

file
Table
Analytical
method

The use of an analytical electron microscope in the analysis of mineral dusts

By F. D. POOLEY

Department of Mineral Exploitation, University College, Cardiff

[Plates 1 and 2]

Dust samples, whatever their source, usually consist of small quantities of very fine particles from which the following information is necessary: (a) the morphology of the mineral particles in the dust, i.e. size and shape; (b) the identity of the mineral particles in the dust; (c) the proportion of each mineral contained in the dust; (d) the mineral concentration in the sample of air, water or biological material from which the dust was recovered.

Information is also required as rapidly as possible from a single preparation so that many samples may be analysed on a routine basis. This paper will outline how this information can be obtained by using an electron microscope analysis system. With such an instrument, dust particles of all sizes may be observed and their size and shape obtained, while the electron microprobe may be used to analyse single particles to determine their chemistry and identify them.

The bulk chemistry of the dust may be obtained in a similar manner by analysing large numbers of particles simultaneously. By using the chemical data obtained from single particles and also the bulk chemistry of the sample, the mineral composition of the dust may be computed. A measure of the mass of dust being analysed can be obtained from a measurement of the X-ray count rate obtained during bulk analysis, measurement of the incident electron-beam intensity and reference to an instrument calibration curve.

INTRODUCTION

Dust particles formed by many minerals play an important part in the incidence and progress of disease of the respiratory tract when inhaled by individuals employed in the production and processing of industrial minerals. The majority of these pathogenic mineral particles are usually less than 5 μm in size if they are compact in shape, but they can be larger in certain dimensions if they are flakey or fibrous in form. The greater part of a dust cloud generated from any rock or mineral consists of particles which can be observed with an optical microscope. Many minerals, however, produce particles which are submicroscopic in size which can only be observed with the aid of electron-optical equipment.

When a mineral dust sample is examined, information is required regarding its mass, particle size distribution, morphology and mineral composition. This information can then be used to estimate the concentration of the dust in the air, water or biological sample from which it was obtained to monitor the environment and also investigate the relationship between dust exposure and the incidence of disease. Many standard mineralogical techniques are employed in this area of research to provide information, but they often require large quantities of material to be effective, are often destructive and may only be useful in detecting and measuring certain mineral phases in a dust. A fully quantitative analysis of a dust sample is therefore rarely performed. An investigative technique which can supply physical and chemical information from a dust sample rapidly, regardless of its size, is therefore extremely useful in this area of research.

[391]

The transmission electron microscope fitted with an energy-dispersive X-ray analysis system is one combination of equipment which can satisfy a large number of requirements. The object of this paper is to outline how such equipment may be used to investigate mineral dust samples and to illustrate the type of results which can be obtained.

THE DEVELOPMENT OF ELECTRON MICROSCOPE MICROPROBE ANALYSIS

Over many years the transmission electron microscope has developed into a piece of equipment capable of imaging fine structure over a wide range of magnification, with a working resolution of 0.2 nm. The instrument has been limited in its analytical capabilities, however, to a morphological examination of material, together with the ability to produce electron diffraction patterns from crystalline phases which could give information about the structure and possible identity of certain features. As the development of transmission electron microscopy was proceeding, a parallel development was taking place with electron-optical equipment using finely focused electron beams in a scanning and fixed mode to produce electron optical images of surfaces, and also to generate X-rays characteristic of the elements contained within the irradiated surface. The analysis of such X-rays with suitable X-ray spectrometers to yield quantitative chemical information resulted in the production of the electron probe micro analyser, while scanning electron microscope instruments were developed to examine surfaces. A generation of instruments has since appeared which combine the capability of producing scanning images of surfaces with the facility for micro-analysis of specific areas of the surface. These instruments, however, do not possess the image resolution and operating advantages of the transmission electron microscope, while the area of analysis of a specimen surface has been limited approximately to a circle 1 μm in diameter.

The desire of researchers involved in the study of fine structures in the transmission electron microscope to analyse the ultrafine features which they observed, resulted in the combination of X-ray spectrometry with the transmission microscope. The first commercial instrument equipped with multi-crystal spectrometers was manufactured by A.E.I. Scientific Instruments Ltd., and code named the EMMA 4; this instrument has been well described in the literature (Cooke & Duncumb 1968). During the development of EMMA 4 a rapid advance in energy-dispersive X-ray technology produced a new form of X-ray spectrometer which, when combined with a transmission electron microscope, gave comparable results to the crystal spectrometer/microscope combination of the EMMA 4. The technique of energy-dispersive X-ray analysis in the transmission microscope has since been used increasingly, especially by biologists, because of its ability to provide a simultaneous analysis of many elements and because of the capability of existing transmission electron microscopes to be readily modified to accept this type of spectrometer.

The operating characteristics and theory of energy-dispersive and wavelength dispersive X-ray analysis have been described by Duncumb 1966 and Gedcke 1972, while the merits of their use for analysis on both scanning and transmission microscopes have been detailed by Russ 1973. Although experience in the analysis of fine particles on either form of electron microscope is limited, most researchers now appear to prefer the combination of transmission electron microscope and energy-dispersive X-ray equipment.

QUANTITATIVE CHEMICAL ANALYSIS IN THE TRANSMISSION ELECTRON MICROSCOPE

It has been demonstrated by several authors (Cliff & Lorimer 1972; Jacobs & Baboravsky 1972; Lorimer & Champness 1973; Lorimer, Razik & Cliff 1973) that quantitative chemical analysis of thin specimens is easily performed with a suitable combination of transmission electron microscope and X-ray analysis system. The most popular procedure employed to produce quantitative chemical information is often referred to as the ratio technique. The application of this procedure is dependent on the fact that as specimen dimensions are reduced X-ray adsorption and fluorescence in the specimen are also reduced to negligible proportions such that the characteristic X-ray intensities I_1 and I_2 produced from a specimen containing atoms of elements 1 and 2 respectively, are related to the atom fractions X_1 and X_2 as follows:

$$\frac{I_1}{I_2} = \frac{KX_1}{X_2} \quad (1)$$

The factor K in equation (1) can be determined for different pairs of elements from the analysis of suitable standard samples, but for ease of calculation, however, it is more convenient to utilize a single element for ratio purposes. In the case of the analysis of dust samples which may contain mainly silicate minerals, silicon is the most appropriate element. We can therefore rewrite equation (1) in the form:

$$\frac{I_E}{I_{Si}} = \frac{KX_E}{X_{Si}}, \quad (2)$$

where I_E, I_{Si} are the characteristic X-ray intensities of element E and silicon respectively, X_E, X_{Si} , the atom fractions of element E and silicon respectively, and K , the calibration constant.

