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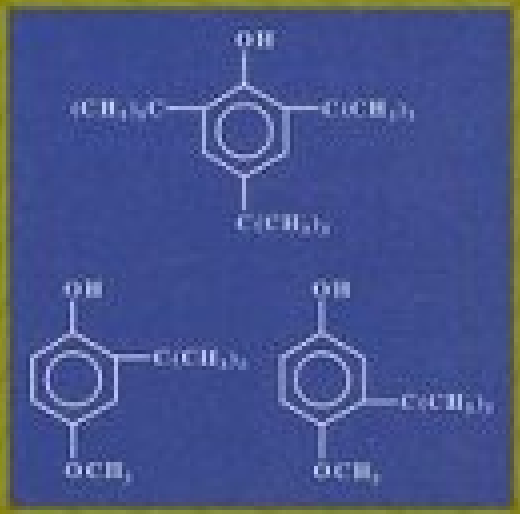

Chemical testing of textiles

Edited by Qinguo Fan

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Chemical testing of textiles

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Qinguo Fan

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Preface

It has long been my desire to contribute to a textbook that is solely devoted to the chemical analysis of textiles. Thus, when Woodhead Publishing contacted me about editing this book, I enthusiastically accepted the offer. Now, with the hard work of a team of contributors who are professors, material researchers and textile analysts from Canada, Britain, Germany and the United States of America, and the great assistance offered by the staff at Woodhead Publishing, this book has become a reality.

The book was initially intended to be read by students in the textile chemistry field who are supposed to have taken organic chemistry. As realized later, this book may also serve as a guide for textile professionals working in laboratories for chemicals testing. Some of these textile professionals may or may not be trained in this specialized area of chemistry, or, if they were trained, they may have been working outside the chemistry specialism for a long time. Therefore, the heavy chemistry content has been reduced and more fundamental chemical concepts and rudimentary procedures have been introduced. It has not been easy to balance the theoretical and practical parts of the content. As it is, this book seems more inclined to the practical with many basic aspects pertaining to the chemical analysis of textiles. Readers who have an avid chemistry mindset or who want to know all the detailed procedures, experimental set-up and data analysis could find the references at the end of every chapter more useful with regard to each individual test introduced in the chapter. In most cases, the chemical analysis is done with a test method regulated and updated by a professional organization, like the American Association of Textile Chemist and Colorists (AATCC), the Society of Dyers and Colourists (SDC), the American Society for Testing and Materials (ASTM) and the International Organization for Standardization (ISO). Some test methods may be adopted by a few organizations.

It should, however, be noted that a particular chemical property of materials can be tested in different ways. The test method introduced in this book may not necessarily be the most suitable one for the job. Sometimes, a new test method may have to be developed or established for new materials coming to the market. For example, nanotechnology can now be employed to process textiles. The claimed

advantages could be novel properties, combined properties by a simple operation or smart properties (intelligent responsive properties). The challenge is how to evaluate the performances and properties associated with nanotechnology. At present, no easily accessible means is available to determine simply whether or not the 'nano' textiles are processed using nanotechnology or if they possess nano-materials. Of course, the traditional properties of 'nano' textiles can still be tested by the currently available methods, but we want to know something about the 'nano' properties in this case. Therefore, test methods must, of necessity, be updated and developed to reflect the trend of new materials. Users of the test methods should be aware of the latest developments and keep using appropriate and updated test methods.

Qinguo Fan

1

Fiber and yarn identification

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1.1 Introduction

The chemical testing of textile fibers has continued to receive special attention from producers, manufacturers, governmental agencies, domestic and industrial consumers. Of particular interest is the number of publications on recent methods of testing and analysis of textiles in general but with specific focus on physical testing, analysis and quality control. This chapter will present selective discussions of the chemical characteristics of major fiber types since an understanding of the fiber chemistry and morphology will aid the chemical analysis of these fibers/yarns. The chapter will also introduce to the reader a selection of chemical tests that are useful in a textile laboratory and document some of the more common chemical methods of analyzing single textile fibers and yarns. Summaries of chemical testing using modern instrumental/analytical tools such as scanning electron microscopy, SEM, transmission electron microscopy, TEM and Fourier transform infrared spectroscopy, FTIR, will be presented.

In practice, all chemical testing must be performed in accordance with specific standards, preferably internationally approved standards. Sometimes, the actual standard may be a mutually agreed and nationally accepted standard method of testing, or one that is based on the end-use of the product and other customer preferences.

1.2 Natural fibers

1.2.1 Chemical composition of cotton

Cotton is the purest form of natural cellulose. Like all the vegetable tissues, it contains a small amount of mineral matter that is left as an ash after cotton is burned. The amount of ash is about 1–1.5%. The mineral matter in cotton consists of chlorides, carbonates and phosphates of potassium, calcium and magnesium. A large variation is observed in the amount of coloring matter found in cotton. The small amount of vegetable protein found in cotton is a little over 1%. The impurity

Table 1.1 Chemical analysis of cotton fiber by McCall and Jurgens, 1951[4]

	Mature cotton (%)	Immature cotton (%)
Cellulose	96.41	92.44
Protein	1.00	2.00
Wax	0.45	1.14
Ash	0.79	1.32
Undetermined	1.35	3.10

found in the largest amount consists of pectinous materials. Also, a small amount of fatty material, which is mostly cottonseed oil, is found in raw cotton. This probably comes from cotton seeds that are slightly damaged during ginning.

Raw cotton contains about 0.5% of a waxy substance which serves as a protective coating on the surface of the fiber. Cotton wax is insoluble in water and because of this, raw cotton is very hard to wet. It is well known that unbleached cotton will not soak up water as easily as bleached cotton. After cotton is purified, all of these impurities are reduced to a total of about 1%.[1,2]

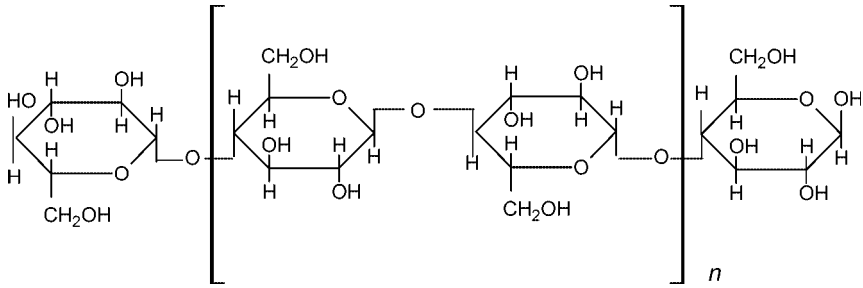
There are several factors that influence the chemical analysis of raw cotton, but we can obtain a general idea from the following figures. If the impurities are calculated on an oven-dry basis, the percentage of fiber should be around 90%. It would be close to 99% after purification.[2,3] Chemical analysis of the cotton fiber has shown the probable composition given in Table 1.1.[4]

The waxes are important in the spinning process but a hindrance to the dyeing operation. Owing to their water-repellent nature, waxes prevent the proper absorption of the dyestuff. The natural color of cotton and the other impurities also interfere, but to a lesser degree, with the ordinary processes of dyeing, printing and finishing.[5]

When all the impurities have been removed from the natural cotton fiber, cellulose remains. Cellulose is a long-chain polymer produced by linking together a large number of glucose units (see Fig. 1.1). Its empirical formula is $(C_6H_{10}O_5)_n$.[3]

Cellulose fiber contains both crystalline and amorphous regions. X-ray diffraction (XRD) diagrams give discernable patterns that indicate the existence of a crystalline arrangement of the molecules in the cellulose fiber. On the other hand, the spots on the XRD diagrams are somewhat blurred and not as clearly defined as those from conventional crystalline substrates.

The main objective in bleaching cotton is the removal of natural and adventitious colorants to produce pure white material. The coloring matters of cotton are associated partly with waxes, proteins and pectins. Some of these coloring matters are partly removed by scouring. However, there is residual natural coloring matter that can only be removed by bleaching. Little is known about these substances, but they appear to contain conjugated carbon double bonds and nitrogen. This coloring matter is capable of being changed into colorless compounds by means of nascent hydrogen, or oxidized into simpler soluble colorless compounds by nascent



1.1 Cellulose structure.

oxygen. The chemicals used for these purposes are termed bleaching agents. The whiteness produced by reducing bleaching agents is not permanent, turning yellow or brown upon exposure to air. The whiteness given by oxidizing bleaching agents does not, as a rule, become yellow. The choice of a bleaching agent is governed by the nature of the fiber, the degree of bleaching required and the cost of the process.[6]

One major treatment that the cotton fibers undergo during processing is mercerization which consists in impregnating the material with a concentrated solution of cold 20–25% sodium hydroxide, keeping the material in contact with this cold solution for a given time with tension and subsequently rinsing it. The structural changes that occur during mercerization induce shrinkage in width and length; this shrinkage has been shown to be caused by swelling which leads to changes in the cross-section of the fibers and improved luster. Ugbolue[7] has summarized the effect of mercerization and other chemical treatments on cotton. It is agreed that mercerized cotton fibers have greater moisture absorption capacity, are more receptive to aqueous chemical agents and are more accessible to dye molecules than unmercerized cottons. The structure of cotton grafted by radiation-induced polymerization with butyl methacrylate and acrylonitrile has been investigated by light and electron microscopy.

The internal structure of the fibers is studied using the transmission electron microscope and changes in fiber surface and type of damage caused by abrasion are evaluated using the scanning electron microscope. The results indicate that the grafting procedure changes the surface as well as the internal fibrillar character of the fibers; the extent of such changes increased with increasing graft polymer content. In a recent study a significant amount of grafting of the polymer on the cotton fabrics was observed and the samples were characterized using SEM and FTIR.[8] Thus, information about textile wet processes helps provide additional resources in our understanding of the chemical testing of these fibers and yarns.

1.2.2 Other vegetable fibers

Some of the other important vegetable fibers include flax, jute, kenaf, hemp, sisal, coir, banana and pineapple. Generally, in vegetable fibers such as cotton and flax,

cellulose is the material that provides the thread-like molecule and fibrillar structure. Differences in the properties of natural fibers of similar chemical constitution can be explained in part by variations in the state of alignment of the molecules. Flax and cotton are chemically almost identical and are both cellulose fibers. But flax has tensile properties quite different from those of cotton; flax has a tenacity of up to 6.3 grams per denier (gpd) compared with 3–5 gpd for cotton. Flax and ramie have highly oriented molecules along the fiber axis and consequently, high tensile strengths. Cotton, with an angle of spirality of about 31 º has a much greater elongation at break than flax, with its spiral angle of 5 º.

Stout[9] has written a detailed review on jute and kenaf. X-ray diffraction patterns show the basic cellulose crystal structure, although in jute and kenaf the crystalline orientation is high and the degree of lateral order is lower than in flax.[9] Batra[10] in a comprehensive review has highlighted the morphological structures and physical, mechanical and chemical properties of other long vegetable fibers.

Gel-permeation chromatography[11] is used to compare the pore structure of jute, scoured jute and purified cotton cellulose. Both native and scoured jute have shown greater pore volumes than cotton. The effects of alkali and acid treatment on the mechanical properties of coir fibers are reported.[12] Scanning electron micrographs of the fractured surfaces of the fibers have revealed extensive fibrillation. Tenacity and extension-at-break decrease with chemical treatment and ultraviolet radiation, whereas an increase in initial modulus and crystallinity is observed with alkali treatment. FTIR spectroscopy shows that the major structural changes that occur when coir fibers are heated isothermally in an air oven (at 100, 150 and 200 ºC for 1 h) are attributable to oxidation, dehydration and depolymerization of the cellulose component.

1.2.3 Protein fibers

Animal fibers are made from proteins and the long molecules are built from some 20 or so different types of amino acid molecule. The proportion and arrangement of these different units determine the structure of the protein molecule and the nature of the protein itself. Wool cells come in two different types: the para cortex and the ortho cortex, which lie on opposite sides of the fiber and grow at slightly different rates. This causes a three-dimensional corkscrew pattern of coiled springs, giving wool high elasticity and a ‘memory’ that allows the fibers to recover and resume normal dimensions.

Wool fibers can be stretched up to 30% without rupturing and still bounce back. The closed-packed wool molecules are joined together by chemical links. These cross-links ensure that when the molecules are stretched out of their normal folded shape, they return to that shape when the stretching force is removed. Also, under suitable conditions wool can absorb half its own weight of water. Cook[13] has suggested that hot water or steam can destroy the cross-links so that the molecules are free to stay in the new positions that they reach when the fibers are stretched.

Moreover, prolonged heating will actually cause new links to form which anchor the molecules firmly in their new position, a transition from α-keratin to β-keratin. Electron microscopy, X-ray diffraction and other forms of evidence indicate that about one-third of the total length of the protein chains in wool is in the coiled-coil, α-helix conformation.

Silk, like wool, is an animal fiber and unlike wool, its molecules are in extended form. The protein molecules in silk are highly oriented in the direction of the fiber and can pack tightly together. The forces of attraction between the molecules interact effectively to give the molecular bundles very great strength. The effect of heat on silk is similar to its effect on wool. Thus, at a high temperature, silk will burn. But the molecules in silk are not joined together by cross-links as in wool; so, there are no cross-links between the molecules to break down or rebuild. Silk is therefore able to withstand higher temperatures than wool.

1.3 Regenerated fibers

Interest in the manufacture of different forms of rayon has resulted in the production of regular rayon, hollow viscose, spun-dyed filaments and staple rayon, crimped rayon and surface modified fibers, high tenacity rayon and high wet modulus (polynosic) rayon fibers. In chemical composition, viscose rayon and cotton are alike; they are both cellulose.

In cotton, the cellulose molecule consists of some 2000 to 10 000 anhydroglucosidic units linked together to give a high proportion of crystalline material (70–85%). The crystallites in cotton are orientated with respect to each other, forming microfibrils which in turn are arranged into fibrils, and the fibrils into filaments. During the manufacture of viscose, natural cellulose fibers are dissolved, resulting in some depolymerization and reduced crystallinity of the cellulose in viscose rayon. This renders the fiber more responsive to water. Thus, viscose rayon will absorb twice as much water naturally from air as cotton does. Viscose rayon has a moisture regain of 13% under standard conditions, and when soaked in water it will increase in length by 3–5% and swell to double its original volume. Viscose rayon loses as much as half its strength when wet, and is more easily stretched.

The differences between regular and high-tenacity rayon are to be found in the degree of degradation of the cellulose which has occurred during preparation of the viscose, the degree of crystallization, the size of the crystallites, the degree of orientation and the fine structure and uniformity of the filament.

1.4 Fiber identification

The identification of textile fibers is a task frequently performed in a textile laboratory. The need to identify fibers arises in fibers research as well as during fabric production and processing. The identification of an unknown fiber in a yarn

or fabric made up of a mixture of fibers is also often carried out. Identification tests are performed by utilizing tests that take advantage of the different chemical (and to some extent physical) characteristics of fibers. While there are some very elaborate analytical instruments that can be used to identify the chemical composition of materials and fibers in most circumstances, the textile laboratory relishes simple qualitative methods of identification of fibers. Here, three procedures are introduced, involving burning, solubility and dye staining tests of the fibers. These experiments will enable the reader to gain some insight in identifying various textile fibers using simple techniques.

1.4.1 Fiber identification by burning

Purpose: To make some observations about the reaction of various fibers to an open flame.

Procedure: Obtain 1–2 cm lengths or tufts of the various fibers or yarns to be tested from the samples provided. Perform the following tasks and carefully record the information in Worksheet 1 provided below. Worksheets may be adjusted as necessary to suit the purpose of the reader.

1. Hold the individual fiber samples to be tested in tweezers or tongs and bring the fibers slowly to the side of a Bunsen burner flame. Make observations. What is the initial reaction? Does the fiber shrink? Melt? Anything else?
2. Place the fiber in the flame and slowly withdraw it. Does the fiber burn?
3. If burning occurs, describe the flame. Color? Sooty?
4. Does burning continue or is fiber self-extinguishing?
5. If burning continues, extinguish it and carefully smell the smoke. Describe the smell.
6. Observe the remains of the ash (burn) product. Color? Black? Pale brown? Does it crumble? Is it hard? Bead-like?

1.4.2 Fiber identification by solubility

Purpose: To examine the reaction of fibers to solvents and to use these observations to identify fibers.

Background: In the burning test, natural fibers like cellulose and wool could be distinguished from the synthetic fibers (nylon, polyester, acrylic) fairly well. Among these synthetic fibers there is some confusion using the burning test. Since fibers are polymeric materials they can react with solvents in different ways. Thermoplastic fibers may dissolve in a common solvent like acetone. Also some highly semi-crystalline (thermoplastic) fibers like nylon and polyester will dissolve only in harsh ‘solvents’ like formic acid or boiling dimethylformamide (DMF). Here chemical dissolution of the fiber polymer occurs. Natural fibers like the cellulosics and protein fibers are thermosetting polymers. They are found to

Worksheet 1 Fiber identification by burning

	Initial reaction	Burning	Description of flame	Self-extinguishing	Smell	Remains
Cotton						
Wool						
Silk						
Acetate						
Polyester						
Acrylic						
Nylon						
Viscose						
Polyolefin						
Glass						

dissolve chemically in strong acid or base solutions. Other 'solvents' have been found that are quite specific in dissolving certain fibers. It is this specificity of solubility that allows for the determination of the quantitative composition of various fibers in blended fiber fabrics, e.g. polyester/cotton, nylon/wool. In this experiment, one can study the solubility behavior of various fibers in a series of solvents and observe the unique solubility behavior of textile fibers.

Worksheet 2 Fiber identification by solubility: synthetic fibers

	Acetone, room temperature	Formic acid, room temperature	DMF, 90 °C
Acetate			
Modacrylic (SEF)			
Polyester (Dacron 64)			
Nylon 6			
Nylon 6, 6			
Acrylic (Orlon)			
Polyolefin (polypropylene)			
Fiber glass			

Procedure

(A) *Identification of synthetic fibers*: Set up a series of 15 test tubes containing about one (1) ml of the following: five with acetone, five with 90% formic acid and five with DMF. (ALL THREE OF THESE SOLVENTS ARE HAZARDOUS!!! EXPERIMENTS MUST BE CARRIED OUT IN THE HOOD AND CARE TAKEN NOT TO SPILL ANYTHING.) To each of the solvents add a 0.5–1 cm length of yarn to determine its solubility. The five fibers to be tested are acetate, polyester, acrylic, nylon and viscose. Gently swirl each test tube and use a glass rod to poke and stir the fiber to effect solubility. Make observations on Worksheet 2, supplied above. Note that it may take a few minutes for these samples to dissolve. For the DMF samples, using a test tube holder, place the test tube in a water bath (IN THE HOOD!!!) and make some observations. Note that complete dissolution may not be possible and may mean weakening to a jelly-like mass of the fiber in the

Worksheet 3 Fiber identification by solubility: natural fibers

	NaOH 10% at room temperature		
	Immediate effect	After 10 min	After 20 min
Cotton			
Wool			
Silk			

	NaOH 10% at 40 °C		
	Immediate effect	After 10 min	After 20 min
Cotton			
Wool			
Silk			

	Sulfuric acid 70% at 40 °C		
	Immediate effect	After 10 min	After 20 min
Cotton			
Wool			
Silk			

liquid. Check this with a glass rod. Make all your observations about the solubility of these five fibers in the three solvents in Worksheet 2.

(B) *Natural fiber solubility tests*: Here the same general procedure and test tube set-up will be used except that we will be testing the solubility of three natural fibers – cotton, wool and silk in two solvents:

- Use three test tubes each with 10% caustic soda (NaOH) at room temperature (and eventually at 40 ºC)
- Use three test tubes each with 70% sulfuric acid at 40 ºC.

Make the same type of observations as described for the synthetic fibers section. Record all the observations in the Worksheets.

1.4.3 Fiber identification by dye staining

Procedure: Following the instructions provided for using DuPont Fabric Dyestain #4, identify the unknown fabric samples assigned for identification. Be sure to:

1. Put a 1 cm wide strip of 'multifiber fabric' in your dyebath as an internal control.
2. Confirm the identity of your fabric by performing a burning or a solubility test on your unknown materials.
3. Report the results of your unknown determinations on Worksheet 4.

Worksheet 4 Fiber identification by dye staining

1. Unknown # (mount samples in spaces)	Identified as
	Dyestain test: _____
	Confirm test: _____
2. Unknown #	
	Dyestain test: _____
	Confirm test: _____
Multifiber control (to be mounted here)	

1.4.4 DuPont Dyestain #4 instructions

(DuPont fiber identification dye #4)

Source: PYLAM Products Company Inc, 2175 East Cedar Street, Tempe, AZ 85281-7431, USA. Tel: +1 480-929-0070, Fax: +1 480-929-0078

Product use: Identify fiber/yarn/fabric types by color 'staining' technique. Also useful for identifying polymers in general.

Product composition: Dye mixture – Acid Blue 298, Acid Red 182, Direct Blue 218, Disperse Orange 25, Disperse Yellow 3, Direct Yellow 11.

Procedure

1. Wet out material (unknown) with hot water.
2. Place material into boiling 1% by weight water solution of DuPont #4 dye stain. Use a 20:1 (liquor:fiber) bath ratio.
3. Boil for 1 min.
4. Remove, rinse and dry.
5. Compare color results with 'standard' color strip.

1.4.5 Quantitative determination of the percentage of fiber in a yarn/fabric blend (solubility test)

Procedure

1. Weigh a watch glass.
2. Take a piece of blend fabric in which one of the components is either cotton or wool and the other is a synthetic. Place it on the watch glass and dry it in a 100 ºC oven for 10 min. Weigh the fabric and watch glass and calculate the weight of fabric.
3. In a fume hood:
   - If it contains cotton, put it in a beaker of 70% sulfuric acid.
   - If it contains wool, put it in a beaker of 5% caustic soda and 'Clorox' bleach.

   Leave for 15 min, stirring occasionally.
4. Remove what is left (the synthetic part of the blend) into a beaker of water with care, and stir once more.
5. After 5 min, remove the synthetic component, rinse carefully and transfer to the watch glass. Dry in the oven.
6. Weigh the synthetic component and calculate the weight of the synthetic component.
7. Calculate the percentage of the blend fabric.
8. Fill the table below with your data.

Fabric tested: Blend of _____

Table 1.2 Calculation of percentage makeup of blend

Weight of watch glass	*a*	g*
Weight of blend fabric and watch glass	*b*	g
Weight of fabric	*b–a*	g
Weight of synthetic component and watch glass	*c*	g
Weight of synthetic component	*c–a*	g
% of synthetic in the blend	100 × (*c–a*)/(*b–a*)	%

*Add data to this column.

Result: Fabric tested consists of % _____ and % _____ .

Table 1.3 Summary of typical observations

Fibre	Burning characteristics	Odour	Ash
Cotton	Burns with a flame. Has an afterglow	Burning paper	Black and powdery
Polyester	Melts and burns with a sputtering flame. Gives off thick black smoke	Faintly sweet, slight geranium odour	Hard, black, round and shiny
Polypropylene	Melts and burns with steady flame. Clear flame, no smoke. Looks like melting glass. Melted portion is clear.	Very little odour. Slight celery odour	Hard, turns opaque
Nylon	Melts and burns with sputtering flame. Gives off white smoke	Burning garbage	Hard, round, gray or brown, shiny
Nomex	Very slow to ignite. Will not support combustion. No melting. Material chars and curls up	Faintly sweet	Black, dull finish crushes into black powder
Acrylic	Melts and burns rapidly. Sputtering flame. Thick black smoke	Faintly sweet, slight 'hot iron' odour	Resembles burned head of wooden match; crucibles into black or brownish orange powder

Details of single fiber analysis have been given by Bresee.[14] Therefore, in this chapter, only highlights of some of the important methods for fiber identification have been considered.

1.5 Density measurement

The density of any material is defined as its weight per unit volume. Textile fiber density is more conveniently determined indirectly by comparing the sample with standards of known density. The two commonly used techniques are the sink–float and gradient density methods.

The sink–float method requires a beaker, pipette, burette and two liquids. The liquids must be miscible and inert to the fiber being tested. One liquid must be less dense than the fiber and the other liquid must be more dense. A known volume of liquid A is pipetted into a beaker and the fiber is immersed in the liquid. The second liquid, B, is then added dropwise from a burette to the beaker with constant stirring. As the density of the liquid solution in the beaker changes, a point is reached where the density of the liquid precisely equals that of the fiber and the fiber will neither sink nor float but will remain suspended in the liquids. The volume of the second liquid added to the beaker is recorded and the density of the fiber is calculated:

$$d_{\text{solution}} = d_{\text{fiber}} = \frac{d_{\text{A}}V_{\text{A}} + d_{\text{B}}V_{\text{B}}}{V_{\text{A}} + V_{\text{B}}} \qquad [1.1]$$

where d refers to density, V refers to volume and A and B refer to the first and second liquids respectively.

The density gradient method is more complicated and can provide density measurements to five significant figures. A density gradient apparatus can either be purchased or constructed inexpensively as detailed elsewhere.[15] Density gradient analysis consists of preparing a density gradient column, calibrating the column and then introducing the fiber sample to the column for measurement of its density. The column is a vertical tube containing two miscible liquids such that the density in the tube changes continuously from top to bottom. The column is calibrated by immersing several objects of known density in the column and then plotting their locations in the column versus their densities on graph paper. Glass spheres of known densities are used as calibration floats. The fiber is dropped in the column and when it has settled in the column, its location is recorded. Finally, the density of the fiber is determined by noting the density on the calibration curve corresponding to its location in the column.

Density measurements can be used in the calculation of the percentage crystallinity of fibers. Fiber degradation has also been monitored by both sink–float and density gradient measurements.[16]

1.6 Use of infrared spectroscopy

The appearance of the first research grade Fourier transform infrared (FTIR) spectroscopy in the early 1970s initiated a renaissance and opened the door for the use of the technique in many analyses, including textile fiber identification. The basis of FITR spectoscopy is the two-beam interferometer. Details of the design, techniques and applications are adequately covered elsewhere.[17,18] The fundamental equation for spectrometric quantitative analysis is known as Beer–Lambert–Bouguer law, sometimes shortened to the Beer–Lambert law. To ensure an acceptable quantitative method, it is important to obtain reference spectra of the analyte and all other components. Also, the best method of sampling must be employed and the system calibrated. Finally, a validation sample must be prepared for evaluation. Polymers and fibers are usually analyzed as pressed films although solid samples can be analyzed directly if the FTIR apparatus has an appropriately attached microscopic unit. Sometimes, absorption band ratios are used and give the best results.

Positive identification of synthetic fibers can be made using standard analytical methods published by AATCC (American Association of Textile Chemists and Colorists), ASTM (American Society of Testing Materials) and The Textile Institute, Manchester.

1.7 Other methods of surface analysis

Many new instruments are now available which can be used to characterize various depths of a specimen. A brief account of the use of these techniques will be presented here.

1.7.1 ESCA (XPS)

Electron spectroscopy for chemical analysis (ESCA) is used for characterizing polymer surfaces and is also known as X-ray photoelectron spectroscopy (XPS). This method is based on the observation that electrons are emitted by atoms under X-ray irradiation. The energy of the emitted electrons yields the binding energy of the electron to the particular atom.[19]

1.7.2 SEM

Scanning electron microscopy (SEM) constitutes one of the older and one of the most widely used instruments for surface analysis. It provides a three-dimensional visual image and, thus, the quantitative analysis is relatively straightforward.

1.7.3 SSIMS

Static secondary ion mass spectroscopy (SSIMS) ranks with XPS as one of the principal surface analytical techniques. Treatment of polymer surfaces to improve their properties with respect to wetting or water repulsion and to adhesion, is by now a standard procedure. The treatment is designed to change the chemistry of the outermost groups in the polymer without affecting bulk properties. One popular surface treatment is plasma etching. The use of SSIMS is most amenable to the surface evaluation of such treated materials.

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2

Chemical analysis of feather and down textile materials

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2.1 Introduction

2.1.1 Feathers and down

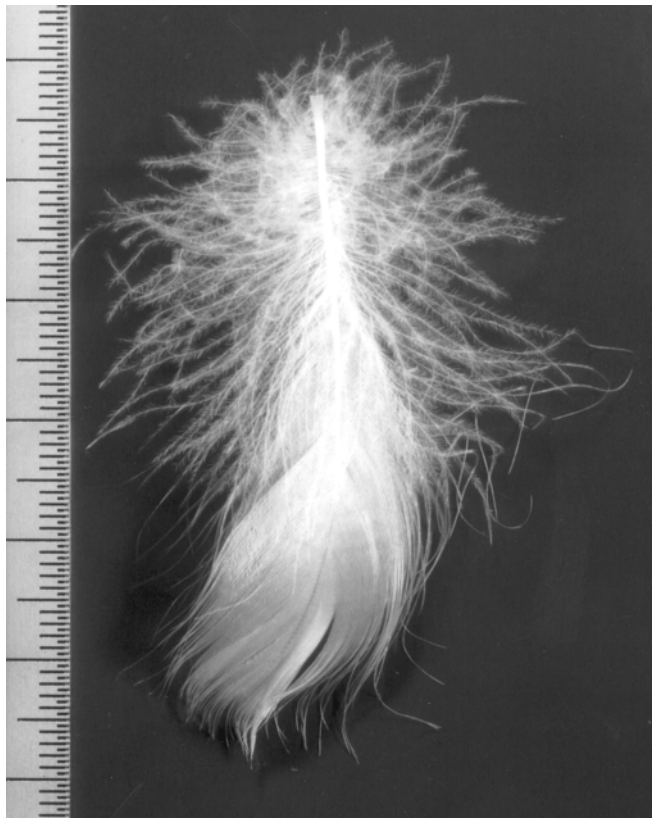
Feathers and down are two of nature's most marvelous products. Together they form the bird's plumage, but they are very different in structure. A feather has a two-dimensional structure, a quill from which barbules extend in two opposite directions like vanes and a compact and flat tip (EN 1885, 1998, p 4). Down has no quill but a small core, from which small clusters of barbs (with barbules and nodes) extend in three dimensions (EN 1885, 1998, p 4). It would be erroneous to assume that down is a small feather or would eventually develop into a feather.

Feathers form the outer, protective coat of the animal's body. They have structural functions, best seen in the strong wing and tail feathers. They are highly resilient. Down, only found in waterfowl, provides the necessary warmth insulation for the bird. The barbs are fluffy-elastic and at least as resilient as feathers. Thanks to its structure, down can trap a large volume of air, resulting in an almost unsurpassed heat insulation capability with respect to weight.

2.1.2 Test standards

Few people buy commodities knowing everything about them, nevertheless most consumers would like to feel comfortable understanding what is on the product labels. This is important because the standardized information provided on the labels enables producers and merchants of down- and feather-filled products to inform customers of their products' quality, and thus sell more goods.

In order to write, read, compare and understand the quality or performance data of down and feathers in a universal language, the International Down and Feather Bureau (IDFB), together with international and national standardization organizations, has developed methods and published standards for both testing and



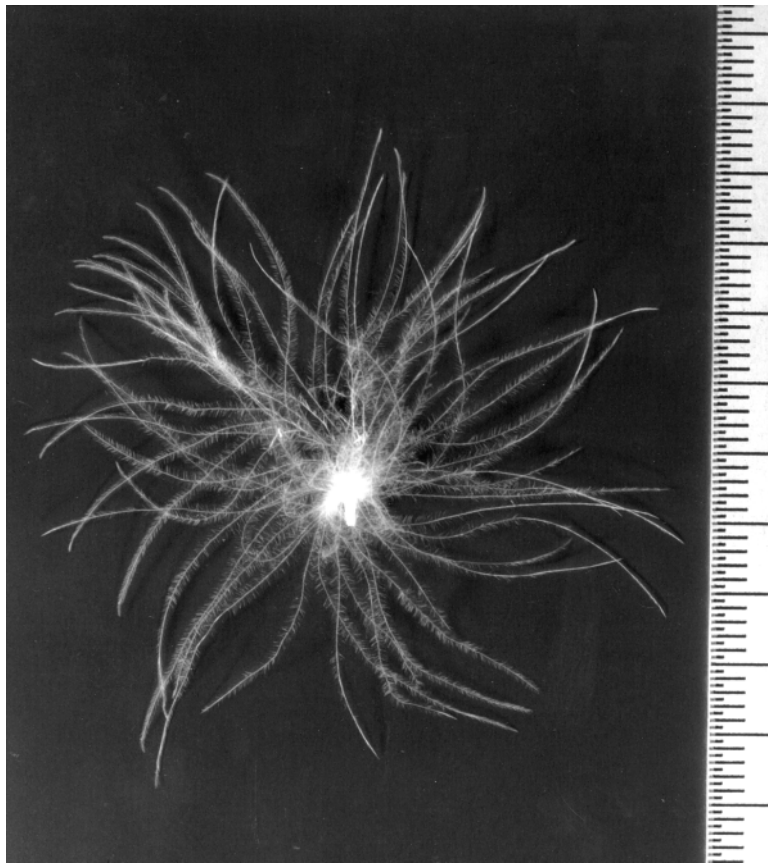
2.1 Micrograph of a feather (*source*: IDFL – International Down and Feather Laboratory and Institute).

characterizing down and feather material and products. In this chapter, information and data on the quality control of feathers and down are summarized, primarily from IDFB testing regulations and from European standards. European standards (EN) are determined by committees acting for the European Union in its effort to standardize regulations for inter-Europe commerce. References are also made to British and Japanese norms**.** When applying any of these methods, it is important that the procedures are followed in their entirety.

The characterization and testing of all materials, natural or synthetic, are determined by their physical structure and chemical composition.

2.1.3 The physical structure of feathers and down

As far as we know, few of nature's products are fully symmetrical, although if we could observe the nano-range of matter not currently visible to our eyes or through current technical vision aids, we may find many more. No feather, for example, is exactly the same on the left and the right side of the shaft, and none are entirely



2.2 Micrograph of a down cluster (*source*: IDFL).

straight. The barbs are not symmetrical (see Fig. 2.1). Furthermore, it is clear that an individual down cluster is not at all as symmetric as an individual snowflake, with which down is sometimes compared (see Fig. 2.2).

2.1.4 The chemical composition of feathers and down

Nature's polymer chemistry has selected two basic molecular building blocks for fibrous products.

- Flora: Cellulose is the construction material for the structural cells in plants. It is probably found in its purest form in cotton, having the general formula of a polysaccharide:

$$-[C_x(H_2O)_y)]_n- \qquad [2.1]$$

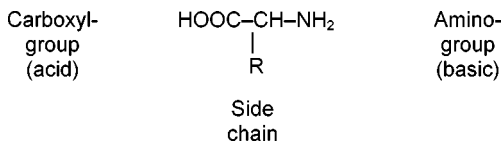
- Fauna: Animal and human tissue, like skin and leather, as well as fibers such as

hair, wool, and feathers and down, have proteins as their main building blocks. These are large molecules, assembled by nature from a variety of not much more than 20 different amino acids. Keratin is the predominant protein in fibers. It, too, is a macromolecule, with cysteine as one of the main amino acids:

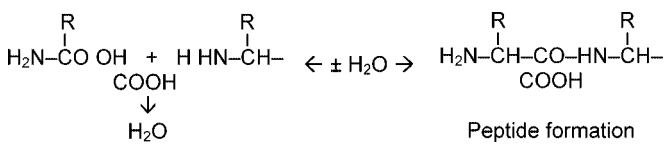
$$HS–CH_2–CH(NH_2)–COOH \qquad [2.2]$$

Amino acids: building blocks for proteins

Proteins are composed by nature from (by weight) about 50% carbon (C), 20–25% oxygen (O), 15–17% nitrogen (N), 7% hydrogen (H) and, particularly in the keratins (the protein building blocks of hair and feathers), between 2.5 and 5% sulfur (S). A closer look at amino acid molecules reveals that they actually have an acidic head (carboxyl group) and an alkaline tail (amino group) (see Fig. 2.3). With this structure, they are capable of head-to-tail reactions, forming first peptides and then proteins, which are large molecules containing chains of amino acids linked by peptide bonds (see Fig. 2.4).



2.3 General chemical formula of amino acids (*source*: IDFL).



2.4 Peptides (*source*: IDFL).

The role of water

As can be seen from the chemical composition of down and feathers, water is an essential part of their chemical makeup. Not only is water a by-product of the polymerization of amino acids to proteins, it can also reverse this chemical reaction. Boiling water will split proteins into shorter chains of polypeptides, which is an intermediate step in the biochemical analysis of down and feathers.

In a manner similar to that of hair and wool, down and feathers have the ability to physically and even chemically absorb moisture from the atmosphere surround-

ing them. The rate is about 13% at standard atmospheric conditions (note: IDFB Testing Regulations Part 1, see References, Section 2.6.3, states that these are 20 ± 2 ºC and 65 ± 2% relative humidity).

As will be shown in Section 2.4, moisture plays an important role for the structural revival or reconditioning of down and feathers that have been vigorously compressed as bulk raw material in bales, or in a finished product, for example in a tightly rolled-up down sleeping bag.

2.2 Chemical analysis of feathers and down

2.2.1 Representative sampling

As the photos above (Fig. 2.1 and Fig. 2.2) indicate, down and feathers are not homogeneous. It is therefore very important to draw representative samples in testing either the raw material or the finished products. If only a single item is to be tested (bag, bale or manufactured article), three individual samples should be collected at three different sites in the item, i.e. from the upper, the middle, and the lower part, respectively. In the case of several packages or items belonging to one lot or batch, the number and quantity of samples are determined according to the following tables. (Sampling norms are somewhat different, and as this difference may be decisive in legal cases, the IDFB and the EN figures are shown in Table 2.1 and Table 2.2.

Table 2.1 Sampling of down and feather products or packages (>500 g/item)

Extent of delivery or lot		Number of packages or items sampled		Weight of each individual sample		Total sample quantity	
IDFB Part 2	EN 1883	IDFB Part 2	EN 1883	IDFB Part 2(g)	EN 1883(g)	IDFB Part 2(g)	EN 1883(g)
1	1	1	1	135	135	405	405
2–8	2–15	2	2	70	70	420	420
9–25	16–25	3	3	45	45	405	405
26–90	26–50	5	4	30	35	450	420
	51–90	(5)	5	(30)	30	(450)	450
91–280	91–150	7	7	20	20	420	420
	151–280	(7)	10	(20)	20	(420)	600
281–500	281–500	9	15	20	15	540	675
501–1200	501–1200	11	20	20	15	660	900
1201–3200	> 1200	15	25	15	15	670	1125
3201–10000		19	(25)	15	(15)	860	(1125)

Source: EN 1883, 1998, Table A.1: Packages filled with more than 500 g (Section 2.6.2); IDFB Testing Regulations Part 2 (Section 2.6.3).

Table 2.2 Sampling of down and feather products or packages excluding pillows (<500 g/item)

Extent of delivery or lot		Number of packages or items sampled		Weight of each individual sample		Total sample quantity	
IDFB Part 2	EN 1883	IDFB Part 2	EN 1883	IDFB Part 2(g)	EN 1883(g)	IDFB Part 2(g)	EN 1883(g)
1	1	1	1	35	40	105	120
2–25	–	2	(2)	17	(20)	102	(120)
–	2-90	–	2	–	20	–	120
26–280	–	3	–	13	–	102	–
	91–150	(3)	3	(13)	14	(102)	126
	151–280	(3)	4	(13)	10	(102)	120
281–500	281–500	5	6	7	7	105	126
501–1200	501–1200	7	7	5	6	105	126
1201–3200	> 1200	9	9	5	5	135	135

Source: EN 1883, 1998, Table A.2: Package(s) filled up to 500 g and manufactured articles (Section 2.6.2); IDFB Testing Regulations Part 2 (Section 2.6.3).

2.2.2 Determination of moisture content

While a lower than normal moisture content may be observed in very dry climates, down should be able to return to its natural moisture percentage of 13% if stored under standard climate conditions. If it does not, however, this may be an indication that the down has been mistreated thermally or chemically during the preliminary processes or while in use. A higher than normal moisture content may indicate that the material has been stored or transported under wet conditions, which may result in microbiological or pest damage. If the moisture content is too low, feathers and down lose their resilience and may become brittle. The determination of moisture content is therefore of chemical, physical and biological importance in the quality control of feathers and down. The IDFB Testing Regulation, Part 5 demonstrates how this is done (also refer to EN 1161: 1995E relating to moisture content, see References, Section 2.6.2):

Four to five grams of the representative down–feather specimen are placed into a weighing bottle which has been dried at 105–110 ºC for at least 1 h, then cooled in a desiccator. The sample is dried at 105–110 °C for 2 h, and then allowed to cool in the desiccator. The weight loss is measured (repeating until the weight is constant within 1 mg), calculated and reported as *xx.x*%.

2.2.3 Ash chemical analysis

The chemical formula of cysteine:

$$HS–CH_2–CH(NH_2)–COOH \qquad [2.3]$$

illustrates that the proteins in feathers and down, mainly keratin, contain sulfur (S) in addition to the main components of amino acids: carbon (C), hydrogen (H), oxygen (O) and nitrogen (N).

Ash analytical methods may thus be used to test for evidence of protein-based matter including waterfowl down and feathers. But the characterization or even identification of bird species can hardly be definitely determined on the basis of chemical element percentage alone. One reason is the difficulty of collecting a chemically representative sample from a fairly non-homogeneous natural product.

Nonetheless, the ash chemical methods used for identifying chemical elements present in down and feathers do serve to find and identify foreign matter and undesirable additives. Two examples are:

1. Barium salts added to increase (illegally) the final weight and to give artificial whiteness to raw or pre-processed down.
2. Metal-based chemicals and halogen compounds added to reduce the (in itself not very risky) potential flammability of feathers and down, or additionally, for pest control. Most of these substances are currently prohibited as additives in natural or synthetic materials meant for human use.

In short, the traditional chemical–analytical methods for detecting specific elements or molecules is (despite the application of modern identification detectors) predominantly used in basic research or for detective investigations, but are rarely applied in the day-to-day quality control of down and feather filling materials.

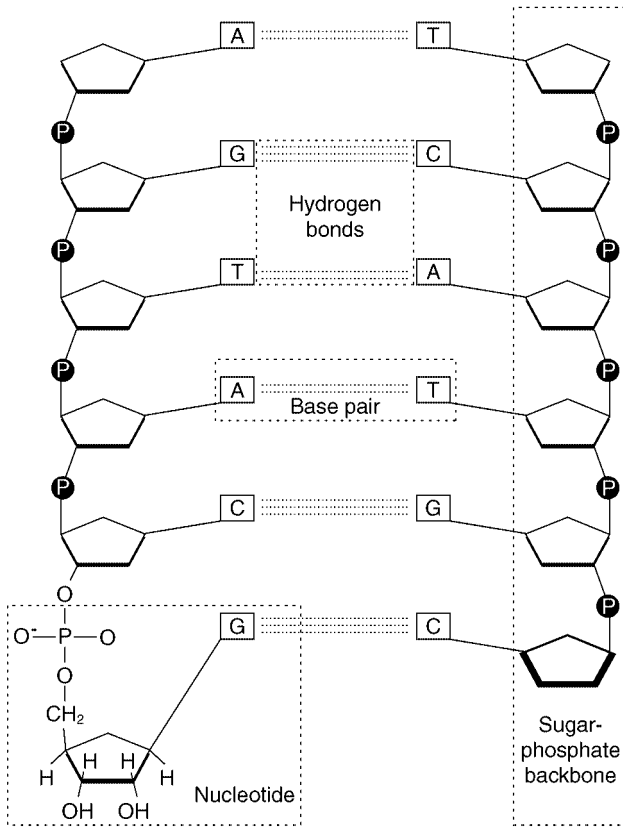
2.2.4 Biochemical analysis

Each cell of an animal, including the structural cells of down and feathers, carries megabytes of genetic information. This is stored in an orderly manner in strands of DNA, nature's 'read only' memory. They most often are found paired with a partner strand, wrapped around each other in the familiar double helix. Most of this information remains stored and protected when it is not actively used either to propagate information or for repairs should it become corrupted (see Fig. 2.5 DNA Chain).

SIAM method for species identification

Specific Identification of Animals by MALDI–TOF mass spectrometry (SIAM) was developed by Wolfgang Altmeyer, Gene-Facts GbR in cooperation with Klaus Hollemeyer and Elmar Heinzle, Saarland University, Saarbrücken, Germany (http://www.gene-facts.com/ENGLISH/SIAM/siam.html).

In this method, proteins are cleaved by specific enzymes, the restriction sites being defined by the amino acid sequences. The fragments generated by this treatment differ in length and molecular weight, according to the species-specific



2.5 DNA chain (*source*: IDFL) The code is quite easy to read. The cells read it by scanning down a messenger RNA (copied from the DNA) and use ribosomes to build proteins based on the code that is read. Researchers read the code by stepping down one nucleotide at a time, clipping it off to identify it, thus determining the sequence of a DNA strand. Hundreds of different proteins are built in to interact with the information contained in the DNA. Their sequence is genetically determined and varies between different animal species.

composition of proteins. Owing to the high content of repetitive sequences, many species-specific (as well as unspecific) peptides are created. These peptides are then separated by highly sensitive MALDI-TOF mass spectrometry (matrix assisted laser desorption ionization time-of-flight mass spectrometry), generating patterns of peaks according to the different molecular weights. The peaks are then analyzed for species-specific patterns.

General description of test method

The feather or down material to be analyzed is put into a PCR (polymerase chain reaction) container, containing a solution of 25 mM NH_4HCO_3 and

2-mercaptoethanol. The PCR container is then placed into a boiling water bath for 20 min, during which time the disulfide bridges of the proteins are opened, thus becoming accessible to the enzymes. The container is then immediately cooled down on ice.

A solution of 25 mM NH_4HCO_3 and trypsin (a protein-cutting enzyme) is added and incubated for 3–4 h at 37 ºC. Following this incubation, the enzyme is chemically deactivated and 1 º µl of the liquid is brought onto a sample plate and evaporated. The sample plate is then placed into the mass spectrometer and analyzed. The time of flight in the mass spectrometer is dependent on the molecular mass of the fragments produced during the preceding 'digestive' procedure. As stated above, the spectrogram can now be analyzed for patterns specific to the bird species.

Test accuracy

To date, the MALDI-TOF spectrometer provides the most specific separation spectrograms. Based on numerous test series with a known reference material, an extensive data base of spectrograms has been acquired. For goose, duck, eider duck, chicken, pheasant and turkey, the accuracy of bird species identification is almost 100%. Accuracy of the visual quantitative method is ±5%. For most quality control purposes, this is sufficient (see also Section 2.4, Visual analytical methods).

2.2.5 Isotopic analysis

Because radioactive elements decay at a known rate, they are increasingly used for identifying sites and objects. Stable isotope ratios can be propagated through the environment from geological formations into water or from food into body tissue. Thus flora and fauna living in such environments will receive a geochemical stamp allowing isotopic analysis to provide information on the origin of materials. This procedure has, for example, been accomplished for meat and grapevines. It may eventually be applied to down and feathers, making it possible to identify the plumage of birds according to their native geographic areas, based on isotopic ratios of trace elements and on isotopic data available on agricultural soil and, in consequence, on plant food consumed by ducks and geese (during analysis, however, it must be taken into account that birds fly long distances, even between continents, and that animal food may also be transported over similar distances).

Until now, these methods have primarily been used in archeology, including the study of ancient nutrition sources of plants or animal diets determined from potsherd residues. However, by plotting data of several elements together, and with more geochemical information, specific maps are becoming available that give very localized indications on the plant source of the food chain of humans or animals. Such maps have already been successfully applied to modern day criminology.

Current instrumentation allows for the analysis of very small samples, and such progress in separation chemistry means that using the above approach is now feasible. Accelerator mass spectrometry (AMS) for detecting the radioactive isotope of carbon (^{14}C) in relation to the stable isotopes once required specimen sizes of one gram or more four decades ago, to sample masses today containing only 0.1–1 mg of carbon are adequate. Measurement times have been reduced from weeks to hours. Stable isotopes of lighter elements such as carbon, nitrogen, oxygen, and even hydrogen (e.g. from proteins) can now be measured with very high precision using isotope ratio mass spectrometry (IRMS).

2.3 Chemical analysis of extracts

Raw down and feathers are obviously not clean and must be washed and separated in various steps. Depending upon how effective the washing equipment is, varying amounts of impurities can be detected through the use of water and solvents.

2.3.1 Aqueous extracts

Acidity (pH)

According to IDFB Testing Regulations, Part 6 (see Section 2.6.3), acidity (pH) is determined in the following manner:

Sample preparation
In a 250 ml Erlenmeyer flask 1 g ± 0.01 g of the test specimen (cut to pieces of approximately 1.5 mm) is macerated with 5 ml of boiled distilled water until all material is wet. Then 65 ml of boiled distilled water is added and the flask is stoppered and allowed to stand for 3 h at room temperature. It must be occasionally shaken mechanically or by hand.

Measurement
Without removing the material, the temperature is adjusted to 25 ± 1 ºC and the pH is measured potentiometrically. Report the pH to the nearest 0.1 pH unit. Occasionally the acidity is measured from the aqueous extract prepared for the determination of oxygen number and turbidity (see below) but this method is not standardized.

Oxygen number (based on IDFB Testing Regulations, Part 7 – see Section 2.6.3; EN 1162, 1996– Section 2.6.3)

Sample preparation
Ten grams ± 0.1 g of the representative down or feather sample is placed into a 2 l plastic jar. One liter of distilled or de-ionized water (grade 3) is added and the jar is closed with a watertight lid. It is then shaken at least 10–15 times by hand to ensure

that the plumage begins to absorb water. Then the jar is placed in a horizontal position on the shaking machine. The jar is shaken at room temperature for 30 min (European Norm (EN) 1162 requires at least 1 h) at a speed of 150 shakes per minute. The resulting liquid is filtered through a sintered glass filter with pore size P160 without squeezing or wringing the liquid from the down and feathers.

Measurement

A 100 ml sample of the liquid is transferred into a 400 ml beaker and acidified by adding 3 ml of 3 mol l^{-1} (ca 25%) sulfuric acid; the beaker is placed onto a magnetic stirrer. By adding N/10 (0.02 mol l^{-1}) potassium permanganate ($KMnO_4$) 0.02 ml at a time, the liquid is titrated until a faint pink color persists for 60 s. The test is repeated with another 100 ml of the liquid sample and a blind test is done with plain water.

Calculation

A = quantity in ml of potassium permanganate solution used by the test sample, B = quantity in ml of potassium permanganate solution used in the blank test, oxygen number = 80 × (A–B). Use the arithmetical mean of the two measurements, rounded to 0.1.

Turbidity

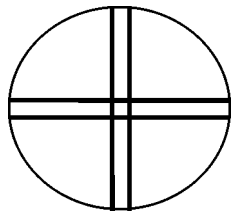
Sample preparation

The test liquid is prepared in the same manner as for the oxygen number; thus, the test liquid prepared for the oxygen number can also be measured for turbidity. Turbidity is measured with a glass turbidity tube (according to IDFB Testing Regulations, Part 11-B – see Section 2.6.3; EN 1164, 1998 – see Section 2.6.2).

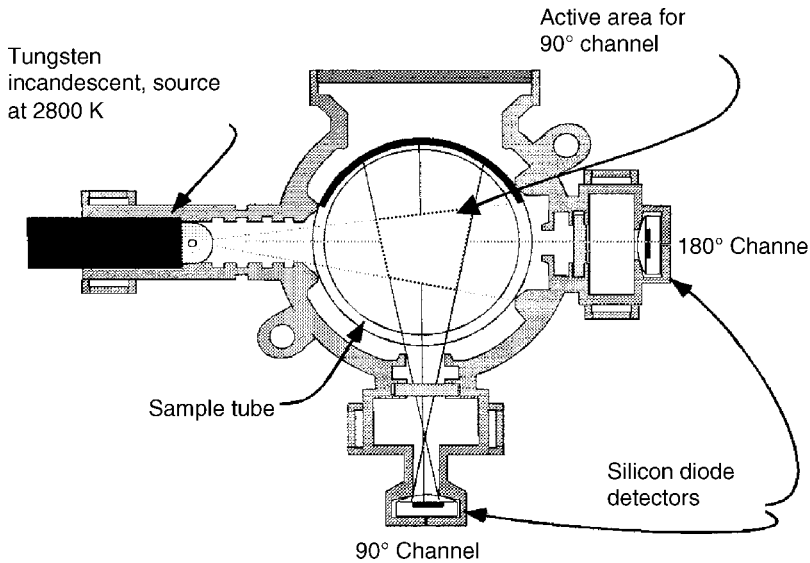
A disk with a double-cross marking (see Fig. 2.6) is placed at the bottom of a 550 mm or longer glass cylinder or tube. A light source of at least 600 lux (e.g. a strong flashlight) is properly positioned to illuminate the double cross marker. The cylinder is then filled with the test liquid. After 60 s, the level of the liquid is lowered until the cross is visible through the liquid. The height of the liquid is at that point recorded as 'turbidity in mm.' Test liquid is again added and then lowered until the cross is visible. The two visibility readings should not differ more than 10 mm, or the refill and lowering steps must be repeated. (EN 1164 recommends connecting the measuring tube to a communicating flask, allowing the liquid level to be raised or lowered more easily to the height of the visibility of the double cross.)

Turbidity is measured with an automated NTU meter (according to IDFB Testing Regulations, Part 11-A – see Section 2.6.3).

In an extensive IDFB round robin test made during spring 2002, the accuracy of the conventional tube-visibility test and the nephelometric measurement of turbidity units, or NTU, was compared. The findings were presented at the June 2002



2.6 Turbidity visibility chip. (*source*: IDFL).



2.7 LaMotte 2020 nephelometric turbidity meter. Light passing through clear water will travel in a straight line. Particles in turbid water will cause the light to scatter, giving it a cloudy or foggy appearance. The turbidity of a sample is determined by measuring the amount of scatter when light is passed through a sample. The higher the turbidity, the greater the amount of scatter. (*source*: *LaMotte 2020 Turbidimeter Instruction Manual*, p 9, source: online www.lamotte.com 2020 Turbidity Meter Instruction Manual; reprinted by permission).

IDFB meeting in Vancouver BC and both methods were approved as equally accurate (source: International Down and Feather Laboratory, IDFL; results on file).

The IDFB Testing Regulations, Part 11-A, as well as the data shown below, are based on tests performed with the LaMotte 2020 turbidity meter (see Fig. 2.7).

Procedure

The vial of the turbidity meter is filled with the liquid which is prepared as prescribed for the oxygen number test. Next, the NTU value is measured as

Table 2.3 Conversion of NTU to mm visibility height (*source*: IDFL)

Test tube visibility height (mm)	100	200	300	400	500	600	750	1000
Nephelometric turbidity unit (NTU)	30.0	15.0	10.0	7.5	6.0	5.0	4.0	3.0

prescribed in the operating instructions of the instrument (a very easy push-button test). At least three readings are taken without removing the vial.

Comparison/conversion
For the range of the 0–1000 mm tube, visibility height and the 0–50 NTU range of nephelometric measurements with the LaMotte 2020 turbidity meter, a conversion of the following relation was determined:

$$y = 3341.2x^{-1.0379} \quad [2.4]$$

where x is mm visibility height and y are the NTU turbidity units.

For practical use, the above relation may be rounded to:

$$x = 3000/y \quad [2.5]$$

For a first estimate, Table 2.3, conversion of NTU to mm visibility height, may be helpful.

The results of the turbidity tests, both tube and NTU above, are indicators for the cleanliness of the down and feather product. It is for this reason that some government regulations already request an NTU value of no more than ten (equaling a visibility level greater than 300 mm).

2.3.2 Solvent extracts

Oil and fat content

Oil and fat content is determined according to IDFB Testing Regulations, Part 4 (see Section 2.6.3) and EN 1163 (1996) – see Section 2.6.2.

Sample preparation
A representative sample of 4–5 g is weighed, put into an extraction thimble and oven-dried for 1 h at 105–110 ºC, then allowed to cool to room temperature in a desiccator. Then it is re-weighed in the same manner as in determining the moisture content (see Section 2.2).

The dried and weighed sample is put into an extraction thimble which is then placed in the Soxhlet extractor, from which the solvent-soluble ingredients are extracted from the down and feathers through at least 20 siphonings.

Solvents

Different norms specify different solvents. Diethyl ether, formerly widely used,

has lost its importance owing to the fear of peroxide explosions and also because its fumes are much heavier than air, allowing them to accumulate on the floor in potentially inflammable concentrations. Furthermore, it has a fairly wide flammability concentration range. Dichloromethane is still specified in some norms, but chlorinated solvents are increasingly being banned from general use by environmental regulations. Therefore, IDFB Testing Regulations Part 4 specifies petroleum, 60–80 ºC fraction (also called naphtha or petroleum ether):

The extract is filtered and the solvent first distilled off in the hot water bath, then evaporated at 100–105 ºC until at a constant weight. The oil and fat content is then calculated as a percentage of the weight of the test sample.

An oil and fat content of 0.5 to 1.5 percent in the pre-processed down–feather filling material is not only considered normal, but also desirable. Markedly higher oil–fat content may indicate insufficient cleanliness. Down and feathers with a too low oil and fat content become brittle and will therefore not be suitable for long-term use. (This is the main reason washing is preferred over chemical cleaning for down-filled products.)

Chemical analysis of the solvent extract

Odor is a first chemical indicator. For instance, natural fats and oils smell different from synthetic finishing chemicals. Chromatographic separation methods will reveal in more detail what has been left on the feathers during cleaning and what has been added during processing. These and other methods for the analysis of solvent extracts are particularly valuable for the verification of biological claims, or for the detection and even identification of traces of both permitted and prohibited chemical treatment methods. Each of these methods is, however, not usually part of routine testing, but is applied in more extensive quality control of down and feather products and the methods are often tools used to investigate complaints further.

2.4 Visual analytical methods

2.4.1 Content analysis

Content analysis according to IDFB Regulations, Part 3 (Section 2.6.3) and EN 12131 (1998) (Section 2.6.2) is as follows:

A separating cabinet (see Fig. 2.8) is equipped with enough weighing containers, usually glass beakers, to segregate the components and to contain them during weighing. A representative sample is placed in the bottom section of the cabinet. This is a 6-g sample with a declared or expected down content equal to or less than 30% or 4 g if the down content is higher than 30%.

First separation
Using tweezers, the individual pieces of plumage are separated into (A) whole

2.8 Separation cabinet (*source*: Peter Lieber).

waterfowl feathers, (B) whole land fowl feathers, (C) broken or damaged waterfowl feathers, (D) residue, and (Q) quill feathers (feathers which are over 100 mm in length or which have a quill point exceeding 9.5 mm in length). In this first separation, down clusters, plumules, nestling down, down fiber, and feather fiber are collected in container (E). The contents of all containers are weighed to an accuracy of 0.1 mg calculated as a percentage of the total weight of all components. (EN 12131 tolerates a maximum weight loss of 2% during this separation step.)

Second separation

A representative minimum sample of 0.2 g from the down/fiber container (E) is then subdivided in a second separation into down clusters (F), down fiber (G), waterfowl feather fiber (H), land fowl feathers and land fowl feather fiber (I) and residue (K). These components are also weighed and expressed as a percentage of the total weight of all components.

Reporting

The components, according to IDFB Testing Regulations Part 3 are reported as follows:

- F % down cluster
- G % down fiber
- A % waterfowl feathers

- H % waterfowl fiber
- C % broken and damaged waterfowl feathers
- Q % quill feathers
- B + I % land fowl feathers and fiber
- D + K % residue
- 100 %

Evaluation and labeling

To represent the visual analysis of the contents of the different components, several quality and labeling standards have been established. Based on EN 12934, down and feather filling materials are qualified in classes (Table 2.4). A problem for both consumer and manufacturer is that it is impossible to produce, for example, products with consistent 100% down content. There are often disparities between what is printed on the label (the manufacturer's claims for the product) and the actual composition of the down–feather filling after it has been laboratory tested. Standards have been developed detailing permissible deviations from the goal percentage. Table 2.5 represents permissible labeling–test disparities. Table 2.6 shows the range of percentages of goose and duck allowed for specific content labeling claims.

2.4.2 Microscopic specie analysis

Biochemical analysis of bird species as described in Section 2.2.4 would in most cases provide a result with the best possible accuracy. However, this method is not readily accessible for production plants using on-site quality control. It is for this reason that visual tests by means of a microscope or microfiche (see Fig. 2.9) are

Table 2.4 Quality classification according to EN 12934 (1999)

Fowl species	Classification	Content of other elements (%)	Down/feather composition
Waterfowl	Class I (also: 'new')	up to 5	down %, feather %
	Class II	more than 5 to 15	down %, feather %
	Class III	more than 15	down %, feather %, other elements %
Land fowl and blends of land- and waterfowl	Class IV (also: 'new')	up to 5	down %, feather %
	Class V	more than 5 to 15	down %, feather %
	Class VI	more than 15	down %, feather %, other elements %
Land fowl and/or waterfowl	Class VII	not specified	unspecified composition

Table 2.5 Permissible disparities between test results and labeling (content analysis)

Denomination on label (%)	Test result range (%)
100	95.0–100.0
90	85.0–94.9
80	75.0–84.9
70	65.0–74.9
60	55.0–64.9
50	45.0–54.9
40	35.0–44.9
30	25.0–34.9
20	17.5–24.9
15	12.5–17.5
10	7.5–12.4

Source: EN 12934 (1999), Table 2, p 8 – see Section 2.6.2

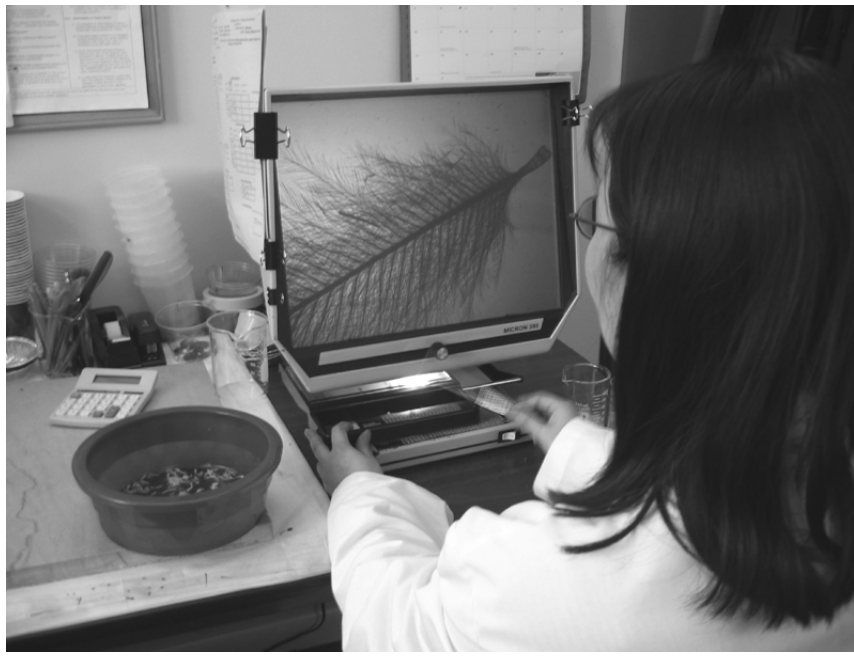
Table 2.6 Goose–duck percentages for labeling

Composition (%)		Denomination
70.0–89.9	goose	
10.0–29.9	duck	goose
50.0–69.9	goose	
30.0–49.9	duck	goose/duck
30.0–49.9	goose	
50.0–69.9	duck	duck/goose
10.0–29.9	goose	
70.0–89.9	duck	duck
0–9.9	goose	
90.0–100	duck	pure duck

Source: EN 12934 (1999), Table 3, p 9 – see Section 2.6.2

still widely performed. Fortunately, nature has equipped the birds' plumage with certain distinctive marks. Best known are the nodes on the down or feather barbules.

IDFB Test Regulation Part 12, Determination of Feather and Down Specie, requires the visual evaluation of all feathers in a 1 g feather sample and all down in a 0.2 g down sample. Several years of research show that testing all pieces at a specific weight is more accurate than testing a certain number of pieces, as was formerly the common practice. This IDFB testing regulation describes the nodes ('fingerprints') of goose, duck, and land fowl feathers and down as follows (see Figs 2.10, 2.11 and 2.12).



2.9 Species identification (*source*: Peter Lieber).

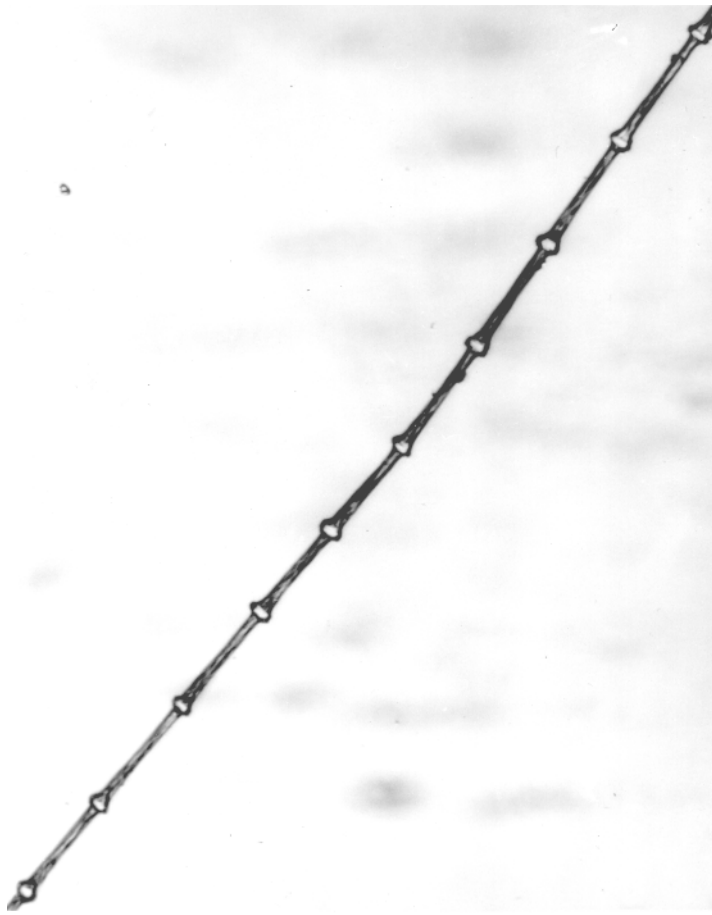
2.4.3 Volume measurement

Filling power

One important feature of feathers, and in particular of down, is their capability to trap air and keep the bird from loosing heat by convection or conduction with a minimum of structural material – a minimum of weight per volume unit, lower than any synthetic product. However, if this were not combined with high resilience and a unique structural 'memory effect' (the sum being what is called filling power or fillpower), feathers and down would be worthless to humans. Several methods are in use; the following description is based on IDFB Testing Regulations Part 10 (see Fig. 2.13):

To measure filling power, 30 g of the down–feather specimen are loosely filled into a cylinder (other test standards use 20 g or one US-ounce) and, according to IDFB Regulations Part 10**,** loaded with a plunger at a specific pressure of 0.149 g cm^{-2} (slightly higher according to the Japanese Industrial Standards, JIS norm). The filling power of down and feathers is usually first measured immediately after the washing and sorting process, and this value is used as one of the quality indicators or claims.

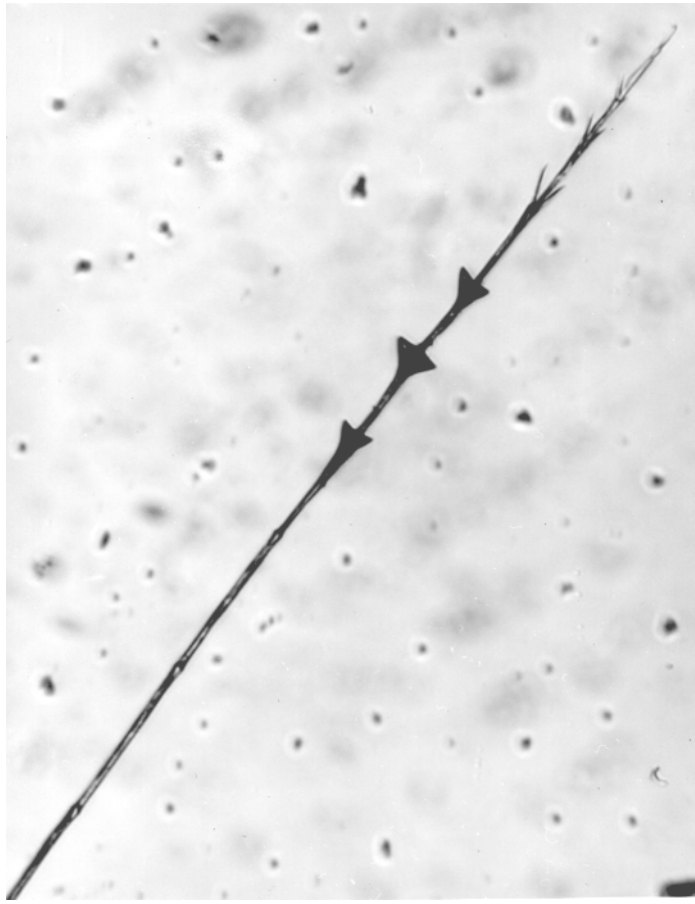
Filling power (in EN 12130, 1998, also called 'massic volume') is expressed in various ways:



2.10 Goose plumage has small nodes which generally begin in the middle area of the barbule. The distance between nodes of a goose feather or down is two times or more the distance between the nodes of a duck (*source*: IDFL).

- in millimeters filling height in a standardized measuring cylinder
- in volume per weight unit, in $cm^3\ g^{-1}$ or $l\ kg^{-1}$ (according to EN 12130, 1998)
- in volume per weight unit, in cubic inches per ounce, cu in/oz (US standards)
- in weight per volume, in $g\ cm^{-3}$ (apparent density)
- in centimeters filling height (according to Japanese standards).

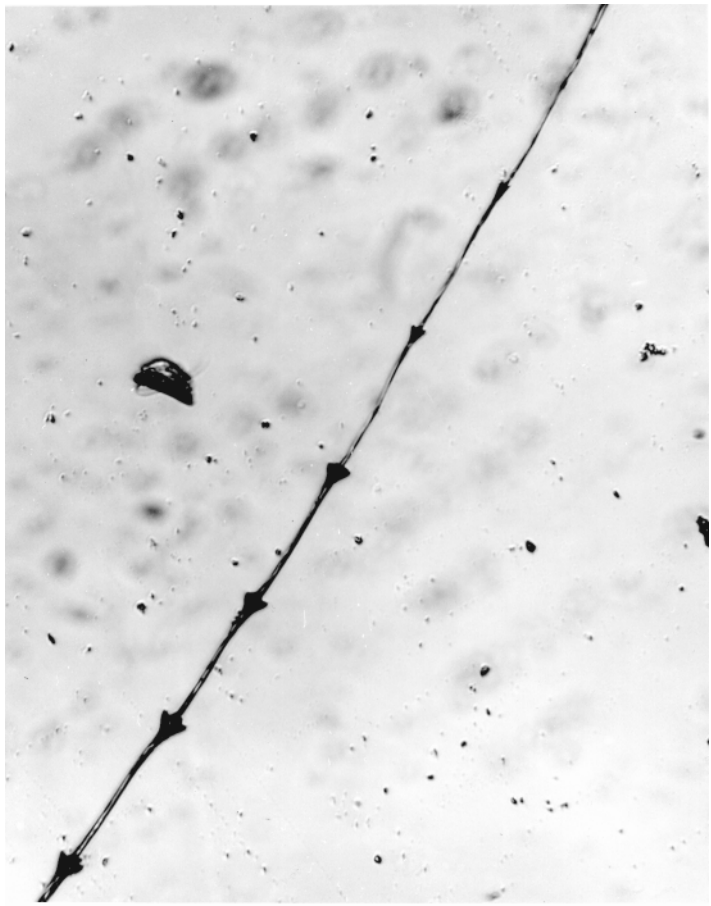
Down and feathers are often vigorously compressed either as processed bulk material in the form of bales or in finished products (e.g. sleeping bags or garments). In this compressed form, they can be transported and stored over longer periods of time. Compression temporarily lowers the filling power of down and feathers.



2.11 Duck plumage has between one and six (often three) nodes near the tip of the barbule. These nodes are relatively large. The distance between the nodes of a duck feather is very short. Prongs are often found beyond the most distant duck node (but are not used in species identification) (*source*: IDFL).

However, in most cases filling power is restored during use and laundering of the product.

Manufacturers, retail buyers and end-use customers would like to be able to verify the filling power quality of the product. This is difficult to do without actually using the product, so product use is often replicated in a laboratory setting. The testing of physical behavior of a natural organic product often makes little sense without taking chemical characteristics into consideration. This is particularly demonstrated in the case of down and feathers owing to their interaction with water molecules. It is this interaction that helps the birds'



2.12 Land fowl (chicken) plumage has a series of evenly spaced slight nodes or swellings which give the barbule the appearance of bamboo. The protrusions or nodes of land fowl extend nearly the entire distance of the barbule (*source*: IDFL).

plumage activate its structural memory and revive it to its filling power potential.

As in any chemical reaction, the absorption or desorption of water is reversible and is connected to a reaction constant, incorporating these physicochemical rules:

- Concentration: obviously, down absorbs water in its liquid form (i.e. the down is submerged in the water) faster than from water present in the atmosphere as humidity. Likewise, it absorbs more in moist air (e.g. steam) than in dry air.
- Time: every chemical reaction, even the most vigorous explosion, takes time each reaction has a specific speed, based on its individual reaction constant.

2.13 Filling power cylinders. Manual (left) and automated (right) (*source*: Peter Lieber).

- Temperature: a chemical reaction generally doubles its speed with every 10 °C rise in temperature.
- Motion: down and feather barbules may be physically restricted from regaining their original geometrical form. Shaking will loosen these restrictions.
- Conditioning: down and feathers require conditioning. Usually, they are box conditioned in screened boxes which are placed in a standard climate room (see Fig. 2.14). At least 72 h of adjusting must be allowed for loose down specimens. Elevated temperatures help speed up the revival. Knowing this, manufacturers and testers have simulated what is done in the cleaning process through tumble drying.

A further developmental step in conditioning is the simulation of body perspiration (which is known to help sleeping bags or comforters to 'rise') by adding a wet towel to the tumbler. Reconditioning the down and feathers to their original volume quality level, which is measured immediately after the original washing and drying, may require 'steaming', that is, direct steam injection into the conditioning box, then allowing the sample to dry off by means of a hair dryer and finally allowing it to adjust to standard climate. Looking at the graph (see Fig. 2.15), it becomes obvious that about 80% of the original filling power (here in

2.14 Conditioning box (*source*: Peter Lieber).

cu in/oz) may be reached in a short time. But to regain the final 20%, the down needs either time or a temperature/moisture boost.

Warmth–insulation

Down and feathers are designed to keep the bird warm. Likewise, we use them to keep ourselves warm and comfortable. It follows that manufacturers and quality control organizations are constantly searching for a meaningful comfort factor. TOG values (describing the thermal insulation properties of textiles as 1 TOG =

0.1 m^2 K W^{-1}) are well known in Great Britain and are used for bed covers as well as for down clothing. The sleeping bag industry has also developed regulations that specify the comfort range of environment temperatures. Other branches of the down and feather industry will soon follow with similar specifications or classifications. In the end, these comfort factors all relate to filling power.

Down–feather ratio

It is obvious from Figs 2.1 and 2.2 that down provides a better insulation per unit of weight than do the feathers. It is therefore useful to include with this description of quality control methods for feathers and down, a graph which shows the filling power in approximate relation to the down/feather ratio (see Fig. 2.16).

2.5 Finished product quality

Textile fabric testing is vital to the quality control of down and feather products. Fabric that can confine down and feathers within predetermined volumes and shapes also prevents dust or mites from contaminating the down filling. Consequently, some basic testing of textiles is necessary for good quality control.

Figure 2.16 does not take into consideration the absolute top range of filling power qualities of around 900 cu in/oz. It does demonstrate that the filling power value drops quickly with even a small addition of feathers. But the resilience-force of feathers is usually higher, making them (or admixtures to down) well suited for pillows.

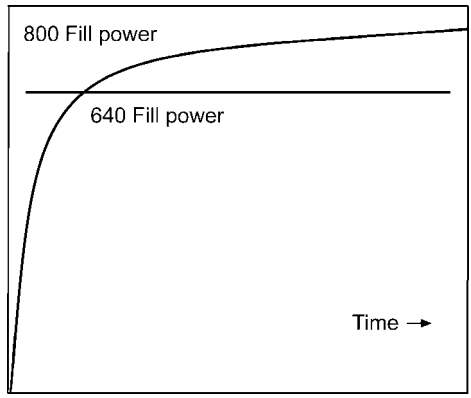
Figure 2.16 raises two questions:

Q1: Why is filling power represented in cu in/oz and not in metric units, cm^{-3} g^{-1} or g cm^{-3}, or in millimeters filling height, the actual reading the instrument takes before converting it into filling power values based on the filling weight?

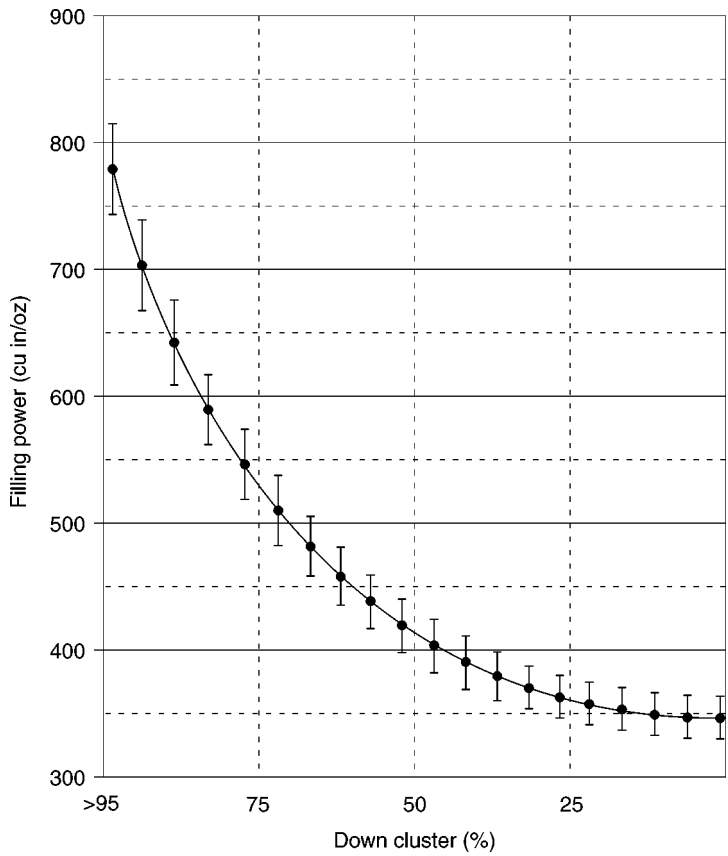
A1: As an example, 800 cu in/oz, if converted to the metric unit (at an identical specific load of 0.149 g cm^{-2}), equals 436.8 l kg^{-1}, and is expressed in this form according to EN 12130 (1998). Psychologically, the larger cubic inch measurement is automatically identified with better quality. In addition, the easy to read, comma-free three digit cubic inch figure (in most cases displayed only in 10 or even 50 unit steps, which is easier yet to read and to conceive) is historically older. It is most likely to remain in friendly co-existence with metric units.

