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1987/57. Determination of concentration, and evaluation of, airborne dust: Analysis of quartz by X-ray diffraction

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Abstract

Dusts on membrane filters are being analysed by X-ray diffraction in the Department of Mines laboratories for quartz (crystalline silica). The basis of the method is elaborated, with statistical analysis of the results.

INTRODUCTION

Airborne dusts can provide a number of hazards, particularly that of silicosis, a complaint thought to be related primarily to the content of crystalline silica in dusts. Quartz (or strictly, at room temperature, alpha quartz) is the most common form of crystalline silica, and is a major component of many rocks, soils and industrial materials.

The airborne dusts are normally assessed by collection on membrane filters in miniature cyclone separators, calibrated for the respirable size range (1-10 μm). Static samples are collected when the cyclone is in a fixed location, but of more direct use are personal samples, where the cyclone is worn by a worker.

These dusts on membrane filters are assessed by :

(1) **Gravimetry** (weight measured before and after sampling)

(2) **Microscopy** (polarised light or electron microscopy), usually for asbestos studies.

(3) **Mineralogy** by X-ray diffraction or infra-red spectroscopy, etc., principally for the determination of the quartz content.

(4) **Chemistry** by X-ray fluorescence, etc.

X-ray diffraction is one of the most specific and sensitive techniques for dust assessment, and is the only method discussed here. Optical microscopy is ineffective for dusts in the respirable size range, and electron microscopy is relatively expensive and inconvenient for routine use. Chemical analysis will give total silica but not the proportions of quartz, silicates, etc. Colorimetry and differential thermal analyses are difficult to use for this purpose (National Health and Medical Research Council, 1984).

X-RAY DIFFRACTION

X-ray diffraction is an optical effect resulting from interference of X-rays passing through crystalline substances. The regular, planar, arrangement of atoms results in a 'diffraction-grating' effect (fig. 1a, 1b), the resulting diffraction pattern being detectable by various electronic and photographic methods. The diffraction pattern for a single crystal can be recorded on photographic film as an array of spots surrounding the primary beam (fig. 1c), and this is the principal technique for crystal structure analysis.

Powdered samples give a series of concentric circles on photographic film (fig. 2a, 2b), but are more commonly studied with a diffractometer. This

