

Table 9.4. Numbers of oxygen atoms and total cations in formulae of common minerals

Mineral	No. O atoms	No. cations
amphibole	23	15
chlorite	28	20
cordierite	18	11
epidote	25	16
feldspar	8	5
garnet	24	16
ilmenite	3	2
kaolinite	18	8
kyanite	5	3
mica	22	16
mullite	13	8
nepheline	16	12
olivine	4	3
pyroxene	6	4
spinel	4	3

More detailed structural formula calculations can be carried out, in which assumptions are made about the distribution of cations between lattice sites. A general-purpose computer program for calculating structural formulae has been described by Rock and Carroll (1990). Special programs have been developed by Spear and Kimball (1984) and by Richard and Clarke (1990) for amphiboles, also by Knowles (1987) for garnets. A spreadsheet-based program for amphiboles, which is convenient for processing large batches of tabulated data, has been described by Tindle and Webb (1994).

Unambiguous mineral formula calculation is not always possible, as in the case of micas containing lithium, though Tindle and Webb (1990) have shown that in the case of trioctahedral micas (excluding those with high MgO, e.g. phlogopite), an empirical relationship exists between  $\text{Li}_2\text{O}$  and  $\text{SiO}_2$  contents, resulting from Li and Si increasing simultaneously at the expense of Fe, with a redistribution of Al. This can be used to estimate  $\text{Li}_2\text{O}$  contents for micas analysed with the electron microprobe.

## Sample preparation

### 10.1 Preparation of sample materials

Most types of geological specimen require some treatment before mounting for examination in the SEM or analysis by EMPA. Often cleaning is necessary to eliminate unwanted contaminants. Sediments (and soils) commonly need drying. Friable and porous materials usually require impregnation, especially if polished samples are to be produced. Hand specimens have to be cut to a slice of an appropriate size for mounting and polishing. These processes are described in the following sections.

For further information on these topics and other aspects of specimen preparation the reader is referred to Humphries (1992), Hutchison (1974), Laflamme (1990), Miller (1988), and Smart and Tovey (1982).

#### 10.1.1 Cleaning

As collected, many samples contain unwanted components which hinder examination of the specific features of interest and need to be removed. For example, sediments and soils often require washing (with distilled water) to remove soluble salts (mainly chlorides). Only gentle agitation should be used as a rule, ultrasonic cleaning being liable to damage the mineral grains. Unwanted carbonate can be removed with hydrochloric acid, iron oxides with stannous chloride, and organic matter with an oxidising agent such as potassium permanganate or hydrogen peroxide. Hydrocarbons can be removed by soaking in a solvent such as trichlorethane (pressure may be required in the case of low-porosity materials).

#### 10.1.2 Drying

Some sample materials are wet in their normal state and must be dried before introduction into the SEM or EMP vacuum. This can be carried out by gentle

heating in air (temperatures above about 50 °C can cause loss of structural water from clay minerals). Other approaches are required, however, where fragile structures need to be preserved. Damage can be limited by replacing water with a volatile liquid of lower surface tension (e.g. amyl acetate) before drying. Other techniques, developed for drying fragile biological materials, can be adapted for clays and soils (McHardy, Wilson and Tait, 1982). For example, in 'freeze drying', water is removed from the frozen sample by sublimation in vacuum. The sample must be frozen rapidly to minimise ice crystal growth: this is achieved by immersing the sample (which should be as small as practicable) in a liquid such as freon, cooled by liquid nitrogen.

The least damaging, but slowest, technique is 'critical-point drying', which relies on conversion of liquid to vapour above the temperature of the critical point, so that there is no phase change. For water this temperature is inconveniently high, so the water in the sample is replaced by a more suitable liquid before drying. A typical procedure entails first replacing the water by methanol, then by liquid carbon dioxide. The sample temperature is raised just above the critical point of the latter (32 °C) and carbon dioxide is vented slowly from the chamber.

### 10.1.3 Impregnation

Friable materials require impregnation with a suitable medium to impart the necessary mechanical strength for normal specimen preparation procedures to be applied. Also, the filling of pores and cavities is desirable to avoid entrapment of polishing materials etc. and difficulties caused by outgassing in the instrument vacuum. Epoxy resins are most commonly used for impregnation. A type with low viscosity should be selected. Viscosity can be reduced by heating, but the temperature should not be such as to accelerate setting too much. In some cases it is desirable to dilute the medium with a solvent such as toluene or acetone, which evaporates before setting is complete.