Using equation (2), and with the analysis of suitable standard specimens, values of K relating equal atom fractions of various elements and silicon can be produced to form a calibration curve relating to K to atomic number, in which the value of K for silicon itself is unity. Using the ratio procedure several authors (Cliff & Lorimer 1975; Rowse *et al.* 1974; Pooley 1975) have demonstrated that accurate quantitative chemical information can be obtained from mineral particles. The ratio procedure has also been shown by White, Denny & Irving (1966) to be applicable to the quantitative analysis of fine mineral particles in the conventional electron microprobe analyser.

Some researchers, however (Henderson *et al.* 1975; Beaman & File 1976) still prefer to use only simple elemental X-ray intensity ratios to describe material. This does not allow comparison to be made with results obtained by other investigators, as elemental X-ray intensity ratios are affected by the type of X-ray spectrometer equipment employed, its geometrical configuration with the transmission electron microscope, and also the microscope operating conditions.

CALIBRATION OF AN ANALYTICAL TRANSMISSION ELECTRON MICROSCOPE

Instrumental calibration for quantitative analysis in an analytical transmission electron microscope can be performed in a number of ways. Morgan, Davies & Erasmus (1975) demonstrated that droplets (approximately 3 μm in diameter) from iso-atomic solutions which were sprayed onto a prepared electron microscope grid and dried were suitable for calibration. This

[393]

enabled them to produce calibration specimens containing as many as eight elements in equal proportions covering an elemental range from atomic number 11 to 27 (sodium-cobalt). Rowse *et al.* 1974, employed thin sections of mixed and embedded compounds for calibration purposes and analysed large numbers of particles at a time (approximately 10^4 , $0.5\ \mu\text{m}$ particles) with a $60\ \mu\text{m}$ diameter electron beam to obtain X-ray calibration readings, the composition of the thin particulate films being checked by wet chemical techniques. Other researchers (Lorimer & Champness 1973) used thinned layers of synthetic glasses of known composition for standards.

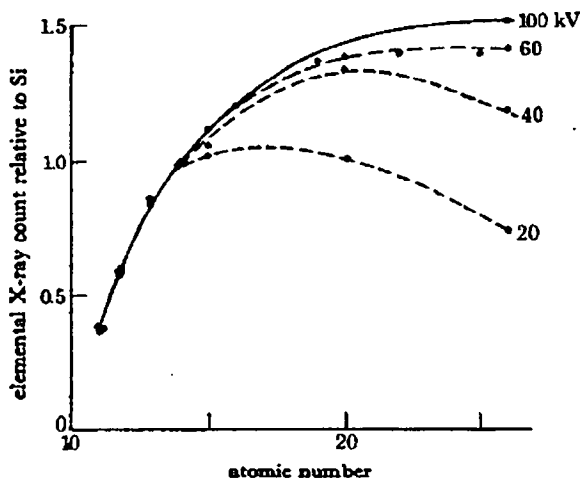


FIGURE 1. Variation of $K\alpha$ X-ray emission for equal atomic proportions of elements in the range sodium to iron relative to silicon obtained at various accelerating voltages.

Fine particles of accurately analysed silicate minerals have also been employed for calibration purposes (Pooley 1975). The shape of the calibration curve obtained using an energy-dispersive spectrometer is defined by the adsorption of low-energy X-rays at the beryllium window of the spectrometer (which limits its detection to elements of atomic number 11 and above), and also by the transparency of the silicon-detecting crystal to high energy X-rays. The final shape of a calibration curve and the values of K , the calibration constants obtained for each element, also depend upon the manner in which the X-ray spectral data are produced and the way in which these data are reduced to a usable form. X-ray counts for each elemental peak may be obtained by integrating the counts under the total peak, or only a portion of the peak, spanning the peak axis. More sophisticated approaches may include fitting the peaks to a Gaussian profile from which the peak intensity may be determined. X-ray data must then be corrected for background either by subtraction of a background reading in close proximity to each peak, or by mathematical prediction of the bremsstrahlung background in the peak region.

Figure 1 illustrates the results obtained from the analysis of standard silicate mineral particles containing elements in the range sodium $\rightarrow$ iron in which the X-ray emission from equal atomic proportions of each element have been expressed as a ratio with silicon for various accelerating voltages in the electron microscope. The X-ray data were obtained using an energy dispersive X-ray spectrometer manufactured by Edax Ltd attached to a Philips 301 transmission electron microscope. The X-ray counts for the various elements were processed using an Edax 707a multi-channel analyser employing a spectrum display in which X-rays were collected in

[394]

channels 20 eV wide. Integrated counts in 3 channels spanning each elemental $K\alpha$ X-ray peak were used for ratio purposes after correction for background. Calibration constants K for each element in the range sodium $\rightarrow$ iron were obtained by expressing the X-ray intensity ratio of equal atomic proportions of each element to silicon as a reciprocal to produce a plot of the form as shown in figure 2. Using the calibration constants K contained in figure 2, X-ray reading obtained for elements in this spectral region were reduced to give percentage atomic proportions of each element present. These were used in constructing the chemical formulae of the feature analysed and readily converted into standard oxide mass percentage data.

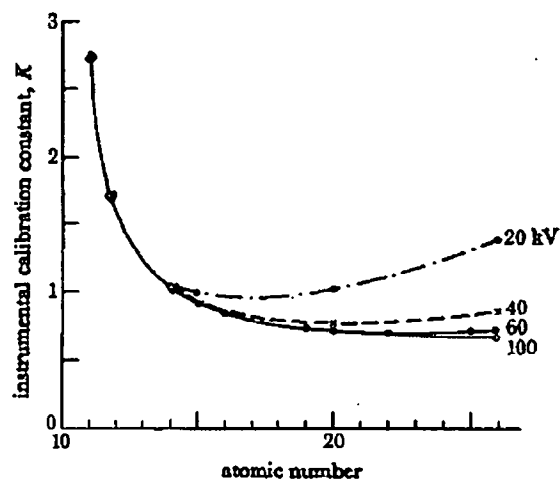


FIGURE 2. Variation of calibration constant K obtained at various accelerating voltages for elements in the range sodium to iron.

An example of the application of the ratio technique to the analysis of single dust particles is illustrated by figure 3, plate 1, which is an electron micrograph of a single fibre of amosite asbestos 0.3 μm in diameter. The mineral fibre has been analysed ten times along its length in the space of 6 μm using an accelerating voltage of 80 kV and an incident beam current of 15 nA. The position of each analysis point is indicated by the electron beam contamination marks along the fibre length. The form of the X-ray spectrum collected at each point for 100 seconds is illustrated by figure 4 in which the peaks corresponding to the various elements that have been detected are labelled. The mean elemental counts for the various peaks obtained from the ten analysis points, together with their standard deviations, are contained in table 1. The mean counts, contained in table 1 have also been converted to atomic proportions using the calibration constants from figure 2, and these figures have been used to obtain oxide weight percentages of the various elements detected. For comparison, chemical data obtained from a bulk analysis of this amosite sample are also included in table 1. The quantity of material analysed at each point along the fibre was approximately 10^{-14} g.