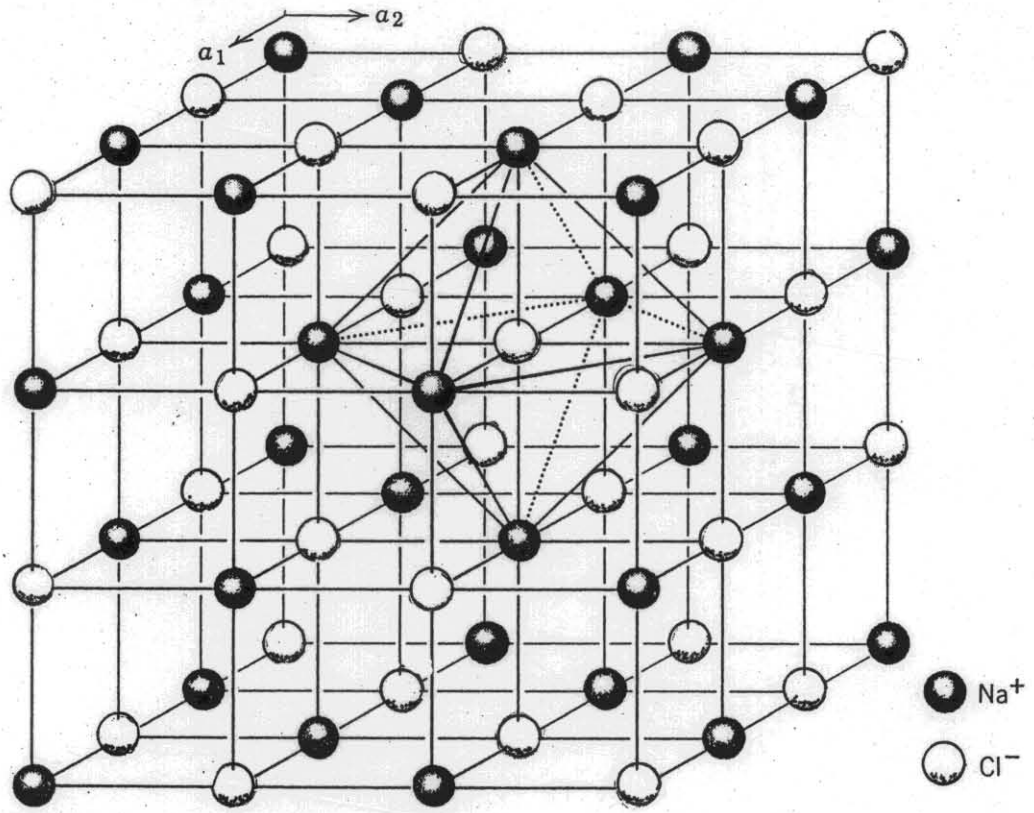


Figure 1a. *Sodium chloride (NaCl) structure based on face-centered cubic lattice type. Note that each ion is surrounded by 6 neighbouring ions of opposite charge (CN=6), outlining octahedral polyhedra.*

Figure 1b.
Geometry of X-ray "reflection".

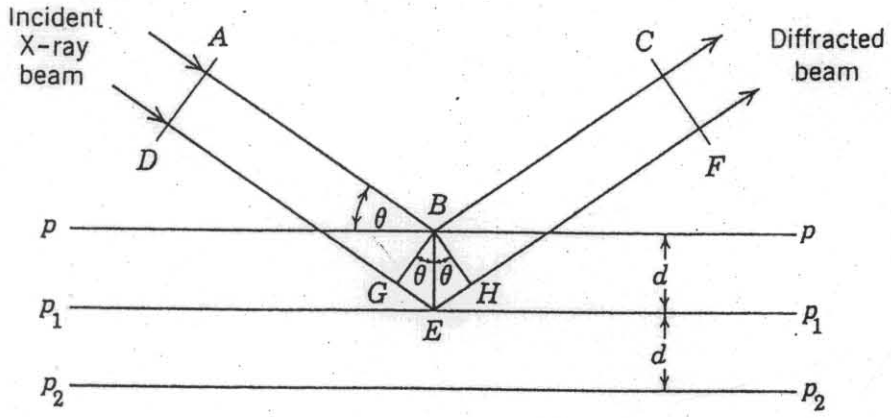
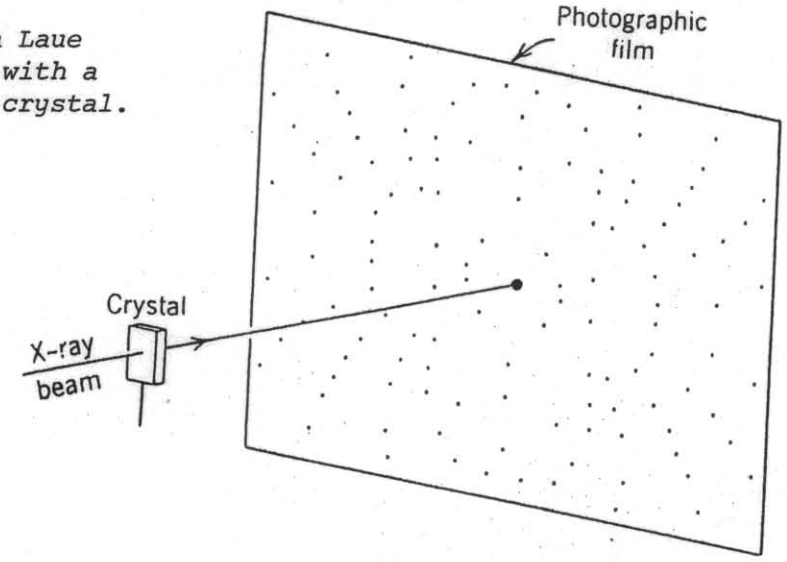
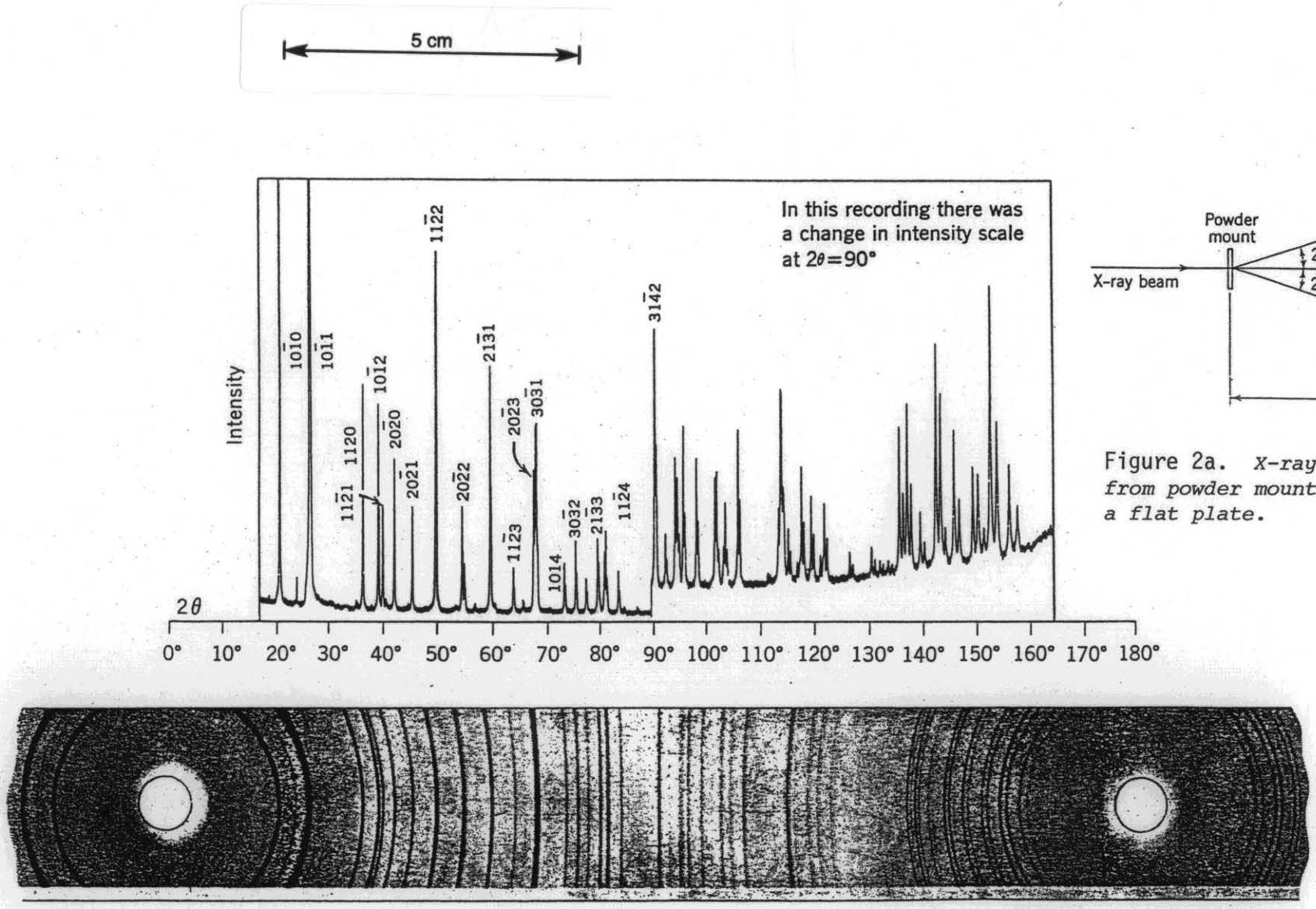