The effectiveness of impregnation can be improved by removing air under vacuum and utilising atmospheric pressure to force the medium into the pores. This can be achieved by lowering the sample into liquid medium under vacuum, then admitting air. (Note: for epoxy resins the pressure should not be below 10 torr, or excessive frothing will occur.) Alternatively, the liquid medium is poured onto the sample (fig. 10.1), and, on admitting air to the sample chamber, is forced into the pores. To achieve maximum penetration several pumping and venting cycles may be necessary. Higher pressures can be applied by using gas from a cylinder.

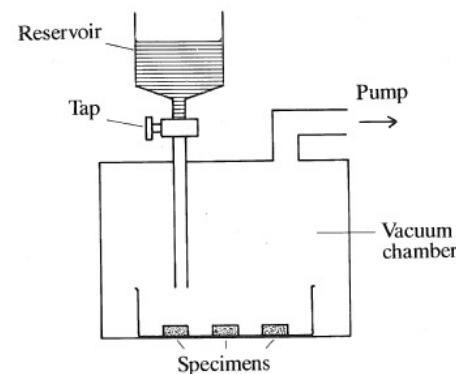


Fig. 10.1. Vacuum impregnation: chamber is evacuated to remove air from pores in specimens; liquid embedding medium (e.g. epoxy resin) is introduced by opening stopcock; on venting chamber, medium is forced into pores by air pressure.

### 10.1.4 Making replicas and casts

In applications where pore structures are of interest, it is useful to produce replicas or casts for examination in the SEM. This entails impregnation, as described above, followed by dissolution of the sample material using hydrochloric acid for carbonates, and hydrofluoric acid for silicates. Pittman and Duschatko (1970) used a procedure entailing repeated pumping and venting cycles to obtain maximum penetration by the medium. Details of methods suitable for chalk specimens have been given by Walker (1978) and Patsoules and Cripps (1983).

Latex rubber casts of fossil plant impressions can be used for scanning electron microscopy, which reveals original topographic details preserved in negative form on the rock surface (Chaloner and Gay, 1973). Latex may be applied in several successive layers, allowing each to dry before applying the next. The resulting cast is adequately resistant to vacuum and electron bombardment for SEM examination.

### 10.1.5 Cutting rock samples

Hand specimens of rocks require cutting to give pieces of suitable size and shape for mounting and polishing. Usually cutting is done with a circular diamond saw, a parallel-sided slice (typically a few mm thick) being cut off and then trimmed to the size required for the mounted section. Friable specimens need to be impregnated (as described in section 10.1.3) before cutting. Damage to the specimen occurring during these operations may extend to

considerable depth, possibly affecting the final product, therefore the methods used should be as gentle as possible.

## 10.2 Fused rock powders

Whole-rock analyses can be obtained by EMPA, using glass samples made by fusing rock powders (section 8.8.3). Also standards may be made from rocks of known composition, as determined by bulk analysis. Various fusion techniques can be used. Rucklidge *et al.* (1970) described a method involving fusion of about 100 mg of powder in a graphite crucible placed in a furnace, with a hydrogen atmosphere. Nicholls (1974) used an iridium-strip heater operated at 1600–1800 °C in air, with about 10 mg of powder (iridium being preferred to platinum because the latter tends to absorb iron from the sample). Brown (1977) adopted a similar approach but used a molybdenum-strip heater in an argon atmosphere, whereas Foland and Wagner (1981) employed a platinum foil 'boat' heated in a graphite furnace used for atomic absorption spectrometry (iron loss was not found to be a serious problem).

