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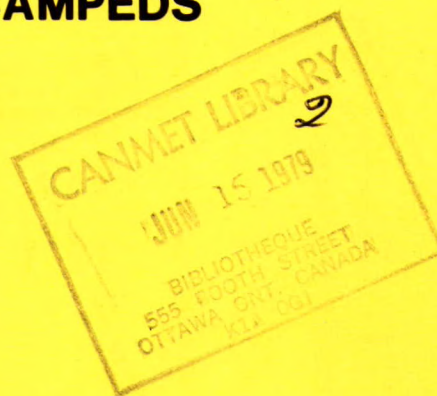
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REPORT 78-7

MINE DUST SAMPLING SYSTEM — CAMPEDS

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MINERALS RESEARCH PROGRAM
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PREFACE

This is a record of experimental work at the Elliot Lake Laboratory in developing a method of dust sampling for mines using both gravimetric assessment and X-ray diffraction analysis for quartz. The field work undertaken in this connection is reviewed briefly.

The report emphasizes laboratory aspects of a dust sampling program using respirable dust samplers and X-ray diffraction analysis for quartz, and is intended mainly for staff setting up a sampling and XRD assessment system. It may also be useful to other personnel heavily committed to a dust sampling program. Report MRP/MRL 77-56, "Guide to gravimetric Sampling with Quartz Analysis in Mines" by the same author describes the field techniques of interest to most users of dust sampling equipment.

PREFACE

Ce rapport contient un compte rendu des recherches effectuées au Laboratoire d'Elliot Lake ayant pour but de mettre au point une méthode d'échantillonnage de la poussière dans les mines à l'aide de l'évaluation gravimétrique et de l'analyse par diffraction des rayons X (DRX) du quartz. On décrit brièvement les recherches à cet effet effectuées en chantier.

Le présent rapport met l'emphase sur l'analyse en laboratoire du programme d'échantillonnage de la poussière à l'aide d'un échantillonneur de poudre respirable et l'analyse du quartz par la diffraction des rayons X. Il a été rédigé à l'intention des personnes responsables de la mise sur pied de système d'échantillonnage et d'évaluation par la DRX et de celles qui s'occupent présentement d'un programme d'échantillonnage. Le rapport MRP/MRL 77-56 intitulé "Guide to Gravimetric Sampling with Quartz Analysis in Mines" du même auteur décrit les techniques employées en chantier et susceptibles d'intéresser ceux qui se servent d'un équipement d'échantillonnage de la poussière.

MINE DUST SAMPLING SYSTEM - CAMPEDS

by

G. Knight*

ABSTRACT

This report describes an improved method of sampling for air-borne dust in mines. Aerodynamic size selection is used to simulate dust deposition in the alveolar region of the lungs and dust is collected on a filter for periods of 2 to 10 hours. The dust is assessed by weighing before and after ashing to give estimates of total respirable dust and "respirable combustible dust". Respirable quartz dust is assessed on individual samples by X-ray diffraction. Silver membrane filters have been found most suitable for both gravimetric and X-ray diffraction analysis. They make it possible to measure directly without any transfer operation.

The X-ray diffraction analysis of quartz is improved by using the most intense beam possible with wide slits. The graphite diffracted-beam monochromator increases intensity and peak-to-background ratio. The choice of X-ray target material is a compromise between intensity, resolution and absorption with cobalt being the most suitable. More than one X-ray diffraction line is used to minimize the effects of interference.

Because of uneven dust deposition over the filter and uneven illumination by X-rays, the X-ray diffraction must be calibrated against the mass of quartz on samples collected with the sampler in a pure quartz dust cloud. Permanent quartz standards are required to eliminate effects of secular variations in X-ray intensity.

A robust personal dust sampler combined with the cap lamp battery called CAMPEDS was developed for convenient personal sampling in mines. The respirable size-selection characteristics of dust samplers are affected by small changes in dimensions and layout of components. It is essential that calibrations on complete instruments be carried out to test both the design and reproducibility of manufacture.

METHODE D'ECHANTILLONNAGE DE LA POUSSIERE DANS UNE MINE — CAMPEDS

par

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RESUME

Le présent rapport décrit une méthode améliorée d'échantillonnage de la poussière dans l'air d'une mine. La méthode de sélection aérodynamique selon la granulométrie est employée afin de simuler le dépôt de la poussière dans la région alvéolaire des poumons. La poussière est accumulée sur un filtre pendant 2 à 10 heures. Cette poussière est pesée avant et après avoir être réduite en cendre pour estimer la quantité totale de poussière respirable et de "poussière combustible respirable". La quantité de poussière de quartz respirable est mesurée sur chacun des échantillons par la diffraction des rayons X. Les filtres composés d'une membrane d'argent conviennent mieux aux analyses gravimétriques et de diffraction des rayons X. Par ce fait il est possible de mesurer directement sans effectuer de transfert.

On améliore l'analyse du quartz par la diffraction des rayons X en employant un faisceau lumineux le plus intense possible et des fentes plus larges. La méthode avec monochromateur graphite à faisceau diffracté fait augmenter l'intensité et le rapport sommet à fond. Le choix du matériau cible pour l'analyse aux rayons X nécessite un compromis entre l'intensité, la résolution et l'absorption. Le cobalt est la meilleure cible. On utilise plus d'une ligne de diffraction des rayons X afin de minimiser les effets d'interférence.

Comme la poussière ne se dépose pas uniformément sur le filtre et que l'illumination par les rayons X est inégale, la diffraction des rayons X doit être étalonnée selon la masse du quartz sur les échantillons prélevés d'un échantillonneur placé dans un nuage de poussière de quartz pur. Les normes de quartz permanentes sont requises afin d'éliminer les effets des variations séculaires de l'intensité des rayons X.

On a donc mis au point un échantillonneur robuste et personnel appelé CAMPEDS combiné à la pile de l'ampoule du casque. Les caractéristiques de sélection granulométrique des particules respirables des échantillonneurs de poussière sont affectées par les menus changements de la dimension et de la disposition des composantes. Il est essentiel que les réglages sur les instruments soient effectués afin de vérifier la conception et la facilité de reproduction.

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CHAPTER 1

INTRODUCTION

Airborne dust that can be inhaled and deposited in the lungs of miners represents a potential health hazard. Measurements are required to indicate the extent of this hazard and the need for dust control. Such measurements should include the determination of physical and chemical parameters of the dust cloud and should relate to its biological effects.

The development of suitable measuring methods forms part of the Minerals Research Program of the Department of Energy, Mines and Resources. It developed from previous studies in which a number of types of dust sampling instruments were compared when used in various laboratory dust clouds (1). It was found that for one type of cloud at various concentrations, any two types of instrument would indicate the same ratio of concentration within reasonable limits of ± 10%, although for different clouds — varying in type of material and particle size distribution — the indicated ratio of concentration ranged at least from 1:1 to 4:1. Thus one instrument could assess one working place as, say, twice as hazardous as another, whereas a second type of instrument could reverse the relationship. Clearly, all the instruments cannot give an adequate single-parameter estimate of the health hazard; the choice of a suitable instrument requires consideration of biological effects.

Dust sampling should be directed toward estimating the potential hazard of pneumoconiosis in its many forms — silicosis, anthracosis, etc. To do this, it is necessary to consider the physiological processes involved and to measure dust in terms of appropriate parameters. Factors to be considered in relating the onset of pneumoconiosis to the characteristics of the dust cloud are:

1. deposition of dust in the lungs,
2. clearance of dust from the lungs,
3. biological effect of dust in the lungs.

1.1. Deposition of Dust in Lungs

The only dust that can be deposited in the alveolar region of the lung where it may lead to pneumoconiosis, is that which remains in the inhaled air after passing through the respiratory tract or mucus-swept airways. Three physical mechanisms — impaction, gravitational settling and diffusion — are instrumental in depositing dust in both the respiratory tract and the alveolar region, and one appropriate parameter for describing the behaviour of a dust particle is its "aerodynamic size". This is defined as the diameter of a sphere of unit density having the same settling velocity as the particle in question.

The general dependence of alveolar and respiratory-tract deposition on size is shown in Fig. 1.1; however, precise values vary with the breathing pattern and with the individual (2). The extent of the variability is indicated by the hatched areas. In general, a minimum deposition occurs for particles about 0.5 μm in size. Impaction and gravitational settling increase with particle size and are responsible for most of the deposition at sizes above the minimum. Diffusion deposition increases inversely with size and is the main mechanism below 0.5 μm size.

To define the alveolar-deposition potential of an airborne dust cloud, size distribution should be specified in terms of aerodynamic size. Other measures of particle size may give misleading results, e.g., coal particles with an aerodynamic size of 5 μm may have projected areas equivalent to that of 5- to 15-μm diameter circles (3).

Size selectors have not been designed that simulate the entire effect, i.e., the increased deposition of very small particles, the minimum at 0.5 μm, the maximum at 1 μm, and the decrease at larger sizes. However, in airborne dust clouds resulting from mineral breakage, most of the mass and surface area of the dust is associated with the coarser portion — i.e., that part of the respirable dust above 1 μm — and most size selectors have been designed to simulate the alveolar dust deposition in the size range above
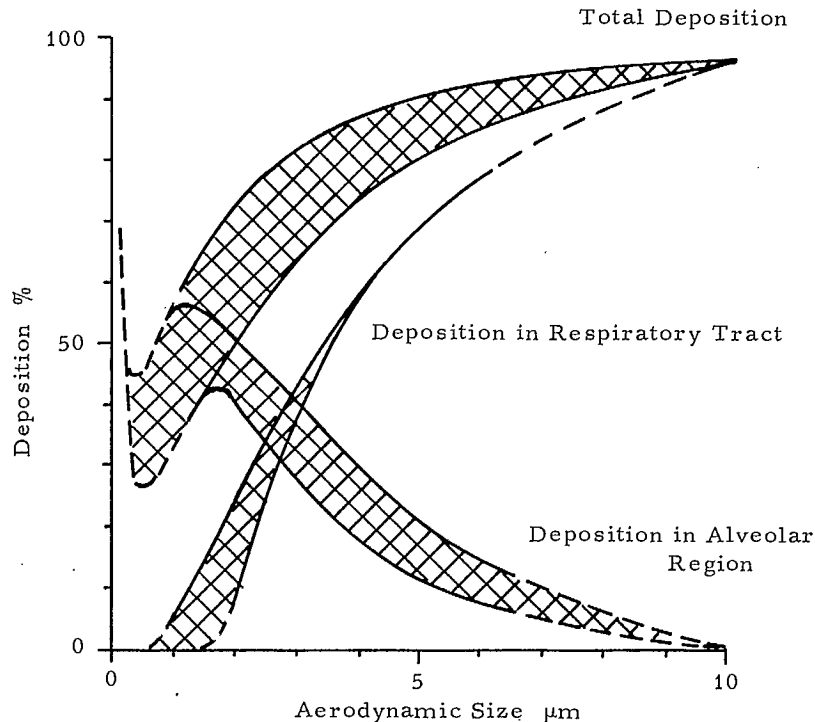
Fig. 1.1 - Dust deposition in lungs showing range of variation between individuals and different breathing rates. After Hatch and Gross (2).

1 µm, with a maximum efficiency of nearly 100% rather than the 40% shown in the figure. Usually all particles finer than this are collected with high efficiency and are included in the "respirable" dust portion.

Aerodynamic size selection should be used on all dust samplers for estimating the pneumoconiosis hazard, because of the difficulty of ascertaining the original state of aggregation and density after collection (4).

1.2. Clearance of Dust from Alveolar Region

The mechanisms of clearance are not as clearly understood as those of deposition. Experimental studies, reviewed by Hatch and Gross, have suggested that clearance depends on composition, size distribution, shape, and concentration of the deposited dust (2).

Experimental studies (2) have suggested that the clearance has a half-life of 20 days or more, and only at extremely high dust concentra-

tions has there been suggestion of a breakdown. This slow rate of clearance suggests that the average dust exposure over a period of at least 20 days would be more significant than peak exposures, unless these are extremely high; however, the most relevant parameters for expressing these factors are not known. As a first approximation, dust exposure should be estimated as an average over long periods, not as peak concentrations.

1.3. Biological Effect of Dust in Lungs

The physical and chemical factors determining biological effects are: concentration, size distribution, composition, shape and residence time. The composition of dust is very important as shown by the very great differences in recommended threshhold limit values (TLV), such as 2 mg/m³ for coal mine dust and 0.1 mg/m³ for pure quartz dust (5). Other minerals which have low TLV's are other crystalline and amorphous

varieties of silicon dioxide, asbestos, talc, and other fibrous minerals. In mining, quartz is the most common and wide-spread of these more harmful substances, both in the pure form and mixed as fine crystals with other minerals.

This report is concerned with methods of analyzing dust samples for quartz and with methods of collecting suitable samples of airborne dust in the respirable size range. Clearly, the choice of physical parameter — number, surface area, or mass — to be assessed has a great effect on the relative assessment of dust concentration in atmospheres of differing dust size distributions, and the parameter chosen should be related to the biological effect.

It has been shown that the health hazard of coal mine dust is closely related to mass in the respirable size range (6). It is widely assumed that mass is also the best measure for other dusts which do not give rise to a specific biological reaction. For free silica, the position is not clear and it is assumed on the basis of both theories of the physiological action of silica, that the surface area of the silica dust in the respirable size range is most closely related to its health hazard (4). However, some experiments on the intratrachael injection of sized quartz particles suggested that mass may be a better indicator of the silicogenic effect than is surface area (7).

At present no method exists for specifically measuring surface area of the silica in airborne dust and all the available analytical techniques measure parameters that are more closely associated with the mass than with the surface area of the silica particles. Page-Shipp and Harris concluded there is a high correlation between respirable surface area and respirable mass of airborne dust in South African gold mines as determined by microscopy on ashed thermal precipitator slides (8).

In routine dust analysis it is not practicable to measure a large number of parameters, and it is suggested that free silica, (quartz) should be specified by the single parameter, mass, as determined by an analytical method.

However, because of doubt as to which parameter is most closely related to the biological activity and the effect of its admixture with other components, detailed analyses of size distribution and composition should be made in research studies on a range of samples of airborne dust. A suitable start might be to collect routine gravimetric respirable dust samples, bulking those from each job in each mine or section and analyzing them to obtain at least the following additional information: size distribution of all respirable dust, size distribution of respirable quartz dust, major mineral components, trace elements, and major organic constituents, as well as the form in which free silica occurs.

1.4. Requirements for Dust Sampling System in Hard Rock Mines

Consideration of the physiological processes described above led to the following requirements on which a new dust sampling technique should be developed for routine use in hard rock mining:

1. aerodynamic size selection to match deposition of dust in the alveolar region of the lung,
2. long-period sampling — a full shift is a convenient time interval,
3. quartz analysis to be carried out on individual dust samples.

Further non-physiological requirements are:

4. sampling instrument should be readily portable and self-contained,
5. sensitivity of dust assessment should be about one tenth of the appropriate threshhold limit values,
6. repeatability of the method need be only 10 to 20% because of the great variability of the airborne dust clouds in mines.

Dust sampling instruments meeting requirements 1, 2 and 4 have been developed for coal mines and iron foundries respectively (9, 10). These were examined as to suitability for collecting samples for quartz analysis and some were purchased. Requirement 3 is considered in detail in the next section.

1.5. Methods of Analysis for Quartz and/or Free Silica

Free silica or silicon dioxide crystallizes in a number of forms — α-quartz, high quartz; low, middle, and high tridymite; low and high crystobalite; keatite; coesite; stiskovite, and also occurs in non-crystalline form as glasses (11). These forms affect the analytical techniques to various extents. While all are more hazardous than combined silica (silicates) in most of its forms, α-quartz is the most common and its occurrence can be separated into two classes: coarse-crystalline (amethyst, etc.) and fine-crystalline (chalcedony, agate, flint, chert, jasper, etc.). The latter may have to be distinguished when certain of the analytical techniques are used.

A number of analytical techniques have been proposed and some have been extensively used:

1.5.1. Wet chemical

This technique separates free silicas from silicates by their relative solubilities in hot phosphoric acid. Almost all silicates are dissolved more quickly than the free silicas. The original technique used gravimetric assessment of the undissolved silica but more recent developments have used colorimetric methods of assessing the silica after dissolving the separated silica in hydrofluoric acid and have achieved sensitivities down to 10 μg of free silica (12). In assessing this method, it must be remembered that some silica dissolves in the hot phosphoric acid from the surface of each free silica particle, and that the complete solution of the large particles of silicate is not achieved. The time and temperature of phosphoric acid attack is set to balance these two errors; however, the balance achieved is dependent on the particle size distribution and on the varying solubilities of the silica and silicate varieties present. The technique requires very careful control of time and reagent purity to achieve consistent results (12), and has been used extensively in some laboratories.

This method is believed applicable to all varieties of free silica.

1.5.2. Infrared absorption

Certain infrared absorption spectral lines are specific to various chemical bonds, and the doublet at 12.5 μm wavelength has been widely used for silicon dioxide analysis. The usual technique has been that of mixing the finely-ground dust with a transparent salt (KBr), pressing the mixture into a pellet, and measuring the absorption. Recent work has shown that absorption can be measured directly on a dust deposit as collected on a filter, with a sensitivity of about 10 μg (13).

Some minerals interfere with the silica assessment and ashing is recommended for coal dust to reduce interference (13, 14).

The method is believed to be applicable to all forms of free silica.

1.5.3. X-ray diffraction

X-ray diffraction can be used for qualitative and quantitative analysis of most crystalline materials. The strongest diffraction line, that from the 3.34 Å spacing in the quartz crystal, has been widely used for quantitative analysis. While many materials interfere with this, qualitative analysis in conjunction with the extensive tables available has normally been used to identify possible interferents (15, 16). The technique has been developed to a sensitivity of less than 10 μg, and the method is applicable to all crystalline varieties of silica.

1.5.4. Differential thermal analysis

Quartz and the other crystalline varieties of free silica undergo marked phase changes with emission or absorption of heat at specific temperatures. This effect can be used to analyze them quantitatively; so far the sensitivity has been considerably less than the best achieved by the other methods listed above (17).

1.5.5. Choice of quartz analysis technique

It was expected that, if a method were

developed for use in mines, there would be thousands of quartz analyses to be done each year and therefore techniques using as little handling as possible should be tried before examining transfer techniques which might reduce the compromises required between dust sampling and assessment, and possibly give greater sensitivity and accuracy.

Preliminary studies on quartz collected directly on silver and vinyl membrane filters using both X-ray diffraction and infrared absorption were undertaken at other laboratories within CANMET. It was found that both techniques had sensitivities of about 0.1 mg quartz on a 25-mm diameter filter. The Elliot Lake Laboratory elected to purchase X-ray diffraction equipment because of its applicability to qualitative and quantitative analysis of other minerals as well as of quartz. The starting point for the X-ray diffraction technique was J. Leroux's excellent studies in Ottawa (18 to 22), based on the thin-film technique which largely avoids the need for corrections due to absorption in the matrix. Dr. Leroux proposed the use of silver membrane filters as they give a low background compared with other types. He also proposed the use of MoKα X-rays to minimize absorption effects.

It is recommended that the area of the diffraction peak should be measured for quantitative analysis (23). To enable this to be carried out on a large number of samples requires computer processing and equipment was therefore purchased with a computer-compatible output on punched paper tape.

The design of the Elliot Lake Laboratory dust sampling and assessment system for use in mines was developed during many studies over the past few years and is now named the Canadian Mining Personal Dust Sampling System — CAMPEDS.

Many major facets have to be taken into account and these are treated in separate chapters. However, many details and some ancillary studies are relegated to Appendices.

Accurate assessment of quartz in mine air involves both analysis and sampling, all aspects of which have to be considered.

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CHAPTER 2

OUTLINE OF DEVELOPMENT

The design of the Elliot Lake Laboratory dust sampling and assessment system, now called CAMPEDS, involved many separate studies. Advances in the design of the different components were made at various times and this chapter outlines that development.

The major emphasis at the start of the program in 1970 was in sensitivity for a quartz assessment and involved collecting as much quartz as possible on as small a filter as practicable. The major types of small battery operated gravimetric samplers with respirable size selectors were first compared with a horizontal elutriator in the laboratory dust chamber with the results given in Table 2.1.

These results suggested that Casella personal samplers would present much more quartz to the small X-ray beam than would any of the other samplers. It was also found there was considerable disagreement between the two U.S. coal mine samplers using the same size selector. This was found to be due to pulsations in the airflow given by the single acting diaphragm pumps used and has since been corrected by the manufacturers, thereby bringing the relative dust concentrations to 0.7 by the Cassella 113A. It should also be noted that with the Bendix, 25 to 50% of the dust collected was deposited on the internal surface of the cassette rather than on the filter where it could be analyzed.

The next stage of development was checking performance of the X-ray diffraction equipment on samples collected in a pure quartz dust

cloud. These tests brought out four major observations:

1. quantities of quartz down to 0.25 μg in the X-ray beam could be detected by the X-ray system,

2. response was not linear, and apparently at the start of sampling some 30% of the quartz was not seen by the X-ray beam,

3. there was disagreement between the weight of quartz on the sample filter and that determined by the X-ray system when calibrated for evenly deposited quartz. This led to a complete calibration against dust collected on the filters,

4. a copper X-ray target was preferable to molybdenum.

This laboratory study was followed by a period of field work carried out with funding from the McIntyre Research Foundation. The major factors discovered during this period were:

5. quartz analysis could be carried out on most samples collected by the Casella personal sampler in mines,

6. interference by other minerals occurred fairly often and had to be allowed for,

7. in mines with diesel vehicles, clogging of the 25-mm diameter filters could occur in as little as 2 hours; however, as concentrations as indicated by weight loss on ashing, up to 10 mg/m^3 were found, it was hoped the sampling problem could be solved by controlling diesel exhaust rather than by increasing the filter area with the resultant loss in sensitivity for quartz,

8. as a personal sampler in mines two components of the Casella-plastic pump case was prone to damage, and the smoother needed

Table 2.1 - Dust collection characteristics of samplers

	Filter diam mm	Flowrate L/min	Relative respirable dust		
			mass	mass/unit area	concentration
Casella MRE 113A	55	2.5	1	1	1
MSA coal mine sampler	37	2.0	0.27	0.7	0.34
Bendix coal mine sampler	37	2.0	0.41	1	0.51
Casella personal sampler	25	1.9	0.8	4	1

frequent repair; however, a metal cased version is now available.

After the system was proven in the field, studies have concentrated on the following considerations:

9. interference with quartz analysis,
10. absorbtion of X-rays in the dust layer,
11. methods of analyzing rock samples,
12. search for alternative filters,
13. X-ray diffraction analysis of varieties of free silica,
14. refinement of the X-ray diffraction technique for quartz analysis,
15. development of sampling head pump system for mounting on the miner's cap lamp battery,
16. development of a small combined impactor size-selector with a filter-cassette,
17. dust sources in mines as measured by gravimetric and quartz analysis,
18. the variation of full-shift personal samples preparatory to designing personal dust sampling programs.

Studies on consideration 9 to 16 have been completed and are dealt with either in the text or in the appendices; those on considerations 17 and 18 are incomplete and only preliminary results are given.

CHAPTER 3

QUARTZ ANALYSIS

Little difficulty was found in obtaining adequate sensitivity for X-ray diffraction assessment of quartz in the small quantities collected by portable battery operated dust samplers. However, many precautions are necessary to minimize errors and the major ones — permanent standards, calibration, interference, and absorption — are dealt with in the sections of this chapter which follow.

The detailed set-up of the equipment for optimizing high sensitivity quantitative analysis of quartz is given in Appendix A and for computer processing is given in Appendix C. Appendix D describes a method of preparing rock samples for analysis by this technique and Appendix E describes the ancillary studies carried out on varieties of free silica.

3.1. Permanent Quartz Standards

Leroux (1) in his development of the thin layer technique for X-ray diffraction analysis of quartz used the diffraction from an aluminum plate as an intensity standard. The diffraction angle is not the same as for quartz and is thus not easily used in conjunction with the automatic sample changer and step scanning. Therefore, permanent quartz samples were developed which ideally should simulate the dust deposit on the filters in particle size and surface density distribution.

In the first attempt, quartz samples taken on silver membranes were mounted on the automatic sample changer holders and sprayed with various lacquers. The samples were not sufficiently robust and the lacquer increased the background excessively.

The second method tried was to place a mixture of quartz and setting resin in a recess in a steel plate. This technique, although giving a high background -- mainly a very broad band about the cellulose d-spacing -- , was robust. A number of attempts were made before

the standards were uniform across the area and the quartz sufficiently finely ground.

The procedure finally selected for preparing permanent standard quartz samples was as follows:

1. cut steel plate to fit automatic changer,
2. surface grind both sides,
3. turn 0.25 mm deep cylindrical depression the same diameter (22 mm)* as the dust deposit on the filter paper,
4. grind quartz (silica sand) in jet mill and collect in cloth bag,
5. disperse quartz in alcohol and let coarser dust settle,
6. mix suspension with resin and hardener and place in sample holder,
7. finish dust in resin and plate flat on surface grinder and reduce the layer thickness to about 0.012 mm.

These permanent quartz standards are not an ideal match in particle size distribution and surface density distribution for the Casella samples and are satisfactory as standards only if the X-ray diffraction arrangement is similar to that used in calibrating them.

Five quartz standards have been prepared, four for 25-mm diameter filters and 22-mm diameter dust deposits*, and one for 13-mm diameter filters and 10-mm diameter dust deposit. The four standards for 25-mm diameter filters were calibrated by comparing with the thicker samples collected in a pure quartz dust cloud and described in Section 3.2. and Appendix B. These comparisons were carried out 3 or 4 times on each of three strongest quartz diffraction lines, 1,0,0; 1,0,1; and 1,1,2. The repeat comparisons gave a standard deviation of about 4% in the estimate of the mass of quartz on each standard for each diffraction line. This variation is considerably greater than that, 0.5% calculated from counting statistics using the formula given by Klug and Alexander (2). Two factors contributing

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* Other changes have led to the dust deposits being 20.5 mm in diameter in Casella samplers and matching standards should be used.

to this greater variation are the finite size and variability of position relative to the peak of each step, and variations in position of the limits of integration as chosen by the peak area computation program on a statistical basis.

In using these calibrations it is essential that the divergent slit be big enough for the beam to cover the full width of the standard and sample.

The use of permanent standards is essential, both for detecting malfunctions in the equipment and allowing for the long term decrease in X-ray tube output of about 30% in 2000 hours as shown in Table 3.1.

Table 3.1 - Variations in X-ray
intensity with time

Date (1971)		X-ray intensity
July	16 a.m.	37034
	16 p.m.	38380
	19	38001
	20	37199
	21	36113
	22	32822
	23	31549
	26 a.m.	30463
	26 p.m.	30379
Sept.	7	33156
	8	35012
	9	32744
	10	33674
	23	32448
Nov.	5	31600
	10	31380
	15	28717
Feb.	10	28730
	11	27765
	22	27832
	23	27628
	23	27940
	25	28331
	25	27744

3.2. Calibration

The calibration of X-ray diffraction analysis of quartz was carried out by comparing X-ray intensity given by the standards with that given by samples collected in a pure quartz dust cloud. Detailed results are given in Appendix B. A number of major factors were found:

1. some quartz is lost in filter pores before dust bed builds up, resulting in shielding from the X-ray beam; this loss depends on the filter pore size and on size distribution of the quartz as well as of other dust; it is corrected by a thin sample correction factor;

2. absorption of X-rays in dust layer;

3. uneven deposition of dust on the filter -- heavier at the centre than at the edge is characteristic of many dust samplers;

Minor factors were also noted:

4. precise location of sample in the X-ray beam;

5. position of step with respect to peak centre;

6. variations in X-ray intensity over area of beam;

7. variations in X-ray intensity with time.

The effect of dust penetrating into the filter and of absorption is shown in outline in Fig. 3.1. together with the calibration, shown as a dotted line, obtained by taking the mean of the heavier samples. It can be seen that the dotted line is within 7% for all samples which have less than 20% absorption and small thin sample corrections and thus for most samples, adequate results are obtained without correcting for absorption. However, the dust losses on thin samples are appreciable and the use of the thin sample correction factor is desirable. The experimental derivation of the thin sample correction factor is difficult and may vary from batch to batch of filters. The best available values for silver membrane filters are given in Table 3.2., both for full effect and for correction to the mean calibration.

To minimize errors due to these factors it is essential to calibrate against dust samples
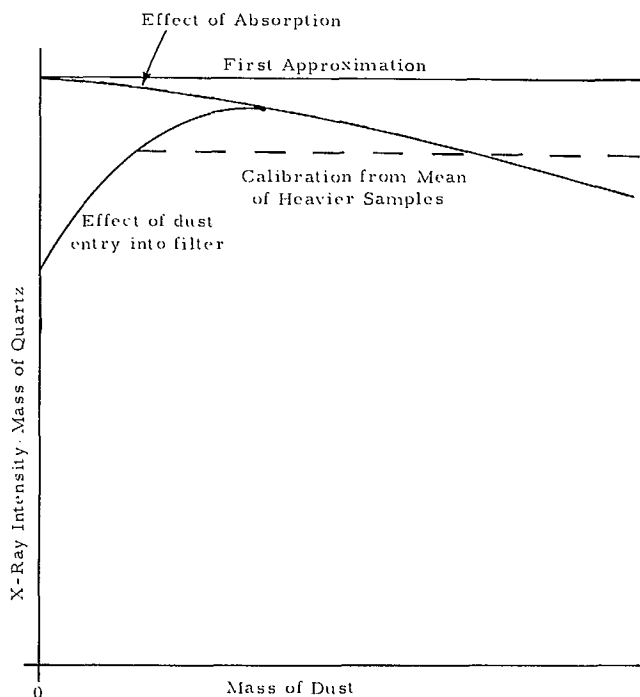
Fig. 3.1 - Schematic of effects of absorption and penetration of dust into filter at start of sampling.

Table 3.2 - Thin sample correction factors

Sample weight mg	Thin sample correction factor		
	Full effect	Correction to mean calibration	
0.0	1.5	1.4	1.16*
0.05	1.42	1.33	1.13*
0.10	1.35	1.26	1.19*
0.15	1.30	1.21	1.07*
0.2	1.24	1.15	1.05*
0.3	1.16	1.08	--
0.4	1.10	--	--
0.5	1.05	--	--

*Estimated values for 3-μm pore size silver membrane filters. Others are experimental values for 5-μm pore size.

prepared by a method as similar as possible to the field technique and to use "standard" samples that are as close a match to field samples as practical. Although it has been possible to produce reasonable samples for calibration using the appropriate dust sampler in a pure quartz dust cloud in the laboratory test chamber, the standards match the filter in diameter but not in uniformity of deposition.

A small zero error was observed when comparing measurements of pure quartz samples made on the four lines using cobalt radiation. The origin of this zero error appears to be in the calculation of area using a linear approximation for the background pattern from the silver filter, whereas this background is curved or irregular, particularly for the 1,0,0 and 2,1,1 lines. This zero error amounts to adding approximately 10 μg to estimates on the 1,0,0 line and 4 μg to those on the 2,1,1 line. More work is required to explain this problem.

3.3. Interference

A large number of minerals produce X-ray diffraction (XRD) patterns in which one or more lines are similar or quite similar to quartz. For instance, the common mineral muscovite has a strong line at a crystal lattice spacing of 3.32A, close to the strongest quartz line at 3.34A and interference with quartz analysis occurs.

Figure 3.2 shows two of the conditions that can occur with two close lines. In the first, Form 1, the two lines merge and appear as a single slightly wider line, and in the second, Form 2, the peaks are clearly resolved. When computing the area under the peak assuming a linear background, the hatched area would be omitted.

A number of approaches towards avoiding or correcting for interference are possible — the following have been examined:

1. identifying minerals present in the ore from mine geologists' data and choosing a quartz line that is clear of interference,

2. XRD scanning of ore and airborne dust samples from the mine and identifying minerals present and choosing a quartz line that is clear of interference,

3. visual checking of the XRD scan of each sample for adjacent peaks and departure

FORM 1 INTERFERENCE

FORM 2 INTERFERENCE
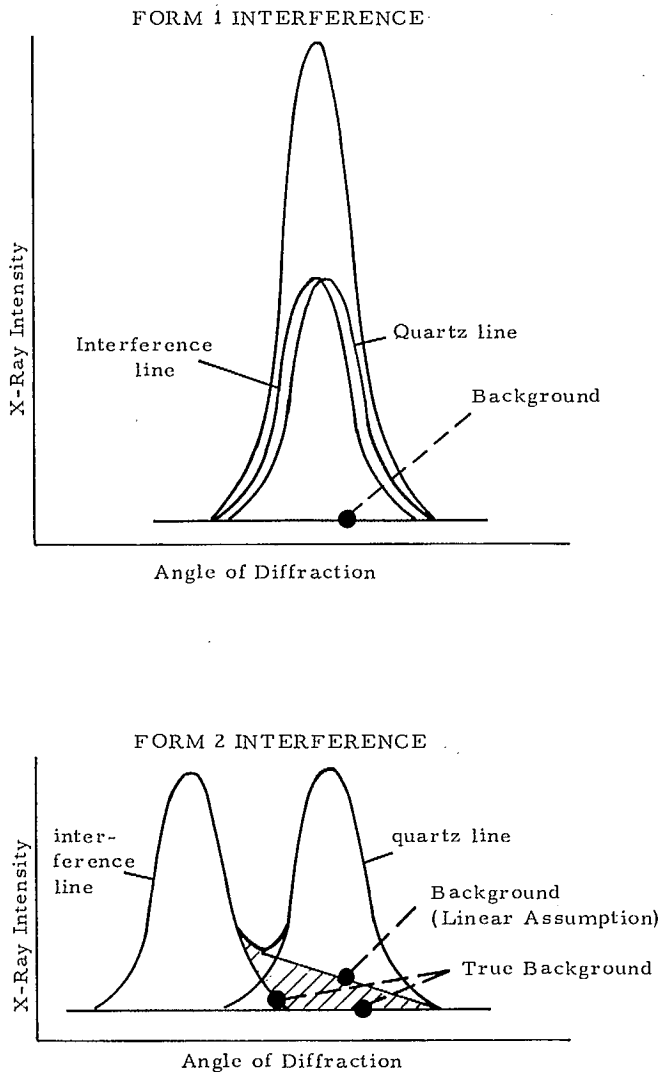
Fig. 3.2 - Interference effects of adjacent diffraction line on line area estimation.

from normal shape,

4. examination of the ratios of intensity of the various quartz diffraction lines and eliminating the lines which give rise to ratios markedly different from pure quartz samples,

5. comparing estimates of quartz on each sample obtained by using a number of diffraction lines,

6. computer analysis of each scan using curve-fitting with least squares criterion.