TABLE 1. RESULTS OBTAINED FROM THE ANALYSIS OF TEN INDIVIDUAL POINTS ON A SINGLE AMOSITE ASBESTOS FIBRE OPERATING AT 60 kV AND A BEAM CURRENT OF 15 nA

	Si	Na	Mg	Al	Mn	Fe	
mean X-ray counts/element	1405	4	158	35	56	1115	average elemental counts obtained from 10 consecutive analyses of a single fibre
% standard deviation of counts	1.6	200	16	20	11	4.2	
counts corrected with calibration constants and expressed as a % of the total count	53.0	0.5	10.6	1.5	1.7	32.8	% atomic proportions of each element detected in the sample
	SiO ₂	Na ₂ O	MgO	Al ₂ O ₃	MnO	FeO	
X-ray data expressed as oxide mass %	51.6 (50.16)	0.3 (0.3)	7.0 (6.9)	1.2 (1.17)	1.9 (1.85)	38.1 (37.03)	figures in brackets adjusted for 2.8 % H ₂ O in the fibre
oxide mass % data obtained by bulk analysis of this sample	49.51	0.12	6.76	n.d.	1.80	36.40	

n.d., Not detected.

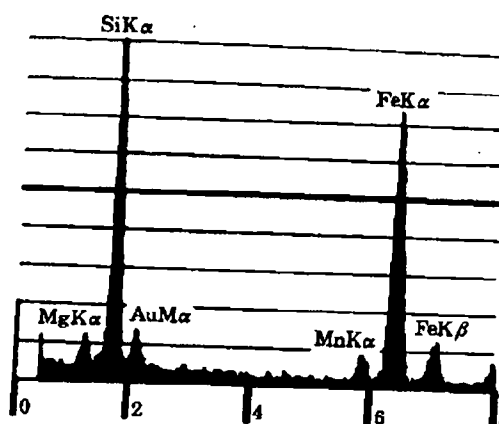


FIGURE 4. X-ray spectrum 0-8 keV obtained from a 100 s point analysis of the fibre illustrated in Figure 3.

FACTORS AFFECTING PARTICLE ANALYSIS IN THE TRANSMISSION ELECTRON MICROSCOPE

Accurate analysis of single mineral particles in the transmission electron microscope depend upon the collection of X-ray spectra which are characteristic of the materials being analysed and which have not been modified by deficiencies in the instrumentation, its operation, or faulty sample preparation. Microscope construction can influence the form of the X-ray spectra collected during the analysis of a particle by contributing X-rays to the spectra which have been generated from the various metal surfaces of the specimen holder and the surrounding specimen stage by electron scatter. X-rays from this source can be reduced to negligible proportions by use of a collimator and also by constructing, or coating, the surface in close proximity

[396]

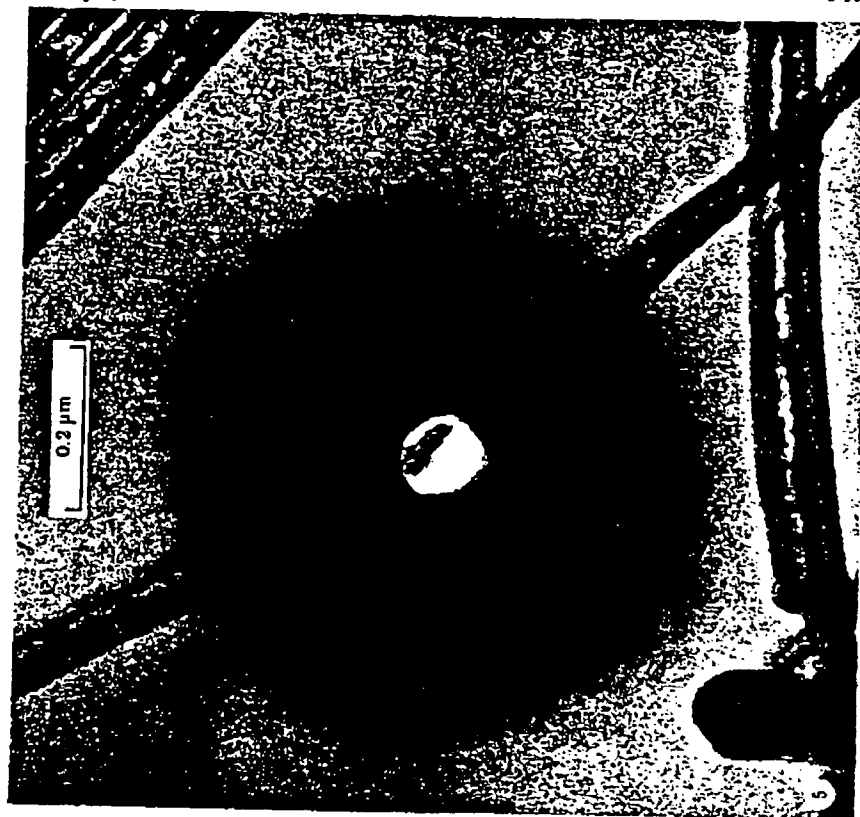


FIGURE 3. Electron micrograph of a single amosite asbestos fibre illustrating the location of ten analyses points along the length of the fibre.