## 10.3 Mounting

### 10.3.1 The SEM 'stub'

SEM specimens are commonly mounted on a 'stub', which takes the form of a disc, usually made of aluminium and typically about 1 cm in diameter, with a spigot for attachment to the stage mechanism (fig. 3.9). (Sometimes graphite stubs are used, to minimise X-ray background, especially for particulates.) The sample is glued to the stub and coated to provide conduction (see section 10.6). A quick alternative method of attachment is to use double-sided sticky tape, though this is to be avoided if possible. Quick-setting glue can be used instead. It is important that mounting materials and adhesives should have a low vapour pressure so that the instrument vacuum is not adversely affected. Whatever arrangement is used, there must be an electrical path to the holder: if necessary this should be provided by applying conducting paint, e.g. carbon or silver 'dag' (fig. 10.2). For small specimens such as micro-fossils the use of a vacuum-compatible wax has some advantages (Finch, 1974). The wax is warmed so that it flows over the surface of the stub and the specimens are pressed into the wax while it is soft. On cooling they are firmly held. For some purposes it is desirable to mount an electron microscope grid with numbered bars on the stub, so that individual specimens can be relocated by means of their 'grid reference'.

## Mounting

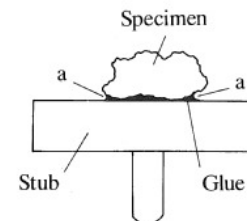


Fig. 10.2. SEM specimen mounted on 'stub'; note that conductive coating may not connect across overhanging regions (a), which should therefore be painted with silver or carbon 'dag'.

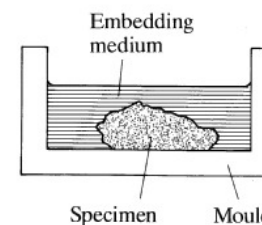


Fig. 10.3. Embedding specimen for polishing: liquid medium (e.g. epoxy resin) is poured into 'non-stick' mould and allowed to set (with heating if necessary).

The special problems arising in the mounting of soil samples have been treated in detail by Lohnes and Demirel (1978).

### 10.3.2 Embedding

For some specimens (e.g. ore minerals) it is not necessary to use thin sections, and embedding in a solid block is appropriate. The sample (e.g. a piece of rock prepared as described in section 10.1) is placed in a mould (made of non-stick silicone rubber, for example) and the embedding medium in liquid form poured in (fig. 10.3). Alternatively, a metal or plastic ring can be temporarily stuck down to serve the same purpose, remaining part of the mount after the medium has set. Bakelite (supplied as a powder and polymerised by application of pressure and heat) can be used for embedding, but has been superseded by epoxy resins which are either cold setting or require only relatively mild heating, and therefore are less likely to cause damage to the specimen. Bubbles can be removed by applying the moderate vacuum obtained with a water pump, for example. There is some advantage in using a conducting medium, e.g. epoxy resin filled with fine carbon or metal particles.

For further details about impregnation, see Smart and Tovey (1982).

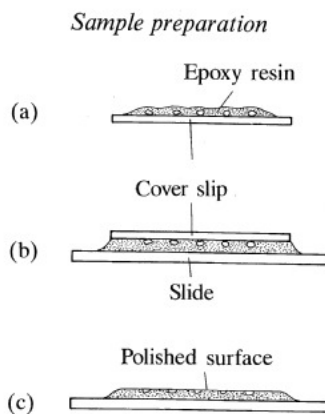


Fig. 10.4. Mounting small grains: (a) grains embedded in thin layer of epoxy resin on cover slip; (b) embedded grains mounted on microscope slide; (c) cover slip ground away and exposed grains polished.

### 10.3.3 Thin sections

In many applications, thin sections are required so that viewing by transmitted light is possible. The preparation procedure is as for ordinary thin sections in the first stages but, because of the stress of polishing, a strong adhesive (e.g. epoxy resin) should be used for attaching the rock slice to the glass slide (instead of Lakeside cement). Special epoxy resins with suitable optical properties are available. The slice is ground to a thickness somewhat greater than the 30  $\mu\text{m}$  final thickness required, before commencing polishing. The standard 75  $\times$  25 mm microscope slide is undesirably long for SEM or electron microprobe work, but can be cut down to a length of 25–35 mm (either before or after polishing). Other rectangular sizes are sometimes used, while 1 inch (25.4 mm) diameter round sections are also used, especially in the USA.

### 10.3.4 Grain mounts

Special techniques are required for mounting small grains. One possibility is to mix the grains with embedding medium (e.g. bakelite or epoxy resin) and set in a mould. Alternatively the grains may be pressed into a thin layer of epoxy resin on a glass cover slip. After setting, this is inverted and mounted on a glass slide, and the cover slip ground away, leaving the grains lying in one plane ready for polishing (fig. 10.4). This makes more efficient use of the material. If it is desirable for grains not to form clumps, mixing them with crushed graphite particles of similar size prior to embedding is an effective way of keeping them separate (Reid *et al.*, 1985).