Figure 1c.
Obtaining a Laue photograph with a stationary crystal.





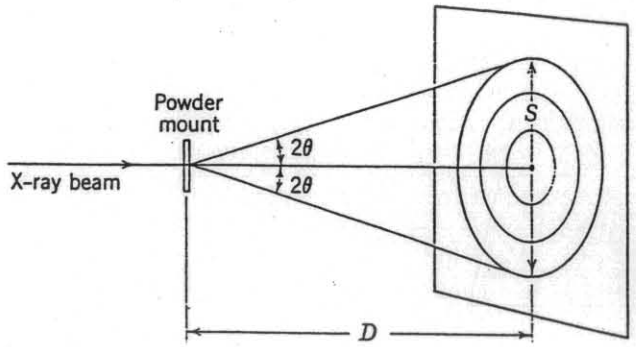


Figure 2a. *X-ray diffraction from powder mount recorded on a flat plate.*

Figure 2b, 2c. *Comparison of diffractometer record and powder film of quartz. On the diffractometer recording are given the Miller indices of the crystal planes that gave rise to the various low angle diffraction peaks.*

method uses a scintillometer (or geiger, etc.) detector, rotating about the sample over angles up to 0-160°, to record the pattern on a chart recorder and/or a computer (fig. 2c). The positions (°2θ) of the "reflections" are dependant on the lattice spacings (d) of the sample and the X-ray wavelength (λ) used, by the Bragg law:

$$n\lambda=2d\sin\theta$$

The lattice spacings are dependant on the chemical composition as well as the crystal structure of the sample. The X-ray diffraction pattern can thus indicate the identity of unknown crystalline compounds - few patterns overlap exactly. Information can also be obtained on the composition and crystallinity of the compounds. Amorphous materials, in contrast, usually only provide a broad peak of limited use (fig. 3).

