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April 13, 1976

Mr. Doug Jones
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Dear Doug:

This is sent to you at the request of Jack Walsh.

Best regards,

Harry

H. B. Rhodes
Technology Manager

HBR:cjb
Enclosure

CC: Mr. J. E. Walsh

NIOSH RECOMMENDED STANDARD -

OCCUPATIONAL EXPOSURE TO CRYSTALLINE SILICA

On November 11, 1974, the National Institute for Occupational Safety and Health (NIOSH) transmitted their recommended standard for occupational exposure to crystalline silica to OSHA. OSHA will now consider these recommendations and the supporting evidence in the Criteria Document and publish a proposed standard in the Federal Register. Written and oral testimony on the proposed regulations will be received by OSHA and a final version of the regulation will then be promulgated. This procedure could easily take a year or more.

The proposed standard is intended to protect the worker from "adverse effects of silica exposure for up to a 10-hour workday, 40-hour workweek, over a working lifetime." Crystalline silica includes the common minerals, quartz, tridymite, and cristobalite, plus microcrystalline silica and also materials containing minute grams of free silica cemented together with amorphous silica. These include tripoli, flint, chalcedony, agate, onyx, and silica flour. Amorphous silica itself is not included.

An allowable limit of 50 micrograms per cubic meter for a full shift time-weighted average is recommended. This is approximately one half of the limit presently in force.

"Exposure to free silica" would be clearly defined as exposure to levels more than 25 micrograms per cubic meter. The regulations would not apply below this level.

Medical examinations, including X-rays and breathing function tests, would be required before exposure to free silica and at least every three years thereafter. Records must be kept for 30 years after termination of employment.

Warning signs would be required at the approaches to and in the work areas where there is a "potential exposure to free silica." Warning labels would be required for all new materials, mixtures, and other products containing more than 5% free silica. A material safety data sheet would be necessary for any product or material containing free silica.

Engineering controls would be mandated to maintain the dust levels below the prescribed level. Exceptions would be made for places where a variance has been granted, for the interim period while controls are being implemented, where levels cannot be met, for certain nonroutine operations, and emergencies. For these exceptions, various types of respirators, depending on the exposure level, are prescribed.

Employees exposed or to be exposed to free silica would be required to receive detailed instruction on the hazards and how to handle the materials safely. The increased risk due to smoking must be described.

A series of work practices including substitution, moisture for dust suppression, ventilation, and recommended housekeeping procedures would be specified. It is recommended that "sand" blasting with materials containing more than 1% silica be prohibited.

Very extensive monitoring would be required for areas where workers are exposed to free silica. Complete records must be maintained for 30 years.

Sampling and analytical procedures are specified in detail. The main tool is X-ray diffraction.

NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH CRITERIA DOCUMENT RECOMMENDATIONS FOR A CRYSTALLINE SILICA STANDARD

The National Institute for Occupational Safety and Health (NIOSH) recommends that employee exposure to crystalline silica in the workplace be controlled by adherence to the following sections. The standard is designed to protect the health and safety of workers for up to a 10-hour workday, 40-hour workweek, over a working lifetime. Compliance with the standard should prevent adverse effects of crystalline silica on the health and safety of workers. The standard is measurable by techniques that are valid, reproducible, and available to industry and government agencies and are attainable with existing technology. The criteria and the standard recommended in this document will be subject to review and revision as necessary.

Crystalline silica, hereafter referred to in this document as free silica, is defined as silicon dioxide (SiO_2). "Crystalline" refers to the orientation of SiO_2 molecules in a fixed pattern as opposed to a nonperiodic, random molecular arrangement defined as amorphous. The three most common crystalline forms of free silica encountered in industry are quartz, tridymite, and cristobalite. Micro- and cryptocrystalline varieties of free silica, also included in the recommended standard, are composed of minute grains of free silica cemented together with amorphous silica and include tripoli, flint, chalcedony, agate, onyx, and silica flour. Other forms of free silica which, upon analysis, are found to have a crystalline structure as part of their composition are also subject to the recommended standard.

"Exposure to free silica" means exposure of the worker to an airborne concentration of free silica greater than half of the recommended environmental level in the workplace. Worker exposure at lower environmental concentrations will not require adherence to the following sections.