For SEM work, polishing may not be required. In this case, grains can be scattered onto a sticky surface or onto partly dried carbon paint, etc., or alternatively suspended in a liquid, drops of which are transferred to the substrate and then evaporated. (In the latter case, it may be necessary to de-coagulate the particles with the aid of an ultrasonic bath.) Suitable substrate materials include beryllium (which gives minimal X-ray emission), carbon (which is almost as good in this respect, but is difficult to obtain with a very smooth surface), and silicon (this is available in very highly polished form, but emits more X-rays, which is a drawback in some applications.)

### 10.3.5 EMPA standards

Methods used for mounting standards are essentially similar to those already described. Usually fairly small (e.g.  $\sim 1$  mm) pieces of standard materials are used, so a reasonable number can be mounted in the specimen holder at one time. Standards can be prepared individually, allowing selection of those required for each application. Alternatively a single block containing many standards can be used. This latter approach saves space, but obtaining a good polish on a wide variety of materials with different physical properties can be difficult. Prepared standard blocks are obtainable from commercial suppliers. It is convenient for commonly used standards to be mounted in the specimen holder semi-permanently, but those needed only occasionally can be inserted in the holder as and when required for calibration measurements and then removed to make more space for specimens.

## 10.4 Polishing

For X-ray analysis and BSE imaging it is extremely desirable to avoid topographic effects: specimens should therefore be flat and well polished. Polishing procedures for ore microscopy (e.g. Taylor and Radtke, 1965) can be adapted to rocks consisting predominantly of silicates (e.g. see Lister, 1978). Starting with a flat ground surface, polishing is carried out with progressively finer grades of abrasive (carborundum or emery in the coarser grades and diamond in the later stages). Paper or woven nylon laps are preferable to cloth with a 'nap', since they have less tendency to produce surface relief between minerals of different hardness. Either rotating or vibrating motion of the lap is used, the former being preferable. The specimens should be thoroughly cleaned after each stage, to avoid carry-over of abrasive material in pores and cracks. For soft phases a final hand polish using very fine alumina may be necessary to obtain a good result. A single-stage polishing technique using only alumina

has been described by Allen (1984). Special procedures are required for electron channelling pattern studies (section 5.9.3), the damaged surface layer left by conventional polishing being removed by a final polish with alkaline colloidal silica slurry (Lloyd *et al.*, 1981).

Polished thin sections are usually made by polishing a section previously ground to a thickness somewhat greater than  $30\ \mu\text{m}$  (fig. 10.5). However, the final thickness is then poorly constrained, creating problems for polarised light microscopy. This can be avoided by polishing one face of the rock slice first, temporarily mounting face down on a glass slide, grinding off surplus material to give a thickness of  $30\ \mu\text{m}$ , mounting permanently with epoxy resin on another glass slide (ground face down), and finally removing the first slide.

### 10.5 Etching

Chemical etching enables chemical and crystallographic differences to be converted into topography which can be observed in SE images. (It is inappropriate for EMPA, where flat, smooth, surfaces are required, especially for quantitative analysis; also, etching may alter surface composition.) Carbonates can be etched with dilute hydrochloric acid (1–5%), acetic acid (20%), or EDTA, by immersion in the acid, the most delicate effect being obtained with the last two. In some cases heavy etching to remove carbonate cement, leaving exposed grains of quartz, etc. for SEM study, is appropriate. Quartz grains may be etched with concentrated hydrochloric acid for surface texture studies. Etching of polished sections with hydrofluoric acid can be used to reveal textures of quartzitic sandstones, for example, and fine exsolution textures in silicates (section 5.7.3). The sections can be suspended above an acid bath, to be etched by the fumes, or immersed for a stronger effect. (The glass slide may be protected from frosting by covering with paraffin wax.)