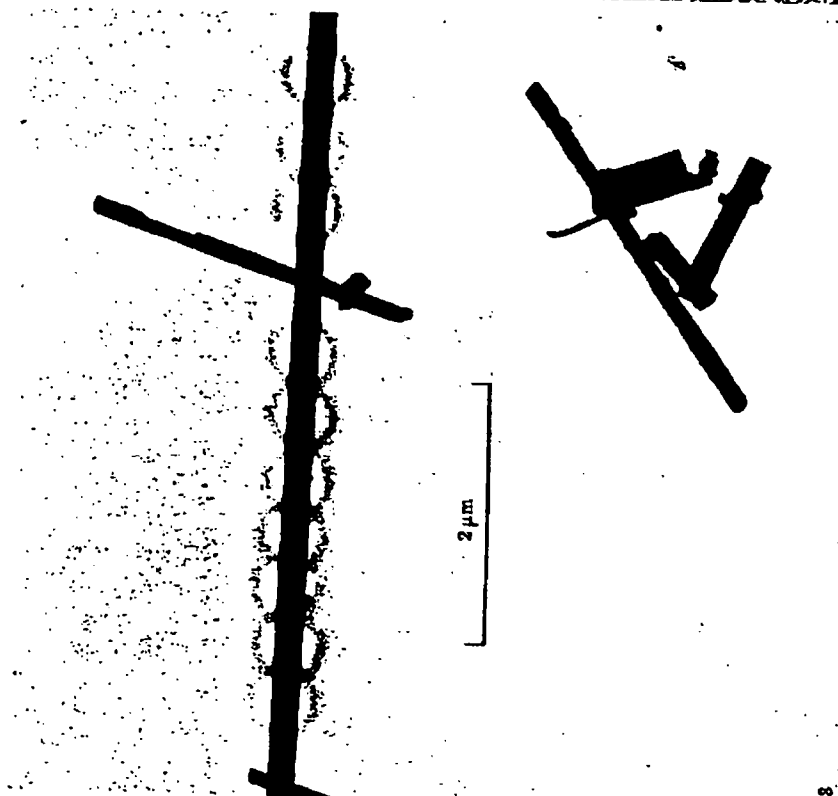


FIGURE 5. Electron micrograph of a single chrysotile asbestos fibril which had been analysed with a high intensity electron beam illustrating the damage to the fibril and also beam contamination.

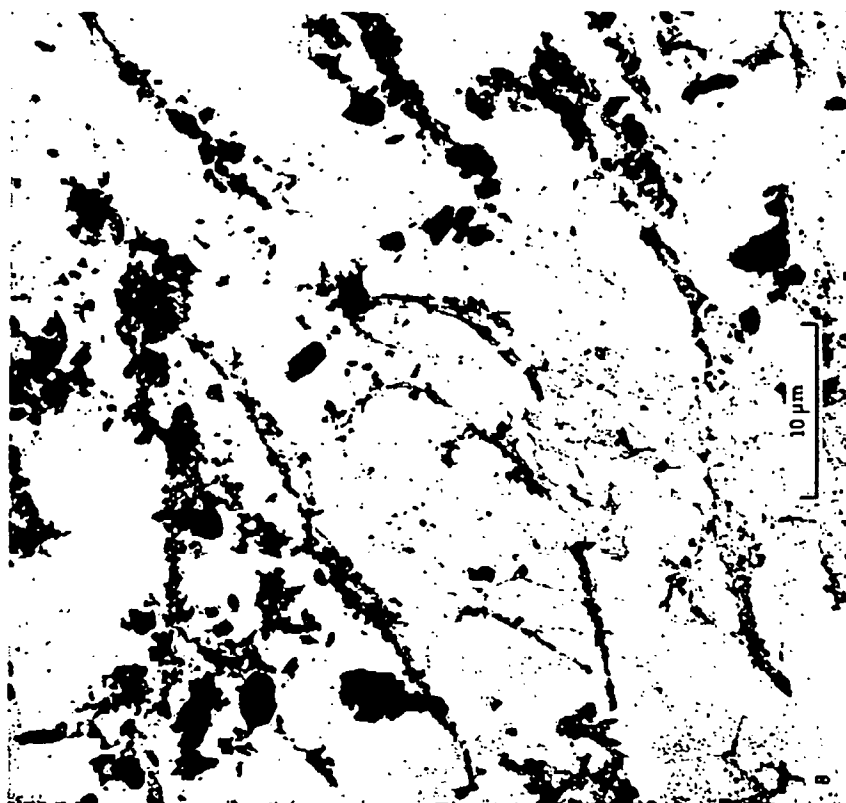


FIGURE 6. Electron micrograph of a slate dust sample collected on a millipore membrane filter.

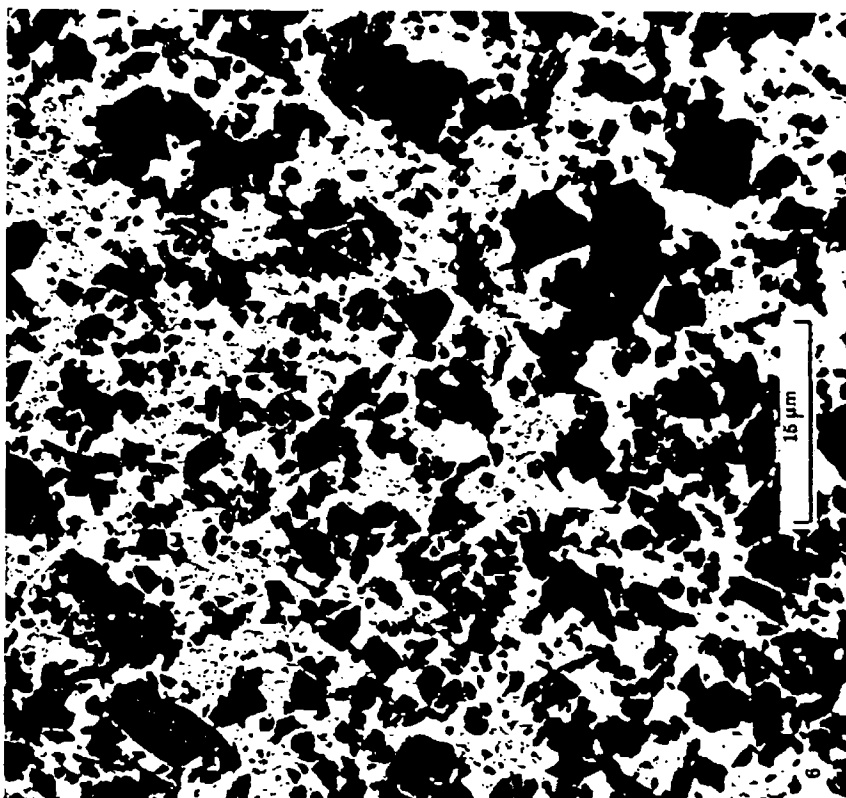


FIGURE 7. Electron micrograph of dust sample obtained from the *post mortem* lung tissue of a slate quarry worker.

to the specimen with materials of low atomic number, which produce X-rays of too low an energy to be detected by the spectrometer, e.g. graphite or beryllium.