The first approach entailed obtaining mineralogical reports from the mine geologists.

However, these reports were not adequate to determine the XRD patterns using standard references for many minerals, particularly those with variable composition such as the plagioclases (3,4), it was thus necessary to confirm the patterns using the second approach. In this approach a number of samples of ore and host rock were obtained from each mine, crushed and scanned by XRD. This was successful in some cases where the number of minerals present in significant quantity was small. For the Elliot Lake uranium mines the only interference found was muscovite (sericite) on the 1,0,1, quartz line. The analysis could not be completed for mines with a large number of minerals present in significant quantity, such as the Timmins gold mines. For these, even after identification and confirmation of seven minerals in the XRD pattern, some medium strength lines were not allocated to minerals.

The third approach is useful in detecting Form 2 errors and, incidentally, in detecting samples which become misplaced in the automatic sample changer, but for only one other sample has useful information been gained from the shape of the diffraction line. When a Form 2 error is recognized, the quartz diffraction line may be expected to provide a low estimate of the quartz content and so the reliability of the result should be discounted.

In investigating the fourth approach, the ratios of intensities of three quartz diffraction lines were measured. The range of results obtained from four types of dust samples are shown in Table 3.3.

Table 3.3 shows that only in the case of uranium mines are the results compatible with the assumption that there is no significant interference on two of the lines — the 1,0,0 and the 1,1,2. The range of ratios for the other mines for all three comparisons are such that no conclusions can be drawn.

In the fifth approach, four estimates of the quartz in each sample are made using the four strongest diffraction lines of quartz that are clear of the diffraction pattern of the filter material (silver metal). The results obtained

Table 3.3 - Ratio of intensities of
quartz diffraction lines

Airborne dust samples	Range of intensity ratios (Integrated line areas)		
	1,0,0/1,0,1	1,1,2/1,0,1	1,1,2/1,0,0
Pure quartz	0.20-0.22	0.083-0.10	0.4 -0.44
Uranium mines	0.16-0.21	0.06 -0.10	0.4 -0.45
Gold mine	0.05-0.60	0.15 -0.18	0.17-1.9
Nickel mine	0.12-0.38	0.05 -0.12	0.23-0.5

from a representative range of samples are shown in Table 3.4. It can be seen there is reasonable agreement between the estimates in many cases, but in others they differ by as much as 300%. Form 2 errors were found on some lines on certain samples. It is assumed that as Form 1 errors are not observable and give rise to high estimates of quartz, the best estimate is given by the lowest one that does not show Form 2 errors.

The sixth approach — form fitting with least squares criterion using a computer — has been used successfully for separating overlapping lines in many similar problems, for instance in gas chromatography (5). However, in the case in question, with diffraction lines that are weak with respect to background and are distorted due to bent filters, the preliminary examination suggested that long counting times and extended scanning widths would be necessary for a successful analysis. This approach does not seem as promising as producing multiple estimates of · quartz from different diffraction lines — approach 5 — and has not been investigated further.

It is clear that interference is a problem in quartz analysis and that considerable effort could be spent in checking each sample and it is thus necessary to consider the object of dust sampling and quartz analysis in mines. The requirement in most sampling is to demonstrate that the dust level is below a legally defined limit and all samples with a lower level than this and free of Form 2 errors can be reported as

having a maximum rather than an estimated quartz content. Form 2 errors can be detected on the computer print-out by:

1. an adjacent peak,
2. a marked change in background or background slope from similar samples, or
3. a marked disagreement between estimates of quartz by peak height and by line area.

Samples with Form 2 errors or quartz content above the threshold limit must be analyzed on a second line to determine the maximum content or to confirm the high estimate. It may be necessary to extend this analysis to a third or fourth line for some mines.

Ideally, the quartz estimate should be based on a weighted mean of measurements on the various lines allowing for their different accuracies and for indications of interference. In many mines with low dust concentrations, the disagreement between lines appears more often to be due to errors than to interference, and thus if one uses only lines not prone to interference the simplest process is to average the measurements obtained.

In the mine samples analyzed to date it appears that the 1,1,2 quartz line is the least subject to interference and most suitable for the first estimate. However, the 1,0,1 line has eight times the intensity, a slightly greater sensitivity, and is more suitable in some mines. It is thus a close choice between these two lines for obtaining the first estimate. The 1,0,0 line is least sensitive because of the higher background at the lower angle and to date has appeared to be the least useful of the four lines examined.

Interference has frequently been found and appears to be a disadvantage of the X-ray diffraction method. However, in most cases interference has been observed only because of disagreement between the independent estimates. The chemical method — separating silicates from free silica by dissolving in hot phosphoric acid — can provide only a single answer, and the variable dissolution rates of silicates and free silica with type of mineral and particle size give rise

Table 3.4 - Comparison of quartz analyses using some
of the diffraction lines available

Mine	Mass of quartz estimated in mg using the diffraction lines indicated							
	1,0,0		1,0,1		1,1,2		2,1,1	
	Height	Area	Height	Area	Height	Area	Height	Area
A			.017	.019	.025	.024		
			.030	.031	--	--		
				.014		.015		.001
				.022		.01		.022
		.01		.01		.06		.01
B	.023	.049	.006	.007	.007	.002	.010	.003
	.110	.093	.20	.305	.175	.15	.185	.165
	.185[1]	.160[1]	.064	.077	.057	.053	.050	.041
C				.24		.00		
				.32		.27		
D		.86		.45		.24[1]		.60
		.30		.24		.11[1]		.26
E[2]		1.03		.83		.36[1]	.81	1.16
F		.32		.04		.02		
				.05		.03		.04
G				.06		.12		.04
H		3.14		.26		.15		.21
H'		.24		.21		.16		.14
H'[3]		.64		.15		.13		.09

1 Adjacent peak detected.

2 Percentage of quartz in the crushed ore determined by X-ray
diffraction: i.e., 24%, 64%, 15%, and 35% respectively for
each of the four lines. These figures compare with the 30-
40% found by other techniques.

3 The one sample H' from a coal mine was ashed and reanalyzed
with the results given in this line.

to unknown error. Infrared absorption can pro-
vide three semi-independent estimates of free-
silica content — one pair is a doublet, and
serious interference has been reported (6).

3.4. Sample Absorption Studies

'Thin' samples are used in quartz analy-
sis to avoid the need to determine corrections
for matrix and absorption effects and non-linear

calibrations. Although molybdenum radiation, because of its high energy and low absorption, would permit measuring thicker layers, it has very great disadvantages in sensitivity and resolution compared with longer wavelengths.

It is expected that as the thickness of a sample increases, the ratio of intensity of the diffracted peak to the mass will drop due to absorption. This decrease in ratio can be given for small losses simply as:*

$$Ln \ (R_o/R_m) \ = \ \mu_m \ m \ cosec \ \theta$$

where: R_o = ratio of intensity to mass extrapolated to zero mass;

R_m = ratio of intensity to mass at mass m;

m = mass of dust per unit area;

μ_m = mass absorption coefficient for X-rays;

θ = Bragg angle.

This equation assumes that on the average the X-rays pass through half the depth of the dust layer twice. For the silver peaks, X-rays pass through the dust layer twice and a factor of 2 is added to the right-hand side of the equation.

Using the values for mass absorption given in the X-ray handbook (7) mass limits for selected minerals can be calculated corresponding to R_m 20% less than R_o due to absorption. The selected minerals are: SiO_2, representative of silicates and quartz; FeS_2 representative of iron, the commonest mineral-forming element that is a heavy absorber of copper radiation; and $CaCO_3$ representative of calcium, the commonest element that is a heavy absorber for cobalt, iron, and chromium radiations. Table 3.5 shows that mass limits for each radiation for each of the four lines of quartz together with that for the strongest silver line from the supporting filter. It can be seen that the mass limits

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* J. Leroux (8) has given a more rigorous treatment of absorption in dust samples which is necessary for thicker samples than considered here.

decrease generally in the order from Mo to Cr.

For 25-mm diameter filters with an effective area of 3.5 cm^2 the absorption mass limit for molybdenum radiation is well above the threshold limit value for all dusts, while with copper radiation, the element iron is a limiting factor. With chromium radiation, the quantities of mineral-forming elements — potassium and calcium — are limited to 1.4 mg on the filter for analysis by the quartz 1,0,1 diffraction line. Considerations of elemental abundancies in the earth's crust show that of the elements which could be problems with these characteristic radiations — iron at 5%, calcium at 3.6%, and potassium at 2.6% — are the most important. From absorption characteristics, on average, cobalt and iron radiation might well be preferable to copper because they have less absorption in the common rock-forming element, iron. Chromium radiation would seem more likely to give rise to absorption problems than iron radiation.

It should be possible to check absorption by measuring the intensity of the silver 1,1,1 line through the dust deposit. Figure 3.3 shows a plot of this intensity, as peak height, against mass of some samples using copper radiation. It can be seen that with pyrite samples the loss in intensity with mass is about half that predicted (Table 3.5). Figure 3.4 shows the effect of sample thickness on X-ray intensity mass ratio of the four quartz lines for the mixed pyrite-quartz samples shown in Fig. 3.3. The fall in intensity with thickness is less than expected from absorption of the silver line shown in Fig. 3.3 and from comparisons between quartz and silver lines shown in Table 3.5.

With field samples, distortion of the filters sometimes leads to line broadening and reduction in peak height and it is necessary to determine peak area. This has been done by multiplying net peak height by half the width on the recorder trace with the results shown in Fig. 3.5 for all field samples received in a given period using Cu radiation. Figure 3.6 shows some of these repeated using Cr radiation. It can be seen that the variation in silver peak

Table 3.5 - Calculated mass limits for 20% departure from linear
calibration with a selection of materials and radiations

Substance	Diffraction line	Mass limit mg/cm^2 for radiations from				
		Mo	Cu	Co	Fe	Cr
SiO$_2$	Q 1,0,0	5.3	1.7	1.1	0.77	0.63
	Q 1,0,1	6.8	2.1	1.4	1.0	0.82
	Q 1,1,2	12	3.9	2.5	1.8	1.5
	Q 2,1,1	14	4.6	3.0	2.1	1.7
	Ag1,1,1	4.8	1.5	1.0	0.7	0.58
CaCO$_3$	Q 1,0,0	2.6	0.62	0.44	0.35	0.28
	Q 1,0,1	3.4	0.78	0.56	0.45	0.37
	Q 1,1,2	6.0	1.45	1.05	0.85	0.67
	Q 2,1,1	7.0	1.7	1.2	1.0	0.75
	Ag1,1,1	2.4	0.56	0.4	0.32	0.26
FeS$_2$	Q 1,0,0	0.85	0.22	0.50	0.39	0.31
	Q 1,0,1	1.1	0.27	0.6	0.5	0.41
	Q 1,1,2	2.0	0.5	1.4	0.95	0.76
	Q 2,1,1	2.3	0.6	1.5	1.1	0.85
	Ag1,1,1	0.75	0.2	0.45	0.35	0.29
Oxygen[1]	Q 1,0,0	30	10	7	5	5

1 This is entered as an ultimate possible low mass for organic
compounds (combustible dust).
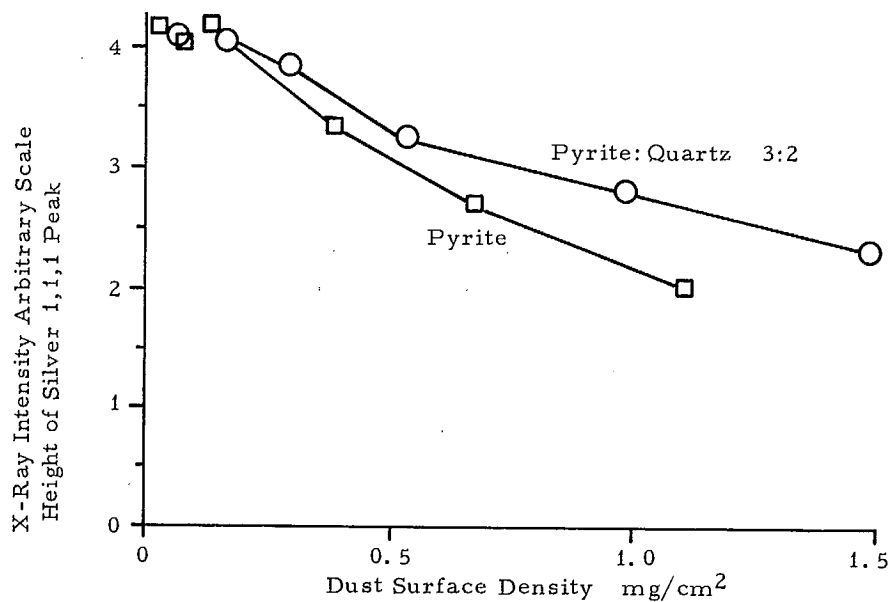
Fig. 3.3 - Absorption of CuKα X-rays in dust layer as measured by intensity of silver 1,1,1 peak.
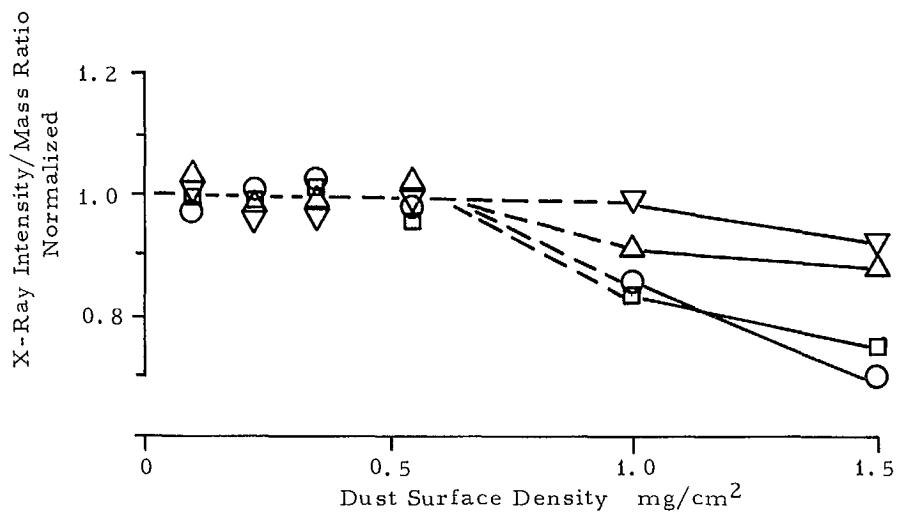
Fig. 3.4 - Effect of absorption on intensity of quartz peaks in 3.2 pyrite-quartz dust deposit.
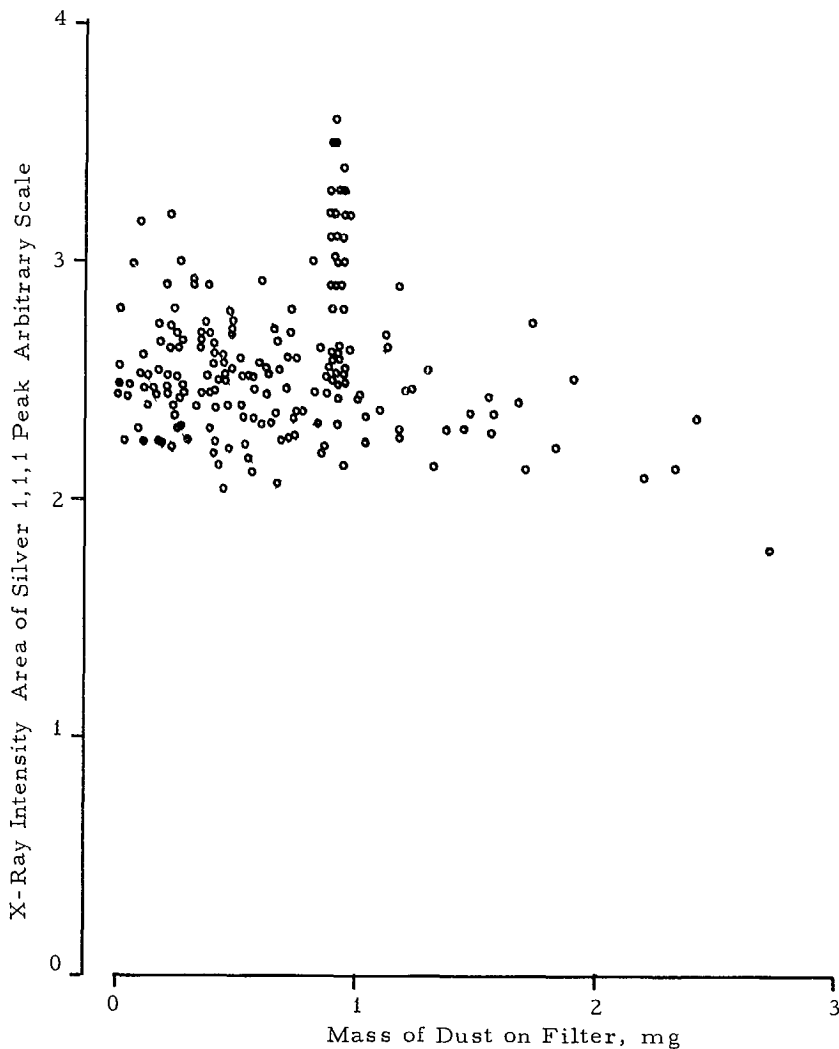
Fig. 3.5 - Intensity of silver peak measured through dust deposit on field samples — copper radiation.
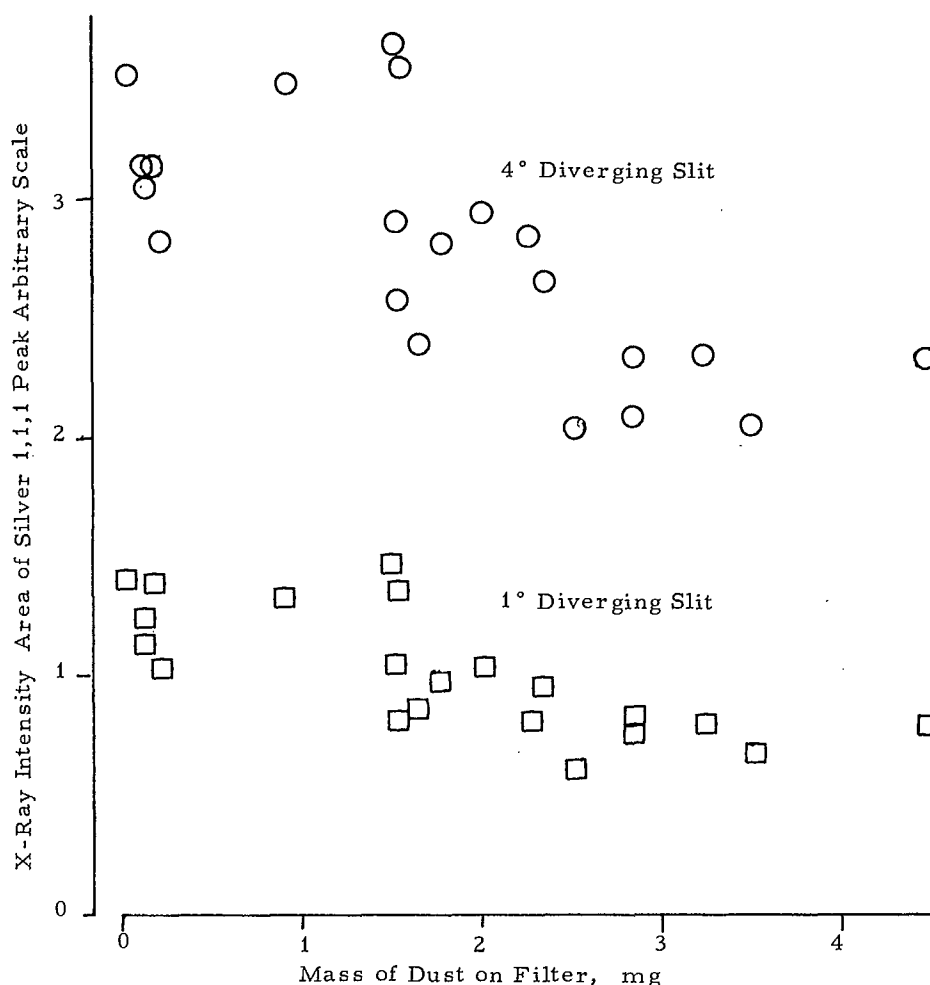
Fig. 3.6 - Intensity of silver peak measured through dust deposit on field samples — chromium radiation.

intensity is much greater than the possible effect of absorption for most of these samples, and one cannot be sure that there is significant absorption until the peak height is less than 2 for Cu radiation or less than 2.5 for Cr; the absorption loss could then be as high as 50% or as low as 10%.

These results were obtained with a wide slit and it is possible that the edges of the filter outside the dust deposit caused errors in estimating absorption of the dust layer. Also the centre of the dust deposit is heavier than the edges. Figure 3.6 shows intensity of the silver peak through the dust deposit when illuminated over two areas, 26 x 12 and 10.5 x 12 mm. This suggests that the relative absorption is

about twice as great in the central portion of the sample as at the edges. In these experiments the second type of filter holder was used and a 22-mm diameter dust deposit was exposed through a 23-mm diameter orifice with some clear silver showing. This does not explain most of the variations found in field samples and it is assumed the main reason is the 'tarnishing' of the silver metal leaving a highly X-ray absorbent silver compound on the surface. Leroux has suggested that intensity of the silver peak from the back of the filter should be compared with that from the front through the dust deposit as a measure of absorption in the dust layer (8). Although this procedure corrects the batch-to-batch variation found for clean filters, it gave little

improvement on the single dust-side measurement when applied to field samples, and as well, it is easier to use the samples with little dust as a control for the heavier. A significant factor appears to be preferential tarnishing on the dust side, either during collection or by reaction with the deposited dust. It is known that hydrogen sulphide, a not uncommon gas, reacts with silver metal to produce silver sulphide, which has occasionally been detected by XRD.

It is concluded that errors greater than 20% are only likely to occur in a few airborne dust samples even if chromium radiation is used. Gross errors greater than 50% can probably be detected and corrected by measuring intensity of the silver diffraction peak through the dust layer using the relative masses given in Table 3.5. Observing intensity of the silver peaks should be carried out as a routine on heavier samples until such time as further experience indicates if it is worthwhile.

Cobalt-target X-ray tubes can be obtained in a high intensity version. The absorption by silicon, calcium, and potassium minerals would be intermediate to those for Cu and Fe radiations, although the absorption by iron-bearing minerals would be less and is recommended as the best compromise.

3.5. Summary of Quartz Analysis

Permanent standards must be used to avoid effects of changes in X-ray intensity with time and setting. Although any standard substance could be used, it is simpler to use quartz of at least the same diameter as the dust samples as it will minimize errors due to changes in beam angles and can be processed with the same scanning limits and computer program. Internal standards with transfer to a second filter have been used by some analysts but although this overcomes matrix errors, it appears to increase the possibility of error due to interference (9).

Calibration using samples collected in a pure quartz dust cloud appears desirable in direct analysis on the collecting filter to minimize errors from uneven deposition and to

collection of dust in the body of the filter where it is hidden from the X-ray beam. Because dust collected in the body of a filter is difficult to remove it is possible that this effect also occurs in transfer techniques and that calibration of the whole process is desirable.

The deposition of dust in the body of the filter at the start of sampling before the dust bed builds up has been handled by the use of a thin sample correction factor determined during calibration in a pure quartz dust cloud. Clearly the deposition and the factors depend both on the pore size of the filter and on the size distribution of the dust. The results obtained suggest that the factors would differ from 1 by a factor of about 2 for 5-μm pore size compared with 3-μm pore size silver membrane filters and thus there might be a slight batch to batch variation due to changes in average pore size. The effect of particle size distribution on dust bed build-up and penetration into the filter might be significant for mineral dusts compared with the much finer diesel exhaust particulates. However, as it is very difficult to estimate and to carry out experiments, the assumption is made that the thin sample correction factors for the weight of quartz on the filter determined in pure quartz dust are applicable to other samples if the weight of total respirable dust is substituted for the weight of quartz. Thus, build-up of the dust bed and its penetration by quartz bears the same relation to its total weight as does that of a pure quartz dust bed.

Because determination of the thin sample correction factors is difficult, possibly not too accurate, and does not introduce substantial errors in samples above half the suggested target values, it is suggested that the values given in Table 3.2. can be used without excessive error for all silver membrane filters.

Interference, as indicated by disagreement between the estimates using the four diffraction lines of quartz, occurs frequently and would appear to be a disadvantage of the X-ray method; however, there is no such easy method of

checking for interference in the other methods — chemical and infrared — and minor interference would therefore not be detected. However, adjacent peaks and the resultant low value for quartz are readily detectable and, except in these cases, one can take the measured value as an upper limit for quartz in the sample. Consideration should be given to carrying only confirmatory analyses on a second diffraction line for the heavier samples.

The results obtained suggest that absorption or matrix effects are not significant for most field samples that do not exceed the suggested target value of 2 mg/m³ (2 mg per filter) of total respirable dust, and thus are not important. However, the use of a cobalt target X-ray tube gives rise to least absorption by the commoner mineral-forming elements and still having the longer wavelength desirable for increasing resolution, minimizing interference, and giving a high intensity.

Computation of peak area is desirable to minimize effects of distorted filters broadening the diffraction lines. The program used defines the background areas to avoid adjacent peaks. It appears probable that the use by many programs of fixed positions for counting background increases errors due to interference and curved background on very thin samples, found to have a width of less than one third of that for heavy samples.

The advantage of a high count rate obtained by running the X-ray diffraction equipment with the maximum slit widths normally supplied outweighs the disadvantage of the resultant slight reduction in resolution. The graphite monochromator in the diffracted beam has the advantage of decreasing the background, particularly at high diffraction angles and on field samples, as well as increasing the intensity compared with filters to remove the Kβ radiation.

The emphasis in the development of the X-ray analysis technique has been on the rapid processing of large numbers of samples rather than on the accurate analysis of individual samples. Field results have shown good reproducibility of side by side samples ± 15%, but very great variations of up to 10:1, between the highest and lowest full shift samples taken with one man nominally doing the same job in the same working place on different days. Duplicate analyses on one line, either 1,0,1 or 1,1,2, suggest that the accuracy of quartz analysis can be better than ± 5 µg or 10% whichever is the greater. Larger errors can creep in due to interference, filter damage, transmission and transcription. It is believed that if simple precautions are taken, only a few single analyses will have errors greater than 25%. These precautions are:

1. examining filters for damage, estimating correction factor for section of cake missing;

2. checking interference on heavier samples from each mine, choosing one line least subject to interference;

3. checking the printout on each sample for an unusual background slope and disagreement between peak height and peak area estimates of quartz, repeating analysis or computation.

Because of variations in dust concentration, better results would be obtained by taking multiple samples and doing single analyses rather than by spending the same effort in doing multiple analyses of single samples. For critical work on undamaged samples, greater accuracy can be obtained by performing multiple analyses with rotation of samples in the holder.

3.6. References

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CHAPTER 4

FILTER CHARACTERISTICS

The filter is required to collect a
sample of dust from the air, to support it in the
X-ray beam for analysis, and to enable it to be
weighed before and after ashing. Clearly, a
number of factors affecting these processes must
be considered:

1. collection efficiency,
2. site of dust deposition on the surface or
   in the body of the material,
3. airflow and pressure drop,
4. shape and size,
5. background for X-ray diffraction analysis,
6. hygroscopicity,
7. ashing.

4.1. Dust Collection Efficiency

A sensitive method is readily available
in the Elliot Lake Laboratory for determining the
passage of airborne quartz through filters by
estimating the quartz deposited on a back-up
filter of fine pore size using X-ray diffraction.

This method was applied to a number of
filter materials of 25-mm diameter with nominal
pore sizes of 3 to 8 μm by sampling fine quartz
dust clouds (80% respirable) produced by a fluid
energy mill from silica sand (Ottawa, Illinois)
(1). Silver membrane filters of 0.8-μm pore-size
were used as backup filters. The experiments
were carried out in two ways: firstly, by making
single runs in which 0.8 mg of dust was collected
on the first filter at a flow rate of 1 L/min;
and secondly, by making a run in which the first
filter was changed three times while a total of
about 1 mg of dust was collected. The quantities
of quartz found on the second filter are shown in
Table 4.1 to be, with one exception, the indicat-
ed amounts on the backup filter of 1 to 5 μg,
which is at the lower limit of detection for
quartz by X-ray diffraction and corresponds to
less than 1% penetration of dust through the
filters. The one exception with 58 μg on the
filter was not confirmed by a replicate run and

was assumed to be due to contamination during
handling. This suggests that the other measure-
ments may also have overestimated the penetra-
tion. Recent work has shown that 40 to 70% of
0.3-μm DOP aerosol penetrates the 5-μm pore size
silver membrane filters, while 2 to 5% penetrates
the 3-μm pore size (2). Even so, it is concluded
that all these filters collect respirable mine
dusts adequately, and that the amount of quartz
penetrating the silver membrane filters is much
less than the amount corresponding to the light-
sample correction factor as shown in Appendix B.
This implies that the light-sample correction is
due to entry of the quartz into the body of the
filter at the start of sampling and its shielding
from the X-ray beam by the highly absorbent
silver.

It is assumed that all the finer pore
sizes have a higher collection efficiency than
the coarse ones listed.

4.2. Site of Dust Deposition

Even though all the dust is collected by
the filter, there is a possibility that some of
it may enter the pores where it is partially or
completely shielded from the X-ray beam by the
filter material. The significance of this
depends both on the degree to which dust enters
the pores and absorption of X-rays by the filter
material. The effect has only been examined for
silver membrane filters. In the original
calibration (Appendix B) it was found there was a
reduction in the X-ray intensity/mass ratio for
very light samples. This was explained by fine
dust penetrating through or entering into the
body of the filter prior to the dust bed building
up. Once a dust bed is formed it can be expected
that no dust will penetrate it. The effect is
given in detail in the section on calibration and
the dependence of this effect on the pore size of
silver membrane filters is outlined in Table 4.2.

It can be seen that the X-ray intensity/
mass ratio is less for light dust deposits than
for the heavy for the three larger pore sizes but
is slightly greater for the 0.8-μm pore size.
This last relationship is explained approximately

Table 4.1 - Dust passing through filter materials

Filter	Pore size μm	Quartz on backup filter, μg 1st test	2nd test
Flotronics	5	1	30
Flotronics	3	2	2
Metricel	5	2	2
Versapor	5	4	5
Millipore	5	2	3
Nucleopore	5	2	5
Sartorius	8	2	2
Acropor	3	2	5
GF/A	5	2	2
GF/E	5	4	2

Table 4.2 - Dependence of body deposition of dust on filter pore size

Pore size μm	Ratio X-ray intensity to mass 400-500 μg dust	30-50 μg dust
5	146	101
3	142	125
1.2	157	135
0.8	154	158

by the expected effect of absorption in the quartz (Section 3.4).

4.3. Airflow and Pressure Drop

The airflow through and the pressure drop across a filter varies greatly with pore size and much less markedly with type. It has been found that with filters of pore size of 3 μm or larger the main limiting factors on the thickness of a dust bed have been the suction available from the pump, the airflow per unit area, and resistance of the dust bed. With smaller pore sizes than this, the higher resistance of the filter itself leads to a decrease in the attainable thickness of the dust bed. Five μm pore size filters have been used in most of the field measurements.

4.4. Shape and Size of Dust Deposit

Clearly, sensitivity depends on the mass of dust in the X-ray beam and thus on the shape and size of the dust deposit as well as on its thickness. As has been shown, the thickness of the dust deposit is limited by its resistance to airflow. Thus, if other things — sampling time, air velocity normal to the filter surface and concentration — are taken as constant, the mass of dust in the beam is proportional to the area of dust deposit and reaches a maximum when this area is equal to that of the beam.

If dimensions of the dust deposit were made equal to those of the beam, the accuracy would depend on alignment, but not on the uniformity of the dust deposit. With a larger deposit the dependence on accuracy of alignment decreases and the uniformity of deposition becomes important. For deposits smaller than the beam, neither alignment nor uniformity of deposition are important, but sensitivity is less.

The projection of the beam on the sample is normally rectangular, but rectangular filter holders could only reasonably be made in large numbers from moulded plastic. Some prototype metal units have been made and used successfully. The compromise of using circular filters of a diameter less than or equal to that of the beam has been used on some laboratory apparatus. For

field use this would result in the flow rate being reduced to 1 L/min with available battery-operated portable pumps, thus rendering the gravimetric assessment less sensitive.

The other compromise of using circular filters larger in diameter than the beam has been used in most cases. It is found that most dust samplers do not give a uniform dust deposition and that the calibration technique must allow for this. Dust samplers give errors of up to 40% if the X-ray is calibrated with filters having uniform dust deposits.

Considering all these factors it has been concluded that the possible merits in using filters smaller than 25 mm diameter in dust samplers intended for underground use do not justify the considerable expense involved in changing the available dust-sampler pumps and size selectors. However, if a dust sampler were to be designed there could be merit in choosing a rectangular deposit about 1 mm less in size than the beam and choosing a flow rate to suit.

4.5. Background for X-ray Diffraction Analysis

It has been shown that quartz determination in airborne dust can be carried out directly on dust samples collected on filter papers. Silver membrane filters have been recommended (3) as the most suitable for this purpose. The suitability of a filter lies in its providing a low even background of scattered or diffracted X-rays at the positions of the quartz lines. The diffraction patterns from the six types of clean filter examined using CuKα X-rays are shown in Fig. 4.1. Similar results were obtained using CrKα X-rays.

Assuming a linear background in the neighbourhood of the diffraction line, the sensitivity for determination of quartz can be calculated from the formula given by Klug and Alexander (4):

$$P = 0.675 \ (N_T + N_B)^{\frac{1}{2}} \ (N_T - N_B)^{-1}$$

where P is the relative probable error, N_T is the total count (including the background count $\sim N_B$)

adapted approximately for the step scanning assessment of the area under the line used in the Elliot Lake Laboratory.