### 10.6 Coating

Most geological samples, being nonconductors of electricity, require a conductive coating to prevent charging under electron bombardment unless this is avoided by using a low accelerating voltage (section 5.6.7) or an 'environmental' SEM (section 3.9.2). The preferred coating element for X-ray analysis is carbon, because it has a minimal effect on the X-ray spectrum. It is also the best choice for cathodoluminescence studies. However, it is not ideal for SEM imaging, owing to its low secondary electron yield. For this

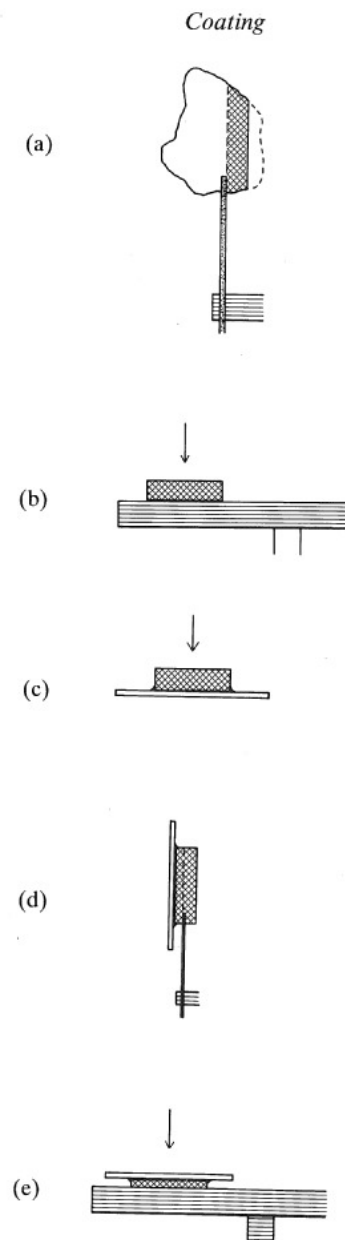


Fig. 10.5. Preparation of polished thin section: (a) slice of rock cut with diamond saw and trimmed to size; (b) one face of slice ground and lapped; (c) slice attached to glass slide, lapped face down; (d) surplus material cut off with fine diamond saw; (e) surface ground and polished leaving  $\sim 30\ \mu\text{m}$  thickness.

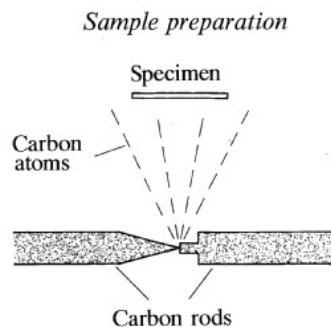


Fig. 10.6. Evaporation of carbon to give conductive coating on sample, using pointed carbon rods and large current.

purpose a metal with a higher SE yield is preferable, e.g. gold or gold-palladium alloy (which has a finer grain structure). This type of coating is, however, less suitable for X-ray analysis or BSE imaging.

### 10.6.1 Carbon coating

The usual method of coating with carbon is to place the specimen in a vacuum chamber with a carbon evaporation source consisting of pointed carbon rods (3–6 mm diameter) in contact under light pressure (fig. 10.6). A current of around 100 A is passed through the rods for a few seconds, causing carbon to be evaporated from the hottest region where the rods are in contact. The pressure should be less than  $\sim 10^{-4}$  torr, as obtained with either a diffusion pump or a turbo pump. (Carbon films produced under poor vacuum conditions are 'sooty' and lack adhesion.) Since the evaporated carbon atoms travel in straight lines this coating method is suitable only for flat specimens and not irregularly shaped objects. In the latter case, better coverage can be obtained by rotating the sample during coating.

The optimum thickness of carbon is about 20 nm. The thickness can be controlled approximately by using a fixed current and evaporation time. It can also be estimated from the colour of a coated polished brass surface (Kerrick *et al.*, 1973): orange = 15 nm, indigo red = 20 nm, blue = 25 nm, bluish green = 30 nm. (Other highly reflective materials show similar colours.) More accurate monitoring can be achieved by means of a quartz crystal forming part of an electronic oscillator circuit, with one surface exposed to the evaporant, the oscillator frequency being used to indicate the coating thickness. Other methods of thickness monitoring are based on the electrical resistance or the optical density of the coating on a blank glass slide (for a normal coating thickness, light transmission is about 70%). Specimens should be equi-distant from the carbon source to ensure uniformity of coating thickness.