Section 1 — *Environmental (Workplace Air)*

(a) Concentration

Occupational exposure shall be controlled so that no worker is exposed to a time-weighted average (TWA) concentration of free silica greater than 50 micrograms per cubic meter of air (50 ug/cu m; 0.050 mg/cu m) as determined by a full-shift sample for up to a 10-hour workday, 40-hour workweek.

(b) Sampling, Calibration, and Analysis

Exposure to free silica shall be determined by a personal (breathing zone) sample.

Procedures for sampling, calibration of equipment, and analysis of environmental samples shall be as provided in Appendices I and II, or by methods show to be equivalent in sensitivity, accuracy, and precision to the method specified.

Section 2 — *Medical*

(a) Medical examinations shall be made available to all workers subject to "exposure to free silica" prior to employee placement and at least once each 3 years thereafter. Examinations shall include as a minimum:

(1) A medical and occupational history to elicit data on worker exposure to free silica and signs and symptoms of respiratory disease.

(2) A chest reentgenogram (posteroanterior 14 inches by 17 inches or 14 inches by 14 inches) classified according to the 1971 ILO International Classification of Radiographs of Pneumoconioses. [ILO U/C International Classification of Radiographs of Pneumoconioses 1971, Occupational Safety and Health Series 22 (rev). Geneva, International Labor Office, 1972]

(3) Pulmonary function tests including forced vital capacity (FVC) and forced expiratory volume at one second (FEV 1) to provide a baseline for evaluation of pulmonary function and to help determine the advisability of the workers using negative- or positive-pressure respirators. It should be noted that pulmonary function tests may vary significantly in various ethnic groups. For example, in black persons, the test values for the FVC should be divided by 0.85 before the percentage value is compared with normal figures.

(4) Body weight.

(5) Height.

(6) Age.

(7) Initial medical examinations for presently employed workers shall be offered within 6 months of the promulgation of a standard incorporating these recommendations.

(b) Medical Management

An employee with or without roentgenographic evidence of silicosis who has respiratory distress and/or pulmonary functional impairment should be fully evaluated by a physician qualified to advise the employee whether he should continue working in a dusty trade.

(c) These records shall be available to the medical representatives of the Secretary of Health, Education, and Welfare, of the Secretary of Labor, of the employee or former employee and of the employer.

(d) Medical records shall be maintained for at least 30 years following the employee's termination of employment.

Section 3 — *Labeling (Posting)*

(a) The following warning shall be posted to be readily visible at or near entrances or accessways to work areas where there is potential exposure to free silica.

WARNING!
FREE SILICA WORK AREA
Unauthorized Persons Keep Out

(b) The following warning shall be posted in readily visible locations in any work area where there is potential exposure to free silica.

WARNING!
FREE SILICA WORK AREA
Avoid Breathing Dust
May Cause Delayed Lung Injury (Silicosis)

The posting required under sections 3 (a) and 3 (b) shall be printed both in English and in the predominant language of non-English-speaking workers, unless they are otherwise trained and informed of the hazardous areas. Illiterate workers shall receive such training.

(c) The following warning label, in addition to or in combination with labels required by other statutes, regulations, or ordinances, shall be affixed to all new materials, mixtures, and other products containing more than 5% free silica, or to their containers.

WARNING!
CONTAINS FREE SILICA
DO NOT BREATHE DUST
May Cause Delayed Lung Injury (Silicosis)

Section 4 — *Personal Protective Equipment and Work Clothing*

Engineering controls shall be used to maintain free silica dust exposures below the prescribed limit. Subsection (a) shall apply whenever a variance from the standard recommended in Section 1 is granted under provisions of the Occupational Safety and Health Act, or in the interim period during the application for a variance. When the limits of exposure to free silica prescribed in paragraph (a) of Section 1 cannot be met by limiting the concentration of free silica in the work environment, an employer must utilize, as provided in subsection (a) of this section, a program of respiratory protection to effect the required protection of every worker exposed.

(a) Respiratory Protection

Appropriate respirators, as prescribed in Table I-1, shall be provided and used when a variance has been granted to allow respirators as a means of control of exposure to routine operations and while the application is pending. Administrative controls may also be used to reduce exposure. Respirators shall also be provided and used for nonroutine operations (occasional brief exposures above the environmental standard and for emergencies); however, for these instances a variance is not required but the requirements set forth below continue to apply. Appropriate respirators as described in Table I-1 shall only be used pursuant to the following requirements:

(1) For the purpose of determining the type of respirator to be used, the employer shall measure the atmospheric concentration of free silica in the workplace when the initial application for variance is made and thereafter whenever process, worksite, climate, or control changes occur which are likely to affect the free silica concentration. This requirement shall not apply when only atmosphere-supplying positive pressure respirators are used. The employer shall ensure that no worker is exposed to free silica in excess of the stand because of improper respirator selection, fit, use, or maintenance.