QUANTITATIVE X-RAY DIFFRACTOMETRY

Quite complex mixtures can usually be interpreted if not too many unknown or complex phases are present (fig. 3). Most common minerals can be recognised by experienced users from the strongest 1-3 reflections but overlap and absorption effects can cause problems.

The intensity (I_i) of a reflection is a function of the concentration (X_i) of diffracting component i in a mixture according to the formula of Klug and Alexander (1954):

$$I_i=kX_i/\mu_i$$

where k is a constant, dependant on the instrument, reflection and component, and μ is the mass absorption coefficient of the sample. A number of methods are used for quantitative or, more commonly, semi-quantitative analysis. A series of known standards are usually prepared, enabling calculation of k, and μ can be measured, calculated or estimated. The internal standard technique is very common; this relies on adding known amounts of some component and measuring intensity ratios, which are independant of μ.

Difficulties may be major, due to variations in crystallinity, grain size, composition, crystallite orientation, etc. Analyses can seldom be produced with accuracy better than ± 10% relative, and detection limits may vary from 0.3% to perhaps 40% (e.g. glass). Best results are obtained on samples of size range 1-30 micrometres.

QUARTZ ANALYSIS ON MEMBRANE FILTERS

Most workers on environmental dusts use an X-ray or infra-red method to determine the contents of alpha-quartz and other forms of silica. Our laboratory has adopted the 'Direct on Filter' technique (similar to the internal standard method) recommended by the National Health and Medical Research Council (1984) for such analyses. This technique is a variation of that developed by Altree-Williams *et al.* (1977).

In our laboratory, dust samples are received on 25, 37 or 45 mm Millipore polycarbonate membrane filters, which are placed above a silver membrane filter in sample holders. The strongest silver and quartz peaks are located and measured automatically, the backgrounds measured and subtracted, and the resulting peak intensities ratioed and multiplied by a predetermined constant to give a calculated weight of quartz (fig. 4). The measurements

