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Phase 1 Air Sampling and Monitoring Work Plan

TVA Widows Creek Spill

Stevenson, Alabama Jackson County

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1.0 Introduction and Purpose

At approximately 0600 hrs on January 9, 2009, a release of spent Flue Gas Desulfurization (FGD) material (calcium sulfate, or “gypsum”) was discovered by TVA contractor. The material is produced when limestone slurry (calcium carbonate) is used to scrub sulfur dioxide (SO₂) emissions from flue gas. The release occurred through a 36” retired-in-place standpipe from FGD Pond #2B. The cap on the pipe dislodged, releasing liquid and solid contents from the bottom of FGD Pond #2B into the Stilling Pond located below it. The material overflowed the Stilling Pond and released into Widows Creek. Widows Creek feeds into the Tennessee River approximately 2 miles downstream from the release. Gypsum also overflowed the weir on the Stilling Pond and released through NPDES outfall number DSN008 to the Tennessee River.

On January 18, 2009, the unified command suggested that TVA begin a proactive air sampling program onsite and offsite to document any potential concern of airborne particulate issues arising from drier weather conditions in the Stevenson, AL area. At approximately 18:00 hrs, R. L. Pope with Tennessee Valley Authority (TVA) contacted CTEH and requested a Toxicology Emergency Response Program (TERP) response to Stevenson, Alabama to assess potential airborne presence of particulates associated with the TVA gypsum and fly ash spill. The CTEH TERP team mobilized on the evening of January 18, 2009 and arrived onsite at the Widows Creek Plant at 06:50 hrs on January 19, 2009. CTEH will collect eight consecutive rounds (12 hrs per round for a total of four days) of integrated analytical samples at the perimeter of the Widows Creek Fossil Plant. During these four days, CTEH will also conduct continuous real-time air sampling in the community and in the work areas.

This work plan addresses air sampling at the Widows Creek TVA gypsum and fly ash spill site location.

The purpose of this sampling includes the following:

- Monitor the perimeter of the TVA facility site to protect the community and response workers in close proximity to the incident site.
- Monitor the work site or incident site to protect the workers and other personnel located within the incident site.
- Monitor air within the community to assess potential off-site impact from airborne contaminants originating from the gypsum and fly ash spill.
- Monitor to assist with compliance of exposure standards and guidelines,
- Provide toxicology and industrial hygiene consulting support.

The air sampling data will be summarized daily and made available for review onsite.

2.0 Air Sampling, Monitoring Locations, and Target Analytes

Real time¹ air monitoring and analytical² air sampling may be performed at the following locations:

- The TVA facility site and work area,
- At perimeter locations offsite to the TVA facility,
- Locations throughout adjacent community and or residential areas.
- At selected locations that will address potential off-site receptors, accounting for possible changes in wind-direction.
- At selected locations that will address potential on-site receptors in regards to workers.

3.0 Constituents of Interest

Based on a review of the Material Safety Data Sheet (MSDS) for gypsum and coal fly ash, CTEH has focused air monitoring and sampling efforts on the following constituents (crystalline silica, heavy metals, respirable dust, and total dust.

4.1 Exposure Standards and Guidelines

The Occupational Safety and Health Administration (OSHA) establishes workplace standards to protect the safety and health of workers. Table 1 lists the OSHA values for silica dust, heavy metals, respirable dust, and total dust. When applicable, sampling data results will be compared to health- and risk-based ambient air and exposure guidelines such as Minimal Risk Levels from the Agency for Toxic Substances and Disease Registry, Acute Exposure Guideline Levels from the EPA, Emergency Response Planning Guidelines from the American Industrial Hygiene Association, and Temporary Emergency Exposure Limits from the US Department of Energy.

¹ The term “real–time air monitoring” generally refers to using handheld, portable direct reading instruments that rapidly detect and display the airborne concentration of a chemical.

² The term “analytical air sampling” refers to air sampling methods that involve collection of air samples over a specified period, followed by analysis at a laboratory. The results of these samples represent the average airborne concentration for the sample period. These methods typically involve passing a known volume of air through a collection medium (e.g. charcoal sample tube or filter cassette) that efficiently traps and retains the compound until it can be analyzed by the laboratory. By knowing the volume of air collected, and the quantity of chemical absorbed onto the collection medium, the average air concentration can be calculated.

**Table 1
Occupational Exposure Standards and Guidelines***

Analytes	OSHA PEL-TWA^a
Silica	10.0 mg/m ³
Heavy Metals, Arsenic	0.01 mg/m ³
Total Dust	15 mg/m ³
Respirable Dust	5 mg/ m ³

NE= Not Established

- a. OSHA PEL-TWA = The permissible concentration in air of a substance that shall not be exceeded in an 8-hour work shift or a 40-hour work week (OSHA, 1989).

Additionally, community total dust averaged values will be compared to the National Ambient Air Quality Standards (NAAQS) 24-hour average value of 0.150 mg/m³ for particulate matter less than 10 micrometers (PM₁₀).

5.0 Real-Time Monitoring

The term “real-time” refers to direct reading instruments that allow nearly instantaneous determinations of a chemical concentration in air. Real-time measurements provide immediate information for worker and community exposure scenarios and, with the use of appropriate site safety measures, help prevent overexposures. Real-time air monitoring equipment will be used on the site in Stevenson, Alabama as an indicator of current air concentrations of particulate matter. This will assist in the protection of workers in the event of a change of concentrations and allow TVA to gain a good understanding of exposure scenarios in different areas. Real-time measurements are not directly comparable to OSHA TWA values nor to community exposure standards or guidelines. Instantaneous real-time samples do not necessarily represent conditions experienced throughout the workday and can substantially underestimate or overestimate exposures potentially experienced by workers. Direct reading instruments perform sampling and analyses within the instrument and concentration readings can usually be obtained immediately. These instruments have fast response times and can follow rapid changes in concentration.



CTEH will monitor at locations in response to incident site changes and/or community concerns or requests. Real-time monitoring will be conducted using the TSI AM510 particulate monitor.

Table 5.1 Real-Time Air Monitoring Equipment Summary

Instrument	Analyte	Correction Factor	Detection Limit
TSI AM-510	Particulate Matter	N/A	0.001 mg/m ³

5.1 TSI AM510 Particulate/Aerosol Monitors

Particulate matter is measured using a real-time TSI Aerosol Monitor Model AM-510. The AM-510 Aerosol Monitor is a portable, battery-operated, laser-photometer that measures airborne dust concentrations. The sensing mechanism consists of a laser diode directed at the aerosol stream. Scattered light is collected with optics and a photo detector perpendicular to the light beam. The intensity of the scattered light is a function of the particle mass concentration. The data is conveyed in milligrams per cubic meter (mg/m³). Real-time air monitoring for particulate matter will be conducted in the 10 µm impactor (PM₁₀). The TSI AM510 is sent for annual factory calibration and will be zero calibrated onsite daily as suggested in the manufacturer’s operation manual. Calibrations will be logged manually in CTEH’s field forms or electronically on the hand-held data collection device that is synchronized to the CTEH server multiple times daily.

6.0 Real-Time Air Monitoring Locations

Real-time air monitoring for particulates will be conducted at the following locations: in the clean-up work area, in the surrounding community, the TVA facility, and other locations deemed necessary. Daily maps will be produced to highlight the location of the sampling locations for the previous day.

7.0 Analytical Sampling

Analytical air sampling will be conducted for the purpose of collecting data that represents TWA concentrations of particulates throughout the day. When applicable, sampling will be conducted and analyzed for crystalline silica, metals, respirable dust, and total dust. This monitoring may be focused according to resulting laboratory data to include the constituents that were identified at or near levels of concern. Monitoring will be responsive to onsite activities. In accordance with the EPA and ADEM requests, CTEH will collect eight rounds of analytical sampling (two rounds per day) for the aforementioned constituents. The first round of samples will be analyzed as same day turn around at the laboratory. All subsequent samples will be analyzed as standard turn-around time. Samples will



be numbered sequentially using CTEH's bar code system. The numbers are 9-character alpha numeric and start with SMP followed by the 6 digit sample number (SMP004601).

All samples will be held according to method/laboratory requirements and will be shipped to Galson Laboratories, an AIHA accredited laboratory, for subsequent analysis. Analytical air sampling methods for the analytes listed above are summarized in Table 7.1 and copies of the methods are available in Appendix A.

**Table 7.1
Summary of Analytical Air Sampling Methods**

Analyte	Analytical Method	Sample Media	Flow Rate (L/min)	Sample Volume (12 hr.)
Silica, crystalline	NIOSH 7500	37 mm, 5-µm PVC filter	2.5	1800 L
Metals	NIOSH 7300	37 mm, 0.8 µm MCE filter	2.0	1440 L
Total Dust	NIOSH 0500	37 mm, 0.8 µm MCE filter	2.0	1800 L
Respirable Dust	NIOSH 0600	37 mm, 5-µm PVC filter	2.5	1440 L

8.0 Data Management

- All analytical air samples will be sent to Galson Laboratories, an AIHA Accredited Laboratory located in East Syracuse, N.Y.
- The following data will be logged for analytical sampling
 - Sample ID
 - Start time
 - Stop time
 - Pump period
 - Sample period
 - Flow rate pre cal
 - Flow rate post cal
 - Flow rate average
 - Sample volume (in liters)
- A request for complete data packages will be made to the laboratory for all samples analyzed.
- The data packets will be reviewed and the data will undergo a data validation process.
- All real-time instruments will be calibrated according to the manufacturer recommendations or as determined necessary by CTEH personnel.
- Calibration logs will be completed daily for real-time equipment.
- Real-time readings will be documented by handwritten notes, handheld PDA, or by the use of data logging capabilities of the instrument, if available.