(2) Employees experiencing breathing difficulty while using respirators shall be evaluated by a physician to determine the ability of the worker to wear a respirator.

(3) A respiratory protective program meeting the requirements of Section 1910.134 of the Occupational Safety and Health Standards shall be established and enforced by the employer. [29 CFR 1910.134 published in the *Federal Register*, vol 39, page 23671, dated June 27, 1974, as amended]

(4) The employer shall provide respirators in accordance with Table I-1 and shall ensure that the employee uses the appropriate respirator.

(5) Respiratory protective devices in Table I-1 shall be those approved either under 30 CFR 11, published March 25, 1972, or under the following regulations:

(A) Filter-type dust, fume, and mist respirators — 30 CFR 14 (Bureau of Mines Schedule 21B)

(B) Supplied air respirator — 30 CFR 12 (Bureau of Mines Schedule 19B)

(6) A respirator specified for use in higher concentrations of free silica may be used in atmospheres of lower concentrations.

(7) Employees shall be given instruction on the use of respirators assigned to them, on cleaning respirators, and on testing for leakage.

TABLE I-1

REQUIREMENTS FOR RESPIRATOR USAGE AT CONCENTRATIONS ABOVE THE STANDARD

Concentrations of Free Silica in Multiples of the Standard	Respirator Type*
Less than or equal to 5x	Single use (valveless type) dust respirator.
Less than or equal to 10X	Quarter or half mask respirator with replaceable dust filter or single use (with valve) dust respirator.
	Type C, demand type (negative pressure), with quarter or half mask facepiece.
Less than or equal to 100X	Full facepiece respirator with replaceable dust filter.
	Type C, supplied air respirator, demand type (negative pressure), with full facepiece.

Concentrations of Free Silica in Multiples of the Standard	Respirator Type*
Less than or equal to 200X	Powered air-purifying (positive pressure) respirator, with replaceable applicable filter.**
Greater than 200X	Type C, supplied air respirator, continuous flow type (positive pressure), with full facepiece, hood, or helmet.

*Where a variance has been obtained for abrasive blasting with silica sand, use only Type C continuous flow, supplied air respirator with hood or helmet.

**An alternative is to select the standard high efficiency filter which must be at least 99.97% efficient against 0.3 μm dioctyl phthalate (DOP).

(b) Work Clothing

Where exposure to free silica is above the recommended environmental limit, work clothing shall be vacuumed before removal. Clothes shall not be cleaned by blowing or shaking.

Section 5 — *Informing Employees of Hazards from Free Silica*

((a) Each employee exposed to free silica shall be apprised at the beginning of his employment or assignment to a free silica exposure area of the hazards, relevant symptoms, appropriate emergency procedures, and proper conditions and precautions for safe use or exposure. The employee shall be instructed as to availability of such information including that prescribed in (b) below. Such information shall be kept on file and shall be accessible to the worker at each place of employment where free silica is involved in unit processes and operations. Workers shall also be advised of the increased risk of impaired health due to the combination of smoking and free silica dust exposure.

(b) Information, to the extent applicable to free silica, as specified in Appendix III shall be recorded on US Department of Labor Form OSHA-20, "Material Safety Data Sheet" (see Appendix III) or on a similar form approved by the Occupational Safety and Health Administration, US Department of Labor.

Section 6 — *Work Practices and Control Procedures*

(a) Substitution

(1) Wherever a hazard of silicosis can be eliminated by a reasonable substitution of other less toxic materials for free silica, the substitution shall be made unless the silica sand has been so processed before use to make it nonrespirable such as by washing to remove fine particles. Examples of such substitution are the use of alumina instead of flint for china placing in potteries, and the substitution of a quartz-free grit in abrasive blasting.

(2) Uncontrolled abrasive blasting with silica sand is such a severe silicosis hazard that special attention must be given to this problem. Silica sand, or other materials containing more than 1% free silica, should be prohibited as an abrasive substance in abrasive blasting cleaning operations.

(b) Dust suppression

Moisture shall be added where such addition can substantially reduce the exposure to airborne respirable free silica dust.