For the sensitivity limit in the step scanning (0.04°2θ per step was used), let P be 0.5, then:

$$MT^{\frac{1}{2}} = (1.8 \ M/A + 25 \ B/A)^{\frac{1}{2}}$$

where M is the sensitivity limit in μg of quartz,
T is the counting time per step in seconds,
A is the area of the diffraction peak per
  unit mass of quartz
  (counts $sec^{-1} \ \mu g^{-1}$), and
B is the background (counts sec^{-1}).
Note, on very light samples the peak is very narrow and the background to peak count ratio gets very large.

It has been found that the maximum useful counting time per step is limited to 100 seconds by small random 'diffraction' peaks on the silver membrane filters and assuming the same counting time limit is found for other filters the calculated sensitivity limits are given in Table 4.3 together with other relevant data for the stronger independent quartz diffraction lines using CuKα radiation.

It is necessary to analyze for quartz using all available independent diffraction lines because of interference by other minerals. It can be seen that silver membrane filters are most sensitive and have four lines available and that nucleopore filters (1), with five lines available, are almost as sensitive. The other filters are less sensitive and, on the original traces, also show more random small peaks than do silver or nucleopore filters, which would decrease the maximum useful counting time per step, and therefore the sensitivity.

4.6. Hygroscopicity of Filter Material

Filter materials which absorb water require carefully controlled atmospheric humidities prior to and during weighing, which greatly increases the time and effort required. Thus low

1. Sartorius 11303
2. Sartorius 12804
3. Millipore SMWP 5.0 μ
4. Gelman VM4
5. Nucleopore
6. Flotronics silver membrane
7. Blank aluminium holder
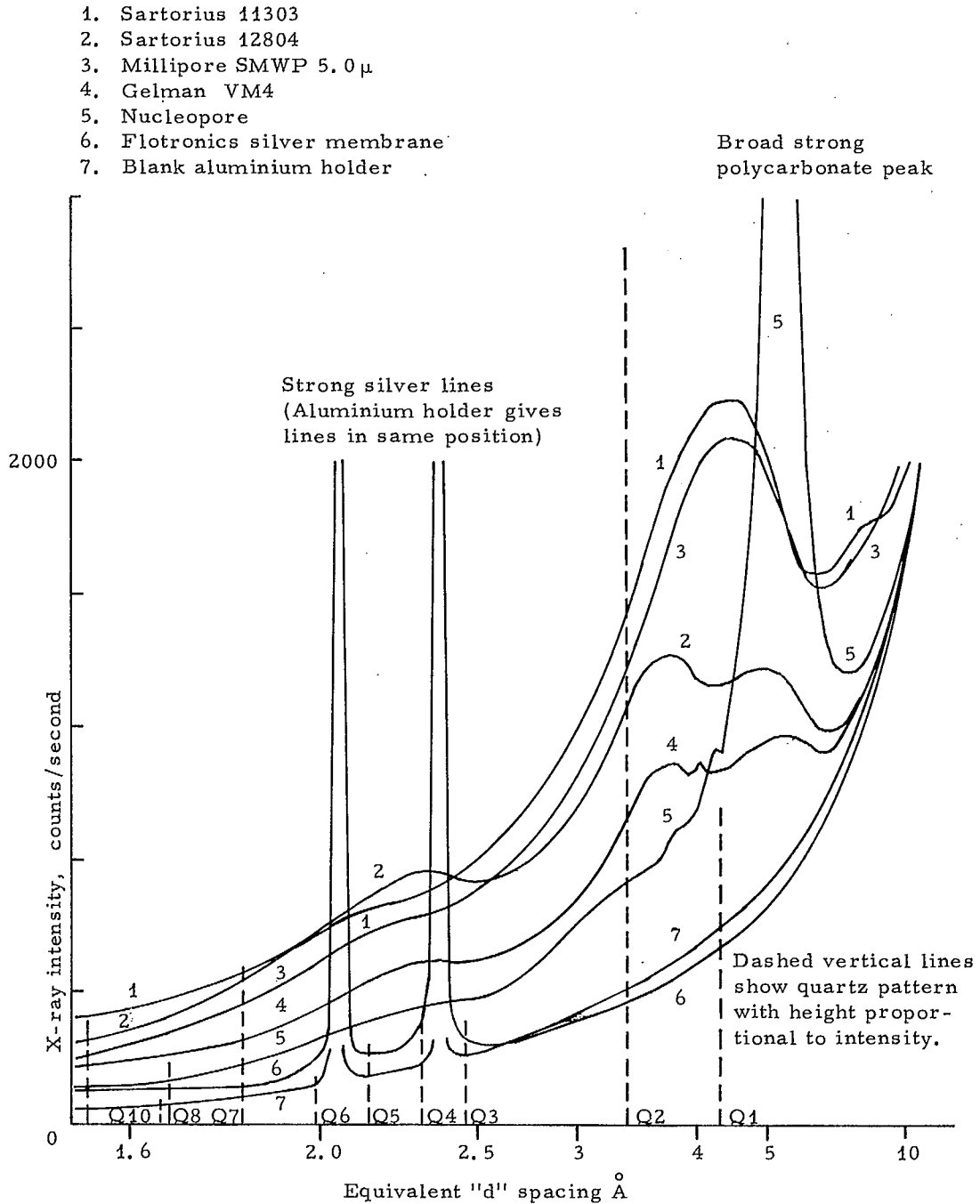
Fig. 4.1 - X-ray diffraction patterns from clean filters.

water absorption is desirable and is claimed by the manufacturers for many types of filter material. Experience with glass fibre, vinyl, silver and polycarbonate filters have confirmed this and drying to a specific relative humidity is not required. However, moisture will deposit in the pores at high humidities and all filters must be conditioned and weighed at relative humidities below 80%. The Elliot Lake Laboratory uses a domestic type dehumidifier in the balance room to achieve this in humid weather.

4.7. Ashing

Ashing of the dust samples is desirable

Table 4.3 - Characteristics of filter papers relevant to quartz
analysis for the six strongest quartz lines

Filter type[1]	Quartz lines					
	Q1	Q2	Q3	Q4	Q7	Q10
	100	101	110	102	112	211

X-ray intensity[2] of quartz peaks in counts sec^{-1} μg^{-1}

	5.5	28	3.3	3.3	4.5	2.2

Background from filters in counts sec^{-1}

1	2150	1500	800	700	450	320
2	1300	1250	720	750	430	255
3	2000	1350	700	600	360	205
4	1050	900	500	500	250	180
5	1100	700	370	350	175	110
6	500	350	270	300	105	110

Sensitivity for quartz determination in μg for 100 second counting time per step

1	NLB[3]	NLB	8	7.3	5	6
2	NLB	NLB	7.4	7.5	5	5
3	9.5	NLB	7.3	6.7	4.5	5
4	6	NLB	6	6	3.5	4.5
5	NLB	2.5	5.3	5	3	3.5
6	5	1.8	NLB	NLB	2.5	3.5

(1) See captions on Fig. 4.1.

(2) Given as peak area with a step size of $0.04^{\circ}2\theta$

(3) NLB - Not usable except for very large quantities of quartz
     because the background is not linear.

to determine the mineral and combustible portions separately and to identify the significance of their respective dust sources. Silver filters can be ashed at temperatures between 480 and 500°C with very little distortion of the filter or disturbance of the mineral dust layer. The change in tare weight is less than 0.03 mg. Nucleopore filters can be ashed completely, leaving a negligible ash from the filter; however, the dust layer is loose in a dish and needs further handling for X-ray analysis.

4.8. Choice of Filter

To summarize, it is believed that silver membrane filters are the most suitable for the gravimetric — X-ray diffraction dust sampling system because of robustness, negligible weight change on ashing, and low background for X-ray diffraction, and are worth somewhat greater cost.

Nucleopore filters are difficult to handle and readily lose a dust cake. They could be more suitable than silver, however, if other analyses were required such as by infrared absor-

ption. Their handling and dust retention might be improved by mounting and handling them in a rigid clip such as is used on the Casella 113a gravimetric dust sampler (5).

Consideration is being given to the use of quartz analysis using relatively cheap infrared absorption equipment at the mine with confirmation on the heavier samples at a central laboratory using X-ray diffraction. Preliminary results suggest that Gelman DM 5000 filters are sufficiently transparent to infrared and have background suitable for XRD analysis of quartz down to less than 50 µg.

4.9. References

1.   Filter material identification and manufacturers: Flotronics silver membrane FM-5 — Selas Flotronics, Spring House, Pa. Metricel VM-1, Versapor 6424, Acropor AN5000, GF/A Glass fibre and GF/E Glass fibre — Gelman Instrument Co., Ann Arbor, Mich. Millipore SMWP 5.0 µm — Millipore Corp. Nucleopore — General Electric. Sartorius SM11301 — Sartorius Membrane Filter GmBH, Gottingen, West Germany.

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4.   Klug, H.P. and Alexander, L.E. "X-ray diffraction procedures"; (Eq. 5.25); John Wiley and Sons, Inc., New York; 1954.

5.   Manufacturer; Casella Ltd., London, England.

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CHAPTER 5

DUST SAMPLERS

The major components of the sampler are: size selector, filter holder, filter, flow smoother, pump and motor, and battery. There are also various optional components such as flowmeter and running time indicator. This chapter discusses laboratory work carried out on dust samplers other than filters which were discussed in Chapter 4. Details are given in Appendices F and G.

5.1. Respirable Size Selection

It was found using simple comparisons in a laboratory dust cloud that many commercial dust samplers showed unexpected variation in indicated respirable dust concentrations attributed to the following effects:

1. pulsating airflows from single acting pumps leading to an increase in dust deposition in a cyclone size selector compared with smooth airflows;
2. passages between size selectors and filters modifying the size selection of the dust reaching the filter;
3. electrostatic effects under dry laboratory conditions;
4. variations in dimensions of machined cyclones.

These effects require that calibration of the size selection of complete dust samplers be carried out. The standard method using monodisperse dusts would have required a lot of time both to set up and operate (1). Thus, at Elliot Lake a simpler method was chosen comparing with a standard dust sampler in a dust cloud prepared in a specific manner. The horizontal elutriator built to the British Medical Research Council Specification (2,3) was chosen for a number of reasons — its availability, its expected 25% greater dust collection than the ACGIH specification, its simple theory, and the apparent variability of instruments intended to

meet the ACGIH specification (4).

The choice of size selectors for the Elliot Lake program was reduced to the Casella 10-mm metal cyclone. However, this showed some variability traced to variations in dimensions, and was fairly heavy. Although the 10-mm nylon is attractive because of low cost and high reproducibility, its effective size is only about 70% of the Casella cyclone.

Eventually an impactor size selector-filter holder was designed which was smaller than either cyclone, and because the main critical dimension was one drilled hole, it was not subject to machining variations; also its sensitivity to pulsating flow was less than that of a cyclone. The first unit used a single-hole single-stage impactor, but after collecting about 2 mg of dust, part of the oversize could easily be loosened and penetrate to the filter. This was overcome by using a two-stage impactor, each stage having single holes. The unit is described in Appendix G.

The effective flow rate or size cut of the impactor can readily be changed by changing the hole size and it is thus a very flexible design. To date the sampling head has been produced in three versions:

1. normal flow, 2.0 L/min,
2. low flow, 1.5 L/min,
3. "open filter" in which the impact block is omitted, which however still leaves some, as yet unmeasured, size selection as with all "open filter" configurations.

It can be expected that any dust sampler fitted with a size selector can reasonably match specifications for lung deposition by adjusting the flow rate. Table 5.1 shows the expected equivalent flow rates at which some samplers would match the ACGIH and the BMRC specifications in a comminuted mineral dust cloud (2,3).

Cyclones and impactors show two important advantages compared with horizontal elutriators — freedom from orientation effects and, in mineral dusts at least, virtually no change in mass of "respirable" dust collected with a change

Table 5.1 - Size selector comparisons

	Size selection criterion	
	ACGIH	BRMC
Expected airflows L/min to match size selector		
Casella 113A horizontal elutriator	1.7	2.5
CAMPEDS	2.5	2.0
Casella cyclone		
10-mm nylon cyclone		
coal mine Cassette[1]	1.7	1.4
Millipore filter holder[1]	1.3	1.0
Expected relative respirable dust concentration		
Mineral dusts	1.0	1.25
Diesel exhaust particulates	1.0	1.0

1 Tests indicated substantial differences between the two filter
 holders supplied with the M.S.A. sampling head, whether this applies
 to other makes or to more recent units is unknown.

in flow rate. Thus, flow rate control is not very important and the "respirable" dust concentration should be calculated using the nominal flow rate rather than the average during sampling.

5.2. Sampling Position

One study showed that on average a personal sampler indicates a 25% higher dust concentration than does a fixed position sampler. A fixed position sampler was hung as near to the miner as possible to avoid likelihood of damage. Stope drillers often moved more than 20 ft during the shift and although slusher operators spent most of their shift at the controls near the sampler, they also spent some time in the stope adjusting cables, etc. Fixed position long period sampling requires more effort to obtain proper samples than simply issuing personal samplers on surface.

Thus, for a routine program personal sampling is probably simpler and gives a better indication of exposure. Fixed position sampling and observation may be required to identify dust sources and determine corrective measures.

In personal sampling, the sampler intake should ideally be close to the nose, but this is a nuisance to the wearer and a position on the lapel is the usual alternative. For miners, a pump and sampling head attached to the cap lamp battery would be the least hindrance and least subject to damage. A few tests were carried out to examine the effect of position of the sampler on indicated dust concentration.

In these tests each miner wore two Casella personal samplers with one sampling head on his lapel and a second on his belt. The samplers were worn throughout the shift as described previously (5). The results expressed as a ratio of respirable silica dust concentration measured at the belt to that measured closer to the breathing zone at the lapel, are shown in Table 5.2.

The mean ratio of dust concentration at the two positions — excluding readings with insufficient samples and those with sampling heads covered by oilskins — is 1.04 with a range of 0.7 to 1.6 suggesting that the belt position is

Table 5.2 - Comparison of lapel and belt sampling positions

Operation	Ratio of belt to lapel dust concentrations					
Drilling	0.7,	1.1,	1.0,[1]	2.0,[1]	1.2,	0.8,[1]
		1.0,[1]	0.5,[2]	0.25[2]		
Slushing		1.0,	1.1,	0.8,	1.2	
Haulage	0.7,	0.2[1]				
Muck and clean up	1.0,	1.6				

1 Ratio inaccurate as sample weight was small.

2 Sampling head on belt covered by protective clothing (oilers).

satisfactory unless protective clothing is worn over the sampling head.

These results suggest that combining the sampling head with the caplamp battery could be the most satisfactory compromise between accuracy of sampling and wearer comfort for general mining operations. However, it leaves two problems:

1. Possible interference from clothing which requires training and checking by supervisors to assure that the battery-mounted dust sampler is worn outside all clothing.

2. The possible pronounced over- or under-estimation of dust levels if the source is above or below the operator such as on a sorting table or at screens feeding a crusher.

Another alternative, the Casella SIMPEDS has the pump on the battery and sampling head on the cap lamp (6), but was rejected because miners found the extra stiff connector to the helmet a nuisance and the dust deposit on the filter could be jarred and shaken off rendering the quartz analysis subject to error.

5.3. Filter Holders

The functions of a holder are to support the filter in a leak-free container and to present a uniform flow to the face. It consists of an inlet cone, a clamping device, an air seal, a backing plate, and an outlet connection. It

has been found desirable to:

1. use mainly metal components, as erratic effects have been experienced with plastic inlet cones;

2. use an inlet cone with a minimum surface area, an included angle of 60°, and rounded corners;

3. let inlet and outlet masked areas of the filter coincide to give a uniform deposition area for X-ray analysis;

4. avoid rotation of the filter and consequent damage during clamping by using low friction washers of Teflon or nylon between filter and rotating member if any;

5. prevent leakage around the edge of filter into the outlet connection from both the inlet cone and the ambient air by using air seals;

6. prevent the silver membranes from sticking to the inlet cone which happens under some conditions, as yet unexplained. This is now avoided by using a thin plastic washer between the filter and the cone. The problem seems to occur most often in humid conditions and has occurred with aluminum, stainless steel and brass.

5.4. Flow Smoothers and Flow Measurement

Most small battery-powered samplers have single acting diaphragm pumps with an oscillating

suction. A continuous smooth airflow is preferred as it avoids modifying the size selection characteristics and gives a true reading on the commonly used taper tube flowmeters. Although both these effects could be compensated by calibration, there is no guarantee that the compensation would be uniform over the entire operating range.

The Elliot Lake Laboratory did some work in developing smoothers as described in Appendix G.

The smoothers examined consisted of one or more chambers in the suction line to the pump, each with a rubber diaphragm separating it from the ambient air. The major requirements identified were:

1. the connection between the final smoother and the pump should be as short and large as possible;

2. the volume in each chamber should be as large as possible;

3. the rubber diaphragm should be as thin or elastic as possible without collapsing under maximum suction — coil spring supports may help; and

4. there should be a restrictive orifice between each pair of chambers.

In measuring flow of dust samplers, errors due to pulsating flows have to be avoided. Taper tube flowmeters, because they read the root mean square flow, are not suitable as primary standards although they are almost universally used for sampling pumps. Bubble burettes, wet test gas meters, or spirometers can be used as primary standards for calibrating taper tube flowmeters.

Some dust samplers have built-in flowmeters and some have external units. The Elliot Lake Laboratory used external flowmeters attached to the air inlet to the size selector. These formed a check on the entire samplers, and in many cases low readings led to discovery of leaks in filter holders and smoothers which would not be revealed in a changed reading on the internal flowmeter as mounted in many sampling pumps. A

simple leakage check for many samplers is to see if blocking the inlet stalls the pump.

Checks were made with the flowmeter underground. Very high readings were found in deep mines due to the response of the flowmeter to air density. This renders flow checking by untrained staff difficult and experience with the Casella pump is that only occasionally during a shift do significant changes in airflow due to high dust loading occur. One mine found overloading only on 15% of the samplers issued to operators of diesel powered Scooptrams. It is thus better to set up the pump for maximum stability rather than for easy flow adjustment, and to accept that thick samples may be slightly underestimated because of the drop in flow rate.

5.5. Sampling Pumps

CANMET's experience has been mostly with the Casella pump and has indicated the following features:

1. A by-pass flow adjustment is undesirable because it increases the drop in flow rate as dust thickness increases.

2. A throttle flow adjustment is undesirable because it limits the thickness of dust deposit.

3. The least response of flow to dust thickness was obtained using a stroke adjustment.

4. The response to pressure and temperature in a mine is complex and the flow characteristics of the pump and flowmeter should be calibrated over the possible pressure and temperature ranges.

5. A running time indicator is useful for indicating faulty samples due either to malfunction or being turned off by the wearer.

The Casella SIMPEDS pump used in the Elliot Lake Laboratory has adjustments for both motor speed and stroke and is fitted with a running time indicator.

The response to pressure of depth in the mine was investigated in the laboratory. It was found that the flowmeter reading increased

steadily with depth while the true airflow at that pressure decreased. The response to temperature was small and was opposite on the two units tested. However, erratic changes of up to 5% in airflow have been noticed when the pump differed in temperature from the ambient air. The details are given in Appendix G.

5.6. References

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CHAPTER 6

DISCUSSION

In judging the suitability of the personal sampler for assessing pneumoconiosis hazard and for reporting the results, it has been necessary to develop standards for permissible dust levels. Perusal of published standards in the world and laboratory correlation between instruments suggest that the threshold limit values for mines should lie in the ranges of (1):

from 2.0 to 4.3 mg/m³ for total respirable dust, from 0.5 to 3.0 mg/m³ for respirable combustible dust, from 0.06 to 0.5 mg/m³ for respirable quartz dust.

Sensitivity of the method is about one tenth the lower limit of the above range for each component respectively.

So far this report has only considered the pneumoconiosis hazard of the airborne dust. However, a number of studies have suggested a relationship between bronchitis and dust exposure, and it seems possible that in future dust standards may be controlled by the bronchitis hazard as well as by the pneumoconiosis hazard. Although very little is known about parameters of dust affecting bronchitis, it presumably is that which is deposited in the bronchia and thus coarser than the respirable dust fraction considered for pneumoconiosis. A better terminology might be 'alveolar dust' for that entering the deep portion of the lung, avoiding the term 'respirable' as this implies that entering the nose. The dust collected in the second impact stage of the CAMPEDS cassette could form a useful estimate of dust in the bronchial tract and thus of the bronchitis hazard. Possibly a target value should eventually be set for a mass concentration measured thus.

6.1. Dust Sampling

Preliminary results in mining showed that personal dust sampling instruments indicated 25% higher dust concentrations on the average than samples fixed in position in the working place. It was also shown that dust concentrations vary greatly with time. For assessing dust exposure it is clear that long period personal dust samplers are most suitable.

The Canadian mining personal dust sampler was developed by the Elliot Lake Laboratory for convenience in use by underground miners and is called the CAMPEDS. A cassette is used to minimize filter handling outside the laboratory and the sampler is mounted on and is powered by the cap lamp battery. It has had ready acceptance by miners and by ventilation staff. The mines need experience in using it to develop a system for switching it on, issuing and returning the sampler, for recording the relevant data and in interpreting the results and applying them to dust control.

Because the cap lamp battery is heavy, a version using a much lighter battery has been built for use where a cap lamp is not required, and this can be used either as a personal sampler on surface or as a fixed-position sampler underground.

It has been shown that alterations in any component of a size selective dust sampler may affect the size selection characteristics. Calibration of the complete sampler as intended for use is clearly desirable.

6.2. Gravimetric Assessment of Dust

This assessment is susceptible to errors as described in Appendix H. It is found that 90% of the samples have errors less than 0.1 mg; some 3% of the samples have substantially greater errors than this due to loss of filter material in handling or to errors in transcribing.

It should be appreciated that these errors in weight of dust can result in very large errors in calculating percentages of quartz in airborne dust. Reasonably accurate percentages can only be obtained with thick samples or by calculating a mean from a number of samples. Thus the quartz quantity should be compared with the basic value rather than with the percentage formula for the threshold limit value for quartz (2,3).

6.3. X-ray Analysis

Anderson has reviewed the literature on free silica analysis and has shown there are a number of problems (4):

1. particle size distribution in the sample,
2. the amorphous high solubility layer on the surface of quartz particles,
3. the various forms in which free silica occurs in nature, and
4. interference.

In addition to these problems there are related difficulties in interpretation of the analysis for estimating the health hazard, and these are:

5. biological effects of composition and structure, and
6. synergistic and inhibitory effects.

In mines, free silica occurs mainly in the coarse crystalline form of α-quartz. There are also some occurrences of the fine crystalline varieties such as chert. Crystobalite and tridymite can occur in younger rocks. Most samples analyzed in the laboratory have contained the coarse crystalline form of a quartz.

Particle size distribution of quartz from comminution of quartz-bearing rock tends to be constant below the original grain size, because it is usually the strongest mineral present. Because the original grain size is usually larger than the respirable size, it is found that the quartz particle size distribution in the respirable portion of the airborne dust collected near the dust source is reasonably constant (5). Some loss of the coarser respirable particles occurs by settlement, etc. when samples are collected at a distance from the dust source. However, the largest proportion by mass of the quartz particles falls into the most sensitive size range for XRD analysis, and this effect is unlikely to lead to significant error using XRD.

The amorphous high-solubility layer on quartz particles appears to be an effect of heat and stress in crushing, but is not likely to cause significant error in quartz analysis by XRD of respirable dust samples from comminution, as most of the quartz would be above the 1 μm size,

at which a significant effect occurs (4).

Both these effects would in part be compensated by calibrating with a quartz material produced by a comminution process.

The various forms in which free silica occurs in nature certainly raise considerable difficulty for the analyst, a specific study of the X-ray analysis of varieties of crystalline silica is given in Appendix E. This suggests that a coarse crystalline form of quartz should be used as the main standard in mining. The errors in using this for fine crystalline quartzes may rise to 40% but this is probably insignificant in relation to the unknown differences in toxicity and their rare occurrence. The errors in analysis could be considered as part of their structure to be examined in epidemiological studies with their concentrations expressed as XRD equivalent in coarse crystalline quartz. Calcined diatomaceous earths have been analyzed for crystobalite with success, but tests on tridymite showed only low intensity lines.

Interference has been found to be very common, but is usually detected and circumvented by making measurements on more than one diffraction line and is minimized by using as long a wavelength as possible.

The effects of composition, structure, synergism and inhibition require elucidation from both laboratory experiments and epidemiology. However, epidemiology will be of little value without good estimates of exposures to quartz and other dusts in the field which can in the meantime be measured in terms of an analytical standard based on a specific quartz.

In addition to the above factors, the XRD analysis of quartz is limited in accuracy and sensitivity by the following:

1. lack of accuracy of size selection and airborne dust sampling procedures,
2. gain or loss of dust between time of collection and measurement,
3. evenness of dust deposit and presentation of a representative portion to the X-ray beam,

4. penetration of dust into filter and hiding from X-ray beam,

5. absorption of X-rays by the dust layer,

6. stability of X-ray intensity and equipment alignment,

7. variations in background XRD from a clean filter, i.e., small, apparently random, peaks,

8. errors in data handling.

Size selection and sampling procedures are common to all respirable dust analyses and calibration on complete systems is desirable if not essential. The dust samples as collected on filter membranes are easily damaged and have to be handled with care.

Uneven distribution of dust over the surface of the filter occurs on most types of sampler, usually with the centre being thicker. Systematic differences between types of dust samplers have given 40% differences in the ratio of XRD intensity to mass of quartz and the effect on analysis is minimized by calibrating with samples collected by the selected sampler in a pure quartz dust cloud.

Fine dust penetrates into the pores of the filters used at the start of sampling, before a dust bed builds up. This dust may be hidden from the X-ray beam by the filter material and the effect is allowed for by using thin sample correction factors determined during calibration with samples collected in a pure quartz dust cloud.

Absorption has only been found to be a problem on heavily laden filters. All 25-mm diameter filters so far examined which have less than 2 mg of total respirable dust (the target value for a full shift sample), as well as many heavier ones, have not needed significant corrections for absorption. However, substantial absorption has occurred on 13-mm diameter filters, and samples thin enough to avoid absorption corrections are too light to weigh accurately.

The stability of the X-ray intensity is dependent on the high voltage generator, X-ray tube and alignment of the equipment. No short-term stability problems have been detected but a regular decrease of about 20% per 1000 hours of operation does occur. The main cause of this is believed to be pitting of the target by the electron beam generating the X-rays. The long-term drift is controlled by the use of standard permanent samples prepared from a quartz and setting resin mixture.

The small background XRD peaks from the clean silver membranes limit the sensitivity to between 0.5 and 10 µg for the various diffraction lines of quartz. This limit has been found to correspond to a maximum counting time of 100 to 200 seconds per step. A counting time of 10 to 40 seconds is normally used.

Errors in transmitting data over the 350-mile phone line to the shared-time computer are frequent, leading to detectable errors in about 1 in 3 samples and gross errors in about 1 in 10 samples. During thunderstorms the error rate is higher and the computer is unusable. Enough redundant items of information have to be returned from the computer to detect significant errors; probably many, leading to errors in quartz estimates of less than 20%, slip through. Data transcription errors occasionally occur in the production of punched paper tape.

Repeat quartz analyses four weeks later have shown differences of 10 µg or 3%, whichever is the greater (Appendix C). Comparisons (6) between analyses by this and other laboratories on sets of field samples have shown that some are in good agreement with CANMET results, but others range from half to one and a half times as much quartz. It was suggested that these differences arose largely from the calibration procedures not being matched to the specific field samples examined.

6.4. Sampling and Analysis Time Study

The CAMPEDS is intended to take full shift samples in routine analysis and for this about 1/4 hour per sampler per day is required to issue, receive, change filter cassette, check

sampler, and keep records. The CAMPEDS has not been in use long enough to know maintenance requirements, but based on experience with the earlier Casella pump, the loss of samples due to various causes is expected to be less than 10%, that samplers would require repair or maintenance about once per month, and that one full day per month should be sufficient to maintain and repair 5 samplers.

Weighing is done with the Elliot Lake Laboratory Mettler Grammatic balance and has taken about 2 minutes for both tare and gross weights per filter; ashing requires about 5 to 10 minutes per sample in batches of 6, mainly because the oven does not have thermostatic control and ashing temperature is fairly critical — too low and the filters do not ash fully, too high and the silver membrane filters distort.

A time study of the X-ray analysis procedure is given in Table 6.1 which shows the time required for each operation and how it could be fitted into the working day. It is based on a one-batch unit, i.e., an automatic sample changer magazine containing 2 standards and 33 samples.

Throughput can be compared with the most likely Canadian requirement which is estimated at 20,000-30,000 samples per year based on a total of about 10,000 miners working with medium- to high-quartz ores and samples from about 10% of the remaining 40,000 Canadian miners in low-quartz mines at two samples per year.

6.5. Composition of Airborne Dust

To date over 5000 airborne dust samples have been analyzed for quartz and over 2000 for combustible dust and their results are summarized in Table 6.2. The analysis of mine working place samples and special dust studies measuring air entering and leaving the working place has led to a fairly clear understanding of the main factors affecting the composition of dust in mine air as follows:

1. The quartz content as measured by X-ray diffraction and expressed in terms of the ash portion of the respirable dust is usually less than the quartz content of the ore and agrees reasonably well with that measured in the fine-sized fractions of ore

Table 6.1 - Time study of analysis procedures

Batches per day	1	2	3	4
Magazine change time[1]	9	9,14	9,14,20	7,12,17,22
	Technician time required, h			
Sample handling, setting X-ray	1/2	1	1 1/2	2
Computer operation	2	3 1/2	5 1/2	7
Calculating, checking, reporting	1	2	3	4
Totals	3 1/2	6 1/2	10	13
Samples/5-day week[2]	100	180	280	360
Technicians required	1/2	1	1 1/2	2

1 Hours on 24-hour clock.

2 Allowing for repeating heavy samples on a second line and only running four nights/wk.

Table 6.2 - Composition of the respirable airborne dust in various mines: ranges and means

Mine		Combustible dust %	Ash %	Quartz as % of		Quartz in ore %
				Total dust	Ash	
A	Range	--	--	0-100		99+
	Mean[1]	--	--	80		
	Mean[1]	--	--	50		
B	Range	--	--	0-100		65
	Mean	--	--	25		
C	Range	8-91	9-92	0-70	0-100	65
	Mean	57	43	22	52[2]	
D	Range	5-100	0-95	0-15	0-30	30
	Mean	49	51	7.5	15	
E	Range	19-96	6-81	0-2	0-30	10
	Mean	50	50	1.5	3	
F	Range			0-15		15
	Mean			1.2		
G	Range			0-12		10
	Mean			1.7		
H	Range	10-95	5-90	0-10	0-20	40
		50	50	5	10[3]	

1 Two means were obtained before and after the mean dust concentration dropped from 0.3 mg/m^3 to 0.1 mg/m^3 during a concentrated effort on dust control.

2 Chemical analysis of one "rafter" dust sample from near the crusher gave, after removal of +5 μm sizes by sedimentation, 49%.

3 Chemical analysis of "rafter" dust samples from near the underground crusher gave 15% free silica.

samples by other methods. The ash portion of the respirable dust in mines appears to be mainly of mineral origin. Presumably the main reason for the quartz content of the respirable sized mineral dust usually being less than that of the ore is that quartz is stronger than many other minerals and is therefore broken less readily.

2. The mineral portion of the airborne dust in mines has been found to be significantly

diluted by oil mist which is collected on filters and weighed as dust from lubrication of compressed air operated equipment and by particulates in diesel exhausts, as shown in Table 6.2. While not yet identified, atmospheric dust and solids in atomized water could form significant diluents. As an example, in two mines with ore containing 60 to 70% quartz, the quartz per cent in respirable dust ash averaged 52%, but in the total respirable dust in one mine it was 25% and in the other 10 to 15%. The first mine used a few diesel-engine powered locomotives for rail haulage, whereas the second used many diesel load-haul-dump units.

3. The sulphuric acid content of diesel exhaust particulates is about 50% by weight.

4. The major portion of mineral dust in mines is produced from ore handling and the control of dusty air leaving these operations should be very effective in reducing miners' dust exposure.

5. Quartz constitutes the main health hazard in most mines having more than 20% quartz in the ore. However, in some cases diesel operation gives rise to high concentrations of exhaust particulates. While there are no standards for these, it would be imprudent to wait for pneumoconiosis to develop before controlling them.

6. The average dust concentration measured in the limited number of mines examined with significant quartz in the ore are close to the suggested permissible level of 0.1 mg quartz per cubic metre.

7. Dust concentrations vary from day to day even though full shift samples are being taken. The ratio of maximum to minimum concentration was found to range from 1.5:1 to 30:1 in a group of 20 men examined for 3 to 6 shifts each.

6.6. Further Developments

Two main problems with the X-ray diffraction analysis of quartz which could possibly be improved are that data-feeding to the remote computer requires too much technician time both directly and in correcting for transmission errors, and that unevenness of the dust deposit leads to sampling errors.

The use of an on-line computer to control the X-ray equipment, to calculate the mass of quartz from the area, and to repeat measurements on second lines when necessary, would greatly decrease technician time by permitting one technician to handle at least 400 samples per week and would also reduce X-ray time.

The area of sample covered by the X-ray beam has already been increased by 20% by machining the slits controlling the "vertical" dimension, along the goniometer axis, and increasing the size of the beam. However, the full benefit has apparently still not been obtained because of limited response to the outer parts of the sample in the graphite monochromator. Changing the X-ray optics to permit the full diameter of the filter to be illuminated and modifying the detector system to respond to the outer regions of the filter could diminish problems due to uneven deposition. Possible approaches are a larger graphite monochromator or the use of a solid state X-ray detector. Further possible improvements are:

i) the use of a vacuum system with chromium radiation,

ii) the use of an X-ray target to give the same beam width as the receiving slit recommended could increase intensity or tube life by a factor of 2.

The dust sampling and assessment system as a unit has one major problem of making rapid dust assessments and permitting immediate remedial action to be taken or studies of control failures to be undertaken. This requirement can be met by weighing before and after ashing for mines with small proportions of quartz in the ore but is not possible with high proportions. Two possible approaches are either to use much cheaper equipment for measuring quartz or to use more sensitive, more accurate techniques for de-

termining the mass of dust and ash on the filters.