A more important source of interference are those X-rays generated from the electron microscope support grid. These can be reduced to minimal proportions by using grids with very large apertures so that particles being analysed are as distant from the metal support as possible, and also by selecting grids which are constructed from elements which are not likely to be found in the specimen, or which contribute X-ray peaks to areas of the spectrum where there is little analytical interest. For the analysis of silicate dusts, gold grids have been found to be most useful as they contribute only a weak *Ma* peak to an X-ray spectrum in the 2300 eV region which coincides with the approximate position of the sulphur *Kα* peak. Electron beam currents are normally maintained at levels which provide adequate X-ray count rates without overheating the sample as this may produce the loss or migration of more volatile elements away from the point of analysis. Rowse *et al.* 1974 noted potassium loss from thin mica flakes when operating at current densities of $10 \text{ nA } \mu\text{m}^{-2}$ to and considered $0.1 \text{ nA } \mu\text{m}^{-2}$ to be a more suitable

TABLE 2. RESULTS OBTAINED FROM THE ANALYSIS OF SINGLE CROCIDOLITE FIBRES OF DIFFERENT DIAMETER USING A $0.5 \text{ } \mu\text{m}$ DIAMETER FOCUSED BEAM AND AN INCIDENT BEAM CURRENT OF 50 nA

fibre diameter μm	oxide mass percentage				
	SiO_2	Na_2O	MgO	Al_2O_3	FeO
0.05	61.4	5.5	2.5	0.2	30.3
0.09	59.5	6.4	4.0	1.0	29.1
0.14	58.9	6.9	3.7	0.8	28.8
0.26	58.5	6.0	3.8	0.6	31.2
0.49	58.5	6.0	4.3	1.0	30.1
mean values	59.36	6.16	3.66	0.72	30.1

These results have not been adjusted for theoretical water contents.

value for this type of material. High accelerating voltages are normally used for analysis to ensure adequate excitation of heavier elements and also to obtain optimum peak to background ratios. Low excitation voltages reduce the penetration thickness of the electron beam the thickness varying approximately in linear proportion to the accelerating voltage. An inherent property of electron guns allows that the beam intensity increases with increase in voltage, thus producing an apparent increase in intensity of spectral lines. Electron microscopes are therefore normally operated for analytical purposes at 60–100 kV.

To prevent the simultaneous collection of X-ray spectra from different mineral particles care must be taken to ensure that mineral particles prepared for examination are adequately spaced and do not overlap. A single layer of well-spaced particles is most conveniently produced by filtering a dilute suspension of particles on to fine-pore organic filters. The particles can be removed from the filter by coating the filter surface and particles with a layer of carbon and dissolving the filter to leave the particles embedded in a carbon support film which can then be transferred to microscope support grids. Particles prepared so that they are embedded in, rather than resting on, a carbon support film have been found to be more suitable for analytical purposes as they are rigidly held by the carbon film which also conducts heat away from the particles while they are being analysed. Silicate mineral particles with a thickness greater than $1 \text{ } \mu\text{m}$

have been analysed in the electron microscope without any noticeable X-ray adsorption and fluorescence effects; however, variation in the spectral response of particles of mineral have been noted as they decrease in size below 0.4 μm (Beaman & File 1976). Table 2 illustrates the results obtained from the analysis of crocidolite fibres of different diameter using identical analytical conditions. They show that no alteration in the spectral response was observed with variation in particle size over the range 0.05 $\rightarrow$ 0.5 μm . It is possible as particle size decreases and the mass of material available for analysis is reduced for electron beam intensities to be increased to maintain a high X-ray count rate; this produces a marked increase in heating of the particle and may produce volatile losses. Figure 5, plate 1, illustrates electron beam damage on a single particle of chrysotile which resulted in an apparent 10% magnesium loss in the analysis of the particle.

TABLE 3. A COMPARISON OF THE CHEMISTRY OF MINERAL SAMPLES BY SINGLE PARTICLE ANALYSIS IN THE ELECTRON MICROSCOPE AND BULK CHEMICAL ANALYSIS

mineral sample	method of analysis	composition of mineral as oxide mass percentage								e.m. reading adjusted for
		SiO ₂	Na ₂ O	MgO	Al ₂ O ₃	K ₂ O	CaO	MnO	FeO	
amaragdite	bulk	27.05	0.16	26.68	23.82	n.d.	0.03	0.08	8.76	12.8% H ₂ O
	e.m.	27.02	n.d.	26.86	22.70	n.d.	n.d.	n.d.	8.62	
hornblende	bulk	42.95	1.35	10.41	10.52	0.75	11.36	0.38	17.31	2.5% H ₂ O
	e.m.	46.26	1.52	11.25	9.98	0.69	11.73	n.d.	16.33	
talc	bulk	62.08	0.31	31.20	0.70	n.d.	0.15	n.d.	0.29	5.5% H ₂ O
	e.m.	61.43	0.66	30.50	1.61	n.d.	n.d.	n.d.	0.38	
richerite	bulk	53.25	5.64	18.94	1.47	1.04	6.55	7.73	1.61	2.3% H ₂ O
	e.m.	55.94	4.65	18.69	2.62	1.07	6.39	7.46	0.90	

n.d., Not detected.

EXPERIMENTAL RESULTS OBTAINED WITH AN ANALYTICAL ELECTRON MICROSCOPE IN THE ANALYSIS OF MINERAL DUSTS

The results presented in this section were obtained using a Philips 301 transmission electron microscope and an Edax energy-dispersive X-ray spectrometer. The X-ray counts were processed using an Edax 707a data processing system, X-ray data being converted to chemical information using the ratio technique previously outlined and the calibration constants contained in figure 2. All the analyses reported were obtained operating the microscope at an accelerating voltage of 80 kV.

Analysis of many preparations of fine mineral particles have shown that accurate chemical information can be obtained from single mineral particles. Table 3 contains the analytical results from four samples of silicate minerals together with chemical data for these minerals obtained by more orthodox methods. The electron microscope results have been adjusted to take account of water of crystallization determined in the bulk analysis of these mineral samples. The results in table 3 illustrate that the chemistry of single particles is sufficiently accurate to act as a base on which to make an identification of the mineral. This identification can also, whenever possible, be strengthened by the use of the selected area electron diffraction facility available with the transmission electron microscope.

Because of the excellent electron beam control in the transmission microscope it is possible not only to focus the beam on very fine individual particles but also to defocus the beam to

larger than 100 μm diameter and still maintain reasonably high current densities. This enables large numbers of mineral particles to be irradiated simultaneously so that the X-ray spectra collected are representative of the bulk sample and all the minerals it may contain. To illustrate this procedure several samples of the United State Geological Survey standard rock specimens were prepared as fine powder and analysed in this fashion. The results obtained are contained in table 4, together with published average values for these standard rock specimens (Flanagan 1969). The results show that the equipment employed is capable of producing bulk chemical information which is reasonably representative of the material being analysed.