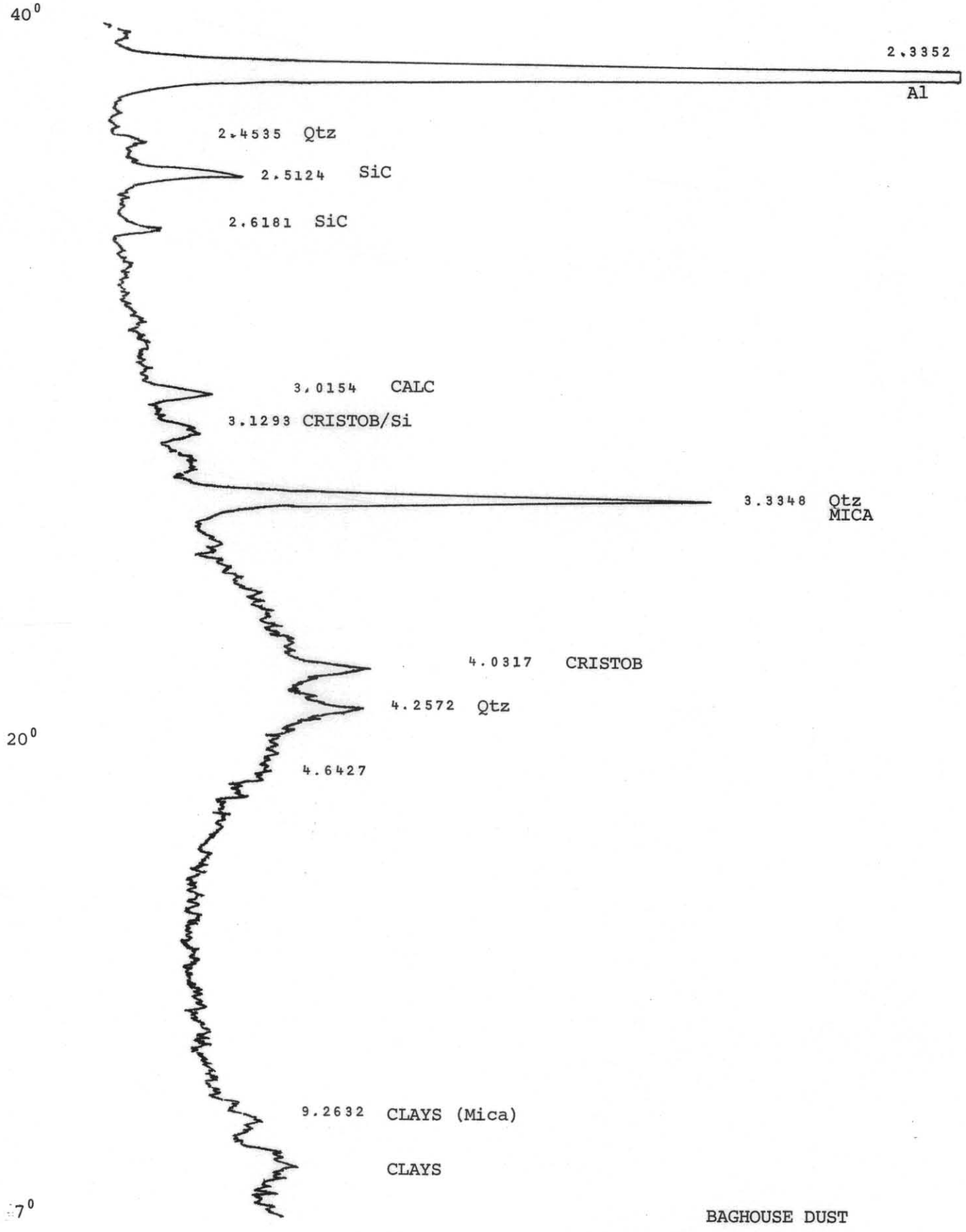


Figure 3. *A chart record for a sample of dust containing about 90% amorphous silica (broad peak), about 7% quartz, and ≤2% cristobalite, silicon, silicon carbide, calcite, micas and clay. The aluminium peaks are from the sample holder.*

5 cm

PHASE	DEG 2THETA	D-SPACE	INTENSITI	BGROUND	I-BGROUND
ILLITE	8.85	9.9916	178	188	-10

	SIO2 POSN	I-SIO2	B-GROUND	AG-POSN	I-AG	B-GROUND	RATIO	WT.SIO2-MG
AUE.	0.742MG							
	26.74	435	186	37.90	3339	97	0.130	0.713
	26.72	457	188	37.90	3314	97	0.138	0.755
	26.74	446	183	37.90	3333	88	0.134	0.732
	26.72	469	191	37.90	3347	87	0.140	0.766
	26.73	455	191	37.91	3336	85	0.137	0.747

i25

	SIO2 POSN	I-SIO2	B-GROUND	AG-POSN	I-AG	B-GROUND	RATIO	WT.SIO2-MG
AUE.	0.001MG							
	26.77	6	189	37.89	3605	95	0.002	0.009
	26.67	-4	185	37.88	3684	86	-0.001	-0.005
	26.61	1	190	37.88	3645	91	0.000	0.001
	26.74	-5	197	37.88	3675	87	-0.001	-0.007
	26.63	3	181	37.88	3657	93	0.001	0.005

Blank

Figure 4. *Results output from two runs, one a blank filter and one a pure quartz standard (No 125). The output shows the position of the main quartz peak, its intensity and background: ditto for silver; the peak ratio (I(quartz)/I(silver)) and the calculated quartz content. Note that illite is automatically searched for in 125, the 'quartz peak position' is widely variable for the blank, and the intensity variability is related to the absolute intensity.*

6/0

are repeated five times to give a suitable mean result, and this takes about twenty minutes in total. Resolution and reproducibility are improved by use of a sample spinner and a graphite monochromator. Samples are run with normal-focus, nickel-filtered copper radiation at 50 kV, 25 mA, with slits 1°/0.2/1°, and a Philips (Norelco) diffractometer, proportional detector and microprocessor.

The microprocessor-based control system automatically checks for interference from micas; interference from other compounds (e.g. graphite or iron carbide) is checked for manually when suspected. The second strongest quartz peak may be used if interference is suspected, but with about 30% of the resolution. The position of the peaks is output, giving an indication of accuracy, and all results are monitored closely and rechecked where necessary.

Statistical work on about thirty pure quartz standards (prepared in a small dust chamber) (see Appendix 1) indicates, by regression analysis (fig. 5a):

$$\text{Weight of quartz (mg)} = 3.58 \times I(\text{quartz})/I(\text{silver}) \quad (R^2=0.994)$$

The standard deviation of the mean ($Sm=s.d./\sqrt{N}$, where $N=5$ repeats) was found by regression (fig. 5b) to be:

$$Sm\ (mg) = 0.004 + 0.004 \times (\text{wt. quartz}) \quad (R^2=0.886)$$

The detection limit is thus about 0.004 mg, where Sm = 100%. For example, for 0.1 mg of quartz, Sm = 4.4%, i.e. there is a 68% probability of the real value being within the confidence limits (0.1000 ± 0.0044 mg). In actual practice, results are given to two decimal places, as the presence of other components has an unquantified effect. In comparison, the detection limit with infra-red is about 0.02 mg, with results ±5% (National Health and Medical Research Council, 1984).