Infrared absorption has been used for quartz analysis and the least expensive equipment costs about $5000, which would seem a reasonable expenditure for individual mines or mining camps. To set this up would require finding a technique and a filter compatible with the dust sampler (7), gravimetric assessment before and after ashing, and X-ray diffraction assessment of quartz. Interference can also be expected with infrared absorption and results would need checking by X-ray diffraction but the method could be of immediate use making corrections by XRD for long-term estimation of exposure.

A more sensitive assessment of total mass and ash could be based on β-ray absorption (8,9) and X-ray absorption (10). Low energy β-rays with very thin filters have been shown to give a sensitive measurement of mass with little dependence on atomic number. X-ray absorption depends on atomic number and both methods could probably be used and calibrated for each mine to give sensitive and sufficiently accurate assessments of total respirable dust and ash. In most cases these two estimates would probably also give respirable quartz dust with sufficient accuracy for immediate application.

6.7. References

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ACKNOWLEDGEMENTS

APPENDIX A

DEVELOPMENT OF X-RAY INSTRUMENTAL TECHNIQUES

This appendix is devoted to a detailed description of the settings and modifications for each component of the X-ray equipment. It should be appreciated that the results given were obtained with one particular apparatus having some custom features and with optimum settings for analyzing small quantities of quartz. Usually only one variable was studied at a time using preliminary best compromises on the others. These recommendations should be used as a guide for purchasing and setting up the equipment.

The equipment, mostly manufactured in Holland and supplied by Philips Electronics Ltd. will be examined in a logical order starting with filter mounting and finishing with data printing. Results for the four strongest diffraction lines of quartz will be given where the difference between them was significant. The requirement for more than one quartz line to minimize errors caused by interference was discussed in Chapter 3.

A.1. Filter Mounting

A Philips automatic sample changer is used which restricts filter mounting methods and prevents rotation of samples because of close spacing in the magazine. Two mounting methods have been tried, both ensuring that the centre of the filter coincides with the centre of the X-ray beam. The axial mounting surface on the goniometer had to be machined to clear part of the filter.

For the first method, a 22-mm diameter hole was drilled through the mounting plates supplied with the unit and a recess 0.25 mm deep and 25.5 mm in diameter was turned to receive the filters. The filters are held in the recess by petroleum jelly dabbed on the supporting surface in two or three places with a brush and smoothed out with a mating cylindrical tool. The filter is placed in the recess and the edges are pressed down with a clean mating tubular tool. This

method was used for most studies and worked well except in a few instances when distorted filters loosened from the supporting surface and became caught in the sample changer. Filters can be ashed after X-ray analysis as the petroleum jelly is burnt off.

In the second method, the recess was taken nearly through to the top surface of the mounts. The top surface was chamfered to permit full illumination of the surface of the dust deposit down to 20°2θ, i.e., the lowest angle for a quartz diffraction line using CuKα radiation. The filter is held in place by a spring clip one size smaller than the 25-mm diameter hole as a high retaining force is not required. The surface of the dust deposit is below the axis of the goniometer causing an error of about -0.25°2θ in the peak position which has to be allowed for in mineral identification. This method is now in routine use and has fewer problems than the first. The arrangement is shown in Fig. A.1.

For holding 13-mm filters a similar arrangement is used in circular plates 25 mm in diameter which fits into the 25-mm filter holders. For filters with larger diameters of 32 and 37 mm, similar mounts have been made which have to be changed manually. However, for most samples the 25-mm diameter centre is punched out and mounted in the 25-mm filter holders with automatic sample changing.

A.2. Generator and Ancillary Equipment

The ultra-stable generator, PW1140, has required a few minor repairs and the addition of switch guards to prevent accidental operation when working on the X-ray table. X-ray tube cooling has used recirculation from a tank fitted with a water-to-water heat exchanger because dirt in the mains water supply rapidly clogged the recommended filter.

A.3. X-ray Tube

The use of three target materials — molybdenum, copper and iron were originally examined systematically. This suggested the examination of two further materials — cobalt and
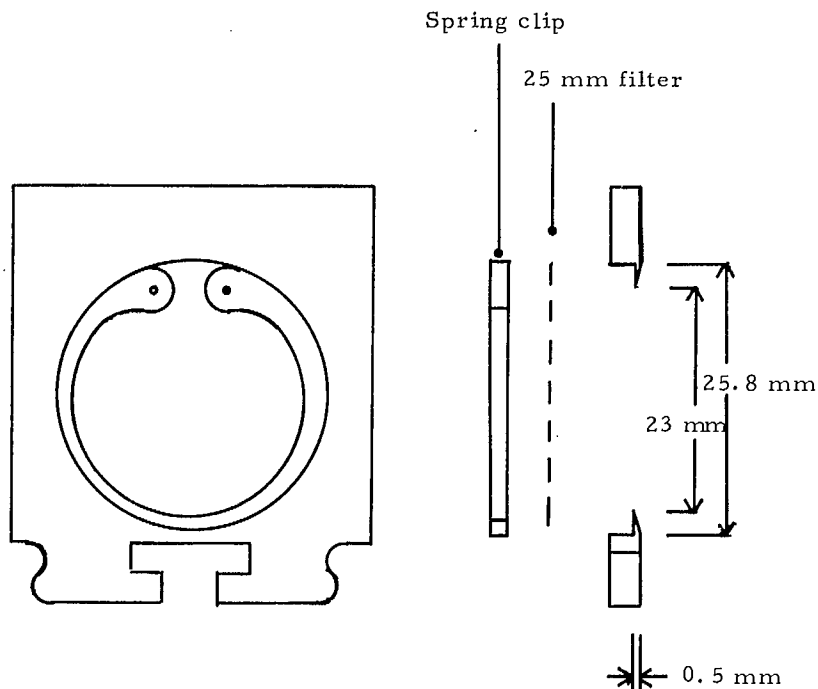
Fig. A.1 - Filter holder for automatic sample changer.

chromium. The following four quantities, which depend on target materials must be considered with respect to their effect on quartz analysis while maintaining other factors constant:

1. Intensity — area of diffraction line using the strongest emission line of the target, the unresolved $K\alpha_1\alpha_2$ doublet; high intensity shortens the analysis time.

2. Peak-to-background ratio; a higher ratio is associated with higher sensitivity.

3. Resolution, i.e., width of the line in equivalent "d" spacing. Clearly there is less chance of other mineral diffraction lines interfering with or overlapping the quartz line if the lines are narrower.

4. Wavelength of the characteristic X-ray affects absorption in the sample and therefore affects the limit of the linear range of analysis.

A.3.1. Intensity of characteristic radiation

Each tube was operated at its maximum rating as given by the manufacturer with the voltage and amperage adjusted to give the maximum peak height on the 1,0,1 quartz line. It was found that the optimum voltage based on intensity for the molybdenum tube was at or above the safe maximum voltage for the tube shield and it was operated at 55 kV and 18 mA. The copper tube was operated at 50 kV and 40 mA, the iron at 35 kV and 10 mA, and the chromium at 40 kV and 50 mA. The optimum for the cobalt tube was 40 kV and 50 mA.

Table A.1 shows the effect of target material on the intensities as peak heights of the diffraction lines from quartz and the silver membrane filter support. The first part of the table shows the values actually obtained and the second part shows the values corrected linearly for the energy input to the X-ray tube. It can be seen that the intensity for the quartz peaks increases from molybdenum through copper to iron even after allowing for the effect of "use" on the copper target. The chromium target gives slightly lower intensities than the copper tube did when new, possibly because of the effect of

air absorption. The intensity of the peaks from the highly absorbing silver filter backing, however, falls as the atomic number of the target is reduced and the radiation is more readily absorbed.

The cobalt target was purchased after the copper and chromium targets were worn out and could not be compared directly. Records show that the cobalt target was not as intense when first installed, but improved after installation. These three targets give essentially the same intensity over the period of use considering the normal effect of wear.

Table A.1 - Intensities of diffraction lines (peak heights) relative to those using a copper target by net peak height

	Mo/Cu[1]	Fe/Cu[2]	Cr/Cu[2]
As measured			
Quartz 1, 0, 0	--	0.35	1.2
1, 0, 1	0.14	0.37	1.1
1, 1, 2	--	0.28	0.75
2, 1, 1	--	0.28	0.88
Average	0.14	0.32	0.98
Silver 1, 1, 1	0.85	0.2	0.31
Corrected for power[3]			
Quartz 1, 0, 0	--	2.0	1.2
1, 0, 1	0.28	2.1	1.1
1, 1, 2	--	1.6	0.75
2, 1, 1	--	1.6	0.88
Average	0.28	1.82	0.98
Silver 1, 1, 1	1.7	1.14	0.31

1 When molybdenum radiation was used at the normal settings for copper radiation the resolution was poor and only the 1, 0, 1 line of quartz was measurable.

2 These comparisons are unfavourable to a copper target because the copper tube had been operated for more than 1000 hr and its output was down to about 2/3 of the value when new, whereas the molybdenum, iron and chromium tubes were almost new.

3 The tubes and settings used were:

	Focus, mm	mA	kV	W
Mo	1.0 x 0.1	18	55	1000
Cu	1.2 x 0.12	40	50	2000
Fe	1.0 x 0.1	10	35	350
Cr	1.2 x 0.12	50	40	2000

It is not clear what factors affect the decrease in intensity with time, but on the particular tubes used the life to half intensity at full rating was about 4000 hours on the copper and 3000 hours on the chromium. The cobalt tube was run at half rating and so far has run 4000 hours with only about a 20% drop in intensity, most of which has occurred in the 1500 hours since the rating was increased to 60%.

A.3.2. Peak-to-background ratio

Table A.2 shows the average effect of target material on the peak-to-background ratio obtained on a small number of field samples. It can be seen that the ratio increases as one progresses from molybdenum through to iron. Chromium was compared with copper on different samples at a later date and although preferable to copper, it apparently showed lower ratios than iron.

A.3.3. Resolution

Table A.3 shows the average effect of target material on the width of the peak as the mean on a small number of pure quartz samples. The width of the peak was measured at one-half of the net peak height above background, and was

Table A.2 - Net peak height to background ratio relative to that with copper target

	Mo/Cu[1]	Fe/Cu	Cr/Cu[2]
Quartz 1,0,0		1.5	
1,0,1	0.09	1.9	1.4
1,1,2		2.1	1.6
2,1,1		2.35	
Silver 1,1,1	0.17	1.37	

1 When molybdenum radiation was used on normal settings for copper radiation the resolution was poor and only the 1,0,1 line of quartz was measurable.

2 Comparisons were obtained at a later date on different field samples which had been analyzed earlier with Cu radiation on these two lines.

Table A.3 - Width of diffraction lines

			Absolute copper radiation	Relation to copper		
				Mo/Cu	Fe/Cu	Cr/Cu
By angle at 1/2 height in °2θ						
Quartz	1,0,0		0.25	1.6	1.0	1.0
	1,0,1		0.27	1.6	0.9	1.0
	1,1,2		0:31		0.9	1.0
	2,1,1		0.33		1.0	1.2
Silver	1,1,1		0.27	1.5	0.85	1.0
Average			0.29	1.55	0.93	1.0
By "d" spacing at 1/2 height in Å						
Quartz	1,0,0		0.05		0.8	0.67
	1,0,1		0.033	3.3	0.67	0.67
	1,1,2		0.0105		0.67	0.67
	2,1,1		0.0076		0.74	0.65
Silver	1,1,1		0.016	2.7	0.63	0.65
Average				3.0	0.70	0.66

expressed as an angle in degrees 2θ, or as equivalent increment in "d" spacing in angstrom units. The angular width is about the same for each line using one target with a marked difference between Mo and the others. The width in equivalent increment in "d" spacing decreases markedly with increasing angle and with target material in the order — Mo, Cu, Fe and Cr — suggesting that the longer the X-ray wavelength the greater is the resolution and the less likely is interference from minerals with close "d" spacings.

A.3.4. Absorption

Table A.4 shows the relative effects of target materials on absorbance by four samples. The three filters with samples had a lower silver peak than the blank with each target material being much more marked with the Cu, Fe and Cr radiations. This may be connected with tarnishing of the silver as the blank was a recent filter, whereas the others were 1 to 4 years old. There appears to be no significant differences in

absorption between the three samples with any of the four radiations, suggesting that any of the radiations are suitable. However, studies on many samples are required to determine the upper limit of linearity for quartz analysis and to determine methods of detecting absorption as reported in Section 3.4.

The choice of target material depends on conflicting requirements and is a balance between higher absorption and improved intensity, peak-to-background ratio and resolution as the wavelength is increased.

It is clear that the disadvantage of low resolution and intensity when using a molybdenum target is not counterbalanced by its low absorption. The differences between the other four targets is not large and a high power cobalt tube is preferred because of the relative rarity of elements with high absorption for CoKα X-rays.

A.4. Take-off Angle

As the effect of increasing take-off angle in increasing the width of the diffraction

line is much less than that due to other factors, efforts were made to maximize intensity. It was found that the advantages expected were not obtained at angles above 7°, presumably because of mechanical restrictions in the tube or tube shield and therefore 6° take-off angle given by the alignment tools is used. A specially designed or modified tube to give the same effective beam width as the receiving slit should provide greater intensities or longer tube life and be worth the possible extra cost. The Krottky tube will give a greater angle but some modifications to the tube shield and vertical goniometer are required.

Table A.4 - Absorption in sample - intensity of silver lines relative to those given by the absorbed radiation - Mo (Corrected for power) by net peak height

	Relative[1] intensity	Cu/Mo	Fe/Mo	Cr/Mo
Blank filter	1.0	0.9	1.02	0.27
Quartz 0.1 mg	0.85	0.57	0.58	0.16
Quartz 2.0 mg	0.88	0.64	0.66	0.24
Mine sample[2] 2.3 mg	0.8	0.54	0.54	0.15

1 Relative intensity of the silver line from each filter using molybdenum radiation.

2 The mine sample was chosen as containing some iron which has a high absorption for copper radiation.

A.5. Beam Height

The windows and shields on the goniometer were set to restrict the beam height along the goniometer axis to 10 mm. The later equipment by Philips Electronics Ltd. uses optics 12 mm wide. However, the new high-intensity tubes are supplied with a source 12 mm long and by machining all slits and shields to 12.5 mm, the illuminated area of the 22-mm diameter dust deposit was increased by nearly 20% and the intensity of the X-ray peak by about 15%.

A.6. Vertical Divergence of Incident Beam

The term "vertical divergence" is used in most texts to mean the angular divergence of the beam along the axis of the goniometer, even though with the goniometer used this is actually a horizontal direction. The vertical divergence is normally controlled to about 2° by Soller slits in the incident beam; that in the emergent beam is controlled by the graphite monochromator. If those in the incident beam are removed, its divergence is controlled at about 8° by source and sample. The effect for copper radiation of removing the Soller slits is shown in Table A.5 and Fig. A.2. There is a gain in intensity of 200 to 300% accompanied by a drop in peak-to-background ratio and distortion of the peak with a longer tail on the low angle side.

The removal of the Soller slits gives a considerable gain in intensity but at too great a loss in resolution. Coarser Soller slits might be a useful compromise.

A.7. Diverging Slit

The diverging slit regulates the width of sample illuminated by the X-ray beam at a set diffraction angle and tests have shown that intensity increases almost linearly with slit size until the sample is completely illuminated. The background also increases linearly and thus the peak-to-background ratio is constant until the beam is as wide as the sample. A secondary effect of increasing the slit size is to increase the peak width, but as this increase is less than 10% the gain in intensity far outweighs the loss in resolution.

Ideally the slit width should be set so that the beam just covers the sample at each of the angles used. However, the slits are manufactured in steps and the next larger slit width is used, with a slight loss in peak height-to-background ratio. Above 70°2θ it is not possible to illuminate the entire width of the sample and measurements using chromium radiation on the 1,1,2 and 2,1,1 quartz lines were carried out with less than the full width illuminated.
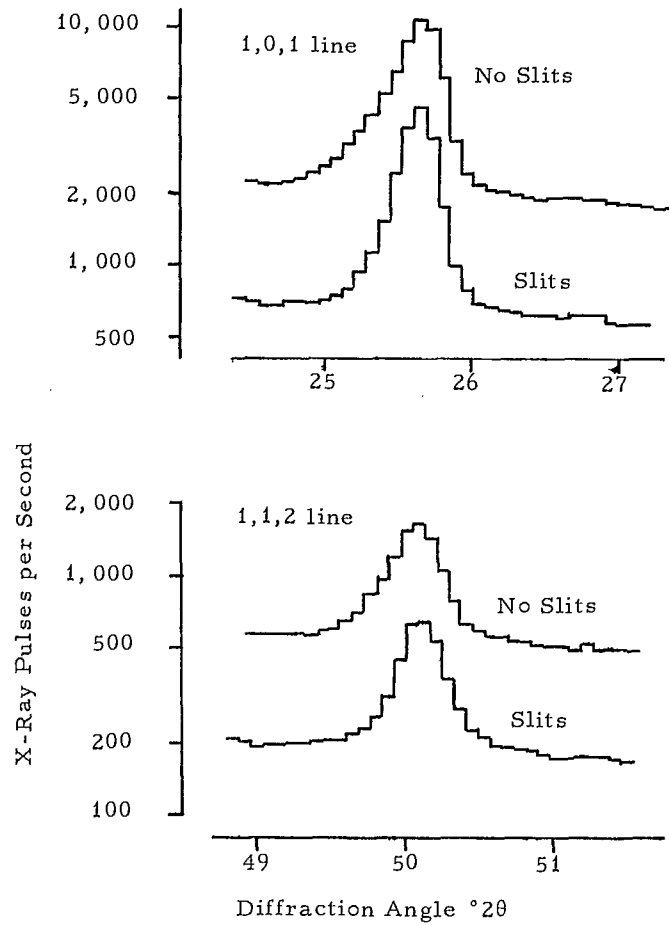
Fig. A.2 - Effect of Soller slits on diffraction lines from quartz.

Table A.5 - Effect of vertical divergence

	Ratio $\frac{\text{Soller slits in}}{\text{Soller slits out}}$ on quartz line			
	1,0,0	1,0,1	1,1,2	2,1,1
Intensity by area	0.38	0.40	0.37	0.39
Peak height-to-background ratio	1.45	1.45	1.2	1.05
Width at 1/2 height	0.83	0.85	0.82	0.85

Automatic adjustment of slit width to angle would be useful and a still further improvement for circular filters would be elliptical slits to match (1). To avoid variations in peak intensity due to slight misalignment of the samples, the width illuminated should be either greater or less than the sample in all its possible alignments.

A.8. Receiving Slit

When a crystal monochromator is used on the vertical goniometer, the receiving slit assembly differs from the usual arrangement in that the diffracted beam Soller slits are omitted and the scatter slit is mounted differently.

Table A.6 shows the effect of various receiving-slit widths on the peak area of the quartz diffraction line (1,1,2) using copper radiation and the diffracted beam monochromator. The gain in intensity more than compensates for the decreased signal-to-noise ratio as the slit width increases from 0.091 to 0.434 mm; however, it does not do so for the very wide slit at 1.5 mm. It is possible there is an optimum slit width at about 0.6 mm. The 0.434-mm slit width is about 10% of the width of the quartz diffraction line and does not degrade the resolution appreciably.

A scatter slit of about 4° angle based on the receiving slit as axis is used. Its removal, however, has not been found to increase background and the inner end of the beam tunnel has about the same angle of view.

A.9. Step Size

The system used counts the height across the diffraction line by step scanning. It has been shown that receiving slits up to 0.2°2θ can be used with a gain in intensity and there are advantages in both counting and computing time if only a few wider steps are used. Table A.7 shows the effect of step size and shifts in step position relative to the peak maximum on the integrated intensity using copper radiation of the 1,0,1 line of a pure quartz sample.

The corrected peak area is independent of step size in the range of 106 to 113 but shows some variation with the position of the peak within the step in the larger sizes. It is concluded that the variation found with the 0.083°2θ step size is within satisfactory limits, but that found with the 0.167°2θ is unsatisfactory. A step size in the range of 0.06 to 0.1°2θ is probably the most suitable and the values available depend on the drive. The goniometer drive is obtained from a motor controlled by a microswitch operated by a cam on the drive shaft with the variables — gear ratio and number of faces on the cam. The original motor supplied by the manufacturer ran on from 1/10 to 1/3 of a revolution depending on the friction applied to the shaft and was difficult to control. This was replaced by a motor fitted with a solenoid-operated clutch and brake which has a very small run-on and can be used with a multi-rise cam. However, the printout of the data for each step takes 4 to 5 seconds and control was modified to occur in the

Table A.6 - Effect of receiving slit width

| Slit width | | Peak | Intensity/unit width | | Signal/noise |
mm	°2θ	area	Total	Incremental	ratio*
0.091	0.03	28.8	317	317	3.7
0.203	0.067	62.8	310	304	3.5
0.253	0.084	74.9	296	242	3.28
0.434	0.144	102.8	227	154	3.02
1.5	0.5	147.2	98	42	2.58

*Expressed as (peak-height - background)/background.

Table A.7 - Effect of step size and position relative to the peak maximum

Step size °2θ	Shift °2θ	Receiving slit width °2θ	Peak area Indicated	Peak area Corrected[1]
0.021	-	0.03	1490	107
0.042	-	0.03	737	106
0.083	0.00	0.084	963	111 } mean 108
0.083	0.04	0.084	929	106
0.167	0.00	0.144	641	107
0.167	0.04	0.144	716	119 } mean 113
0.167	0.08	0.144	692	115
0.167	0.12	0.144	665	111

1 Corrected for variations in peak area with slit width (Table A.6) and for number of steps (divide by number of steps per °2θ). This factor is effectively equal to change in counting time with step size.

same period. Using a 6-rise cam — the motor output shaft is 2 rpm — and the 1°2θ/minute gears, a step size of 0.083°2θ and motor advance time of 5 seconds can conveniently be obtained with minimum machining. The time constant of the one-shot circuit switching on the motor in the PW 1364 step scan control unit was reduced to 3 seconds by disconnecting one of the two capacitors.

A.10. Diffracted Beam Monochromator

The Norelco graphite monochromator replaces a filter to eliminate the Kβ radiation from the target.

A comparison between the graphite monochromator and the normal Ni filter on a pure quartz sample using CuKα radiation is shown in Table A.8. It can be seen using the monochromator that intensity is 40% higher and that the major gain is in the very great reduction in background of 2 to 6 times, increasing both with angle and with the presence of other materials mixed with the quartz. The peak width is essentially the same for both techniques.

The check on the resolution of the graphite monochromator was on the relative intensities of the Kα and Kβ peaks when the monochromator is set to maximum intensity for unresolved

Kα₁ - Kα₂ or for Kβ radiation. The tests were carried out on a blank filter using the silver 1,1,1 peak and copper radiation. It was found that the intensity of the Kα peak was reduced by a factor of 1500 when the monochromator was set on Kβ rather than on Kα. The Kβ peak showed about the same reduction when the monochromator was set to Kα radiation. The Kβ peaks from the very strong lines of the silver metal filter do appear at intensities comparable with those of weak lines from mineral samples collected on the filter paper and should be recognized. However, they do not interfere in the analysis of quartz or crystobalite and "ghost Kβ" lines, as expected, have not been detected from any minerals as they very seldom reach 10% of the intensity of the silver lines.

A.11. Detector

The doped sodium iodide crystal and scintillation detector have been used throughout. Voltage applied to the detector has been 880 as this appeared to be in the middle of the plateau and the lower level and window width were set to cut off at 10% of full height above background. This reduces the total count by about 10% from that in the range-count minimum below the peak to the shoulder of the flat background above the peak. Output from the scintillation detector and monochromator is shown in Fig. A.3, both on the quartz peak and an adjacent background for copper radiation.

Table A.8 - Comparison of graphite monochromator and nickel filter using CuKα radiation

	Monochromator/Ni filter for quartz line	
	1,0,1	1,1,2
Intensity: peak height	1.35	1.55
peak area	1.4	1.45
Peak height/background	1.9-2.7[1]	1.85-6.0[1]
Width at 1/2 height	1.05	1.0

1 The gain in peak height-to-background ratio using the monochromator is greater for light samples and samples containing other minerals.
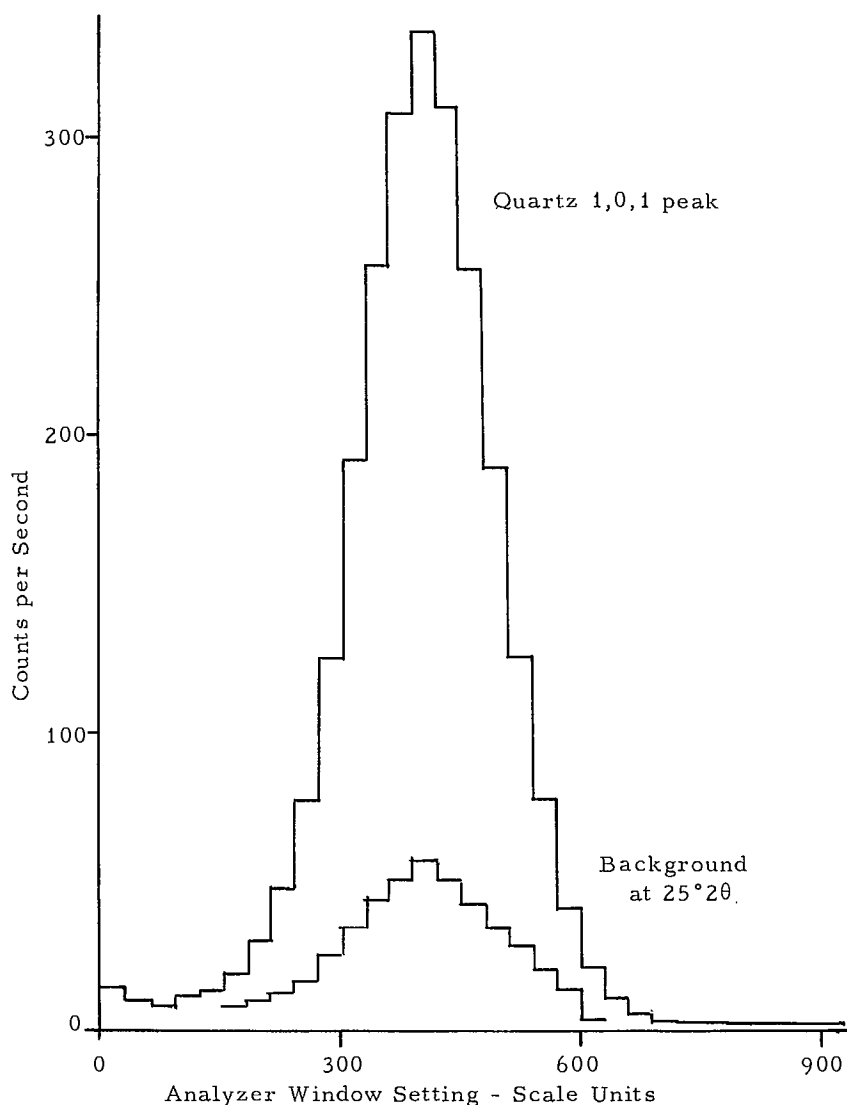
Fig. A.3 - Pulse size distribution from X-ray scintillation detector.

A.12 Evenness of X-ray Illumination Over Sample

Some preliminary tests were carried out with masks on the sample to check on alignment; however, the results were not conclusive, and a sample holder was made up in which a powder quartz test sample 3 mm in diameter could be set at any position in the sample area. The peak height from this test sample was measured on the 1,0,1 diffraction peak using CrKα radiation. The peak height was maximized by adjusting the diffraction angle, which varied over a range of 0.03°2θ and was approximately equal to the expected flat-sample correction. The background without the quartz sample was also measured and amounted to about 50% of the maximum peak height, much greater than the net peak height at the edges of the sample. The peak height was measured on grid points spaced 1.5 mm apart in both directions; Fig. A.4 shows the net peak height contours drawn in the sample plane. Also shown are the circles 10 and 22 mm in diameter outlining the two sample sizes used and the edges of the beam as defined by the shield components. It can be seen that intensity falls off very markedly towards the edges of the sample. As this fall-off could be due to variations in illumination or to variations in detector response, a photographic plate was placed in the

sample position and exposed. This showed two deviations from uniform intensity — shadows of the plates in the Soller slit, and the expected drop in intensity with increased distance from the source.

The 3-mm diameter of the quartz test sample is larger than the Soller slit spacing and

thus its effect should be smoothed out in Fig. A.4. The increase in distance from source to sample from one side of the sample to the other should be compensated for by the corresponding decrease in distance to the detector.

Thus it appears that the major cause of the decrease in peak height towards the edges of
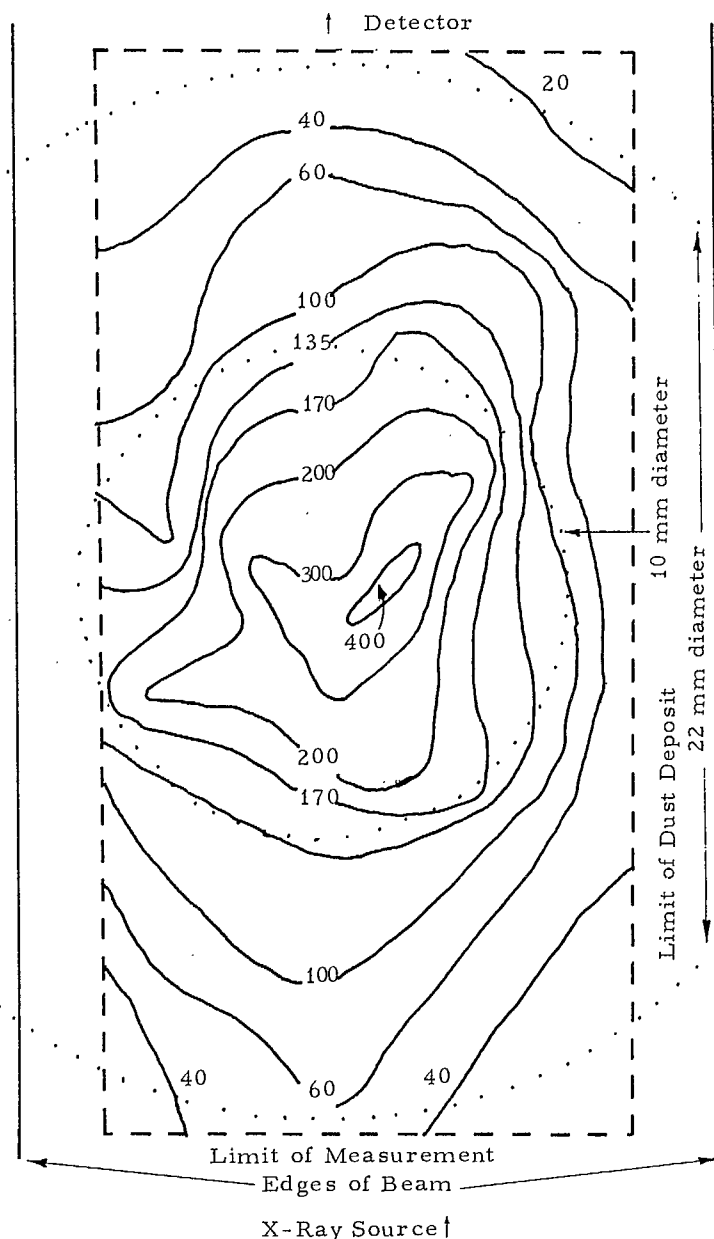
Fig. A.4 - Contours of diffracted beam intensity from a 3-mm diameter quartz sample — 1,0,1 line CrKα radiation.

the sample area is in the detection system. It is believed that the graphite monochromator crystal is the component responsible. It is possible that a larger crystal could give a greatly increased intensity from field samples. Philips Electronics Ltd. now supplies a larger crystal. Certainly an even response over the whole sample area would increase the intensity by a few hundred per cent. A possible alternative would be to use a solid state, lithium-drifted silicon detector in place of the monochromator and scintillator detector.

A.13. Noise Suppression

Spurious bursts of counts were observed on the chart recorder at irregular intervals when first received. Some of these were traced to the operation of electrical switches both in the system and external to it. The incidence of these bursts was greatly reduced by adding an extra stage of capacitor-resistance smoothing on the power input to the scintillation detector pre-amplifier. The manufacturers have since issued modifications which increase the smoothing of this power supply. A few other switches on the equipment also give noise problems and these must either be suppressed by fitting capacitors across the contacts or else not used during counting. The problems identified are:

a) step scan microswitch on goniometer drive — suppressed by adding capacitor across terminals;

b) switching recorder off is very noisy — suppressed by adding capacitors across PW 2500 supply terminals and ground;

c) fluorescent light on recorder table — removed.

Some spurious signals occasionally interfere with the control and data transfer signals producing difficulty in operating the computer program as well as unwanted stops in running through a set of samples on the X-ray equipment; their sources have not yet been identified.

A.14. Comparison of Angle and Energy Resolution Systems

Solid-state detectors for X-rays have been greatly improved, and the latest versions can resolve X-rays into fine energy bands. It has been suggested these detectors could be used for diffractometry instead of the normal practice of scanning through an angle with monochromatic X-rays (2). This would give the advantage that the whole spectrum would be received at one time; calculations suggested that the technique would be close to the technique now used in this laboratory.

An opportunity, by courtesy of Radionics Ltd., was found to test an Ortec high-resolution lithium-drifted silicon solid-state detector on the Philips X-ray equipment with a vertical goniometer, using a Northern Scientific multichannel analyzer.

A.14.1. Experimental technique

The energy resolution was compared with angle resolution diffractometry under as similar conditions as possible. The same diverging and receiving slits were used. The graphite crystal diffracted-beam monochromator (Philips part PW 1152) and scintillation detector were replaced by a scatter slit, Soller slits and the Ortec silicon solid-state detector, mounted on an elevating table.

Output from the solid-state detector and pre-amplifier, operated at liquid nitrogen temperatures, was amplified and counted on a Northern Scientific ADC and multichannel analyzer.

Three fixed diffraction angles were chosen based on the relationship between the energies of copper $K\alpha$ (from the tube) and silver $K\alpha$ (from the membrane filters used to collect the dust samples) radiations and the energies corresponding to the quartz and silver metal diffraction patterns.