Q2: Does 900 filling power (i.e. 900 cu in/oz) really exist, as sometimes claimed?

A2: Yes, but only in very rare cases and the supply of such down is very small. Since market demand may be much higher than the available down, buyers should be cautious before accepting a 900 filling power claim.



2.15 Filling power increases with conditioning time. (*source*: IDFL).



2.16 Filling power plotted against down cluster (content 0–95%) (*source*: IDFL).

2.5.1 Physical downproofness

Downproofness describes the ability of fabric to keep down and feathers enclosed. There are several test methods which simulate the conditions of actual product use in a time-lapse manner.

US method

A small pillow made of the fabric to be used in the finished product is filled with down and feathers and tumbled in a chamber with rubber stoppers. Both chamber and pillow are examined for leakage counts and rated from 1 (not downproof) to 5 (excellent downproofness) on a comparative basis.

EN method

EN methods EN 12132-1 (1998) and 12132-2 (1998) describe methods of determining downproofness. Sample cushions are filled with specified down and feather mixtures, then tested by either a rubbing motion (EN 12132-1) or by impact (EN 12132-2), simulating the shaking and pounding that occurs in the normal use of bedding or clothing. The samples are then inspected for feathers penetrating the fabric and are rated (see Table 2.7).

2.5.2 Air permeability

Determining air permeability of a fabric is another standard test used in the quality analysis of textiles. Measuring air flow through a specific area of the fabric at standardized differential pressure is a good indicator of downproofness. In general, the lower the air permeability of the fabric tested, the less likely it is that feathers and down will penetrate it. However, these test results are not necessarily conclusive. Some fabrics may fail the air permeability test but pass the physical downproof test and vice versa.

2.5.3 Thread count

Thread count claims are commonly printed on down product labels. The number

Table 2.7 Down proof tests according to EN 12132 (1998)

Impact test (EN 12132-1)	Quality rating	Rubbing test (EN 12132-2)
0 to 5 penetrations	Good	0 to 10 penetrations
6 to 15 penetrations	Acceptable	11 to 20 penetrations
More than 15 penetrations	Not acceptable	More than 20 penetrations

of threads used in weaving is counted by the square inch (or square centimeter). For example, a thread count of 180 may mean a weave of 100 vertical threads (the warp) and 80 horizontal threads (the weft) per square inch. In metric units, it would be designated a 40–32 weave (40 warp threads and 32 weave threads per square centimeter). The thickness of the thread is also a factor in this equation. The finer the thread, the more there will be in one square unit, producing a higher thread count. Normally, the higher the thread count, the better the downproofness. However, yarn size and weaving techniques make some high thread count material unacceptable for down products whereas some low thread count fabrics are acceptable. Before using new fabrics, a careful evaluation of downproofness should be completed.

What is considered a 'high thread count' in down and feather products? A thread count of between 200 and 400 (per square inch) is sufficient, but thread count can go as high as 800 or 1000 threads. (It is important to note that for down and feather quality control purposes, two-ply threads are counted as one thread).

2.5.4 Product labels

As mentioned at the beginning of this chapter, uniform testing procedures provide the methods used to control the quality of down and feather products. By using standardized terms to reflect the quality of down and feather products on the product label, the consumer can be confident that a pillow labeled '100% goose down,' is what it is claimed to be. In Europe, for instance, the European Norm (EN) is standard. In reference to product labeling, the following norms are applied:

EN 12131 (1998) 'Determination of the quantitative composition of feather and down,' describes how the composition of down samples is to be analyzed, calculated and reported.

EN 1885 (1998) 'Terms and definitions,' supports EN 12131 by identifying and defining the components that are to be separated and includes pictures.

EN 12934 (1999) 'Composition labeling of processed feathers and down for use as the sole filling material,' establishes provisions for how the composition of the plumage for use as fillings, and of the fowl species from which such components are derived, are to be represented on the product label (see also Figs 2.9 and 2.10 in Section 2.4.2).

Other norms are created to present these values on labels in a concise form. Despite such attempts to standardize labeling, the problem of standardizing norms worldwide is on-going.

Although the CEN (European Committee for Standardization) is working to solve this problem within Europe, these standardized procedures have not necessarily been adopted by manufacturers outside Europe, whereas the quality control testing procedures are more widely accepted. However, tolerances used to classify feather and down products can vary widely. As an example, EN 12934 (1999)

clearly requires down content ranges to be identified in numbers. According to Table 2.5 in Section 2.4.1, a product labeled '90% down' must test between 85.0% and 94.9% down clusters. Yet in other areas of the world, a product containing a minimum of 75% down may still be labeled as 'down.' The problem is summed up well in EN 12934: 'Fillings of feather and down have not been covered by national standards dealing with denomination and composition in all CEN countries. Where standards exist they often differ from each other.'

2.6 References

2.6.1 Normative references

Table 2.8 shows which IDFB Regulations and European Norms should be followed for each type of test.

2.6.2 Sources for citations

CEN (European Committee for Standardization/Comité Européen de Normalisation), rue de Stassart, 36 B-1050 Brussels.

EN 1161: 1996 E, 'Feather and down – Test methods – Determination of moisture content'. CEN: Brussels, 1996.

EN 1162: 1996 E, 'Feather and down – Test methods – Determination of the oxygen index number'. CEN: Brussels, 1996.

EN 1163: 1996 E, 'Feather and down – Test methods – Determination of the oil and fat content'. CEN: Brussels, 1996.

EN 1164: 1998 E, 'Feather and down –Test methods –Determination of the turbidity of an aqueous extract'. CEN: Brussels, 1998.

Table 2.8 Normative references

Test	IDFB-Regulation	European Norm
Feather and down–sampling in view of tests	Part 2	EN 1883
Moisture content	Part 5	EN 1161
Acidity (pH)	Part 6	N/A
Oxygen number	Part 7	EN 1162
Turbidity (nephelometric)	Part 11-A	N/A
Turbidity (tube visibility)	Part 11B	EN 1164
Oil and fat content	Part 4	EN 1163
Content analysis	Part 3	EN 12131
Quality classes	N/A	EN 12934
Terms and definitions	N/A	EN 1885
Filling power (volume measurement)	Part 10	N/A
Comfort range (sleeping bags)	N/A	EN 13537
Downproofness	N/A	EN 12132-1/2
Species identification	Part 12	N/A

EN 1883: 1998E, 'Feather and down – Sampling in view of tests: Table A.1 and Table A.2. CEN: Brussels, 1998.
EN 1885: 1998/prA1:2003, 'Feather and down – Terms and definitions – Amendment 1'. CEN: Brussels, 1998.
EN 12130: 1998 E, 'Feather and down – Test methods – Determination of the filling power (massic volume)'. CEN: Brussels, 1998.
EN 12131: 1998 E, 'Feather and down – Test methods – Determination of the quantitative composition of feather and down (manual method)'. CEN: Brussels, 1998.
EN 12132-1: 1998 E, 'Feather and down – Methods of testing the down proof properties of fabrics – Part 1: Rubbing test'. CEN: Brussels, 1998.
EN 12132-2: 1998/prA1: 2003 E, 'Feather and down – Methods of testing the down proof properties of fabrics – Part 2: Impact test'. CEN: Brussels, 2003.
EN 12934: 1999 E, 'Feather and down – Composition labeling of processed feathers and down for use as sole filling material'. CEN: Brussels, 1999.

2.6.3 IDFB Testing Regulations

The IDFB Testing Regulations cited below were published by IDFB, Aschaffenburg, Germany. The IDFB moved to Dornbirn in January 2005 (see below). These documents are not paginated, nor are they available on-line.

IDFB (International Down and Feather Bureau)
Current address: Marktplatz 9, A-6850 Dornbirn, Austria
Contact: Mr Siegfried Böhler, Secretary
Tel: +43 5572 382223
Fax: +43 5572 31393
Email: idfb@idfb.org

IDFB Testing Regulations:

1. Part 1 Conditioning
2. Part 2 Sampling
3. Part 3 Determination of the composition (content analysis)
4. Part 4 Determination of the oil and fat content
5. Part 5 Determination of the moisture content
6. Part 6 Determination of the acidity (pH factor)
7. Part 7 Determination of oxygen number
8. Part 10 Determination of filling power (volume measurement)
9. Part 11-A Determination of turbidity (with automated NTU meter)
10. Part 11-B Determination of turbidity (with glass turbidity tube)
11. Part 12 Determination of feather and down species

2.6.4 Other sources

For the 'LaMotte 2020 Turbidity Meter' in Fig. 2.7, see www.lamotte.com/pages/common/pdf/manuals/1799.pdf

Although the above is the internet page title, if you type it in, the page is apparently unavailable. To find it, go to www.lamotte.com, click on 'product manuals' and then click on '2020 Turbidity Meter.' This takes you to the 2020 Turbidity Meter Instruction Manual. The image shown in Fig. 2.7 is on page 9 and the specification for 'Nephelometric turbidity, calibrated in NTU' is given on page 5.

3

Chemical analysis of leather

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3.1 Introduction

Leather is one of the materials used earliest as clothing by humans to protect them from the cold and as shields when combating animals and fighting enemies. Nowadays, it still has wide application in the making of garments, gloves, shoes, wallets, suitcases, upholstery, sporting goods, book covers, pipe organs and much more. Leather is produced in three steps (Thorstensen, 1993). The first step is removal of the unwanted components from the animal skin, leaving a network of fibres of hide protein and cutting the skin to the desired layers. Cow or pig skin can be cut into between one and three layers for different end uses. The second step is to treat this network of hide with tanning materials to produce a stabilized fibre structure. The third step is to build on to the tanned leather surface characteristics of fullness, colour, softness and lubricant, producing a useful product.

The purpose of tanning is to apply chemical stability to the leather by creating stable chemical bonds to the chemically active sites on the collagen fibres. Some tanning agents also promote cross-links among the collagen fibres (Piltingsrud and Tancous, 1994). Tanning materials (tannages) can be divided into three groups: vegetable tannins, inorganic agents (salts of bi- or trivalent metals, including chromium, aluminium and zirconium) and synthetic tannages (syntans). Sometimes, in order to improve the properties of the leather, a re-tanning with chromic salt can be performed after vegetable tanning. The vegetable tanning imparts a natural brown colour to the leather, whereas the chrome tanning gives the leather a pale blue colour.

Materials used for leather dyeing are usually acid dyes, direct dyes, mordant dyes (Thorstensen, 1993) and reactive dyes (Shao and Zhao, 1984). Basic dyes are primarily used for dyeing vegetable tanned leather (Sandoz, 1949).

Based on the production processes of leather, this chapter will discuss the chemical tests which allow identification of leather from its synthetic substitutes and analyses of tanning materials. Some tests of important leather properties, such as pH, fat, chrome and ash content will also be described. The azo dye tests will be illustrated here since many countries have already adopted mandatory regulations

prohibiting the use of certain azo dyes in consumer articles. This chapter will only discuss some important properties of leather such as resistance to chemical penetration, resistance to oil, cut resistance, water vapour permeability, water absorption and leather stability (ageing). Regular physical tests, including tensile strength, shear strength, elongation, colour fastness, which are similar to physical tests of textiles, have been described elsewhere (Saville, 1999).

Resin finishing and coating are widely used to improve the leather properties (Thorstensen, 1993). Chemical analyses of finishes and coating are often required. Description of such analyses can be found in Chapter 6 and Chapter 7 of this book, respectively.

Leather making produces a large quantity of effluents, which contain a considerable amount of chromium. Chapter 9 of this book discusses the treatment of wastewater including heavy metals. Section 3.3.2 of this chapter will discuss the analysis of chromium content in solutions and the recycling of chromium briefly.

This chapter does not purport to explain all of the safety concerns. The users of the following test methods must have knowledge of and obey all the laboratory safe policies to avoid injury during testing.

3.2 Identification of leather

More and more products made from synthetic materials substituting for leather have been introduced into the market. Synthetic leather substitutes are usually non-woven fabrics coated or laminated with some kind of polymer. It is very often desired to identify if a product is a genuine leather or a synthetic substitute. The following four test methods can be used to identify the samples.

3.2.1 Burn test

Cut a small piece of the sample and burn it in the fume hood. Leather burns without flame but releases a smell of burning protein. However, the synthetic leather burns without smell of burning protein. The burn test is simple and quick. It can be used as a preliminary test and confirmed by the other methods.

3.2.2 Sodium hydroxide test

Naturally, leather is composed of collagen fibres which have been modified or cross-linked by tanning. Collagen fibres that are not cross-linked can be dissolved in a solution of sodium hydroxide on boiling (Shao and Filteau, 2004a). Prepare a solution of 10% (w/w) sodium hydroxide. Boil a piece of the sample (around 0.2 g) in 100 ml solution of 10% (w/w) sodium hydroxide in a 250 ml flask with a condenser in a fume hood for 30 min. After cooling, observe the sample in the solution. A dispersion of the sample in the solution suggests that the sample is a genuine leather because collagen fibres that are not cross-linked dissolve in the

solution, while those that are cross-linked do not dissolve and leave particles in the solution. The synthetic leather substitutes, usually with super-microfibres of nylon, polyester and polypropylene, do not dissolve in the solution of 10% (w/w) sodium hydroxide under the above conditions.

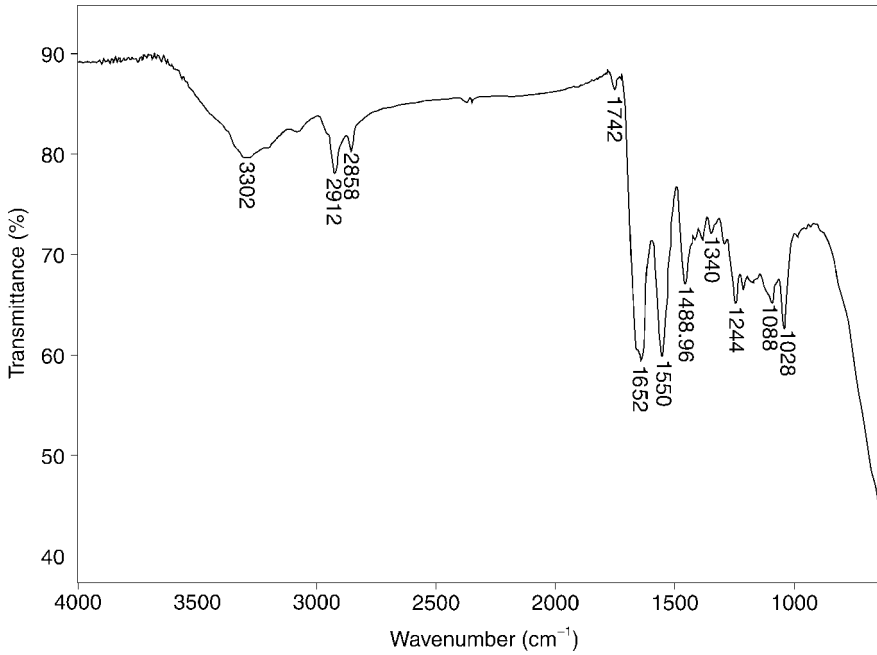
3.2.3 Infrared spectroscopic analysis

Infrared spectroscopic analysis is a useful method for distinguishing genuine leather from the synthetic type. The energy of most molecular vibrations corresponds to that of the infrared region of the electromagnetic spectrum (William and Fleming, 1998). Molecular vibrations may be detected and measured in an infrared spectrum usually ranging from a wavenumber of 4000 cm^{-1} to 400 cm^{-1}. Each functional group has a vibration frequency with well-defined infrared spectrum characteristics for the group. These different functional groups are summarized in the literature (Nakanishi, 1962; Sadtler Research Laboratories, 1974; Skoog and Leary, 1992). Infrared spectroscopic analysis is carried out by identification of the functional group or by comparison of the spectrum of the tested material with those of known materials. Spectra that are to be compared should be obtained by the same technique and under the same conditions. Before the leather sample is analysed, the surface layer of the sample should be peeled off because most leather is finished on the surface with wax, nitrocellulose, resin or other materials.

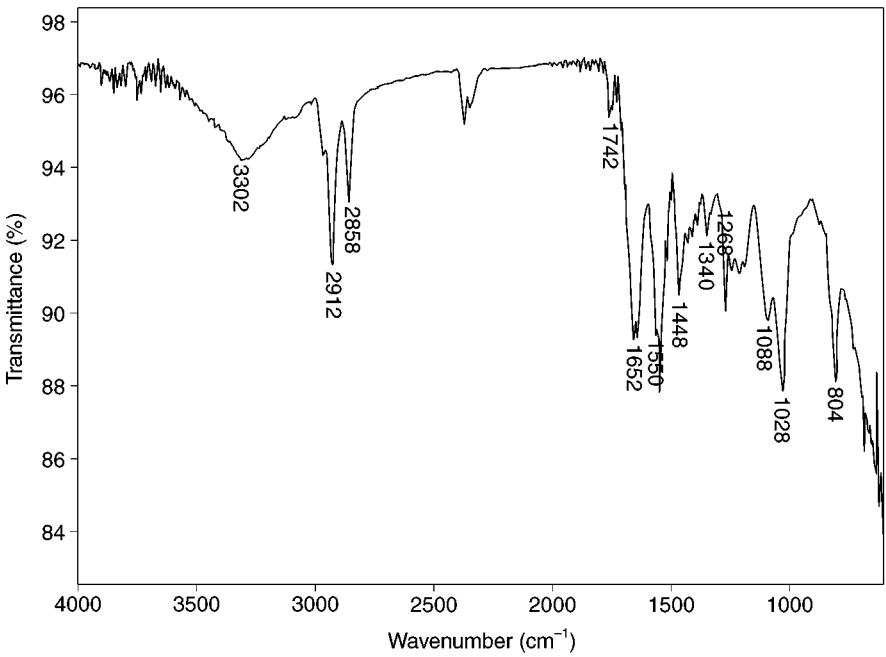
The infrared spectrum of the sample can be obtained either by an alkali halide pressed pellet technique or by different reflection techniques. The sample powder is ground into small particles and 3–10 mg are mixed uniformly and pressed with approximately 300 mg of alkali halide powder (such as sodium chloride (NaCl) or more commonly potassium bromide (KBr)) by means of the apparatus electrohydraulic press with an evacuable KBr die. The quantity of the leather powder used for the pellet should be determined so that the spectrum that will be obtained has an absorbance of the strongest band of around 1 unit. The transmission spectrum can be obtained by placing the thin and uniformly pressed pellet of leather powder–KBr perpendicular to the infrared radiation.

A method of horizontal attenuated total reflectance (HATR) by Fourier transform infrared spectroscopy (FTIR) is considered more useful for infrared spectroscopic analysis of leather samples. By this method, the sample is simply put on the flat plate of ZnSe crystal or KRS-5 crystal of the HATR accessory. The Fourier transformation of the interferogram is converted by the computer into a plot of absorption against wave number that resembles the usual IR spectrum (William and Fleming, 1998).

Figure 3.1 and Fig. 3.2 are FTIR spectra of cow leather and sheep leather, respectively. They are obtained by the HATR method for 20 scans at a resolution of 4 cm^{-1} in transmittance over wavenumber. From the figures, it can be seen that the spectra of leathers have most important absorption bands at 3300, 2910, 2860, 1742, 1650, 1550, 1445, 1340, 1244, 1088 and 1028 cm^{-1}. The assignment of the



3.1 FTIR spectrum of a type of cow leather.



3.2 FTIR spectrum of a type of sheep leather.

Table 3.1 IR absorption bands of leather (adapted from Bienkiewicz, 1983)

Wave number (cm^{-1})	Properties of the bands	Assignment
3302	Amine band	Stretch of =N–H group
2912		Asymmetric stretching bonds of =NH and – CH_3, –CH_2– groups
2858		Symmetric stretching of –CH_2– groups
1742	Increases in acids and with heating	–COOH un-ionized group
1651	Very strong	Amide band I and –C=O stretching in helical structure and in coiled structure
1550		Amide band II
1448		Bonding oscillations of –CH_3, –CH_2– groups
1340	Very strong	Amide band III
1244	Appears by action of acids or heating	Amide band III of helix structure
1088 and 1028		Stretching of C–O group or –C=S group (some amino acids with sulphur)

molecular vibrations is explained in Table 3.1 (Bienkiewicz, 1983). The different absorption bands (at 1268 and 804 cm^{-1}) between the spectrum of the cow leather and that of the sheep leather are due to the different chemical structures between these two kinds of leather. An absorption band at around 2400 cm^{-1} comes from carbon dioxide in the environment.

Based on the absorption bands of leather listed in Table 3.1, it can be determined whether the tested sample is a genuine leather or synthetic polymer. However, care should be taken with the spectra of nylon, silk and wool which could have many of the absorption bands listed in Table 3.1, because they have the structures of amide bands. They can be distinguished from the genuine leather by the other three methods described in this section.

3.2.4 Microscopic observation

After the surface layer of the leather sample is peeled off, the sample can be observed under a microscope. The collagen fibres of leather differ in appearance from non-woven fabrics and from the uniform polymers of coating and lamination in the synthetic substitutes. However, some artificial leathers in the market do better than the real leather. It has been reported that some leather substitutes with super-microfibres of nylon, polyester and polypropylene can have similar views of cross-section under the microscope (Cheng, 1998). A combination of the burn test, the chemical test, the infrared spectroscopic analysis and/or the microscopic

observation is able to identify a genuine leather from artificial ones with high confidence.

3.3 Analysis of tanning materials

Tannages are substances which have the chemical and physical properties necessary to convert animal hides and skins into leather. Tanning materials are commonly divided into three groups: vegetable, metal and synthetic tannages. The vegetable tannins can be obtained from various types of plant barks (such as hemlock, wattle), leaves (such as sumac), nuts (such as chestnut) and roots. The most important metal tannage is chrome compound. The others are salts of aluminium, titanium or zirconium. One group of synthetic tannages is syntans which contain phenolic hydroxyl groups, and as such have the ability to react with the hide protein in the presence of formaldehyde or its like to produce leather. The second group of synthetic tannages contains other materials in an aldehyde-type condensation, including melamine–formaldehyde, dicyandiamide–formaldehyde, dialdehyde starch and glutaraldehyde (Thorstensen, 1993). Because of the importance of the tanning materials to leather production, methods for analysing the vegetable tannins, chromium sulphate and formaldehyde will be described in the following section.

3.3.1 Analysis of vegetable tannins

Analysis of vegetable tannins is used to determine the tannin content in the extract solution from the raw or spent materials. The tannin analysis method set up by the American Leather Chemists Association (ALCA, 1954a) is based on the absorption of materials from the extract by hide protein. It is not based on chemical analysis of a true tannin molecule.

Filter a testing solution prepared from tannin extracts from the raw or spent materials on a standard filter paper. Pipette 50 ml of the filtrate to a preweighed beaker with stopper. Dry the testing solution overnight in a forced-air oven at 100 ± 2 ºC. Cool the beaker with the stopper in a desiccator. Weigh the beaker containing the solid residue. The solid residue converted to each litre of the filtrate is defined as the total soluble solids of the testing solution (g l^{-1}).

Dry the hide powders in an oven for 16 h and cool in a desiccator. Add 1 ml of 3% chrome alum $CrK(SO_4)_2$ solution for each gram of air-dried hide powders at 25 ± 2 ºC for 2 h. Wash the pretanned hide powders thoroughly with water at 25 ± 2 ºC. Filter the suspended hide powders and squeeze the powders to obtain about 75% of the moisture in the powders. Weigh 50 g of the wet hide powders (containing approximately 75% moisture), equivalent to 12.5 ± 0.3 g of dried powders, and add them to a 200 ml volumetric flask. Fill the flask with testing solution to the 200 ml mark. Close the bottle and keep the solution at 25 ± 2 ºC for 15 min. Filter the solution immediately into a beaker containing 2 g of kaolin.

Squeeze the drained hide powder. Mix the filtrate and kaolin thoroughly. Filter the solution on a standard filter paper. Collect the filtrate and transfer the filtrate to a preweighed beaker with a stopper using the same pipette (50 ml) for total solid measurement. Dry the testing solution overnight in a forced-air oven at 100 ± 2 °C. Cool the beaker with the stopper in a desiccator. Weigh the beaker containing the solid residue. The solid residue converted to each litre of the filtrate is defined as the non-tannins of the testing solution (g l^{-1}). The concentration of the tannins in the testing solution is calculated by:

$$\text{Tannins (g l}^{-1}\text{)} = \text{total soluble solids (g l}^{-1}\text{)} - \text{non-tannins (g l}^{-1}\text{)} \quad [3.1]$$

3.3.2 Chrome recycling and analysis of chromium sulphate

Chrome tanning is the most important tanning method in leather production. The effluents from the tannery house contain a considerable amount of chromium. A limit to the chromium discharge is mandated by pollution regulations in almost every country. It is necessary to recycle chrome tanning materials from the effluents. The most common way of recovering the spent chromium salts is by precipitation (Thorstensen, 1993). The pH of the effluents may be raised to the precipitation point of the chromium salts, which precipitate as a hydrated chromium oxide.

The precipitation of chromium hydroxide is complicated by the amphoteric nature of chromium. At pH below 5–6, chromium is predominately cationic with chromium accepting hydroxyl ions. At pH 7–8, chromium hydroxide acts as a weak acid and becomes an anion. Only in a very narrow pH range (pH 6–7) will the precipitation have a minimum charge and minimum hydration. Precipitation with sodium hydroxide or sodium carbonate will result in a gelatinous precipitate. If calcium hydroxide (lime) is used, better precipitation will be obtained. Very good success has been attained by precipitation with magnesium hydroxide, which is less soluble than calcium hydroxide and as a result, the hydroxyl ion concentration is less and the pH lower. At pH 5–7 the magnesium hydroxide will come into equilibrium with the chromium so that the precipitate will be formed with minimum hydration. The precipitate can be dissolved by adding sulphuric acid and be reused for tanning.

No matter what the source of chromium tannages, either from raw materials or from recycled solutions, care must be taken to maintain the quality of the leather. This can be only achieved by constant chemical analysis and chemical control. The chromium content in the solution can be tested by the following two methods, titration and atomic absorption analysis:

Titration method

The concentration of chromium sulphate can be titrated by an oxidization–

reduction reaction (Meites, 1963). The principle of the test method is to oxidize all of the chromium compounds in the tanning solution to Cr^{6+}, followed by the addition of potassium iodide to the solution. The released iodine is then titrated with a standard solution of the reduction agent sodium thiosulphate. The reactions can be expressed as (Strouts *et al.*, 1955):

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 = Cr_2(SO_4)_3 + 3I_2 + 4K_2SO_4 + 7H_2O \quad [3.2]$$

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6 \quad [3.3]$$

The concentration of the initial chromium sulphate solution for practical tanning is around 15–20% (w/w), which should be diluted for analysis. Pipette 10 ml of the initial chromium sulphate solution into a 1 l volumetric bottle. Dilute the solution with distilled water to the 1 l mark. Pipette 100 ml (V_1) of the diluted solution into a 250 ml triangular beaker. Add 5 ml of hydrogen peroxide (around 33% w/w of H_2O_2) and 5 ml of 10% potassium hydroxide (or sodium hydroxide). Boil the solution gently for 1 h to oxidize Cr^{3+} to Cr^{6+} and to get rid of excess peroxide. Add 10 ml of 6 N H_2SO_4 to acidify the solution. After standing in the dark for 5 min, add 20 ml of 10% (w/w) potassium iodide. The solution turns to a dark reddish brown owing to the formation of iodine. Titrate the iodine in the solution with 0.1 N standard solution of sodium thiosulphate until the colour of the solution turns to yellow. Add 1–2 ml of starch solution (1% w/w) as an indicator. The colour of the solution turns to dark blue. Continue titration until the colour just disappears. Record the volume of the standard solution of sodium thiosulphate used (V_0). The concentration C (g l^{-1}) of initial chromium sulphate solution can be calculated by the following equation:

$$C_{Cr_2(SO_4)_3}\ (g\ l^{-1}) = \frac{1000}{10} \times \frac{N_0 \times V_0}{V_1} \times \frac{392}{6} \quad [3.4]$$

where 10 and 1000 are the volumes (ml) of the initial solution withdrawn and the volume diluted, respectively; N_0 and V_0 are the normality and the volume used of the standard sodium thiosulphate solution. The molecular weight of chromium sulphate and the number of electrons transferred during the reaction for each molecule of chromium sulphate are 392 and 6, respectively. The concentration of the standard solution of sodium thiosulphate should be standardized frequently at least once a month.

To prepare and standardize 0.1 N sodium thiosulphate (Strouts *et al.*, 1955), weigh 25 g of sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$) and dissolve in distilled water which has been boiled and cooled free from carbon dioxide to a volume of 1 l. Allow the solution to stand overnight. Dry potassium dichromate ($K_2Cr_2O_7$) in an oven at 130 ºC for 2 h and cool in a desiccator. Weigh about 0.2 g of $K_2Cr_2O_7$ to the nearest 0.0001 g and dissolve in 50 ml of distilled water in a 250 ml triangular beaker. Add 5 ml of 6 N H_2SO_4 to acidify the solution. After standing in the dark for 5 min, add 20 ml of 10% (w/w) potassium iodide. Titrate the solution of

$K_2Cr_2O_7$ with the solution of $Na_2S_2O_3$ till the colour of the solution turns from dark reddish brown to yellow. Add 1–2 ml of starch solution (1% w/w) as an indicator. The colour of the solution turns to dark blue. Continue titration until the colour just disappears. Record the volume of the standard solution of $Na_2S_2O_3$ used (V). The normality N of the standard solution of $Na_2S_2O_3$ is:

$$N = W/(0.04903 \times V) \quad [3.5]$$

where N is the normality of the standard solution of $Na_2S_2O_3$, W is the weight of $K_2Cr_2O_7$ and V is the volume (ml) required for titration.

Method of atomic absorption analysis (AAA)

As we can see, titration of the chromium sulphate and preparation of the standard sodium thiosulphate solution are relatively long procedures. By means of AAA, the test for chromium can be simplified.

The atomic absorption process is essentially the reverse of atomic emission. In the latter, the atoms are excited by introduction of energy in a form of electricity or heat. The energy absorbed promotes valence electrons to the excited states. When the electrons fall back to lower energy states, the energy reappears as radiation. In the case of atomic absorption, radiation from an external light source emits spectral lines that correspond to the energy required for an electronic transition from the ground state to an excited state. The radiation passes through a flame. The flame gases are treated as a medium containing unexcited free atoms capable of absorbing radiation from the external source when the radiation corresponds exactly to the energy required for a transition of the test element from the ground state to the excited state. Unabsorbed radiation then passes through a monochromator, which isolates the exciting spectral line of the light source, and into a detector. The absorption of radiation from the light source depends on the population of the ground state, which is proportional to the solution concentration sprayed into the flame (Willard *et al.*, 1988).

The flame gases used for AAA can be pairs of air–acetylene, nitrous oxide–acetylene or air–hydrogen. The nitrous oxide–acetylene flame has a maximum temperature of about 2900 ºC and is used for the determination of elements which form refractory oxides. The air–hydrogen flame burns at a temperature of approximately 2000 ºC and is used for the determination of alkali metals (Cs, Rb, K, Na) as its lower flame temperature reduces ionization interferences. Air–acetylene is the preferred flame, which has a temperature of approximately 2300 ºC, for the determination of about 35 elements including chromium by atomic absorption (Perkin Elmer, 1982).

The procedures for determinating the chromium concentration by atomic absorption are:

(1) Prepare the testing solution. The concentration of the testing solution should be in a linear range between radiation absorption and the solution concentration

(sensitivity). For example, the sensitivity of the instrument Perkin Elmer Lamda 4B for chromium test is 7 mg l^{-1} (ppm). If the concentration of $Cr_2(SO_4)_3$ in the initial chrome tanning solution is 15% (w/w), the chromium concentration is around 4% (= 15 × 104/392)% (392 is the molecular weight of $Cr_2(SO_4)_3$, 104 is the weight of two atoms of Cr). Pipette 10 ml of the initial tanning solution into a 1 l volumetric flask and dilute to the mark with deionized water. Then pipette 10 ml of the diluted solution to a 1 l volumetric flask and dilute to the mark with deionized water. This is the testing solution and it has a chromium concentration of around 4 ppm.

(2) Prepare the standard chromium solutions for calibration. Pipette respectively, for example, 0.1 ml, 0.2 ml, 0.4 ml, 0.5 ml and 0.7 ml of a concentrated standard chromium solution (such as 1000 ppm, commercially available) into 100 ml volumetric flasks. Dilute them to the mark with deionized water. The concentrations of the diluted standard solutions are 1 ppm, 2 ppm, 4 ppm, 5 ppm and 7 ppm, respectively.

(3) Put the discharge lamp corresponding to the element to be tested in the light source position. For the chromium test, the lamp emits the spectral line at a wavelength of 357.9 nm.

(4) Turn on the instruments and select the element to be tested. Enter the values of the concentrations of the diluted standard chromium solutions.

(5) Adjust the gas flow by computer. In the chromium test using the Perkin Elmer Lamda 4B instrument, a 6.2 l min^{-1} flow rate of air and a 3.9 l min^{-1} flow rate of acetylene is preferred.

(6) Turn on the flame and auto-zero the base line.

(7) Pump the diluted standard solutions one by one in order from the lowest to the highest concentration and read the values of ppm tested. The test results should show a linear relationship on the diagram. If the relation between the concentration of the standard solutions and the tested values is not linear, re-do the calibration.

(8) After the successful calibration, pump the testing solution and read the ppm value at least three times.

(9) Calculate the concentration of $Cr_2(SO_4)_3$ in the initial tanning solution by :

$$Cr_2(SO_4)_3\ (g\ l^{-1}) = R \times (\text{'number of times diluted by'}\ 1000) \times (392/104) \qquad [3.6]$$

where R is the average reading of the testing solution in ppm. The 'number of times diluted by' is the ratio of solution to be diluted to diluent. After the instrument has been calibrated, a large number of samples can be easily tested by AAA.

3.3.3 Analysis of formaldehyde

Formaldehyde is a main component in synthetic tannages. The concentration of formaldehyde can be tested mainly by two methods: titration and colorimetric analyses (Meites, 1963).

Titration method

Dilute the initial formaldehyde solution to around 5 g l^{-1} for testing. Pipette 50 ml of 1 M sodium sulphite (Na_2SO_3) into a 250 ml beaker. Add 2–3 drops of thymolphthalein indicator. Pipette 10 ml of the formaldehyde testing solution into the beaker. A blue colour appears. Titrate the solution with a 0.05 N standard sulphuric acid until the blue colour just disappears. Record the volume V_0 (ml) of the standard sulphuric acid used. Calculate the concentration of the formaldehyde testing solution:

$$\text{Formaldehyde (g l}^{-1}) = \frac{N_0 \times V_0 \times 30}{10} \quad [3.7]$$

where N_0 is the normality of the standard sulphuric acid (0.05 N), the molecular weight of formaldehyde is 30 and 10 ml of testing solution is used. The concentration of the initial formaldehyde solution should be the concentration of the testing solution multiplied by the number of dilutions. Standard sulphuric acid can be prepared by dissolving 3 ml of concentrated sulphuric acid (98% w/w) in distilled water in a 1 l volumetric flask (sulphuric acid must be added into water) and diluting to the mark. The acid solution is then standardized by sodium hydroxide.

Colorimetric method (Japanese Standard Association, 1983)

Prepare a formaldehyde stock solution with a concentration of roughly 2 g l^{-1} and leave it overnight. Standardize it by titration with the sulphuric acid as described above. Pipette, for example, 1 ml, 2 ml, 5 ml, 7 ml, 10 ml and 15 ml of the stock solution and dilute each in a 1-l volumetric flask to the mark. The concentrations C_i of the standard solutions will be around 2 ppm, 4 ppm, 10 ppm, 14 ppm, 20 ppm and 30 ppm. Dilute the sample of initial formaldehyde solution to be tested to a concentration of around 10 ppm. Pipette 5 ml of the standard solutions and 5 ml of the testing solution into different test tubes. Pipette 5 ml of acetylacetone reagent into each test tube. Pipette 5 ml of distilled water and 5 ml of acetylacetone reagent into a test tube as a blank. Warm the test tubes in a water bath at 40 ºC for 30 min. Use the blank as a reference, measure the absorbance A_1, A_2, A_3, A_4, A_5 and A_6 of the standard solutions and A of the testing solution using a UV-visible spectrophotometer at the wavelength of 415 nm. Use the absorbance A_i and the corresponding concentration C_i of the standard solutions to draw a calibration curve. The concentration of the initial formaldehyde solution to be tested is:

$$\text{Formaldehyde (g l}^{-1}) = (D \times C)/1000 \quad [3.8]$$

where D is the 'number of times diluted by' dilutions from the initial solution to the testing solution; C (ppm) is the corresponding concentration at the absorbance A from the calibration curve.

The stock solution of formaldehyde (around 2000 ppm) can be kept for 4 weeks.

The acetylacetone reagent is prepared by dissolving 150 g of ammonium acetate in around 500 ml of distilled water in a 1-l volumetric flask, then adding 3 ml of glacial acetic acid and 2 ml of acetylacetone and diluting to 1000 ml with distilled water. Keep the acetylacetone reagent in a dark reagent bottle for no longer than 6 weeks.

3.4 Tests for leather properties

Most of the test methods in Section 3.4 and Section 3.5 are standard test methods. The test procedures of the standard methods will be only described briefly as an introduction. The information presented here can be used together with the details of the test procedures, reagents and apparatus given in the standard test methods in the literature.

3.4.1 Sampling of leather

Leather is a natural product and is subject to extensive variability. The physical and chemical properties vary considerably depending on the location from which the leather test sample is taken. The standard test method from the American Society for Testing and Materials (ASTM D2813, 1997) ensures random sampling of finished leather and fabricated leather items for physical and chemical tests. Test specimens should be cut from only one side of the backbone with their long dimension perpendicular to the backbone line. Test specimens should be taken from different parts of the shoulder, belly and tail of the leather. The number of specimens taken depends on the reliability of the test results, the deviation and the error of the testing procedures and should be recorded on the test report. Physical tests of leather and leather products, unless otherwise specified, should be performed under the standard atmospheric conditions of 50 ± 4% relative humidity at 23 ± 1 ºC.

3.4.2 Tests for fats in leather

The preliminary processes of unhairing and batting remove most of the natural oils from the skin. The leather at the time of the completion of tannage dose not contain sufficient lubricants to prevent it from drying into a hard mass (Thorstensen, 1993). Proper lubrication or fat-liquoring greatly affects the physical properties of break, stretch, stitch tear, tensile strength, water repellency, and comfort of the leather. The amount of fats and oils in leather can be determined by solvent extraction (ASTM D3495, 2000b). Weigh 5 g of ground leather to the nearest 0.001 g. Loosely pack the ground leather in an extraction thimble and cover with a pad of fat-free cotton. Place the loaded thimble in a Soxhlet extraction tube. Dry an extraction flask in an oven at 100 ± 2 ºC for 1 h. Cool in a desiccator and weigh to the nearest 0.001 g. Fill the flask to around two-thirds with hexane. Then

assemble the apparatus (the loaded thimble, Soxhlet extraction tube and the flask) in a fume hood with water cirulating through the condenser. Heat the flask until at least 50 siphons have been extracted. The solvent evaporates in the tube and then condenses in the thimble. When the condensed solvent in the thimble reaches the level of the outlet, it flows into the flask. This process constitutes one siphon. At the end of the extraction, remove the flask and continue heating to drive off the solvent until around 10 ml of solvent remains. Heat the flask gently in a steam bath until no solvent is visible. Place the flask in an oven at 100 ± 2 ºC for 2 h. Cool to room temperature in a desiccator and weigh the flask. Heat the flask in the oven again until a constant weigh is obtained. The content of fats and oils in the leather is calculated by the equation:

$$\text{Fats and oils (hexane soluble materials)}\% = (W_1 - W_0)/W \times 100\% \quad [3.9]$$

where W_1 is the constant weight of the flask with extracted matter, W_0 is the original weight of the flask and W is the weight of the leather specimen.

3.4.3 Measurement of pH of leather

The pH of leather is an important property for indicating the quality of leather as well as reflecting the stability of leather over a long period of time. Usually, leather has the pH of a weak acid.

Cut three specimens from the leather sample by the sampling method in Section 3.4.1. Each specimen consists of approximately 5 g of leather. Cut the specimen to small pieces of around 1 cm in diameter. Soak the specimen in a 250 ml flask with distilled water that is 20 times the weight of the specimen (ASTM D2810, 2001b). Stopper the flask and shake thoroughly. Keep it in a conditioned room (temperature 23 ± 1 ºC) for 6 h. Remove the leather specimen from the flask and measure the pH of the solution with a pH meter that has been calibrated against standard pH solutions. Standard pH solutions (pH 4.0, pH 7.0 and pH 10.0) are commercially available.

3.4.4 Test of chromic oxide in leather

A very important process in converting hide to leather is tanning. In chrome tanned leather, the chromium is presented in a combined form with the hide protein. Though the chromium in leather is usually reported to be chromic oxide (Cr_2O_3), this does not mean that the chromium is present as the oxide.

Chromium analysis can be performed on the ash sample from leather or can be performed on the leather directly. ASTM D2807 is a method for testing chromium by leather digestion (ASTM D 2807–1998). In this method, weigh 1 g of leather to the nearest 0.0001 g and cut it into small pieces 0.5 cm in diameter. Transfer the specimen to a 250 ml flask and add sequentially 20 ml of concentrated nitric acid (HNO_3), 15 ml of perchloric acid ($HClO_4$) and 10 ml of sulphuric acid (H_2SO_4).

Add a few glass beads. Heat the solution gently under reflux conditions in a fume hood until all the organic materials are destroyed and the colour changes to a clear red-orange indicating oxidation of chromium. Cool and dilute to 125 ml with distilled water. Heat to boiling and continue for 7 min. The solution after cooling can be analysed by titration (ASTM D2807, 1998) or by AAA.

Titration method

Add 30 ml of phosphoric acid (H_3PO_4, 40%) and 20 ml potassium iodide (KI 10%) to the solution obtained by digestion. Keep the solution standing for 5 min. Titrate the solution with a 0.1 N standard solution of sodium thiosulphate ($Na_2S_2O_3$) until the colour of the solution turns to yellow. Add 2–3 ml of starch solution (1% w/w) as an indicator. The colour of the solution turns to dark blue. Continue titration until the colour just disappears. Record the volume (V_0 ml) used of the standard solution of $Na_2S_2O_3$. The percentage of chromic oxide in leather can be calculated by the following equation:

$$Cr_2O_3\% = V_0 \times N_0 \times 2.533/W \quad [3.10]$$

where V_0 is the volume of $Na_2S_2O_3$ used in millilitres, N_0 is the normality of $Na_2S_2O_3$ and W is the weight of the leather specimen. If ash from the leather was used, $W = A/C$, where A is the weight of ash and C is the ash content (%) given by ash content measurement (see the following section). **Caution**: The hot perchloric acid digestion gives off strong toxic fumes so a good fume hood is needed. Moreover, the hot solution may explode caused by the reaction between perchloric acid and the organic matter.

Atomic absorption analysis

The solution from leather digestion can also be tested by AAA. Dilute the solution digested from the leather specimen from 125 ml to 1000 ml, then pipette 25 ml of the diluted solution to 250 ml for testing. Analyse the testing solution by the same AAA procedures described in Section 3.3.2. The chromium concentration (ppm) of the testing solution can be read directly from the instrument when the solution is pumped into the gas flame. The percentage of chromic oxide in leather can be calculated by the following equation:

$$Cr_2O_3\% = (R \times 1.8269/W)\% \quad [3.11]$$

where R is the average value in ppm read from the instrument and W is the weight of the leather specimen. A chromium tanned leather normally contains 2–4% of chromic oxide.

Using different discharge lamps emitting spectral lines for different elements and following the same AAA procedures, we can measure the content of chromium as well as that of aluminium, lead, magnesium, iron or zirconium in leather after obtaining the solution from digestion. These elements are either tannages or toxic

Table 3.2 Spectral wavelength and flame gases for AAA (adapted from Perkin Elmer, 1982)

Element	Wavelength (nm)	Preferred flame gases
Aluminium	309.3	Nitrous oxide–acetylene
Chromium	357.9	Air–acetylene
Iron	248.3	Air–acetylene
Lead	283.3	Air–acetylene
Magnesium	285.2	Air–acetylene
Zirconium	360.1	Nitrous oxide–acetylene

heavy metals in leather. Information about their content in leather is often required. Table 3.2 shows the wavelength of the spectral lines and the preferred flame gases for measurement of aluminium, chromium, iron, lead, magnesium and zirconium by AAA (Perkin Elmer, 1982).

3.4.5 Test for ash content of leather

Total ash content in leather can be measured by the standard test methods ASTM D2617-96 or by thermogravimetric analysis (TGA).

Muffle furnace method (ASTM, 2001a)

Cut 5 g of leather and weigh to the nearest 0.0001 g. Place the specimen in a weighed platinum dish. Heat the specimen in the dish in an oven at 43 ºC for 16 h, then at 93 ºC for 2 h. Cool the specimen with the dish in a desiccator. Weigh the dry specimen. The percentage of the total solids of the leather sample is:

$$\text{Total solids}\% = W_d/W \times 100\% \quad [3.12]$$

where W_d is the dry weight of the leather specimen and W is the original weight of the specimen under the standard conditions (RH 50 ± 4%, 23 ± 1 ºC).

Put the dry specimen in a clean preweighed crucible. Burn the specimen in the crucible on a flame until there is no smoke released from the specimen. Place the crucible in a muffle furnace at 600 ± 25 ºC for 1 h. Cool the sample in a desiccator and weigh the residue in the crucible. The percentage of the total ash of the dry leather sample is:

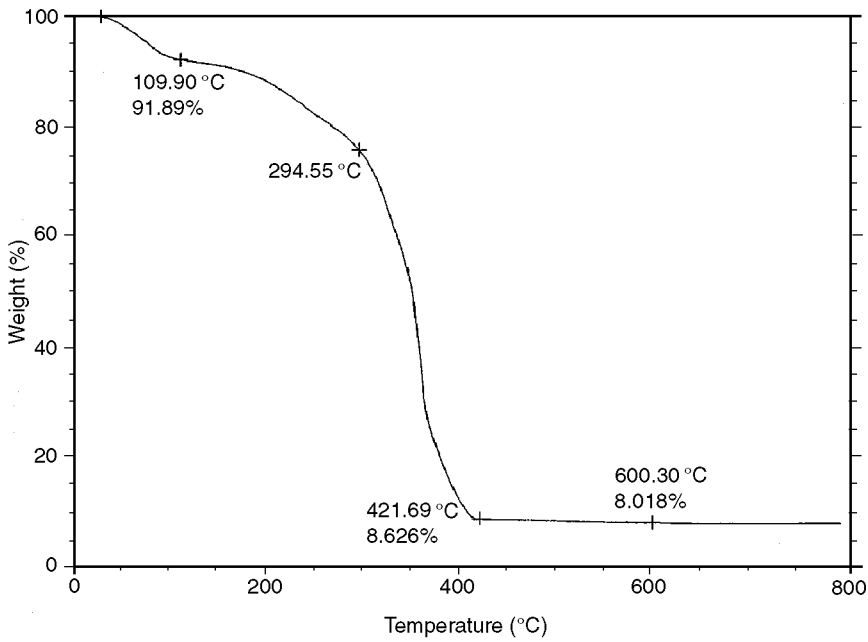
$$\text{Total ash}\% = R/W_d \times 100\% \quad [3.13]$$

where W_d is the dry weight of the leather specimen and R is the weight of the residue.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a method for the continuous measurement

of the weight of a material as a function of time or temperature as it is heated, preferably at a linear rate. It provides an analysis with a quantitative measurement of any weight change during heating. For example, TGA can directly record the weight loss with time or temperature caused by dehydration or decomposition (Willard *et al.*, 1988). Weigh around 20 mg of leather sample and place the specimen in the platinum pan which has been weighed and auto-zeroed to the TGA instrument. The weight of the specimen is measured by the instrument and considered to be 100%. Figure 3.3 is a TGA curve of a goat leather. The curve was obtained under the following conditions: specimen weight, 9.4770 mg; instrument, TGA Q500 (TA Instrument, USA); air flow rate, 60 ml min^{-1}; heating rate, 20 ºC min^{-1}; heating range, 30–800 ºC. From the curve, it can be seen that the specimen of goat leather lost around 9.1% weight at 110 ºC. The weight loss was due to the evaporation of water, low boiling point lubricants and so on. The specimen started fast decomposition and carbonization at 290–300 ºC. Before 290 ºC, the weight loss of the specimen could be caused by both evaporation of the high boiling point materials and the onset of the decomposition. According to the standard test method (ASTM D2617-96), the ash content was measured at 600 ºC. From the TGA curve, we can see that the ash content of the specimen is 8.02% at 600 ºC. Decomposition and carbonization of the specimen was almost complete at 420 ºC with a weight of residue 8.83%.



3.3 TGA curve of a type of goat leather.

Table 3.3 Aromatic amines specified by Directive 2002/61/CE (adapted from European Parliament *Directives 2002/61/EC*, 2002)

No	CAS number	Index	Substances
1	92-67-1	612-072-00-6	Biphenyl-4-ylamine; 4-Aminobiphenyl xenylamine
2	92-87-5	612-042-00-2	Benzidine
3	95-69-2		4-Chloro-*o*-toluidine
4	91-59-8	612-022-00-3	2-Naphthylamine
5	97-56-3	611-006-00-3	*o*-Aminoazotoluene; 4-*o*-Tolylazo-*o*-toluidine 4-Amino-2',3-dimethylazobenzene
6	99-55-8		5-Nitro-*o*-toluidine
7	106-47-8	612-137-00-9	4-Chloroaniline
8	615-05-4		4-Methyoxyl-*m*-phenylenediamine
9	101-77-9	612-051-00-1	4,4'-Methylenedianiline; 4,4-Diaminodiphenylmethane
10	91-94-1	612-068-00-4	3,3'-Dichlorobenzidine 3,3'-Dichlorobiphenyl-4,4'-ylenediamine
11	119-90-4	612-036-00-x	3,3'-Dimethoxybenzidine; *o*-Dianisidine
12	119-93-7	612-041-00-7	3,3-Dimethylbenzidine; 4,4'-Bi-*o*-toluidine
13	838-88-0	612-085-00-7	4,4'-Methylenedi-*o*-toluidine
14	120-71-8		6-Methoxy-*m*-toluidine; *p*-Cresidine
15	101-14-4	612-078-00-9	4,4'-Methylene-bis-(2-chloro-aniline) 2,2'-Dichloro-4,4'-methylene-dianiline
16	101-80-4		4,4'-Oxydianiline
17	139-65-1		4,4'-Thiodianiline
18	95-53-4	612-091-00-x	*o*-Toluidine; 2-Aminotoluene
19	95-80-7	612-009-00-3	4-Methyl-*m*-phenylenediamine
20	137-17-7		2,4,5-Trimethylaniline
21	90-04-0	612-035-00-4	*o*-Anisidine; 2-Methoxyaniline
22	60-09-3	611-008-00-4	4-Aminoazobenzene

3.4.6 Analysis of azo dyes in leather

To protect human health and improve consumer safety, the European Parliament and the Council of the European Union (EU) published Directives 2002/61/EC and 2003/3/EC on September 11, 2002 and January 6, 2003, respectively. These restrict the use of carcinogenic azo-dyes in textiles and leather articles and prohibits the sale of such articles dyed with the restricted azo dyes. Directives 2002/61/EC and 2003/3/EC had been transposed into national laws and put into effect in the member states respectively by September 11, 2003 and June 30, 2004. Aromatic amines (azo dyes) (22 kinds) specified and prohibited by Directive 2002/61/EC are listed in Table 3.3.

The analysis of azo dyes is based on the standard test methods NF EN 14362 Part 1 and Part 2 (Association Française de Normalisation, AFNOR, 2004a and b). The principle of the test method is to extract the azo dyes (aromatic amines) from

the testing material. The extraction is analysed by thin layer chromatography (TLC), by gas chromatography (GC), by high-performance liquid chromatography (HPLC) or by HPLC/mass spectroscopic analysis.

Without extraction (EN 14362-1) (AFNOR 2004a)

Heat 17 ml of the tampon solution pH 6, which contains 0.06 mol l^{-1} citrate and sodium hydroxide in a flask with stopper to 70 ºC. Place 1.00 g of the testing material into the tampon solution in the flask, which is shaken well for 30 min. Add 3 ml of the sodium dithionite aqueous solution into the flask and keep reaction at 70 ºC for 30 min. Then, cool the solution to 20–25 ºC within 2 min. The solution is extracted by 40 ml of t-butylmethyl ether. After extraction, condense the solution of t-butylmethyl ether to around 1 ml and use for the chromatographic analysis.

Extraction (EN 14362-2) (AFNOR, 2004b)

Extract 1.00 g of the testing material in 25 ml of chlorobenzene in a Soxhlet for 30 min. Eliminate the solvent in a fume hood and add 2 ml of methanol in the residue, then add 15 ml of citrate/sodium hydroxide tampon solution (pH 6) and 3 ml of sodium dithionite. Extract the solution with 40 ml of t-butylmethyl ether. After extraction, condense the solution of t-butylmethyl ether to around 1 ml and use for the chromatographic analysis.

TLC only offers a qualitative result. HPLC and HPLC/mass spectroscopic analysis give both qualitative and quantitative results. For HPLC analysis, the test results should be calibrated with the standard aromatic amines at known concentrations.

The test conditions for HPLC specified by the standard method (EN 14362) are: mobile phase I, methanol; mobile phase II, 0.575 g of ammonium dihydrogenphosphate + 0.7 g disodium hydrogenphosphate in 1 l of distilled water (pH 6.9); stationary phase, Zorbex SB-Phenyl® (5 μm) (250 × 4.6) mm; flow rate, 0.6–1.0 ml min^{-1}; gradient, start at 10% of mobile phase I and increase to 50% of mobile phase I for 50 min, then to 100% mobile phase I for the next 20 min; injection volume, 15.0 μl; column temperature, 30 ºC; detector, UV detector at wavelength 240 nm, 280 nm or 305 nm.

After injection of the extraction from the testing material, absorption peaks appear at different retention times (RT). Under fixed HPLC conditions, a specific compound has a fixed retention time. By comparing the retention time and the peak area of the extraction from the testing material with the standard azo dyes (aromatic amines) at the known concentration, we can confirm the type and the quantity of the azo dyes existing in the testing material. According to the Directive 2002/61/EC, the listed azo dyes (aromatic amines) should be below 30 mg kg^{-1} in the testing materials.

3.5 Tests of leather performance

3.5.1 Test of leather permeability to water vapour

Water vapour permeability is essential for the comfort of leather shoes, garments or sporting goods. Water vapour permeability helps dissipate metabolic heat and avoids the heat accumulation that causes heat stress (Shao and Filtreau, 2004a). The test method (ALCA, 1954b) measures the water vapour in grams passing through the sample per square centimetre per hour.

Cut a specimen of 5.70 cm in diameter from the conditioned sample. Fill an aluminium cup 5.65 cm in diameter and 3.2 cm in depth, with fresh desiccator (anhydrous calcium chloride) to a height around 5 mm below the level of the rim. Cover the cup with the testing specimen grainy side downwards. Press gently the specimen on the rim of the cup and seal with melting microcrystalline wax (melting point lower than 70 ºC). Place the assembly at a constant temperature in a humidity chamber (23 ± 1 ºC and RH 50 ± 4%) with the specimen side up. Adjust the air flow so that the velocity over the specimen is 2.54 m s^{-1}. At the end of 1 h, weigh the assembling to the nearest 0.001 g. This is considered the initial weight W_0. Shake the assembly after the weighing to distribute the desiccator evenly. Weigh the assembly at 1-h intervals and shake after each weighing. Total test time should be not less than 4 h and not more than 24 h. The last weighing is recorded as the final weight W. The permeability to water vapour of the specimen is calculated by:

$$P = (W - W_0)/AT \qquad [3.14]$$

where A is the exposure area of the specimen (normally 25 cm^2) and T is the total test time in hours. Usually, the leather used for garments should have a minimum permeability to water vapour of 0.005 g cm^{-2} h^{-1}.

3.5.2 Test for water absorption of leather

Naturally, leather absorbs some liquid water but mainly is water resistant. The leather industries do not claim that it is 'waterproof'. So-called 'waterproof' leathers are finished with water repellent agents such as organo-silicon, fluorocarbon and so on. Water absorption of leather can be tested by a static absorption method (ASTM D1815, 2000a). Cut the conditioned specimen with a circular cutter. Measure the diameter and thickness of the specimen. Calculate its volume in cubic centimetres. Weigh the specimen to the nearest 0.01 g. Immerse the specimen in distilled water at 23 ± 1 ºC in a horizontal position with the grain side up. Leave the specimen immersed for a period of 30 min. At the end of immersion, take out the specimen and blot the surface of the specimen with filter paper to remove excess water. Weigh the specimen immediately to the nearest 0.01 g. Calculate the amount of water absorbed by the specimen:

$$\text{Water absorbed (g cm}^{-3}) = (W_1 - W_2)/V \quad [3.15]$$

where W_1 and W_2 are the weights of the specimen before and after immersion respectively and V is the volume of the specimen.

3.5.3 Test of resistance to chemical penetration

Leather is often used as a material for protective clothing (as well as gloves and shoes) because of its properties. The protective suit must have good resistance to chemical penetration, to oil and to cutting.

The chemical challenges used for the test of resistance to penetration of protective clothing for fire fighters by the standard test method (National Fire Protection Association, NFPA, 2000) are: (a) 3% of aqueous film-forming foam (AFFF); (b) battery acid (37% w/w of sulphuric acid); (c) fire-resistant hydraulic fluid (phosphate ester base); (d) surrogate gasoline fuel C (50/50 v/v of toluene and iso-octane); and (e) swimming pool chlorinating chemical containing at least 65% of free chlorine. Items described in (a) and (c) can be obtained from the fire department or service, and items (b), (d) and (e) can be prepared in the laboratory. In agreement between the supplier and the buyer, the chemicals can also be used as challenges.

The main part of the apparatus is a cell, which can resist different chemicals, and is normally made of PTFE (polytetrafluoroethylene). The cell is used to restrain the specimen during contact with the pressurized test liquid via a restraining ring. It consists of a chamber which can contain approximately 60 ml of the challenge liquid. The cell has an outer diameter of approximately 10 cm and an inner diameter of 6 cm. It has a viewing port which allows observation of the specimen during the test.

Cut a round specimen in a diameter of 10 cm and cut four small holes at the positions corresponding to the four screws on the cell. Place the specimen to the cell with the outside surface facing the cell chamber. Put the restraining ring between the cover and the specimen. Tighten the cover with screws. There are different testing procedures for chemical penetration. The following procedures are more similar to the conditions under which the protective clothing is attacked by chemicals. Add 55 ml of the challenge liquid into the chamber from the inlet to the cell and record the starting time. Wait for 5 min and observe if there is any liquid penetrating through the specimen. If there is no penetration, continue the test. Apply an air pressure of 2 psi (13.8 kPa) gradually (at a rate no more than 0.5 psi s^{-1}) (3.5 kPa s^{-1}) on to the liquid by the inlet of the cell. Keep the pressure for 1 min and observe if there is liquid penetration. If there is no penetration, continue the test. Release the air pressure gradually (at a rate no more than 0.5 psi s^{-1}) (3.5 kPa s^{-1}), and keep the assembly at 0 psi for an additional 54 min and observe if there is liquid penetration. Record the test results as 'penetration' or 'no penetration' at each step. Three specimens should be tested for each chemical. Report the test results for each specimen.

Table 3.4 Standard test liquids for oil repellency (adapted from AATCC, 1997)

AATCC grade number	Test liquid	Surface tension (dyn cm^{-1} at 25 °C)[a]
1	Kaydol (a white mineral oil)	31.5
2	65/35 (v/v) Kaydol/*n*-hexadecane	–
3	*n*-Hexadecane	27.3
4	*n*-Tetradecane	26.4
5	*n*-Dodecane	24.7
6	*n*-Decane	23.5
7	*n*-Octane	21.4
8	*n*-Heptane	14.8

[a] 1 dyne = 0.981 mg cm^{-1}.

3.5.4 Test for oil repellency

This test detects the leather's resistance to wetting by a selected series of liquid hydrocarbons with different surface tensions. The standard test liquids are listed in Table 3.4 (American Association of Textile Chemists and Colorists, AATCC, 1997).

Place the test specimen flat on white textile blotting paper on a smooth horizontal surface. Start with the lowest numbered test liquid (Kaydol) and carefully place small drops approximately 5 mm in diameter or 0.05 ml in volume on the test specimen in five locations. The drops should be at least 4 cm apart. Do not touch the specimen with the dropper tip. Observe the drops for 30 s, viewing at an angle of around 45°. If there is no penetration, no wicking or no wetting at the liquid–fabric interface, continue with the next numbered test liquid at an adjacent site on the fabric. Continue this procedure until one of the test liquids shows obvious wetting or wicking of the fabric under or around the drop within 30 s. The number of the last test liquid is reported as the AATCC oil repellency grade. If there is wetting or wicking when testing with the first numbered liquid, the oil repellency grade is reported as 0. The oil repellency grade should be tested on two specimens. If the two results agree, report the value. If the two grades are not in agreement, test the third specimen. Report the grade of the third determination if the value is the same as either of the first two tests. When the third determination is different from either of the first two, report the median value to the nearest 0.5.

3.5.5 Test of cut-resistance

Cut-resistance is an important property of leather against mechanical forces, especially for products that are more at risk of cutting such as gloves, shoes or sport goods. The test method is to measure the force needed to cut through the sample at a distance of 20 mm (International Organization for Standardization, ISO , 1999).

Figure 3.4 is a schematic diagram of the apparatus for testing cut-resistance. It

consists of a motor-driven balanced arm (A) holding the cutting edge (B) in contact with the specimen mounted on a mandrel (C). As the arm is driven, the blade moves across the specimen until the force, generated by the weights (D) mounted on the lever arm assembly, causes the specimen to sustain a cut through. The top surface of the mandrel (C) has a round form. The blades should be made of stainless steel with a solidity greater than 45 HRC. The blades should be of 1.0 ± 0.5 mm thick and have a cutting edge length greater than 65 mm. Before the test, the blades should be calibrated by a standard material of neoprene. The standard neoprene should have a hardness of 50 ± 5 Shore A and a thickness of 1.57 mm (± 10%).

Weigh the mandrel to the nearest 0.01 g. Place the mandrel on the apparatus and balance the level by the screw on the lever arm. Cut the standard neoprene to dimensions of 50 mm × 100 mm. Use a double face tape to stick the neoprene onto the mandrel. In between the neoprene and the tape, place an approximately 1 cm wide aluminium foil strip along the middle line of the round surface of the mandrel. Thus, when the blade cuts through the neoprene, the electricity which is conducted by the blade and the aluminium foil stops the cutting and the length of the cut through can be recorded. Weigh the assembly, which is composed of mandrel, neoprene, double face tap and aluminium foil, to the nearest 0.01 g. Place a load of 5 N on the blade in addition to the balance weight for the neoprene, double face tap and aluminium foil (usually, the lever arm is designed and calibrated so that each 1 g of the weight on the lever arm applies 2 g of load on the blade). Record the length of the cutting edge on the neoprene. It must be between 18 and 38 mm. The cut through length for the five tests should not differ in length by more than 10 mm. Each blade can be used only once for the cut-resistance test. The calibration factor f of the blades is:

$$f = 20 \text{ mm}/D_c \qquad [3.16]$$

where D_c is the average length of cut through of neoprene.

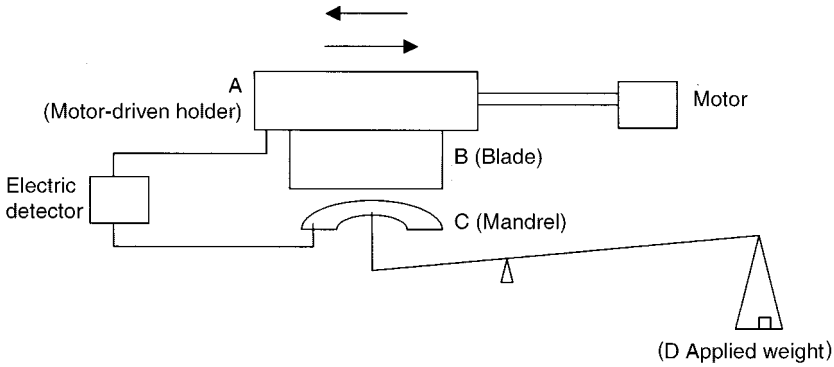
Cut at least three specimens of the leather sample to dimensions of 50 mm × 100 mm. Follow the same procedures as for calibration. Adjust the load on the blade to let the cut through length to be in the range of five times 5–15 mm, five times 15–30 mm and five times 30–50 mm. Draw a curve of the load F against the cut through length D and use an exponential regression equation between F and D in:

$$F = A \cdot D^b \qquad [3.17]$$

where A and b are constants obtained by the regression equation of the test results. Calculate the force F_{20} by the Equation [3.17] when D is 20 mm where F_{20} is the force needed to cut through the leather sample to a cut through length of 20 mm. The calibrated force needed to cut through the leather sample to a cut through length of 20 mm $(F_{20})_{\text{calibrated}}$ is:

$$(F_{20})_{\text{calibrated}} = f \cdot F_{20} \qquad [318]$$

where f is the calibration factor from Equation [3.16].



3.4 Schematic representation of the apparatus used to measure cut-resistance.

3.6 Tests of leather stability (ageing)

Since leather is a high quality textile material, a longer service lifetime is required, especially when it is used in furniture, book covers and pipe organs and so on. In the early 1950s, it was found that the higher the chrome content, the better the protection against ageing of leather (Beebe *et al.*, 1956). Vegetable tanned leather after retanning with chrome or aluminium also has a long service lifetime. The removal of water-soluble tanning materials from the leather can enhance deterioration. The addition of some salts, such as calcium oxalate, results in a better durability (Hannigan, 1965).

3.6.1 Accelerated ageing

To test the durability of leather, accelerated ageing was recommended (Piltingsrud and Tancous, 1994). The main part of the apparatus for the accelerated ageing test is a stainless steel bomb, which must be safe when it is applied at a pressure of 90 psi (621 kPa). The test specimen is cut to a size suitable for tensile strength measurement, e.g. 3 inches (7.6 cm) wide and 6 inches (15.2 cm) long for tests by the Grab method. Eight specimens in four pairs are cut from the different parts of the leather sample. Each pair of the specimens is used for ageing and for reference, respectively. Put the four ageing specimens in the test bomb, then purge the bomb with sulphur dioxide gas (SO_2). Warm the bomb to 35 ºC and connect the bomb to a source of filtered compressed air saturated with water to nearly 100% of relative humidity until the pressure inside the bomb reaches 90 psi (621 kPa). Close the connection valve, leave the bomb at a constant pressure and temperature for either 168 or 336 h depending on the possible residue of the tensile strength. Lower the pressure of the bomb to normal air pressure before opening the bomb and take out the aged specimens. Test the tensile strength of the aged specimens and the reference specimens. The thickness of the specimens should be also measured and

reported. Optionally, the ageing test can be performed without sulphur dioxide or with different humidities to observe the effect of sulphur dioxide and humidity on the durability of leather.

3.6.2 Kinetic analysis

The ageing test described above is a test method that makes relative comparisons between test samples. It cannot predict the service lifetime of the sample. By analysis of the ageing kinetics and the measurement of activation energy of leather reacting with the environment, it is possible to predict the lifetime of the sample and to analyse the effect of different factors on it. Many attempts have been made to use the kinetic analysis to investigate the ageing process of cellulose, paper and textiles (Steiger, 1958; Miller *et al.*, 1967; Grey, 1969).

The kinetic analysis of ageing is based on the concept that the rate of most chemical reactions increases when the temperature increases, and that the physical properties of materials, which react with the environment, are affected by their chemical changes. The basis of the kinetic analysis is the law of chemical reaction kinetics:

$$V = \frac{\mathrm{d}C}{\mathrm{d}t} = -kC^n \qquad [3.19]$$

where V is the reaction rate, C is the concentration of the reactants, n is the reaction order, t is the reaction time and k is the rate constant. In the early study (Steiger, 1958; Miller *et al*., 1967; Grey, 1969), the loss of tensile strength was used as an indication of fibres' degradation and a first-order kinetic equation obtained with some assumptions:

$$\frac{1}{F_t} - \frac{1}{F_0} = kt \qquad [3.20]$$

where F_t and F_0 are tensile strength at time t and at the beginning respectively and k is the reaction rate constant which depends on the temperature. Zou and co-workers found that the number-average degree of polymerization of the fibres had better linear relationship with the reaction time (Zou *et al.*, 1994, 1996), that is:

$$\frac{1}{DP_{(t)}} - \frac{1}{DF_{(0)}} = kt \qquad [3.21]$$

in which $DP_{(t)}$ and $DP_{(0)}$ are number-average degree of polymerization of cellulose fibres at time t and at the beginning, respectively.

The temperature-dependence reaction rate constant is described by the well-known Arrhenius equation:

$$k = A\mathrm{e}^{(-E/RT)} \qquad [3.22]$$

or in the form:

$$\ln k = -(E/RT) + \ln A \qquad [3.23]$$

where A is the frequency factor (the same units as k), E is the activation energy (kJ mol^{-1}), R is the gas constant (kJ mol^{-1} K^{-1}) and T is the absolute temperature (K). Plot ln k versus ($1/T$); there will be a straight line with a slope ($-E/R$) and an intercept of ln A. From the slope and the intercept, the values of E and A can be calculated. Thus determination of degradation at different temperatures T and different times t allows the activation energy E to be calculated by combination of Equation [3.20] (or Equation [3.21] and Equation [3.23] as:

$$\ln(\frac{1}{t})(\frac{1}{F_t} - \frac{1}{F_0}) = -(E/RT) + \ln A \qquad [3.24]$$

Suppose the sample is kept at a temperature of 20 ºC, the degradation takes place very slowly. Since the activation energy E is a difference in potential energy between the reactants and the transition state, different temperatures do not change the energy barrier of the reaction. A higher temperature only results in more molecules of reactants with a higher energy than the energy barrier of the reaction (Solomons, 1980). Determination of tensile strength (F_t and F_0) of the sample at different times (t) and at a high temperature (T) (accelerated ageing) produces a straight line, allowing the calculation of A and E in Equation [3.24]. With the calculated A and E values, we can predict the service lifetime t_{life} of the sample at different temperatures (T) by the equation:

$$\frac{1}{t_{\text{life}}} = \left(\frac{F_t F_0}{F_0 - F_t}\right) \cdot A e^{-(E/RT)} \qquad [3.25]$$

Catalysts, such as acids and humidity, can change the activation energy E. Keeping a test condition at a fixed acid concentration and humidity, we can preview the service lifetime at the specified conditions by the same procedures as described above. We can also predict the service lifetime of a sample under different conditions. The better relation in Equation [3.20] or Equation [3.21] between the parameters selected (such as yellowing, viscosity, tensile strength and number-average polymerization degree etc.), the less is the deviation in the measurement of activation energy. Though there is deviation to some extent in the measurement of activation energy owing to the assumption of a first order reaction (Equation [3.19]), this method of kinetic analysis of material durability is still valuable in both the theoretical and practical fields of study.

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4

Analysis of common chemicals used in textile wet processes

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4.1 Introduction

Chemical analysis always involves the use of different chemicals. In order to assure accurate analysis results, the chemicals used need to be standardised, the procedures must be followed exactly and the data obtained have to be analysed statistically. If an instrument is used, it should be maintained and calibrated properly. A detailed description of analytical chemistry is not the purpose of this book. Readers can refer to analytical chemistry books in the literature.[1] During the last five decades, sophisticated instruments in the market have made chemical analysis much easier than before. However, the price of the instruments plus high operation costs have limited their applications in many textile businesses. Therefore, the analytical methods discussed in this chapter are mainly those of traditional wet chemistry based analyses.

In a chemical analysis, especially involving quantitative analysis, the amount of chemical used is critical and can be determined by the measurement of concentration if it is a solution, or by weight, if it is a solid. Sometimes, the concentration of a solution can be easily determined by using another known solution through titration. For acids and bases, if the concentration is sufficiently low, the pH concept is generally used to represent the concentration of the acid or base in the aqueous solution. For the analysis of common chemicals, such as caustic soda, acetic acid, soda ash, sodium dithionite, hydrogen peroxide, and so on, titrimetric analysis and gravimetric analysis are widely used. For the analysis of surfactants and other chemicals, qualitative spot tests and specialised instruments should be utilised.

4.1.1 Concentration

The concentration of a solute is usually expressed as the amount of a solute in a unit volume of a solution. The amount of a solute can be in grams (g), kilograms (kg), moles (mol), or normals (n). The unit volume of a solution is always in litres (l). A

mole of a specific chemical has the mass of 6.02205×10^{23} molecules. As a weight, the mole is the mass formular weight in grams, known as molecular weight, MW. If moles per litre is the concentration unit, it is known as molarity, M; if normals per litre is the case, it is known as normality, N. The normality of a solution is obtained by multiplying the molarity value by the number of equivalents in a mole. The number of equivalents is the number of protons or electrons per molecule participating in a specific balanced chemical reaction. Sometimes, mass percentage concentration (w/v%) is used (weight in volume percentage concentration).

The conversion among these concentrations can be carried out by using the following equations:

$$N = M \times \text{number of equivalents} \quad [4.1]$$

$$M = \frac{w/v \times 10}{MW} \quad [4.2]$$

4.1.2 Titration

Titration is a method by which the concentration of an unknown solution can be determined using a standardised solution with a known concentration through a stoichiometric reaction. The end point of the chemical reaction is indicated by the colour change of an indicator or an instrumental reading. The standard solution of a known reagent is the titrant and the unknown solution is the titrand. The unknown concentration can be determined using Equation [4.3]:

$$V_A N_A = V_B N_B \quad [4.3]$$

where V is the volume used in the titration and N is the normality of the solution, subscripts A and B denote the known and unknown solutions, respectively.

The most common titrations are based on acid–base neutralisation (acid–base titration), or oxidant–reductant reaction (redox titration) principles. With these two titration methods, many textile chemicals can be analysed. The common indicators used in these titrations are listed in Table 4.1[2] and 4.2.[3] For an accurate titration, the consumption of the standard solution is ideally between 35 and 45 ml in a 50 ml burette.

4.1.3 Weighing

Weighing is an important operation in gravimetric analysis. Usually it involves the use of an electronic balance with a minimum readability of 0.1 mg. In order to ensure reproducible results, sample handling is very critical especially when hygroscopic materials are weighed. For most textile materials, an accurate weighing result can only be obtained by repeated heating–cooling–weighing until a constant weight is reached. During the weighing operation, the following precautions should be taken:

Table 4.1 Some common indicators for acid–base titration[2]

Indicator	pH range	Low pH colour	High pH colour	Preparation
Methyl violet	0.1–1.5	Yellow	Blue	0.05% in water
Thymol blue (acid range)	1.2–2.8	Red	Yellow	0.1 g in 21.5 ml 0.01 N NaOH + 229.5 ml water
Methyl yellow	2.9–4.0	Red	Yellow	0.1% in 90% ethanol
Bromphenol blue	3.0–4.6	Yellow	Blue	0.1 g in 14.9 ml 0.01 N NaOH + 235.1 ml water
Bromcresol green	3.8–5.4	Yellow	Blue	0.1 g in 14.3 ml 0.01 N NaOH + 235.7 ml water
Methyl red	4.8–6.0	Red	Yellow	0.02 g in 60 ml ethanol + 40 ml water
Bromcresol purple	5.2–6.8	Yellow	Purple	0.02% in ethanol
Bromthymol blue	6.0–7.6	Yellow	Blue	0.1% in 50 % ethanol
Phenol red	6.4–8.0	Yellow	Red	0.1% in ethanol
Thymol blue (base range)	8.0–9.6	Yellow	Blue	0.1% in ethanol
Phenolphthalein	8.2–10.0	Colourless	Red	1% in ethanol
Thymolphthalein	9.4–10.6	Colourless	Blue	0.1% in ethanol
Alizarin yellow R	10.2–12.0	Yellow	Red	0.1% in water
Tropeolin O	11.0–13.0	Yellow	Orange	0.1% in water
Nitramine	10.8–13.0	Colourless	Brown	0.1% in 70% ethanol
1, 3, 5-trinitrobenzene	11.5–14.0	Colourless	Orange	0.1% in ethanol

Table 4.2 Some common redox indicators[3]

Indicator	Oxidised colour	Reduced colour	Transition potential (V)	Solution condition
5-Nitro-1,10-phenanthroline iron (II) complex	Pale blue	Red-violet	+1.25	H_2SO_4 1M
2,3′-Diphenylamine dicarboxylic acid	Blue-violet	Colourless	+1.12	H_2SO_4 7–10 M
1,10-phenanthroline iron (II) complex	Pale blue	Red	+1.11	H_2SO_4 1M
Erioglaucin A	Bluish red	Yellow-green	+0.98	H_2SO_4 0.5 M
Diphenylamine sulphonic acid	Red-violet	Colourless	+0.85	Dilute acid
Diphenylamine	Violet	Colourless	+0.76	Dilute acid
p-Ethoxychrysoline	Yellow	Red	+0.76	Dilute acid
Methylene blue	Blue	Colourless	+0.53	Acid 1 M
Indigo tetrasulphonate	Blue	Colourless	+0.36	Acid 1 M
Phenosafranine	Red	Colourless	+0.28	Acid 1 M

- The balance must be properly calibrated and kept level at all times.
- There should be no vibrations nearby.
- The sample should be weighed without air flowing through or nearby.
- The laboratory environment and the sample should be kept clean.
- The temperature and humidity of the environment should be controlled.

