COLLABORATIVE TESTS OF TWO METHODS FOR DETERMINING FREE SILICA IN AIRBORNE DUST

Final Report

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16. Abstract (Limit: 200 words)

Two methods were collaboratively tested in 15 laboratories:

- XRD Method--PCAM 259, Free Silica (Quartz, Cristobalite, Tridymite) in a Airborne Dust.
- IR Method--Method for Infrared Determination of Quartz in Respirable Coal mine Dust.

Samples for the tests were collected from aerosols prepared in a specially adapted laboratory generation system. For the XRD method, the percent relative standard deviation (%RSD) for samples containing between 50 and 200 µg of silica and varying amounts of background matrix ranged from 15%-23%. The major component of variability was due to between-laboratory differences (10%-15%) with a lesser contribution from intralaboratoy differences (7%-10%). The use of personal sampling pumps added significantly to the interlaboratory variability, with an estimated error of 17% found for sampling pump variability. For the IR method, a %RSD of 13%-22% was found over the range of 25 to 160 µg silica in coal mine dust. The between-laboratory differences (8%-14%) were the major component of variability with this method; intralaboratory differences were 7%-10%. Collection of samples with personal sampling pumps increased the interlaboratory error, the estimated sampling pump error being 24%. The methods were found to be unbiased. Both remained classified as B methods under NIOSH criterion that a B method measure within 25% of the "true" value 95% of the time, in a single laboratory.

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ABSTRACT

A collaborative study of the determination of free silica in airborne dust was conducted in which an x-ray diffraction (XRD) and an infrared (IR) method were examined and compared. These methods are:

- XRD Method--PCAM 259, Free Silica (Quartz, Cristobalite Tridymite) in Airborne Dust.
- IR Method--Method for Infrared Determination of Quartz in Respirable Coal Mine Dust.

The study's objectives were to obtain information on the precision and bias of these methods for monitoring worker exposure. Fifteen laboratories participated in each test, in a program structured to assess both sampling and analytical errors and to determine the analytical error sources. Samples for the collaborative tests were collected from aerosols prepared in a specially adapted laboratory generation system. For the XRD method, the percent relative standard deviation (%RSD) for samples containing between 50 μg and 200 μg of silica and varying amounts of background matrix ranged from 15% to 23%. The major component of variability was due to between-laboratory differences (10% to 15%) with a lesser contribution from intralaboratory differences (7% to 10%). The use of personal sampling pumps added significantly to the interlaboratory variability, with an estimated error of 17% found for sampling pump variability.

IR method results were similar. A %RSD of 13% to 22% was found over the range of 25 μg to 160 μg silica in coal mine dust. The between-laboratory differences (8% to 14%) were the major component of variability with this method also. Intralaboratory differences were 7% to 10%. Collection of samples with personal sampling pumps increased the interlaboratory error, the estimated sampling pump error being 24%.

The methods were found to be unbiased and gave similar results for coal mine dust samples. Both remained classified as B methods under the NIOSH criterion that a B method measure within 25% of the "true" value 95% of the time, in a single laboratory.

In a preliminary study, both methods were evaluated for ruggedness. Factors tested included the mailing of samples, use of either a low-temperature asher or a muffle furnace, and procedures involved in the material transfer steps.

Evaluations of the size distributions of several quartz materials were made in a separate study to select specific quartz material for use as a calibration standard. The basis for selection was that the size distribution of the bulk

material should adequately match the size distributions of materials penetrating the cyclones when sampling at 1.7 L/min. Min-U-Sil 5, a commercially available quartz powder, fits this criterion and is recommended as a calibration standard.

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Mr. David Ingersoll was a key SRI person. In addition to his contributions to design of the ruggedness studies, he prepared the samples and did the laboratory studies associated with selection of a calibration standard. Dr. Wesley R. Harris carried much of the responsibility for the ruggedness study of the XRD method. Mr. William R. Peifer did the laboratory studies for the ruggedness test of the IR method and contributed to that report. Mr. Curtis W. Beeman helped establish the generation system and helped conduct the two sampling sessions at SRI. XRD analyses were done by Mr. Eldon P. Farley. Dr. Francis Dresch, senior statistician, was a major contributor to the design and evaluation of the tests.

Ms. Helen Lang, U.S. Bureau of Mines, has been generous with her time in support of the project. The IR method was developed by Ms. Lang, and she shared the results of her laboratory studies.
Thirty laboratories participated in the collaborative tests. Many of these volunteered their time and efforts. During the several meetings and many phone calls, laboratory representatives were helpful with suggestions and comments. These laboratories are listed alphabetically below:

XRD Collaborative Studies

American Foundrymen's Society
Bethlehem Steel Corporation Environmental Health Laboratory
Clayton Environmental Consultants, Inc.
Commonwealth of Virginia Consolidated Laboratory Services
Coors Spectro Chemical Laboratory
IIT Research Institute
Indiana State Board of Health
Martin Marietta Laboratories
Mine Safety and Health Administration, Denver, Colorado
Mine Safety and Health Administration, Pittsburgh, Pennyslvania
Minnesota Department of Health
NIOSH, Cincinnati, Ohio

The Travelers Insurance Company
USDOL-OSHA, Salt Lake City
Wisconsin Occupational Health Laboratory

IR Collaborative Studies

Alberta Workers' Health, Safety and Compensation
State of Connecticut Department of Health
Commercial Union Insurance Company
Fireman's Fund Insurance Company
Galson Technical Services
Health Sciences Associates
Indiana Analytical Laboratory, Inc.
Industrial Hygiene Laboratory
Kennecott Environmental Laboratory
Mine Safety and Health Administration, Pittsburgh, Pennsylvania
Minnesota Department of Health
NIOSH, Cincinnati, Ohio
Tennessee Eastman Company
State of Washington Department of Labor/Industry
U.S. Bureau of Mines.

SECTION I

INTRODUCTION

The inhalation of crystalline silica is one of the oldest workplace hazards known to man. Early workers in stone suffered from silicosis, which has been known by various terms over the decades (1); there is still significant potential for exposure to silica. Today it is estimated that 1,200,000 workers may be exposed to atmospheres of free silica, mostly quartz, in mining, manufacturing, construction, and agriculture. Silica is a component of much of the earth's crust; its physical properties and morphology in fine powder form make it an ideal additive for products such as paint and soap powders. The importance of control of worker exposure must not be underestimated, for inhaled crystalline silica lodges in the lung where it damages the tissues.

Effectiveness of worker protection is measured by collecting airborne samples from a worker's breathing zone. Adequate methods are required to make these measurements. Three general types of methods are readily available for analysis of silica. These use x-ray diffractometry (XRD), infrared analysis (IR), or spectrophotometry to estimate the amount of silica in each sample. The first two techniques measure the free silica; in the third, the silica is dissolved and a blue silicomolybdate complex is formed.

NIOSH has developed a sampling and analysis method for free silica based on the analysis by XRD. This method has been extensively tested in the NIOSH laboratories and has been published as PCAM 259, Analytical Method for Free Silica (Quartz, Cristobalite, Tridymite) in Airborne Dust. This method, or variations of it, is in widespread use. Appendix A contains the full XRD method, which is summarized here:

- Airborne dust is collected from the breathing zone of the worker with a personal sampling pump. Air is drawn through a 10-mm nylon cyclone at a rate of 1.7 L/min; the respirable fraction penetrating the cyclone is trapped on a PVC filter.

- The PVC filter and organic fraction of the dust are destroyed in either a muffle furnace or a low temperature asher (LTA).

- Silica and other residue are suspended in solvent and deposited uniformly on a silver membrane filter.

- The silica is analyzed by x-ray diffraction, and the intensity of the peak is compared with that of calibration standards.

- The silver filter serves as an external standard to detect and correct for sample self-absorption. The intensity of the

diffracted silver peak of the sample is compared with that for a clean silver filter, and a correction is applied, if necessary, to the silica result.

A second method, based on the IR analysis of silica, was developed by the U.S. Bureau of Mines. This method, which has not been published previously, is specific for quartz in respirable coal mine dust and is an alternative to the XRD procedure for these sample types. This method relies on the use of an IR-transparent filter rather than the more commonly used KBr pellet. This method, included in full as Appendix B, is summarized below:

- Coal mine dust is sampled from the breathing zone of the worker with a personal sampling pump. Air is drawn through a 10-mm nylon cyclone at 2.0 L/min; the respirable fraction penetrating the cyclone is trapped on a preweighed PVC filter.

- The PVC filter is reweighed to determine total mass, then the filter and the organic fraction of the deposit are destroyed in either a muffle furnace or an LTA. If the laboratory uses a muffle furnace, and the sample contains calcite, the filter is rinsed in acid before ashing.

- The residue from ashing is suspended in solvent and redeposited on an IR-transparent filter.

- IR analysis of the filter is done by measuring absorption at 800 cm^{-1}. Calibration standards are prepared on similar filters. If the laboratory uses an LTA, a correction must be made for kaolinite, a common contaminant in coal mine dust, which absorbs at 800 cm^{-1}. The correction is made by using a second band of kaolinite, at 915 cm^{-1}, to subtract its absorbance at 800 cm^{-1}.

The main purpose of this study was to collaboratively test each of these methods to determine what levels of precision and bias may be expected in their application. It is well known that, even though good precision may be obtained for samples analyzed in one laboratory, the same method will give poorer results for samples analyzed in many laboratories. One factor is responsible for this difference in precision between laboratories: each laboratory may have its own systematic error, or bias, which differs from that of other laboratories. Although a laboratory may improve its own precision by practicing a method, the laboratory will be unaware of bias unless its results are compared with results from other laboratories. An adequate evaluation of the method, therefore, requires that samples be analyzed by many laboratories, as is done in a collaborative study.

In a collaborative test, three statistics are derived: the total standard deviation of the method, the within (intra) laboratory standard deviation, and the between (inter) laboratory standard deviation. These statistics can be applied in several ways. For example:

- The total standard deviation gives confidence limits to the results for any individual measurement. If a future sample is analyzed by the tested method, the total standard deviation for the method should be applied to the result.

- The intralaboratory standard deviation, a measure of the precision of samples analyzed in one laboratory, can be applied when comparing samples taken at several locations or at different times. For example, we may be interested in comparing samples taken before and after installation of production control operations, in which case the intralaboratory standard deviation can be used if the samples are analyzed in one laboratory.

- The interlaboratory standard deviation for systematic error indicates the range of bias. We hope, of course, to eliminate bias, but once we know its magnitude we can attempt to make improvements in the method.

Since both methods tested here are for sampling as well as analysis and since the sample collection process is a major potential source of error, the standard deviation for sampling error was also estimated. Two types of collection techniques were compared: first, all filter cassettes of a set were prepared by one individual, and samples were collected using a matched group of critical flow orifices; second, a number of individuals prepared the filter cassettes, and samples were collected using a group of battery-operated personal sampling pumps. The difference in variability of results for the two sets was used to estimate errors due to sample collection.

For accuracy of measurements, calibration materials for both methods must have the appropriate size distribution. We did not know if all laboratories used the same type of standard materials, and the XRD collaborative test was an opportunity to compare the results of using many standards to those using one standard material. XRD test collaborative laboratories reported results based on their normally used calibration curve and on a curve prepared from a standard supplied by SRI. From these two types of results, we were able to compare the variability due to change in calibration.

Sufficient preliminary study was required to justify collaborative study of the methods. The analysis of crystalline silica is difficult, and there are numerous problems not found with other materials. For example:

- Standards for calibration must have particle size distributions matching those of the samples.

- Standards must be prepared from suspensions rather than solutions; this requires considerable care and practice.

- There are several material transfer steps in the analysis--all potentials for sample loss.

- Many materials interfere in the analysis either by giving positive response for the silica measurement or by depressing the response.

Before the collaborative tests, both methods were evaluated for ruggedness in our laboratory. In a ruggedness test, parts of the procedure are deliberately varied, in minor but reasonable ways, to discover which steps must be carefully controlled. For example, if it is critical that the ashing time be controlled to no greater than 2 hours, rather than 2.5 hours, this must be specified in the method writeup. Sections III and IV are detailed reports of the ruggedness studies for the XRD and IR methods, respectively. Although the ruggedness studies preceded the collaborative testing, they are presented in later sections of the report since it is not necessary to read them for an understanding of the collaborative study, which is the main topic of this report.

Min-U-Sil 5 was chosen by SRI as a calibration material for use by all the collaborative laboratories, on the basis of the experimental studies described in Section V. The particle size distributions of bulk Min-U-Sil materials were compared with size distributions of the same materials after passage through 10-mm nylon cyclones. Samples for both the ruggedness studies and the collaborative tests were prepared in the test atmosphere generation facility described in Section VI. As with the reports of the ruggedness studies, we have presented these two descriptions in later sections of the report.

In this report the words silica, crystalline silica, and free silica are used interchangeably and refer to alpha-quartz. The IR method is specific for quartz in coal mine dust; PCAM 259 is applicable to any of the silica polymorphs--quartz, tridymite, and cristobalite--but was studied collaboratively using quartz.

SECTION II

COLLABORATIVE TEST

PLANNING

Ruggedness Tests

Before the collaborative testing program, the XRD and IR methods were tested for ruggedness. Ruggedness testing is a formalized study of the method in one laboratory to efficiently assess whether there are steps in the method that must be closely controlled. Certain steps of each procedure were selected, and these variables were systematically varied to observe the effect of making minor but reasonable modifications. Also, because users may elect to ash the the filters in either a muffle furnace or a low temperature asher (plasma asher), we compared results for these two asher types for each method. These studies are described in Sections III and IV of this report, but are summarized here. The variables examined were:

- XRD Method

  Asher type--Muffle furnace or low temperature asher (LTA) including variables unique to each asher type.
  - --LTA: Ashing time, power to asher, oxygen flow rate.
  - --Muffle furnace: Ashing time and temperature.

  Amount of matrix material deposited with the silica

  Effect of mailing of samples

  Material transfer steps
  - --Rinsing of chimney during redeposition of ashed residue.
  - --Length of time for sonicating residue, to resuspend it in solvent.
  - --Ashing time and temperature.

- IR Method

  Asher type--Muffle furnace or low temperature asher, including variables unique to each asher type.
  - --LTA: Ashing time and LTA power.
    Amount of calcite on the sample.
    Amount of kaolinite on the sample.

--Muffle furnace: Ashing time and temperature.
Amount of calcite on the sample.
Amount of kaolinite on the sample.
pH of solvent used to remove calcite.

Some of the variables, such as mailing of samples and the material transfer steps, are common to both methods and were not repeated in the IR ruggedness study if they were evaluated in the XRD study.

Effects of calcite and kaolinite were studied because these two materials are frequently collected on the coal mine dust samples. In the IR method, calcite must be removed from the filter before ashing if a muffle furnace is used, because calcite reacts with silica at high temperature. Calcite does not interfere in the analysis if left on the filter during low temperature ashing.

Kaolinite, however, may interfere if samples are ashed at low temperature. The IR absorption band for kaolinite is superimposed on the silica band; this band disappears after high temperature ashing but not after low temperature ashing. Laboratories with an LTA must construct a kaolinite calibration curve from which a correction is made. (Refer to Section IV for more detail or to Sections 8 and 9 of the IR method in Appendix B).

Both methods were found to be rugged with respect to minor variations of the procedural steps. For the XRD method, we could not resolve the question of whether the sample self-absorption correction (see Section 10 of PCAM 259) caused overestimation of silica if a large amount of dust was codeposited with the silica. For the IR method, precision of analyses was better for samples treated in a low-temperature asher than for those ashed at high temperatures.

Selection of Calibration Standard

The accuracy of quantitation for both the XRD and IR methods depends on matching the particle size distributions of standards to those of samples. From our particle size studies, described in Section V, Min-U-Sil 5 was selected as a standard. Each participating laboratory was supplied with several grams of this material from a common supply.

Selection of Laboratories

Fifteen laboratories participated in each collaborative test. All the laboratories were proficient in silica analysis, as determined by their participation in the American Industrial Hygiene Association (AIHA) Proficiency Analytical Testing (PAT) program. Each laboratory was assigned an identification number.

Both private and government laboratories participated. Of the 54 PAT laboratories proficient in silica analysis using XRD, 2 are associated with universities, 17 are government (state or federal), and 35 are private. The XRD collaborative test had 7 private laboratories, 4 from state governments, and 4 from the federal government. Although some laboratories normally varied specific steps of the method, all were able to carry out the exact procedure for this testing.

Twenty-five laboratories, including nine government, one university, and fifteen private, are proficient in silica analysis by IR. The IR collaborative test had 3 federal and 3 state laboratories, 1 Canadian provincial laboratory, and 8 private laboratories. Since the IR method was newly proposed, only one laboratory had been doing silica analysis by IR directly from a filter. Other laboratories used a KBr pellet, as described in NIOSH Method PCAM 110, Quartz in Coal Dust by Infrared Spectroscopy.

EXPERIMENTAL DESIGN

General

The numbers of collaborators, samples, and sample types were chosen to meet the goals of the study, using the statistical techniques for collaborative tests described in the "Statistical Manual of the AOAC" (2). The concepts and data analysis are described later in the subsection "Treatment of Data."

Tests of the two methods were run in parallel and were similar in design and management. Except for one laboratory, there was no duplication of collaborators for the two programs.

The collaborative test program was divided into two phases. Phase I consisted of a practice round or preliminary test, followed by a briefing session. Phase II constituted the actual collaborative program, which was divided into two stages: one to test for the analytical errors and one to evaluate errors associated with sampling.

Phase I - Preliminary Test

In the first round of this study, collaborators received a Pretest Set of samples and a copy of the analysis method with instructions that the method should be followed exactly. All laboratories had already received a copy of the method and were prepared to use it.

IR laboratories also received a 2-gram supply of kaolinite and a specially fabricated 1-cm-ID glass chimney required to make filter deposits (see Section 6.4.4 of IR method). These chimneys, which are not available from a commercial source, were supplied by H. Lang of the U.S. Bureau of Mines.

After completion of this Pretest Set, a briefing session was held to review the results, evaluate if further clarification of procedure descriptions were necessary, find out the source of gross differences between individual laboratories, and demonstrate laboratory procedures as required. An analyst from each laboratory and representatives from NIOSH, the U.S. Bureau of Mines, and SRI attended.

Phase II - Actual Collaborative Test

Table 1 is a summary of the various sample sets of Phase II, their method of collection and distribution, and purpose.

The first stage of Phase II consisted of distributing and analyzing sample sets collected by SRI personnel using the test atmosphere generation system's flow orifices to draw samples. The results of this stage were used to determine errors associated with analysis. The variability due to sampling error was assumed to be negligible when samples were collected using the flow orifices rather than sampling pumps. These samples correspond to XRD-Set I and IR-Set I in Table 1.

The second stage of Phase II was the analysis of sample sets collected by laboratory representatives using personal sampling pumps. Representatives met at the SRI generation facility in a three-day sampling session to collect this sample set. These individuals were either the industrial hygienist associated with the laboratory or a person selected by SRI who was familiar with sample collection procedures. Results from these samples were used to estimate errors associated with sample collection by personal sampling pumps. These are the XRD-Set II and IR-Set II samples listed in Table 1.

Both groups of collaborative laboratories received these two sets. In addition, XRD laboratories received a third set, which was identical to IR-Set I and is called XRD-Set III. Results from this set were used to compare performance of the two methods.

For each group of laboratories, all Phase II samples were distributed at the same time. Samples collected by SRI were sent to the laboratories at the conclusion of the sampling sessions. The appropriate method, with revisions proposed at the briefing session of Phase I, accompanied the samples.

Sample sets consisted of eight samples (four pairs), referred to as Levels 1, 2, 3, and 4, and two filter blanks. The samples themselves were PVC filters loaded with quartz only or with quartz and a background matrix, as listed in Table 2. The quartz-only samples served as a "baseline" sample, with the assumption that performance of the methods was optimum for this sample pair. The target range of quartz in the samples was 50 to 200 g, representative of amounts of interest for worker exposure for an 8-hour sampling time, although the actual sampling time in the generation facility was shorter.

Table 1. Summary of sample sets for XRD and IR collaborative tests.

Sample type	Method of collection	Distributions and identification		Purpose
		XRD Labs	IR Labs	
Containing XRD matrix of calcite/ kaolinite/talc/ iron oxide	By SRI, using matched flow orifices	XRD-Set I	--	Evaluate variance due to analytical errors, XRD
Containing XRD matrix of calcite/ kaolinite/talc/ iron oxide	By laboratory representatives, using sampling pumps	XRD-Set II	--	Evaluate variance due to sampling errors, XRD
Containing IR matrix of coal mine dust/kaolinite/ calcite	By SRI, using matched flow orifices	XRD-Set III	IR-Set I	Evaluate variance due to analytical errors, IR, and compare methods (XRD and IR)
Containing IR matrix of coal mine dust/kaolinite/ calcite	By laboratory representatives, using sampling pumps	--	IR-Set II	Evaluate variance due to sampling errors, IR

Table 2. Composition of sample sets.

Sample Component	Level 1	Level 2	Level 3	Level 4
XRD-Set I and XRD-Set II*				
Silica, μg	54.0 ± 3.6†	102 ± 4.0†	207 ± 6.7†	104 ± 8.1†
Matrix, mg	1.1	--	1.8	1.8
Iron oxide, mg	--	--	--	0.78
IR-Set I/XRD-Set III				
Silica,‡ μg	107 ± 7.7†	150 ± 37∇	122 ± 5.9†	65 ± 10†
Coal mine dust, mg	--	0.81	2.0	0.71
Kaolinite,§ mg	--	0.81	--	--
Calcite, mg	--	--	--	0.81
IR-Set II				
Silica,‡ μg	84.2 ± 4.6†	170 ± 8.3†	27.0 ± 1.8†	36.7 ± 4.2†
Coal mine dust, mg	--	1.4	1.45	0.62
Kaolinite,§ mg	--	0.14	--	--
Calcite, mg	--	--	--	0.2

*Sets were collected at the same time.
†One standard deviation for n = 6 samples.
‡Total silica, including amount contained in coal mine dust and amount added separately.
§Added separately.
∇An uncertainty of 25% (37 μg) was estimated; problems with the instrumentation during analysis caused imprecision in analysis.

For XRD-Sets I and II, the matrix was a mixture of inorganic minerals (calcite, kaolinite, and talc) and, in one level, iron oxide. The matrix amount was chosen to cover a reasonable range representative of actual samples. Because iron oxide is a strong x-ray absorber, its presence on one sample pair challenged the method's capability of correcting for sample self-absorption.

The IR test background matrix was coal mine dust. One level also contained calcite, which is used in coal mining areas to reduce the dust level, and kaolinite was added to one level. Although calcite does not interfere in the IR analysis, it does cause loss of silica in the high temperature asher if not removed. Kaolinite is a minor component of the coal mine dust used to prepare these samples, but more kaolinite was added to one sample pair because this method may also be used with other coal mine dusts containing a higher fraction of kaolinite. Kaolinite interferes in the analysis because it absorbs radiation at 800 cm^{-1}, where the quartz measurement is made.

Reporting

For XRD laboratories, results were reported twice for each sample: once based on use of the laboratories' normally used calibration curves and once based on calibration with material (Min-U-Sil 5) supplied by SRI. Except when noted, all data analyses in this report are based on the Min-U-Sil 5 calibration curve. Laboratory reports also included details of the XRD intensity measurements.

A net weight for XRD-Set II samples was also reported. Although method PCAM 259 does not direct users to determine sample weights, the gravimetric determinations made by the laboratories do provide additional information for users who calculate the OSHA standard based on percent silica. These sample weights are not part of the collaborative test.

IR laboratories reported results in micrograms silica per sample and in percent silica. The IR method requires that a net sample weight be taken.

EXPERIMENTAL STUDIES

Materials

Collection Unit for XRD Tests--
The filter unit consists of a polyvinyl chloride (PVC) membrane filter (37-mm diameter, 5-μm pore size) and a backup pad (Millipore catalog no. PVC503700) contained in a two-piece cassette filter holder.

Collection Unit for IR Tests--
The filter is a 37-mm diameter, 5-μm pore size PVC filter, preassembled in a three-piece inner packet, which is contained in a lightweight cassette (Mine Safety Appliances preweighed dust cassette, part number 457193). The inner packet, which weighs approximately 250 mg and is preweighed by MSA to the nearest 0.1 mg, is the PVC filter layered between a lightweight backup pad and aluminum cover piece.

Cyclone--
10-mm Dorr Oliver nylon cyclones were used.

Silica--
Min-U-Sil 5 was used as the calibration standard. However, Min-U-Sil 15 was used as the feed for the test atmosphere to make the test more realistic. Almost 45% of Min-U-Sil 15 is removed by the cyclone (compared with only a few percent of Min-U-Sil 5). The particles retained in the cyclone may become reentrained or in other ways affect the precision of samples from the generation facility, and this potential source of error was deliberately included.

Coal Mine Dust--
Dust from Pittsburgh Seam Coal (-200 mesh), naturally contaminated with both kaolinite and crystalline silica, was obtained from the U.S. Bureau of Mines, Department of the Interior.

Kaolinite--
This Georgia Kaolin product is sold under the name Hydrite UF, with a reported median particle size of 0.2 μm.

Calcite--
Microwhite 25, particle size range 0.5 to 15 μm, mean size 3 μm (as reported by the supplier) was used.

Talc--
Magnesium Silicate No. 399 from Whittaker, Clark & Daniels, Inc., was used. The average particle size is estimated to be 5 μm. (Approximately 85% of the test atmosphere passes through the 10-mm cyclone and is collected on the filter.)

XRD matrix--
The matrix consisted of talc, kaolinite, and calcite, with the following composition:

Component	Wt (%)
Talc	33.4
Kaolinite	33.7
Calcite	32.9

Iron oxide--
Hematite was obtained from the Frank D. Davis Company.

Independent Analysis of Samples

The amounts of coal mine dust, kaolinite, calcite, and iron oxide deposited on the filter samples were determined by gravimetric analysis or by knowledge of the generation rate. For each of the two tests, a method other than that being collaboratively tested was used to obtain an independent estimate of the amount of quartz on the sample filters. For the IR test, six samples per level were analyzed by the XRD procedure. For the XRD test, the independent method, adapted from NIOSH Method PCAM 106, was to treat the filter samples, containing only silica, with hydrofluoric acid to solubilize the silica, which was treated to form a blue silicomolybdate complex. The absorption at 620 nm was measured to quantify the silica.

Sample Preparation

All samples were collected from test atmospheres prepared in the SRI dust generation system described in Section VI. The individual sample components were loaded sequentially. For example, a test atmosphere of the matrix was prepared, and samples were collected until the target amount was achieved. Then a test atmosphere of silica was prepared and sampled to obtain the amount of silica needed.

For the XRD test samples, the silica source was a test atmosphere of Min-U-Sil 15. For the XRD matrix, kaolinite, talc, and calcite were generated as a three-component mixture; iron oxide was loaded separately.

For the IR test, a specified amount of coal mine dust was loaded. The coal mine dust naturally contains both silica and kaolinite. When a greater deposition of either of these materials was desired, separate test atmospheres of either Min-U-Sil 15 or kaolinite were prepared and sampled. Calcite was loaded separately.

Test air was sampled through 10-mm nylon cyclones. Sample flow rates were 1.7 L/min for XRD test samples and 2.0 L/min for IR test samples. Approximate collection rates for the various materials were as follows:

Silica	4 μg/min
Three component matrix of calcite, kaolinite, talc	40 μg/min
Iron oxide	50 μg/min
Coal mine dust	20 μg/min
Kaolinite	50 μg/min
Calcite	50 μg/min.

Precision of Sample Generation

There is a certain variability in the samples distributed to collaborators, which we need to know in order to evaluate the results. Based on several experiments, we estimated the precision of generation to be between 2% and 6%, for samples collected onto filters using the generation system's matched critical flow orifices to draw aerosol, and with the 10-mm cyclones in place. The lower limit of 2% is based on variability of the orifices (with no filter in line), which were evaluated by measuring the flow rates using a bubble meter and timer. The upper limit is derived from results of analysis of samples by evaluating SRI's data for a number of sample sets. The variance is a combination of collection and analysis errors, and although we cannot identify these separately, we are able to estimate a maximum sampling error as described below.

First, we estimate a minimum analyses error for SRI of 3.2% based on the data in Table 2, and an average %RSD of 7% for total error. Assuming that the collection and analyses errors are linearly added to form the total error, we estimate collection error from the relationship

$$(7\%)^2 = C^2 + (3.2\%)^2$$

where

C^2 = represents the collection error

and then calculate collection error to be 6%. This 6% represents the maximum variability of samples distributed to the laboratories for the sets collected with critical flow orifices

Distribution of Samples

For each run (level), enough samples were prepared so that each laboratory received one pair. Samples from each level were assigned to laboratories on a random basis so that there was no correlation between sample port location and laboratory. Except by chance, no two samples of a set were taken from the same sampling port for any one laboratory.

Sampling Sessions

Two separate sampling sessions, each of three days duration, were held at the SRI test atmosphere generation facility. Samples were collected as described in Section VI except that 30 individual personal sampling pumps were used to draw samples. Representatives of each laboratory were responsible for collecting two samples per run.

Sample pumps were calibrated at the beginning of each day with a cyclone and filter unit in line. For the XRD test, individuals were supplied with PVC filters, backup pads, and cassettes and were responsible for assembling the filter unit. Preassembled dust cassettes were supplied to the IR lab representatives. If the laboratory representatives had their own cyclones, which fit into the cyclone holder of the collection chamber, they used their own. Most cyclones were supplied by SRI, but there were no obvious differences in any of the cyclones.

When the filter unit/cyclone was assembled, it was handed to an SRI employee to place in the collection chamber of the test atmosphere system. The outlet of the filter cassette was connected to the associated personal sampling pump by connecting both to opposite ends of a permanently mounted port in the sidewall of the chamber, using Tygon tubing. Sampling lines from pumps to the samples were kept as short as possible. Once all samples and pumps were in place, the collection chamber was closed and sealed. The 30 pumps were then turned on briefly to ensure that they were operating properly. A test atmosphere was prepared, and after approximately 20 minutes, the signal was given to activate the pumps.

During sampling, the flow rate was adjusted, as required, by bringing the float of the pump's rotameter back to its original position. When two or more components were deposited on the filters, the pumps and samples were left in place during changeover of the generation system. At the conclusion of the sampling period, the signal was given to turn off the pumps. Samples were removed by an SRI employee and returned to the laboratory representatives.

Determination of Sample Weights

- XRD-- Clean desiccated PVC filters were weighed by laboratory representatives during the sampling sessions. The second weighing of these same filters was made at the collaborative laboratory when the filter was removed for analysis. These PVC filters weigh approximately 12 mg.

- IR-- Both Phase II sets were weighed. Phase II, IR-Set I, total sample weight was found from the difference between the final weight (made by collaborative laboratories) and the initial weight (made by MSA). Weighings were made to 0.1 mg.

  For Set II, initial and final weighings were made by laboratory representatives at the time samples were collected. The inner packet of the MSA dust cassette was

removed and weighed to the nearest 0.01 mg, then resealed into the same cassette. After sample collection, the packet was reweighed on the same balance. Samples were desiccated for at least 12 hours before each weighing.

TREATMENT OF DATA

Estimation of Components of Variance

The techniques of Youden and Steiner (2) for evaluating collaborative test results were followed to estimate precision and bias for the methods. In this "paired sample" scheme, each laboratory analyzes a set of matched pairs of samples, where the composition of the pairs extends over the range of applicability of the method. The total standard deviation and its components due to intralaboratory and interlaboratory error are calculated for each set of sample pairs. If the standard deviations are uniform over the range of samples used for the test, pooled or combined standard deviations may be calculated.

For our tests, each of 15 laboratories received sets of samples consisting of four "paired samples," referred to as Levels 1, 2, 3, and 4; the pairs of each level differed in some respect, either in amount of silica or in amount of matrix or both. For each level, several statistics were obtained, as defined below:

The total data standard deviation, S_d:

This standard deviation represents the overall performance of the method for the sample type of that level. It is composed of intralaboratory and interlaboratory errors, plus errors introduced by sample collection. Each laboratory's results for a pair are added together, and a standard deviation, S_d, is calculated from these totals.

The intralaboratory standard deviation, S_r:

This standard deviation, due to random errors, represents the inherent imprecision in the method. To obtain S_r, we find the difference for each laboratory's results for a pair, and calculate S_r from these differences. By using the differences to determine S_r, we eliminate the effect of change of bias since each laboratory's bias, which is presumed to be the same for each sample of the pair, drops out.

The interlaboratory standard deviation, S_b:

S_b is the component due to bias, or more exactly, the interlaboratory differences in bias. The term "systematic error" is also used for bias. The S_b is calculated from S_d and S_r, as described below. If there were no bias, or if each laboratory had the same bias, S_d and S_r would be equal.

The sampling pump standard deviation, S_p:

S_p represents errors introduced because personal sampling pumps, rather than critical flow orifices, were used to collect the samples. It is obtained as a difference between standard deviations of the samples taken with sampling pumps and those collected with flow orifices.

When the sample results for a set were returned and tabulated, and after elimination of outlier results as described later, the following calculations were made to arrive at the standard deviations for each of the four levels for each set of samples.

First, we found the total and the difference for each laboratory's pair at that level and inserted these values in the following formulas for the variance, or square of the standard deviations:

$$S_d^2 = \frac{\sum (T_i - \overline{T})^2}{2 (n - 1)} \quad (1)$$

and

$$S_r^2 = \frac{\sum (D_i - \overline{D})^2}{2 (n - 1)} \quad (2)$$

where:

T_i = total of paired sample results for laboratory i

$\overline{T}$ = average of T_i for n laboratories

D_i = difference of paired sample results for laboratory i

$\overline{D}$ = average of D_i for n laboratories.

These are the usual formulas for estimating variances, except that each is divided by two, in effect increasing the degrees of freedom, because both T_i and D_i are derived from two samples.

The total standard deviation, S_d, is composed of both S_r and S_b, the intra- and interlaboratory standard deviations. Since S_r and S_d were obtained from the laboratory results, S_b could be found from the relationship:

$$S_b^2 = 1/2 \quad (S_d^2 - S_r^2) \quad (3)$$

One-half the difference $S_d^2 - S_r^2$ is used because the estimate S_r^2 is obtained from the difference of two samples.

In an ideal method, interlaboratory errors would be negligible; that is, $S_d^2 \approx S_r^2$. To detect the significance of differences of S_d^2 and S_r^2 for each level, we compare the F-ratio

$$F = \frac{S_d^2}{S_r^2} \tag{4}$$

with values tabulated in statistical tables. At the 95% confidence level (15 laboratories), F-ratios greater than 2.48 must be reached to conclude that S_d^2 is significantly greater than S_r^2.

These calculations were repeated for each of four levels for each set of samples.

Three other definitions are useful:

$\overline{X}$ = average value of samples for any level, calculated as $\overline{T}$ divided by 2.

$\frac{\overline{X}}{S}$ = Relative standard deviation (RSD) or coefficient of variation (CV); this may also be expressed as a percent when multiplied by 100.

S^2 = variance, or squared standard deviation.

Test for homogeneity of variance was applied to the data for all levels, using the criterion of Youden and Steiner (2), to determine whether it was acceptable to combine the data for two or more levels within a set to arrive at a standard deviation for the total range of samples. If the data could not be pooled because the variances differed by too great an amount, the various statistics could only be summarized for each level. However, if the RSDs were found to be independent of the mean and the RDSs could be pooled, these were combined over as many levels in one set as possible.

The sampling pump error was estimated by comparing the data of samples collected by SRI (XRD-Set I or IR-Set I) with the data of samples collected with the pumps (XRD-Set II or IR-Set II). As it happened, when there was an increase in variability for the pump samples, it could be identified with an increase in interlaboraotry error, S_b. Thus the sampling pump standard deviation, S_p, was calculated from

$$S_p = \left[S_{b(II)}^2 - S_{b(I)}^2 \right]^{1/2} \tag{5}$$

where $S_{b(II)}$ and $S_{b(I)}$ are the interlaboratory standard deviations for Set II and Set I, respectively.

Identification of Outliers

Before the standard deviations were computed, data were tabulated and examined for extreme results. A sample was rejected if the laboratory reported loss due to any reason such as spillage. Each report was scrutinized for obvious computation errors or discrepancies. The data were then examined to see whether any laboratory showed consistently high or low values using the ranking scheme suggested by Youden and Steiner. Laboratories having a significant rank total (at the 5% level) were removed. Several of the laboratories having significant rankings or other extreme results were contacted to see whether the cause could be found. One laboratory found and corrected a computation error.

Individual outlier pairs were removed after application of Dixon's test (2), using the 95% confidence level. The process of rejecting outlier pairs was complicated by the interaction of sampling errors and outliers. On XRD Set II samples, for example, poor collection could be readily detected because of the presence of red iron oxide on the backup pad. Although these results could have been rejected as outliers, we chose to retain them to point out a possible source of error when assembling cassettes.

Another type of judgment was made. When the tabulated data were scrutinized, some individual points appeared to be outliers for that level, even though the pair was not. For example, within a set of 30 points, one result of a pair would be extreme, although the sum of that pair was not. The decision was this: if for an individual laboratory there was close agreement between individual pairs for all levels except one, an individual sample, Y_i, was considered to be an outlier if it failed the following outlier test:

$$\left| \frac{\overline{Y} - Y_i}{S} \right| > T = 2.9 \qquad (6)$$

where $\overline{Y}$ is the mean and S the standard deviation for all individual sample results for that level (usually 30) before rejection of individual pairs or exclusion of laboratories with significant high or low ranked totals. The rationale is that some event may have occurred during sample collection that made that particular sample not a fair sample. Exclusion of this type of sample pair tended to reduce S_r^2 with little effect on S_d^2.

Determination of Systematic Error of the Method

At each sample level, the "taken" value found by the SRI independent analysis was used as a reference value to test for systematic error of the method, that is, to detect an inherent bias in the method. Again, using the formula of Youden, a Student's t-value was calculated for each level:

$$t = \frac{(\overline{X} - R)\sqrt{2n}}{S_d} ; \quad 2(n-1) \text{ degrees of freedom} \qquad (7)$$

where:

$\overline{X}$ = average of results for n laboratories

R = reference value for that level

S_d = standard deviation of sums of duplicates for one level for n laboratories (see definition above).

In this formula, $\sqrt{2n}$ rather than $\sqrt{n}$ is applied because each of n laboratories had two values. From the t-value we are able to decide whether the difference in the laboratory averages and the reference value is attributable to random errors, or if a true difference is indicated, by referring to probability tables. For most of the comparisons we make here, a t-value with absolute value less than 2.0 indicates there is a 95% chance that there is no difference in the values being compared. It should be remembered that the ability to detect differences is a function of the standard deviation, the test being more sensitive for smaller values of S_d.

Comparison of the Two Methods

For the sample set common to the two collaborative tests (IR-Set I and XRD-Set III), the F-ratio test was used to compare variances of the two methods on a level-by-level basis. The significance of the difference of means was estimated using a standard Student's t-test, similar to that described above.

RESULTS AND DISCUSSION - XRD TEST

Phase I - Preliminary Test

Samples for the Pretest Set are tabulated in Table 3. As in each of the tables of data to follow, the laboratory numbers are listed in the left-hand column, with the results for the four sample pairs (four levels) in the remaining columns. Underlined results were not used in the calculations, either because the laboratory reported a problem in handling the sample or because they were detected as outliers by the statistical criteria described in the Treatment of Data section. Elimination of one of a sample pair meant that neither sample could be included.

Presented below the tabulated values in the table are the various statistics calculated from these values. The number of pairs remaining after elimination of outliers, n, is shown. The three relevant standard deviations, S_d for the total, S_r for intralaboratory (random) errors, and S_b or interlaboratory error (difference in bias), are listed in the two columns of data below the values for each level. Each standard deviation is given twice, once in micrograms of silica, then as the percent relative standard deviation (%RSD).

Next are the average values found by the test method ($\overline{X}$) and the SRI reference value, and below that the t-value calculated using Equation (7). Significant t-values (95% confidence level) are indicated with an asterisk. Sample components other than silica are listed below the double line.

Table 3. Data from XRD pretest set samples (values tabulated as micrograms silica).

Laboratory	Level 1		Level 2		Level 3		Level 4	
1	54.9	28.1	77.3	31.1	353.8	243.7	51.2	134.9
2	70.0	69.0	82.0	123.0	262.0	259.0	133.0	153.0
3	61.3	49.2	87.0	69.7	211.8	198.5	115.3	105.8
4	65.8	74.1	109.2	81.3	215.6	222.8	147.0	149.1
5	56.6	49.4	93.0	106.2	225.2	221.2	131.9	150.4
6	60.7	34.8	89.0	94.2	117.3	185.2	88.2	104.2
7	80.4	52.3	90.5	85.2	224.5	190.7	107.4	105.8
8	62.0	63.0	107.0	101.0	218.0	231.0	139.0	123.0
9	53.1	58.3	72.3	76.8	213.6	242.2	223.5	138.6
10	82.6	17.0	97.0	120.8	293.2	278.8	163.7	181.1
11	62.4	69.2	89.0	96.6	238.6	237.1	141.0	154.2
12	45.7	58.6	85.0	90.9	166.3	167.0	85.1	77.4
13	82.3	82.9	167.9	99.2	231.8	245.1	146.9	147.2
14	39.0	51.0	83.3	88.2	211.6	185.1	118.6	107.2
15	89.9	84.6	100.3	77.5	306.8	318.2	162.0	189.1
	n: 14	%RSD	n: 13	%RSD	n: 13	%RSD	n: 12	%RSD
S_d:	19.1	31.1	14.0	15.2	53.7	23.2	35.7	26.2
S_r:	6.8	11.1	8.2	8.9	7.5	3.2	5.8	4.3
S_b:	12.6	20.6	8.1	8.8	37.6	16.2	24.9	18.9
$\bar{X}$:	61.0		92.2		231		136	
Reference:	40		106		191		114	
t:	5.8*		-5.02*		3.83*		3.02*	
	Other sample components							
Matrix:	1.3		--		1.9		0.60 mg	
Iron oxide:	--		--		--		0.57 mg	

*Significant difference.

We see from these data that although S_d ranges from 14.0 μg (Level 2) to 53.7 μg (Level 3), the intralaboratory standard deviation, S_r, goes only from 5.8 to 8.2 μg. The interlaboratory differences in systematic error, S_b, are obviously the dominant factor of variability. The differences between the test method and the reference method were significant at all four levels, as seen by the t-values.

These data were presented and discussed at a briefing session attended by representatives of most of the laboratories. Many of the participants believed that a major source of error could be attributed to the making of standards and to the choice of pipets used to deliver the silica suspension when making standards. We discussed the technique of withdrawing the aliquot from the suspension and whether to do so while the suspension was being stirred or immediately after shaking it. We concluded that vigorous stirring with a magnetic stirrer caused the particles to be unevenly distributed in the solvent, so that a representative aliquot could not be withdrawn. The technique for making standards, including more detailed instructions on rinsing out the pipets, was revised (Section 9.1 of PCAM 259) based on these discussions.