Arrangement 1. The diffraction angle was set at $38.1°2\theta$ where the $CuK\alpha$ coincides with the first line in the diffraction pattern of

silver; the supporting filter is made from silver metal. The CuKβ almost coincides with the second line of silver. Fluorescence from iron and near elements can interfere with quartz.

Arrangement 2. The diffraction angle was set at 17.6°2θ where the AgKα coincides with the first silver diffraction line. This gives very little interference with the quartz 1,0,0; 1,0,1; 1,1,2; 2,0,2; and 2,1,0 lines. The arrangement might be improved by using a silver target tube.

Arrangement 3. The diffraction angle was set at 6.0°2θ where all the quartz diffraction lines occur at energies greater than the silver Kβ line.

A.14.2. Results

Some results from a pure quartz sample are shown in Table A.9. Arrangement 2 apparently gives the best results, and these are shown in Fig. A.5 to A.8. Figures A.5 to A.7 show comparisons between high and low quartz samples on both angle and energy resolution for the three main diffraction lines of quartz; Fig. A.8 shows

results obtained by energy resolution for the three quartz lines 1,1,2; 2,0,2; and 2,1,0.

The results show that the diffraction peaks are broader for energy than for angle resolution and that this is likely to introduce more difficulties from interference by other minerals. This was observed on samples of mine dusts known to contain minerals interfering with some of the quartz lines. Some gain in resolution might be obtained by improving the arrangement but as the diffraction line is only 1-1/2 times as broad as a fluorescence line there is not much room for improvement without an improved detector resolution. The detector used had a width of 300 keV at half height for CuKα radiation.

The energy resolution technique gives much lower peak height counts than the angle resolution technique but as it gathers all its data simultaneously rather than consecutively, this disadvantage is partly offset. The difference between the two as tested is about 1700:1. The energy resolution detector is smaller than the X-ray beam and the energy technique could probably be improved by a better choice of

Table A.9 - Results from pure quartz sample

| | Angle resolution | | Energy resolution | | | |
| | | | Set up 1 | Set up 2 | | Set up 3 |
	101	112	101	101	112	101
Diffraction angle °2θ	26.64	50.12	38.1	17.6		6.0
Diverging slit	1.0	2.0	1.0	0.5		0.25
Scatter slit °2θ	(1)		1.0	0.5		0.25
Receiving slit mm	0.56	0.156	0.156	0.156		0.156
Detector	scintillation		(2)			
Analysis	PHA		MCA			
Scanning	0.04°2θ steps		1024 channels, 0.05 keV/channel			
Channel width = d A	0.005	0.0014	0.03	0.011	0.0033	0.005
Width at 1/2 height = d A	0.025	0.009	0.22	0.085	0.03	0.11
Peak-background cps	2700	175	2.56	1.55	0.06	0.175
Area cps · d	68	1.6	0.56	0.132	0.0018	0.019
Peak-background	14.3	1.95	0.46	11.4	2.1	21

(1) Graphite monochromator is used; eliminates interference by fluorescence.

(2) Ortec 6-mm diam, 3-mm sensitive depth lithium drifted silicon.
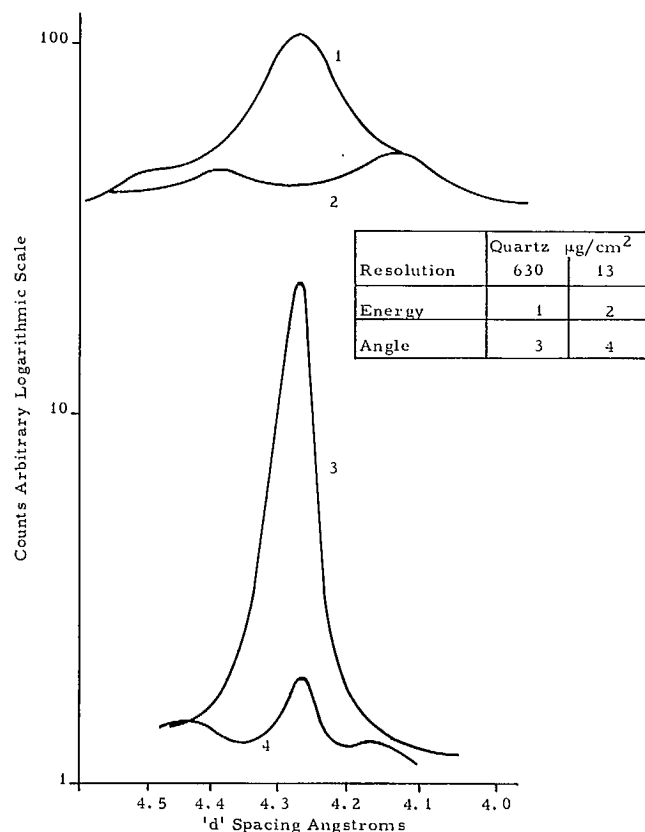
Fig. A.5 - Comparison of energy and angle resolution for samples with high and low densities of quartz — 1,0,0 diffraction line of quartz.

Fig. A.6 - Comparison of energy and angle resolution of samples of high and low densities of quartz — 1,0,1 diffraction line of quartz.

components making it comparable in sample time; however, there would be no advantage unless the resolution can be brought nearer to that of angle resolution.

The sensitivity for quantitative analysis of quartz using energy resolution was about one tenth of that using angle resolution. The lower sensitivity is due to the broader diffraction lines suffering from interference.

A.15. Data Printout

The data printout as originally supplied consisted of three seven-figure numbers separated by single blanks together with carriage return and line feed control signals for each count. The three numbers were the step number, the time, and the count. This format took 7 seconds for the printout on each step and was wasteful because only 15 of the 26 characters were used. Sample change could only be detected by carrying out logic computations on the step numbers. A second numerator was added to count samples and the format was changed so that one seven-figure number was made up of a two-figure sample number, a two-figure step number, and a three-figure preset count. The blanks were replaced by commas to simplify computer input processing. This reduced the number of characters per line to 18

	Quartz $\mu g/cm^2$	
Resolution	630	13
Energy	1	2
Angle	3	4
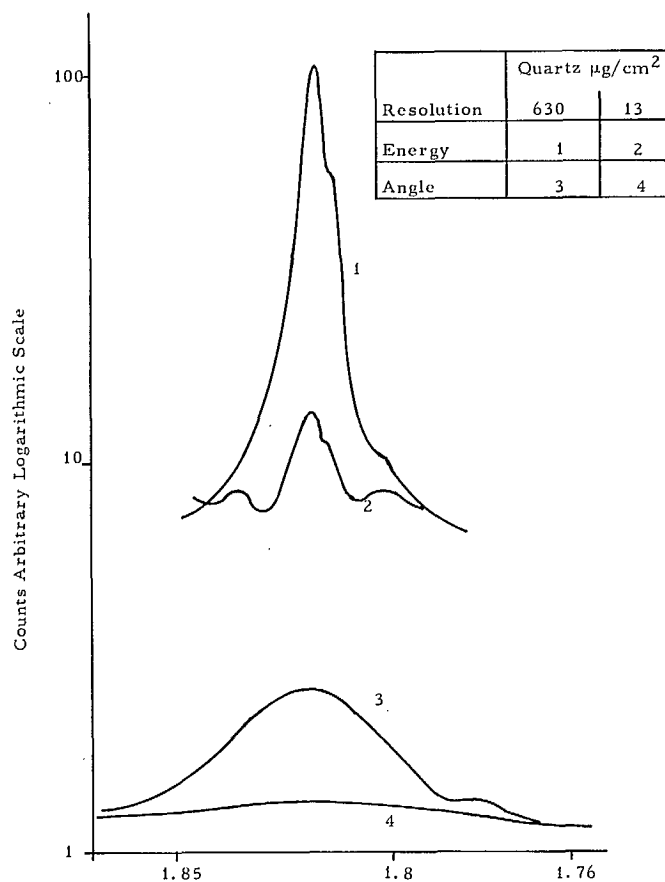
Fig. A.7 - Comparison of energy and angle resolution of samples with high densities of quartz — 1,1,2 diffraction line of quartz.
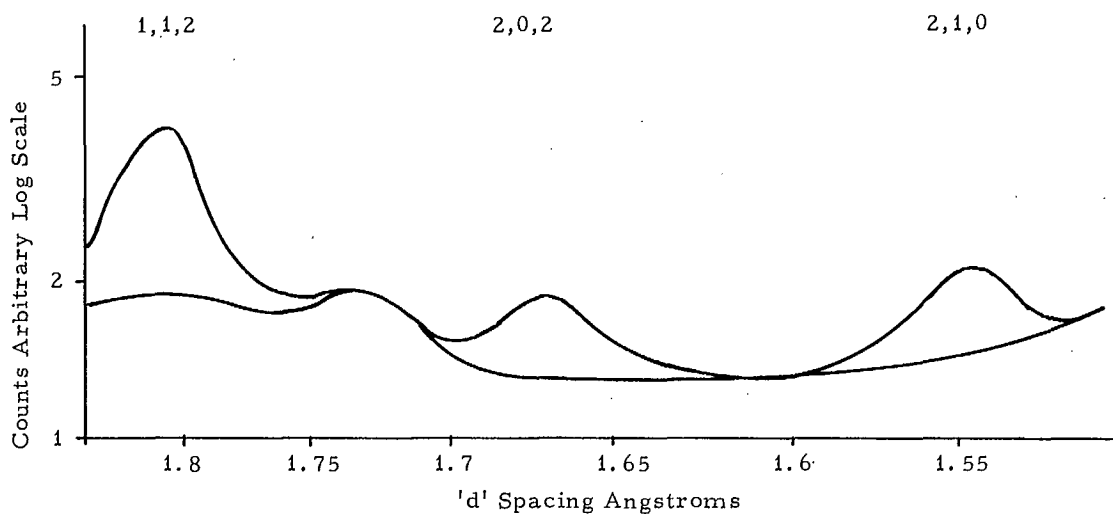
Fig. A.8 - Energy resolution chart for region covering the 1,1,2; 2,0,2 and 2,1,0 diffraction lines of quartz for samples with high and low quartz.

with a substantial saving in the time taken to transmit data to the computer.

A.16. References

1.   Jenkins, R. and Paoline, F.R. "An automatic divergence slit for the powder diffracto-meter"; Norelco Rep; 21:1:9-14; 1974.

2.   Giessen, B.C. and Gordon, G.E. "X-ray diffraction: new high speed technique based on X-ray spectrography"; Science; 159:3818:973; 1968.

APPENDIX B

CALIBRATION OF QUARTZ ANALYSIS

It was decided that the primary calibration of the X-ray analysis system would be carried out by collecting dust samples on filters from pure quartz dust clouds in conditions as closely as possible resembling field use. This would minimize any effect of particle size and systematic variations in particle deposition over the area of the filter and resultant errors in the proportion of quartz in the X-ray beam.

The first calibration was carried out on dust deposits collected on 25-mm diameter filters using Casella T13040 personal size-selecting gravimetric dust samplers (1).

B.1. Preparation of Pure Quartz Samples in Laboratory Dust Chamber

To calibrate the technique of determining respirable quartz in air down to the threshold limit value of 0.1 mg/m^3 of shift-period samples, it was necessary to prepare samples with as little as 0.05 mg of quartz. This quantity could not be weighed sufficiently accurately and the quantities of dust on the filters were determined indirectly.

A quartz dust cloud was prepared by continuous breakage and dispersion of silica sand (Ottawa, Illinois) into filtered air in the laboratory dust chamber using a twin-jet fluid energy mill. Samples were taken with four Casella personal samplers at 1.9-2.0 L/min and one Casella Hexhlett sampler at 50 L/min for various periods from 1 to 90 minutes (1). Filters from all the samplers in the longer runs were weighed and the ratios between the masses collected by the personal samplers and those by the Hexhlett were determined. Then, on the short runs, the masses of respirable dust collected by the Hexhlett were weighed and those on the personal samplers were calculated from these ratios.

The mass of quartz on the filters ranged from 0.04 to 3.3 mg, equivalent to a surface density of 10 to 850 µg quartz/cm^2.

B.2. Calibrations of Quartz Samples

Intensity measurements were made on the 101 quartz peak of samples collected by personal samplers in a pure quartz dust cloud using both copper and molybdenum Kα radiations. The results obtained are given in Table B.1 and are shown plotted in Fig. B.1 and B.2. Figure B.1 shows a plot of peak height against mass of quartz using a linear scale and Fig. B.2 shows the ratios of the peak height area to mass of quartz on the filter plotted against the mass of quartz. The logarithmic scale was chosen so that the shapes of the curves could be compared directly with one another.

The results show that the ratio of X-ray intensity to mass calculated from the mass of the 50-L/min Hexhlett samples of samples collected by the personal samplers decreases markedly for thin samples. This is presumably due to fine quartz either passing through or into the body of the 5-µm pore size silver membrane filters where it is screened from the X-rays. It is assumed that penetration decreases as the dust bed builds up and stops at 200 µg of quartz/cm^2. It is presumed that penetration is dependent on the mass of all dust collected and that a thin sample correction factor based on total respirable mass

Table B.1 - Calibrations of quartz samples (1,0,1 line) for copper and molybdenum Kα radiation

Mass of quartz µg/cm^2	Peak height C . sec^{-1}		Peak area C .°2θ . sec^{-1}		Signal/noise ratio	
	Cu	Mo	Cu	Mo	Cu	Mo
Samples collected by Casella personal sampler						
842	4700	774	1430	280	73	9.4
208	1198	194	357	66	28	3.4
121	690	110	210	37.4	17	2.3
99	545	83	156	26.4	14	1.6
52	244	36.5	72	12.6	6.5	0.8
33	137	21.4	47	7.0	4.3	0.5
22	88	14.6	29	4.6	2.3	0.45
10.5	41	6.6	13.4	2.0	1.1	0.17
10.5	39	6.3	13.6	2.1	1.2	0.16
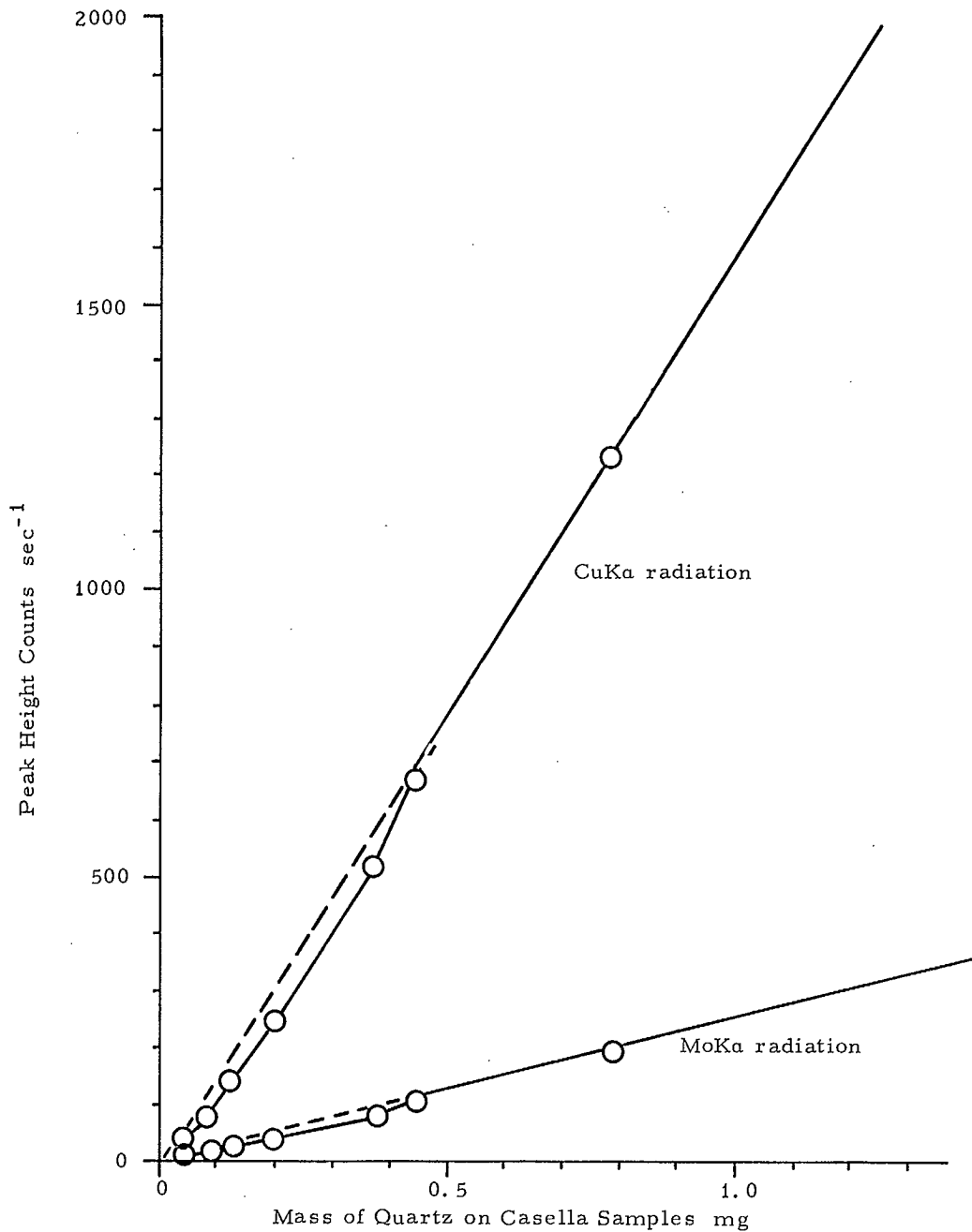
Fig. B.1 - Quartz calibration of X-ray with Casella samples.

can be applied. It can be expected this factor would depend on size distribution of the dust, penetration increasing with a finer size of quartz dust at the start of sampling but decreasing more rapidly as the bed of finer dust particles became less permeable. In practice, respirable-sized quartz shows little change in size distribution and total respirable dust tends to be finer in mines due to diesel particulates, and thus the correction factor would be overestimated, leading to a safe but small overestimate of quartz.
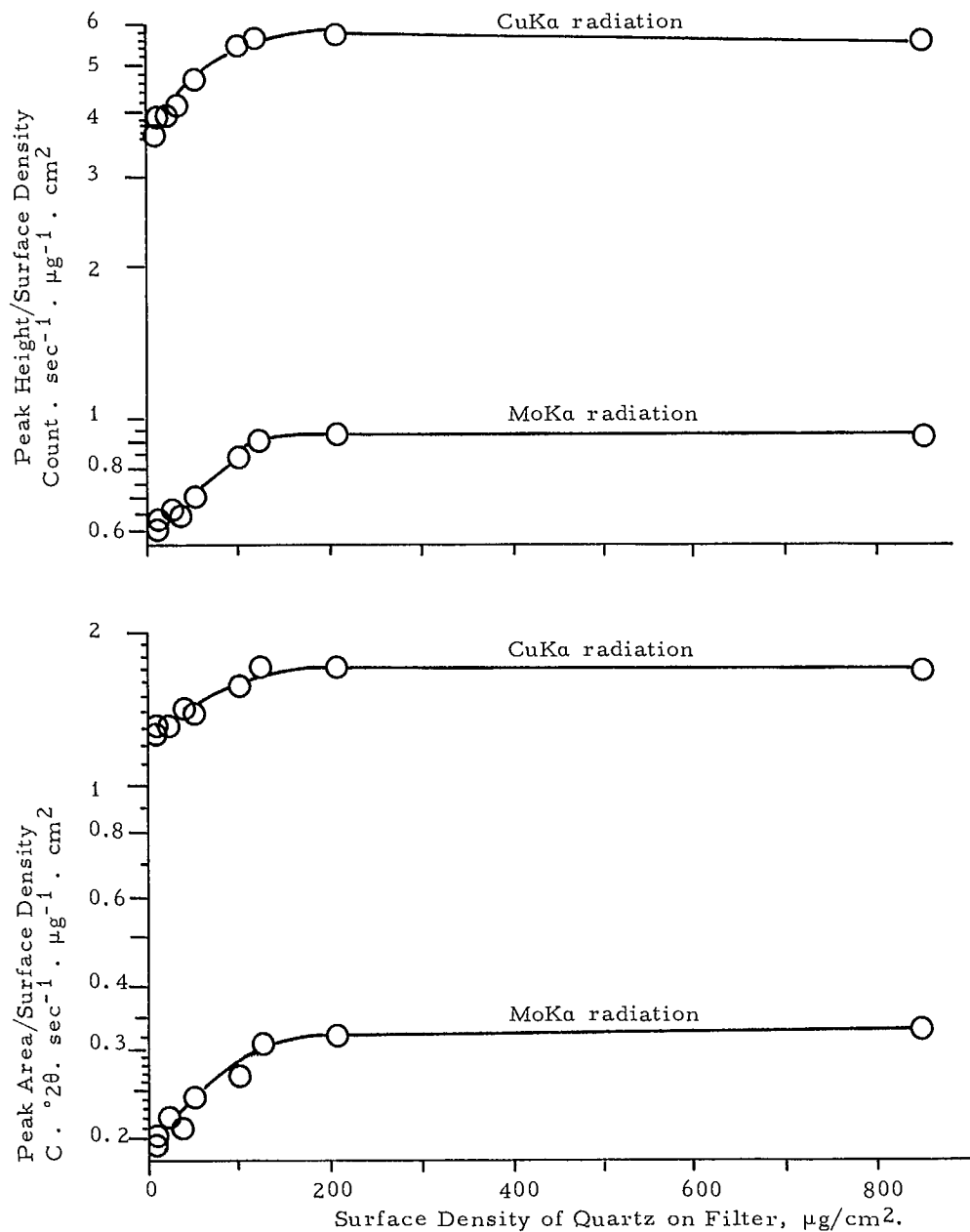
Fig. B.2 - Quartz calibration of X-ray with Casella samples.

B.3. Calibration of Other Dust Sampling Instruments Used in Elliot Lake Laboratory

A set of samples was collected in a pure quartz dust cloud using a number of dust samplers as listed below:

a)   2 Casella personal samplers, type 13040, airflow 2 L/min,

b)   2 modified Casella personal dust samplers with 37-mm diameter filter holders, airflow 2 L/min,

c)   1 open filter, 25 mm in diameter, airflow 1 L/min,

d)   1 open filter, 13 mm in diameter, airflow 1 L/min,

e)   a set of 7 horizontal elutriator size-
     selecting samplers operated with either 25-
     or 13-mm diameter filters at a flow rate of
     1 L/min.

Samples were also prepared from liquid suspensions which gave an even deposition of dust over the surface of the filter with the values given in Table B.2. It can be seen that the results are more variable than with airborne samples. In particular, the 1,0,1 line is stronger on the liquid dispersion than on airborne dust, suggesting that preferred orientation can occur.

The set of horizontal elutriator samplers was made with a range of airflow settlement area ratios to give measurements of particle size distribution in accordance with the technique proposed earlier (2). The X-ray intensity mass ratios are shown for the 1,0,1 quartz line on all instruments examined. Only measurements of reasonably dense samples have been included in this table to avoid the effect of lower intensity mass ratios on thin samples discussed previously.

Table B.3 shows there are appreciable differences in calibrating this range of dust samplers, most of which can be accounted for by

Table B.2 - Calibration of permanent quartz standards

Sampler description Filter size mm	Quartz line	Mass of quartz dust on standard expressed as equivalent on sample filter				13 mm
		22 mm diameter				
		St1	St3	St4	St5	St2
Casella personal sampler						
25	1,0,0	2.28[1]	3.55	7.4	5.56	--
	1,0,1	2.51	3.50	7.08	5.12	--
	1,1,2	2.51	3.63	8.01	5.78	--
37	1,0,1	5.9	8.23	16.6	12.0	--
Open filters						
25	1,0,1	2.87	4.01	8.1	5.85	--
13	1,0,1	1.52[2]	2.07[2]	4.4[2]	3.12[2]	0.765
HE[3](7.1 μm)						
25	1,0,1	2.89	4.03	8.15	5.90	--
HE(5.0 and 3.5 μm)						
25	1,0,1	3.04	4.22	8.53	6.17	--
HE(2.5 and 1.75 μm)						
13	1,0,1	--	--	--	--	0.72
HE(1.25 μm)						
13	1,0,1	--	--	--	--	0.93
25-mm liquid suspension	1,0,0	--	3.7	--	5.2	--
	1,0,1	--	2.6	--	3.9	--
	1,1,2	--	4.1	--	6.2	--
	2,1,1	--	4.7	--	7.4	--

1   This standard shows a fairly high variability, ±10%, in repeat calibrations on the 1,0,0 line due apparently to the low peak-to-background ratio.

2   This comparison was undertaken with a divergent slit large enough to cover the 22-mm dust deposit on the standard.

3   Horizontal elutriator samplers.

Table B.3 - Calibration of dust sampling instruments

Sampler description			X-ray intensity[1]	
Filter	Size selector		/Mass on	/Mass in
size	Type	Size 50%	filter	beam[2]
mm		Cut[3] µm		
37	Cyclone[4]	5	74	235
	Cyclone	5	68	216
25	Cyclone[5]	5	162	337
	Cyclone	5	172	358
	None	--	146	304
	HE[6]	7.1	145	302
	HE	5	139	290
	HE	4	138	2B7
	HE	3.5	139	290
	HE	1.25	74	154
13	None	--	232	249
	HE	7.1	247	265
	HE	5.0	255	274
	HE	3.5	256	275
	HE	2.5	245	264
	HE	1.75	245	264
	HE	1.25	190	204

1   X-ray intensity to mass ratios after correction
    for secular variation in X-ray intensity.

2   Calculated mass in the X-ray beam assuming even
    dust deposition over the active area of the
    filter.

3   Approximate aerodynamic size (diameter of unit
    density sphere with same falling speed) at which
    50% of the particles are collected in the size
    selector and 50% pass through to the filter.

4   Modified Casella personal gravimetric sampler
    with 37-mm filter holder.

5   Casella personal gravimetric sampler.

6   Laboratory set of horizontal elutriator samplers.

two factors: uneven distribution of quartz over the surface of the filter — the Casella personal samplers show a visibly thicker deposit in the centre than at the edges, and the effect of quartz particle size which will be described in the next section.

B.4. Effect of Quartz Dust Size

The horizontal-elutriator size-selecting samplers remove some of the coarser dust particles before they collect on the filter. This set of samplers has a range of ratios of settle-ment area/airflow and thus rejects different fractions of the dust (2). The results are shown in Table B.4. The penultimate column shows the results of calculations for each increment of dust as the elutriators are steadily decreased in area/flow ratio and larger particles pass through and collect on the filter. The particle size range in which most of the increment of dust occurs is shown in the last column.

It can be seen that particle size has some effect on the intensity/mass ratio. The effect is not the same on both sizes of filter

Table B.4 - Effect of particle size on diffracted intensity
of X-rays from quartz

50% size cut aerodynamic size μm	Mass on filter relative	X-ray intensity, arbitrary units	X-ray intensity/ Mass of qtz in beam		Particle size range of increments, μm
			Total	Each dust increment	
25-mm filters					
1.25	0.104	7.7	154		0.5-1.5
				308	1-4
3.5	0.42	54.5	270		
				334	3-6
5.0	0.60	83.5	290		
				342	4-8
7.1	0.78	113	302		
				322	6-10
Open	1.0	147	306		
13-mm filters					
1.25	0.104	20	207		0.5-1.5
				326	1-2
1.75	0.16	37	249		
				247	1.5-3
2.5	0.31	76	264		
				313	2-4
3.5	0.42	108	276		
				269	3-6
5.0	0.60	153	274		
				239	4-8
7.1	0.78	193	266		
				191	6-10
Open	1.0	232	249		

and is presumably confused with the effects of uneven deposition on the area and with different thicknesses. The results in Table B.4 suggest that the X-ray intensity/mass ratio is greatest for 3- to 8-μm aerodynamic size particles with a sharp decrease for particles smaller than 1 μm and a slow decrease for larger ones.

B.5. References

1. Casella Ltd.; London, U.K.; manufacturer.

2. Knight, G. "A simple method for determining size distribution of airborne dust by its settling velocity"; Amer Ind Hyg J, 33:8:526-532; Aug. 1972.

APPENDIX C

COMPUTER PROCESSING OF DATA

The data from step scanning over peaks is collected on punched paper tape and transmitted by telephone to a shared computer service in Toronto. Kemper and Van Kempen's program for γ-ray spectroscopy is the basis for determinating areas of the X-ray diffraction peaks (1). It was necessary to make minor modifications and prepare a program for reading data input and separating it into samples. In using this program it became apparent that some major modifications were desirable, as follows:

1.   The original program had a set value of 2 for the "width". This was used for finding a peak by determining whether the count in channel N was significantly greater than counts in both channels N-2 and N+2. This could fail to find quartz peaks of low but significant intensity. The program was modified to make the width a variable input and a search was conducted for a peak which was the highest in a range rather than only being compared with a set channel on either size.

2.   The program attempted to separate doublets such as the $K\alpha_1$ $K\alpha_2$ peaks of the high angle quartz lines into two areas and then obtained an unsatisfactorily high background between them. This was solved by using the variable "width" entry to indicate how far the program should scan over a secondary peak and decide whether it is separate or not. Values up to eight have been used for integrating close triplets (2°2θ) in some minerals.

3.   The program originally computed the significance of a count relative to horizontal background. It was found that fewer errors occurred due to adjacent peaks if a linear sloping background was assumed. The first estimate of the slope is obtained from the first six and the last six counts in each sample. If the background slope found when integrating over the peak differs significantly from the first estimate, an error message is produced and the area can be redetermined with a new value for the slope.

4.   The modified program also calculates the mass of substance in the sample from both the net peak height and the area by comparing with the values obtained on the standard. If the two values of mass are not close it is indicative of some form of interference or distortion in the filter. Distortion can be checked by visual inspection and should be noted when unloading the filters from the magazine.

The program used is in BASIC language and is given on the next few pages. The program has provisions for correcting input data on-line when alphabetic or non-type characters are introduced as quite frequently happens in data transmission to the computer in Toronto. Some redundant information is returned to Elliot Lake to assist in checking the accuracy of the input data used by the computer. The program could be made available on punched paper tape in an updated version.