TABLE 4. ELECTRON MICROSCOPE ANALYSIS OF U.S.G.S. STANDARD ROCK SPECIMENS WITH AVERAGE DATA FOR COMPARISON

code No.	G.S.P.-1		P.C.C.-1		B.C.R.-1	
	published values	c.m. values	published values	c.m. values	published values	c.m. values
SiO ₂	67.27	68.2	41.87	44.0	54.48	56.7
Na ₂ O	2.88	2.6	0.05	0.5	3.31	2.6
MgO	0.96	1.2	43.56	43.1	3.28	2.6
Al ₂ O ₃	15.11	15.3	0.85	1.1	13.85	13.5
K ₂ O	5.48	5.2	0.01	n.d.	1.68	2.2
CaO	2.03	1.8	0.53	0.6	6.95	7.0
TiO ₂	0.69	1.0	0.02	0.1	2.23	2.3
MnO	0.04	n.d.	0.17	0.7	0.17	0.8
FeO	4.20	3.4	8.20	9.6	13.0	12.3
P ₂ O ₅	0.28	0.8	0.01	n.d.	0.38	0.4

n.d., Note detected. Published values obtained from Flanagan (1969).
c.m. values not corrected for H₂O content of the rock samples.

When referring to the accuracy of analysis in the electron microscope it must be remembered that when analysing a single dust particle, only $10^{-12} \rightarrow 10^{-13}$ g of material is available for analysis while the analysis of bulk samples involves only $10^{-10} \rightarrow 10^{-12}$ g of material. Accurate estimation of elemental values in a sample below 1 % by mass from this quantity of material are therefore very difficult to obtain.

The ability to analyse both single particles and also the bulk sample can be put to very good use, in the examination of dust specimens. Figure 6, plate 2, is an electron micrograph of a sample of slate dust generated in a laboratory dust chamber and prepared for examination by collection of a fine-pore cellulose acetate filter. By probing individual particles in the dust sample it was established that four distinct mineral phases were present. Examples of the X-ray spectra obtained from the four mineral phases are illustrated by figures 7a-d. Computation of the chemistry of these four phases showed that they correspond to the minerals muscovite, quartz, chlorite and an iron oxide mineral. Bulk chemical readings from the dust sample were also obtained and the form of the bulk X-ray spectra is illustrated by figure 7e. The chemistry of the four phases plus the chemistry of the bulk sample is contained in table 5. Using the chemical information obtained from the individual particles and also the bulk dust a series of simultaneous equations were formed to determine the percentage contribution of each mineral to the bulk chemistry. These values are also contained in table 5 from which it can be seen that to obtain the bulk chemistry of the sample from the four minerals detected would require a composition of 53.86 % muscovite, 34.85 % quartz, 8.23 % chlorite and 3.07 % iron as FeO on a mass

[399]

55-2

basis. These figures have not been corrected for theoretical water contents which would alter the mass composition figures slightly. Using the chemistry of the individual mineral phases in the dust and also the bulk chemistry of the sample (all of which were determined by using the electron microscope), the mineralogical composition of the dust has thus been established.

Another example of the use of this procedure to determine the mineralogical composition of a dust sample is illustrated by figure 8, plate 2, which is an electron micrograph of the dust found in the *post mortem* lung tissue of a slate worker. The analyses of the particles found in the tissue and also the bulk analysis of the tissue residue are contained in table 6. The tissue was prepared using an ashing procedure (Pooley 1972) with a portion of the ashed residue being

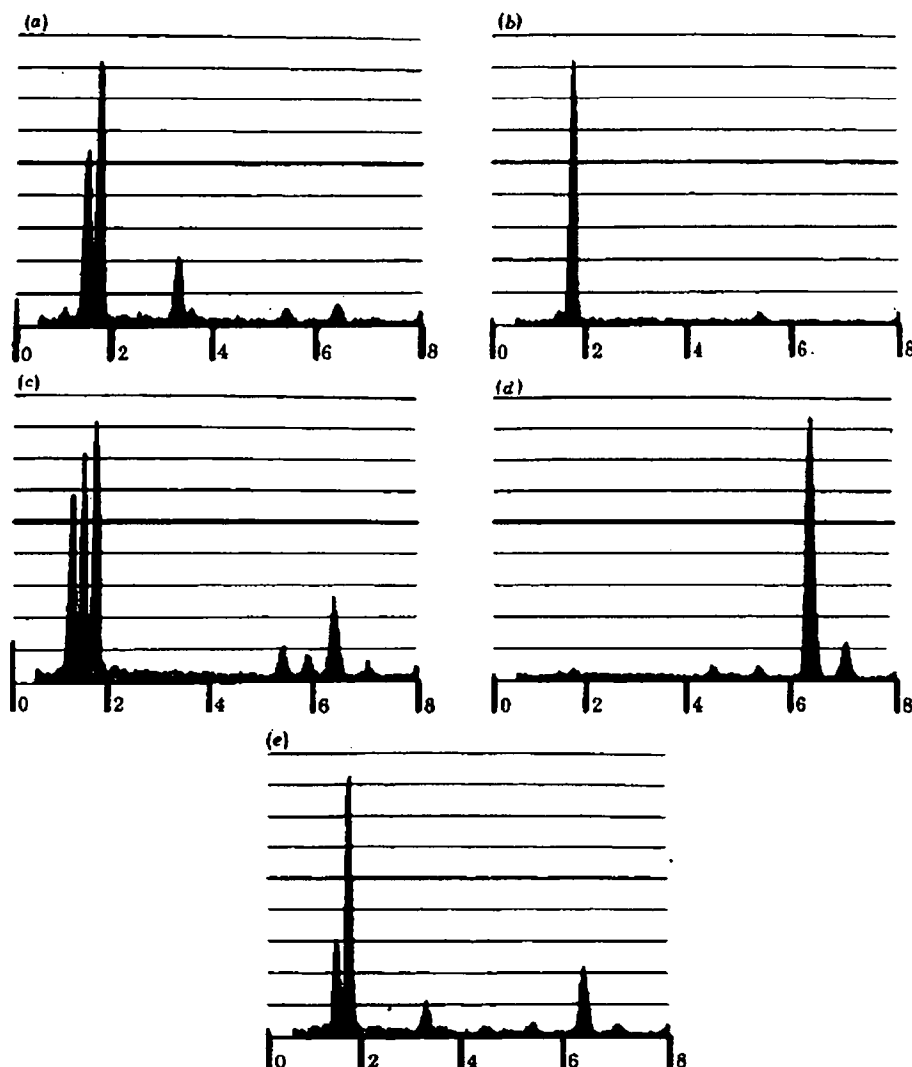


FIGURE 7. X-ray spectra 0-8 keV obtained from the various mineral phases detected in the slate dust sample illustrated by figure 6 and also from the bulk sample. (a) Phase 1, muscovite; (b) Phase 2, quartz; (c) Phase 3, chlorite; (d) Phase 4, iron oxide; (e) X-ray spectrum obtained from bulk sample.

[400]

examined directly and a second portion being washed in dilute HCl to leave the dust particle free of tissue residue. The difference in chemistry between the ash residue and acid-washed sample corresponded to the chemistry of the tissue ash. Using an identical procedure, as outlined for the previous slate dust sample, the mineralogical composition of the dust in the tissue has been calculated and the proportion of each mineral in the tissue residue determined.