The results in Table 3 are based on calibration with Min-U-Sil 5, supplied to each laboratory by SRI. Because some laboratories were unable to duplicate their normally used curve even when Min-U-Sil 5 had been used previously, the question was raised whether individual portions of the bulk material differed in either purity or in size distribution. Participants from laboratories that have automatic data systems suggested that the difference in results for the two curves arose because of the data manipulation, which differed from the normally used curve. For example, some analysts fit the data points to a nonlinear curve. The question of reproducibility of the standard curve was not resolved, but each laboratory was asked to prepare new standards for the next phase of the study. Additional data on the difference for the two curves were gathered in Phase II and are given later (Table 13).

Based on suggestions at the briefing session, the method was also revised to instruct that the blank silver membrane filters, used to detect sample self-absorption, be rinsed with isopropanol as if making a standard. Section 8.4.5 of PCAM 259 contains this change.

Phase II - Collaborative Test

After the briefing session, all three of the collaborative test sets were distributed to the XRD laboratories at the same time. XRD-Set I were samples collected with critical flow orifices; XRD-Set II were collected by laboratory representatives using personal sampling pumps; XRD-Set III were collected with the critical flow orifices but differed from the other two sets in having coal mine dust as a background matrix. This last set is the same as the IR-Set I, to be described later.

Collaborative Test Results--
Results for XRD-Set-I are given in Table 4. The format of the table follows that of Table 3, with the standard deviations for total data, intralaboratory and interlaboratory errors included, plus the test method and reference method averages, and Student's t-value for testing the differences of these two

Table 4. Data from XRD-Set I. Test for analysis errors—samples collected by SRI (values tabulated as micrograms silica).

Laboratory	Level 1		Level 2		Level 3		Level 4	
1	67.5	73.0	195.2	212.3	110.9	82.0	118.2	101.9
2	50.0	40.0	120.0	110.0	90.0	80.0	100.0	90.0
3	51.5	60.2	201.2	177.4	94.6	117.7	111.8	102.8
4	75.2	72.2	203.3	246.3	98.0	226.8	153.7	149.8
5	77.5	124.0	192.5	198.5	105.1	90.3	159.9	105.2
6	59.2	56.0	70.5	—	87.7	86.5	98.6	119.6
7	53.8	58.8	178.2	180.6	93.7	80.4	68.9	58.2
8	77.8	62.2	154.2	172.4	88.8	95.6	107.2	113.3
9	64.1	57.4	201.3	189.2	79.4	82.5	113.7	113.0
10	71.1	73.0	234.2	207.4	106.0	100.6	135.8	141.0
11	78.5	70.1	205.8	220.8	109.9	118.1	190.4	147.7
12	71.1	71.9	175.8	190.1	85.6	92.6	84.6	83.7
13	65.9	85.1	249.2	229.2	47.6	138.2	140.2	142.4
14	68.3	100.3	156.0	247.8	122.4	124.3	101.0	167.9
15	65.5	76.2	271.7	225.1	105.3	103.0	153.6	147.6
	n: 13	%RSD	n: 13	%RSD	n: 12	%RSD	n: 12	%RSD
S_d:	11.6	16.7	34.4	16.9	17.4	17.7	29.1	22.2
S_r:	6.1	8.8	16.6	8.1	6.2	6.3	16.0	12.2
S_b:	7.0	10.1	21.3	10.4	11.5	11.7	17.2	13.1
$\bar{X}$:	69.4		204		98.4		131	
Reference:	54		207		102		104	
t:	6.77*		-0.38		-1.00		6.50*	
	Other sample components							
Matrix:	1.1 mg		1.8 mg		--		1.8 mg	
Iron oxide:	--		--		--		0.8 mg	

*Significant difference.

means. Values that are underlined were excluded from the statistical analysis, as described in the later section on Ranking of Laboratories.

From the statistics of the individual levels of XRD-Set I, we derived estimates of the total error and the intra- and interlaboratory standard deviations (not including contributions from the sampling pump) for the XRD method. Table 4 shows that the standard deviations for the total data, S_d, range from 11.6 to 34.4 μg over the four levels and increase in proportion to the amount of silica. For each of Levels 1, 2, and 3 the %RSD is about the same, so we may pool these values to arrive at an average estimate of 17% for the total error. Level 3, which contains only silica, might be expected to yield the best data, but errors for these samples are similar to those for the Level 1 and 2 samples, which also contain the three-component matrix of calcite, kaolinite, and talc.

At each level we find the difference between S_d and S_r to be significant, using Equation (4) to calculate the F-ratio of variance. Random, intralaboratory errors (S_r) follow the same pattern as for total errors, being approximately proportional to the mean value, rather than constant, for Levels 1, 2, and 3. We may also pool these and calculate that the intralaboratory error is 8%. These standard deviations are similar to those found by SRI for samples analyzed in the ruggedness study, where for a set of 32 samples, a standard deviation of 7.3 μg (mean of 112.3 μg) was found.

The interlaboratory, or systematic error, likewise, may be estimated by averaging the Level 1, 2, and 3 values, and we find an average of 11% for S_b. Again, the interlaboratory error is the dominant factor in the distribution of errors.

Errors for Level 4 samples, which contain 0.8 mg of iron oxide in addition to 1.8 mg of the other matrix, are greater for both the total error (22.2%) and the random error (12.2%). Clearly, Level 4 was made more difficult by the high mass loading and the strong x-ray absorber, since the amount of silica on Level 3 and Level 4 is almost identical, and Level 3 errors are less.

The estimates derived from these data fall into two groups, one for samples containing only silica or silica and the weakly absorbing matrix, and one for samples bearing iron oxide, as follows:

Error Component	Samples with 0-2 mg Matrix	Samples with Iron Oxide
Total (not including pump)	17%	22%
Intralaboratory	8%	11%
Interlaboratory	11%	13%

The samples containing iron oxide are reviewed in more details in the Discussion of Sources of Errors.

The average of values found by the laboratories for Levels 2 and 3 were not significantly different from the reference values, as seen by the t-values of

-0.38 and -1.00, respectively. However, neither Levels 1 nor 4 agree with the reference, both being much higher. A t-value greater than 2.05 is needed to detect differences at the 95% confidence level. Looking back at the Pretest Set in Table 3, we observe that, here also, the laboratory averages for the lowest loading of silica and for the iron oxide-fortified samples are higher than the reference. Although we can find the probable cause of the difference for the iron-oxide-loaded samples, there is no ready explanation for the apparent bias at Level 1, for if the reference value is low, or the matrix has a positive interference, these effects should also be detected in Level 3.

Table 5 gives the data from XRD-Set II, which together with XRD-Set I were used to estimate sampling pump error. (Special problems occurred with some of the Level 4 samples, which are described below.) Both XRD-Set I and XRD-Set II were collected from the same test atmosphere, the only difference being that sampling pumps, rather than flow orifices were used for XRD-Set II. Therefore, the reference values are identical for both of these sets. Were there no effect from the sampling pumps, the errors and averages for both sets would be equivalent.

We first calculated the F-ratio to decide whether there were significant differences in the several standard deviations for the data of XRD-Set I and XRD-Set II. The F-ratios of the four levels were as follows:

Level	F-ratio
1	2.15
2	0.87
3	2.91
4	1.27

Although there is an increase in variability for each of the XRD-Set II levels, only the increases at Levels 1 and 3 are significant. The value 2.91 is significant at the 95% confidence level; the Level 1 F-ratio of 2.15 is significant at the 90% level.

The next thing to observe is that the intralaboratory or random error has not increased when using the sampling pumps. The largest difference in S_r is found in the Level 2 values, but this slight decrease is not statistically significant. Except for Level 2, the use of pumps increases the interlaboratory differences, as reflected by the increase in S_b. To produce this effect each pair of pumps must have the same degree of bias. Because the effect of the sampling pumps is seen in the bias component, S_b, the magnitude of this effect, S_p, is calculated from differences in S_b. The %RSDs of Levels 1, 2, and 3 of XRD-Set I are homogeneous, and they were pooled to obtain an average of 11% for S_b for that set. The XRD-Set II samples are not as uniform, but it is reasonable to estimate the S_b from a pooled average of Levels 1 and 3, which turns out to be 20.0%.

By calculating S_p from these estimates, using Equation (3), we arrive at a value of 17% for the sampling pump error. This leads to the following summary of errors for samples collected with pumps.

Table 5. Data from XRD-Set II. Test for sampling pump error--samples collected with personal sampling pumps (values tabulated as micrograms silica).

Laboratory	Level 1		Level 2		Level 3		Level 4	
1	42.7	66.1	190.3	122.0	64.3	83.4	123.4	124.2
2	49.0	48.0	134.0	131.0	73.0	91.0	100.0	165.0
3	40.8	44.5	169.9	125.5	74.6	54.7	115.6	58.0*
4	51.7	23.3	142.9	155.9	60.0	84.0	57.1*	112.4
5	75.1	79.7	155.9	161.1	109.9	118.6	130.4	145.7
6	67.9	73.8	204.8	213.2	77.6	107.5	89.1	98.4
7	56.4	58.9	193.2	201.0	105.9	110.4	84.4	86.7
8	—	—	—	—	—	—	—	—
9	55.6	50.0	184.9	170.2	67.3	65.7	112.0	119.1
10	56.0	67.4	195.5	195.2	137.8	109.8	74.3*	129.1
11	68.2	55.1	194.8	196.2	107.3	101.4	140.0	132.6
12	66.2	67.0	189.0	180.6	95.7	94.5	76.6	68.3
13	74.6	76.2	210.5	202.7	124.5	120.1	135.1	134.7
14	62.1	68.9	185.3	181.8	71.8	84.5	97.5	106.9
15	60.2	82.1	223.3	198.1	98.7	110.9	161.7	136.3
	n: 13	%RSD	n: 13	%RSD	n: 13	%RSD	n: 12	%RSD
S_d:	17.1	27.8	32.2	17.6	29.7	31.6	32.8	29.1
S_r:	6.4	10.5	13.9	7.6	7.1	7.6	15.9	14.1
S_b:	11.1	18.2	20.5	11.2	20.4	21.7	20.3	18.0
$\bar{X}$:	61.1		182		93.9		113	
Reference:	54		207		102		104	
t:	2.14†		-3.88†		-1.39		-1.29	

	Other sample components			
Matrix:	1.1 mg	1.8 mg	--	1.8 mg
Iron oxide:	--	--	--	0.8 mg

*See text regarding these values. Statistics for this level, after excluding these three pairs, are: S_d: 31.2, S_r: 5.6, S_b: 21.7.

†Significant difference.

Error Component	%RSD
Total (including pump)	29
Intralaboratory	8
Interlaboratory	11
Sample pump	17

Since the Level 2 error did not increase when using a sampling pump, we may hav overestimated the sampling pump error. However, we also found a sizable effect for sampling pump error in the IR collaborative test.

In addition to increasing the variability at three of the levels, the use of pumps also caused a systematic error for Level 2. Comparison of the Level 2 means for XRD-Sets I and II reveals that XRD-Set II values are significantly lower than XRD-Set I ($t = 2.40$). These samples were prepared by first loading 1.8 mg matrix onto the filters, then loading the silica. It appears that the average collection rate of the sampling pumps decreased because the pumps were unable to maintain the flow when filters contained a high dust loading. (The differences in averages of Levels 1 and 3 for XRD-Sets I and II were not identified as significant.)

We have ignored the Level 4 samples so far, because an additional source of sampling error was noted on three of these samples (marked with an asterisk in Table 5). Red material from the iron oxide matrix was noticed on the backup pads on these samples, suggesting that the filter cassettes may not have been tightly sealed. These values, which increased S_r, could have been treated as outliers, but they do point out a sampling problem. Had these values been rejected, we would have obtained the statistics shown in the bottom on Table 5 based on only 9 laboratories. We must question whether similar breakthrough occurred for other levels, but was unnoticed because the matrix was not colored. Because of the number of defective samples in XRD-Set II Level 4, no information is to be gained from comparing XRD-Sets I and II at this level, except to emphasize the necessity of properly closing the cassettes.

The final set of data for the XRD test is found in Table 6. These samples, which were collected with the critical flow orifices, are from the same test atmospheres as IR-Set I. In addition to having a different background matrix from the matrix of the other XRD sets, they also differed from those sets in that an MSA dust cassette, rather than a two-piece 37-mm cassette, was used.

In the experimental design, XRD-Set III samples were included to permit comparison of the XRD and IR methods on a similar sample set. However, estimates of error may be obtained from these also, using the statistics in Table 6. Again, we have one level containing only silica, and the other three with various other components. The variability of Level 4 samples can be attributed to the calcite, as discussed in the Discussion of Sources of Error. For the moment, the Level 4 data should be excluded from the discussion.

In contrast to XRD-Set I, the S_d was approximately constant for these sample types, with the %RSD decreasing for larger amounts of silica. The silica-only sample, Level 1, has a higher S_d for these samples than for the comparable

Table 6. Data from XRD-Set III. Test for comparing XRD and IR methods--samples collected by SRI (values tabulated as micrograms silica).

Laboratory	Level 1		Level 2		Level 3		Level 4	
1	61.6	98.4	168.5	197.8	125.6	98.3	59.8	32.9
2	62.0	77.0	148.0	138.0	87.0	88.0	<10.0	26.0
3	73.8	87.0	147.0	201.3	94.1	117.7	40.0	31.1
4	81.0	89.9	158.2	186.1	134.5	110.9	60.0	72.3
5	113.0	138.4	297.7	190.1	134.6	154.8	36.8	43.8
6	38.9	51.3	164.9	10.6	57.8	101.7	20.4	13.4
7	122.4	76.1	217.2	183.4	89.8	99.1	61.0	56.8
8	100.2	110.7	142.9	189.8	100.3	105.9	39.9	45.5
9	74.3	80.4	166.8	165.1	121.6	106.2	63.5	64.0
10	103.1	100.2	213.4	210.6	120.5	137.9	40.8	38.8
11	101.7	106.1	181.0	182.5	119.3	137.7	51.2	46.1
12	72.2	72.4	150.7	186.2	77.7	103.8	44.1	5.5
13	120.6	117.2	187.4	195.2	138.7	146.5	55.3	50.8
14	94.8	90.2	157.5	198.2	106.2	112.5	73.9	66.7
15	—	—	—	—	—	—	—	—

	n: 12	%RSD	n: 11	%RSD	n: 12	%RSD	n: 11	%RSD
S_d:	23.8	25.8	20.9	11.5	24.6	21.1	16.8	32.7
S_r:	10.3	10.8	13.6	7.5	5.6	4.8	5.0	9.7
S_b:	15.2	16.0	11.2	6.2	16.9	14.5	11.3	22.0
$\bar{X}$:	95.2		181		116		51.4	
Reference:	107		150†		122		62	
t:	-2.41*		--		-1.09		2.96*	

	Other sample components			
Coal mine dust:	--	0.81 mg	2.0 mg	0.71 mg
Calcite :	--	—	—	0.18 mg
Kaolinite :	--	0.18 mg	--	--

*Significant difference.

†Uncertainty of ±25%; therefore, t-value not calculated.

samples of Table 4. Since XRD laboratories may not have been familiar with the MSA preweighed dust cassettes before receiving these samples, some imprecision due to unfamiliarity with the sample unit might be factored into these results.

For these samples the following estimates, not including an error for the sampling pump, are obtained by pooling Levels 1, 2, and 3:

Error Component	µg Silica	Range of %RSD
Total (not including pump)	23	15%-23%
Intralaboratory	10	6.7%-10%
Interlaboratory	15	10%-15%

Here, since the absolute amount was uniform over the samples, the standard deviations are expressed in mass of silica, with the range of %RSDs also indicated. The %RSDs found for the XRD-Set I samples are within these ranges. The average of Level 1 samples is significantly different from the reference value, although Level 3 average does agree. Because of the large uncertainty in the reference value of Level 2, the t-value was not calculated.

This data set is discussed again in the section on Comparison of XRD and IR Test Results.

Ranking of Laboratories and Detection of Outliers--
The values underlined in the data tables were identified as outliers by the following process. For each of the four sample levels, the laboratories were ranked from 1 to 15 in terms of the lowest to the highest values reported. These rankings were then summed to indicate laboratories that reported consistently very high or very low results. Rank sums below 8 and above 56 were considered significant. These ranks are shown in Table 7.

The XRD laboratories analyzed three sets (12 pairs), and the question to be decided was whether to base the total rankings on one, two, or all three of these sets. Using either XRD-Set I or XRD-Set III, or XRD-Set I and XRD-Set III, Lab 2 would be excluded as having extremely low results, but no laboratories would be excluded because of high rank. Since these two sets were collected using flow orifices rather than sampling pumps, it made sense to use them. The ranking scheme was complicated by the fact that individual samples were sometimes outliers, causing the ranking process to be inexact.

Several laboratories had high rankings, near the upper limit, but were retained. Labs 13 and 15 had high rankings in both the Phase I and Phase II tests; Lab 15 was unable to complete Set III samples so it did not fall into the elimination process. Lab 6 ranking of five for Set III was significantly low.

Lab 12 results were low for Level 4 samples, Sets I and II, and were excluded for this pair since this lab was also low for a similar sample pair in the Pretest Set. This sample pair contained iron oxide in the matrix.

Table 7. Ranking for XRD laboratories.

	Set I					Set II					Set III				
	Level				Rank	Level				Rank	Level				Rank
Laboratory	1	2	3	4	Sum	1	2	3	4	Sum	1	2	3	4	Sum
1	7	10	8	6	31	5	4	4	9	22	5	10	8	8	31
2	1	2	2	3	8	3	1	6	10	20	2	2	2	1	7
3	2	6	12	4	24	2	2	1	4	9	6	7	6	4	23
4	11	13	15	14	53	1	3	3	2	9	7	6	10	13	36
5	15	8	9	9	41	14	5	12	13	44	14	14	14	6	48
6	4	1	4	5	14	11	13	7	5	36	1	1	1	2	5
7	3	4	3	1	11	6	11	11	3	31	9	10	4	11	34
8	6	3	6	7	22	–	–	–	–	–	12	4	5	7	28
9	5	7	1	8	21	4	6	2	8	20	4	3	9	13	29
10	10	12	10	11	43	8	9	14	6	37	10	13	12	5	40
11	12	11	13	15	51	7	10	9	12	38	11	9	11	9	40
12	9	5	5	2	21	10	8	8	1	27	3	5	3	3	14
13	13	14	7	12	47	13	12	13	11	49	13	11	13	10	47
14	14	9	14	10	34	9	7	5	7	28	8	8	7	14	37
15	8	15	11	13	47	12	14	10	14	50	–	–	–	–	–

Significant ranges for four Levels are: 14 laboratories: 8, 52
15 laboratories: 8, 56

Outlier Pairs--
The following comments apply to individual sets and explain the reasons for excluding outlier pairs.

XRD-Set I-- Three individual outlier pairs were identified by Dixon's test; Lab 6's Level 2 sample was missing. Lab 13's Level 3 value was rejected because the pair difference of 90.6 μg was significantly high and caused overestimation of the intralaboratory error.

XRD-Set II-- Lab 8 did not receive this set. Laboratories reported micrograms of silica for all four levels and the net filter weight for the samples at three levels. The two reports could be compared to assist in detecting sources of errors.

Labs 3 and 10 commented that there was evidence of leakage to the backup filter on the Level 4 samples. Since these filters contained the red iron oxide, leakage was easy to spot. Also, the representative who collected samples for Lab 4 reported at the conclusion of the sampling session that leakage was suspected on this pair. For each of the sample pairs in question, the weight difference between the two samples is greater than for other pairs at the same level, i.e., 0.68, 0.69, and 0.65 mg difference compared with the next highest weight difference for this level of 0.17 mg.

Two Level 2 pairs showed large weight differences between samples of a pair. Lab 3 reported a weight difference of 0.92 mg; this pair difference, as micrograms silica, was 44.4 μg, second highest of this level. Lab 11's Level 2 pair had a weight difference of 1.61 mg, but a difference of only 1.4 μg silica. Lab 4 had the lowest value for Level 1, leading to the suspicion that some leakage may have occurred with one of these samples as well as their Level 4 sample.

The probable source of error in these samples is not variation in the sampling pumps but improper sealing of the filter in the cassette. If the top section of the cassette is not pressed down hard enough, sampled air will leak around the filter. This problem is separate from that of leakage through the side of the cassette, for which many people use shrink-tape to make a seal.

The Youden scheme would reject these individual sample pairs as outliers. However, because this set was included specifically to evalute the sampling errors, the data should not be rejected outright. Statistical tests were done with and without inclusion of suspect pairs. During the sampling session, the participants informally discussed the problem of seating these filters so the possibility of loss from this source is recognized.

Lab 1 reported values of 190.3 and 122.0 (D = 68.3) for the Level 2 pair. Values reported for this same pair, based on the normally used curve, were 151.2 and 151.4 (D = 0.2). This is a change in repeatability of 68 μg, just from use of different standard curves, and this type of difference was not expected. The lab explained that the samples are analyzed twice; when using their normal method, the instrument data processor is programmed to correct for background automatically. They do use Min-U-Sil 5 for calibration standards for both runs. These sample pairs were not rejected; they will increase S_r for Level 2.

XRD-Set III--Two individual outlier pairs were identified by Dixon's criteria.

Discussion of Sources of Error--

Effects of self-absorption correction--Materials codeposited with the silica may reduce the intensity of the x-ray beam (sample self absorption), causing a low reading. PCAM 259, the XRD method, includes the following procedure to correct for self-absorption: the sample transmittance (T), that is, the ratio of silver peak intensities (samples versus clean silver filter) is first determined; then a function of this ratio f(T) (see Section 10 of PCAM 259) is applied to the silica results. A sizable correction is required for samples with a strong x-ray absorber, such as iron oxide; for example, for T = 0.80, f(T) = 1.1663; for (T) = 0.60, f(T) = 1.4050, when using the primary silica and silver peaks. We wanted to discover the effect of this correction in the hands of many laboratories.

Table 8 lists the transmittance values for XRD-Set I, derived from the laboratory reports.

Table 8. Transmittance values for XRD Set-I samples.

Laboratory	Level 1		Level 2		Level 3		Level 4	
1	1.00	1.00	0.95	0.96	1.00	1.00	0.73	0.75
2	0.69	0.67	0.65	0.66	0.81	0.82	0.52	0.51
3	0.94	0.98	0.87	0.93	0.90	0.87	0.77	0.68
4	0.89	0.90	0.83	0.81	1.00	1.01	0.61	0.60
5	1.00	0.92	0.84	0.85	0.90	0.86	0.62	0.69
6	0.79	0.84	1.00	---	0.93	1.00	0.48	0.46
7	0.70	0.77	0.61	0.63	0.92	0.99	0.35	0.33
8	0.84	0.87	0.83	0.75	0.95	0.95	0.55	0.54
9	0.92	0.92	0.90	0.83	1.00	0.97	0.67	0.66
10	0.88	0.85	0.76	0.87	1.01	0.99	0.68	0.59
11	0.90	0.93	0.83	0.83	1.05	0.93	0.57	0.60
12	0.73	0.76	0.65	0.68	1.00	1.00	0.46	0.49
13	0.91	0.86	0.79	0.80	1.00	0.98	0.53	0.53
14	0.83	0.81	0.87	0.69	0.99	1.00	0.53	0.53
15	0.81	0.95	0.80	0.80	1.03	1.04	0.68	0.68

From the composition of Level 3 samples, which contain only silica, we expect to see values hovering around 1.00. Because Level 2 samples contain more silica and matrix than Level 1 samples, the transmittance should on the average be lower, as it is. Level 4 samples contain a high amount of matrix and iron oxide, and the low transmittance values we have here are to be expected. Lab 2's transmittance values are significantly low, as were their results for silica mass; however, the micrograms reported for silica (Table 4) would be lower still for higher transmittance. Lab 7's low transmittance values are a result of their use of a filtration chimney with a smaller diameter than most laboratories use.

To see the effect of the sample self-absorption correction, we used the transmittance values of Table 8 to "uncorrect" XRD-Set I results from Table 4 using the appropriate f(T) from Table 1 of PCAM 259. Table 9 compares statistics for "uncorrected" data with the statistics in Table 4.

Table 9. Comparison of statistics of XRD-Set I for results corrected for sample self-absorption versus "uncorrected" values.

	Level 1		Level 2		Level 3		Level 4	
	Corr.*	Uncorr.	Corr.*	Uncorr.	Corr.*	Uncorr.	Corr.*	Uncorr.
$\bar{X}$	69.4	63.5	204.0	179.0	98.4	97.0	131.0	93.2
S_d:	11.6	10.1	34.4	32.7	17.4	17.7	29.1	20.1
S_r:	6.1	5.6	16.6	10.0	6.2	6.3	16.0	9.8
S_b:	7.0	5.9	21.3	22.0	11.5	11.7	17.2	12.4
Reference	54		207		102		104	

*Repeated from Table 4.

Examination of these summaries in Table 9 reveals that, as expected, the correction factor has little effect on Level 3 (the silica-only sample), or on Level 1 samples with 1.1 mg matrix and 54 μg of silica. There is more random error in Level 2 samples, but failure to use the correction factor would cause underestimation of silica (the difference in means is significant at the 95% confidence level). However, application of correction factors to Level 4 samples, which contain 1.8 mg matrix plus 0.8 mg iron oxide, causes overcorrection. There is also a significant increase in both S_b and S_r for corrected samples for Level 4.

The effectiveness of the sample self-absorption correction depends on whether the absorbing materials affect the silver and silica peaks to the same degree. This may not always be the case. For example, a finely divided powder may deposit in a uniform layer over the surface of the silver membrane filter, but leave a high proportion of the silica particles protruding above the layer. The intensity of the beam will be attenuated to a greater degree for the silver peak than for the silica peak, causing the silica amount to be overestimated.

The degree of correction also varies by laboratory, the reason for which is not entirely understood. Looking back at the data in Table 8, we see transmittance values ranging from below 0.5 to 0.75 for the Level 4 samples. The "fine tuning" of the correction procedure will be difficult to achieve while maintaining a wide applicability for the method; however, a better understanding of the various contributing influences is desirable.

Effect of calcite on XRD results--Returning to XRD-Set III, Level 4 (Table 6), the large standard deviation can be explained by looking at the effect of calcite. As mentioned earlier, and discussed at length in the description of the IR method ruggedness test (Section IV), calcite reacts with silica at muffle furnace temperatures. The IR method directs those laboratories using a muffle furnace to wash the filter in acid if the presence of calcite is suspected, but the XRD laboratories were not asked to do this step. The effect of calcite is seen in the Level 4 sample results.

Of the 14 laboratories reporting on this Level 4 sample, 5 used low temperature ashers (LTA) and 11 used the muffle furnaces (M). One of each type was an outlier. Table 10 shows the ranks in order of increasing amount of silica of the remaining laboratories for Level 4, along with their furnace type.

Table 10. Laboratory rankings for XRD-Set III, Level 4, compared with type of furnace.

Rank	Laboratory	Type of Furnace	Average Micrograms Silica for Level 4 Pair	
			M	LTA
1	12	M	24.8	--
2	3	M	35.6	--
3	10	M	39.8	--
4	5	M	40.3	--
5	8	M	42.7	--
6	1	LTA	--	46.7
7	11	M	48.6	--
8	13	M	53.0	--
9	7	LTA	--	58.9
10	9	LTA	--	63.8
11	4	M	66.1	--
12	14	LTA	--	70.3
		Mean	43.9	59.8

The rank sum for laboratories with LTA is 37 (6 + 9 + 10 + 12). Since there is less than a 5% probability that a random set of four laboratories would have a rank sum this high, the difference in means for the two asher types (43.9 versus 59.8) is significant. The mean of 59.8 µg for the LTA laboratories compares quite well with the reference value of 62 µg (see Table 6). We do not find a similar difference between laboratories with different ashers for the other three levels, so we conclude that calcite caused values for muffle furnace users to be low.

The effect of calcite depends, apparently, on what other materials are on the filter. The regular XRD matrix loaded on XRD-Set I and XRD-Set II also contains calcite, meaning that all sample pairs, except Level 3, had calcite along with talc and kaolinite. For example, of the 1.8-mg matrix on Level 2 samples of XRD-Set I (Table 4), approximately 0.36 mg was calcite. Yet when the results are tabulated by asher type there is no detectable differences in the two means, or in the variability, as shown below for Level 2:

	Average µg silica	S_d
LTA laboratories (5)	205.8	36.3
Muffle furnace laboratories (8)	203.6	35.4

The probable explanation is that the matrix for the XRD test, being composed entirely of inorganic matter, survives the high temperature ashing and acts as a diluent during the ashing step, preventing intimate contact of the calcite and silica. Most of the coal mine dust, however, is removed during ashing, leaving only a small fraction of inorganic residue, not enough to prevent interaction of calcite and silica.

Only two kinds of background material, coal mine dust and the XRD matrix, were evaluated in these tests. Undoubtedly the calcite-to-silica ratio as well as the type of codeposited aerosol are important. Therefore, if the method is to be used for calcite-loaded samples, the laboratory should either wash the filter as recommended in the IR study, or determine by some means that silica is not lost in the ashing step. Those using an LTA need not be concerned with this problem.

Comparison of Results from Two Different Calibration Curves--
Laboratories were asked to report results based on their normally used calibration curve, in addition to those from a calibration curve constructed using standards prepared from a Min-U-Sil 5 furnished by SRI. Laboratory rankings for XRD-Set I based on the normally used curve are given in Table 11; these may be compared with the XRD-Set I rankings in Table 7. Three of the laboratories (6, 9, 14) reported the same results for the two curves.

Table 11. Laboratory rankings for XRD-Set I results based on normally used curves.

Laboratory	Level 1	2	3	4	Rank Sum
1	4	9	4	3	20
2	1	2	2	2	7
3	2	3	5	5	15
4	14	14	15	15	58
5	15	8	9	10	42
6	6	1	7	7	21
7	5	5	6	1	17
8	11	11	13	12	47
9	7	12	3	8	30
10	9	13	10	11	43
11	8	10	12	14	44
12	13	7	8	4	32
13	3	4	1	6	14
14	10	6	14	9	39
15	12	15	11	13	51

Two significant rankings were identified: Lab 2 was again low, and Lab 4, which had the highest rank by the new curve, was higher yet and was considered an outlier. Individual outlier pairs were also identified and removed. In general, pairs identified as outliers by one curve were also found to be outliers by the other.

The data of the normally used curve are shown in Table 12, along with the relevant statistics. To detect differences due to the two calibration curves, these statistics should be compared with those in Table 4, as summarized in Table 13.

Table 12. Data from XRD-Set I. Samples based on normally used curves (values tabulated as micrograms silica).

Laboratory	Level 1		Level 2		Level 3		Level 4	
1	53.3	46.3	193.6	188.2	85.4	85.0	86.7	67.1
2	40.0	30.0	90.0	80.0	80.0	70.0	70.0	60.0
3	41.8	49.0	165.2	145.5	77.3	94.7	91.4	84.0
4	74.8	71.6	199.4	236.3	97.9	211.7	155.4	146.0
5	71.9	117.9	185.4	191.5	98.9	84.1	151.8	97.8
6*	59.2	56.0	70.5	—	87.7	86.5	98.6	119.6
7	53.4	55.3	180.7	174.0	92.5	80.4	68.9	51.7
8	88.0	56.2	184.9	201.3	105.7	114.4	123.7	135.0
9*	64.1	57.4	201.3	189.2	79.4	82.5	113.7	113.0
10	64.6	66.3	212.6	188.3	96.2	91.3	123.3	128.0
11	68.4	60.8	185.5	199.3	97.7	105.0	169.9	130.8
12	72.1	72.9	178.3	192.8	86.8	93.9	85.8	84.9
13	41.1	54.6	171.3	157.1	28.4	93.0	91.7	93.2
14*	73.1	67.9	137.1	219.2	117.8	109.7	115.0	122.8
15	70.6	73.9	237.2	198.6	97.6	95.7	140.7	135.7
	n: 12	%RSD	n: 12	%RSD	n: 12	%RSD	n: 12	%RSD
S_d:	14.1	23.1	23.3	12.4	14.4	15.4	32.4	28.7
S_r:	5.9	9.6	15.0	8.0	3.8	4.0	11.8	10.4
S_b:	9.1	14.9	12.6	6.7	9.8	10.5	21.3	18.8
$\bar{X}$:	61.1		187		93.6		113	
Reference:	54		207		102		104	
t:	2.46†		-4.29†		-2.85†		1.32	

*Same results as for new curve.

†Significant difference.

Table 13. Summary of XRD-Set I results reported by two different calibration curves.

	Level 1		Level 2		Level 3		Level 4	
	Normal	New	Normal	New	Normal	New	Normal	New
$\bar{X}$:	61.1	67.6	187.0	203.0	93.6	97.6	113.0	129.4
S_d:	14.1	10.2	23.3	35.9	14.4	15.2	32.4	29.5
S_r:	5.9	3.8	15.0	15.1	3.8	6.0	11.8	12.1
S_b:	9.1	6.7	12.6	23.0	9.8	9.9	21.3	19.0

"Normal" refers to normally used curve.
"New" refers to curve constructed from Min-U-Sil 5 standard.

In every case the mean found, $\bar{X}$, is higher for the new curve, although none of the differences were statistically significant. Most laboratories were, in fact, already using Min-U-Sil 5 for calibration. Many of these labs have modified the analysis steps of PCAM 259, with regard to both the normalization technique and the subtraction of background, which may be reflected in the results of the "normal" curve.

Since the same pairs of samples are used for both curves, S_r could be expected to remain constant for the two results; it is expected that S_b, the change in systematic error, would differ. In fact, the only significant increase in variance (95% confidence level) is for the bias component of Level 2, where $F = 3.33$.

Weighing Errors, XRD-Set II--
Only a limited amount of weight data was obtained. Although PCAM 259 does not give directions to determine percent silica, laboratories were asked to measure percent silica on three levels of the XRD-Set II samples, those collected with personal sampling pumps.

The weight data are given in Table 14. As before, the outlying pairs are underlined and statistics are in the lower section. Level 3 samples contained silica only, 102 µg. In the calculations for this level, if the silica amount found by XRD was greater than the mass found by weighing the filter, a value of 100% was entered. This reduces the scatter of data, of course, but it is a reasonable assumption for an analyzing laboratory to make.

Comparison of the statistics in Table 14 and Table 5 reveals some correspondence of the statistics calculated for silica mass with those for percent silica (remembering, of course, that Level 3 values were adjusted to 100% in some cases). The relative errors for the percents are approximately the same as for mass determinations, and it appears that measurement of percent silica is not significantly poorer than measurement of mass. Only limited conclusions can be drawn from these data, except to comment that this is probably a "worst case" situation, since weighings were made on different balances in 14 different laboratories.

Table 14. Data from XRD-Set II. Test for analysis errors—samples collected by SRI (values tabulated as percent silica).

Laboratory	Level 1*		Level 2		Level 3		Level 4	
1	—	—	10.1	6.4	76.5	93.7	5.0	5.0
2	—	—	4.9	4.8	77.0	38.8	2.8	4.9
3	—	—	8.8	12.5	152.0†	160.0†	5.1	3.6
4	—	—	9.3	11.1	54.5	56.3	5.3	6.4
5	—	—	8.4	9.0	183.0†	148.0†	5.5	6.0
6	—	—	10.5	11.6	69.7	91.8	3.7	4.2
7	—	—	10.1	10.6	70.0	88.7	3.4	3.8
8	—	—	—	—	—	—	—	—
9	—	—	10.1	8.9	102.0†	87.6	4.7	5.2
10	—	—	10.3	9.6	95.7	79.7	4.8	5.9
11	—	—	10.2	643.0	87.9	80.1	6.4	5.8
12	—	—	—	—	—	—	—	—
13	—	—	9.8	9.8	80.3	75.5	5.8	6.0
14	—	—	6.7	6.5	308.0	384.0	3.0	3.2
15	—	—	11.8	9.7	72.5	80.9	7.0	5.7
			n: 11	%RSD	n: 11	%RSD	n: 12	%RSD
S_d:	—	—	1.9	19.8	19.7	24.7	1.5	30.0
S_r:	—	—	0.9	9.4	5.6	7.0	0.3	6.0
S_b:	—	—	1.2	12.5	13.4	16.8	1.0	20.0
$\bar{X}$:	—	—	9.6		79.8		5.0	
Reference:	—	—	10		100		3.7	

*Data not collected for Level 1.

†Value adjusted to 100% in statistical analysis.

Several laboratories reported weights for filter blanks (i.e., filters weighed at SRI, then reweighed at the collaborative laboratories). These weights are given below.

Lab No.	Amount Found (mg)
3	-0.005; -0.003
4	-0.026
5	0
7	+0.017; +0.022
9	+0.222; +0.095
10	+0.021; +0.040
11	+0.055; +0.066
13	-0.002; -0.003
14	+0.01; +0.03
15	+0.019

An improvement in the results for percent silica would have been seen if all weighings had been in one laboratory, since there are obviously some differences between balances. These blank filters were not clamped into cassettes, but were transported in PetriSlides.

RESULTS AND DISCUSSION - IR TEST

Phase I - Preliminary Test

The IR method test began by having collaborators analyze a preliminary test, or practice, set. Data for this set are given in Table 15. Lab 4 did not report this set; Lab 7 inadvertently used the wrong filter in the "washing step" so their data were excluded. Lab 14 did not wash the filters to remove calcite, although this is required for labs having a muffle furnace; therefore, the one sample pair containing calcite was removed from consideration. The excluded values are underlined in the table.

The sample components, other than silica, were coal mine dust, kaolinite, and calcite in various combinations, as displayed in the table. Level 1 sample contained only silica. The most "natural" samples are those of Level 3, which were not fortified with kaolinite or calcite. As mentioned before, the Pittsburgh Seam Coal is naturally contaminated with kaolinite as well as silica, so all samples with coal mine dust have some kaolinite, estimated to be 0.02 mg per milligram of coal mine dust. If it were known that this ratio of kaolinite to coal mine dust in our supply is representative of all worker exposure situations, kaolinite would not have been added to the samples, since it was not our aim to test this method for material other than coal mine dust. Likewise, the appropriate amount of calcite was estimated to be less than 0.3 mg per sample for field samples, and this is the maximum amount of calcite added.

The results tabulated in Table 15 show a significant scatter in data for all levels, as reflected in the statistics at the bottom of the table. The %RSD is greater than 30% for all levels, even for the samples containing only silica. The intralaboratory error, S_r, is lower for samples containing only

Table 15. Data from IR pretest set samples (values tabulated as micrograms silica).

Laboratory	Level 1		Level 2		Level 3		Level 4	
1	169.0	181.0	208.0	262.0	54.0	63.0	71.0	100.0
2	162.2	207.5	324.5	210.5	48.2	46.5	87.9	89.4
3	175.0	168.0	110.0	138.0	49.0	60.0	105.0	22.0
4	—	—	—	—	—	—	—	—
5	103.0	68.5	188.2	150.0	49.5	46.5	74.2	66.0
6	111.5	107.3	170.6	181.9	22.7	36.1	70.2	57.8
7	71.8	68.4	25.3	12.3	10.9	17.8	21.8	26.7
8	167.0	167.0	260.0	242.0	71.0	65.0	64.0	94.0
9	115.2	105.2	102.4	99.8	53.8	35.8	30.7	47.4
10	183.5	156.7	180.7	350.5	53.4	57.1	62.6	81.1
11	153.0	164.0	190.0	184.0	56.0	56.0	82.0	81.0
12	153.5	144.9	68.8	184.1	42.3	53.6	86.4	90.2
13	90.0	90.0	158.0	105.0	65.0	78.0	55.0	78.0
14	164.8	125.4	219.0	129.6	36.2	34.2	33.0	26.5
15	240.0	206.0	184.0	226.0	38.0	29.0	48.0	48.0

	n: 13	%RSD	n: 13	%RSD	n: 13	%RSD	n: 12	%RSD
S_d:	56.8	38.1	79.6	42.8	17.8	35.6	22.0	31.2
S_r:	11.2	7.5	36.0	19.4	3.9	7.8	16.1	22.8
S_b:	39.4	26.4	50.2	27.0	12.3	24.6	10.6	15.0
$\bar{X}$:	149		186		50.0		70.5	
Reference:	172		234		54.7		81.0	
t:	-2.04		-3.10*		-1.35		-2.34*	

Other sample components

Coal mine dust:	—	0.79 mg	1.98 mg	0.88 mg
Calcite :	—	—	—	0.30 mg
Kaolinite:	—	0.18 mg	—	—

*Significant difference.

silica, or coal mine dust and silica, than for samples with added kaolinite or calcite (Levels 2 and 4). For these levels, the intralaboratory and interlaboratory differences were higher than anticipated.

This IR method for analyzing quartz on a filter rather than in a KBr pellet was not familiar to most of the laboratories, except for whatever practice they were able to do between the time they joined the study and the time they received the first sample set. Important differences between this new method and the KBr pellet are as follows:

(1) After ashing of the PVC collection filter, the residue is redeposited on one-half of a DM-450 membrane filter (the other half is used in the reference beam of the spectrophotometer). A 1-cm-ID filtration chimney, of special fabrication, is required.

(2) If a muffle furnace is used and calcite is a suspected sample component, the calcite must be removed before ashing by rinsing the collection filter. The acid wash is done in a filtration unit, so the solubilized calcite and the acid may be removed easily by suctioning it through a 0.5-μm pore size PVC filter, upon which the quartz is retained.

(3) If an LTA is used, a correction for kaolinite in the sample is needed. Kaolinite has a sharp absorption band at 915 cm^{-1}, as well as the band at 800 cm^{-1}, which interferes with silica. The amount of kaolinite in the sample is determined based on the 915 cm^{-1} band, from which a correction is made.

When the data in Table 15 were presented at the briefing session, we discussed the difficulty of carrying out the procedure to remove calcite. In the method that was distributed with the Pretest Set, the procedure for rinsing the filter with acid was to carefully position a clean, 37-mm-diameter PVC filter over a frit of the base of the filtration unit, place the sample filter on top of this, then clamp down the 47-mm chimney. Acidified isopropanol was added to the chimney. Many people had trouble with this procedure and believed it to be at fault in the poor precision. The 47-mm chimney has an internal diameter of about 34 mm, making it hard to place precisely over the 37-mm sample filter. After further laboratory studies at SRI, this step was modified, by going to a 25-mm chimney in which the folded collection filter was placed.

The original procedure for making kaolinite standards was also modified after the briefing session discussion. At first, the standards were prepared by depositing an aliquot of kaolinite in suspension onto a PVC filter, ashing this filter, and making a redeposit onto the DM-450 filter. The revised procedure calls for making a homogeneous deposit directly onto the DM-450 filter.

The source of interlaboratory differences could not be identified, although it was suspected that the standard curves were significantly different. Several laboratories described the regression lines for calibration curves, and even in cases where the calibration curves were similar, interlaboratory agreement for samples was poor.

Phase II - Collaborative Test

Collaborative Test Results--
The IR method was collaboratively tested with two sample sets, similar to those in the preliminary test. One set was collected by SRI using critical flow orifices; the second was collected by laboratory representatives with personal sampling pumps. Both sets were distributed at the same time, along with a copy of the IR method, which had been revised after the briefing session. Samples of the two sets were collected from different test atmospheres, IR-Set I having been prepared at the same time as XRD-Set I. The sample compositions of the two sets are similar but not identical. Laboratories made weighings of the MSA dust cassettes for most of the samples and reported both silica mass and silica percent.