C.1. References

1.   Kemper, A., and Van Kempen, "A simple program for high resolution gamma ray spectroscopy"; J Rad Chem, 6:461-475; 1970.

```
 620 X(I)=(P1*SQR(B)+0.5)/T
 630 C(I)=B/T
 640 T2=T2+T
 650 IF I=1 GO TO 780
 660 IF K(I)=K(I-1)+1 GO TO 780
 670 REM CHECK FOR MISSING STEP.  TO CONTINUE AS IS ENTER 0  TO INTERPOLA
TE 1 STEP ENTER 1.  IF THE MISSING STEP IS ON THE PEAK IT MAYBE NECESSAR
Y TO RERUN THE SAMPLE ON THE XRAY.
 680 PRINT 'STEP MISSING BETWEEN';K(I-1);'AND';K(I);'.  ACTION';
 690 INPUT K7
 700 IF K7=0 GO TO 780
 710 K(I+1)=K(I)
 720 K(I)=K(I)-1
 730 X(I+1)=X(I)
 740 X(I)=(X(I-1)+X(I))/2
 750 C(I+1)=C(I)
 760 C(I)=(C(I-1)+C(I))/2
 770 I=I+1
 780 NEXT I
 790 GOTO 810
 800 K6 =1
 810 N7=I-1
 820 IF N7<(2*K1+7) GOTO 230
 830 T1=T2/N7
 840 REM            BACKGROUND SLOPE
 850 X3=-(C(2)+C(3)+C(4)+C(5)-C(N7-1)-C(N7-2)-C(N7-3)-C(N7-4))/(N7-6)/4
 860 X4=0
 870 REM           FIND SIGNIFICANT PEAK N4 BY COMPARING WITH STEPS A
         SEARCH WIDTH EITHER SIDE
 880 X2=X3
 890 FOR N=(N4+K1) TO (N7-3-K1)
 900 FOR I=K1+1 TO K1-1 STEP-1
 910 IF C(N)>C(N-I)+X(N) GOTO 940
 920 NEXT I
 930 GOTO 970
 940 FOR I=K1+1 TO K1-1 STEP-1
 950 IF C(N)>C(N+I)+X(N) GOTO 990
 960 NEXT I
 970 NEXT N
 980 GOTO 2170
 990 I1=N-K1+1
1000 F=0
1010 FOR N=I1 TO I1+2*K1-1
1020 IF C(N)<F GOTO 1050
1030 F=C(N)
1040 N4=N
1050 NEXT N
1060 REM           FIND PEAK SHOULDERS N3 AND N5
1070 FOR N=N4+3 TO N7-K1
1080 IF C(N+K1)>=(C(N)-X(N)+K1*Y2) GOTO 1100
1090 NEXT N
1100 N5=N
1110 FOR N=N4-3 TO K1+1 STEP -1
1120 IF C(N-K1)>=(C(N)-X(N)-K1*Y2) GOTO 1140
1130 NEXT N
1140 N3=N
1150 REM           DEFINE RIGHT BACKGROUND   N5 TO N6
 110 REM    PROGRAM "GKXRA" ; ANALYSIS OF XRAY DIFFRACTION DATA
 120 DIM K(100),C(100),X(100)
 130 K6 =0
 140 D2=0
 150 PRINT'ENTER PROBABILITY,SEARCH WIDTH;PEAK HEIGHT ,PEAK AREA AND MASS
OF STANDARD';
 160 INPUT P1,K1,H5,S5,N5
 170 OPEN 1,'XRAY2',INPUT,LINE
 180 ON EOF 1 GOTO 800
 190 ON ERR GOTO2200
 200 L1=100
 210 IF K6=1 GOTO 2220
```

```
220 N4=4
230 T2=0
240 K4=K5
250 REM            READ,CORRECT AND TRANSLATE INPUT DATA AND SEPARATE INTO
    SAMPLES
260 FOR I=1 TO 100
270 IF D2 >0 GOTO 310
280 GET L
290 IF L=L1 GOTO310
300 PRINT 'ERROR IN LINE NO ':L; ' CHECK XRAY2 ?'
310 D2 =0
320 ON ERR 1 GOTO 350
330 GET A2
340 GOTO 400
350 GET A$
360 REM CHECK FOR ERROR IN SAMPLE STEP NO. TIME COMPLEX 'A'.  IF ERROR P
RINTOUT INCLUDES ONLY A ENTER 0,A,0   IF THE COUNT IS INCLUDED IN THE ER
ROR PRINTOUT ENTER 1,A,COUNT
370 PRINT 'A=';A$;' PREVIOUS A=''A.' REVISION';
380 INPUT D1,A2,B1
390 IF D1>0 GOTO 470
400 ON ERR 1 GOTO 430
410 GET B1
420 GOTO470
430 GET  B$
440 REM CHECK FOR ERROR IN THE COUNT.  IF ONLY THE COUNT IS IN ERROR ENT
ER 0,COUNT  IF THE ERROR PRINTOUT INCLUDES THE FOLLOWING LINE NUMBER ENT
ER 1,COUNT.
450 PRINT 'COUNT=';B$;' A=';A;'PREVIOUS COUNT=''B;' REVISION';
460 INPUT D2 ,B1
470 A=A2
480 L1=L+10
490 B=B1
500 A1=A/100000
510 K5=INT(A1)
520 IF K5<>K4 GOTO 810
530 A1=(A-100000*K5)/1000
540 K(I)=INT(A1)
550 A1=A-100000*K5-1000*K(I)
560 T=INT(A1)
570 IF T>0 GOTO 620
580 T1=T2/I
590 REM CHECK FOR ERROR IN THE COUNTING TIME
    ' PRINT 'TIME IN ERROR';L;A;B;'PREVIOUS';T1;C(I-1);' ENTER TIME';
      NPUT T
1730 IF S1<.5 GOTO 2160
1740 S2=SQR(T+((N5-N3+1)**2)*(B1/K3+B2/K2))/4/S1/SQR(T1)*100+0.005
1750 H=C(N4)-(B1*(N4-N2)+B2*(N6-N4))/(N6-N2)
1760 M1=(H/H5)*M5
1770 M2=(S1/S5)*M5
1780 PRINT USING 1790 K4,K(N4),C(N4),K(N3),K(N5),S2,B2,K2,B1,K3,X2,Y4,H,
M1,S1,M2
1790: ### *### ######.# ### ### ####.##*#####.# ## #####.# ## ####.## #
#     NET HEIGHT######.# MASS####.### AREA#######.# MASS####.###
1800 REM OUTPUT GIVES SAMPLE NO;PEAK STEP,HEIGHT AND REGION;AREA SD; BAC
KGROUND VALUE &NO STEPS,LEFT & RT:SLOPE & NO. OF LOOPS
1810 REM            CHECK BACKGROUND SLOPE
1820 X7=(B1-B2)/(N5+N6-N2-N3)*2
1830 Y6=ABS(X7-X2)
1840 IF Y6 <(X(N2)+X(N6))/20 GOTO1940
1850 REM CHECK TO SEE IF THE BACKGROUND SLOPE HAS CHANGED SIGNIFICANTLY
DURING THE CALCULATION.
1860 REM TO CONTINUE ON TO THE NEXT PEAK ENTER 0,0
1870 REM TO RECALCULATE THE PEAK HEIGHT AND AREA ENTER 1,TRUE WHERE THE
VALUE OF TRUE IS ROUNDED OFF TOWARD SLOPE
1880 PRINT 'SLOPE= ';Y2;'TRUE= ''X7;' 0,0 OR 1,TRUE';
1890 INPUT X5,X7
1900 IF X5=0 GOTO1930
```

```
1910 X2=X7
1920 GOTO1160
1930 REM  TEST PEAK WIDTH AND LIMIT IT IF NECESSARY
1940 J1=INT(12.5*H*(N6-N2)/(B1*(N4-N2)+B2*(N6-N4)))
1950 J2=0
1960 REM LIMIT THE EXTENT OF THE RIGHT EDGE OF THE PEAK.
1970 IF N5<=N4+4+J1 GOTO 2040
1980 J2=1
1990 N5=N4+4+J1
2000 J9=2*N5-N3+3
2010 IF N6<J9 GOTO2040
2020 N6=J9
2030 REM LIMIT THE EXTENT OF THE LEFT EDGE OF THE PEAK.
2040 IF N3>=N4-4-J1 GOTO2100
2050 J2=1
2060 N3=N4-4-J1
2070 J8=2*N3-N5-3
2080 IF N2>J8 GOTO 2100
2090 N2=J8
2100 IF J2=0 GOTO 2140
2110 H1=H*(N6-N2)/(B1*(N4-N2)+B2*(N6-N4))
2120 REM NOTIFY USER THAT THE PEAK WIDTH HAS BEEN LIMITED.
2130 PRINT 'WIDTH LIMITED; H1=';H1
2140 IF J2=0 GOTO 2160
2150 GOTO 1550
2160 GOTO 860
2170 PRINT USING 2180 K4,L1,C(1),K(1),C(N7),K(N7),T1
2180: ###    NO MORE PEAKS   LAST LINE IS###### #####.# ## ####.# ##T@##
#.#  ***
2190 GOTO 210
2200 PRINT 'ERROR TYPE  ';ERM;'  IN SAMPLE ENDING ON LINE  ';L1
2210 GOTO 210
2220 CLOSE 1
2230 END


1160 X4=X4+1
1170 F=0
1180 FOR N=N5 TO 2*N5-N3+3
1190 F=F+C(N)-X2*(N-N5)
1200 Z=F/(N-N5+1)
1210 IF N+1>N7 GOTO 1260
1220 IF Z>=(C(N+1)-X(N+1)-X2*(N-N5+1)) GOTO 1250
1230 IF N+2>N7 GOTO 1250
1240 IF Z<(C(N+2)-X(N+2)-X2*(N-N5+2))GOTO1260
1250 NEXT N
1260 N6=N
1270 F=0
1280 FOR N=N6 TO N4+1 STEP -1
1290 F=F+C(N)+(N6-N)*X2
1300 Z=F/(N6-N+1)
1310 IF Z>=C(N-1)-X(N-1)+X2*(N6-N+1) GOTO 1330
1320 IF Z<C(N-2)-X(N-2)+X2*(N6-N+2) GOTO 1340
1330 NEXT N
1340 N5=N
1350 REM        DEFINE LEFT BACKGROUND N2 TO N3
1360 F=0
1370 FOR N=N3 TO2*N3-N5-3 STEP -1
1380 F=F+C(N)+X2*(N3-N)
1390 Z=F/(N3-N+1)
1400 IF N<2 GOTO 1450
1410 IF Z>=(C(N-1)-X(N-1)+X2*(N3-N+1)) GOTO1440
1420 IF N<3 GOTO 1440
1430 IF Z<(C(N-2)-X(N-2)+X2*(N3-N+2)) GOTO 1450
1440 NEXT N
1450 N2=N
1460 F=0
1470 FOR N=N2 TO N4-1
```

```
1480 F=F+C(N)-X2*(N-N2)
1490 Z=F/(N-N2+1)
1500 IF Z>=(C(N+1)-X(N+1)-X2*(N-N2+1)) GOTO 1520
1510 IF Z<(C(N+2)-X(N+2)-X2*(N-N2+2)) GOTO 1530
1520 NEXT N
1530 N3=N
1540 REM              CALCULATE BACKGROUND
1550 K3=N6-N5+1
1560 F=0
1570 FOR N=N5 TO N6
1580 F=F+C(N)
1590 NEXT N
1600 B1=F/K3
1610 K2=N3-N2+1
1620 F=0
1630 FOR N=N2 TO N3
1640 F=F+C(N)
1650 NEXT N
1660 B2=F/K2
1670 REM              CALCULATE AND PRINT RESULTS
1680 T=0
1690 FOR N=N3 TO N5
1700 T=T+C(N)
1710 NEXT N
1720 S1=T-(B1*(N5-N2)+B2*(N6-N3))*(N5-N3+1)/(N6+N5-N3-N2)
```

APPENDIX D

PREPARATION OF ROCK SAMPLES FOR ANALYSIS

During these studies, samples of rock dust were prepared for comparing with the samples of airborne dust to assist in understanding the compositional changes and interference effects. A simple liquid dispersion technique was developed to give even deposition over the filter and was found to give reasonable agreement between X-ray analysis for quartz and the free silica analyses obtained from mine sources. It is realized that this simple technique could suffer errors from two sources — preferred orientation and mineral segregation by size in the settling process, but to date these have not appeared to give rise to significant error in quartz analysis. However, other minerals can give markedly different intensity ratios for the various diffraction lines when prepared by this method compared with the preparation method for standards; mixing with resin and setting in a recess in the sample holder. No efforts have yet been made to solve these problems; their extent is shown in Table D.1 where the calibrations for standards of various pure minerals are given.

The liquid dispersion technique gives an even dust deposit and lower X-ray intensity/mass ratios than samples collected by the personal dust sampler, and thus a different calibration is required as was given in Table B.2.

Preparing rock samples for X-ray diffraction analysis requires the following steps:

1. Handgrind 0.1 ± 0.01 gm of dust in a pestle and mortar under ethyl alcohol for 10 to 15 minutes.

2. Wash the groundrock into a 50-ml bottle with alcohol and make up to about 40 ml.

3. Place a tared 25-mm diameter 0.8-μm pore-size silver membrane filter in a specially made filter funnel, 22 mm internal diameter and 50 mm high on a smooth backing plate and seal with an O-ring.

4. Place distilled water to a depth of 25 mm in the filter funnel and nearly fill with alcohol. The use of a denser solvent minimizes density convection and uneven deposition on the filter.

5. Shake up the ground material in the bottle and let settle for one minute.

6. Remove 2 ml of suspension from near the top of the bottle using a pipette and transfer it to the funnel.

7. Turn on vacuum under funnel.

8. Remove vacuum when funnel has drained, i.e., do not wash down.

9. Dry and weigh the filter.

It is essential that even dispersion be obtained over the surface of the 22-mm dust deposit on the filter and this is difficult to achieve with dense minerals. An alternative technique using 13-mm diameter filters has been tried, but samples that are heavy enough to weigh accurately require substantial corrections for absorption. Although these can be obtained from measurements of the intensity of the silver 1,1,1 line through the dust deposit and from the back of the filter, allowance has to be made for the uncovered portion of the filter surrounding the dust deposit as well as for variations in X-ray intensity over the dust deposit. Calibration is complex and time-consuming.

Table D.1 - Calibration of pure mineral standards:
usable diffraction lines

	d-spacing Å	Calibrated mass on standard, mg			d-spacing Å	Calibrated mass on standard, mg
Sulphides				**Carbonates**		
Chalcopyrite				Dolomite		
	3.03	3.8			2.88	2.7
	1.85	5.4			1.80	0.6
	1.59	6.5			1.78	1.1
	1.08	6.9			1.39	3.0
Pentlandite		St.I	St.III*	Siderite		
	5.84	0.42			3.60	4.7
	3.04	0.47	0.68		2.80	2.8
	1.94	0.99	0.58		2.14	5.1
	1.78	0.72	0.71		1.97	3.2
	1.31	0.53	0.76		1.74	4.0
Pyrite					1.36	5.5
	3.12	2.3		**Silicates**		
	2.70	1.8		Albite	6.39	1.45
	2.42	2.6			4.03	3.9
	2.21	2.9			3.78	3.6
	1.92	2.2			3.67	5.0
	1.63	2.8			3.19	1.9
	1.04	2.3		Chlorite		
Pyrrhotite					14.0	4.4
	3.00	2.5			7.0	2.75
	2.65	4.4			4.7	2.0
	2.08	4.0			3.5	1.8
	1.73	4.2			2.85	2.8
	1.62	3.9			2.0	3.5
Sphalerite	3.12	3.8		Labradorite		
	1.91	3.9			6.4	4.2
	1.63	4.5			4.0	3.2
Oxides					3.6	2.3
Magnetite	4.84	2.2		Microcline		
	2.96	2.2			4.2	4.0
	2.53	2.6			3.77	1.6
	2.09	2.1		Muscovite		
	1.71	3.2			10.0	1.7
	1.61	3.2			5.0	1.8
	1.12	3.3			4.5	4.3
	1.09	3.3			3.32	1.5
Uraninite					3.2	1.9
	3.15	3.5			3.0	3.0
	2.73	5.4			2.56	3.2
	1.93	5.3			2.13	2.9
	1.65	5.3		Pyroxene		
	1.58	3.8			3.04	4.8
	1.25	5.2			2.5	3.5
	1.11	4.8			1.62	5.8
	1.05	6.1				
	0.93	7.3				

*More than one attempt at preparing standards was required for some materials.
It so happened there were two good standards for pentlandite.

APPENDIX E

VARIETIES OF FREE SILICA

Free silica, or silicon dioxide, SiO_2, occurs in a variety of crystalline and non-crystalline polymorphs. All these forms appear to be substantially more hazardous to health than most other minerals and must be considered in assessing respirable dust. The polymorphs of silica with their occurrences and properties have been described in detail [1]. Free silica occurs chiefly in the form of quartz. Crystobalite and tridymite occur occasionally in younger rocks. Semi-amorphous forms such as opal and amorphous forms such as glasses can be found in nature. Quartz occurs in many varieties depending on origin and impurities.

Because of the complexity and variety of free silica in nature it is desirable to check the X-ray response to many forms rather than to compare all samples with a particular variety.

The Geological Survey of Canada and other sources supplied a number of mineral samples of nearly pure quartz in a variety of forms as well as samples of crystobalite and pure synthetic tridymite. One sample of crystobalite was scraped off an obsidian matrix. Samples for X-ray analysis were prepared using the technique described in Appendix D. The minerals are described in Table E.1 and the relative X-ray intensities compared with the standard materials used for each crystalline form are given in Table E.2.

Dana classifies quartz into two main classes — "coarse crystallized" and "fine crystalline to dense" [1]. Samples 1 and 2 are examples of the first class and are in very close agreement. Samples 3 to 11 are fine crystalline to dense varieties. Sample 3, novaculite, shows good agreement with the coarse crystalline varieties except for the strongest quartz line, 1,0,1, which is about 20% lower in intensity. The reduction on this one line is also found on the Jasper sample. The other fine crystalline varieties, 4 to 11, show generally weaker intensity/mass ratios and variations in intensity between the diffraction lines. Jasper is the

Table E.1 - Description of free silica samples

Code No.	Description	Origin
1	Laboratory 'standard' quartz	
	Silica sand	Ottawa, Illinois
	Quartz varieties	
2	Massive white	Elliot Lake, Ontario
3	Novaculite	Hot Springs, Arkansas
4	Jasper	Pink Lake, P.Q.
5	Chalcedony	Kamloops Lake, B.C.
6	Chalcedony	Tranquille Lake, P.Q.
7	Chalcedony	Red Deer, Alta.
8	Agate centre	Western U.S.A.
9	Agate edge	Western U.S.A.
10	Flint	Dover Cliffs, U.K.
11	Chert	Mogul mine, Eire
12	Prepared respirable quartz DQ12	Dr. Robock, Germany*
13	Prepared respirable quartz GQ12	Dr. Robock, Germany*
14	Crystobalite	Valleyview, Alta.
15	Crystobalite in obsidian	Millar County, Utah

*See reference 2.

Table E.2 - X-ray intensities of silica varieties

Code		X-ray diffraction line			
		1,0,0	1,0,1	1,1,2	2,1,1
	Quartz Intensity[1]/mass ratio for each variety compared with Type 1				
2	Massive white[2]	1	1	1	1
3	Novaculite	1.04	0.82	0.97	1.03
4	Jasper	0.74	0.61	0.71	0.80
5	Chalcedony	0.62	0.60	0.86	0.76
6	Chalcedony	0.39	0.57	0.68	0.54
7	Chalcedony	0.55	0.67	0.79	0.75
8	Agate centre	0.52	0.65	0.81	0.65
9	Agate edge	0.53	0.64	0.79	0.66
10	Flint	0.62	0.65	0.81	0.79
11	Chert	0.63	0.59	0.81	0.81
12	Prepared	--	0.72	0.50	0.57
13	Prepared	--	0.74	0.62	0.62
	Crystobalite Intensity/mass ratio for 15 compared with 14				
15		0.79	0.36	0.40	0.44

1 X-ray intensity determined as area of the diffraction peak.
2 Within ±5% on three samples.

only material in this group reputed to have more than 10% impurities — non-quartz material — which was confirmed by the X-ray scan. If allowance is made for the amount expected, results are close to those obtained for Novaculite. The chalcedonies, agates, flint and chert, although reputedly composed of more than 90% quartz, may contain inclusions of impurities (1). However, only in the case of chert is sufficient crystalline impurity indicated by X-ray diffraction scans to account for the lower intensity/mass ratio.

It appears that the 1,1,2 line gives the highest and most consistent estimate of the fine-grained varieties, but this is difficult to apply because of the effects of interference.

Samples 12 and 13 are of quartz dust prepared by grinding and elutriation to have a particle size of less than 5 μm and are intended for biological experiments on silicosis. These show low X-ray intensity/mass ratios which may be attributed to small particle size, surface de-crystallization or impurities. Examination of industrial products prepared in Canada from massive white quartz suggested that the sericite intensities found in it were due to an impurity of less than 1% in the ore being concentrated into the fine fraction. It formed about 30% of the dust less than 2 μm in size as determined by the non-quartz discrete lines in the X-ray diffraction pattern. While the concentration of silicate impurities into the fine DQ12 fraction of the German quartz sand would be expected, this is not confirmed by the German analyses or by CANMET X-ray diffraction scans.

Two samples of crystobalite were examined and found to have large differences in the X-ray intensity/mass ratios. This is believed due to the inclusion of obsidian in sample 15 because of difficulties in separation.

A sample of tridymite was found to give a complex pattern with low intensity/mass ratios;

a much simpler pattern with much higher ratios should be found if it is heated above the phase change at 163°C to form high tridymite and thus a heated specimen holder is required for analyzing airborne dust containing tridymite (3).

This very limited study has demonstrated that large differences in X-ray intensity/mass ratio of up to 2:1, can arise with different samples of quartz. Although this is partly due to impurities, there seems to be a remaining real effect possibly as great as 40%. This needs to be borne in mind in considering the health hazard due to airborne dust. Most, but not all, occurrences of significant quantities of quartz in airborne mine dust arise from coarse crystalline sources and it is fortunate that the X-ray diffraction method gives a reasonable consistent assessment. Fine crystalline varieties of quartz can occur in significant proportions in some mines and the possibility of underestimating the quartz content using X-ray diffraction should be considered.

E.1. Conclusions

1. There are differences between X-ray intensity/mass ratios for different varieties of quartz.
2. Coarse crystalline quartz is most common

and in most cases should be used for calibration of the X-ray equipment.

3. Special studies should be undertaken for each mine with significant quantities of fine crystalline quartz, i.e., chert or other silica varieties. These studies should measure the X-ray intensity/mass ratios and the purity of hand picked samples of the purest possible free silica.

4. Because of uncertainties about impurities in fine crystalline quartz and their biological effects it is suggested that fine crystalline quartzes be expressed in terms of equivalent coarse crystalline quartz as given by the analytical method.

E.2. References

1. Frondel, C. "Dana's system of mineralogy"; III; Wiley, New York; 1962.

2. Robock, K. "Standard quartz DQ12<5 μm for experimental pneumoconiosis projects in the Federal Republic of Germany"; Ann Occ Hyg; 16:63-66; 1973.

3. Borg, I.Y. and Smith, D.K. "Calculated X-ray powder patterns for silicate minerals"; Geol Soc of Am; Boulder, Colorado; 1969.

APPENDIX F

CALIBRATION OF CHARACTERISTICS OF SIZE SELECTIVE
DUST SAMPLERS

During these studies it was found that commercial dust samplers intended to measure respirable dust to the same specification, could give significantly different estimates of concentration under certain test conditions as summarized in Table F.1 (1). These were traced to a number of causes such as variations in dimensions and filter holders and it was concluded that calibration of the size selection characteristics of the completely assembled sampler rather than its size selection component alone is essential.

The basic requirements of any measuring instrument are accuracy, repeatability and reliability. For two-stage dust sampling instruments intended to simulate the collection of dust in the two main regions of the lungs, one of the major factors is performance of the size selector in separating the dust into two parts. Three specifications for the size selector have been set down by the British Medical Research Council (2,3), by the U.S. Atomic Energy Commission (4), and by the American Conference of Governmental Industrial Hygienists (5) — a modification of the second specification.

It has been shown that the theoretical difference between these three specifications would be about 20% in most polydisperse industrial dust clouds (6,7). This is less than the difference between individual persons or for one person using different breathing patterns.

The first specification has the advantage for reproducibility of specifying a size selection curve based on a calculable physical process horizontal elutriation, and approximately to a lung curve (8). The other two are based on a mean lung curve to which the size selection curve of real instruments can only be approximately matched by a difficult and time-consuming laboratory calibration. Size selective sampling has been reviewed (9,10). An instrument for use

with the first specification has been adopted as a standard in both the U.K. (11) and the U.S.A. (12, 13).

The horizontal elutriator size selector, however, has to be used in a position close to horizontal and is not suitable for personal sampling. Cyclone size selectors can be used in any position and although they do not give the same curve as a horizontal elutriator, instruments fitted with them can be adjusted to indicate approximately the same respirable dust concentration (14). This approach should give more reproducible measurements than using a mean factor to correct from one size selection curve to another in dust clouds of differing size distribution as has been done in the U.S.A. (12,15). The latter procedure has been criticized as giving a very poor prediction of the concentration measured by the instrument on which the dust standard is based (15).

A second important criterion is the flow rate through the dust sampling instrument. With the horizontal elutriator, correct flow rate is very important as a 10% increase in flow leads to a 20% increase in mass of dust collected on the filter. With a cyclone, flow control is not as important because a 10% increase in flow has hardly any effect on the mass collected. This is because of the compensating effects of flow rate and collection efficiency of the cyclone (14). Of course, in very fine dust clouds the mass collected is proportional to flow rate for both types of size selector.

Most small air samplers use battery-powered single action pumps producing a pulsating airflow that affects the size selection characteristics (15) and indication of airflow by a taper tube flowmeter which tends to read the root mean square rather than the average flow. It is thus desirable that the airflow in all instruments should be sufficiently smooth to give a negligible error in size selection and flowmeter reading which are supplied by manufacturers with a calibration based on smooth airflow. The pulsating airflows from single action pumps can be

Table F.1 - Performance of size selector - dust sampler

Size selector	Dust sampler	Flow L/min	Code[1]	Relative[2] respirable dust concentrations
10-mm nylon cyclone	Lab A-E	1.7	C	0.74 - 0.84
	F	1.7	C	0.82
	F	1.7	PS	0.74
	Man 1	1.7	P	0.63
	Man 2 A	1.7	P	0.49
	" "	1.7	PS	0.67
	" B	1.7	P	0.41
	" "	1.7	PS	0.56
	" "	1.7	C	0.55
	" "[3]	1.7	PS	0.79
	" "	1.7	C	0.81
	" "[4]	1.7	PS	0.77
	" "	1.7	C	0.79
3/8-in. metal cyclone	Man 3 A	2.0	PS	0.76
	" B	2.0	PS	0.85
	" C-J	2.0	PS	0.92 - 1.06
	" K[5]	2.0	PS	1.21
	" L[5]	2.0	PS	1.13
	" M-P	2.0	PS	1.0 - 1.08
Horizontal elutriator	Lab A	2.83	C	1.0
	"[6]	2.83	C	0.94
	"[7]	2.83	C	0.86
	Man 3 Q	50.00[8]	C	0.95
	" R-T	2.5	P	0.98 - 1.05
	" R	2.5	PS	0.99 - 1.02
	" "[9]	2.5	C	0.97 - 1.01

1 Code for evenness of flow: C - critical orifice (very smooth), P - pump, PS - pump and smoother.

2 Dust concentration relative to that given by the Hexhlett in a coarse coal dust cloud. External flow control used and internal critical orifice removed.

3 Commercial unit with alternative filter holder.

4 Commercial unit with laboratory fitted metal filter holder.

5 Some dimensions on these 2 cyclones were outside reasonable tolerances.

6 Laboratory unit with filter facing down (Reference 1).

7 Laboratory unit with small orifice between elutriator and filter.

8 Hexhlett as manufactured with critical orifice between elutriator and filter.

9 Cassella 113A as recommended for standard instrument.

smoothed using pulsation dampers (Appendix G).

A third factor in these instruments is electrical conductivity of the components as this may affect deposition of charged particles. The mucous fluid in the bronchial passages is moderately conducting in common with other physiological fluids. Dust deposition on plastic components of dust samplers, attributed to electrostatic effects has been found in tests in this laboratory under dry conditions. This deposition has been associated with a 20% lower estimate of respirable dust in a plastic filter holder compared with a metal holder.

A fourth factor is attaching the size selector to the filter. It was found that dust can deposit on intermediate surfaces causing changes in the effective size selection characteristics.

A fifth factor is the type of filter used. It is widely accepted that a relatively coarse filter of 5-μm pore size or equivalent will collect airborne dust from comminution with high efficiency but that a finer pore size may be required for smokes or fumes.

A sixth factor is the direction and magnitude of the air stream passing over the dust sampler. It has been shown that the dust collected by the 113A dust sampler is dependent on airflow direction and velocity (16). This is also probably true of other dust sampling instruments and of the human nose and mouth (17).

Comparison tests between instruments should be carried out at low air velocities of about 0.5 m/s to avoid inertial effects. Although velocity and direction effects on each sampler should be determined, corrections cannot readily be applied because little is known about their effects on nasal entry and dust deposition in lungs.

F.1. Dust Collection Specifications

For proving instrument types, accurately calibrated airflow equipment such as a spirometer or wet test gas meter is required. However, for checking individual instruments of an approved design, calibrated high-accuracy glass rotameters provide satisfactory secondary standards.

1. Standard size-selection specification. The gravimetric sampler designed by the Mining Research Establishment of the National Coal Board, U.K., and manufactured by Casella uses a horizontal elutriator to the BMRC specification and is readily available. This design was chosen as a standard in the Elliot Lake Laboratory. For critical work, such as setting up and proving other instruments, a much closer specification on airflow is required; a flow rate of 2.5 ± 0.025 L/min from a critical orifice with the filter holder and horizontal elutriator is recommended. Checks should also be made to ensure that the leakage is very low.

2. All other respirable dust samplers should be so adjusted as to choice of airflow, etc. that the estimated respirable dust concentration based on the average of at least 5 instruments should be within 5% of that of the standard instrument in a 'test' dust cloud. The test dust cloud is dispersed from dry pulverized coal by an air ejector. The dust should be 40-60% respirable by mass.

3. The airflow through the size selection device and filter holder should be smooth enough for the dust collection to be within 5% of that obtained with a smooth airflow.

4. Components of samplers from each manufacturer should have equal ability within 5% of collecting dust in the test cloud, and be numbered in series each instrument kept intact or retested when components are changed.

5. The cyclone and filter should be constructed of materials having surface conductivities greater than 10^{-6} S/cm to avoid build-up of electrostatic charge and possible interference with dust deposition.

6. Individual instruments are considered satisfactory if they agree within 10% of the

standard in the test dust cloud.

7. Airflow from a pump and damper must be smooth enough to give less than 5% error on a rotameter calibrated on a smooth airflow. Note, however, that for cyclone size selectors, specification 3 is approximately equivalent to a 2% error in this test.

8. The flow rate should not drop more than 10% after collecting 10 mg/m³ of the test dust in an 8-hr shift when the flow is set 5% higher at the start of sampling and no further adjustment of the flow controls is made.

9. Test procedures and standards should be established for each instrument to determine
   i) leakage, including inlet fitting,
   ii) pressure drop and flow rate,
   iii) pump and valve maintenance.

10. Calculation of respirable dust concentrations should be based on:
    i) nominal flow rate for cyclone size selectors rather than by using the mean of before and after flows,
    ii) mean of flow before and after, for horizontal elutriator size selector,
    iii) mass airflow relationship found in test dust cloud for other size selectors.

11. The pumping performance of a dust sampler can depend on air density. The effect of operating it at pressures experienced in a deep mine should be determined and an appropriate adjustment made to the flow rate established on surface prior to sampling and calculated to minimize error at depth in the mine.

F.2. Test Methods

Test dust cloud

Dry coal is crushed and then ground in a rotating plate pulverizer with plates set at 0.125-mm separation. It is dispersed using an air ejector at a pressure of 60 kN/m² (9 lb/in.²). The dust cloud should have a concentration of 10-30 mg/m² and contain between 40 and 60% respirable dust by mass.

Dust collection

Standard size selection

The 113A gravimetric dust sampler as manufactured by Casella is used as the standard instrument (18). When testing it is necessary to adjust the flow rate as accurately as possible; however, this is easier to achieve if the elutriator and filter holder are operated on a smooth airflow produced by a vacuum pump acting through a critical orifice rather than by the instrument pump.

The Hexhlett dust sampler is useful as a secondary standard because of its large sampling rate of 50 L/min and correspondingly low weighing errors (18) GF/A filters of 5.5 cm in diameter are used. The Hexhlett indicates a respirable dust concentration between 0.85 and 1.0 times that of the standard instrument depending on the flow control used. The use of the critical orifice supplied leads to a low estimate of respirable dust because of dust deposition on metal surfaces between it and the filter. The mass of dust collected by the standard and test instruments should be about 2 mg.

Tests with pump or smooth flow
(9.1. para 3)

A sampling head with filter holder is alternately tested in the test cloud with airflow produced by its own pump, including a pulsation damper, and with a smooth flow derived from a critical orifice (19). The smooth airflow has to be carefully adjusted using a wet test gas meter or similar meter to be equal to the pump flow.

Airflow

Accuracy of rotameter reading on pump flow

The wet test gas meter, or similar instrument, and the rotameter are set up in series and air is drawn through them with either the instrument pump including pulsation damper or a critical orifice and vacuum pump (Fig. F.1). The difference in rotameter reading on the pump flow with its pulsations and that given by a critical
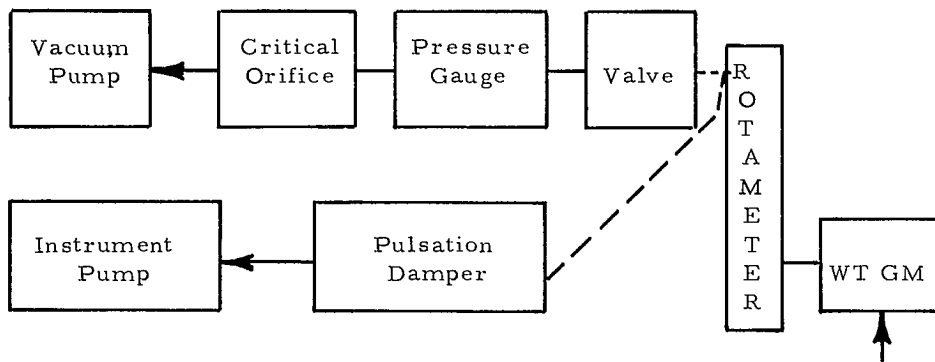
Fig. F.1 - Accuracy of rotameter reading on pump flow test.

orifice adjusted to the same flow rate as indicated by the wet test gas meter gives a measure of whether the pulsations are sufficiently smoothed by the pulsation damper or not.

Flow rate control

The instrument flow rate is set at 5% above nominal and then collects dust in the dust chamber for eight hours at a rate of 8-12 mg/m³. The final flow rate is measured and the flow rate drop corresponding to a dust concentration of 10 mg/m³ is calculated on the assumption that the measured drop is linearly proportional to the respirable dust concentration measured by the instrument. Alternatively this can be determined from separate measurements of pressure drop on the filter and the effect of pressure drop on the airflow of the pump.

(i) Leakage tests

Leakage tests should be carried out on the complete unit excluding the pump, making it essential to have a leakproof fitting attached to

the sampler inlet. The test layout is shown in Fig. F.2. Leakage is indicated by change in rotameter reading as valve 1 is adjusted from fully open to a gauge pressure drop of 2.5 kPa.

(ii) Flow and pressure drop

Figure F.3 shows layout for testing the pump over its complete pressure range. A useful test point is the suction developed at a flow 10% low after the pump is set to 5% high on a clean filter because this is considered the limit on a valid sample; another useful point is the maximum suction developed as the inlet is closed. The motor current should also be measured.

(iii) Maintenance procedures

Specifications on the performance of the units in tests 9(i), (ii) should be set up to indicate the need for pump and motor maintenance. A daily schedule should be set up to indicate the need for more complete testing and maintenance as outlined above.

Fig. F.2 - Leakage tests.

```
┌─────────────────┐     ┌──────────┐     ┌─────────┐     ┌───────────┐
│ Instrument      │     │  Inlet   │     │  Valve  │     │ Flowmeter │
│ complete with   │◄────│ Fitting  │     │         │────►│           │
│ Clean Filter    │     │          │     │         │     │           │
└─────────────────┘     └──────────┘     └─────────┘     └───────────┘
        │                    │                                 ▲
┌─────────────────┐     ┌──────────────┐
│    Ammeter      │     │  Manometer   │
└─────────────────┘     └──────────────┘
        │
┌─────────────────┐
│    Battery      │
└─────────────────┘
```

Fig. F.3 - Flow and pressure-drop test.

F.3. References

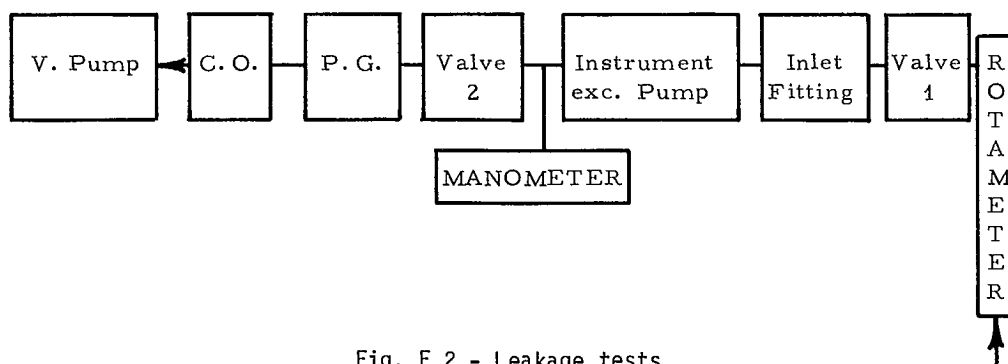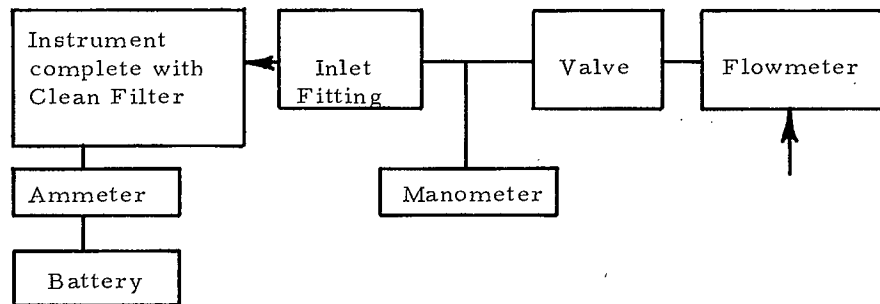1. Cochrane, T.S., Knight, G., Richards, L.C., and Stefanich, W. "Comparison of dust sampling instruments"; Mines Branch Research Report R250; Oct. 1971.