4.1.4 pH

pH is a scale between 0 and 14 used to express the concentration of hydronium (H_3O^+, or H^+) ions in a solution. It is defined by Equation [4.4].

$$pH = -\log [H^+] \quad [4.4]$$

where $[H^+]$ is the molar concentration of hydronium. For pure water, the hydronium concentration at 25 ºC is 1×10^{-7} M. If the pH scale is in place, we can use pH 7, instead of 1×10^{-7} M to express the strength of the hydronium ion in pure water. Because at this pH, pure water has the same amount of hydronium ion and hydroxide ion (OH^-), we call this pH point as neutral. Any pH under 7 is an indication of an excess amount of hydronium ions in the solution, which is an acidic solution; any pH over 7 is the opposite, an excess amount of hydroxide ions in the solution, which is a basic solution. Similarly, the concept of negative logarithm of a concentration can also be applied to other chemical solutions. For instance, pK_a is used to express the magnitude of K_a, the dissociation constant of a weak acid. The lower the pK value, the stronger the chemical.

pH measurement is very important in textile wet processes. In scouring of wool, pH should be controlled between 9 and 10.5, otherwise the protein fibres would be damaged. For hydrogen peroxide bleaching, a basic pH ranging from 10 to 12 is required for best whiteness results. In fibre reactive dyeing of cellulosic fibres, an acidic pH (pH < 7) should be avoided or hydrolysis of fibres and dyes would occur. A pH meter is a convenient tool for pH measurement though pH paper is also widely used, especially in a harsh environment where colour does not interfere with the results. However, a pH meter is susceptible to damage and chemical interference. If possible a stainless steel probe/electrode should be used. After each measurement, the probe should be cleaned to avoid any cross-contamination. In order to maintain the performance of the probe, it is also advisable to keep the probe moist and neutralised when not in use.

4.2 Acids, bases and salts

Acid can react with base to produce salt and water in the reaction shown below. It is a neutralisation reaction. Based on this reaction, acid–base titration is used to analyse the concentration of many acids and bases used in textile wet processes:

$$\text{acid} + \text{base} \rightarrow \text{salt} + \text{water} \quad [4.5]$$

The following standard solutions are used in the acid and base analysis. They are usually prepared in advance and consumed within a certain period of time.

1. H_2SO_4, 0.1 N, 0.25N, 0.5 N and 1 N;
2. HCl, 0.1N, 0.25 N, 0.5 N and 1 N;
3. HNO_3, 0.1 N;
4. NaOH, 0.1 N, 0.5 N and 1 N;
5. KOH, 0.5 N.

4.2.1 Inorganic acids

H_2SO_4

The concentration of sulphuric acid (H_2SO_4) can be determined by using Baume's (ºBé) hydrometer. Table 4.3 shows the relationship between ºBé and sulphuric acid concentration.[4] The conversion of Baume to specific gravity (*SG*) for liquids heavier than water can be conducted using Equation [4.6]:

$$°\text{Bé} = 145 - \frac{145}{SG} \qquad [4.6]$$

The titration of sulphuric acid is carried out using sodium hydroxide in the presence of phenolphthalein as an indicator. The end point is reached when a faint

Table 4.3 ºBé and concentration of sulphuric acid at 20 ºC[4]

ºBé	Concentration of H_2SO_4		Specific gravity
	(w/w%)	(g l^{-1})	
0	< 0.26	< 2.6	1.000
3.4	4.00	41.0	1.025
6.7	7.70	80.9	1.050
10.0	11.26	121.0	1.075
13.0	14.73	162.0	1.100
18.8	21.38	245.9	1.150
24.0	27.72	332.6	1.200
28.8	33.82	422.7	1.250
33.3	36.68	515.8	1.300
37.4	45.26	611.0	1.350
41.2	50.50	707.0	1.400
44.8	55.45	804.0	1.450
48.1	60.17	902.5	1.500
54.1	69.09	1105.4	1.600
59.5	77.63	1319.7	1.700
64.2	87.69	1578.4	1.800
65.4	93.64	1713.6	1.830

Table 4.4 Specific gravity and concentration of hydrochloric acid at 15 °C[5]

Specific gravity	Concentration of HCl	
	(w/w%)	(g l^{-1})
1.000	< 0.16	< 1.6
1.010	2.14	22.0
1.020	4.13	42.0
1.030	6.15	64.0
1.040	8.16	85.0
1.050	10.17	107
1.060	12.19	129
1.070	14.17	152
1.080	16.15	174
1.090	18.11	197
1.100	20.01	220
1.110	21.92	243
1.120	23.82	267
1.130	25.75	291
1.140	27.66	315
1.150	29.57	340
1.160	31.52	366
1.170	33.46	392
1.180	35.49	418
1.190	37.23	443
1.200	39.11	469

pink color is persistent. Depending on the original concentration of sulphuric acid, dilution may be needed. It is worth mentioning here that the dilution of sulphuric acid should be carried out with acid being added into water – never the reverse. Otherwise, a splash of sulphuric acid can cause serious problems.

HCl

The concentration of hydrochloric acid (HCl) can be determined using a hydrometer, in a very similar manner to the determination of sulphuric acid concentration. Table 4.4 shows the relationship between specific gravity (SG) and the concentration of hydrochloric acid at 15 °C.[5] Hydrochloric acid is a volatile acid at high concentration. Caution must be taken to avoid errors in determination of the concentration. The weighing of the concentrated HCl should be under confined conditions using Lunge-Rey weighing pipette, Dely weighing tube or snake weighing tube. The titration of HCl is also very similar to that of sulphuric acid. Methyl red or methyl orange may be used as the titration indicator.

HNO_3

The concentration of nitric acid (HNO_3) can be determined using a hydrometer.

Table 4.5 Specific gravity and concentration of nitric acid at 15 °C[5]

Specific gravity	Concentration of HCl	
	(w/w%)	(g l^{-1})
1.000	< 0.10	< 1.0
1.010	1.90	19.0
1.020	3.70	38.0
1.030	5.50	57.0
1.040	7.26	75.0
1.050	8.99	94.0
1.060	10.68	113
1.070	12.33	132
1.080	13.95	151
1.090	15.53	169
1.100	17.11	188
1.110	18.67	207
1.120	20.23	227
1.130	21.77	246
1.140	23.31	266
1.150	24.84	286
1.160	26.36	306
1.170	27.88	326
1.180	29.38	347
1.190	30.88	367
1.200	32.36	388
1.210	33.82	409
1.220	35.28	430
1.230	36.78	452
1.240	38.29	475
1.250	39.82	498
1.260	41.34	521
1.270	42.87	544
1.280	44.41	568
1.290	45.95	593
1.300	47.79	617
1.310	49.07	643
1.320	50.71	669
1.330	52.37	697
1.340	54.07	725
1.350	55.79	753
1.360	57.57	783
1.370	59.39	814
1.380	61.27	846

Table 4.5 shows the relationship between specific gravity (SG) and the concentration of nitric acid at 15 °C.[5] If titration is used to determine the concentration, phenolphthalein is the indicator.

Table 4.6 Weight percentage and specific gravity of phosphoric acid

% w/w	SG, 25 °C/15.5 °C	% w/w	SG, 25 °C/15.5 °C
22.0	1.1271	62.0	1.4425
24.0	1.1400	64.0	1.4617
26.0	1.1534	66.0	1.4813
28.0	1.1669	68.0	1.5013
30.0	1.1807	70.0	1.5216
32.0	1.1948	72.0	1.5424
34.0	1.2092	74.0	1.5635
36.0	1.2238	76.0	1.5849
38.0	1.2387	78.0	1.6067
40.0	1.2539	80.0	1.6290
42.0	1.2694	82.0	1.6516
44.0	1.2852	84.0	1.6745
46.0	1.3014	86.0	1.6977
48.0	1.3178	88.0	1.7214
50.0	1.3347	90.0	1.7455
52.0	1.3518	92.0	1.7688
54.0	1.3692	94.0	1.7937
56.0	1.3870	96.0	1.8186
58.0	1.4051	98.0	1.8436
60.0	1.4236	100.0	1.8686

H_3PO_4

The concentration of phosphoric acid (H_3PO_4) can be determined in a similar manner to that discussed for H_2SO_4, HCl and HNO_3. Table 4.6 shows the relationship between the specific gravity and the concentration of phosphoric acid at 15.5 °C.[5] If P_2O_5 percentage is needed, Equation [4.7] can be used:

$$\% P_2O_5 = H_3PO_4 \times 0.72425 \quad [4.7]$$

The constant 0.72425 is the ratio of the weight of one molecule of P_2O_5 to that of two molecules of H_3PO_4 because one molecule of P_2O_5 can produce two molecules of H_3PO_4 in the following chemical reaction:

$$P_2O_5 + 3\ H_2O = 2\ H_3PO_4$$

$$141.943 \qquad 2 \times 97.9937 \quad [4.8]$$

$$\frac{141.943}{2 \times 97.9937} = 0.72425$$

4.2.2 Organic acids

HCOOH

HCOOH (formic acid) is the simplest organic acid in terms of its organic structure.

Concentrated HCOOH is usually 88% in strength. Since formic acid is a volatile acid, precautions should be taken to prevent loss of strength in the sample preparation stage. The concentration of formic acid can be determined by acid–base titration as well as by redox titration owing to the reduction power of formic acid. The acid–base titration is conducted just like the titration for the inorganic acids mentioned above. Phenolphthalein is used as an indicator.

The redox titration is carried out using permanganate and oxalic acid. First, a known excess amount of $KMnO_4$ is added into the sample HCOOH solution, which is adjusted to alkaline pH using Na_2CO_3 prior to the addition of permanganate; warm the solution to facilitate the redox reaction; then add a known excess amount of oxalic acid solution and a small amount of H_2SO_4 to the mixture to dissolve the precipitated MnO_2. Excess oxalic acid is back titrated with $KMnO_4$. A blank titration should be conducted to determine the background values of the reagents and the water used.

CH_3COOH

Acetic acid is a weak acid. It is available at different concentrations. Highly concentrated acetic acid at 98% and above is called glacial acetic acid because its freezing point range is between 13.3 ºC (98%) and 16.7 ºC (100%). Glacial acetic acid is flammable. The concentration of acetic acid can easily be determined using acid–base titration with phenolphthalein as an indicator. The water used should be free from CO_2, prepared by boiling before use.

4.2.3 Inorganic bases

NaOH

Sodium hydroxide (NaOH) is also called caustic soda. It is available in solution at different concentrations or in solid form. Commercial NaOH often contains a little sodium carbonate (Na_2CO_3) as a by-product of the manufacturing process. This small amount of Na_2CO_3 will usually not influence its use in textile wet processes. Owing to its strong alkalinity, NaOH can react with CO_2 in air easily. It can also absorb water very quickly. Therefore storage and sample preparation should be arranged with caution. Weighing solid NaOH should be conducted with a weighing bottle. A concentrated solution should be diluted as near as possible to the following acid-base titration to determine its concentration. The water used should be CO_2 free. The titration is done using either sulphuric acid (H_2SO_4) or hydrochloric acid (HCl) with methyl red as an indicator.

Total alkalinity is sometimes used to evaluate the strength of NaOH. The percentage total alkalinity can be expressed as % Na_2O. A NaOH sample solution is prepared first, to which an excess amount of a strong acid solution with a known concentration is added. This mixture is back titrated with a strong base. An equivalent coefficient (E) of the known acid solution to the known base solution

should be determined. Let E = number of millilitres of the known acid solution, equivalent to 1 ml of the known base solution. The total alkalinity as Na_2O is calculated as follows:

$$\% \text{ total alkalinity as NaOH} = \frac{(\text{volume of acid in ml} - \text{volume of base in ml}) \times E \times \text{normality of acid} \times 0\ 031}{\text{weight of NaOH in grams in the sample solution}} \times 100\% \quad [4.9]$$

The total alkalinity as NaOH can be calculated as follows:

$$\% \text{ total alkalinity as NaOH} = \frac{(\text{volume of acid in ml} - \text{volume of base in ml}) \times E \times \text{normality of acid} \times 0\ 04}{\text{weight of NaOH in grams in the sample solution}} \times 100\% \quad [4.10]$$

The detection of a small amount of Na_2CO_3 can be done using a gas analysis method. This method is based on the principle of CO_2 being released from acidified carbonate solution. A special glassware assembly should be used for the accurate measurement of CO_2 released.

An indirect titrimetric method can be used to determine the hydroxide and carbonate in NaOH. A standardised HCl solution is added into a mixture of 50 ml sample NaOH and 50 ml 10% $BaCl_2 \cdot 2H_2O$ neutralised to pastel pink with phenolphthalein. The end point is reached when the pink color disappears. The calculation is as follows:

$$\% \text{ NaOH} = \frac{\text{volume of HCl in ml} \times \text{normality of HCl} \times 0.04}{\text{weight of NaOH in grams}} \times 100\% \quad [4.11]$$

$$\% \text{ } Na_2CO_2 = \% \text{ total alkalinity } Na_2O \times 1.71 - \% \text{ NaOH} \times 1.325 \quad [4.12]$$

Na_2CO_3

Sodium carbonate (Na_2CO_3) is also called soda ash. In textile wet processes, it is often available in anhydrous form. Its purity can be > 99% Na_2CO_3 (58% Na_2O). If the concentration of a Na_2CO_3 solution needs to be determined, a titrimetric method identical to the ones listed for NaOH in this section can be used. If the existence of bicarbonate is a concern (very rarely in textile wet processes) the following method can be used to determine the content of bicarbonate in sodium carbonate.

To the Na_2CO_3 sample solution, an excess amount of a known NaOH solution is added to convert bicarbonate to carbonate. A $BaCl_2$ solution is added to the above mixture to precipitate carbonate as $BaCO_3$ in the presence of phenolphthalein as an indicator. Without filtration, a final back titration is carried out to determine the excess amount of NaOH using a standardised acid solution. If the bicarbonate

exists in a large content, NaOH can be used to titrate the bicarbonate using silver nitrate as an external indicator. The end point is reached when precipitation occurs after a drop of the solution mixed with a drop of $AgNO_3$ solution.

$$\% \ NaHCO_3 = \frac{(\text{ml of NaOH} - \text{ml of acid} \times E) \times \text{normality of NaOH} \times 0.084}{\text{weight of } Na_2CO_3 \text{ in grams of the sample solution}} \times 100\% \quad [4.13]$$

NH_4OH

Ammonium hydroxide (NH_4OH) is a water solution of ammonia gas (NH_3). It can also be called aqua ammonia or ammonia water. The concentration determination can be done using either a hydrometer or an acid–base titration. Since ammonia is volatile, the concentration determination should be done with care to avoid any loss of strength. If a hydrometer is used, the sample and the hydrometer should be cooled to 5–10 ºC. Table 4.7[5] lists the relationship between the concentration (% w/w) and ºBé of NH_4OH at 10 ºC.

Table 4.7 Relationship between the concentration (%w/w) and ºBé of NH_4OH at 10 ºC[5]

ºBé	% w/w
14.02	6.74
14.52	7.61
15.02	8.49
15.52	9.38
16.02	10.28
16.52	11.18
17.03	12.10
17.53	13.02
18.03	13.96
18.53	14.90
19.03	15.84
19.53	16.80
20.04	17.76
20.54	18.72
21.04	19.68
21.54	20.64
22.04	21.60
22.54	22.56
23.05	23.52
23.55	24.50
24.05	25.48
24.55	26.46
25.05	27.44
25.56	28.42
26.06	29.40

Acid–base titration can also be used to determine the concentration of NH_4OH. The procedures are exactly the same as those for NaOH or Na_2CO_3. Standardised H_2SO_4 or HCl is used. Phenolphthalein is the indicator. For more accurate results, back titration can be applied.

4.2.4 Organic bases

Triethanolamine

Triethanolamine, $N(CH_2CH_2OH)_3$, is a strong organic base miscible with water, methanol and acetone. The pH of its 0.1N aqueous solution is 10.5. Analytical grade $N(CH_2CH_2OH)_3$ is a highly hygroscopic and viscous liquid with a pale yellow or no colour. Its melting point is between 18 and 21 ºC. Its density is about 1.12. Without using analytical instruments like gas chromatography,[6] its accurate content analysis is complex for textile chemical applications.[7] A direct titration in aqueous solution with an acid is often a common practice for aliphatic amines. An estimate of its alkalinity can be conducted. A 1 N HCl or H_2SO_4 is used to titrate a 100 ml sample solution at 10 g l^{-1} concentration with methyl orange as an indicator. If the consumption of the acid is between 6.7 and 7.2 ml, the concentration of $N(CH_2CH_2OH)_3$ would be > 80%.

Ethylenediamine

Ethylenediamine, $(H_2NCH_2)_2$, is a strong organic base miscible with water and alcohol. It is a colourless and viscous liquid with a density of 0.898 and a melting point of 8 ºC. The pH of a 25% aqueous solution is 11.5. Like triethanolamine, it is an aliphatic amine soluble in water and, therefore, can be determined by the acid–base titration with methyl orange as an indicator.

4.2.5 Salts

Salts are the products of the acid-base neutralisation reaction. The salts used most in textile wet processes are common salt (NaCl, sodium chloride) and Glauber's salt (Na_2SO_4, sodium sulphate). The content analysis of salts is usually conducted by using a precipitation titration method which may be followed by filtering and weighing procedures to obtain the final results.

Sodium chloride

Industrial grade NaCl has a content of 92–98%. The precipitation titration can be conducted using 0.1 N $AgNO_3$ as the titrant and 5% K_2CrO_4 as the indicator (the Mohr method). The sample chloride solution should be buffered with calcium carbonate to a pH between 6.3 and 7.2 in order to avoid any interference from other

ions present in the solution. After adding potassium chromate solution, the silver nitrate solution is added into the sample chloride solution slowly until a reddish colour appears. The following reactions occur:

$$NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl\downarrow \text{ (white precipitate)} \quad [4.14]$$

$$2AgNO_3 \text{ (excess)} + K_2CrO_4 \rightarrow 2KNO_3 + Ag_2CrO_4\downarrow \text{ (reddish precipitate at end point)} \quad [4.15]$$

The content of NaCl can be calculated using Equation [4.16]:

$$\%\ NaCl = \frac{\text{ml of 0.1 N } AgNO_3 \times 0.005845}{\text{sample weight}} \times 100\% \quad [4.16]$$

Sodium sulphate

Na_2SO_4 is available in two types, anhydrate and decahydrate. Its content analysis can be conducted based on the precipitation method using barium chloride ($BaCl_2$). An excess amount of barium chloride is added into the sample solution which has been filtered beforehand to form $BaSO_4$ precipitate as indicated by the following reaction:

$$Na_2SO_4 + BaCl_2 \rightarrow 2NaCl + BaSO_4\downarrow \quad [4.17]$$

Keep the mixture warm for at least 2 h to complete the precipitation reaction. Filter off, wash and dry the precipitate. Weigh the totally dried white precipitate. The Na_2SO_4 content can be calculated using the following equation:

$$\%\ Na_2SO_4 = \frac{\text{weight of } BaSO_4 \times 0.6094}{\text{sample weight in solution}} \times 100\% \quad [4.18]$$

4.3 Surfactants

Surfactants are widely used in textile wet processes for the purpose of wetting, dispersing, emulsifying and cleaning. The molecular structures of surfactants have a distinctive hydrophilic moiety and a distinctive hydrophobic moiety. When they are used at a sufficient concentration, the surface/interface tension of the solution is lowered and micelles are formed, which give the solution extra properties. According to their ionic properties in aqueous solution, traditional surfactants can be divided into four categories: anionic, cationic, amphoteric and non-ionic. The comprehensive analysis of surfactants is beyond the scope of this book. Readers with this in mind can gain more information from elsewhere.[8] In this section, only simple ionic tests are introduced.

4.3.1 Anionic surfactants

Acidic methylene blue test[9]

Methylene blue is a cationic dye soluble in water and insoluble in chloroform. It can form a blue compound with anionic surfactants which is soluble in chloroform.

Acidic methylene blue solution
Slowly add 12 g H_2SO_4 to 50 ml water; after cooling down, add 0.03 g methylene blue and 50 g Na_2SO_4 anhydrate; dilute the whole solution to 1 l.

Test
Add 5 ml of 1% sample surfactant solution into a mixture of 10 ml methylene blue solution and 5 ml chloroform in a test tube; shake vigorously then allow it to stand until two layers are formed. If the chloroform layer (bottom layer) shows blue, add another 2–3 ml of the surfactant solution. Shake well and leave for layers to form. The chloroform shows as dark blue and the water layer is almost colourless. This is a positive result of the existence of anionic surfactant in the sample solution. This test is suitable for alkylsulphate and alkylbenzolsulphonate surfactants. Soap cannot be tested because it would precipitate in the strong acidic medium.

Basic methylene blue test[10]

Add 1 drop of 5% sample solution to a mixture of 5 ml 0.1% methylene blue solution, 1 ml 1 N NaOH solution and 5 ml chloroform. Shake well and observe the colour of the chloroform layer. If a blue-purple colour is shown, there is an anonic surfactant in the sample. This test is suitable for any type of anionic surfactant.

Thymol blue test[8]

Thymol blue solution is prepared by adding 3 drops of 0.1% thymol blue in every 5 ml of 0.005 N HCl solution.

For the test, add 5 ml neutralised sample solution to 5 ml thymol blue solution. Shake well and observe the colour of the mixture. A reddish-purple colour is the evidence of existence of anionic surfactants in the sample solution.

Precipitation test[11]

A few drops of sample solution are added into 5 ml of 5% *p*-toluidine hydrochloride aqueous solution. If a white precipitate appears, there is anionic surfactant in the sample solution.

4.3.2 Cationic surfactants

Methylene blue test

Cationic surfactants can also be tested using methylene blue solution. First add 2 drops of a known anionic surfactant solution to a mixture of 5 ml methylene blue solution and 5 ml chloroform, shake well and leave to stand until the chloroform layer shows as blue. Then add a few drops of the sample solution, shake well and leave for layers to form. If the blue colour in the chloroform layer becomes lighter or colourless, the existence of cationic surfactants in the sample solution can be confirmed.

Bromophenol blue test[12]

Bromophenol blue solution is prepared by adding 20 ml of 0.1% bromophenol blue in 96% ethanol to a mixture of 75 ml 0.2 N sodium acetate and 925 ml 0.2 N acetic acid. Adjust the pH of the solution to 3.6–3.9.

For the test, add 2–5 drops of a neutralised sample solution to 10 ml of bromophenol blue solution. Shake well and observe the colour of the mixture. If a blue colour is shown, the existence of a cationic surfactant is confirmed.

Alternatively, add 1 drop of 5% sample solution to a mixture of 5 ml chloroform, 5 ml 0.1% bromophenol blue dilute ethanol solution and 1 ml 6 N HCl. Shake well and observe the colour of the chloroform layer. If a yellow colour appears, there is a cationic surfactant in the sample.

Precipitation test[8]

A diluted aqueous solution of either sodium salicylate, sodium benzoate, or sodium succinate can precipitate cationic surfactants.

4.3.3 Non-ionic surfactants

Methylene blue test

The test is conducted as in Section 4.3.1, acidic methylene blue test. If the aqueous layer is emulsified to a milk-like state, or both layers have the same colour, the existence of non-ionic surfactants can be confirmed.

Cloud point test[13]

The solubility of polyoxyethylene surfactants is dependent on their hydrogen bonding with water. At a high temperature, the hydrogen bonds of the surfactants would be dissociated leading to lower solubility of the surfactant. Therefore, the solution of the surfactant becomes cloudy at the high temperature. Based on this principle, the polyoxyethylene surfactants can be detected.

A 1% sample solution is gradually heated with a thermometer in the solution to monitor its temperature. When the solution becomes cloudy, stop heating. Let the solution cool down slowly. The cloud point is reached when the solution turns clear.

4.3.4 Amphoteric surfactants[10]

Amphoteric surfactants contain both anions and cations. They should show positive results when tested using either the basic methylene blue test for anionic surfactants or the alternative bromophenol blue test for cationic surfactants.

A saturated bromine aqueous solution can also be used to determine the type of amphoteric surfactant. Add 5 ml of 1% sample solution to 1.5 ml saturated bromine aqueous solution. Observe the colour of the precipitate. Heat the mixture and observe the change in the precipitate. If the precipitate is a yellow to yellow-orange colour and is dissolved to form a yellow solution after heating, the sample is an imidazoline or alanine type of amphoteric surfactant. If the precipitate is a white to yellow colour and insoluble after heating, the sample is the other type of amphoteric surfactant.

4.4 Oxidising agents and reducing agents

Oxidising agents are mainly used for bleaching and reducing agents are mainly used for vat dyeing in textile wet processes. These agents are often strong chemicals and need to be handled with care. The assay of these agents is almost always based on the redox titration. In a redox reaction, an oxidising agent (oxidant) is reduced (it gains electrons) and a reducing agent (reductant) is oxidised (it loses electrons). The redox reaction can be written as two half reactions shown below:

Oxidation reaction: reducing agent $\rightarrow$ oxidized form + n e^-

Reduction reaction: oxidising agent + n e^- $\rightarrow$ reduced form

The net reaction is: reducing agent + oxidising agent $\rightarrow$ oxidised form + reduced form

4.4.1 Oxidising agents

Hydrogen peroxide[14]

Hydrogen peroxide (H_2O_2) can be titrated with potassium permanganate ($KMnO_4$) in an acid medium. H_2O_2 is the reducing agent and $KMnO_4$ is the oxidising agent.

Accurately prepare 500 ml 0.4% H_2O_2 sample solution containing 2 ml 33% H_2SO_4. Transfer 20 ml of the sample solution to a 500 ml conical flask containing 15 ml 33% H_2SO_4 and 60 ml distilled water. Titrate the mixture with a standardised

0.1 N $KMnO_4$ until a faint pink colour appears for about 30 s. Record the millilitres of the $KMnO_4$ solution consumed. The H_2O_2 concentration can be calculated using the following equation:

$$\%\ H_2O_2\ (w/w) = \frac{\text{ml of } KMnO_4 \times \text{normality of } KMnO_4 \times 1.701 \times 50}{\text{weight of } H_2O_2 \text{ in the sample solution}} \times 100\% \quad [4.19]$$

The AATCC Test Method 102 can also be used to determine the concentration of H_2O_2. It is based on the same principle redox mechanism using potassium permanganate.[15]

Sodium Hypochlorite[16]

In hypochlorite bleaching of textiles, active chlorine is the species measured for the control of the bleaching process. Iodometry is the method used to determine the content of active chlorine.

Prepare a sample solution by dissolving 1 g sample in a minimum amount of water. Add it to a mixture of 20 ml 10% KI, 15 ml 6 N acetic acid and 100 ml distilled water. Titrate the mixture with 0.1 N $Na_2S_2O_3$ until the solution shows a pale yellow colour. Add 3 ml 1% starch solution and continue the titration until the blue colour disappears. Active chlorine concentration can be obtained by using Equation [4.20]:

$$\%\ \text{active chlorine} = \frac{\text{ml of 0.1 N } Na_2S_2O_3 \times 0.00355}{\text{sample weight}} \times 100\% \quad [4.20]$$

Sodium perborate[17]

Either sodium permanganate or potassium iodide can be used to titrate the sodium perborate ($NaBO_3 \cdot 4H_2O$). Dissolve 0.2 g of sample in 200 ml distilled water, add 40 ml 6 N H_2SO_4, titrate with 0.1 N sodium permanganate until a pink colour appears. The assay of sodium perborate can be calculated using Equations [4.21] and [4.22]:

$$\%\ NaBO_3 \cdot 4H_2O = \frac{\text{ml of } KMnO_4 \text{ solution} \times \text{normality of } KMnO_4 \times 0.07695}{\text{sample weight}} \times 100\% \quad [4.21]$$

$$\%\ \text{active oxygen} = \frac{\text{ml of } KMnO_4 \text{ solution} \times \text{normality of } KMnO_4 \times 0.008}{\text{sample weight}} \times 100\% \quad [4.22]$$

4.4.2 Reducing agents

Sodium hydrosulphite ($Na_2S_2O_4$)[17]

Dilute 10 ml 40% formaldehyde with 50 ml distilled water. Dissolve 1 g sample in the diluted formaldehyde solution. Shake well and leave it to stand for 20 min. Dilute the solution to 500 ml. Take 50 ml out of the 500 ml solution and dilute it to 150 ml. Titrate the solution with 0.1 N aqueous bromine solution until a red brown colour appears. Back titrate the red brown solution with 0.1 N $Na_2S_2O_3$ until a pale yellow colour is shown. Add 2–3 drops of 1% starch solution and continue to titrate until the blue colour disappears. $Na_2S_2O_4$ concentration can be calculated using Equation [4.23]:

$$\% \ Na_2S_2O_4 = \frac{(N_{I_2} \times V_{I_2} - N_{Na_2S_2O_3} \times V_{Na_2S_2O_3} \times 0.04353}{\text{sample weight} \times \dfrac{50}{500}} \times 100\% \quad [4.23]$$

where N_{I_2} and V_{I_2} are the normality and volume in ml of I_2 solution used, $N_{Na_2S_2O_3}$ and $V_{Na_2S_2O_3}$ are the normality and volume in ml of $Na_2S_2O_3$ solution used.

Glucose[17]

Glucose ($C_6H_{12}O_6$) can be used as a reducing agent in vat and sulphur dye applications. It can be analysed by iodometry. Accurately prepare a 0.5% glucose solution. To 50 ml 0.5% glucose solution containing 0.25 g glucose, add 50 ml 0.1 N I_2 and 75 ml 0.1 N NaOH. Shake and leave it to stand for 15 min. Add 4–5 ml 2 N H_2SO_4 and shake. With 3–5 ml of 1% starch solution as an indicator, titrate using 0.1 N $Na_2S_2O_3$ until a blue colour disappears:

$$\% \ C_6H_{12}O_6 = \frac{(N_{I_2} \times V_{I_2} - N_{Na_2S_2O_3} \times V_{Na_2S_2O_3} \times 0.09005}{0.25} \times 100\% \quad [4.24]$$

Sodium thiosulphate[17]

Sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$) can be titrated easily by iodometry. Accurately weigh a 5 g sample and dissolve it in 500 ml distilled water to make a 1% sample solution. To 50 ml of 1% sample solution, add 50 ml distilled water and 3–5 ml 1% starch solution. Titrate with 0.1 N I_2 solution until a blue colour is shown:

$$\% \ Na_2S_2O_3 = \frac{(N_{½} \times V_{½} \times 0.15812}{\text{sample weight} \times \dfrac{50}{500}} \times 100\% \quad [4.25]$$

4.5 Miscellaneous chemicals

4.5.1 Organic solvents

Ethanol

The specific gravity of ethanol (C_2H_5OH) is directly related to its content. Table 4.7 lists the relationship between the volume% (weight%) and the specific gravity of ethanol at 15 ºC.

Ethylene glycol and glycerol

ASTM method D1615[18] may be used to estimate the concentration of ethylene glycol and glycerol in an aqueous medium. Though this method was withdrawn in 2004, it is still a method that could give a good result when no alternatives are available. A brief description of the modified method is listed below:

1. Accurately weigh 1–2 g of sample and make up a sample solution of 100 ml. Mix 20 ml of the sample solution with 2 drops of methyl purple indicator and 50 ml of freshly prepared 11g l^{-1} periodic acid solution. Shake well.
2. Prepare two 20 ml blanks and leave them to stand for about 1 h at room temperature.
3. Add 100 ml of distilled water and 3 drops of methyl purple indicator to the sample solution and the blank. Titrate with 0.1 N NaOH to neutral pH.
4. Add 150 ml distilled water, 30 ml 200 g l^{-1} KI solution and 25 ml 16.7% sulphuric acid to the solution that has just been titrated in step 3. Titrate with 0.2 N $Na_2S_2O_3$ solution until a pale yellow colour is obtained. Add 5 ml of 1% starch solution and continue to titrate until the blue colour disappears.

The following equations are used to calculate *G*, the glycerol percentage; *T*, the glycerol and ethylene glycol percentage expressed as the percentage of glycerol; and *E*, the ethylene glycol percentage.

$$\% G = \frac{(A - B) \times N \times 0.09206}{W \times 0.2} \times 100\% \quad [4.26]$$

where *A* is the volume in ml of NaOH for the sample solution, *B* is the volume in ml of NaOH for the blank solution, *N* is the normality of NaOH solution, 0.09206 is the number of grams of glycerol equivalent to 1 ml of 1 N NaOH solution, *W* is the weight in grams of sample and 0.2 is the aliquot fraction of sample.

$$\% T = \frac{(B' - A') \times N \times 0.023015}{W \times 0.2} \times 100\% \quad [4.27]$$

Table 4.7 Ethanol volume % versus specific gravity at 15 °C

Volume %	Weight %	Specific gravity
5	4.00	0.99281
10	8.04	0.98680
15	12.13	0.98114
20	16.23	0.97608
25	20.43	0.97097
30	24.66	0.96541
35	28.96	0.95910
40	33.35	0.95185
45	37.84	0.94364
50	42.52	0.9343
55	47.29	0.9242
60	52.20	0.9134
65	57.24	0.9021
70	62.50	0.8900
75	67.93	0.8773
80	73.59	0.8639
85	79.55	0.8496
90	85.75	0.8340
95	92.46	0.8164
100	100	0.7946

where A' is the volume in ml of $Na_2S_2O_3$ for the sample, B' is the volume in ml of $Na_2S_2O_3$ for the blank, N is the normality of $Na_2S_2O_3$ solution, 0.023015 is the number of grams of glycerol equivalent to 1 ml of 1 N $Na_2S_2O_3$ solution, W is the weight in grams of sample and 0.2 is the aliquot fraction of sample.

$$E = 1.348\ (T–G) \qquad [4.28]$$

4.5.2 Others

Urea[17]

Urea is tested for the content of nitrogen using H_2SO_4 and formaldehyde. The indicator used is a mixed indicator containing 0.5 g phenolphthalein and 0.5 g thymol phthalein dissolved in 100 ml ethanol. A 25% formaldehyde solution used should be neutralised before use. The procedures of the method is briefly described below.

1. Dissolve 1 g fully dried sample in a small amount of water; add 3 ml concentrated H_2SO_4; mix well and heat on a hot plate.
2. Heat until the release of CO_2 (bubbling) has stopped and dense white smoke (SO_3) is emitted; leave to cool down.
3. Add 50 ml distilled water and 2 drops of methyl red indicator.

4. Neutralise the acidity of the solution with 6 N NaOH added dropwise until the red colour changes to a pink colour; add 0.5 N NaOH slowly to change the solution colour to a faint pink.
5. Add 40 ml 25% neutralised formaldehyde solution and 5 drops of the mixed indicator; stand for a few minutes.
6. Titrate with 1 N NaOH until a violet colour that can last for 1–1.5 min.

The concentration can be calculated using Equations [4.29] and [4.30]:

$$\% \text{ N} = \frac{N_{\text{NaOH}} \times V_{\text{NaOH}} \times 0.014}{\text{sample weight}} \times 100\% \quad [4.29]$$

$$\% \text{ CO(NH}_2)_2 = \frac{N_{\text{NaOH}} \times V_{\text{NaOH}} \times 0.03}{\text{sample weight}} \times 100\% \quad [4.30]$$

Fluorescent whitening agents

Fluorescent whitening agents (FWA) are a special type of chemical that can significantly increase the apparent whiteness of treated fabrics. They absorb UV radiation and re-emit the absorbed energy in the blue visible light range which makes the treated fabrics appear whiter. The easiest test for the effect of FWAs is simply a visual examination of the whiteness of treated fabrics. Manufacturer's recommendations should be followed in order to achieve the best whitening effect.

Ethylenediamine tetraacetate (EDTA)

Ethylenediamine tetraacetate (EDTA) can form a few different water soluble salts with calcium, potassium and sodium, for example, calcium disodium, trisodium and tetrasodium salts. EDTA tetrasodium salt is used most widely in many industrial applications as a powerful chelating agent. Its 1% solution has a pH of 11.3. It can chelate with many divalent and trivalent metal ions to form water-soluble metal complexes. The chelation value can then be used to evaluate the chelating power of EDTA-based chelating agents.[19] According to AATCC Test Method 149, the active content of ethylenediaminetetraacetic acid (EDTA), *N*-hydroxyethylethylenediaminetriacetic acid (HEDTA) and diethylene-triaminepentaacetic acid (DTPA) and their salts can be expressed by the calcium chelation value (CaCV). The testing requires a pH 12 medium and use of calcium carbonate as a titrant and sodium oxalate as an indicator. The titration end point is reached when a slight turbidity occurs which is caused by calcium oxalate precipitate. CaCV can be calculated by using Equation [4.31]:[19]

$$\text{CaCV} = \frac{100.1 \times 0.250 \times V}{W} \quad [4.31]$$

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5

Analysis of chemicals used in fibre finishing

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5.1 Introduction

A very important concept in the textile operations is that fibre, as the fundamental component of textiles, should be protected as much as possible during processing. Starting before spinning and progressing through fabric formation, fibres are exposed to many harsh processing environments including physical (temperature, friction, tension and compression), chemical (pH, inorganic and organic compounds) and biological (bacteria and enzyme) variables. Fibre finishing is usually the first step in textile processes where chemicals are used to give fibres protective and functional properties. For instance, sizing agents are added to fibre assembly-yarn to facilitate the weaving operation, lubricating agents are needed to smooth the yarn spinning process and different additives are used to improve the spinning, yarn formation and fabric formation.

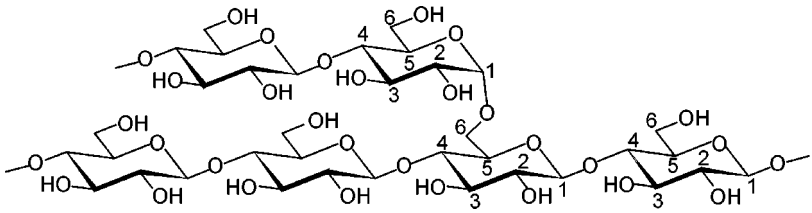
5.2 Sizing agents

As mentioned briefly above, sizing agents are added to the yarns that are used in the weaving operation. More specifically, sizing agents are added only to warp yarns, not to filling yarns. This is because the warp yarns are under high tension and constant friction during the weaving operation. Without sizing, the warp yarn cannot be used for weaving; it would be broken easily and quickly, causing the weaving machine to stop and result in very low and even no productivity for the weaving operation. The sizing agents can give warp yarns extra strength to withstand the high tension and a smooth surface to reduce friction.

5.2.1 Natural sizing agents

Starch and its derivatives

Starch is a natural polymer from the group called polysaccharides which has multi-anhydroglucose units. The chemical formula of starch is $(C_6H_{10}O_5)_n$. Starch has chemically two moieties, an amylose part which consists of anhydroglucopyranose



5.1 Chemical structure of amylopectin.

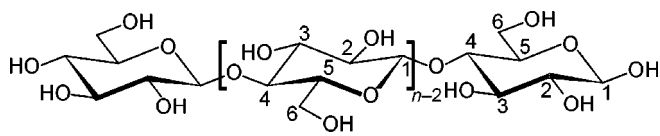
units joined by α-D 1,4 glycosidic bonds and an amylopectin part which consists of anhydroglucopyranose units linked by α-D 1, 6 glycosidic bonds as shown in Fig. 5.1. Amylose has a linear chain and amylopectin has a branched chain.

Starch can be decomposed by pyrolysis and acidic hydrolysis. British gums and dextrins are products derived from starch. They have a lower molecular weight and better water solubility. A qualitative test of starch and its derivative can be conducted using an aqueous solution containing 1.4 g l^{-1} I_2 and 2.4 g l^{-1} KI.[1] The existence of starch (specifically amylose) will turn the yellow-orange colour of the solution to a dark blue colour. When tested with I_2/KI solution, British gums and completely degraded dextrins give a reddish brown colour, partially degraded dextrins give a violet colour and white dextrin give a blue colour.[2]

Cellulose derivatives

Cellulose is another natural polymer belonging to the polysaccharides group. The chemical formula for cellulose is $(C_6H_{10}O_5)_n$. It has a chemical structure very similar to amylose. Instead of α-D 1,4 glycosidic bonds, cellulose has only β-D 1, 4 glycosidic bonds as shown in Fig. 5.2. Because of these β-D 1, 4 glycosidic bonds, the molecular chain of cellulose can extend quite linearly, making it a good fibre-forming polymer. In order to use cellulose for sizing purposes, it should be modified to shorten the molecular structure. Two of the most-used cellulose derivatives are carboxymethyl cellulose (CMC) and hydroxyethyl cellulose (HEC).

Carboxymethyl cellulose (CMC) is manufactured from alkali cellulose and sodium chloroacetate. The hydrogen atoms of hydroxyl groups on C2 and C6 are partially substituted with $–CH_2COONa$ or $–CH_2COOH$ depending on reaction conditions. The degree of substitution (DS) is usually between 0.2 and 1.5 (0.2 to 1.5 carboxymethyl groups ($–CH_2COOH$) per anhydroglucose unit). CMC with DS



5.2 Chemical structure of cellulose.

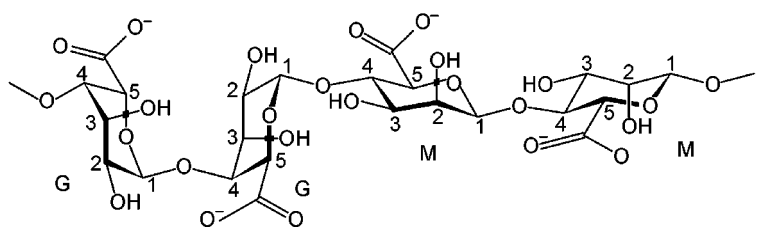
1.2 or below is water soluble. The final product always contains sodium salt. A foaming test can distinguish sodium CMC from other cellulose ethers, alginates and natural gums.[3] Sodium CMC solution, after vigorous agitation, would not produce any foam layer. Uranyl nitrate can be used to detect the existence of CMC. A 4% uranyl nitrate is used to precipitate CMC between pH 3.5 and 4.[4] A 0.5% methylene blue methanol solution may also be used to detect CMC on the fabric.[5] After rinsing in distilled water and drying, the methylene blue treated sample may show a blue/purple colour which confirms the existence of CMC or acrylic sizes. A separate extraction of the fabric with toluene can exclude the acrylic sizes from the test.

When the hydrogen atom of the hydroxyl group on C6 of cellulose is partially substituted with a hydroxyethyl ($-CH_2CH_2OH$) group in a reaction with ethylene oxide under alkaline condition, hydroxyethyl cellulose (HEC) is produced. So far there are no known testing methods for HEC detection. However, if one wants to distinguish CMC from HEC, an ion tolerance test can be conducted. CMC is anionic and can be precipitated from an aqueous solution with a cationic surfactant. Since HEC is non-ionic, its aqueous solution is compatible with cationic surfactants. Based on the same ionic tolerance principle, a high salt concentration can precipitate CMC, not HEC.

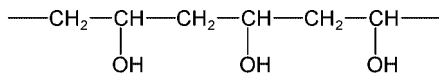
Alginates

Alginates are linear co-polymers of randomly arranged β-D 1, 4 mannuronic acid (M) and α-L 1, 4 guluronic acid (G) blocks as represented in Fig. 5.3. Its chemical structure is similar to that of cellulose except that it has a carboxylic group on the C5 position instead of a methylol group in the case of cellulose.

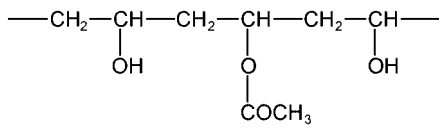
Alginates have good water solubility. Di- and higher valent metal ions, strong acids and bases can precipitate alginates out of its aqueous solutions. In order to distinguish alginates from other thickening agents, precipitation methods can be tried.[3] A 2.5% $CaCl_2$ can cause a 0.5% sodium alginate solution to precipitate. Aqueous solutions of gum arabic, sodium carboxymethyl cellulose, carrageenan, gelatin, gum ghatti, karaya gum, carob bean gum, methyl cellulose and tragacanth gum would not be affected. Saturated $(NH_4)_2SO_4$ would not precipitate 0.5%



5.3 Chemical structure of alginate.



(a)



(b)

5.4 Chemical structures of PVA. (a) Fully hydrolysed and (b) partially hydrolysed PVA.

sodium alginate. But agar, sodium carboxymethyl cellulose, carrageenan, de-esterified pectin, gelatin, carob bean gum, methyl cellulose and starch would be affected. The existence of sodium alginate can be tested with acid $Fe_2(SO_4)_3$.[3] When the sample has been in contact with a ferric sulphate solution for 5 min, a cherry-red colour appears and gradually changes to a deep purple colour. This confirms the presence of sodium alginate in the sample.

5.2.2 Synthetic sizing agents

Polyvinyl alcohol

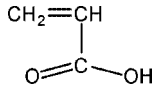
Polyvinyl alcohol (PVA) is the hydrolysis product of polyvinyl acetate. Depending on the hydrolysis conditions, there are fully hydrolysed PVA and partially hydrolysed PVA, as shown in Fig. 5.4a and b, respectively.

Fully hydrolysed PVA usually has a degree of hydrolysis (DH) of 98–99.8% and can dissolve in water only at > 80 ºC. The solubility of partially hydrolysed PVA with a DH between 85 and 90% is dependent upon its molecular weight. Partially hydrolysed PVA with the higher molecular weight requires a high temperature to dissolve.

Specific detection of PVA on fabrics can be achieved using potassium dichromate ($K_2Cr_2O_7$).[4] Two solutions are used. Solution A consists of 11.88 g $K_2Cr_2O_7$ and 25 ml concentrated H_2SO_4 in 50 ml distilled water. Solution B contains 30 g NaOH in 70 ml distilled water. After solutions A and B are applied to a white fabric sample sequentially, the brown colour developed indicates the existence of PVA. A yellow-green colour can be triggered by unsized goods, potato starch, styrene-maleic anhydride copolymer, alginates, guar, gelatin or CMC.

Acrylics

Acrylic is a generic term for a large group of homopolymers and copolymers



5.5 Chemical structure of acrylic acid.

derived from acrylic acid, shown in Fig. 5.5. Since the hydrogen atoms of the carboxylic group and the vinyl group can be substituted by many different chemical groups, a huge variety of polyacrylic acid and polyacrylates is currently available for many different applications. Most of them are used as an emulsion.

The analysis of acrylics is almost impossible without using sophisticated instruments. There are no known simple methods for the tests that need to be done in wet chemistry, which could be because (1) analysis with wet chemistry is too complicated; (2) analysis has to deal with too many different types of polymers; (3) analysis involves the use of many toxic organic solvents. If an analysis is needed, it is recommended that either Fourier transform infrared spectroscopy (FTIR) or gas chromatography (GC) be used to obtain results quickly and accurately. FTIR analysis of acrylics can show very distinctive absorption peaks between 1100 and 1150 cm^{-1} for the alkyl C–O–C stretching band and at 1750 cm^{-1} for the C=O stretching band. If the acrylic polymer system contains some vinyl monomers, a broad peak at 3020 cm^{-1} and a strong peak at 1660 cm^{-1} indicate the stretching bands of C–H and C=C in CH=CH structure, respectively.[6] With GC analysis, acrylic acid, ethyl methacrylate, *n*-butyl acrylate, 2-ethylhexyl acrylate, isobutyl acrylate, methyl methacrylate, ethyl acrylate and methyl acrylate can all be detected and determined quantitatively.[7] ASTM Test Method D3362[8] is a standardised method to determine the purity analysis of acrylate. It is certain that more types of acrylates can be successfully analysed nowadays with modern instruments.

5.3 Lubricants and cohesive agents

Lubricants are added into fibre finishes to reduce the friction between fibres and the hard surface of the spinning equipment, whereas cohesive agents are used to increase the frictions between fibres. The overall purpose of using lubricants and cohesive agents is to run the spinning process faster, to reduce fibre damage as much as possible and to make the spinning process run at high speed for as long as possible, which means high quality, large volume and better productivity.

5.3.1 Waxes

Waxes are a group of organic compounds consisting mainly of heat-sensitive hydrocarbons which are insoluble in water but soluble in most organic solvents and, most of them, free from glyceride.[9] Sources of waxes can be animal, vegetable, mineral, synthetic and petroleum. The waxes used for fibre finishing are

mostly petroleum-based. Paraffin wax is one of them. They are inexpensive and easily available. However, their performance is not as good as synthetic compounds. If used alone, waxes are very difficult to remove in the textile processes that follow their application and use, causing dyeing and finishing problems. Tests for waxes are mainly for their physical properties, such as melting point, flash point, colour, density, odour and so on. Readers interested in more specific tests are recommended to refer to ASTM D1168.[10]

One chemical test that is useful for textile wet processes may be the spot test. By using hydroxamic acid, waxes and fatty oils can be distinguished from their mineral counterparts.[11] In a small crucible, one drop of a saturated ethanol solution of hydroxamic acid is mixed with one drop of an ethanol solution of the sample and one drop of an ethanol solution of KOH. The mixture is heated to bubbling (evaporation) and then allowed to cool and is acidified with HCl. A drop of $FeCl_3$ is added to the acidified sample. A violet colour confirms the existence of waxes and fatty oils. Carboxylates may also give a positive result. If the saponification number of waxes needs to be known, ASTM D1387 can be used.[12] ASTM D1386 can be used to determine the acid number of waxes.[13]

5.3.2 Oils and greases

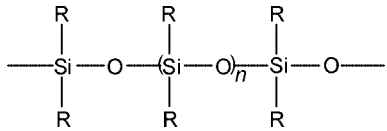
Oils and greases belong to the same type of organic compounds as waxes but have lower molecular weights. Oils have a lower viscosity and are used at lower temperature than greases.

Quantitative analysis of oils and greases can be conducted using methods regulated by IUPAC.[14] Many ASTM methods can also be used to determine the specific chemical properties of oils and greases. For example, ASTM D1980 can be used for the analysis of the acid value;[15] ASTM D1965 for the unsaponifiable matter;[16] ASTM D1957 for the hydroxyl value;[17] and ASTM D1541 for the total iodine value.[18] For the purpose of a qualitative test, two simple but not specific methods can be tried with some interference from other chemicals present in the sample. The first method is based on the fact that oils can usually show fluorescence clearly with UV light. The second method is based on the fact that oils can dissolve solvent dyes but not acid dyes and other water-soluble dyes.

The total content of oils, fats and waxes on fabrics can be extracted with 1,1,1-trichloroethane using the Soxhlet extractor. By comparing the fabric weight before and after extraction, the weight percentage of oils, fats and waxes can be easily calculated.[19] It was reported that supercritical CO_2 can be used instead of the toxic organic solvent to extract the commercial finishes from polyester, nylon and polypropylene fibres.[20]

5.3.3 Synthetic compounds

Many synthetic compounds can be used as lubricants and cohesive agents. In the



5.6 Chemical structure of silicones.

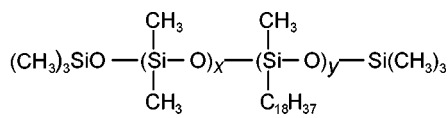
lubricant group, many are esters of organic acids, such as octyl isononanoate, decyl adipate and tridecyl stearate. In the cohesive agent group, many are non-ionic surfactants, such as ethoxylated decyl alcohols, ethoxylated oleyl alcohol and their derivatives. Similar to the case of acrylics, these synthetic compounds vary widely. It is difficult to analyse them chemically using a simple wet chemical mechanism. However, the methods mentioned in Chapter 4, Section 4.3.3 and Section 5.3.2 here can meet most requirements for the textile applications.

5.3.4 Silicones

Silicones are a special group of polymers containing –Si–O– as the backbone of the structure, as shown in Fig. 5.6. The R groups in the structure may be the same or different chemical groups. The most popular are methyl, phenyl and chlorophenyl groups. Silicones can be used as high-performance lubricants in spandex spinning, sewing threads treatment, knitting operation and rope manufacturing.

However, they are not used for yarns that are dyed in the later process because silicone lubricants are difficult to remove, and silicones removed from the yarns can deposit on the surface of machine parts, causing many processing problems.

The most-used silicone lubricants in the fibre finishing applications are polydimethylsiloxane, polymethylphenylsiloxane, oleophilic silicone/organic copolymer (Fig. 5.7a), and poly(glycol silicone copolymer) (Fig. 5.7b). The analysis of silicones can be conducted by FTIR. A strong and often broad absorption in the 1000–1100 cm^{-1} region can be attributed to the Si–O vibration. A peak at 1100 cm^{-1} shows the Si–O–Si vibration. A sharp peak at 1260 cm^{-1} indicates the Si–CH_3 stretching absorption.[21]



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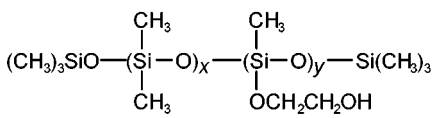
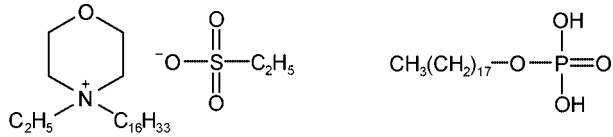


(b)

5.7 Chemical structures of the two most used silicone lubricants.



(a) (b)

5.8 Chemical structures of two common antistats.

5.4 Other additives

In a good fibre finishing formulation, lubricants are always the most important component. However, lubricants alone cannot make the formulation work perfectly. Usually, an antistatic component is included to control the static charge generated during the spinning process, an antimicrobial agent is used to control the growth of microorganisms, an antioxidant is used to prevent the formulation from oxidation damage and a defoamer and an emulsifier are also used to facilitate the production of the final finish. These components, often used in a small quantity, are not necessarily all used together, depending very much on the application and formulation.

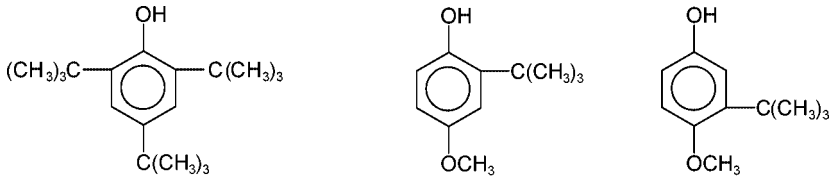
5.4.1 Antistatic agents

'Antistatic agent' can also be called 'antistat' in the industry. The best antistatic agents used in fibre finishes are quaternary amines and alcohol phosphate esters. For example, *N*-cetyl-*N*-ethylmorpholinium ethylsulphate shown in Fig. 5.8a and stearyl alcohol phosphate shown in Fig. 5.8b are representative antistats.

Figure 5.8a is clearly a cationic surfactant. Indeed, the structure shown in Fig. 5.8a can be used as a multifunctional agent, being an antistat, as a cationic surfactant, as a lubricant and even as an antimicrobial agent. The detection of this type of quaternary amines can be followed by the methods described in Chapter 4, Section 4.3.2. Figure 5.8b is an alcohol phosphate that can be easily neutralised as the –OH group connected to the P atom can be dissociated to show the required charge conductivity. When neutralised, it is actually an anionic surfactant. Similar to quaternary amines, stearyl alcohol phosphates can be used as emulsifiers as well as being excellent antistats. Accordingly, they can be detected using the methods presented in Chapter 4, Section 4.3.1.

5.4.2 Antimicrobials

There is a wide range of chemicals suitable for antimicrobial application to fibre finishes. However, for practical reasons, amine-based chemicals, especially quaternary amines are used most because they can show multifunctionality as mentioned in Section 5.4.1.



(a) (b1) (b2)

5.9 Chemical structures of (a) BHT and (b) BHA.

5.4.3 Antioxidants

Antioxidants are used to protect the finishes and the treated fibres from attack by oxygen and heat. Many antioxidants are used in rubber, plastic, composite, paint and coating/laminating materials. Hindered phenols are widely used as antioxidants, especially in the food industry. Two representative ones are butylated hydroxytoluene (BHT, 2,6-di-*t*-butyl-4-methyl-phenol as shown in Fig. 5.9a) and butylated hydroxyanisole (BHA, a mixture of 2- and 3-*t*-butyl-4-hydroxyanisole, shown in Fig. 5.9b1 and b2, respectively).

Apart from the alkylated phenols, phenyl-β-naphthylamine, acetone diphenylamine reaction products and alkylated diphenylamines are also used in different industrial applications and they can absorb UV light. Using proper solvents, these antioxidants can be both qualitatively and quantitatively analysed. Table 5.1 shows the solvents and test conditions for determination of antioxidants.[7]

Sometimes, chelating agents are used to diminish the catalytic effect of metal ions which, if present in the finish system, can promote the autoxidation reaction. EDTA is one of the most commonly used chelating agents. EDTA sodium salt can chelate nickel ions thus preventing the formation of red nickel dimethylglyoxine. Two solutions are needed, one being 0.008% nickel sulphate and the other 1% dimethylglyoxine in alcohol.[4]

5.4.4 Defoamers

Defoamers are used in fibre finishes in order to inhibit the formation of foam during the manufacturing and application of the finishes. Silicones and fluorochemicals are outstanding defoamers. They have very low surface tension and limited solubility in many organic compounds. They can quickly reduce the local surface tension of bubbles to create an imbalance of surface tension which leads to the easy rupture of bubbles. Silicones can be analysed using FTIR. The analysis of fluorochemicals is difficult because fluorochemicals, especially perfluoro compounds, are resistant to many reagents. One microdetermination of fluorine by alkali fusion in a metal bomb was reported.[22] Since it is too complicated and specialised apparatuses are used, this method is not introduced here.

Table 5.1 Solvents and test conditions for determination of antioxidants

Antioxidant	Solvent	Detection wavelength (nm)
Phenyl-β-naphthylamine	Toluene	309
Acetone diphenylamine reaction products	85% Methylcyclohexane 15% Ethanol	288
Alkylated diphenylamines	Methylcyclohexane	288

5.4.5 Emulsifiers

Emulsifiers are used to help immiscible components become compatible with each other to form an easily applicable finish, usually in a liquid form. Since emulsifiers are surfactants, they can be tested using the methods presented in Chapter 4, Section 4.3.

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6

Chemical analysis of fabric finishes and performance-related tests

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6.1 Introduction

Textile finishing is the final process in converting greige fabricated textile materials into a condition that allows formation of garments, home furnishings and other consumer goods. Chemical finishing, that is, applying chemicals to textiles to achieve specific performance results, is a major part of the finishing process. Desirable physical and chemical properties of the textile can be enhanced and undesirable properties minimized. In order properly to control, evaluate and optimize the chemical finishing process, analysis of the finished fabric and performance evaluation are necessary. The following sections discuss the various methods that can be used to test chemical finishes and treated fabrics.

6.2 Analysis of fabric finishes

The identification of chemical finishes on fabrics can serve several purposes. Often a fabric with an unknown finish needs to be analyzed for forensic or competitive reasons. Fabrics that do not perform as expected need to be analyzed to determine if the correct finish was applied in the proper concentration. Regular analysis of production fabrics forms a basis for process improvement through application of statistical process control methods.

The special character of textile finishes can make chemical analysis less than straightforward. A typical chemical finish for textiles has numerous components including the active agent, surfactants, softeners and miscellaneous processing aids. In addition, many finishes undergo chemical changes during the finishing process, that is, the cross-linking reactions that occur in durable press finishing. If the fabric has been washed after finish application either as part of the finishing process or by a consumer after purchase, the water-soluble components may have been partially or completely removed. The most useful approach is often to prepare fabrics with known finishes and use these as internal standards when analyzing unknown or questionable fabrics.

Table 6.1 Infrared frequencies associated with chemical finishes

Absorption frequency (cm^{-1})	Chemical bond
3700–3300	O–H
3500–3200	N–H
2967–2857	C–H
2252–2062	C≡N
1750–1735	C=O (esters)
1725–1700	C=O (saturated aliphatic acids)
1725–1705	C=O (saturated aliphatic ketones)
1680–1630	C=O (amides)
1600–1500	C=C (aromatic)
1570–1515	N–H (secondary amides)
1250–1150	C–O (esters)
~ 1250	P=O
720–730	C–H

The following sections discuss a variety of analysis methods that can be used to examine textile finishes. The discussion is divided into two sections, one for methods that can be used with fabrics without separation techniques and the other for techniques that require extraction of the finish or finish component of interest from the fabric.

6.2.1 Non-extractive methods

Infrared spectroscopy

One of the most useful analytical methods for examining chemical finishes on fabrics is infrared spectroscopy.[1–3] By using a reflectance infrared sampling process, the finish does not need to be separated from the fabric. In this technique, the fabric sample to be analyzed is exposed to infrared radiation in the 600–4000 cm^{-1} range. After reflection, the resultant energy spectrum is recorded. The chemical bonds in the sample absorb specific wavelengths of the incident radiation depending of the nature of each molecule's vibrations. Specific absorption frequencies in the infrared region have been assigned to particular chemical bonds. Table 6.1 lists some of the frequencies associated with chemical finishes used with textiles.

By studying the absorbed frequencies from a sample, the presence or absence of specific functional groups can be inferred.

Of the various infrared techniques available, Fourier transform infrared (FTIR) spectroscopy has become the most useful for textile finish analysis. The entire spectrum is recorded simultaneously and scanning is not necessary. In this way, many spectra can be recorded and averaged in a short time. FTIR utilizes a computer interface to store and manipulate the recorded spectra. The spectra can then be easily compared with libraries of standard spectra to aid in the identifica-

tion of the fabric finish. FTIR is often combined with the attenuated total reflectance (ATR) data collection technique. The ATR technique involves placing the fabric sample horizontally on a zinc selenide crystal. The incident infrared radiation enters the crystal at one end and exits the other after multiple internal reflections between the sample surface and the crystal interior. The radiation typically only penetrates the sample to a depth of a few micrometers, so the technique is limited to surface studies. An example of the use of FTIR with textile finishes is given by Morris *et al*.[4] The authors determined the amount of a durable press finish (dimethyloldihydroxyethylene urea or DMDHEU) on finished fabric by first generating fabrics with known levels of DMDHEU and then analyzing them with both FTIR and elemental nitrogen analyses. The percent DMDHEU found by FTIR compared very favorably with the amounts found by nitrogen analysis.

Another very useful technique similar to infrared spectroscopy is near infrared (NIR) spectroscopy.[5] With this method, radiation in the 4000–12 500 cm^{-1} range is employed. This radiation is energetic enough to excite overtones and harmonics of molecular vibrations. The method can be used to determine organic functional groups such as O–H, N–H, and C=O quantitatively if adequate calibration samples are available. The instrumentation used with NIR makes it quite suitable for in-process monitoring of textile finishing processes.[6] NIR has also been used to determine DMDHEU and DMDHI (1,3-dimethyl-4,5-dihydroxy-2-imidazolidinone) concentrations on cotton fabric.[7] In this study, excellent correlation was found between the NIR results and elemental analyses.

X-ray fluorescence

When a material is exposed to a beam of high-energy X-ray radiation, the inner shell electrons of the material's atoms are ejected by the absorbed X-rays and outer shell electrons fall into the vacant orbitals, emitting characteristic fluorescence.[8] The intensity of each individual fluorescence is proportional to the amount of that element present. The radiation for X-ray fluorescence is generated with tungsten, molybdenum or chromium target tubes in high-voltage electrical fields. X-ray fluorescence instrumentation can provide concentrations of suitable elements accurate to 0.1% in less than 1 min. No special sample preparation is needed, however, calibration with known standards should be done if quantitative results are desired. The elements that are most suitable to be studied by X-ray fluorescence are those with atomic number 12 (magnesium) and higher. Flame-retardant finishes are particularly convenient to analyze with this technique since they usually contain elements in that atomic number range (i.e. phosphorous, chlorine, bromine, antimony). A study has shown that X-ray fluorescence and elemental analyses gave comparable results for a series of phosphorus-based flame-retardant fabrics.[9]

X-ray photoelectron spectroscopy (XPS), sometimes called electron spectroscopy

for chemical analysis (ESCA), is an analysis technique similar in some ways to X-ray fluorescence.[10] In XPS, the sample to be analyzed is exposed to high energy X-rays generated from magnesium and aluminum targets by high voltages. As in X-ray fluorescence, inner shell electrons are ejected when the X-rays are absorbed. However, in the XPS technique, the ejected electrons are collected and their energies measured. Only surface atoms can be studied by XPS owing to the short range of the electrons involved. In addition, the sample chamber must be kept under ultra high vacuum conditions (10^{-9} millibar) to avoid interference from molecules in the atmosphere adsorbed on the sample surface. The ejected electron energies are characteristic of the binding energies of the atoms on the material's surface. The shapes of the peaks in the electron energy spectrum are influenced by chemical bonding, so XPS can provide both elemental and chemical bond information. The only elements not able to be detected by XPS are hydrogen and helium. This technique is particularly useful in studying textiles that have been plasma treated, since the treatments are restricted to the surface of the material. In a recent study of cotton treated with a fluorochemical containing atmospheric plasma,[11] XPS showed that both CF_4 and C_3F_6 plasmas introduced C–F bonds at the fabric surface, with the C_3F_6 treatment providing a higher level of modification. Fewer COH and COOH groups were also detected after the plasma treatments.

6.2.2 Extractive methods

Separating a chemical finish from the textile to which it has been applied can be a daunting task. Some finishes, especially those intended to be non-durable might simply be removed by rinsing with the appropriate solvent. However, finishes that are expected to provide performance over the life of the textile cannot usually be removed that easily. In these situations, the entire finish–textile assembly must be broken down by chemical or thermal means and the resulting components analyzed.

Elemental analysis

Elemental analysis is probably the oldest method that has been used to analyze textile finishes. It is still the 'gold standard' in that all newly developed methods are judged by how well results from the new method compare to results from elemental analysis. Traditional wet chemical methods, such as Kjeldahl nitrogen analysis,[12] continue to have a place in finish analysis. Elemental analysis can be qualitative or quantitative, depending on the need.

Qualitative elemental analysis

Spot tests are very useful in determining the presence or absence of particular elements. Several good references are available for elements commonly used in

textile finishes.[13,14] A few tests, for example, iron or copper that are present in large amounts can be done directly on the fabric. However, the usual practice is to prepare solutions, either from fabric extracts or from fabric digestion. These solutions can be concentrated by evaporation if necessary and the appropriate masking agents added. The specific reagents for a particular element are added and a distinctive color change or precipitation indicates the presence of that element.

Quantitative elemental analysis

In atomic spectroscopy,[15] a material is exposed to high-energy conditions (2000–6000 °K) in a flame, furnace or plasma. The resulting gaseous atoms can absorb or emit ultraviolet (UV) or visible radiation in quantities proportional to their concentration. Atomic absorption (AA) measures the absorption of radiation from atoms produced from a solution injected into a flame. A hollow-cathode lamp containing the element under investigation emits radiation into the flame. Any atoms of that element in the flame absorb that radiation and decrease the intensity of the lamp in proportion to their concentration. With appropriate calibration curves, accurate concentration levels of the element in the original material can be determined. Most metals found in textile finishes, such as magnesium, aluminum and zinc, can be measured. Some disadvantages of AA are that only one element at a time can be analyzed and that a separate hollow-cathode lamp is needed for each element. Inductively coupled plasma spectroscopy (ICP) measures the emission of radiation by atoms generated by injecting a liquid sample into a plasma. This method allows for the simultaneous determination of multiple elements. In addition, more elements likely to be found in textile finishes can be detected with ICP including halogens (except fluorine), phosphorous, sulfur and silicone.

Formaldehyde tests

Formaldehyde is an important constituent of many textile finishes, especially finishes for cellulosic textiles. As the main chemical route to cross-linking cellulose, formaldehyde or a reactant made from formaldehyde is found in a variety of finishes, ranging from durable press agents to water repellents.

Although a very useful and versatile chemical, formaldehyde also causes breathing difficulties and headaches if inhaled, causes eczema and allergies with skin contact and is a suspected human carcinogen. As a result, several countries have enacted laws to control the level of free or easily released formaldehyde in textiles. These levels are specified with particular test methods since there can be significant differences in results obtained with different test methods. Formaldehyde in durable press-treated fabrics can exist in several forms since the formaldehyde reactions are all equilibrium reactions and the 'bound' formaldehyde can be converted to free formaldehyde to varying degrees depending on the test conditions. Therefore, when analyzing fabric for formaldehyde, the test

method used must be reported with the data. Some of the more common fabric test methods for formaldehyde[16] are summarized below.

A qualitative test for the presence of formaldehyde is to add a small piece of the fabric to 3 ml of a solution of 10 mg chromotropic acid per 100 ml of 72% sulfuric acid. The solution is warmed in a test tube to 100 ºC for 1 min. A red to violet color indicates the presence of formaldehyde.

In the USA, the regulatory focus is on consumer and worker exposure to formaldehyde vapors released from the fabric, so the test method specified is AATCC Test Method 112-2003.[17] In this method, 1 g of fabric is suspended over 50 ml of distilled water in a sealed quart jar. The jar is placed in an oven for either 4 h at 65 ºC or 20 h at 49 ºC. Any formaldehyde vapors generated are absorbed by the water. An aliquot of the formaldehyde–water solution is taken and analyzed colorimetrically using the Nash reagent.[18] Typical levels of formaldehyde found in properly processed fabrics treated with modern cross-linking reagents are less than 100 ppm. The Nash method is based on the reaction of acetylacetone with formaldehyde and an ammonium salt to form a yellow complex with an absorbance maximum at 414 nm. The mild conditions of the reaction (pH 7, 5 min at 58 ºC) eliminate many potential interferences.

In Japan, the concern for formaldehyde is the dermatological effect of wearing formaldehyde-containing textiles and the specified test method reflects that concern. Japanese Law 112-1973[19] provides a procedure for extracting 1 g of fabric with 100 ml of distilled water at 40 ºC for 1 h. An aliquot of the water is then analyzed colorimetrically using Nash reagent. The maximum level of allowable formaldehyde is 75 ppm in children's and adult clothing, no formaldehyde is allowed in infant wear.

Chromatographic methods

Several reviews of the use of chromatographic methods to analyze textile chemicals have appeared.[20,21] Since most textile finishes are either polymeric in nature or covalently bonded to the textile, the finishes must be separated from the fabric and solubilized prior to chromatographic analysis. These separation techniques tend to break down the finish into its component parts making unambiguous analysis difficult. Some of the more useful chromatographic methods are summarized below.

Pyrolysis chromatography involves heating samples to temperatures in the range of 600–1000 ºC in a very short period of time (ms). The volatile products of this pyrolysis can then be analyzed by gas chromatography (PY–GC), mass spectrometry (PY–MS) or their combination (PY–GC–MS). In gas chromatography, adsorption–desorption between the gaseous material and the solid column packing causes retention time differences between the various components allowing their identification by comparison of retention times to standards. By placing a mass spectrometer at the exit end of the column, additional information can be

learned about the components. Fabrics treated with phosphorous-[22] and bromine-containing flame retardants[23] have been studied by these procedures.

High-pressure liquid chromatography (HPLC) allows the separation of soluble materials into component parts based on the partitioning of the materials between a mobile (solvent) and stationary (column packing) phase. With proper choice of solvent and column packing, separation of many types of materials is possible. HPLC has been used successfully to determine reagent residues on fabrics treated with durable press finishes[24,25] as well as determining formaldehyde levels in aqueous solutions obtained by the AATCC Test Method 112.[26]

6.3 Finish performance tests

Chemical finishing is an important area in textile processing and requires a diligent fabric testing program to maximize the benefits of the chemical treatments. Many chemical finishes have an optimum level of application, too much chemical can be wasteful, too little can compromise the desired fabric properties. The development of the appropriate performance test methods is just as important to the commercial success of a chemical finish as the development of the finish itself. A test method is appropriate if it provides useful, reproducible results that correlate with actual 'real world' performance. The best test methods utilize simple, inexpensive equipment with easy to follow procedures and yield precise, accurate data.

Organizations such as the Association of American Textile Chemists and Colorists (AATCC) and the American Society for Testing and Materials (ASTM) in the USA, the British Standards Institute in the United Kingdom, the Deutsches Institut für Normung (DIN) in Germany and the International Organization for Standardization (ISO) headquartered in Switzerland publish test methods that can be used to evaluate the performance of chemical finishes.

The following sections will discuss some of the more important test methods in use for fabrics with durable press, flame-retardant, soil release, repellent, UV protective, antimicrobial, anti-insect, anti-felting, hand building and weighting finishes.

6.3.1 Durable press testing

Cellulosic textiles, although valued for their comfort, have the unfortunate disadvantages of wrinkling while being worn and wrinkling and shrinking during laundering. Chemical finishes have been developed that can provide dimensional stability, wrinkle resistance and shape retention to cellulosic and cellulosic blend fabrics. These finishes are referred to as 'easy care', 'wrinkle resistant', 'permanent press' or 'durable press' finishes. These fabric property improvements are achieved by cross-linking the cellulosic polymer chains into the desired configuration.[27] A variety of tests has been developed to determine the effectiveness of the treated fabrics. Some of the more common procedures are discussed below.

Performance tests

AATCC Test Method 135-2003[28] determines the dimensional changes of fabrics when subjected to controlled home laundering. Different wash temperatures, agitation cycles, rinse temperatures and drying procedures can be chosen for any particular home laundering condition. Several options for sample preparation are available based on fabric size. The fabrics are marked with benchmarks prior to laundering and the distance between the marks is compared before and after laundering. The percentage dimensional change can then be calculated.

AATCC Test Method 124-2001[29] is a procedure that attempts to standardize the home laundering process. Choices of hand- or machine laundering, wash cycles, wash and rinse temperatures and drying procedures are provided. The method specifies washing machine, load size, detergent composition, tumble dryer and visual rating procedures. Any fabric construction can be evaluated, but the most meaningful results are obtained with woven fabrics. Three fabric samples (each 38 × 38 cm) are laundered and dried with a ballast load (total weight of 1.8 kg). After conditioning, the appearance of the samples is then visually compared to plastic replicas (AATCC three-dimensional smoothness appearance replicas) that allow ratings on a 1–5 scale, with 5 being the smoothest appearance. A typical commercially acceptable rating is ≥ 3.5.

AATCC Test Method 128-1999[30] determines the tendency of fabrics to wrinkle under carefully controlled laboratory conditions. Fabrics made from any fiber or fiber combination can be evaluated. A special apparatus (AATCC wrinkle tester) provides consistent wrinkling force to the 15 × 28 cm preconditioned fabric samples with a 3500-g weight. After being wrinkled for 20 min, the samples are allowed to hang vertically for 24 h under standard conditions and then compared to plastic replicas (AATCC three-dimensional wrinkle recovery replicas) to obtain a smoothness rating on a 1–5 scale. An average of nine determinations is reported.

AATCC Test Method 66-2003[31] provides a quantitative measure of a woven fabric's ability to recover from induced wrinkling. Fabric samples (15 × 40 mm, six with the long dimension parallel to the warp direction of the fabric and six with the long dimension parallel to the filling direction) are folded and compressed under controlled conditions of time and force to create a wrinkle. The wrinkled sample is then suspended in one of two recommended testers (AATCC wrinkle recovery tester or James H. Heal crease recovery angle tester) for a controlled recovery period after which the recovery angle is measured. The sum of the average warp recovery angle and the average filling recovery angle is reported. The test can be done with dry or wet samples.

The ISO test method 2313: 1972[32] is essentially the same procedure as option 2 of AATCC Test Method 66-2003.

AATCC Test Method 88B-2003[33] is designed to evaluate the smoothness appearance of fabric seams after laundering. Any fabric with any type of seam is suitable for testing with this method. Fabric samples (38 × 38 cm) are cut in half

and then seamed back together using the chosen seaming method. A choice of hand- or machine washing, machine wash cycles, wash temperatures and drying procedures is provided. Two sets of AATCC photographic seam smoothness replicas (one for single needle seams, one for double needle seams) can be used to rate the seam appearance on a 1–5 scale, with 5 having the smoothest appearance.

AATCC Test Method 88C-2003[34] allows the evaluation of the durability of intentional pressed-in creases to home laundering. Creased fabric samples are laundered and dried under controlled conditions similar to those in AATCC Test Method 124-2001. The washed and dried samples are then visually compared to plastic replicas (AATCC three-dimensional crease replicas) which allow ratings from 1–5, with 5 being the sharpest crease.

AATCC Test Method 143-2001[35] applies the washing, drying and evaluation procedures of test methods AATCC TM 124, 88B, 88C to apparel and other textile products.

In addition to these tests, which measure the enhanced performance properties, fabrics that have been treated with durable press treatments also need to be tested for strength (tensile and tear) and abrasion resistance since the cross-linking reaction leads to fiber and fabric strength losses. Appropriate tensile strength tests include ASTM D5034 and D1424 for woven fabrics and D3786 for knitted fabrics. Tearing strength for all fabrics can be determined by ASTM D5587 and D2261.[36]

6.3.2 Flame retardancy testing

One of the more important functional textile finishes is the flame-retardant finish. Firefighters and military personnel have obvious needs for such protective apparel. In addition, textiles used in public buildings are required to have similar protection. Flame retardancy can be achieved by several chemical means[37] which usually involve phosphorous and/or bromine chemistry. The tests that have been developed for evaluating flame retardancy are typically designed for specific textiles under specific testing conditions and these conditions may or may not be comparable to real world fire situations. In addition, these tests are continually being revised. Nonetheless, many of these tests have been established by various legislative bodies and fabrics being sold into markets covered by the legislation must meet the requirements.

The United States Consumer Product Safety Commission (CPSC) has published several test methods that are used to qualify apparel for sale in the USA.[38] Test 16 CFR 1610 is a test for general apparel.[38] A fabric sample (2 × 6 inches, 5 × 15 cm) is placed on a sample rack in a draft proof ventilated chamber at an angle 45° from the horizontal and a cotton cord is placed 5 inches (13 cm) from the narrow fabric edge. A butane flame is held to the narrow edge for 1 s. The test ends when the cord is burned through or the fabric fails to ignite. The fabric passes if it does not ignite or if only one of five tested samples burns the cord after more than 4 s. There are special grading rules for raised surface fabrics.

Children's sleepwear have separate tests, 16 CFR 1615/1616,[38] depending on the size of the garment. These tests are quite similar, both impinging a methane flame for 3 s to the bottom edge of a 3.5 × 10 inch (8.9 × 25.4 cm) fabric sample suspended vertically in the draft-free test chamber. In order to achieve a passing grade, five samples of the tested fabric must have an average char length of 7 inches (17.8 cm) or less with no sample having a char length of 10 inches (25.4 cm).

The National Firefighters Protection Association (NFPA) has developed a specific flame retardancy test for the protective clothing worn by firefighters.[39] NFPA 1971 is a compilation of requirements for coats, trousers, helmets, gloves, footwear and interface items that make up a firefighter's protective ensemble. The flame retardancy test exposes a vertically held 3 × 12 inch (7.6 × 30.5 cm) fabric sample for 12 s to a flame produced by a special gas mixture (540 BTU/cubic foot (4806 kcal m^{-3})). An acceptable fabric will have an average char length of 6 inches (15.2 cm) or less, an after-flame of less than 2 s, and an afterglow of less than 4 s.

A very useful test for flammability is ASTM D2863-00.[40] This method provides a procedure for measuring the minimum oxygen concentration that will just support flaming combustion in a flowing mixture of oxygen and nitrogen. This minimum concentration, also known as the limiting oxygen index or LOI, can be used to quantify flammability behavior of plastics and textiles. A sample of the material to be tested is placed in an open top glass column and a flow of oxygen and nitrogen is begun at the bottom of the column. A natural gas flame is used to ignite the top of the sample. The amount of oxygen is adjusted until the flaming sample just continues to burn. The concentration of oxygen at that point is the LOI. For example, materials that will continue to burn in air have LOIs of ~20. Materials that have good flame retardancy can have LOIs of 30 or greater, meaning that they will burn in an atmosphere of 30% oxygen, but not in air.