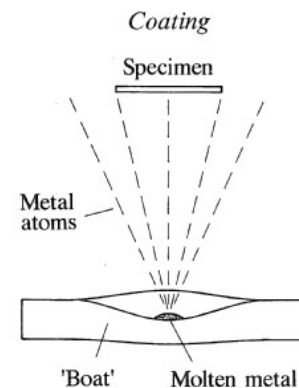


Fig. 10.7. Evaporation of metal (e.g. Ag, Al) by heating in molybdenum 'boat' carrying large current.

Carbon films can be produced by using carbon fibre 'string' in place of the pointed rods described above. By 'flash heating', that is briefly passing a large current which generates a very high temperature for a short time, heating of the sample (which can be significant when the conventional technique is used) is minimised. However, this method is unsuitable for coating batches of several specimens at a time.

### 10.6.2 Metal evaporation

Although carbon is usually the preferred coating material for samples which are to be analysed, the enhanced thermal conductivity obtained with a relatively thick metal coat is advantageous in reducing the effects of electron bombardment for certain types of sample (section 9.6). Gold, as used for SEM samples, is best avoided because of its X-ray lines: the Au M lines occur around 2.1–2.2 keV (see fig. 7.3) and interfere with the K lines of P and S, as well as the L lines of elements around Nb. Alternative metals such as aluminium, copper or silver are therefore sometimes used. Coating with these metals can be carried out by vacuum evaporation, using a wire basket made of tungsten, or a 'boat' made from molybdenum sheet, heated by passing a large electric current (fig. 10.7). In some cases sputter coating may be used instead (see next section).

### 10.6.3 Sputter coating

This alternative method can be used for producing coatings of some metals, including the gold and gold-palladium alloys used for SEM specimens. The 'diode' type of sputter coater is shown in fig. 10.8. The chamber is first evacuated with a rotary pump; argon is then admitted to give a pressure of about

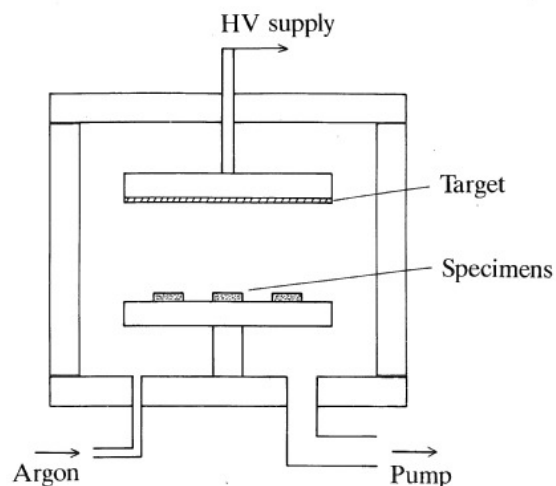


Fig. 10.8. Sputter coating: air is removed from chamber and replaced by argon at low pressure; high voltage applied to top electrode causes discharge in gas; specimens are coated with metal atoms (e.g. Au) removed from target by 'sputtering' due to bombardment with argon ions.

$10^{-1}$  torr. When a high voltage is applied across the electrodes a discharge occurs and the metal foil target is bombarded with ions, which remove atoms by sputtering. These are deposited on the specimen, the coating thickness being determined by the discharge current and time. The current is controlled by varying the argon pressure. The specimen is heated significantly by electron bombardment, which can cause damage to fragile materials. 'Cold' coaters are available, in which the electrons are deflected by a magnet.

Sputter coating is quick and convenient, and is especially suitable for gold and its alloys, as used for SEM work. It lends itself readily to automation, thereby saving time for the user. Since the sputtered atoms are strongly scattered by gas molecules they travel in all directions, which is advantageous for coating specimens of irregular shape.

#### 10.6.4 Removing coatings

It may be desirable to remove a coating applied for SEM or EMP work, for example to allow unhindered examination by optical microscopy, or to permit a gold coating applied for SEM examination to be replaced by carbon for X-ray analysis (or vice versa). Carbon deposited under high vacuum conditions adheres strongly to the substrate, but can be removed from polished sections with the aid of a fine polishing medium (e.g.  $0.25\ \mu\text{m}$

diamond on a cloth lap). Gold and other metals can be wiped off with a tissue, etc., but the above treatment helps to remove traces in cracks, etc. (which give rise to undesirable bright spots in BSE images). SEM specimens with strong three-dimensional topography require a different approach. Gold can be removed from such samples by treatment with a 10% aqueous solution of sodium cyanide (Sela and Boyde, 1977), with appropriate precautions in view of the toxicity of this substance. Silver has the advantage that it can be removed easily with less toxic hazard, using photographic 'Farmer's reducer' (Mills, 1988).