- Real-time data will be entered onsite and drafts made available upon request.

9.0 Project Organization

CTEH will be responsible for the following:

- Air monitoring
- Toxicology support
- Quality Assurance/Quality Control
- Air Data evaluation
- Air Reporting

CTEH site management:

Project Manager

- Cory Davis, Industrial Hygienist, Manager, Toxicology Emergency Response Program

10.0 Equipment Decontamination

If required, equipment will be decontaminated by the decontamination group where all entries and exits occur. The decontamination will be with damp cloths as the equipment cannot be submerged under water.

11.0 Field Documentation

During the project, the team members will maintain various field books, reports, electronic database, and logs. Each of the components of the field documentation is described below. All documents and logs generated onsite will be produced to the Environmental Branch Manager.

12.0 Calibration and Maintenance of Field Instruments

The calibration and maintenance of field equipment and instrumentation will be in accordance with each manufacturer's specifications or applicable test/method specifications, and shall be documented in the Calibration Logs or Site Safety and Health Logbooks.

13.0 Sample Labels and Chain of Custody (COC)

All sample labels used on sample containers will include, at a minimum, a sample identification code, the date of the sample, and the analyte. Each sample will be identified on a chain of custody record.

The analytical sample numbering system will include site name, date, analyte, and identification code unique to each sample.

14.0 Packaging and Shipping

Packaging and shipping of samples will vary depending upon sample media, contaminant concentration, preservation technique, and sample container. The person packaging the samples is responsible to ensure that the sample packaging is in suitable condition for shipping.

Appendix A

Analytical Sampling Methods

PARTICULATES NOT OTHERWISE REGULATED, TOTAL

0500

DEFINITION: total aerosol mass CAS: NONE RTECS: NONE

METHOD: 0500, Issue 2

EVALUATION: FULL

Issue 1: 15 February 1984
Issue 2: 15 August 1994

OSHA : 15 mg/m³
NIOSH: no REL
ACGIH: 10 mg/m³, total dust less than 1% quartz

PROPERTIES: contains no asbestos and quartz less than 1%

SYNONYMS: nuisance dusts; particulates not otherwise classified

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (tared 37-mm, 5-µm PVC filter)	TECHNIQUE:	GRAVIMETRIC (FILTER WEIGHT)
FLOW RATE:	1 to 2 L/min	ANALYTE:	airborne particulate material
VOL-MIN:	7 L @ 15 mg/m ³	BALANCE:	0.001 mg sensitivity; use same balance before and after sample collection
-MAX:	133 L @ 15 mg/m ³	CALIBRATION:	National Institute of Standards and Technology Class S-1.1 weights or ASTM Class 1 weights
SHIPMENT:	routine	RANGE:	0.1 to 2 mg per sample
SAMPLE STABILITY:	indefinitely	ESTIMATED LOD:	0.03 mg per sample
BLANKS:	2 to 10 field blanks per set	PRECISION (S_r):	0.026 [2]
BULK SAMPLE:	none required		
ACCURACY			
RANGE STUDIED:	8 to 28 mg/m ³		
BIAS:	0.01%		
OVERALL PRECISION (S_{r,T}):	0.056 [1]		
ACCURACY:	± 11.04%		

APPLICABILITY: The working range is 1 to 20 mg/m³ for a 100-L air sample. This method is nonspecific and determines the total dust concentration to which a worker is exposed. It may be applied, e.g., to gravimetric determination of fibrous glass [3] in addition to the other ACGIH particulates not otherwise regulated [4].

INTERFERENCES: Organic and volatile particulate matter may be removed by dry ashing [3].

OTHER METHODS: This method is similar to the criteria document method for fibrous glass [3] and Method 5000 for carbon black. This method replaces Method S349 [5]. Impingers and direct-reading instruments may be used to collect total dust samples, but these have limitations for personal sampling.

EQUIPMENT:

1. Sampler: 37-mm PVC, 2- to 5- μ m pore size membrane or equivalent hydrophobic filter and supporting pad in 37-mm cassette filter holder.
 2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing.
 3. Microbalance, capable of weighing to 0.001 mg.
 4. Static neutralizer: e.g., Po-210; replace nine months after the production date.
 5. Forceps (preferably nylon).
 6. Environmental chamber or room for balance (e.g., 20 °C \pm 1 °C and 50% \pm 5% RH).
-

SPECIAL PRECAUTIONS: None.

PREPARATION OF FILTERS BEFORE SAMPLING:

1. Equilibrate the filters in an environmentally controlled weighing area or chamber for at least 2 h.
NOTE: An environmentally controlled chamber is desirable, but not required.
2. Number the backup pads with a ballpoint pen and place them, numbered side down, in filter cassette bottom sections.
3. Weigh the filters in an environmentally controlled area or chamber. Record the filter tare weight, W_1 (mg).
 - a. Zero the balance before each weighing.
 - b. Handle the filter with forceps. Pass the filter over an antistatic radiation source. Repeat this step if filter does not release easily from the forceps or if filter attracts balance pan. Static electricity can cause erroneous weight readings.
4. Assemble the filter in the filter cassettes and close firmly so that leakage around the filter will not occur. Place a plug in each opening of the filter cassette. Place a cellulose shrink band around the filter cassette, allow to dry and mark with the same number as the backup pad.

SAMPLING:

5. Calibrate each personal sampling pump with a representative sampler in line.
6. Sample at 1 to 2 L/min for a total sample volume of 7 to 133 L. Do not exceed a total filter loading of approximately 2 mg total dust. Take two to four replicate samples for each batch of field samples for quality assurance on the sampling procedure.

SAMPLE PREPARATION:

7. Wipe dust from the external surface of the filter cassette with a moist paper towel to minimize contamination. Discard the paper towel.
8. Remove the top and bottom plugs from the filter cassette. Equilibrate for at least 2 h in the balance room.
9. Remove the cassette band, pry open the cassette, and remove the filter gently to avoid loss of dust.
NOTE: If the filter adheres to the underside of the cassette top, very gently lift away by using the dull side of a scalpel blade. This must be done carefully or the filter will tear.

CALIBRATION AND QUALITY CONTROL:

10. Zero the microbalance before all weighings. Use the same microbalance for weighing filters before and after sample collection. Maintain and calibrate the balance with National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights.

11. The set of replicate samples should be exposed to the same dust environment, either in a laboratory dust chamber [7] or in the field [8]. The quality control samples must be taken with the same equipment, procedures and personnel used in the routine field samples. The relative standard deviation calculated from these replicates should be recorded on control charts and action taken when the precision is out of control [7].

MEASUREMENT:

12. Weigh each filter, including field blanks. Record the post-sampling weight, W_2 (mg). Record anything remarkable about a filter (e.g., overload, leakage, wet, torn, etc.)

CALCULATIONS:

13. Calculate the concentration of total particulate, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_2 - W_1) - (B_2 - B_1) \cdot 10^3}{V}, \text{ mg}/\text{m}^3.$$

where: W_1 = tare weight of filter before sampling (mg)
 W_2 = post-sampling weight of sample-containing filter (mg)
 B_1 = mean tare weight of blank filters (mg)
 B_2 = mean post-sampling weight of blank filters (mg)

EVALUATION OF METHOD:

Lab testing with blank filters and generated atmospheres of carbon black was done at 8 to 28 mg/m^3 [2,6]. Precision and accuracy data are given on page 0500-1.

REFERENCES:

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 [2] Unpublished data from Non-textile Cotton Study, NIOSH/DRDS/EIB.
 [3] NIOSH Criteria for a Recommended Standard ... Occupational Exposure to Fibrous Glass, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-152, 119-142 (1977).
 [4] 1993-1994 Threshold Limit Values and Biological Exposure Indices, Appendix D, ACGIH, Cincinnati, OH (1993).
 [5] NIOSH Manual of Analytical Methods, 2nd ed., V. 3, S349, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
 [6] Documentation of the NIOSH Validation Tests, S262 and S349, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
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 [8] Breslin, J.A., S.J. Page, and R.A. Jankowski. Precision of Personal Sampling of Respirable Dust in Coal Mines, U.S. Bureau of Mines Report of Investigations #8740 (1983).

METHOD REVISED BY:

Jerry Clere and Frank Hearl, P.E., NIOSH/DRDS.

PARTICULATES NOT OTHERWISE REGULATED, RESPIRABLE 0600

DEFINITION: aerosol collected by sampler with 4- μ m median cut point CAS: None RTECS: None

METHOD: 0600, Issue 3

EVALUATION: FULL

Issue 1: 15 February 1984
Issue 3: 15 January 1998

OSHA: 5 mg/m³
NIOSH: no REL
ACGIH: 3 mg/m³

PROPERTIES: contains no asbestos and quartz less than 1%; penetrates non-ciliated portions of respiratory system

SYNONYMS: nuisance dusts; particulates not otherwise classified

APPLICABILITY: The working range is 0.5 to 10 mg/m³ for a 200-L air sample. The method measures the mass concentration of any non-volatile respirable dust. In addition to inert dusts [4], the method has been recommended for respirable coal dust. The method is biased in light of the recently adopted international definition of respirable dust, e.g., \approx +7% bias for non-diesel, coal mine dust [5].

INTERFERENCES: Larger than respirable particles (over 10 μ m) have been found in some cases by microscopic analysis of cyclone filters. Over-sized particles in samples are known to be caused by inverting the cyclone assembly. Heavy dust loadings, fibers, and water-saturated dusts also interfere with the cyclone's size-selective properties. The use of conductive samplers is recommended to minimize particle charge effects.