(c) Ventilation

Where a local exhaust ventilation and collection system is used, it shall be designed and maintained to prevent the accumulation or recirculation of free silica dust into the workplace. The total system shall be inspected periodically for efficiency of operation. In addition, necessary measures shall be taken to ensure that discharge outdoors will not produce a health hazard to humans, animals, or plants.

(d) General Housekeeping

(1) Cleaning by blowing with compressed air or dry sweeping shall be avoided and dustless methods of cleaning such as vacuuming or washing down with water be substituted.

(2) Emphasis shall be placed upon cleanup of spills, preventive maintenance and repair of equipment, proper storage of materials, and collection of dusts containing free silica. Sanitation shall meet the requirements of 29 CFR 1910.141 as amended.

Section 7 — *Monitoring and Recordkeeping Requirements*

Work environments where it has been determined, on the basis of a professional industrial hygiene survey or by the judgment of a compliance officer, that the workers' exposure does not exceed half of the standard shall not be considered to have exposure to free silica. Records of these surveys, including the basis for concluding that air levels are at or below half of the standard shall be maintained. Surveys shall be repeated when any process change indicates a need for reevaluation or at the discretion of the compliance officer. Requirements set forth below apply to areas in which there is "exposure to free silica."

Employers shall maintain records of the workers' exposure to free silica based upon the following sampling and recording schedules:

(a) In all monitoring, samples representative of the exposure in the breathing zone of employees shall be collected. An adequate number of samples shall be collected to permit construction of a full-shift exposure for every

operation or process. The minimum number of time-weighted average determinations for an operation or process shall be based on the number of workers exposed as provided in Table I-2 or as otherwise indicated by a professional industrial survey.

(b) The first work environment (breathing zone) sampling shall be completed within 6 months of the promulgation of a standard incorporating these recommendations.

(c) Work environment (breathing zone) samples shall be taken within 30 days after installation of a new process or process changes.

TABLE I-2

SAMPLING SCHEDULE

Number of Employees Exposed	Number of Time-weighted Average Determinations
1-20	50% of the total number of workers
21-100	10 plus 25% of the excess over 20 workers
over 100	30 plus 5% of the excess over 100 workers

(d) Samples shall be collected and analyzed at least every 6 months in accordance with Appendices I and II for the evaluation of the workers' exposure with respect to the recommended standard.

(e) When monitoring of the workers' exposure indicates a free silica concentration in excess of the recommended standard, suitable controls shall be initiated to reduce the exposure level to or below the recommended standard. In such cases monitoring shall continue at 30-day intervals until 2 consecutive surveys indicate the recommended standard is no longer exceeded. Periodic review and evaluation of environmental and medical data shall be performed to determine the effectiveness of control measures.

(f) Records shall be maintained of medical examinations and all sampling schedules to include the sampling and analytical methods, type of personal protection devices, if any, in use at the time of sampling and the determined free silica dust concentration. Records shall be maintained for at least 30 years following termination of workers' employment. Each employee shall be able to obtain information on his exposure.

VIII. APPENDIX I
AIR SAMPLING METHOD FOR FREE SILICA

General Requirements

To evaluate the worker's exposure, environmental sampling for free silica dust requires the application of respirable dust sampling techniques such as those presented in the ACGIH *Air Sampling Instruments* [145] and those recommended by the AIHA-ACGIH Aerosol Technology Committee. [82] The dust is collected with a size-selective personal sampler positioned in the worker's breathing zone. Dust penetrating the precollector is collected on a low ashing polyvinyl chloride (PVC) filter and the free silica content is determined by X-ray diffraction (Appendix II) after redeposition of the dust on a silver membrane filter.

(a) Samples collected shall be representative of the individual worker's exposure.

(b) Sampling data sheets shall include:

(1) The date and time of sample collection.

(2) Sampling duration.

(3) Volumetric flowrate of sampling.

(4) The name of the worker being sampled or the description of the sampling location.

(5) Sampler serial number.

(6) Name of person taking sample.

Personal Sampling

(a) Size-selective device

Personal samples shall be collected using a two-stage, 10-mm nylon cyclone size-selective sampler.