For IR-Set I, the data for the silica mass are tabulated in Table 16. Outlier values, detected as discussed in a later section, are underlined. There is a marked improvement in these samples over the Pretest Set, either because of the laboratories' experience with this method or the improvements made in several of the steps. In attempting to find a single set of statistics to describe the data, we find that neither the standard deviations nor the %RSD are uniform for the four levels. Rather, there are two groups, Levels 1 and 4 and Levels 2 and 3, having similar errors.

Level 1, containing only silica, was expected to yield the most precise data, but Level 4, with both calcite and coal mine dust, has even slightly better data. Apparently calcite on the Level 4 samples was effectively removed. Since most of the laboratories have muffle furnaces, poor results for Level 4 would have shown up if calcite was not adequately rinsed from the filters.

Level 2 and Level 3 variabilities (%RSD) are similar, except that the random error, S_r, of 12.2% for Level 3 is higher than the 7.4% for Level 2. The increased error of Level 2, over Levels 1 and 4, is readily explained by the presence of kaolinite on these samples, which we know makes the IR analysis less precise. The interlaboratory error of Level 2 is almost double the intralaboratory error, reflecting perhaps that each laboratory was internally consistent in treating the kaolinite, but different from the other laboratories. Level 3 should be of the same degree of difficulty as Level 4, but it may be that the amount of kaolinite naturally found in this coal mine dust (2% in the respirable fraction) was enough to reduce the precision. Another possible cause of the increased variability of Level 3 is that, with a higher loading, there was more likelihood of losing material from the filter when the inner packet of the dust cassette was unsealed.

Because the errors are not uniform for the four levels, we pooled values of Levels 1 and 4 and Levels 2 and 3 to arrive at the following two sets of statistics to describe the variability of the method:

	%RSD	
Error Component	Level 1 and 4	Level 2 and 3
Total	13%	22%
Intralaboratory	7%	10%
Interlaboratory	8%	14%

Table 16. Data from IR-Set I. Test for analysis errors--samples collected by SRI (values tabulated in micrograms silica).

Laboratory	Level 1		Level 2		Level 3		Level 4	
1	100.0	115.0	148.0	185.0	185.0	115.0	67.0	67.0
2	43.5	69.3	3.5	44.8	131.3	18.4	55.1	44.2
3	102.0	125.0	205.0	206.0	115.0	112.0	67.0	68.0
4	94.5	96.0	200.0	197.0	134.0	121.0	78.0	82.0
5	89.0	71.0	125.0	107.0	91.0	94.0	63.0	61.0
6	110.7	108.7	165.9	179.6	119.4	114.6	63.7	72.8
7	92.8	102.4	152.7	152.7	88.1	100.5	76.7	68.2
8	89.0	108.0	128.0	156.0	140.0	112.0	100.0	128.0
9	100.1	94.5	50.4	59.2	43.1	74.6	70.4	56.7
10	89.5	80.6	148.7	151.7	94.0	94.3	17.7	39.7
11	112.0	112.0	172.0	130.0	87.0	112.0	69.0	71.0
12	83.3	92.7	182.3	170.5	117.7	108.7	56.3	73.4
13	30.0	25.0	50.0	95.0	85.0	30.0	75.0	95.0
14	109.5	100.6	175.9	132.6	137.9	109.3	64.4	55.5
15	121.0	80.0	148.0	148.0	93.0	83.0	60.0	66.0

	n: 13	%RSD	n: 12	%RSD	n: 12	%RSD	n: 11	%RSD
S_d:	14.7	14.7	34.8	21.6	26.2	23.5	8.0	11.9
S_r:	7.8	7.8	11.9	7.4	13.6	12.2	3.9	5.8
S_b:	8.8	8.8	23.1	14.3	15.8	14.2	4.9	7.3
$\bar{X}$:	99.7		161*		112		67.2	
Reference:	107		150*		122		65	
t:	-2.53†		---		-1.94		0.64	

	Other sample components			
Coal mine dust:	---	0.81 mg	2.0 mg	0.71 mg
Calcite :	--	---	---	0.18 mg
Kaolinite:	--	0.18 mg	--	--

*Uncertainty of ±25%; therefore, t-value not calculated.

†Significant difference.

These represent the lower and upper values that should be applied to the sample results. Clearly, we can say that if samples contain less than 1 mg of coal mine dust, which is naturally contaminated with less than 2% kaolinite, the first set of statistics should be applied. The second set of statistics apply if there is up to 2 mg of coal mine dust or if significant amounts of kaolinite are present, even at lower loadings.

We may compare the intralaboratory values with those obtained in our laboratory during the ruggedness study of the IR method. A %RSD of 9.3% was found for each of two sets of 12 filters ashed in an LTA (means of 86.5 and 135.9 μg). The %RSDs for similar sets of filters ashed in the muffle furnace were 22.7% and 17.8%, much higher than LTA samples. In the ruggedness tests 0.6 mg of kaolinite was added to some of the filters, and we concluded that the high variability for muffle furnace results could be attributed to the kaolinite.

Of the laboratories in the IR test, four used LTA (Labs 2, 4, 10, and 13) and the remainder had muffle furnaces. We could find no difference in results based on furnace type, but it would be difficult to detect differences with this few LTA users. The intralaboratory precision is quite satisfactory and probably reflects the best achievable for the type of samples studied.

Only the average value for Level 1 was found to be different from the SRI reference value, having a t-value of -2.53. Although the difference is only 7.8 μg, the t-test is more sensitive because the standard deviation is smaller for this level.

The data for these same samples, when converted to percent silica, are in Table 17. The interlaboratory error, S_b, is again dominant, meaning that systematic errors for the analysis were carried through in calculations for percent. Were there a significant improvement in the systematic error component, we would theorize that there was a true difference in sample pairs given to individual laboratories. These data were averaged to arrive at S_d of 20%, S_r of 6%, and S_b of 14%.

The statistics for percent silica for the Level 1 sample, containing only silica, were not calculated because the IR method is for quartz in coal mine dust. Also, when using the MSA dust cassette, a mass loading of 100 μg is on only 0.04% of the total mass, since the inner packet weighs 250 mg. Although the IR method is suitable for analyses of low loadings of silica, another type of cassette unit, in which the PVC filter itself is weighed, should be used if the total mass loading is low.

The results for samples collected with sampling pumps are tabulated in Table 18. Estimates of sampling pump errors are made by comparing these data with the IR-Set I data. The first thing to notice is the increase in S_d for all IR-Set II levels except Level 2, the pair containing kaolinite. Most of this increase is seen as an increase in interlaboratory error. Level 1 (with only silica), for example, has a bias component, S_b, of 26.7% for IR-Set II compared with 8.8% for IR-Set I. Therefore, to obtain an estimate of sampling pump error, we compare the interlaboratory errors of IR-Sets I and II. Except for Level 2, the bias component is uniform when expressed as a percent and we

Table 17. Data from IR-Set I. Test for analysis errors--samples collected by SRI (values tabulated as percent silica).

Laboratory	Level 1		Level 2		Level 3		Level 4	
1	34.5	57.5	11.4	12.4	4.7	5.0	5.9	6.5
2	21.7	50.5	2.4	3.5	6.0	.8	5.3	4.0
3	17.0	17.9	12.8	12.9	4.6	4.3	5.6	4.5
4	45.0	87.3	14.9	11.9	5.9	5.3	7.3	8.2
5	29.7	35.5	8.9	8.2	3.8	4.1	6.3	7.3
6	92.2	108.7	13.7	14.4	5.1	5.2	7.1	7.0
7	54.6	68.3	12.2	10.5	5.2	4.9	7.4	6.8
8	>100.0	38.6	10.5	12.1	6.7	4.9	9.3	12.5
9	50.0	31.5	3.4	3.7	1.9	3.0	5.4	4.7
10	—	—	12.4	11.7	3.9	3.9	2.0	4.4
11	56.0	28.0	10.7	10.0	4.1	4.7	6.3	5.9
12	20.8	23.2	12.2	12.2	4.7	4.5	5.1	6.1
13	7.5	8.3	6.3	6.8	3.5	7.5	6.3	4.8
14	100.0	50.3	16.0	6.0	5.3	4.4	3.6	4.0
15	60.5	80.0	12.3	12.3	4.7	4.0	6.0	6.7
			n: 11	%RSD	n: 12	%RSD	n: 11	%RSD
S_d:	--*	--	2.04	17.3	0.84	17.8	1.61	25.8
S_r:	--	--	0.65	5.5	0.34	7.2	0.22	3.5
S_b:	--	--	1.36	11.5	0.54	11.5	1.13	18.2
$\bar{X}$:	--	--	11.8		4.7		6.2	
Reference:	--	--	13.2		5.7		6.5	
t:	--	--	-1.68		-5.61†		-1.17	

*Not applicable to Level 1 samples, which contain silica only.

†Significant difference.

Table 18. Data from IR-Set II. Test for sampling pump error--samples collected with personal sampling pumps (values tabulated as micrograms silica).

Laboratory	Level 1		Level 2		Level 3		Level 4	
1	78.0	78.0	174.0	174.0	31.0	31.0	44.0	48.0
2	88.7	82.2	156.4	191.3	15.1	16.4	46.1	24.2
3	92.5	102.0	190.0	207.0	27.0	32.0	42.5	55.6
4	113.0	115.0	158.0	174.0	8.0	22.5	46.0	42.0
5	87.0	81.0	135.0	88.0	41.0	21.0	27.0	33.0
6	125.2	115.5	111.6	115.5	52.4	42.7	38.8	39.8
7	25.9	45.6	103.5	54.2	7.2	11.1	15.7	19.6
8	150.0	141.0	130.0	134.0	97.0	75.0	75.0	75.0
9	79.1	48.3	81.9	52.0	32.6	33.6	63.0	53.9
10	85.3	108.5	149.4	112.5	51.0	23.1	34.4	21.4
11	77.0	80.0	164.0	177.0	29.0	34.0	55.0	50.0
12	48.8	88.9	154.0	144.0	22.1	26.6	28.8	30.2
13	25.0	58.0	50.0	72.0	96.0	96.0	70.0	51.0
14	65.1	43.9	172.1	163.6	28.2	36.5	47.2	50.3
15	114.0	100.0	134.0	53.0	26.0	46.0	40.0	50.0

	n: 13	%RSD	n: 10	%RSD	n: 12	%RSD	n: 13	%RSD
S_d:	35.7	38.9	36.3	23.0	12.5	41.1	18.5	41.5
S_r:	8.5	9.2	8.9	5.6	6.3	20.7	4.4	9.9
S_b:	24.5	26.7	24.9	15.8	7.6	25.0	12.7	28.5
$\bar{X}$:	91.8		157.6		30.4		44.6	
Reference:	84.2		170		27.0		36.7	
t:	0.55		-0.76		0.67		1.09	

Other sample components				
Coal mine dust:	—	1.44 mg	1.45 mg	0.62 mg
Calcite :	—	—	—	0.20 mg
Kaolinite:	—	0.14 mg	—	—

may average (or pool) the three values of 26.7%, 25.0%, and 28.5% to obtain an average S_b of 26.8% for IR-Set II. For IR-Set I results, the three S_b values for Levels 1, 3, and 4 are not homogeneous, so rather than pooling all three, we may pool only the 8.8% of Level 1 and 7.3% of Level 4, to obtain 8.5%.

Two estimates of sampling pump error may be made, then, by comparing the pooled %RSD of 26.8% with both 8.5% and the IR-Set I, Level 3, value of 14.2%. Using Equation (5), these estimates are derived as follows:

$$S_p = \left[(26.8)^2 - (8.5)^2\right]^{1/2} = 25.4\%$$

$$S_p = \left[(26.8)^2 - (14.2)^2\right]^{1/2} = 22.7\%$$

Thus, although the Level 2 results indicate an absence of sampling pump error, the results for the other three levels are a strong indication that there is a significant error from the sampling pump of 23% to 25%.

From the t-values we find no significant difference between the reference methods and the average of the laboratory values.

When the data of Table 18 were converted to percent silica, as shown in Table 19, we observe that both random (intralaboratory) error and bias error have increased over those for percent silica of IR-Set I in Table 17. A pooled %RSD for random error of 10.4% (IR-Set II) versus 5.7% (IR-Set I) is calculated.

When we compare the data for percent silica with the mass silica data for the same samples of IR-Set II (Tables 18 and 19), we find that there is an improvement in the precision for the Level 3 samples containing only coal mine dust. The overall error is now only 22.0% rather than the 41.1% found on a mass basis, with commensurate decreases in S_r and S_b. We would expect this decrease in interlaboratory error when calculated as percent silica if the only factor in the increase in variability arose from different rates of sampling. However, neither Level 2 nor Level 4 results are improved when reported as percent.

We conclude from this test that the effect of the sampling pump is complicated, being dependent on the type of sample components as well as on the mass of silica. This is reasonable if we consider that the properties that affect collection, such as mass agglomeration rate or probability of reentrainment of material from the cyclone, differ for various materials.

Table 19. Data from IR-Set II. Test for sampling pump error--samples collected with personal sampling pumps (values tabulated as percent silica).

Laboratory	Level 1		Level 2		Level 3		Level 4	
1	30.0	27.9	7.7	7.8	1.8	1.6	4.7	4.7
2	100.0	39.1	7.0	9.0	.7	.8	3.3	2.5
3	18.4	17.0	7.9	7.1	1.5	1.7	4.6	4.7
4	59.5	57.5	7.2	8.3	.4	1.2	4.7	4.4
5	21.8	40.5	5.9	4.0	1.5	1.2	2.7	3.2
6	69.6	82.5	5.2	6.0	2.7	2.1	3.9	4.1
7	10.0	25.0	4.5	2.7	.4	.6	1.7	2.0
8	48.4	38.1	5.7	6.7	5.2	4.7	7.4	7.7
9	99.9	48.3	3.7	2.4	1.7	1.8	7.0	5.4
10	—	—	7.5	4.9	2.5	1.1	3.4	2.2
11	25.0	80.0	7.8	8.0	1.6	1.7	3.6	1.7
12	24.4	44.5	5.0	8.0	1.2	1.3	3.0	3.1
13	25.0	38.7	2.3	3.6	4.8	4.1	7.5	5.4
14	1.2	.8	2.4	2.2	1.4	1.9	5.0	5.1
15	57.0	91.8	8.4	2.5	>100.0	2.4	3.1	3.1

			n: 10	%RSD	n: 11	%RSD	n: 13	%RSD
S_d:	--*	--	2.4	35.8	0.66	22.0	2.11	50.2
S_r:	--	--	0.72	10.7	0.29	9.7	0.45	10.7
S_b:	--	--	1.62	24.2	0.42	14.0	1.46	34.8
$\bar{X}$:	—		6.7		3.0		4.2	
Reference:	—		9.7		1.9		4.5	

*Not applicable to Level 1 samples, which contain silica only.

Rankings of Laboratories--
Rankings of IR-Sets I and II are given in Table 20. The basis for ranking was results reported in mass rather than percent silica. In IR-Set I the rank sum of 8 is significant for Lab 2, although it appears that this laboratory had outlier samples at three levels rather than a significant bias. Values for Lab 2 were excluded from Set I.

Lab 13 had an unusual pattern, being either at the high or the low end of the rankings for both IR-Set I and IR-Set II. It was suspected that some mixup in the labeling of these samples may have occurred, so results for this lab were excluded.

Table 20. Rankings for IR laboratories based on micrograms found.

	Set I					Set II				
	Level				Rank	Level				Rank
Laboratory	1	2	3	4	Sum	1	2	3	4	Sum
1	12	11	15	8	46	14	6	9	6	35
2	2	1	3	2	8	13	3	5	9	30
3	15	15	10	9	49	15	5	11	11	42
4	6	14	14	13	47	10	2	7	13	32
5	3	4	5	4	16	5	7	4	8	24
6	13	12	11	10	46	6	13	6	14	39
7	8	9	7	12	36	3	1	1	1	6
8	9	5	13	15	42	8	14	15	15	52
9	7	2	2	6	17	2	10	13	4	29
10	4	7	6	1	18	7	12	2	10	31
11	14	8	8	11	41	12	8	12	7	39
12	5	13	9	7	34	9	4	3	5	21
13	1	3	1	14	19	1	15	14	2	32
14	11	10	12	3	36	11	9	10	3	33
15	10	6	4	5	25	4	11	8	12	35

Outlier Pairs--
In IR-Set I, individual outlier pairs were excluded for Lab 9 (Levels 2 and 3) and for Labs 8 and 11 (Level 4). The relatively large difference in Lab 1's values for Level 3 (70 µg) contributes heavily to the S_r of 13.6 µg for this level; rejection of this pair would reduce S_r to 7.3 µg, but have small effect on S_d.

In IR-Set II, Lab 7's values were rejected because they had inadvertently used a 5-µm pore size rather than a 0.5-µm pore size filter in the "washing step" of the method. Lab 5 reported one sample partially lost for Level 2; Lab 15's Level 2 pair had one low result due to sampling error. Lab 9's Level 2 pair was significantly low, and Lab 8's Level 3 pair was significantly high.

COMPARISON OF XRD AND IR TEST RESULTS

Data for the sample sets common to both collaborative tests are given in Tables 6 and 16 and are summarized below in Table 21. In this table the standard deviations by each test are listed together under the headings of the four levels. Below that are the lab averages, $\bar{X}$, the number of laboratories, and the t-value comparing the XRD and IR averages. The sample components are listed at the bottom.

Table 21. Statistics for comparing XRD and IR methods.

	Level 1		Level 2		Level 3		Level 4	
	XRD	IR	XRD	IR	XRD	IR	XRD	IR
S_d	23.8	14.7	20.9	34.8	24.6	26.2	16.8	8.0
S_r	10.3	7.8	13.6	11.9	5.6	13.6	5.0	3.9
S_b	15.2	8.8	11.2	23.1	16.9	15.8	11.3	4.9
$\bar{X}$:	95.2	99.7	181.0	161.0	116.0	112.0	51.4	67.2
n:	12	13	11	12	12	12	11	11
t:	0.83		2.34		0.54		---	
Silica taken, µg	107		150		122		65	
Coal mine dust, mg	---		0.81		2.0		0.71	
Calcite, mg	---		---		---		0.18	
Kaolinite, mg	---		0.18		---		---	

The methods were compared first by the t-values for difference in means. For Level 2, the t-value of 2.34 is significant at the 99% confidence level. The t-value of 0.83 and 0.54 for Levels 1 and 3, respectively, are not significant; there is good agreement between the two methods. Level 4 test results were not compared statistically because the presence of calcite caused extensive bias in XRD results, as described earlier.

Next, the F-ratios were calculated to determine if there are significant differences in the variances of the two methods, and it was determined that differences are significant (95% level) for Levels 1 and 2. The Level 2 samples, containing kaolinite, are particularly difficult to analyze by the IR method, and the variability is greater by IR. For the Level 1 samples, the XRD method had a higher error. However, the total error for a similar "silica only" sample that was done in XRD-Set I had much better precision, with S_d of 17.4 µg for a loading of 102 µg.

From these data, it is concluded that the methods will give similar results for samples of quartz in coal mine dust. Significant amounts of kaolinite cause greater variability for the IR method. Calcite-containing samples must be treated to remove the calcite before ashing at high temperatures, and this information should be added to PCAM 259.

SUMMARY OF THE COLLABORATIVE TESTS

XRD Test

The XRD method was collaboratively tested in 15 laboratories, using eight types of samples prepared from laboratory-generated test atmospheres. The range of silica was 50 to 200 μg, codeposited with one or more background materials in amounts from 0 to 2.6 mg. Samples were collected either by SRI using matched critical flow orifices, or by laboratory representatives, permitting the estimation of sampling pump errors as well as analytical errors.

The performance of the method depended on the type, but not the amount, of material codeposited with silica. For samples containing 0 to 2.0 mg of a mixture of talc, kaolinite, and calcite (all weak x-ray absorbers) the total percent relative standard deviation (%RSD) and its components for intralaboratory and interlaboratory error (not including variability for the sampling pump) were as follows:

	Estimated %RSD
Total error for analysis	17%
Intralaboratory error	8%
Interlaboratory error	11%

These estimates encompass errors in sampling through a 10-mm cyclone (but not with a personal sampling pump) as well as errors in analysis. For the type of sample with the inorganic matrix, the variations in results were proportional to the amount of silica, so the average percent relative standard deviation is tabulated.

The use of personal sampling pumps for these same samples caused the interlaboratory error to become as great as 20%, the increase being due to an estimated sampling pump error of 17%. The intralaboratory error is not increased with the use of personal sampling pumps. For samples collected with the pumps, then, estimated errors are as follows:

	Estimated %RSD
Total error, sampling and analysis	29%
Intralaboratory error	8%
Interlaboratory error	11%
Sampling pump error	17%

There is some uncertainty in the magnitude of the pump error, since in one case no increase in variability was observed for samples collected with pumps compared with those collected with the matched critical flow orifices. Even so, there is sufficient evidence of large pump error, both from this test and from the IR test, to warrant the estimate of 17%.

Inadequately sealed filter cassettes introduced errors, which were not quantitated but may be a factor in the pump error estimate. Samples collected with the pumps had cassettes assembled by many individuals, in contrast to assembly by one person for nonpump samples.

When the method was applied for samples of silica (100 to 150 μg) in coal mine dust (0 to 2.0 mg) and kaolinite, the total variability was approximately constant, at an average of 23 μg. There was more fluctuation in both intra- and interlaboratory error over the range of sample types, with no apparent pattern. The errors were neither proportional to the means nor did they increase (or decrease) with the means. Estimates of the errors, not including pump error, for the coal mine dust samples are as follows:

	Estimated Standard Deviation μg silica	Range of %RSD
Total error, analysis	23	15%-23%
Intralaboratory error	10	6.7%-10%
Interlaboratory error	15	10%-15%

The %RSD ranges bracket those for the inorganic matrix samples listed above, so the data for the two sample types are in agreement.

For samples containing a high loading (0.8 mg) of iron oxide (a strong x-ray absorber), the intralaboratory error is 12%, higher than for any of the other samples types. This kind of sample, which was included to challenge the method, is obviously more difficult to handle, since the silica amount was overestimated by an average of 25% due to the correction for sample self-absorption.

Using SRI's "taken" value obtained by a colorimetric procedure as a reference, the XRD method was found to be free from systematic error for samples containing 100 to 200 μg silica, but the silica amount was overestimated by an average of 15 μg at the 54 μg level. The XRD method results agree with those of the IR method on the average.

The XRD method must be used with caution for samples containing calcite if the laboratory ashes the filter at high temperature. In some situations, calcite may react with the silica, as was found to be the case for coal mine dust samples also containing calcite.

When samples containing a final loading of 2.0 mg of matrix were collected with sampling pumps, there was a significantly lower average than for samples collected with flow orifices, suggesting that the sampling rate decreases with increased loading of the filters. This decrease is not detected by observing the rotameter of the pump.

There was no distinct improvement in results when calibration material from a common supply was used by all the laboratories, compared with results from the laboratories' normally used curves.

This method should remain classified as a B method under the criterion established by NIOSH in 1977 that a B method (sampling and analysis) should come within 25% of the "true" value 95% of the time in a single laboratory.

IR Test

The IR method was collaboratively tested in 15 laboratories, using four types of samples prepared from laboratory-generated aerosols. The samples, which covered the range of interest for monitoring worker exposure to quartz in coal mine dust, contained Pittsburgh Seam coal mine dust. Kaolinite, calcite, or silica (in addition to that naturally occurring in the coal mine dust) was added to some samples. One sample pair contained only silica. Measurements of both silica mass and silica percent were made on most of the samples.

The variability of the method depended on the type of sample, and the statistics obtained for total errors (excluding the sampling pump) represent the upper and lower values that should be applied to results. The easier type of samples were those containing from 0 to 1 mg of coal mine dust with less than 2% kaolinite. More difficult samples were those containing 2.0 mg of coal mine dust or even a lower level of coal mine dust but more than a few percent kaolinite. The upper and lower values of the %RSD for the method, not including variability of the sampling pump, are as follows:

	Estimated %RSD	
	Lower	Upper
Total error for analysis	13%	22%
Intralaboratory error	7%	10%
Interlaboratory error	8%	14%

The amount of silica ranged from 62 to 150 μg.

The error contributed by the sampling pump was obtained by comparing the results for samples collected with pumps with the results for samples collected by SRI with a matched set of critical flow orifices. The error for using a personal sampling pump was estimated to be 23% to 25%, which increased the interlaboratory variability for both the easier and the more difficult sample types. For samples collected with a pump, the standard deviations (using an average for the pump of 24%) are estimated to be:

	Estimated %RSD	
	Lower	Upper
Total error, sampling and analysis	36%	40%
Intralaboratory error	7%	10%
Interlaboratory error	8%	14%
Sampling pump error	24%	24%

There is more variability in the results when they are reported as percent silica. Relative standard deviations ranged from 17% to 50%, with the best

data obtained for samples collected by SRI rather than with sampling pumps. Initial weights for these filters were furnished by MSA. Pooled data for samples are given below, based on percent silica:

	Estimated %RSD
Total error, as percent silica	20%
Intralaboratory error	6%
Interlaboratory error	14%

Using values obtained by XRD analysis at SRI as references, the method was found to be free from systematic error at seven of the levels tested. At the remaining level, a difference of 7 μg was determined to be significant. The averages for the IR method agree with the averages for the XRD method for the set that was distributed to collaborative laboratories in both tests.

This method should be classified as a B method under the criterion established by NIOSH in 1977 that a B method (sampling and analysis) should come within 25% of the "true" value 95% of the time.

RECOMMENDATIONS

For both methods, the source of errors for the sampling pumps should be investigated. Because the "pump effect" increased interlaboratory differences, there must be an interaction betwen the "pump effect" and laboratories (or sampling personnel). Any further study of the sampling problem should include experiments similar to those done here. That is, to estimate the pump error for sampling silica, the experiment should include sampling of silica and a reasonable amount of matrix through the 10-mm cyclones.

The intralaboratory precision is quite good for both these methods and we would not expect to be able to reduce these errors significantly, nor would it be reasonable in view of the sampling errors.

For the IR method, some improvement would be expected if the laboratories could eliminate the acid-washing of the sample filter. If the industrial hygienist who collects the samples knows with certainty that there is no calcite, the laboratory should be informed to make the analysis easier.

For the XRD method, further investigation of the effects of the correction for sample self-absorption is warranted. Because the magnitude of the correction may be significant, depending on the material collected with the silica, we recommend that further studies include various materials and, especially, various size distributions. PCAM 259 has wide applicability, and for most situations where weakly absorbing materials are collected, the correction improves the results, but there are some samples for which the correction is not right. Preliminary treatment of the filter may help; for instance, acid treatment may solubilize iron oxide particles. The effectiveness of the treatment should be thoroughly evaluated before it is incorporated into the method since it would require additional handling of the filter.

The magnitude of the interlaboratory errors for both the XRD and IR methods was disappointing, and it is recommended that an attempt be made to understand and reduce this type of error. In this study we attempted to reduce the errors due to differences in calibration by providing laboratories with supplies of the same calibration materials. We believe the next step would be to provide actual calibration standards, that is, silver membrane or IR-transparent filters containing silica, or to arrange for the exchange of standards. Certified standards, such as those now obtainable from the National Bureau of Standards for other materials, could be made available to the laboratories.

SECTION III

RUGGEDNESS STUDY OF THE XRD METHOD

GENERAL

The objective of this task was to test for ruggedness of the XRD method PCAM 259, Free Silica (Quartz, Cristobalite, Tridymite) in Airborne Dust (see Appendix A), in preparation for the collaborative test of this method. A ruggedness study is a formalized technique for assessing the vulnerability of the measurement to small, but reasonable, modifications to the procedures. This provides safeguards for the collaborative study in that participating laboratories may be alerted to those steps requiring close control. If significant adverse results are found to be caused by minor alterations in the procedures, changes may be made as required before the collaborative study is initiated. Descriptive details may be added to more carefully guide users of the method.

PCAM 259 can be summarized in four steps:

(1) Collection of a respirable dust fraction on a polyvinyl chloride (PVC) filter.

(2) Destruction of the filter and other organic matter in the sample using either a low temperature asher (LTA) or a muffle furnace.

(3) Redeposition of the residue onto a silver membrane filter.

(4) Quantification of the silica by x-ray diffraction (XRD) analysis using the silver as an external standard to correct for sample self-absorption.

Workers are exposed predominately to α-quartz, and this study concentrated on that polymorph. The words silica and quartz are used here interchangeably and refer to alpha-quartz. Neither tridymite nor cristobalite was studied.

Samples for both the ruggedness and collaborative tests were made up to resemble actual field samples as closely as possible. This is important for silica measurement because the analysis is sensitive to particle size distribution. A matrix material was added to the samples so that the procedures could be tested in the presence of possible interfering materials. Both the silica and matrix materials were collected onto PVC filters from aerosols in a laboratory generation system. The 10-mm nylon cyclones were used to collect only the respirable fraction of the total aerosol.

The initial problem was to identify those variables that may affect analysis results and to select an experimental design to efficiently determine which of these candidate variables can cause significant errors in the analysis if not closely controlled. A design was chosen that permitted the estimation of main effects for a number of variables and gave information on interactions.

APPROACH

Design of the Tests

The statistical design for the ruggedness tests followed the procedures described by Youden and Steiner (2), but used a larger number of filters (16 and 32) as given by Plackett and Burman (3). The basic idea is not to study one variation at a time, but to introduce a number of procedural modifications all at once, using a design that permits detection of individual effects. For a number of variables, n, each having two alternatives, we would need to run the 2^n experiments if we attacked the problem by changing one variable at a time, while holding the others constant. Fortunately, there are subsets of 2^n experiments that permit us to evaluate a number of variables simultaneously, and we chose these for the experiments. The full design patterns are described in the section on experimental results. For the moment it is only necessary to know that some of the steps in the XRD method were selected for study and, for each, two probable conditions were selected.

The Youden procedure assumes that the variables to be considered can be set at two levels corresponding to a reasonable range of laboratory exactitude, or at each of two dichotomous conditions (for contrasting yes-no procedural alternatives). Each filter can thus be processed at a selected setting for each of the variables in question. The conditions for any one filter can be treated as a series of plus ones or minus ones, corresponding to two different values for each continuous variable or to distinguish the alternatives in a dichotomous variable (e.g., the decision to mail the filter cross-country or not, or the choice between plasma asher or muffle furnace).

The XRD method directs the user to destroy the filter matrix using either a low temperature asher (LTA) or a muffle furnace. If a choice between asher and furnace is considered, the design is applicable only if all the other variables make sense for both. However, some variables, such as temperature of the furnace, are irrelevant for filters processed in the asher. The remedy for this problem was to apply the Youden procedure separately for the LTA and again for the muffle furnace (in designs using 16 filters) in an initial stage to analyze the significance of variables peculiar to each ashing procedure. Then, in a second stage (in a design using 32 filters), conditions or variable alternatives relevant to the total method were evaluated. In the second stage, variables peculiar to the asher or to the furnace were held at preselected values, and the muffle furnace/LTA was treated as one of the variables.

In each of the two first-stage tests, four variables were included for each asher type. The designs used could accommodate 15 variables, of which 11 were dummy variables and so were not varied in the procedure. In the second stage, there were 7 active variables and 24 dummy variables, providing 23 degrees of

freedom for estimating experimental error. In both stages, assignment of variables to columns was made by a random process. Although some economy in the test design could have been achieved by reducing the number of samples, there had been some question of the precision of generation of replicate samples. Therefore, the relatively large number of degrees of freedom was desired to estimate the standard error.

Selection of Variables

Variables unique to either the muffle furnace or the LTA are listed in Tables 22 and 23, along with their two conditions, "+" and "-", values. The designations "+" and "-" are used for convenience and do not imply that one condition is higher or more positive than the other. These variables relate to the corresponding ashing process. Since the residue from these two processes may require different sonication times, the variable for resuspension time was included.

Table 22. Variables associated with a muffle furnace.

Variables	(+)	(-)	Design column*
Ashing time	2 hr	1 hr	X_7
Ashing temperature	600°	500°	X_1
Amount of isopropanol used to transfer residue from crucible used in ashing	3 10-mL rinses	1 10-mL rinse, then 1 5-mL rinse	X_3
Time taken to resuspend residue in ispropanol (i.e., time of sonication)	4 min	2 min	X_{15}

*See section entitled Treatment of Data.

Table 23. Variables associated with use of a low temperature asher.

Variables	(+)	(-)	Design column*
Ashing time	2 hr	1 hr	X_{10}
Radio frequency generator wattage	300	200	X_{15}
Oxygen flow rate	75 mL/min	50 mL/min	X_4
Time taken to resuspend residue in isopropanol (i.e., time of sonication)	4 min	2 min	X_9

*See section entitled Treatment of Data.

Table 24 lists variables tested in the full 32-filter experimental design. The use of either the muffle furnace or LTA was treated as one variable for this expanded test. The LTA was operated with 300 watts for 2 hours at an oxygen flow rate of 75 mL/min. Samples for the muffle furnace were treated for 2 hours at 600°C. The amount of matrix was varied in preparation for the collaborative study and because the absorption correction factor was expected to be perturbed by the loading of co-deposited materials.

Table 24. Variables tested for the complete XRD method.

Variables	(+)	(-)	Design column*
Rinse chimney	Do not rinse	Rinse chimney	X_5
Time delay between sonication of residue and deposition onto a 0.45-μm silver filter	15 min	2 min	X_{12}
Mailing of samples	Mailed	Not mailed	X_{13}
Sonication time	10 min	3 min	X_{17}
Volume of isopropanol rinses used to transfer sonicated sample to funnel	3 5-mL rinses	3 10-mL rinses	X_{25}
Amount of matrix material	2.17 mg	1.07 mg	X_{26}
Type of ashing	Muffle furnace	Plasma asher	X_{31}

*See section entitled Treatment of Data.

For the third variable, mailing of samples, half of the samples were sent by Federal Express to the NIOSH offices in Cincinnati and returned to us. Filters were left in the cassettes. Here again, the matrix amount could affect the result of mailing since any tendency of the deposit to crack and flake off would occur at higher sample loadings.

The other variables in Table 24 were concerned with transfer of the material during the redeposition steps. These were selected based on past experience of various users of the method. For instance, it had been observed that some filter residues are difficult to break up in the sonicator and require more lengthy treatment than other similar filter samples.

A ruggedness study of variables associated with preparation of standards had been done previously (4), so we did not include any variables for the preparation of standards. The method directs that the quality of the standard curve be verified before it is used for calibration by requiring that replicates by prepared if there is a significant scatter in the points. For the ruggedness study, the precision and/or accuracy of the standard curve is unimportant because sample results are compared with each other. However, it is our experience that the standard preparation requires some practice.

We did not include any variables associated with measurement of the XRD intensity of the silica and silver peaks or alignment of the instrument. In most laboratories, the XRD analysis is performed by a specialist. This technique is more sensitive than some others to operator experience and quality control practices, and the success of the method relies to a great extent on these factors.

EXPERIMENTAL PROCEDURES

Equipment

The following equipment was used in these experiments:

Muffle furnace: Model M15A from Blue M Electric Company, Blue Island, IL.

Low temperature asher (LTA): Plasma System IPC 1003B, from International Plasma Corporation, Hayward, CA. It contains two 3-inch-diameter by 6-inch-long cylindrical chambers, with a total capacity for six 50-mL beakers. Radio frequency generator power range is 0-300 watts.

Ultrasonic bath: Model DR 50 AH from Acoustica Associates, Inc., Los Angeles, CA. Tank size is approximately one gallon.

X-ray diffraction system: Phillips x-ray diffractometer, 1800-watt high intensity copper x-ray tube; Bicron scintillation detector; Canberra data system.

Generation facility: System built at SRI for use in the Proficiency Analytical Testing (PAT) program and modified (5) to provide for collection of multiple samples either at 1.7 or 2 L/min using 10-mm nylon cyclones to remove nonrespirable aerosol (see Section VI).

Materials

Silica--
Min-U-Sil materials were supplied by PGS Floridin (a subsidiary of ITT). Selected physical properties are listed in Section V. Min-U-Sil 15 was used as a feed dust to prepare aerosols for sample preparation.

Min-U-Sil 5 was used as a calibration material. The XRD pattern of Min-U-Sil 5 matches that of JCPDS Card No. 5-490. A semiquantitative spectrographic analysis gave the following results, reported as oxides of the elements indicated.

Si	Principal constituent	Cu	<0.001%
Fe	0.07%	Ti	0.001%
Mg	0.008%	Ca	0.003%
Mn	<0.001%	Sr	<0.003%
Al	0.01%	Ba	<0.001%

Kaolinite--
This Georgia Kaolin product is sold under the name Hydrite UF, with a reported median particle size of 0.2 μm.

Calcite--
Microwhite 25, particle size range 0.5 to 15 μm, mean size 3 μm (as reported by the supplier).

Talc--
Magnesium Silicate No. 399 from Whittaker, Clark & Daniels, Inc., was used. The average particle size is estimated to be 5 μm. (Approximately 85% of test atmosphere passes through the 10-mm cyclone and is collected on the filter.)

Background Matrix for Samples

A background matrix for the samples was prepared by adding weighed amounts of talc, calcite, and kaolinite to a dry solids mixer of V-type (6) and mixing for 36 hours. One kilogram of mixture with the following composition was prepared:

Component	Wt %
Talc	33.4
Kaolinite	33.7
Calcite	32.9

Characteristics of Matrix Mixture

X-ray diffraction pattern for talc agrees with JCPDS Card No. 13-588. Samples prepared for the Proficiency Analytical Testing (PAT) program have this talc as a background matrix.

The x-ray diffraction patterns from 0° to 90° were recorded for bulk samples of calcite, kaolinite, and Min-U-Sil 5. The purity of the calcite and Min-U-Sil was confirmed by comparing their XRD patterns with the d spacings tabulated by the Joint Committee of Powder Diffraction Standards. The kaolinite XRD pattern was compared with both the tabulated d values and with a recorded XRD pattern of a kaolinite sample from the Source Clay Minerals Repository, Department of Geology, University of Missouri. The commercial bulk kaolinite satisfactorily matches both the SCMR sample and the literature values.

There are very few overlapping XRD peaks between Min-U-Sil, calcite, and kaolinite. The scan for a 1:1:1 mixture of these components is shown in Figure 1. The peaks are easily assigned to the various components based on

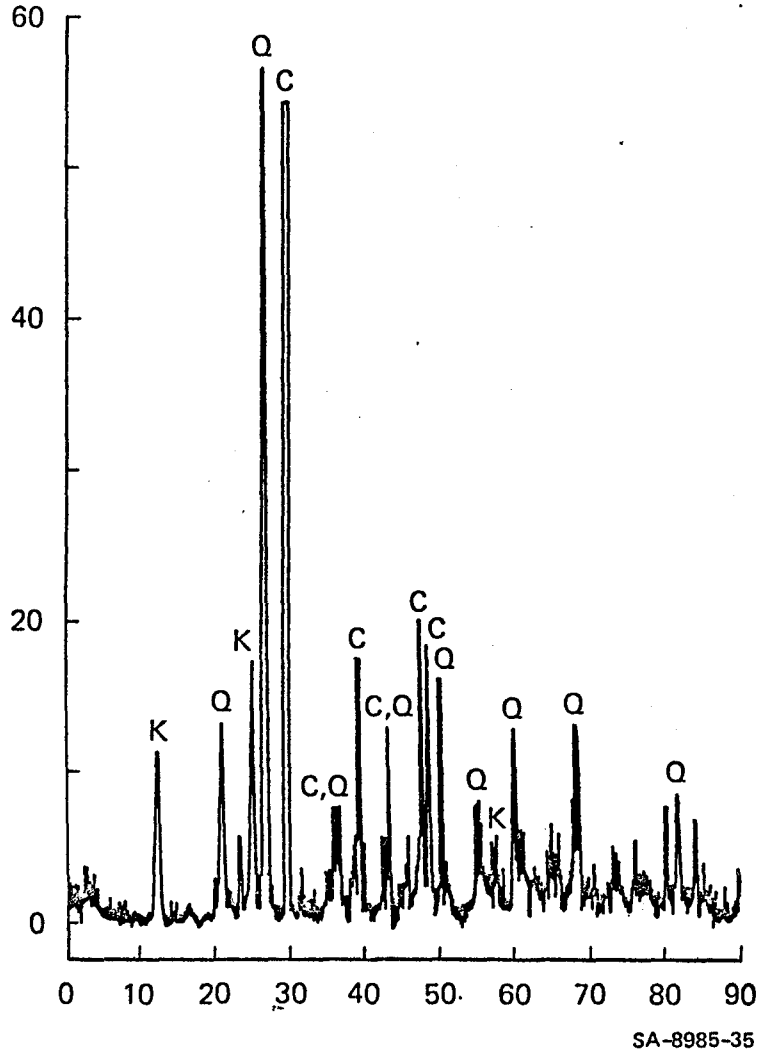


FIGURE 1 POWDER X-RAY DIFFRACTION SCAN OF A 1:1:1 MIXTURE OF CALCITE (C), KAOLINITE (K), AND QUARTZ (Q)

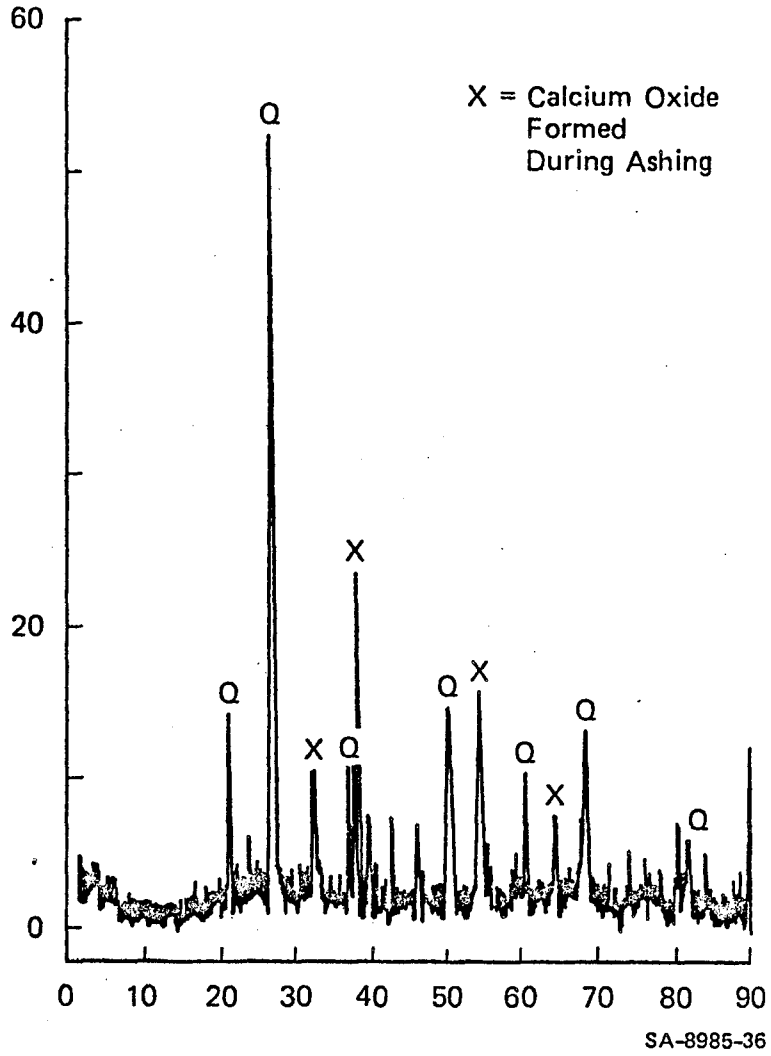


FIGURE 2 POWDER X-RAY DIFFRACTION SCAN OF SAME MIXTURE AFTER IT HAS BEEN ASHED AT 800°C FOR 2 HOURS

their individual XRD patterns. Kaolinite is easily detected by the two strong peaks at 2θ values of 12.5° and 25° (d = 7.07 and 3.56 Å calculated using λ = 1.54 Å for Cu K_α radiation). Calcite is characterized by a very intense band at 29.6° (d = 3.00 Å) and two smaller peaks at 47.6° (1.83 Å) and 48.7° (1.78 Å). The calcite peak at 39.6° (2.27 Å) overlaps a background peak that appears in all samples. The Min-U-Sil is easily detected by several intense, well-separated peaks.