Recently the State of California has passed a stringent flammability requirement for mattresses sold in the state beginning in January 2005. Since the size of the California market is so large, California standards tend to become national standards as manufacturers decide for business reasons to have all of their products comply with California law. The requirement (Technical Bulletin 603 of the Bureau of Home Furnishings and Thermal Insulation, Department of Consumer Affairs, State of California) specifies a burner apparatus and testing conditions for mattresses. The measured quantity is the total heat evolved 30 min after subjecting the mattress to severe flame exposure.

6.3.3 Soil release testing

Most consumers would like to be able to clean their garments effectively during laundering. The ability of textiles to release soil during laundering is a function of many factors including the nature of the soil, the mechanical action imparted by the washing machine, the composition of the detergent, the structure of the textile, the

washing temperature and the surface characteristics of the textile fiber. In order to release oily soil easily, the most difficult soil to remove from synthetic fibers, the fiber surface should be both hydrophilic and oleophobic. A variety of chemical materials have been used commercially to achieve this goal.[41] Evaluating soil release finishes is best done by subjecting the fabrics to simulated home launderings under carefully controlled conditions.

AATCC Test Method 130-2000[42] has been developed to measure the ability of fabrics to release an oily stain when laundered. Fabric samples (15 × 15 inches) (38 × 38 cm) are stained with corn oil, then a specified weight is used to force some of the oil into the fabric interior. After laundering with a specified detergent under a choice of laundering conditions, the samples are dried in a tumble dryer and compared to photographic standards (stain release replica with the usual AATCC 1–5 scale).

6.3.4 Repellency testing

Repellent finishes are important components of many protective textiles. Applications for repellent textiles range from medical textiles to raincoats. The low surface energies provided by repellent finishes can keep solid and liquid soils from adhering to treated fiber surfaces. Finishes based on hydrocarbon and silicone chemistries can yield water repellent textiles, while fluorochemicals are necessary to achieve the low surface energies needed for dry soil and oil repellency.[43]

AATCC Test Method 22-2001[44] is a simple test for rapid screening of water repellency. The fabric sample (7 × 7 inches) (18 × 18 cm) is stretched tight in an embroidery hoop, held at a 45° angle in the test apparatus and sprayed with 250 ml of water through a specified spray head from a height of 150 mm. Photographic standards are used to evaluate any wetting pattern that is formed. A completely non-wetting fabric is given a 100 rating, while a fabric that wets completely is given a 0 rating.

AATCC Test Method 35 -2000[45] is designed to simulate a rain event. A special apparatus is used to hold the 20 × 20 cm fabric sample in a vertical position backed by a weighed piece of blotter paper. The fabric face is sprayed with water under constant hydrostatic pressure for 5 min and the blotter paper reweighed. The increase in weight of the backing paper is a measure of the resistance of the fabric to penetration by the simulated rain.

A more severe simulation of a rain event is provided by ISO 9865.[46] This test method is similar to AATCC Test Method 35 except that the water is sprayed for 10 min and the undersides of the fabric samples are rubbed while the spraying takes place. A rather elaborate apparatus is required. The appearance of the fabric face, the amount of water absorbed by the fabric and the amount of water passing through the fabric are all factors in determining the repellency rating of the fabric.

Oil repellency can be evaluated by AATCC Test Method 118-2002.[47] Drops of hydrocarbon with various surface tensions are applied to the fabric sample and the

fabrics observed to determine if wetting has occurred. The hydrocarbon series varies from mineral oil (rating of 1) to n-heptane (rating of 8). The fabric is assigned a repellency rating based on the hydrocarbon with the lowest surface tension that does not wet the fabric. For example, a fabric that is not wetted by n-heptane in this test is given a rating of 8.

INDA, the Association of the Nonwoven Fabrics Industry, has published repellency test methods specifically designed for the nonwoven fabric structure. IST 80.5(01)[48] is designed to measure a nonwoven material's ability to resist gravity-only penetration by a saline solution. This property is useful in assessing the degree of water repellency needed by nonwovens in a number of applications. A sample of the nonwoven to be tested is placed in the mouth of a quart size Mason jar containing saline solution. The jar is then inverted and placed on an electric grid that senses when the solution has penetrated the nonwoven. The time to complete penetration is recorded as a measure of repellency.

Another INDA repellency test especially useful for nonwovens intended for medical use is IST 80.8(01).[49] This test is similar to AATCC 118 in that a series of liquids with varying surface tensions are placed dropwise on the sample to determine at what point the nonwoven is wetted. The difference in this test is that the liquids used are composed of varying concentrations of alcohol and water from 100% water (rating 0) to 100% alcohol (rating 10). Methanol, ethanol and isopropanol may be used as the alcohol component. The higher the rating, the higher the level of repellency of the nonwoven.

Upholstery and carpets are often treated with repellent finishes to minimize soiling during use. Since much of the soiling that occurs is due to dry soil, a test to evaluate dry soiling behavior is useful. AATCC Test Method 123-2000[50] can be used for upholstery and carpet samples. Either 10 g of actual vacuum cleaner soil or 10 g of a synthetic soil is rotated with pebbles in a rotary ball mill with two samples (3 × 7 inches) (7.6 × 18 cm) of the fabric to be tested. After a predetermined exposure time, the fabrics are removed, vacuumed and visually compared to previously soiled standards.

6.3.5 UV protective testing

The harmful effects of exposure to ultraviolet radiation from sunlight on human skin were recognized by the medical community in the early 1990s. Long-term exposure to ultraviolet light can result in accelerated skin ageing, acne, phototoxic reactions with drugs, sunburn, skin cancer, cornea damage and DNA mutations. The textile industry has responded to this recognized need by providing chemical treatments that absorb ultraviolet light. Government agencies around the world have also responded by providing standards for clothing designed to protect the wearer from ultraviolet rays. The standards define an ultraviolet protection factor (UPF) to be included on clothing sold as ultraviolet protective. The higher the UPF, the greater the ultraviolet protection provided.

The early test methods for determining the ultraviolet protective effects of clothing involved exposing volunteers to ultraviolet radiation until their skin reddened (erythema) to a specific degree. Fortunately, instrumental methods of evaluation have been developed that eliminate the need for sunburned assistants. AATCC Test Method 183-2000[51] determines the transmittance of ultraviolet light through fabric samples. Through the use of established tables and formulas, the UPF is calculated.

6.3.6 Antimicrobial testing

The growth of microorganisms on textiles can cause functional, hygienic and aesthetic problems. Fungi and bacteria are the most troublesome organisms. Fungi can cause discoloration and fiber damage, while bacteria can produce unpleasant odors and a slimy feel to fabrics. Of course, growth of pathogenic bacteria on textiles presents health hazards to the wearer and to the general public. A successful antimicrobial textile finish must be effective against the target organisms, yet not harm the wearer or the environment. Textiles marketed as biocidal, that is, capable of killing organisms, are mandated by law to meet strict efficacy requirements, whereas biostatic (growth inhibiting) textile finishes are held to much more lenient standards. In the USA, biocidal products must be registered with the Environmental Protection Agency before they can be sold.

Antibacterial tests

Qualitative and quantitative test methods have been developed for evaluating the antibacterial properties of textiles. AATCC Test Method 147-1998[52] provides a qualitative measure of a textile's antibacterial effects. A small sample of the textile (25 × 50 mm) is placed in a sterile agar-containing plate that has been streaked with either a gram positive- or gram negative bacteria-containing solution. After incubation for 18–24 h at 37 ºC, the plate is examined for bacterial growth. If the bacteria did not grow on the textile, an antibacterial effect can be claimed. Although this method is suitable for a rapid assessment, a more quantitative test is needed to determine if the effect is biocidal or biostatic.

AATCC Test Method 100-1999[53] was developed to provide a quantitative evaluation of a textile's antibacterial properties. A swatch of the antimicrobial treated textile (1.9 inch (4.8 cm) diameter disk) is inoculated with a bacteria-containing solution (either gram positive or gram negative) and incubated for 18–24 h at 37 ºC. The swatches are then extracted and the number of bacteria in the extract determined by serial dilutions placed on sterile agar containing plates and incubated for 48 h at 37 ºC. Calculations are made to find the percentage reduction of bacteria found on the antimicrobial treated textile compared to the number of bacteria found on an untreated textile of similar construction. Care must be taken

to ensure that bacteria actually grow on the untreated textile sample. This can be accomplished by incorporating a small amount of growth medium in the initial inoculating solution.

Antifungal testing

AATCC Test Method 30-1999[54] provides four methods for determing the antifungal properties of a textile. The first method involves covering the textile samples (1.5 × 6 inches) (4 × 15 cm) with fungi-containing soil and incubating the mix for 2–16 weeks at 28 ºC. In the second method, cellulosic fabric (1.5 inch (4 cm) diameter disk or 1.5 × 6 inch (4 × 15 cm) strip) is inoculated with a standard fungus (*Chaetomium globosum*) solution and incubated on a sterile agar-containing plate. The third method is similar to the second except that the fungus *Aspergillus niger* is used as the inoculum. The fourth method exposes 1 × 3 inch (2.5 × 7.6 cm) textile samples to a high humidity environment for 14–28 days in a sealed jar after inoculation with a mixture of three fungi. In all methods, the extent of fungal growth is determined visually and reported as either 'no growth', 'microscopic growth' or 'macroscopic growth'. In all the methods except the third, fabric strength losses can also be measured.

6.3.7 Anti-insect and mite testing

Although desirable from an aesthetic and comfort sense, animal fibers have the disadvantage of being damaged by a variety of insects that have the ability to digest keratin. These insects include clothes moths, carpet beetles and fur beetles. The main defenses against these insect pests are digestive poisons and nerve poisons. These materials must be used carefully to prevent harm to other non-destructive insects or to the environment in general.

To evaluate the effectiveness of anti-insect finishes, populations of the target insects must be established. AATCC Test Method 24-1999[55] provides detailed procedures for rearing and handling clothes moths and carpet beetles in the testing laboratory. Options are available for evaluating fabrics, yarns, and carpets. The textile materials to be tested (samples of 2 inch^2 (12.9 cm^2)) are placed in glass or metal containers with ten larvae of the target species. After 14 days of incubation at 27 ºC and 55% relative humidity, the samples are removed and examined for damage. The extent of the damage can be measured by weight loss of the samples or by the total mass of insect excrement generated. The number of living and dead insects is also recorded. This test method is usually used in conjunction with AATCC Test Method 28-1999[56] to evaluate potential anti-insect finishes under conditions of ordinary use.

Recently concerns over the adverse effect of house dust mite fecal matter on asthma sufferers has led to interest in textile treatments to control mite populations in mattresses, sheeting, pillows and bed covers. Dust mites are not insects but are

more closely related to spiders. Chemical treatments, both biocidal and biostatic, are available. The AATCC has a test method under development to evaluate the effectiveness of these treatments. Fabrics to be tested are inoculated with dust mites and a growth medium. The number of mites surviving after six weeks incubation at 23 ºC and 74% relative humidity gives an indication of the anti-mite property of the treated textile.

6.3.8 Anti-felting testing

Wool fibers have a scaly covering that leads to an interesting phenomenon referred to as felting. When wool fabrics are laundered, the individual fibers can slide along each other in one direction (the 'with-scale direction'), but not the other (the 'against-scale direction'). This situation causes irreversible shrinkage of the fabric. Chemical treatments that address this problem can either remove the scales by chemical reaction or 'fill in' the rough areas with a polymer deposit to give a smoother surface and allow the fiber to return to its original position more easily, or 'spot weld' adjacent fibers to prevent movement in the first place. The success of 'washable wool' in the market place attests to the usefulness of these finishes.

The Woolmark Company Test Method TM31[57] provides a method of washing wool in a special washing machine designed to duplicate the mechanical action found in home laundering. The wool fabric is marked before and after being laundered under controlled conditions and the shrinkage calculated.

6.3.9 Hand building and weighting testing

Often a textile fabric requires a firm feel or hand. This can be accomplished by adding a chemical finish to increase the fabric stiffness. These finishes are usually low-cost water-soluble polymers such as starch or polyvinyl alcohol. If a durable stiffening effect is needed, vinyl acetate polymers, polyurethanes and thermosetting resins can be used.

The effects of a fabric stiffening treatment can be quantified by the cantilever method described in ASTM D1388-96.[58] A sample of specified length and width is placed on top of the test device. The device has a horizontal surface connected to a downward incline. The fabric is pushed over the incline until the sagging leading edge just touches the inclined plane of the device. The length of fabric that has passed over the point where the horizontal and incline meet is used to calculate the fabric's flexural rigidity.

Some of the same chemicals used to stiffen fabrics can also be used to increase a fabric's weight, an important sales specification. Silk fabrics can be conveniently weighted by the application of tin salts. Measurement of the degree of weighting can be done by comparing the final weight of the fabric in g m^{-2} to the initial weight.

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7

Chemical analysis of textile coatings and membranes

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7.1 Introduction

Coated and laminated textiles usually consist of a textile substrate, which will typically be a woven, knitted or nonwoven fabric, combined with a thin, flexible film composed of a natural or synthetic polymeric substance. A coated fabric is one in which the textile substrate has a polymer film applied directly to one or both surfaces as a viscous liquid in a solvent or water, the thickness of which is controlled by application via a blade or similar aperture. A transfer coated fabric is an intermediate product in which a thermoplastic film is first prepared on a release paper prior to thermally bonding to the textile substrate. A laminated fabric usually consists of one or more textile substrates that are combined with a pre-prepared polymer film or membrane by adhesives or heat and pressure (Hall, 2000).

7.2 Chemical types used in coatings and membranes

A wide range of polymers which form thin, flexible films are used. They can be split into two categories, polymeric elastomers and rubbers. The polymers include polyurethanes, polyvinyl chloride, polyvinylidene chloride, polyethylene, polytetrafluoroethylene, silicone elastomers, polyacrylates, and chlorinated and chlorosulphonated polyethylenes.

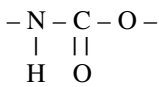
7.2.1 Polyurethanes (PU)

These are widely used in coatings and membranes for many purposes. Their chemistry is very complex, so is dealt with separately in Section 7.2.2. Molecular weights vary considerably, depending on the application. Specific gravities (SG) of film-forming PUs are between 1.05 and 1.31. Polyester PUs are used in lightweight (25–45 g m^{-2}) direct coated fabrics for rainwear. Polyether PUs are used in heavier (70–200 g m^{-2}) transfer coated fabrics that are thermoplastic in nature. Thus, they can be welded to form materials with good air or liquid-holding

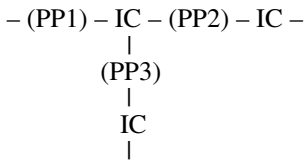
properties. Hydrophilic PUs are segmented copolymers of polyester or polyether PUs together with polyethylene oxide which form waterproof, water vapour-permeable solid films. Microporous PUs are formed by coagulation of the liquid PU in a solvent by exposure to water or steam. This forms a microporous gel structure that is then washed and dried. Both the above are used in high-performance weatherproof and protective clothing and associated personal equipment (Scott, 1995; Roff and Scott, 1971).

7.2.2 Chemistry of polyurethanes

The polyurethanes are a wide class of polymers ranging from rubbers and elastomeric fibres to surface coatings, adhesives and flexible or rigid foams. They are widely used in lightweight coated fabrics for waterproof clothing. They are derived from the reaction of polyesters or polyethers with di- or polyisocyanates to produce complex structures containing urethane linkages. The fundamental unit is based upon the urethane group:



Polyurethanes used in coating are complex polymers, the major component of which is a segmented prepolymer. These are composed of a linear polyester or polyether that has been extended several fold in chain length by coupling through urethane linkages. The prepolymer molecule (– PP –) can be further extended and cross-linked with a multifunctional isocyanate (– IC–) to produce the following general structure (Roff and Scott, 1971):



The first step in the production of complex polymers is to prepare segmented prepolymers by coupling a hydroxyl-terminated polyester or polyether to a polyfunctional isocyanate. This extends the molecular size through the urethane linkages.

A typical polyester could be poly (diethyleneglycol adipate) with a molecular weight of between 2000 and 3000. A typical polyether is obtained by polymerisation of propylene oxide, usually in the presence of a small proportion of glycerol or sorbitol to provide branched structures. Two of the most commonly used isocyanates are 2,4- and 2,6- tolylene di-isocyanate (TDI). These are chosen because of their reactivity, cheapness and relative low toxicity. The resulting prepolymer has –OH terminal groups when a deficiency of isocyanate is used, but –NCO terminal groups if an excess of isocyanate is employed.

7.2.3 Polyvinyl chloride (PVC)

This is an addition polymer made from the vinyl chloride (CH_2–CHCl) monomer with a molecular weight of 62.5, an SG of 1.1–1.7 and a degree of polymerisation of 800–2000. PVC coating formulations must be plasticised using high boiling point esters of C_8 to C_{10} alcohols (typically phthalates, phosphates and sebacates) to render them flexible at low temperatures. PVC is resistant to acids and oxidising agents and is flame retardant, but is dissolved by many common solvents, oils and petrol. It has been widely used for heavy duty, cheap, coated fabrics, such as leather cloth, tentage, liners, truck covers, shelters, awnings, etc.

7.2.4 Polyvinylidene chloride (PVDC)

This is similar to PVC, but made from the monomer 1,1-dichloroethylene ($CH_2 = CCl_2$). It has a specific gravity of 1.67–1.71 and a degree of polymerisation of over 200. The molecular weight of commercial polymers is about 20 000. It is often used in the form of a copolymer with vinyl chloride or ethyl acrylate to improve its properties. Coating formulations are plasticised with highly chlorinated aromatics, as common plasticisers are ineffective.

7.2.5 Polyethylene (PE)

PE has one of the simplest fundamental units in organic chemistry, $–(CH_2–)_n$. It is produced in both a low-density (0.915–0.94 specific gravity) and high-density (0.94–0.97 SG) form. Both are prepared from ethylene (CH_2=CH_2). It is a relatively low-melting point polymer (130–140 °C). PE is usually prepared in film form for lamination to a range of textile structures. Products are used where resistance to solvents, alkalis, concentrated acids and oils is required. It is ideal for chemically protective clothing, especially cheap disposable clothing based upon nonwoven polyolefin substrate, a well-known example being 'Tyvek' (Du Pont).

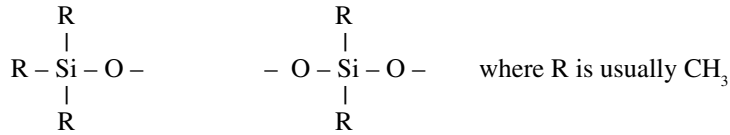
7.2.6 Polytetrafluoroethylene (PTFE)

PTFE has a remarkable range of properties. It possesses the simple monomer unit, $–(CF_2–CF_2)–$, with a molecular weight of 100, an SG of 2.1–2.3 and a degree of polymerisation of 10 000. PTFE is extremely stable and inert, is not soluble in any known liquid solvent and is unaffected by concentrated acids and alkalis. It will not burn in air, is flexible down to –80 °C and dimensionally stable up to +250 °C. It has a low coefficient of friction, good abrasion resistance and has excellent liquid repellency properties. It is predominantly available as a thin membrane that is laminated to one or more textile fabrics. PTFE is thus well suited for use against chemicals and liquids in harsh environments. One of the special uses of the membrane is in a shock-expanded microporous form, which confers high liquid barrier properties with high water vapour permeability. In this form laminates are

used in high performance wet weather clothing and equipment, under the trade name 'Gore-Tex'®.

7.2.7 Silicone elastomers

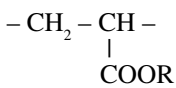
These silicon-based polymers for coatings are usually primary linear chains of difunctional polysiloxane units with monofunctional end groups as follows :



Silicones are soluble in ketones, esters and ethers. They are unaffected by water, some mineral oils, petrol, cold acids and alkalis. They remain flexible at temperatures down to –70 °C and resist heat-ageing well. When used in thin coatings on lightweight nylon or polyester fabrics they maintain high tear strength and soft handle. When vulcanised with organic peroxides they resist microbiological attack. They are odourless, tasteless, physiologically inert and water repellent. This makes them ideal for outdoor purposes such as lightweight tents, shelters and covers. They are also used in the food, engineering and medical product industries.

7.2.8 Acrylic (polyacrylates)

Polyacrylates have the basic structure



The R can be an alkyl or aryl group. The molecular weight of a typical monomer is 71, the degree of polymerisation is 5000–10000 and the SG is 1.05–1.11.

Acrylates are soluble in most chlorinated hydrocarbons, esters, ketones and aromatic hydrocarbons. They can be plasticised by esters similar to those used in PVC. Acrylate polymers used in coatings possess excellent fastness to light, weathering and microbiological attack, retaining light colours and good whiteness. The rubbers have good resistance to flex-cracking, oxidation, ozone, ultraviolet radiation and lubricating oils. These properties make them ideal for sun blinds, white hat covers and snow camouflage (Scott 2000).

7.2.9 Chlorinated and chlorosulphonated polyethylenes (Hypalon)

Chlorinated polyethylenes are prepared by passing gaseous chlorine through a hot suspension or emulsion of polyethylene in carbon tetrachloride. They contain

about 25–30% of chlorine in chlorinated groups [–$CH_2CH(Cl)$–]. Chlorosulphonated polyethylenes are similarly prepared, but both gaseous chlorine and sulphur dioxide are introduced simultaneously into the hot emulsion. They contain about 1–2% of the [–$CH_2CH(SO_2Cl)$ –] group. The SO_2Cl groups provide reactive sites for cross-linking, as in the case of general purpose rubbers.

Compared with straight polyethylene, these polymers possess outstanding resistance to heat ageing and they have a degree of flame retardance. They are also highly resistant to weathering, ozone, abrasion and general chemical attack. These properties make them ideally suited for products such as tentage, chemically protective clothing, flexible fuel tanks, roofing and flooring.

7.3 Natural and synthetic rubbers

Specially compounded rubbers have been used widely for heavy duty coated fabrics. Practical rubber compounds are a complex mixture of organic and inorganic substances that must be mixed carefully to obtain uniform high-strength barrier properties. The presence of some of these compounding agents helps to identify rubber coatings. They may contain the following:

- A vulcanising agent, usually sulphur, which forms sulphur bridge bonds between the chain molecules, produces the tough practical elastomeric form.
- Accelerating agents which are usually metal oxides (MgO, PbO) or organic substances such as thiazoles, mercaptobenzthiazoles (MBT) or sulphenamides. Activators are required to make the organic accelerators function effectively. These can typically be zinc oxide and stearic acid. Stearic acid also acts as a lubricant, softener and plasticiser.
- Diluting fillers such as clays, talc, and barytes act as diluents to cut costs.
- Reinforcing fillers such as finely divided carbon black increase the tensile and tear strength of the mix. Finely divided coloured pigments can also be added instead of carbon black.
- Antioxidants such as ketone–amine condensation products or phenols are used to prevent natural ageing and atmospheric ozone cracking.

7.3.1 *cis*-Polyisoprene (natural rubber)

The simplest unit is 1,4-isoprene, although there are two distinct *cis* and *trans* isomeric configurations of 1,4-polyisoprene.

$$-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CH-CH_2-$$

The *cis* form, where the chains substituent to the double bond lie on the same side

of the chain, is the natural elastomeric rubber used in coating formulations; the formula is C_5H_8, molecular weight is 68, degree of polymerisation is 1500–5000 and SG is 0.93.

Natural rubber is obtained by cutting (tapping) the bark of *Hevea braziliensis,* a wild tree originally found in South America. The rubber is in a milky form containing about 35% latex. The latex is separated by coagulation with a weak acid and it is soluble in a range of solvents, including hydrocarbons, chlorinated hydrocarbons, certain ketones, esters and carbon disulphide.

7.3.2 Polychloroprene rubber (neoprene)

The simplest unit is:

$$-CH_2-\underset{\displaystyle Cl}{\underset{|}{C}}=CH-CH_2-$$

The formula is C_4H_5Cl, molecular weight is 88.5, degree of polymerisation is 1000–3500 and SG is 1.20–1.25. The vulcanised forms of polychloroprene are known as 'neoprene'. It has good resistance to heat and flames, oils, acids and ozone, which makes it useful for outdoor end-uses such as shelters, covers and industrial protective clothing.

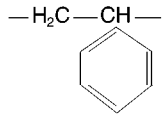
7.3.3 Polyisobutylene rubbers (butyl)

The simplest fundamental unit is based upon butylene groups attached to 1,4-isoprene units:

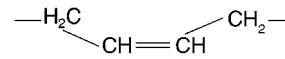
$$-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}---CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2-$$

The formula for isobutylene is C_4H_8, the molecular weight is 56, the 1,4-isoprene formula is C_5H_8, molecular weight is 68, the degree of polymerisation varies from 20 to 200 and SG is 0.91–0.98.

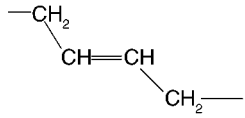
Butyl rubber is unaffected by oxygen, alkalis, hydrogen peroxide, alcohols, phenols, animal and vegetable oils, and some ketones, ethers, esters and fatty acids. Its compact structure gives it excellent resistance to gas and liquid permeation, hence it is used in tyres, balloons, tank and pond liners. It has specialist military uses in protective clothing, covers and shelters against chemical warfare agents. The heat and flame retardance of butyl rubbers can be enhanced for protective clothing by combining small proportions of chlorine or bromine in the milling process.



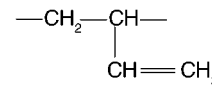
Styrene
(1)



cis-1,4-butadiene
(2)



trans -1,4-butadiene
(3)



1,2- or vinyl butadiene
(4)

7.1 The structure of components for styrene–butadiene rubbers.

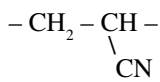
7.3.4 Styrene–butadiene rubbers (SBR)

The simplest fundamental units are based upon a mixture of styrene (1) with various molar proportions of *cis*- or *trans*-isomers of 1,4-butadiene (2, 3) or 1,2-butadiene (vinyl butadiene) (4). The structures of the components are shown in Fig. 7.1.

The above units are randomly arranged in emulsion copolymers, but in solution the polymers may occur in uniform blocks of varying length. These block copolymers are resilient and rubber-like at room temperature, but are thermoplastic at higher temperatures. SBRs are similar to natural rubber, in that they are susceptible to atmospheric oxidation and ozone cracking when stretched in air. They are swollen and weakened by hydrocarbons and halogenated hydrocarbons. However, their resistance to abrasion and ageing is superior to natural rubber.

7.3.5 Nitrile rubbers

The structure is similar to SBR, in that they contain butadiene isomers (2), (3) and (4) above, together with acrylonitrile:



Nitrile rubbers are classified according to the content of acrylonitrile, which can be from a low of 20% up to a high content of 45%. The butadiene units are predominantly in the *trans*-1,4 form. Nitrile rubbers have low tensile strength unless filled with reinforcing carbon blacks. Their resilience is low and low-temperature flex-cracking is worse than that of natural rubber. However, their advantage over natural rubber is their superior resistance to heat ageing and light.

Nitrile rubbers have good resistance to oils, greases and other hydrocarbon liquids and are therefore used in mechanical engineering applications.

7.4 Preparation of coatings for analysis

Ideally, it is easiest to analyse the polymer before application, to prevent any interference by the fabric substrate, adhesives or any finishing processes such as water repellency or colouration by printing. However, this is not practical on the finished coated fabric or laminate.

7.4.1 For thick coatings

When the strength of the coating exceeds the strength of the fibre/coating bond, there are several approaches:

- Using a sharp blade or grinder scrape off and discard any topical treatment, then collect subsequent scrapings or small cuttings for analysis (British Standards Institution, 2000).
- Freeze the fabric specimen down to below –20 ºC or –40 ºC then crack off the coating or membrane, ensuring that residues of fibre or finish are discarded.

7.4.2 Dissolution tests

These tests are used for thin coatings, but are also recommended for all polymer coatings and membranes to minimise contamination by substrates and finishes:

- For rubberised composites based upon natural, SBR and butyl rubbers, expose the material to the vapours of methylene chloride or 1,1,1-trichloroethane for a short time. Afterwards the solvent should be removed from the swollen rubber by drying in air at room temperature. The coating can then be carefully removed by scraping, grinding or by cryogenic crushing to pass a sieve, which has a mesh grating width of approximately 1.7 mm (International Standards Organization, 1996).
- Use a range of solvents for other polymer coatings, as detailed in Table 7.1. Tetrahydrofuran will dissolve and separate PVC and PVDC from nylon and polyester substrates in the cold. Carbon tetrachloride will dissolve and separate chlorinated polyethylene from nylon and polyester substrates. Toluene will dissolve and separate polyethylene from synthetic fibre substrates, apart from polyolefins, when the whole material should dissolve.
- An alternative method is to dissolve away the fabric substrate and leave the coating behind. Nylon can be dissolved in cold *meta*-cresol in about 1 min, or 90%v/v formic acid. Polyester (polyethylene terephthalate) will dissolve in hot *meta*-cresol, but PVC may also be affected. Alternatives are *ortho*-cresol and chloroform or *ortho*-chlorophenol.

Table 7.1 Preliminary identification tests

Appearance	Thin, clear coating	PU, acrylic, silicone, PE
	Thin white membrane	PTFE, microporous PU
	Thick, dense coating	PVC, PVDC
	Thick, dense, black/grey coating	Natural, butyl, neoprene, SBR, nitrile rubbers
Appearance under microscope	Microporous fibrillar voids or bubbles	PTFE, microporous PU
Smell	Sulphurous 'plastic' smell	Vulcanised rubbers, plasticised PVC, PVDC
Beilstein test (heated copper wire)	Blue/green flame in bunsen	PVC, PVDC, neoprene, all chlorine-containing coatings
Heating in tube	Smell of almonds (cyanide poisonous)	Acrylonitrile
	Burns with blue flame	Polyacrylonitrile
Dissolution	In tetrahydrofuran	PVC, PVDC
	In carbon tetrachloride	Chlorinated polyethylene
	In toluene	Polyethylene

- After dissolution, separate the components by filtration, washing solid residues in ethanol and/or remove the solvent by careful distillation.

7.4.3 Preliminary identification tests

A great deal of useful information can be obtained from simple tests on unknown coatings. Mere visual examination, touching and smelling the polymer can determine the type of polymer or eliminate some others. For example, PVC and many rubber coatings have distinctive colour, texture and smell. Preliminary tests are shown in Table 7.1.

7.5 Elemental analysis

These are the most important tests for additional elements other than carbon, hydrogen and oxygen. The additional elements found in coatings are nitrogen, sulphur, chlorine, fluorine, phosphorus and silicon. For many years this analysis was carried out using the sodium fusion test. However, applying this test to the mixtures that can make up coatings and laminates can cause problems. For example, nitrogen can be missed if it is present in small quantities and accompanied by chlorine, and it is said that PVC reduces the effectiveness of the fusion process (Haslam *et al.*, 1983) A more effective method is to use the oxygen flask combustion method.

7.5.1 Oxygen flask combustion method

This apparatus consists of a strong Pyrex flask fitted with a platinum gauze basket on the end of a sealed support adapter containing a platinum and tungsten wiring system through which can be passed a high-tension spark from a suitable source. In use a sample of the unknown substance is wrapped in filter paper and placed in the platinum basket. About 25 ml of 1 N sodium hydroxide solution is placed in the bottom of the flask. The flask is filled with oxygen, the electrode adapter is sealed to it, the apparatus is placed inside a suitable safety enclosure and the HF spark ignition system is activated. The sample is allowed to burn to completion, the combustion products being absorbed by the NaOH. This solution is then diluted with distilled water for further analysis.

Test for chlorine

Prepare an analar solution of 12 g ammonium ferric sulphate in water and add 40 ml of analar nitric acid. Dilute to 100 ml. Prepare a solution containing 0.4 g of mercuric thiocyanate crystals in 100 ml of absolute alcohol. Mix 5 ml of the test solution from the oxygen flask combustion method (described above) with the ammonium ferric sulphate solution. Add 1.5 ml of mercuric thiocyanate solution. When chlorine is present an orange to red colour will develop in the test sample. If a semi-quantitative estimation of chlorine is required, set the solution aside for 10 min, then measure the optical density of this coloured solution against the blank solution at 460 nm in 20 mm cells. Typical calibration figures for the examination of plastic coatings such as PVC are as follows:

Chlorine in plastic coating	= 1% up to 2%
Optical density (D20/460) measured against blank	= 0.4 up to 0.75.

Test for sulphur

Dissolve 0.2 g of peptone in 50 ml of 1% w/v barium chloride solution. Buffer to a pH of 5.0 with 0.02 N hydrochloric acid and add 10 g of analar sodium chloride, diluting to 100 ml. Heat in a water bath for 10 min at below boiling and add a few drops of chloroform, followed by filtration. This is solution A. Dissolve 0.4 g of gum ghatti in 200 ml of distilled water by warming. Then add 2.0 g of barium chloride and filter if necessary. This is solution B. Just before use, add 10 ml of A to 100 ml of B. This is the precipitating reagent C.

Transfer 5 ml of the above unknown test solution to a test tube and add 2 drops of 100 volume hydrogen peroxide followed by 1.2 ml of 1 N HCl. Mix well and add 2.0 ml of the precipitating agent C. A distinct turbidity will be produced if sulphur is present. If a semi-quantitative estimation of sulphur content is needed, add 5 ml of distilled water to both a blank and the turbid solution, mix and leave for 30 min.

Measure the optical density of the test solution in a 40 mm cell at 700 nm. Useful calibration figures are given below:

Sulphur in plastic/rubber coating	= 1% up to 2%
Optical density (D40/700) measured against blank	= 0.2 up to 0.4.

Test for nitrogen

Weigh 0.1 g of resorcinol into a clean dry beaker and dissolve in 0.5 ml of glacial acetic acid. Add 5 ml of the test solution, mix and add 0.1 g of ammonium ferrous sulphate. Prepare a blank test solution for comparison. A green colour in the test sample, compared with a pale yellow in the blank indicates the presence of nitrogen.

Test for fluorine

Prepare a buffered alizarin complexan solution by weighing 40.1 mg of 3-aminomethylalizarin-*N*,*N*-diacetic acid into a beaker and add 1 drop of 1 N NaOH followed by 20 ml of distilled water. Warm to dissolve, then cool and dilute to 200 ml. Prepare a separate solution of 4.4 g of sodium acetate in water. Add 4.2 ml of glacial acetic acid and dilute to 42 ml. Pour this sodium acetate solution into the alizarin complexan and mix to form the buffered solution.

Transfer 2.4 ml of the buffered alizarin and 20 ml of distilled water to a 50 ml beaker. Add 1 ml of test solution and mix. Finally add 2 ml of cerous nitrate solution and mix again. Prepare a similar blank solution. When fluorine is present a mauve colour will be developed in the test solution compared with a pink colour in the blank. If a semi-quantitative estimation of fluorine is required measure the optical density of the test solution against the blank at 600 nm in 10 mm cells. Useful calibration figures are given below:

Fluorine in plastic film	= 1% up to 2%
Optical density (D600/20) measured against blank	= 0.07 up to 0.135.

Test for silicon

It is important to note that any polymer coating sample used must be free from any silica fillers or water-repellent silicone surface treatment, otherwise interference will occur. However, most silicone finishes are applied to the outer textile face only.

A sample of the coating is ignited in a test tube or wet-ashed with concentrated H_2SO_4 and HNO_3. This leaves a residue of silica and the glass tube will become hydrophobic to acid and water. The presence of silicon is confirmed by:

- Adding ammonium molybdate solution to the silica residue, when a blue colour develops.
- Dissolving the residue in concentrated hydrofluoric acid. This does not leave a residue on evaporation.

Table 7.2 Classification by detection of elements

Element found	Principal coating polymers and materials indicated
Chlorine only	PVC, PVDC, chlorinated polyethylene, chloroprene rubber (neoprene), hydrochlorinated rubber, chlorinated butyl rubber
Nitrogen only	Polyurethanes, polyacrylate, polyamide, nitrile rubber (unvulcanised)
Sulphur only	All vulcanised natural and synthetic rubbers
Chlorine + nitrogen	Vinyl or vinylidene chloride/acrylonitrile copolymers
Chlorine + sulphur	Chlorosulphonated polyethylene, vulcanised chloroprene, chlorinated butyl rubber
Nitrogen + sulphur	Vulcanised nitrile rubber
Fluorine only	Polytetrafluoroethylene (PTFE)
Silicon only	Silicone elastomer or resin
Carbon + hydrogen only	Polyethylene, polypropylene, natural rubber latex, unvulcanised butyl rubber

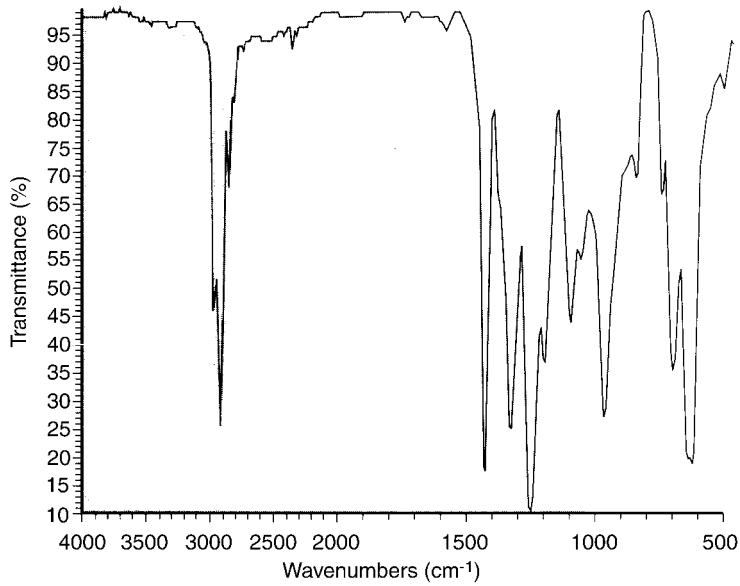
7.6 The Burchfield colour reaction test for elastomers

The Burchfield colour reaction test is used to confirm the specific identity of a range of elastomers. The test results in colour changes before and after heating the test mixture (Braun, 1986).

In the procedure, a few grams of the finely chopped test elastomer are placed in a fusible glass tube. Another boiling tube is prepared containing 2 ml of dimethylaminobenzaldehyde solution (in hydroquinone and methanol).To this add 5 ml of concentrated HCl and 10 ml of ethylene glycol. The sample tube is then heated strongly and the vapours passed into the prepared solution. The colour change of the solution is noted after shaking and cooling. Next dilute this coloured solution with 5 ml methanol and heat for 3 min before noting the colour again. Table 7.3 gives the colour changes of several elastomers used in coating fabrics.

Table 7.3 Colour changes for elastomers in the Burchfield test

Elastomer	Burchfield colour reaction		
Polychloroprene rubber	Yellow-green	→	Dark green
Butyl rubber	Light blue	→	Violet
Natural rubber	Brown	→	Dark blue-violet
Nitrile rubber	Orange-red	→	Burgundy
Polyurethane rubber	Yellow	→	Yellow
Silicone	Colourless	→	Yellow
Styrene–butadiene rubber	Light green	→	Dark green



7.2 Typical Fourier transform (FTIR) spectrum of polyvinyl chloride.

7.7 Infrared spectroscopy of coatings

Spectroscopy is the study of the interaction of electromagnetic radiation with matter. Infrared radiation is absorbed by matter in the form of bands which have a discrete frequency. The nature of the absorption is related to the types of atoms present and their arrangement in the molecule. IR rays have wavelengths in the range 1–1000 μm. They are expressed as wavenumbers in cm^{-1}. Full descriptions and reviews of IR spectroscopy are found in (Roeges, 1994) and (Hervey, 2000). It is concluded that during the absorption process, molecules use the energy of the radiation to create or intensify vibrations in groups of atoms. The stronger the vibrating atoms are bonded together, the higher the wavenumber. The wavenumber also increases when the masses of the vibrating atoms are smaller. Each non-linear molecule displays $3N–6$ fundamental vibrations, in which N represents the number of atoms of a structural unit from which the polymer, in this case, is built up. Bonds or groups of atoms can vibrate in different modes such as stretching, bending, wagging, rocking, scissoring, or as in-plane or out-of-plane vibrations, to give characteristic peaks on the graph which aid identification (Billmeyer, 1984; Geil, 1996), see Fig. 7.2 above.

A dispersive IR spectrophotometer scans the compound by means of a monochromator, and gives the absorption for each wavenumber, which is called a spectrum. A machine based upon Fourier transformation determines the absorption for each wavenumber at the same time, using a Michelson interfero-

Table 7.4 Typical infrared spectra for coating elastomers

Elastomer	Type of group vibration		Wavenumber (cm^{-1})
Polyethylene	CH_2	in-plane bend	1463
	CH_2	in-plane rocking	725
Polyacrylonitrile (PAN)	C≡N	stretch	2245
	CH_2	out-of-plane bend	1455
	CH	wagging	1363
Polyvinyl chloride (PVC)	Phthalate	plasticiser	1728
	CH_2	in-plane bend	1426
	CH	in-plane bend	1255
	C–C	stretch	966
	CCl	stretch	615
Polytetrafluoroethylene (PTFE)	CF_2	stretch	1220–1195
	CF_2	in-plane bend	639
	CF_2	wagging	505
Silicone	CH_3	in-plane bend	1261
	Si–O–Si	stretch	1078 & 1020
	CH_3	rocking	808
Polyurethane polyester type	NH	stretch	3400
	C=O	stretch	1730
	Phenyl	stretch	1600–1400
	NH	in-plane bend	1531
	C=O–O	stretch	1223
	O–C	stretch	1111
	N–C	stretch	1000
	CH_2	stretch	809
Polyurethane polyether type	NH	stretch	3400
	C=O	stretch	1730
	Phenyl	stretch	1600–1400
	NH	in-plane bend	1540
	CH_2	wagging	1374
	C–O–C	stretch	1110

Note: all listed except PTFE exhibit CH_3 and CH_2 stretch at 3000–2840 cm^{-1}

meter, and then generates the spectrum graphically (Kealey and Haines, 2002; Hervey, 2000).

Typical spectral peaks to aid in the identification of coating elastomers and rubbers are shown in Tables 7.4 and 7.5 (Verleye *et al.*, 2001). The tables show that the infrared spectroscopic technique is invaluable in detecting characteristic peaks to identify the differences between chemically similar hydrocarbon polymers, such as polyolefins, natural and butyl rubbers. It is also sensitive enough to show the difference between polyester and polyether urethanes. Modern FTIR machines can store, retrieve and compare spectra to enable manufacturers to check quality, identity and characteristics of the polymer materials they use (RAPRA, 2004).

Table 7.5 Typical infrared spectra of vulcanised coating rubbers

Rubber	Type of group vibration		Wavenumber (cm^{-1})
Natural rubber	C = C	stretch	1645
	CH_3 and CH_2	in-plane bend	1452–1375
	CH	out-of-plane bend	886
	CH_2	rocking	798
SBR(Styrene–butadiene)	CH	stretch	3150–3000
	Phenyl	stretch	1600–1380
	C=C	stretch	1601
	CH	in-plane bend	1186 & 1028
	Phenyl	in-plane bend	756
	Phenyl	out-of-plane bend	697 & 540
Butyl rubber (isobutene–isoprene)	C=C	stretch	1641
	CH_3 & CH_2	in-plane bend	1470
	CH3	in-plane bend	1395 & 1365
	=CH	in-plane bend	1230
	=CH	out-of-plane bend	890
Polychloroprene	C=C	stretch	1636
	CH_2	in-plane bend	1458
	=CH	out-of-plane bend	884
	C–Cl	stretch	814
Nitrile (polyacrylonitrile–butadiene)	C≡N	stretch	2237
	C=C	stretch	1592
	CH_2	in-plane bend	1455
	C–CN	stretch	828
	CH_2	rocking	758

Note: All the rubbers listed exhibit CH_3 and/or CH_2 stretch peak at 3000–2840 cm^{-1}

7.8 British and international standard chemical test methods

Standard test methods that have been trialled, tested and approved by independent committees are the main methods accepted by government purchasing departments, manufacturers and quality assurance systems. Many traditional British Standards have been incorporated into International Standards (ISO) and European Norme (BS EN) standards for use throughout the world. The following list contains some of the important test methods for the chemical analysis of rubbers, plastics and other elastomers used in coated fabrics.

7.8.1 Chemical tests for raw and vulcanised rubbers

Most tests form part of British Standard 7164 (British Standards Institution, 1996; ISO, 1996).

BS 7164-2 (= ISO 4661–2) Part 2 concerns sample preparation (see Section 7.4 above)

BS 7164-6.1 Part 6 Methods for the determination of volatile matter in rubber
BS 7164-7.1 (= ISO 5945) Part 7 Methods for the determination of polyisoprene content
BS 7164-11.1 Part 11 Determination of the microstructure of butadiene
BS 7164-13 Part 13 Determination of total hydrocarbon content
BS 7164-21 (=ISO 1656) Part 21 Determination of nitrogen content (see Section 7.5.1, Test for nitrogen)
BS 7164-22.1 Part 22 Determination of chlorine content using the Parr Bomb method
BS 7164-22.2 (ISO 7725) Part 22 Determination of bromine and chlorine content using the oxygen flask method (see Section 7.5.1, Test for chlorine)
BS 7164-23.1 (ISO 6528-1) Part 23 Determination of total sulphur content (see Section 7.5.1, Test for sulphur)
BS 6057-3.25 Methods of test for synthetic rubber latices

7.8.2 Methods of test for coated fabrics and plastics

BS 3424 is entitled Methods of test for coated fabrics (British Standards Institution, 2000). There are 38 parts to this standard; most of the tests are physical tests such as strength, abrasion, flex resistance, tear, mass, thickness, ageing, liquid proofness, air permeability, and so on. However, BS 3424 Part 7 (similar to ISO 2411) covers coating adhesion strength, which includes cleaning and preparation of the coating. BS 3424 Part19 is the determination of sulphur staining. BS 3424 Part 21 is determination of fusion of PVC and state of cure of rubber coatings and BS 2782 concerns Methods of test for plastics.

7.9 Analysis of components, additives and compounding ingredients

Many coating polymers contain additives and compounding ingredients to improve the physical durability, flexibility and performance. Rubber coatings in particular usually include carbon black and inorganic fillers to improve physical properties or reduce costs.

7.9.1 Determination of carbon black in rubbers and plastic coatings.

The method involves the pyrolysis of a weighed amount of the polymer in a stream of nitrogen in an electric furnace at 300–500 ºC and is very reproducible (Haslam *et al*., 1983). The carbon residue after heating is cooled, desiccated and weighed. The percentage of carbon is determined from the original polymer sample weight.

7.9.2 Analysis of plasticisers in polymer coatings

Coatings, especially PVC, contain plasticisers to render the film coating flexible over a range of utility temperatures. There are a wide variety of plasticisers available in the form of aliphatic and aromatic phthalates, sebacates, ricinoleates, adipates, phosphates, oleates, stearates, palmitates, lactates and glycollates. Dioctyl phthalate is typically known for its use in PVC coatings.

Qualitative analysis of common plasticisers is complicated by the fact that there may be other fillers and additives in the coating polymer. It is important to dissolve out the plasticiser in a reflux apparatus with suitable solvent such as ether, methanol or carbon tetrachloride.

Phthalates can be identified by adding the acidified test solutions to resorcinol or phenol, followed by heating in an oil bath at the boil for a few minutes. After cooling and diluting, 1 N sodium hydroxide solution is added and stirred. If phthalates are present, the resorcinol test shows a pronounced green fluorescence. In the phenol test, a red colouration caused by phenolphthalein is produced. Both sebacates and ricineolates also give a faint positive fluorescence in the resorcinol test, but do not produce colour in the phenol test.

Another test for phthalates involves polarography (Whitnack and Ganz, 1953). The plasticiser is mixed with tetramethyl ammonium chloride and diluted with methanol. After removal of oxygen the solution is polarographed over the range –1.0 to –2.0 V. Dibutyl phthalate is reduced at about –1.45 V. Dimethyl, dihexyl, dioctyl and dinonyl phthalates are reduced at about –1.5 V.

Separation of mixtures of plasticisers can be achieved by thin layer chromatography on a Kieselgel plate using mixtures of benzene and ethyl acetate as solvents. The separated bands obtained can be examined by infrared techniques.

7.9.3 Analysis of fillers and pigments

Rubber compounds can contain a range of fillers such as silicates, sulphates, oxides, carbonates, phosphates, nitrates, titanium dioxide, barium sulphate and various clays. Analysis of mixtures of these additives is complicated and it is necessary to separate the constituents by dissolution in suitable inorganic solvents and/or filtration of insoluble substances such as silicates. The residues can be examined in several ways:

- Visual examination under the microscope can identify common substances such as silica (sand).
- The residues can be tested for the presence of metallic sulphates, carbonates and sulphides using inorganic analytical techniques.
- The residue can be heated until ash forms and the product is examined.
- The nature of the elements present can be established by emission and/or X-ray fluorescence spectroscopy.
- Infrared spectroscopy can be used to examine inorganic species, as many of the

Table 7.6 Infrared absorption bands for inorganic anions

Anion	Structure	Wavenumber (cm^{-1})	Comments
Carbonate	CO_3^{2-}	1450–1410 880–830	Broad and strong; split in basic carbonate
Bicarbonate	HCO_3^-	1350–1300 700–690	Broad and strong; broad medium intensity
Nitrate	NO_3^-	1410–1390 840–820	Broad and strong; sharp and weak
Phosphate	PO_4^{3-}	1100–1000	Often complex
Sulphate	SO_4^{2-}	1130–1080	Complex with strong bands
Silicate	SiO_4^{2-}	1100–900	Many silicates have complex band patterns

fillers are metallic salts in which the anion contains oxygen, i.e. in carbonates, bicarbonates, phosphates, nitrates, silicates and sulphates. Strong absorption bands due to the C–O, Si–O, P–O, N–O and S–O vibrations within the ion occur in the fingerprint regions of the IR spectrum (Haslam *et al.*, 1983).

Table 7.6 shows characteristic peak wavenumbers for common inorganic anions.

7.10 Conclusions

This chapter has attempted to give guidance on the qualitative and quantitative analysis of polymeric coatings and membranes used in textiles. The coatings are often complex mixtures of polymers, composites with textile fibres, additives, finishes, fillers and plasticisers which makes them difficult to analyse without interference. Separation and isolation of a representative pure sample requires skill and a wide range of chemical techniques. Some coatings, such as PVC are relatively easy to identify by touch, smell, and rudimentary preliminary tests. Rubber coatings are relatively easy to recognise owing to their colour, smell and appearance, but analysis of the detailed composition is complicated.

Health and safety legislation is driving the coated fabric industry towards the use of less toxic, environmentally friendly processes. Many coatings are now applied from water-based pastes or as thermoplastic elastomers , so that the complications surrounding the use and recycling of organic solvents can be avoided. There is continual discussion in the western world about limiting or controlling the use of halogen-containing polymers such as PVC, PVDC and PTFE, and fillers containing heavy metals such as lead and cadmium.

Some of the identification methods must be carried out with great care and attention to health and safety considerations. Toxic vapours or gases such as HF or

HCN can be evolved as products and some additives and chemical reagents need careful handling in modern laboratory conditions. The modern textile coating and laminating industry continues to thrive and innovate, with performance requirements becoming more challenging, whilst the range of applications for high-performance technical textiles is continually increasing.

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8

Chemical analysis of damage to textiles

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8.1 Introduction

The chemical analysis of damage to textiles is a fascinating special area of chemical testing of textiles. It has significant practical relevance, considerable charm but also many difficulties. Determining the exact cause of damage can often be a real challenge. Those who carry out damage analysis need wide-ranging knowledge and some experience but also intuition and the ability to reason and weigh up evidence like a detective.

With a little imagination, textile damage analysis and its prerequisites can be compared to a building. The foundations consist of an extensive knowledge of textile fibres, their conversion to yarns and fabrics, dyeing and finishing, making-up processes and typical usage. Thus the base is a knowledge and understanding of textile technology, including textile physics and textile chemistry. The roof of this imaginary building is the damage analysis itself. It is supported by several rows of columns resting on the foundations. One group of columns is made up of the experience, intuition and detective-like reasoning mentioned above. The next group of supporting columns consists of the most important methods used in damage analysis, such as microscopy, chromatography, infrared (IR) spectroscopy and thermal analysis. Further supporting columns are peripheral information, starting with the conditions used in producing, dyeing and finishing the damaged textile, including the processes and machines used, further processing stages, storage, transport and, where appropriate, usage. This analogy is intended to give an idea of the requirements for successful analysis of damage to textiles and the knowledge and skills which successful analysts should have.

Analysis of damage to textiles is not usually an exact science although it does use scientific methods. In many cases several different tests are necessary. Their results can sometimes be contradictory. These then have to be evaluated and weighed up against each other very critically, whereby comparison of samples, experience with similar cases and information about the circumstances of the damage can be useful. In many ways this process is similar to a court trial when only circumstantial evidence is available but fortunately in the laboratory the damage can often be imitated and the evidence thus verified.

8.2 Practical importance of textile damage assessment and analysis of causes of damage

Textiles can become damaged during their production as well as during distribution and usage. Experience shows that consumers are less likely to make complaints than are those people involved in the chain of textile production. For example, textile manufacturers often dispute with textile dyers and finishers about who might be responsible for faults, although this can usually be clarified quickly by means of a film imprint, as shown in Section 8.4.6. As well as the question of who is responsible and therefore who has to bear the costs, it is naturally also of interest to know how the damage can be repaired and also how it can be avoided in future. In the case of large lots or continuous production it is often important to find out very quickly what the cause is in order to stop producing the fault as soon as possible. In this respect damage analysis plays an essential role in quality assurance. Lack of quality and subsequent complaints should not be underestimated in terms of the image problem they present for the supplier. Experts in damage analysis are thus often employed by well-known companies.

In spite of modern process control, optimization and quality control faults cannot be avoided completely. They occur at all stages of textile production including storage and transportation. The experts in damage analysis at the fibre, dyestuff and auxiliary agent producers, as well as those at the testing and research institutes, still have their hands full, dealing with many cases of damage where the costs caused by the fault can be quite high. Some disputes about damage are settled by a court but more usually the customer and producer agree on a settlement. Depending on the importance of the business relationship, fair dealing and price discounts play an important role here. Occasionally unjustified complaints are also made in the hope of obtaining just these benefits. In order to remain in charge of investigations of complaints, most of the West European producers of fibres, dyestuffs and auxiliary agents have their own testing laboratories with damage analysis experts. The alternative, namely to let testing institutes carry out this work, is usually rejected because, amongst other reasons, the companies would have to reveal too much detailed knowledge and also because it often takes too long. Some producers of textile auxiliary agents choose another, risky path. They take care of complaints simply by giving price reductions without carrying out their own laboratory investigations.

Most textile companies do not have the personnel or equipment required for the clarification of complicated faults. On the other hand they do have the best insight into peripheral information required for damage analysis. However, when they hand over the fault to an institute or, more usually, to their suppliers of fibres, dyestuffs or auxiliaries for investigation they often only pass on part of this information. Analysis of the fault is then often regarded as technical customer service in order to promote and cement customer relationships. The intensity of

these external analyses of damage then sometimes reflects that of the business relationship.

Although there are no figures available for the economic importance of textile damage analysis it can be roughly estimated from the expenses incurred by producers of fibres, dyestuffs and auxiliary agents in dealing with complaints and analysing damage. These expenses for personnel and equipment are very high even though some decades ago they were even higher. The authors know of at least two dozen specialized laboratories that undertake such analyses in German-speaking countries, in industry and in testing and research institutes. If it is assumed that on average two or three employees are involved with a corresponding annual budget of about 300 000 to 400 000 euros per laboratory this would amount to a total of up to 10 million euros just for Germany, Switzerland and Austria.

8.3 Fundamentals of textile damage analysis

8.3.1 Definition of faults, damage and quality

Faults are defects which lower the value and usefulness of goods. According to DIN 40 080, faults are defined as any kind of deviation from prescribed requirements. Damage is the disadvantage arising from faults. Thus damage analysis is a wider ranging term than analysis of faults. It is damage which leads to complaints and, as a rule, to demands to repair the damage or compensate for it. Quality is defined as the total sum of characteristics relating to suitability in use, which fulfil defined and prescribed specifications. Damage analysis is an important part of quality control and contributes to quality assurance.

8.3.2 Manifestations of damage

The manifestation of damage to textiles can vary widely. It ranges from obvious, for example visible or easily recognizable defects, to hidden ones, for example defects that are hard to detect or those that can only be detected later. It is the latter type which is generally the reason for giving guarantees.

Perception and description of the fault are the first steps in damage analysis. Damage can be perceived visually, macro- and/or microscopically, often only with a specific type of illumination, such as reflected, oblique or transmitted light, or with a specific light source, for example ultraviolet (UV) or polarized light. Some faults are detected by other senses, usually in the form of a handle assessment, or they can be registered by measurements. Examples for the latter are colour measurement, tensile and abrasion strength, extensibility, shrinkage and fastness properties. These technical properties can be supplemented by thermophysiological comfort properties and care requirements, where significant deviations from the agreed or specified values can be claimed as faults.

Damage is manifested most commonly as stains followed by streaks and

barriness. Other types of damage manifestation, such as differences in hue or depth of shade, unlevelness of dyeing, lack of strength, deposits, abrasion and holes, occur with less frequency.[1]

It is important here to describe the fault as exactly as possible. All the typical characteristics and peculiarities, their frequency and possible regularity have to be noted and also whether they can be localized to individual fibre or thread systems. This makes it easier or even possible to determine the cause of the damage later.

8.3.3 Damage causes

There are mechanical, thermal, chemical and biological causes of damage to textiles. They may be attributed to different causal agents, in particular to textile manufacturers, dyers and finishers, garment producers, distributors or consumers. Although there are cross-relations between all the above-named causes and other causal agents, it is usual, for example, to attribute mechanical damage to the textile manufacturer and chemical damage to the dyer and finisher.

Although there are different types of damage manifestation, there is no especially typical cause of damage. In the statistical investigation, based on 550 cases of damage, there were 81 different causes of damage where more than 10 cases were registered. Their proportion ranged from 2% to a maximum of 6%.[1] Other sources also report a similarly wide range of damage causes with a relatively low percentage in each case.[2] This enormous range of causes is typical for damage to textiles and makes its analysis difficult.

This statement is also applicable to the causes of the most frequent manifestation of damage, namely stains. Statistical analysis of 258 cases of damage by stains resulted in 29 types of cause, each represented in more than seven cases.[1] The most common types of cause gave frequencies in the range from 7–8%. These are, for example, stains caused by mechanical and chemical influences, dyestuffs, grease or oil, silicone and dead or immature cotton.

8.3.4 Chemical and physical assessment of textile damage

Of the many possibilities for investigating damaged textiles, two main groups can be ascertained: chemical and physical testing. Corresponding to this, two types of textile laboratories are often to be found, namely chemical and physical testing laboratories. Each offers different advantages for damage investigation. Physical testing does not require any chemicals and often gives results which are easily interpretable and may allow a direct quality assessment such as ‘just acceptable’, ‘second choice’ or ‘reject’. On the other hand with chemical testing the cause of the damage can be ascertained, which is what is actually meant by analysis of damage. But this advantage often has to be paid for in the form of higher costs for personnel and equipment.

8.3.5 Procedure for textile damage analysis

Unfortunately there are no hard and fast rules on how to proceed with textile damage analysis. The variety of cases and causes is too great for this. Nevertheless, some companies and institutes use their own preprinted forms with long lists of tests for this purpose. This has the advantage that none of the rare tests is overlooked but also the disadvantage of inflexibility and unnecessary work on certain types of damage. Such preprinted forms may be of help to less experienced testers but experienced testers tend to have their own specific procedures, depending on the case, and are often guided by their intuition. As a general rule preliminary tests are made, followed by more painstaking specific tests.

The usual steps taken in an investigation are illustrated here using the example of stain analysis:

1. Manifestation of the damage with a description of the type, distribution and possible regularity of the stains
2. Microscopy with increasing magnification, beginning with a magnifying glass or stereomicroscope and progressing to 300 to 1000-fold magnification. Use of different types of illumination and contrast, such as reflected, oblique and transmitted light, UV, polarization or fluorescence
3. Preliminary tests such as solubility and staining tests
4. Isolation of the substance causing the stains (for example by extraction in a Soxhlet apparatus) and concentration of the extraction residue. It is recommended here to cut out the stained areas from the specimen and to extract an equivalent quantity of unstained material for comparison. If the stain is in the form of insoluble deposits an attempt can be made to dissolve the fibre material and thus isolate the stain substance
5. Comparison and identification, usually by means of thin layer chromatography and/or IR spectroscopy. Comparison is made with the blank sample (extract from unstained areas) and with authentic substances which could have caused the stain. If the stain cannot be extracted, IR spectra from stained and unstained areas can be compared and the spectra subtracted in order to identify the stain substance. The limits of detection of typical stain substances in IR spectra and a comparison of IR methods have been given in the literature[3,4]
6. Reproduction, if possible, of the damage in order to verify the findings, for example comparison with authentic stain substances on the same textile material, using conditions as close as possible to those used with the damaged sample
7. Further verification, for example, if possible, by means of consultation with the persons concerned in the stage of production suspected of causing the damage. It is important here to consider alternatives and to test the plausibility of the findings critically
8. Summary of the findings, discussion of the results. If the cause has not been clearly identified the results should be formulated carefully and alternatives mentioned. Documentation including photographs and possibly samples.

9. If possible hints should be given on how to avoid such stain formation in future and also on how to remove the stains (suitable solvents and procedures).

The last steps in this stain analysis demonstrate that comparative samples and information from peripheral areas of the case can be particularly useful aids in damage analysis. An archive with similar cases of damage can also be very useful here. If the archive is very extensive, retrieval of information on all damage cases according to different criteria should be possible, such as type of textile and fibre, damage manifestation, cause of damage, method and procedure leading to clarification and, if available, the source and client for the analysis.

In many cases, but unfortunately not in all, about halfway through these steps, or at least after the preliminary tests, the cause of the damage may be suspected and this may lead to a working hypothesis. This hypothesis then has to be either unequivocally verified or rejected on the basis of further tests. It is often hard to give up a hypothesis and look for a better one. Self-criticism and experience can be helpful here as well as literature searches and discussions with interested colleagues or other experts.

8.3.6 Literature on textile damage and its analysis

A very useful book, in which many typical cases of damage are described and illustrated, has been published by Mahall.[5] In this book he has summarized his years of experience in damage analysis and his many publications in such a way that readers receive valuable stimulation for their own work. Further books which may be of assistance in damage analysis include those from Hearle *et al.*,[6] Agster,[7] Stratmann,[8] Greaves and Saville[9] and from the Textile Institute.[10]

Most of the articles on damage analysis published in journals are not recent.[11–21] This is also true of company brochures on this topic.[22–24] In the selection mentioned here, the last article is cited if it is part of a series of articles. Citations for previous articles in the series can be obtained there.

8.4 Methods of textile damage analysis

8.4.1 Preliminary examination

The subject of preliminary examination is as varied as a later part of this section, namely miscellaneous methods. There may also be no clear-cut separation between the two. Preliminary examination is composed of simple tests, carried out in a short time and with little effort, which give the first clues in damage analysis.

It is usual to begin with an exact visual examination, if possible in comparison with an undamaged sample. Notice should be made of any peculiarities in appearance. Sometimes abraded and raised areas, holes, thin places and pressure marks can be easily recognized without optical aids. With the use of a magnifying glass they can be seen more clearly and in more detail. The same is true for many

visible deposits of foreign matter such as silicates, calcium and magnesium salts (for example oxalate, phosphate), polyester oligomers and mildew spots.

As a next step, easily determinable differences between the damaged sample and undamaged comparison samples can be sought, for example handle assessments, wetting behaviour (TEGEWA drop test[25]) or pH value. The latter can be determined with moist pH paper or more accurately by adding a drop of liquid indicator or with a flat-bottomed pH electrode. The microscopical detection of acid residues by the formation of methyl orange crystals is described in Section 8.5.2. Simple tests of mechanical strength (stretching between the thumbs), crocking fastness tests (dry and wet) and, where appropriate, a test of wet fastness, for example in cold and then heated dimethylformamide, also belong in this group.

After marking the damaged area, woven fabrics can be separated into warp and weft threads and knitted fabrics unravelled in order to investigate the isolated threads more thoroughly. Do the threads from the damaged area show differences in diameter, twist level or yarn composition? Are stray fibres discernible?

Rapid methods of separating fibre blends for damage analysis

Part of the preliminary examination of textile blends consists of dissolving out one fibre component and examining the residual fibre to see which fibre components are damaged. The following methods of separation have proved useful:

1. Polyester residue in blends with cellulose, acetate or nylon: The sample is treated with 72% sulphuric acid for 5 min at 70 °C or in 75% sulphuric acid for 20 min at 50 °C. It is then thoroughly rinsed with water, neutralized with diluted ammonia, rinsed again and dried. (Acrylic fibres may dissolve.)
2. Polyester residue with polyester/wool blends: The sample is boiled for 1–2 min in 3.25% caustic soda, then rinsed with water, neutralized with diluted acetic acid, rinsed again and dried.
3. Cellulose or wool residues in blends with polyester fibres: Dissolution of the polyester fibre is carried out in a 50% solution of trichloroacetic acid in chloroform at room temperature for 15 min (liquor ratio 1:50). The sample is then rinsed twice with about 100 ml of a 15% solution of trichloroacetic acid in chloroform. The sample is subsequently rinsed with cold chloroform until, in the case of dyed samples, the solvent is no longer dyed. As a rule about 200 ml of chloroform are required. A final rinse is made with hot water.
4. Nylon residue with nylon/wool blends: The wool is dissolved with caustic soda as in method 2.
5. Wool or cellulose residues in blends with nylon: The nylon fibres are dissolved out by treating the sample two to three times with concentrated formic acid for 15 min each time at room temperature. The sample is then thoroughly rinsed with concentrated formic acid, hot water, diluted ammonia and cold water and then dried.

6. Acrylic residue with acrylic/wool blends: The wool is dissolved with caustic soda as in method 2.
7. Cellulose, wool, nylon or polyester residues in blends with acrylic fibres: The fibre sample is treated at 90–100 °C for 1 h in dimethylformamide, preferably in a boiling water bath. The fibre residue is then extracted with fresh dimethylformamide for 30 min in the boiling water bath. It is then washed with 1–2 l of hot distilled water and dried.
8. Diacetate fibres can be dissolved out by two treatments with acetone and triacetate fibres by three treatments with dichloromethane, in each case for 10 min at room temperature. In this way they can be separated from cellulose, wool, silk, polyester or acrylic fibres, which then remain as a residue.
9. Wool and silk fibres can also be dissolved out by treating with sodium hypochlorite solution for 20 min at room temperature (35 g l^{-1} active chlorine and 5 g l^{-1} caustic soda), followed by rinsing, anti-chlorine treatment with natrium thiosulphate solution and further rinsing. Cellulose, nylon, polyester, acrylic or polyvinylchloride fibres remain as residue.

Fibre identification

Determination of the fibre type, including checking of the stated fibre type, is one of the most important preliminary tests. If no IR spectrometer is available, standard fibres can be most readily identified using the characteristic reactions according to Stratmann.[8] For modified fibres or high-performance and speciality fibres the more complicated classification on the basis of solubility groups and their subdivisions[8, 26] or other methods of analysis[27] have to be used.

Qualitative analysis of standard fibres by means of microscopy and characteristic reactions can be carried out as follows:

1. Wool can be easily recognized in the longitudinal microscopic view on account of its typical scales.
2. Cotton has typical irregular convolutions in the longitudinal microscopic view. When raw cotton is embedded in cuoxam the fibres show a typical balloon formation.
3. Flax is stained blue by zinc chloride–iodine reagent (see Section 8.5.6), as are all other cellulose fibres. In addition the typical V- and X-shaped transverse structures can be seen more clearly. Differentiation from hemp can be made by means of a cross-sectional sample. Flax shows clearly visible irregular polygons with lumen, hemp shows relatively indistinct and often conglomerate structures.
4. Viscose shows typical longitudinal striations in the longitudinal microscopic view. Cupro, lyocell and some polynosic fibres have round cross-sections and can be confused with mercerized cotton, which, however, appears more irregular. Lenzing modal fibres can be recognized by one clearly visible longitudinal striation. Further helpful details are described by Reiter.[28]

5. In the longitudinal microscopic view raw or degummed silk appear as double or single filaments, respectively. Silk gum residues can be visualized by staining with direct dyes or Neocarmin W (see Section 8.5.3). Silk dissolves in cuoxam as do the cellulose fibres. It can be distinguished from them by the lack of blue staining in the zinc chloride–iodine reagent and by its irregular longitudinal form.
6. Cellulose di- and triacetate fibres (CA, CT) as well as acrylic fibres (polyacrylonitrile, PAN) are all soluble in the zinc chloride–iodine reagent. An initial differentiation is made using the acetone test on a watchglass: only CA and CT fibres dissolve (evidenced by a cloudy evaporation residue). Differentiation between CA and CT fibres: CA dissolves in Frotté II reagent (see Table 8.1), CT only swells. Results are similar in zinc chloride/formic acid, but with a less distinct difference (CT swells more markedly). PAN fibres dissolve in cold concentrated nitric acid and in dimethylformamide at 100 °C. They swell in boiling 85 % formic acid and decompose at about 280 °C without melting.
7. The nylon fibres PA 6 and PA 6.6 show the typical crenellation of the fibre surface in Frotté I reagent after maximally 5 min at room temperature. In the weaker Frotté II reagent this reaction only occurs with PA 6 (see Table 8.1). Further differentiation is by determination of melting point (PA 6 = 215 °C, PA 6.6 = 255 °C, PET also at 255 °C).
8. When polyester fibres (polyethylene terephthalate, PET) are heated in 15% alcoholic potassium hydroxide (KOH) on a microscope slide with a cover slip, typical needles are formed from the potassium salt of terephthalic acid.[29] This characteristic reaction for polyester is simpler and less problematical than the staining of fibre ends with Oil Red in *m*-cresol as described by Stratmann.[8]
9. Polypropylene (PP) and polyethylene (PE) fibres float in water, they are not soluble in cold concentrated sulphuric acid but soluble in boiling perchloroethylene. They are also easily recognizable and distinguishable by their melting points: PE 124–138 °C (occasionally up to 155 °C) (low density PE 105–129 °C), PP = 160–175 °C (if based on metallocene catalysis 15–20° C lower).
10. Elastic fibres can be easily recognized by their great extensibility and elasticity as well as their longitudinal microscopic view (often quasi-monofil from coalesced single fibrils). As opposed to rare rubber threads, elastane fibres based on polyurethane dissolve in boiling dimethylformamide and swell markedly in 85% formic acid.

Further preliminary tests

Sometimes it can be appropriate to carry out preliminary tests for readily detectable elements or compounds, for example the Beilstein test for organically bound

Table 8.1 Frotté reagents and reactions (according to Stratmann[8] except acetylated polyvinyl alcohol fibres)

Reagent	Main reaction	Side reactions
Frotté reagent I 100 g anhydrous $ZnCl_2$ are dissolved in 50 ml water and the density adjusted to 1.900 (g cm^{-3}), then 5 parts by volume of this solution mixed with 1 part by volume of methanol	Frotté reaction (crenellation) within 5 min at room temperature with nylon 6 and nylon 6,6; with nylon 11 and nylon 12 the reaction only occurs after heating on the microscope slide until boiling	Swelling with regenerated cellulose fibres, dissolution of acetate and acrylic fibres, swelling reaction with polyvinyl acetate fibres, swelling and core contraction reaction with acetylated polyvinyl alcohol fibres resulting in a characteristic zigzag form
Frotté reagent II 100 g anhydrous $ZnCl_2$ are dissolved in 100 ml water and the density adjusted to 1.566 (g cm^{-3}), then 5 parts by volume of this solution mixed with 1 part by volume of methanol	Frotté reaction (crenellation) within 5 min at room temperature with nylon 6 (not with nylon 6,6, nylon 11 or nylon 12)	Swelling with regenerated cellulose fibres, differentiation of acetate fibres: CA soluble, CT only shows swelling, swelling reaction with polyvinyl acetate fibres, swelling and core contraction reaction with acetylated polyvinyl alcohol fibres resulting in a characteristic zigzag form

chlorine (green coloration of the flame when heating a copper wire with a small fibre sample in the non-luminous region of a gas flame). In this way fibres containing vinyl chloride can be easily recognized.

A further example is the detection of iron in the combustion residue of a textile sample or directly on the fibre material. For example, after adding a few drops of 1 N hydrochloric acid p.a. and 1 N ammonium thiocyanate a red iron complex is formed which can be concentrated by extraction with ether so that the detection limits are very low (more detailed description in Section 8.5.1).

Hints on the presence of silicone deposits are given by the adhesive strip test (lowering of the adhesion due to silicone) and the foam test (marked formation of foam when the textile sample is shaken with chlorinated hydrocarbons). Detection by means of IR spectroscopy is discussed in Section 8.4.4.

Staining, swelling and solubilty tests as well as extraction are seldom so simple that they might be included under preliminary examination. As a rule they belong to the miscellaneous methods discussed in Section 8.4.6.

8.4.2 Microscopy

Microscopy is certainly the most important method used for damage analysis of textiles. Without microscopy and its supporting techniques the elucidation of most cases of damage would not be possible. The extensive literature on this topic also demonstrates the great importance of textile microscopy for damage analysis.[5, 6, 8–13, 22, 24, 30–38] A number of well-known textile microscopists who also worked intensely on elucidation of faults deserve mention here: A. Herzog (Vienna, Dresden), H. Reumuth (Jena, Mannheim, Karlsruhe), P.-A. Koch (Dresden, Zurich, Krefeld), M. Stratmann (Krefeld), N. Bigler (Basle), K. Mahall and I. Goebel (Düsseldorf) and G. Schmidt (Ludwigshafen).

Microscopical methods are used in the textile industry to investigate raw materials, for product development and analysis of competitor's samples, and to check production and control effects and quality. Typical examples of their use are shown in Table 8.2. Textile microscopy is indispensable in dealing with complaints and analysing damage as well as in avoiding faults and repudiating unjustified claims. Microscopy is, of course, just as important in textile research (for example in the analysis of the fine structure of fibres, surface modifications and investigations on the distribution of dyes and auxiliaries).

Stereo microscope

The microscopical investigation of damage usually begins with a stereo microscope at low magnification (about 5X), which can then be increased to about 100X. If necessary the damaged areas can often be marked and thus distinguished from their intact surroundings. The large distance between sample and objective enables individual threads, foreign fibres or deposits to be easily manipulated. Further advantages of the stereo microscope are the spatial, three-dimensional image obtained and the fact that different types of illumination can be readily used, depending on what is to be examined. For example, reflected light falling obliquely from one side or opposite sides can be used as well as even, shadow-free illumination with a ring lamp or contrasts with strong shadows using extremely flat illumination from one side. Transmitted light is also possible with the stereo microscope but is seldom used in damage analysis.

Compound microscope

More detailed information can be obtained from light microscopes with up to 1000X total magnification. They are also known as compound microscopes because they have two complementary light paths, the illuminating and the imaging light path, which are adjusted to each other by means of the condenser and aperture diaphragms (Köhler illumination). Such microscopes are available with transmitted light for single fibre investigations or for thin cross-sections and with reflected light for non-transparent objects. Brightfield illumination is usually used

Table 8.2 Examples of the use of microscopy in textile production and fault analysis[35]

Production stage	Examples
Primary spinning	Cross-sectional form
	Fineness
	Delustrant
	Vacuoles
	Drawing
	Core-sheath structure
	Bicomponent fibre structure
Secondary spinning	Fibre identification
	Blend distribution
	Hairiness
	Twist
	Slubs, neps
	Fibre slippage
	Variation in thickness
Texturizing	Type of texturizing
	Fibre deformation
	Bulking effect and evenness of bulk
Weaving preparation	Distribution of size
Weaving and knitting	Fibre type and state
	Weave/knit pattern and pattern faults
	Deposits, waxes, grease
Pretreatments	Fibre type and state
	Degree of alkalization, mercerization, saponification
	Bleaching effect, bleaching damage
	Mechanical effects such as extent of raising, pile position
Dyeing	Evenness, macro- and micro-levelness
	Penetration
	Deposits
	Migration
	Bicolour effect with blends
Printing	Clarity of print
	Print penetration
	Distribution of binder
Finishing	Distribution
	Crosslinking
	Mechanical effects such as chintz, embossing, raising, emerizing

with transmitted light. Darkfield illumination allows edge structures such as projecting fibres from yarns, scales on animal hairs and delustrants to be more easily observed. Polarized light is used for the determination of the melting point of synthetic fibres (see Section 8.4.5), for their identification by means of birefringence and also for damage analysis.[39] Differences in tension and drawing as well as fibres deformed under pressure can be seen more easily between crossed polars. The same is true for the typical transverse structures in natural fibres, such

Table 8.3 High-magnification microscopic methods for textiles: types of contrast and illumination[40]

Method, contrast	Reflected light	Transmitted light
Brightfield	Seldom	Very common
Darkfield	Seldom	Common
Polarization	Very seldom	Common
Fluorescence	Common	Seldom
Scanning electron microscopy	Common	Seldom

as ramie or tussah silk.[38] Phase contrast and interference contrast methods are very seldom used in microscopical investigations of textile damage. For fibre identification with polarization and interference microscopy, see Section 8.7.1. The usual contrast and illumination methods at high magnification as used here are summarized in Table 8.3.

Fluorescence microscopy

In damage analysis the most important microscopical contrast method is selective staining of structures of interest. Unfortunately there are cases where no normal dyes are known that give selective staining. However, if selective staining with fluorescent dyes is successful, fluorescence microscopy can be a particularly useful method of investigation for the analysis of damage to textiles. It is more or less independent of the original dyeing of the textile and it can create strong contrasts and thus mark substances present in low concentrations. In rare cases the natural fluorescence of the material can be sufficient for the investigation, for example with wool where it occurs in direct relation to yellowing.[41] However, the samples are usually selectively stained with fluorescent dyes, the so-called fluorochromes. The exciter and barrier filters of the microscope then have to be adjusted for the particular fluorochrome. Otherwise the relatively weak fluorescence would be superimposed by the intensive excitation light. The best-known excitation is with UV light for optical brighteners, which then emit blue light. In this case a barrier filter which does not transmit UV light is necessary. Further examples are shown in Table 8.4. The most common method of illumination in fluorescence microscopy is the reflected light/brightfield method. In sample preparation care should be taken to use non-fluorescent embedding agents and extremely clean slide glasses and cover slips so that the background is not brightened by dust, scratch marks, fingerprints or similar. Although this suggests that expensive apparatus and time-consuming sample preparation are required, the following examples will serve to show that the effort is worthwhile. These examples are directly or indirectly related to damage analysis.