OTHER METHODS: This method is based on and replaces Sampling Data Sheet #29.02 [6].

EQUIPMENT:

1. Sampler:
 - a. Filter: 5.0- μ m pore size, polyvinyl chloride filter or equivalent hydrophobic membrane filter supported by a cassette filter holder (preferably conductive).
 - b. Cyclone: 10-mm nylon (Mine Safety Appliance Co., Instrument Division, P. O. Box 427, Pittsburgh, PA 15230), Higgins-Dewell (BGI Inc., 58 Guinan St., Waltham, MA 02154) [7], aluminum cyclone (SKC Inc., 863 Valley View Road, Eighty Four, PA 15330), or equivalent.
2. Personal sampling pump, 1.7 L/min \pm 5% for nylon cyclone, 2.2 L/min \pm 5% for HD cyclone, or 2.5 L/min \pm 5% for the AI cyclone with flexible connecting tubing.
NOTE: Pulsation in the pump flow must be within \pm 20% of the mean flow.
3. Balance, analytical, with sensitivity of 0.001 mg.
4. Weights, NIST Class S-1.1, or ASTM Class 1.
5. Static neutralizer, e.g., Po-210; replace nine months after the production date.
6. Forceps (preferably nylon).
7. Environmental chamber or room for balance, e.g., 20 °C \pm 1 °C and 50% \pm 5% RH.

SPECIAL PRECAUTIONS: None.

PREPARATION OF SAMPLERS BEFORE SAMPLING:

1. Equilibrate the filters in an environmentally controlled weighing area or chamber for at least 2 h.
2. Weigh the filters in an environmentally controlled area or chamber. Record the filter tare weight, W_1 (mg).
 - a. Zero the balance before each weighing.
 - b. Handle the filter with forceps (nylon forceps if further analyses will be done).
 - c. Pass the filter over an anti-static radiation source. Repeat this step if filter does not release easily from the forceps or if filter attracts balance pan. Static electricity can cause erroneous weight readings.
3. Assemble the filters in the filter cassettes and close firmly so that leakage around the filter will not occur. Place a plug in each opening of the filter cassette.
4. Remove the cyclone's grit cap before use and inspect the cyclone interior. If the inside is visibly scored, discard this cyclone since the dust separation characteristics of the cyclone may be altered. Clean the interior of the cyclone to prevent reentrainment of large particles.
5. Assemble the sampler head. Check alignment of filter holder and cyclone in the sampling head to prevent leakage.

SAMPLING:

6. Calibrate each personal sampling pump to the appropriate flow rate with a representative sampler in line.
NOTE 1: Because of their inlet designs, nylon and aluminum cyclones are calibrated within a large vessel with inlet and outlet ports. The inlet is connected to a calibrator (e.g., a bubble meter). The cyclone outlet is connected to the outlet port within the vessel, and the vessel outlet is attached to the pump. See APPENDIX for alternate calibration procedure. (The calibrator can be connected directly to the HD cyclone.)
NOTE 2: Even if the flowrate shifts by a known amount between calibration and use, the nominal flowrates are used for concentration calculation because of a self-correction feature of the cyclones.
7. Sample 45 min to 8 h. Do not exceed 2 mg dust loading on the filter. Take 2 to 4 replicate samples for each batch of field samples for quality assurance on the sampling procedure (see Step 10).
NOTE: Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.

SAMPLE PREPARATION:

8. Remove the top and bottom plugs from the filter cassette. Equilibrate for at least 2 h in an environmentally controlled area or chamber.

CALIBRATION AND QUALITY CONTROL:

9. Zero the microbalance before all weighings. Use the same microbalance for weighing filters before and after sample collection. Calibrate the balance with National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights.
10. The set of replicate field samples should be exposed to the same dust environment, either in a laboratory dust chamber [8] or in the field [9]. The quality control samples must be taken with the same equipment, procedures, and personnel used in the routine field samples. Calculate precision from these replicates and record relative standard deviation (S_r) on control charts. Take corrective action when the precision is out of control [8].

MEASUREMENT:

11. Weigh each filter, including field blanks. Record this post-sampling weight, W_2 (mg), beside its corresponding tare weight. Record anything remarkable about a filter (e.g., visible particles, overloading, leakage, wet, torn, etc.).

CALCULATIONS:

12. Calculate the concentration of respirable particulate, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_2 - W_1) - (B_2 - B_1)}{V} \cdot 10^3, \text{ mg}/\text{m}^3$$

where: W_1 = tare weight of filter before sampling (mg)
 W_2 = post-sampling weight of sample-containing filter (mg)
 B_1 = mean tare weight of blank filters (mg)
 B_2 = mean post-sampling weight of blank filters (mg)
 V = volume as sampled at the nominal flowrate (i.e., 1.7 L/min or 2.2 L/min)

EVALUATION OF METHOD:

1. Bias: In respirable dust measurements, the bias in a sample is calculated relative to the appropriate respirable dust convention. The theory for calculating bias was developed by Bartley and Breuer [10]. For this method, the bias, therefore, depends on the international convention for respirable dust, the cyclones' penetration curves, and the size distribution of the ambient dust. Based on measured penetration curves for non-pulsating flow [1], the bias in this method is shown in Figure 1.

For dust size distributions in the shaded region, the bias in this method lies within the ± 0.10 criterion established by NIOSH for method validation. Bias larger than ± 0.10 would, therefore, be expected for some workplace aerosols. However, bias within ± 0.20 would be expected for dusts with geometric standard deviations greater than 2.0, which is the case in most workplaces.

Bias can also be caused in a cyclone by the pulsation of the personal sampling pump. Bartley, et al. [12] showed that cyclone samples with pulsating flow can have negative bias as large as -0.22 relative to samples with steady flow. The magnitude of the bias depends on the amplitude of the pulsation at the

cyclone aperture and the dust size distribution. For pumps with instantaneous flow rates within 20% of the mean, the pulsation bias magnitude is less than 0.02 for most dust size distributions encountered in the workplace.

Electric charges on the dust and the cyclone will also cause bias. Briant and Moss [13] have found electrostatic biases as large as -50%, and show that cyclones made with graphite-filled nylon eliminate the problem. Use of conductive samplers and filter cassettes (Omega Specialty Instrument Co., 4 Kidder Road, Chelmsford, MA 01824) is recommended.

2. Precision: The figure 0.068 mg quoted above for the precision is based on a study [3] of weighing procedures employed in the past by the Mine Safety and Health Administration (MSHA) in which filters are pre-weighed by the filter manufacturer and post-weighed by MSHA using balances readable to 0.010 mg. MSHA [14] has recently completed a study using a 0.001 mg balance for the post-weighing, indicating imprecision equal to 0.006 mg.

Imprecision equal to 0.010 mg was used for estimating the LOD and is based on specific suggestions [8] regarding filter weighing using a single 0.001 mg balance. This value is consistent with another study [15] of repeat filter weighings, although the actual attainable precision may depend strongly on the specific environment to which the filters are exposed between the two weighings.

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METHOD REVISED BY: David L. Bartley, Ph.D., NIOSH/DPSE/ARDB and Ray Feldman, OSHA.

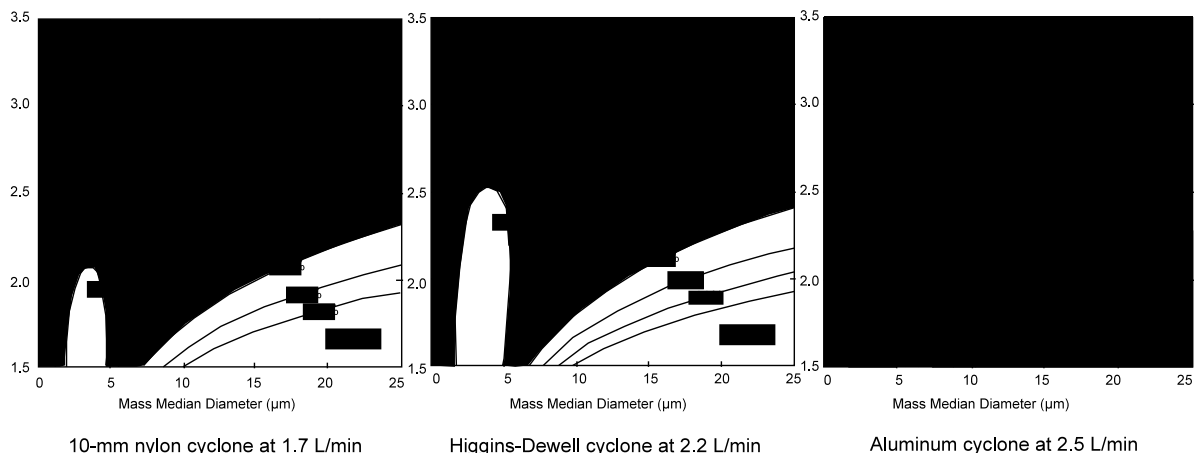


Figure 1. Bias of three cyclone types relative to the international respirable dust sampling convention.

APPENDIX: Jarless Method for Calibration of Cyclone Assemblies

This procedure may be used in the field to calibrate an air sampling pump and a cyclone assembly without using the one-liter "calibration jar".