This mixture was ashed in a muffle furnace at 800°C for 2 hours. The XRD pattern of this ashed mixture is shown in Figure 2. All calcite and kaolinite peaks disappear after ashing. The quartz peaks all remain and are joined by a new set of peaks at 32.4° (2.77), 37.5° (2.41), 54.0° (1.70), and 67.6° (1.39), which can all be assigned to calcium oxide. The small peaks at 42.6°, 40.5°, 46.0°, and 64.3° have not been assigned. Thus it appears that the calcite is converted to CaO by the ashing, but the quartz is unaffected. The XRD peaks for kaolinite disappear because the kaolinite is converted to amorphous metakaolin between 500° and 900°C.

Preparation of Filter Samples

Two separate sample generation runs were required. Silica aerosols were prepared using Min-U-Sil 15. The sample collection rate through 10-mm nylon cyclones onto 5-μm PVC filters was 1.7 L/min.

For the first generation run, silica was deposited over a period of 30 minutes; 0.889 mg of matrix material was then deposited. These filters were used for the two ruggedness tests for factors associated with the ashing steps.

In the second generation run, silica was again deposited first over a period of 22 minutes. Matrix material was then generated and collected until 1.027 mg of matrix had been deposited. One-half of the filters were removed, and generation of matrix was continued until the other half of the filters contained 2.173 mg matrix. Samples from this run were used in the 32-filter matrix design test of the total method.

Silica levels were determined by removing and analyzing two filters immediately after generation of the silica aerosol. The colorimetric method of analysis was used to estimate silica loadings on these two filters. Matrix material loadings were determined by gravimetric analysis of filters that were used to collect only matrix materials.

The fraction of matrix material penetrating the 10-mm nylon cyclones was determined by collecting filter samples with no cyclone in place and comparing them with samples collected with a cyclone present. The percentage of matrix material penetrating the cyclone was 76.3%.

XRD Procedures

Calibration--
Standards were prepared from suspensions of Min-U-Sil 5. A polycrystalline quartz wafer was used daily for instrument calibration. A calibration curve of net intensity [Net (I)] versus micrograms of silica per filter (w) was

established covering the range of 16 to 160 μg. This curve can be described by the equation

$$\text{Net (I)} = 63.471\ w - 108. \qquad (8)$$

Data Collection--
The net intensities for the quartz (101) peaks for standards and samples were obtained by subtracting the sum of the background counts from each side of the peak from the total integrated peak count. Peak scanning was from $2\theta = 27.63°$ to $2\theta = 25.75°$ at 0.125°/min. The background count was made by scanning each side of the peak and calculating an average background value.

The net intensity of the (111) silver peak was measured by scanning from $2\theta = 41.44°$ to $2\theta = 34.76°$ at a rate of 1.00°/min. Background counts were made as for the silica peak.

Filters for both samples and standards were attached to glass slides with two-sided tape.

Colorimetric Analysis

For the colorimetric analysis, samples were treated with hydrofluoric acid to solubilize the silica. A blue silicomolybdate complex was formed and was measured at 620 nm. Standards made from bulk Min-U-Sil 5 were used to prepare a calibration curve. This procedure is adapted from PCAM 106.

TREATMENT OF DATA

Computation of Main Effects

Tables 25 through 27 show the N x N matrices used. The design patterns for the individualized tests of variables unique to either the muffle furnace or LTA are the same (Tables 25 and 26), except that column assignments of the variables tested are different. Table 27 is the full design for the combined testing strategy.

The elements in each row indicate which condition, "+" or "-", of the variable was applied in the treatment of the filter associated with that row. Columns to which variables were assigned are indicated by an asterisk. These variables, which are identified in Tables 22 through 24, are shown as notes to the tables. All other columns were unassigned and were used to estimate the experimental error. There are N - 1 columns available for assignment of variables; the Nth column, identified as Y_i, is a tabulation of the responses, in micrograms of silica, for the filter associated with each row.

To conduct the experiments, we used SRI's test generation system to prepare the number of silica containing filter samples listed in the left-hand column. Each filter was analyzed independently, using the "+" or "-" designations as guidelines. For filter 1 of Table 25, for example, the ashing temperature was set at the "+" condition, as directed by the first column X_1; the second column, a "dummy" variable, was ignored; the "+" value of the procedure

Table 25. Matrix elements and results for the 16-filter ruggedness test of the muffle furance.

Filter	X_1^*	X_2	X_3^*	X_4	X_5	X_6	X_7^*	X_8	X_9	X_{10}	X_{11}	X_{12}	X_{13}	X_{14}	X_{15}^*	Y_i
1	+	+	+	+	-	+	-	+	+	-	-	+	-	-	-	120.2
2	-	+	+	+	+	-	+	-	+	+	-	-	+	-	-	156.3
3	-	-	+	+	+	+	-	+	-	+	+	-	-	+	-	163.3
4	-	-	-	+	+	+	+	-	+	-	+	+	-	-	+	110.0
5	+	-	-	-	+	+	+	+	-	+	-	+	+	-	-	157.8
6	-	+	-	-	-	+	+	+	+	-	+	-	+	+	-	175.0
7	-	-	+	-	-	-	+	+	+	+	-	+	-	+	+	172.0
8	+	-	-	+	-	-	-	+	+	+	+	-	+	-	+	175.5
9	+	+	-	-	+	-	-	-	+	+	+	+	-	+	-	165.8
10	-	+	+	-	-	+	-	-	-	+	+	+	+	-	+	166.7
11	+	-	+	+	-	-	+	-	-	-	+	+	+	+	-	173.5
12	-	+	-	+	+	-	-	+	-	-	-	+	+	+	+	159.6
13	+	-	+	-	+	+	-	-	+	-	-	-	+	+	+	165.0
14	+	+	-	+	-	+	+	-	-	+	-	-	-	+	+	155.8
15	+	+	+	-	+	-	+	+	-	-	+	-	-	-	+	183.1
16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	163.4
δ_j:	+1.9	+0.1	+2.3	-8.4	-2.6	-8.5	+0.2	+3.1	-5.2	+4.0	+3.9	-7.0	+6.0	+6.1	+0.8	160.2 (Avg)

* X_1 = Ashing temperature.
X_3 = Isopropanol rinses.
X_7 = Ashing time.
X_{15} = Time of sonication.

s = 22.2 µg.
δ_{min} = 12.2 µg. (95% confidence level)

Table 26. Matrix elements and results for the 16-filter ruggedness test of the low temperature ashing procedure.

Filter	X_1	X_2	X_3	X_4*	X_5	X_6	X_7	X_8	X_9*	X_{10}*	X_{11}	X_{12}	X_{13}	X_{14}	X_{15}	Y_i
1	+	+	+	+	-	+	-	+	+	-	-	+	-	-	-	146.1
2	-	+	+	+	+	-	+	-	+	+	-	-	+	-	-	166.6
3	-	-	+	+	+	+	-	+	-	+	+	-	-	+	-	156.2
4	-	-	-	+	+	+	+	-	+	-	+	+	-	-	+	152.8
5	+	-	-	-	+	+	+	+	-	+	-	+	+	-	-	157.6
6	-	+	-	-	-	+	+	+	+	-	+	-	+	+	-	163.7
7	-	-	+	-	-	-	+	+	+	+	-	+	-	+	+	160.0
8	+	-	-	+	-	-	-	+	+	+	+	-	+	-	+	167.5
9	+	+	-	-	+	-	-	-	+	+	+	+	-	+	-	163.5
10	-	+	+	-	-	+	-	-	-	+	+	+	+	-	+	164.1
11	+	-	+	+	-	-	+	-	-	-	+	+	+	+	-	139.7
12	-	+	-	+	+	-	-	+	-	-	-	+	+	+	+	172.9
13	+	-	+	-	+	+	-	-	+	-	-	-	+	+	+	158.4
14	+	+	-	+	-	+	+	-	-	+	-	-	-	+	+	157.9
15	+	+	+	-	+	-	+	+	-	-	+	-	-	-	+	170.6
16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	140.6
δ_j:	1.0	+4.5	-0.9	-1.2	+3.7	-1.5	-0.03	+3.2	+1.2	+3.0	+1.1	-1.6	+2.7	+0.4	+4.4	158.6 (Avg)

* X_4 = Oxygen flow rate.
X_9 = Time of sonication.
X_{10} = Ashing time.
X_{15} = Radio frequency generator wattage.

s = 9.3 µg.
δ_{min} = 5.1 µg. (95% confidence level)

Table 27. Matrix elements and results for the ruggedness test of the total method.

Filter	X_1	X_2	X_3	X_4	X_5^*	X_6	X_7	X_8	X_9	X_{10}	X_{11}	X_{12}^*	X_{13}^*	X_{14}	X_{15}	X_{16}	X_{17}^*	X_{18}	X_{19}	X_{20}	X_{21}	X_{22}	X_{23}	X_{24}	X_{25}^*	X_{26}^*	X_{27}	X_{28}	X_{29}	X_{30}	X_{31}^*	Y_i
1	-	-	-	-	+	-	+	-	+	+	+	-	+	+	-	-	-	+	+	+	+	+	-	-	+	+	-	+	-	-	+	112.4
2	+	-	-	-	-	+	-	+	-	+	+	+	-	+	+	-	-	-	+	+	+	+	+	-	-	+	+	-	+	-	-	123.0
3	-	+	-	-	-	-	+	-	+	-	+	+	+	-	+	+	-	-	-	+	+	+	+	+	-	-	+	+	-	+	-	118.9
4	-	-	+	-	-	-	-	+	-	+	-	+	+	+	-	+	+	-	-	-	+	+	+	+	+	-	-	+	+	-	+	112.9
5	+	-	-	+	-	-	-	-	+	-	+	-	+	+	+	-	+	+	-	-	-	+	+	+	+	+	-	-	+	+	-	115.3
6	-	+	-	-	+	-	-	-	-	+	-	+	-	+	+	+	-	+	+	-	-	-	+	+	+	+	+	-	-	+	+	126.8
7	+	-	+	-	-	+	-	-	-	-	+	-	+	-	+	+	+	-	+	+	-	-	-	+	+	+	+	+	-	-	+	115.8
8	+	+	-	+	-	-	+	-	-	-	-	+	-	+	-	+	+	+	-	+	+	-	-	-	+	+	+	+	+	-	-	117.5
9	-	+	+	-	+	-	-	+	-	-	-	-	+	-	+	-	+	+	+	-	+	+	-	-	-	+	+	+	+	+	-	122.8
10	-	-	+	+	-	+	-	-	+	-	-	-	-	+	-	+	-	+	+	+	-	+	+	-	-	-	+	+	+	+	+	103.6
11	+	-	-	+	+	-	+	-	-	+	-	-	-	-	+	-	+	-	+	+	+	-	+	+	-	-	-	+	+	+	+	116.6
12	+	+	-	-	+	+	-	+	-	-	+	-	-	-	-	+	-	+	-	+	+	+	-	+	+	-	-	-	+	+	+	113.0
13	+	+	+	-	-	+	+	-	+	-	-	+	-	-	-	-	+	-	+	-	+	+	+	-	+	+	-	-	-	+	+	125.1
14	+	+	+	+	-	-	+	+	-	+	-	-	+	-	-	-	-	+	-	+	-	+	+	+	-	+	+	-	-	-	+	106.6
15	+	+	+	+	+	-	-	+	+	-	+	-	-	+	-	-	-	-	+	-	+	-	+	+	+	-	+	+	-	-	-	119.6
16	-	+	+	+	+	+	-	-	+	+	-	+	-	-	+	-	-	-	-	+	-	+	-	+	+	+	-	+	+	-	-	120.0
17	-	-	+	+	+	+	+	-	-	+	+	-	+	-	-	+	-	-	-	-	+	-	+	-	+	+	+	-	+	+	-	108.6
18	-	-	-	+	+	+	+	+	-	-	+	+	-	+	-	-	+	-	-	-	-	+	-	+	-	+	+	+	-	+	+	114.7
19	+	-	-	-	+	+	+	+	+	-	-	+	+	-	+	-	-	+	-	-	-	-	+	-	+	-	+	+	+	-	+	106.9
20	+	+	-	-	-	+	+	+	+	+	-	-	+	+	-	+	-	-	+	-	-	-	-	+	-	+	-	+	+	+	-	114.8
21	-	+	+	-	-	-	+	+	+	+	+	-	-	+	+	-	+	-	-	+	-	-	-	-	+	-	+	-	+	+	+	97.7
22	+	-	+	+	-	-	-	+	+	+	+	+	-	-	+	+	-	+	-	-	+	-	-	-	-	+	-	+	-	+	+	110.1
23	+	+	-	+	+	-	-	-	+	+	+	+	+	-	-	+	+	-	+	-	-	+	-	-	-	-	+	-	+	-	+	100.0
24	+	+	+	-	+	+	-	-	-	+	+	+	+	+	-	-	+	+	-	+	-	-	+	-	-	-	-	+	-	+	-	101.3
25	-	+	+	+	-	+	+	-	-	-	+	+	+	+	+	-	-	+	+	-	+	-	-	+	-	-	-	-	+	-	+	113.8
26	+	-	+	+	+	-	+	+	-	-	-	+	+	+	+	+	-	-	+	+	-	+	-	-	+	-	-	-	-	+	-	99.9
27	-	+	-	+	+	+	-	+	+	-	-	-	+	+	+	+	+	-	-	+	+	-	+	-	-	+	-	-	-	-	+	114.0
28	+	-	+	-	+	+	+	-	+	+	-	-	-	+	+	+	+	+	-	-	+	+	-	+	-	-	+	-	-	-	-	115.7
29	-	+	-	+	-	+	+	+	-	+	+	-	-	-	+	+	+	+	+	-	-	+	+	-	+	-	-	+	-	-	-	96.2
30	-	-	+	-	+	-	+	+	+	-	+	+	-	-	-	+	+	+	+	+	-	-	+	+	-	+	-	-	+	-	-	120.8
31	-	-	-	+	-	+	-	+	+	+	-	+	+	-	-	-	+	+	+	+	+	-	-	+	+	-	+	-	-	+	-	98.4
32	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	+	+	-	+	-	-	+	+	-	-	-	-	-	-	108.6
δ_j:	0.3 |	0.8 |	-0.1 |	-2.6 |	1.1 |	-0.7 |	-0.6 |	-1.5 |	-0.2 |	-2.2 |	-0.9 |	0.9 |	-2.1 |	0.4 |	1.1 |	-0.4 |	-0.7 |	-0.9 |	0.9 |	-1.0 |	2.9 |	0.3 |	1.3 |	3.0 |	-0.6 |	4.5 |	0.1 |	0.5 |	0.7 |	-0.5 |	-0.4 |	112.3 (Avg)

*X_5 = Chimney rinse.
X_{12} = Time delay after sonication.
X_{13} = Mailing of samples.
X_{17} = Sonication time.
X_{25} = Isopropanol rinses.
X_{26} = Amount of matrix.
X_{31} = Muffle furnace or LTA.

s = 7.3 µg.
δ_{min} = 2.7 µg (95% confidence level).

for the isopropanol rinse was used, from the column X_3; the "-" condition for ashing time, column X_7, and the "-" condition for the time of sonication variable, column X_{15}, were used. Finally, the amount of silica (120.2 μg) determined for that filter was tabulated in the last column.

The main effects of each variable were computed as follows:

$$\delta_j = \frac{\sum^{+} Y_i - \sum^{-} Y_i}{N} \tag{9}$$

where

δ_j = main effect (μg silica) associated with the variable assigned to the j^{th} column (j = 1 to q, where q is the number of assigned variables)

Y_i = response (μg silica) for the filter in the i^{th} row

$\sum^{+} Y_i$ = summation of Y_i associated with a "+" in column j

$\sum^{-} Y_i$ = summation of Y_i associated with a "-" in column j

N = number of filters.

Each column has an equal number of "+" and "-" signs. Within these two groups, all other variables are included an equal number of times at their "+" and "-" values. Thus each δ_j reflects half the difference between the mean results corresponding to the two conditions of the variable assigned to column j. The sign of δ_j indicates if the effect is greater at the "+" or "-" value of the variable. All the individual Y_i values and the effects associated with each column are listed in Tables 25 through 27.

The standard deviation of Y_i is calculated from the effects determined for the unassigned columns.

$$s = \left[\frac{N}{N - q - 1} \sum_{k=q+1}^{k=n} \delta_k^2 \right]^{1/2} \tag{10}$$

(q = number of assigned columns)

The minimum significant effect (δ_{min}) is taken to be

$$\delta_{min} = \frac{s}{\sqrt{N}} \cdot t \tag{11}$$

where t is the value of Student's "t" at the desired probability level for N - q - 1 degrees of freedom.

Test for Interactions

Interactions between assigned variables were determined by identifying a matrix column representing interaction. The effect associated with this derived column was compared with the minimum significant effect. To find the appropriate column, we compared, row by row, the two columns associated with the variables under test. Combinations of +, + or -, - were assigned a + value; whereas combinations of -, + or +, - were assigned a - value. As before, the Y_i values associated with the + or - values (for the new column) were summed, and the effect was found. This had the result of testing if the effect of one variable differs for different levels of the second variable.

Power Function Calculations

Estimates of standard error were used to calculate power functions. The power function is defined as the probability that a test for significance of observed difference in effect between the "+" and "-" values for a variable would reject the null hypothesis (that no significant effect was indicated) if the true effect $(\mu_i - \mu_0)$ actually differed from zero by alternate amounts. Here μ_i is defined as one-half the difference between the "+" and "-" conditions and $\mu_0 = 0$.

For N filters, this power function is derived from tables of the noncentral t distribution with $N - q - 1$ degrees of freedom, level of significance α, and the means of N/2 observations at each of the two levels of each test condition. This power function is obtained as $(\mu - \mu_0) = \frac{s}{\sqrt{N}} \cdot d$,

where d is the so-called noncentrality factor in Owen's (7) table for the noncentral t distribution using the row for $N - q - 1$ degrees of freedom.

Table 28 is a tabulation of the power functions. The values closest to the minimum significant effects for the three tests are underlined, showing there is a 50% probability that an effect as great as the observed minimum would have been detected.

Table 28. Power function projections for the XRD method.

	Power	Centrality parameter d (α = 0.025)*		Detectable effect ($\mu - \mu_0$) in µg		
				N = 16		N = 32
β	1 - β	f = 11	f = 24	s = 9.3	s = 22.2	s = 7.3
0.01	0.99	4.73	4.47	11.0	26.3	5.8
0.05	0.95	3.97	3.76	9.2	22.0	4.9
0.10	0.90	3.57	3.38	8.3	19.8	4.4
0.20	0.80	3.08	2.92	7.2	17.1	3.8
0.30	0.70	2.73	2.59	6.3	15.2	3.3
0.40	0.60	2.43	2.31	5.6	13.5	3.0
0.50	0.50	2.15	2.04	5.0	11.9	2.6
0.60	0.40	1.87	1.78	4.3	10.4	2.3
0.70	0.30	1.57	1.50	3.7	8.7	1.9
0.80	0.20	1.22	1.16	2.8	6.8	1.5
0.90	0.10	0.74	0.71	1.7	4.1	0.9

Note: f = degrees of freedom.

*Corresponding to α = 0.05 for a two-tailed test with 16-4-1 = 11 degrees of freedom or 32-7-1 = 24 degrees of freedom.

RESULTS AND DISCUSSION

Test of Variables Unique to Ashing

Tables 29 and 30 summarize the main effects of the variables for each of the 16-filter tests. A comparison of the effects of the variable with the minimum significant effect reveals that none of the variables tested had a significant effect on the results for either set of samples. In addition, there were no significant interaction effects for either test.

There is much more scatter in the data for the filters treated in the muffle furnace than for those treated in the LTA as evidenced by the standard error of 22.2 µg for the muffle furnace versus only 9.3 µg for the LTA data. We believe this increased variability is due to only two filters (1 and 4), both of which had low values. (Of the four variables tested, it happened that each had a "+" and "-" value for these two filters.) Also, both Level 1 and Level 4 values would be rejected as outliers if the data in Table 25 were tested. In the ruggedness test for the total method (decribed later), we found that the standard deviations for LTA and muffle furnace procedures were almost identical.

Table 29. Summary of computations of main effects of variables related to muffle furnace.

Minimum significant effect: 12.2 μg (5% level of significance)
Estimated standard deviation: 22.2 μg

Variable	Effect (μg)
Ashing temperature	1.9
Ashing time	0.2
Crucible rinse volume	2.3
Sonication time	0.8

Average μg: 160.2

Table 30. Summary of computations of main effects of variables related to low temperature asher.

Minimum significant effect: 5.1 μg (5% level of significance)
Estimated standard deviation: 9.3 μg

Variable	Effect (μg)
Ashing temperature	1.9
O_2 flow rate	-1.2
RF wattage	4.4
Sonication time	1.2

Average μg: 158.6

The average of all filters for the muffle furnace was 160.2 μg; for the LTA the average was 158.6 μg. All the filters for both of these tests were collected simultaneously, so the averages were expected to agree.

Test of Total Method

Table 31 summarizes the main effects of the variables for the total method. The average amount found was 112.3 μg, with an estimated standard error of 7.3 μg.

Table 31 shows that there is a significant effect (4.5 μg) due to the amount of matrix loadings; the sign of the effect (+) reflects that those filters having a greater amount of matrix were also estimated to have a greater amount of silica. None of the other variables had an effect, as can be seen by comparing the size of each effect with the minimum significant effect of 2.7 μg.

Table 31. Summary of computations of main effects of variables for total method.

Minimum significant effect: 2.7 μg (5% level of significance)
Estimated standard deviation: 7.3 μg

Variable	Effect (μg)
Chimney rinse	+1.09
Time between sonication and filtration	+0.90
Mailing of samples	-2.1
Sonication time	-0.68
Volume of isopropanol rinses	-0.60
Amount of matrix material	+4.5
Type of asher	-0.36

Average μg: 112.3

We found that the apparent matrix effect could be explained by examining the effect of the sample self-absorption correction. To do this, we tabulated the XRD results for mass of silica, for the same filters, before the correction factor was applied. These values, when analyzed statistically yielded the results in Table 32. We find a lower average amount, 101.4 μg rather than 112.3 μg, but comparable minimum significant effects, 2.9 μg versus 2.7 μg. The effect for matrix amount is now 1.3 μg, which is not significant. We conclude from this evaluation that, when the correction factor is applied, it causes overestimation of the amount of silica because the intensity of the silver peak is attenuated to a greater degree than the intensity of the silica peak.

Table 32. Summary of computations of effects of variables on silica measurement, not corrected for absorbance.

Minimum significant effect: 2.9 μg (5% level of significance)
Estimated standard deviation: 8.0 μg

Variable	Effect (μg)
Chimney rinse	+1.09
Time between sonication and filtration	+0.81
Mailing of samples	-2.4
Sonication time	-1.1
Volume of isopropanol rinse	-0.09
Amount of matrix material	+1.3
Type of asher	+0.81

Average μg: 101.4

In a further attempt to identify the source of the effect we tabulated the transmittance values (based on silver peaks) for these samples and evaluated them in the Plackett and Burman scheme (3). Again, a significant effect was found for the amount of matrix variables.

The mean and standard deviations for filters done by either the LTA or muffle furnace (from those used for the 32-filter test, not corrected for absorbance) were calculated and found to be:

Muffle furnace	100.6 ± 7.3 μg
LTA	102.8 ± 8.5 μg

These data agree with the results of the 16-filter tests (Tables 29 and 30), in that there is no significant difference from the type of asher used.

Complete XRD spectra were obtained for two of the samples, one from the muffle furnace and one from the LTA (see Figures 3 and 4). The different effects of muffle furnace or LTA can be seen by comparing the matrix component peaks. Each sample contained 1 mg of the matrix mixture before ashing.

Accuracy

It is difficult to establish the accuracy for silica because there is no accepted calibration standard proved applicable for all samples and methods. We compared the results of our XRD analyses with the results of analyses by the colorimetric method. When samples are collected from test atmospheres, we are able to obtain a group of samples containing only silica; this is easily done because the various sample components (matrix materials and silica) are loaded sequentially. When it is time to load silica, we place clean filters into the sampling chamber and remove them after the target amount of silica is loaded.

Because there are no interfering materials, the colorimetric procedure is specific for silica without preliminary treatment of the filter to remove other minerals. The silica is dissolved in hydrofluoric acid directly on the collection filter and is treated to form a blue silicomolybdate compound. To calibrate the spectrophotometer, an aliquot of bulk Min-U-Sil 5 is weighed into a Teflon® beaker and dissolved in hydrofluoric acid, after which it is brought to volume. Aliquots of this standard are run at the same time as the samples.

When compared to the colorimetric analysis, the XRD analysis overestimates the amount of silica by approximately 15%. Tabulated below, in micrograms silica, are the results of ruggedness test samples by XRD and by colorimetry (also listed are the average values before correcting for absorbance).

	XRD		
	Silica	Silica corrected for absorbance	Colorimetric
Filters for asher test	149	159	124
Filters for total test	101	112	86.3

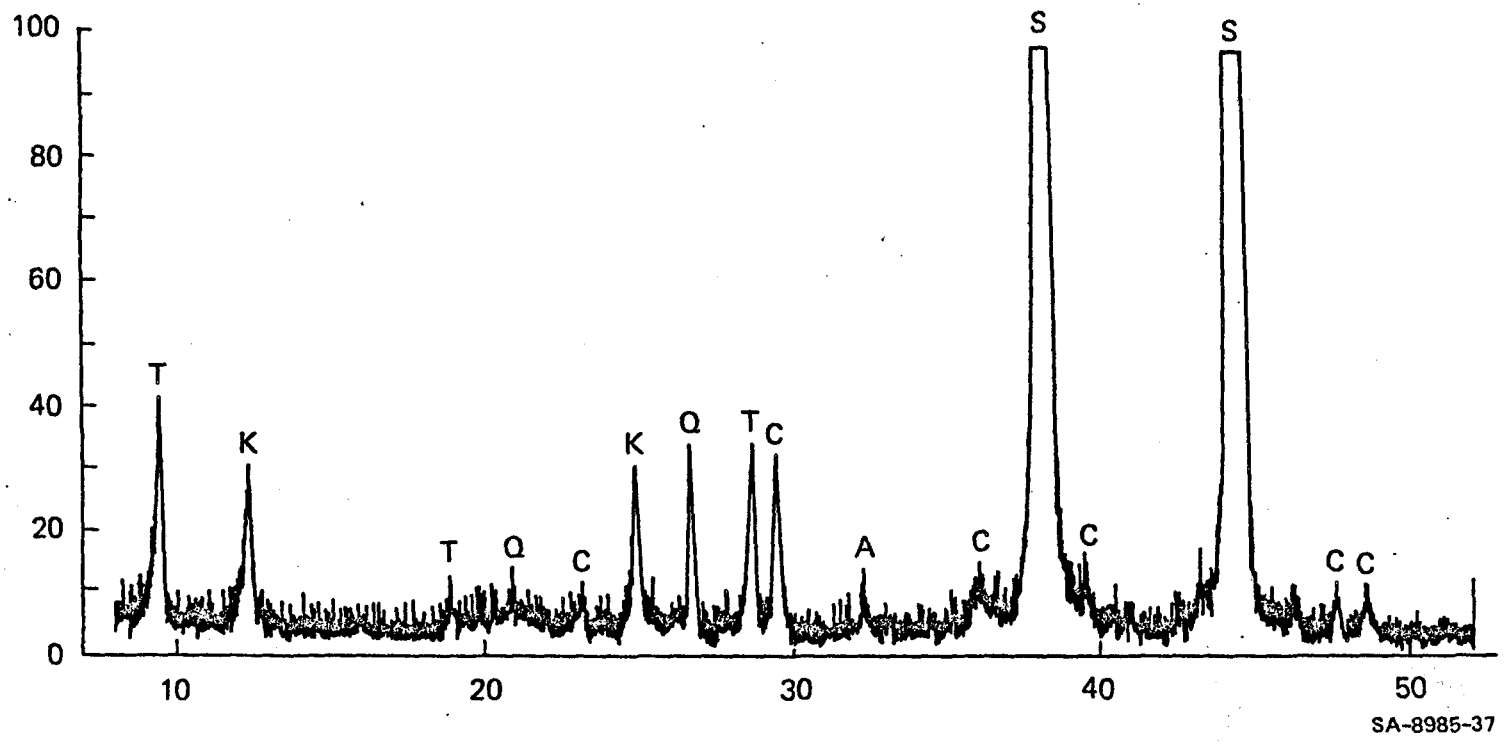


FIGURE 3 X-RAY DIFFRACTION PATTERN OF FILTER SAMPLE 28 FROM 32-FILTER DESIGN

PVC filter containing quartz, kaolinite, calcite, and talc was ashed in the LTA. Residue redeposited on solver membrane filter.

Q = Quartz; T = Talc; K = Kaolinite; C = Calcite; A = Silver chloride; S = Silver

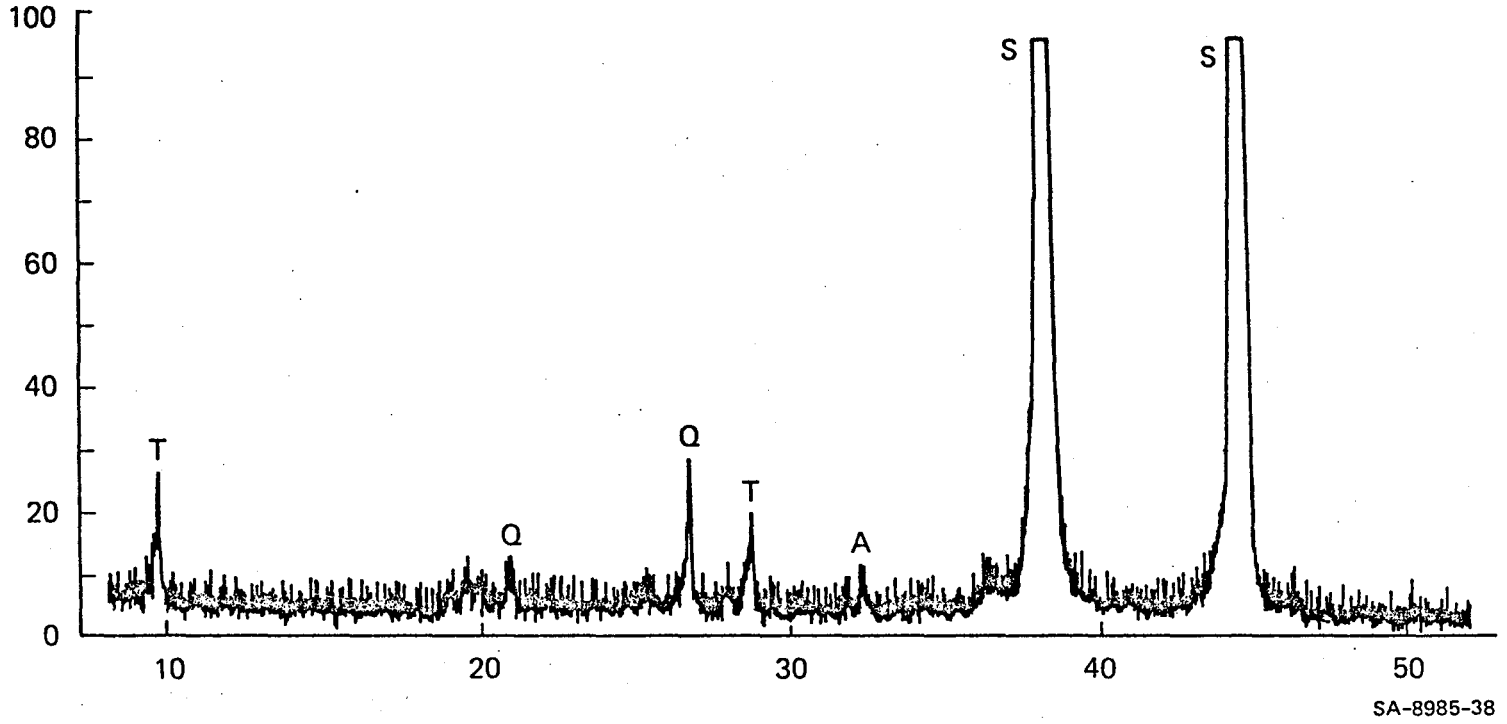


FIGURE 4 X-RAY DIFFRACTION PATTERN OF FILTER SAMPLE 11 FROM 32-FILTER DESIGN

PVC filter containing quartz, kaolinite, calcite, and talc was ashed in the muffle furnace. Residue redeposited on silver membrane filter.

Q = Quartz; T = Talc; A = Silver chloride; S = Silver

The ratio of the colorimetric to the XRD results averages 0.84 for samples not corrected for absorbance and 0.78 for those corrected. Because of the lack of agreement, it would seem that the size distributions of samples and standards are not well matched. However, this ratio is similar to those we obtain for other types of samples.

For example, SRI prepares Proficiency Analytical Testing (PAT) samples in the same manner as the filters for the ruggedness study, with two exceptions:

(1) Min-U-Sil 5, rather than Min-U-Sil 15, is used to prepare the aerosol.

(2) Samples are collected on the 0.5-μm PVC filters contained in open-faced cassettes; the sampled air stream does not pass through a cyclone.

Because we are sampling a Min-U-Sil 5 atmosphere, without a cyclone, the size distribution of the PAT samples should be very close to the distribution of the bulk material. We then have a situation where two different analytical methods (colormetric and XRD) are calibrated with the same bulk standard material, and the samples have this material in the same particle size distribution, as in the bulk. The results should agree.

For a number of PAT rounds, sets of samples were analyzed by SRI by both the colorimetric and XRD methods. Filters for colorimetric assay contain only silica and were analyzed to establish that the target level had been reached; those analyzed by XRD contain silica plus approximately 100 μg of talc. The XRD calibration curve from Min-U-Sil 5 standards, $I_q = 63.471\ w - 108$, was used. Table 33 shows the results for seven runs.

Table 33. Comparison of results for silica using colorimetric and XRD methods (PAT samples).

μg Silica Measured				
Colorimetric (n = 4)		XRD* (n = 10)		Ratio of Colorimetric to XRD
47.5	(14.1%)†	54.5	(12.6%)†	0.87
65.6	(4.1%)	82.0	(4.1%)	0.80
79.2	(2.5%)	85.0	(5.0%)	0.93
87.5	(4.8%)	99.1	(7.5%)	0.88
89.7	(2.1%)	104.7	(7.8%)	0.86
93.9	(4.0%)	101.7	(4.9%)	0.92
125.0	(3.0%)	132.4	(7.0%)	0.95

*In these analyses it is assumed that an absorbance correction is not necessary.

†Percent relative standard deviation.

We find the same discrepancy in averages for these filters. For the PAT samples the average ratio (colorimetric to XRD) is 0.88, similar to the average ratio of 0.84 (colorimetric to XRD) for the ruggedness study samples.

We have also compared results for the XRD method with those obtained by analyzing samples by IR. During the ruggedness studies of the IR method (see Section IV), XRD analysis was done on a set of samples with coal mine dust as a background matrix. There was no difference in the different method averages. Here we also used Min-U-Sil 5 to calibrate the IR spectrometer, as well as for XRD standards. The data are tabulated below. The IR procedure was performed using either a muffle furnace (MF) or a low temperature asher (LTA); thus there are two values for IR.

	Method		
	XRD	IR	
µg Silica		MF	LTA
Average	127.5	125.9	135.9
Standard deviation	10.1	20.4	12.5
n	6	12	12

When tested using a Student's t-statistic, these averages were found not to be significantly different.

We can summarize the data on accuracy by saying that, for the types of samples we have considered, the XRD method overestimates the amount of silica by about 15% when compared with the colorimetric analysis we used, but it agrees with values found by the IR method.

CONCLUSIONS AND RECOMMENDATIONS

The XRD method, PCAM 259, was demonstrated to be rugged with respect to minor procedural variations when similar samples were analyzed. The sample matrix is a statistically significant factor, however, because of the use of the correction factor. The silica amount was overestimated because of the correction factor, although the magnitude of the effect was less than 5 µg for the weakly absorbing matrix used. Further work with other matrix materials would be required before a recommendation could be made to modify the use of this absorption correction.

It was recommended that the method be distributed for a collaborative test, using the same type and amounts of matrix materials in the sample preparation.

SECTION IV

RUGGEDNESS STUDY OF THE IR METHOD

GENERAL

The objective of this study was to test the ruggedness of the method for Infrared Determination of Quartz in Respirable Coal Mine Dust (see Appendix B), in preparation for the collaborative test. This method was developed at the U.S. Bureau of Mines and is used in its laboratories as an alternative to the x-ray diffraction (XRD) method.

In the ruggedness study, the vulnerability of the measurement to small, but reasonable, modifications to the procedures is scrutinized. This provides safeguards for the collaborative study in that participating laboratories may be alerted to those steps requiring close control. If minor variations in the procedural steps are found to cause significant adverse results, changes in the procedures must be made before beginning the collaborative study. Descriptive details may be added to guide the users of the method more carefully.

We revised the method as originally written to include provisions for treating interferences from kaolinite and calcite, both of which are known to be present in many coal mine dust samples. Ruggedness testing was then done on the revised procedure.

This IR method can be summarized as follows:

- Collection of a respirable dust fraction on a polyvinyl chloride (PVC) filter.
- Destruction of the filter and other matter in the sample, using either a low-temperature plasma asher or a muffle furnace.
- Redeposition of the residue onto an IR transparent filter.
- Quantification of the silica by IR analysis.

It had been decided that the samples used in both the ruggedness and collaborative tests should resemble actual field samples as closely as possible. This is important for silica measurements because the analysis is sensitive to particle size distribution. Samples were prepared in a laboratory sample generation apparatus, and all samples were made using aerosols as a source of deposit. The 10-mm nylon cyclones were used to collect only the respirable fraction.

The initial problem was to identify those factors that may affect the analytical results and select an experimental design to efficiently determine whether any of these candidate factors, if not closely controlled, causes significant errors in the analysis. A design was chosen that permitted estimating main effects for a number of variables and gave information on interactions.

MODIFICATIONS TO THE PROCEDURE

The originally proposed method for infrared determination of crystalline silica in respirable coal mine dust was modified to include an acid wash to eliminate calcite before ashing in a muffle furnace and a correction curve to deal with kaolinite interference after low-temperature ashing. Details of the changes are described below.

Removal of Calcite

In calcite-containing samples ashed at high temperature, the absorbances by silica at 800 cm^{-1} were drastically diminished below values expected from calibration curve data; in most instances, the 800 cm^{-1} peak virtually disappeared. XRD analysis verified that silica levels had indeed been reduced after high-temperature ashing in the presence of calcite (see Figures 5 and 6).

The reaction between silica and calcite under high temperature is well documented (8) and is illustrated by the equation:

$$CaCO_3 + SiO_2 \rightleftarrows CaSiO_3 + CO_2 \qquad (12)$$

In an attempt to eliminate calcite interference, samples were washed with hydrochloric acid before high-temperature ashing. Both alcoholic and aqueous acid solutions were tested for the ability to wet the filter material and dissolve the calcite. Alcoholic solutions were able to wet the filter material, but they were not as effective as aqueous solutions in dissolving calcite; however, aqueous solutions did not wet the filter material.

It was decided that a 25% v/v solution of concentrated hydrochloric acid in distilled water would be used for the washing step and that a few milliliters of isopropyl alcohol would be added to the filter funnel during the wash to wet the filter material. The method was modified to include these steps.

Kaolinite Correction Method

Kaolinite, which is a component of coal mine dust, interferes in the IR analysis for silica because it has an absorption band (doublet) at about 800 cm^{-1}, as well as a more intense band at 915 cm^{-1}. The procedure for handling kaolinite depends on the type of asher used.

If the filter is to be ashed in a muffle furnace, no special procedures are required; however, the method is simply not usable if the kaolinite loading is too high. The problem is illustrated by the IR spectrum shown in Figure 7.