Hesse and Pfeifer[43] described the fluorescent detection of oil stains, the analysis of the distribution of optical brighteners in polyester/cotton blends and the

Table 8.4 Examples of the relationship between excitation range, object colour and fluorochrome[42]

Excitation range (nm)	Excitation colour	Fluorescence/object colour	Examples of fluorochromes
340–380	UV	Blue	Optical brighteners
450–490	Blue	Yellow to yellow-green	Auramine (C.I. Basic Yellow 2)
515–560	Green	Red	Rhodamine B (C.I. Basic Violet 10) Phloxine B (C.I. Acid Red 92)

detection of photolytic damage by means of macroscopical and microscopical fluorescence techniques. Nettelnstroth showed how several cases of damage arising from fibres with different degrees of optical brightening could be elucidated with the aid of fluorescence microscopy.[44] Meyer and Zürcher were able to analyse the distribution of cross-linking agents in cotton by means of bicolour fluorescence, whereby the cross-linked areas were stained with Rhodamine B and the non-cross-linked areas with an optical brightener.[45] Meyer was able to visualize the distribution of anti-felting agents on wool by means of bicolour fluorescence, including the use of a filter dye which lessened the disturbance caused by stray light.[46] Based on this work further publications have dealt with the investigation of dye transport in wool[47] and polymer distribution (for example silicones) on wool.[48, 49] On account of the natural fluorescence of many kinds of fungi, biological damage to textiles could be analysed.[50, 51] The distribution of applied spin finishes has been studied with fluorescent staining.[52] Amongst the many publications in which the diffusion of dyes, surfactants and other substances in textile fibres has been studied using fluorescence microscopy, those of Lewis and Smith, in which the role of reactive dyes in the prevention of damage to wool are described, may be mentioned here.[53, 54] Use of fluorescent marking to check the distribution of binding agents applied to nonwovens[55] and the fibre-dependent distribution of silicones[42] has been described.

Scanning electron microscopy

Because of the high costs of equipment and personnel, including sample preparation (sputtering or vaporizing with carbon or gold in high vacuum), scanning electron microscopes (SEM) are seldom used for damage analysis of textiles. Only black and white images can be obtained and the staining, swelling and dissolution reactions which play such an important role in light microscopy are not possible with SEM. On the other hand SEM offers considerable advantages. Because of the very short wavelength of the electrons used, much greater magnification is possible than with light microscopy. More importantly for damage analysis, SEM images have a large focal depth and appear strongly contrasted and spatial. For example, with SEM determination of the cuticle height, wool (0.6 μm) and mohair

or cashmere (0.4 μm) fibres can be differentiated and quantitatively analysed in wool/mohair or cashmere blends.[56] SEM combined with energy dispersive analysis (EDA) can detect elements quantitatively with atomic numbers of 11 (sodium) or higher on the sample surface. Thus, for example, delustrants, heavy metal, phosphorus or chlorine content, and deposits of silicone, silicates or calcium salts can be analysed.[57, 58]

Microphotography and image analysis

To conclude this section on microscopy textile in damage analysis the production of cut or ground cross-sections should be mentioned. Also, surface imprints of fibres, yarns and fabrics, which are of such importance for damage analysis, are usually, but not always, evaluated microscopically. They are therefore discussed in Section 8.4.6. Illing-Günther and Hanus[37] analysed spots using microspectrophotometry. Finally, digital image analysis, which has now reached a high stage of development, should be mentioned, since it allows easy evaluation, archiving and distribution of microphotographs. The demands made on good micro-images are almost self-explanatory. They should show the object of interest as sharply as possible and with high contrast; as a rule they should not be manipulated, although selective colouring can be used to highlight the object, and the microphotographs should be evenly illuminated.

Cross-sections and grinding techniques

Cut or ground cross-sections of fibres, yarns and fabrics are of interest for fibre identification, in fault analysis in primary and secondary spinning and in checking the penetration of dyes into fibres, filaments, yarns and fabrics. These methods are also used to investigate hollow and multicomponent fibres, the build-up, adhesion and evenness of coating layers and the analysis of other textile composites. All of this can be useful for damage analysis. Grieve[59] has written a review on cross-section preparation methods for fibres.

If high-quality images are not required simple, rapid methods are advantageous, for example manual cross-sections using the cork or metal plate methods[28, 32] or the ITF or Hardy hand microtome.[60] The wet grinding methods developed by Rohner and Wagner[24, 61–63] have proved useful, where normal buttons are used for smaller samples and easily prepared small Perspex plates are used for larger samples. The samples are fixed with rapid adhesive in the holes of the button or the ridges of a Perspex sandwich. By grinding with increasingly fine-grained emery paper, high-quality thin sections can be obtained in 10 to 20 min. These provide long-lasting microscopic slides. Even fibre types which cannot be cut smoothly or easily, such as aramides and other high-tenacity fibres, glass and metal fibres, can be easily prepared as microscopic cross-sections in this way. However, with fibres which swell greatly in water there is a danger that after prolonged wet grinding the thin sections break away from the glass slide.

Cross-sections of particularly high quality are made with rotary or slide microtomes. A rotary microtome controlled by foot has the distinct advantage that both hands are free to take up the delicate thin sections with tweezers and paintbrush. Before they can be cut, textile samples have to be embedded. The embedding agent should as far as possible be transparent and colourless. It should not damage the sample or alter it, for example by heat of polymerization, or by dissolving, swelling or staining it and its hardness should be as close as possible to that of the fibre to be cut. If the embedding agent is too soft, the fibre is dislodged laterally when cutting, if it is too hard the thin sections become brittle and break and the microtome blades have to be resharpened too often. It is also important that there is good adhesion between the embedding agent and the fibres. In addition, air bubbles must be avoided or else they must be easily removable before hardening takes place (wetting behaviour and viscosity). In the authors' laboratories three polymer systems have proved their worth for this purpose.

1. Mixtures of the methyl and butyl esters of polyacrylic acid
The methyl ester of polyacrylic acid is relatively hard whereas the butyl ester is soft. By varying the proportions of these two esters the hardness of the embedding copolymer can be made to suit the fibre to be cut. For example, Peter[24] recommended a mixture of methyl and butyl ester in the ratio 30:70 for cellulose and nylon fibres and 40:60 for the harder polyester fibres, and 1% of dibenzoyl peroxide is added as a catalyser. Polymerization then takes place for 4 h at 70 °C in a water bath. The water bath initially supplies the heat required for the start of polymerization but it then has the advantage that it quickly takes up the heat of polymerization and prevents overheating of the sample. Peter used aluminium tubes as the form for the reaction since these could be easily bent to hold cardboard frames. The fibres, yarns or fabrics are stapled under tension to the frames. Disadvantages of this embedding system are the marked odour of the monomers and the fact that they have to be separated from their stabilizers before use. During mixing they have to be stirred carefully to avoid air bubbles. Such bubbles can be removed by short evacuation in a low vacuum; under high vacuum the monomers evaporate.

2. Epoxide resin (for example Araldite D with 20% hardener HY 956 from Ciba)
At room temperature the polymerization of this embedding system lasts about 10 h; at 70 °C in a water bath it only lasts 1 h, with the additional advantage of protection against overheating as mentioned above. The handling is easier (no removal of stabilizers) but the hardness cannot be varied. Peter recommended use of this embedding agent when the acrylic acid esters dissolve the fibres or dyes.[24] However, disperse dyes are also taken up by epoxide resins so that the dyed fibres become lighter.

3. Embedding agent hardened by light (Technovit 200 LC[64])
This embedding agent based on mono- and difunctional methacrylate does not

need to be mixed and hardens in 30 min after illumination with blue light. In daylight and the usual forms of artificial light the medium is relatively stable so that there is enough time for preparation. It is odourless and does not form bubbles or cracks. A special advantage is the possibility of building up the embedded sample in layers, making it easier to hold the sample or the frame with the sample, and reducing the heating of the sample by the heat of polymerization (maximum 90 °C). A disadvantage is the cost of purchasing the necessary polymerization instrument with blue light (Technotray CU). This embedding system was developed for grinding techniques. It is therefore relatively hard but it can be mixed with other acrylic acid derivatives thus modifying the hardness.

For demanding cross-sectional investigations on samples which cannot be cut or which contain fibre types which break randomly when cut, grinding and polishing machines as used in materials analysis (for example metals, ceramics) are required.

8.4.3 Chromatography, preferably thin layer chromatography

Chromatography comprises an important group of separation methods in which mixtures of substances are separated into their components using a mobile and a stationary phase. With textile damage analysis the possibility of identifying the separated substances by comparing them with authentic samples is often as important as the separation itself. This identification is successful when the separation behaviour in one or, preferably, more separation systems is the same and when additional findings such as the same staining or reaction behaviour show that the substances are identical. A prerequisite for such chromatographic identification is that the identity of the substance is already suspected so that the relevant substances can be chromatographed at the same time for comparison. An even more fundamental prerequisite is that the substances to be analysed are soluble in the mobile phase. Naturally it is also important that a suitable separation system is known or can be developed.

Of the many chromatographic methods used in analysis the one preferably used in textile damage analysis is thin-layer chromatography (TLC). The reason for this is that TLC delivers results quickly, simply and cheaply, with usually sufficient accuracy for elucidation of damage cases. Dyestuffs, optical brighteners, soluble textile auxiliaries and fibre finishes are especially suitable for TLC. Many pigments are also sufficiently soluble. Cross-linked finishes, fibres, coatings and other polymers are unsuitable. For the analysis of these insoluble or polymeric substances the more costly pyrolysis gas chromatography (P-GC) and variations of high-performance liquid chromatography (HPLC) or, often simpler in the case of almost homogeneous polymers, infrared spectroscopy can be used.

The procedure in TLC consists of:

- depositing the samples on the starting line of the TLC plate
- chromatographical separation, also known as development

- detection of the spots if they are not already visible due to their colour
- evaluation and documentation.

All these steps are also available in an automated form, which can be advantageous for routine investigations. If a very high degree of separation is required high-performance TLC can be used (HPTLC). Here the layers have smaller grains with a narrower distribution of grain size (for example 5 µm instead of the conventional 12–20 µm). On account of their higher separation performance HPTLC plates are usually smaller (5 × 5 cm). The use of horizontal separation chambers further shortens the time for their chromatographic development.

The extensive literature makes it easier to find suitable separation systems (coating of the plate and eluent) and to visualize colourless spots, usually with colouring reagents or by derivatizing to coloured compounds. Classical books on TLC have been written by Stahl,[65] Randerath[66] and Kirchner.[67] Newer books have been written by Nyderi[68] and Fried and Sherma.[69] There have been many publications on TLC of textile dyes (for example Rettie and Haynes[70] and Anonymous[71]). Schweppe gave a detailed description of TLC of dyes, pigments and optical brighteners.[72] An interesting sideline to damage analysis is detection with TLC as a rapid preliminary test of textiles in relation to their content of dyes which can be cleaved to carcinogenic aromatic amines.[73]

TLC is particularly useful for analysing cases of damage caused by soluble stains or oily or greasy soiling. The following examples serve to illustrate this.

1. Identification of grease and oil stains is by means of TLC of hexane extraction residues of the stains in comparison to similarly sized samples without stains, and mineral oils and oleine,[74, 75] (see also Section 8.6.1):
   - stationary phase: ready-made TLC plates with Silica Gel 60 F 254 (Merck)
   - mobile phase: (a) *n*-hexane or (b) *n*-hexane/diethyl ether/glacial acetic acid 80:20:1 by volume
   - detection by molybdatophosphoric acid or anisaldehyde
   - mineral oil Rf value in eluent (a) 0.67 and in (b) 0.78
   - oleine Rf value in eluent (a) 0 and in (b) 0.12 with tailing to the start
   - many machine oils fluoresce in UV light.[43] This can more easily be seen with oil stains when the residue of the extract is tested in UV light (concentration of the oil).
2. TLC of carriers for polyester:[74, 75]
   - stationary phase: ready-made plates with Silica Gel 60 F 254 (Merck)
   - mobile phase: *n*-hexane/diethyl ether/glacial acetic acid 80:20:1 by volume
   - detection by UV light (254 nm) or, in the case of phenolic compounds, by 2,6-dichloroquinone chlorimide (1% solution in ethanol = spray solution A; spray solution B = 10 g anhydrous sodium carbonate dissolved in 60 ml distilled water and 30 ml methanol. After spraying with A and before spraying with B the TLC plate is dried with cold air from a hair dryer).
   - The Rf values of some authentic substances (phthalic acid dimethyl ester 0.1;

o-phenylphenol 0.2; biphenyl 0.6; benzoic acid phenyl ester 0.45) demonstrate the broad separation possible with this TLC method.

3. Polyester oligomers are a frequent cause of faults. They can be identified by TLC in comparison with authentic oligomers. Their detection by means of melting point determination and IR spectroscopy will be discussed in Section 8.5.5. Authentic oligomers can be readily obtained by extracting polyester with methylene chloride (which dissolves the core oligomers), dioxane or perchloroethylene. It is recommended that polyester goods should be cleaned first with petroleum ether and acetone and that the oligomers be recrystallized from boiling dioxane. Kobayashi has named several TLC systems for their analysis,[76] see also Lang and Makart.[77] A further method based on a TLC system that is also usable for disperse dyes is as follows:[78]
   - stationary phase: ready-made plates with Silica Gel 60 F 254 (Merck)
   - mobile phase: toluene/glacial acetic acid 9:1 by volume
   - detection by UV light and/or with Dragendorff reagent as a blue coloration obtained from barium bismuth iodide, Rf 0.8 (depending on purity with tailing to 0.3)
   - Preparation of the reagent: solution A = 1.7 g basic bismuth nitrate dissolved warm in 20 ml glacial acetic acid and 80 ml distilled water; solution B = 40 g potassium iodide in 100 ml distilled water; Dragendorff reagent is prepared freshly before using by mixing these solutions A and B, adding 200 ml glacial acetic acid and then distilled water to make 1 l. The spray solution is made freshly by combining two parts by volume of this solution with one part by volume of 20% barium chloride solution.

Many low-molecular weight textile auxiliary agents can be analysed with TLC and this can be useful in elucidating certain cases of damage. Known examples are stains caused by carriers or softeners. Cross-linking agents for cellulose, as used in easy-care finishes, can be identified by TLC after degradation with dimedone. Surfactants can be separated using TLC and identified by comparison with authentic surfactant.[79, 80] When mixtures of surfactants with different ionic forms are present it is recommended that they be separated first with an ion exchanger. Ethoxylated products can be separated by TLC into the individual species up to an ethoxylation degree of 20 to 25. This results in an impressive row of spots like a pearl necklace and the size of the spots gives a rough idea of the distribution of the degrees of ethoxylation.[81–83]

- stationary phase: ready-made plates with Silica Gel 60 F 254 (Merck)
- mobile phase: butanone/distilled water 50:50 by volume
- detection: Dragendorff reagent, then vapourized with iodine.

8.4.4 IR spectroscopy

Infrared spectroscopy (IRS) is often a useful supplement to TLC especially in the

analysis of insoluble or macromolecular substances. However, with mixtures of substances the superimposed IR spectra are often so complex that they can hardly be interpreted. A previous separation, including that with TLC, is very useful for IRS. Several books on IRS can be recommended.[84–86]

Molecules can be excited by absorption of IR rays to give stretching vibrations (in the direction of the bond) and also the somewhat less energetic bending vibrations with three or more atoms in the molecule. Thus as a rule spectra with many bands and containing a high degree of information are formed. The position and the shape of the IR bands are characteristic of the particular molecular structure which has been excited. IRS in the intermediate IR range from 2.5–25 μm, corresponding to 4000–400 cm^{-1} (wavenumber) enables the identification of functional groups and other structural parts of molecules. It can also be used for testing identity. If all the essential bands in the IR spectra of the sample and the authentic substance correspond, including those in the so-called fingerprint range of carbon backbone vibrations at about 1500–1000 cm^{-1}, the two substances are identical.

This shows that IRS is a particularly powerful method for damage analysis. With this method fibres, coatings and other deposits, textile auxiliaries and substances causing stains can be identified. Chemical damage to fibres can also be detected by means of specific structural changes. All states of matter can be investigated with IR spectroscopy. Thus in damage analysis the composition of mostly liquid extraction residues is of particular interest. As well as qualitative IRS, quantitative applications are also available, where on the basis of the Lambert–Beer law the determination of the concentration of dissolved substances, the blend ratio in fibre mixtures or estimation of the comonomer content in copolymers is possible.

On account of its high energy flow and favourable signal-to-noise ratio, modern Fourier transform IRS (FT-IRS) enables the use of very low energy analysis methods such as IR microscopy[87] and many interesting reflection methods including directed and diffuse reflection as well as attenuated total reflection (ATR). With the ATR technique the methods suitable for solids and liquids, namely horizontal multiple reflection and single reflection diamond ATR, are of particular interest. The advantages and disadvantages of the different IR sampling and measuring techniques suitable for textile applications, especially for damage analysis, can be found in the literature.[4, 88, 89]

The following examples serve to give an idea of the many possiblities for the use of IRS in investigating damage to textiles. The identification of fibres, including unwanted foreign fibres, of coatings, stains and other fibre deposits are the applications which spring most easily to mind.

The IR spectra of polyester oligomers are almost identical to those of polyester fibres. The oligomers can be prepared as KBr pellets, as a molten film between NaCl or KBr platelets or else they can be investigated directly by the diffuse reflection or the diamond ATR method.

Silicone stains still occur quite often and with the aid of IRS they can be readily

Table 8.5 Suitability of IR bands for identifying silicone stains, depending on the type of fibre[3]

Wave number (cm^{-1})	Cotton	Viscose	Wool	Nylon 6,6	Polyester
770–800	++	++	++	++	0 (+)
1020–1120	–	–	+	+	–
1260	+	+	0 (+)	–	–
2965	0 (+)	0	–	–	0 (+)

Explanation of symbols: ++ indicates very good suitability (single, non-overlapping bands); + good suitability; 0 means that because of superimposition silicone can only be detected by the markedly higher intensity of the bands; – means that no increase in intensity of the superimposed bands is recognizable.

and fairly sensitively detected by means of the $Si–CH_3$ rocking band at 800 cm^{-1}, several intensive Si–O–Si bands in the range from 1020–1120 cm^{-1} and $Si–CH_3$ bending vibrations at 1260 cm^{-1}. Table 8.5 lists the suitability of these bands for the detection of silicones depending on their superimposition with fibre bands.[3] Other types of stains such as paraffins, sizes, softeners and carriers are somewhat more difficult to identify by IRS.[3] On account of the intensive F–C main bands at 1200 and 1150 cm^{-1} fluorocarbon finishes can be detected by IRS at application levels of fluorocarbon polymer from about 0.3–1.2%, depending on the overlapping with fibre bands.[4] When dealing with complaints or analysing competitor's samples concerning bonded nonwovens the composition of the binder is of interest as well as the type of fibre. The binder can also be determined by IRS.[90]

Weber-Kälin[75] has given further examples that show how IRS can be used to elucidate cases of damage caused by stains:

- Very small stains on cotton were shown to be the carboxylate of an organic acid, partly on account of bands at 1550 cm^{-1}.
- Light stains on a wool fabric were identified as a mixture of mineral oil (using TLC) and fatty acid ethanolamide (using IRS). Such mixtures are used as antifoaming agents.
- Small fluorescent spots on a white polyester/cotton fabric were extracted and compared with extracts from samples without spots. With the aid of TLC and IRS the spots were shown to be a mixture of silicone and a disperse optical brightener.
- Tiny spots on cotton were shown by comparative IRS to be the calcium salt of polyacrylic acid.
- IRS on other small spots suggested after searching in an IR spectra library the presence of silicic acid, which could be confirmed by classical analytical chemistry (alkaline melt, yellow precipitate with ammonium molybdate after exclusion of silicone).[7]

Self-collected or purchased IR spectra libraries[91–94] are very useful for the identification of unknown substances. With computer-aided library searches a correspondence

of about 80% of the bands is often sufficient to obtain a first idea or working hypothesis. If several possible identity solutions are offered it is the discrepancy between the first suggestion and the next which is more important than the absolute degree of correspondence with the spectrum of the substance being sought after. If several suggestions are made with only a few per cent discrepancy between them, all of these substances should be included in the clarification of the damage.

8.4.5 Thermal analysis

Thermal analysis (TA) is the comprehensive name for a group of analytical methods in which physical or chemical properties of a sample are measured as a function of temperature and time. The sample, contained in a defined atmosphere (usually air or nitrogen), is subjected to a controlled temperature programme, for example it can be tested isothermically or with a constant rate of heating or cooling. TA has been indispensable in polymer technology and research for a long time. In the area of textiles it has increased in importance owing to the fast-growing market segment of technical textiles, for example in quality control and in analysis of products, competitor's samples and damage. In the other textile market segments, namely apparel and household textiles, TA is especially important in damage analysis.

A database research using the keywords textile and TA (including the methods DSC, TGA and TMA, which are explained below) showed a marked difference in their relevance for textiles. By far the most important is differential scanning calorimetry (DSC), followed by thermogravimetric analysis (TGA) and finally thermomechanical analysis (TMA). Several books can be recommended for further information on these methods.[95–97]

Determination of melting point

The determination of melting point as used for fibre identification can itself be included under TA, because here the phase change is determined as a function of temperature. It can be carried out very easily using a Kofler hot bench.[98] This has a temperature range from about 50–260 °C. Fibre snippets are moved with tweezers from the colder to the warmer end until they begin to melt. The relevant

Table 8.6 Temperature range for softening and melting of fibres, arranged in order of increasing melting point or decomposition temperature.

Type of fibre, chemical basis (trade names)	Softening range	Melting range
Polyethylene, PE (HD = high density)	105–120	**124–138 (up to 155)**
Polypropylene, isotactic, iPP	150–155	**160–165 (175)**
Polypropylene based on metallocene catalyst, more highly isotactic, **iPP(Mc)**		**147–158 (130–160)**
Polyoxymethylene, POM (Delrin, Tenac)		165

Polylactic acid, PLA (e.g. Ingeo, Lactron, Lacty, Lacea)		140–178
Poly(vinyl chloride), PVC	65–90	150–180 d
Poly(vinyl chloride) postchlorinated, PVC+	85–110	150–180 d
Poly(vinylidene chloride), PVDC	90–140	150–180 d
Polyamide 12, PA 12 (Grilamid)		172–175
Polyamide 11, PA 11 (Rilsan)		180–190
Polyamide 6.10, PA 6.10 (Brulon, Decalon, Platon, Survon)		214
Polyamide 6, Nylon 6, PA 6	170–200	**215–220**
Polyurea, PUA (Urylon)		216
Copolyester A-Tell (Polyesterether PEE)		218–219
Polystyrene, PS	70	218–220
Polyglycolic acid, PGA (Merilon)		215–223
Poly(butylene terephthalate), PBT (e.g. Trevira ESP, Nylstar Elite)		221–225
Poly(trimethylene terephthalate), PTT (e.g. Corterra, Solo, Solona)		228
Copolyester Grilene, PES(G) (Polyesterether PEE)		229
Polyvinylalcohol, PVA		232
Copolyester Vycron, PES(V) (Comonomer isophthalic acid)		237
Polyurea Urylon, PUA		237
Polyacrylonitrile, PAN or **PAC**	190–250	from **260–270 d**
Elastane (e.g. Lycra, Dorlastan), **PUR(E)** or **PUE**	170–210	**230–260**
Diacetate, CA		**255–260 d**
Polycarbonate, PC		245–256 (150–300)
Polyester normal type, PES(N) or **PET**	230–240	**254–256 (250–260)**
Polyamide 6.6, Nylon 6,6, PA 6.6	220–235	**255–260**
Polyamide 4, PA 4 (Taimir)		256–265
Poly(ethylene naphthalate), PEN		270
Qiana (alicyclic polyamide)		270–275
Poly(dimethylcyclohexane terephthalate), Kodel, Vestan, PES(K),	260–265	282/295
Triacetate, CT		**290–300 d**
Basofil (Melamine-formaldehyde-polycondensate)	> 220 (d)	330–350 d
Kynol (Phenol-formaldehyde-polycondensate)	230 (d)	350 d
Polyetherketone, PEK, also PEEK (e.g Zyex)	> 250	324–366
m-Aramid, *m*-AR, PMPIA (e.g. Nomex, Conex)	320	370 d
Polyamideimide, PAI (Kermel)		380–400 d
Polytetrafluoroethylene, PTFE (Teflon)	330 (d)	410 d
p-Aramid, *p*-AR, PPTA (e.g. Kevlar, Twaron)		425–500 d
Polyimide, PI (P84)	> 260	> 500 d
Poly-*p*-phenylene-2,6-benzoxazol, PBO (Zylon)		650 d
Polybenzimidazol, PBI		660 d

Approximate values in °C (d = decomposition). Standard fibres emphasized.

temperature is then read off a scale which has to be previously calibrated. In this way the melting point or melting range can be determined in a few minutes with an accuracy of about ±2 °. As the melting points for fibres given in Table 8.6 show, this accuracy is usually sufficient for fibre identification. With intimate fibre blends a melting point or hot stage microscope is necessary. This has a heated microscope stage as well as a simple polarizer and analyser. Since the crystalline structure of the fibres collapses on melting the melting point can be determined very exactly in polarized light because the interference colours seen here, arising from the crystalline structure, disappear as soon as the fibre melts. In this way the melting point can be determined with an accuracy of ±0.5 °. However, during the last 5–10 ° before melting, the heating must take place very slowly (2–3 ° min^{-1}) in order for optimal transfer of heat from the stage to the fibre sample to be assured. If heating takes place too rapidly the melting point obtained is too high. An advantage of the hot stage microscope is that in fibre blends the melting behaviour of all the fibres can be observed consecutively. Even if a fibre does not melt when heated up to 300 °C, for example, this can still be a useful piece of evidence for its identification.

Differential scanning calorimetry (DSC)

Using DSC the temperature range for melting (T_m) or for decomposition (T_d) and, during cooling, that of crystallization (T_c) can be determined along with the corresponding enthalpies (heat of fusion H_m, heat of decomposition H_d and heat of crystallization H_c). Furthermore the characteristic temperature for the amorphous areas, the glass temperature (T_g) and the so-called effective temperature or middle endotherm peak temperature (MEPT) can be determined. By comparing the measured heat of fusion with the theoretical value, the purity or content can be determined. This is particularly relevant for fibre recycling. Similarly the measured heat of reaction can be compared with the theoretical value in order to calculate the extent of reaction, for example with cross-linking reactions.

For damage analysis of textiles made from polyester the MEPT is especially interesting because it gives insight into the thermal prehistory of the fibres.[99–101] The MEPT is the maximum temperature of a small endothermic peak between the small endothermic stage of glass transition and the large endothermic melting peak. The position of this MEPT peak is variable and depends on the temperature of thermal pretreatments (T_p). Its size depends on the intensity, and thus mainly on the duration of the thermal treatment and also on the tension, for example during setting. The measured MEPT usually lies several degrees above the temperature of a preceeding thermal treatment (MEPT > T_p). It gives useful information for damage analysis. For example, it is possible to determine from this temperature whether polyester goods were dyed at the boil (with carrier), under high-temperature (HT) conditions or using the thermosol process. Conclusions about setting temperature are also possible, in particular differences in setting conditions

can be determined exactly. Unfortunately, this thermal memory also has notable restrictions. It can be superimposed by mechanical influences; for example differences in tension also affect the MEPT. The way in which the heat was applied (steam, hot air, conducted heat) also causes significant differences. Finally, a strong thermal influence should not have taken place subsequently as this extinguishes the memory of the weaker influence.

The model of Jeziorny[102] to explain the phenomenon of MEPT helps to make these factors understandable. According to this model, small increasingly ordered areas, the so-called microcrystals, are formed under increased heat input from initially unordered structures on the surface of the crystalline areas of the fibre. These then melt during the DSC measurement. If the sample is cooled after the first DSC measurement and then subjected to a second run, a MEPT peak is no longer found. Comparing the first and second run thus makes it easier to find and interpret this thermal event. If the DSC instrument is sufficiently sensitive a MEPT peak can also be found with nylon fibres. Its allocation to thermal pretreatments is, however, more difficult than with polyester because, among other reasons, the rate of crystallization is higher for nylon.

DSC is also useful for characterizing bicomponent fibres, film-forming finishes and coatings. For example, with polysiloxane a very low glass temperature (about –120 °C) is characteristic, followed by a crystallization peak (at about –100 °C) and a large melting peak (–40 °C). As a matter of interest the enthalpies obtained by integration of these peak areas enable the crystalline ratio to be calculated: $(H_m - H_c):H_m$. This calculation is also possible with polyester, especially with granules, on account of their higher amorphous content. Fischer has described a relation between the glass temperature of film-forming finishing agents and the hardness or softness of the corresponding finishes.[103]

Thermogravimetric analysis (TGA)

With TGA the change in weight of the samples on heating is determined (usually possible up to 1000 °C). In a nitrogen atmosphere the decomposition of the sample can thus be studied; in air the ability to be oxidized is additionally determined. In this way fibres modified to be flame-resistant can be distinguished from standard fibres. In fibre composites, for example fibre-reinforced rubber, it is thus possible to determine the proportions of the components with relatively little effort: moisture and softeners in the first stage of weight loss up to about 220 °C, then the fibre and rubber components up to 500 °C and finally after changing from a nitrogen atmosphere to air the carbon used as a filling burns and above 700 °C the non-burnable inorganic filling remains. The first derivative of the weight loss curve, the derivative TG (DTG), enables a more exact determination. By coupling TGA with a mass spectrometer or a FT-IR spectrometer the decomposition products can be analysed. Because of the higher costs such methods are only used in exceptional cases for textile damage analysis.

Thermomechanical analysis (TMA)

Thermomechanical analysis (TMA) investigates the changes in the dimensions of a sample as a function of the temperature, for example shrinkage or extension of fibres.[104] It is easier to work here with filaments than with staple fibres. Fibre composites and other materials are also analysed by dynamic loading. This dynamic mechanical analysis (DMA) enables, for example, the glass temperature of elastomers to be determined exactly. But in textile damage analysis TMA is seldom used.

In conclusion the most important advantages and disadvantages of thermoanalytic methods, both in general and in textile damage analysis, can be summarized:

- variety of applications and sophisticated instruments
- information about the thermal prehistory of polyester
- small quantities of sample are sufficient (about 5 to 10 mg)
- difficulties in obtaining representative samples
- the sample is usually damaged or destroyed by the heat (important for example in forensic applications, see Section 8.7.1)
- danger of misinterpretation of the results (correct allocation of the thermal events is made easier by simultaneous TA, for example DSC and TGA simultaneously).

8.4.6 Further methods

There are a large number and variety of methods which can be used for damage analysis of textiles and these methods can naturally also be combined. It is economic restraint which most affects the imagination of the damage analyst. In other words, any method can be considered for damage analysis if it is or could be useful, does not cost too much and does not take too long.

In addition to the important methods of damage analysis described above three further methods will be briefly described here.

Techniques for surface immprints

Imprint techniques have been a proven and important method in damage analysis of textiles for a long period of time. It is often advantageous not to investigate the original object under the microscope but rather the negative imprint of its surface:

- In an imprint it is often possible to see if a fault in a coloured textile was caused during textile manufacture or during dyeing and finishing. Spinning faults, such as use of different fibre counts or differences in yarn twist, and faults in fabric production can be seen in the imprint as well as in the original (and in the same location). On the other hand, faults arising from dyeing or printing are eliminated in the imprint.
- The imprint is transparent and the colour of the sample does not interfere. Thus

Table 8.7 Comparison of the advantages of the most important surface imprint methods

Imprint with gelatine-coated plates	Imprint with thermoplastic films
No thermal influence on the sample No special equipment necessary	No swelling of hydrophilic fibres With a commercial instrument[107] larger areas (approximately 20 x 30 cm) can also be tested
No false indication of structural differences, arising from diffusion of grease, oil or wax deposits (possible effect on films)	Detection of grease, oil or wax deposits possible due to diffusion into and dulling of the film

with dark-dyed wool fibres the cuticle scales can only be easily recognized in the imprint. The same applies to abraded places and other types of mechanical damage to the surface of dark dyeings.

- Since the surface imprint is very thin (about 0.02 mm) the depth of focus is usually much better than in direct microscopy of the uneven, three-dimensional textile surface and possible fibre lustre and transparency do not interfere. In direct microscopy with reflected light the image is usually not sharp because the fibre interior and the underside of the fibre also reflect light.
- Since the transparent imprints are examined in transmitted light, it is not necessary to have a microscope with reflected light. In addition, the original sample remains unchanged.

There are two different widely used imprint methods in damage analysis, namely imprints on gelatine-coated plates[105] and on thermoplastic films, usually polypropylene or polystyrene.[5, 106] In Table 8.7 the most important advantages of these complementary imprint methods are compared.

Principle of the method with gelatine-coated plates

Two grams of gelatine are swollen in 40 ml of distilled water for 1 h at about 35 °C. One part of this swollen gelatine is diluted with three parts distilled water, and 10–20 ml of this solution are sufficient for about 100 cm² of glass plate surface. The solution is brought evenly onto clean glass plates, for example microscope slides, with a pipette. After drying for 24 h in a dust-free place the plates are ready for storage or use. Before use they are dipped briefly into water and the adherent water then removed by shaking. The fabric is then laid on the swollen gelatine and covered with a filter paper and a further glass or metal plate. A weight is added, which should cover the upper plate evenly. For glass plates that are the same size as microscope slides the weight should be about 500 g. After pressing for 30 min the textile side is dried briefly with a warm hair dryer and then carefully removed from the imprint. Further details can be found in the publications by Bigler[105] and

Peter,[24] who was able to obtain structured shadows (pseudo stereo effect) by displacing the condensor sideways (oblique transmitted light).

Principle of surface imprints with thermoplastic films

The thickness of the films (usually with polypropylene 30–40 μm, or with polystyrene 100–200 μm) depends on the thickness of the individual fibres and yarns or the structure of the fabric. Polystyrene films are preferred for large-scale imprints (up to about 20 × 30 cm) in the Streak Analyzer.[107] For small-scale imprints a piece of film cut to a suitable size is pressed firmly together with the textile sample between two polished metal plates, for example in the size of microscope slides, with two screw clamps. The assembly is placed in a drying oven at 105 °C, in the case of polypropylene for 30 min and with polystyrene for 45 min. After cooling as rapidly as possible with cold air the sample is separated from the film. The film can then be examined in transmitted light in the microscope without the use of embedding agent. Further details are given by Mahall.[5, 106]

Extraction methods

A typical textile laboratory is characterized by several Soxhlet extractors standing in the fume cupboard. That is to say, the extraction of textile samples is a routine or standard procedure. During extraction, substances soluble in organic solvents or water are removed from the textile, then, as a rule, concentrated by distillation and the extraction residue is analysed qualitatively and/or quantitatively. Examples of extracted substances are stains, fibre spin finishes, lubricants, residual grease in wool, residues of surfactants and other chemicals such as acids, bases or thickeners, soluble finishes, dyes and optical brighteners, pesticides and other biocides, carriers, heavy metal salts and formaldehyde. Stepwise extraction using solvents of increasing polarity (for example first hexane, then methylene chloride, then absolute alcohol and finally water) can give a first indication of the nature of the extracted substances.

Different extraction methods and apparatus can be used. Some of the procedures are standardized.[108] Mini versions of the Soxhlet extractor are prefered for very small samples such as stains. As alternatives to the Soxhlet extractor, automated apparatus have been developed. The Morapex rapid extractor[109, 110] enables the test sample to be extracted non-destructively in a very short time with either water or organic solvents.

Average degree of polymerization of fibres

Many types of damage, including chemical, thermal, photolytical, biological and some types of mechanical damage, are based on degradation of the polymer chains in the fibre. Thus determination of the average degree of polymerization (DP)

gives a direct scale for assessing the extent of such damage but not its cause. The time and cost of determining DP is, however, so great that, whenever possible, simpler but less accurate methods are preferred. Examples of these are loss of tensile strength and abrasion resistance or the pinhead reaction with cotton (see Section 8.5.1). An advantage of DP determination is that it allows quantitative estimation of the damage. For example, Eisenhut[111] defined a damage factor s for cellulose fibres based on the decrease in DP, which allows comparative assessment of damage for cotton and regenerated cellulose fibres:

$$s = \log [(2000 : P_1) - (2000 : P_2) + 1] : \log 2$$

where P_1 = DP before damage and P_2 = DP after damage.

Damage factors of $s < 0.5$ are said to be acceptable after bleaching treatments, but with $s > 0.75$ the goods are said to be badly damaged. It must be borne in mind that the damage factors are also dependent on the method used, they are higher with the cuoxam method than with the EWNN method.[112]

Of the many methods known for determining DP, measurement of viscosity according to Staudinger is the one preferred in damage analysis because it can be carried out in any textile laboratory. The viscosity is measured indirectly via the times taken for the polymer solution and the solvent to run through an Ubbelohde or Ostwald viscosimeter. A prerequisite is that a suitable solvent is available for the fibre and that the corresponding constants for the calculation are available. The solvent must not damage the fibres and it should be easy to handle. Sometimes, however, health-damaging m-cresol has to be used (polyester, nylon). Schefer[113] has listed solvents and viscosity constants for 16 undamaged fibre types.

In order to give an idea of the other methods which are used for damage analysis[7, 5] the following examples are listed:

- detection of metals, such as Fe, Cu, Ca, Mg, and non-metals, such as N, P, S, Cl, F, which can help to elucidate the damage
- swelling and solubility tests, especially, but not only, with natural fibres
- determination of concentration, for example by means of titration, gravimetry or colorimetry
- staining tests which mark, for example, setting differences, oil and grease deposits or fungi. They generally have the disadvantage that the samples have to be undyed or only lightly dyed. It is time-consuming if the original dyeing first has to be removed in order for staining with test dyes to be carried out and there is also the danger that additional damage may occur during stripping of the dyeing.

Instead of describing these methods here for the general case it would appear more suitable to discuss them in relation to the type of fibre involved in the damage. This is covered in the next section.

Choice of the most suitable method is made more difficult if there is very little sample material available. An ideal method should be highly sensitive,

reproducible and give clear-cut results. A common combination of methods, especially when analysing stains, begins with microscopy, followed by concentration after extraction. The extract from an undamaged area serves for comparison. For identification the preferred methods are TLC (if authentic samples are available for comparison) and IR spectroscopy. Reference spectra are also very useful here but it is possible to identify the substances causing damage by direct interpretation of the spectra.

8.5 Damage analysis according to the type of fibre

The extensive subject of damage analysis of textiles can be divided into typical cases of damage depending on the stage of processing or the technology of yarn and fabric production such as:

- filaments, threads and yarns[114, 115]
- woven fabrics[116]
- knitted fabrics[117–120]
- nonwovens
- textile composites, coated fabrics.

An additional type of damage occurs during cleaning operations, such as washing[121] and dry cleaning. Although this division may be useful for many typical types of faults, a division according to the type of fibre appears even more suitable. In this way the types of damage typical for a particular fibre can be meaningfully grouped. For example, cellulosic, protein and synthetic fibres each have their own characteristic strengths and weaknesses, which are enlightening when analysing damage to them. In the following section the most important methods of damage analysis will be described for the respective types of fibre.

8.5.1 Damage analysis of cellulosics, especially cotton

In contrast to wool, cellulosic fibres are relatively stable to alkali but sensitive to acid. In addition, cellulosic fibres can be damaged by strong oxidizing agents, excessively high temperatures and microorganisms. The extent of this damage (the damage factor) can, among other means, be assessed by viscosimetric determination of the degree of polymerization, as described in Section 8.4.6. A much easier method is the following reaction.

'Pinhead' reaction with cotton[122, 123]

This rapid microscopic test indicates chemical damage to cotton and enables the degree of damage to be roughly estimated. The cotton fibre to be tested is cut with very sharp scissors or a razor blade to snippets of about 1 mm length and embedded with 15% sodium hydroxide on a glass slide. After covering the sample with a

Table 8.8 'Pinhead' reaction and damage to cotton[122, 24]

Type	Formation of pinheads	DP range
1 Undamaged	Well-rounded pinheads on about ¾ of all fibre snippets	> 1500
2 Clearly damaged	Mostly flat protuberances with some semi-rounded pinheads	1600–1000
3 Heavily damaged	Cut ends mostly flat with some flat protuberances	1100–700
4 Very heavily damaged	All cut ends smooth with varying width of lumen, fibres partially convoluted	800–400
5 Extremely damaged	Surface notches, longitudinal and transverse splits, fibrillation and marked deformation	< 400

DP = average degree of polymerization

cover slip and leaving for 2–3 min the formation of 'pinheads' at the cut ends is evaluated. In Table 8.8 the appearance of the 'pinheads' is described corresponding to different stages of damage and approximate ranges of the degree of polymerization.[24, 122] In undamaged cotton the primary wall surrounding the secondary wall is intact so that the cellulose in the secondary wall, which swells strongly in sodium hydroxide, is pressed out at the cut ends and thus forms the pinhead shapes. After chemical damage to the primary wall the fibre can swell laterally without restriction and thus does not form pinheads. This 'pinhead' reaction is said to be applicable to cotton after every stage of processing and finishing but it does not work with flax or ramie.[122] Cotton which has been given easy-care properties with cross-linking agents only swells slightly and thus does not show any marked pinheads. This can suggest a higher degree of chemical damage than is actually present. Since more than 90% of cross-linking agents for cellulose contain formaldehyde the results of the pinhead reaction should be confirmed by testing for formaldehyde with chromotropic acid: a small sample of fibres is heated carefully to a maximum of 100 °C in 1–2 ml of 72% sulphuric acid in which a little chromotropic acid is dissolved (about 10 mg in 100 ml). The formation of a reddish-violet colour after 1–2 min indicates the presence of formaldehyde.

If the pinhead reaction demonstrates chemical damage the next point of interest is to determine the exact cause. The tests described below for damage caused by chemicals or fungi are applicable to all cellulosic fibres.

Detection of acid damage with Fehling's solution

Since cellulosic fibres are sensitive to acids they can be easily damaged by the acid catalysts used in easy-care, silicone, fluorocarbon and flame-retardant finishes as well as by drops of concentrated acid or faulty dyeing of cellulose/wool blends.

Carbonization of wool is based on this sensitivity of cellulose to acid. Acid damage is also known to occur in sulphur dyeing (cleavage of sulphuric acid during storage) and in contact between cellulose textiles with easy-care finishes and chlorinated bathing water or detergents containing chlorine bleach (chloroamines are formed, which decompose to hydrochloric acid and oxygen).

The 1,4-glucosidic bonds in the cellulose chains are cleaved hydrolytically by acids. Cellulose damaged in this way, so-called hydrocellulose, is characterized by the shorter length of the molecules and thus a higher concentration of end groups. One end of the chain has a ring-forming hemiacetal structure in equilibrium with the open-chain aldehyde form. This chemical test for damage is based on the higher concentration of aldehyde groups after acid cleavage.

Fehling's solution is prepared freshly by mixing equal amounts of Fehling's solution A and B (A = 6% copper sulphate solution, B = 20 g of sodium potassium tartrate and 10 g of sodium hydroxide in 100 ml distilled water) and diluting with an equal amount of distilled water. The sample, which was previously degreased and soaped at the boil, is boiled in this test solution for 5 min, during which it is kept below the liquid level and prevented from contact with air by means of a glass rod. If this is not done, an interfering green colour occurs. After rinsing with water and very dilute acetic acid the formation of a red colour due to precipitated copper (I) oxide indicates acid damage. In principle during this redox reaction the aldehyde groups of the cellulose chains are oxidized to carboxylic acid groups and the copper is reduced from copper (II) to copper (I). It is important here to compare with acid-damaged reference samples and undamaged goods, since the latter also show a slight red coloration. The aldehyde groups may already have been partially oxidized by atmospheric oxygen. Only a marked red coloration is a sure sign of acid damage. In cases of doubt this test should be repeated. The following reverse conclusion may also be useful here: if the pinhead reaction indicates chemical damage and the oxycarmine test described below is negative, there is a high probability that acid damage has occurred.

The detection of aldehyde groups with ammoniacal silver solution, as recommended in the literature,[7, 124] is dangerous because the reagent can explode after standing for longer periods.

Detection of oxidative damage with oxycarmine

Cellulosic fibres are often oxidatively damaged when the most commonly used bleaching agent, namely hydrogen peroxide, decomposes catalytically. This unwanted decomposition to aggressive radicals is catalysed especially by heavy metals. Traces of iron (abraded metal, rust from water or steam pipes), for example, are sufficient to cause severe catalytic damage during peroxide bleaching. The damage is manifested as a marked loss of strength or even formation of holes. Naturally, it is difficult to detect traces of iron around the edge of these holes. This will be discussed in the next section.

Oxidatively damaged cellulose, known as oxycellulose, is characterized by polymer chain degradation and an increased concentration of carboxylic acid groups. These arise not only from the aldehyde groups at the end of the chains, such as described for hydrocellulose, but also to a much larger extent from the primary alcohol groups of the C-6 atoms of the many β-glucose constitutional elements. These primary alcohol groups are fairly readily accessible. They can thus be easily oxidized to carboxylic acids via the aldehyde intermediates. Under strongly oxidizing conditions the secondary alcohol groups of the C–2 and C–3 atoms can be oxidized to keto structures, which after cleavage of the bond between the C–2 and C–3 atom also form carboxylic acid groups.

These numerous carboxylic acid groups, distributed along the cellulose molecule, are the basis for the chemical detection of oxidative damage. As a rule this detection is more intensive and unequivocal than that for acid damage with Fehling's solution, which is based only on the end groups. The carboxylic acid groups formed by oxidation bind basic dyes via salt links, whereas these dyes do not stain undamaged cellulose. A well-known example is the staining test with Methylene Blue:[125] the sample is stained with a 0.1% aqueous Methylene Blue solution either cold for 20 min or at 60–100 °C for 5 min and then thoroughly rinsed. Staining with the test dye oxycarmine[126] is said to be four times as sensitive as with Methylene Blue[123] and is specific for oxycellulose. The test dye has to be freshly prepared from two storeable components and can only be used for one day. The dyeing conditions are simple and explained in the product information. It is also important here to have comparative stainings on undamaged and oxidatively damaged goods in order to interpret the blue coloration correctly.

Catalytic damage and detection of iron

Typical evidence of catalytic damage is a local marked loss of strength and often tiny holes, where the cellulose has been so severely destroyed by oxidation that it has been dissolved out of the fabric. In the case of dyed fabrics the edges of these holes are usually lighter coloured or colourless since oxycellulose has a decreased affinity for the usual cellulose dyes. In fabrics with optical brighteners a decreased or quenched fluorescence in UV light may be observed around the holes; areas containing metal appear darker. The edges of the holes are dyed intensively blue with oxycarmine. In the case of cotton the severe chemical damage in these areas is indicated by the lack of formation of pinheads in the corresponding test. These detection reactions become more difficult if the edges of the holes have been broken off by mechanical stresses during bleaching, dyeing or scouring. In spite of this, additional tests for traces of metals such as iron or copper should be made. Although all the heavy metals catalyse the decomposition of hydrogen peroxide, iron is most often involved.[127] Detection of other metals has been described by Agster.[7]

Iron can be detected on the fabric as well as in the combustion residue. The best-

known methods for detecting iron are with thiocyanate or as Prussian blue. In each case either the fabric is wetted at the relevant places with 1–2 drops of semi-concentrated analytical grade hydrochloric acid (10–15% or 6 N) or the combustion residue is dissolved in the porcelain crucible in 1–2 ml of this hydrochloric acid. After adding a few drops of ammonium or potassium thiocyanate solution (about 10%) an intensive red colour is formed. By adding a little diethyl ether to the solution in a test tube and shaking the colour can be concentrated in the ether phase. For detection in the form of Prussian blue a few drops of a 10% solution of tetrapotassium hexacyanoferrate solution are added to the acidified fabric or the solution. The fabric can also be tested by adding directly drops of a test solution consisting of 1 g of tetrapotassium hexacyanoferrate, 100 ml of 1 N hydrochloric acid p.a. and 50 ml of ethanol.[74] In the presence of ferric iron an intensively blue precipitate of $Fe_4[Fe(CN)_6]_3$ is formed. Schliefer and Heidemann[127] recommend the detection of iron as Prussian blue, which precipitates on the fabric within a narrow area and is not absorbed and distributed by the fibre capillaries, as is the case with soluble iron thiocyanate, which makes this detection method less sensitive. Also, in contrast to iron thiocyanate, Prussian blue is very stable. If technical grade hydrochloric acid is used instead of analytical grade a blank sample should be tested since traces of iron in technical hydrochloric acid can be falsely assigned to the fabric.

Mechanical damage

Mechanical damage can best be seen in longitudinal mounts under the microscope or in surface imprints. Since individual mechanically damaged fibres may not be representative of the sample, a fairly large number of fibre samples should be examined (up to 100 according to the particular case).

Damage by microorganisms

Cellulosic fibres are more often damaged by fungi than by bacteria. The microscopic detection of fungi will be described in more detail in Section 8.6.3. Storage of moist fabric overnight in a warm environment can be sufficient to cause fungal attack, leading to variously coloured mildew patches, which are difficult to remove.

Alkali spots

Cellulosic fibres, especially cotton, are pretreated with alkali. After rinsing off, a certain amount of residual alkali usually remains in the fabric and this is often distributed unevenly.[128] This can lead to faults in subsequent processes where alkali interferes, for example with acid-catalysed finishes (easy-care, water-, oil- and soil-repellent, stretch finish). Another problem caused by alkali is alkali spots,

usually caused by uneven addition of alkali (for example, splashes). The cellulose fibres swell more in these places and thus take up more dye, causing dark spots in the fabric. In undyed fabric alkali spots can occasionally be seen on account of their yellowish colour. The more markedly swollen fibres can be detected in an exact microscopic comparison of the longitudinal view of fibres from the spots and fibres from undamaged areas. According to Schmidt[40] the effect of the alkali can be recognized by a marked green coloration in the red/green test (dyed fabrics must be previously stripped of dye under gentle conditions). The red/green test is briefly described in a following section.

Differences in mercerization

During mercerizing, a treatment with concentrated sodium hydroxide under tension, the structure of the cotton fibre is irreversibly changed. The convolutions are removed and the cross-section becomes almost round. Dyeability, dimensional stability, handle and lustre of the fabric are improved. Since this process is influenced by many factors it is not surprising that differences in degree of mercerization, and thus complaints, can arise. Therefore the degree of mercerization is determined in order to express the quality of the mercerization. A comparison of suitable methods for this purpose was given by Hermanutz *et al.*[129] It is understandable that microscopical methods including image analysis have been developed to evaluate the degree of mercerization and the maturity of cotton. Examples can be found in the literature.[130–133] The assessment of the degree of mercerization is also possible with near-IR spectroscopy.[134] For damage analysis it usually suffices to carry out microscopic investigations, preferably on surface imprints, and in difficult cases also on cross-sections. Differences in tension during mercerization are a widespread cause of uneven dyeing. They can be detected by the red/green test (with increasing tension redder).[135]

Damage by heat and light (pyro- and photocellulose)

Cellulosic fibres are not particularly sensitive to heat and light. However, they do turn yellow after over-exposure to heat or light and lose strength owing to decomposition reactions. Pyrocellulose is said by Agster to show the reactions of both hydro- and oxycellulose.[136] Cotton damaged by light is said to react more like hydrocellulose whereas cellulose-regenerated fibres delustred with titanium dioxide are said to respond more to the reaction for oxycellulose after damage by light.[137]

Faulty quality in cotton, in particular neps from immature and dead cotton

Differences in fibre quality in one lot of cotton can lead to uneven fabric appearance. These differences cause higher costs in dyeing and finishing and represent a

difficult challenge for the dyer. They are also often the reason for customer complaints. Immature and dead cotton as well as the so-called hard or red cotton (with high concentrations of calcium or iron compounds) are not themselves typical forms of damage but are a frequent form of faulty quality with similar negative effects.

Calcium and iron compounds can be removed with weak acids or sequestering agents during pretreatment. Immature and dead cotton fibres have a secondary wall which is too thin and thus they have a low flexural rigidity. During processing these fibres entangle with each other and form so-called neps. Especially with dyed fabrics these pill-like entanglements often first become irritatingly noticeable after dyeing. They cannot be removed and lower the fabric quality. The annual losses thus caused were estimated in 1996 to be US$200 million for the US textile industry alone.[138] Covering of immature and dead fibres differs according to the dyestuff class and the individual dye. Problems with uneven fabric appearance occur especially with direct and vat dyes. Unfortunately, there is no textile auxiliary agent which solves this problem. The quality of immature cotton can, however, be greatly improved by mercerization. The treatment with caustic soda causes the relatively thin secondary walls of the immature fibres to swell. As with mature cotton, the fibre cross-section remains approximately circular after mercerizing and drying and the uptake of dye is improved. Dead cotton hairs have died off at an early stage of growth so that the secondary wall, if present at all, is very thin. Their cross-section is correspondingly flat. After mercerization they are said to be disadvantageously modified, their neps become flatter and reflect incident light even more than immature cotton, which swells more strongly. Light-coloured neps are one of the most frequent causes of complaint with cotton textiles.[120, 139]

There are many publications on the subject of neps and their detection, for example Furter and Frey,[140] and on the determination of the degree of maturity of cotton.[141, 142] Here, only the principle of the so-called red/green test will be briefly described, since it is easy to carry out in any textile laboratory[5, 7, 143] and it gives a quick idea of the proportion of immature cotton. It does not correlate well with other tests of maturity.[130–133, 144, 145] On the other hand, cotton samples which show the same degree of maturity after the usual maturity test with the air-flow method often show subsequent differences in depth of dyeing,[145] thus underlining the importance of this dyeing test.

The red/green test was introduced by Goldthwait, Smith and Barnett and is thus also known as the GSB test.[143] It was developed for raw cotton. However, Denter *et al.* recommend previous alkaline scouring.[145] When the red/green test is used on yarns and fabrics neps become more clearly visible as small green spots. Using a mixture of a red direct dye with small molecules and a green direct dye about twice as large (Table 8.9) the mature, thick-walled cotton fibres are dyed mostly red and the immature, thin-walled fibres, but also very fine mature fibres, are dyed mostly green. This effect is based on differences in substantivity, rates of diffusion and

Table 8.9 Commercial dyes for the red/green test

Colour Index	Direct Red 81	Direct Green 26
Literature references	Sirius Red 4 B (Bayer/DyStar) Solar Red B (Sandoz/Clariant) Diphenyl Red 5 BL (Ciba-Geigy) Diphenyl Red 5B 182% (Ciba-Geigy)	Sirius Light Fast Green B (Bayer/DyStar) Solar Brilliant Green BL (Sandoz/Clariant) Solophenyl Green BL (Ciba-Geigy)
Commercially available replacement dyes	Ciba Pergasol Red 2B 182% (Ciba SC) Levacell Red 5B liq. (Bayer, paper dye) Direct Red 81 (Aldrich)	Ciba Solphenyl Green BLE 155% (Ciba SC) Sirius Green S-4B (DyStar)

washing-off of these dyes and also on differences in the structure, accessibility, pores and affinity of the cotton fibres. It is of interest for damage analysis that the red/green test can also be used for the detection of differences in cotton caused by alkali treatment or mercerization[40, 135] (see the previous sub-section on alkali spots).

Swelling of regenerated cellulosic fibres in caustic soda

Reiter described the microscopic identification of regenerated cellulose fibres.[28] Kornreich[146] was able to distinguish between mechanical and chemical damage by means of a microscopic swelling test in 30% caustic soda. Damaged fibres and undamaged ones for comparison are placed next to each other on a microscope slide and covered with a cover slip. While the fibres are being observed, 30% caustic soda is drawn through the dry sample and the cover slip immediately pressed down evenly with a dissecting needle. Chemically damaged viscose fibres then break in a longitudinal direction or fall apart into fragments. Fibres which are not chemically damaged only show swelling, which recedes after the pressure is released.

Further tests for damage on regenerated cellulosic fibres, such as iodine absorption, core/sheath differentiation, peeling methods, detection of traces of sulphur or copper as well as some hints for investigations on bast fibres are given in the literature.[147]

Diacetate and triacetate fibres

Diacetate (CA) and triacetate (CT) fibres, being esters of acetic acid, can in principle be hydrolyzed with acids and alkalis. They are resistant to dilute acids. Up to pH 9.5 alkali is said not to damage CT, CA is more sensitive. With CT an intentional alkaline hydrolysis of the fibre surface is known as an S-finish

(saponification). Alkali stains on acetate fibres are caused by cellulose arising from partially hydrolyzed acetate. They can be detected by selective dyeing with direct dyes, for example with Sirius Red 4B,[5] alternatively by Levacell Red 4B (a Bayer paper dyestuff)[148] or with 6% Benzo Black AT (Type 8000), 20% Glauber's salt, 2 min at 80 °C, liquor ratio 1:50 (different grey shades corresponding to the saponification of the acetate fibre)[149] and also by dyeing blue with zinc chloride–iodine reagent.[8]

CA is also more easily damaged by oxidizing agents than CT. The maximum ironing temperature for CA is 150 °C but it is 220–230 °C for CT. This shows that the two types of fibre also differ in their thermal resistance. Their resistance to light, ageing, microorganisms and insect attack is said to be good. Quantitative analysis of damage (damage factor) can be carried out by viscosimetric determination of the degree of polymerization. Microscopic swelling reactions with 9% caustic soda, in comparison with undamaged acetate fibres, show up chemical damage if the swelling occurs more rapidly and thermal damage when it occurs more slowly.[146]

8.5.2 Damage analysis of wool

Wool chemistry and types of damage

The chemistry of protein fibres, especially that of wool, is more complex than that of most other types of fibre. The amide groups which link the repeat units are also to be found in nylon fibres. Amides can be cleaved hydrolytically by strong acids and bases. However, the inter- and intramolecular bonds in wool are particularly numerous. There are hydrogen and disulphide bonds, salt links and hydrophobic attraction. All of these bonds are important for understanding chemical damage to wool and the possibilities for its detection.

Hydrogen bonds are already weakened by swelling in water. Urea forms a large number of hydrogen bonds and thus destabilizes the wool structure to a marked extent (see the urea/bisulphite solubility test described below). The reducing agent bisulphite attacks the disulphide bonds in cystine, another important link between protein chains. It thus also causes marked destabilization of the structure. The cystine links can also be cleaved hydrolytically, for example with hot water, steam and especially with alkali. They are relatively stable to acids. The disulphide bonds are also destroyed by strong oxidation, being converted via intermediates to cysteic acid, which can be detected by IR spectroscopy by means of the bands at 1040 and 1170 cm^{-1}.[18] In a later section it will be described in more detail how determination of the content of cystine, cysteine and cysteic acid enables conclusions to be made about damage (for example, by reduction or oxidation).

To a much larger extent than silk, wool contains many α-amino acids which either contain an additional carboxylic acid group (monoamino dicarboxylic acids such as glutamic acid and aspartic acid) or additional amino or other basic groups

(the diamino monocarboxylic acid lysine as well as arginine, tryptophan and histidine). Salt links are formed between these acid and basic side groups in the protein chain. Their maximum concentration is found in the isoionic range at about pH 4.9. Since there are more acid than basic side groups and the wool has a negative surface charge, the pH range in which wool is most stable lies slightly on the acid side (isoelectric point at about pH 4.5). The basic and acid side groups are also the reason for the high capacity of wool to bind acids and alkalis (amphoteric behaviour). Amino acids with non-polar side groups, such as leucine, proline, valine and phenylalanine, result in hydrophobic bonding and also explain the capacity of wool to absorb hydrophobic substances, for example organic solvents.

This short review is meant to illustrate the chemical bonds in wool and also to demonstrate its weaknesses. It thus becomes clear why wool is particularly sensitive to alkali, but is also damaged by strong acids, reducing agents and oxidizing agents. The effect of bifunctional wool protecting agents, such as aldehydes which cross-link amino side groups, can thus also be understood.

Indications of wool damage

First indications of possible damage to wool are a harsh handle or yellowing, both, where possible, in comparison to a wool sample before the potential damage. Heavy felting and change of shade in dyed fabrics are also signs of possible damage. Microscopic indications are usually more unequivocal, since the characteristic scale structure of wool fibres not only enables their identification and characterization but also analysis of damage to them. Changes in the scale structure can be seen particularly well in surface imprints (see Section 8.4.6). It is important here that several samples (at least 10, in critical cases up to 100) taken from different parts of the fabric are examined in order to gain a representative impression. Even in high-quality wool fabrics some individual damaged fibres can be found. Easily recognizable signs of damage under the microscope are:

- abraded scale edges or other types of scale damage (mechanical damage, kinks, rupture)
- projecting, bulky scales (for example after damage by acids, alkalis, chlorine or light)
- longitudinal striations in the interior of the fibre (damage caused by alkali or bleaching)
- pore-like openings, especially visible in embedding agents with a similar refractive index to wool (n_D 1.55, for example Canada balsam), caused, for example, by too heavy chlorination[150]
- fibrillar delamination of the wool hairs with release of the spindle cells (heavy chemical or enzymatic damage)
- frayed fibre ends (brush ends, damage by tearing, possibly indicating shoddy wool)

- root ends and skin remnants (possibly indicating slipe wool)
- crescent-shaped bites (insect attack).

Staining tests

Many dyestuffs have been described in the literature as staining tests for wool damage. Examples are:

- Methylene Blue/C.I. Basic Blue 93[7] (0.1% aqueous solution, 3 min at room temperature),
- Neocarmin W[5] and Neocarmin MS[126] (5 min at room temperature),
- Cotton Blue/Water Blue B or Telon Blue AGLF(DyStar)/Lactophenol[5, 7] (see also Section 8.6.3),
- Indigocarmin (cold saturated solution and 40 ml/l sulphuric acid),[151]
- Sirius Light Grey GG/C.I. Direct Black 77 and Sirius Light Red 4BL/C.I. Direct Red 79 (0.5% solutions, 3 min at the boil),
- Rhodamine B/C.I. Basic Violet 10[150, 125] (1% aqueous solution, 1 min at the boil),
- Congo Red/C.I. Direct Red 28 [152]

and other test dyes which are no longer commercially available (e.g. Crystal Poinceau 6R/C.I. Acid Red 28, Benzopurpurine 10B).

It is recommended that the sample be separated into the individual fibres before the staining test and that these be treated for 10 min in a solution of about 0.5% wetting agent. After staining the sample should be thoroughly rinsed.

A common factor in these staining tests is that damaged wool usually takes up more dye. Most types of damage destabilize the wool structure so that deeper dyeing takes place than in undamaged wool. Cross-linking wool protecting agents can reduce the amount of dye uptake. These staining tests should only be regarded as a rough indication of wool damage, compared with the methods described below.

The Pauly reaction as an important indication of damage

The diazo reaction according to Pauly[5, 7] is especially useful in damage analysis of wool. It shows up mechanical, chemical and biological damage and demonstrates destruction or peeling off of the cuticle (scale layer). The Pauly reaction is based on the fact that the cuticle layer contains considerably fewer aromatic amino acids than the cortex layer lying beneath it. These aromatic amino acids, especially tyrosine, react with the Pauly reagent (diazotized sulphanilic acid) to form a red monoazo dyestuff. The intensity of the coloration thus obtained, ranging from yellow-brown via orange-brown to red-brown, corresponds as a rule to the degree of damage.

The preparation of the relatively unstable diazobenzenesulphonic acid is not

very difficult,[5, 7] even in the modified form according to Doehner and Reumuth[150] as explained here: 5 g of sulphanilic acid p.a. are dissolved completely in about 2.5 ml of 10% potassium hydroxide. If necessary a few drops of potassium hydroxide are added until the solution shows a weakly alkaline reaction (pH paper). After cooling in an ice bath, 20 ml of an ice-cooled 10% sodium nitrite solution are added. This mixture is placed in a separating funnel and added dropwise to an ice-cooled solution of hydrochloric acid (8 ml concentrated hydrochloric acid and 4 ml water). After a few minutes the diazonium chloride precipitates in the form of small crystals. It is filtered off in a G2 glass filter, rinsed on the filter with a little ice-cooled water and then with alcohol. Diazobenzenesulphonic acid can also be obtained as a moist powder[153] which can be kept in the refrigerator for several months. By contrast, the light- and heat-sensitive Pauly reagent has to be prepared freshly each time. Even when cooled with ice it can only be used for a few hours.[123]

Preparation of the Pauly reagent: 0.5 g of diazobenzenesulphonic acid are dissolved in 50 ml of 10% sodium carbonate solution. After complete dissolution (careful stirring or shaking) 50 ml of distilled water cooled to 4 °C or 50 g of crushed ice are added. The solution is filled into a brown bottle and kept cooled in an ice bath during use.

To carry out the Pauly reaction the wool sample must be easily wettable. If necessary it is wetted out for 15 min in a 0.5% solution of wetting agent and rinsed carefully. The sample is then placed for 10 min in the ice-cooled diazotate solution (at a maximum of 5 °C) and then rinsed carefully with ice-cooled distilled water. A few wool fibres, still in the moist state, are then examined one at a time under the microscope, initially with intermediate magnification. Since the unavoidable decomposition products of the Pauly reagent also dye undamaged wool it is recommended to test in parallel a blank sample of undamaged wool and comparison samples with defined damage. The Pauly reaction can also be interfered with by acid and alkali residues in the wool sample, wetting agents based on fatty acids and wool protecting agents containing proteins.[150] By counting fibres under the microscope the Pauly reaction can be evaluated semi-quantitatively.[7, 150] However, Mahall[5] has reported that after very heavy alkaline damage the colour intensity of the Pauly reaction can decrease. For this reason also this test dyeing should always be combined with a microscopic examination. The Pauly reaction can also be carried out with dyed wool. However, the red coloration is difficult to see on deeply dyed wool, for example at the edges of the fibres.[5] The Pauly reaction also works with other animal hairs. In addition it shows up hair roots and skin particles, which can sometimes be present in wool yarns.

The KMV reaction for detecting acid or alkali damage

Whereas the Pauly reaction is a useful indicator of every type of damage to the cuticle layers of wool, the swelling reaction with ammoniacal potassium hydroxide according to Krais, Markert and Viertel (KMV reaction) enables the cause of

the damage to be determined, namely whether damage due to acid or alkali is present.[5, 7, 154, 155,] A further advantage of this swelling reaction is that it can also be carried out on dyed fibres. For example, fibres dyed by the Pauly reaction can be used here (after drying) so that this analysis of damage can be concentrated on the more heavily damaged fibres.

Preparation of the KMV reagent: 20 g of potassium hydroxide are dissolved in portions in 50 ml of at least 25% ammonia solution cooled in ice with occasional careful shaking or stirring. This solution is placed with a loose cover in a fume cupboard for 2 h in order for superfluous ammonia to escape. It can then be kept in the refrigerator for several months but its activity should be checked on wool samples with defined damaged before use.

Procedure for the KMV swelling reaction: the wool fibres to be tested are laid on a microscope slide, a few drops of the KMV reagent are added and the fibres observed under the microscope at intermediate magnification. The time is noted from the addition of the reagent to the appearance of the first small, hemispherical blisters on the fibre surface. The evaluation of the findings is given in Table 8.10. Irregular small protuberances slowly become larger until they finally break up. With coarse wool fibres the time taken for the appearance of the first blisters is longer than that for fine fibres. Again this illustrates that a comparison with undamaged wool and wool with defined damage is a useful aid to interpretation. In particular, the comparison of samples before and after a potentially damaging process enables a more exact explanation of the damage. When acid and alkali damage have taken place sequentially, the results of the KMV reaction are not unequivocal. Long swelling times can occur without alkaline damage if the wool has been treated with aldehydes or other cross-linking agents (as fibre protecting agents).

This qualitative analysis of acid and alkaline damage is complemented by quantitative tests as described in the sub-section below. Short swelling times in the KMV reaction are a sensitive and discriminating indication of acid damage. The longer swelling times after alkaline damage provide less discerning evidence. A further indication of alkaline damage is the particularly heavy staining with Lactophenol/Water Blue, but this is not specific, since other chemical, biological and mechanical forms of damage also cause deeper staining. Rolling up of the fibre ends to crosier forms or even more pronounced ringlet forms is, on the other hand, alone typical of alkali-damaged wool.[5]

Detection of alkali and acid residues, including formation of methyl orange crystals

A simple indication of possible damage can be obtained by measuring the pH value of the wool (liquid indicator, flat-ended pH electrode) or that of the aqueous extract, according to IWTO-2 or DIN 54275 and 54276, for example. The determination of the alkali content (IWTO-21) and acid content (IWTO-3, DIN

Table 8.10 Time until commencement of swelling of wool with KMV reagent[7,150,154]

Time until commencement of KMV reaction (min)	Conclusions about type and extent of damage
1–2	Very heavy acid damage
2–6	Acid damage
6–10	Treated with acid but scarcely damaged
10–12	Normal undamaged wool, depending on fineness and origin
15–30	Possibly treated with alkali but without noticeable damage
More than 30	Treated with alkali, in most cases also alkaline damage

54280) are standardized methods.[156] In cases where only small amounts of sample are available for damage analysis microscopic investigations with methyl orange can be useful as an alternative to these methods of direct pH measurement. A few fibres on a microscope slide are covered with a cover slip, 0.1% aqueous methyl orange solution is then added from the side. In the presence of acid, thin orange-coloured needles are rapidly formed at the fibre surface. They consist of the free acid of methyl orange, which at pH values of 4 or below is hardly soluble in water.[33, 24] This elegant method of detecting acid residues is also applicable to all other types of fibre.

Detection of damage caused by heat and light

After longer periods of exposure to heat, wool textiles can discolour above temperatures of about 120 °C. The allowable temperature for rapid pressing is about 160 to 170 °C.[157] At higher temperatures and longer periods of time wool yellows. In strong light, wool is at first bleached (photo bleaching) and then yellows (photo yellowing). This effect is intensified by additional thermal stress, for example with wool textiles in automobiles. UV absorbers lessen this damage. Alkali residues increase the extent of yellowing by heat. Further indications of this type of damage are markedly lowered peracetic acid/ammonia and urea/bisulphite solubility as well as lower cystine content. Alkali solubility and Methylene Blue uptake are increased slightly by dry heat treatments and markedly by damage caused by light and moist heat.[18] Peracetic acid/ammonia solubility enables differentiation between damage due to dry heat (markedly reduced solubility) and damage due to light (increased solubility). Additionally this is said to be a good indicator of cross-linked wool (reduced solubility). The tryptophan content can also be used as an indicator of photodegradation.[158, 159] These quantitative methods are described in more detail in following sub-sections. The increased values for solubility can be ascribed to the cleavage of cross-links, especially the disulphide bonds. The formation of new cross-links, for example the formation of lanthionine, contributes to a decrease in solubility.

Detection of biological damage to wool

Bacterial damage to animal fibres is described more often than fungal damage.[5, 147, 150] Dyed fabric damaged by bacteria, for instance, often has light spots or streaks which cannot be repaired. Typical observations on the damaged fibres are intensified striations and splitting up into cortex cells. The fact that only the orthocortex has been attacked and the paracortex remains is characteristic.[5] In order to differentiate from acid damage, in which the cortex cells can also be exposed, the KMV reaction, which is very sensitive to acid damage, is recommended. The extent of damage by bacteria can be assessed by the Pauly reaction. Bacteria can be stained with Lactophenol/Water Blue (as can fungi) and also with carbolfuchsin (1 g fuchsin, 10 ml alcohol, 5 ml liquid phenol, 100 ml distilled water; 3 min at room temperature[147]). However, the bacteria are often washed off during dyeing or scouring so that only the changes in the fibre, as mentioned above, remain as evidence. Mahall has described the procedure and the problems of detecting bacterial damage in detail.[5] The same is true for fungal damage, the microscopic detection of which is described in Section 8.6.3

Wool can also be damaged by insects. For example, the larvae of the clothes moth (*Tineola biselliella*), the furniture carpet beetle (*Anthrenus flavipes*) and the black carpet beetle (*Attagenus*) feed on keratin. Treatment with moth- and beetleproofing agents can largely prevent such damage. The damage caused by insects to non-treated wool can be easily recognized under the microscope.[120] If fibres with crescent-shaped bites are found at the edge of holes, the holes can be said to originate from the furniture carpet beetle, which sometimes also leaves behind typical hairs. According to Peter, moth larvae usually bite off the end of the fibre and leave behind typical traces of a transparent, voluminous substance, which exudes from the mouth of the larva when feeding in the vicinity of the fibre end.[24] Moth bites are sometimes also found on cellulosic and synthetic fibres, the fibre substance then being excreted without being digested. Excrement is further evidence of moth damage.

Staining tests for detecting shrinkproof treatments

The detection of shrinkproof treatments is not itself part of damage analysis but it can contribute to clarifying cases of damage. To detect chlorinated wool and Hercosett shrinkproof treatments Bayer has suggested the following staining test:

- 0.8% Supramine Yellow GW/C.I. Acid Yellow 61, replaceable by Telon Yellow GW micro (DyStar)
- 1.0% Acilan Fast Navy Blue R/C.I. Acid Blue 92, replaceable by Acid Blue 92 (Aldrich) or Sandolan Navy Blue P-RLp125 (Clariant)
- 5% sodium sulphate
- 6 ml l^{-1} acetic acid
- 2 g l^{-1} sodium acetate

- 10 min at 40 °C.

Untreated wool is dyed greenish-yellow, chlorinated wool is dyed a dirty green, Hercosett-treated wool is navy blue and wool treated with Basolan SW is dark green.

Polymer films applied to wool as shrinkproofing treatments can also be selectively stained with optical brighteners and then detected by fluorescence microscopy. The levelness of their application can also be tested in this way: the wool sample is treated with a 0.5% solution of the optical brightening agent Ciba Uvitex BHT 180% for 30 min at 0– 2 °C (cooled with ice) at a liquor ratio of about 1:100, then rinsed three times for half a minute each with cold water and dried. After UV excitation the polymer film can be recognized by its strong blue fluorescence.[49, 148]

Quantitative analysis of wool damage

The quantitative methods described here enable the degree of wool damage to be estimated and sometimes also the type of damage. The principle of solubility tests is to determine the weight loss after an exactly defined treatment and to compare this with the weight loss of undamaged wool. The weight loss is always calculated on the basis of the dry weight of the fibres and given as a percentage. As a rule, the greater the difference to the weight loss of undamaged wool the more extensive is the damage. By analogy, this also applies to the methods where the content of certain amino acids (cystine, cysteine, cysteic acid, lanthionine) or the amount of dye uptake (for example, Methylene Blue) is determined. Here also the difference from the reference value for undamaged wool is used to evaluate the damage. Table 8.11 lists the most important quantitative methods for wool damage analysis.

Solubility tests are sensitive indicators of changes to the natural surface protection layers of the wool fibre, for example, the enlargement of the porosity or penetrability after damage to the epicuticle.[160] Reagents which cause formation of new cross-links (aldehydes, chrome dyes, multifunctional reactive dyes) reduce the solubility. Since values for the solubility of undamaged wool given in the literature usually show a relatively large variation, the accuracy of the analysis is increased by comparison with a sample taken before the potentially damaging treatment. This is especially important for detecting slight damage. Sakli and Schutz[160] have described the influence of fibre fineness (increasing solubility with increasing fineness), test temperature and mechanics (shaking) on common solubility tests. Schefer[18] explained the connection between usual wool treatments in practice and the typical changes in the wool resulting from these, including possible chemical damage.

As a complement to Table 8.11 the most important simple quantitative test methods, which as a rule can be carried out in any textile laboratory, are commented on below. More complicated methods are only used for wool damage

Table 8.11 Important quantitative methods for wool damage analysis[18]

Method	Principle	Main conclusions	Value for undamaged wool	Value with very heavy damage
Alkali solubility IWTO-4 (1) ASTM D-1283 (2) BS 3568 (3) SNV 195 587 (4) DIN 54281 (5)	Treatment with 0.1 N NaOH at 65 °C, 60 min	Increase after treatment with acids or oxidizing agents, also after steaming above 100 °C	12–17%	50–80%
Urea/bisulphite solubility IWTO-11 DIN 54279	Treatment with a urea/bisulphite solution at 65 °C, 60 min	Increase after treatment with acids or oxidizing agents; marked decrease after treatment with alkali or cross-linking agents	40–50%	about 5 or 80–90%, respectively
Peracetic acid/ammonia solubility SNV 195 586	Oxidation of cystine with peracetic acid and treatment with 0.2 N ammonia	Decrease after treatment with alkali, cross-linking agents or dry heat	90–86%	60–40%
Cystine and cysteine content IWTO-15 EMPA-Methode (6)	Hydrolysis of wool with sulphuric acid, reduction of cystine with sulphite, colorimetric determination of the blue colour formed with phosphotungstic acid	Decrease in cystine content after treatment with alkali, peroxide, reducing agents (not with acids), increase in cysteine content after reduction	Cystine 11–12.5% Cysteine 0.3–0.4%	Cystine 6–8% Cysteine 1–2%
Cysteic acid IWTO-23 DIN 54286 and IR spectroscopy	Total hydrolysis, electrophoretic separation and colorimetry or FTIR preferably with ATR	Increase after heavy oxidation, for example with peroxide or chlorine	0.2–0.5%	3–5%
Methylene Blue-uptake SNV 195 588	Staining with Methylene Blue and colorimetry of the residual liquor	Global parameter, increase with almost all types of chemical damage to wool	3–5 mmol/100 g	25–35 mmol/100 g

(1) International Wool Textile Organisation; (2) American Society for Testing and Materials; (3) British Standards Institution; (4) Schweizerische Normen-Vereinigung; (5) Deutsches Institut für Normung; (6) Eidgenössische Materialprüfanstalt

analysis in exceptional cases. They often involve the chromatographic separation of the total hydrolysate of wool samples, which is available in automated form. Schefer[161] names some exceptions to the rule that the results of quantitative wool damage analysis correlate well with mechanical textile tests, for example after cross-linking reactions.

Alkali solubility

Since alkali solubility increases particularly markedly after acid damage (from about 15% to as much as 80%) it is a sensitive indicator for this kind of damage. Damage caused by peroxide bleaching or chlorination causes a much smaller increase in solubility (usually up to about 20–30% weight loss). Alkali solubility also increases noticeably after reductive as well as oxidative damage and also after HT steam treatments. Dry heat and damage by light increase alkali solubility to a lesser extent. After damage by alkali a small decrease in alkali solubility is observed (for example, down to 10%). If the aqueous extract of the wool sample indicates a pH value below 4, the acid content of the wool should be determined and taken into consideration when calculating the solubility in the alkali solubility test as well as the urea/bisulphite solubility test.[7]

Urea/bisulphite solubility test

Since urea cleaves hydrogen bonds and bisulphite cleaves disulphide bonds, the weight loss with undamaged wool is high (40–50%). It is increased further by acid damage (up to more than 80%) and greatly reduced by alkaline damage (down to a few per cent, for example 5 to 10%), because under alkaline conditions wool forms new cross-links (lanthionine and lysinoalanine formation). Urea/bisulphite is therefore particularly useful for investigating alkali damage. Damage caused by chlorination or peroxide bleaching causes a slight increase in urea/bisulphite solubility (up to 50–60%), steaming and dry heat lead to a slight decrease.