- (1) Connect the pump to a pressure gauge or water manometer and a light load (adjustable valve or 5- μ m filter) equal to 2" to 5" H₂O with a "TEE" connector and flexible tubing. Connect other end of valve to an electronic bubble meter or standard bubble tube with flexible tubing (See Fig. 2.1).
NOTE: A light load can be a 5- μ m filter and/or an adjustable valve. A heavy load can be several 0.8- μ m filters and/or adjustable valve.
- (2) Adjust the pump to 1.7 L/min, as indicated on the bubble meter/tube, under the light load conditions (2" to 5" H₂O) as indicated on the pressure gauge or manometer.
- (3) Increase the load until the pressure gauge or water manometer indicates between 25" and 35" H₂O. Check the flow rate of the pump again. The flow rate should remain at 1.7 L/min \pm 5%.
- (4) Replace the pressure gauge or water manometer and the electronic bubble meter or standard bubble tube with the cyclone having a clean filter installed (Fig. 2.2). If the loading caused by the cyclone assembly is between 2" and 5" H₂O, the calibration is complete and the pump and cyclone are ready for sampling.

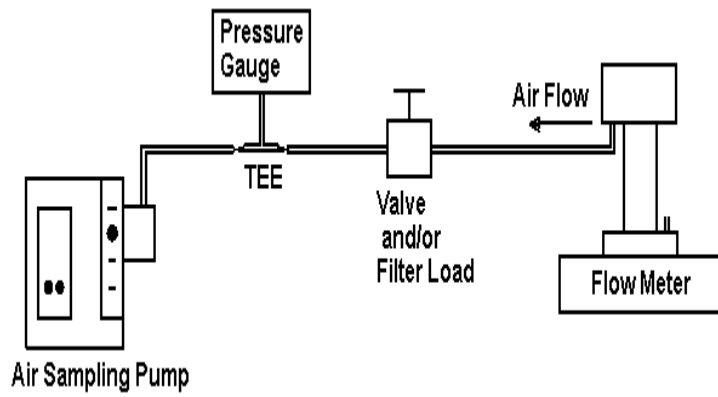


Figure 2.1 Block Diagram of Pump/Load/Flow Meter Set-up.

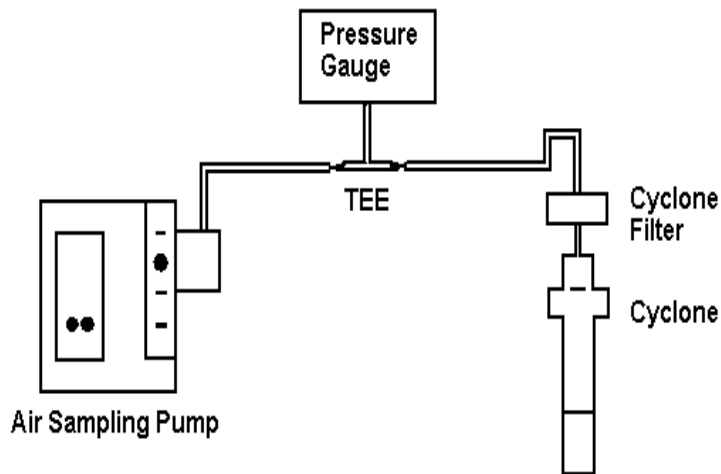


Figure 2.2. Block Diagram with Cyclone as the Test Load.

ELEMENTS by ICP (Nitric/Perchloric Acid Ashing)

7300

MW: Table 1

CAS: Table 2

RTECS: Table 2

METHOD: 7300, Issue 3

EVALUATION: PARTIAL

Issue 1: 15 August 1990
Issue 3: 15 March 2003

OSHA: Table 2

PROPERTIES: Table 1

NIOSH: Table 2

ACGIH: Table 2

ELEMENTS:	aluminum*	calcium	lanthanum	nickel	strontium	tungsten*
	antimony*	chromium*	lithium*	potassium	tellurium	vanadium*
	arsenic	cobalt*	magnesium	phosphorus	tin	yttrium
	barium	copper	manganese*	selenium	thallium	zinc
	beryllium*	iron	molybdenum*	silver	titanium	zirconium*
	cadmium	lead*				

*Some compounds of these elements require special sample treatment.

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (0.8- μ m, cellulose ester membrane, or 5.0- μ m, polyvinyl chloride membrane)	TECHNIQUE:	INDUCTIVELY COUPLED ARGON PLASMA, ATOMIC EMISSION SPECTROSCOPY (ICP-AES)
FLOWRATE:	1 to 4 L/min	ANALYTE:	elements above
VOL-MIN:	Table 1	ASHING	
-MAX:	Table 1	REAGENTS:	conc. HNO ₃ / conc. HClO ₄ (4:1), 5 mL; 2mL increments added as needed
SHIPMENT:	routine	CONDITIONS:	room temperature, 30 min; 150 °C to near dryness
SAMPLE		FINAL	
STABILITY:	stable	SOLUTION:	4% HNO ₃ , 1% HClO ₄ , 25 mL
BLANKS:	2 to 10 field blanks per set	WAVELENGTH:	depends upon element; Table 3
ACCURACY		BACKGROUND	
		CORRECTION:	spectral wavelength shift
RANGE STUDIED:	not determined	CALIBRATION:	elements in 4% HNO ₃ , 1% HClO ₄
BIAS:	not determined	RANGE:	varies with element [1]
OVERALL PRECISION ($\hat{S}_{r,r}$):	not determined	ESTIMATED LOD:	Tables 3 and 4
ACCURACY:	not determined	PRECISION (\hat{S}):	Tables 3 and 4

APPLICABILITY: The working range of this method is 0.005 to 2.0 mg/m³ for each element in a 500-L air sample. This is simultaneous elemental analysis, not compound specific. Verify that the types of compounds in the samples are soluble with the ashing procedure selected.

INTERFERENCES: Spectral interferences are the primary interferences encountered in ICP-AES analysis. These are minimized by judicious wavelength selection, interelement correction factors and background correction [1-4].

OTHER METHODS: This issue updates issues 1 and 2 of Method 7300, which replaced P&CAM 351 [3] for trace elements. Flame atomic absorption spectroscopy (e.g., Methods 70XX) is an alternate analytical technique for many of these elements. Graphite furnace AAS (e.g., 7102 for Be, 7105 for Pb) is more sensitive.

REAGENTS:

1. Nitric acid (HNO₃), conc., ultra pure.
2. Perchloric acid (HClO₄), conc., ultra pure.*
3. Ashing acid: 4:1 (v/v) HNO₃:HClO₄. Mix 4 volumes conc. HNO₃ with 1 volume conc. HClO₄.
4. Calibration stock solutions, 1000 µg/mL. Commercially available, or prepared per instrument manufacturer's recommendation (see step 12).
5. Dilution acid, 4% HNO₃, 1% HClO₄. Add 50 mL ashing acid to 600 mL water; dilute to 1 L.
6. Argon.
7. Distilled, deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size; or polyvinyl chloride membrane, 5.0-µm pore size; 37-mm diameter, in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Inductively coupled plasma-atomic emission spectrometer, equipped as specified by the manufacturer for analysis of elements of interest.
4. Regulator, two-stage, for argon.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.**
6. Volumetric flasks, 10-, 25-, 100-mL, and 1-L**
7. Assorted volumetric pipets as needed.**
8. Hotplate, surface temperature 150 °C.

** Clean all glassware with conc. nitric acid and rinse thoroughly in distilled water before use.

SPECIAL PRECAUTIONS: All perchloric acid digestions are required to be done in a perchloric acid hood. When working with concentrated acids, wear protective clothing and gloves.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 200 to 2000 L (see Table 1) for TWA measurements. Do not exceed a filter loading of approximately 2 mg total dust.

SAMPLE PREPARATION:

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 5 mL ashing acid. Cover with a watchglass. Let stand 30 min at room temperature.
NOTE: Start a reagent blank at this step.
5. Heat on hotplate (120 °C) until ca. 0.5 mL remains.
NOTE 1: Recovery of lead from some paint matrices may require other digestion techniques. See Method 7082 (Lead by Flame AAS) for an alternative hotplate digestion procedure or Method 7302 for a microwave digestion procedure.
NOTE 2: Some species of Al, Be, Co, Cr, Li, Mn, Mo, V, and Zr will not be completely solubilized by this procedure. Alternative solubilization techniques for most of these elements can be found elsewhere [5-10]. For example, aqua regia may be needed for Mn [6,12].
6. Add 2 mL ashing acid and repeat step 5. Repeat this step until the solution is clear.
7. Remove watchglass and rinse into the beaker with distilled water.
8. Increase the temperature to 150 °C and take the sample to near dryness (ca. 0.5 mL).
9. Dissolve the residue in 2 to 3 mL dilution acid.
10. Transfer the solutions quantitatively to 25-mL volumetric flasks.
11. Dilute to volume with dilution acid.
NOTE: If more sensitivity is required, the final sample volume may be held to 10 mL.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate the spectrometer according to the manufacturers recommendations.
NOTE: Typically, an acid blank and 1.0 µg/mL multielement working standards are used. The following multielement combinations are chemically compatible in 4% HNO₃/1% HClO₄:
 - a. Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, La, In, Na
 - b. Ag, K, Li, Mg, Mn, Ni, P, Pb, Se, Sr, Tl, V, Y, Zn, Sc
 - c. Mo, Sb, Sn, Te, Ti, W, Zr
 - d. Acid blank
13. Analyze a standard for every ten samples.
14. Check recoveries with at least two spiked blank filters per ten samples.