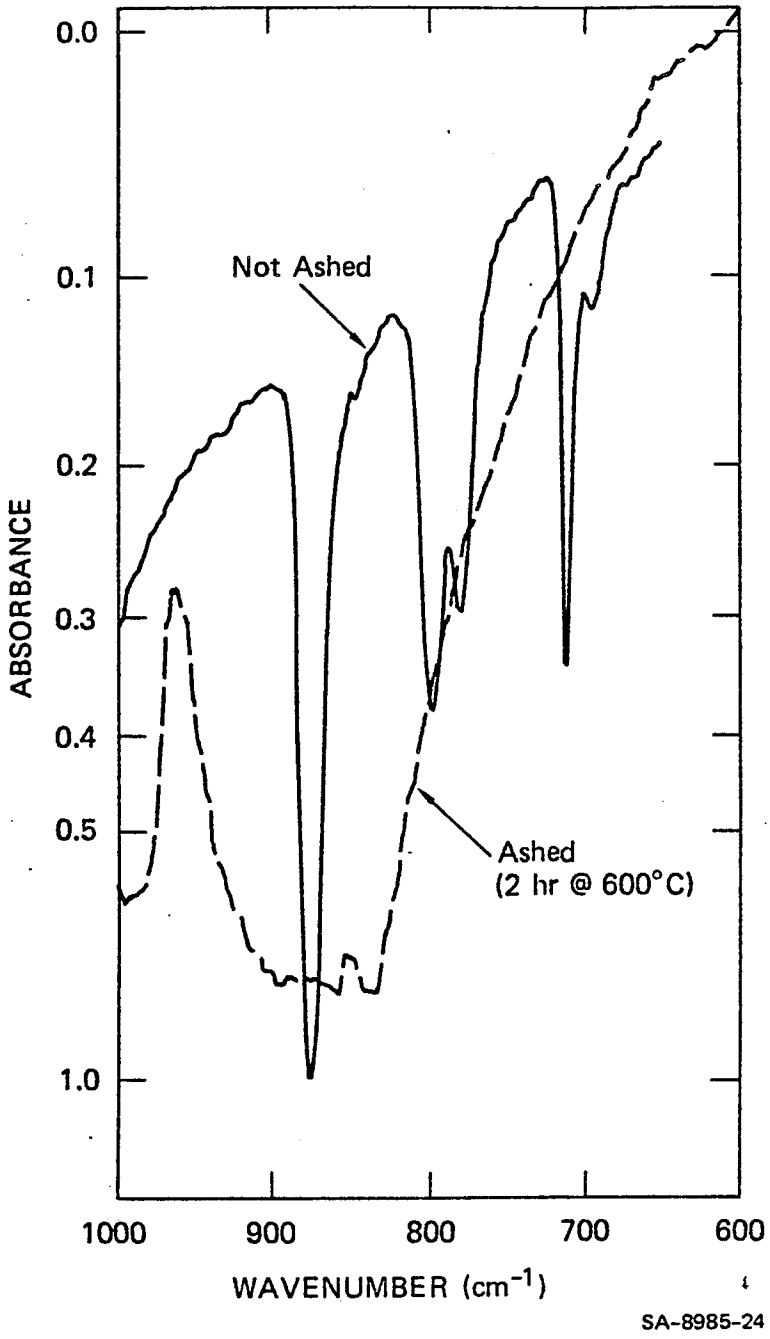


FIGURE 5 IR SPECTRA OF CALCITE/SILICA SAMPLES
(200 μg Silica and 800 μg Calcite)

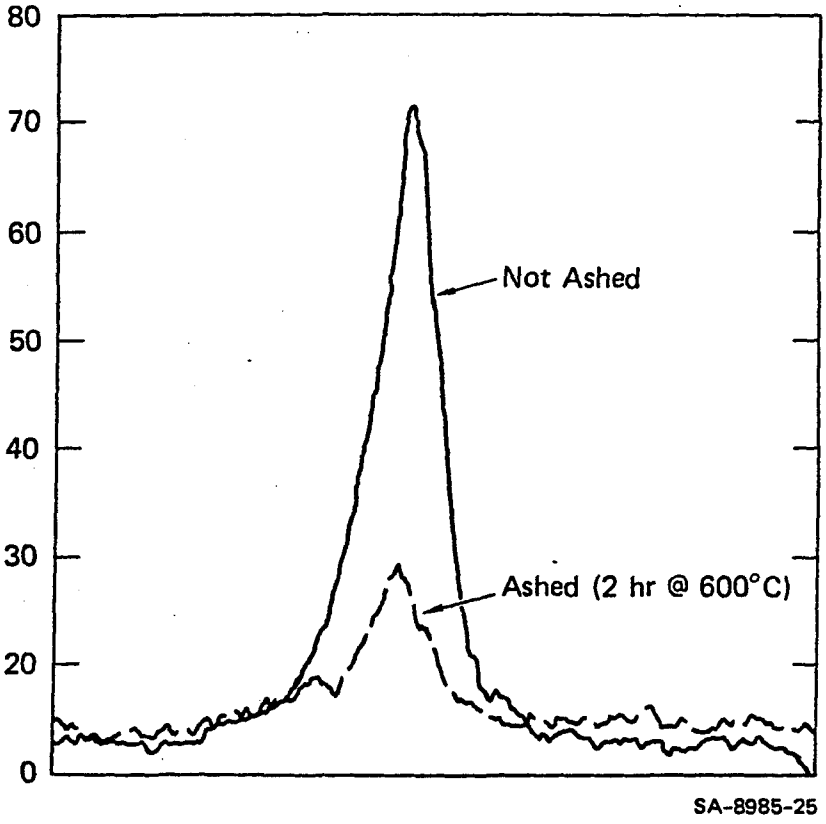


FIGURE 6 XRD SPECTRA OF CALCITE/SILICA SAMPLES
Quartz 101 peak.
(100 μg Quartz and 400 μg Calcite)

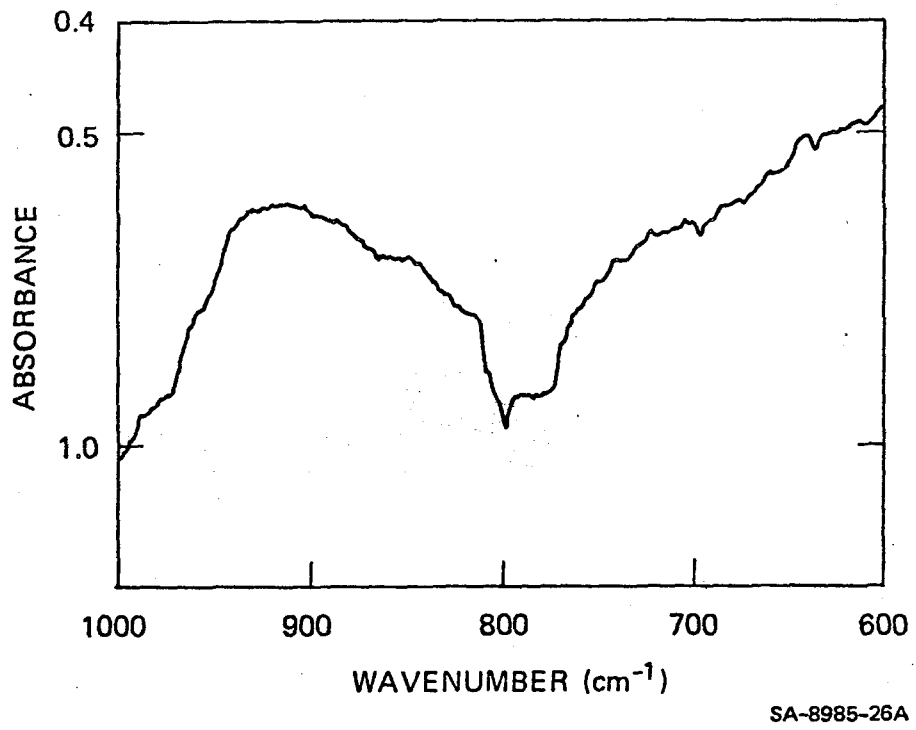


FIGURE 7 IR SPECTRUM OF A SILICA/KAOLINITE SAMPLE THAT WAS ASHED IN A MUFFLE FURNACE AT 600°C FOR 2 HOURS
(200 μg Silica and 800 μg Kaolinite)

As seen from this sample, containing 800 μg kaolinite, there is a broad absorption band in the 700 cm^{-1} to 900 cm^{-1} region, above which a poorly defined peak at 800 cm^{-1} can be seen. This broad band is due to amorphous meta-kaolin, formed when kaolinite is heated at 500° to 900°C. Since we cannot eliminate kaolinite from the samples, the problem was to determine its effect at various levels and to find how much kaolinite could be tolerated. The amount of kaolinite was included as a variable in the ruggedness test.

When using an LTA, some means must be taken to compensate for the kaolinite. When the filter is ashed at low temperatures, kaolinite (like silica) does not change its crystalline form; the spectrum before and after ashing is the same. An IR spectrum of a kaolinite standard (400 μg) ashed at low temperature is shown in Figure 8, from which we can observe the 800 cm^{-1} band as well as the more intense peak at 915 cm^{-1}. Next, in Figure 9, the spectrum of a mixture of silica and kaolinite is displayed, and it is seen that the kaolinite peak coincides with the silica peak at 800 cm^{-1} whose intensity we want to measure. The remedy for this situation was to determine the amount of kaolinite, using the 915 cm^{-1} band, and then subtract out the absorbance due to kaolinite at 800 cm^{-1}.

To derive the best correction curve, we analyzed a number of kaolinite standards. Unlike for silica, no precise relationship could be found between kaolinite mass and absorption at either 915 cm^{-1} or 800 cm^{-1} as can be seen by the scatter in the points in Figures 10 and 11. A better correction curve was

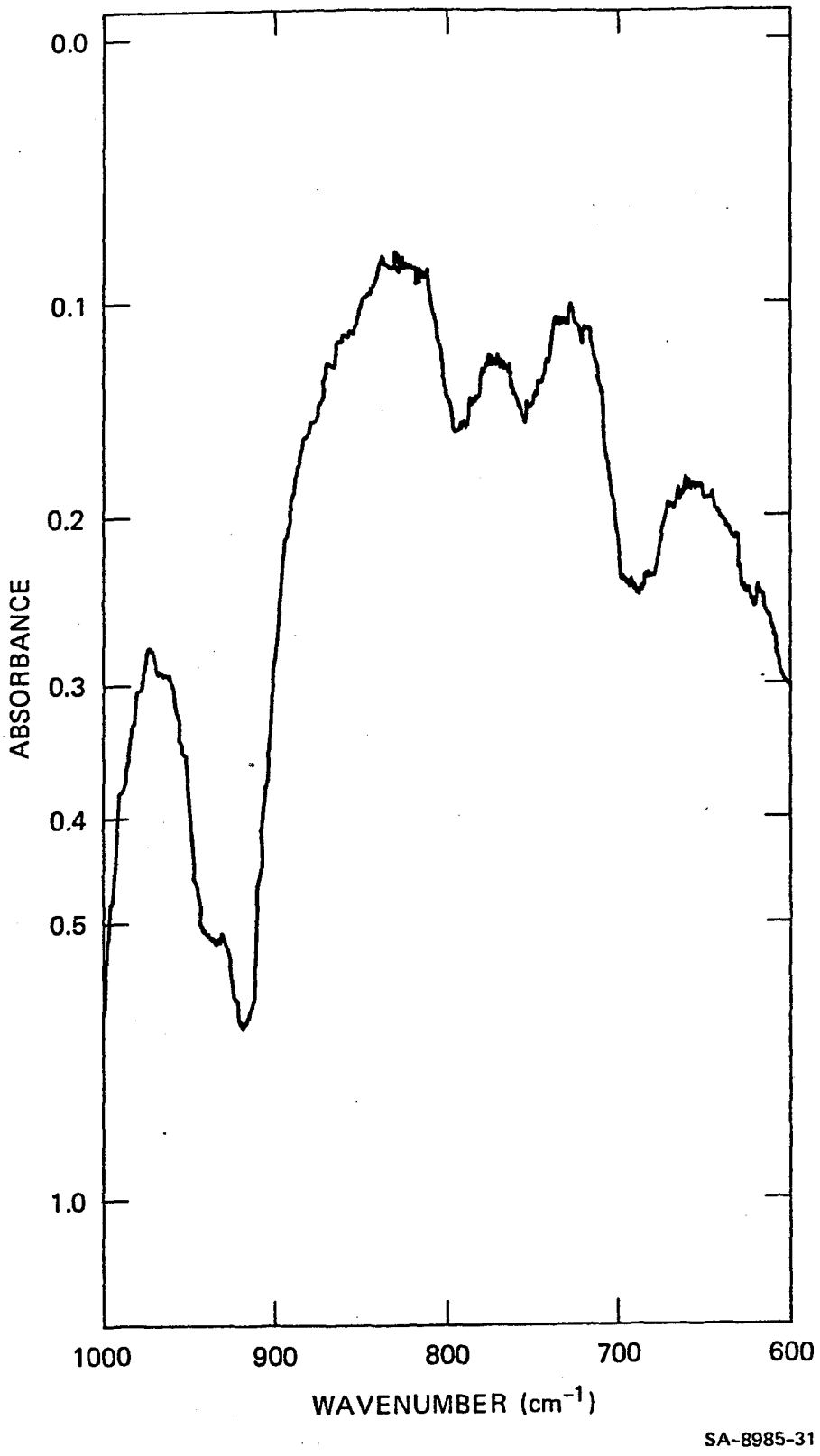


FIGURE 8 IR SPECTRUM OF KAOLINITE STANDARD (400 μg) ASHED IN A LOW TEMPERATURE ASHER

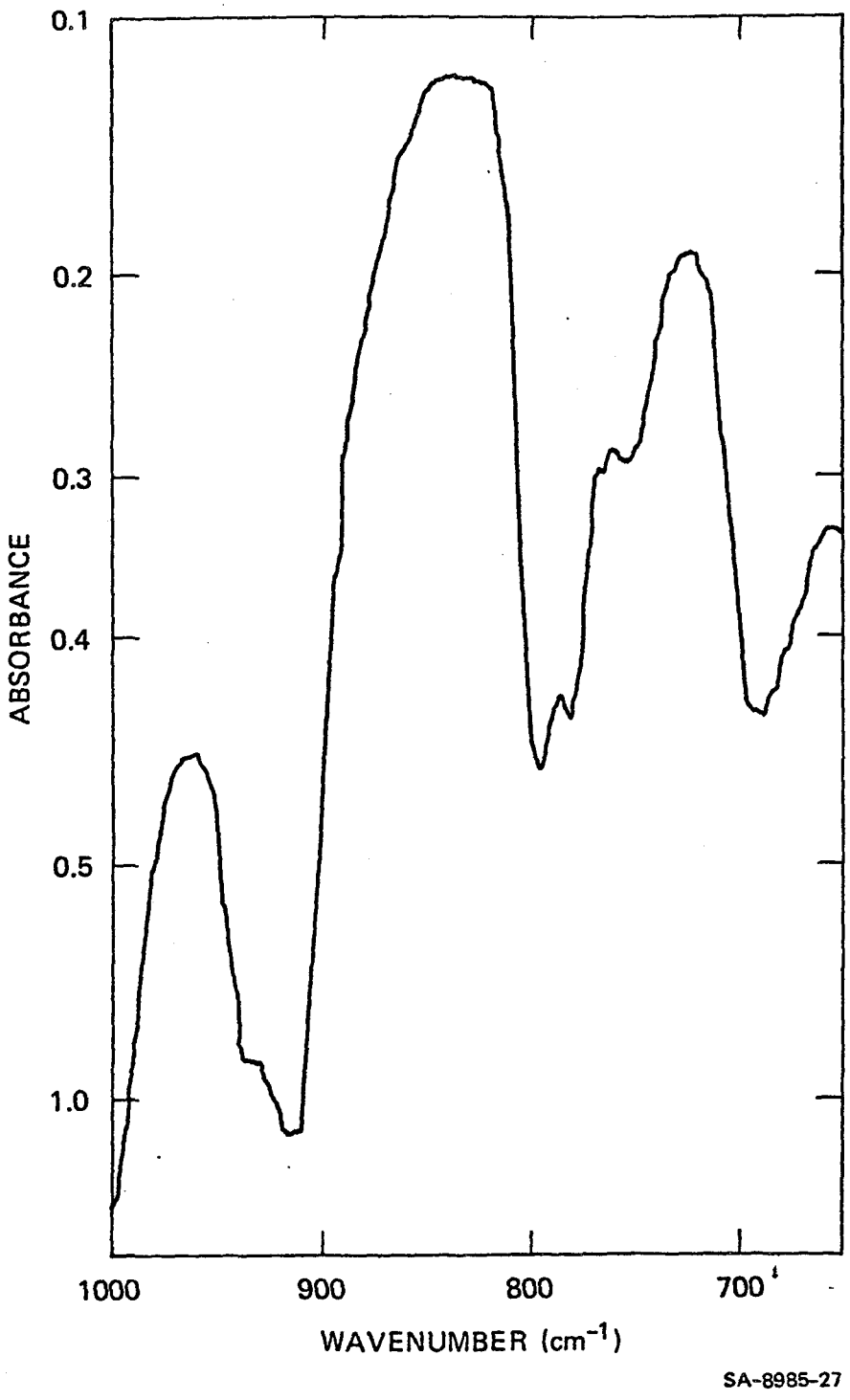


FIGURE 9 IR SPECTRUM OF A SILICA/KAOLINITE SAMPLE THAT WAS ASHED IN A LOW TEMPERATURE ASHER

(200 μg Silica and 800 μg Kaolinite)

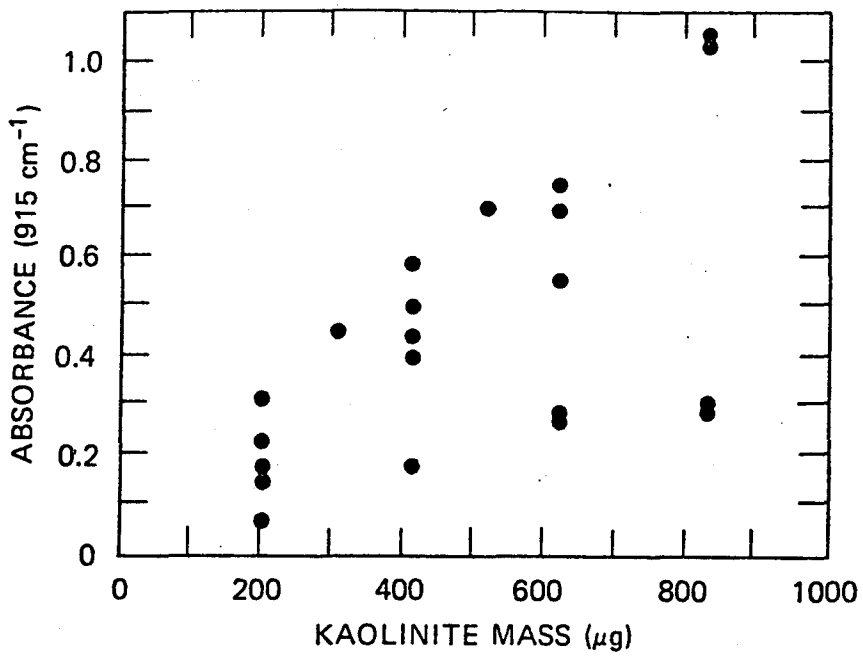


FIGURE 10 KAOLINITE ABSORBANCE AT 915 cm^{-1} VERSUS MASS

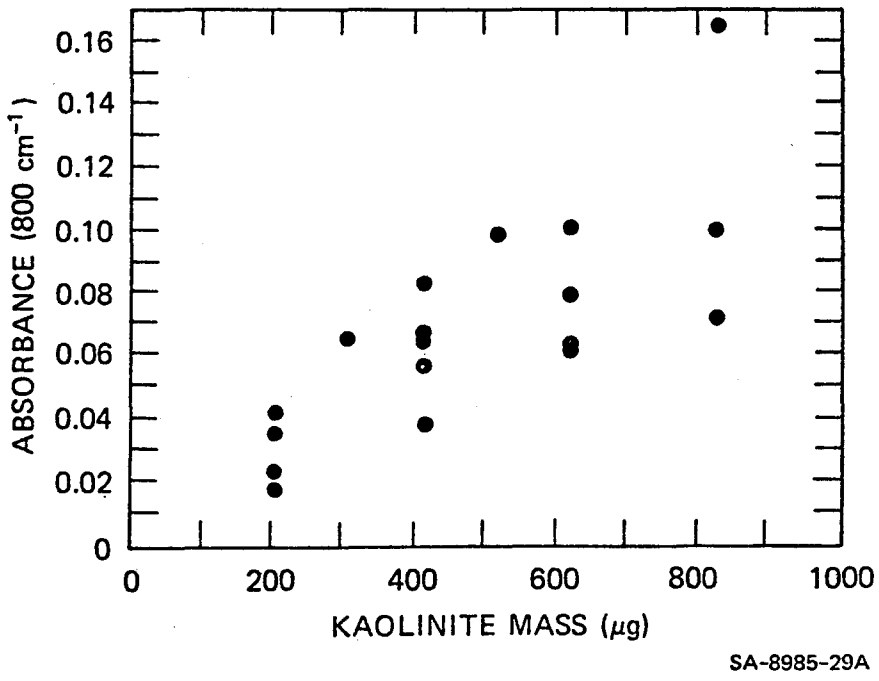


FIGURE 11 KAOLINITE ABSORBANCE AT 800 cm^{-1} VERSUS MASS

obtained by plotting absorption at 915 cm^{-1} versus absorption at 800 cm^{-1} (Figure 12). Although this curve is satisfactory, there is a good deal of scatter in the data, due undoubtedly to the difficulty of drawing an appropriate baseline under the 915 cm^{-1} peak, which protrudes from a sharply sloping baseline. Even though the correction curve is not well defined, the effect is not too severe if we do not try to measure a small amount of silica in the presence of a high loading of kaolinite. For example, 200 µg of kaolinite will contribute an 0.034 absorbance unit to the 800 cm^{-1} peak. This same absorbance would be seen for only about 20 µg of silica. An error as high as 50% in this kaolinite determination would cause only 10 µg error in the silica amount, which may be tolerated for high but not low loadings of silica.

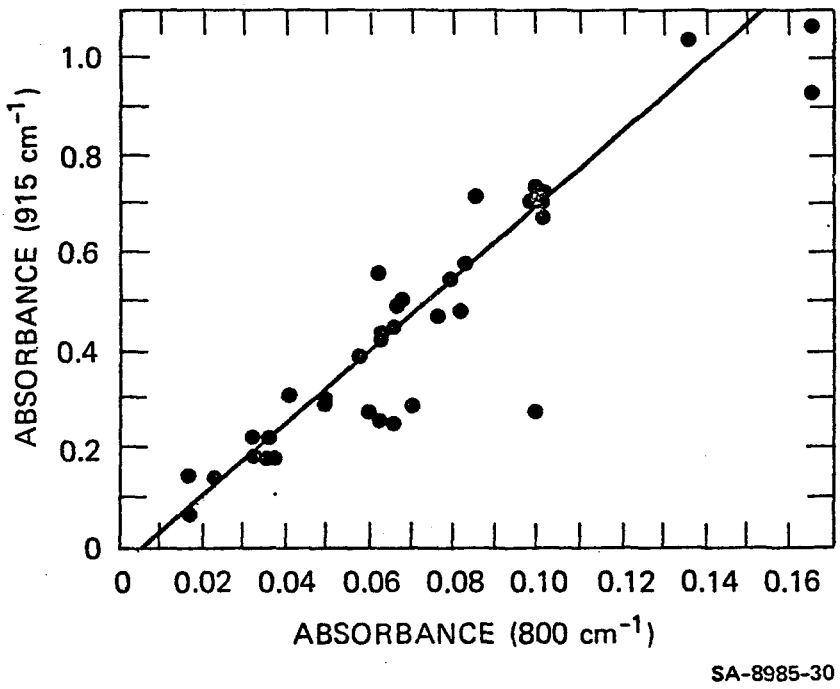


FIGURE 12 RELATIONSHIP OF ABSORBANCE AT 915 cm^{-1} TO ABSORBANCE AT 800 cm^{-1} FOR KAOLINITE STANDARDS

TEST DESIGN

The statistical design for the ruggedness tests followed the procedures described by Youden and Steiner (2), but with a larger number of filters as given by Plackett and Burman (3). The basic idea is not to study one variation at a time, but to introduce a number of procedural modifications all at once, using a design that permits detection of individual effects, as discussed in Section III.

The procedure assumes that the factors to be considered can be set at either of two levels: (1) the plausible range of laboratory exactitude, which allows two conditions to be set, or (2) dichotomous conditions of a factor, which allow for yes/no procedural alternatives. The condition used for any one filter can be treated as a plus or minus one, corresponding to two values or to a yes/no condition for each factor.

The IR analytical method directs the user to ash the filter sample, using either a low-temperature plasma asher or a muffle furnace. If such a choice between low-temperature asher and muffle furnace is considered, the design is applicable only if all the other factors make sense for both. However, as previously described, the original IR method of analysis was unsatisfactory because of interference from calcite and kaolinite, and as a result the method was modified so that different procedural steps were performed depending on the ashing technique used. Therefore, some of the factors associated with the use of one ashing method are unique to that method and irrelevant for the other. The remedy for this problem was to apply the Youden procedure separately to the low-temperature asher and muffle furnace in designs using 12 filters. This allows a determination of which, if any, of the factors peculiar to each ashing procedure result in a significant effect.

The 12-filter designs were applied at each of two silica levels. The designs used could accommodate up to 11 factors. Six of these were dummy factors and so were not varied in the procedure. The dummy factors were used to calculate the standard deviation, estimate the minimum significant effect, and calculate the power of the test. Designs using 12 filters were chosen to permit collection of enough samples in one run for both the low-temperature asher and muffle furnace tests. The original plan called for an additional ruggedness test using the muffle furnace or low-temperature asher as a factor, and a set of eight samples were reserved. This test was not required, however, because results from the 12-filter tests were adequate for comparing the two ashing techniques.

SELECTION OF FACTORS

The factors associated with the low-temperature asher and the muffle furnace are listed in Tables 34 and 35. The tables also show two conditions designated "+" or "-", and column assignments selected for each conditions. The choice of "+" or "-" does not mean that one condition is higher or more positive, but only distinguishes the two.

Table 34. Factors associated with the use of the low-temperture asher.

Factor	(+)	(-)	Column Assignment*
Amount of calcite in sample†	0	600 µg	X_1
Radio frequency generator power (wattage)	200 W	300 W	X_2
Ashing time	1-3/4 hr	3 hr	X_3
Amount of kaolinite in sample†	100 µg	600 µg	X_4
Kaolinite correction factor‡	Use ratio of peaks at 800 to 915 cm^{-1}	Use calibration curves	X_5

*See section entitled Treatment of Data.
†See section entitled Generation of Filter Samples for exact sample loadings.
‡See section entitled Kaolinite Correction Method for discussion.

Table 35. Factors associated with the use of the muffle furnace.

Factor	(+)	(-)	Column Assignment*
Amount of calcite in sample†	0	600 µg	X_1
Ashing time	1-3/4 hr	3 hr	X_2
Ashing temperature	500°C	700°C	X_3
Amount of kaolinite in sample†	100 µg	600 µg	X_4
Acid wash before ashing‡	25% v/v conc. HCl in H_2O	1% v/v conc. HCl in H_2O	X_5

*See section entitled Treatment of Data.
†See section entitled Generation of Filter Samples for exact sample loadings.
‡See section entitled Modifications to the Procedure for discussion.

The amount of calcite or kaolinite used as the "-" value was based on sample loadings of field samples. A loading of 600 µg of kaolinite is close to the upper limit that would permit measurement of silica, since with higher amounts there would be too high a background even on the ashed sample. The "+" value of kaolinite was the lowest amount obtainable because of the presence of kaolinite in coal mine dust used.

EXPERIMENTAL PROCEDURES

Equipment

The following equipment was used in the experiments:

Muffle furnace: Model M15A from Blue M Electric Company, Blue Island, IL.

Low-temperature asher (LTA); Plasma System IPC 1003B, from International Plasma Corporation, Hayward, CA. It contains two 3-inch-diameter by 6-inch-long cylindrical chambers, with a total capacity for six 50-mL beakers. Radio frequency generator power range 0-300 watts.

Ultrasonic bath: Model DR 50 AH from Acoustica Associates, Inc., Los Angeles, CA. Tank size is approximately one gallon.

IR spectrophotometer: Perkin-Elmer Model 457 dual-beam scanning infrared spectrophotometer, equipped with SRI-fabricated magnetic sample holders.

X-ray diffraction system: Phillips x-ray diffractometer, 1800-watt high-intensity x-ray tube; Bicron scintillation detector; Canberra data system.

Generation facility: System built at SRI for use in the Proficiency Analytical Testing (PAT) program and modified to provide for collection of multiple samples either at 1.7 or 2 L/min, using 10-mm nylon cyclones to remove nonrespirable aerosol (see Section VI).

Materials

Silica--
The silica materials used were standard Min-U-Sil materials obtained from PSG Floridin, a subsidary of ITT. Selected physical properties are described in Section V. Min-U-Sil 5 was used as the standard silica material for the preparation of calibration curves. Min-U-Sil 15 was used to prepare aerosols for the preparation of samples.

Kaolinite--
This Georgia Kaolin product, sold under the name Hydrite UF, was used to prepare both the ruggedness samples and the calibration curves. The median particle size, as reported by the manufacturer, was 0.2 μm. The purity of this material was confirmed by comparing the XRD pattern with the XRD pattern of the kaolinite sample obtained from the Source Clay Materials Repository, University of Missouri, and with JCPDS values.

Calcite--
The calcite material used was Microwhite 25. As reported by the supplier, Harrison and Crossfield, the particle size range of the material was 0.5 to 15 μm, with a mean particle size of 3 μm. The purity of the material was confirmed by comparing its XRD pattern with that reported by the JCPDS.

Coal Mine Dust--
The coal mine dust used for the preparation of the ruggedness studies was obtained from the U.S. Department of Interior, Bureau of Mines. This material was Pittsburgh Seam Coal with a reported particle size of -200 mesh. The material contained both kaolinite and silica, the latter at a level of <2% by weight.

Filters--
The filters used for sample collection were 5-μm PVC filters obtained from Millipore. The filters used for redeposition of the ashed samples were Gelman Instrument Company DM-450 series filters, with a reported pore size of 0.45 μm.

Generation of Filter Samples

Two separate sample generation runs were required. Silica aerosols were prepared using Min-U-Sil 15. The sample collection rate through 10-mm nylon cyclones onto 5-μm PVC filters was 2.0 L/min.

Sample generation consisted of preparing two sets of 12-trial runs for each ashing method. Set I of filter samples contained a silica loading of approximately 94 μg, and Set II contained a silica loading of 148 μg. (We planned to use approximately 40 μg and 150 μg of silica for these two loadings, but were unable to achieve the lower loading because the amount of silica deposited with the coal mine dust was considerably higher than 40 μg; silica levels were estimated by IR analysis of filter samples containing only coal mine dust and supplementary silica.) Several 8-trial run filter samples were also prepared at both the low and high silica levels. A number of additional filters were used to estimate loadings of the generated materials.

The filter samples were prepared along the following guidelines:

Step 1--Generation of Coal Mine Dust. The coal mine dust was generated until the target level of 2 mg was deposited. Mass determinations of desiccated PVC filters were used to estimate coal mine dust loadings. The amounts of coal mine dust deposited for Generation Sets I and II were 1.53 and 2.03 mg, respectively.

Step 2--IR Analysis. Two filters were removed from the generation system for silica analysis by IR. On the basis of these analyses, additional silica was generated, if necessary, to reach the desired loadings.

Step 3--Generation of Supplementary Silica. It was necessary to supplement only Generation Set II with additional silica. Additional silica was generated until the target level was reached. Silica levels were estimated by IR analysis of filter samples containing only the silica and by

IR analysis of filter samples containing coal mine dust and the supplementary silica.

Step 4--Generation of Calcite. The appropriate filters were mounted in the generation facility, and calcite was generated until the desired level was reached. Mass determinations of desiccated PVC filters were used to estimate calcite loadings.

Step 5--Generation of Kaolinite. The coal mine dust used in this study was also contaminated with kaolinite. It was determined by IR analysis of a generated coal mine dust sample that the lower amount of kaolinite to be used in the ruggedness test was present in the sample. For this reason, it was necessary to deposit additional kaolinite onto only those samples that required the higher amount of the kaolinite level. Mass determinations of desiccated PVC filters and IR analysis of generated coal mine dust were used to estimate kaolinite sample loadings.

Step 6--Analysis of Samples. The samples were removed from the aerosol generation facility for analysis.

The amounts of calcite and kaolinite generated for the "+" and "-" values for both generation sets are listed below. The kaolinite levels shown are estimates only because the coal mine dust is contaminated with kaolinite and its contribution to the level generated is not accurately known.

	Kaolinite	Calcite
Generation Set I, low silica		
"+" condition, µg	100	0
"-" condition, µg	563	480
Generation Set II, high silica		
"+" condition, µg	115	0
"-" condition, µg	603	504

The fraction of matrix material penetrating the 10-mm nylon cyclones was determined by collecting filter samples with no cyclone in place and comparing them with samples collected with a cyclone present. The fractions of material penetrating the cyclones are as follows:

Coal mine dust	28%
Kaolinite	91%
Calcite	46%

IR Procedure

Analysis was done by the steps in the IR method, with the procedures under scrutiny being adjusted according to the design used. Silica calibration standards were prepared from suspensions of Min-U-Sil 5. Suspensions were deposited directly onto 47-mm DM-450 filter halves through a 10-mm chimney and

allowed to air dry before IR analysis. The IR spectrophotometer was calibrated each time samples were analyzed. A standard curve of absorbance at 800 cm^{-1} versus micrograms of silica was constructed for the range of 27 to 122 μg from IR data gathered on the day of analysis of ruggedness test samples. This curve, shown in Figure 13, can be described by the equation:

$$AU(800) = 0.00138\ (\mu g\ silica) + 0.0048 \qquad (13)$$

Kaolinite standards were prepared from suspensions of respirable-sized Georgia kaolinite. Suspensions were deposited onto 0.5-μm PVC filters through a 16-mm chimney; then the filters were ashed in a low-temperature asher at 300 watts for 2 hours. Residual ash samples were resuspended into about 10 mL each of isopropyl alcohol by sonicating for 10 minutes; suspensions were then redeposited through a 10-mm chimney onto one-half of the 47-mm DM-450 filter. (The second half is reserved to use in the reference beam of the spectrometer.) Filters were allowed to air dry before IR analysis. Several lots of standard filters were prepared and analyzed over a period of one month, and the data were pooled. A representative set of four standard filters was analyzed on the same day as the ruggedness test samples.

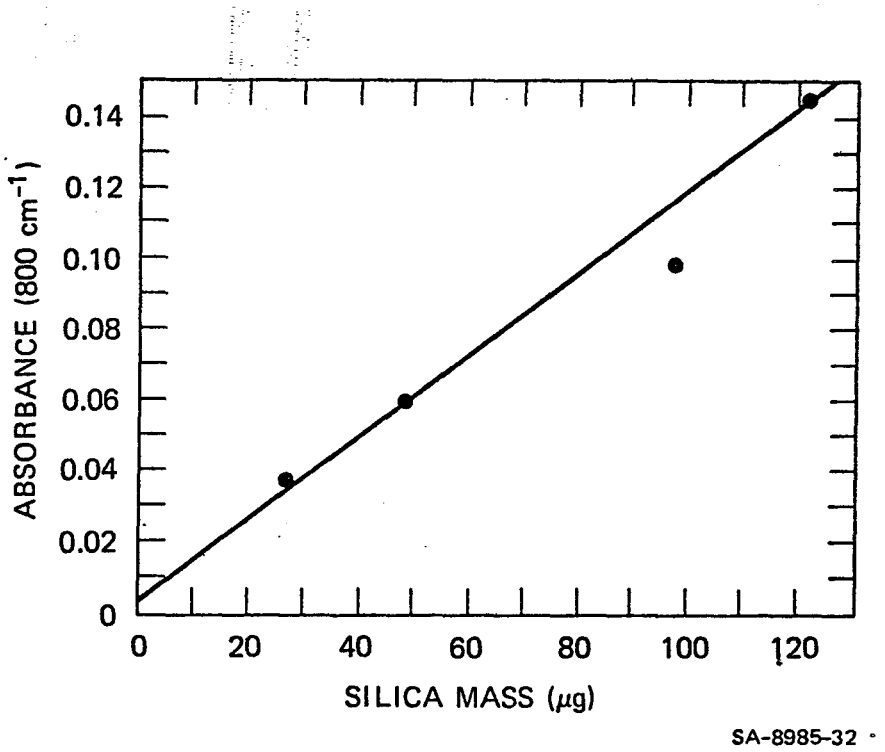


FIGURE 13 SILICA CALIBRATION CURVE

Standard curves were constructed from pooled data for absorbance at 915 cm^{-1} versus micrograms of kaolinite, absorbance at 800 cm^{-1} versus micrograms of kaolinite, and absorbance at 915 cm^{-1} versus absorbance at 800 cm^{-1}, for the range of 200 to 1000 μg of kaolinite. After removal of some of the lower points, the standard curves derived from the data collected over several weeks are described by the following equations:

$$AU(915) = 0.0012927\ (\mu g\ kaolinite) - 0.0325 \quad (14)$$

$$AU(800) = 0.000165\ (\mu g\ kaolinite) \quad (15)$$

$$AU(915) = 7.41\ [AU(800)] - 0.035 \quad (16)$$

Four kaolinite standards and a blank were analyzed on the same day as the ruggedness test samples, and a curve of absorbance at 915 cm^{-1} versus absorbance at 800 cm^{-1} was constructed. This curve can be described by the equation:

$$AU(915) = 7.17\ [AU(800)] - 0.045, \quad (17)$$

which agrees closely with the corresponding curve above, generated from pooled data.

Ruggedness test samples were prepared for analysis in the following manner. Dust deposits on 5-μm PVC filters were either washed with a hydrochloric acid solution, placed in porcelain crucibles, and ashed at high temperature in a muffle furnace, or they were placed in 50-mL glass beakers (without acid wash) and ashed in a low temperature asher. Residual ash samples were resuspended in about 10 mL each of isopropyl alcohol by sonicating for 10 minutes. These suspensions were then redeposited through a 10-mm chimney onto 47-mm DM-450 filter halves. Filters were allowed to air dry before IR analysis.

TREATMENT OF DATA

Computation of Main Effects

The 12-filter matrix designs used and the results obtained are shown in Tables 36 to 39. Tables 36 and 37 show those results from the use of the LTA at low and high silica levels, and Tables 38 and 39 show the results with the muffle furnace at the low and high levels of silica.

When the "-" of the kaolinite correction method was used, it was not possible to estimate the kaolinite background contribution to the silica peak with any degree of accuracy because of the large amount of scatter in the data. For this reason, the low temperature plasma asher data were reevaluated, using only one kaolinite correction method (the ratio method described in the section entitled Kaolinite Correction Method). These data are given in Tables 40 and 41.

Table 36. Matrix elements and results for the 12-filter ruggedness test of the low-temperature asher at low silica levels.

Filter	X_1*	X_2*	X_3*	X_4*	X_5*	X_6	X_7	X_8	X_9	X_{10}	X_{11}	Y_i
1	+	+	-	+	+	+	-	-	-	+	-	75
2	+	-	+	+	+	-	-	-	+	-	+	80
3	-	+	+	+	-	-	-	+	-	+	+	91
4	+	+	+	-	-	-	+	-	+	+	-	91
5	+	+	-	-	-	+	-	+	+	-	+	76
6	+	-	-	-	+	-	+	+	-	+	+	81
7	-	-	-	+	-	+	+	-	+	+	+	84
8	-	-	+	-	+	+	-	+	+	+	-	82
9	-	+	-	+	+	-	+	+	+	-	-	82
10	+	-	+	+	-	+	+	+	-	-	-	95
11	-	+	+	-	+	+	+	-	-	-	+	100
12	-	-	-	-	-	-	-	-	-	-	-	101
δ_j =	-3.5	-0.7	3.3	-2.0	-3.2	-1.2	2.3	-2.0	-4.0	-2.5	-1.2	86.5 (Avg.)

$s = 8.3$

$\delta_{min} = 5.9$ at the 95% confidence limit

*X_1 = Amount of calcite

X_2 = Radio frequency generator wattage

X_3 = Ashing time

X_4 = Amount of kaolinite

X_5 = Kaolinite correction method

Table 37. Matrix elements and results for the 12-filter ruggedness test of the low-temperature asher at high silica levels.

Filter	X_1*	X_2*	X_3*	X_4*	X_5*	X_6	X_7	X_8	X_9	X_{10}	X_{11}	Y_i
1	+	+	-	+	+	+	-	-	-	+	-	137
2	+	-	+	+	+	-	-	-	+	-	+	155
3	-	+	+	+	-	-	-	+	-	+	+	123
4	+	+	+	-	-	-	+	-	+	+	-	127
5	+	+	-	-	-	+	-	+	+	-	+	152
6	+	-	-	-	+	-	+	+	-	+	+	131
7	-	-	-	+	-	+	+	-	+	+	+	146
8	-	-	+	-	+	+	-	+	+	+	-	112
9	-	+	-	+	+	-	+	+	+	-	-	136
10	+	-	+	+	-	+	+	+	-	-	-	129
11	-	+	+	-	+	+	+	-	-	-	+	137
12	-	-	-	-	-	-	-	-	-	-	-	146
δ_j =	2.6	-0.6	-5.4	1.8	-1.3	-0.4	-1.6	-5.4	2.1	-6.6	4.8	135.9 (Avg.)

s = 14.3

δ_{min} = 10.1 at the 95% confidence limit

*X_1 = Amount of calcite

X_2 = Radio frequency generator wattage

X_3 = Ashing time

X_4 = Amount of kaolinite

X_5 = Kaolinite correction method.

Table 38. Matrix elements and results for the 12-filter ruggedness test of the muffle furnace at low silica levels.

Filter	X_1*	X_2*	X_3*	X_4*	X_5*	X_6	X_7	X_8	X_9	X_{10}	X_{11}	Y_i
1	+	+	-	+	+	+	-	-	-	+	-	55
2	+	-	+	+	+	-	-	-	+	-	+	63
3	-	+	+	+	-	-	-	+	-	+	+	81
4	+	+	+	-	-	-	+	-	+	+	-	65
5	+	+	-	-	-	+	-	+	+	-	+	85
6	+	-	-	-	+	-	+	+	-	+	+	56
7	-	-	-	+	-	+	+	-	+	+	+	52
8	-	-	+	-	+	+	-	+	+	+	-	70
9	-	+	-	+	+	-	+	+	+	-	-	81
10	+	-	+	+	-	+	+	+	-	-	-	72
11	-	+	+	-	+	+	+	-	-	-	+	110
12	-	-	-	-	-	-	-	-	-	-	-	98
δ_j =	-8.0	5.5	2.8	-6.7	-1.5	0	-1.3	0.2	-4.7	-10.8	0.5	74.0 (Avg.)

$s = 16.8$

$\delta_{min} = 11.9$ at the 95% confidence limit

*X_1 = Amount of calcite

X_2 = Ashing time

X_3 = Ashing temperature

X_4 = Amount of kaolinite

X_5 = Acid wash of sample.

Table 39. Matrix elements and results for the 12-filter ruggedness test of the muffle furnace at high silica levels.

Filter	X_1*	X_2*	X_3*	X_4*	X_5*	X_6	X_7	X_8	X_9	X_{10}	X_{11}	Y_i
1	+	+	-	+	+	+	-	-	-	+	-	130
2	+	-	+	+	+	-	-	-	+	-	+	120
3	-	+	+	+	-	-	-	+	-	+	+	131
4	+	+	+	-	-	-	+	-	+	+	-	158
5	+	+	-	-	-	+	-	+	+	-	+	98
6	+	-	-	-	+	-	+	+	-	+	+	95
7	-	-	-	+	-	+	+	-	+	+	+	101
8	-	-	+	-	+	+	-	+	+	+	-	119
9	-	+	-	+	+	-	+	+	+	-	-	154
10	+	-	+	+	-	+	+	+	-	-	-	132
11	-	+	+	-	+	+	+	-	-	-	+	134
12	-	-	-	-	-	-	-	-	-	-	-	139
δ_j =	-3.8	8.3	6.4	2.1	-0.6	-6.9	3.1	-4.4	-0.9	-3.6	-12.8	125.9 (Avg.)

s = 22.5

δ_{min} = 15.9 at the 95% confidence limit

*X_1 = Amount of calcite

X_2 = Ashing time

X_3 = Ashing temperature

X_4 = Amount of kaolinite

X_5 = Acid wash of sample.

