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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.

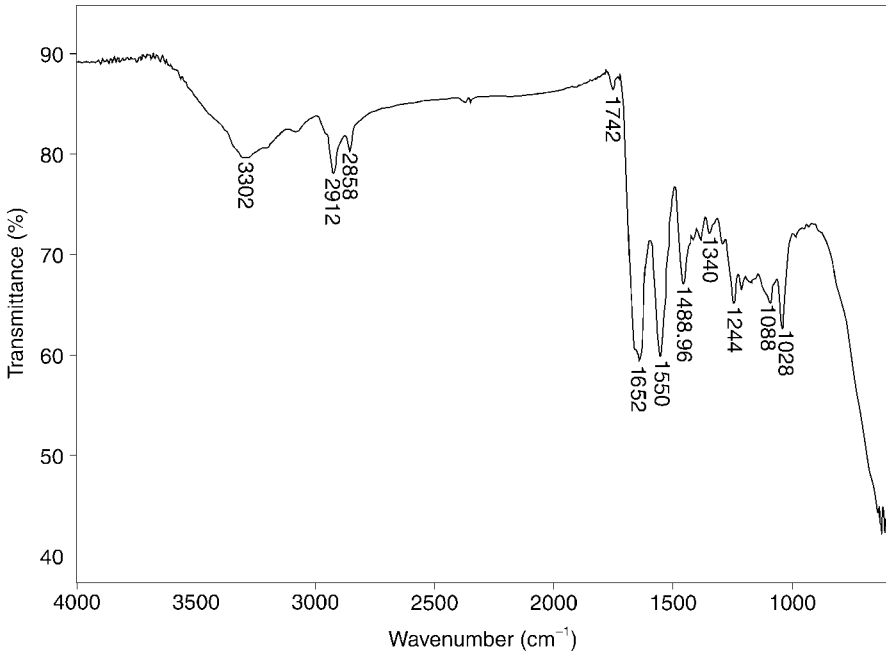
3.2.3 Infrared spectroscopic analysis

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.

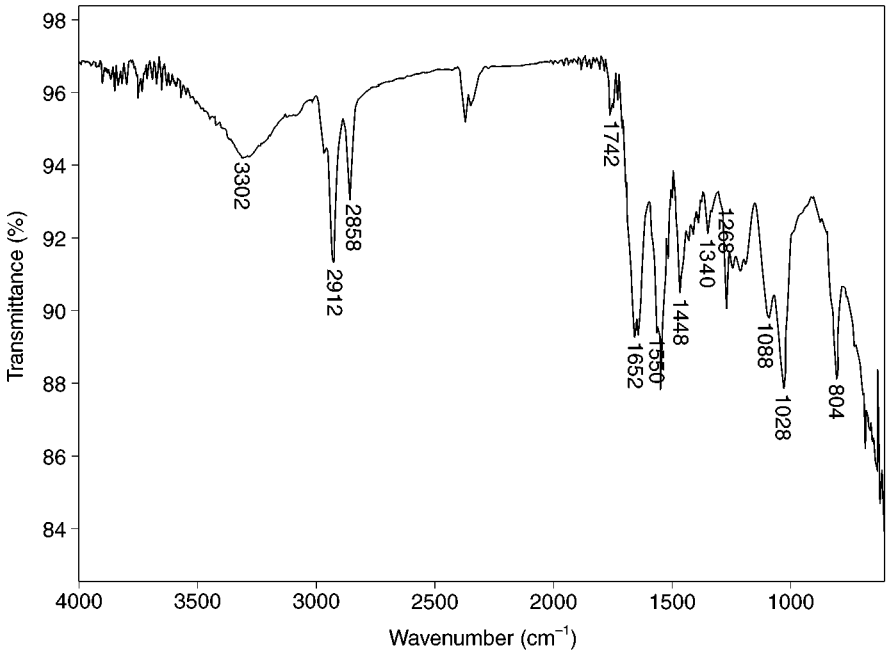
The infrared spectrum of the sample can be obtained either by an alkali halide pressed pellet technique or by different reflection techniques. The sample powder is ground into small particles and 3–10 mg are mixed uniformly and pressed with approximately 300 mg of alkali halide powder (such as sodium 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 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 non-tannins of the testing solution (g l^{-1}). The concentration of the tannins in the testing solution is calculated by:

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

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:

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

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 :

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

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:

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

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:

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

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:

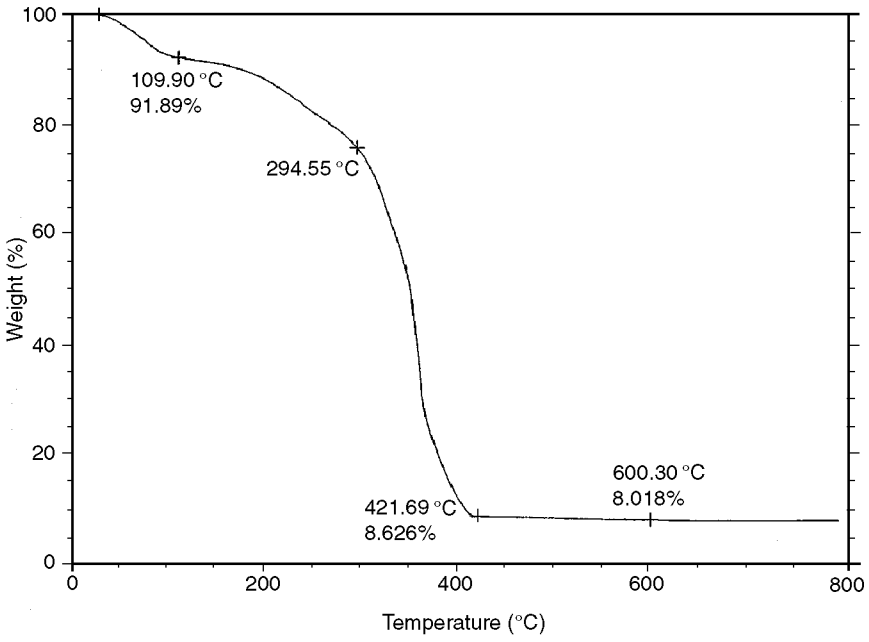
$$\text{Total ash}\% = R/W_d \times 100\% \quad [3.13]$$

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.

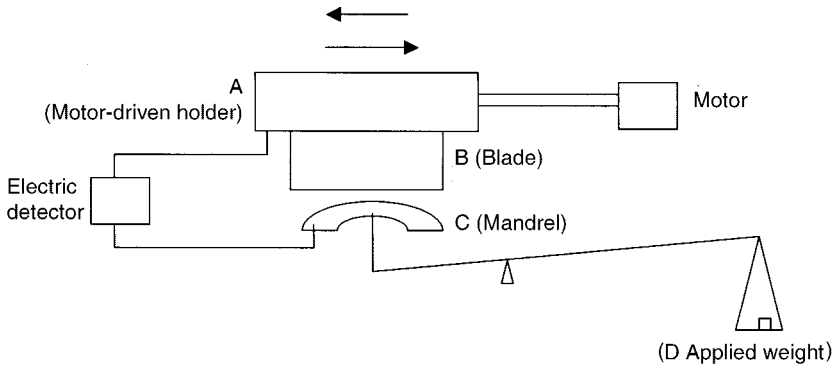
Cut at least three specimens of the leather sample to dimensions of 50 mm × 100 mm. Follow the same procedures as for calibration. Adjust the load on the blade to let the cut through length to be in the range of five times 5–15 mm, five times 15–30 mm and five times 30–50 mm. Draw a curve of the load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

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

$$\% \text{ Na}_2\text{CO}_2 = \% \text{ total alkalinity Na}_2\text{O} \times 1.71 - \% \text{ NaOH} \times 1.325 \quad [4.12]$$

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.

$$\% \text{ NaHCO}_3 = \frac{(\text{ml of NaOH} - \text{ml of acid} \times \text{E}) \times \text{normality of NaOH} \times 0.084}{\text{weight of } Na_2CO_3 \text{ in grams of the sample solution}} \times 100\% \quad [4.13]$$

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]:

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

$$\%\ \mathrm{CO(NH_2)_2} = \frac{N_{\mathrm{NaOH}} \times V_{\mathrm{NaOH}} \times 0.03}{\text{sample weight}} \times 100\% \qquad [4.30]$$

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]

$$\mathrm{CaCV} = \frac{100.1 \times 0.250 \times V}{W} \qquad [4.31]$$

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