MEASUREMENT:

15. Set spectrometer to conditions specified by manufacturer.
16. Analyze standards and samples.
NOTE: If the values for the samples are above the range of the standards, dilute the solutions with dilution acid, reanalyze and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

17. Obtain the solution concentrations for the sample, C_s (µg/mL), and the average media blank, C_b (µg/mL), from the instrument.
18. Using the solution volumes of sample, V_s (mL), and media blank, V_b (mL), calculate the concentration, C (mg/m³), of each element in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \text{mg} / \text{m}^3$$

NOTE: µg/L ≡ mg/m³

EVALUATION OF METHOD:**Issues 1 and 2**

Method, 7300 was originally evaluated in 1981 [2,3]. The precision and recovery data were determined at 2.5 and 1000 µg of each element per sample on spiked filters. The measurements used for the method evaluation in Issues 1 and 2 were determined with a Jarrell-Ash Model 1160 Inductively Coupled Plasma Spectrometer operated according to manufacturer's instructions.

Issue 3

In this update of NIOSH Method 7300, the precision and recovery data were determined at approximately 3x and 10x the instrumental detection limits on commercially prepared spiked filters [12] using 25.0 mL as the final sample volume. Tables 3 and 4 list the precision and recovery data, instrumental detection limits, and analytical wavelengths for mixed cellulose ester (MCE) and polyvinyl chloride (PVC) filters. PVC Filters which can be used for total dust measurements and then digested for metals measurements were tested and found to give good results. The values in Tables 3 and 4 were determined with a Spectro Analytical Instruments Model End On Plasma (EOP)(axial) operated according to manufacturer's instructions.

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METHOD REVISED BY:

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Method originally written by Mark Millson, NIOSH/DART, and R. DeLon Hull, Ph.D., NIOSH/DSHEFS, James B. Perkins, David L. Wheeler, and Keith Nicholson, DataChem Laboratories, Salt Lake City, UT.

TABLE 1. PROPERTIES AND SAMPLING VOLUMES

Element (Symbol)	Properties		Air Volume, L @ OSHA PEL	
	Atomic Weight	MP, °C	MIN	MAX
Silver (Ag)	107.87	961	250	2000
Aluminum (Al)	26.98	660	5	100
Arsenic (As)	74.92	817	5	2000
Barium (Ba)	137.34	710	50	2000
Beryllium (Be)	9.01	1278	1250	2000
Calcium (Ca)	40.08	842	5	200
Cadmium (Cd)	112.40	321	13	2000
Cobalt (Co)	58.93	1495	25	2000
Chromium (Cr)	52.00	1890	5	1000
Copper (Cu)	63.54	1083	5	1000
Iron (Fe)	55.85	1535	5	100
Potassium (K)	39.10	63.65	5	1000
Lanthanum	138.91	920	5	1000
Lithium (Li)	6.94	179	100	2000
Magnesium (Mg)	24.31	651	5	67
Manganese (Mn)	54.94	1244	5	200
Molybdenum (Mo)	95.94	651	5	67
Nickel (Ni)	58.71	1453	5	1000
Phosphorus (P)	30.97	44	25	2000
Lead (Pb)	207.19	328	50	2000
Antimony (Sb)	121.75	630.5	50	2000
Selenium (Se)	78.96	217	13	2000
Tin (Sn)	118.69	231.9	5	1000
Strontium (Sr)	87.62	769	10	1000
Tellurium (Te)	127.60	450	25	2000
Titanium (Ti)	47.90	1675	5	100
Thallium (Tl)	204.37	304	25	2000
Vanadium (V)	50.94	1890	5	2000
Tungsten (W)	183.85	3410	5	1000
Yttrium (Y)	88.91	1495	5	1000
Zinc (Zn)	65.37	419	5	200
Zirconium (Zr)	91.22	1852	5	200

TABLE 2. EXPOSURE LIMITS, CAS #, RTECS

Element (Symbol)	CAS #	RTECS	Exposure Limits, mg/m ³ (Ca = carcinogen)		
			OSHA	NIOSH	ACGIH
Silver (Ag)	7440-22-4	VW3500000	0.01 (dust, fume, metal)	0.01 (metal, soluble)	0.1 (metal) 0.01 (soluble)
Aluminum (Al)	7429-90-5	BD0330000	15 (total dust) 5 (respirable)	10 (total dust) 5 (respirable fume) 2 (salts, alkyls)	10 (dust) 5 (powders, fume) 2 (salts, alkyls)
Arsenic (As)	7440-38-2	CG0525000	varies	C 0.002, Ca	0.01, Ca
Barium (Ba)	7440-39-3	CQ8370000	0.5	0.5	0.5
Beryllium (Be)	7440-41-7	DS1750000	0.002, C 0.005	0.0005, Ca	0.002, Ca
Calcium (Ca)	7440-70-2	--	varies	varies	varies
Cadmium (Cd)	7440-43-9	EU9800000	0.005	lowest feasible, Ca	0.01 (total), Ca 0.002 (respir.), Ca
Cobalt (Co)	7440-48-4	GF8750000	0.1	0.05 (dust, fume)	0.02 (dust, fume)
Chromium (Cr)	7440-47-3	GB4200000	0.5	0.5	0.5
Copper (Cu)	7440-50-8	GL5325000	1 (dust, mists) 0.1 (fume)	1 (dust) 0.1 (fume)	1 (dust, mists) 0.2 (fume)
Iron (Fe)	7439-89-6	NO4565500	10 (dust, fume)	5 (dust, fume)	5 (fume)
Potassium (K)	7440-09-7	TS6460000	--	--	--
Lanthanum	7439-91-0	--	--	--	--
Lithium (Li)	7439-93-2	--	--	--	--
Magnesium (Mg)	7439-95-4	OM2100000	15 (dust) as oxide 5 (respirable)	10 (fume) as oxide	10 (fume) as oxide
Manganese (Mn)	7439-96-5	OO9275000	C 5	1; STEL 3	5 (dust) 1; STEL 3 (fume)
Molybdenum (Mo)	7439-98-7	QA4680000	5 (soluble) 15 (total insoluble)	5 (soluble) 10 (insoluble)	5 (soluble) 10 (insoluble)
Nickel (Ni)	7440-02-0	QR5950000	1	0.015, Ca	0.1 (soluble) 1 (insoluble, metal)
Phosphorus (P)	7723-14-0	TH3500000	0.1	0.1	0.1
Lead (Pb)	7439-92-1	OF7525000	0.05	0.05	0.05
Antimony (Sb)	7440-36-0	CC4025000	0.5	0.5	0.5
Selenium (Se)	7782-49-2	VS7700000	0.2	0.2	0.2
Tin (Sn)	7440-31-5	XP7320000	2	2	2
Strontium (Sr)	7440-24-6	--	--	--	--
Tellurium (Te)	13494-80-9	WY2625000	0.1	0.1	0.1
Titanium (Ti)	7440-32-6	XR1700000	--	--	--
Thallium (Tl)	7440-28-0	XG3425000	0.1 (skin) (soluble)	0.1 (skin) (soluble)	0.1 (skin)
Vanadium (V)	7440-62-2	YW2400000	--	C 0.05	--
Tungsten	7440-33-7	--	5	5 10 (STEL)	5 10 (STEL)
Yttrium (Y)	7440-65-5	ZG2980000	1	N/A	1
Zinc (Zn)	7440-66-6	ZG8600000	--	--	--
Zirconium (Zr)	7440-67-7	ZH7070000	5	5, STEL 10	5, STEL 10

TABLE 3. MEASUREMENT PROCEDURES AND DATA [1].
Mixed Cellulose Ester Filters (0.45 µm)

Element (a)	wavelength nm	Est. LOD µg/ Filter	LOD ng/mL	Certified 3x LOD (b)	% Recovery (c)	Percent RSD (N=25)	Certified 10x LOD (b)	% Recovery (c)	Percent RSD (N=25)
Ag	328	0.042	1.7	0.77	102.9	2.64	3.21	98.3	1.53
Al	167	0.115	4.6	1.54	105.4	11.5	6.40	101.5	1.98
As	189	0.140	5.6	3.08	94.9	2.28	12.9	93.9	1.30
Ba	455	0.005	0.2	0.31	101.8	1.72	1.29	97.7	0.69
Be	313	0.005	0.2	0.31	100.0	1.44	1.29	98.4	0.75
Ca	317	0.908	36.3	15.4	98.7	6.65	64.0	100.2	1.30
Cd	226	0.0075	0.3	0.31	99.8	1.99	1.29	97.5	0.88
Co	228	0.012	0.5	0.31	100.8	1.97	1.29	98.4	0.90
Cr	267	0.020	0.8	0.31	93.4	16.3	1.29	101.2	2.79
Cu	324	0.068	2.7	1.54	102.8	1.47	6.40	100.6	0.92
Fe	259	0.095	3.8	1.54	103.3	5.46	6.40	98.0	0.95
K	766	1.73	69.3	23.0	90.8	1.51	96.4	97.6	0.80
La	408	0.048	1.9	0.77	102.8	2.23	3.21	100.1	0.92
Li	670	0.010	0.4	0.31	110.0	1.91	1.29	97.7	0.81
Mg	279	0.098	3.9	1.54	101.1	8.35	6.40	98.0	1.53
Mn	257	0.005	0.2	0.31	101.0	1.77	1.29	94.7	0.73
Mo	202	0.020	0.8	0.31	105.3	2.47	1.29	98.6	1.09
Ni	231	0.020	0.8	0.31	109.6	3.54	1.29	101.2	1.38
P	178	0.092	3.7	1.54	84.4	6.19	6.40	82.5	4.75
Pb	168	0.062	2.5	1.54	109.4	2.41	6.40	101.7	0.88
Sb	206	0.192	7.7	3.08	90.2	11.4	12.9	41.3	32.58
Se	196	0.135	5.4	2.3	87.6	11.6	9.64	84.9	4.78
Sn	189	0.040	1.6	0.77	90.2	18.0	3.21	49	21.79
Sr	407	0.005	0.2	0.31	101.0	1.55	1.29	97.3	0.65
Te	214	0.078	3.1	1.54	102.0	2.67	6.40	97.4	1.24
Ti	334	0.050	2.0	0.77	98.4	2.04	3.21	93.4	1.08
Tl	190	0.092	3.7	1.54	100.9	2.48	6.40	99.1	0.80
V	292	0.028	1.1	0.77	103.2	1.92	3.21	98.3	0.84
W	207	0.075	3.0	1.54	72.2	10.1	6.40	57.6	14.72
Y	371	0.012	0.5	0.31	100.5	1.80	1.29	97.4	0.75
Zn	213	0.310	12.4	4.60	102.2	1.87	19.3	95.3	0.90
Zr	339	0.022	0.9	0.31	88.0	19.4	1.29	25	57.87

- (a) Bold values are qualitative only because of low recovery.
(b) Values are certified by Inorganic Ventures INC. at 3x and 10x the approximate instrumental LOD
(c) Values reported were obtained with a Spectro Analytical Instruments EOP ICP; performance may vary with instrument and should be independently verified.