TABLE 5. EXAMPLE OF THE ANALYSIS OF A SLATE DUST SAMPLE USING AN ANALYTICAL ELECTRON MICROSCOPE

	oxide mass percentages						
	SiO ₂	Na ₂ O	MgO	Al ₂ O ₃	K ₂ O	MnO	FeO
bulk analysis of the dust using the e.m.	62.7	1.8	2.7	23.2	4.2	0.2	5.1
analysis of individual mineral phases detected in the dust							
(1)	50.1	2.1	1.4	36.4	7.6	0.1	2.4
(2)	93.9	0.3	1.4	3.7	0.3	0.2	0.3
(3)	34.2	0.6	27.3	27.7	0.3	1.4	8.5
(4)	n.d.	n.d.	n.d.	0.2	n.d.	0.2	99.6

Contribution of each mineral phase to the bulk: Phase 1 (muscovite) 56.86%; Phase 2 (quartz) 34.85%; Phase 3 (chlorite) 8.23%; Phase 4 (iron oxide) 3.07%.

	SiO ₂	Na ₂ O	MgO	Al ₂ O ₃	K ₂ O	MnO	FeO
chemistry of the dust calculated from the individual mineral proportions	62.5	1.2	3.5	23.2	4.2	0.2	5.1
bulk chemistry as determined by the e.m.	62.7	1.8	2.7	23.2	4.2	0.2	5.1

n.d., Not detected.

TABLE 6. AN EXAMPLE OF THE ANALYSIS OF DUST EXTRACTED FROM THE TISSUE OF AN INDIVIDUAL EXPOSED TO SLATE DUST USING AN ANALYTICAL ELECTRON MICROSCOPE

	oxide mass percentages									
	SiO ₂	Na ₂ O	MgO	Al ₂ O ₃	K ₂ O	CaO	MnO	FeO	TiO ₂	P ₂ O ₅
analysis of tissue ash residue	50.9	4.3	1.0	19.6	5.4	4.0	0.2	5.8	1.2	7.7
analysis of tissue ash residue acid washed	62.0	2.0	1.0	23.9	5.4	n.d.	0.1	4.2	1.3	n.d.
analysis of mineral phases detected in the acid washed residue										
(1)	94.7	0.2	0.6	2.6	0.5	n.d.	n.d.	0.7	0.4	0.1
(2)	49.1	1.2	1.1	35.5	0.1	n.d.	0.2	3.3	0.7	n.d.
(3)	0.2	n.d.	n.d.	n.d.	n.d.	n.d.	0.2	99.7	0.1	n.d.

n.d., Note detected.

Composition of acid washed tissue residue: Phase 1 (quartz) 32.0%; Phase 2 (muscovite) 65.0%; Phase 3 (iron oxide) 2.2%.

Ashed lung composition; 82.1% mineral and 17.9% tissue ash.

tissue ash analysis					
P ₂ O ₅	Na ₂ O	MgO	K ₂ O	CaO	FeO
43.3	15.2	0.6	5.6	22.5	12.9

[401]

The use of this procedure to determine the composition of a dust has been extensively investigated using synthetic mixtures of minerals and has been found to be accurate in estimating the proportion of one mineral phase in another to the 1 % level by mass. For its success, however, the method requires that the number of elements detected are equal to, or exceed, the number of mineral phases present. The major mineral phases detected in the two examples outlined were confirmed by the preparation of X-ray powder photographs of the dusts.

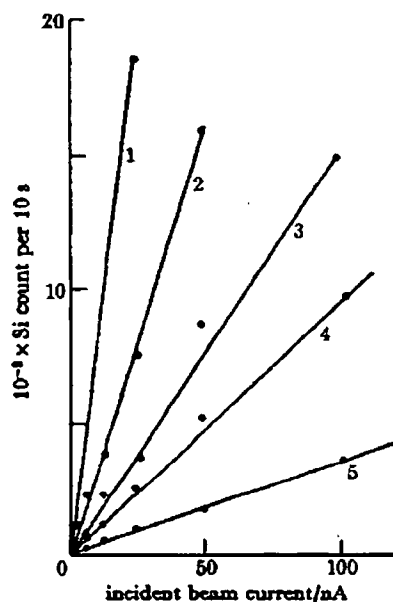


FIGURE 9. Variation of silicon count/unit time with incident beam current obtained from the analysis of 60 μm diameter areas of specimens containing different quantities of quartz particles/unit area. (1) 40 $\mu\text{g}/\text{cm}^2$; (2) 20 $\mu\text{g}/\text{cm}^2$; (3) 10 $\mu\text{g}/\text{cm}^2$; (4) 5 $\mu\text{g}/\text{cm}^2$; (5) 2.5 $\mu\text{g}/\text{cm}^2$.

The X-ray spectra collected during the bulk analysis of a dust sample in the electron microscope not only provide a means of obtaining the chemistry of the dust but it is extremely useful in estimating the mass of dust per unit area of the sample being analysed. Experimental results have shown that the rate of production of elemental characteristic X-rays during analysis is directly proportional (over a wide range of values), to the incident electron beam current. This relation is illustrated by figure 9 which is a plot of the silicon counts per unit time against incident electron beam current obtained from dust particles of pure quartz deposited on to filters so that the mass concentrations of dust per unit area of each preparation varied from 40 $\mu\text{g}/\text{cm}^2$ to 2.5 $\mu\text{g}/\text{cm}^2$.

The results were obtained by irradiating areas of the prepared specimens equivalent to a 60 μm diameter circle using incident beam currents varying from 10–100 nA. The silicon counts collected per 100 s of analysis time were recorded and plotted against incident beam current to produce the plots shown in figure 9. It can be seen that the silicon count rate increases in a linear manner with increase in the beam current and that the slope of the plots vary directly in proportion to the mass of quartz deposited per unit area of filter. This relation can be used to obtain the mass of SiO_2 in a dust per unit area of an unknown filter sample by

[402]

simply monitoring the silicon count rate obtained during the analysis of an identical area on the sample, equivalent to a 80 μm diameter circle, measuring the incident beam current and relating these readings to the values obtained from a standard specimen with a known mass of SiO_2 per unit area. Having obtained a value for mass of SiO_2 per unit area on the unknown filter, the total mass of dust can be calculated from the bulk chemical analysis of the sample with the knowledge that the SiO_2 content of the dust represents only a specific percentage of the oxide mass of the sample.