Determination of the cystine content

Undamaged wool contains 11–12.5% of the important amino acid cystine. Alkali damage reduces this value markedly (for example, down to 8%). A smaller decrease (by about 2%) is caused by peroxide bleaching. Chlorination, acid damage, steaming and strong exposure to light also reduce the cystine content slightly. Determination of cystine content is particularly suitable for determining the extent of damage by alkali. However, it is much more complicated to carry out than the determination of urea/bisulphite solubility, which is also suitable in this case. For determination of cystine the wool sample is hydrolysed by heating with dilute sulphuric acid. The disulphide groups are then reductively cleaved by adding sodium sulphite or sodium pyrosulphite. The cysteine thus formed, together

with the cysteine originally present, give a blue coloration on addition of phosphotungstic acid (Folin's reagent). The colour is then assessed colorimetrically. This method of determining cystine content can be interfered with by some dyestuffs on dyed wool. Interference can also occur after oxidative or reductive treatments.[7]

Determination of the cysteine content

The cysteine content is determined analogously to the cystine content but without addition of reducing agent. The cysteine content has to be taken into consideration when calculating the cystine content, even though undamaged wool only contains 0.3–0.4% cysteine. This value is increased markedly by reductive treatments (bleaching, anti-chlorine treatments, stripping of azo dyes), which can thus be checked by this method. The cysteine content is lowered by alkaline scouring, setting and decatizing processes and oxidative treatments such as peroxide bleaching. Complexing agents based on ethylenediamine tetra acetic acid can interfere with the determination of cysteine.[162] Damage caused by reductive treatments should be readily assessable by determining cysteine content. However, according to Schönberger, increased cysteine values are seldom found in investigations of complaints.[163]

Determination of the tryptophan content

Tryptophan can be used as an indicator amino acid for the photolysis of protein fibres, such as wool, silk or human hair. Schäfer[158] has compared different methods for the quantification of tryptophan and the interference to the colorimetric method (with dimethylaminobenzaldehyde) caused by pigments and dyes.

Cumulative wool damage

Damage to wool is often due to a combination of several causes, whereby according to Doehner and Reumuth[150] the effects can be developed, added, multiplied or even increase exponentially. When more than one chemical acts on wool, as is usually the case in dyeing and finishing, damage can occur which would have been harmless if each of these chemicals had acted alone. This effect is known as cumulative damage. For example, intensive peroxide bleaching and dyeing in strong acid conditions can each be carried out alone in such a way that the performance of the wool is not lessened and other undesirable effects are also avoided. If, however, these treatments are carried out under the same conditions in sequence, the wool suffers considerable damage. Sanger[164] explained this by the catalytic effect of the cysteic acid formed during oxidation on the acid hydrolysis of the neighbouring amide group. The proton from the cysteic acid is transferred via a hydrogen-bond-stabilized six-membered ring structure to the amide nitrogen, which makes this amide group easier to hydrolyze.

In this section on wool damage analysis we have hoped to show that the fascinating, multifaceted chemistry and structure of wool give rise to many possibilities for wool damage but also to many methods of chemical analysis.

8.5.3 Damage analysis of silk

Reports on faults with silk fabrics are more common than would be expected from their share of the world fibre market (about 0.1%). One reason for this is that silk is particularly delicate. Mechanical treatment, especially in the wet state (dyeing and finishing as well as household laundering), causes irreparably abraded areas, the so-called blanched places. Defibrillation and splitting off of the silk filaments causes incident light to be scattered diffusely. The silk lustre is no longer present, the fabric appears dull and lighter. This is particularly noticeable with dark dyeings. The abraded fibres can be identified in direct microscopy and even better in surface imprints. The same is true for silk lousiness (exfoliation), which is not actually a case of damage but does represent a quality problem. Silk lousiness is the term for pills formed from fine fibrils which become separated from the filaments of the silk. They are laid bare during degumming and during further processing they are twisted together into pills.[165] Again they represent an aesthetical problem especially for dyed fabrics.

A further common type of damage in silk is alkali damage, which usually occurs during degumming, especially when fibre protective agents are not used. Typical mechanical and chemical damage during scouring has been described in the literature.[166] According to Kornreich[167] chemically damaged silk dissolves in cupriethylenediamine, whereas undamaged silk does not dissolve. Damage to silk by alkali was evaluated by determination of the content of amino groups by the ninhydrin method and by determination of the tensile strength.[168] Silk should not be washed with products that contain hypochlorite or proteases, which are recommended for cellulose textiles. Further typical forms of damage to silk and their analysis have been described by several authors.[169–174]

Mahall and Goebel have reported that the Pauly reagent as used in wool damage analysis can also detect mechanical and chemical damage to silk, although the silk fibre does not have a cuticle layer but only a thin fibroin sheath.[5, 165] With silk the Pauly reaction thus has to be carried out for a short time and with cooling (1–2 min, ice-cooled). To help verify the results it is recommended that comparisons be carried out on undamaged silk and on silk with defined damage. In addition, before this analysis is made Bombyx mori silk has to be carefully checked to see if it is completely degummed, since residues of sericin are stained red in a similar way to damaged fibroin. Undamaged Bombyx mori silk is stained yellow. Degummed tussah silk is stained yellow-brown by the Pauly reagent and bleached tussah silk light orange, thereby indicating a slight degree of bleaching damage.

Similar staining tests have been described for the detection of sericin and for

controlling the degumming process: staining of silk with a 2% aqueous solution of C.I. Direct Red 80 at a liquor ratio of 1:40 for 2 min at the boil[175] or with 1 g l^{-1} C.I. Direct Red 80 at a liquor ratio of 1:200, also for 2 min at the boil.[176] C.I. Direct Red 80 is now available as Sirius Red F3B (DyStar), Ciba Solophenyl Red 3BL 140%, and Direct Red 80 (Aldrich). Former trade names mentioned in the literature are Sirius Red F3B 200%, Solar Brilliant Red BA 150% and Solophenyl Red 3BL 140%. Mahall and Goebel[165] have described a staining test with a 1 % solution of C.I. Direct Red 80 for 1 min at room temperature. In all these staining tests the fibroin is colourless after rinsing and the sericin is stained red. According to the manufacturer's information[126] Neocarmin W stains fibroin gold-yellow and sericin blue to violet, according to Mahall, Neocarmin W also stains degummed Bombyx mori silk blue, brownish violet or reddish violet, depending on its origin, but the colour is lighter than that with sericin.[5] Checking the stained samples under the microscope is in all cases useful in verifying the findings. Testing of degumming can also be made, in a time-consuming way, by quantitative determination of the primary amino groups after staining with ninhydrin.[176]

In order to distinguish cultivated Bombyx mori silk from wild silks such as tussah the so-called silk reagent is used. In contrast to tussah silk, Bombyx mori silk dissolves completely after 2–5 min at room temperature.[29] Preparation of the silk reagent: 10 g of copper sulphate are dissolved in 100 ml of distilled water and 5 g of glycerine added. 40% sodium hydroxide is added dropwise until the copper hydroxide precipitate initially formed is completely dissolved. Two further reactions for differentiation have been described by Agster.[7] Bombyx mori silk dissolves in boiling zinc chloride solution (45° Bé) after 1 min, whereas tussah silk is hardly affected. Unlike tussah silk, Bombyx mori silk is also dissolved after boiling for 5 min in 5% sodium hydroxide. Mahall[5] has illustrated the microscopic differentiation between cultivated and wild silk by means of longitudinal views and cross-sections.

Since weighted silk is more easily damaged mechanically and the detection of weighting is an important aspect of quality control, this subject will be mentioned briefly. Weighting with minerals, usually with tin-phosphate-silicate, results in a light-coloured skeleton residue of ash after burning. At higher levels of weighting the structure of the yarn or fabric is retained in the ash. Agster[7] has described conventional chemical detection reactions for weighting. Silk can also be weighted by grafting-polymerization with methacrylamide,[177] which can be detected by conventional chemical analysis or by IR spectroscopy.[178]

8.5.4 General types of damage to synthetics (thermal, light and mechanical damage)

In contrast to natural fibres only a few simple test methods are known for damage analysis of synthetic fibres. On the other hand the standard synthetic fibres are also generally much less heavily damaged by acids, alkalis and microorganisms than

are cellulosic and protein fibres. But there are also typical faults and types of damage to synthetic fibres, as is briefly described in this section.

Thermal damage

Thermal damage is one of the most frequent causes of complaints about synthetic fibres, especially if they have a relatively low melting point. It causes, amongst other things, hardening of handle, yellowing, loss of strength, uneven fabric appearance (light reflection) and dyeing behaviour (spots, streaks and other types of unlevelness such as warp splashes). Thermal damage can occur at many stages in processing. Examples are texturizing, setting, singeing, pressing and sewing. During texturizing the originally circular fibre cross-sections are usually flattened to polygons. When setting is at too high a temperature or for too long, the yarns are flattened at the interlacing points. During singeing of staple fibre blends with cellulosics or wool, protruding synthetic fibres can melt to form small balls, which cause a hard handle and which dye more deeply in exhaust processes (small dark spots, deeper dyeing being caused by the high amorphous content and the decrease in relative surface area) and after continuous dyeing are lighter than the undamaged fibres (the diffusion time is too short for the melt balls).[5] Pressing at too high a temperature causes flattening and bonding of thermally sensitive synthetic fibres. Thermal damage also occurs through friction, impact, striking, cutting or punching out during textile production and garment manufacture. Mahall has shown many typical examples of this.[5] The most important methods of investigation of thermal damage are microscopy in longitudinal view (also with surface imprints) and on cross-sections, dyeing tests and thermal analysis (see Section 8.4.5). Schwertassek[179] has compared methods for determining the degree of setting in synthetic fibres, since differences in setting are a common cause of unlevel dyeing:

- The critical solubility temperature, which also depends strongly on fineness, crimp, delustrant and residues of auxiliaries. In addition, relatively long sections of yarn are necessary.
- Iodine sorption, which can be used for many types of fibre. Residues of some chemicals interfere. Also, only fibres of the same fineness can be compared, since the adsorption is strongly dependent on the specific surface area.

Buchanan and Hardegree described the influence of heat and tension (for example during drawing, texturizing and occasonally dyeing) on faults in yarns made of polyester, nylon 6,6 and polypropylene.[180]

Damage by light

According to their chemical constitution and stabilization synthetic fibres show differing degrees of sensitivity to light, for example aliphatic and aromatic polyamides are more sensitive and polyacrylonitrile fibres less so. Apart from

some technical fibres, synthetic fibres are usually delustred with titanium dioxide. This catalyses photolytic degradation (photolysis), which can be recognized by an apparent coarsening of the grains of the delustrant. The delustrant pigments appear larger because they are surrounded by a sphere of degraded fibre substance with a different refractive index.[33, 34] Damage by light can usually be detected by fibre-specific reactions and also by non-specific effects such as yellowing, loss of strength and decrease in the average degree of polymerization.

Mechanical damage

Mechanical damage to synthetic fibres can be just as easily detected under the microscope as with natural fibres. In the case of thermoplastic fibres mechanical damage is often accompanied by thermal damage. This causes deformations which can be clearly seen in the longitudinal view and in fibre cross-sections. The change in reflection of light in the damaged area interferes with the uniform appearance of the fabric. Well-known examples are shuttle marks and warp splashes, caused by the shuttle striking yarns in the shed of the loom and thus deforming warp or weft threads made from synthetic fibres. The higher lustre of the deformed threads then shows up at a certain distance from the selvedge in the form of short, irregular and diffuse streaks in weft direction.[5] Hearle studied the structure of ruptured fibres (polyester, nylon, acrylic) under the light microscope and with electron microscopy and also the damage caused by abrasion and torsional stress, the samples mainly coming from damage in use.[181]

Differences in drawing ratio, fineness or texturizing of synthetic fibres are often the reason for streaks and barriness in fabrics made from them. They can be identified by marking the threads, stripping off the dye and redyeing, in which case they reappear at the marked places. These faults can usually be recognized under the microscope (surface imprints) and differences in drawing ratio can be seen particularly well in polarized light.[182] A milky dullness in synthetic fibres can be caused by tiny gas bubbles formed either during coagulation in the precipitating bath or by thermal degradation during finishing. They can be easily recognized under the microscope.[21] Irregular distribution of the fibre components in yarns made from staple fibre blends, usually from synthetics with natural fibres, can lead to a skittery fabric appearance. This can be checked by microscopy of the yarn cross-section.[23]

Chemical damage

The chemical weak spots and the corresponding types of damage vary greatly with synthetic fibres depending on their structure. Thus they are described in the next section in relation to the type of fibre. However, a general difference in chemical stability exists between fibres formed by polymerization or polycondensation. At extreme pH values polycondensate fibres are hydrolytically degraded, for example

by cleavage of ester or amide bonds between the constitutive elements. The carbon backbone chain of the polymerisate fibres is stable to hydrolysis but sensitive side groups such as the nitrile groups of acrylic fibres can be hydrolyzed.

Microfibres

Microfibres are especially sensitive to light damage, owing to their large specific surface. Light damage is intensified by the catalytic effect of some dyes and their light degradation products. Also a much higher dyestuff concentration is needed for microfibres, compared to the same shade on normal fibres. Fastness problems can arise from residual size that is usually not completely washed off from the microfibres.

8.5.5 Analysis of damage to polyester fibres

Polyester fibres (PET) are chemically relatively stable, so that damage caused by acid or alkali is seldom. At extreme pH values, however, hydrolytic degradation occurs, for example as used in the alkaline titre reduction of polyester textiles. Thermal damage is more common, caused by setting, pressing, pleating or singeing fibre blends containing PET or thermally bonding nonwovens at too high temperatures. Another form of thermal damage is the thermal deformation caused by heat of friction, which can occur during sewing and cutting or punching out. Mahall has described many examples of this.[5] The damage caused by excessive heat and mechanical effects, for example during primary spinning,[183] secondary spinning[184] or tension during setting, primarily causes structural differences in the PET fibres which lead to barry dyeings and shade differences across the fabric. Differences in shade can be detected with as little as 2 °C difference in setting temperature, depending on the sensitivity of the disperse dye used. Generally speaking, at setting temperatures above 185 °C markedly deeper dyeings are obtained.

As a test dyeing to detect structural differences in PET, C.I. Disperse Blue 79 (for example Dianix Navy Blue NNG, Foron Navy S-2GL or Ostacet Navy Blue 2 GLS) has been recommended, for example for 30 min at 130 °C.[185] Another test dyeing uses a mixture of a blue dye which shows up structural differences very markedly and a yellow dye which does not have this property:[186]

- 0.3% C.I. Disperse Blue 130, for example Ciba Terasil Navy BGLN 200%
- 0.15% C.I. Disperse Yellow 122, for example Ciba Terasil Yellow 2GL
- 1 gl^{-1} ammonium sulphate
- 0.5 gl^{-1} Uvadin DP
- pH 5, set with formic acid, liquor ratio 1:20

Heat at a rate of 5 °/min to 50 °C, then at 1.5 °/min to 90 °C and at 0.5 °/min to 130 °C. Treat at 130 °C for 30 min and cool at 3 °/min to 60 °C (or dye at the boil for 60 min with 1 g l^{-1} carrier)

Table 8.12 Validity of test methods for changes in structure of PET due to heat and tension[187]

Test method	Effect of heat	Effect of tension	Equipment costs	Effort
Dye uptake during HT dyeing *	–	–	Large	Large
Residual shrinkage ** (hot air)	+	++	Low	Low
Tensile strength	–	–	Large	Low
Elongation at break	–	+	Large	Low
Work at 5–10% elongation	–	++	Large	Low
Elongation at 200–300 cN	–	++	Low	Low
Residual extension	–	++	Low	Low
Critical solution time * (phenol)	–	–	Low	Large
Density (graduated column[188])	++	–	Medium	Medium
Differential scanning calorimetry (DSC)	++	–	Large	Low
Thermomechanical analysis ** (TMA)	+	++	Large	Low
X-ray (long period)	+	–	Large	Large

Effects of heat and tension: * simultaneously, ** separately.
Validity: – none, + good, ++ very good.

Rinse hot and cold and reductively clear with:

- 5 ml l^{-1} sodium hydroxide 36 ° Bé
- 2 g l^{-1} hydrosulphite
- 1 g l^{-1} Eriopon OL

for 20 min at 70 °C, then rinse, neutralize and dry.

Differences in draw ratio in PET fibres can be analysed by microscopic determination of their specific birefringence, whereby higher tension results in a higher birefringence whereas the influence of temperature varies.[39] In Section 8.4.5 it was described how the thermal prehistory of PET can be analyzed with the aid of the so-called effective temperature or middle endotherm peak temperature (MEPT) determined by differential scanning calorimetry. The term 'effective temperature' was introduced by Berndt and Heidemann.[187] In this publication a review of many other testing methods for analysing structural differences in PET is given, including an evaluation of how well they respond to the influence of heat and tension. Table 8.12[187] shows that the methods of thermal analysis are fairly well suited to this purpose. Investigation of the fine structure of PET with the aid of iodine sorption has been described by Gacén and coworkers.[189,190]

According to Richter[191] damage caused by alkali can be recognized from the partial saponification number and damage by heat from the iodine sorption. Bobeth[192] analysed thermal damage and damage caused by dyeing and finishing on the basis of swelling of cut ends and microsolubility times. Schwertassek[193] determined differences in degree of setting by various methods. According to Küppers[194] the influence of strong heat and in particular of setting conditions can be seen under the microscope in a 90% phenol solution (Table 8.13). Since the

Table 8.13 Setting conditions and swelling time of PET fibres in 90% phenol solution[194]

Commencement of longitudinal swelling after (min)	Exposure to heat, setting conditions
15 to 30	Untreated or slightly set
About 60	Normal setting
More than 120	Overset, thermally damaged

swelling time is dependent on the origin of the polyester fibres, comparisons should only be made between fibres from the same batch, for example from samples before and after thermal damage. In addition, the samples should not be heated during the swelling test, for example by leaving them for a longer period of time on a heated microscope stage (this results in shorter swelling times). The older methods for investigation of damage to PET fibres mentioned in this paragraph are seldom mentioned in the recent literature. More common is the determination of the average degree of polymerization of damaged polyester by means of viscosimetry in *m*-cresol.[195] According to Tetzlaff and co-workers normal DP values range from 80 to 150.[196]

A simple staining test which indicates mechanical, thermal and chemical damage to polyester fibres consists of staining with an oil dye dissolved in *m*-cresol, which according to Stratmann[8] is also used to identify different polyester fibres (a more advantageous alternative with alcoholic potassium hydroxide is discussed in Section 8.4.1).

Preparation of the test staining solution: 0.5 g of C.I. Solvent Red 27, for example Oil Red O (Aldrich, Fluka, Sigma), in the literature recommended as Oil Red 5B, is wetted with a little methanol and then dissolved in 50 ml *m*-cresol.

Carrying out the test: to identify the fibre short snippets of fibres are squeezed off with blunt scissors. To analyse the damage the fibre is treated as gently as possible and, if necessary, cut with a sharp instrument. The fibre sample is treated for 5 min at room temperature with the solution of oil dye. It is then rinsed thoroughly with methanol, very briefly with acetone and immediately thereafter again with methanol. The squashed areas of the polyester fibres are dyed intensively, fibres damaged mechanically, chemically or thermally are dyed deeply in the damaged area whereas undamaged Kodel fibres are dyed overall.

Using a staining test with C.I. Basic Blue 3 (Astrazon Blue BG) PET fibres which have undergone titre reduction by alkali treatment can be identified,[197] whereas by spraying with Astrazon Pink FG (0.5% in dichloromethane) they can be tested for barry dyeing.[198]

Photolytically damaged polyester fibres can be recognized under the microscope by the apparent coarsening of delustrant grains,[199] as described in Section 8.5.4, and by fluorescence in UV light of the degradation products oxy- and 2,5-dihydroxy terephthalic acid.[200, 201] This fluorescence microscopy enables a

differentiation to be made between photo and thermal damage, but only if optical brighteners do not superimpose on the weak fluorescence of the terephthalic acid derivatives.

Since they are hydrophobic, PET fibres show great affinity for other hydrophobic substances, not only to disperse dyes but also for oils, grease and waxes as used in textile production. If these contaminants are not removed during pretreatment and they can diffuse into the PET fibres during thermal treatments (such as setting, thermosol dyeing or pressing) they are often well fixated and are thus a typical cause of stains, streaks and other similar types of complaint. They can be detected by extraction followed by TCL or IRS as well as under the microscope by staining with oil dyes and also by dulling the film in surface imprints (see Section 8.6.1).

Polyester oligomers as a cause of damage

PET oligomers are low molecular weight side products of the polycondensation reaction with two to about 10 repeat units. These linear and cyclic oligoesters are possibly also formed during the melt spinning process. The total content of oligomers is 1–3% and 70 to 90% of this amount is in the form of the cyclic trimer *cyclo*-tris-ethylene glycol terephthalic acid ester, $c(G–T)_3$. A large percentage of the cyclic trimer diffuses onto the fibre surface under HT dyeing conditions and from there into the dyebath. $c(G–T)_3$ is practically insoluble in water up to 100 °C and at 100–140 °C only to the extent of 1–5 mg l^{-1}. Thus during dyeing and in particular during cooling down of the dyebath it can precipitate and deposit on the goods being dyed or on the interior surfaces of the dyeing vessel. The problems which thus arise are particularly great when dyeing loose fibres or yarns. These problems include dust formation, poor running properties, difficult spinnability and increased wear on thread guides and needles. With piece dyeings the oligomer deposits can cause light spots, especially due to a filtration effect on the HT beam dyeing machine (possible perforation imprints on the fabric roll),[44] but less so with knitted goods in jet dyeing machines. In addition, the fabric then lacks brilliance; a cloudy greyness gives an uneven fabric appearance. Oligomers which adhere to the fibre surface particularly interfere (surface oligomers, as opposed to core oligomers). They are often mixed with spinning oils and other auxiliaries or with dyes and can be difficult to remove. In spite of many known methods of avoiding oligomer problems, such as pretreatment in an alkaline medium or with organic solvents, alkaline dyeing, addition of auxiliaries, dropping the dye liquor under HT conditions and alkaline reductive clearing, PET oligomers still repeatedly cause complaints.

The first indication of damage caused by PET oligomers is often the appearance of the fault: light grey deposits, which are partially easy to remove mechanically and form dust. In addition, when an isolated sample is shaken in isopropanol a marble-like suspension with mother-of-pearl lustre is formed.[202] Detection methods

for PET oligomers, especially for $c(G–T)_3$ have in some cases already been described:

- IR spectra resemble that of the PET fibre (see Section 8.4.4);
- TLC detection, especially by comparing with authentic samples (see Section 8.4.3);
- melting range 305–327 °C, according to their purity (marked difference to PET fibre dust, which melts at 250–255 °C), possible confirmation by means of mixed melting points: a mixture of approximately equal parts of sample and authentic cyclotrimer should not show any marked depression of the melting point;
- microscopic detection by recrystallization on the microscope slide: dissolve in dichloromethane, $c(G–T)_3$ crystallizes out after concentration by evaporation of the solvent[202] or formation of crystals after melting the sample on the microscope slide.[5] The crystals thus formed are usually hexagonal, sometimes also in the form of needles or are star-shaped and they appear golden yellow to multicoloured in polarized light.[202]

Quantitative determination is usually made gravimetrically, after extraction with dichloromethane or dioxane, whereby a separate extraction with petroleum ether is made to determine the quantity of extractable spinning oils. In this way the maximum fraction of extractable oligomers is determined, not the total oligomer content.[202] The marked UV absorption at 250 nm also enables quantitative determination. More details of quantitative analysis can be found in the literature[7, 202] and further information, also on repairing faulty pieces, is available.[202]

8.5.6 Analysis of damage to nylon fibres

In terms of quantity standard nylon fibres were overtaken by polyester fibres around 1975. The reason that the latter fibres are now by far the most important group of synthetic fibres has also to do with the fact that nylon 6 and 6,6 fibres are more sensitive to light and less stable to hydrolysis than polyester fibres. Nylon fibres also have a greater tendency to yellowing in heat, nylon 6 in particular being less stable to heat than PET (see Table 8.6). On the other hand the abrasion resistance and bending strength of nylon fibres is very high. Hearle has described the microscopic analysis of fatigue appearance in nylon fibres.[181] Under extreme conditions of use and also during dyeing and finishing oxidative damage can occur, often intensified by heat and/or light. UV radiation damages aliphatic polyamides and the aramids. With nylon 6 and 6,6, acid damage and, less commonly, alkaline damage are usually the result of inappropriate dyeing and finishing treatments. At extreme pH values their amide bonds are cleaved hydrolytically. Comparison of the sensitivity to damage of the standard nylon fibres shows that nylon 6 is more sensitive to hydrolysis and heat whereas nylon 6,6 is more easily damaged by oxidation.

Table 8.14 Extent of damage and staining of acid-damaged nylon fibres with Rhodamine B[203]

Extent of acid damage	Staining	Loss of strength (%)
No damage	Colourless	0
Slight damage	Pale pink	about 5
Medium damage	Pink	about 15
Heavy damage	Red	about 30
Very heavy damage	Deep red	about 70

Detection of acid damage

According to Bubser and Modlich[203] acid damage to nylon fibres can be detected in a simple way by a staining test with Rhodamine B (C.I. Basic Violet 10, available from Aldrich, Fluka, Sigma): the sample is placed for 5 min at room temperature in an aqueous solution of 0.1% Rhodamine B, to which 10 ml l^{-1} of 60% acetic acid have been added. The sample is then rinsed cold until the rinsing water is colourless. Depending on the degree of acid damage, staining of the sample ranges from colourless via pale pink with slight damage to dark red with heavy damage (Table 8.14). Nylon fibres damaged by heat, light or oxidation are not stained in this test.

According to the literature[21] (see section S087 there) damage due to mineral acids can easily be recognized under the microscope by means of the irreversible swelling of the nylon fibres. Acid residues can also be detected microscopically by embedding the sample in 0.1% Methyl Orange solution (typical needle formation, see Section 8.5.2).

Detection of thermal damage

When treatments such as setting, pressing, pleating or singeing of nylon fibres are carried out at too high temperatures, and also during thermal bonding of nonwovens or during cutting and sewing, fibre deformation, fibre bonding and formation of melt balls at the fibre ends can occur, all of which can be easily recognized under the microscope. The melt balls usually dye more deeply[148] and give rise to a hard handle. Damage caused by setting can be roughly estimated by measuring the swelling time in sulphuric acid.[179, 204] Differences in degree of setting can be determined by means of a test dyeing in a 1% solution of C.I. Direct Blue 71, for example Sirius Blue S-BRR from DyStar (pH 5 set with acetic acid, liquor ratio 1:50, 60 min at the boil): with increasing degree of setting the dye uptake at first decreases; with overset fabric, however, it increases. The same test dyeing (or also with just 0.25% dye and an additional 1% salt) is also used to identify structural differences that have other causes which also affect dye uptake capacity, for example differences in draw ratio or texturizing. Setting differences in carpet yarns

giving streaky dyeings can be rapidly detected by spectroscopy in the near-infrared region.[205] Damage from the effect of dry heat for longer times can lead to a reduction in the concentration of amino end groups so that the staining test with ninhydrin gives a lighter colour.[206]

Detection of damage by light

Despite photostabilization during fibre production and, in some cases, additionally during finishing, damage by light (especially UV light) is fairly common with nylon fibres. The complex photolysis reactions are accelerated by delustrants as well as by contaminants within and external to the fibre (and, among many other things, by nitrous gases).[206–208] These reactions cause yellowing and loss of strength and can be recognized under the microscope by the apparent coarsening of the delustrant grains (see Section 8.5.4). According to Bubser and Modlich[203] damage by light can also be recognized microscopically by a dark dulling of the nylon fibres when embedded in olive oil. The reduction in content of amino end groups as a result of damage by light is the basis for two dyeing tests: a lighter dyeing with C.I. Direct Blue 67 (Aldrich, former Solar Brilliant Blue A 330%) (0.1% solution, 2% fatty amine ethoxylate as a levelling agent, for example Sandogen NH liquid, pH 6, 60 min at the boil)[75] and a lighter coloration with ninhydrin (0.5% solution, 2 min at the boil, short rinse and dry between filter papers). This is in contrast to damage by acid or oxidation, which gives a deeper colour in the ninhydrin reaction.[194, 206] In exceptional cases, if the effort can be justified, determination of the amino end groups with 1-fluoro-2,4-dinitrobenzene (FDNB method) gives a more exact analysis of the damage than is possible with ninhydrin. This method is also suitable for aramid and polyimide fibres.[209]

Detection of damage by oxidation

With the ninhydrin staining reaction mentioned above a darker colour than normal is obtained after oxidative damage.[194] Using modified zinc chloride solutions (Frotté reagent I and II) nylon fibres can be distinguished and identified by the so-called Frotté reaction according to Koch[31] (crenellated, finely structured transverse folds and cracks on the fibre surface, which gradually change to coarser structures and then dissolve, see Table 8.1). With solutions of zinc chloride, potassium iodide and iodine (zinc chloride–iodine reagent: 66 g $ZnCl_2$ and 6 g KI in 34 ml water, plus as much iodine as will just dissolve), modified according to Bubser and Modlich (three parts by volume of zinc chloride–iodine reagent, one part by volume of 96% ethanol, 1 part by volume of distilled water), the Frotté reaction only occurs after oxidative damage, but not after damage by acid, heat or light.[203]

This is described in more detail in Table 8.15 and is shown in Table 8.16 in a review together with other methods for detecting damage to nylon fibres. The conclusions which can be drawn from these microscopic methods are unfortunately

Table 8.15 Damage to nylon fibres and Frotté reaction with modified zinc chloride–iodine reagent, according to Bubser and Modlich[203]

Type of damage	Loss of strength (%)	Swelling behaviour after 3 min at room temperature
None (grey fabric)	0	Marked Frotté reaction
Slight acid damage	about 5	Marked Frotté reaction
Medium acid damage	about 15	Moderate Frotté reaction
Heavy acid damage	about 35	Marked flattening of the crenellations
Very heavy acid damage	about 70	No Frotté reaction
Heat set	about 15	Marked Frotté reaction
Overset	about 30	Marked flattening of the crenellations
Thermal damage	about 60	No Frotté reaction
Damage by light	about 40	No Frotté reaction, dulling of the unswollen part
Oxidative damage	about 80	Marked Frotté reaction

Table 8.16 Review of detection methods for damage to nylon fibres[148, 194, 203]

Damage due to:	Acid	Heat	Light	Oxidation
Rhodamine B staining	+	–	–	–
Swelling in modified zinc chloride–iodine reagent	–	–	–	+
Ninhydrin colour reaction	Darker	Lighter	Lighter	Darker than normal
Embedding in olive oil		Normal	Dull	
Staining with acid dye				Darker than normal

often not exact enough and can only serve as a rough guide,[123] probably also because in practice different types of damage are superimposed, for example, light and heat or light and oxidation (photo-oxidation) or even all three causes of damage together.

Viscosimetric determination of the average degree of polymerization (DP), usually in *m*-cresol,[210] enables the extent of many types of damage to nylon fibres to be determined exactly, since most types of damage occur with chain degradation. But the type of damage itself cannot be analysed in this way. In addition, contaminants which deposit on the fibre during production, dyeing and finishing or in use, and which are sometimes difficult to remove, interfere with the determination of DP. According to Zaremba *et al.* usual DP values for PA6 range from 100 to 180 and for PA6.6 from 50 to 80.[211]

Nylon oligomers

In the production of nylon fibres, especially nylon 6, oligomers can also be formed. They are soluble in water, as is also the monomer caprolactam, and thus they do not

usually lead to problems as do the polyester oligomers. An exception to this has been described by Schwertassek.[212] Insufficient removal of caprolactam and nylon 6 oligomers can lead to marked fibre deformation and cracks during heat setting. These deformations can be seen by embedding microscope samples in iodine/Glauber's salt solution (40 g of potassium iodide and 5 g of iodine in 50 ml of distilled water, then diluted 1:5 with Glauber's salt solution saturated at room temperature), which also serves to identify the cause of the damage. Caprolactam and oligomers take up more iodine and can be readily seen under the microscope as yellowish brown droplets (Glauber's salt hinders their dissolution).

8.5.7 Analysis of damage to acrylic fibres

Acrylic fibres (PAN) for the home furnishings and garment sector are one of the fibre types with the greatest range of variation in their commercial types, similar to the elastane fibres. Two possibilities of variation in the manufacture of acrylic fibres are characteristics of this: first, the type and amount of comonomers added to make the structure more flexible and to enable dyeing with basic dyes and secondly the possibility for wet or dry spinning with different solvents. Additional special features are dope dyeing and gel dyeing. The resulting variety of types is a cause of many cases of damage caused by mistaken types and dyeing faults. PAN fibres have good resistance to acid up to medium concentrations and somewhat poorer resistance to alkalis. Their biological resistance is good. PAN fibres are very resistant to non-polar organic solvents, oxidizing agents and weathering. Their abrasion resistance is low because of a tendency to fibrillation.[213] Resistance to heat is also relatively low; above 150 °C they show yellowing and, depending on the type of fibre, from 200–250 °C an exothermic cyclization takes place (discoloration from yellow to brown and then black, caused by naphthyridine structures). This short review shows that with PAN fibres one can expect damage from heat, abrasion, polar solvents and effects of strong alkalis to be predominant. In addition, damage is also caused by too great or uneven shrinkage, the reason for which can be found in fibre manufacture, textile production or dyeing and finishing.

Mechanical damage

Mechanical damage is usually easy to recognize under the microscope, especially in surface film imprints. Hearle has analysed abrasion and torsional damage with light and electron microscopy.[181] Microscopic swelling and solubility tests have been developed for analysing mechanical and, in particular, thermal damage. The microsolubility time in 56% nitric acid decreases after mechanical damage to an extent which depends on the form of the fibre cross-section.[192] Abraded spots, fibrillated and squashed fibres and thermomechanical damage appear lighter in dyed fabrics because of the greater scattering of light.[5]

Thermal damage

The influence of cold or hot stretching in combination with heat setting has been investigated by many physical and chemical methods, which are also suitable for corresponding damage analysis (amongst others porosity, density, strength, extensibility, differential thermal analysis, molecular weight, electron microscopy).[214] The iodine adsorption number according to Schwertassek (mg iodine taken up by 1 g fibre) is very dependent on the PAN fibre type and is reduced by the effect of heat.[191] With the same fibre material, differences in solubility in dimethylformamide demonstrate differences in thermal effects (lower solubility after more drastic thermal effects).[194] With some types of PAN fibre so-called vacuoles are formed at temperatures around 90 °C. These are hollow spaces which have an effect like delustrants and feign apparent unlevelness of dyeing. They are particularly visible under the microscope when the sample is embedded in benzene/chlorobenzene 1:1.[194] Schmidt[34] reported a case of damage in which a deepening of the colour occurred during steaming for form setting. This was due to a reduction in the number of vacuoles during steaming.[34] A large amount of acrylic fibre production is used to produce high-bulk yarn. This is made from a blend of acrylic fibres with different morphology (fully shrunk fibres and shrinkable fibres, where the shrinkage is produced by heat treatment after spinning the yarn, the bulk effect then arises from the loops formed by the preshrunk fibres). By measuring the critical solubility time in common solvents (dimethylformamide, dimethylsulphoxide, dimethylacetamide) Gacén and Arias[215] developed a simple test which shows differences in fibre structure and shrinkage behaviour sensitively and accurately (the less the fibres have been shrunk the shorter the solubility time). This method was also used for development and endurance testing of technical textiles, including those made of PAN fibres.[216]

Damage by acids and alkalis

Since the main polymer chain of PAN fibres consists of carbon atoms, it is stable to hydrolysis. The nitrile side groups and many of the comonomers used to make the structure more flexible, such as methyl acrylate, methyl methacrylate or vinyl acetate, are cleaved at extreme pH values. The ester groups are hydrolysed to the original acids and alcohols and the nitrile groups are saponified to the acrylic acid structure via the amide intermediate. The loss of nitrogen or ammonia which thus occurs forms the basis of an analysis of alkali damage to PAN fibres, namely the determination of the partial nitrogen number according to Richter.[191] This also decreases owing to the effects of dry and wet heat, whereby the latter (steam) causes more damage (cleavage of the strong intermolecular hydrogen bonds in PAN). Richter also investigated the copper binding capacity of PAN fibres, which decreases after steam treatment (cupro numbers I and II). Polyacrylonitrile modified with vinyl chloride (modacrylic fibres) is especially sensitive to alkali; it can be damaged by hot alkaline scouring.

Further types of damage, reasons for faults and detection methods

The widely varying dyeing behaviour of the different types of PAN fibres is a common cause of faults, for example by mistaking the type of fibre or using unsuitable dyeing methods. PAN fibre types can be distinguished microscopically by their different swelling and fibrillation in zinc chloride–iodine reagent. Simple staining tests have been published for testing differences in dye uptake capacity (1% C.I. Basic Blue 5, Aldrich, formerly Astrazon Blue B, 1.5% sodium acetate, 1.5% acetic acid 60%, 1% Avolan IW[194] or 1% C. I. Basic Blue 3, for example Astrazon Blue BG micro 200% or Maxilon Blue 5G, set to pH 4.5 with acetic acid[217]). Heinkel has also described dyeing tests to distinguish PAN fibres with sulphonic and carboxylic groups (2% Maxilon Black T, pH 2 set with sulphuric acid: light blue with carboxylic groups, khaki to dark olive with sulphonic groups) and to distinguish between basic and acid dyeing PAN fibre types (with 1% C.I. Basic Blue 3 and 1% C.I. Acid Red 151, for example from Aldrich or Ciba Erionyl Red B, 10% Glauber's salt, set to pH2 with sulphuric acid, 1–2 min at the boil).[217] Rather than relying on the rough orientation given by staining tests it would appear better to consider the fibre-specific data, in particular the rate of dyeing and the fibre saturation value, which depends on the concentration of anionic groups in the PAN fibre.[218, 219] If this data is not supplied by the fibre producer and if enough material is available it can be easily determined in the laboratory.[220] This information is also useful for clarifying cases of damage concerned with dyeing. Neal has described some methods of correction for dyeing faults with PAN.[221] If after piece-dyeing PAN is cooled down too quickly in the rope form (jet) undesired creases can be set in the cloth. A further cause of faults is excessive shrinkage, for example when dry cleaning is carried out at too high temperatures.[222, 223]

Average degree of polymerization and analysis of PAN damage

Determination of the viscosimetric degree of polymerization or simply the relative viscosity of PAN fibres can be carried out relatively easily in the solvents used for spinning such as dimethylformamide or concentrated sulphuric acid (SNV 195592 according to Schefer[113]). In this way, for example, the extent of damage after thermal degradation can be determined, especially if comparable material from the same fibre lot can be tested at the same time. Usual DP values range from 1200 to about 2000 [224] and for gel-spun PAN from 10 000 to 20 000.[213] This method is not suitable for the analysis of damage caused by hydrolysis, since this does not involve chain degradation but changes in the structure of the side groups (nitrile, ester, amide). In addition, the new side groups formed during hydrolysis (mostly carboxylic acid groups) change the viscosity of the PAN solutions and thus reduce the accuracy of the viscosimetric DP determination. More costly methods for determining DP and its distribution, such as gel chromatography, are only rarely used in exceptional cases for PAN damage analysis.

8.5.8 Analysis of damage to elastane (spandex) fibres

Elastic fibres are usually elastane fibres, which according to ISO 2076 are made up from at least 85% by weight of segmented polyurethanes. In the USA they have the generic name spandex. The definition of elastane does not include the newly developed elastic fibres on the basis of pure polyester or polyolefin.[225] Although the share of elastane fibres on the world fibre market is still less than 1% they have achieved increasingly greater importance in the last decades. In the meantime about half of all clothing fabrics contain elastane fibres and around 85% of elastane fibres are used for clothing. This increasing distribution is the first reason for the frequency of complaints relating to textiles containing elastane. The second reason is that they can be overstrained during production, dyeing and finishing and in use. This already suggests the third reason, namely the relatively high sensitivity of elastane fibres to certain types of damage. They are particularly susceptible to thermomechanical damage (by heat and tension) and are also attacked and degraded by hydrolysis (acids and alkalis) and photolysis (especially by UV light). When the conditions are not too aggressive they are stable to oxidizing and reducing agents, except for the heavy damage caused by chlorine.

The urethane link, which binds the segments of the elastane repeat units, can be described as half ester and half amide of a carboxylic acid. The stability of polyurethanes is thus similar to that of polyamides and polyesters. The latter are more stable because of their high crystallinity and compactness, which is reflected in their density (elastane 1.2–1.3 and PET 1.38 g cm^{-3}). As with all elastic substances elastane fibres are cross-linked at wide intervals. They consist of so-called soft and hard segments. The latter are the fixed points in the network, they determine elasticity (recovering force), setting and heat behaviour. The hard segments are highly crystalline and contain urethane and, in some cases, additional urea groups, both groups form strong intermolecular hydrogen bonds (cross-linking via secondary valency). The soft segments are the flexible structures with little order, located between the fixed points, and they are responsible for the extensibility. With molecular weights in the range from 1000 to 3000 they are relatively large[226] and consist mainly of aliphatic polyethers (such as polytetrahydrofuran) or aliphatic polyesters. The former are more stable to hydrolysis whereas the latter are more resistant to oxidation (for example chlorine or photo-oxidation). The hard segments contain mainly aromatic structures which, as with the aramids, increase cohesion between the chains because of their mutual attraction. On the other hand because they absorb UV light strongly they contribute greatly to damage by light. This review is intended to show the main structural weaknesses in elastane fibres. It has already been mentioned that elastane is the fibre class with the greatest variation of types. The most important points of variation in their manufacture are:

- the type and size of the macrodiol (polyether or polyester), which makes up the soft segments;

- the type of polyisocyanate (for example diphenylmethylene and toluylene diisocyanate, MDI and TDI), with which the macrodiol is reacted and whose reaction products form the greater part of the hard segments;
- the type of chain extension, with diols extending to further urethane structures or with diamines extending to urea derivatives;
- the type of spinning process, dry or wet, reactive (chemical spinning) and, increasingly, melt spinning.

The number and association of the primary filaments to multifil yarns, the kind of thermal after-treatment (hot air, hot water) as well as the kind and amount of spinning oils varies between the many commercial varieties of elastane. Additional variety arises from further processing in the bare or covered form (elastic co-twisted, covered, core-spun or co-tangled threads). This variety can lead to mistaken identity and thus cause faults if the specific properties of each type are not given sufficient attention during processing.

Mechanical damage

Elastic multifilament yarns are less damaged during sewing than monofils because usually only a few of the primary filaments are damaged by the needle and the remainder is sufficient to hold the yarn together. Although the extensibilty at break of elastane fibres is 400–800 % mechanical damage can occur with overstretching. This does not necessarily mean that a tear occurs, large residual extension (set) and lower recovery forces can be reasons for complaint. Drastic damage includes thread breaks due to too high mechanical stress during knitting or weaving. A tear in the elastane core of a covered elastic yarn is referred to as a core break. It occurs particularly often with knitted fabrics; with woven fabrics loss of elasticity is the greater problem in practice.[227] This type of damage is easy to recognize visually. Mechanical overstraining and fatigue (ageing) can be analysed by mechanical testing methods:

- Stress/strain behaviour: a flatter form of the stress/strain curve is an indication of noticeable loss of elasticity. At higher extension the resistance of the elastane yarn increases exponentially until the thread reaches the maximum strength or extensibility, respectively, and breaks. Both values are lowered in cases of damage. As a simple manual test the extension at break can be determined as a rough guide with a scaled ruler, by measuring the initial length of an isolated section of the elastane thread and comparing with the length at break. The accuracy of this length measurement can be increased by grasping the ends of the thread with tweezers instead of with fingertips.
- Hysteresis curves: the elastic properties are determined by repeated extension and recovery at a constant rate between fixed limits (hysteresis behaviour, for example according to DIN 53835, five cycles to 300% extension). In the literature[226] extensive work on the dynamometric properties of elastic fibres and rubber threads has been cited. From their experience with many complaints

concerning elastane, Gähr and Lehr recommend that conclusions about the cause of damage should not be made from the hysteresis behaviour of an elastic thread isolated from the fabric.[227] They justify this by an extension limit of 300% in the test and by the fact that stresses which occur before the actual damage takes place can have a large effect on the hysteresis behaviour.

Thermal damage

Depending on the type of elastane fibre, noticeable thermal damage can occur when the fibres are heated above about 170 °C. Mainly yellowing accompanied by loss of strength and elasticity occurs. Under the microscope deformed elastomer fibres can then frequently be seen together with others which have taken on the contours of the covering component or adhere to it.[227] The temperature range for softening of elastane fibres lies between 170 and 230 °C, depending on the type, and for melting and commencement of degradation between 230 and 290 °C.[226] Water lowers the bonding in the hard segments (secondary valence bonding by means of hydrogen bonds); hydrothermal treatments therefore cause more damage than dry heat at the same temperature. Additional tension also increases the thermal damage considerably (thermomechanical damage). Especially if undamaged material is available for comparison damage by heat can be investigated by means of the stress/strain behaviour mentioned above or by thermomechanical methods of analysis:

- An elastane yarn set under excessive extension has a stress/strain curve lying to the 'left' of the curve for undamaged yarn. It has lower tenacity and much lower extensibility.[227]
- By determination of the hot breaking time; this is the time taken for an elastomer thread stretched by 100% to break at 193.5 °C.
- by determination of the heat distortion temperature (HDT); this is the temperature at which an elastomer thread under a pre-tension of 0.2 mN tex^{-1} and heated at a rate of 20K min^{-1} reaches an extension of 0.25%.[226]

The HDT differs greatly depending on the type of elastane fibre and often lies between 170 and 190 °C; with melt-spun fibres it can be lower. In order to avoid damage the setting temperature should not noticeably exceed the HDT of the respective elastane fibre type.[227, 228]

Marked thermal damage, leading to degradation of the polyurethane chains, can also be analysed by means of viscosimetric determination of the average degree of polymerization or the relative viscosity on which this is based. The spinning solvents dimethylformamide and dimethylacetamide[229] or hexamethylphosphoric acid triamide[113] can be used as solvents for this purpose. These viscosimetric analyses cannot be used with elastane fibres which have been covalently cross-linked and are thus not sufficiently soluble without degradation.

Yellowing after heat treatment of elastane can also be done to antioxidants in the fibre, especially of the sterically hindered phenol type.

Damage by light (photolysis)

In spite of the incorporation of stabilizers, elastane fibres are frequently damaged by light, especially when it has a high UV component (for example when wearing sport or bathing textiles outdoors). Photolysis causes discoloration as well as loss of strength and elasticity or even fibre breakage. The UV stabilizers can be partially washed out during dyeing and finishing.[226] Photolysis can be accelerated by oils and skin creams as well as sebaceous oils. The latter effect was demonstrated by Küster and Herlinger with model substances (squalene and linoleic acid methyl ester) on the basis of the decrease in relative viscosity of the damaged elastane fibres dissolved in dimethylacetamide. Perspiration, on the other hand, is said not to accelerate photolysis.[229] Küster and Herlinger list hypotheses and many citations concerning photochemical degradation. In the cases of elastane fibres based on polyether damage by light is accompanied by oxidation (photo-oxidation).

Chemical damage

Acids: elastane fibres are stable to dilute mineral and organic acids at room temperature. At higher concentrations and higher temperatures damage occurs including dissolution. The structural relationship to nylon fibres becomes apparent here, as it also does in respect to dyeing behaviour.

Alkalis: at room temperature elastane fibres are astonishingly resistant to alkalis. According to Hueber[230] it is possible to causticize and mercerize cotton/elastane blends at low temperature. At the boil, damage occurs with more than 2 g l^{-1} of soda.

Reducing and oxidizing agents: under the usual conditions of dyeing and finishing elastane fibres are relatively resistant. The limits for peroxide bleaching in blends with cotton are said by Naroska[231] to lie at pH 11 and 100 °C. The resistance to chlorinated water in swimming pools is said to be good,[226] on the other hand cases of damage have been reported. Chlorine bleach causes heavy damage, as does ozone.

Exhaust gases, especially nitrous gases (NO_x) cause damage by yellowing and loss of strength. Yellowing can also occur when nitrous gases from stenters directly heated with gas react with spinning oils, fibre lubricants and knitting oils used with elastane fibres, if these have not been completely removed by scouring.[232]

Oils and fats such as mineral oil, paraffin, wax, unsaturated fatty acids (spinning oils[228]), cosmetic oils and sun protection agents are absorbed by elastane fibres and can lead to loss of strength and elasticity due to loosening of the fibre structure. Some of these products also accelerate photolysis.[229] If dry cleaning is carried out carefully with the usual solvents such as perchloroethylene or benzene no damage occurs to elastane, except when stabilizers to light are extracted.[226] Highly polar organic solvents such as dimethylformamide, dimethylacetamide, cyclohexanone, butyrolacetone and phenols damage elastane fibres due to swelling or even dissolution.

Further types of damage, sources of faults and their detection

Many of the types of damage already mentioned are worsened in combination. Known examples are photo-oxidation and thermomechanical damage. Resistance to ageing also results from a mixture of many types of influence, for example mechanical, thermal and chemical influences such as atmospheric oxidation and the detergents and cleaning agents commonly used in laundering. The resistance to ageing of elastane fibres is much better than that of the rubber threads previously used, which were particularly susceptible to oxidation. As already described for wool, elastane fibres also appear to suffer from cumulative damage. For example, wet processing treatments during dyeing and finishing which normally have tolerable effects lead to noticeable fibre damage after intensive presetting.[228] Dyeing of polyester/elastane blends, often also with a wool component, is relatively problematical. Elastane fibres are damaged above 115 °C (as is wool also) (softening of the elastane and loss of elasticity[227]). The alternative, namely to dye with carriers at lower temperatures, is also difficult because many carriers can cause swelling of elastane fibres and thereby reduce their elasticity. During heat setting of piece goods the elastane fibre component is irreversibly damaged by too high temperatures and tension together with excessive duration (stretching without recovery).[227] Recommendations for finishing treatments for elastic textiles have been published, for example by Naroska[231] and Hueber.[230]

A frequent cause of faults is silicone stains on textiles containing elastane. During primary spinning elastane fibres require 2–6% of spinning oils,[226] this being 6 to 8 times more than on other yarns. These oils contain a large percentage of silicone oil, which in a normal pre-scour (without special detergents) is only partially removed. This is particularly a problem with cotton/elastane blends because cotton also retains a large amount of silicone. The silicone residues assist the thermomigration of dyes, which can lead to poor crocking fastness and the dyes can be deposited as stains on the fabric. Silicone stains are often first noticed after coloration and are difficult to remove. Their detection is described in Section 8.6.1.

Identification and differentiation of elastane fibres

Elastic fibres can be easily recognized on account of their elasticity. A differentiation between elastane and rubber threads is seldom necessary because rubbber threads are hardly used now. In contrast to rubber, elastane dissolves in boiling dimethylformamide. In order to clarify some cases of damage it can be important to know what type of elastane fibre has been used. Initial differentiation can be made under the microscope in the longitudinal view, and especially in cross-section, both can show large differences.[226] On account of their differing resistance to hydrolysis and oxidation it can be of particular interest to determine whether the fibre is of the polyether or polyester type. A microscopic differentiation is possible by embedding in 2 N methanolic potassium hydroxide. The ester type breaks up

Table 8.17 Test methods for damage to elastane fibres[226–228, 233]

Method	Comments
Stress/strain behaviour Also as a simple manual method for determining elongation at break	For all types of damage, especially for analysing mechanical and thermal damage. Flat form of the curve shows loss of elasticity, decrease in tensile strength and elongation at break.
Hysteresis or tensile–elastic behaviour	Loss of elasticity and residual extension (set) with almost all types of damage. During textile production modified to such an extent that this method is not recommended for analysing damage in dyeing and finishing or in use.[227, 228]
Thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA)	Testing of the temperature dependence of the extension and shrinkage behaviour at low (TMA) or oscillating (DMA) yarn tension: glass temperature, elasticity and other parameters for exact differentiation of elastomeric fibres.
Heat distortion temperature, HDT	The HDT is the temperature at which a pre-tensioned elastane thread at a defined rate of heating reaches a certain extension (usually around 200 °C). Suitable for determining heat setting conditions and for testing thermal damage.
Hot breaking time	The time taken for an elastane thread stretched by 100% to break at 193.5 °C (usually > 20 s), especially suitable for analysis of thermo-mechanical damage.
Relative viscosity and average degree of polymerization	Quantitative analysis of chain degradation and degree of damage possible. Used for analysis of photo-chemical damage[229], also suitable for analysing other degradation reactions, for example by acids, alkalis, chlorine, exhaust gases or heat

within a few minutes as opposed to the ether type, where the thread structure remains.[233] Both types of elastane fibre can also be readily identified and differentiated by IR spectroscopy. The ester type is characterized by bands at 1730, 1220 and 1170 cm^{-1}, the ether type has a typical band at 1100 cm^{-1}.

Table 8.17 gives a review of the methods commonly used for analysis of damage to elastane fibres. They usually require a relatively large effort or high costs. There is a disproportional relation between the many possibilities for damage to elastane

fibres and the small number of simple detection methods known and suitable for this purpose. It would be helpful to have simple staining and solubility tests as well as microscopic methods similar to those used for studies of damage to wool, cellulosic and nylon fibres. The following methods should be tested for their suitability for detecting damage to elastane fibres:

- staining with basic dyes such as Rhodamine B, Methylene Blue and Oxycarmin. There will be greater affinity for these dyes if an increase in the number of carboxylic acid groups has occurred during damage to the elastane fibre, for example by hydrolysis of ester groups in the soft segments;
- staining with ninhydrin, which responds to amino groups, since these could be increasingly formed after damage (for example by hydrolysis or pyrolysis);
- solubility tests in dimethylformamide or dimethylacetamide, with a critical solution time (similarly to that with polyester);
- investigations by IR spectroscopy and thermal analysis, although these cannot be included under simple methods on account of the expensive instruments. However, many damage analysists have access to an IR spectrometer.

8.5.9 Analysis of damage to polyolefin fibres, especially polypropylene

Of the two polyolefin fibres polypropylene (PP) and polyethylene (PE), polypropylene has by far the greater importance. PP is the second most important synthetic fibre type after polyester and continues to grow at a remarkable rate.

PP fibres are relatively cheap. According to Schmenk and *et al.*[234] they are very resistant to acids, alkalis and organic solvents at room temperature. Damage can be caused by oxidizing substances, such as chlorine bleach and concentrated nitric acid at higher temperatures, as well as hydrocarbons and chlorinated hydrocarbons above 100 °C (swelling and dissolution). Their abrasion resistance is high. Tensile strength and extensibility can be varied within a wide range during fibre production. A great disadvantage of polyolefin fibres, which is particularly noticeable with PE fibres, is the large amount of deformation under stress, so-called creep. This is also the reason for their low degree of elastic recovery after compression, an important property with carpets. Further weaknesses are their low resistance to heat and light, especially UV light, which can lead to loss of strength. Heat stabilizers can increase the temperature for long-period thermal resistance from the usual 80 °C up to as high as 125 °C. Stabilizers to light and UV enable PP textiles to be used outdoors. Unmodified PP fibres cannot be dyed by the usual dyeing methods. Dope dyeing with pigments gives high fastness but is only economical for large quantities. For analysis of damage it is important to know that PP fibres exist in many further modifications, such as:

- those based on Ziegler-Natta catalysts (ZN-PP) or on metallocene catalysts

(mPP), the latter having a more uniform chain length and being more highly isotactic with a melting point about 15 °C lower;
- as microfibres and hollow fibres;
- antimicrobial, flame-resistant or antistatic modifications.

Recently elastic polyolefin fibres have also been introduced (generic name: lastol), they are cross-linked and stable at temperatures up to 220 °C and above.[235] High-tenacity polyethylene fibres, with ultra high molecular weight (UHMW-PE, Dyneema) have been available for some time; they are produced by a gel-spinning process at high dilution.

This review serves to illustrate that PP fibres are fairly commonly damaged by heat and light, by mechanical overstraining and long periods of strain and by oxidation, including photo-oxidation. PE fibres are even more sensitive to heat than PP fibres, but are less damaged in principle by light and oxidation. This last point is difficult to generalize about because their behaviour is strongly dependent on the type and amount of added stabilizers to light and oxidation.

Mechanical damage to polyolefin fibres

Polyolefin fibres have relatively good abrasion resistance. Their tensile strength and extensibility can be varied over a wide range by means of the chain length and draw ratio. An extreme example is high-tenacity UHMW-polyethylene Dyneema, which is used, amongst other things, for bullet-proof vests. Mechanical damage to polyolefin fibres can occur at many stages during processing and also in use. Sewing damage to PP knitted goods has been investigated by Wang *et al.*[236] Mechanical damage during needling of PP nonwovens has been described by Qian and Chu, who investigated the dynamic creep behaviour and ageing of PP geotextiles as a function of the type of bonding of the web.[237] Residual extension and deformation after longer periods of strain are also typical types of mechanical damage to polyolefin fibres. Mechanical damage can be detected by the usual physical testing methods and under the microscope, preferably in the form of surface film imprints.

Thermal and thermomechanical damage to polyolefin fibres

Low temperatures for the softening ranges of PP (150–155 °C) and especially for PE (105–120 °C) are the reason for many cases of damage caused by excessive heat, often combined with mechanical stress, that can occur in heat setting, sewing or pressing. According to Chidambaram *et al.*[238] the loss of strength in PP fibres during thermal bonding of nonwovens is due more to the temperature than to the mechanical strain. With the aid of the methods for thermal analysis (DSC, TGA, TMA, see Section 8.4.5) polyolefin fibres and their modifications can be easily identified. The melting range enables, for example, differentiation between low

density and high density PE (LD-PE and HD-PE) as well as ZN-PP and mPP. By comparing the measured value for the latent heat of fusion with the theoretical value, the purity of raw and recycled material can be determined. The degree of crystallinity can also be evaluated in this way. The stability to oxidation of PE fibres can be determined with isothermal DSC at 200 °C by measuring the time (oxidation induction time OIT) until commencement of oxidation (onset of the exothermal reaction). Buchanan and Hardegree investigated the influence of spinning conditions on the shrinkage behaviour of PP fibres by means of TMA.[180] With PE a thermal memory has also been noted, an effect which is particularly interesting for the analysis of damage. Thermal treatments cause a so-called melting gap, usually just before the DSC melting curve reaches its maximum. This effect has been explained by the fact that during thermal treatments the amorphous areas of the fibre form crystallites with a sufficiently high melting point. After complete melting of the fibre this thermal prehistory is erased, so that a comparison of the curves for the first and second run of the DSC can improve the validity of the interpretation.

Thermal degradation of PP fibres can be analysed quantitatively by viscosimetric determination of the chain length in decalin at 135 °C. More common is the determination of the melt flow index MFI, which can be carried out in an automated form.[234] The fact that marked damage is possible by thermolysis is demonstrated by the decrease in the chain length of PP granulate or PP chips to about half their initial value during melt spinning of PP fibres.[239] The molecular weight of PP fibres is given as 150 000–600 000, but usually 200 000–300 000,[234] this corresponds to an average degree of polymerization of 3600–14 300, or usually 4700–8300.

Damage by light and oxidation to polyolefin fibres, including photo-oxidation

The relatively high sensitivity of PP fibres to light and oxidation arises, amongst other reasons, from the fact that radical intermediate products are energetically favoured. The methyl groups on the tertiary carbon atom are weak electron donors. They thus stabilize free electrons on the tertiary C atoms. Cleavage by radicals of the C–H bonds of the tertiary C atoms is thus favoured. The necessary activation energy can be supplied by heat (thermolysis), light (photolysis) or by reaction with free radicals. In the presence of oxygen, peroxide radicals are formed at the tertiary C atoms in the chain. These react with other tertiary C–H groups, forming hydroperoxides and new PP radicals. The hydroperoxides decompose with chain cleavage, whereby carbonyl and alkene structures are formed.[240] Heat stabilizers are radical catchers, for example sterically hindered phenols or phenol-free compounds. Phosphites, for example, which reduce the peroxides, are used as antioxidants. Hindered amine stabilizers, HALS, can be used as UV stabilizers.[234]

The above-mentioned types of damage are manifested by chain degradation and yellowing, accompanied by brittleness and loss of strength. They can be detected

and analysed by the appropriate methods described in the two preceding sections. However, loss of fibre strength often does not correlate with viscosity or chain length. Martin explains this by the supposition that with damage by light the amorphous areas are preferentially degraded.[241] Pezelj *et al.*[242] have investigated damage to PP fibres by ozone and light, whereby low concentrations of ozone sufficed to cause brittleness, loss of strength and increase in hydroperoxide content.

Hydrolytic damage to polyolefin fibres

Because of the continuous carbon chain and the lack of sensitive side and end groups, polyolefin fibres are particularly stable to hydrolysis. They are stable even at extreme pH values, if other factors are not involved. Thus PP is soluble in hot, concentrated nitric acid because it also acts as an oxidizing agent. Polyolefin fibres are not soluble in cold concentrated sulphuric acid (that is, at room temperature). The solubility groups developed by Stratmann[8] for the identification of fibres (SG I to VI, see Table 8.18) clearly show the differing resistance to acids of the fibre types. Only SG I is an exception. Here, the cellulose fibres, which would interfere with a further division according to increasing acid stability, are identified with cuoxam. Cellulose acetate and nylon fibres, which already dissolve in glacial acetic acid, are relatively sensitive to acid (SG II). Acrylic fibres need cold concentrated nitric acid to dissolve (SG IV). Even more resistant to acid is polyester, which dissolves in cold concentrated sulphuric acid (SG V). All types of fibres which are not soluble in this acid are grouped together in SG VI. Here the polyolefin fibres can be found together with chlorovinyl fibres and polytetrafluoroethylene, which all have a continuous carbon chain and acid-resistant substituents.

Further types of damage to polyolefin fibres

Polyolefin fibres are themselves very hydrophobic and therefore absorb hydrophobic substances such as oils, greases and waxes. The intermolecular bonding, which is not very strong in the first place, is decreased further, leading to a loss of strength. A number of organic solvents also cause damage by swelling or dissolution, although these generally only take place at higher temperatures (> 100 °C). Formation of clumps with PE and PP fibres, without complete dissolution, occurs with boiling dimethylformamide, cyclohexane, γ-butyrolactone, benzyl alcohol, phenol and *m*-cresole. Both polyolefin fibres are dissolved by boiling tetrachloroethylene and tetrachloromethane, mono- and dichlorobenzene, amyl acetate, toluene and xylene.[8] In this way PP contamination (packing material) can be dissolved out of wool with perchloroethylene at 115–118 °C. After repeated dry cleaning with perchloroethylene or laundering, PP textiles show increasing ageing and an increased content of peroxide groups, probably caused by washing out of stabilizers.[242] Chlorine damage to PP fibres is also known, for example

Table 8.18 Classification of manufactured fibres in solubility groups (SG) according to Stratmann[8, 123]

SG	Solvent	Type of fibre	Abbreviation
I	Cuoxam (under the microscope)	Cellulosics	CO, CV, CC, CD, CLY
II a	Glacial acetic acid, cold	Diacetate, triacetate	CA, CT
II b	Glacial acetic acid, boiling	Aliphatic PA (nylon) fibres, polyurea, poly (lactic acid)	PA 6, PA 6,6, PA 4, PA 11, PA 12, PUA, PLA
III	6 N Hydrochloric acid	Vinylal fibres (polyvinylacetal)	PVA+
IV	conc. Nitric acid	Acrylic fibres, poly-(phenylene sulphide) (elastane fibres usually disintegrate, Tohalon dissolves)	PAN PPS EL (PUE) CT (Tohalon)
V	conc. Sulphuric acid, cold	Polyester with modifications	PET, PES(V), PES(G), PES(A), PES(K), PEN, PTT, PBT
		m-aramid,	*m*-AR
		polyimide,	PI
		poly(ethylene naphthalate),	PEN
		polyetherketone,	PEK
		poly(glycolic acid),	PGA
		some multipoly-merisate fibres and alginate	PVM(V), PVM(D), AL
V and VI	Partially soluble in cold conc. sulphuric acid	*p*-aramid, polybenzimidazole, Kynol, Tenax, Kermel	*p*-AR, PBI
VI	Insoluble in the solvents of SG I to V	Polyolefin fibres,	PP, PE
		polytetrafluor-ethylene,	PTFE
		chlorovinyl fibres,	PVC, PVC+, PVD
		multipolymerisate fibres,	PVM(D), PVM(Ac)
		polycarbonate fibres,	PC
		modacrylic,	MAC, PAM
		fibres from regenerated proteins	e.g. KA

Ulmann has described damage caused by sodium hypochlorite, whereby the strength decreased markedly and the PP fibres were no longer soluble in decalin.[243] Damage to PP fibres by aerial pollution was investigated by Cunko and Pezelj, whereby strength and isotacticity decreased, even without the effect of light, and the content of hydroperoxide groups increased.[244]

Unfortunately there are not enough simple methods of detection of damage to

polyolefin fibres. On the other hand there are also not so many cases of complaint, based on damage to PP and PE fibres, which are difficult to analyse, although these fibres are increasingly present in all three segments of the textile market. They are particularly important in the field of technical textiles, including nonwovens (for example hygienic, agricultural, building, industrial, protective and medical textiles, geotextiles, vehicle interiors, packing materials, filters, ropes) but also in home furnishings and household textiles (carpets, furnishings, bathroom accessories, cleaning cloths). They are also to be found in some clothing areas (for example sportswear, functional underwear, socks).

8.6 Special types of damage and their analysis

As a supplement to damage analysis in relation to specific fibres this section deals with important types of causes of damage. Mahall divided his book[5] entirely on the basis of types of damage, namely:

- chemical damage
- mechanical damage
- thermal and thermomechanical damage to synthetics
- streaks and bars in textile fabrics due to yarn differences and technological reasons
- causes of the formation of tight threads and their effects
- defects caused by deposits and encrustations on the fibre material
- other defects in the quality of textiles
- microbiological damage to fibres.

If the titles of this book *Chemical Testing of Textiles* and this chapter 'Chemical analysis of damage to textiles' are taken narrowly only chemical types of damage and chemical testing methods for other types of damage should be discussed here. But there is no clear-cut borderline and a too narrow treatment would not do credit to the broad subject of chemical analysis of textile damage. Thus, for example, technological faults due to using mistaken material or caused by foreign fibres can often be most simply clarified by chemical identification of the fibres. In practical damage analysis, physical methods are often combined with chemical ones, for example microscopic staining, swelling and dissolution reactions or colour reactions and derivatization in chromatography. IR spectroscopy, a physical method, requires chemical knowledge for the identification of fibres, textile auxiliaries and stains. The selection of special types of damage causes described here is restricted to the investigation of deposits on fibres, especially stains, the detection of the causes of streaks and barriness, and to biological damage.

8.6.1 Analysis of unwanted deposits on textiles

Since these deposits are usually not distributed evenly on the fibres and textile

fabrics they often consist of more or less large stains, spots or streaks. They are one of the most frequent causes of damage (see Section 8.3.3). Deposits of lime or PET oligomers show up as greyness on white fabric or light-coloured structures on dyed fabric. The identification of PET oligomers is described in Section 8.5.5. Lime is soluble in acid and can be washed off with, for example, acetic acid or sequestering agents. Calcium ions can be detected by precipitating them as oxalate.[7] Mahall has described a simple microscopic detection method for lime.[5] The textile sample is ashed and the residue taken up in a little 2 N hydrochloric acid. A small drop of this solution is placed on a microscope slide and next to it a small drop of 2 N sulphuric acid p.a. is placed. A cover slip is then laid carefully over both drops. If lime deposits are present needle-shaped crystals of calcium sulphate can be seen in the mixed liquids under the microscope.

Detection of oil, grease, paraffin and wax deposits

These hydrophobic substances can often be marked and detected by staining with oil dyes. Mahall[5] and others recommended the oil dyes Sudan Red 460 and Sudan Red 7B (C.I. Solvent Red 19), Fat or Oil Red 5B (C.I. Solvent Red 27) and Duranol Blue PP (ICI). Nowadays Sudan Red 7B and C.I. Solvent Red 27 as Oil Red O are available both from Aldrich and Fluka. According to Mahall about 1 g l^{-1} of oil dye is used to prepare the oil dye reagent for macroscopic tests. The dye is first stirred with 10 ml methanol for about 3 min, water warmed to 40 °C is then poured over this and 10 ml of concentrated hydrochloric acid is added. The sample under investigation is treated for about 10 min at 40 °C with this reagent, if staining is faint the time can be lengthened or the temperature increased to 70 °C. It is recommended that a flat vessel be used in which the sample is not pressed or creased. The sample is then rinsed thoroughly for 3 min under running water and dried at a maximum of 100 °C. Oily deposits can then generally be distinctly seen on account of their coloration. For microscopic investigations it is recommended that a solution of 3–5 g of oil dye in 50 ml ethanol, to which 50 ml of glycerine is added, be used as an embedding agent. In this way, oil or grease contamination which has diffused into the fibre (for example into PET or PP fibres) can be seen.[5] A similar recipe for microscopic detection of oils was given by Bigler:[13] three parts by volume of alcohol and one part water are mixed and saturated with oil dye. One part by volume of glycerine is then added to this solution. Peter[24] modified this recipe by doubling the amount of glycerine.

Even more sensitive than these staining tests for detecting grease and oil contamination is an imprint on thermoplastic films (see Section 8.4.6). During production of the imprint, hydrophobic deposits diffuse into the film and can usually be easily recognized by the local cloudiness they cause. The natural waxes of cotton do not interfere here because they are evenly distributed. Spots caused by pigments or disperse dyes are also transferred onto the film imprints and are then easier to investigate microscopically.[5]

In addition, grease, oil, waxes and paraffins can be detected by IR spectroscopy, either by a direct comparison of spectra from the stain and from unstained areas, with the possibility of subsequent subtraction of spectra, or after extractions and concentration by spectroscopy of the extraction residue.

In the latter case it is also recommended that extracts from a stained area be compared with a similarly sized area without stains. Long alkyl chains are characteristic of these compounds, which can thus be identified, for example, by the intensive C–H bands just below 3000 cm^{-1}. Apart from these stretching bands, intensive deformation bands at about 1500 cm^{-1} and a weaker band at 720 cm^{-1} are also found, the last one being characteristic of a chain structure with more than three methylene groups. The extracted fats and oils can also be analysed more exactly by thin layer chromatography (see Section 8.4.3). An indication of oil deposits is given by fluorescence in UV light[43] on the fabric (if it has not been optically brightened) as well as in the extraction residue and on the TLC plate.

Detection of unwanted film-like deposits

This kind of deposit interferes by causing, for example, a harsh handle, dye reservation or other optical effects, and also chalky streaks when the fabric is scratched. Typical causes are size residues, printing paste thickeners which have not been washed off or unevenly distributed finishing agents. They can usually be identified with the aid of film imprints, since they often show up in the form of flat cakes or crumbly deposits.[5] Film-like deposits usually cause a somewhat blurry appearance of the surface imprint, for example blurred scale structures in wool. Size residues can be detected by colour reactions on the fabric or in an extract (combined with precipitation reactions).[245] An advantage of the imprint method here is that the textile fabric can be investigated without being separated into individual fibres, which would destroy film-like deposits. However, deposits can sometimes be better analysed by means of staining tests and the preparation of cross-sections of yarn or fabric. Mahall[5] investigated fibre adhesion and size residue (including distribution of size and over-sizing) in this way.

Detection of other deposits in the form of stains

The high frequency of stains as a manifestation of damage was mentioned in Section 8.3.2. The reasons for the occurrence of stains are very numerous. Several examples of stain analysis were described in Section 8.4.4 and the typical method of approach in Section 8.3.5. Löffel[74] has also described the comparative selective extraction of stains with subsequent identification, preferentially with TLC and IRS. In Section 8.4.3 details of TLC analysis of stains caused by grease and oil or polyester carriers are presented. In Section 8.4.4 information is given on the identification of silicone stains and fluorocarbon deposits using IRS. The detection of silicones with fluorescence microscopy is described in the literature.[42]

Table 8.19 Types of stain and the processing stage where they occur[3]

Occurrence	Type of stain and cause
Production of yarns and fabrics	Oil and paraffin stains (usually wet paraffinizing), often together with abraded metal, which darkens the stain Small spots due to fly and clumps of foreign fibres
Pretreatment	Residues of size (usually widely distributed on the warp, blurry warp streaks) Residues of sizing auxiliaries such as paraffins, oils, waxes, fats, softeners and smoothing agents Preserving agents (often inhibit enzymes) Silicone stains from antifoaming agents Acid and alkali stains
Dyeing	Antifoam stains based on mineral oils or silicones, sometimes also containing silicic acid (see Section 8.4.4) Stains caused by PET carriers and oligomers Precipitation of auxiliaries with opposite charges Lime and phosphate deposits Spots due to undissolved or precipitated dye Stain-like lighter dyeing due to air bubbles in wound packages Stains due to drips of water or chemicals (change in dye affinity)
Finishing	Silicone stains (often darker, from softening, stretch or hydrophobic finishes and antifoaming agents) Softeners, hydrophobic agents, flame retardants and other finishing agents which have precipitated due to faulty treatment conditions, usually colourless and uncommon
Storage and transport	In addition to soiling, stains due to yellowing, caused by antioxidants in plastic films and cartons together with nitrous oxides in the air (combustion engines) and cationic substances[246]

Schindler *et al.*[3] have published a comprehensive review of the relevant literature and of types and causes of stains formed during production and dyeing and finishing of textiles (see Table 8.19). In this review the fibre-dependent limits of detection by IRS of stains caused by mineral oil and paraffin, sizes based on polyacrylate, fabric softeners and polyester carriers are described. Stains which arise during textile usage are often easier to analyse because the circumstances of their occurrence are mostly known or are fairly easy to determine.[247] Illing-Günther and Hanus have described a stain analysis with microspectrophotometry.[37]

As well as the most common form of stain, namely that caused by deposits of foreign substances, there are two further kinds. One occurs owing to localized effects of chemicals which modify the fibres in such a way that they reflect light or take up dye differently, for example splashes of caustic soda on cellulose. For the

detection of this chemical damage the fibre-specific methods of analysis described in Section 8.5 can be used. In addition, residues of the chemical which caused the stain can sometimes be detected directly on the fabric or in an extract. With the third type of stain arising as a result of mechanical influences, the local reflection of light is modified in such a way that a manifestation of damage in the form of a stain occurs. This can best be detected under the microscope, for example by starting with a stereomicroscope and different types of illumination.

Identification of the substances which caused the stain is usually the prerequisite to determining who is responsible, who carries the blame and how best to repair the damage. Optimal removal of the staining substance requires knowledge of the fibre involved in order to avoid further damage to the textile during stain removal. As a rule small individual stains are removed by stain removing agents. With larger or more frequent stains, dry cleaning or scouring, depending on the type of stain, is carried out with possible addition of surfactants, sequestering agents, enzymes, acids or bases.

8.6.2 Detection of the causes of streaks and barriness in woven and knitted fabrics

Streaks and bars are second only to stains as one of the most common manifestations of damage. They occur in numerous forms,[248] for example:

- parallel or oblique to the warp or weft direction
- with a repeat pattern or irregularly
- in bands or bars
- running along short or long sections of thread or across differing numbers of wales or courses.

The cause of the fault can usually be clarified here with the aid of a microscope and film imprint. The causes are as numerous as the forms the faults take. This is illustrated by the 24 relevant examples in Mahall's book[5] and the 10 examples in Goebel's publication on the formation of streaks.[248] As a rule streaks and bars are caused by faults in textile production. Examples of this are:

- mistaken material, usually use of the wrong yarn
- differences in yarn count, yarn bulk, yarn twist, thread tension, plying, pile opening, hairiness, inhomogeneous blends
- faults during texturizing or mercerizing
- with pile fabrics, more deeply incorporated tuft rows or differences in needling.

Faults arising from dyeing and finishing are also known:

- wet abrasion and other types of mechanical damage in jet dyeing machines
- plaiting-down faults in cotton pretreatment: squashed fibres, notches, cracks and splits in the fibres which occur when the goods, swollen with alkali, are packed down too densely

- greasy deposits and resinated mineral oil, which have a carrier effect on polyester, leading to deeper dyeing.

8.6.3 Detection of biological damage

As well as damage to wool by the larvae of clothes moths and carpet beetles, as discussed in Section 8.5.2, microbiological damage to fibres is of interest here. This damage is usually caused by fungi and, less commonly, by bacteria. Bacterial damage to wool is known to occur, it causes fibre degradation and an unpleasant odour. Bacteria often live in symbiosis with fungi on fibres. Both types of microorganism can feed on natural fibres and many types of textile auxiliary based on natural substances, for example sizes, spinning oils, fabric softeners, starching agents and stiffening agents, printing paste thickeners and other types of digestible agents. Synthetic fibres are not completely resistant to microorganisms, for example elastane fibres and polyurethane coatings can be damaged by them. Humidity, warmth and time favour microbial damage. It leads to loss of strength and occasionally to mildew stains, unpleasant handle, odours and loss of colour. Microbial damage frequently occurs after lengthy transport of goods packed when damp or containing size, or when damp fabric is stored overnight or over a warm weekend in a textile dyeing and finishing mill. Antimicrobial treatments can prevent such damage but it still occurs repeatedly in practice.

Musty smelling mildew stains are often a first indication of fungal attack. They occur particularly frequently on cellulosic textiles and their colour varies depending on the type of fungus, from black to olive green, reddish brown to orange and yellowish brown. According to Nopitsch[249, 250] actual detection of the fungus is best made under the microscope by staining with Lactophenol Blue reagent. The Cotton Blue dye, which gave this reaction its name, is no longer available. This is also the case for the replacement dyes Water Blue B[13] and Lanaperl Blue RN 150[5] (C.I. Acid Blue 281). Mahall[5] recommends the still available substitute Telon Blue AGLF (DyStar) and in addition he mentions a 0.5% solution of Methylene Blue as a possible alternative.

Preparation of the Lactophenol Blue reagent: Solution A consists of 20 ml of lactic acid, 20 g of phenol, 40 ml of glycerine and 20 ml of distilled water. Solution B consists of 2 g of dye in 100 ml of distilled water. The reagent is prepared by mixing 50 ml of solution A and 10 ml of solution B.

Method for Lactophenol Blue staining: several fibres from the sample are cut to a suitable size, embedded directly in the Lactophenol Blue reagent and covered with a cover slip. Since the reagent itself is dark blue the stained mycelium threads and spores of the fungus cannot always be easily recognized. For this reason after at least 10 min and up to a maximum of 30 min the reagent solution is sucked out by a strip of filter paper (rider) bent upwards in the middle, which is placed at the side of the cover slip. At the same time drops of solution A are placed on the opposite side of the cover glass so that the sample does not dry out. This rinsing

treatment, which increases the colour contrast, is critical because if the solution is drawn through too quickly fragments of the fungus can be washed away. On the other hand the blue-stained mycelium threads and possible spores and bacteria colonies only become clearly visible after this rinsing treatment. This detection method becomes more difficult and requires much patience and preparative skill if the sample under investigation was washed after the microbial attack, so that only traces of the microorganisms can be found.