TABLE 4. MEASUREMENT PROCEDURES AND DATA [1].
Polyvinyl Chloride Filter (5.0 µm)

Element (c)	wavelength nm	Est. LOD µg per filter	LOD ng/mL	Certified 3x LOD (b)	% Recovery (a)	Percent RSD (N=25)	Certified ¹⁷ 10x LOD (b)	% Recovery (a)	Percent RSD (N=25)
Ag	328	0.042	1.7	0.78	104.2	8.20	3.18	81.8	18.9
Al	167	0.115	4.6	1.56	77.4	115.24	6.40	92.9	20.9
As	189	0.140	5.6	3.10	100.7	5.13	12.70	96.9	3.2
Ba	455	0.005	0.2	0.31	102.4	3.89	1.270	99.8	2.0
Be	313	0.005	0.2	0.31	106.8	3.53	1.270	102.8	2.1
Ca	317	0.908	36.3	15.6	68.1	12.66	64.00	96.8	5.3
Cd	226	0.0075	0.3	0.31	105.2	5.57	1.27	101.9	2.8
Co	228	0.012	0.5	0.31	109.3	4.67	1.27	102.8	2.8
Cr	267	0.020	0.8	0.31	109.4	5.31	1.27	103.4	4.1
Cu	324	0.068	2.7	1.56	104.9	5.18	6.40	101.8	2.4
Fe	259	0.095	3.8	1.56	88.7	46.82	6.40	99.1	9.7
K	766	1.73	69.3	23.4	96.4	4.70	95.00	99.2	2.2
La	408	0.048	1.9	0.78	45.5	4.19	3.18	98.8	2.6
Li	670	0.010	0.4	0.31	107.7	4.80	1.27	110.4	2.7
Mg	279	0.098	3.9	1.56	54.8	20.59	6.40	64.5	5.7
Mn	257	0.005	0.2	0.31	101.9	4.18	1.27	99.3	2.4
Mo	202	0.020	0.8	0.31	106.6	5.82	1.27	98.1	3.8
Ni	231	0.020	0.8	0.31	111.0	5.89	1.27	103.6	3.2
P	178	0.092	3.7	1.56	101.9	17.82	6.40	86.5	10.4
Pb	168	0.062	2.5	1.56	109.6	6.12	6.40	103.2	2.9
Sb	206	0.192	7.7	3.10	64.6	22.54	12.70	38.1	30.5
Se	196	0.135	5.4	2.30	83.1	26.23	9.50	76.0	17.2
Sn	189	0.040	1.6	0.78	85.7	27.29	3.18	52.0	29.4
Sr	407	0.005	0.2	0.31	71.8	4.09	1.27	81.2	2.7
Te	214	0.078	3.1	1.56	109.6	7.49	6.40	97.3	3.8
Ti	334	0.050	2.0	0.78	101.0	9.46	3.18	92.4	5.5
Tl	190	0.092	3.7	1.56	110.3	4.04	6.40	101.9	2.0
V	292	0.028	1.1	0.78	108.3	3.94	3.18	102.5	2.6
W	207	0.075	3.0	1.56	74.9	15.79	6.40	44.7	19.6
Y	371	0.012	0.5	0.31	101.5	3.63	1.27	101.4	2.5
Zn	213	0.310	12.4	4.70	91.0	68.69	19.1	101.0	9.6
Zr	339	0.022	0.9	0.31	70.7	54.20	1.27	40.4	42.1

- (a) Values reported were obtained with a Spectro Analytical Instruments EOP ICP; performance may vary with instrument and should be independently verified.
- (b) Values are certified by Inorganic Ventures INC. at 3x and 10x the approximate instrumental LOD [12].
- (c) Bold values are qualitative only because of low recovery. Other digestion techniques may be more appropriate for these elements and their compounds.

SILICA, CRYSTALLINE, by XRD (filter redeposition)

7500

SiO₂ MW: 60.08 CAS: 14808-60-7 (quartz) RTECS: VV7330000 (quartz)
 14464-46-1 (cristobalite) VV7325000 (cristobalite)
 15468-32-3 (tridymite) VV7335000 (tridymite)

METHOD: 7500, Issue 4

EVALUATION: FULL

Issue 1: 15 August 1990

Issue 4: 15 March 2003

OSHA : quartz (respirable) 10 mg/m³/(%SiO₂+2);
 cristobalite and tridymite (respirable) ½ the above
NIOSH: 0.05 mg/m³; carcinogen
ACGIH: quartz (respirable) 0.1 mg/m³
 cristobalite (respirable) 0.05 mg/m³
 tridymite (respirable) 0.05 mg/m³

PROPERTIES: solid; d 2.65 g/cm³ @ 0 °C; crystalline
 transformations: quartz to tridymite
 @ 867 °C; tridymite to cristobalite
 @ 1470 °C; α-quartz to β-quartz
 @ 573 °C

SYNONYMS: free crystalline silica; silicon dioxide

SAMPLING		MEASUREMENT	
SAMPLER:	CYCLONE + FILTER (10-mm nylon cyclone, Higgins-Dewell (HD) cyclone, or aluminum cyclone + 5-µm PVC membrane) *see sampling section	TECHNIQUE:	X-RAY POWDER DIFFRACTION
FLOW RATE:	Nylon cyclone: 1.7 L/min; HD cyclone: 2.2 L/min; aluminum cyclone: 2.5 L/min	ANALYTE:	Crystalline SiO ₂
VOL-MIN:	400 L	ASH:	Muffle furnace or RF plasma asher or dissolve in tetrahydrofuran
-MAX:	1000 L	REDEPOSIT:	On 0.45-µm Ag membrane filter
SHIPMENT:	Routine	XRD:	Cu target X-ray tube, graphite monochromator Optimize for intensity; 1° slit Slow step scan, 0.02°/10 sec Integrated intensity with background subtraction
SAMPLE STABILITY:	Stable	CALIBRATION:	NIST SRM 1878a quartz, NIST SRM 1879a cristobalite, USGS 210-75-0043 tridymite suspensions in 2-propanol.
BLANKS:	2 to 10 per set (see step 13.g.)	RANGE:	0.02 to 2 mg SiO ₂ per sample [2]
BULK SAMPLE:	High-volume or settled dust; to identify interferences	ESTIMATED LOD:	0.005 mg SiO ₂ per sample [2]
ACCURACY		PRECISION (Ŝ_r):	0.08 @ 0.05 to 0.2 mg per sample [1]
RANGE STUDIED:	25 to 2500 µg/m ³ [1] (800-L sample)		
BIAS:	None known		
OVERALL PRECISION (Ŝ_{r,T}):	0.09 (50 to 200 µg) [1]		
ACCURACY:	± 18%		

APPLICABILITY: The working range is 0.025 to 2.5 mg/m³ for an 800-L air sample.

INTERFERENCES: Micas, potash, feldspars, zircon, graphite, and aluminosilicates. See APPENDIX.

OTHER METHODS: This is similar to the method in the Criteria Document [3] and P&CAM 259 [4] which has been collaboratively tested [1]. This method is similar, except for sample collection, to S315 [5,6]. Method P&CAM 109 [7,8,9], which incorporates an internal standard, has been dropped. XRD can distinguish the three silica polymorphs and silica interferences can be eliminated by phosphoric acid treatment. IR (methods 7602 and 7603) can also quantify quartz, cristobalite and tridymite if amorphous silica and silicates are not present in large amounts. However sensitivity is reduced if multiple polymorphs are present and secondary peaks must be used. Crystalline silica can also be determined by visible absorption spectrophotometry (e.g., Method 7601), but polymorphs can not be distinguished. Visible absorption methods also have larger laboratory-to-laboratory variability than XRD and IR methods and therefore are recommended for research use only [10].