(b) Filters and filter holders

The size-selective sampler shall be connected to a 2-piece, 37-mm cassette containing as the collecting medium a 37-mm, low-ashing polyvinyl chloride (PVC) filter with a 5.0-um pore size. (Gelman VN-1 filters are unacceptable for use in the analytical method recommended because of the high background reading produced by the filter upon ashing.) Duplicate filters shall be subjected to identical handling, but without air being drawn through them, so that they may serve as blanks or controls.

(c) Personal sampling pumps

A portable battery operated pump, conforming to the requirements of 30 CFR-47, which is equipped with a pulsation dampener and which will draw 1.7 liters of air per minute (liters/minute) for at least 8 hours shall be used. Present technology of personal sampling pump batteries limits the sample collection time to approximately 8 hours.

(d) Sampling time

The sampling time shall be for a full work shift and the exposure calculated for a continuous 8-hour exposure. Multiple, shorter (2-4 hours) samples may be collected over a full shift and pooled for determination of an individual's average exposure to free silica during the total work shift.

Workroom (General) Air Sampling

(a) Size-selective sampling devices

When high volume respirable dust samples are required from the area of the worker's environment, a 1/2-inch metal cyclone or its equivalent shall be used to obtain samples.

(b) Filters and filter holders

The size-selective sampler is connected to the filter holder cassette containing the appropriate filter. Samples collected for chemical analysis must be collected on a 37-mm low-ashing polyvinyl chloride (PVC) filter with a 5.0-m pore size.

(c) Sampling pumps

Any nonpulsating flow pump with a capacity of at least 10-15 in. Hg at 9 liters/minute will be adequate if the 1/2-inch cyclone is used. For larger samplers a pump of greater capacity will be required.

(d) Sampling time

The general air samples should be collected for a period of 4 consecutive hours taken during collection of the personal samples.

Collection and Shipping of Samples

(a) The quantity of dust collected in the filter holder cassette assembly should not exceed 5 mg. The filter is kept in the cassette for shipment.

(b) Whenever an air sample or series of air samples is collected, a bulk sample of the suspected parent material of the atmospheric contaminant should be obtained and shipped back to the laboratory with the air samples.

(c) After sampling, remove the filter cassette from the sampling train. Stopper the end of the cassette. Ship the cassette to the analytical laboratory in a suitable container to prevent damage in transit.

Sampling Methods for Quantitative and Qualitative Analysis of Free Silica

There are several difficulties, especially from small sample size, in analyzing for the percent and/or form of free silica on each personal sample, so the following methods of sampling are recommended to provide an appropriate sample size for such determinations: higher volume respirable dust samples as collected with a 1/2-inch cyclone; groups of pooled personal samples; any other method shown to be equivalent in collection of a suitable size sample.

A minimum total sample of 500 um of dust or a minimum free silica dust sample of 25 um is needed for accurate analysis of the collected dust.

Calibration of Sampling Trains

Since the accuracy of an analysis is no greater than the accuracy of the volume of air which is measured, accurate calibration of a sampling pump is essential for correct interpretation of the pump's indicated volume. The frequency of calibration is dependent on the use, care, and handling to which the pump is subjected. In addition, pumps should be recalibrated if they have been misused or if they have just been repaired or received from a manufacturer. If the pump receives hard usage, more frequent calibration may be necessary.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. The accuracy of calibration is dependent on the type of instrument used as a reference. The choice of calibration instrument will depend largely on where the calibration is to be performed. For laboratory testing, primary standards such as a spirometer or a soapbubble meter are recommended, although other standard calibrating instruments such as a wet-test or a dry-gas meter can be used. The actual setup will be the same for these instruments.

Instructions for calibration with the soapbubble meter follow. If another calibration device is used, equivalent procedures should be followed.

The calibration setup for a personal sampling pump with a filter cassette is shown in Figure XI-1. The procedure is described below.

(a) Check the pump battery with a voltmeter to assure adequate voltage for calibration. Charge the battery if necessary.

(b) Place the PVC filter in the filter cassette.

(c) Assemble the sampling train as shown in Figure XI-1.

(d) Turn the pump on and moisten the inside of the soapbubble meter by immersing the buret until they are able to travel the entire length of the buret without bursting.

(e) Adjust the pump manometer to insure that the pressure drop across the sampling train does not exceed 13 inches of water (1 in. of Hg).

(e) Adjust the pump rotameter to provide a flowrate of 1 liter/minute.

(f) Check the water manometer to insure that the pressure drop across the sampling train does not exceed 13 inches of water (1 in. of Hg).