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APPENDIX G

DEVELOPMENT OF THE CANADIAN MINING PERSONAL
DUST SAMPLER (CAMPEDS)

Most studies carried out by the Elliot Lake Laboratory in mines used the Casella 13040 personal size-selecting gravimetric dust sampler (1,2). Although this instrument has proved capable of collecting samples suitable for gravimetric and direct quartz analyses using X-ray diffraction on the filter some problems have occurred:

(a) flow rate adjustment by bleed valve was a source of dust entering the pump and increased the need for maintenance;

(b) flow smoother was bulky, awkward, and leaked frequently;

(c) the instrument is too fragile as a personal sampler in mines;

(d) miners are reluctant to carry extra equipment.

However, these problems have been overcome through a number of improvements.

It is believed unnecessary to adjust airflows underground because the mass of respirable dust collected is almost independent of airflow except in dust clouds with unusually high proportions of fine particles (3). If it were possible to adjust the airflow underground, it seems unlikely it would be carried out sufficiently systematically by mine staff in routine use to be of any value.

Tests on flow smoothers led to a much smaller and convenient design; specifications are given in Appendix F.

The problem of the fragile dust sampler could have been met by using a more robust and heavier case, but was approached by combining the sampler with a piece of existing miners' equipment. Its combination with cap lamp and battery terminal, SIMPEDS, was developed by the Safety in Mines Research Establishment (4,5). This showed promise but could not collect samples for direct quartz analysis on the filter because of the coarse pre-filter used to catch any of the dust layer dislodged by rough handling. The SIMPEDS is also cumbersome to wear because of the extra hose and cap lamp-mounted sampling head.

Making the sampler as inconspicuous as possible by combining both the sampling head and pump with the cap lamp battery was proposed and tests were made (Section 5.2).

The concept of combining the dust sampler with the cap lamp battery is termed the Canadian Mining Personal Dust Sampler with its acronym, CAMPEDS. The first prototype was made using standard Casella 13040 personal sampler components mounted in a metal case to fit the top of the Wheat battery, as shown in Fig. G.1. These prototypes have been operated by mine staff under the direction of the Mines Accident Prevention Association of Ontario (6). Although wearing the units was voluntary, few refused (7). The main problem has been changing filters between shifts, because the men available for this purpose had no previous laboratory experience (7). The sampling head was designed so that the filter could not be handled when exposed but it has occasionally been dropped and damaged. This problem led to a second prototype using a smaller impaction size selector instead of the cyclone, following the suggestion of M. Jacobsen (8,9), making it a part of the reloadable cassette as shown in Fig. G.2. This prototype uses the SIMPEDS pump unit with minor modifications.

The Casella SIMPEDS pump used in the CAMPEDS is for mounting on the Oldham cap lamp battery but both the MSA and the Wheat cap lamp batteries can be machined to fit it. In laboratory tests both types of battery were hand filed to fit.

G.1. Impaction Size Selector

The size selector combined with a filter holder for 25-mm diameter filters is shown in Fig. G.2.

The first model used a single impaction orifice, but it was found that on heavy dust loads of about 2 mg, an oversize dust cone built up under the orifice and that parts of this could

PULSATION DAMPER

FLOW ADJUSTMENT

REVOLUTION COUNTER

MOTOR

COVER

PUMP

BATTERY

FLOWMETER
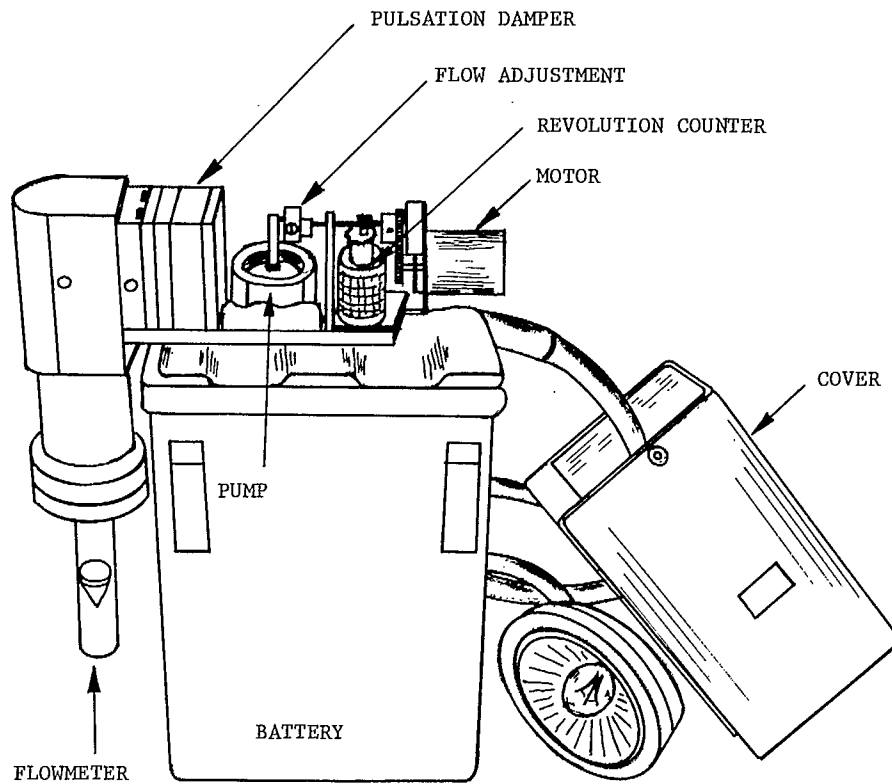
Fig. G.1 - The pump set up for adjusting flow rate.

1st stage impact block

2nd stage impact block

2nd stage orifice

O-ring

Air entry

1st stage orifice

Cassette cover

Mounting position

Cone

Battery clamp

Washer

Filter

Modified SIMPEDS pump and case

Air entry

Support grid

O-ring

Filter holder

CAP LAMP BATTERY

Air outlet

Cassette - exploded view

Assembled sampler
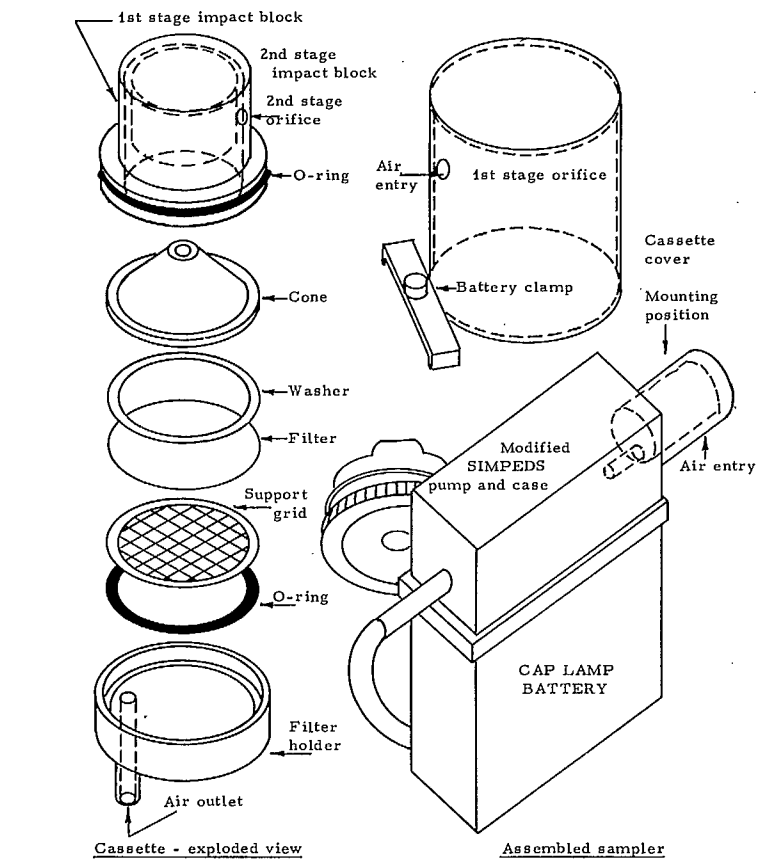
Fig. G.2 - Filter holder and size selector for the CAMPEDS.

be readily dislodged and pass through to the filter. The problem was solved by using two orifices in series with the first only slightly larger than the second so that most of the dust was trapped there. The suggestion (9) of using a lip, although possible with this construction, was not practicable because of the difficulties of cleaning behind it. Impact surfaces are lightly coated with vaseline to decrease the possibility of coarse dust penetrating to the filter. The flow rate chosen for this sampler was 2 L/min as a round figure within the range of the specially built Rotameter taper-tube flowmeters supplied by Casella. Some consideration was given to the flow of 2.08 L/min which would give the exact volume of 1 m^3 in an 8-hr period normally used to define the period of exposure for threshold limit values, but it is slightly too high for convenience with the high accuracy flowmeter custom-manufactured for Casella.

Circular impaction orifices were chosen for the size selector for ease of construction and ready checking. The diameter of these orifices was adjusted so that the completed unit, when operated at 2 L/min, indicated the same respirable dust concentrations as the 113A dust sampler, as described in the section on calibration in Appendix F. The effect of orifice size is shown in Table G.1 both for single orifices and two in series.

Tests were carried out on size selection characteristics of the final CAMPEDS impactor and a horizontal elutriator, the 113A, designed to the BMRC specification (10). The technique used is similar to that described by Tomb and Treaftis (9). The Coulter counter, an electronic size analyzer classifying particles by volume, was used to compare coal-dust samples collected on silver membrane filters following the various selectors with those collected on an open filter in the laboratory test chamber. The dust samples were redispersed in ethyl alcohol and an aliquot transferred to the electrolyte, 4% sodium hexametaphosphate, for counting. The detailed results are given in internal reports and summarized herein. The number of particles in each size range for some of the experiments are shown plotted against size on an approximately logarithmic scale in Fig. G.3. These results were obtained using two Coulter counter aperture sizes. Figure G.4 shows results obtained from percentage penetration through the respirable-dust size selectors plotted against particle size by volume. Also shown is the design performance plotted against aerodynamic particle size. It can be seen that the results are not very consistent, presumably due to difficulties in removing all the dust from the filter, dispersing the dust, and avoiding contamination. These experiments show no significant differences between the CAMPEDS and the horizontal elutriator size selectors, but they are not accurate enough to detect the expected slight differences in slope.

G.2. Laboratory Tests on CAMPEDS Sampler

The SIMPEDS 70 Mark 2 flow smoother and flowmeter was found to have a high resistance to airflow — about 10 mm of mercury at 2.0 L/min. This left little spare capability for drawing air through the size selector, filter, and dust deposit, especially when a 25-mm diameter filter is used instead of the specified 37 mm. Resistance of the flow smoother was greatly reduced by opening up the outlet to 4.0 mm, the hole between the two chambers to 2.5 mm, and removing the 30-mm long by 1.3-mm diameter orifice in the smoother inlet. It was then found that tests 9.3.3 and 9.3.7 were satisfactory and that a gauge pressure of 2.5 kPa across the filter was equivalent to a drop in flow rate of 10%. If this is not sufficient to handle the dust load in mines with high diesel usage, it will be necessary to try the unit without the built-in flowmeter or to modify the size selector and use a lower flow rate.

Air density increases with mine depth and this affects flowmeter calibration — the reading is about 10% high at 2000 m below surface. It is possible that the pump performance is also affected. A temperature effect was noticed in the mine tests. Therefore an experiment was carried out in the laboratory in which

Table G.1 - Effect of diameter and number of
orifices on the characteristics of
an impact size selector

Diameter of orifice mm		Indicated respirable dust concentration relative to
1st	2nd	that of the 113A
NU*	4.4	1.68
NU	3.2	1.25
NU	2.5	1.5
4.4	4.1	1.34
4.4	3.8	1.28
4.4	3.2	0.93
3.8	3.2	0.88
3.8**	3.5**	1.00

*Not used.

**Values chosen for the CAMPEDS dust samplers.
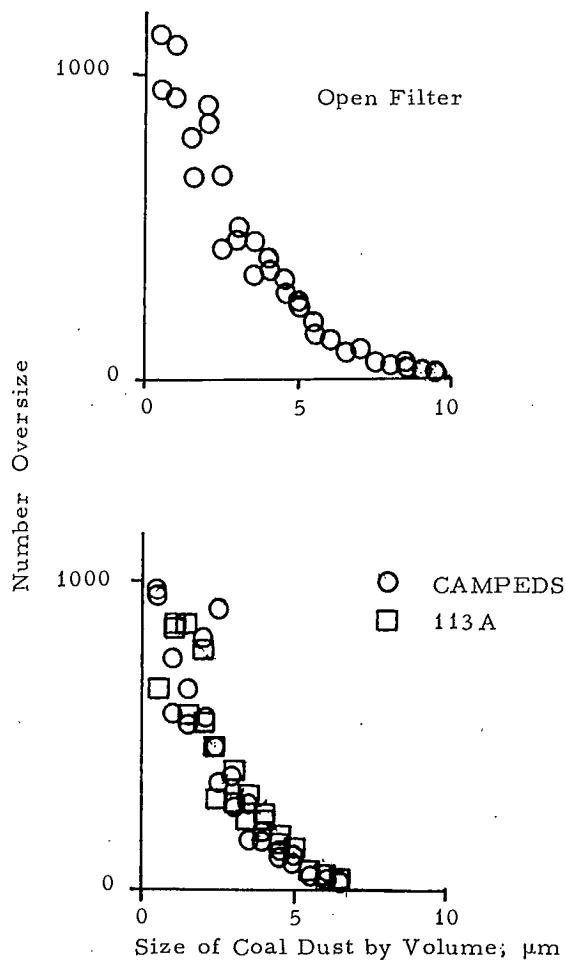
Fig. G.3 - Size distribution of particles determined by Coulter Counter.
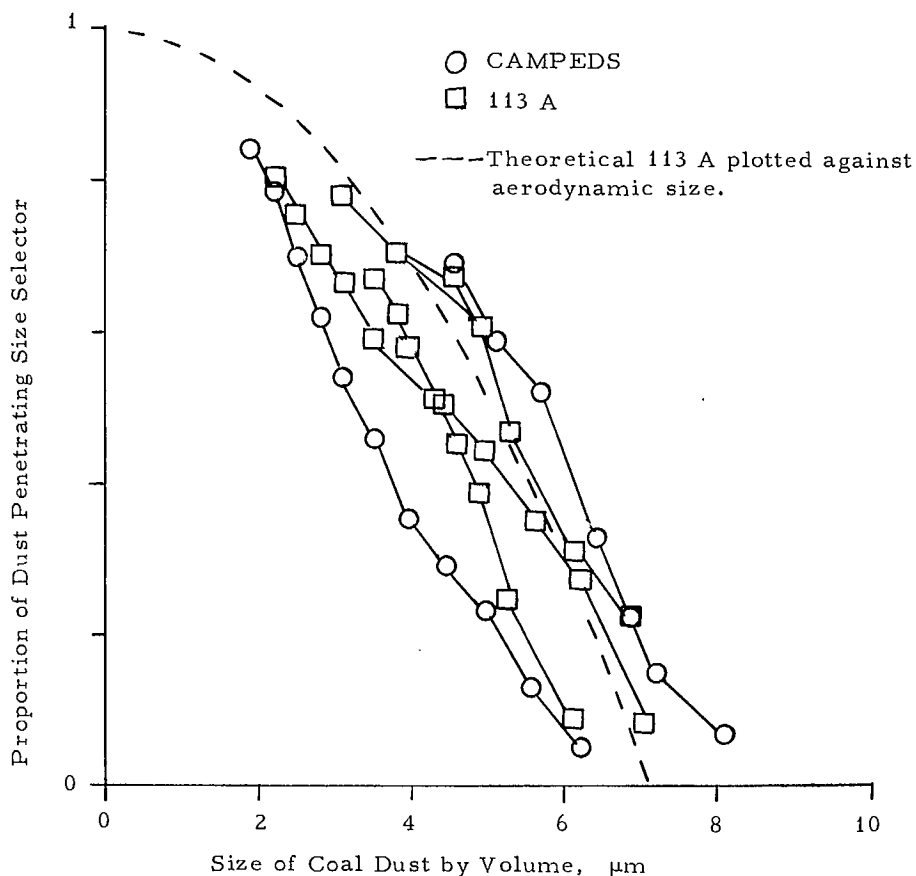
Fig. G.4 - Efficiency of collection of particles by size selectors
determined by Coulter Counter.

two CAMPEDS units were assembled in a pressure
chamber and measurements were made over a range
of pressures under two temperatures. Figure G.5
shows the results obtained for motor speed (ex-
pressed as true seconds per indicated minute on
the running time meter), for rotameter reading
and for volume flow obtained by correcting the
rotameter reading to test pressure and
temperature.

It can be seen that increasing pressure
leads to decreased motor speed, increased indi-
cated flow, and decreased true volume under test
conditions. Qualitatively this is expected be-
cause of increased air density increasing the
load on the pump and the rotameter indication.

Lowering the temperature by 20°C reduced
airflow slightly and altered motor speed by about
2% on each unit but in opposite directions.

It is concluded that setting up at room

temperature and pressure will not give signifi-
cant errors until mine depths are greater than
1000 m. However, the effect on the rotameter
reading is enough to take the float off scale at
depths greater than 1500 m.

Recommended values for setting up the
pump based on depth and an allowance for pressure
drops on the loaded filter are given below.

Average depth below surface (m)	Airflow (L/min)	Motor speed (sec/indicated min)
0 - 300	2.05-2.15	59 -60
300 - 1000	2.1 -2.2	58.5-59.5
1000 - 2000	2.15-2.25	58 -59
2000 - 3000	2.2 -2.3	57 -58
Nominal values	2.0	60
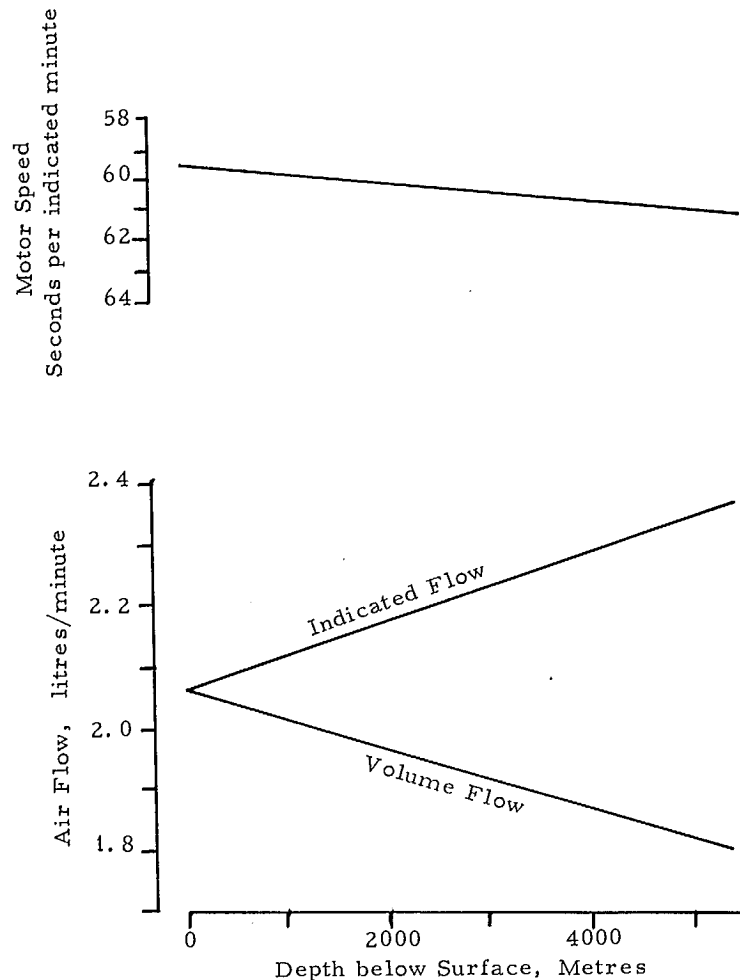
Fig. G.5 - Effect of mine depth on pump characteristics

G.3. Underground tests

Five CAMPEDS units were built for the Elliot Lake Laboratory and tested in one of the local mines. The samplers were worn by a representative section of the underground staff and miners. Careful measurements of airflow and motor speed were made both with the clean filter installed and after collecting the sample.

The first set of tests started with supervisors and progressed to the miners after a few days. The mine ventilation department arranged the issue of dust samplers and laboratory staff changed the cassettes and checked the instruments daily. A total of 86 samples were taken in 18 days. Sample losses occurred due to both mechanical faults and human error.

The results obtained in the trials are shown in Tables G.2 to G.6 where the mass of respirable dust collected or net weight flow rate before and after sampling, motor speed before and after sampling expressed as seconds per one-minute indication on dial, indicated running time in minutes, and clock running time in minutes for each instrument are given.

It can be seen that the samples averaged 0.5 mg in weight with a maximum of 1.1 mg and that on the average little change in airflow or motor speed occurred between measurements made before and after the sampling period. However, it was noticed that cold pumps indicated high airflow and presumably airflows after sampling were biased on the high side because the pumps

Table G.2 - Tests on dust sampler No. 1

Filter no.	Net wt	Flow rate L/min		Motor speed Sec/ind. min		Running time, min		
		Before	After	Before	After	Indicated	Clock	Diff, (I-C)
1	0.23	2.1	2.1	58.4	58.4	450	450	0
6	0.35	2.1	2.1	58.4	58.2	437	435	2
11	0.30	2.05	2.08	58.0	58.2	547	525	22
16	0.86	2.1	2.08	58.0	58.0	238	225	13
21	0.46	2.1	2.1	58.0	58.0	294	285	9
26	0.46	2.1	2.1	58.0	58.0	232	220	12
31	0.62	2.13	2.1	58.0	58.0	230	225	7
36	0.53	2.1	2.1	58.4	58.6)	955	420	40
41	0.64	2.1	2.1	58.4	58.4)		495	
46	0.48	2.1	2.0	58.2	58.0	528	510	18
51	0.34	2.1	2.15	57.2	58.0	510	490	20
56	0.52	2.1	2.1	57.6	57.6	525	515	10
61	0.19	2.14	2.15	59.4	59.4	525	518	5
65	0.62	2.12	2.2+	58.4	60.2	467	460	7
70		2.1		59.2	)	1008	1010	-2
70	0.55		·2.11		58.8)			
71	0.44	2.1	2.1	58.8	58.4	499	495	4
82		2.09	2.1	58.4	58.0	511	510	1
Mean	0.475	2.102	2.102	58.3	58.4			+9

Table G.3 - Tests on dust sampler No. 2

Filter no.	Net wt	Flow rate L/min		Motor speed Sec/ind. min		Running time, min		
		Before	After	Before	After	Indicated	Clock	Diff, (I-C)
2	0.16	2.1	2.1	58.6	58.8	271	360	-89
7	0.28	2.1	2.0	58.6	59.6	245	235	10
12	0.39	2.12	2.15	58.4	59.0	456	450	6
17	1.03	2.05	2.08	59.0	59.2	485	475	10
22	0.30	2.05	2.17	59.0	58.0	483	470	13
27	0.20	2.08	2.1	58.6	58.6	229	220	9
32	0.21	2.1	2.07	58.6	59.6	229	225	4
37	0.33	2.1		59.6	)	849	360	9
42	0.35		2.1		59.2)		580	
47	0.85	2.05	2.05	59.0	59.0	524	520	4
52	0.73	2.18	2.0	58.0	58.4	503	490	13
57	0.40	2.0	2.1	58.4	58.0	518	495	23
62	0.42	2.12	2.2+	58.4	46.4	610	510	100
66	0.75	2.1	2.13	58.8	60.0	440	460	-20
78	0.37	2.12	2.0	58.8	62.0	471	490	-19
83		2.1	2.1	58.8	59.2	516	510	6
Mean	0.518	2.095	2.08	58.75	59.2			5

Table G.4 - Tests on dust sampler No. 3

Filter no.	Net wt	Flow rate L/min		Motor speed Sec/ind. min		Running time, min		
		Before	After	Before	After	Indicated	Clock	Diff, (I-C)
3	0.32	2.1	2.0	58.2	58.4	544	505	39
8	0.15	2.13	2.13	59.4	59.6	251	240	11
13	0.52	2.1	1.9	59.2	59.6	455	450	5
18	0.95	2.1	1.88	59.6	59.6	495	480	15
23	0.33	2.08	2.08	59.4	59.6	290	290	0
28	0.22	2.08	2.02	59.6	59.6	229	220	9
33	0.34	2.05	1.95	59.6	59.6	472	465	7
38	0.28	2.03		59.6	)	526	225	-69
43	0.21		2.1		59.2)		370	
48	0.59	2.1	2.05	59.2	58.4	528	515	13
53	0.38	2.1	2.05	59.4	59.4	461	470	-9
69	0.47	2.08	2.16	59.0	58.8	495	507	-12
72	0.56	2.09	2.1	59.0	58.0	509	497	12
75	0.41	2.08	2.09	58.0	59.0	515	497	18
79	0.52	2.1	2.1	59.0	57.6	521	502	19
84		2.06	2.04	59.0	58.8	529	513	16
Mean	0.423	2.085	2.04	59.15	59.0			10

Table G.5 - Tests on dust sampler No. 4

Filter no.	Net wt	Flow rate L/min		Motor speed Sec/ind. min		Running time, min		
		Before	After	Before	After	Indicated	Clock	Diff, (I-C)
4	0.46	2.1	2.1	58.4	58.0	275	255	20
9	0.17	2.08	2.0	58.0	59.2	137	235	-98
14	0.19	2.08	2.1	58.0	59.0	138	450	-312
19	0.59	2.1	2.13	58.4	58.0	85	470	-385
24	0.39	2.08	2.08	58.4	58.0	75	480	-405
34	0.24	2.1	2.2+	58.0	58.0	475	465	10
39	0.84	2.13	2.05	58.4	58.4)	694	165	3
44	0.91	2.1	2.1	59.0	58.4)		492	
49	0.50	2.1	2.1	58.2	58.0	542	520	22
54	0.47	2.1	2.18	57.6	56.4	517	515	2
59	0.42	2.1	2.18	55.6	56.0	538	515	23
67	0.52	2.1	2.1	58.0	58.0	492	485	7
73	0.41	2.09	2.12	60.0	57.2	528	516	12
76	0.92	2.1	2.05	58.6	60.0	498	495	3
80	0.49	2.1	2.02	60.0	60.0	489	495	-6
85		2.1	1.84	58.4	60.0	479	473	6
Mean	0.515	2.075	2.085	58.3	58.2			13

Table G.6 - Tests on dust sampler No. 5

Filter no.	Net wt	Flow rate L/min		Motor speed Sec/ind. min		Running time, min		
		Before	After	Before	After	Indicated	Clock	Diff, (I-C)
5	0.74	2.1	2.1	58.4	58.8	278	275	3
10	0.35	2.12	2.2+	58.4	58.4	360	345	15
15	0.64	2.1	2.1	58.4	59.6	456	450	6
20	0.30	2.13	2.13	58.6	58.6	236	225	11
25	0.50	2.13	2.1	58.2	59.2	445	405	40
30	0.38	2.14	2.1	59.0	59.0	230	220	10
35	0.23	2.07	2.05	59.0	59.2	228	225	3
40	0.42	2.1	2.2	58.4	56.4)	954	420	34
45	0.58	2.1	2.1	58.4	58.4)		500	
50	0.66	2.13	2.1	58.2	59.0	517	505	12
55	0.38	2.1	2.1	59.0	58.8	473	500	-27
60	1.10	2.08	2.1	59.2	57.0	516	495	21
64	0.41	2.11	2.1	58.8	59.2	527	--	
68	0.43	2.1	2.14	59.6	58.8	526	513	13
74	0.43	2.1	2.1	58.4	58.9	513	505	8
77	0.25	2.11	2.03	59.2	60.6	248	243	5
81	0.31	2.03	2.1	60.0	59.0	505	493	12
86		2.1	2.1	59.2	59.0	496	485	11
Mean	0.476	2.103	2.103	58.8	58.75			10

had not always reached room temperature when the flow checks were made. Mostly, good agreement existed between running times by the instrument indicator and the clock except when the instrument was switched off or failed.

Mechanical and electrical problems in the first series of tests and their solutions are listed below.

1. It was difficult to achieve a seal between the O-ring on the cassette and the cassette cover, due partly to distortion of the unmachined tube from which the covers were made. These were machined, using a larger O-ring and the O-ring groove on the cassette was remachined.

2. Big end bearings on two pumps seized up occasionally. The bearings were cleaned and oiled.

3. The electronic speed control failed on instrument No. 2, leading to a high motor speed throughout most of one shift. A temporary repair was made using a 22-ohm fixed resistor and a 5-ohm 1-watt potentiometer in series.

4. Exit pipes on the cassettes leaked. These were glued in place with epoxy resin.

5. One pump case came off a battery underground. Adequate care must be taken in machining the batteries to fit the pump case.

On completing these modifications a further set of underground tests was carried out, with mine staff looking after all procedures, except quartz analysis. A total of 130 samples were taken with very few samples lost due to human error or mechanical problems. The mine ventilation department staff was satisfied and ordered these samplers for routine use.

G.4. Pulsation Dampers

Work in the Elliot Lake Laboratory showed considerable differences in dust collection characteristics among three dust samplers from different manufacturers using the same size selector (3). Some of these differences are attributed to the effect of pulsating flow on dust collection in the cyclones used for size selection of respirable dust (3,11,12). The pulsating flow gives rise to greater deposition in the cyclone than a smooth flow and, therefore, to

a lower estimate of the respirable dust concentration. The laboratory calibrations of cyclones reviewed by Lippmann were based, it is believed, on smooth flows (13).

The pulsating flow arises from using single-action diaphragm or piston pumps in the samplers and has a secondary effect on airflow calibration. Taper tube flowmeters are used as secondary standards and, if the float does not follow the pulsations, the root mean square of the airflow is read rather than the average, i.e., the flowmeter will read high, up to twice the average flow. Pulsation dampers have been used to give a reasonably accurate reading on a taper tube flowmeter calibrated on a smooth airflow (14).

This section describes studies on pulsation dampers for the modified Casella sampler combined with the cap lamp battery, as well as on some dampers built for the existing Casella pumps after Higgins and Dewell (2). Similar work on the MSA personal respirable dust sampler has been carried out in this laboratory.

The pulsation damper supplied with the Casella personal gravimetric sampler is a bulky separate component which can be awkward to use in some mining locations. It has also been found that frequent replacement of the rubber finger cotts is required and that they are prone to leakage.

Combining the personal gravimetric dust sampler with the cap lamp battery involves fitting the pump and pulsation damper into a minimum-sized holder above the battery. The layout of the unit was described earlier (G.1). Following the USBM study on symmetrical two-chamber pulsation dampers (15), it was decided to build a symmetrical four-chamber unit to fit the space available.

This unit was found to control dust collection adequately but too much error remained in the flowmeter reading. Some experimental units were therefore built to attach directly to

the case of the original Casella personal sampler pump so that some of the variables could be investigated with less restriction on overall size (1). The parameters of the various dampers and the results of tests described in the two following sections are given in Tables G.7 and G.8.

Following this, a modified three-chamber version was prepared for the unit combined with the cap lamp battery and was tested.

G.4.1. Effect of pulsation dampers on dust collection

Tests on various pulsation dampers placed between a Casella personal sampling pump and its cyclone filter unit were carried out in an approximately 50% respirable coal dust cloud in the laboratory chamber. This dust cloud was chosen because it had shown the largest difference between size-selective dust samplers (3). The dust collected on each filter was compared with that collected by the large volume — 50 L/min — Hexhlett respirable dust sampler as this could be weighed with negligible error. Tests were also carried out with the same cyclone filter unit and a smooth airflow obtained from a vacuum pump and a critical orifice. The results are shown in Table G.7. It should be noted that the combination of the units — pump, pulsation damper, and filter-cyclone — were altered for each run so as to average out variations between the individual pumps and filter-cyclones.

It can be seen that the absence of a pulsation damper on this sampler leads to a low estimate of respirable dust (Code 1). The Casella (Code 2) and the laboratory-built damper with thin rubber (Code 5) are adequate to keep the dust collection within 5% of that with a smooth flow, while the laboratory damper with thick rubber (Code 4) and the single chamber proprietary damper (Code 6) do not. It should be noted that at the sampler's recommended airflow of 1.9 L/min the estimate of respirable dust is 10 to 15% higher than that given by the Hexhlett.

Table G.7 - Effect of pulsation dampers on dust collection
with the Casella personal gravimetric dust sampler

Code	No. of chambers	Volume cm^3	Rubber thickness mm	Individual runs	Mean
1	None			0.43, 0.68, 0.61, 0.55, 0.78	0.65
2	2	32	0.18	1.04, 1.12, 1.20, 1.06, 1.18, 1.04	1.11
3	3	17	0.48*	1.04, 1.21, 1.12, 1.07, 1.11, 1.06	1.10
4	2	16	0.71	0.98, 0.96, 1.03	0.99
5	2	16	0.48	1.06, 1.18, 1.08, 1.10, 1.13, 1.03	1.10
6	1	9	0.35	1.15, 1.06, 1.04, 1.12, 1.06, 1.03	1.07
7	Smooth flow			1.07, 1.13, 1.21, 1.11, 1.18, 1.21	1.15

Column headers over "Dust collection expressed as fraction of that by Hexhlett"

*Final design of smoother for the prototype Casella personal samplers combined with the cap lamp battery.