REAGENTS:

1. Silica Standards.
 - a. Quartz* (SRMs 1878a, 2950, 2951, 2958) and Cristobalite* (SRMs 1879a, 2960, 2957), available from Standard Reference Materials Program, Rm. 204, Bldg. 202, National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899; www.nist.gov.
 - b. Tridymite* (210-75-0043) available from U.S. Geological Survey, Box 25046, MS 973, Denver, CO 80225.
2. 2-Propanol*, reagent grade.
3. Desiccant.
4. Glue or tape for securing Ag filters to XRD holders.
5. Optional: tetrahydrofuran (THF)* (if LTA or muffle furnace are unavailable).
6. 1.5 % parlodion solution. (Dissolve 1.5 g of parlodion* in isopentyl acetate* and dilute to 100 mL with isopentyl acetate.)
7. Optional (if calcite present): 25% v/v concentrated hydrochloric acid* (ACS reagent grade) in distilled water and 25-mm filters of PVC or cellulose ester with pore size of 1 µm or less.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
 - a. Filter: Polyvinyl chloride (PVC) filter, 37-mm, 5.0-µm pore size supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
NOTE: Check each new lot of PVC filters by analyzing one or more by this method. For example, Gelman VM-1 filters (all lots) were found to be unacceptable because of high ash and background. If THF is used, check for complete dissolution by dissolving a blank PVC filter and following steps 5c through 8.
 - b. Cyclone: 10-mm nylon, Higgins-Dewell (HD), Aluminum (Al), or equivalent [11].
2. Area air sampler: PVC membrane filter, 37-mm diameter, 5-µm pore size; three-piece filter cassette.
3. Sampling pumps with flexible connecting tubing, capable of the following flow rates: nylon cyclone, 1.7 L/min; HD cyclone, 2.2 L/min; Al cyclone, 2.5 L/min; and bulk sampler, 3 L/min.
4. Silver membrane filters, 25-mm diameter, 0.45-µm pore size, available from Sterlitech Corp., 22027 70th Ave S, Kent, WA 98032-1911; www.sterlitech.com.
5. X-ray powder diffractometer (XRD) equipped with copper target X-ray tube, graphite monochromator, and scintillation detector.
6. Reference specimen (mica, Arkansas stone, or other stable standard) for data normalization.
7. Low-temperature radio-frequency plasma asher (LTA) or muffle furnace, or ultrasonic bath (≥ 150 W), for filter preparation.
8. Vacuum filtration assembly and side-arm vacuum flask with a 25-mm filter holder.
9. Sieve, 10-µm, for wet sieving.
10. Analytical balance (0.001 mg); magnetic stirrer with thermally insulated top; ultrasonic bath or probe; volumetric pipettes and flasks; Pyrex crucibles with covers (muffle furnace); 40-mL wide-mouth or 50-mL centrifuge tubes (THF method); desiccator; reagent bottles with ground glass stoppers; drying oven; polyethylene wash bottle.
11. Explosion-resistant hot plate.
12. Teflon sheet, 0.3 to 1 mm thick.

SPECIAL PRECAUTIONS: Avoid inhaling silica dust [3]. THF is extremely flammable and should be used in a fume hood. 2-Propanol, parlodion and isopentyl acetate are flammable. Hydrochloric acid is corrosive and should be used in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at $1.7 \pm 5\%$ L/min with nylon cyclone or $2.2 \pm 5\%$ L/min with HD cyclone for a total sample size of 400 to 1000 L. Do not exceed 2 mg dust loading on the filter.
NOTE 1: Do not allow the sampler assembly to be inverted at any time when using a cyclone. Turning the cyclone to anything other than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.
NOTE 2: A single sampler/flow rate should be used for a given application. Sampling for both crystalline silica and coal mine dust should be done in accordance with the ISO/CEN/ACGIH/ASTM respirable aerosol sampling convention. Flow rates of 1.7 L/min for the Dorr-Oliver nylon cyclone and 2.2 L/min for the Higgins-Dewell cyclone have been found to be optimal for this purpose. Outside of coal mine dust sampling, the regulatory agencies currently use these flow rates with the Dorr-Oliver cyclone in the United States and the Higgins-Dewell sampler in the United Kingdom. Though the sampling recommendations presented in a NIOSH Criteria Document have been formally accepted by MSHA for coal mine dust sampling, the Dorr-Oliver cyclone at 2.0 L/min with 1.38 conversion factor is currently used in the United States for the purpose of matching an earlier sampling convention [12]. In any case, a single sampler/flow rate should be used in any given application so as to eliminate bias introduced by differences between sampler types and sampler conventions [11].
3. Take an area air sample or collect a settled dust sample, if dust in the work environment has not been previously characterized.

SAMPLE PREPARATION:

4. Samples may be characterized by one of the following methods, as appropriate.
 - a. **Interference check.** Prepare area dust sample or settled dust bulk sample for XRD analysis by mounting the collection sample directly on an XRD sample holder, or by depositing or redepositing the dust on another filter for mounting, or by packing an XRD powder holder. Proceed to step 11.
 - b. **Qualitative Analysis.** Prepare the area air sample or settled dust sample for qualitative analysis by grinding and/or wet sieving to best match the airborne dust particle size. Wet sieve with a 10- μ m sieve, 2-propanol, and an ultrasonic bath [13], followed by evaporation of excess alcohol, drying in an oven for 2 hours, and overnight storage in a desiccator. Deposit the end product on a filter (steps 7-8) or pack in a conventional XRD powder holder.
NOTE 1: For quantitative determination of % SiO₂, weigh out, in triplicate, 2 mg sieved dust, transfer to a 50-mL beaker, add 10 mL 2-propanol, and continue with step 6.
NOTE 2: In a bulk sample, if there is an interfering compound(s) that renders the identification and quantitation of quartz very difficult, the sample will need to be carefully treated in hot phosphoric acid [14] to dissolve the interfering compound(s) and avoid the loss of quartz. This treatment can be used to dissolve several 50-mg sample aliquots in order to concentrate the quartz content for the purpose of lowering the LOD.
5. Use one of the following methods to prepare filter samples and blanks:
 - a. **Low Temperature Ashing:** Place the filters in 50-mL beakers within the low temperature asher so that the sample exposure to the plasma is optimized. Ash according to manufacturer's instructions. After ashing, carefully add 15 mL 2-propanol to each beaker; or
 - b. **Muffle Furnace Ashing:**
 - i. If the samples contain a significant amount of calcite (>20% of total dust loading), silica may be lost due to formation of CaSiO₃. Remove the calcite by the following procedure: Place a 0.5- μ m, 25-mm PVC filter in the filtration apparatus and clamp the filter funnel over it. Remove the sample filter from the cassette, fold, and drop it on the 25-mm filter. Add 10 mL 25% v/v HCl and

- 5 mL 2-propanol to the filter funnel and allow to stand for 5 min. Apply vacuum and slowly aspirate the acid and alcohol in the funnel, washing with three successive 10-mL portions of distilled water. Release the vacuum. Carry both filters through the ashing step together.
- ii. Place the filter samples in porcelain crucibles, loosely cover and ash in muffle furnace for 2 h at 600 °C (800 °C if graphite is present). Add several mL 2-propanol to the ash, scrape the crucible with a glass rod to loosen all particles and transfer the residue to a 50-mL beaker. Wash the crucible several more times and add wash to beaker. Add 2-propanol to the beaker to bring the volume to about 15 mL; or
 - c. **Filter Dissolution:** Using forceps and a spatula, remove the filter from the cassette, fold the filter three times, and place in the bottom of a 40- or 50-mL centrifuge tube. Add 10 mL THF and allow to stand for at least 5 min. Cap the centrifuge tube with aluminum foil to prevent contamination. Gently agitate the centrifuge tube by hand or with a vortex mixer making sure the THF does not go near the top of the tube. Place the tube in an ultrasonic bath (water level 2.5 cm from top) for at least 10 min. (The filter should be totally dissolved.) Just prior to filtering, agitate the sample for 10 to 20 sec on a vortex mixer. Continue with step 6, substituting THF for 2-propanol and centrifuge tube for beaker.
6. Cover the beaker with a watchglass and agitate in an ultrasonic bath for at least 3 min. Observe the suspension to make sure that the agglomerated particles are broken up. Wash the underside of the watchglass with 2-propanol, collecting the washings in the beaker.
 7. Place a silver filter in the filtration apparatus. Attach the funnel securely over the entire filter circumference. With no vacuum, pour 2 to 3 mL 2-propanol onto the filter. Pour the sample suspension from the beaker into the funnel. After the transfer, rinse the beaker several times and add rinsings to the funnel for a total volume of 20 mL. In order to minimize feathering of the sample outside the deposition area, allow the suspension to settle for a few minutes prior to applying vacuum. Do not rinse the chimney after the material has been deposited on the silver filter. Rinsing the chimney can disturb the thin layer deposition.
 8. Leave the vacuum on after filtration to produce a dry filter. Place 2 drops of 1.5% parlodion solution on a glass slide. Remove the silver filter with forceps and fix the material to the filter by placing the bottom side of the filter in the parlodion solution. Place the saturated filter on top of the Teflon sheet which has been heated on the hot plate at a low temperature setting. When thoroughly dry, mount the silver filter in the XRD sample holder.

CALIBRATION AND QUALITY CONTROL:

9. Prepare and analyze at least 6 levels of standard filters.
NOTE 1: Calibration standards are limited to NIST and USGS certified standards of known purity, particle size, and sample-to-sample homogeneity. At least 12 materials, including 5- μm Min-U-Sil, previously used by laboratories throughout the United States and Canada, have been evaluated, and none have been found to be acceptable alternatives to the certified standards cited within this method [10]. Standard reference materials should be corrected for phase purity.
NOTE 2: Crystalline silica methods require calibration standards of known purity, specific particle size and distribution, and sample-to-sample homogeneity. Establishing traceability of secondary calibration standards to the specified NIST and USGS primary standards requires the use of measurement methods with better precision and accuracy than the XRD, IR and visible absorption spectrophotometry methods commonly used in the industrial hygiene field can provide. In addition, particle size distribution measurements have considerable error. Therefore, the use of secondary calibration standards that are traceable to NIST and USGS certified standards is not appropriate.
NOTE 3: NIST SRM 2950 calibration set (α -quartz) and NIST SRM 2960 calibration set (cristobalite) may be useful for preparing working standards at known concentrations.
 - a. Prepare two suspensions of each analyte in 2-propanol by weighing 10 and 50 mg of the standard material to the nearest 0.01 mg. Quantitatively transfer each to a 1-L glass-stoppered bottle using 1.00 L of 2-propanol.
 - b. Suspend the powder in 2-propanol with an ultrasonic probe or bath for 20 min. Immediately move the bottle to a magnetic stirrer with thermally insulated top and add a stirring bar. Allow the solution to return to room temperature before withdrawing aliquots.