CONCLUSIONS

Using a transmission electron microscope and suitable X-ray analytical equipment it is possible to analyse a dust sample to obtain morphological information, i.e. size and shape of particles, and also accurate chemical information from both single and large numbers of particles. The chemical information from single particles can serve as the basis for an identity of the minerals contained in the dust, while the analysis of large numbers of particles simultaneously provides a chemical analysis of the total dust. Using the chemical data obtained from single particles and the bulk sample it is possible to calculate the percentage composition of each mineral phase in the dust. X-ray readings recorded from the bulk material can also be used to estimate the mass concentration of dust present per unit area of a prepared specimen which can then be related back to the total area of the sample from which the specimen was prepared to obtain mass concentration data. Using an analytical electron microscope in the manner outlined in this paper it is possible to derive information from dust samples that cannot be obtained by other analytical techniques.

The application of the procedures outlined is not limited by sample size as they are based on the ability to analyse single dust particles. In the future it is to be expected that the analytical transmission microscope will become a major tool not only in the area of dust research but also in the study of all fine grained mineral assemblages.

I would like to thank the Medical Research Council for their financial support of the work reported in this article, and also Professor D. R. Bowes of the Department of Geology, University of Glasgow for his bulk analyses of the samples used.

REFERENCES (Pooley)

- Beaman, D. R. & File, D. M. 1976 Quantitative determination of asbestos fibre concentrations. *Anal. Chem.* **48**, 101-110.
- Cliff, G. & Lorimer, G. W. 1972 Quantitative analysis of thin foils using EMMA 4 - the ratio technique. *Proc. Fifth Europ. Congr. on Electron Microsc. Manchester*, Pp. 140-141. London: Inst. of Physics.
- Cliff, G. & Lorimer, G. W. 1975 The quantitative analysis of thin specimens. *J. Microsc.* **103**, 203-207.
- Cooke, C. J. & Duncumb, P. 1968 *5th Int. Conf. X-ray Optics and Micro-analysis Tübingen* (eds G. Mollenstadt & K. H. Gaulker), pp. 245-247. Berlin: Springer Verlag.
- Duncumb, P. 1966 Precipitation studies with EMMA - a combined electron microscope and X-ray analyser. In *The electron microscope* (eds T. D. McKinley, K. F. J. Heinrich & D. B. Wittry). Pp. 490-498. John Wiley, New York.
- Flanagan, F. J. 1969 U.S. Geological Survey Standard II First compilation of data for the new U.S.G.S. rocks. *Geochim. cosmochim. Acta*, **33**, 81-120.
- Gedcke, D. A. 1972 The Si (Li) X-ray energy analysis system: operating principles and performance. *X-ray Spectrom.* **1**, 129-141.
- Henderson, W. J., Melville-Jones, C., Barr, W. T. & Griffiths, K. 1975 Identification of talc on surgeons' gloves and in tissue from starch granulomas. *Br. J. Surg.* **62**, 941-944.

- Jacobs, M. H. & Baboravská, J. 1972 Quantitative micro-analysis of thin foils with a combined electron microscope-micro-analyser (EMMA-3). *Proc. Fifth Europ. Congr. on Electron Microsc. Manchester*, pp. 136-137. London: Institute of Physics.
- Lorimer, G. W. & Champness, P. E. 1973 Combined electron microscopy and analysis of an orthopyroxene. *Am. Mineral.* 58, 243-248.
- Lorimer, G. W., Razik, N. A. & Cliff, G. 1973 The use of the analytical electron microscope EMMA-4 to study the solute distribution in thin foils - some applications to metals and minerals. *J. Microsc.* 99, 153-164.
- Morgan, A. J., Davies, T. W. & Erasmus, D. A. 1975 Analysis of droplets from iso-atomic solutions as a means of calibrating a transmission electron analytical microscope. *J. Microsc.* 104, 271-280.
- Pooley, F. D. 1972 Electron microscope characteristics of inhaled chrysotile fibre. *Br. J. Industr. Med.* 29, 146-153.
- Pooley, F. D. 1975 The identification of asbestos dust with an electron microscope microprobe analyser. *Ann. Occup. Hyg.* 18, 181-186.
- Rowse, J. B., Jepson, W. B., Bailey, A. T., Climpson, N. A. & Soper, P. M. 1974 Composite elemental standards for quantitative electron microscope microprobe analysis. *J. Phys. E: Scient. Instrum.* 7, 512-514.
- Russ, J. C. 1973 X-ray spectrometry on the electron microscope. *X-ray Spectrom.* 2, 11-14.
- White, E. W., Denny, P. J. & Irving, S. M. 1966 *Quantitative microprobe analysis of microcrystalline powders in the electron microprobe* (eds T. D. McKinley, K. F. J. Heinrich & D. B. Wittry), pp. 791-804. New York: John Wiley.

Discussion

J. V. SMITH (*Dept. of the Geophysical Sciences, University of Chicago, Chicago, Illinois 60637, U.S.A.*). Your description of the use of a solid-state detector in the identification of small particles was illuminating, and I would like to ask for details on some technical points: (a) was a peak-stripping procedure used such as the ones developed by Reed & Ware and by Statham?; (b) have you considered using Be to coat the specimen rather than Au (Be is a toxic poison when gaseous, but has been used successfully at E.T.H., Zürich, as a coating during electron microprobe analysis; the gold M lines unfortunately overlap with the sulphur K lines thereby making difficult the identification of S-bearing specimens); (c) have you considered using magnetite or haematite as the iron-oxide rather than the FeO listed on one of your slides (these minerals are more likely under the oxidizing conditions at the Earth's surface than wüstite); (d) have you considered making corrections for efficiency-of-generation, fluorescence and absorption using idealized shapes such as cubes or hemispheres flooded by the electron beam? I suspect that neglecting these factors may cause serious errors for the light elements Na to Si.

F. D. POOLEY. (a) No peak stripping procedure was used to obtain the chemical data illustrated in the paper, only single peak minus background subtractions; (b) I agree that Be is a more suitable element to use for specimen support grids, but its expense and toxic nature preclude its use except in the most critical of analyses; (c) the use of FeO as a means of expressing iron as an oxide is simply a matter of choice as it is not possible at present to distinguish between the various oxide forms of iron using the analytical technique described; (d) with the very small size of particles analysed it has not been found necessary to make any corrections for efficiency-of-generation, fluorescence or absorption effects.

R. C. MACKENZIE (*The Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen*). For bulk chemical analysis it is essential that the field examined be representative of the whole sample. Since it is always difficult to ensure that the material on an electron microscope grid is representative, how were sampling errors avoided or minimized?

F. D. POOLEY. It is never possible to avoid errors when sampling fine particulate material for electron microscopy. Errors were, however, minimized by ensuring the sample was reduced to particles of a very fine size, i.e. usually less than 5 µm, and care was taken to ensure adequate mixing and dispersion while splitting and reducing samples to a size suitable for microscopy.