(g) Start a soapbubble up the buret and, with a stopwatch, measure the time it takes the bubble to move from one calibration mark to another. For a 1000-ml buret, a convenient calibration volume is 500 ml.

(h) Repeat the procedure in (g) above at least twice, average the results, and calculate the flowrate by dividing the volume between the preselected marks by the time required for the soapbubble to traverse the distance.

(i) Data for the calibration include the volume measured, elapsed time, pressure drop, air temperature, atmospheric pressure, serial number of the pump, pump number, date of the calibration, and name of the operator.

IX. APPENDIX II
ANALYTICAL METHOD FOR DETERMINATION OF FREE SILICA IN ATMOSPHERIC DUST

The following method for determination of the polymorphs and/or free silica content in airborne dusts employs X-ray diffraction as recommended in the *NIOSH Manual of Analytical Methods*. [146] This method is based upon the work of Bumsted, [135] Leroux and Powers, [130] Talvitie and Brewer, [147] Bradley, [148] the *Handbook of X-rays*, [149] and Leroux et al. [150]

(a) Principle of the Method

(1) Atmospheric dust samples are collected on low-ashing PVC membrane filters.

(2) The filters are ashed and the residues along with an internal calibration standard are redistributed onto silver-membrane filters.

(3) Each sample is scanned by X-ray diffraction to determine the polymorphs of free silica that may be present.

(4) If present, the mass of each polymorph is determined by measuring the ratio of the diffraction peak intensities of the free silica polymorph and the internal standard, and comparing this ratio to a calibration curve.

(b) Range and Sensitivity

(1) The analytical range extends from 5 ug/sq cm to 200 ug/sq cm for each free silica polymorph; the total atmospheric dust loading on the filter must not exceed 1 mg/sq cm.

(2) The sensitivity is 5 ug for each free silica polymorph.

(3) A minimum total dust sample of 500 ug or a minimum free silica dust sample of 25 ug is needed for accurate analysis of collected dusts.

(c) Interferences

(1) Several minerals have diffraction peaks that correspond in position to the major peak for quartz; these include micas (biotite, muskovite, potash, feldspars [microcline], plagioclase), sillimanite, graphite, iron carbide, and zirconium silicate. The presence of these interferences is usually encountered in specific, recognizable situations and can be seen in the X-ray diffraction pattern. Analytical measurements can be carried out at a secondary quartz peak with a commensurate decrease in sensitivity.

(2) Comparable interference may occur from other free silica polymorphs such as cristobalite and tridymite. This can be determined by X-ray diffraction analysis. If interference occurs, secondary peaks must be used.

(3) Diffraction peak interference may also occur for the fluorite (CaF_2) internal calibration standard. Compensation must be made for increased peak intensity from the interfering minerals, or an alternate standard must be employed.

(4) In certain cases, some elements (iron and iron compounds) present in the sample may give rise to appreciable X-ray fluorescence leading to high background intensity. This situation may be circumvented by using a diffracted beam monochromator or by utilizing an alternate X-ray tube target material.

(d) Precision and Accuracy

(1) Leroux et al [150] stated that dust deposits may be analyzed with a precision of better than plus or minus 3%.

(2) Bumsted [135] reported 21 replicate measurements of quartz in 2 mg of coal dust as having an average of 0.63% (12.6 ug), a range of 0.51-0.91% (10.2-18.2 ug) and a standard deviation of 0.114 (plus or minus 1.4 ug); he reported an accuracy of plus or minus 30% (plus or minus 3.8 ug) of the quartz present in these samples. No information is

available regarding the accuracy for cristobalite or tridymite.

(e) Advantages and Disadvantages

(1) The X-ray diffraction method offers sensitivity equivalent to or greater than other methods (infrared or colorimetric), is nondestructive to the sample and is rapidly performed.

(2) The X-ray diffraction method is limited to a sample size of a few milligrams. Application of the method requires a rather high degree of technical skill and expensive equipment.

(f) Apparatus

(1) X-ray diffraction equipment, including copper and/or molybdenum target X-ray tubes. (Gelman VM-1 filters are unacceptable for use with X-ray diffraction because of the high background reading produced by the filter upon ashing.)

(2) Low temperature radiofrequency asher or muffle furnace.

(3) Ultrasonic bath.

(4) Filtration apparatus.

(5) 25-mm diameter silver membrane filters having a 0.45 um pore size.

(6) Aluminum weighing pans.