Table 40. Matrix elements and results for the 12-filter ruggedness test of the low-temperature asher at low silica levels using only one kaolinite correction method.

Filter	X_1*	X_2*	X_3*	X_4*	X_5	X_6	X_7	X_8	X_9	X_{10}	X_{11}	Y_i
1	+	+	-	+	+	+	-	-	-	+	-	75
2	+	-	+	+	+	-	-	-	+	-	+	80
3	-	+	+	+	-	-	-	+	-	+	+	89
4	+	+	+	-	-	-	+	-	+	+	-	84
5	+	+	-	-	-	+	-	+	+	-	+	69
6	+	-	-	-	+	-	+	+	-	+	+	81
7	-	-	-	+	-	+	+	-	+	+	+	82
8	-	-	+	-	+	+	-	+	+	+	-	82
9	-	+	-	+	+	-	+	+	+	-	-	82
10	+	-	+	+	-	+	+	+	-	-	-	93
11	-	+	+	-	+	+	+	-	-	-	+	100
12	-	-	-	-	-	-	-	-	-	-	-	94
δ_j =	-3.9	-1.1	3.8	-0.8	-0.9	-0.8	2.8	-1.6	-4.4	-2.1	-0.8	84.3 (Avg.)

$s = 7.8$

$\delta_{min} = 5.3$ at the 95% confidence limit

*X_1 = Amount of calcite

X_2 = Radio frequency generator wattage

X_3 = Ashing time

X_4 = Amount of kaolinite.

Table 41. Matrix elements and results for the 12-filter ruggedness test of the low-temperature asher at high silica levels using only one kaolinite correction method.

Filter	X_1*	X_2*	X_3*	X_4*	X_5	X_6	X_7	X_8	X_9	X_{10}	X_{11}	Y_i
1	+	+	-	+	+	+	-	-	-	+	-	138
2	+	-	+	+	+	-	-	-	+	-	+	155
3	-	+	+	+	-	-	-	+	-	+	+	122
4	+	+	+	-	-	-	+	-	+	+	-	120
5	+	+	-	-	-	+	-	+	+	-	+	145
6	+	-	-	-	+	-	+	+	-	+	+	133
7	-	-	-	+	-	+	+	-	+	+	+	145
8	-	-	+	-	+	+	-	+	+	+	-	114
9	-	+	-	+	+	-	+	+	+	-	-	138
10	+	-	+	+	-	+	+	+	-	-	-	128
11	-	+	+	-	+	+	+	-	-	-	+	140
12	-	-	-	-	-	-	-	-	-	-	-	138
δ_j =	1.8	-0.8	-4.8	3.0	1.7	0.3	-0.7	-4.7	1.5	-6.0	5.3	134.7 (Avg.)

$s = 12$

δ_{min} = 8.4 at the 95% confidence limit

*X_1 = Amount of calcite

X_2 = Radio frequency generator wattage

X_3 = Ashing time

X_4 = Amount of kaolinite.

In all six tables, the elements in each row indicate whether the "+" or "-" value of the factor was applied in the treatment of the filter used for that row. The columns are identified as X_1, X_2, X_3, etc. Eleven columns are available for assignment of factors. The columns indicated by an asterisk were assigned to real factors, as shown in notes to the table. All the remaining unassigned columns were used to estimate the standard deviation, the minimum significant effect, and the power of the test. The last column, Y_i, is a tabulation of the responses, in μg of silica, for the filter used.

To conduct the experiments, the analyst referred to the design columns for direction. Filter 1 in Table 36, for instance, had the "+" values of both calcite and kaolinite as directed by columns X_1 and X_4. When this filter was analyzed, the "+" setting of the radiofrequency generator wattage was applied (column X_2), the "-" values for the ashing time (column X_3), and the "+" condition for correcting for kaolinite (column X_5) were used. The other columns are "dummy" variables and were ignored during the filter analysis. The amount of silica for that filter (75 μg) is recorded in the last column. Each of the other 15 filters was then treated according to its respective column assignments.

The main effect for each factor was calculated as

$$\delta_j = \frac{\sum^{+} Y_i - \sum^{-} Y_i}{N} \qquad (18)$$

where:

δ_j = main effect (μg silica) associated with the variable assigned to the j^{th} column (j = 1 to q where q is the number of assigned variables)

Y_i = response (μg silica) for the filter in the i^{th} row

$\sum^{+} Y_i$ = summation of Y_i associated with a "+" in column j

$\sum^{-} Y_i$ = summation of Y_i associated with a "-" in column j

N = number of filters.

Each column has an equal number of + and - signs. Within each of these two groups for any one column, there are an equal number of + and - signs for all the remaining columns. Thus, each δ_j reflects half the difference between the main results corresponding to the "+" and "-" value of the factor assigned to column j. The sign of δ_j indicates if the effect is greater at the "+" or "-" value of the factor.

The standard deviation of Y_i is calculated from the main effects, δ_j, of the unassigned columns. The following equation was used:

$$s = \left[\frac{N}{N - q - 1} \sum_{j=q+1}^{j=N} \delta_j^2 \right]^{1/2} \qquad (19)$$

where:

q = the number of assigned columns.

The minimum significant effect, δ_{min}, is given by

$$\delta_{min} = \frac{s}{\sqrt{N}} \cdot t \qquad (20)$$

where t is the value of the Student's "t" at the desired probability level for N - q - 1 degrees of freedom.

Test for Interactions

Interactions between assigned factors were evaluated by creating a new matrix column, which represented the desired interaction. The effect indicated by this derived column was then compared with the minimum significant effect. This new column was created by performing a row-by-row addition of the two columns of interest. Combinations of +, + or -, - were assigned a + ; whereas combinations of +, - and -, + were assigned values of -. As before, the Y_i values associated with a + or - value for the new columns were summed and the effect was found. This had the result of testing if the effect of one variable differs for different levels of the second variable. Table 42 summarizes this test for all two-factor interactions.

Power Function Calculations

Estimates of standard error were used to calculate power functions. The power function is defined as the probability that a test for significance of any observed difference in effect between the "+" and "-" values for a variable would reject the null hypothesis (that no significant effect was indicated) if the true effect ($\mu_i - \mu_0$) actually differed from zero by varying amounts. Here μ_i is defined as one-half the difference between the "+" and "-" conditions and $\mu_o = 0$.

For N filters, this is derived from tables of the noncentral t distribution with N - q - 1 degrees of freedom, test level of significance α, and the means of N/2 observations at each of the two levels of each test conditions.

This power function is obtained as $(\mu - \mu_0) = \frac{s}{\sqrt{N}} \cdot d$

where d is the so-called noncentrality factor in Owen's (7) table for the noncentral t distribution, using the row for N - q - 1 degrees of freedom.

Table 42. Test for two-factor interactions

Filter Number	X_1X_2	X_1X_3	X_1X_4	X_1X_5	X_2X_3	X_2X_4	X_2X_5	X_3X_4	X_3X_5	X_4X_5
1	+	-	+	+	-	+	+	-	-	+
2	-	+	+	+	-	-	-	+	+	+
3	-	-	-	+	+	+	-	+	-	-
4	+	+	-	-	+	-	-	-	-	+
5	+	-	-	-	-	-	-	+	+	+
6	-	-	-	+	+	+	-	+	-	-
7	+	+	-	+	+	-	+	-	+	-
8	+	-	+	-	-	+	-	-	+	-
9	-	+	-	-	-	+	+	-	-	+
10	-	+	+	-	-	-	+	+	-	-
11	-	-	+	-	+	-	+	-	+	-
12	+	+	+	+	+	+	+	+	+	+

Matrix	δ_{min}	δ_{ij}									
Low-temperature asher											
Low silica level	5.9	-1.7	2.3	2.3	-1.2	4.8	-1.2	3.0	0.8	0.7	-2.3
High silica level	10.1	0.8	3.9	0.1	3.8	0.9	-5.1	2.6	3.4	5.4	6.3
Muffle furnace											
Low silica level	11.9	-3.2	-2.2	4.0	6.5	3.0	0.5	4.0	1.8	5.7	0.5
High silica level	15.9	-1.8	8.1	3.1	-6.6	0.4	2.1	5.8	-6.8	-7.4	7.3
Low-temperature asher One kaolinite correction method											
Low silica level	5.3	-3.3	1.6	3.1	NA	4.1	-0.4	NA	0.1	NA	NA
High silica level	8.5	-1.3	2.7	0.8	NA	-1.7	-4.2	NA	2.2	NA	NA

Appropriate tabulations of the power functions are set forth in Table 43, where the minimum significant effects of each ruggedness test are underlined. For the LTA test using two kaolinite correction methods, there is a 60% probability that an effect as great as the δ_{min} would have been detected as a true effect; for the remaining two tests the probability is 50%.

RESULTS AND DISCUSSION

Test of Variables

Table 44 summarizes of the information displayed in Tables 36 through 43. The left side of the table reviews the experiments, showing that, for each of the two asher types, separate tests with a low and high silica loading were done. The second listing for the LTA in this section is for the data were obtained by reevaluation of the LTA test, but using only one kaolinite correction method. The middle section of the table lists the variables and the effects found for each; if the variable was not used, "NA" is entered. The pertinent statistics, which were calculated as described in the footnotes, are in the third section of the table. First is the mean, or average, of all the filters, then the standard deviation calculated from the unassigned columns of the test design. The minimum significant effect, δ_{min} , is the value against which all the δ_i of that row should be compared. Finally, we have the relative standard deviation calculated with the usual formula, and its percent, %RSD.

By comparing each δ_i with its corresponding δ_{min}, we see that none are significant. That is, varying the procedural steps by the amounts chosen for "+" and "-" did not affect the analysis. Observe that there is much greater variability in the data for the muffle furnace than for the LTA, with standard deviations of 8.30 and 14.30 μg for LTA samples (first 2 rows) versus 16.80 and 22.50 μg for muffle furnace (next 2 rows). Based on our preliminary studies, we had expected to find that the high amount ("-" level) of kaolinite would affect both the LTA and muffle furnace results, but in neither case was the kaolinite amount significant.

Accuracy and Precision

Examination of the data for all tests described above reveals that the observed means for muffle furnace tests are consistently 10 μg less than the corresponding means for low temperature ashing tests. Although this difference is not significant here, it may indicate a trend. A more important observation is that coefficients of variation for the muffle furnace tests are very high (over 20% for low silica loading), about twice as high as those for the low temperature ashing tests. Apparently, the poor precision of the muffle furnace tests is due largely to the high amount of background absorbance present in those samples.

Table 43. Power function projections for IR method.

β	Power (1 - β)	Centrality parameter d (α = 0.025)† f = 6	f = 7	Detectable effect (μ - μ0)* in μg: Low-temperature plasma asher (f = 6) Silica level Low (s = 8)	High (s = 14.3)	Muffle furance (f = 6) Silica level Low (s = 16.8)	High (s = 22.5)	Low-temperature plasma asher: one kaolinite correction method (f = 7) Silica level Low (s = 7.8)	High (s = 12.5)
0.01	0.99	5.22	5.06	12.1	21.5	25.3	33.9	11.4	18.3
0.05	0.95	4.37	4.23	10.1	18.0	21.2	28.4	9.5	15.3
0.10	0.90	3.91	3.80	9.0	16.1	19.0	25.4	8.6	13.7
0.20	0.80	3.37	3.27	7.8	13.9	16.3	21.9	7.4	11.8
0.30	0.70	2.98	2.89	6.9	12.3	14.5	19.4	6.5	10.4
0.40	0.60	2.64	2.57	6.1	10.9	12.8	17.1	5.8	9.3
0.50	0.50	2.34	2.27	5.4	9.7	11.3	15.2	5.1	8.2
0.60	0.40	2.03	1.98	4.7	8.4	9.8	13.2	4.5	7.1
0.70	0.30	1.70	1.66	3.9	7.0	8.2	11.0	3.7	6.0
0.80	0.60	1.32	1.29	3.0	5.4	6.4	8.6	2.9	4.7
0.90	0.10	0.80	0.78	1.8	3.3	3.9	5.2	1.8	2.8

*$(\mu - \mu_0) = \frac{s}{\sqrt{N}} \cdot d$

†Corresponding to α = 0.05 for a two-tailed test with 12-5-1 = 6 degrees of freedom or 12-4-1 = 7 degrees of freedom.

Note: f = degrees of freedom.

Underlined values are those closest to δ_{min} for each test.

Table 44. Summary of effects of real factors.

Matrix	δ_i (µg)							Mean* $\bar{Y}$ (µg)	s† (µg)	δ_{min}# (µg)	SD‡ (µg)	%RSD§
	Calcite	Power	Temperature	Time	Kaolinite	Correction	Wash					
Low-temperature asher												
Low silica	-3.5	-0.67	NA	3.33	-2.0	-3.17	NA	86.5	8.30	5.87	8.9	10.3
High silica	2.58	-0.58	NA	-5.42	1.75	-1.25	NA	135.9	14.30	10.11	12.5	9.2
Muffle furnace												
Low silica	-8.0	NA	2.83	5.5	-6.67	NA	-1.5	74.0	16.80	11.89	17.8	24.0
High silica	-3.75	NA	6.42	8.25	2.08	NA	-0.58	125.9	22.50	15.91	20.4	16.2
Low-temperature asher (only one kaolinite correction method used)												
Low silica	-3.92	-1.08	NA	3.75	-0.75	NA	NA	84.2	7.84	5.34	8.6	10.2
High silica	1.83	-0.83	NA	-4.83	3.0	NA	NA	134.7	12.55	8.55	11.83	8.8

*Mean calculated from the equation $\bar{Y} = \frac{1}{N}\sum Y_i$.

†s is the standard deviation calculated as described in the section entitled Computation of Main Effects.

#δ_{min} at 95% confidence level.

‡SD calculated from the equation $SD = \left[\frac{\sum (\bar{Y} - Y_i)^2}{N - 1}\right]^{1/2}$

§%RSD calculated from the equation $\%RSD = 100 \cdot (SD/\bar{Y})$.

CONCLUSIONS AND RECOMMENDATIONS

The infrared method for determining of crystalline silica in coal mine dust was demonstrated to be rugged with respect to minor procedural variations. Although none of the experimental factors tested was significant, two recommendations were made. First, low temperature ashing should be preferred over high temperature muffle furnace ashing because sample handling is minimized (i.e., no acid wash is needed), background absorbance is decreased, and the coefficient of variation for the method is reduced. Second, the kaolinite correction for samples ashed at low temperature should be made from a curve of kaolinite absorbance at 915 cm^{-1} against that at 800 cm^{-1} rather than from absorbance versus mass curves, simply because the former method involves the gathering of fewer, less-scattered data than the latter.

The correction for kaolinite must be applied carefully for "real" samples. Absorbance in the infrared is a function of the particle size distribution; for example, the slope of the silica calibration curve decreased with increasing average particle size. The kaolinite particle size distribution of the ruggedness test samples was presumably closely matched with that of the kaolinite standards, since 91% of the kaolinite penetrated the cyclones during sample generation. This will not always be true for field samples; therefore, additional studies should be done with other kaolinite standards.

It was recommended that the method be distributed for a collaborative test, using the same types and amounts of matrix materials in sample preparation.

SECTION V

SELECTION OF A CALIBRATION STANDARD

BACKGROUND

Various investigators (9-11) have noted that the x-ray diffraction intensity per microgram of silica deposited on a filter is a function of particle size distribution. This is seen in Figure 14, which gives the calibration curves prepared using the standard silica materials Min-U-Sil 5 and Min-U-Sil 10. The reported average particle sizes of these materials are 1.9 and 3.5 μm, respectively.

Because of this dependence, accuracy in the analytical x-ray diffraction results dictates that the standard material used to prepare the calibration curves must have a particle size distribution that closely matches that of the samples. Since it would be impractical and expensive for individual laboratories to attempt to obtain a supply of standard material to match the size distribution of each set of field samples, NIOSH elected to select one material for universal use. We evaluated various size distributions of Min-U-Sil to select the bulk materials whose size distribution most closely resembles the size distribution of materials passing through the cyclones used to collect respirable samples.

EXPERIMENTAL PROCEDURES

Materials

The silica materials used in this study were Min-U-Sil 5, Min-U-Sil 15, and Min-U-Sil 30, which are available commercially (12). The physical properties of these materials, as reported by the supplier, are given below.

	Min-U-Sil 5	Min-U-Sil 10	Min-U-Sil 30
Surface area (m^2/g)	2.06	0.84	0.54
Average particle size (μm)	1.9	4.0	8.8
Specific gravity (g/cm^3)	2.650	2.650	2.650
Silicon dioxide content (SiO_2)(%)	99.46	99.46	99.46

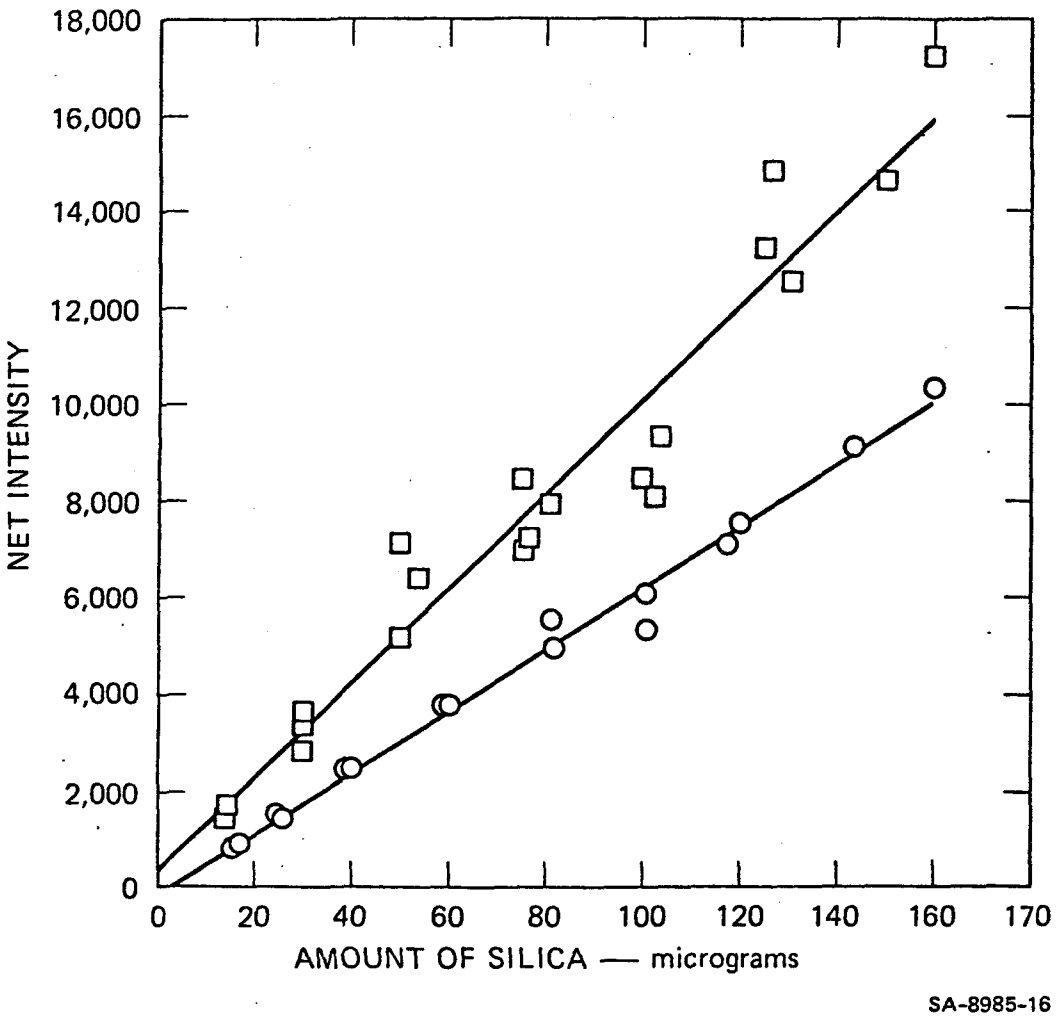


FIGURE 14 XRD CALIBRATION CURVES OF MIN-U-SIL 5 (○) AND MIN-U-SIL 10 (□)

Apparatus

A schematic of the aerosol sampling chamber is shown in Figure 15. The air flow rate through the chamber is 820 L/min, at a linear velocity of greater than 40 cm/s. At this velocity, an upward drag force sufficient to overcome the gravitational force was maintained for particles greater than 50 μm (equivalent spherical diameter). The cyclone sampling assembly is shown in Figure 16, and a schematic of the aerosol generation system is shown in Figure 17.

The particle size distribution curves were prepared using California Measurements Systems' piezoelectric cascade impactor (13). The impactor stack of this unit consists of a nine-stage Andersen sampler, each stage of which is fitted with a matched set of piezoelectric crystals coated with a thin film of adhesive. After the air stream is sampled, the frequency change per stage is used to calculate the mass collected on that stage. The air flow rate through the impactor stack is 200 mL/min. Based on this air flow rate and a specific gravity for silica of 2.650, the 50% cutoff sizes (Dp 50) for the nine stages would be as follows:

Stage	Dp 50 (μm)	Stage	Dp 50 (μm)
1	16.372	6	0.4056
2	6.344	7	0.1946
3	3.132	8	0.1043
4	1.566	9	0.0749
5	0.8632		

Particle size distribution data on the silica material were collected with and without a 10-mm nylon cyclone connected to the inlet of the impactor stack. The required air flow rate through the cyclone is 1.7 L/min. However, at this air flow rate through the impactor stack, a very limited amount of information is available because the first stage has a Dp 50 of 5.1 μm. Therefore, only a portion of the air stream from the 10-mm cyclone outlet was used in the stack. The 1.7 L/min air flow rate required for the correct operation of the cyclone was obtained by connecting a critical flow orifice operating at 1.5 L/min in parallel with the impactor stack operating at 0.2 L/min. A special isokinetic sampling tube, shown in Figure 18, was used to connect the cyclone to both the impactor stack inlet and the critical flow orifice. This tube was designed so that the linear velocity to each device was the same, thereby preventing any bias in the measured size distribution due to the splitting of the aerosol stream.

RESULTS AND DISCUSSION

Using the special sampling chamber and the piezoelectric cascade impactor, we determined size distribution curves for Min-U-Sil 5, Min-U-Sil 15, and Min-U-Sil 30 with and without 10-mm nylon cyclones in place. Figure 19 shows the particle size distribution curves of the Min-U-Sil materials when the cyclones were not in place. The average particle sizes for Min-U-Sil 5 and Min-U-Sil 15 were found to be 1.5 and 3.5 μm, respectively. These values match the

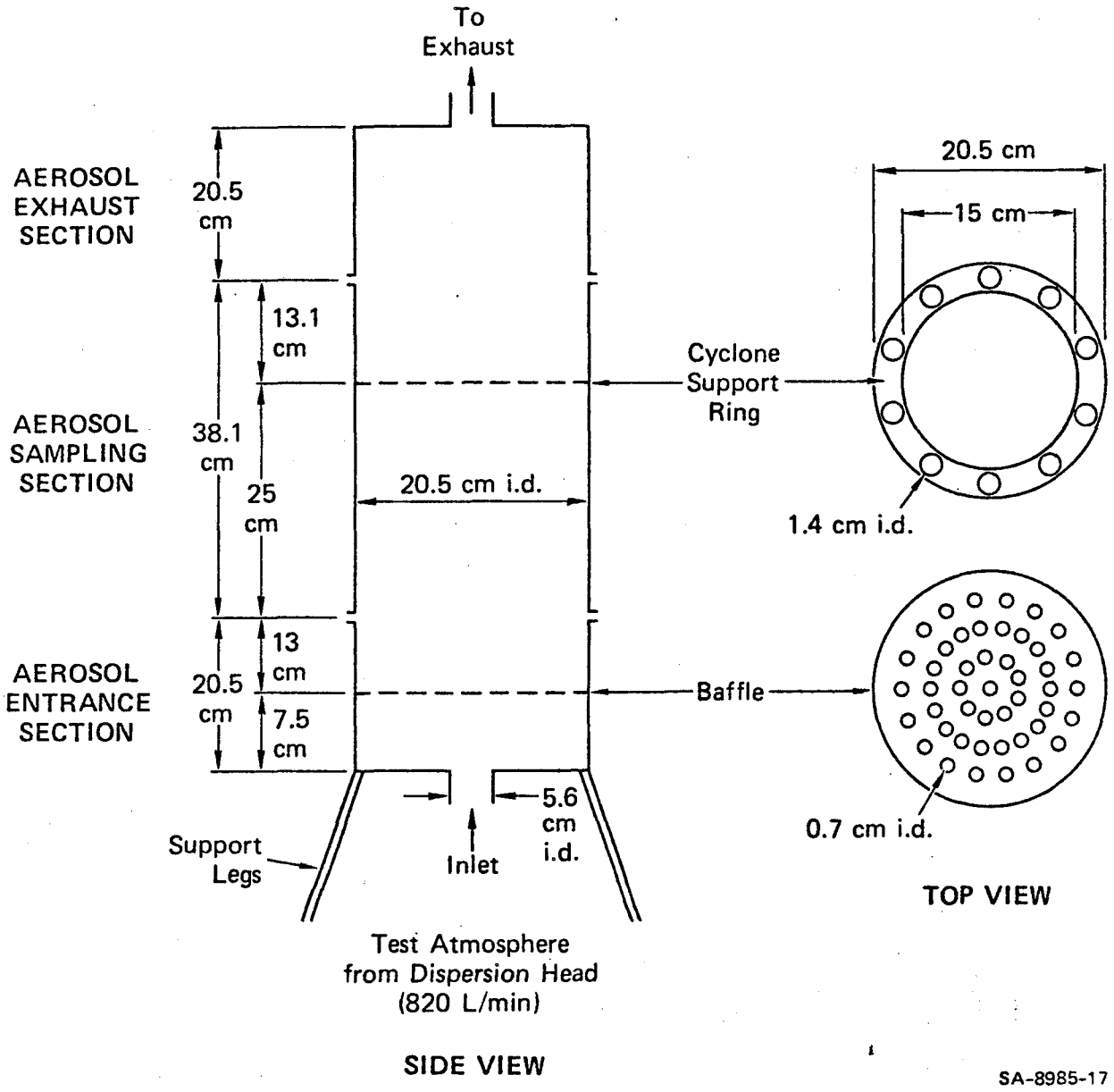
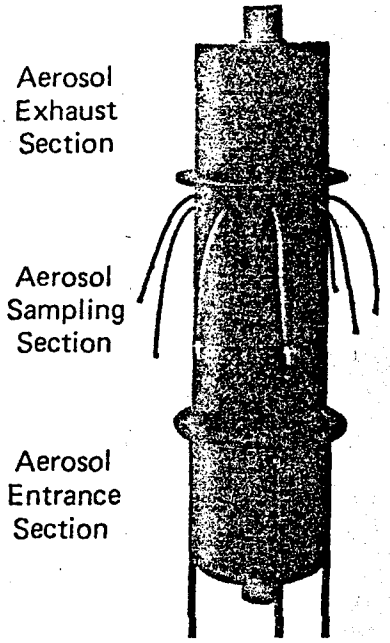
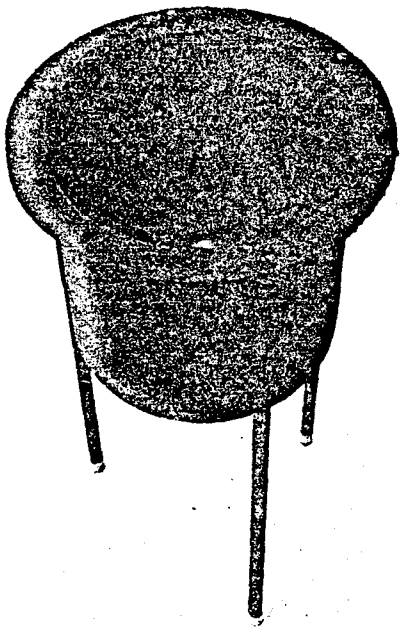


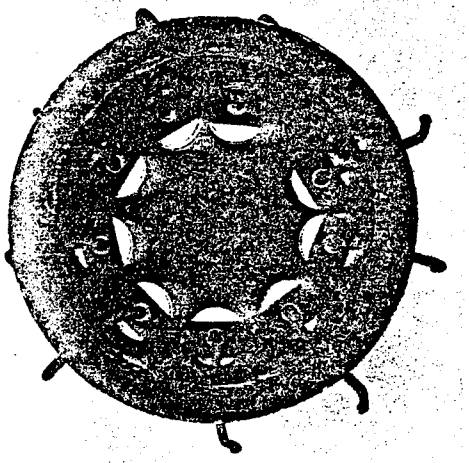
FIGURE 15 SCHEMATIC OF AEROSOL SAMPLING CHAMBER



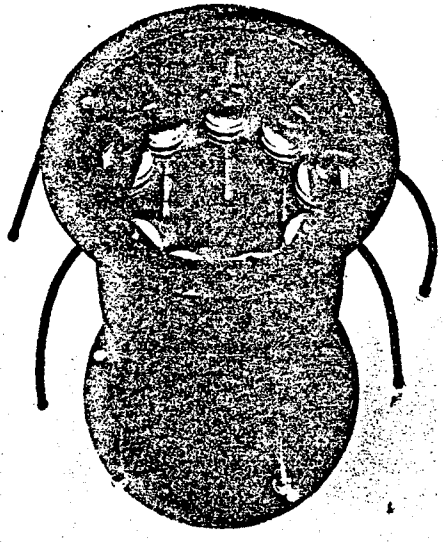
(a) Side view of aerosol sampling chamber



(b) Oblique view of aerosol entrance section with baffle in place



(c) Top view of aerosol sampling section with cyclones and collection filters in place



(d) Oblique view of aerosol sampling section with cyclones and collection filters in place

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FIGURE 16 PHOTOGRAPHS OF AEROSOL SAMPLING CHAMBER USED FOR PARTICLE SIZE STUDIES

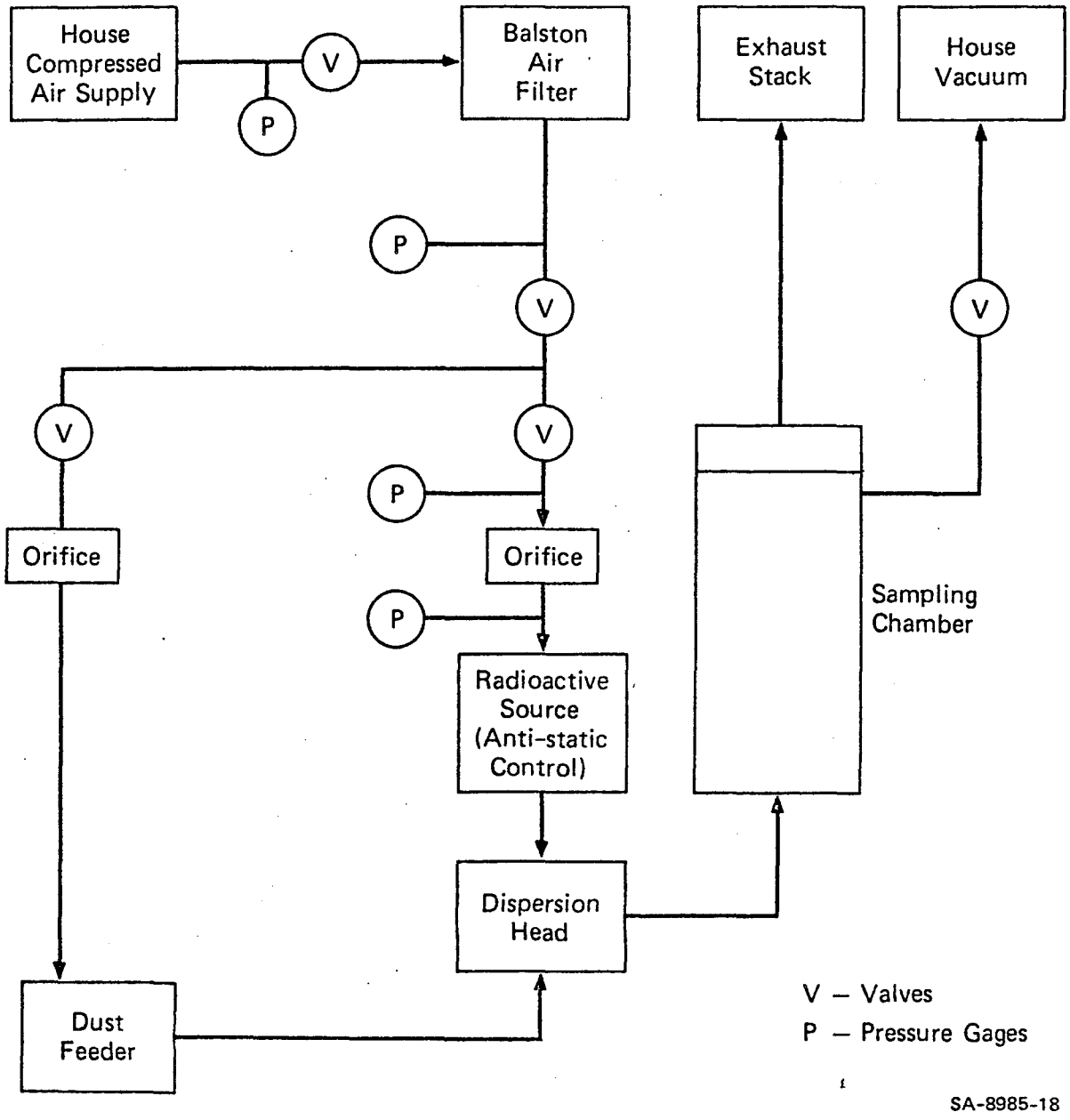


FIGURE 17 SCHEMATIC OF AEROSOL GENERATION SYSTEM

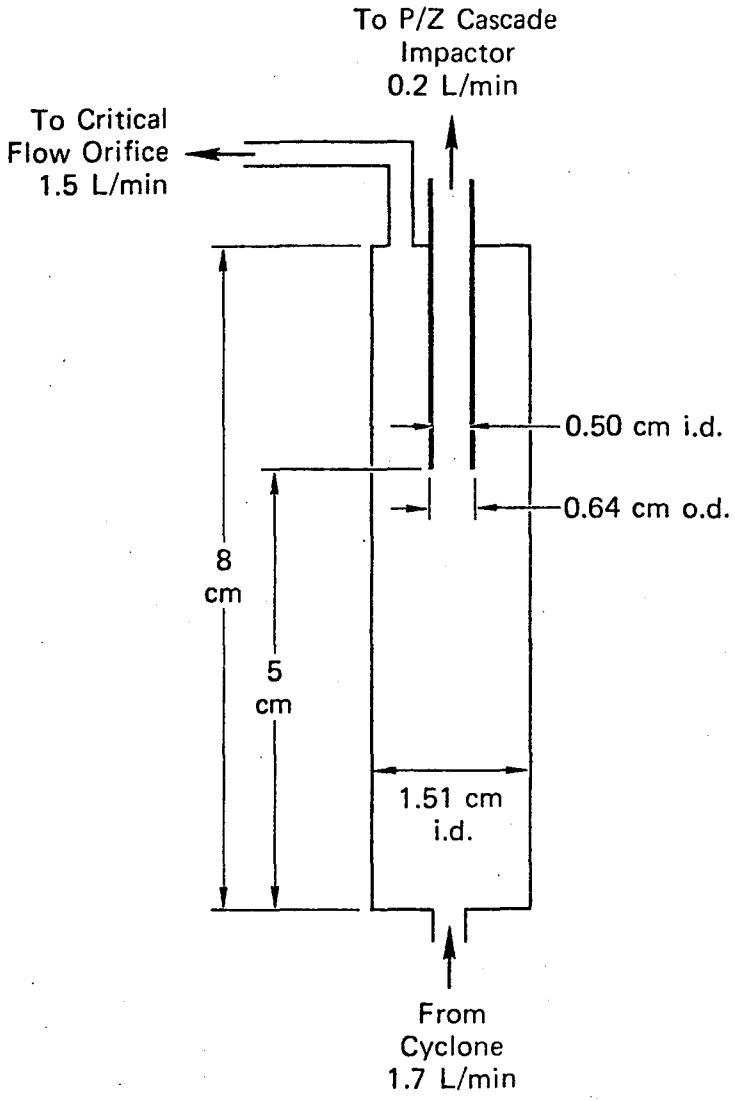


FIGURE 18 ISOKINETIC SAMPLING TUBE

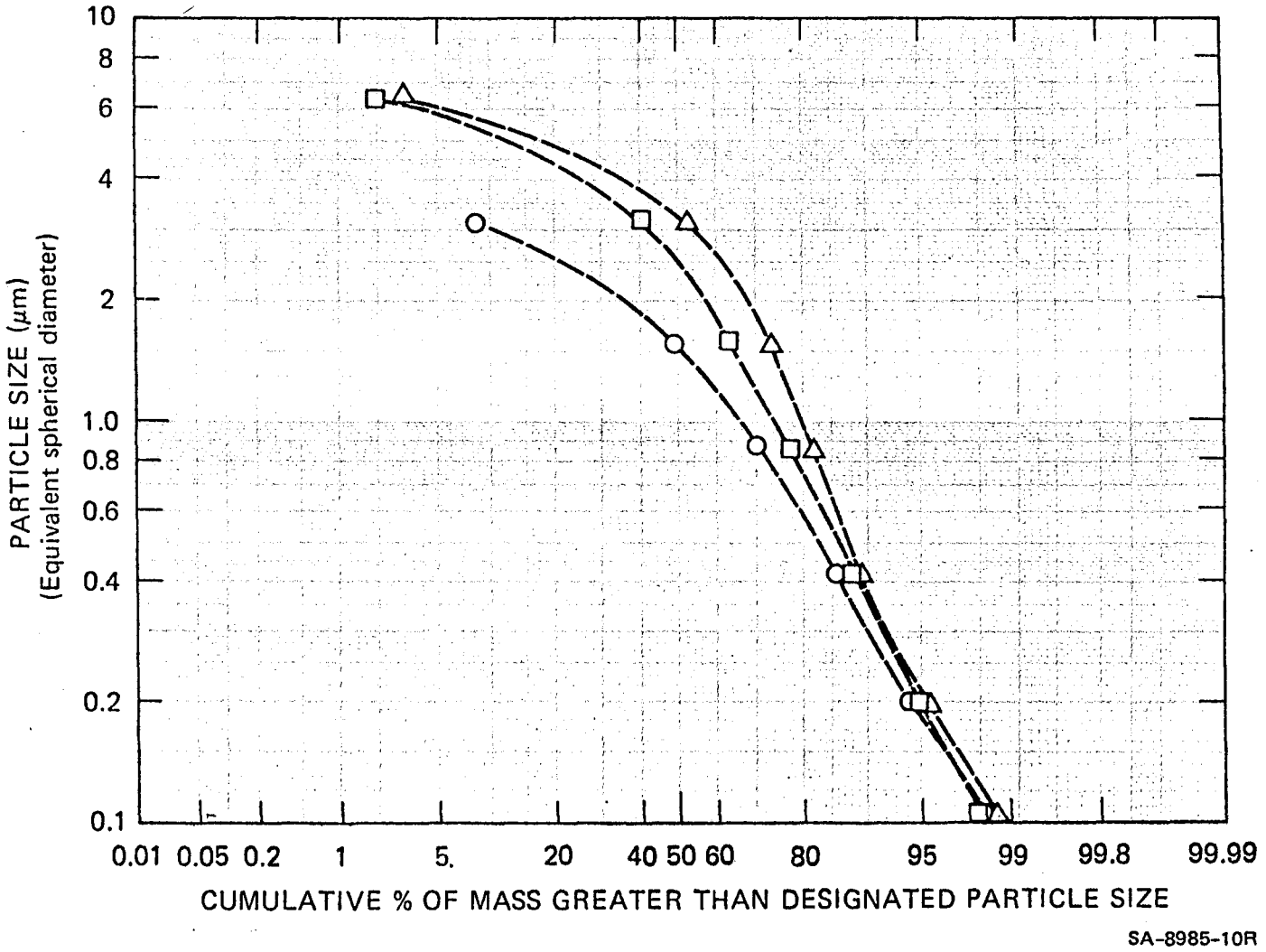


FIGURE 19 PARTICLE SIZE DISTRIBUTION CURVES FOR MIN-U-SIL 5 (○), MIN-U-SIL 15 (△), AND MIN-U-SIL 30 (□) DETERMINED WITH A PIEZOELECTRIC CASCADE IMPACTOR WITHOUT 10-mm NYLON CYCLONES

average particle sizes of 1.9 and 4.0 μm reported by the manufacturer. The measured averge particle size for Min-U-Sil 30 was found to be 3.5 μm, which is significantly less than the reported value of 8.8 μm. It appears likely that either the generation/sample system cuts out larger particles, or the piezoelectric cascade impactor does not accurately measure particle size distribution when the aerosol being sampled contains a greater percentage of large particles.

When 10-mm nylon cyclones are placed in the sampling system, the distribution curves of all the Min-U-Sil materials shift toward smaller particle sizes. The cyclone cuts out a fraction of particles even from Min-U-Sil 5. (The 50% cut size of the 10-mm cyclone when operated at 1.7 L/min is reported to be 2.2 μm for silica.) The size distribution curves of the aerosols that penetrate the 10-mm cyclones are remarkably similar, as shown by the distribution curves shown in Figure 20. The average particle sizes of cycloned Min-U-Sil 5, Min-U-Sil 15, and Min-U-Sil 30 are 1.16, 1.2, and 1.2 μm, respectively.

These results from the piezoelectric cascade impactor studies are corroborated, at least qualitatively, by visual inspection of scanning electron photomicrographs of samples collected at the time of the impactor studies. Figure 21 shows scanning electron photomicrographs of the various silica materials collected on 0.4-μm Nuclepore polycarbonate filters after penetration through 10-mm nylon cyclones. Despite the differences in sample loadings on these filters, it is apparent that the particle size distributions of these samples are quite similar to each other.

Figure 22 shows scanning electron photomicrographs of the Min-U-Sil materials deposited from isopropanol suspensions onto 0.4-μm Nuclepore polycarbonate filters. The effect of the generation processes on particle size distribution is quite evident from comparisons of Figures 21 and 22. The Min-U-Sil 5 deposits seen in the photomicrographs are not notably different from one another or from the other cycloned materials.

There does appear to be a higher fraction of larger particles in the samples prepared from suspension. However, Min-U-Sil 15 and Min-U-Sil 30 materials deposited from suspension have significantly larger particles than their cycloned counterparts.

Although not directly related to the particle size distribution studies, one additional set of experiments was performed. These experiments were concerned with the possibility of breakthrough of the 5-μm PVC collection filter by the silica particles during sample collection. To determine if any of the silica genetrates the 5-μm PVC filter, we mounted several filters in the aerosol generation system with either 0.2- or 0.4-μm Nuclepore polycarbonate backup filters. Figure 23 shows photomicrographs of a typical PVC filter sample and the 0.2-or 0.4-μm backup filters with breakthrough silica. The backup filters were then examined by scanning electron microscopy. The results showed very little breakthrough. We found some localized silica deposits that may be due to small flaws in the PVC filters. We believe that, despite the fairly large pore size, an insignificant fraction of the silica passed completely through the filter.