Mildew stains can be removed by intensive bleaching. Previously, chlorine bleach was regarded as the best method for this with many types of fibres, except wool, silk, nylon and elastane. Overdyeing to black was the only solution for fibres sensitive to chlorine. In all cases the more or less marked loss of strength, depending on the degree of damage, remained a problem. In Mahall's book[5] there are many well-illustrated practical examples of fungal damage and also three examples of bacterial attack on wool. To analyse this type of damage to wool, the book by Doehner and Reumuth[150] can also be recommended.

Bacterial damage to wool is also favoured by warmth, humidity and time. A neutral to weakly basic environment supports bacterial growth; low pH values inhibit it. Level souring-off of the fabric is the simplest method of protection against bacteria when wool has to be stored moist for longer periods of time. With wool not only the fungi and bacteria cultures are stained with the Lactophenol Blue reagent but also the damaged areas of the wool are clearly and specifically more deeply stained. This is helpful in damage analysis when the actual microorganisms have been washed out during scouring. In bacterial damage, longitudinal striations first appear on the wool fibre and the spindle-shaped cells of the orthocortex are then laid bare. This results in a characteristic appearance of bacterial damage.[5] Only after further, more extensive damage are the spindle cells of the paracortex laid bare, since these contain a greater concentration of stabilizing disulphide links. Since wool is also fibrillated by acid damage, it is recommended that this be differentiated from bacterial damage by carrying out the KMV reaction with ammoniacal potassium hydroxide (see Section 8.5.2). Macroscopically, stains caused by bacterial attack appear lighter because the fibrillation leads to a greater scattering of incident light.

8.7 Special applications and particularities of textile damage analysis

8.7.1 Forensic application of textile damage analysis methods

Forensic science and its application in criminal investigative technology are used to help clarify criminal cases. Textiles can play an important role here, usually in the form of clothing but also including household and automobile textiles, furnishings and in rare cases also technical textiles, for example strings and ropes used to

bind, strangle or hang victims. Textiles used by criminals can also include stocking masks, gloves, bags, sacks or adhesive tapes. Sometimes it is possible to solve cases of murder unequivocally with the aid of a few typical fibre traces transferred from the murderer to the victim and/or vice versa.

Although the aims and tasks of textile damage analysis are usually less dramatic, the methods used are often the same as those in textile-related criminal investigative technology. For this reason, colleagues from the German Federal Criminal Bureau have been present at all the Münchberg symposia on textile damage analysis. An important difference from textile damage analysis is that in criminal investigations there is often very little fibre material available. In addition, most of this material has to be retained unchanged as evidence and possibly as material for a further expertise. Therefore, in such cases non-destructive methods of identification and further analysis are preferred. Dissolution, melting, staining and so on are only permissible when larger samples are available. Microscopy with its many modifications such as comparative, polarization, interference, fluorescence, thermo- and FT-IR microscopy play a dominant role as well as microspectrophotometry and scanning electron microscopy with energy dispersive X-ray spectroscopy.

In order to identify fibres non-destructively by polarization microscopy the birefringence is determined.[35, 36] This is based on the refraction of polarized light in the crystalline areas of the fibre. The birefringence is the difference between the refractive index parallel and the refractive index perpendicular to the fibre axis. For this method of fibre identification the birefringence is determined more easily via the retardation, using a Michel-Lévy Colour Chart. In this chart the retardation and the birefringence are plotted against the fibre thickness. For each type of fibre a straight line approximately passing through the origin and with a characteristic slope is obtained. Less common and more costly, but more accurate for criminal investigations, is the identification of fibres by interference microscopy. Here the refractive indexes of the fibre are determined parallel and perpendicular to the fibre axis. The unknown fibre can then be localized in a plot of these refractive indexes, where it can be identified by its correspondence to the values for known fibre samples.[251] Especially fine differences in crystallinity due to different speeds during spinning of polyester fibres can be detected by interference microscopy.

The methods mentioned above show that the effort required for cases of criminal investigation can be considerably greater than that for the usual analysis of damage to textiles. Both fields have the problem of obtaining representative samples. In damage analysis this will determine how conclusive and representative the detection of the damage or the specific changes in the fibres from the case in hand will be. Since there will always be a few stray fibres, sometimes as many as 100 samples have to be investigated in order to obtain a representative picture. This question of the strength of evidence based on a few investigated fibres is even more critical in criminal investigations because the result of the investigation is often the basis for the court's verdict. Therefore it has to be perfectly clear whether typical fibres, for example from the victim's or suspect's clothing, have been unequivocally

detected on a certain piece of evidence. From the many kinds of transferred fibres certain target fibres may be selected as evidence, such as:

- those with special properties (colour, type of polymer, morphology),
- synthetic fibres, which usually produce more solid evidence than natural fibres,
- fibres which are very easily transferred and can also distribute themselves in the environment of the victim or suspect,
- fibres which are to be found in the most relevant places (for example underwear in cases of rape).[252]

It is essential for the court to know how highly the results based on fibre traces are to be rated as evidence. In order to assess the evidential value of transferred fibres their frequency has to be taken into account as well. This so-called degree of discrimination is obtained from studies on fibre population (frequency of occurrence at certain places or on certain objects) and from databases, which, for example, give information about the frequency of certain types of fibres in the relevant types of clothing.

It is also interesting in damage analysis to know which fibre characteristics are determined in criminal investigations. Typical characteristics are:

- the morphology, such as length and thickness and their distribution, fine structure and cross-sectional shape,
- then the chemical basis, including possible types of modification, especially with acrylic and polyurethane copolymers,
- the degree of delustring including the particle size and distribution of these pigments,
- the state of finishing, including method of coloration and type of dyes and finish,
- characteristics of textile care such as wet laundering or dry cleaning,
- typical traces of use such as wear, ageing and soiling.

The variety of available methods of investigation is usually greater for synthetic fibres than natural fibres. With cotton and wool an exact allocation is often only possible on the basis of their dyeing, which is analysed on single fibres using a microspectrophotometer, with similar results to colour measurements in a textile mill. If the amount of sample is a little larger the dyes are also identified by means of TLC and HPLC. Thus, in the case of a murderer who had used a red acrylic scarf it was not only possible to determine the scarf manufacturer and the dyeing mill but also to show that the dyeing recipe used for the suspect's scarf and that for the sample scarf used for comparison were different.

A special case of fibre identification involves vehicle accidents with fatal injuries to the occupants. The high pressure of impact causes such a high frictional heat that fibres are embedded in plastic surfaces which are momentarily softened and the fibres are retained there after the plastic cools down. With these traces, known as fusion marks, it is possible to reconstruct where the passengers were

sitting and to determine who was driving. Fibre traces on the seats are not so conclusive because they can have gathered there over a longer period of time.

The criminal investigator attempts to use the characteristics of fibre traces and their environment to obtain a degree of certainty as great as possible for the evidence of fibre transfer and its conclusiveness and, in the long run, whether with this evidence the suspect can be found, incriminated or exonerated. Extensive literature is available on forensic analysis, for example from Grieve.[59, 253, 254]

8.7.2 TESS, an expert system for textile damage analysis

Another particularity of textile damage analysis is the expert system TESS. This abbreviation stands for Textiles Experten-System für Schadensfälle (Textile Expert System for Cases of Damage). It will be briefly described here because this enables an interesting survey of the method of approach and uses of such systems as well as giving an idea of the complexity and problems of damage analysis in textiles. TESS was developed from about 1993 by the Eidgenössische Materialprüfungs- und Forschungsanstalt (EMPA) in St. Gallen, Switzerland, in close cooperation with a dozen project partners and has been in industrial use since 1998.[255–258]

TESS is a Windows-based diagnostic system for all stages of textile production including dyeing and finishing. The knowledge gained from numerous experts was continuously structured and implemented in a knowledge base. This consists of a network of about 2000 nodes. The initial nodes of the network are five simplified manifestations of damage (stains, streaks, holes, surface differences and differences in handle). These are further sub-divided according to size, direction, frequency, colour and position of the fault. For an exact determination of the cause of the damage further investigations are requested, for example observation of the fault in reflected and transmitted light and possibly UV light, surface film imprint, determination of whether the fault runs parallel to the threads, determination of count and fastness or extraction. In the form of a dialogue TESS suggests further stepwise tests, delineates the area of possible causes and, if successful, names the cause of the fault and ways to repair it and avoid it in future.

Further advantages of TESS are that it supports and relieves experts during damage analysis, and is especially useful in training new staff. It is always available, it considers very many possibilities and notes the steps taken (transparent logic). It serves to preserve the specialized knowledge of experts who retire and sometimes enables shorter diagnosis times and earlier recognition of the cause of faults. Disadvantages of TESS are that until now it has mainly been successful with faults arising from textile production and it appears to be limited in its suitability for the numerous types of damage connected with textile dyeing and finishing. In spite of the large amount of work invested in its development, much more experience has to be included. Since this continuing effort appeared to be too time-consuming and expensive, further work on this difficult project ceased in 2002. In

the long run TESS was not able to cope with the enormous variety of cases of damage in textile dyeing and finishing, the complexity of the manifestations of damage and, in particular, their causes. On the other hand this emphasizes the importance and illustrates the performance of experienced damage analysts.

8.8 Concluding remarks

The previous section again shows the great variety and complexity of damage analysis on textiles in general and textile chemical damage analysis in particular. These challenges correspond to the demands made on damage analysts in terms of broadly based, thorough knowledge, great experience and the right combination of logical and intuitive approaches depending on the problem at hand. In addition, these experts require many kinds of information, not only concerning the particular case of damage but also on approaches and solutions to similar cases. Private collections of cases of damage, study of the literature and exchange of ideas with colleagues are always helpful. Useful ideas (sometimes generated just by aside comments), that help in interpreting one's own work can arise while reading the many published cases of damage in practice. Well-known experts have described in these publications their often very individual approaches based on their particular experience in analysing textile damage. Occasionally they are honest enough to confess that in spite of much effort a case could not be solved under the given circumstances. Compared to this, the results of a database research on damage analysis of textiles were rather disappointing. Only a small percentage of the finds proved to be useful. Presumably the choice of keywords when preparing the abstracts was not sufficiently adapted to the contents and questions which are of interest here.

Many interesting details of the published examples of damage analysis did not fit into the structure of this comprehensive chapter, in particular they did not fit into the division into methods and damage analysis in relation to the type of fibre. In conclusion, reference is again made to the analogy used in the introduction to this chapter: by reading this chapter the temple-like structure and in particular its roof may have become more familiar to the reader and it is hoped that the foundations and columns have been sufficiently reinforced so that the ponderous roof now appears somewhat lighter.

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9

Water and wastewater analysis

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9.1 Introduction

This introduction provides an overview of water use and properties in textile manufacturing. The role of water in textiles, especially in wet processing, and sources and types of water, including raw material and wastewater, are briefly reviewed. Contaminants and impurities common to various types of water in textile manufacturing and the impact of contaminants are briefly described. In addition, water standards for various uses, for example, drinking water, raw water, process water, stream standards and wastewater are identified. Finally, general categories of water tests are listed and sampling, laboratory practices, limitations and potential improvements are noted.

The second part of this chapter presents descriptions of specific tests, including purpose and scope; accuracy, precision and correlation with key 'real-world' items and events; applicability and limitations; method employed; reporting and interpretation of results; and cost. Perspectives regarding anticipated future improvements in testing, with emphasis on issues pertaining to cost, accuracy and precision, correlation with 'real-world' items and events, applicability, analytical methods and sampling, and reporting and interpretation of results are also presented.

Finally, this chapter concludes with an annotated bibliography of references for the text as well as those that provide sources of further information and advice. Comments concerning the scope of various references are provided, to aid readers in their search for information regarding particular types of water or wastewater tests.

9.1.1 Water and textile wet processing – an overview

Textile wet processing is highly water intensive. Table 9.1 shows water consumption for processing of various types of textiles, based on a study of several hundred factories.

Water is used mainly in textile wet processing (preparation, coloration and

Table 9.1 Water quantities used in some types of textile wet processing (l kg^{-1})

Type of processing	Min	Av	Max
Wool finishing	4.2	11.7	77.6
Woven fabric preparation, coloration and finishing	5.0	113.4	507.9
Knit fabric preparation, coloration and finishing	20.0	83.4	377.8
Hosiery processing	5.8	69.2	289.4
Carpet processing	8.3	46.7	162.6

Source: USEPA, 1996.

finishing), and to a lesser extent in some other manufacturing operation steps in the textile production sequence, that is water jet weaving, synthetic fiber finishing, slashing, and the like. However, the vast majority of the water used is in the wet processing operations, and this is the focus of this chapter.

Water serves many purposes in textile processing, as indicated by Table 9.2.

In order to supply water to textile processes and other needs in textile manufacturing, there are many different water systems and sub-systems in a typical facility. These are listed in Table 9.3 below.

Perspectives regarding the importance of water

Water quality can have a significant effect on the efficiency and quality of textile processing. The effects may be positive or negative. Examples of interferences include the following (Smith, 1987):

- alkalinity or buffer systems: inhibits acid-catalyzed resin curing; increases hydrolysis rates for solutions of fiber reactive dyes;
- alum: flocking agent used in municipal water purification can be present as an impurity in water supplies, leading to filtering and spots on dyed goods, especially in beam and package dyeing;
- bacterial and organic chemical contamination: potable water supplies must be free of harmful contaminants;
- chlorine: many dyes, especially fiber reactive types, are severely degraded by the presence of residual chlorine used to disinfect drinking water, as is the common practice in municipal water systems;
- hardness: calcium and magnesium hardness ions cause precipitation of soaps, as well as saponification products (fatty acids) from scouring cellulosic fibers. Also, hardness causes precipitation of certain cellulosic dyes and causes difficulties in washing-off fiber reactive dyes;
- metals: iron, copper and other metal ions can cause undesirable decomposition of peroxide in bleach baths, resulting in foam, loss of bleaching effectiveness and pinholes in fabric. Heavy metals also can react with colorants, especially disperse dyes, to cause shade changes on dyed goods. In addition, less active

Table 9.2 Properties and roles of water in textile processing

Role	Comments or explanation
Solvent	Dissolves polar solutes to produce processing solutions
	Removes soluble impurities from substrates, washing
	Dissolves oxygen and other atmospheric gases (Henry's Law)
	Serves as media for homogeneous aqueous phase reactions
	Serves as liquid media for heterogeneous reactions and equilibria
	Serves as continuous phase for dispersions and emulsions
	Hydrates dyestuffs in solution, as well as dye sites in fibers
Chemical	Participates in hydrolysis and polymerization reactions
	Participates in buffer systems
	Promotes corrosion, especially if salt or acid is present
	Hosts galvanic reactions and ion exchange in metal parts
Electrical	Dielectric effects charge interactions in aqueous solutions
	Sorbed water increases conductivity and weight of substrates
	Humidity in processing areas reduces static electrical charges
	Immersed fibers can develop electrical charge (zeta potential)
Biological	Has no specific biological or nutrient activity per se
	Excellent medium for enzyme activity and biodegradation, e.g. of waste
	Develops osmotic pressure within cells, thus drives biological processes
	Dissolves nutrients
	Swells certain fibers
	Hosts biological growth
	Used for human consumption
Thermal	Efficient heat transfer fluid
	Cooling for machines, motors, bearings, etc
	Unusually large liquid range
	Relatively low viscosity, easy to pump, convective
	Conducts heat
	Steam (high enthalpy)
	Heat recovery from wastewater is common practice
Mechanical	Lubricant
	Transport substrates, e.g. in jet dyeing machines
Surface	Effective foaming medium, when used with surfactants
Polarity	Hydrogen bonding solvent
	Greater structure at low temperature, less structure at high temperature
	Hydrogen bonding structure can be chemically disrupted, e.g. with salt
Optical	High index of refraction, can make colors appear more intense
	Dissolves many dyestuffs (color)
	Can suspend particulates (turbidity)
Other	Moisture regain adds weight to textile substrates
	Fire suppression systems
	Environmental control in processing areas for comfort and efficiency

Table 9.3 Typical water systems/types in textile processing factories

Water type/system	Examples or comments
Process	Raw water from primary source
	Filtered/softened (cold) water, stored in clear wells
	Hot process water (preheated from heat recovery)
	Cold process wastewater
	Hot process wastewater (to heat recovery)
	Recycle/reuse process water (e.g. countercurrent wash water)
	Process bath reuse (e.g. dye/bleach bath, countercurrent washing)
	Chilled water
Waste treatment	Influent
	Sludge dewatering
	Effluent
Non-process	Non-contact cooling (recycle to clear well)
	Facility, equipment and implement wash-up
	Filter backwash
	Environmental (humidity) control in processing/storage areas
Laboratory	Distilled
	Deionized
	Aerated biological oxygen demand (BOD) dilution
Potable	For human consumption
Sanitary waste	From restrooms, food storage areas, etc.
Storm	Roof drains
	Parking lot runoff
Boiler	Feed water
	Steam
	Condensate return
	Blow-down
Recovered	From caustic or size recovery
	From wastewater treatment sludge dewatering
Closed systems	Cooling towers
Humidifier	Must be respirable quality

metal ions (e.g. copper) can undergo galvanic ion exchange reactions in metal plumbing systems to produce lead (from solder) and zinc (from galvanized pipe);

- organic chemicals: add color and/or odor to water, demand oxygen from solutions and can react with process chemistry, humans, enzymes, etc;
- reducing agents: reducing agents (e.g. oxygen demanding substances) such as dextrins can reduce and thereby decolorize dyes. This causes poor color repeats, e.g. in the pressure dyeing of polyester cotton blends with disperse and direct dyes;
- suspended solids: finely dispersed materials filter out in package and stock dyeing, producing sedimentary deposits on yarn and fiber;
- temperature: certain solutions used in textile processes are temperature

Table 9.4 Raw water quality in textile mills in the southeastern USA

Impurity	Average concentration for 10 mills studied
Ca^{2+}	12.9 mg l^{-1}
Mg^{2+}	3.8 mg l^{-1}
Na^{+}	36.0 mg l^{-1}
Alkalinity as $-CO_3^{2-}$	1.4 mg l^{-1}
Fe^{3+}	0.1 mg l^{-1}
Cu^{2+}	0.02 mg l^{-1}
Mn^{2+}	0.01 mg l^{-1}
Zn^{2+}	0.11 mg l^{-1}
pH	7.2 standard units

sensitive. For example, fiber reactive dyes hydrolyze more rapidly if made up hot, and mercerization solutions are more effective if the temperature is low.

The above are a few of the types of impact that water impurities can have on textile wet processes. There are many other effects, most of which are site-specific. Testing of water sources and processing solutions is a very important and often overlooked aspect of textile quality control. Typical data for contaminant levels in raw textile process water and in textile processing solutions are shown in Table 9.4.

9.1.2 Sources of water for textile operations

There are primarily four types of water sources for textile factories: surface water, groundwater, municipal systems and recovered/recycled water:

- Surface waters include such sources as rivers, lakes and shallow wells. These are typically contaminated with agricultural runoff, discharged pollutants from municipal and other waste treatment systems. In the USA, there are federal standards, as well as state standards that vary from state to state.
- Groundwater from deep wells typically contains particulates, suspended solids and dissolved solids, especially iron or hardness.
- Municipal or other public water systems typically have contaminants of two types: those that pass through the municipal purification system and those that are residues from the treatment process itself. Bacteria and turbidity are examples of the former. The latter may include materials such as alkalinity, alum, buffers, bromate, chlorine, chlorite, copper, haloacetic acids and trihalomethanes.
- Recycled and recovered water from reclaimed waste streams typically contain salt, surfactants, alkalinity, color and other contaminants that are common to the textile operation itself.

The impact of these contaminants on textile processes can be significant, as discussed above under ‘perspectives’. In the case of surface, ground or municipal

water, water quality is regulated in the USA by state, federal and sometimes local standards. Outside the USA, practices vary. An informative searchable database, maintained by the World Health Organization, contains detailed information on the water quality standards of many countries (http://www.who.int/water_sanitation_health/en).

9.1.3 Water standards

The quality of process water depends, of course, on its source. In the USA, sources are regulated as described below. (The state of North Carolina is used in the following as an example simply because it is a USA state with a significant textile industry. Owing to space limitations, it is not possible to include information from all 50 states.)

Drinking water standards (as produced by municipal systems) are set by the US Environmental Protection Agency (USEPA) and the individual states. National Primary Drinking Water Regulations apply to all public water systems and are designed to protect public health by reducing contaminants in drinking water (USEPA, 2000). National Secondary Drinking Water Regulations regulate contaminants that cause aesthetic effects (e.g. tooth discoloration, taste, odor, color). The EPA recommends these standards but does not enforce them. Some states have adopted them.

In the USA, groundwater standards are set at the state level. For example, the state of North Carolina regulates a list of 141 substances, as adopted by the North Carolina Environmental Management Commission. (North Carolina Administrative Code (NCAC) 2L.0202) In addition, nine other substances are listed in an interim standard (NCAC 2L.0202(c)) (North Carolina Administrative Code, 2002).

Stream standards are set by the states and, in some cases, may vary regionally within a state. Major contributors to contaminants in streams include agricultural and municipal storm water runoff and National Pollutant Discharge Elimination System (NPDES)-permitted point discharge sources. These are regulated by the USEPA under Title 40 CFR. For textile mills the relevant section is Part 410. This lists wastewater discharge limits for textile manufacturing sub-categories. North Carolina General Statutes (NCGS) for the protection of water resources are implemented by the NC Environmental Management Commission as well as the Department of Environment and Natural Resources (NCGS, 2000).

9.1.4 General types of water tests

There are many reasons for testing water, including compliance testing, process quality control, safety and health. There is one definitive source of water testing methods and that is *Standard Methods for the Examination of Water and Wastewater*, a joint publication of the American Public Health Association, The American Water Works Association, and the Water Pollution Control Federation

(Standard Methods, 1998). This reference contains methods of sampling as well as essentially every necessary water test in textile manufacturing. The most important types of tests in textile manufacturing include the following:

- Acidity, alkalinity, pH
- Biological content and contaminants
- Color and appearance
- Human and aquatic toxicity
- Metal ions
- Nutrients
- Organic materials, e.g. surfactants
- Oxygen demand
- Priority pollutants
- Solids.

Although seldom used in the textile area, the taste and odor of water can be assessed using standard methods. Specifically, these properties can be roughly quantified by the threshold odor method (2150 B) and the threshold taste method (2160 B) in which a water sample is diluted with pure odor- and taste-free dilution water until the odor or taste is just barely perceptible. This method is only roughly quantitative, owing to variances between observers, and time-to-time variations of the same observer. Samples collected for odor and taste testing should be collected and stored in completely full glass bottles with glass or tetrafluoroethylene (TFE)-lined closures. Storage should be under refrigeration. Odor tests at 60 ºC give increased sensitivity.

9.2 Samples and sampling

In addition to providing detailed procedures for sample collection for specific test methods, the 'Standard Methods' literature provides an overview of the general considerations associated with the collection and preservation of samples (Standard Method 1060). The principal goal is to ensure the collection of sufficient material for the test and representative of the material sampled yet small enough to be readily transported. A key purpose of sampling is often to determine compliance with regulatory standards. Methods developed for sampling include manual, automated and solid sorbent techniques.

9.2.1 General requirements

Samples are to be handled in a manner that prevents them from decomposing or being contaminated prior to their analysis. Consideration must be given to the filling of sample containers, collection and storage of composite samples, collection of samples containing metals, labeling of samples, description of sampling procedure, frequency of sampling, and the number and distribution of

sampling sites. Normally, sampling is to be avoided in areas of excessive turbulence, at weirs and at composite sites when volatile organic compounds (VOC) analysis is to be conducted. A summary of special sampling and handling requirements is provided in Table 1060:I of Standard Methods (1998).

Safety considerations

Adequate precautions must be taken when collecting and handling. This includes the use of protective apparel, gloves, safety glasses and well-ventilated areas. In the laboratory, sample containers are to be opened in a fume hood.

Types of samples

Test methods include specifications for the collection of grab samples, wastewater sludges, sludge banks, muds and composites. Advantages and disadvantages to composite sampling are reported in Standard Method 1060 B (Standard Methods, 1998). For instance, composite sampling is to be avoided when the components could undergo unavoidable changes during storage. Also, described in this method is the use of discharge-weighted methods. This type of sampling is associated with waters that vary in composition across their width or depth.

9.2.2 Laboratory practices, limitations and potential improvements

It is important to recognize that the various standardized methods developed for the analysis of water-based samples are not fail-proof. In this regard, the utility of specific methods and the reliability of test results are dependent upon the use of proper laboratory practices and understanding the limitations of a given method. This section is designed to illustrate some of the important issues in this area.

Chain of custody procedures

This aspect of the sampling process is critical to insuring the integrity of samples, from the collection stage to the reporting of test results. Consideration must be given to sample labels and seals, field and laboratory log books, chain of custody records, sample analysis requests, sample delivery to laboratory, scheduling of samples for analysis and disposal of samples following analyses.

Sample storage and preservation

While it is clear that is not always possible fully to maintain the original properties of a test sample, guidelines are provided in section 1060C of Standard Methods (1998) to help minimize errors introduced by improper storage and preservation of

samples. The key is to minimize the potential for volatilization or biodegradation between sampling and analysis.

Improper storage of samples can lead to changes in cation concentrations caused by adsorption on the surface of glass containers, leaching out of alkali from glass (thus changing the pH or alkalinity of samples), temperature-induced pH and dissolved gases changes, and changes in the chemical makeup of sample constituents caused by biological activity within the sample. Where possible, test samples should be analyzed on the day of collection. When this is not possible samples should be stored at 4 ºC.

Test method limitations

When employing a given test method, consideration must be given to the nature of the sample to be analyzed, as the presence of certain species either interferes with the detection of the target constituent or the concentrations of the target constituent may render a given method inappropriate. For instance, the presence of suspended matter and other ions that form precipitates with Ba^{2+} will give interferences leading to high results when making gravimetric determinations and colorimetric methods are preferred when non-turbid and colorless samples are employed.

9.3 Specific tests

Due to space limitations, all water tests that might be useful in textiles cannot be described here. The following selected tests are the ones that are most often used in textile manufacturing. These descriptions are abbreviated, and references are given in each case to more detailed explanations of the tests.

9.3.1 Physical and aggregate properties

There are a few very basic and general water tests that indicate important properties of water, but which do not detect the specific chemicals that are present. These include the following.

Alkalinity

The amount of alkalinity in water is typically determined by Standard Method 2320 (Standard Methods, 1998) and is reported as the equivalent amount of $CaCO_3$ in milligrams per liter. The purpose of alkalinity testing is to assess the presence of alkaline materials or buffer systems that might interfere with desired chemical reactions, or might promote underside reactions, as discussed in the introductory section of this chapter.

Samples are not filtered or altered in any way prior to alkalinity titration and all titrations are done at room temperature. Alkalinity may be measured as the amount

of standardized sulfuric or hydrochloric acid titer required to bring the sample to a specific pH end point. The pH may be detected by a well-calibrated pH meter, or by indicator materials. The most common indicators used are phenolphthalein (pH 8.3), *meta*-cresol purple (pH 8.3) or bromcresol green (pH 4.5). If the selected end point is pH 4.5, the alkalinity is reported as 'total alkalinity'. If the end point pH is 8.3, the alkalinity is reported as 'phenolphthalein alkalinity' regardless of the method used to detect the pH 8.3 end point. In the case of samples of very low alkalinity (less than 20 mg l^{-1}), the amount of standard acid required to decrease the pH by 0.3 units may be measured. This corresponds to a doubling of the hydrogen ion concentration. The amount of acid required to bring the pH to the desired end point then can be extrapolated from the result.

In some cases, color or turbidity of the sample may interfere with the visual observation of the end point color change if an indicator chemical is used. On the other hand, if a pH meter is used, certain surfactants, oils and the like can coat the pH probe and cause erroneous readings.

pH

pH, which is the negative logarithm of the hydrogen ion activity in a solution, is determined by a potentiometric method, using a well-calibrated commercial pH meter, as described in Standard Method 4500-H (Standard Methods, 1998). The purpose of pH testing is to detect the presence of the hydroxide or hydrogen ions that are required for various textile process, for example, fixation of fiber reactive dyes or acid dyeing of wool.

pH measurements must be done at room temperature, or using a temperature compensating instrument. Samples are not filtered nor altered in any way prior to measuring. The result is reported as a number, usually to one decimal place. Typically in textile processing solutions the pH value is between 4 and 10. Samples with pH values outside this range can be measured and reported but, owing to the logarithmic nature of the pH measurement unit, total alkalinity is often a better choice. In fact, even within the most appropriate working range for pH, alkalinity can reveal significant information which pH does not, for example, the presence of buffers. In some cases, certain surfactants, oils and the like can coat the pH probe and cause erroneous readings.

Temperature

Temperature measurements are used to characterize wastewater, as well as to make corrections for other tests that are temperature sensitive. Temperature is measured by allowing a thermometer or electronic device to come to thermal equilibrium with the water, by Standard Method 2550 (Standard Methods, 1998). Thermometers should be mercury in glass types, marked to a precision of 0.1 ºC. These should be well calibrated against primary standard thermometers, or against the

normal freezing point and boiling point of pure water. Thermometers are marked to indicate the proper depth for immersion and care must be taken to allow adequate time for the thermometer to equilibrate with the sample being measured.

Electronic methods include the use of well-calibrated commercial thermocouple- or thermistor -based instruments. These are typically built into meters used for other types of electrometric measurements, for example, pH and dissolved oxygen.

Conductivity

Conductance is the ability of water to transport electrical current, owing to the presence of dissolved ions, and is a very sensitive measure of high water purity. Conductance is traditionally measured as the reciprocal of resistance, in micromho's (μmho), which is the reciprocal of megohms of resistance. Owing to variations in cell geometry, conductance measurements on a specific water sample vary and are reported as corrected to a standard geometry of 1 cm^2 of electrode surfaces placed parallel to each other and 1 cm apart. Since the conductance is generally proportional to the area of the electrodes and inversely related to the distance between them, the specific conductance is generally reported as μmho cm^{-1}. The SI unit of conductance is the siemens, which is defined as one reciprocal ohm, and the usual reporting value for conductance is millisiemens per meter (mS m^{-1}). That being the case, one 10 μmho cm^{-1} = 1 mS m^{-1}.

These measurements are made by Standard Method 2510 (Standard Methods, 1998) using a well-calibrated commercial instrument. Prior to measurement, the samples are brought to 25.0 ºC. Any contamination of the electrodes by oils, surfactants and the like can result in inaccurate readings.

Silica

Silica suspended in water can interfere with certain dyeing operations and can cause visible turbidity, as discussed in the introduction to this chapter. Various forms of silica can be determined by any one of several methods as described in Standard Method 4500-Si. For textile use, total silica is the most important. This may be determined gravimetrically by Standard Method 4500-Si-C or by atomic absorption spectrometry by Standard Method 3111D (Standard Methods, 1998). For information of atomic absorption methods, see the 'Metals' section below. Also, since the detrimental effects in textiles are related primarily to filtering of the silica on beam and package machines, it often suffices to measure the total suspended solids (TSS) in the water supply. TSS testing is described later in this chapter and is simpler than silica testing.

Total silica can be determined gravimetrically by Standard Method 4500-Si-C. In this method, hydrochloric acid decomposes the silica into forms that are insoluble and which precipitate. These precipitates are removed by filtration, then

dried at 110 °C and incinerated at 1200 °C. The residues are weighed, then treated with hydrofluoric acid solution, forming SiF_4. These are evaporated at 105 °C, with the addition of a small amount of perchloric acid to ensure complete dehydration. Upon further heating at 1200 °C, the SiF_4 evaporates and is determined by the weight loss. If other materials are known to be not present in the original sample, the weight of the residues upon the first drying and incineration can be taken as the amount of silica, as the entire amount of precipitated material will volatilize.

The method calls for the use of perchloric acid as a dehydrating agent. This is an explosive material and must be handled only by properly trained personnel. Care must be taken also to avoid contact of hydrofluoric acid and other solutions with glass, as glass is composed of silica and contact may contaminate the analysis.

Total hardness

Water hardness may be determined by Standard Method 2340 (Standard Methods, 1998). The results of the test are reported as the equivalent amount of $CaCO_3$ in the sample. There are two methods for this.

The first method is by calculation from independently determined Ca^{2+} and Mg^{2+} concentrations as described in the 'Metals' section below. The total hardness is calculated as follows:

$$\text{Total hardness, as } CaCO_3 \text{ equivalent mg } l^{-1} = 2.497\,[\text{Ca, mg } l^{-1}] + 4.118\,[\text{Mg, mg } l^{-1})]$$

The constants in the equation convert the concentration of Ca^{2+} and Mg^{2+} to the equivalent concentration of $CaCO_3$, where the atomic masses of Ca and Mg are 40.08 and 24.305, respectively, and the molecular mass of $CaCO_3$ is 100.09. Therefore, the factors needed to convert the Ca^{2+} and Mg^{2+} concentrations to the equivalent amount of $CaCO_3$ are 100.09/24.305 = 4.118 for Mg^{2+}, and 100.09/40.08 = 2.497 for Ca^{2+}.

The second method is by ethylene diamine tetra acetic acid (EDTA) titration, in which an indicator, Eriochrome Black T is added to the water sample, which develops a red color due to the presence of Ca^{2+}. When EDTA titer is added, Ca^{2+} is complexed and yields an end point at which the color changes to blue. To ensure a sharp end point, a small amount of magnesium salt of EDTA is added. The titration is performed at room temperature and at a pH of 10.

Some divalent metal ions can interfere including barium, cadmium, lead, manganese, strontium and zinc. These are titrated as hardness. In addition aluminum, cobalt, iron and nickel can interfere with the end point. This interference becomes more severe when phosphates are present above 10 mg l^{-1}. If these metals are present at significant levels, non-EDTA methods for hardness are preferred.

Oxidizing and reducing materials

The presence of oxygen in water is crucial for aquatic life. If discharged to the environment, wastewater that contains oxygen-demanding substances can deplete the oxygen in receiving waters, thereby damaging aquatic life. The measurement of oxygen content and oxygen demand of wastewater is critical to the operation of wastewater treatment systems and process chemical selection. The methods employed for determination of dissolved oxygen and determination of reducing materials are summarized in the sections that follow (i.e. dissolved oxygen biological oxygen demand and chemical oxygen demand).

Dissolved oxygen

Standard Method 4500-O describes two methods for determination of dissolved oxygen (DO) in water: Winkler's iodometric method and the elecrometric method (Standard Methods, 1998). The iodometric method is very accurate and precise, but the electrometric method is far more convenient for field use (e.g. in wastewater treatment system monitoring and control) and produces an electronic output that can easily be converted to digital form for microprocessor monitoring or control of wastewater treatment systems. Also, electrometric methods are not subject to certain interferences (i.e. oxidation or reduction of the iodine indicator). In addition, the iodometric method end point may be obscured by the presence of turbidity or color in textile wastewater samples. The electrochemical method is almost exclusively used in testing of textile wastewater.

The electrometric method (Standard Method 4500-O G) uses either an electrochemical- or a galvanic cell that interacts with the test sample through a membrane that allows dissolved oxygen to pass through. These cells and test instruments are commercially available from a wide variety of vendors. These use varying methods for calibration and temperature compensation, which must be followed explicitly to obtain accurate results.

The condition of the membrane is critical to the test. Physical damage, fouling by oils and surfactants, and other hazards require that the cell be renovated frequently by changing the membrane and the solution inside of the cell on a regular basis. In this regard, it is critical to follow the manufacturer's recommendation explicitly.

The electrometric DO test method can give measurements accurate to within 0.1 mg l^{-1}. These tests are very temperature sensitive, because temperature changes have a large effect on the diffusion of oxygen through the membrane. For this reason most commercial DO meters have built-in temperature compensation features.

High levels of salt can interfere with DO testing. The effects can be large and are also related to the temperature. Typical textile wastewaters from cotton dyeing have salt contents from 100 to 3000 mg l^{-1}. The upper end of this range can affect DO measurement.

Samples for DO testing must be collected and handled very carefully to ensure they are not exposed or shaken in air, which would alter their DO content. Also, samples taken from the surface of water may have a different DO content from samples taken from a greater depth. For this reason, most field instruments are equipped with cells designed to be immersed in the stream itself, rather than taking a sample. Also, it is best practice to analyze samples as soon as practical for DO, rather than storing them for long times prior to analysis. Since the electrometric method can be used to determine DO *in situ*, it can eliminate problems of sampling, handing and storage of samples for DO testing.

Biological oxygen demand

One of the most important characteristics of wastewater is the amount of oxygen required to stabilize it. This quantity is called the oxygen demand, and is determined either as biological oxygen demand (BOD) or chemical oxygen demand (COD). BOD is the quantity of oxygen required to stabilize wastewater in the presence of bacteria that consume the chemical pollutants and oxygen in the sample and can be determined by Standard Method 5210 (Standard Methods, 1998).

The test is conducted by placing the water sample (containing pollutants), plus oxygen buffer and nutrient solution (dissolved in the dilution water), and bacteria in an airtight container for a period of time. For research purposes, the time may vary, however, for NPDES or publicly-owned treatment works (POTW) compliance testing, the time is almost always five days. The sample is stored in an incubator to ensure that the temperature is constant at 20 ºC during the test. The dissolved oxygen content of the sample is determined initially and again after five days storage in an incubator with bacteria and nutrients. After applying certain correction factors, the depletion is converted into a biological oxygen demand (BOD) number, which is reported in milligrams of oxygen consumed per liter of undiluted sample.

The dilution water must contain the oxygen, nutrients and buffers for the test. This is prepared by adding pH 7.2 phosphate buffer solution and several nutrients (magnesium sulfate, calcium chloride and ferric chloride) to the water. This is then brought to 20 ºC in an incubator and thoroughly mixed with air by shaking or bubbling air into it. The DO content of dilution water should be about 8–9 mg l^{-1}. If the dilution water is of acceptable purity, it can be stored in an airtight container for five days with no more that 0.2 mg l^{-1} of oxygen depletion. Higher depletion indicates the presence of impurities in the water that oxidize and compromise the quality of the BOD test.

Owing to the variability of many factors in the BOD test (e.g. quality of the bacterial, see dilution water, incubator temperature), each batch of tests must include a control. The control is water containing 150 mg l^{-1} glucose plus 150 mg l^{-1} glutamic acid (GGA) and 2% of this GGA standard solution is introduced as a known

Table 9.5 Contents of typical test samples

	Contents	Comments
Dilution water blank	Dilution water only	DO depletion must be <0.2 mg l^{-1}
Seed blank	Seed plus dilution water	s = fraction of seed in the bottle
GGA control	Dilution water Seed 2% of GGA solution	t = fraction of seed in the test
Samples to be tested	Dilution water Seed Various amounts of sample	P = fraction of sample in the test

sample and must give a result of 198 ± 30.5 mg l^{-1}. If not, all results in the test batch are invalid.

The bacteria (called 'seed') for the test are generally available from the textile mill (or municipal POTW) waste treatment system. These bacteria, having been exposed to the textile factory wastewater for some time, are 'acclimated' to the pollutions that are present and therefore can degrade them and consume oxygen, which is the purpose of the test. The BOD of the seed itself must be determined by including 'seed blank' samples with each batch of tests.

Each test batch contains the following: water samples to be tested (diluted to various concentrations in test bottles), dilution water blanks, seed blanks and GGA control. Table 9.5 indicates the contents of typical samples. These samples are incubated together for five days. In some cases, longer term 20-day BOD tests may be performed. The DO in each bottle is measured before and after incubation. The BOD of the sample is determined using the following equation:

$$\text{BOD mg } l^{-1} = [\ (DO_{\text{before}} - DO_{\text{after}}) - (B_{\text{before}} - B_{\text{after}}) \times (t/s)\ ]/P$$

In this equation, DO_{before} is the DO in the sample bottle prior to incubation, DO_{after} is the DO in the sample bottle after incubation, B_{before} is the DO in the seed blank bottle prior to incubation, B_{after} is the DO in the seed blank after incubation, t is the fraction of seed in the test, s is the fraction of seed in the seed blank and P is the fraction of water sample in the test.

Samples must be analyzed as soon as practical after collection. If the sample must be stored, it must be refrigerated to avoid spoilage.

In all cases, DO depletion ($DO_{\text{before}} - DO_{\text{after}}$) of at least 2 mg l^{-1} must be observed for sample tests to be valid. If the DO depletion for all samples is less than 2 mg l^{-1}, it is possible that the sample contains materials that are toxic to the seed. Also, there must be a reasonable amount of DO remaining after incubation. If the DO_{after} is less than 2 mg l^{-1}, it is uncertain whether or not the sample would have consumed more DO, if present.

Owing to the inherent variability of many factors in this test, coefficient of variation of test results is about 10% within a laboratory. The differences between laboratories are expected to be greater owing to seed and dilution water variations.

Chemical oxygen demand

The chemical oxygen demand (COD) test may be performed by Standard Method 5220, which has three variants (Standard Methods, 1998). The most common method is 5220 D, the closed reflux colorimetric method. Like the BOD test described above, COD is a measure of the amount of oxygen required to stabilize wastewater. COD is the quantity of oxygen required to stabilize wastewater, reported as mg l^{-1} when exposed to a strong oxidizer, that is, dichromate.

COD testing has several advantages over BOD. Notably the COD test is more rapid, more repeatable, less susceptible to interferences and less labor intensive. On the other hand, BOD is more strongly correlated to processes that actually occur in wastewater treatment systems and receiving waters. For typical textile wastes, the COD:BOD ratio is typically about 3:1. Wastewater with higher ratios (e.g. 7:1) are resistant to aerobic biological treatment. (USEPA, 1996).

In the COD test, various amounts of water sample are added to a solution of dichromate and heated for some time, during which the pollutants in the water consume some of the dichromate. The residual dichromate is determined by titration or by visible spectrophotometry.

In the open reflux method (Standard Method 5220 B), 50 ml of sample (or some dilution of the sample) are put in a 250 ml ground glass stoppered Erlenmeyer flask along with 1 g of $HgSO_4$ and 5 ml of sulfuric acid reagent, composed of 5.5 g Ag_2SO_4 per kg H_2SO_4. The flask is fitted with a water cooled condenser, and 25 ml of 0.417 M potassium dichromate plus 70 ml additional sulfuric acid reagent is added. This mixture is refluxed for 2 h, then cooled. The residual mixture is titrated with nominally 0.25 M ferrous ammonium sulfate using a ferroin indicator (1,10 phenanthroline plus ferric sulfate). A blank, with no water sample in it, is also run. The COD is calculated by the following formula:

$$\text{COD mg } l^{-1} = (A - B)\, M\, 8000/(\text{ml sample in test})$$

In this equation, A is the ml of titer for the blank, B is the ml of titer for the sample and M is the exact molarity of the titrant.

The results are reported to the nearest mg l^{-1} and the coefficient of variation of test results is about 6–14%, depending on the level of COD present, based on interlaboratory studies (Standard Methods, 1998).

In the closed reflux spectrophotometric method (Standard Method 5220 D), a standardized colorimetric reagent, based on dichromate, is provided in a sealed vial. Test samples are added to the vial and heated to 150 ºC for 2 h in an aluminum block with appropriate holes to accommodate the vials. After cooling, the

transmission of the reaction mixture is measured at 600 μm with a spectrophotometer. These instruments and supplies are available for several commercial vendors. The COD is determined from a calibration curve prepared from standardized potassium hydrogen phthalate solutions. The closed reflux methods retains volatiles and therefore can give more exact results. The coefficient of variation for this test is about 9%.

Total organic carbon

Total organic carbon (TOC) indicates the amount of carbon, regardless of its oxidation state prior to testing, whereas the COD or BOD test gives results that vary according to the oxidation state of the carbon (e.g. methane, methanol, formaldehyde, formic acid, carbon dioxide, sodium carbonate). This test provides a different type of information about the organic and inorganic carbon in a sample.

The method is typically performed by an instrument that oxidizes the sample to CO_2 over a catalyst, as described in Standard Method 5310 (Standard Methods, 1998). The amount of CO_2 produced is measured by an infrared analyzer. Calibrations are produced by injecting known materials into the analyzer. The accuracy for solutions is typically 1–2%. The accuracy for turbid samples with suspended matter is 5–10%.

Metals

There are many methods for metal determination (Standard Methods, 1998: section 3000). Some, for example as gravimetric, titrimetric or colorimetric methods, are most effective at high metal concentrations. Others, for example atomic absorption (AA), inductively coupled plasma (ICP) or inductively coupled plasma mass spectrometry (ICPMS) are far more sensitive. The latter are used for typical textile applications, such as compliance testing for water quality or detection of trace impurities in high-volume raw materials.

Metal ions of greatest interest in textiles are: antimony, arsenic, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, nickel, silver, sodium, tin, titanium and zinc.

ICP gives simultaneous determination of many metals, but the detection limits are typically not as low as AA. The actual detection limit varies depending on the specific metal. AA gives lower detection limits, but only analyzes one metal at a time, requiring equipment changes for additional metals. The most recently developed method is ICPMS, which simultaneously gives low detection limits with multiple metal detection capability (Cottingham, 2004). An EPA report (USEPA, 1998) compares five of the above test methods in detail. These were selected because of their low detection limits and because they use widely available, cost-effective technologies. The methods are:

- inductively coupled plasma/mass spectrometry (ICP/MS)

- stabilized temperature graphite furnace atomic absorption spectrophotometry (STGFAA)
- chelation preconcentration and ICP/MS
- chelation preconcentration and STGFAA
- hexavalent chromium by ion chromatography.

Owing to space limitations, all methods for metals cannot be presented here. Standard Methods presents the following methods for metals of interest in textiles. Numbers in parentheses are typical detection limits in $\mu g\ l^{-1}$ for AA and ICP. (Note: there are several AA methods and the detection limits presented are for the direct aspirational method. Other methods vary slightly.)

- colorimetric by Standard Method 3500: arsenic, chromium, copper, iron, lead, mercury, nickel, silver and zinc;
- titrimetric by Standard Method 3500: calcium and manganese;
- gravimetric by Standard Method 3500: magnesium;
- AA by Standard Method 3113: antimony (3), arsenic (1), chromium (2), cobalt (1), copper (1), iron (1), lead (1), manganese (2), nickel (1), silver (0.2) and tin (5);
- ICP (not ICPMS) by Standard Method 3120: antimony (30), arsenic (50), calcium (10), chromium (7), cobalt (7), copper (6), iron (7), lead (40), magnesium (30), manganese (2), nickel (15), silica (20 as SiO_2), silver (7), sodium (30) and zinc (2).

9.3.2 Color and appearance

The appearance of water, especially textile wastewater is systematically described in terms of its visible characteristics (Standard Methods, 1998). In this regard, the presence of color, suspended particles and turbidity is the focus of much of the testing conducted. In the case of textiles, the presence of color in wastewater is extremely important and numerical methods are normally employed to report results from making color assessments. While color in textile wastewater may arise from the presence of transition metal ions, vegetable matter and industrial plant effluents, color derived from unspent dyebaths is of primary importance. Invariably, this color is removed using a number of physical and/or chemical methods (Reife, 1993); however, methods enabling the recycle/reuse of dye-based color have been developed (Reife and Freeman, 1996).

Color assessments include visual and spectrophotometric methods, both of which employ reference standards to aid in the communication of results. For instance, the visual method involves a comparison of the color of the test sample with known concentrations of potassium chloropalatinate (K_2PtCl_5) and cobalt (II) chloride ($CoCl_2$) in distilled water. The estimated color of the test sample is then used to calculate color units, using the following equation:

$$\text{Color units} = \frac{A \times 50}{B}$$

where A is the estimated color and B is the volume of stock color standard employed.

In the visual comparison method, standards having colors of 5–70 are prepared by diluting 0.5–7.0 ml stock color standard with distilled water in Nessler tubes (Standard Method 2120 B). These solutions must be protected against evaporation and contamination.

In the spectrophotometric method, color is assessed by means of a standard absorption spectrophotometer. In this case, a description of the hue, intensity and brightness of a non-turbid colored solution is possible in the visible region (400–700 nm) of the electromagnetic spectrum. Since pH will have a significant impact on the color of certain dyes, the pH of the dye solution employed must be measured and reported. Details regarding the method are provided in section 2120 C of the Standard Methods book, and can be summarized as follows:

1 Make all measurements at room temperature.
2 Record spectra at the original pH of the sample and at pH 7.6 (adjusting the pH with H_2SO_4 or NaOH).
3 Filter to remove insoluble material.
4 Record the visible spectrum.

The American Dye Manufacturers Institute (ADMI) developed a method for measuring sample color independent of hue. This method provides a mechanism for assessing differences in samples that have color characteristics that are significantly different from the Pt–Co standards described above. This is Standard Method 2120E, which determines the percentage of light transmitted through a set of tristimulus light filters. The resultant transmission values are used to calculate tristimulus ($X_s Y_s Z_s$, intermediate (DE) and Munsell color values.

The American Public Health Association (APHA) also developed a method for evaluating the color of wastewater. Initially, this method was used as an indication of water purity and involved making comparisons of test samples with dilutions of a 500-ppm Pt–Co stock solution. In the APHA index system, distilled water is assigned a value of 0 (zero) and the stock Pt–Co solution has a value of 500. Details pertaining to the preparation of solutions and sample measurements are provided in ASTM D1209-93. In addition, ASTM D1209 describes how to correlate data from color measurement instruments with data from physical APHA and Pt–Co color standards.

9.3.3 Biological and microbiological methods

Biological methods for testing water quality emphasize the collection (sampling) and identification of aquatic organisms. Methods of this type aid in the determina-

tion of (1) the cause of color, odor, and taste in water samples; (2) the biological effects of pollution; (3) the progress of self-cleansing of bodies of water; (4) the effectiveness of wastewater treatment methods; and (5) the environmental impact of various natural and human activities. To make these assessments, the status of plankton, peri- and macro-phyton, microinvertebrates, fish and amphibian populations is often measured. The importance of plankton in the total aquatic ecosystem has led to the long-standing use of these microscopic, free-floating organisms as an indication of water quality (Standard Methods, 1998: section 10200). Their short life cycles cause them to respond quickly to environmental changes, making them a good indicator of the surrounding water quality. They are found in fresh and salt water and methods employed in sampling are also reported in Standard Methods (1998, section 10200).

Typical sample sizes are 0.5–1 l. However, water samples expected to have low densities of plankton should be collected in larger amounts (up to 6 l). Plankton nets are preferred over bottles and traps when sampling low density areas. For quick sample collections, a pump is used, giving preference to diaphragm and peristaltic pumps over centrifugal pumps because the latter can damage the organisms. The organisms contained in collected samples are concentrated prior to analyses, using sedimentation, membrane filtration or centrifugation techniques, with sedimentation being the preferred method.

Plankton are counted by using a counting cell or chamber which has a volume and area that facilitates the determination of population densities. The Sedgwick Rafter (S–R) cell is commonly employed, owing to ease of use and reproducibility. However, it is not suitable for nanoplankton because objectives providing high magnification cannot be used. In this case, the Palmer Maloney (P-M) nanoplankton cell was developed and is used despite having its own limitations.

The key purpose of developing methods for microbiological assessments of water is to determine its sanitary quality (Standard Methods, 1998: section 9010). In this regard, the methods developed provide for the detection and listing of indicator organisms, with the presence/absence of coliform bacteria serving as the primary indicator of the suitability of water for various end uses. Two principal methods have been developed for the determination of coliform bacteria levels: (1) the membrane filter method, which involves a direct plating technique for the detection and estimation of coliform densities and (2) the multiple-tube fermentation test, in which the results are reported as a most probable number (MPN) index. The MPN is the most probable number of coliform bacteria that would give the results obtained in the laboratory examination. Unlike direct plating methods such as the membrane filter procedure, it does provide a direct count of coliform colonies. Both methods provide estimates of the density of fecal organisms. This is important because fecal streptococci and enterococci are indicators of water sanitary quality and coliform bacteria is present in the feces of warm-blooded animals.

Microbiological methods have also been developed for the differentiation of the

coliform group, for examination of waters in swimming pools and for the isolation of certain pathogenic bacteria. Samples containing residual chlorine are typically treated with a reducing agent such as sodium thiosulfate ($Na_2S_2O_3$) prior to testing, to ensure an accurate indication of microbial content. Sample sizes of not less than 100 ml are employed.

In the membrane filtration method (Standard Method 9211 B), the test sample is passed through a membrane filter and the filter is placed on the surface of a plate containing M-7 FC agar medium. After incubating for 7 h at 41.5 ºC, the presence of yellow fecal coliform colonies (from lactose fermentation within the FC agar) serves as a positive test.

9.3.4 Organics (priority pollutants)

The control of toxic pollutants is essential to achieving the goals of the Clean Water Act (CWA) because elevated levels of toxic pollutants can accumulate in the tissue of aquatic organisms (especially fish and shellfish) and result in fishing/harvesting advisories or bans (USEPA, 2000). The CWA is designed to ensure all waters are sufficiently clean to protect public health and/or the environment. Consequently, established water quality goals enhance the effectiveness of state and federal water programs that have an impact on aquatic ecosystems and human health, including permitting, coastal water quality improvement, fish tissue quality protection, non-point source controls, drinking water quality and ecological protection.

Water quality standards provide numeric criteria for priority toxic pollutants for each state. For instance, the NPDES permits issued for San Francisco Bay were to be limited to levels not to exceed 5 ppb as a 4-day average and 20 ppb as a 1-h average for fresh water. The combination of a criterion maximum concentration (CMC), which is a short-term concentration limit, and a criterion continuous concentration (CCC), which is a 4-day average concentration limit, is designed to provide protection for aquatic life and its uses from acute and chronic toxicity. Consequently, the terms CMC and CCC refer to the acute and chronic toxicity criteria (values) for a given pollutant. The two-number criteria are designed to identify average pollutant concentrations that will produce water quality generally suited to maintenance of aquatic life and designated uses, while restricting the duration of occurrences exceeding the average. In this way, the total exposure to toxic pollutants will not cause unacceptable adverse effects.

The organic toxic pollutants monitored include: acrolein, acrylonitrile, carbon tetrachloride, chlorobenzene, 1,2-dichloroethane, 1,2-dichloroethylene, 1,3-dichloropropylene, ethylbenzene, 1,1,2,2-tetrachloroethane, tetrachloroethylene, 1,1,2-trichloroethane, trichloroethylene, vinyl chloride, 2,4-dichlorophenol, 2-methyl-4,6-dinitrophenol, 4,6-dinitrophenol, benzidine, bis-(2-chloroethyl)ether, bis(2-ethylhexyl)phthalate, 3,3'-dichlorobenzidine, diethylphthalate, dimethylphthalate, di-*n*-butylphthalate, 2,4-dinitrotoluene, 1,2-diphenylhydrazine,

hexachlorobutadiene, hexachlorocyclopentadiene, hexachloroethane, isophorone, nitrobenzene, *N*-nitrosodimethylamine, and *N*-nitrosodiphenylamine.

Samples containing chlorinated organics, phenols and aromatic amines are analyzed using liquid–liquid extractions followed by gas chromatography (GC)- or liquid chromatography (LC)-mass spectrometry (MS). In the case of chlorinated compounds, extractions are conducted using solvents such as hexanes, *t*-butyl ether and methylcyclohexane. This is followed by GC analysis, in which the retention times of the components are determined and compared with those of compounds in a reference library. When used in combination with mass spectrometry, molecular mass information is obtained and the resultant spectra are also compared against those in a reference library. The detection levels are 0.25–30 μg l^{-1}, depending on the specific type of compound. For samples containing phenols or aromatic amines, extractions are performed using methylene chloride followed by GC- or LC-MS analysis.

When trouble shooting, liquid–liquid extractions with methylene chloride at acidic, neutral and alkaline pH are conducted, followed by neutralization, concentration and GC or GC/LC-MS analyses. This approach is highly effective for unsulfonated organic amines, phenols, carboxylic acids and neutral organics when extensive libraries of retention times and mass spectral data are available.

9.3.5 Solids

Solids

Proper wastewater treatment and drinking water purification system operation depends on solids measurements. There are several types of solids of interest presented in Standard Methods (1998):

- 2540B: Total solids
- 2540D: Total suspended solids
- 2540C: Total dissolved solids
- 2540F: Fixed and volatile solids
- 2540F: Settlability and buoyancy of solids.

Total solids

Standard Method 2540B determines the total solids (TS) in water samples by drying at 105 °C to constant weight. The results are reported in mg l^{-1}, and typically the repeatability of the test is within 6 mg l^{-1}. In some cases where the solids are hygroscopic, the time required for drying may be long and the samples must be cooled before weighing in a dessicator to avoid sorption of moisture from the air.

Total dissolved solids

Standard Method 2540C determines total dissolved solids (TDS) by filtering a water sample through glass fiber disks, then drying the sample at 180 ºC for 1 h. The sample is cooled in a dessicator and weighed, then redried at 180 ºC. This process is repeated until a constant weight is obtained. Coefficient of variation of test values is 7%.

Total suspended solids

Standard Method 2540 D determines total suspended solids (TSS) by filtering a water sample through glass fiber disks, then drying the disc and filtered solids at 105 ºC to constant weight. The resulting test data have a coefficient of variation that is highly dependent on the level of solids in the original sample.

Fixed and volatile solids

For some applications, it is important to distinguish between volatile and non-volatile solids. For example, the bioactive organic portion of mixed liquor suspended solids in secondary activated sludge textile wastewater treatment systems is volatile, whereas grit and other inorganic solids are non-volatile. To determine the volatile component of solids from any of the above three tests, the solid residue is dried to constant weight in a high-temperature muffle furnace at 550 ºC (Standard Method 2540 F).

Settleable solids

Standard method 2540 F determines settleable solids either gravimetrically or volumetrically. In the volumetric method, a 1 l water sample is allowed to settle for 45 min in an Imhoff cone, then is very gently stirred to loosen any settleable particulates that adhere to the sides of the cone. After an additional 15 min of settling, the volume of the settled material is estimated from the marking on the cone. Do not count floating solids.

In the gravimetric method, the TSS is determined from the original sample and also from the supernatant liquid above the settled material. The settleable solids are computed as:

$$\text{settleable solids (mg l}^{-1}) = \text{initial TSS (mg l}^{-1}) - \text{supernatant TSS (mg l}^{-1})$$

9.3.6 Anions

Chloride (Standard Method 4500 Cl^-)

Several methods are available for Cl^- determination, with the choice of method

based largely on personal preference. The argentometric method is suitable for clear waters containing 0.15–10 mg Cl^- in the titrated sample. However, the end point of the mercuric nitrate method has been judged as easier to detect. In this case, special notice must be given to handling of mercury-based wastes. The potentiometric method is suitable for colored or turbid samples that would pose problems with visualization of color-based end points. The ferricyanide and flow-injection methods are automated, with the latter especially useful for large numbers of samples. Cl^- can also be determined using the capillary ion electrophoresis method (Standard Method 4140).

Nitrite (Standard Method 4500 NO_2^-)

Methods developed for NO_2^- determination include a colorimetric method and ion chromatography. In the colorimetric method, NO_2^- ion levels are determined through the formation of an azo red dye from a reagent containing sulfanilamide and *N*-(1-naphthyl)ethylenediamine at pH 2.0–2.5. The applicable range of the method for spectrophotometric measurements is 10–1000 µg NO_2^- l^{-1}.

Single-column ion chromatography measurements afford a retention time of 3.1 min for NO_2^-. In this method the minimum detection limit (MDL) is 0.022 mg l^{-1}.

Nitrate (Standard Method 4500 NO_3^-)

Spectroscopic measurements for detecting NO_3^- are often complicated by the presence of interfering components. Its primary absorbance is at 220 nm, which overlies a number of organic compounds, making this method suitable when the concentration of organics is very low. UV absorption measurements have shown that an NO_3^- calibration curve follows Beer's law at levels up to 11 mg l^{-1}. This allows rapid determination of NO_3^- levels. Single-column ion chromatography measurements have been used and afford a retention time of 5.3 min for NO_3^-. In this method the minimum detection limit (MDL) is 0.035 mg l^{-1}. A nitrate electrode method has also been developed. This selective sensor method responds to NO_3^- ion activity in the 10^{-5}–10^{-1} M region, which corresponds to 0.14–1400 mg NO_3^- N l^{-1}.

Sulfide (Standard Method 4500 S^{2-})

Tests for S^{2-} include the antimony test, silver–silver sulfide electrode test and the lead acetate paper and silver foil tests. In the antimony test, the color produced by treating a 200 ml test sample with 0.5 ml saturated potassium antimony tartrate and 0.5 ml 6 N HCl is compared with colors produced when solutions containing known amounts of S^{2-} are treated in the same way. In the silver–silver sulfide electrode test, the test sample is diluted 1:1 with an alkaline solution of an oxidizing agent and the electrode potential relative to a double-junction reference electrode is measured.

S^{2-}levels are then estimated using a calibration curve. In the third method, the formation of PbS or Ag_2S serves as a positive test for the presence of S^{2-}.

Sulfite (Standard Method 4500 SO_3^{2-})

Iodometric titration is suitable for relatively clean waters having > 2 mg SO_3^{2-} l^{-1}. The phenanthroline colorimetric method is preferred at lower levels. In the former method, an acidic sample containing sulfite is titrated with a standardized solution of potassium iodide/iodate. The end point is signaled by the formation of a persistent blue color formed by the interaction of excess iodine with a starch indicator. In the phenanthroline method, SO_2 is produced and, in turn, converts ferric ions to ferrous ions which form an orange complex with phenanthroline. The complex is measured colorimetrically at 510 nm.

Sulfate (Standard Method 4500 SO_4^{2-})

Chromatographic, electrophoresis, gravimetric and turbidimetric methods are available for determining sulfate, the choice of which often varies with the sulfate levels present and the number of samples to be analyzed. The accuracy of gravimetric and turbidimetric methods has caused them to be preferred. In the gravimetric methods, sulfate is precipitated as $BaSO_4$ by the addition of $BaCl_2$ in HCl near the boil. The precipitate is collected by filtration, washed free of Cl^-, ignited or dried, and weighed to determine the amount of $BaSO_4$. In the turbidimetric method, sulfate is precipitated from an acetic acid solution to give $BaSO_4$ crystals of uniform size. The resultant suspension of $BaSO_4$ is measured using a photometer and the SO_4^{2-} level is determined by comparison of the reading with a standard curve.

Phosphorus (Standard Method 4500 P)

Phosphorus exists predominantly in water samples as phosphates, including orthophosphates, condensed phosphates and organophosphates. The analysis of samples for phosphorus levels involves conversion of the phosphorus species present to orthophosphate followed by colorimetric determination of the orthophosphate. In the case of organophosphorus compounds, a digestion method may be employed to oxidize the organic matter and generate orthophosphate. Oxidizing agents employed include HNO_3/H_2SO_4 and persulfate/UV light. Among the options for colorimetric analysis, the vanadomolybdophosphoric acid, stannous chloride and ascorbic acid methods are most widely used, the choice of which depends on the phosphorus levels present. The vanadomolybdophosphoric acid method is preferred at 1–20 mg P l^{-1} and the stannous chloride and ascorbic acid methods are preferred at 0.01–6 mg P l^{-1}. For further details, see Table 4500-P:I in Standard Methods (1998).

9.4 Laboratory practices

9.4.1 Sample storage and preservation

Metal ions based on aluminum, cadmium, chromium, copper, iron, lead, manganese, silver and zinc are subject to loss by adsorption on the walls of glass containers and should be (1) collected in separate clean bottles and (2) acidified with HNO_3 to pH <2 (to minimize surface adsorption and precipitation). Zero head space is important in preserving samples containing VOCs, making complete filling of containers important when this determination is to be conducted. The time interval between collection and analysis should be minimized. In the case of composite samples, field testing is preferred and the collection time is often specified as the time at the end point of the collection. When immediate testing is not practical, samples should be stored at 4 ºC. Significantly colder temperatures may cause a pH change in the samples and/or damage the sample containers, especially glass. The use of chemical preservatives must be restricted to cases in which the agent used does not interfere with the analysis to be made. Formaldehyde is to be avoided. Normally, the purpose of preservatives is to retard biological activity that, for instance, alters the oxidation state of sample constituents, or retards the hydrolysis of chemical constituents in the sample. A list of preservation methods is provided in Table 1060:I of Standard Methods (1998).

9.4.2 Method development

Method development comes into play when an established standard method does not exist for a particular sample constituent. In this case, a set of experimental steps for measuring a known amount of a given constituent in various matrices is developed. For the new method to become accepted by the scientific community, it must be validated. Validation consists of three steps: (1) determination of the MDL, (2) analysis of independently prepared standards and (3) determination of the stability of the result produced when steps comprising the new method are varied (method ruggedness). New methods passing these three tests are subjected to collaborative testing prior to becoming a standard method.

9.4.3 Expression of results

The units employed are normally based on the International System of Units (SI units) and physical results are expressed in milligrams per liter (mg l^{-1}) unless the constituent concentrations merit using micrograms per liter (μ l^{-1}). Other frequently used units are parts per million (ppm) and percent by weight. To avoid ambiguity in reporting results, significant figures are used, where all digits reported except for the last digit are known definitely.

9.5 Issues and improvements for the future

The science and art of water testing is highly advanced, as analytical instrumentation is available for detecting even parts-per-trillion concentrations of many contaminants. The speed and accuracy of these tests are outstanding. In many cases, the costs of these tests are high, but in view of regulatory requirements for testing at very low levels, there seems to be no reasonable way to reduce these costs. However, the regulatory climate as it exists in developed economies creates a need for lower testing costs. Therefore this is a major unmet need associated with water testing.

Another area of unmet need is in the identification of surfactants in textile wastewater. The effects of surfactants can be readily measured in terms of reduction of surface energy, foaming, aquatic toxicity, turbidity, and the like. However, it is often desirable to identify the exact concentration and identity of surfactants in wastewater. This is helpful, for example, in efforts to evaluate waste treatment system removal efficiency, or to reduce the detrimental effects of surfactants on the environment by pollution prevention (or 'cleaner production' as it is called outside the USA). At present, there is no reasonable scheme for surfactant identification in textile wastewater.

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10

Chemical analysis of colorants

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10.1 Introduction

In a single chapter of this type it is practically impossible to cover all of the techniques and methods that have been used, or even just those that are routinely being used, in analysing and evaluating colorants (and at the same time include information about colorants). This is especially true when these colorants may exist in a very wide range of sample types: pure dyes/pigments; commercially formulated colorants (different physical forms and different additives/impurities present); associated/incorporated with a substrate (textile, paper, leather, hair); or may be in a plastic, a cosmetic, a drug or a food product. However, whilst emphasis has been on the analysis of colorants used in textile coloration, some potentially relevant or interesting examples from other areas have been included to illustrate certain aspects or potential.

The general aim of this chapter is to focus on the major instrumental techniques that are used to analyse colorants associated with the textile coloration industries. The principal techniques that have been covered are spectroscopic techniques and chromatographic techniques. The capability and value of the techniques are highlighted by reference to relevant applications. Prior to focusing on the techniques, consideration is given to the nature of 'colorants' and also general issues, such as sampling, that are important in an overall analytical procedure. Section 10.2 on colorants includes some consideration of the health, safety and environmental considerations linked to colorants, which is a major driver for analysis of colorants. Note, in this chapter there has been a greater focus on the chemical nature, identity and quantitation of colorants (especially by instrumental methods) than on the property and measurement of 'colour'.

10.2 Colorants

'Colorant' is used as a catch all phrase to include any chemical that is coloured or can become coloured in a particular environment/under certain conditions and can be applied/used to impart the property of colour to an item. Dyes, pigments, lakes, toners and stains are all colorants.

A dye (or dyestuff, as they are sometimes referred to, especially in the USA) is a substance, nearly exclusively organic in nature, that is applied to a substrate in order to impart colour with some degree of permanence. At some point during application dyes are unimolecular, that is, they exist as individual molecules. Dye molecules often contain at least one water solubilising group, such as a sulphonic acid group, to aid their normal application route, which is usually from an aqueous medium. By far the main application area for dyes is in textile coloration.

The word pigment comes from the Latin 'pigmentum' meaning coloured material. A modern definition of a pigment would be: a substance consisting of small particles that is insoluble in the applied medium and is used primarily for its colouring properties. Pigments impart colour and some degree of hiding power (opacity) over the surface to which they are applied.

When it comes to defining lakes and toners, both of which are essentially specific types of organic pigment, there is a problem in that the accepted definition/understanding varies in different parts of the world. In the UK the following are accepted:

- A lake is an organic dye (originally natural dyes were used) that has been precipitated on to an inert (usually inorganic) substrate, e.g. alumina, to form an insoluble pigment; this gives a mixture of colorant and substrate.
- Toners can be anionic organic dyes, mainly acid dyes, precipitated as insoluble metal salts, e.g. barium or calcium. If the cation is lithium, potassium, sodium or ammonium the colorant is soluble and therefore a dye. However, salts produced with metals such as calcium, manganese, barium, strontium, and so on, are mainly insoluble. For this type of toner it is the anion that is the source of the colour. This is an easy method of producing relatively simple and economic pigments that find significant usage, especially in printing inks. Alternatively, cationic dyes (providing the coloured part of the molecule) can be precipitated with a complex inorganic acid (an anion), e.g. phosphotungstomolybdic acid. These toner pigments produce very strong, bright colours, but with poor fastness properties, limiting their use somewhat.

The term 'lake' is widely used in the USA, and elsewhere, to describe what are called 'toners' in the UK. To further add to the confusion with respect to American terminology, they often use the name 'Toner' for all organic pigments, as they 'tone' duller inorganic pigments.

A pigment powder consists of a mixture of crystals of different sizes (and often

slightly different shapes), agglomerates and aggregates that give an overall particle size distribution. This size distribution affects the properties of a pigment and can be measured by many methods, for example by microscopy. Some of the properties dependent on particle size distribution are surface area (which in turn affects dispersion properties of a pigment) and the pigment appearance. Particle size and shape greatly influence the amount of light reflected, scattered and absorbed by a pigment. When a pigment is highly scattering it is also very hiding (opaque).

Pigment powders are dispersed into a variety of media in order to impart colour and hiding power, for example, decorative paints, printing inks (for textiles as well as paper and packaging materials), coloured plastics and car paints. Dispersion is a difficult process and the presence of agglomerates and aggregates means some form of grinding must usually take place before the pigment can be used. Grinding is employed to break up large particles, reducing the average particle size (usually also narrowing the particle size distribution) and thus developing the colour strength properties of a pigment in a medium.

Light scattering properties of a pigment depend not only on particle size but also on the refractive indices of the pigment and the medium in which they are dispersed. Increased scattering occurs when the difference between the refractive indices of the pigment and the binder is maximised. Inorganic pigments tend to have high refractive indices (greater than 2) and are more highly scattering, resulting in an opaque appearance. Organic pigments have lower refractive indices and are less scattering and are, therefore, more transparent in appearance. It is also generally true that organic pigments have a smaller mean particle size (sub-micrometre range) than inorganic pigments (micrometre range). Changing the average particle size of a pigment can quite dramatically affect the performance properties (including appearance) of the product the pigment is a part of. For example the white inorganic pigment titanium dioxide (largest volume pigment, renowned for its high opacity) can be manufactured in a small particle size transparent grade that finds use as a UV protecting agent, for example in sun blocks. Additionally, a number of organic pigments have been manufactured to give special higher than normal mean particle size grades with different properties, such as higher opacities, compared to the equivalent pigments with smaller mean particle sizes. Thus particle sizing and particle characterisation techniques are very important for pigments (but are not considered in any detail in this chapter).

Other factors such as safety, cost and handling may also prove important in the choice of a pigment for a particular system. In addition, the pigment must be chemically compatible with the choice of medium, with any other pigments present and with any additives present.

For more detailed information on the chemistry, properties and applications of colorants the reader is advised to consult a suitable text book[1–10] and /or for the latest developments investigate the specialist journals related to colorants.[11–15]

10.2.1 Classification of colorants

There are thousands of different dyes and pigments (in terms of different chemical species) more than those used tens of thousands of years ago, for example from inorganic minerals used in cave paintings to new ones that are still being invented and investigated (for applications from dyeing textiles to those for use in medical treatments for diseases such as cancer). It is interesting to note that the vast majority of these colorants have been discovered over the last 150 years, since the advent of synthetically produced organic colorants following the discovery of mauvine by Perkin in 1856. The number of 'colorants' is multiplied further when different physical forms, different formulations and different suppliers (with often different quality products for basically the same colorant) are taken into account. When this is linked to the fact there are a wide range of uses and users of colorants, the importance of a classification system for colorants is clear.

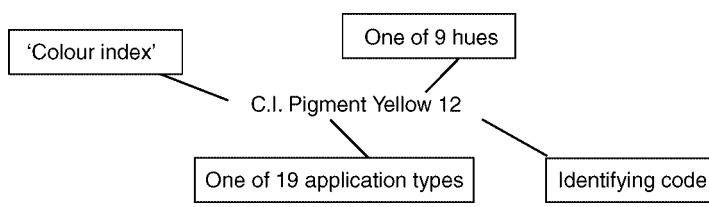
The classification system that is most commonly used for colorants is the one initially developed by the UK Dyer's Company (now transformed into the Society of Dyers and Colourists, SDC), with the first volume of the 'Colour Index' produced in 1924. More recently the Colour Index (CI) has been published on CD-ROM and as an on-line web version, which makes it much more manageable to access. It is now recognised as an exhaustive international classification system for dyes and pigments and is published by the Bradford (UK)-based Society of Dyers and Colourists in partnership with the American Association of Textile Chemists and Colourists (AATCC).

The Colour Index

Each colorant is assigned a C.I. Generic Name and a chemical constitution number (Fig. 10.1).

Generic Name: gives the nature of the product, the colour and a chronological number.

Chemical constitution number: a five figured number which is assigned to a colorant depending upon its chemical structure. Chemically similar colorants are given similar numbers, for example 77000–77996 are numbers of inorganic



10.1 Assignment of generic name to a colorant in the Colour Index.

Table 10.1 Usage categories classified in the Colour Index

Acid dyes	Food dyes	Reactive dyes
Azoic colouring matters	Ingrain dyes	Reducing agents
Basic dyes	Leather dyes	Solvent dyes
Developers	Mordant dyes	Sulphur dyes
Direct dyes	Natural dyes	Condense sulphur dyes
Disperse dyes	Oxidation dyes	Vat dyes
Fluorescent dyes	Pigments	

Table 10.2 Chemical classes classified in the Colour Index

Nitroso pigments	Triaryl methane	Sulphur
Nitro	Xanthene	Lactone
Azo–mono azo	Acridine	Amino ketone
Disazo	Quinoline	Hydroxy ketone
Trisazo	Methine	Anthraquinone
Polyazo	Thiazole	Indigoid
Azoic	Indamine	Phthalocyanine
Stilbene	Azine	Natural organic
Carotenoid	Oxazine	Oxidation bases
Diphenyl methane	Thiazine	Inorganic

pigments. Note, the aromatic structure (series of conjugated double bonds) of colorants was not represented properly in the early versions of the CI (this has been addressed in the latest CD-ROM and on-line versions).

For dyes, details of chemical class, structural formula (where disclosed), preparation methods, constitution number, chemical and physical properties, hue, dyeing properties on various substrates, printing properties, fastness properties, the C.I. Generic Name, references, patents and alternative names for the colorant along with commercial names (when notified by the colorant suppliers) are included. Details of non-textile applications are also provided. In the pigment section (of older versions) similar information is provided but the fastness properties are given as a detailed list of fastness in specific solvents and heat sensitivities. The traditional technical information about fastness properties was largely irrelevant because pigment fastness always depends on the medium in which it is being considered and providing such detailed information would have been fairly impossible. The newer versions give details of C.I. Generic Name, constitution number, structure, hue, chemical class, historical notes, CAS and EU numbers, commercial products, manufacturers, physical form of pigment, application areas and other comments. These details are all provided in one place for each pigment, making the newer versions much easier to use.

Colorants (especially dyes) are primarily classified based on their usage/application type and also on their chemical constitution (or chemical class) – see Tables 10.1 and 10.2.

The most common categories for pigment classification are simply based on chemical constitution:

- inorganic: the coloured oxides, sulphides, hydroxides, sulphates, carbonates, etc. of metals;
- organic: molecules based primarily on aromatic carbons for the backbone structure.

A further division can be made by splitting the pigments into groups depending on how they are obtained/produced:

- natural: pigments obtained from a natural source such as yellow ochre. Natural pigments are a minority group and used only for specialist applications;
- synthetic: pigments which are chemically manufactured. These are commercially the most important pigments.

Many of the naturally occurring pigments are preferentially obtained synthetically for good commercial reasons (especially for quality control of products). Further classifications of pigments can be made by splitting the pigments into colour groups, for example by classifying all red inorganic pigments into the same group. Organic pigments can also be further split by considering more detailed chemical constitution and structure.

Pigment manufacturers have been happy to support the colour index and provide information for its content. This stems from the fact that little industrial advantage can be gained by withholding pigment information and structures from the Colour Index, since most of the differentiation between chemically similar pigments comes about by manufacturing processes and after treatments, which are not revealed. The textile dye industry, on the other hand, has suffered quite badly in the past from 'non-traditional suppliers' using C.I. Generic Names for low quality dyestuffs. This has led to a reluctance to disclose dye information, particularly structures, to the Colour Index.

Colorants are supplied in a variety of physical forms: powder, liquid, presscake, paste, granules, master batch, chip or flake, flush colour or liquid dispersion.

10.2.2 Health, safety and environmental considerations[16–21]

Regulations that affect the colorant industries are numerous and over the last two decades or so they have generally increased in their potential to have an impact on manufacturers and processors of colorants; this is especially true for the more highly developed economies in the world. Companies have had to respond, in order to stay in business, and have generally been successful in doing so, but often after considerable expense (and often with continuing additional costs involved). Regulations can come from a variety of sources such as the European Union (usually in the form of a Directive), national regulations or even a regional or local authority. There are regulations that cover practically all areas of a company's

business and activities, including downstream aspects when chemicals leave one of their sites. Legislation is often based on the philosophies of 'prevention is better than cure' and the 'polluter pays'. This has clearly all resulted in the need for ever greater monitoring and analysis (and obviously not just in the various sectors of the coloration industry, but in all industries). This section will not attempt to cover all areas, but rather will try to focus on the major issues affecting the synthesis and handling of colorants.