(7) Porcelain crucibles with covers.

(8) 100-ml Pyrex beakers.

(9) Glass microscope slides.

(10) Nonserrated, nonmagnetic forceps.

(11) Metal spatula.

(g) Reagents

(1) Quartz, cristobalite, and tridymite powders and other free silica polymorphs as needed: Acid washed and wet-sieved through 10 um sieves.

(2) Fluorite (CaF2): 400 mesh powder, analytical grade.

(3) Wetting agent.

(4) Petroleum jelly.

(h) Procedure-Cleaning of Equipment

It is important that all equipment be kept as free of contaminant dust as possible.

(1) The spatula, forceps, etc., may be satisfactorily cleaned by using ethyl alcohol and disposable nonlinting tissues.

(2) The aluminum weighing pans are cleaned by rinsing them twice with distilled water and twice with ethyl alcohol, and allowing them to dry in a dust-free environment.

(i) Analysis of samples

(1) Either of the following described methods may be used to ash the sample:

(A) With forceps and spatula, place the filter sample in an aluminum weighing pan and situate within the sample compartment of the low-temperature asher so that the sample exposure to the radiofrequency-excited oxygen plasma is optimized. The sample is ashed for 1 hour at 100 watts RF power and at an oxygen flow rate of 75 cc/min, using the techniques recommended in the instrument manual.

(B) Using forceps and spatula, put the filter sample in a porcelain crucible, cover loosely and place in muffle furnace. Maintain for 2 hours at 600 C (800 C if graphite is present in the sample).

(2) Carefully scrape the ash residue into a 100-ml beaker. Rinse the weighing pan (or crucible) several times with about 5 ml of water and pour the rinse water into the beaker. Add 1 ml of the CaF2 standard solution, a few drops of wetting agent, and distilled water to bring volume up to 50 ml.

(3) Ultrasonically agitate the beaker and its contents for 30 minutes at maximum setting.

(4) Filter solution through a 25-mm diameter, 0.45 um pore size silver-membrane filter under suction. Thoroughly wash down the filter holder with distilled water to ensure that all dust particles have been transferred to the filter.

(5) Remove the filter with forceps, place in a Petri dish, and dry at 105 C for 15 minutes.

(6) The silver filter is then attached to a glass microscope slide with petroleum jelly and inserted into the X-ray diffractometer. A portion of the filter should be inserted beneath the clamping surface of the diffractometer.

(7) The diffractometer is then scanned over the 2 Theta-range corresponding to d = 4.5 to 2.8 Angstroms (for a copper tube, 2 Theta = 18-32 degrees and for a molybdenum tube, 2 Theta = 9-15 degrees). The presence of crystalline forms of silica are determined by the occurrence of diffraction peaks as follows:

Mineral	d (Most Intense)	d (Second Most Intense)
Quartz	3.34 Angstroms	4.26 Angstroms
Cristobalite	4.05 "	2.49 "
Tridymite	4.07 "	3.80 "
Calcite Standard	3.15 "	----

The presence of interfering compounds can be determined by the presence and identification of other X-ray diffraction peaks.

(8) The intensity of the most intense diffraction peak for quartz, cristobalite, and tridymite, or other free silica polymorphs is determined by measuring peak height or peak area from the diffraction scan or by scaler (fixed time or fixed count) measurement at peak position. All measurements must be corrected for background. Comparable measurements are made for the fluorite standard at d = 3.15 Angstroms. If diffraction peaks from other compounds interfere with the most intense peak for quartz, cristobalite, tridymite, or other free silica polymorphs, the second most intense peak for these free silicas must be employed.

(9) The free silica to calcite intensity ratios are determined, and the mass of quartz, cristobalite, tridymite, and/or other polymorphs of free silica is determined from the appropirate calibration curve.

(j) Calibration and Standard

(1) Standards

(A) A standard solution of calcite is prepared by adding 20 mg of calcite to 100 ml of distilled water containing a few drops of wetting agent and then agitating.

(B) Known amounts of quartz, cristobalite, tridymite, and/or other polymorphs of free silica are weighed to the nearest 0.1 mg and are added to 100 ml distilled water containing a few drops of wetting agent to provide five standard solutions of each mineral covering a concentration range of 0.01 — 0.3 mg/ml.

(2) Standard curve

(A) One ml of the standard calcite solution and one of the free silica solutions are added to 50 ml distilled water and are analyzed according to steps (i) (4) through (i) (8). Similar data are collected for each of the free silica solutions.