#### 10.7 Marking specimens

Specimens must, of course, be marked for identification purposes. Aluminium SEM stubs can be inscribed with a fine metal stylus, or alternatively written on with a pen. In the case of epoxy blocks in which opaque specimens are mounted for polishing, a label can be embedded with the specimen, or else the identification number can be written or scratched on the back. The paper labels used for ordinary thin sections are less suitable for polished thin sections which are usually smaller and lack free space where the label will not interfere with transmitted light viewing. Normal practice is therefore to inscribe the number on the back using a diamond point.

It is also sometimes desirable to mark areas of interest within specimens to make them easier to find in the electron microprobe or SEM. Ink rings can be drawn on the *back* of thin sections for this purpose, where the instrument concerned has transmitted light viewing facilities. Rings drawn on the *front* are naturally appropriate for opaque specimens, or where transmitted light viewing is unavailable: for this purpose either conducting ink should be used or else the carbon coating must be applied *after* drawing the rings. Ink that is unaffected by the solvents used for cleaning should be selected. The need for marking areas of interest can be obviated by using other approaches described in the following section.

#### 10.8 Specimen 'maps'

Finding areas of interest using the optical microscope in the electron microprobe can be difficult because of the high magnification and small field of view. Scanning electron images, which allow much lower magnification, can be used instead but relevant features are sometimes not easily identifiable in such images. Time can therefore be saved by employing stratagems described below.

A sketch-map or low-magnification photograph of the whole specimen is an invaluable aid. A 'macro' photograph can be obtained in various ways. Transmitted light images can be produced by placing a thin section in the negative holder of a photographic enlarger, though the printed image is of course in negative form. Another possibility is use a slide copier giving a 1:1 image on 35 mm film. Alternatively macro-photographic equipment is available, with variable magnification, down to 1. Yet another possibility is to use a magnifying photo-copier designed for 35 mm slides or microfiche material. Unfortunately there is no readily available method for producing reflected light macro images.

Photo-micrographs of small areas at higher magnifications are also sometimes useful and can be taken with an ordinary photomicrography set-up. It is generally undesirable to rely upon crossed-polar colour micrographs, since polarised light facilities are limited in the typical electron microprobe and absent in SEMs. Opaque grains provide useful 'landmarks' in plain light micrographs which can be easily recognised in the instrument microscope (and in scanning images).

In some cases the need for a 'map' may be obviated by using a bench microscope with  $x$  and  $y$  coordinate read-out. Full microscope facilities – low and high power objectives, polarised light, etc. – are available for finding areas of interest. The positions of these can be recorded relative to a reference mark, so that the same points may be found easily after transfer to the electron microprobe or SEM. It is particularly convenient if the stage read-out is digitised and interfaced to a computer, so that lists of coordinates can be stored and transferred directly to the electron beam instrument (where this is computer-controlled).

A procedure for locating mineral grains using a digital image of the entire sample, obtained with either a video camera or a flat-bed scanner has been described by Potts, Tindle and Stanford (1995).

### 10.9 Specimen handling and storage

Specimens and standards should be kept in a dust-free environment, preferably in desiccators to avoid degradation caused by atmospheric water vapour, etc. In certain cases it is desirable to use a vacuum desiccator (e.g. for pure element standards which oxidise readily and minerals such as sulphides which tend to tarnish). SEM 'stubs' can be stored in plastic boxes available for the purpose.

Cleanliness should be observed when handling specimens, to avoid degradation of the specimen chamber vacuum and enhancement of the rate of

deposition of carbon contamination. Ideally gloves should be used, though these are somewhat inconvenient and are not strictly essential unless minimising contamination is especially important.

Specimens can be cleaned by washing with a residue-free solvent and wiping with a tissue. The solvent should be one which does not attack the specimen, mounting medium, or ink used for labelling. Suitable choices include petroleum ether and ethanol. Dust can be removed with a compressed-air blower.