Table G.8 - Effect of pulsation dampers on flowmeter reading Casella personal sampler pump

Test	Number of chambers	Total volume cm^3	Total rubber area cm^2	Rubber thickness mm	Rotameter[1] L/min	WTGM[2] L/min	Excess reading R - WTGM L/min
1		none			3.4	2.00	1.4
2		smooth flow			2.02	2.02	0.00
3	2	16.0, 16.0	50, 50	0.18[3]	1.86	1.85	0.01
4	1	10.6	22	0.71	2.07	1.93	0.14
5	2	21.2	22	0.71	1.88	1.86	0.02
6	2	5.3, 5.3	11, 11	0.71	2.02	1.91	0.11
7	2	5.3, 5.3	11, 11	0.48	1.96	1.93	0.03
8	1	10.6	22	0.18[6]	1.99	1.96	0.03
9	2	5.3, 5.3,	11, 11	0.18	1.76	1.74	0.02
10	3	5.3, 2.0, 2.0	11, 4, 4	0.18	1.94	1.93	0.01
11	4	2.0, 2.0, 2.0, 2.0	4, 4, 4, 4	0.18	2.04	1.89	0.15
12	2	2.0, 9.0,	0, 18	0.35	2.06	2.00[4]	0.06
13	1	9.0	18	0.35	1.89	1.83[4]	0.06
14	3	12.8, 2.2, 2.2	11.5, 4.6, 4.6	0.28	2.02	1.86	0.16
15	3	12.8, 2.2, 2.2		0.48[5]	1.91	1.89	0.02
16	3	12.8, 2.2, 2.2		0.18[6]	1.94	1.93	0.01

1 Rotameter calibration adjusted to agree with wet test gas meter (WTGM) on smooth flow.
2 WTGM.
3 Supplied with Casella personal gravimetric sampler.
4 Difference in volume between the two tests is presumably due to difference in length of tubing attached to pump inlet.
5 Configuration chosen for modified Casella fitted to cap lamp battery.
6 This rubber has less strength than others used.

G.4.2. Effect of pulsation dampers on reading of taper tube flowmeter

In this study the wet test gas meter, taper tube flowmeter, pulsation damper, and Casella pump were set up in series. The calibration of the flowmeter was adjusted to give the same reading as the wet test gas meter (WTGM), in series, using a smooth airflow from a critical orifice and vacuum pump. Results are given in Table G.8.

Note, the seventh column shows the excess reading on the rotameter due to pulsations in the airflow. In tests 3, 5, 7, 8, 9, 10, 11, 12, 13, 15, and 16 the error in flow rate reading, column 7, is less than 5% and in tests 5, 9, 10, 15 and 16 it is less than 2%.

G.4.3. Discussion on pulsation dampers

The experiments carried out and reported in Tables G.7 and G.8 as well as other less controlled experiments and observations suggest that the following factors should be considered in design and use of pulsation dampers:

(i)   Rubber should be as thin as possible.

(ii)   Volume and rubber area of the chamber nearest the pump inlet should be as large as possible; for the Casella pump tested, 5 cm³ volume and 10 cm² rubber area appear to be the minimum acceptable.

(iii) There appear to be advantages in splitting up the pulsation damper into sections with an orifice between them as small as possible without too great a pressure drop; holes 2.5 mm in diameter were found to be a reasonable compromise.

(iv)   Passage between the pulsation damper and pump should be as short and as large in cross section as practicable.

(v)   Performance under suction is improved by using a support such as a coil spring under the rubber diaphragm to lessen volume decrease; presumable the spring-rubber combination is more elastic than thicker rubber of equivalent strength.

(vi)   One manufacturer claims a dynamic action in the pulsation damper with tuning of spring, rubber diaphragm, and pump speed.

Clearly, both accuracy of dust collection and airflow are important in respirable dust samplers using cyclone size selectors and it is shown that the pulsations in airflow arising from the use of simple single-action air pumps can lead to errors in both these factors. These pulsations and their effects can be controlled by dampers.

Variations in dust collection of these samplers under set conditions in the laboratory are about ±5%, while in the field they may be ±10% or more. Reasonable accuracy is possible if the errors due to airflow pulsations can be kept within 5% for both dust collection and taper tube flowmeter reading. However, the requirement for dust collection at 5% is more stringent for cyclone size selectors and corresponds to a flowmeter reading change of about 2%.

The possibility of decreased effectiveness of the pulsation dampers at high pressure-drops, due to the decreased internal volume of the dampers from stretching of the rubber diaphragms may require a higher efficiency in the clean filter low pressure drop tests.

Inaccuracies in the use of a flowmeter due to pulsations can be overcome by calibrating against a wet test gas meter, spirometer or some other standard, but taper tube flowmeters or rotameters are in widespread use as secondary airflow standards and are the only instruments available in many laboratories. Thus, flow should be smooth enough on all sampling instruments for rotameters to give a sufficiently accurate assessment of flow rate.

Pulsation damper developed for Casella model B personal dust sampler are shown in Fig. G.6 and G.7. The design for the Casella B was elaborate because it was mounted outside the pump case and the rubber diaphragms must be protected from grit.

I, J   → B

I, J

K   K

I, J   I, J

A   A

B

+ I, J   I, J +

K   K
+   +
Y   Y

I, J   I, J
+   +
+   +
Y   Z

PARTS LIST
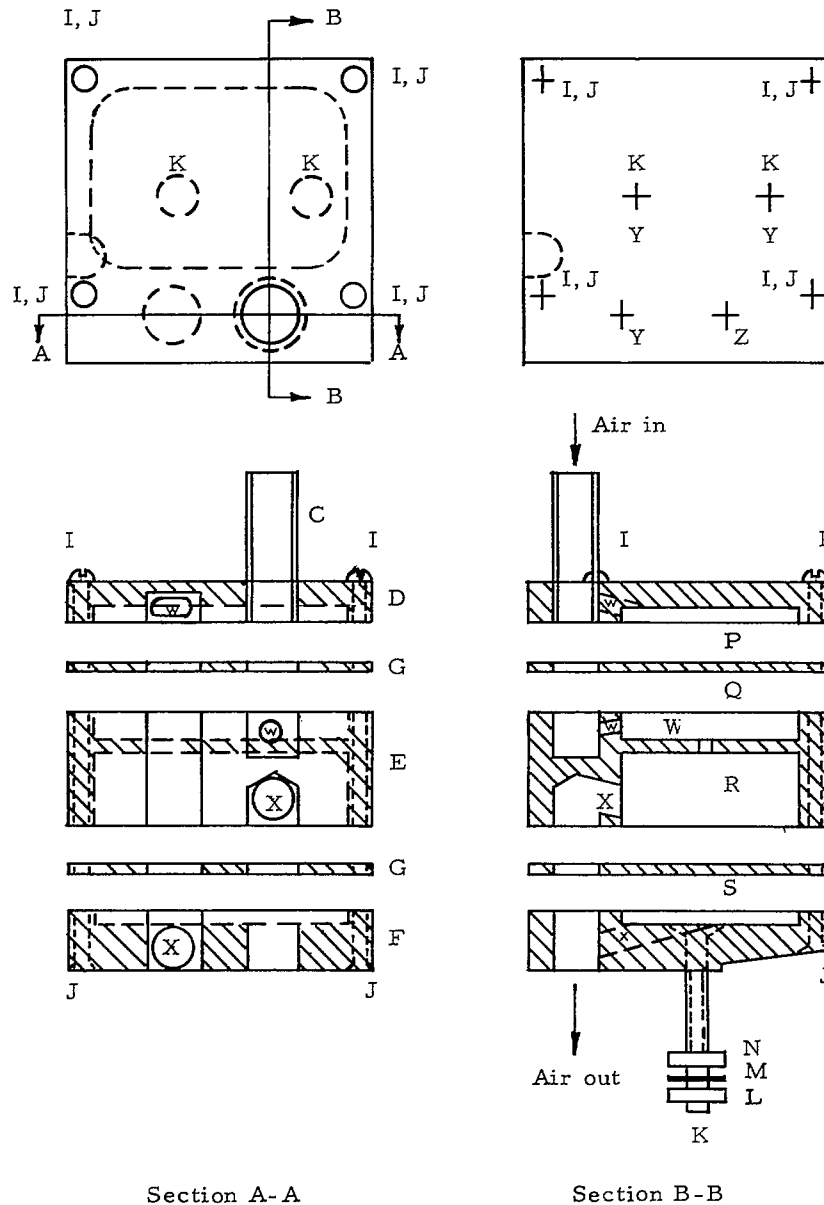
C   - Tube 5/16" O.D. x 3/16" I.D. x 1" Long.
D   - Plate 2" x 2" x 1/4"   Material: light alloy
E   - Plate 2" x 2" x 5/8" or 3/4",   All mating surfaces to be flat
     tapped to receive screw I and J.
F   - Plate 2" x 2" x 3/8".
G   - Rubber, 2 pieces 2 1/2" x 2 1/2" x 0.025"
     These are stuck to piece E
     Holes are cut with hot soldering iron
     Edges trimmed after assembly.
H   - "O" ring 5/16" x 7/16" x 1/16" (set to seal on pump inlet tube)
I   - 4 screws RHD 1/8" O.D. x 1/2" long.
J   - 4 screws CSK 1/8" O.D. x 1/2" long.
K   - 2 screws CSK 1/8" O.D. x 3/4" long.
L   - 2 nuts to fit K.
M   - 2 lock washers to fit K.
N   - Clamping plate 1.25" x 0.25" x 0.125" with 2 clearing holes to fit K.
O   - Milled relief 0.25" x 0.25" x 0.125" deep in part F to clear screw
     on pump case.

Milled recess in plates D, E and F, 1.625" x 1.16" x 0.25" - depth as
shown in B-B.
P   - 0.1"
Q   - 0.187"
R   - 0.375" if E 5/8" thick, and 0.50" if E is 3/4" thick.
S   - 0.1"

Milled relief for opening pump case lid.
T   - 0.70"
U   - 0.13"
V   - 0.07"
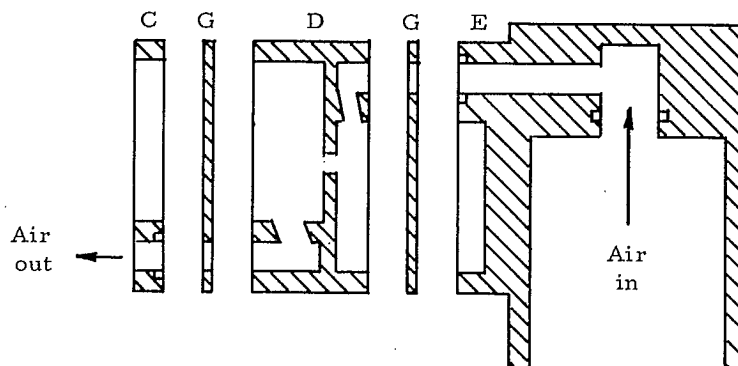
Air passages
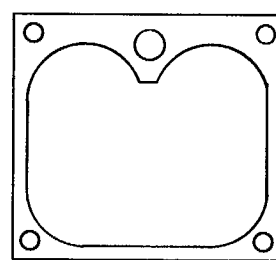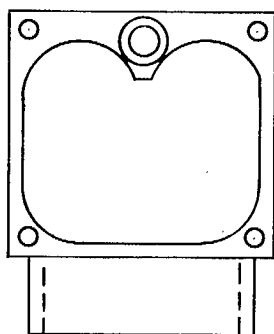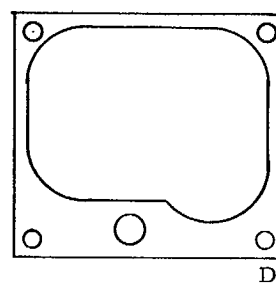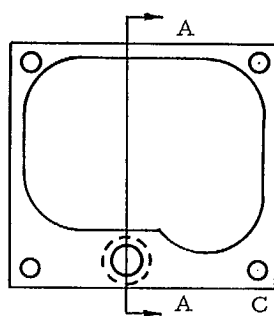W   - 0.125" dia.
X   - 0.3" x 0.125" or equal area.

Attaching to pump case
Y   - Matching holes in pump case.
Z   - Pushes on pump inlet tube. Check size of tube for O ring 'H' seal.
     Remove casting burr if necessary.

Air in

I   C   I
     D

G

E

G

F

I   I
P
Q
W   R
X
S
X
J   J

Air out

N
M
L
K

Section A-A   Section B-B

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Fig. G.6 - Pulsation damper for Casella Model B personal dust sampler

Section A-A

Air out

Air in

C   G   D   G   E

A   C

D

E

Obverse of D

Fig. G.7 - Pulsation damper and cyclone-filter holder for mounting on cap lamp battery.

G.5. References

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APPENDIX H

ANALYSIS OF ERRORS IN GRAVIMETRIC AND X-RAY DIFFRACTION ASSESSMENTS

Random and systematic errors can occur in gravimetric and X-ray diffraction assessments of dust samples. This Appendix describes an experimental assessment of errors. Those detected were mainly random, the only systematic error detected was in calibrating the X-ray diffraction equipment for some samples not taken by the normal method. Types of errors detected were:

1. weighing errors due to balance and interpolation of 5th place in reading the optical scale
2. damage in handling:
    (a) thin slivers of filter material from the cutting operation are often left on the filters and may be lost after taring if they are not removed
    (b) other damage resulting in loss of filter material
    (c) gain of extraneous material from dirty filter holder
    (d) transfer of coarse non-respirable dust from cyclone by either rough handling or horseplay
3. human error — substantial transcription and arithmetical errors have been detected
4. ashing — the observed changes in weight of clean filters when ashed are close to those in 1 above; however, overheating can change the filter weight and careless handling can lead to loss in ash or interchanged filters, with subsequent confusion
5. errors in X-ray assessment.

H.1. Weighing Errors

Since all filters are weighed two and possibly three times, it is important to know the limits of accuracy of the balance. Systematic errors are of little concern here since only a weight difference is needed and the same balance is used for all weighings.

A semi-micro Mettler balance with scale divisions of 0.05 mg, read to 0.01 mg is used for most work. When greater precision is needed a microbalance is used. Random errors in filter weights occur due to variations both in the balance and in fifth-place reading.

To determine the magnitudes of the random errors, ten clean silver membrane filters were selected for repeated weighings. They were read after equal time intervals for one month and the changes in weight readings were determined. The results are given in Table H.1 and a frequency distribution is shown in Fig. H.1. When the subjective nature of estimating the fifth decimal place with possible preferences is taken into consideration, the error curve can be considered to be Gaussian. This method of analysis could also tend to make the peak higher and narrower than it really is. The most probable error is zero and no errors greater than ± 80 µg were observed. The standard deviation, σ of the results is ± 30 µg taken to be the accuracy of weighing and fifth place reading errors.

H.2. Errors in Gravimetric Assessment

A large proportion of the field samples indicating over 100% quartz were low in weight and it seemed likely that errors in gravimetric assessment of total respirable dust could be the main cause of the high quartz indication. Thus, an estimate of the errors in the mass of total respirable dust was made, assuming:

1. X-ray analysis of quartz is accurate
2. quartz content expressed as a percentage is constant in the mineral dust in any one mine
3. proportion of non-mineral dust in the samples showing unduly high quartz percentage is negligible.

For each mine an average quartz content, Q%, was determined from ashed heavy samples of more than 1 mg, and this was used to determine the expected weight of the dust sample on all low weight samples showing higher than expected quartz percentages.

Table H.1 - Distribution of random errors in weighing

| Filter no.	Mean weight (mg)	Frequency of deviation from mean for each value, in mg														
		-.07	-.06	-.05	-.04	-.03	-.02	-.01	0	-.01	.02	.03	.04	.05	.06	.07
W 1	157.15	0	0	0	0	1	1	0	4	0	1	1	0	0	0	0
W 2	148.32	0	0	1	0	2	0	0	1	2	0	1	0	1	0	0
W 3	179.65	0	0	1	0	1	1	1	1	0	1	1	1	0	0	0
W 4	161.51	1	1	0	0	1	0	0	2	0	0	1	0	1	1	0
W 5	179.90	0	0	1	0	1	0	2	0	2	0	2	0	0	0	0
W 6	171.91	0	0	0	1	0	3	0	0	0	2	0	2	0	0	0
W. 7	179.00	0	0	0	1	0	2	0	1	2	2	0	0	0	0	0
W: 8	171.40	0	0	0	0	0	0	2	3	3	0	0	0	0	0	0
W.9	176.52	0	0	0	1	0	0	2	2	3	0	0	0	0	0	0
W10	176.01	0	0	0	1	0	0	4	1	0	0	0	2	0	0	0
Totals		1	1	3	4	6	7	11	15	12	6	6	5	2	1	0

$\sigma = \pm 0.03$ mg
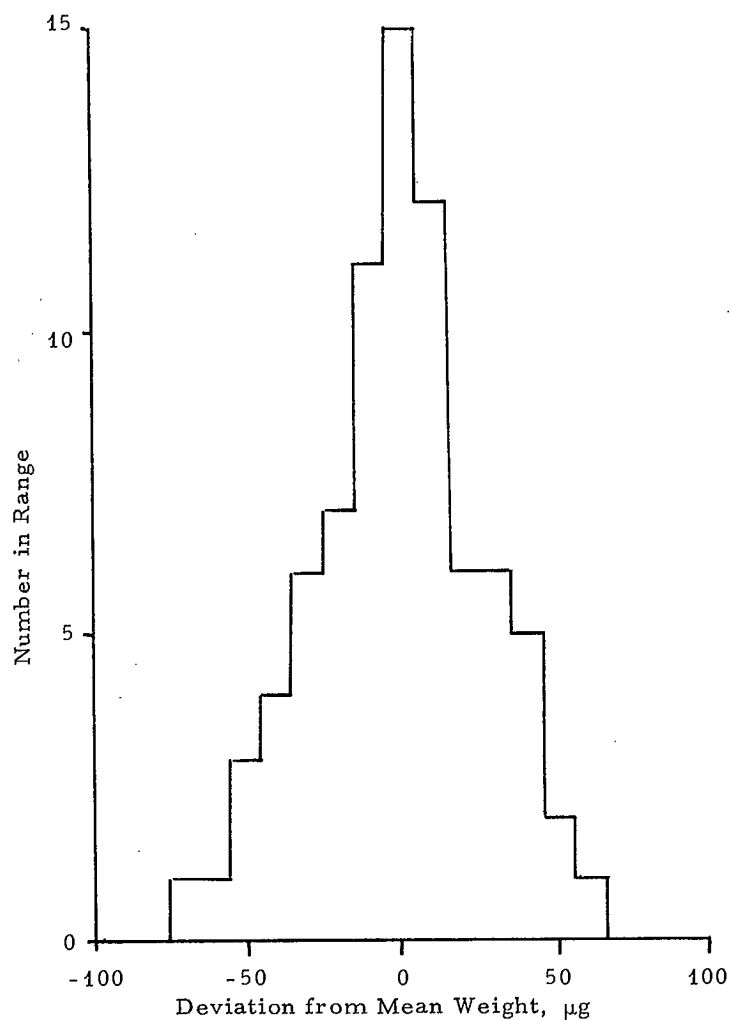
Fig. H.1 - Distribution of errors associated with weighing

$$W_E = 100 \cdot \frac{Q}{Q\%}$$

where Q is the XRD assessment of quartz, and Q% is the appropriate expected quartz percentage for that mine. An estimated error, ϵ, is then determined as:

$$\epsilon = W_M - W_E$$

where W_M is the measured weight of dust.

This procedure determines only those samples which are lighter than expected and thus only the errors with negative values are detected.

The distribution curve of the estimated errors is shown in Fig. H.2. Figure H.3 shows correlation between the estimated error and the expected weight of mineral in the sample, plotted separately for mines with high and low quartz contents. The technique suggests that substantial errors can occur in gravimetric assessment, but it should be noted that method of selecting samples may well omit many samples with small errors and the proportion of large errors is thus likely to be overestimated.

Figure H.4 compares the cumulative probability curve of the estimated errors in gravimetric assessment with weighing errors. The estimated error curves suggest three error terms of substantially different magnitudes:

1. a standard deviation of about 35 µg on all samples
2. a standard deviation of about 80 µg affecting about one third of the samples
3. an error term greater than 100 µg affecting less than 5% of the samples.

The first error term is very close to errors, σ = 30 µg, associated with the balance and fifth-place reading errors.

Identification of the origin of the second error term is difficult but could include handling and transcription errors in fourth-place readings.

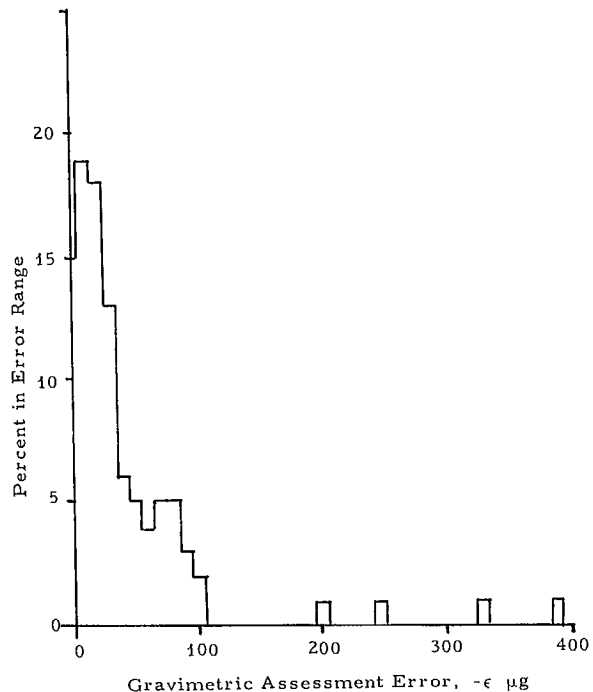The third error term is substantial but fortunately only affects less than 5% of the

Fig. H.2 - Distribution of negative errors in gravimetric assessment calculated from samples showing high quartz contents

samples. This portion of the curve does not contain sufficient points to be accurate.

The presence of combustible dust would lead to an increased magnitude of the expected error equal to the mass of combustible dust. On all ashed samples analyzed to date the combustible portion has formed about 50% of the total respirable dust. Thus, the additional expected error due to ignoring combustible dust could be as great as the expected mineral weight. The average for 95% of the samples showing errors of less than 0.09 mg was 0.18 mg. However, because these samples were selected as showing higher than expected quartz contents they probably average lower in combustible dust. A reasonable description of the errors in gravimetric assessment of total respirable dust is that 90% of the samples have gravimetric assessment errors less than 100 µg in magnitude, and over 97% have errors less than 150 µg. The smaller errors are probably evenly distributed on either side of
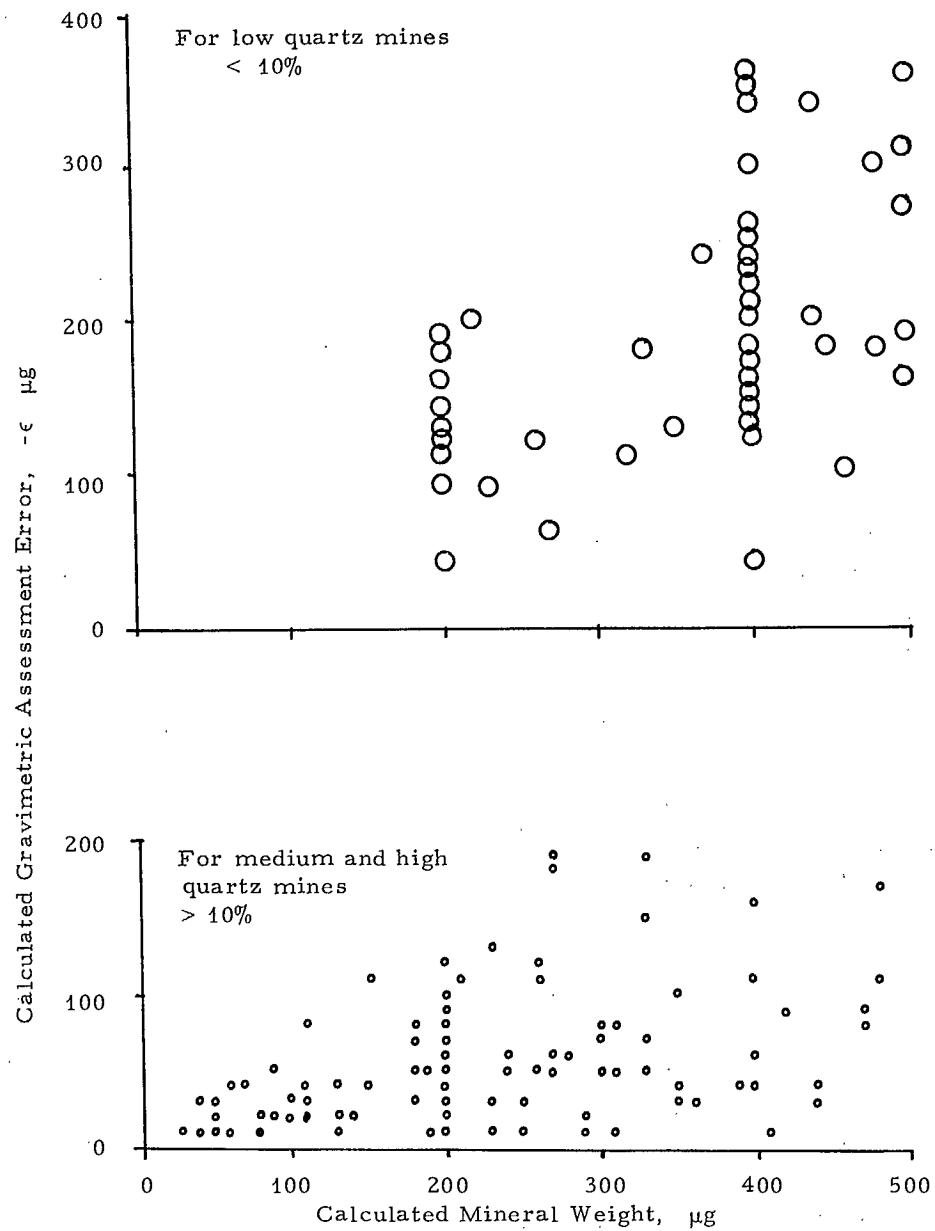
Fig. H.3 - Gravimetric assessment error plotted against calculated mineral weight
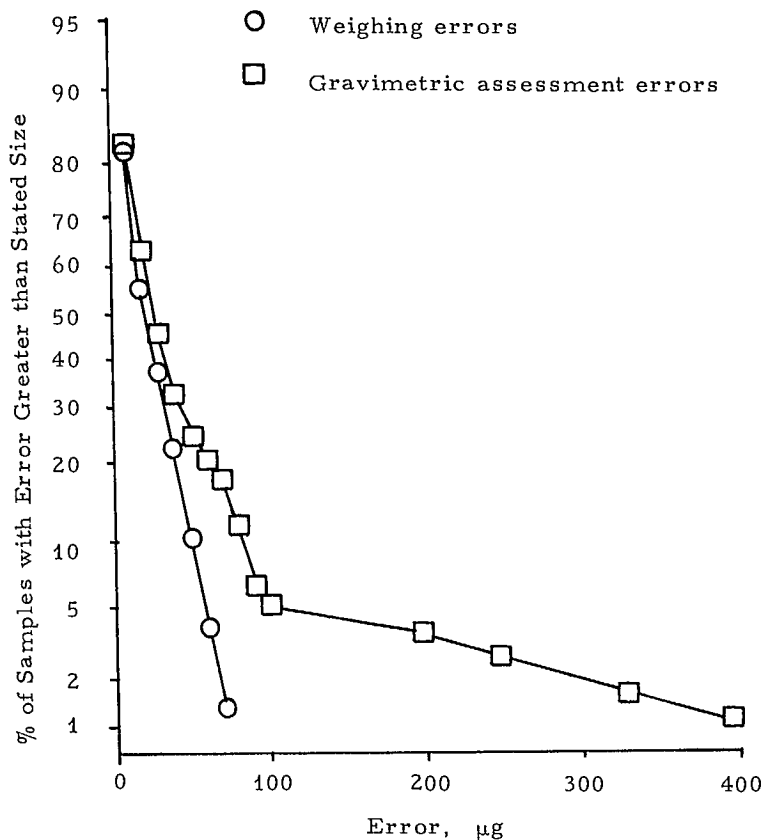
Fig. H.4 - Cumulative probability curves of weighing and gravimetric assessment errors

zero, and errors over 0.15 mg may tend to be more negative than positive if the major cause is filter damage.

As these estimated errors in gravimetric assessment are in reasonable agreement with experience, apparently gravimetric errors can give substantial errors in calculated quartz percentages on individual samples. It is concluded that useful figures for quartz percentages can only be obtained on heavy samples or as the mean of a number of samples.

H.3. Errors in X-ray Assessment

A number of errors can occur in X-ray assessment as discussed previously. In this section relevant experimental results are presented and given in two categories: measurements on standard samples, and duplicate measurements on samples.

Measurements on standard samples

The use of standard quartz samples was introduced to overcome secular variations in X-ray output and in adjustment of the equipment. X-ray intensity from standard samples dropped 50% after installing of a new chromium tube during a target 6-month period and running time of 2200 hours. This is a very significant reduction in X-ray tube output and thus must be included in any assessment of repeatability of measurement. However, running times have not been recorded and the only time variable that can be used is the number of batches or samples run. As the number of batches is easier to check, this has been used in a linear regression analysis of the relationship between batch number and the measured peak area of one of the two standards used. The regression analysis was done on the two most-used

diffraction lines, and results are given in Table H.2.

Table H.2 shows that the average change in X-ray intensity per batch of samples is negligible at about 0.3% and that the standard error of the measurement is 7.5% when corrections are made for decrease in intensity with time (batch number). However, other sources of error in the intensity which apply to both the samples and the standards are:

1. slight variations in setting of the X-ray diffraction equipment
2. changes in X-ray intensity which are not linear with batch number.

Thus, the actual variation from sample to sample because of variation in measuring standards is less than the 7.5% given above and is probably less than 3%.

Duplicate Measurements

The first set of duplicate measurements was undertaken when selecting 125 samples for an interlaboratory check. These covered a wide range of mines and most had been analyzed two years or more previously. The analyses are ex-

pressed as best estimates. Distribution of the differences between the two analyses was approximately Gaussian centered on a zero mean difference. Figure H.5 shows the distribution plotted against mass. It can be seen that the maximum differences range between 30 µg on light samples and 60 µg on heavier samples.

Between these two sets of measurements improvements in technique and equipment were introduced. The samples had been stored possibly damaged leading to loss of quartz or had been contaminated leading to gains in quartz; thus, differences between the two analyses might not be representative of the analyses now undertaken.

The second set of duplicate measurements was made on 33 carefully selected undamaged samples, which were analyzed twice within a 4-week period. Results are given in Fig. H.5, and show that the differences between the two analyses range from 10 µg on light samples to 3% on heavy samples, an improvement over the first set, and probably showing the best repeatability available. However, damage and interference are probably the major factors in limiting accuracy of quartz analysis.

Table H.2 - Statistical linear regression analysis of X-ray intensity (peak area) from one quartz standard

	X-ray diffraction line	
	1,0,1	1,1,2
Intercept (≡ intensity using new tube)	25180	3761
Regression coefficient	-65	-8.5
Change in intensity per batch[1], %	-0.35	-0.3
Correlation coefficient	-0.954	-0.948
Standard error of estimate	1213	215
Reliability of measurement[2], %	7.5%	7.5%

1 Regression coefficient divided by the mean value of the X-ray intensity · 100.

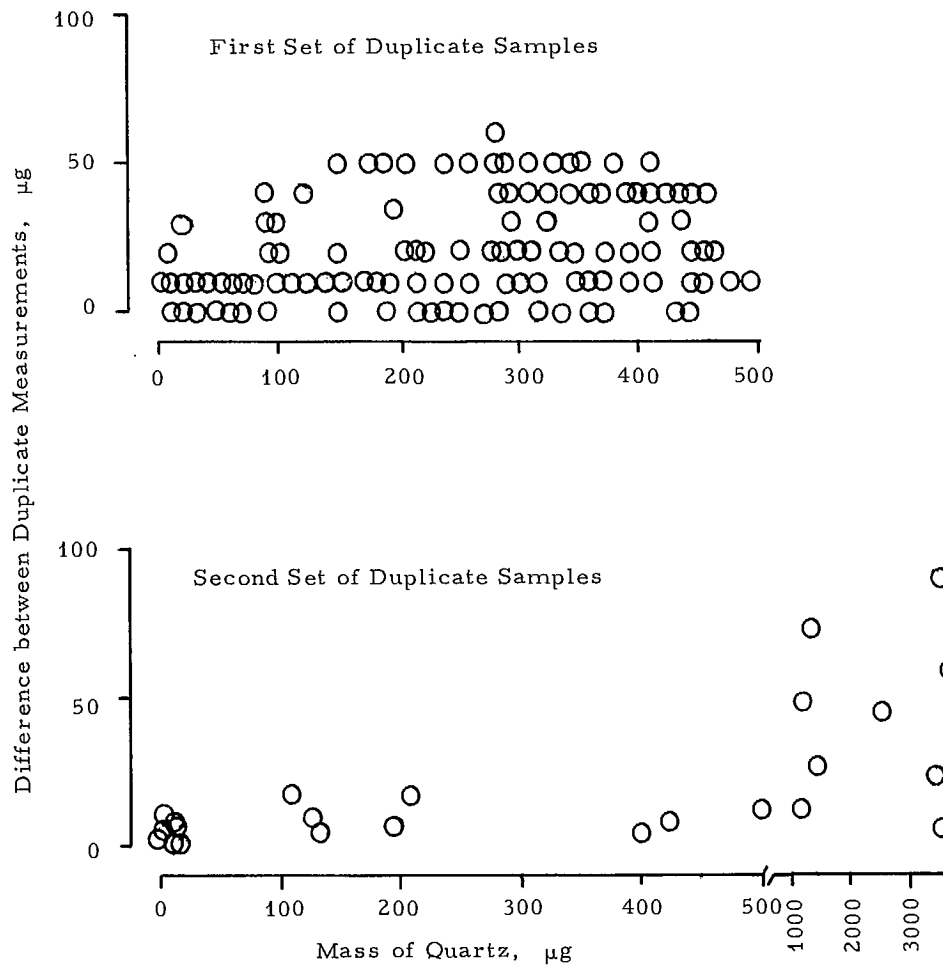2 Standard error divided by the mean value of the X-ray intensity · 100.

Fig. H.5 - Differences between duplicate measurements of quartz

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