(B) Standard curves are prepared for quartz, cristobalite, tridymite, or other forms of free silica in which the intensity ratio of the free silica standard to calcite is plotted against free silica mass in micrograms. This plot should give a nearly straight line that passes through the origin.

(k) Calculations

The concentration of free silica in air can be expressed as micrograms of free silica per cubic meter of air sampled (ug/cu m).

$$\mu g\ SiO2/cu\ m = \frac{\mu g\ Q + \mu g\ C + \mu g\ T + \mu g\ P}{V}$$

where:

μg SiO2/cu m = total micrograms of free silica per cubic meter of air sampled.

μg Q, μg C, μg T, μg P = quantity of free silica as determined from the appropriate calibration curve.

Vs = volume of air sampled in cubic meters.

Q,C,T,P = quartz, cristobalite, tridymite, polymorph of free silica.

X. APPENDIX III
MATERIAL SAFETY DATA SHEET

The following items of information applicable to any product or material containing free silica shall be provided in the appropriate section of the Material Safety Data Sheet or other approved form. If a specific item of information is not applicable (eg, flash point) the initials "na" should be inserted.

(a) Section I. Source and Nomenclature.

(1) The name, address, and telephone number of the manufacturer or supplier of the product.

(2) The trade name and synonyms for a mixture of chemicals, a basic structural material, or for a process material; the trade name and synonyms, chemical name and synonyms, chemical family, and formula for a single chemical.

(b) Section II. Hazardous Ingredients.

(1) Chemical or widely recognized common name of all hazardous ingredients.

(2) The approximate percentage by weight or volume (indicate basis) which each hazardous ingredient of the mixture bears to the whole mixture. This may be indicated as a range or maximum amount, eg 10-20% by volume; 10% maximum by weight.

(3) Basis for toxicity for each hazardous material such as an established standard in appropriate units.

(c) Section III. Physical Data.

Physical properties of the total product including boiling point and melting point in degrees Fahrenheit; vapor pressure in millimeters of mercury; vapor density of gas or vapor (air = 1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatile, indicate if by weight or volume, at 70 degrees Fahrenheit; evaporation rate for liquids (indicate whether butyl acetate or ether = 1); and appearance and odor.

(d) Section IV. Fire and Explosion Hazard Data.

Fire and explosion hazard data about a single chemical or a mixture of chemicals, including flash point, in degrees Fahrenheit; flammable limits in percentage by volume in air; suitable extinguishing media or agents; special firefighting procedures; and unusual fire and explosion hazard information.

(e) Section V. Health Hazard Data.

Toxic level for total compound or mixture. Effects of exposure, and emergency and first-aid procedures.

(f) Section VI. Reactivity Data.

Chemical stability, incompatibility, hazardous decomposition products, and hazardous polymerization.

(g) Section VII. Spill or Leak Procedures.

Detailed procedures to be followed with emphasis on precautions to be taken in cleaning up and safe disposal of materials leaked or spilled. This includes proper labeling and disposal of containers with residues, contaminated absorbants, etc.

(h) Section VIII. Special Protection Information.

Requirements for personal protective equipment, such as respirators, eye protection, protective clothing, and ventilation, such as local exhaust (at site of product formulation, use or application), general, or other special types.

(i) Section IX. Special Precautions.

Any other precautionary information.

XI. TABLE AND FIGURE

TABLE XI-1

PERMISSIBLE CONCENTRATIONS OF DUST CONTAINING FREE SILICA FOR THE PARTICULAR INDUSTRIES IN THE LOCALITIES INDICATED*

Industry	Percentage Silica in the Dust	Permissible Maximum Safe Dust Concentration Million Particles/cu ft
South Africa gold mines**	80	4.5
Ontario gold mines**	About 35 (in the rock)	8.5
Australia sandstone**	90 (in the rock)	6
Barre granite***	31 to 38	10-20
Pennsylvania anthracite coal	35	5-10
Broken Hill, Australia**	10 to 17	14

*National Silicosis Conference, Bulletin No. 13, Division of Labor Standards, United States Department of Labor.
**Based upon engineering practice.
***Based upon clinical studies.

From Reference 33

FIGURE XI - 1. CALIBRATION SETUP FOR PERSONAL SAMPLING PUMP WITH FILTER CASSETTE