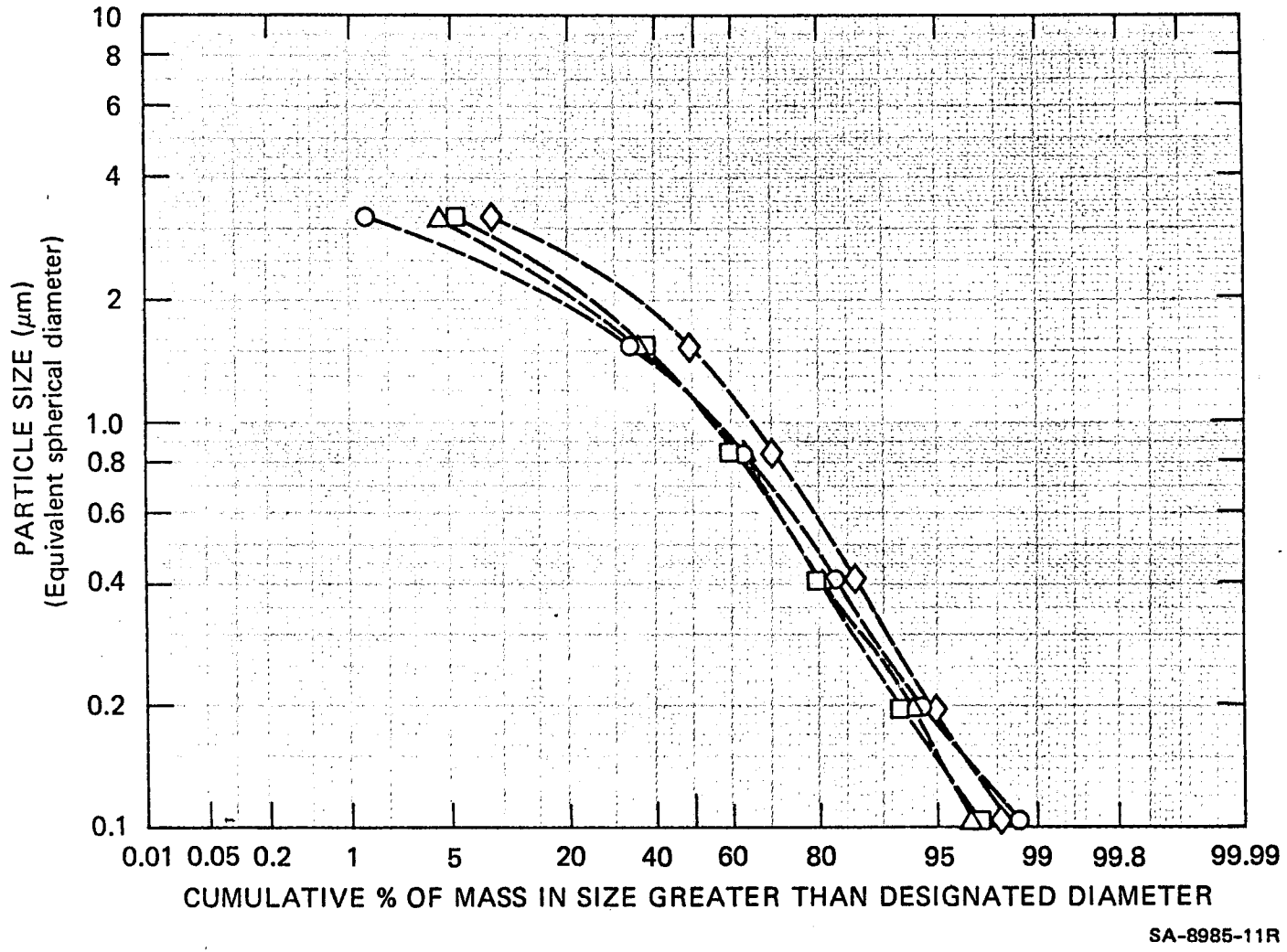
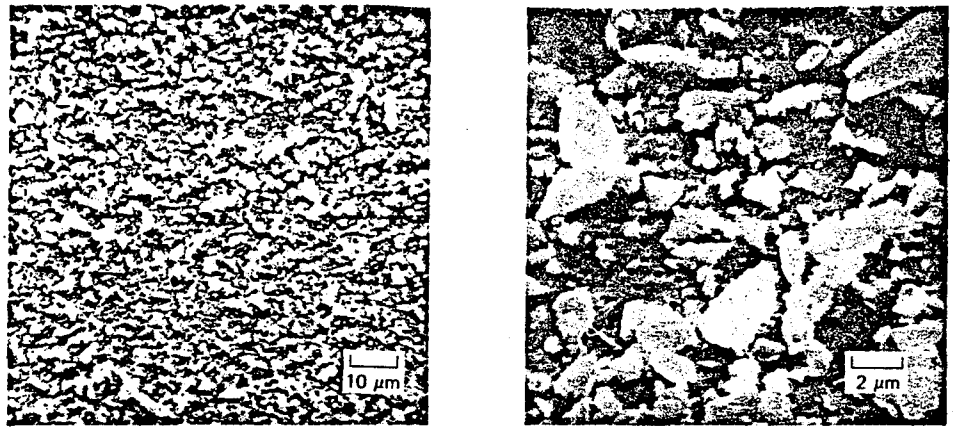
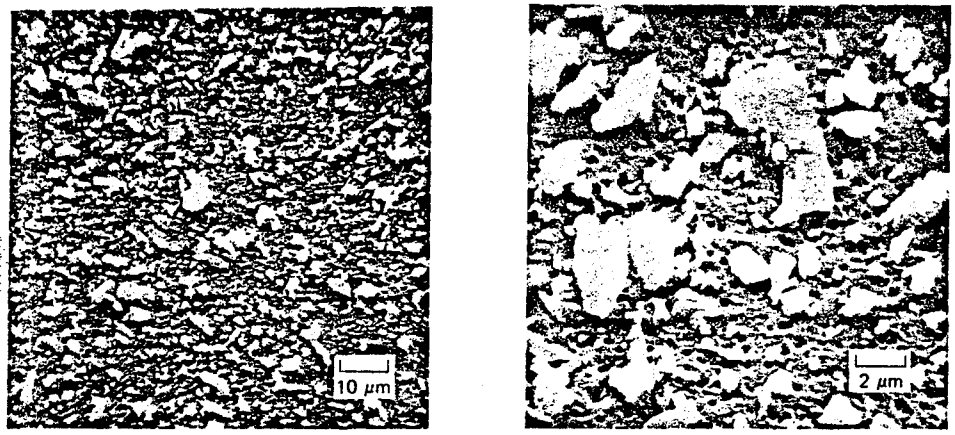


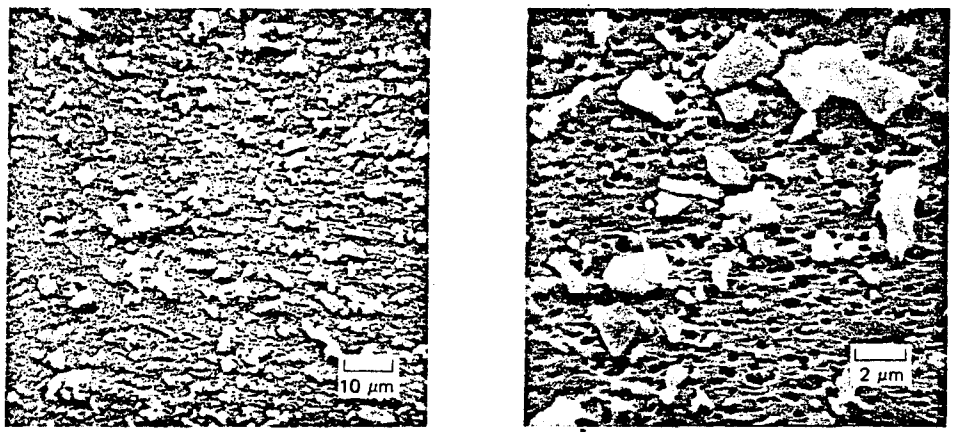
FIGURE 20 PARTICLE SIZE DISTRIBUTION CURVES FOR MIN-U-SIL 5 (○), MIN-U-SIL 15 (□), AND MIN-U-SIL 30 (△) THAT HAVE PASSED THROUGH A 10-mm NYLON CYCLONE AND THE CURVE FOR MIN-U-SIL 5 WITH NO CYCLONE (◇)



(a) MIN-U-SIL 5



(b) MIN-U-SIL 15



(c) MIN-U-SIL 30

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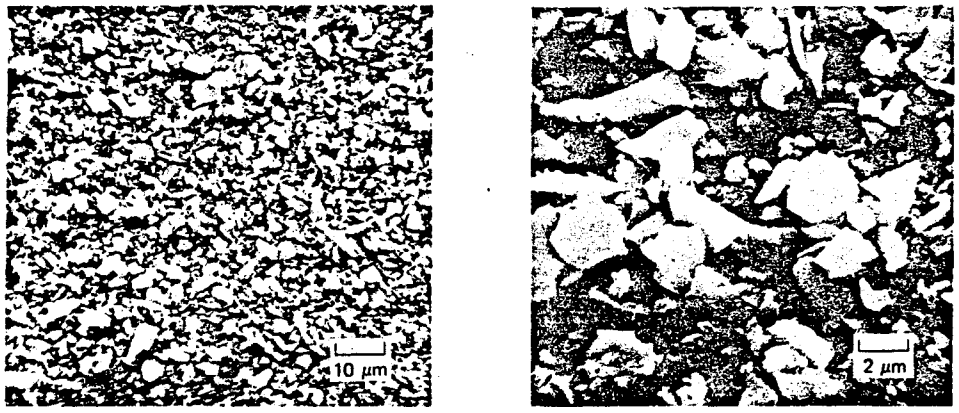
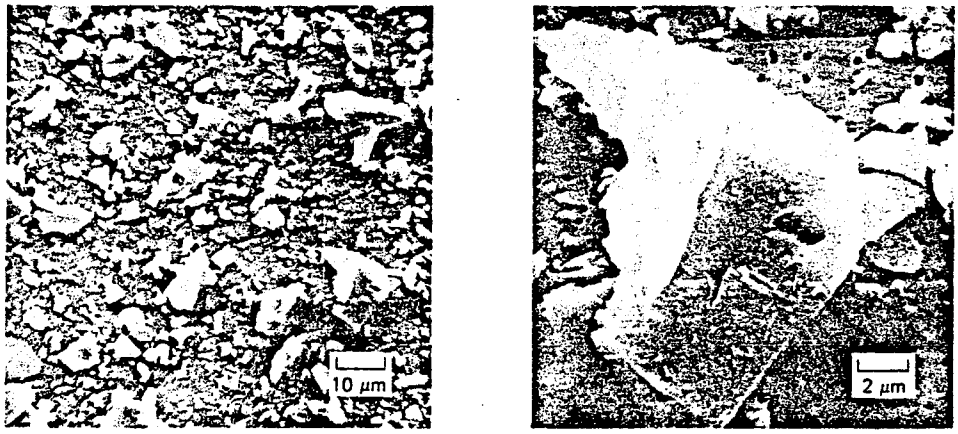
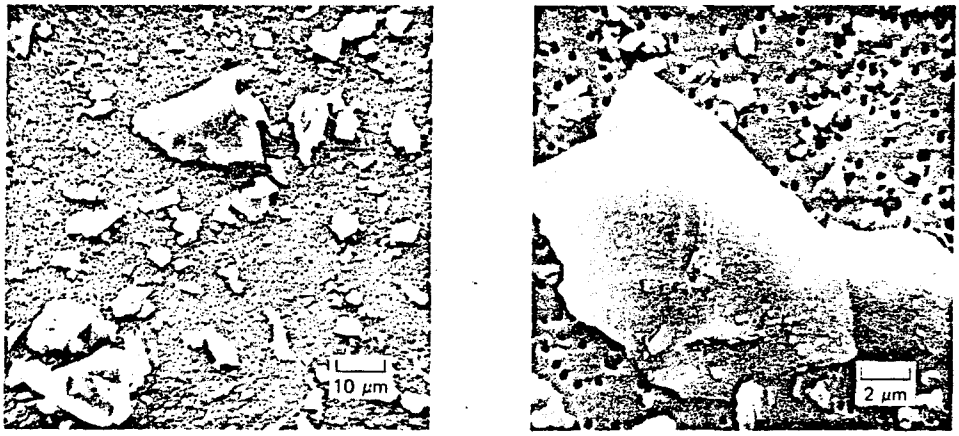
FIGURE 21 SCANNING ELECTRON MICROGRAPHS OF MIN-U-SIL DUSTS THAT HAVE BEEN COLLECTED ON 0.4-μ NUCLEPORE POLYCARBONATE FILTERS AFTER PASSING THROUGH 10-mm NYLON CYCLONES



(a) MIN-U-SIL 5



(b) MIN-U-SIL 15



(c) MIN-U-SIL 30

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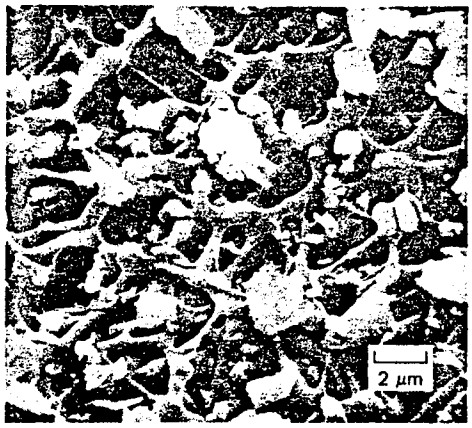
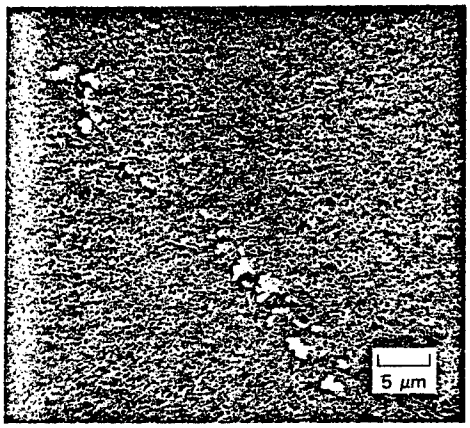
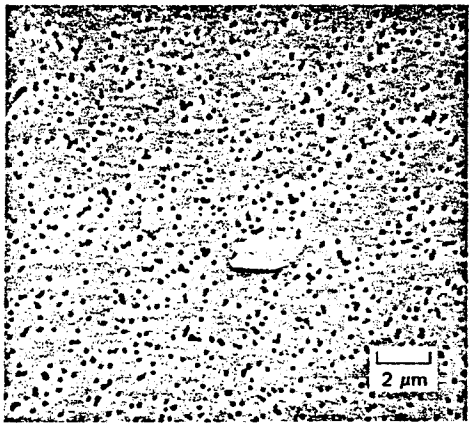
FIGURE 22 SCANNING ELECTRON MICROGRAPHS OF MIN-U-SIL MATERIALS THAT HAVE BEEN FILTERED FROM ISOPROPANOL SUSPENSIONS ONTO 0.4-μ NUCLEPORE POLYCARBONATE FILTERS



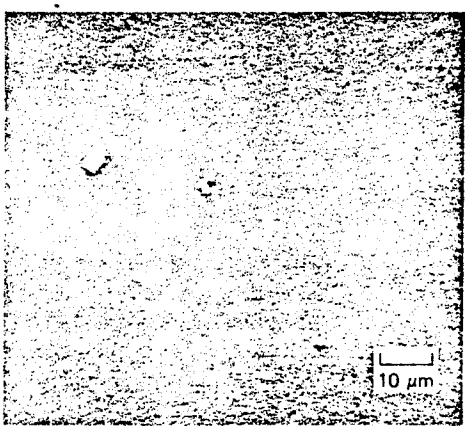
(a) 5-μ PVC FILTER WITH SILICA SAMPLE



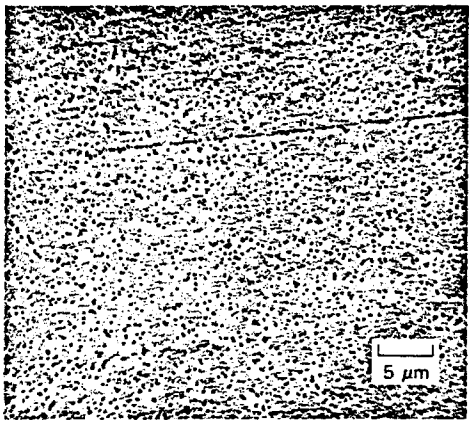
(b) 0.2-μ NUCLEPORE POLYCARBONATE BACKUP FILTER



(c) 0.2-μ NUCLEPORE POLYCARBONATE BACKUP FILTER



(d) 0.2-μ NUCLEPORE POLYCARBONATE BACKUP FILTER



(e) 0.4-μ NUCLEPORE POLYCARBONATE BACKUP FILTER

SA-8985-22

FIGURE 23 SCANNING ELECTRON MICROGRAPHS OF BREAKTHROUGH STUDIES: 5-μ PVC COLLECTION FILTER AND NUCLEPORE POLYCARBONATE BACKUP FILTERS

CONCLUSIONS AND RECOMMENDATIONS

Although none of the particle size distributions of the Min-U-Sil materials deposited from suspension exactly matched those of the cycloned material, Min-U-Sil 5 came the closest. Thus, Min-U-Sil 5 was chosen as the standard material to be used for the preparation of calibration curves.

We recommend that a study be undertaken to attempt to solve the problem of the dependence of the x-ray diffraction intensities on particle size distribution. The objectives of this study would be to:

- Define and explain the exact nature of the interaction between x-ray intensities and particle size distribution, in the respirable range.
- Modify the method, if possible, so that the observed interaction is either lessened or entirely eliminated.

SECTION VI

SRI DUST GENERATION SYSTEM

GENERAL

The SRI dust generation system is shown in Figure 24. The main components are a dust feeder, which delivers a continuous stream of aerosol, a sonic velocity disperser, a settling tower, and four symmetrically located sample collection chambers.

Figure 25 is a schematic of the system. Compressed air, filtered to remove oil mist and particulates, is supplied to the dust feeder at approximately 60 L/min. Air at 750 L/min is delivered to a sonic velocity disperser. Air streams are controlled by separate critical flow orifices.

The feed dust is carried from the dust feeder to the sonic velocity dispersion head through a 1-ft by 1/4-in.-I.D. piece of Tygon tubing. The incoming air stream, at sonic velocity, disperses and deagglomerates the incoming aerosol. Mixing and settling occur in the cylindrical settling tower.

The aerosol is uniformly distributed to the four identical sample collection chambers located in the top section of each chamber. Excess aerosol is exhausted from the settling tower through an absolute filter. The entire system is supported by an aluminum frame structure.

SAMPLE COLLECTION CHAMBER

The base section of the collection chamber (see Figure 26) consists of eight layers of gaskets and machined aluminum sheets. Eighty 37-mm, 2-section Millipore filter cassettes are permanently situated in an 8 by 10 matrix arrangement. Behind each cassette is a critical flow orifice, protected by a fine mesh stainless steel screen. The mounting sheet, in which the 80 critical flow orifices are embedded, forms the upper section of a vacuum chamber so that application of a vacuum to this chamber creates the necessary pressure differential to operate the orifices. The 320 orifices (80 for each sample collection chamber) form a matched set, with a maximum flow rate of about 2 L/min in this system.

Aerosol enters the collection area through 20 symmetrically located passages. The arrows in Figure 26 indicate the air flow directions during sampling. Before sampling, all aerosol is directed out the exhaust line of the settling tower.

Access to the chamber is from the top by removing the cover. Individual samples are connected to the permanently emplaced cassettes using a Luer fitting or tubing, as necessary.

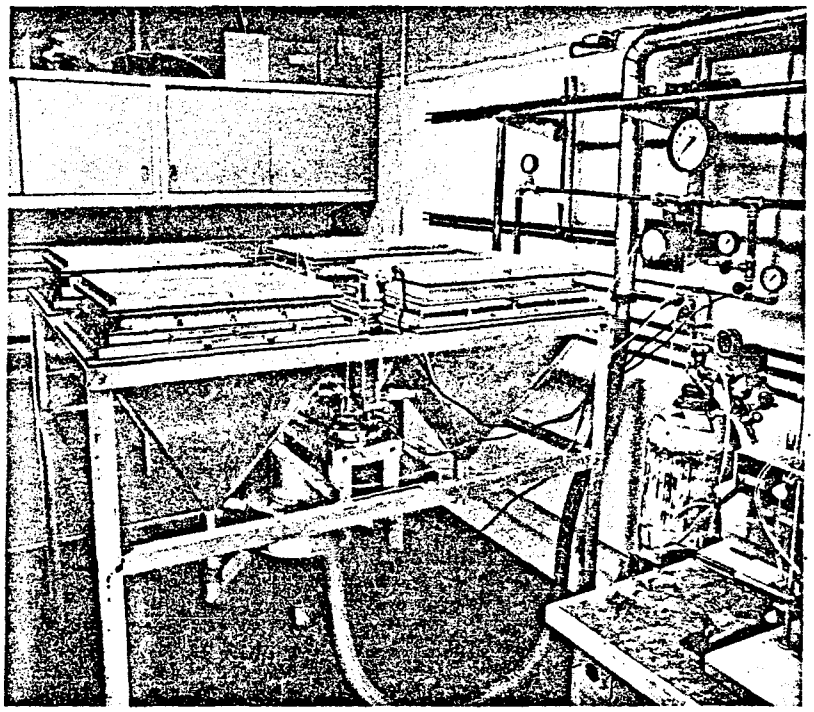


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FIGURE 24 SRI DUST GENERATION SYSTEM

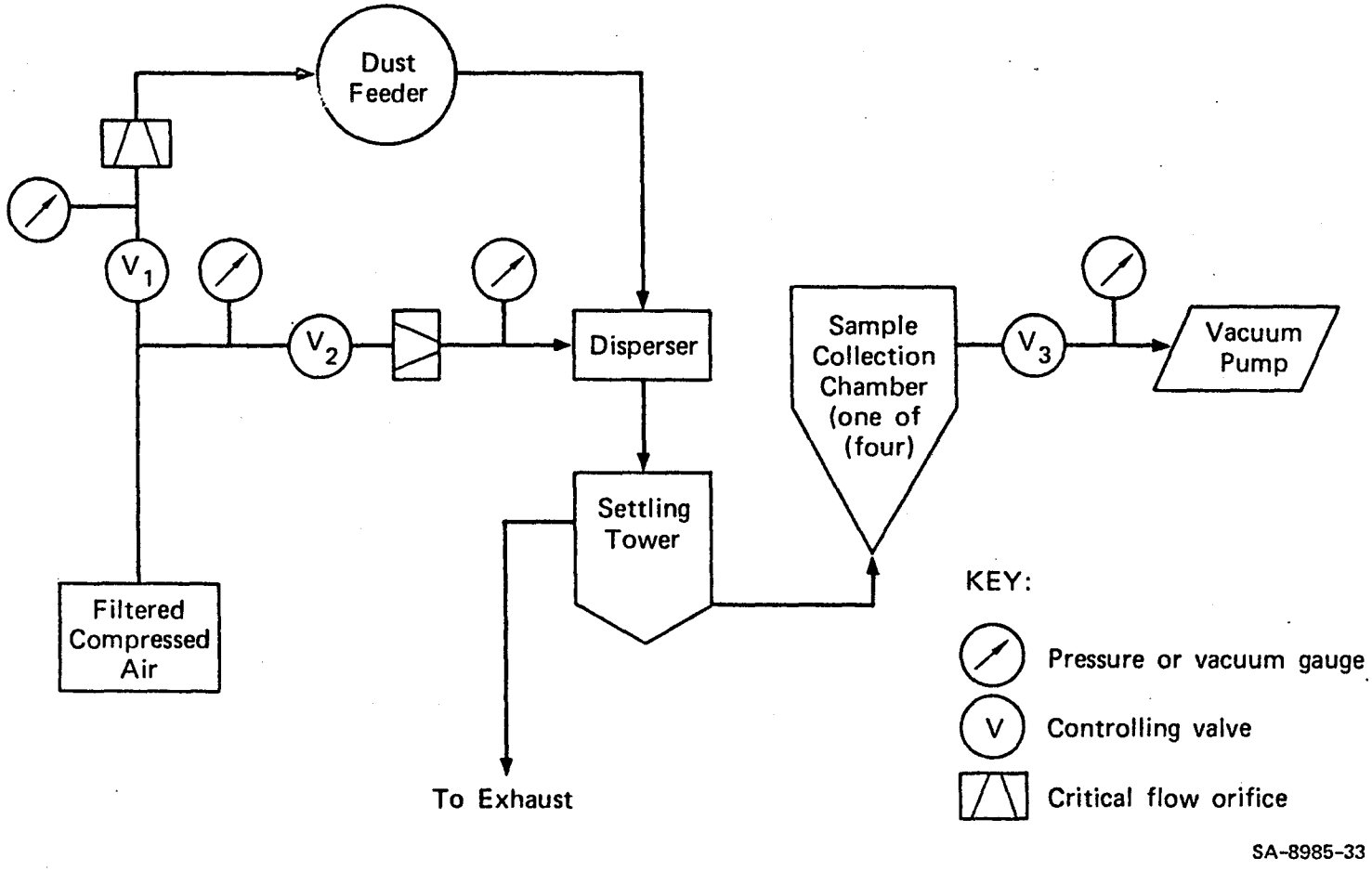


FIGURE 25 SCHEMATIC OF SRI DUST GENERATION SYSTEM

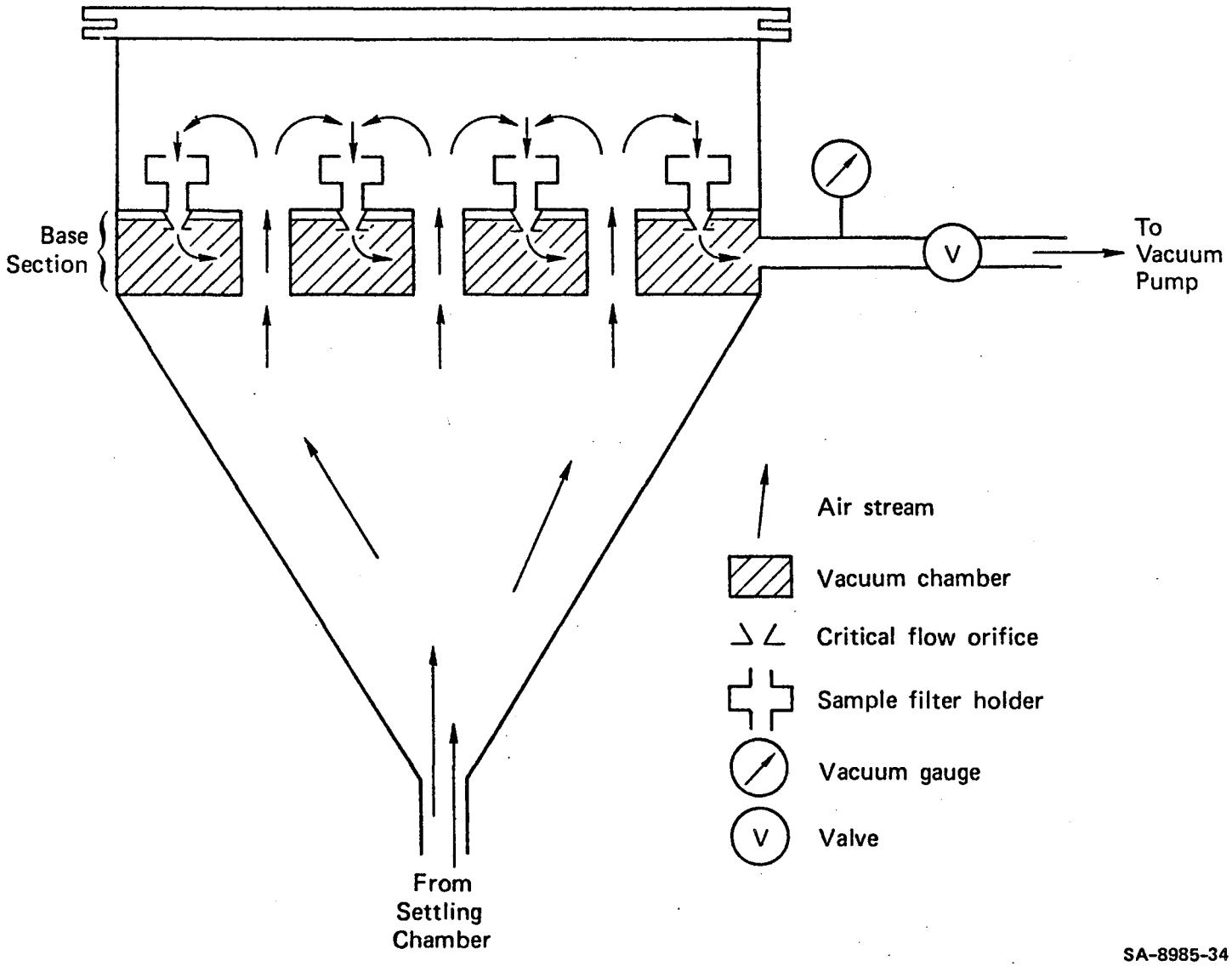


FIGURE 26 SCHEMATIC OF SAMPLE COLLECTION CHAMBER

One chamber has been adapted to accommodate 10-mm nylon cyclones. The cyclones are mounted on support bars, which fit into this chamber. A small flat piece of aluminum fits on the sample cassette and is connected with springs to eye screens on the support bar, creating the tension necessary to force down the vortex section of the cyclone.

Thirty 2.5-cm-long, 0.4-cm-O.D. open brass tubes are sealed horizontally in the sidewall of this same sampling section, permitting sampling from this chamber with externally located pumps. The interior of this chamber is shown in Figure 27, with one row of filter/cyclone units in place.

Maximum sampling rate is about 2 L/min; a lower flow rate is attained by reducing the pressure differential across the sampling orifices. The main vacuum pump creates a vacuum of 27 in. Hg in the vacuum chamber. A controlling valve with a 0.22-in. flow orifice installed in the line between the vacuum chamber and the vacuum pump permits increasing the pressure in the vacuum chamber, and thus decreases the sampling rate.

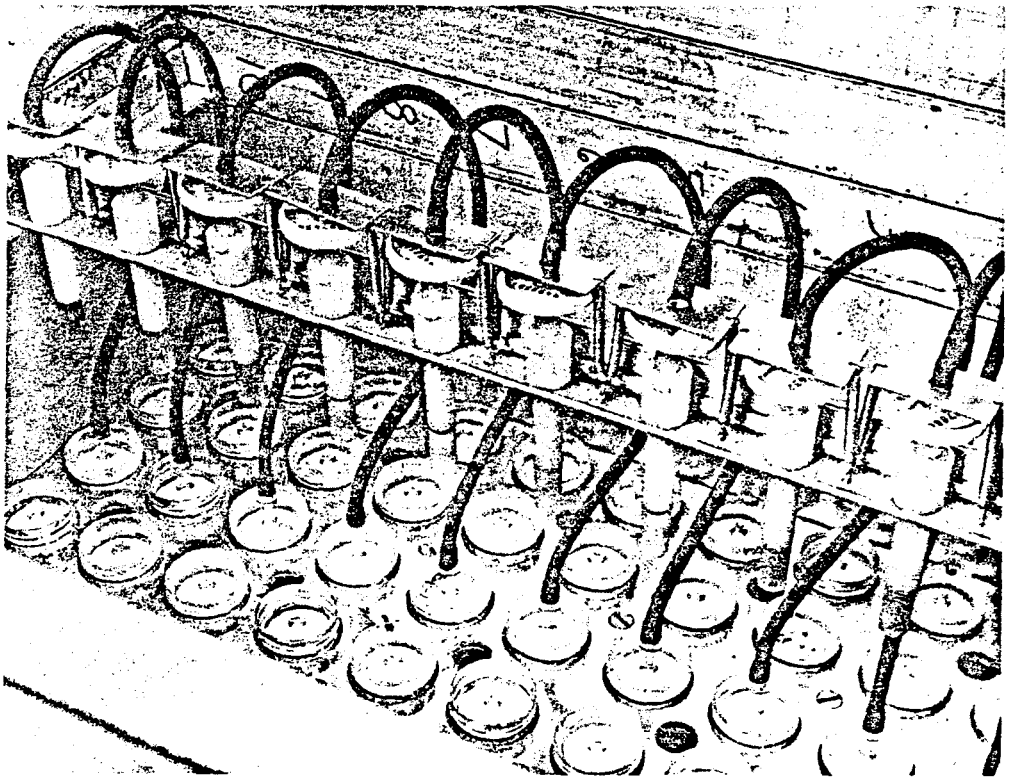
SRI DUST FEEDER

Figure 28 shows the basic elements of the SRI dust feeder. Powder is metered by means of a grooved disk, which rotates at a known rate. The powder is pneumatically unloaded from the disk with a 60-L/min air stream and then conveyed to a sonic velocity disperser.

Powder is loaded into the top of the powder hopper through the powder feed port. It then drops down into the hopper connector where it is pushed into the groove of the disk by the action of rubber wipers attached to the bottom of the agitator shaft. A spring-loaded guard ring surrounds the hopper connector and scrapes the disk to prevent powder from being carried away on the surface of the disk except in the groove. The rotation of the disk continuously carries the powder in the groove to the unloading nozzle, where is removed pneumatically through the action of compressed air that is metered into the bottom of the disk chamber. The grooved disk is rotated by means of a set of pulleys driven by a gearhead motor, the speed of which is controlled. The powder feed rate is determined entirely by the rotation speed of the disk and by the size of the groove.

PREPARATION OF TEST ATMOSPHERES AND SAMPLE COLLECTION

Sample collection filters are placed in the chambers, which are then tightly closed. The feed dust is added to the hopper of the dust feeder, and the feed rate is adjusted by controlling the rotation rate of the feeder's grooved disk. Air to the feeder and the sonic velocity disperser are turned on. After several minutes of operation, the vacuum pump is turned on to initiate sampling. After the appropriate sampling time has elasped, the vacuum pump is turned off and the system is closed down. The required sampling time is determined by calibrating the output of the feeder as a function of disk rotation speed for each dust used.



SP-8985-39

FIGURE 27 INTERIOR OF ONE COLLECTION CHAMBER

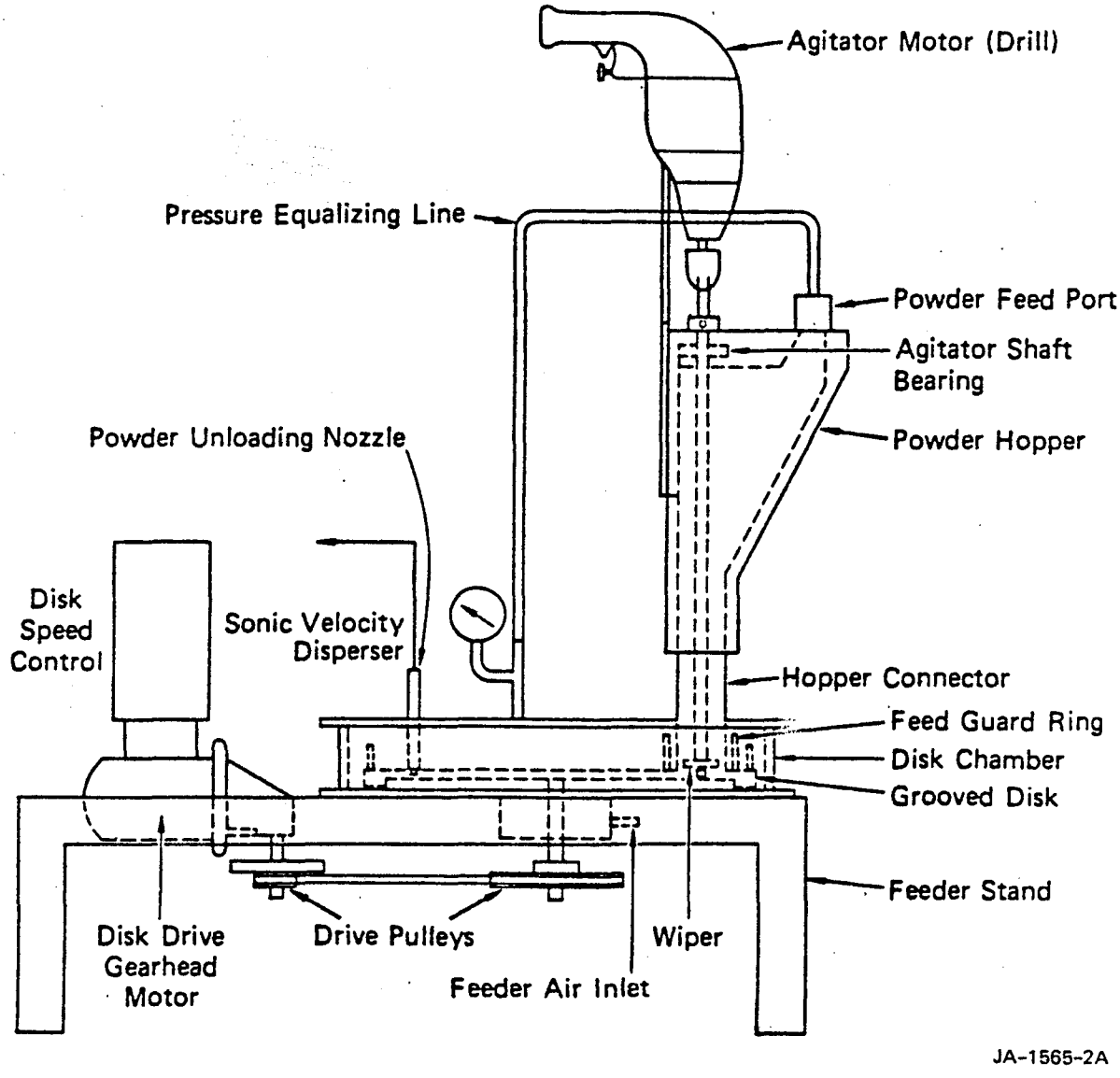


FIGURE 28 COMPONENTS OF SRI DUST FEEDER

REFERENCES

1. National Institute for Occupational Safety and Health: Criteria for a Recommended Standard ... Occupational Exposure to Crystalline Silica. DHEW (NIOSH) Publication No. 75-120, 121 pp. (1974).

2. Youden, W. J., and E. H. Steiner. 1979 Statistical Manual of the Association of Official Analytical Chemists. A.O.A.C., Arlington, Virginia.

3. Plackett, R. L., and J. P. Burman. 1946. The Design of Optimum Multifactorial Experiment. Biometrika 33:305.

4. Peters, E. T. 1976. Evaluation of the NIOSH X-ray Diffraction Method for the Determination of Free Silica in Respirable Dust. Final Report to NIOSH, Contract No. CDC-99-74-45.

5. Anderson, C., and C. Beeman. 1980. Collaborative Test of PCAM 259 for Free Silica, Phase I. Draft Interim Final Report, Contract 210-79-0059.

6. Davis, C. N. 1952. The Separation of Airborne Dust and Particles. Proc. Inst. Mech. Engrs. 1B:185-198.

7. Owen, D. B. 1965. The Power of Student's t Test. Amer. Statis. Assoc.. 60:320-333.

8. Wilhelm, E. 1954. The Physical Chemistry of the Silicates. pp. 884-886. University of Chicago Press, Chicago, Illinois.

9. Alexander, L., P. Klug, and E. Kummer. 1948. J. Appl. Phys. 19:742.

10. Edmonds, J. W., W. W. Hensley, and R. E. Guerra. 1977. Anal. Chem. 49:2196.

11. Gordon, R. L., and R. W. Harris, 1955. Nature, 169:1135.

12. Harrisons and Crosfield (Pacific), Inc., 6285 Christie Ave., Emeryville, CA 94608. (415) 658-8333.

13. California Measurements Systems, Inc., Sierra Madre, California 91024.

Appendix A

XRD METHOD; PCAM 259, FREE SILICA
(QUARTZ, CRISTOBALITE, TRIDYMITE) IN AIRBORNE DUST

DRAFT
02/28/83

SUGGESTED REVISION

FREE SILICA (QUARTZ, CRISTOBALITE, TRIDYMITE) IN AIRBORNE DUST

Measurements Research Branch

Analytical Method

Analyte:	Quartz, Cristobalite, Tridymite	Method No.:	P&CAM 259
Matrix:	Airborne dust	Range:	25-2500 $\mu g/m^3$
Procedure:	Filter collection, redeposition, X-ray diffraction	Precision:	See Section 4
Date Issued:	3/17/77		
Date Revised:	1/31/82; 2/28/83	Classification:	B (Accepted)

1. Synopsis

1.1 A known volume of air is drawn through a membrane filter to trap airborne dust.

1.2 The filters are ashed and the residue redeposited on silver membrane filters.

1.3 The filter samples are scanned by x-ray diffraction to determine the presence of free silica polymorphs (Quartz, Cristobalite, and Tridymite) and other phases which may cause matrix interference.

1.4 The mass of each free silica polymorph present is determined by measuring the diffraction peak intensity of the polymorph and of the silver filter. The mass is calculated from calibration data.

2. Working Range, Sensitivity, and Detection Limit

2.1 The range of the method is 25-2500 $\mu g/m^3$ for a 0.8 m^3 air sample. This corresponds to 20-2000 µg when the sample is pure quartz, cristobalite or tridymite. The range of the method for samples containing mixtures is dependent on the amount of interfering substances and x-ray absorbing substances present.

2.2 The detection limits for the primary and secondary diffraction peaks are 1.3 and 9.8 µg per filter for quartz, 1.7 and 13 µg per filter for cristobalite and 1.3 and 4.7 µg per filter for tridymite. For reliable quantitative measurement using any of these diffraction peaks, approximately fifteen times the detection limit amount is required.

3. Interferences

3.1 Several compounds have diffraction peaks that interfere with the major peak for quartz according to the data in the powder diffraction file (Ref. 11.6). These include micas (biotite, muscovite), potash, feldspars (microcline, plagioclase), montmorillonite, sillimanite, zircon, graphite, iron carbide, *clinoferrosillite, wollastonite, sanidine, leucite, orthoclase,* and lead sulfate. Many of these occur in the various industries where quartz is present but in a study of samples collected in 11 different industrial situations, Altree-Williams (Ref. 11.5) found no signifcant interferences. *The patterns for three forms of aluminum phosphate (JCPDS Nos. 10-423, 11-500, 20-44) are practically identical to those of quartz, cristobalite and tridymite, respectively.* Other interferences may occur for the three silica polymorphs and the three may interfere with each other. The quartz secondary and cristobalite primary peaks are close; the cristobalite secondary peak is overlapped by a quartz peak; and tridymite, if present in sufficient quantity, will interfere with all of the main (primary, secondary, and tertiary) quartz and cristobalite peaks. Silver chloride (if present on the silver filter) may interfere slightly with the primary quartz peak. The presence of interference can be verified by x-ray diffraction analysis.