- c. Mount a silver filter on the filtration apparatus. Place several mL of 2-propanol on the filter. Turn off the stirrer and shake vigorously by hand. Immediately remove the stopper and withdraw an aliquot from the center at half-height of the 10 mg/L or 50 mg/L suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, discard the aliquot in a beaker, rinse and dry the pipet, and take a new aliquot. Transfer the aliquot from the pipet to the silver filter, keeping the tip of the pipet near the surface but not submerged in the delivered suspension.
- d. Rinse the pipet with several mL 2-propanol, draining the rinse into the funnel. Repeat the rinse several times.
- e. Allow the suspension to settle for a few minutes prior to applying vacuum. Apply vacuum and rapidly filter the suspension. Do not wash down the sides of the funnel after the deposit is in place since this will rearrange the material on the silver filter. Leave vacuum on until filter is dry. Place 2 drops of 1.5% parlodion solution on a glass slide. Remove the silver filter with forceps and fix the material to the filter by placing the bottom side of the filter in the parlodion solution. Place the saturated filter on top of the heated Teflon sheet. When thoroughly dry, mount the silver filter in the XRD sample holder. Prepare working standard filters, in triplicate, at e.g., 10, 20, 50, 100, 250, and 500 μg .
- f. Analyze the working standards together with samples and blanks (step 12). The XRD intensities for the working standards (step 12.d) are designated I_x^o and are then normalized (step 12.e) to obtain \hat{I}_x^o . Correct the intensities of working standards $>200 \mu\text{g}$ for matrix absorption (steps 12.f and 13).
- g. Prepare a calibration graph (\hat{I}_x^o , vs μg of each standard).
NOTE: Poor repeatability ($>10\%$ above 0.04 mg silica) at any given level indicates that new standards should be made. The data should lie along a straight line. A weighted least squares ($1/\sigma^2$ weighting) is preferable.
- h. Determine the slope, m , of the calibration graph in counts/ μg . The intercept, b , on the abscissa should be within $\pm 5 \mu\text{g}$ of zero.
NOTE: A large intercept indicates an error in determining the background, i.e., an incorrect baseline or interference by another phase.
10. NOTE: The following procedure for absorption correction is not necessary in situations that have been previously documented as requiring no corrections.
Select six silver membrane filters as media blanks randomly from the same box of filters to be used for depositing the samples. These will be used to test for sample self-absorption. Mount each of the media blanks on the filtration apparatus and apply vacuum to draw 5 to 10 mL 2-propanol through the filter. Remove, let dry, and mount on XRD holders. Determine the net normalized count for the silver peak, \hat{I}_{Ag}^o , for each media blank (step 12.g). Obtain an average value for the six media blanks, \hat{I}_{Ag}^o .
NOTE: The analyst is a critical part of this analytical procedure [12]. A high level of analyst expertise is required to optimize instrument parameters and correct for matrix interferences either during the sample preparation phase or the data analysis and interpretation phase [15]. The analyst should have some training (university or short course) in mineralogy or crystallography in order to have a background in crystal structure, diffraction patterns and mineral transformation. In addition, an intensive short course in the fundamentals of X-ray diffraction can be useful.

MEASUREMENT:

11. Obtain a qualitative X-ray diffraction scan (e.g., 10 to 80 $^{\circ}2\theta$) of the area air sample (or bulk settled dust) to determine the presence of free silica polymorphs and interferences (see APPENDIX). The diffraction peaks are:

Mineral	Peak (2-Theta Degrees)		
	Primary	Secondary	Tertiary
Quartz	26.66	20.85	50.16
Cristobalite	21.93	36.11	31.46
Tridymite	21.62	20.50	23.28
Silver	38.12	44.28	77.47

NOTE: There is an alternative to scanning an area air sample, settled dust sample, or ground bulk sample to prove lack of contamination. A slow scan of the three main peaks of quartz (also cristobalite and tridymite if their absence has not been previously confirmed) on a personal air sample, with verification that their intensity ratios are within 15% of pure quartz, is sufficient evidence that other materials are not interfering in the silica determination.

12. Perform the following for each sample, working standard, and blank filter:
 - a. Mount the reference specimen. Determine the net intensity, I_r , of the reference specimen before and after each filter is scanned. Use a diffraction peak of high intensity that can be rapidly but reproducibly ($S_r < 0.01$) measured.
 - b. Mount the sample, working standard, or blank filter. Measure the diffraction peak area for each silica polymorph. Scan times must be long, e.g., 15 min (longer scan times will lower the limit of detection).
 - c. Measure the background on each side of the peak for one-half the time used for peak scanning. The sum of these two counts is the average background. Determine the position of the background for each sample.
 - d. Calculate the net intensity, I_x , (the difference between the peak integrated count and the total background count).
 - e. Calculate and record the normalized intensity, \hat{I}_x , for each peak:

$$\hat{I}_x = \frac{I_x}{I_r} \cdot N$$

NOTE: Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak, and use this value of N for all analyses. Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently and the net intensities should be normalized to the most recently-measured reference intensity.

- f. Determine the normalized count, \hat{I}_{Ag} , of an interference-free silver peak on the sample filter following the same procedure. Use a short scan time for the silver peak (e.g., 5% of scan time for analyte peaks) throughout the method.
- g. Field blanks may be analyzed by scanning the 2-theta range used for the analyte and silver peaks to verify that contamination of the filters has not occurred. The analyte peak should be absent. The normalized intensity of the silver peak should match that of the media blank. Each laboratory should determine the specifics of field blank use for its application. When contamination does occur, the reason should be investigated and appropriate action taken. In practice, contamination of field blanks is extremely rare and usually is not consistent across filters. The analysis of blanks may be abbreviated if experience indicates that contamination is not likely with current field and laboratory operations; however, occasional confirmation of non-contamination is prudent.

CALCULATIONS:

13. Calculate the concentration of crystalline silica, C (mg/m³), in the air volume sampled, V (L):

$$C = \frac{\hat{I}_x \cdot f(t) - b}{m \cdot V}, \text{mg} / \text{m}^3$$

- \hat{I}_x = normalized intensity for sample peak
 b = intercept of calibration graph (\hat{I}_x^0 vs. μg)
 m = slope of calibration graph, counts/ μg
 $f(t)$ = $-R \ln T / (1 - T^R)$ = absorption correction factor (Table 1)

$$R = \sin(\Theta_{Ag})/\sin(\Theta_x)$$

$$T = \hat{I}_{Ag}/(\text{average } \hat{I}_{Ag}^o) = \text{transmittance of sample}$$

$$\hat{I}_{Ag} = \text{normalized silver peak intensity from sample}$$

$$\hat{I}_{Ag}^o = \text{normalized silver peak intensity from media blanks (average of six values)}$$

EVALUATION OF METHOD:

This method is based on P&CAM 259 which was collaboratively tested [1]. The testing included a ruggedization step to test the effects of the use of muffle furnace or plasma asher (but not the use of THF), shipment of samples, ashing time, and ultrasonication time. None of these factors was found to have an effect. The method was shown to have no bias when referenced to the Talvitie spectrophotometric method [14] and when all standards and samples were Min-U-Sil 5. The relative standard deviations (S_r) for intralaboratory, total measurement and overall (including sampling) variability are:

	Analyte Level (μg)	Measurement Precision (S_r)	Overall Precision (S_{rT})
Intralaboratory	50-200	0.08 [1]	
	20	0.20 [5]	
	10	0.28 [9]	
Total (intra- and interlaboratory)	50-200	0.17 [1]	0.29 [1]

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APPENDIX: INTERFERENCES

Interferences include barite, micas (muscovite, biotite), potash, feldspars (microcline, plagioclase), montmorillonite, sillimanite, zircon, graphite, iron carbide, clinoferrosillite, wollastonite, sanidine, leucite, orthoclase, and lead sulfide.

The patterns for three forms of aluminum phosphate [JCPDS 10-423, 11-500, 20-44] are practically identical to those of quartz, cristobalite and tridymite, respectively. The quartz secondary and cristobalite primary peaks are close; cristobalite secondary peak is overlapped by a quartz peak; 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, interferes slightly with the primary quartz peak. Many of these interferences occur in the presence of quartz; however, in a study of samples collected in 11 different industries, Altree-Williams [20] found no significant interferences.

The presence of elements such as iron can result in appreciable X-ray fluorescence which leads to high background intensity. A diffracted-beam monochromator will minimize this problem.

If calcite is present, loss of quartz will occur when samples are ashed in a muffle furnace. See SAMPLE PREPARATION (step 5.b) for procedure to remove calcite.

If interferences with the primary silica peak are present, use a less sensitive peak. When overlaps are not severe, a smaller receiving slit or chromium radiation may be used; however, a new calibration curve will be necessary.

Table 1. Absorption correction factor as a function of transmittance for some silica-silver peak combinations [16-21].

Transmittance	Silica	f(T) (at indicated degrees 2- θ)							
		26.66	26.66	20.83	20.83	21.93	21.93	21.62	21.62
T	Silver	38.12	44.28	38.12	44.28	38.12	44.28	38.12	44.28
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	1.0635
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	1.3119	1.2713	1.3167
0.74		1.2283	1.2662	1.2965	1.3456	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	1.3682	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
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	1.6858	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