Standards have only been run for 25 mm Millipore filters, and the accuracy of analyses of 37 mm and 45 mm filters is unknown. Multiplication factors need to be used for different sized filters due to the difference in surface areas (e.g. 2.2X for 37 mm filters). There is also a marked concentration of dust in the centre of the filters, suggesting that the measurements may be a slight over-estimate (the X-rays affect an area of about 1 cm^2). Estimates can be made of relative proportions of other components on the filters, and support the results of this method.

OTHER APPLICATIONS

Any crystalline compound could theoretically be treated in a similar manner, if suitable standards are available. It is hoped to analyse cristobalite (a high temperature form of silica) in a similar way in the near future, and perhaps asbestos minerals, although chemical variation and orientation effects could complicate this.

Size analysis of dusts is a theoretical possibility, given suitable standards.

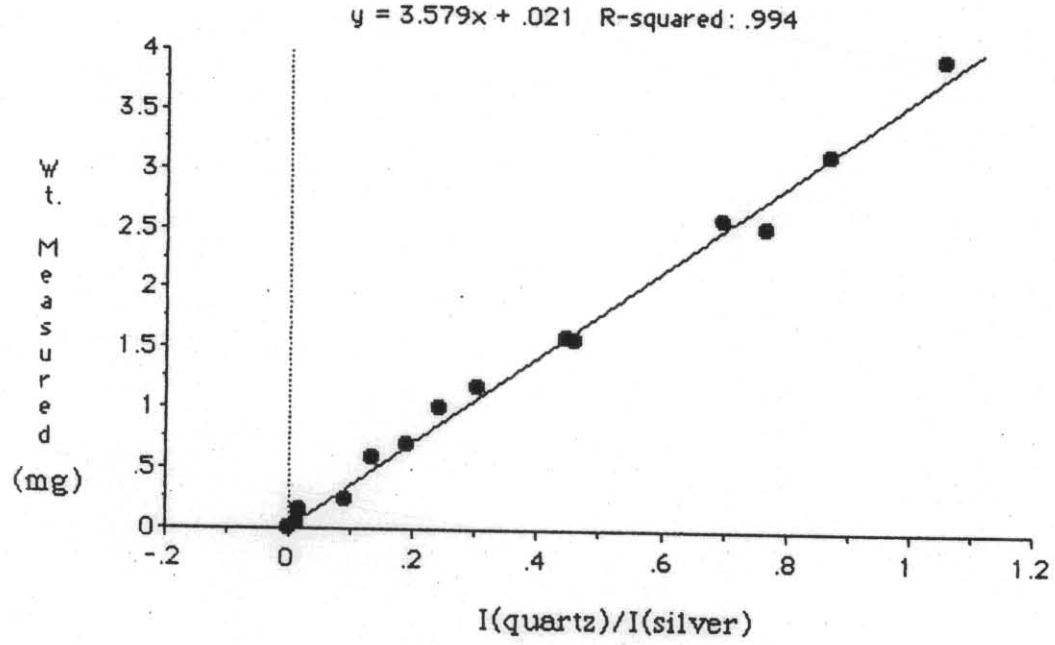


FIG. 5a. Correlation of measured weights of quartz standards with the intensity ratios of X-ray Diffraction peaks.