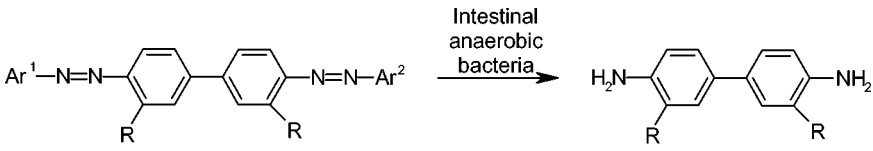
The complexity of the regulations, and the nature of the colorants industry, have caused, and still lead to, many difficulties for companies operating in the industry. Colorants are highly visible in the environment, especially synthetic dyes which can be seen in effluents at very low concentrations owing to their high colouring strengths. Commercial colorants have been designed and developed to possess a number of desirable application and performance properties, such as good fastness properties and high stability (as discussed in previous sections). It should therefore not be surprising to discover that, for example, dyes released in effluents can cause environmental problems since they are not generally biodegradable. Certain dyes are not effectively removed from treated effluents in traditional wastewater treatment plants. The relatively stable aromatic structural units which most dyes are primarily composed of are, at least in part, responsible for the specific environmental and toxic effects associated with the dyes. A number of studies have been carried out into the chemical and into the biochemical degradation of dyes and rely heavily on analytical techniques to study the kinetics of the processes or to aid identification of the products.

When considering the toxicological and ecological properties of pigments, the main factor to remember is that they have extreme insolubility in water and in the application media. Therefore, pigments (when pure) are generally considered to be physiologically and biologically inert.

As has already been mentioned, the most important chromophore system is that based on the azo group. This group is nearly always introduced into colorants via aromatic amines. Certain aromatic amines which were available (and frequently used) from the beginning of the synthetic dye era were later realised to entail considerable hazards and potential impacts. The acute toxicity of a few of these compounds was identified at a relatively early stage; the clinical symptoms that they gave rise to were called anilism. It has also been shown that, for example, benzidine-based azo dyes can be reduced to the free benzidine based diamine by intestinal bacteria[22] and also by UV light[23] (see Fig. 10.2).

Even today the legislation relating to colorants (manufacture, transportation, use, disposal) does vary a lot from one country to the next. Analysis of colorants often relates to checking that the sample does not contain restricted or banned species or will not break down to release any restricted or banned species. Recent German legislation on the use of azo colorants that have been produced from certain known or suspected carcinogenic aromatic amines will be discussed later.

At this point it is worth considering some well-known words of Paracelsus



10.2 Breakdown of benzidine-based azo dyes by intestinal bacteria to generate carcinogenic, free benzidines.

which, if you stop to think about for a while you may agree, are still relevant in modern times:

> 'What exists that is not poison? Every substance is a poison and nothing is no poison, it is merely the dose that makes a substance a poison'

Hence the need for extensive analysis!

ETAD (The Ecological and Toxicological Association of Dyes and Organic Pigment Manufacturers) was set up in 1974, as an international association, to minimise any possible negative impact of colorants on human health and the environment. The ETAD coordinate, and assist, the manufacturers of synthetic organic dyes and pigments with their ecological and toxicological efforts. There are about 46 member companies (based in 15 countries throughout four continents). Member companies are obliged to adhere to the ETAD Code of Ethics, which is based on the principles of responsible care. Further details regarding the ETAD and its activities are available from ETAD, PO Box 4005, Basel, Switzerland (www.etad.com).

Toxicity data

A survey of acute oral toxicity, as measured by the 50% lethal dose (LD_{50}) test, demonstrated that of 4461 colorants tested, only 44 had an $LD_{50} < 250$ mg kg^{-1} and that 3669 exhibited practically no acute toxicity ($LD_{50} > 5$ g kg^{-1}).[24] The rest fell somewhere between these two levels. The evaluation of these colorants by chemical classification revealed that the most toxic ones were found among the diazo (mostly benzidine derivatives) and the cationic dyes. It is widely known that some general cationic compounds have toxic properties. Pigments and vat dyes by comparison were discovered to have extremely low acute toxicity – presumably due to their insolubility/very low solubility in water and in lipophilic systems.

In another survey, summarised by Clarke and Anliker,[25] 3000 dyes in common use were tested for their toxicity to fish. The results showed that 98% of dyes tested had an LC_{50} value (lethal concentration to kill 50% of the test population) greater than 1 mg dm^{-3}. The LC_{50} value was of the order of 0.05 mg dm^{-3} for only 27 dyes (16 of them basic dyes of which 10 had triarylmethane structures), compared, for example, with DDT (a pesticide) at 0.006 mg dm^{-3} .

Toxicity associated with azo colorants

Three different mechanisms for azo dye toxicity have been identified and were reviewed by Brown and DeVito in 1993.[20] In order of decreasing number of published papers, these mechanisms are:

- azo dyes that are toxic only after reductive cleavage of the azo bond to produce aromatic amines (occurring mainly via anaerobic bacteria in the intestines). The aromatic amines are metabolically oxidised to reactive electrophilic species that are then able to bind to DNA;
- azo dyes with structures containing free aromatic amine groups that can be metabolically oxidised, without the need for azo reduction;
- azo dyes that may be activated via direct oxidation of the azo bond to highly reactive electrophilic diazonium salts ($Ar–N_2^+ X^-$).

Note, although it is believed that some bacteria can reduce any azo compound to aromatic amines, not all aromatic amines are toxic and hence not all azo colorants are potentially toxic. In fact, careful selection of intermediates during synthesis means that existing modern azo colorants are likely to be safe.

German ban on use of certain azo compounds in consumer goods

Most colorants are synthesised from aromatic amines and thus in some circumstances may potentially contain these amines as impurities or may, in some instances and under certain conditions, release aromatic amines if they are degraded in subsequent processes.

There has been much concern in the coloration industry since the mid-1990s regarding initially a proposed amendment to the German Consumer Goods Act and then subsequently its approval and implementation. The amendment, which was approved by the German Government in July 1994, placed a ban on consumer goods that contain azo dyes which could, through cleavage of one or more azo groups, form any of 20 specified aromatic amines known as the MAK III amines (see Table 10.3). These aromatic amines are listed by the German MAK Commission (MAK = maximum work place concentration) as either known human carcinogens (MAK III A1 list, compounds 1–4) or known animal carcinogens (MAK III A2 list, compounds 5–20). Although the potential risk to consumers from food and cosmetic products either containing or able to form MAK III amines is fairly self-evident, the toxic risk associated with dyed articles which will come into contact with skin is debatable, but seems likely to be extremely low. However, a cautious approach is surely preferable if human health may be at risk. It is obviously important that legislation is based on facts and sound scientific research so that safety can be ensured whilst at the same time unnecessary burdens are not placed on the coloration industries.

Azo pigments are generally exempted by the Fifth Amendment in the USA

Table 10.3 List of banned (MAK III) aromatic amines

	CAS-No.		CAS-No.
4-Aminodiphenyl	92-67-1	3,3'-Dimethoxybenzidine	119-90-4
Benzidine	92-87-5	3,3'-Dimethylbenzidine	119-93-7
2-Amino-5-chlorotoluene	95-69-2	2-Methoxy-5-methylaniline	120-71-8
2-Aminonaphthalene	91-59-8	3,3'-Dimethyl-4,4'-diaminodiphenylmethane	838-88-0
2-Aminoazotoluene	97-56-3	4,4'-Methylene-bis (2-chloroaniline)	101-14-4
2-Amino-4-nitrotoluene	99-55-8	4,4'-Oxydianiline	101-80-4
4-Chloroaniline	106-47-8	4,4'-Thiodianiline	139-65-1
4-Methoxy-*m*-phenylenediamine	615-05-4	2-Aminotoluene	95-53-4
4,4'-Diaminodiphenylmethane	101-77-9	2,4-Diaminotoluene	95-80-7
3,3'-Dichlorobenzidine	91-94-1	2,4,5-Trimethylaniline	137-17-7

owing to their extremely low solubility, which it is acknowledged means that they do not pose a risk to consumer health. However, some azo pigments are not exempted since they are sufficiently soluble, under the test conditions recommended, to yield detectable amounts of a listed aromatic amine. Note, in order to pass the test there must be less than 30 mg kg^{-1} (i.e. amount of amine present or released under the test conditions from 1 kg of the particular consumer item being tested) of each individual listed amine.

There have been concerns, within the coloration industry, regarding the actual analytical test procedures, since false positives (a result indicating a banned amine is present when the original colorant was not based on any banned amines) have been obtained with some colorants under the rather harsh sample treatment and extraction processes employed. The current official methods published do not use such harsh conditions. Perhaps the real winners in all of this are the contract analytical labs who do all the testing (and possibly the consumers to some extent)! Further details about the analysis of these species are contained in Section 10.6 on separation science.

Note, the German ban only restricts the use of about 5% of azo dyes (the rest are not based on listed/banned amines).

Dyes in effluents

The biggest issue for dyes is probably that of effluent treatment, since at the end of dye application significant amounts of colorant are usually discharged in an aqueous medium. The exact nature of the effluent will depend on the dye and the application method used. Generally reactive dyes are thought to cause the biggest potential problems. Dye effluents and their treatments are not considered in any great detail here, but the following issues are important:

- Presence of dyes in effluent: coloration power, high stability of dyes (wash +

light), chemical state of the dye (especially for reactive dyes) and very low biodegradability (filtration).
- Dyeing auxiliaries: acids, bases, salts, metal ions, surfactants, oxidising/reducing agents, dye impurities, high pollution load.
- Metal ions: very important for certain types of dyeing processes (especially wool), high toxicity but with respect to speciation.

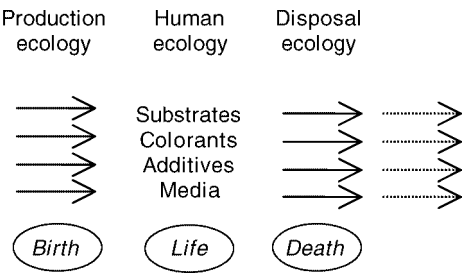
Pigment toxicity

The insolubility and excellent migration fastness of most organic pigments largely eliminate human health hazards. However, care may need to be taken when handling pigments owing to the potential presence of impurities (possibly heavy metals or residual amines). Good manufacturing procedures and appropriate sample clean up methods help to ensure that the levels of impurities are minimised. When pigments are incorporated into formulations it is invariably components other than pigments that are likely to pose the greatest ecological and toxicological risks. Atomic spectroscopy is normally used to test for the presence of heavy metals.

Inorganic pigments that are based on certain heavy metals in certain oxidation states (remember toxicity is dependent on physicochemical form, i.e. speciation) may need special consideration. For example, lead chromate pigments contain both lead and hexavalent chromium and, as a consequence, are defined by the EPA as carcinogenic. Experimentally, however, lead chromates have been found to be non-mutagenic and non-carcinogenic,[26] again presumably owing to their extremely low solubility. Note, the availability of potentially carcinogenic species will be partly dependent on the environmental conditions present (e.g. temperature, pH, etc.). Analytical methods based on atomic spectroscopy need to distinguish between ‘available’ and ‘total’ amounts of analytes of interest.

Life-cycle studies

If companies really want to be responsive to the health and safety needs of their workers and the users/consumers of their products and the welfare of the environment then life-cycle studies should be carried out for each product. The stages to be considered in a life cycle study are illustrated in Fig. 10.3. The creation (birth) and use (life) are of obvious concern to the producers, but should companies also have some responsibility for the safe disposal (death) of products when they reach the end of their useful life time? Can ‘features’ be designed/engineered into products when they are manufactured/formulated that will lessen any detrimental impacts on the environment when the products are disposed of, or could the components be recycled in some way? What happens to the constituents after disposal (life after death)? However, at the end of the day companies need to make money (and workers need to earn a living), therefore it can be argued that there



10.3 Key stages in life-cycle studies.

needs to be a suitable balance between ecology and economy. Analysis is important in the investigation of all of the stages of a life-cycle study in order to understand the species present and to aid the full evaluation of potential impacts.

In terms of the textile coloration industries, for example, investigations into all components – substrates, colorants, auxiliaries and media (likely to be water, but may be a binder-solvent system for a print paste) – need to be made. Additionally, any potential interactions between the different components in a product (e.g. dyed and chemically finished textile garment) or any degradation reactions that may lead to new species being formed (with potential new interactions and possible further species formed) should be considered. The fate of products after disposal has been of increasing concern over recent years. This is generally not an easy thing to investigate, owing to the long-term and complex nature of any breakdown of many products in the environment. For example, what happens to dyes when textiles are discarded? What happens to pigments when plastics degrade? This is an area where much has still to be investigated and learnt.

Conclusions

There are many issues associated with the safe manufacture, use and disposal of colorants and we have covered quite a few in this section. These are areas that will continue to be important, as legislation becomes ever stricter, so the role of analysis will remain important. There are other issues that have not really been covered in this section, but they are still important, for example:

- the special requirements of colorants used in food/cosmetics/pharmaceutical applications;
- the use of natural colorants and their associated problems;
- colorants used in products subjected to harsh conditions/environments (e.g. pigments in plastics that are processed at elevated temperatures).

10.3 General issues in analysis and the steps involved in analysis

Analysis and characterisation of materials is a key aspect of all manufacturing industries and many other industries. There are probably as many, if not more, reasons for carrying out analysis as there are different analytical techniques. Reasons for analysis include: checking the purity of, for example, raw materials, intermediates or finished products to see if they conform to specification; environmental considerations, for example to make sure discharge limits are not being broken – this may be a legal requirement; as a way of adding value to a product; to investigate the nature of a competitors product; trouble shooting when something goes wrong, and so on.

Analysis and characterisation of colorants involves many steps with a range of factors that need to be taken into consideration and not only during the actual analysis. It cannot be emphasised strongly enough that the key steps, in nearly all characterisation tests and analytical measurements, are those that occur before the sample goes anywhere near a characterisation/analytical instrument.

In dealing with materials evaluation, analysis and characterisation, it is worth considering a few general observations:

- The samples being evaluated should have a pedigree that suggests that the samples are worth the effort.
- All analysis and characterisation exercises produce results of one type or another. One major skill lies in being able to establish that the results can be relied upon. Another quality rests in having knowledgeable personnel who can interpret such results, putting them into a meaningful context, whereby appropriate conclusions can be drawn and action can be taken.
- Sample(s) acquisition and storage should be such that the results will never be compromised because of bad/inferior practices.
- The integrity of the samples is of importance. Much emphasis lies in the origin/history of the samples being analysed.
- Samples may have a composition that gives rise to complexities in both the analysis and the interpretation of results.

This chapter deals with these points prior to consideration of highly relevant analytical and characterisation techniques.

As has already been identified there are thousands of colorants and they may be mixed with, incorporated in, deposited on a wide range of different chemicals/materials. Thus there are a number of steps to go through before any actual and meaningful analysis can take place. These steps are considered further in the following Section 10.3.1 based on the approach of Skoog *et al*.,[27] however, just before that it is perhaps worth stating the general meaning of several common terms related to analysis, including ‘qualitative’ analysis versus ‘quantitative’ analysis.

Qualitative analysis: This can be considered in terms of the 'identification of the constituents of a sample without regard to their relative amounts'. Often it refers to elemental analysis, although it can refer to different chemicals within a mixture or even the identification of different functional groups (e.g. by infrared spectroscopy).

Quantitative analysis: Here the 'identification of the relative amounts of substances making up a sample or establishing the amount of one particular compound/element in a sample' is important. Quantitative analysis often refers to elemental analysis, but it may refer to any constituent of the sample.

Accuracy: Refers to the closeness of the agreement between the result of a measurement or analysis and the true value that should have been obtained from the measurement or analysis.

Precision: Refers to the closeness of the agreement between independent test results obtained under stated and closely controlled conditions. Note that precision depends only on the distribution of random errors and does not relate to the actual true value. 'Independent test result' means that each result is obtained in a manner that is not influenced by any previous result.

It is important to remember the terms 'precision' and 'accuracy' are not interchangeable – they mean quite different things.

10.3.1 Stages involved in successful quantitative analysis

The first task in the analysis or characterisation of any sample is to consider the requirements. Why is the sample being tested and what information is actually required? There can be many reasons for carrying out analysis (as discussed at the start of this section) and these reasons can influence the technique used for the analysis, the method selected and the way the test is actually carried out. When considering the requirements and selecting the method it will normally be necessary to take into account a variety of issues including the following:

- the number of different analytes in (or properties of) the sample about which information is required (and whether simultaneous or sequential analysis is possible by just one technique);
- the nature of the analyte(s) of interest;
- the sample matrix (this may help or hinder the analysis);
- the number and frequency of samples;
- the availability of suitable standards (if required);
- the existence of a suitable method(s) (either in-house or in the literature);
- the accuracy and precision needed;
- the urgency and timescale (related to time needed for sample preparation and analysis);
- the equipment available;
- the expertise available;

- the reliability needed;
- the need for more than one technique to be used to increase confidence in the results;
- the type of validation required;
- the full cost involved in the analysis (including sample preparation and staff time).

A number of these points may lead to consideration of whether the analysis should be carried out in-house or sent out externally on a contract basis.

Having decided on a method the next step should be to obtain a representative sample. If you work in an analysis laboratory then it is likely that samples will just be passed on to you, but in many cases it will be worth enquiring (or offering advice) about sample collection. The importance of sampling can be appreciated when you consider that the possible fate of many tons of product is determined based on the results of tests on perhaps just milligrams (mg) of a sample or that the pollution level of a river may be determined by tests on just a few millilitres (ml) or even microlitres (μl) of a sample or that the quality of a batch of thousands of leaflets may be based on maybe just one section of one leaflet. Thus, the sample used for analysis must be representative of the whole (whatever that may be) and the sample should be homogenous. It could well be that the best approach to take would be to obtain a number of samples, from different places in the bulk, and either analyse them individually (to check uniformity) or blend them together to obtain a single representative sample for analysis. The number and selection of samples should be carried out using a suitable statistical basis. You also need to consider whether the sampling process could affect the composition, for example differential adsorption in the sampling system.

Having obtained (or been provided with) a representative sample the next stage will be to prepare the laboratory sample. There are again a number of points to consider, such as will the sample go off (decompose) or change over a period of time or under certain conditions (for example , the hydrolysis of reactive dyes); and does the sample absorb water from the environment (especially important where accurate weighings are required) as this may affect the results obtained by various techniques?

To increase confidence in the results a number of replicates will be needed. You will need to consider how many repeats will be suitable based on the technique and the level of accuracy required. The replicate samples should all be prepared from the start and should not be, for example, just a variety of dilutions from a single stock solution. Any inaccuracy in the initial weighing or making up of the stock solution will lead to subsequent dilutions also being inaccurate (although the precision may be good). Remember accuracy and precision do not mean the same thing!

For performance evaluation it will be important to maintain the physical integrity of each sample prior to testing. Some laboratory samples will need to be

prepared so that they are in the most suitable physical form for the analysis. In many cases this will mean that samples (which are often solids) will need to be dissolved in a suitable solvent. The solvent needs to be suitable not only from the point of view that it can satisfactorily dissolve all the analytes of interest, but that it can be successfully used with the technique being employed for the analysis/characterisation required. Therefore, selected solvents should not interfere (or react) with the sample and should not give a response during the analysis that will in any way affect the response(s) from the analyte(s). For example, certain organic solvents will absorb electromagnetic radiation of the same wavelength as certain analytes and therefore overlapping bands will appear in some cases with techniques such as ultraviolet (UV) and infrared (IR) spectroscopy leading to inaccuracies and/or confusion. Any reagents or solvents used must be of an appropriate quality for the work being carried out; this often means that fresh, high purity materials (which are expensive) are required, in order to avoid the potential confusion/inaccuracies that may be caused by contaminants.

Depending on the analyte(s) of interest and the matrix present, the elimination of interferences could be an essential step in obtaining acceptable results. There is a wide range of techniques available for eliminating interferences, usually aimed at cleaning up the sample and removing the unwanted species or removing the analyte(s) of interest and leaving the other components behind. Eliminating interferences may be part of the sample preparation technique or it could be an automatic feature of a particular technique or instrument. For example, with gas chromatography (GC) only components which are volatile at the injection temperature will enter and be potentially separated in the GC column, additionally many instrumental techniques are available with detectors that are selective (or can be made selective) in what they will actually detect.

For quantitative analysis, especially where accuracy and reproducibility (possibly from month to month or even year to year) are very important, calibration and validation are essential. Calibration of an instrument may be an in-built feature of an instrument (e.g. the internal calibration of the frequency scale of a Fourier transform infrared (FT-IR) instrument using an in-built laser) or may require regular external checking with suitable certified reference materials. When the unknown concentration of a particular analyte in a sample has to be established, a calibration graph (over a suitable concentration range) will need to be produced for the analyte concerned using standards (preferably certified reference materials) of known concentrations. Work may need to be carried out to validate the complete method, including all sample preparation stages and instrumental measurements, and should investigate any effects caused by the sample matrix. Note that an analyte present in deionised water (e.g. a standard) may not give the same response on an instrument as the same analyte at the same concentration when present in a salt solution or aqueous dispersion (e.g. a sample).

When the sample has been prepared properly and the instrument has been set up correctly (check and make a note of all manually set instrument settings, for future

reference or to make sure that none of the instrument variables have been changed since the last time the same type of analysis was carried out) the same should be ready to be analysed/characterised. Then measure a property of the analyte, for example how much electromagnetic radiation it absorbs at a particular wavelength (see Section 10.4), or how much energy it takes in as it is heated (as in thermal analysis). This is what most people would consider to be the actual analysis step, although it can be argued that analysis involves a lot more than simply measuring some property of an analyte. This stage can also be considered as the data acquisition step (where the raw data about a sample is obtained).

After obtaining the raw data (i.e. the original data) for a sample it is nearly always necessary to carry out some data manipulation (this is usually carried out by the instrument or an attached data processor, e.g. a computer) which may include making corrections or calculating concentrations based on calibration work carried out earlier. This stage gets the data into some useful form that is easily recognised and can be used by the analyst.

The results from the analysis/characterisation of a sample may be presented in many different formats, depending on the instrumental technique used and any associated software used for handling the data, including chromatograms, spectra, thermograms, elemental maps, micrographs, tables of data and a single numerical value. In modern times the interpretation of the data/results generated has become easier (and is sometimes carried out automatically by instruments/computers) owing to increases in the speed, power and sophistication of computers and computer software. Having said that, care still needs to be exercised when interpreting or analysing results – always ask yourself if the results and their interpretations make sense – mistakes can be made (e.g. in preparing samples or standards, or in setting up the instrument) and there is a danger that because the information comes from a computer it is automatically assumed to be correct.

Following the interpretation of the data it should be possible to write a report based on the findings. To be truly meaningful and useful the results should report the confidence levels, taking into account the errors (calculated from replicate samples), associated with any values reported. Additionally, units (where relevant) must be included for all values quoted. In most cases it will also be necessary to include the following information:

- the unique sample name/number;
- the experimental method used or reference to a standard method if used (for sample preparation and for analysis);
- instrumental type (and unique identifying label if more than one in the same laboratory) and operational settings;
- the date, place and name of the analyst associated with the work.

Note that operator effects on results obtained can be significant when sample preparation and analysis are not fully automated; this is true even when a standard method is being followed.

You should bear in mind the points made in this section when reading all the other sections. Remember there may not be much point in measuring and reporting results, for example, to three decimal places just because the instrument/computer generates them that way, especially if there are or could be gross errors in your sampling or sample preparation techniques.

Commercial colorants, inks and surface coating formulations are multi-component systems that have generally increased in their chemical complexity owing to the pressures continually to improve formulations and their performance (in a highly competitive market), together with the ever stricter health and safety legislation which is being introduced. Heterogeneous samples such as dyed textiles also present particular potential problems when it comes to analysis.

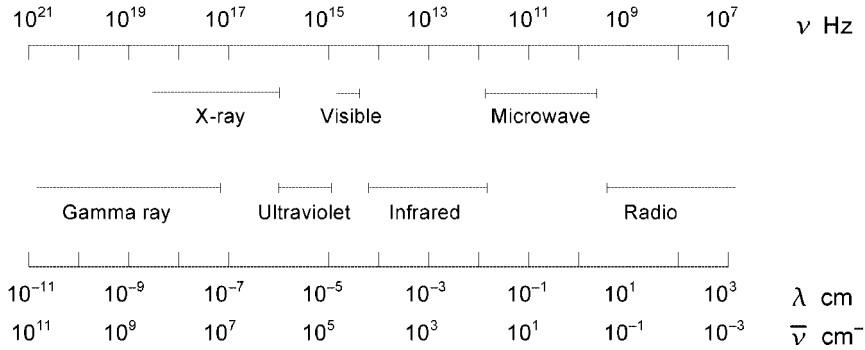
10.3.2 Summary

- Before starting (or requesting) an analysis it is important to consider carefully exactly what information is required and what level of uncertainty (i.e. errors) is acceptable as this will have a big influence on the way the sample is handled and the technique(s) employed.
- There are a number of different steps involved in characterising or analysing a sample – all steps are important to some extent and can influence the result obtained.
- A representative sample must be obtained and used – the consequences of failing to do this could be enormous as wrong decisions could be made based on the results obtained.
- Care with sample preparation is essential especially if quantitative results are required.
- All conditions and instrument parameters should be recorded so that a test could be repeated if required, in exactly the same way, at a later stage.
- Where possible quote the errors and the units associated with any values reported as the results of an analysis or characterisation.

10.4 Molecular spectroscopy/spectrometry

Spectroscopy is the study of the interactions between radiant energy and matter. The frequencies, wavelengths and wavenumbers associated with different regions of the electromagnetic spectrum are shown in Fig. 10.4.

This is of fundamental importance to chemists and materials scientists as the wavelengths at which an organic compound absorbs radiant energy are dependent upon the structure of the compound concerned. Therefore, spectroscopic techniques may be used to determine the structures of unknown compounds and to study the bonding characteristics of known compounds. It must, however, be remembered that most ‘real’ samples contain a number of components and hence the spectral data obtained, which is dependent on a number of factors, including how it is collected, is likely to contain ‘contributions’ from the various



10.4 Regions of the electromagnetic spectrum.

components. Thus, analysing mixtures can lead to problems of interference such as overlapping absorbance bands. However, with experience and the advances that have been made in developing the software packages (that are an integral part of most analytical instruments) data processing and manipulation can assist in the extraction and understanding of a far greater amount of chemical information from mixtures using modern technology and methods. It should be noted that impurities or even analytes of interest within a sample (especially compounds present at low concentrations), unless they contain a particular chemical group (usually needing to be unique to a single chemical within the sample) that interacts (e.g. absorbs a specific wavelength) very strongly, can escape detection on examination by molecular spectroscopy.

Whilst spectroscopy techniques can be used on their own to obtain spectral information about a sample they are also commonly incorporated as a detector as part of another technique, for example the use of an ultraviolet absorbance detector as part of a liquid chromatography system. In recent years there has been much enthusiasm for the research and development of 'hyphenated' techniques, that is the interfacing/linking together of two or more techniques, because of the enhanced additional data that can be generated.

10.4.1 Infrared (IR)

The region of the infrared normally employed for the analysis of materials is in the wavelength range from 2.5×10^{-6} m to 16×10^{-6} m; this is more commonly expressed as the number of waves per cm, i.e. 4000–625 cm^{-1} (in wavenumber units). This region falls within what is often referred to as the mid-infrared region. The full IR region is normally regarded as covering wavelengths from about 750 nm up to 1mm. There has been increasing interest in the near infrared (NIR) region in recent years for process monitoring and quality control (QC) checks of materials, for example, when they enter or leave a site.

The 'fingerprint region' contains numerous and frequently overlapping absorption bands, the exact assignments of which are normally impossible even when a compound of known structure is analysed. The term fingerprint is employed because the pattern of absorption in that part of the spectrum is uniquely characteristic of the compound concerned. The main value of this region is in establishing the identity of samples obtained from different sources. If two samples are identical then their infrared spectra will be exactly superimposable when measured under the same conditions.

It should always be remembered that an infrared spectrum for a mixture of organic compounds will contain contributions (bands that will often overlap) from each of the components present in the mixture. Therefore, interpretation of spectra obtained from mixtures can be very difficult, especially if any or all of the compounds are unknown. It should be noted that impurities (compounds usually present at low concentrations), unless they contain a very strongly absorbing group, can escape detection on examination of infrared spectra.

Infrared instruments

Calibration of instruments

It is good practice to check the accuracy of infrared spectrophotometers (including FT-IR spectrophotometers) at regular intervals by reference to the infrared spectrum of a standard. Conventionally polystyrene has been employed for the purpose (the bands at 1603 and 1028 cm^{-1} being particularly useful). The frequency accuracy of a modern instrument is normally internally calibrated automatically by the instrument.

Evolution of FT-IR technology

Fourier transform infrared (FT-IR) spectroscopy is now one of the most popular techniques in analytical chemistry, this technology having several advantages compared to conventional dispersive infrared instruments. Developments in instrument hardware, in computer software (usually by the instrument manufacturers) and in computing power generally has resulted in very powerful data collection and data handling systems for the analysis and characterisation of all sorts of materials including colorants.

Modern times

Specialised sampling techniques such as attenuated total reflectance (ATR) and diffuse reflectance (DR) have been found to be extremely effective and hence have gained considerable popularity. Microsampling, for measuring very small samples, has become a common technique over the last decade as beam condensers and infrared microscopes (plus accessories) have been improved.

Applications of FT-IR

The physical state of a sample and the information required has to be considered when deciding how best to carry out an infrared analysis of a sample. As has been mentioned previously, sample preparation can be very important and there are examples where this is true for colorants analysed by infrared. For example, if the polymorphism (capable of existing in more than one crystal form) of a colorant is to be studied, then the sample preparation step(s) should not physically nor chemically alter the sample, that is, minimal and mild sample preparation should be used (ruling out the use of the alkali metal halide disk technique, where grinding can cause conversion in crystal forms).

Identification of unknowns

One of the most frequent ways in which infrared spectroscopy is employed is as a qualitative tool for the identification of 'unknown' materials. This is because the absorption bands that a polymer or other material has are very characteristic and reproducible for the chemical functional groups/components within that material. A spectrum may be considered to be a 'fingerprint' for a sample, particularly the region 1400–600 cm^{-1} which is commonly termed the 'fingerprint' region (described briefly earlier in this section). To be a certain material, without any doubts regarding the exact identity, a sample spectrum needs to be in agreement in all respects with a reference spectrum. Thus, all the bands of the reference spectrum need to be present and each band should have the same breadth, that is cover the same frequency range as the reference spectrum. The relative absorbance of each IR band to the others should also agree. If there are additional bands not present in the reference spectrum then the sample material may be a mixture or have a slightly different structure to the reference material. If the match is perfect, it provides a very good basis for identification. It should be remembered, however, that there is always the possibility that a material is a mixture in which the individual substances absorb in common ways. This would be the case for a mixture of polyethylene and paraffin wax. Therefore, other techniques such as thermal analysis may be needed to detect the mixture or confirm the purity of a sample.

Approaches to identifying unknowns: There are a number of different approaches that may be taken to identify unknown compounds from their spectra, the most common ways being:

- frequency–structure correlation charts;
- flow charts based on principal infrared bands;
- collections of reference spectra (these may be stored either in a book or on a computer).

The use of correlation charts can help in piecing together an unknown's identity. For example, carbonyl groups absorb infrared energy over a certain range within

which aldehydes, ketones, carboxyls and other forms of carbonyls are known to absorb at specific frequencies. Although it may not necessarily be possible to identify an entire compound (e.g. a specific dye), it is feasible to identify functional groups based on absorptions in particular regions, for example the carbonyl region, and to which the wavelength corresponds, for example an ester functional grouping. Although it may not be possible to identify a material completely, the spectrum will usually provide an indication of the kind of chemical structure that is present.

Brief details of IR techniques/methods are included in this section. For a more comprehensive explanation of the principles, practicalities and a wide range of applications readers are advised to refer to the excellent book by Chalmers and Dent.[28]

Quantitative analysis of mixtures

Infrared analysis can potentially determine quantitatively the relative amount of different components in a system, such as a mixture of two dyes. The general requirements are that for each component there should be an absorbance band that is relatively sharp and that it should be unique to the component that produces it in the system in which it exists. It is important that sample thickness/concentration (depends on how the samples are prepared and mounted) is adjusted so that absorbance is in a linear range relative to concentration, that is, absorbance should not be too high.

The mass (m) ratio of components is directly proportional to the absorbance ratio of the bands corresponding to each component. Thus for a mixture of two colorants (colorant A with a unique band at 1720 cm^{-1} and colorant B with a unique band at 2235 cm^{-1}) the following can be used:

$$\frac{\text{Concentration of A (m/m)}}{\text{Concentration of B (m/m)}} = K \frac{\text{Absorbance at 1720 cm}^{-1}}{\text{Absorbance at 2235 cm}^{-1}}$$

A common procedure is to produce standards of known composition and then plot the absorbance ratio against the mass percentage of one component or against the mass ratio. The plot should be linear and pass through the origin, that is, the absorbance ratio is zero when one of the components is absent. The constant K is calculated from the slope of the plot. The mass percentage of an unknown may be determined from the graph using the absorbance ratio or directly by calculation using the previously obtained value for K.

For the most accurate quantitative analysis, homogenous samples must be used and care needs to be taken when preparing the samples – dependent partly on the mode of operation. This may involve preparing solutions, however, this requires a solvent whose spectrum does not interfere with the required bands of the analytes in the sample.

Modes of operation

Transmission techniques

When measuring transmission for thin samples, for example films, there is a need to ensure absorption of IR energy is not too strong in any part of the spectrum. For a colorant in a powdered form the traditional way to obtain an infrared spectrum is to dilute the colorant whilst creating a homogenous dispersion either in Nujol (a liquid paraffin) or an alkali-metal halide (normally potassium bromide). Clearly, it is important that the diluent (e.g. Nujol or KBr) does not have absorption bands in the same region of the spectrum as the sample being analysed.

To make a KBr disk the sample is usually pre-ground before mixing (in a ratio of about 1:200–100, depending on the strength of the infrared absorption of the sample) with dried potassium bromide. Following mixing to form a homogenous material the powder is transferred and appropriately packed in a die assembly and then placed in a hydraulic press. A load of about 10 tons (10 000 kg) is normally applied. The resultant disk should be translucent with the colorant homogenously distributed and can be carefully (to avoid contamination, e.g. moisture and grease from fingers, and damage) positioned in the disk holder that is then placed in the infrared instrument ready for data collection.

Reflection techniques

For some sample types, for example a coated substrate, it is not possible to collect an infrared transmission spectrum, whereas in some cases (e.g. when there are concerns over the effects of sample preparation) it may be more desirable to collect a reflected spectrum. The most popular reflection techniques nowadays are internal reflection spectroscopy (IRS) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

DRIFTS: Solids such as powders and fabrics can be studied by collecting the diffusely scattered radiation, without the need for any major preparation of the sample. In reality what happens is that some radiation travels (i.e. is transmitted) through the particles (in the case of a powder) where characteristic wavelengths for the material concerned are absorbed before being scattered at any angle. The infrared spectrum obtained from a sample in a DRIFTS accessory can be more complex than a traditional transmission spectrum, however, because a number of inter-actions and processes happen to the radiation (transmission, absorption, specularly reflected, internally reflected and diffusely scattered). Again the quality of the spectrum obtained for a sample will be dependent on a number of factors including the experimental conditions used (e.g. DRIFTS accessory employed) and sample properties such as homogeneity – both physical (e.g. particle size) and chemical; concentration and packing density (for powders it may be necessary to dilute them with an alkali-metal halide); particle size; refractive index of sample; surface rugosity; and absorption coefficients.

ATR: Internal reflection spectroscopy is sometimes called multiple internal reflectance (MIR), although it is generally better known as attenuated total reflectance (ATR). A further name that has been used is total frustrated reflection (TFR). A variety of geometries and of ATR crystal materials have been utilised in the development of a range of ATR accessories for infrared instruments. These differences result in a wider range of applications and even in differences in the data that can be obtained for a given sample, for example, owing to differences in the refractive indices of different crystal materials the depth of 'sampling' for a given material will depend on the crystal used. The angle of incidence of the infrared beam at the crystal–sample interface also influences the 'sampling' depth. Analysts can sometimes use this phenomenon to their advantage, for example when studying surface coatings/modifications (by using a range of crystal materials and/or angles of incidence).

A potential advantage, that many users utilise, with ATR accessories is that often minimal or no sample preparation is required. Whilst an infrared transmission spectrum of a given colorant will have absorption bands in the same position as an infrared ATR spectrum of the colorant the relative intensities of the bands will vary. The explanation for this phenomenon is again related to the 'sampling' depth, which is actually wavelength-dependent in ATR experiments with the bands becoming relatively stronger with decreasing wavenumber (i.e. with increasing wavelength). Thus, ATR spectra are not equal energy spectra!

FT-IR microscopy

The FT-IR microscope combines microscopy with IR spectroscopy to provide a versatile instrument for molecular microanalysis. The technique has really taken off in the last decade and has embraced a wide range of applications. Nowadays, developments in PC and software products allow for instruments with remote control (including focusing) of microscopes.

Application areas for FT-IR microscopy include:

- composition of plastic laminates (it is necessary to prepare a cross-section of the laminate by conventional microtomy);
- *in situ* analysis of surfaces – particularly well suited for investigating surface coatings and contaminated films;
- characterisation of crystalline substances (including individual particles – if they are not too small);
- analysing evidence in forensic investigations, e.g. fibres or paint chips from the suspect/scene of the crime;
- identification of fibres.

Table 10.4 General comparison of spectroscopic techniques

Infrared	Raman
Requires functional groups to exist which are capable of forming dipoles	Requires functional groups to exist which are not generally capable of forming dipoles
i.e. asymmetric bonds	i.e. symmetrical bonds
Examples of IR active bonds are: >C=O, >N–H, –O–H, S=O, –C≡N	Examples of Raman active bonds are: –C≡C–, >C=C<, C–S, –S–S–, –N=N–, –S–H

10.4.2 Raman

Raman spectroscopy is by no means a new technique, although it is not as widely known or used by chemists as the related technique of infrared spectroscopy. However, following developments in the instrumentation over the last 20 years or so Raman spectroscopy appears to be having something of a rebirth. Raman, like infrared, may be employed for qualitative analysis, molecular structure determination, functional group identification, comparison of various physical properties such as crystallinity, studies of molecular interaction and determination of thermodynamic properties.

Raman spectroscopy is a light scattering method that is non-intrusive; sampling, sample form and sample size are generally not restrictions for the analysis. Like infrared, it can be employed equally successfully for the analysis of solids, liquids and gases.

The reason why Raman spectroscopy has never really been widely practised, certainly nowhere near as much as infrared spectroscopy, is because a large proportion of samples either fluoresce or contain impurities that fluoresce or the samples 'burn out' when excited by the visible lasers commonly employed in conventional Raman measurements; this has been especially true for colorants. The origins of this fluorescence and the thermal heating comes from electronic transitions occurring in samples at or near the laser frequency; the fluorescence is generally many times stronger than the Raman scattering signals and thus swamps out the Raman signals in a spectrum.

When considering Raman spectroscopy it is useful to compare it to infrared spectroscopy since the two techniques are often considered complementary. The selection rules for the two techniques can be stated simply as in Table 10.4.

Strengths and potential advantages of Raman spectroscopy

Raman spectroscopy actually has quite a few benefits and can for certain samples be a better technique to use than infrared spectroscopy. The major strengths of Raman spectroscopy as an analytical technique are:

- Water is only a weak Raman scatterer, hence analyses in aqueous solutions are possible.
- Glass is only a very weak Raman scatterer, hence samples can be analysed in glass vessels (useful for volatile and/or toxic samples).
- Analysis is easy (plus no/minimal sample preparation) – this is often also true with FT-IR analysis (depending on the mode of operation).
- Samples may be in any physical state and investigated under a range of temperatures and pressures.
- Only small quantities are required and Raman microscopes are available (with greater resolution than FT-IR microscopes and even greater resolution as the excitation wavelength from the laser becomes shorter.
- Raman optics do not need to be purged since CO_2 and H_2O, generally, do not interfere with Raman spectra unlike in infrared spectra (this is not such an issue as modern software can often compensate for this phenomenon).
- Investigation of low wavenumber bands is possible compared with infrared which has a much higher wavenumber cut-off (for infrared this is variable and dependent on the mode and infrared accessory used).
- Raman bands are sharp and there are fewer of them, hence interpretation can be easier;
- Raman scattering intensity is linearly related to concentration.

Developments in Raman spectroscopy, with applications for colorants, have included resonance Raman, surface enhanced Raman spectroscopy (SERS), surface enhanced resonance Raman spectroscopy (SERRS) and near-infrared Fourier transform Raman spectroscopy (NIR-FT-Raman), with the latter technique discussed in the next section.

Near infrared Fourier transform-Raman spectroscopy

This technique has emerged and developed within the last 15 years or so. A Nd:YAG near infrared laser is normally used that emits its energy at 1064 nm (i.e. in the NIR); this is a much higher wavelength than in conventional Raman spectroscopy (which uses lasers that emit in the visible region). The major advantage of this is that there is a reduced (but not totally eliminated) problem of fluorescence, that is, fewer samples fluoresce. A potential disadvantage may be a reduction in the sensitivity of the detector used.

Advantages of the Fourier transform technique

Many of the advantages of Fourier transform infrared (FT-IR) over dispersive infrared also apply to FT-Raman over conventional Raman, for example signal averaging and spectral subtractions, together with all frequencies are measured simultaneously and hence there is increased speed of analysis.

Use of NIR energy as the mode of information transport provides the potential for high signal throughput and the use of fibre optic cables over long distances for

remote on-line analysis; this is not a viable option for mid-infrared analysis since there are not the materials available which could carry the mid-IR signals unaltered over long distances.

Applications of Raman spectroscopy

The application areas are as varied and numerous as those found in infrared spectroscopy, however, the technique has not been employed quite so widely (due largely to the cost of the instruments, the problems of fluorescence and 'burn out' mentioned earlier, and the time taken by older instruments to obtain a reasonably good quality spectrum).

In addition to being capable of helping in the elucidation of the structure of a colorant, Raman spectroscopy can be used to monitor organic reactions in aqueous media, such as the diazotisation of an aromatic amine, the coupling reaction and the condensation reaction in the synthesis of a reactive azo dye.[29,30] It is interesting to note that the preparation of samples as an IR KBr disk, or for very sensitive, highly coloured or strongly absorbing samples as IR Nujol mulls between salt flats, can give good strong Raman spectra even for some black azo dyes that burn out when analysed as the neat powder (as illustrated by Chalmers and Dent[28]). Applicability and difficulties with some phthalocyanines (linked to fluorescence caused by transition metals such as copper) have been investigated.[31] Additionally, obtaining spectra of colorants whilst they are in a polymeric matrix (such as dyes on textiles) is possible, for example, with coloured cellulose film, since cellulose is a very weak Raman scatterer.[28] Raman spectroscopy is also widely used for many polymer systems (from fibres to films, to paint systems).

10.4.3 Nuclear magnetic resonance (NMR)

Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for an organic chemist for the characterisation of molecular structure and may be used for samples in the liquid or solid state. NMR has been used traditionally to provide a map of the carbon/hydrogen framework of a chemical. Many nuclei behave as if they are spinning about an axis and because they are charged appear to act as bar magnets. The two most important nuclei that act in this way are ^{1}H and ^{13}C. Examples of other nuclei that are sometimes utilised, and are present in the structures of some colorants, include ^{19}F and ^{15}N. NMR and IR are often used to complement one another. Again though, the technique works best for relatively pure, single component, samples.

Fourier transform can be used with NMR experiments and allows simultaneous irradiation at different frequencies to be performed. This is controlled by a computer which does the mathematical calculation (transformation) to convert the signals obtained into a spectrum. This means multiple scans can be carried out much faster. Typically four scans are used for ^{1}H, while typically 1000–10 000

scans are averaged for ^{13}C (to reduce noise, i.e. increase the signal to noise ratio). Solvents will also give peaks (these must be away from the region of interest). The use of deuterated (^{2}H) solvents, such as D_2O, to avoid the appearance of ^{1}H peaks from the solvent in ^{1}H-NMR is common practice. It is now possible to use NMR in a variety of ways (including two-dimensional NMR) to obtain all sorts of information.

Applications of NMR

NMR is a firmly established technique, however, its full analytical potential has clearly not, as yet, been fully realised with new applications and experiments carried out by this method still being regularly reported.

Solid state NMR

The early investigations with NMR by physicists in the late 1940s and the 1950s, examined both solutions and solids extensively. When chemists adopted the technique – and transformed NMR into one of the most powerful methods for the characterisation of compounds – only solutions and liquids were studied, with few exceptions (between 1956 and 1976). However, in modern times it has become accepted that solids are (almost) as amenable to NMR as solutions.

In isotropic solutions of low viscosity, linewidths for typical spin = ½ nuclei, such as ^{1}H and ^{13}C, are substantially less than 1 Hz (i.e. very narrow). Crystalline samples, such as pigments, and rigid amorphous materials, however, usually exhibit such extreme broadening that all the information on chemical shifts and coupling constants appears to be lost. Carbon-13 and proton NMR linewidths for typical organic solids in powdered or microcrystalline form are roughly 30 kHz and 60 kHz respectively – hence the lack of interest by chemists 20–30 years ago. The chemical information content of solid state NMR is, however, far greater than that of solutions, the problem is extracting it.

The reasons for the complexity of solid state NMR spectra are:

- Orientation dependence of the NMR interactions which give the chemical information.
- Severely restricted mobility of molecules in solids so that little averaging can take place; in contrast, in solution molecules 'tumble' rapidly, isotropically and chaotically, at a sufficient rate that the NMR parameters are averaged to their isotropic values.

Magic-angle spinning (MAS)

What is required for solids is obviously the equivalent of the molecular tumbling in liquids and solutions. The approach normally employed is to spin a bulk sample coherently about an axis making an angle, β. If β is set at 54° 44', all anisotropy

effects are removed from the spectrum, and each powder pattern will collapse to a single line at a frequency governed by the relevant isotropic chemical shift.

Although in principle MAS should be effective for obtaining spectra of dilute spins (including ^{13}C) in the presence of abundant spins (such as ^{1}H or ^{19}F), in practice the usually available spinning speeds are inadequate. Instead, double resonance (decoupling) techniques, as often employed in solution state NMR, are used. The powers necessary for solids are orders of magnitude greater than for solutions. This high-power proton decoupling (HPPD) technique combined with MAS, provides high-resolution spectra of dilute spins (e.g. ^{13}C) for most solids.

Other NMR modes of operation include:

Cross-polarisation (CP), which involves a cross-pulsing sequence. Under the appropriate conditions, magnetisation flows from protons to ^{13}C during the contact time, when resonant radio frequencies are applied to both protons and the nuclei to be observed (e.g. ^{13}C).

Combined rotation and multiple-pulse spectroscopy (CRAMPS). A special pulse sequence, in addition to MAS, is required for high-resolution proton NMR in solids. This technique is known as CRAMPS.

10.4.4 Ultraviolet (UV)/visible (vis) spectrophotometry

Ultraviolet and visible spectrophotometry is usually carried out with solutions for the quantitative determination of components that absorb in the UV or visible regions of the electromagnetic spectrum. Solvents must be selected that do not absorb in the region of interest. The usual region of absorbance that is of interest is within the range 180–780 nm and is associated with electronic transitions in double bonds (e.g. the carbonyl (>C=O) group at ~280 nm or a benzene ring group at ~250 nm); the linking of two aromatic groups, such as benzene rings, through an azo (–N=N–) results in a bathochromic shift (to longer wavelength) into the visible region. Some spectrophotometers extend their wavelength range significantly beyond 700 nm and cover the near-infrared, where some colorants (often specialist ones) absorb electromagnetic radiation.

A suitable detector measures the percentage transmission, which can be converted to an absorbance value for quantitative analysis, for example, in quality control for the quantitative determination of the strength of a particular dye. Calibration with solutions of known compositions and concentrations are normally required so that the concentration of a dye solution of unknown concentration (e.g. a residual dyebath or wash-off solution) can be determined; this is possible through the use of the Beer–Lambert equation ($A = \varepsilon cl$), where ε is the molar extinction absorption coefficient (also known as molar absorptivity or sometimes spectral absorption coefficient) for the absorbing material in molars $dm^3\ mol^{-1}\ cm^{-1}$ (this is wavelength dependent and usually measurements are carried out at the wavelength of maximum absorption), c is the concentration of the absorbing material in moles and l is the optical path length of the absorbing material in cm.

As with IR, this technique is not capable of separating components, thus if two compounds are present that both absorb at the same frequency then they both contribute to the overall absorbance of the sample being analysed. However, it is possible if at least one of the components has a unique absorbance band to carry out at least partial quantitative analysis. Again advances in software, including data manipulation, such as taking derivatives, for example looking at the rate of change of absorbance with respect to wavelength, can sometimes help to resolve the data for simple mixtures of dyes.

In cases where confirmation of identity is required, the UV and/or visible spectrum of a colorant may supplement the IR spectrum or any other means of identification. Note that a UV/visible absorbance spectrum is unlikely to be sufficiently unique to be conclusive on its own.

UV/visible systems often make very good detectors to attach to other instruments, especially liquid chromatography and capillary electrophoresis, that separate the components prior to their spectroscopic detection. Fixed wavelength detectors, multiple wavelength detectors, variable wavelength detectors and diode array detectors exist to monitor UV/visible light absorbance of a mobile phase (carrying analytes) after it has passed through a separation column or capillary (as in high-performance liquid chromatography and capillary electrophoresis). Fluorescence detectors are also sometimes utilised.

UV/visible spectrophotometry has been and continues to be important in the characterisation of dyes (with literally thousands of papers on dyes having some mention of this technique) and, additionally, can be used to monitor the decolorisation of solutions. One interesting collection of papers that helps to highlight the potential usefulness of UV/visible spectrophotometry is that produced by Oakes and coworkers.[32–35]

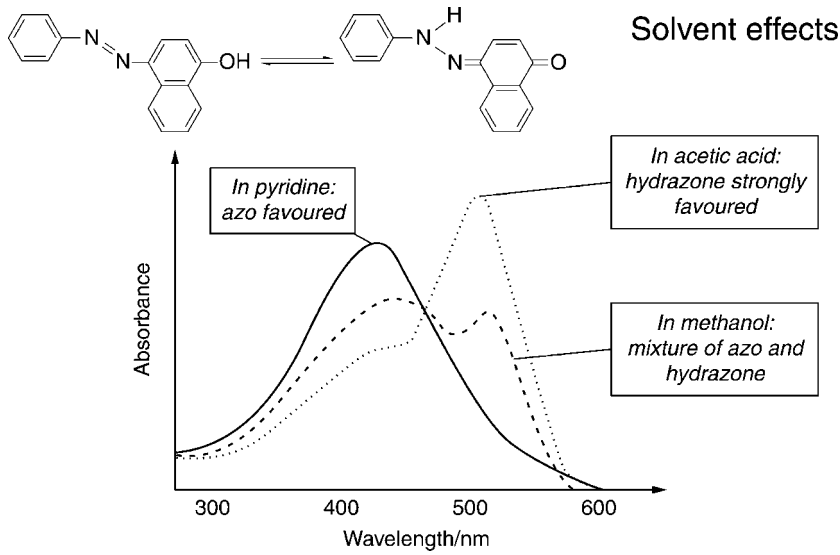
However, to obtain more information (especially for mixtures or unknowns) chromatographic techniques are frequently used, as discussed later.

The pH sensitivity of some dyes (some are used as pH indicators) are well known, others less so. Solvatochromism in colorants can also be important and similarly be investigated by UV/visible spectrophotometry (an example of this is shown in Fig. 10.5).

The use of online colour measurement for process control purposes has been reviewed by Gilchrist[36] and Ferus Comelo.[37]

10.4.5 Mass spectrometry

Mass spectrometry (MS) has become one of the most versatile analytical techniques since a variety of interfaces can be used in order to analyse a wide range of sample types in different physical states (both volatile and non-volatile) from different sources. The fact that MS can be hyphenated to several other techniques in order to, for example, resolve components in mixtures prior to the MS analysis, makes it an extremely powerful technique. The good sensitivity and high specificity



10.5 Solvent effects on the absorbance spectrum of an azo-hydrazone dye.

of MS means that it would be the method of choice (subject to available funds) in the analysis of a wide range of samples, including many environmental samples. MS has been widely used in the analysis of dyes for many years. Applications of liquid chromatography-mass spectrometry (LC-MS) in environmental chemistry is the subject of a book edited by Barceló, which includes sections on the analysis of dyes by LC-MS.[38]

10.5 Atomic spectroscopy (and elemental analysis)

Atomic spectroscopy is employed for the qualitative and quantitative determination of around 70 elements; primarily for the analysis of a wide range of 'metals' (often for trace analysis). Atomic spectroscopy can provide information regarding the identity and concentration of atoms in a sample irrespective of how these atoms are combined. In contrast, molecular spectroscopy gives qualitative and quantitative information about the molecules (or particular functional groups present in molecules) in a sample.

Sensitivities of atomic methods lie typically in the parts per million (mg dm^{-3}) to parts per billion (μg dm^{-3} or μg kg^{-1}) range, although in some cases in the parts per trillion (ng dm^{-3}) range. (You may wish to think about the implications of this !!!). Additional virtues associated with these methods include speed, convenience, unusually high selectivity and moderate instrument costs (although not for an inductively coupled plasma–mass spectrometry system!).

The first key step in all atomic spectroscopic techniques is 'atomisation', a

process in which a sample is volatilised and decomposed in such a way as to produce an atomic gas. This is by far the most important step in atomic spectroscopy. As atomic spectroscopy relies on the analyte being atomic, the efficiency and reproducibility of atomisation will largely determine the entire method's overall sensitivity, precision and accuracy.

Atomic emission spectra are produced when an atom or ion excited by the absorption of energy from a hot source relaxes to its ground state by giving off a photon of radiation (with a characteristic wavelength). In contrast, atomic absorption takes place when a gaseous atom or ion absorbs a photon of radiation (with a characteristic wavelength) from an external source and is thus excited.

Atomic absorption spectroscopy (AAS) is probably still the most widely employed of all the atomic methods because of its simplicity, effectiveness and relatively low cost. A 'line source' of radiation is required for AAS (they do not employ a continuous source of radiation) hence a complete spectrum is not obtained. The sources (which are changed depending on the element of interest) emit certain lines of radiation that have the same wavelength as that of the absorption peak of the analyte of interest.

Sample preparation is again a key step in the analysis. The sample to be analysed is usually in solution in order to be efficiently introduced and atomised in the flame or plasma. For many solid samples, such as dyed/printed textiles, this will involve digestion in strong acid followed by ashing in a furnace (to break down organics and drive off carbon and hydrogen). After ashing the sample is taken up in some acid and diluted to volume prior to atomic analysis.

Atomisation in plasmas

Commercial plasma atomisers became available in the mid 1970s and offer several advantages over flame atomisers. A plasma is a conducting gaseous mixture containing a significant concentration of cations and electrons.

In the argon plasma employed for emission analyses, argon ions and electrons are the principal conducting species, although cations from the sample also contribute. Argon ions, once formed in the plasma, are capable of absorbing sufficient power from an external source to maintain the temperature at a level at which further ionisation sustains the plasma indefinitely; temperatures as great as 10 000 K are encountered. Of the power sources investigated, the radiofrequency, or inductively coupled plasma (ICP), source was found to give the greatest advantage in terms of sensitivity and freedom from interference. The excellence of these results stems from the high stability, low noise, low background and freedom from interferences of the sources when operated under appropriate experimental conditions.

Generally, the detection limits with the ICP source are comparable to or better than those of other atomic spectral procedures. Additionally, ICP allows you to scan for multiple analytes simultaneously, unlike AAS, for instance, which

traditionally can only test for one element at a time (although modern instruments and lamps are now available that have a limited capability for multi-element analysis, for certain popular elements). The biggest disadvantage of ICP is that the instrumentation is expensive to purchase.

Reasons for metal ions/elements to be present in colorants include: they are an integral part of the colorant, such as in an inorganic pigment or a metal–dye complex; they are an impurity, possibly from a raw material/intermediate, a reagent/catalyst used in the synthesis or a species present in the water/media used during synthesis/isolation.

Readers should note that other analytical techniques also exist for investigating the elemental make up of samples, such as CHN analysers (especially for compositional analysis of pure organic chemicals) and X-ray fluorescence (XRF) instruments, and techniques such as X-ray photoelectron (XPS) spectroscopy are available for surface-specific analysis, but expensive.

10.6 Separation science

Most real samples that are analysed are, unless they have been deliberately purified (and even then they may still be), actually made up from a number of different chemicals; this is certainly true for most colorants. As has already been discussed when considering molecular spectroscopy techniques, analysis of mixtures can lead to complex, incomplete or even unresolvable data. The answer/solution to problems of this type normally involves separation science, where there is selective or differential interaction/behaviour of the different components in the separation system. The principle separation sciences are chromatography and electrophoresis.

10.6.1 Chromatography

Chromatography is generally considered to be a technique for separating (and identifying) organic molecules, especially those of low to medium molecular masses (typically up to about 1000 atomic mass units, amu), although chromatography is much broader than this (with variations, mostly in the technology of the stationary/fixed phases, for small inorganic ions and large macromolecules). The separation of colorants has been a very popular application area for chromatography techniques over the 100 years since its initial development. In fact its first reported use was the separation of plant colorants, which lead to its name ‘chromatography’ – colour writing. Chromatographic techniques are many and may be employed on a micro scale for quantitative and qualitative analysis or may be adapted to a macro scale for preparative work.

Dyes have been traditionally analysed by thin-layer chromatography (TLC) and then more recently by high-performance liquid chromatography (HPLC). GC is not normally suitable for dyes since dyes are generally non-volatile ionic or strongly polar compounds. The most popular form of dye analysis by HPLC

usually employs a reversed phase column and an ion-pairing agent to complex with the charged sites on the dye molecule. Advances in chromatography for dyestuffs have been reviewed by Evans and Truslove.[39]

Thin-layer chromatography (TLC)

Thin-layer chromatography is generally considered to be a low-tech approach that is cheap and cheerful, which is especially useful for quick checks on samples in almost any location (from the factory floor to the research laboratory to out in a field!). Whilst it is normally used in this way, it can also be linked with automatic densiometers and spectrophotometers to form quite a sophisticated analysis system capable of generating quantitative as well as qualitative results.

Examples of applications include:

- monitoring the synthesis of a colorant (following the consumption of raw materials – often using a UV lamp to check for their presence, the formation of the required product(s) – a coloured spot or spots, the formation of side products (again may be coloured) and the formation of impurities);
- checking the organic purity of a colorant (note, inorganic species, such as salts will not show up), although care should be taken as an organic impurity may not be 'seen' – either masked by an analyte spot or, if it does not absorb visible light (and it is not checked for with a UV lamp), it may just be 'missed';
- checking an environmental sample (possibly from a watercourse or an extracted sample, e.g. extracted from soil) for the presence of colorants;
- following the decolorisation/breakdown of colorants (e.g. via a biochemical or chemical reaction).

Often analysis by TLC will be followed up by further analysis using liquid chromatography (or capillary electrophoresis), especially if more quantitative analysis is required.

Gas chromatography (GC)

In gas chromatography (GC) the mobile phase is a gas (e.g. nitrogen, N_2) and moves rapidly compared to the movement of the separated substances. Thus, R_f values (retardation factor, i.e. the distance travelled by an analyte divided by the distance travelled by the mobile phase (these values are routinely used in TLC)) would be very small and hard to determine. Retention times are therefore employed in preference to R_f values. The retention time of a compound (also used in liquid chromatography) may be described simply as the length of time it takes a compound to be detected following injection. This quantity has units of time, that is, seconds or minutes.

GC is sometimes referred to as gas liquid chromatography (GLC) since the stationary phase in modern capillary columns behaves (although it is normally

covalently bonded to sites on the internal wall of the capillary) as if it is a liquid and the analytes partition into this phase. GC column packings and liquid phases are available in considerable diversity to achieve sharp separation of a variety of compounds. The oven may be operated isothermally or temperature programmed to as high as about 350 ºC depending upon the particular packings and liquid phases employed, this allows separation of compounds of widely different volatility. To improve resolution and reduce tailing, some polar compounds, such as acids, alcohols and amines, may first be converted to a derivative. For example, conversion of acids to methyl esters is common.

Most colorants, because of their ionic (most dyes) or particulate (pigments) nature with strong intermolecular forces and low volatility cannot be analysed by GC, however, lower molecular weight species, such as certain starting materials, impurities, additives and breakdown products from colorants can be analysed. These include aromatic amines such as those in the German MAK III list, which were discussed earlier in this chapter in Section 10.2.2.

A frequent use of GC with polymers is in the quantitative determination of residual monomer and solvent content, even at sub parts per million levels. This is especially important in food contact applications (e.g. printed packaging materials) where taint and odour issues are important. There are a range of sample preparation and injection techniques to deal with a vast range of samples including, for example, 'headspace' sampling where a solid can be incubated for a period of time and then the vapours from above the solid are transferred into the GC capillary.

There are a variety of detectors for GC systems, however, mass spectrometry (MS) is generally accepted as the best overall. GC-MS is a very powerful and popular technique and therefore has a wide range of different application areas. The major reasons for using GC-MS are:

- identification of unknown analytes;
- target analysis – looking for specific compounds (usually quantitative analysis, requiring suitable calibration);
- post chromatography separation (it is possible to 'separate' and resolve co-eluting analytes in the MS);
- matrix elimination (when MS is needed).

Pyrolysis

Identification of non-volatile compounds by GLC can be carried out using pyrolysis to decompose the polymer into volatile products prior to analysis by GLC. Pyrolysis chromatography constitutes an important section of gas chromatography practice. It is of particular use in characterising compounds that have distinctive thermal degradation products.

The pyrolytic chromatogram is sometimes called the pyrogam. In most cases it is difficult (especially without MS detection) to identify accurately the decomposition products because of their large number. Such pyrograms are primarily suited

to comparisons as 'fingerprints' or for the detection of the presence of certain components or contaminants. The pyrolytic chromatogram is analogous to an IR spectrum as a 'fingerprint' of the compound. Comparison of the chromatogram of an unknown with those of reference standards may permit a positive identification.

Inverse gas chromatography (IGC)

An alternative way of using gas chromatography is exploited in the technique of 'inverse gas chromatography'. IGC allows for the investigation of a stationary phase (e.g. polymer or pigment) with 'unknown' properties to be studied by passing compounds (probes), whose properties are known, through the packed column/capillary and studying the interactions that occur; this type of information can be particularly useful when considering compatibility and behaviour of components (including colorants) in formulations (such as paints and inks).

Liquid chromatography

For charged species, such as most dyes, reversed phase (RP) ion-pair chromatography is employed.

Ion-pair (or paired ion) chromatography is a form of reversed-phase partition chromatography that is employed for the separation and determination of organic ionic species. The mobile phase in ion-pair chromatography consists of an ion pairing agent, containing a counter ion of opposite charge to the analyte(s) of interest, in an aqueous buffer based on an organic solvent such as methanol or acetonitrile. The combination of the counter ion with the analyte ion results in an ion pair. The actual ion pair is more hydrophobic than the parent dye ion (and may be a neutral species) and will demonstrate some degree of retention on a reversed-phase packing material (usually a C18 or a C8 column). For anionic dyes quaternary ammonium species are used as the counter ion, with probably the most common ion-pairing agent being tetrabutylammonium bromide [$(C_4H_9)_4N^+ Br^-$].

10.6.2 Capillary electrophoresis (CE)

Capillary electrophoresis (CE) is a relatively new separation technique and often comparisons are made to the better established technique of high-performance liquid chromatography (HPLC), since they are generally capable of analysing a similar wide range of chemicals. It should be emphasised, however, that the separation principles are quite different. Conventionally in CE, species are separated based on their electrophoretic mobilities (determined mainly by their mass to charge ratios), in an aqueous electrolytic buffer media inside a fused silica capillary. The two ends of the capillary are immersed in separate reservoirs of the buffer and a high voltage is applied across the capillary to induce a bulk (electro-osmotic) flow of buffer through the capillary. Note that the detector (usually a

Table 10.5 Factors affecting capillary electrophoresis separations

Factor	Variables to be considered
Analytes	Nature, state, concentration, solubility and solvent
Buffer	Type, additives, concentration, pH
Capillary	Length, diameter, surface properties, maintenance
Detection	Type, sensitivity
Separation Parameters	Current strength, temperature, separation time

UV/visible detector) is on-line (actually measuring the analytes whilst they are still in the analytical capillary).

The technique is therefore particularly suited to water-soluble species which possess a charge, which includes most dyes. Variations from the main technique (often referred to as capillary zone electrophoresis, CZE) do exist and these include the use of surfactants in the buffer to create micelles (often thought of as creating a pseudo-stationary phase inside the capillary) which then improve the separation of neutral species (and frequently charged molecules) owing to hydrophobic interactions. The term micellar electrokinetic chromatography (MECC or MEKC) is often used for CE separations carried out with the aid of a micellar buffer solution.

Factors affecting capillary electrophoresis analysis

There are many factors that can affect the results that are obtained from the analysis of samples by CE and the major ones are listed in Table 10.5.

One of the most important variables, as with many techniques, is the 'state' of the sample to be analysed. Questions which should be considered prior to CE analysis include: What is the sample dissolved in? What are the known or likely impurities/additives present? How might these 'impurities' affect electrophoresis results? Are sample modifications possible under the separation conditions employed (e.g. pH or temperature-sensitive compounds)? Could aggregation or precipitation be a problem? What is the concentration of the sample – does it need to be diluted or concentrated? Finally it is important to consider any known properties of the samples to be analysed, for example charge, spectral absorption and adsorption characteristics, as these will aid in the setting of some of the other variables for the analysis.

Typical applications in CE

Commercial CE instruments only became readily available in the late 1980s, however, a vast array of information about different applications has been published. As well as the dyes themselves, CE can be used, for example, for the analysis of low molecular weight/simple ions (such as small anions, e.g. chloride, bromide, nitrate, chlorite, acetate, phthalate or small cations, e.g. alkali + alkali earth metals, ammonium, transition metals) or for aromatic amines.

The high resolving power of CE techniques has been recognised and investigated by many scientists. The use of CE for the analysis of environmental samples has been extensive. Good sampling, handling and preparation procedures are usually crucial in environmental analysis. A comprehensive review of different handling and preparation techniques for environmental samples analysed by CE has been presented by Brumley;[40] consideration was given to samples contained in both aqueous and solid matrices.

CE is ideally suited to the analysis of most dyes. Relatively simple aqueous buffers such as phosphate, borate and citrate, depending on the nature of the dyes, have been found to be suitable for a wide range of dyes.[41–44] The use of micellar buffer systems have proved beneficial for the analysis of some dyes, their intermediates, precursors and impurities.[45–48] These analyses have been either with or without an organic modifier depending on factors such as the nature of the analytes and the matrix they are in, since commercial dyes exist in formulations which, in addition to possibly being a blend of more than one dye, may contain a wide range of diverse components. The fact that dyes absorb light in the visible region, as well as the UV region, of the electromagnetic spectrum means that a greater degree of selectivity can be obtained by using detectors which are capable of monitoring absorbance of light in the visible region.

When analysing reactive dyes care needs to be taken in the interpretation of the results. Certain ranges of reactive dyes may be supplied in the form of a precursor of the actual reactive dye. Reactive dyes can undergo hydrolysis in aqueous environments (especially if alkaline). In recent years there has been an increase in the number of bifunctional reactive dyes. For all of the reasons mentioned, a multitude of peaks may be detected from the different derivatives of dyes such as Remazol Black B (C.I. Reactive Black 5).[48] The full chemistry of reactive dyes has not always been appreciated by workers analysing them leading to misinterpretations, for example in the work of Oxspring *et al.*[44]

10.7 Summary of instrumental analysis

There are many reasons for the analysis of colorants, for example, from trying to identify the structure of a new compound, to checking the purity of a known colorant, to checking the concentration of known/target impurities associated with a particular compound, to monitoring processes involving colorants (synthesis/coloration/decolorisation), to trying to identify (and often to also quantitate) unknown colorants (possibly at trace levels) in 'complex' samples. Legislation has become a bigger driving force behind quite a lot of this legislation and, as developments (especially lower limits of detection) in analytical techniques have been made, difficult questions surrounding the safety (and the safe level, since specifying 'undetectable' is not sensible/realistic) of chemicals including colorants need to be carefully considered. Analysis costs for the coloration industries are significant. There are of course companies making money out of all this

analysis, thus appreciation of the possibilities, pitfalls and implications of analysis (and also not doing analysis) is important for companies.

There are a wide range of techniques and a vast array of methods associated with these techniques. This chapter has covered a great number of techniques, but there are gaps. Hopefully, after reading this chapter the reader will have a better appreciation of colorants, issues associated with the analysis of colorants and some of the techniques and methods used for analysing colorants.

Active areas of research and development in terms of analysis include miniaturisation of analytical instrumentation with the idea of 'Lab on a chip'; this could possibly lead to mass production and thus cheaper instruments, so much so that for some techniques they become disposable (this should also make analysis much quicker). The hyphenation of techniques continues to be a very active area owing to the potential benefits that can accrue from linking techniques together, work on the interfaces usually being key. Work on sensors is ongoing for both specific chemicals and groups of related chemicals. There is also a lot of ongoing effort into developing process analysis (with the monitoring and auto-feedback, leading to greater control and optimisation) with spectroscopic techniques probably receiving the most attention. Many of the developments will not necessarily be targeted at colorants first, but opportunities will arise from developments/applications demonstrated with other chemicals, as has happened previously.

10.8 Colorant analysis without using instruments

The analysis of dyes and pigments for textile applications is really a very broad subject because it usually involves many different types of analyses and the use of many sophisticated instruments. It is difficult to provide a detailed coverage in a short section here. Therefore, only some basic and simple analyses are introduced. Readers who want to know more can access the books published elsewhere.[49,50] Analysis of colorants can also mean many different things. Identification of colorants on textile materials is an important aspect of forensic analysis and also very useful for textile dyers. Characterisation of colorants is critical for colour chemists to know what chemical structures the colorant has. Determination of dye classes has its practical significance in making up dyeing and printing recipes as well as in the analysis of historical textiles.

10.8.1 Dye purification and detection of ionic type

When commercial colorants reach the users, usually they are in the form of liquid or solid. The liquid form can be in dispersion, emulsion or high concentration solution. The solid form can be in granule or powder. The effective assay of solid dyes is usually between 85 and 95% with the exception of indigo which can have a purity level as high as 99.5%. For the analysis of the colorants in their original package, dyeing using standard fabrics under standard conditions developed by

individual laboratories can be used as a quality check tool. This quality check is a necessity for quality assurance purposes. It is the easiest and most convenient way to determine the quality of the colorants. Before the colorant is used in mass production, a lab dip can always give an indication of whether or not the colorant is up to the standard in terms of both the colour strength and the dyeing performance, including the fastness properties of the dyeing which are often the determining factors for a dyeing operation. Of course, a simple spectrophotometric measurement of a colorant sample solution can indicate the colorant strength if the standard reading of the same colorant is available.

If an unknown colorant needs to be analysed, an imporatant step is usually the removal of salt from the dye sample. The salt removal method quoted by Mehta *et al*.[51] can be used for dyes containing the sulphonate group. The dye sample is first dissolved in a minimum volume of cold dimethylformamide (DMF) and then filtered through a sintered glass funnel. Acetone is then added to the stirred filtrate and the dye recrystallised. The solution should be cooled in a fridge to aid the recrystallisation over night. If necessary, the procedure should be repeated until the UV/vis absorbance of an aqueous solution of the dye sample is constant. The advantages of this method are that it can avoid the dye hydrolysis and eliminate the possibility of water of crystallisation in the samples, which would interfere with the elemental analysis results of dye analysis. Another method for salt removal of sulphonated dyes involves the use of sodium thiocyanate.[52] The dye sample is first dissolved in a minimum amount of distilled water. Solid sodium thiocyanate is added into the dye solution to precipitate the dye. The precipitated solid is washed with acetone to remove the sodium thiocyanate until the spend acetone shows no trace of thiocyanate peak in the vicinity of 2080 cm^{-1} in its FT-IR spectrum. One of the advantages of using this method is that water soluble dyes are insoluble in acetone, so no dye is lost in the washing step. The dye obtained in this way is readily redissolvable in water.

It was also reported that some alcohol-soluble dyes like C.I. Direct Yellow 12 can be purified using a mixture of toluene and absolute alcohol.[53] Some water-soluble and alcohol-insoluble dyes can be purified from a 60:40 ethanol:water mixture.[54] Precipitation with sodium acetate repeatedly can give a highly purified dye.[55] This method involves as many as five times of precipitation, filtration and redissolving. The final precipitate will be washed with boiling ethanol until no acetate is detected in the spend alcohol by the cacodyl test.[56]

The ionic type of a dye sample can be determined by using ionic surfactants. The anionic dyes can be precipitated by cationic surfactants and vice versa. If a colorant sample would not be affected by either cationic or anionic type of surfactants, it could be a disperse dye with non-ionic dispersants. The surfactant test should be carried out at room temperature and a surfactant solution is added into the dye solution dropwise with the help of a magnetic stirrer. The mixture should then be allowed to stand for 30–60 min for precipitation to develop. Precipitation is the positive indication of the opposite type of ion for dyes in relation to the ionic

surfactant used. With a carefully designed analytical procedure using standardised surfactant solutions, the colorant concentration in the sample can be determined. An experienced textile chemist should also be able to use other types of ionic compounds to do similar analysis, both quantitatively and qualitatively.

10.8.2 Determination of dye purity level

The methods presented here are classical analyses. They are based upon either a redox reaction or an acid–base neutralisation reaction. Since there are a variety of chemical constituents, these methods have their limitations.

Reduction with titanous chloride[57]

This method is suitable for almost all azo dyes and some other water-soluble dyes. The titration should be conducted in a well-ventilated fume hood. A dye sample is dissolved in a hydrochloric acid solution. An excess amount of titanous chloride solution is added into the boiling acidic dye solution under the protection of a CO_2 atmosphere. A back titration is then conducted using a standardised ferrous ammonium sulphate solution with ammonium thiocyanate as the indicator. The titanous chloride solution should be freshly standardised.

Oxidation with potassium dichromate[58]

This method is suitable for nitrogen-containing dyes. The analysis is based on the measurement of nitrogen gas released from the strong oxidation reaction. A dye sample solution is boiled together with dichromate solution in the presence of sulphuric acid. The nitrogen gas generated is collected in a stream of CO_2 and measured. Before the start of the reaction, the entire reaction assembly is purged and filled with CO_2. Some nitrogen-containing impurities can lead to errors.

Titration of acid dyes with basic compounds[54]

A solution of a basic compound, such as Fixanol,[59] which is essentially cetyl pyridinium bromide and cetyl trimethylammonium bromide, is added to the acid dye sample solution to precipitate the acid dye. The end point of the titration is reached when the colour of a drop of the titrated solution on filter paper is different from that of the precipitate. The drawback of this method is that the end point determination is difficult, which could lead to titration errors. A few repeated titrations may reduce the error level.

10.8.3 Identification of dyes on fibres

There are a few sets of identification systems available. A scheme developed by

Green is the first known useful system for identifying the classes of dyes on wool and cellulosic fibres.[60] Clayton updated the Green system with more effective reagents and covering more dyes.[61] Hurwitz, Salvin and McConnell presented a system to identify dyes on cellulosic fibres, animal fibres and synthetic fibres in an AATCC publication.[62]

According to the AATCC system,[62] dyes on cellulosic fibres can be divided into four groups. Group 1 is basically for direct dyes. A dyed sample is boiled with an ammonia solution to extract the dye from the dyed sample. The dyed sample is then removed from the coloured extraction solution and a white piece of cotton fabric and a small amount of salt are put into the same solution for redyeing at the boil for about 1 min. A direct dye is evidenced by the similar shade and depth of the redyed cotton fabric in comparison to the original dyed sample. Group 2 dyes can go through first reduction, then oxidation reactions and can revert to their original colours. They are usually vat dyes and sulphur dyes. The sample usually should be tested for Group 1 before testing for Group 2. The reduction reaction of the dyed sample is carried out using an alkaline sodium hydrosulphite solution at the boil for 2–5 s. The discoloured dyed sample is removed from the reduction bath, dried on filter paper and left to oxidise in air. If the original colour is recovered in about 5 min, it is the positive indication of sulphur or vat dye on the original dyed sample. For sulphur dyes, the confirmative indication is a reduction with sodium sulphide in the presence of sodium carbonate and redyeing of a white piece cotton fabric to a same but lighter shade with the same reduction bath plus some salts. Group 3 dyes are those dyes that can be reduced by sodium hydrosulphite but cannot be oxidised back. They are direct dyes after-treated with metals and formaldehyde, naphthols and insoluble azo dyes, and diazotised and developed dyes. These dyes are all damaged by the reduction reaction at prolonged boiling. Group 4 is for those colorants that cannot be identified by the tests listed in the first three groups. They are very likely to be pigments or maybe reactive dyes. Pigment cannot penetrate the fibre. Therefore a microscopic examination of the pigment coloured fibre cross-section will display a circular coverage of the fibre surface. A DMF extraction can also be used to distinguish pigments from reactive dyes. A 100% DMF treatment at the boil can extract pigments but not reactive dyes from coloured samples. DMF can also be used as a 1:1 DMF:water solution for the identification of other dye classes. The possible results are shown in Table 10.6.[62]

If a fibre sample can be dissolved in 5 % NaOH at the boil, it is a protein fibre, commonly wool or silk. Protein fibres can be dyed most often by acid dyes, metallised acid dyes and chrome dyes. According to the AATCC system, acid dyes on protein fibres can be identified as follows. A coloured sample is boiled in an ammonia solution for 1–2 min. After removing the coloured sample, the ammonia solution is slightly over-neutralised with sulphuric acid. A small piece of white wool sample is then redyed with the ammonia solution at the boil for 1–2 min. A positive indication of acid dyes on the original sample is evidenced by the colour of the redyed wool sample. If chrome dyes are on the dyed sample, no redyeing can

Table 10.6 DMF extraction test of dyes at boiling

1:1 DMF:water	100% DMF
Extraction coloured by:	Extraction coloured by:
All direct	Vats
Diazotized and developed	Leuco vats
Some basic	Naphthols
Some mordant	Sulphurs
	Pigments
Extraction not coloured by:	Some basic
Fibre reactive	Some mordants
Leuco vat	
Naphthols	Extraction not coloured by:
Pigments	Fibre reactive
Some basic	
Some mordants	

occur on the white wool fabric. Metallised dyes are characterised by the presence of chromium, cobalt or manganese. An ash test should be able to distinguish between them. The dyed sample is fused with five times its amount of a mixture of equal parts of sodium carbonate and sodium nitrate in a crucible. A royal blue colour of the cooled melt indicates the presence of cobalt; yellow, chromium; and blue-green, manganese.

The AATCC system is a very detailed dye class identification system. The brief description of some basic tests in this chapter is only for the purpose of introduction. Readers are recommended to obtain the book *Analytical Methods for a Textile Laboratory* by the AATCC in order to comprehend the complexity of the dye analysis. Of course the other books and journal articles listed in the references are also excellent information sources. Whenever possible, reading these materials would definitely help develop a better understanding of colour chemistry, which will ultimately ensure that the dye analysis is performed more effectively and efficiently.

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