3.2 If interferences are present, analytical measurements are made using a different diffraction peak of the free silica polymorph with a commensurate decrease in sensitivity and precision. When overlaps are not severe, a smaller receiving slit or chromium radiation may be used. A new calibration curve must be constructed for each of these situations.

3.3 The presence of specific elements in the sample (iron, in particular) can result in appreciable x-ray fluorescence leading to high background intensity. This situation may be circumvented by employing a diffracted beam monochromator.

3.4 The interfering effects of x-ray absorption by the sample result in attenuation of the diffracted beam and corrections must be made (see Sections 10.4 and 10.5).

3.5 *If calcite is a significant fraction of the total dust loading, loss of quartz may occur when samples are ashed in a muffle furnace. These samples may be treated to remove the calcite, as described in Section 8.4.2.*

4. Precision and Accuracy

4.1 For quartz, the relative standard deviation for a set of 75 filter standards (three operators) was determined to be approximately 20% for 20 µg per filter, 13% for 40 µg per filter and 10% for 60 or more µg per filter. The precision for cristobalite and tridymite are comparable. The precision of quartz determinations

(single operator) for foundry area samples collected simultaneously on a manifold was 9.5% at 25 µg per filter (five filters) and 14.5% at 21 µg per filter (six filters).

4.2 *A precision of 28.5% was found at the 10 µg level.*

4.3 *In a collaborative study with 15 laboratories (Ref. 11.7), for samples collected from laboratory generated aerosols using a set of matched flow orifices, the percent relative standard deviations (%RSDs) for 50 to 200 µg quartz were:*

Total error	*17%*
Intralaboratory error	*8%*
Interlaboratory error	*11%*

From 0 to 2 mg of a weakly-absorbing matrix were present with the quartz.

For samples heavily loaded with iron-oxide (0.8 mg) the intralaboratory error (%RSD) was 12%.

When samples were collected with a personal sampling pump, the total error (%RSD) was 29%. The pump error was 17%, which increased the interlaboraotry error but not the intralaboratory error.

4.4 **The average recovery was determined for nine sets of 10 samples each over the range 20-100 µg. Except for the 20 and 80 µg levels (73 and 84%, respectively), average recoveries were all greater than 90%.**

4.5 *The accuracy is dependent on how well the particle size distributions of the samples and standards are matched. For quartz, if Min-U-Sil 5 is used for standards, the method is assumed to be unbiased. Results by this method and an IR method are equivalent when used on coal mine dust or pure quartz (Ref. 11.7).*

4.6 *If a high laoding of a strong x-ray absorber, such as iron oxide, is present on the sample, the method may be biased, by as much as 25%, but the exact degree of bias is unknown.*

4.7 **The precision and accuracy of the method for cristobalite and tridymite have not been determined.**

5. Advantages and Disadvantages

5.1 The x-ray diffraction method is specific and can determine the individual polymorphs of free silica. The sensitivity of the method is equivalent to or greater than that of other known methods (infrared and colorimetric). The method is non-destructive of the analyte but the ashing step helps to eliminate organic and other volatile compounds that may interfere. The method can be automated.

5.2 The equipment is relatively expensive.

6. Apparatus

6.1 Personal Sampling Equipment. The sampling unit for respirable dust collection has the following components:

6.1.1 Ten-mm nylon cyclone.

6.1.2 Filter unit consisting of the filter media (Section 6.1.4) and appropriate three-piece cassette filter holder.

6.1.3 Personal sampling pump calibrated to ± 5% at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.1.4 Polyvinyl chloride membrane filters, 37 mm, 5 µm pore size. *Representative blank filters should be analyzed for silica interference before use. Only filters from manufacturers' lot numbers known to be interference free should be used.* (Gelman VM-1 filters are unacceptable because of the high background produced by the ash.)

6.2 Area Sampling Equipment. The sampling unit for high volume respirable dust collection has the following components:

6.2.1 Calibrated Gast 1022 vacuum pump equipped with a needle valve flow controller or equivalent.

6.2.2 HASL cyclone, one inch (Bendix No. 240 cyclone).

6.2.3 Polyvinyl chloride membrane filter, 47 mm, 1 µm pore size.

6.2.4 Filter holder.

6.3 X-ray diffraction equipment with a copper target x-ray tube. The equipment should be optimized for intensity rather than resolution.

6.4 Silver membrane filters, 25-mm diameter and 0.45 µm pore size: Selas Flotronics, Spring House, Pennsylvania 19477.

6.5 *Filtration apparatus and side arm vacuum flask. Millipore unit consisting of frit support No. XX10 02500, funnel No. XX10 02514, and clamp, or equivalent.*

6.6 Volumetric flask, 1 L.

6.7 Reagent bottles with ground glass stoppers, 1 L.

6.8 Low temperature radiofrequency *plasma* asher or muffle furnace.

6.9 Porcelain crucibles with covers for muffle furnace.

6.10 Pyrex beakers, 50 mL, *and appropriately-sized watch glasses.*

6.11 Reference specimen (mica, Arkansas stone or other stable standard) for data normalization, Section 3.4.4, Step 3.

6.12 Dessicator.

6.13 Filter storage cassettes.

6.14 Forceps.

6.15 Polyethylene wash bottle.

6.16 Microbalance.

6.17 Ultrasonic bath or probe.

6.18 Magnetic stirrer and stirring bars.

6.19 Volumetric pipets for use in preparing standards: Various sizes up to 10-mL.

6.20 Filter washing unit. If the sample filter is to be treated to remove calcite, the following components are needed:

6.20.1 PVC filter, 37 mm diameter, 0.5-μ pore size, known to be interference free.

6.20.2 25% v/v concentrated hydrochloric acid (ACS reagent grade) in distilled water.

6.21 Drying oven.

7. Reagents

ACS Analytical Reagent Grade or equivalent.

7.1 Quartz, cristobalite and tridymite standards. Min-U-Sil 5, a commercial product of Pennsylvania Glass Sand Company, Berkley Springs, West Virginia 25411, should be used for quartz.

7.2 Glue, tape or other material necessary for attaching silver filters to filter holders.

7.3 Isopropanol.

7.4 Dessicant (Drierite).

8. Procedure

8.1 Cleaning of Equipment. All glassware should be detergent washed, thoroughly rinsed with tap water followed by distilled water and dried.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative filter cassette in the line. Cyclone assemblies should be cleaned before using and a visual check for scoring of the surfaces made. Replace the cyclone if it is scored.

8.3 Collection and Shipping of Samples

8.3.1 Attach the cassette and cyclone assembly to the worker.

8.3.2 Collect an eight-hour sample at a flow rate of 1.7 liters per minute. As it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently and the sampling should be terminated at any evidence of a problem.

8.3.3 Terminate sampling after the predetermined time and note sample flow rate, collection time, date, ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.4 After sample collection, the filter cassette should be firmly sealed with plugs in both the inlet and outlet ends.

8.3.5 Carefully record sample and identify all relevant sample data.

8.3.6 With each batch of ten samples, submit one filter from the same lot of filters that was used for sample collection and which is handled in the same way as the samples except that no air is drawn through it. Label this as a blank.

8.3.7 The filter cassettes should be shipped in a suitable container designed to prevent damage in transit.

8.3.8 *Collect a bulk (settled dust) sample of* the suspected parent material of the airborne dust in a suitable container and ship with the filter samples.

8.3.9 If the laboratory needs a bulk air sample, a high volume respirable dust sample should be taken using the equipment listed under 6.2. A sample of 27,000 liters should be taken at 75 liters per minute.

8.4 Analysis of Samples

8.4.1 Obtain a qualitative x-ray diffraction scan (broad 2 θ range) of the bulk and/or high volume respirable sample to determine the presence of free silica polymorphs and any matrix interference. The expected diffraction peaks are as follows:

Mineral	2 Theta, Primary	2 Theta, Secondary
Quartz	26.66	20.85
Cristobalite	21.93	36.11
Tridymite	21.62	20.50
Silver	38.12	44.28

8.4.2 *Ashing the Samples and Blanks*

One of the following methods should be used.

1. **Low Temperature Ashing**

Using forceps, place the filter samples in 50 mL beakers and situate within the sample compartment of the low temperature asher so that the sample exposure to the plasma is optimized. The samples should be ashed for two hours at *300* watts RF power and at an oxygen flow rate of 75 mL/min, using the techniques recommended in the instrument manual. After ashing, add 15 mL of isopropanol to each beaker. *Be careful not to disturb the ash when adding alcohol.*

2. **Muffle Furnace Ashing**

If it is suspected that the samples contain a significant amount of calcite, the filters should be washed with acid, using the unit described in Section 6.5. (Otherwise proceed to the next paragraph.) Place a 25-mm glass fiber filter over the frit area, then position a 0.5 µm 37-mm PVC filter over the glass fiber filter. Clamp down the filter funnel. Add 5-mL of IPA to the funnel and check for leakage. Remove the sample filter from the cassette. Fold it in half (with the collection surface inside) then into quarters. Place this folded filter into the funnel. If necessary use a glass rod to gently force the filter to the bottom half of the funnel. Add 10-mL of HCl solution, then 5-mL IPA. Leave filter undistrubed for 4-5 minutes, then apply suction to remove the liquid. Wash down the chimney walls generously several times with IPA. Continue suction until all of the

liquid has been removed. It may be necessary to gently press the folded sample filter onto the surface of the collecting filter to make sure no liquid is trapped in the folds of the filter. Remove both filters and place in a porcelain curcible. Allow filters to completely air-dry, then proceed to ash the filters as described in the next paragraph.

Using forceps, place the filter samples in porcelain crucibles, loosely cover and place in muffle furnace. Hold for two hours at 600°C (800°C if graphite is present in the sample). After ashing, add several mL of isopropanol to the ash, scrape the cru-cible with a glass rod to loosen all particles and transfer to a 50 mL beaker. Wash the crucible several more times and add wash to beaker. Add isopropanol to the beaker to bring the volume to about 15 mL.

8.4.3 Redeposition of Residue onto Silver Filters

1. Ultrasonically agitate the beaker contents for at least three minutes. Place a watch glass over each beaker to avoid losses and cross contamination. Make a visual check of the suspension to make sure that the agglomerated particles are being broken up. Use additional ultrasonic power or agitation time as needed. Wash the underside of the watch glass with isopropanol, collecting the washings in the beaker.

2. Set aside six silver membrane filters randomly selected from the same box of filters to be used for depositing the samples. These will be used to test for sample self-absorption (Section 8.4.5).

3. Place a silver filter in the filtration apparatus and attach the chimney. Make sure that the chimney is clamped securely and evenly over the entire circumference. Pour several mL of IPA onto the filter. With no suction, very little IPA will penetrate the filter. Pour the suspension from the beaker into the chimney, and apply vacuum. During filtration, rinse the beaker several times with IPA from a wash bottle and add rinsings to funnel. Control the filtration rate to keep the liquid level in the funnel near the top during rinsing. After filtration is complete leave the vacuum on for sufficient time to produce a dry filter. Do not wash the chimney walls, or add IPA to the chimney when the liquid level is lower then 4 cm above the filter. Remove the filter with forceps, and attach it to the sample holder for XRD analysis.

8.4.4 XRD Analysis

1. Analyze the most intense diffraction peak of each free silica polymorph that is free from matrix interference by step scanning the peak and integrating the counts. Measure the background on each side of the peak for one half the time used for peak scanning and add the counts from each side for a total (average) background. The position of the background must be determined for each sample. The net count or intensity, I_q, is the difference between the peak integrated count and the total background count.

   Determine the net count, I_{Ag}, of the appropriate silver peak following the *same procedure.* Scan times should be shorter for silver filters but should be consistent throughout the method.

2. *After each unknown is scanned, determine the net count,* I_r°, *of the reference specimen. Select a convenient normalization scale factor,* N, *which is approximately numerically equivalent to the net count for the reference specimen peak. Record the value of* N *as it will be used for all standards and samples. Calculate the normalized intensity,* $\hat{I}$, *for the sample peak by multiplying the peak intensity by the ratio of the factor* N *to* I_r°. *Examples for the quartz and silver peaks are:*

$$\hat{I}_q = \frac{N}{I_r^\circ} \cdot I_q$$

$$\hat{I}_{Ag} = \frac{N}{I_r^\circ} \cdot I_{Ag}$$

   Record the normalized intensities.

   Normalizing to the reference specimen intensity permits compensation for long-term drift in the x-ray tube intensity. If experience with the XRD equipment has shown that intensity measurements are stable, the reference specimen may be run less frequently. In this case the net intensities of the silica and silver peaks (I_q and I_{Ag}) should be normalized to the average I_r° for that run.

8.4.5 Mount each of the six clean silver filters (Section 8.4.3) on the filtration apparatus and suction 5 to 10 mL of IPA through the filter. Remove, let dry, and mount on XRD holders. Determine the net count for the silver peak, I°_{Ag}, for each filter. Calculate the normalized intensities

$$\hat{I}^{\circ}_{Ag} = \frac{N}{I^{\circ}_{r}} \quad I^{\circ}_{Ag}$$

and record the $\hat{I}^{\circ}_{Ag}$.

8.4.6 For each blank, scan the same 2θ range used for the silica and silver peaks. These analyses serve only to verify that contamination of the filters has not occurred. The silica peak should be absent. The normalized intensity of the silver peak should match that of the clean silver filters (Section 8.4.5).

9. Calibration and Standardization

9.1 Preparation of Free Silica Standards

9.1.1 Min-U-Sil 5 may be used as received for quartz. Dry the powder in 110 °C oven for 1 hour, cool and store in a desiccator.

9.1.2 For cristobalite and tridymite wet sieve the standard material through a 10 μm sieve with isopropanol. Evaporate the alcohol and dry the powder in a 110°C oven. Cool the powder in a dessicator.

9.1.3 Prepare two suspensions of the standard in isopropanol by weighing approximately 10 and 50 mg of the dry powder to the nearest 0.01 mg. Quantitatively transfer each to a 1-L glass-stoppered bottle using 1.00 liter of isopropanol.

9.1.4 Disperse the powder in isopropanol by using an ultrasonic probe or bath for 20 minutes. Immediately move the flask to a magnetic stirrer with thermally insulated top, and add a stirring bar to the suspension. Be sure the solution has returned to room temperature before withdrawing aliquots.

9.1.5 Prepare a series of standard filters using the 10 and 50 mg/L suspensions. Using appropriate pipets, prepare a sufficient number of standards in triplicate to cover the analytical range (or sample range, if known). Standards at 20, 30, 50, 100, 200 and 500 μg are usually sufficient.

9.1.6 Mount a filter on the filtration apparatus. Place several mL of isopropanol on the filter surface. *Turn off the stirrer. Pick up the bottle and hand shake vigorously. Within a few seconds of setting the bottle down, remove the lid and withdraw an aliquot from the center of the suspension* Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, return all of the suspension to the bottle, rinse and dry the pipet.

Transfer the aliquot from the pipet to the filter. Keep the tip of the pipet near the surface but not submerged in the suspension.

.. Rinse the pipet with several mL of isopropanol and drain the rinse into the chimney. Repeat the rinse several more times.

Apply the vacuum and rapidly filter the suspension. Leave the vacuum on for sufficient time to dry the filter. Do not wash down the sides of the chimney after the deposit is in place since this will rearrange the material on the filter. Transfer the filter to the sample mount that is to be used in the diffractometer.

9.2 Perform step scans on the standards and reference specimen using the same conditions as those used for the samples. Using the procedure of Section 8.4.4, determine and record the normalized intensity, $\hat{I}_q^o$, for each peak measured. *The normalization factor, N, should be the same one used for samples.*

10. Calculations

10.1 Calculate the exact weights of quartz deposited on each standard filter from the concentrations of the standard suspensions and aliquot volumes. Record the weight, w, of each standard. Prepare a calibration curve by plotting $\hat{I}_q^o$ as a function of w. Poor reproducibility at any given level indicates problems in the sample preparation technique and new standards should be made. The data should lie along a straight line for low weights *(at least up to 200 µg per filter for Min-U-Sil) and the points that sho* curvature at high weights should be ignored when determining the line of best fit. *A weighted least squares (1/σ weighting) is preferable.*

10.2 Determine the initial slope, m, of the calibration curve in counts/µg. *(Alternatively, curvature can be eliminated with absorption corrections based on the mass absorption coefficient of SiO_2 - Ref. 11.1.)*

The intercept, b, of the line with the $\hat{I}_q^o$ axis

should be approximately 0. A large negative intercept indicates an error in determining the background. This may arise from incorrectly measuring the baseline or from interference by another phase at the angle of background measurement. A large positive intercept indicates an error in determining the baseline or that an impurity is included in the measured peak.

10.3 Calculate and record the average normalized intensity, average $\hat{I}^{o}_{Ag}$ from those determined for the clean silver filters (Section 8.4.5).

$$\text{ave } \hat{I}^{o}_{Ag} = \frac{\sum_{n=1}^{6} \hat{I}^{o}_{Ag,n}}{6}$$

10.4 Using the normalized intensities, $\hat{I}_{Ag}$, for the silver peaks of each sample (Section 8.4.4) and the average $\hat{I}_{Ag}$ calculated for the clean silver filters, calculate the transmittance, T, of each sample as follows:

$$T = \frac{\hat{I}_{Ag}}{\text{ave } \hat{I}^{o}_{Ag}}$$

10.5 Determine the correction factor, f(T), for each sample according to the formula:

$$f(T) = \frac{-R \ln T}{1 - T^{R}}$$

where: $R = \dfrac{\sin \theta_{Ag}}{\sin \theta_{q}}$

and θ_{Ag} and θ_{q} are the angles θ (not 2θ) of the silver and quartz peaks. Table I lists f(T) values for T values from 0.5 to 1.0 for common $2\theta_{q}$ and $2\theta_{Ag}$ combinations.

10.6 Calculate the weight in micrograms of the quartz in each sample:

$$w(\mu g) = \left(\frac{\hat{I}_{q} - b}{m}\right) \times f(T)$$

10.7 For personal sampling pumps with rotameters only, the following correction should be made:

$$V = f \cdot t \left[\frac{P_1 \ T_2}{P_2 \ T_1}\right]^{1/2}$$

where: V = corrected air volume (L)
f = sample flow rate (Lpm)
t = sampling time (min)
P_1 = pressure during calibration of sampling pump (mm Hg)
P_2 = pressure of air sampled (mm Hg)
T_1 = temperature during calibration of sampling pump (^oK)
T_2 = temperature of air sampled (^oK)

10.8 Calculate the airborne concentration of silica dust in micrograms per cubic meter:

$$SiO_2\ (\mu g/m^3) = \frac{1000\ w}{V}$$

11. References

11.1 Leroux, J. and C. Powers, "Direct X-Ray Diffraction Quantitative Analysis of Quartz in Industrial Dust Films Deposited on Silver Membrane Filters," Occup. Health Rev. 21:26, 1970.

11.2 *Williams, D.D., "Direct Quantitative Diffractometric Analysis," Anal. Chem. 31:1841, 1959.*

11.3 Bumsted, H. E., "Determination of Alpha-Quartz in the Respirable Portion of Airborne Particulates by X-Ray Diffraction," Am. Ind. Hyg. Assoc. J. 34:150, 1973.

11.4 Peters, E. T., "Evaluation of the NIOSH X-Ray Diffraction Method for the Determination of Free Silica in Respirable Dust," Final Report of Contract CDC-99-74-51, May 1976.

11.5 Altree-Williams, S., J. Lee and N. V. Mezin, "Quantitative X-Ray Diffractometry on Respirable Dust Collected on Nuclepore Filters," Ann. Occup. Hyg. 20, 109-126, 1977.

11.6 Joint Committee for Powder Diffraction Standards, International Centre for Diffraction Data, 1601 Park Lane, Swarthmore, Pennsylvania 19081.

11.7 *Anderson, C. C., "Collaborative Tests of Two Methods for Developing Free Silica in Airborne Dust," Final Report of Contract 210-79-0059, February 1983.*

Revised 2/28
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Table 1. Commonly Used Correction Factors
Silica/Silver Peaks, Degrees Two Theta

Silica	26.66	26.66	20.83	20.83	21.93	21.93	21.62	21.62
Silver	38.12	44.28	38.12	44.28	38.12	44.28	38.12	44.28
T	f(T)	f(T)	f(T)	f(T)	f(T)	f(T)	f(T)	f(T)
1.00	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.99	1.0071	1.0082	1.0091	1.0105	1.0087	1.0100	1.0088	1.0101
0.98	1.0144	1.0166	1.0184	1.0212	1.0174	1.0201	1.0177	1.0204
0.97	1.0217	1.0251	1.0278	1.0321	1.0264	1.0305	1.0268	1.0309
0.96	1.0292	1.0337	1.0373	1.0432	1.0355	1.0410	1.0360	1.0416
0.95	1.0368	1.0425	1.0470	1.0544	1.0447	1.0517	1.0453	1.0524
0.94	1.0445	1.0514	1.0569	1.0659	1.0541	1.0625	1.0548	1.0747
0.93	1.0523	1.0605	1.0670	1.0776	1.0636	1.0736	1.0645	1.0747
0.92	1.0602	1.0697	1.0772	1.0894	1.0733	1.0849	1.0743	1.0861
0.91	1.0683	1.0791	1.0876	1.1015	1.0831	1.0963	1.0844	1.0977
0.90	1.0765	1.0886	1.0982	1.1138	1.0932	1.1080	1.0945	1.1096
0.89	1.0848	1.0983	1.1089	1.1264	1.1034	1.1199	1.1049	1.1216
0.88	1.0933	1.1081	1.1199	1.1392	1.1137	1.1320	1.1154	1.1339
0.87	1.1019	1.1181	1.1311	1.1522	1.1243	1.1443	1.1261	1.1464
0.86	1.1106	1.1283	1.1424	1.1654	1.1350	1.1568	1.1370	1.1592
0.85	1.1195	1.1387	1.1540	1.1790	1.1460	1.1696	1.1481	1.1722
0.84	1.1286	1.1493	1.1657	1.1927	1.1571	1.1827	1.1595	1.1854
0.83	1.1378	1.1600	1.1777	1.2068	1.1685	1.1959	1.1710	1.1989
0.82	1.1471	1.1709	1.1899	1.2211	1.1800	1.2095	1.1827	1.2126
0.81	1.1566	1.1821	1.2024	1.2357	1.1918	1.2232	1.1946	1.2266
0.80	1.1663	1.1934	1.2150	1.2506	1.2038	1.2373	1.2068	1.2409
0.79	1.1762	1.2050	1.2280	1.2658	1.2160	1.2516	1.2192	1.2555
0.78	1.1863	1.2168	1.2411	1.2812	1.2284	1.2663	1.2319	1.2703
0.77	1.1965	1.2288	1.2546	1.2971	1.2411	1.2812	1.2447	1.2855
0.76	1.2069	1.2410	1.2683	1.3132	1.2540	1.2964	1.2579	1.3009
0.75	1.2175	1.2535	1.2822	1.3297	1.2672	1.3199	1.2713	1.3167
0.74	1.2283	1.2662	1.2965	1.3465	1.2806	1.3278	1.2849	1.3328
0.73	1.2394	1.2792	1.3110	1.3637	1.2944	1.3440	1.2989	1.3493
0.72	1.2506	1.2924	1.3259	1.3812	1.3084	1.3605	1.3131	1.3661
0.71	1.2621	1.3059	1.3410	1.3991	1.3226	1.3774	1.3276	1.3883
0.70	1.2738	1.3197	1.3565	1.4174	1.3372	1.3946	1.3424	1.4008
0.69	1.2857	1.3337	1.3723	1.4362	1.3521	1.4122	1.3576	1.4187
0.68	1.2979	1.3481	1.3885	1.4553	1.3673	1.4303	1.3730	1.4370
0.67	1.3103	1.3628	1.4050	1.4749	1.3829	1.4487	1.3888	1.4558
0.66	1.3230	1.3777	1.4218	1.4949	1.3987	1.4675	1.4050	1.4749
0.65	1.3359	1.3931	1.4390	1.5154	1.4150	1.4868	1.4215	1.4945
0.64	1.3491	1.4087	1.4567	1.5363	1.4316	1.5064	1.4383	1.5145
0.63	1.3626	1.4247	1.4747	1.5578	1.4485	1.5266	1.4556	1.5350
0.62	1.3765	1.4411	1.4931	1.5797	1.4659	1.5472	1.4732	1.5560
0.61	1.3906	1.4578	1.5120	1.6022	1.4836	1.5684	1.4913	1.5775
0.60	1.4050	1.4749	1.5314	1.6252	1.5018	1.5900	1.5098	1.5995

Silica	26.66	26.66	20.83	20.83	21.93	21.93	21.62	21.62
Silver	38.12	44.28	38.12	44.28	38.12	44.28	38.12	44.28
T	f(T)	f(T)	f(T)	f(T)	f(T)	f(T)	f(T)	f(T)
0.59	1.4198	1.4925	1.5511	1.6488	1.5204	1.6122	1.5287	1.6221
0.58	1.4349	1.5104	1.5714	1.6730	1.5394	1.6349	1.5481	1.6452
0.57	1.4504	1.5288	1.5922	1.6978	1.5590	1.6582	1.5679	1.6689
0.56	1.4662	1.5476	1.6135	1.7233	1.5790	1.6820	1.5883	1.6932
0.55	1.4824	1.5670	1.6353	1.7494	1.5995	1.7065	1.6092	1.7181
0.54	1.4991	1.5868	1.6577	1.7762	1.6205	1.7317	1.6306	1.7437
0.53	1.5161	1.6071	1.6807	1.8037	1.6421	1.7575	1.6525	1.7699
0.52	1.5336	1.6279	1.7043	1.8319	1.6642	1.7840	1.6751	1.7969
0.51	1.5515	1.6493	1.7285	1.8609	1.6870	1.8112	1.6982	1.8246
0.50	1.5699	1.6713	1.7534	1.8908	1.7103	1.8391	1.7220	1.8531

Appendix B

IR METHOD; INFRARED DETERMINATION OF QUARTZ IN RESPIRABLE COAL MINE DUST

DRAFT
02/28/83

SUGGESTED REVISION
OF THE METHOD FOR
INFRARED DETERMINATION OF QUARTZ
IN RESPIRABLE COAL MINE DUST

Analyte:	*Quartz*	Method No.:	
Matrix:	*Airborne Coal Mine Dust*	Range:	10-250 µg/m
Procedure:	Filter collection, redeposition, infrared spectrometry		
Date Issued:	*1981*	Precision:	See Section 4
Date Revised:	*2/28/83*	Classifications:	*B*

1. Synopsis

1.1 A known amount of air is drawn through a 10-mm nylon cyclone and a preweighed dust cassette containing a PVC filter.

1.2 The dust cassette is reweighed and the PVC filter is removed and ashed in a low temperature plasma asher or a muffle furnace, and the ash is put into suspension in IPA. The alcohol suspension of dust is filtered through an IR transparent filter.

1.3 The weight of quartz is determined by measuring the height of the infrared quartz peak at 800 cm^{-1} and converting this to weight based on calibration curve data. The percent of quartz can be calculated from quartz weight and sample weight.

2. Working Range, Sensitivity, and Detection Limit

2.1 The range of this method is 10 to *250* µg of quartz, which is 10-250 $\mu g/m^3$ of air for an 8-hour, 2-L/min sample. The ideal sample range is 0.5 to 2 mg *of total dust.*

2.2 The detection limit is 10 µg of quartz.

3. Interferences

3.1 Cristobalite, tridymite and amorphous silica all have absorbance peaks at 800 cm^{-1}. None of these, however, have been detected in coal mine dust.

3.2 Kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), if present in sufficient quantity, may interfere. Coal mine dust frequently contains a significant fraction of kaolinite, which is not destroyed when samples are ashed at low

temperature. Since kaolinite has an absorption band at the same frequency as quartz, its presence will cause an overestimation of the quartz amount. However, kaolinite also absorbs infrared radiation at 915 cm^{-1} and therefore a correction may be made. If samples are ashed in a muffle furnace the kaolinite absorbance band at Ca. 800 cm^{-1} disappears and no correction is required.

3.3 If calcite is a significant fraction of the total dust loading, loss of quartz may occur when samples are ashed in a muffle furnace. These samples may be treated to remove the calcite, as described in Section 8.4.2. Calcite is used as a dusting agent in coal mines, and has been found frequently in coal mine dust samples.

3.4 Muscovite does not interfere.

4. Precision and Accuracy

4.1 Precision for pure quartz samples is about 5 percent in the 100 to 500 µg range (Ref. 11.1). Precision for actual samples is not as good and depends on sample size and ashing technique.

4.2 *In a collaborative study with 15 laboratories participating (Ref. 11.2) the total errors, and interlaboratory and intralaboratory errors were found to be dependent on the type of samples. For samples collected from laboratory-generated aerosols, using a set of matched flow orifices, the lower and upper limits of the percent relative standard deviation (%RSD) over the range of 60 to 150 µg quartz, were:*

	Lower	Upper
Total error	*13%*	*22%*
Intralaboratory error	*7%*	*10%*
Interlaboratory error	*8%*	*14%*

The lower limit applies to samples containing up to 1 mg coal mine dust, with less than 2% kaolinite; the upper limit was found for samples with 2.0 mg coal mine dust or a lower amount of coal mine dust with more than a few percent kaolinite.

The total error was increased to 36% to 40% (lower and upper range) when personal sampling pumps were used to collect the samples. The pump error increased interlaboratory error.

4.3 *Accuracy is dependent on how well the particle size distributions of standards and samples are matched. When using Min-U-Sil 5 for calibration, the method is assumed to be unbiased. Reuslts by this method and XRD method are equivalent (Ref. 11.2).*

5. Advantages and Disadvantages

5.1 The working range extends lower than either the x-ray diffraction method or the Talvitie method.

5.2 The filters used for redeposit are compatible with both infrared and x-ray analytical techniques.

5.3 The equipment is less expensive than that for x-ray diffraction.

6. Apparatus

6.1 Sampling apparatus:

6.1.1 Ten mm nylon cyclone.

6.1.2 Preweighed filter unit consisting of the filter media (Section 6.1.4) and appropriate cassette filter holder.

6.1.3 Personal sampling pump calibrated to ±5% at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.1.4 Polyvinyl chloride membrane filter, 37 mm, 5-µm pore size, such as Mine Safety Appliances FWSB. Representative number of blanks should be analyzed before sampling to ascertain that filters are interference free.

6.2 Double-beam infrared spectrophotometer.

6.3 Sample holders for infrared instrument. Metal, preferably steel, plates with center hole to match diameter of sample deposit. Small ring magnets can be used to hold filter in position on the plate.

6.4 Apparatus for redepositing samples and preparing standards.

6.4.1 Filters for redeposit. Gelman DM450, vinyl chloride-acrylonitrile copolymer membrane, 47-mm diameter, 0.45-µm pore size, Gelman Instrument Company, Ann Arbor, Michigan 48106.

6.4.2 Glass fiber filters, 25-mm diameter, for backup during filtration.

6.4.3 Filtration apparatus for redepositing sample after ashing, consisting of fritted support (Millipore XX 1002502) and side arm vacuum flask.

6.4.4 Special funnels. To increase the sensitivity of the method, a special filtration funnel is used. This is similar to the Millipore XX 1002514 but with a smaller internal diameter of 1 cm. This may be made of *glass with a bakelite base.*

6.5 Apparatus for treating filters to remove calcite (required only when using a muffle furnace).

6.5.1 Filtration apparatus. Fritted support and side arm vacuum flask (same as 6.4.3 above) and glass funnel, 15 ml capacity (Millipore XX1002514 or equivalent). Funnel I.D. should be approximately 1.6 cm.

6.5.2 Hydrochloric acid, 25% v/v, prepared from ACS reagent grade acid and distilled water.

6.5.3 Glass fiber filters, 25-mm diameter for backup during filtration (same as 6.4.2).

6.5.4 Filters to recollect residue. PVC filter, 37-mm, 0.5 µm pore size.

6.6 Low temperature radio frequency asher (LTA) or muffle furnace.

6.7 Ultrasonic bath.

6.8 Beakers, 50 mL

6.9 Porcelain crucibles (with covers), 10 mL, for muffle furance.

6.10 Microbalance. Cahn electrobalance or equivalent.

6.11 Analytical balance, Mettler H64 or equivalent.

6.12 Desiccator cabinet.

6.13 Magnetic stirrer, and stirring bars.

6.14 Reagent bottles with ground glass stopper, 500 mL.

6.15 Tweezers, stainless steel, flat end.

6.16. Plastic Petri dishes for 47-mm diameter filters. Millipore PD1504100 or equivalent.

6.17 Polyethylene wash bottles.

6.18 Metal spatulas.

6.19 Serological pipets. Miscellaneous sizes as required.

6.20 Lighted viewing box (optional).

7. Reagents

7.1 Isopropanol (IPA), ACS reagent grade

7.2 Quartz for standard samples. Min-U-Sil 5, a commercial product of Pennsylvania Glass Sand Company, Berkeley Springs, West Virginia 25411

7.3 Kaolinite for standard samples. A Georgia Kaolin product, sold under the name "Hydrite UF." (Not required if a muffle furnace is used to ash samples.)

8. Procedure

8.1 All glassware should be detergent or acid washed and thoroughly rinsed first with distilled H_2O and then with isopropanol. These should be dried in a dust-free area.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative filter cassette in the line. Cyclone assemblies should be cleaned before using and a visual check for scoring of the surfaces made. Replace the cyclone if it is scored.

8.3 Collection and Shipping of Sample

8.3.1 Filters should be preweighed to the nearest 0.01 mg.

8.3.2 Attach the cassette and cyclone assembly to the worker.

8.3.3 Collect an 8-hour sample at a flow rate of 2.0 L/min. As it is possible for filters to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently and the sample should be terminated at any evidence of a problem.

8.3.4 Terminate sampling after the predetermined time and note sample flow rate, collection time, date, ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.5 After sample collection, the filter cassette should be firmly sealed with plugs in both the inlet and outlet ends.

8.3.6 With each batch of ten samples, submit one filter from the same lot of filters that was used for sample collection and which is handled in the same way as the samples except that no air is drawn through it. Label this as a blank.

8.3.7 The filter cassettes should be shipped in a suitable container designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 The filters should be reweighed under conditions identical to those for preweighing. The difference is the sample weight, W (mg).

8.4.2 Ashing the Samples and Blanks

One of the following methods should be used.

1. Low Temperature Ashing

Using forceps, place the filter samples in 50 mL beakers and situate within the sample compartment of the low temperature asher so that the sample exposure to the plasma is optimized. The samples should be ashed for two hours at 300 watts RF power and at an oxygen flow rate of 75 mL/min, using the techniques recommended in the instrument manual. After ashing, add 15 mL of isoporpanol to each beaker.

2. Muffle Furnace Ashing

If it is suspected that the samples contain a significant amount of calcite (greater than 20% of the total dust loading), the filters should be washed with acid, using the unit described in Section 6.5. (Otherwise proceed to the next paragraph.) *Place a 25-mm glass fiber filter over the frit area, then position a 0.5 µm 37-mm PVC filter over the glass fiber filter. Clamp down the filter funnel. Add 5-ml of IPA to the funnel and check for leakage. Remove the sample filter from the cassette. Fold it in half (with the collection surface inside) then into quarters. Place this folded filter into the funnel. If necessary use a glass rod to gently force the filter to the bottom half of the funnel. Add 10-ml of HCl solution, then 5-ml IPA. Leave filter undisturbed for 4-5 minutes, then apply suction to remove the liquid. Wash down the chimney walls generously several times with IPA. Continue suction until all of the liquid has been removed. It may be necessary to gently press the folded sample filter onto the surface of the collecting*

filter to make sure no liquid is trapped in the folds of the filter. Remove both filters and place in a porcelain crucible. Allow filters to completely air-dry, then proceed to ash the filters as described in the next paragraph.

Using forceps, place the filter samples in porcelain crucibles, loosely cover and place in muffle furnace. Hold for two hours at 600°C. After ashing, add several mL of isopropanol to the ash, scrape the crucible to loosen all particles and transfer to a 50 mL beaker. Wash the crucible several more times and add wash to beaker. Add isopropanol to the beaker to bring the volume to about 15 mL.

8.4.3 Redeposition of sample residue. Use the apparatus described in Section 6.4

1. With slight vacuum applied, place a glass fiber filter on the fritted base.

2. Cut a 47-mm DM450 filter in half. Superimpose one half on the other, glossy sides down, and place on the glass fiber filter. The lower half of the DM450 serves as a treated blank and is used in the reference beam of the infrared spectrometer. (See Section 8.4.4.)

3. Position filter funnel, apply clamp and turn off vacuum. Add several ml of IPA to the funnel. (Before proceeding, check that the funnel is securely and uniformly clamped.)

4. Place 50-mL beakers containing dust slurry into ultrasonic bath for at least 30 seconds to insure homogenous dispersion.

5. Remove a beaker, wipe excess water from the outside, transfer slurry to filter funnel and reapply vacuum.

6. During filtration, rinse the beaker twice with alcohol to remove all dust and add rinsings to funnel. Control the filtration rate to keep the liquid near the funnel top during rinsing to avoid disturbing the deposit.

7. When the depth of liquid in funnel reaches about 4 cm above the filter, gently rinse inside of funnel with alcohol and complete filtration.

8. After filtration is complete, remove the clamp and lift off the funnel, taking care not to disturb the deposit. Release the vacuum.

9. The deposit area can be defined by a few marks around the circumference, using a pencil or scriber. This is particularly useful for standards or light-colored samples.

10. Place the DM450 filter halves in Petri dishes and allow to air dry.

8.4.4 Infrared Analysis

1. Set appropriate instrument conditions, such as scan time, slit width, time constant, etc.

2. Place the dry DM450 filter half containing the dust deposit on a holder. Center the deposit over the hole in the holder and secure the filter with a magnet. Use a lighted viewing box, if necessary. Insert the sample into the sample beam of the spectrophotometer.

3. Place the other half of the DM450 filter on another holder, secure with a magnet, and insert it into the reference beam. Note: For best precision the reference filter should be half of the same DM450 filter which contains the redeposit; however, for routine analysis the same alcohol-treated blank can be used for all filters with the same batch number.

4. Run an infrared scan, using linear absorbance mode, from 1000 to 650 cm^{-1}.

5. Draw an appropriate baseline *under the absorbance band at 800 cm^{-1}* from *approximately* 820 to 670 cm^{-1}. Measure and record the absorbance at 800 cm^{-1}, baseline to maximum, in absorbance units.

6. If the sample was ashed at low temperature, the presence of kaolinite will be indicated by an absorption band with a maximum at 915 cm^{-1}. Draw an appropriate baseline *under this band* from *approximately* 1000 to 840 cm^{-1}. Measure and record the absorbance at 915 cm^{-1}, baseline to maximum.

7. Perform analyses of blanks. Results should be examined to check for contamination.

9. Calibration and Standards

9.1 Kaolinite

9.1.1 Prepare a suspension of kaolinite in isopropanol at a concentration of about 100 µg/mL. Weigh out 50.00 ± 0.01 mg of dried kaolinite, quantitatively transfer to a 500-mL volumetric flask, and dilute to volume with IPA. Disperse the kaolinite by placing the flask in an ultrasonic bath for 30 to 45 minutes and transfer to a magnetic stirrer.

9.1.2 Kaolinite standards should cover an analytical range of 100 to *600* µg per filter.

9.1.3 Kaolinite standards. *Use the apparatus described in Section 6.4. Position glass fiber filter and DM450 filter as described in Section 8.4.3. After chimney is clamped into position, add 5 mL of IPA through the funnel.* Withdraw an aliquot of the kaolinite suspension from the center of the flask. Draw liquid to the mark, but do not attempt to adjust volume by draining pipette. Carefully wipe the outside of the pipette and drain the suspension into the filter funnel. Rinse down the inside wall of the pipette with IPA, draining the washings into the filter funnel. Apply vacuum. *Complete preparation of the kaolinite standard as described in Section 8.4.3.*

9.1.4 Perform an IR scan from 1000 to 650 cm^{-1}. Measure the height of the bands, at both 915 cm^{-1} and 800 cm^{-1}. Draw baselines similar to those drawn for samples.

9.1.5 Prepare a graph with absorbance at 915 cm^{-1} as ordinate versus absorbance at 800 cm^{-1} as abscissa. Plot a point for each standard. Use as many data points as possible (at least 5 or 6 different kaolinite concentrations). If possible, generate the correction curve data on the same day that coal mine dust samples are ashed, since curve parameters vary somewhat from day to day. A curve through the points should be linear and pass through the origin.

9.2 Quartz

9.2.1 Prepare a suspension of quartz in isopropanol at a concentration of about 15 µg/mL. Weigh out 7.50 ± 0.01 mg of Min-U-Sil 5, quantitatively transfer to a 500-mL volumetric flask, and dilute to volume with IPA. Disperse the quartz by placing the flask in an ultrasonic bath for 30 to 45 minutes then transfer to a magnetic stirrer. Continue stirring *at a slow rate* while preparing standards.

9.2.2 Quartz standards should cover an analytical range of 15 to 250 µg per filter.

9.2.3 Quartz standards. Use appropriate pipettes to cover specified concentration range. Mount a DM450 filter in the filtration apparatus described in Section 6.4 and add 5 mL of IPA through the funnel. Withdraw an aliquot of the quartz suspension from the center of the flask. Draw liquid to the mark, but do not attempt to adjust volume by draining pipette. Carefully wipe the outside of the pipette, then drain the suspension into the filter funnel. Rinse down the inside wall of the pipette with a few mL of IPA, draining the washings into the filter funnel. Apply vacuum and prepare the standard as described in Section 8.4.3.

9.2.4 Perform an IR scan from 1000 to 650 cm^{-1}. Measure the absorbance at 800 cm^{-1}.

9.2.5 Construct a standard curve of absorbance at 800 cm^{-1} versus microgram of quartz/filter. The curve should be linear and pass through the origin.

10. Calculations

10.1 Correction for kaolinite. Using the sample absorbance at 915 cm^{-1}, refer to the kaolinite curve (Section 9.1.5) to find the absorbance at 800 cm^{-1} due to kaolinite. Subtract this amount from the sample absorbance at 800 cm^{-1}. Use this corrected value in Section 10.2.

10.2 If the correction for kaolinite is not required, use the absorbance at 800 cm^{-1} from Section 8.4.4. Refer to the quartz calibration curve to find the weight of quartz, w (µg). Since the deposition area of standards is the same as the samples, a correction for area is not necessary.

10.3 Calculate the percent quartz by dividing the weight of quartz w (µg), by the total sample weight W (mg). Multiply by 10^{-1} to correct for differences in units.

$$\% \text{ quartz} = \frac{w\ (\mu g)}{W\ (mg)} \cdot 10^{-1}$$

11. References

11.1 Freedman, R. W., S. Z. Toma, and H. W. Lang, "On Filter Analysis of Quartz in Respirable Coal Dust by Infrared Absorption and X-Ray Diffraction," Am. Ind. Hyg. Assoc. J., 35:411, 1974.

11.2 Anderson, C. C., "Collaborative Tests of Two Methods for Determining Free Silica in Airborne Dust," Final Report of Contract 210-79-0059, February 1983.