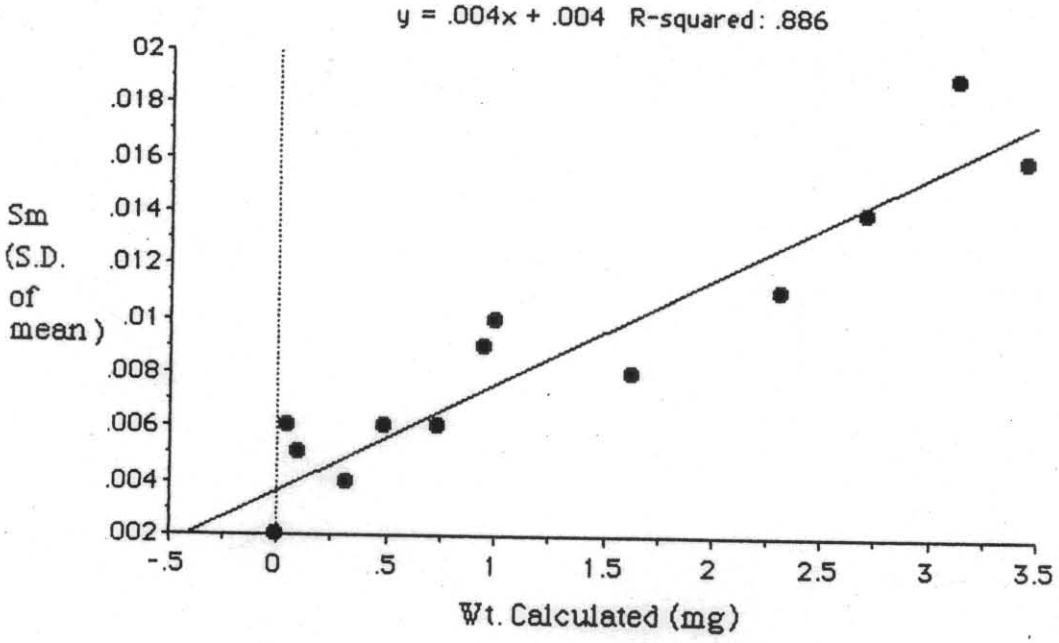


FIG. 5b. Regression analysis of calculated standard deviations of the mean against the calculated mean weights of quartz.

5 cm

REFERENCES

ALTREE-WILLIAMS, S.; LEE, J.; MEZIN, N. V. 1977. Quantitative X-ray diffractometry on respirable dust collected on Nucleopore filters. *Ann. Occ. Hygiene.* 20:109-126.

KLUG, H. P.; ALEXANDER, L. E. 1954. *X-ray diffraction procedures for polycrystalline and amorphous materials.* Wiley.

NATIONAL HEALTH AND MEDICAL RESEARCH COUNCIL. 1984. *Methods for measurement of quartz in respirable airborne dust by infra-red spectroscopy and X-ray diffractometry.* Commonwealth of Australia.

[18 November 1987]

APPENDIX 1.

Preparation of quartz standards

The preparation of standards for determination of the correlation factors used in these analyses is based on the examples shown by the National Health and Medical Research Council (1984). A sample of respirable-sized (1-10 μm) dust, quartz standard A9950 (Aust. 1) was used, and the dust chamber is shown in Figure 6.

A small sample of the standard quartz is placed in the dust chamber, which is then connected to the nitrogen line. Any gas or air under moderate pressure may be used. The dust is given a short, sharp blast of nitrogen, for a few seconds, to send some dust into suspension. It is then left for one minute to settle the coarsest dust, whilst disconnecting the nitrogen line and connecting the sampling pump. The dust is then pumped through the filter for varying times. The relationship between sampling time and weight of dust is shown in Figure 7. Samples of more than 3 mg of dust are unreliable, as dust is readily lost from the filters under such heavy loadings. Membranes must be handled with tweezers (spade-tipped, non-serrated) at all times, and weighed at constant humidity.

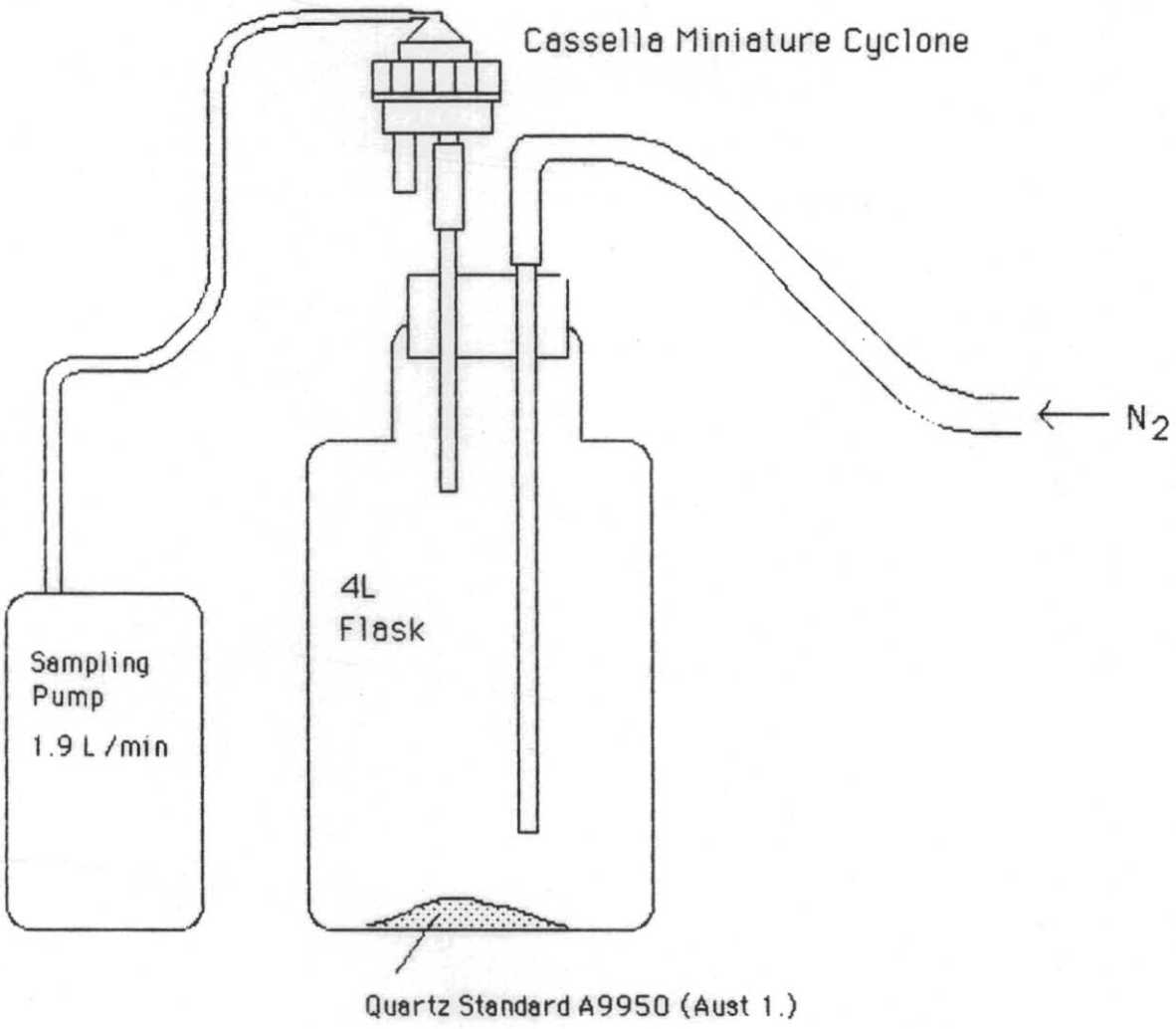


Figure 6. *Dust chamber for preparation of quartz standards*

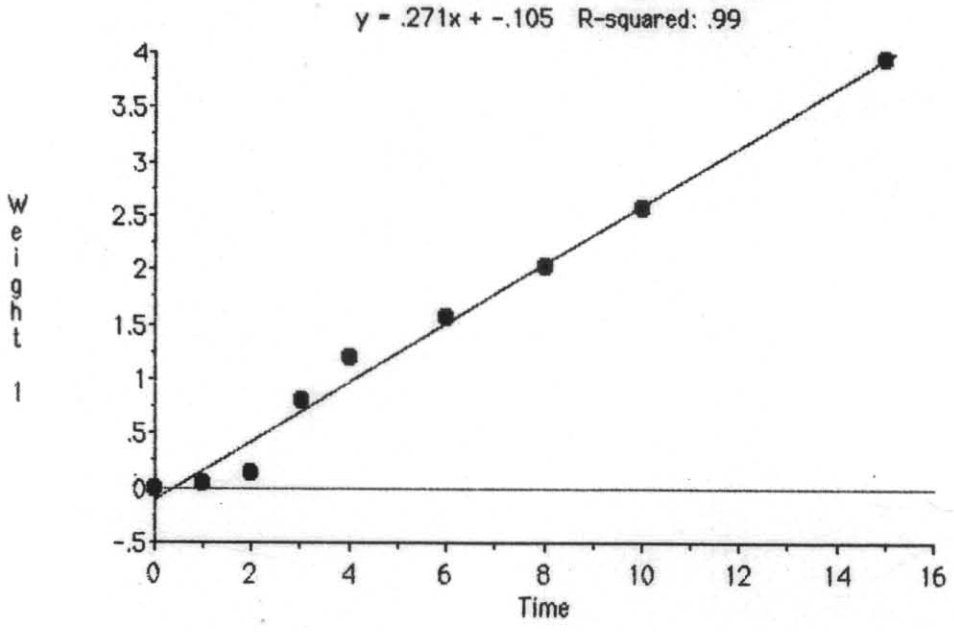


Figure 7. *Correlation of weight of quartz (mg) with pumping time (min)*

5 cm