Method no.: 1008

Control no.: T-1008-FV-01-0609-M

Target concentration: 20 ppm (27.8 mg/m^3)

OSHA General Industry PEL: 20 ppm (Ceiling); 50 ppm (Peak)
OSHA Construction PEL: 10 ppm (15 mg/m^3) (TWA)
OSHA Maritime PEL: 10 ppm (15 mg/m^3) (TWA)
ACGIH TLV: 10 ppm (14 mg/m^3) (TWA)

Procedure: Samples are collected by drawing workplace air through specially constructed hydrogen sulfide samplers containing silver nitrate coated silica gel using a personal sampling pump. During sampling hydrogen sulfide reacts with silver to form silver sulfide. Sulfide is extracted from the samples using NaCN/NaOH then converted to sulfate using hydrogen peroxide and analyzed by ion chromatography using a conductivity detector.

Recommended sampling parameters:

	TWA Sample	Ceiling Sample	Peak Sample
Sampling rate:	0.05 L/min	0.5 L/min	0.5 L/min
Sampling time:	240 min	15 min	10 min
Total air volume:	12 L	7.5 L	5 L

Reliable quantitation limit:

TWA Sample	Ceiling Sample	Peak Sample
0.520 ppm (0.724 mg/m^3)	0.831 ppm (1.16 mg/m^3)	1.25 ppm (1.74 mg/m^3)

Standard error of estimate at the target concentration: 5.1%

Special requirements: The sampling pump must maintain a constant flow at 0.5 L/min with a back pressure of approximately 15 inches of water.

Status of method: Evaluated method. This method has been subjected to the established evaluation procedures of the Methods Development Team.

September 2006

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1. General Discussion

For assistance with accessibility problems in using figures and illustrations presented in this method, please contact the Salt Lake Technical Center (SLTC) at (801) 233-4900. These procedures were designed and tested for internal use by OSHA personnel. Mention of any company name or commercial product does not constitute endorsement by OSHA.

1.1 Background

1.1.1 History

Initially the Occupational Safety and Health Administration (OSHA) used a midget impinger containing an alkaline suspension of cadmium hydroxide to collect hydrogen sulfide (H_2S)[1]. The photosensitivity of the cadmium sulfide formed, and other safety issues associated with impinger sampling, motivated OSHA to develop a hydrogen sulfide method using silver nitrate impregnated cellulose filters (OSHA ID-141)[2]. During sampling the hydrogen sulfide reacted with the silver nitrate on the filter forming silver sulfide. In the laboratory the filter was placed in an alkaline cyanide solution. The cyanide formed a complex with the silver freeing the sulfide that was then analyzed using a polarographic analyzer equipped with a dropping mercury electrode. The use of this method was eventually discontinued due to possible mercury exposure from the polarograph. The method also had several weaknesses and limitations including that the impregnated filters were only stable for three months, the sampler only had capacity for a one hour time weighted average sample, and the calibration standards had to be titrated daily. The sampler also did not have a prefilter to screen out particulate sulfide compounds and the samples had to be analyzed immediately after completion of sample preparation.

OSHA then used a modified version of NIOSH 6013[3] that uses coconut shell charcoal to collect hydrogen sulfide. In the laboratory the charcoal is placed in a solution of ammonium hydroxide and hydrogen peroxide that converts the hydrogen sulfide to sulfate. The sulfate is then analyzed by ion chromatography. This medium, however, collects sulfur dioxide which is a positive interference. The charcoal, depending on lot, can also suffer from high sulfur backgrounds and poor desorption efficiencies.

Because of the limitations of the previous methods used to sample hydrogen sulfide OSHA required a sampler that could collect both long and short term samples, had high extraction efficiency, and did not suffer from interferences from common compounds such as sulfur dioxide. It is preferable to have a relatively easy sample preparation procedure and samples that are stable after preparation. The need for such a sampler resulted in this work.

For the collection of hydrogen sulfide a new sampler was developed and is described in detail in Appendix A. The sampler works by first sending the sample air stream through an uncoated glass fiber depth filter (GFF) to collect particulates. Next, the air stream passes through a sodium carbonate / glycerol coated GFF scrubbing any sulfur dioxide. Finally, the air stream is passed through two sections of 5% silver nitrate coated silica gel to collect hydrogen sulfide. In the laboratory the silica gel is placed in a NaCN/NaOH solution, heated in a hot water bath, and then placed on a shaker. The

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[1] *NIOSH Manual of Analytical Methods (NMAM)*, 2nd ed.; DHEW/NIOSH Pub. No. 77-157-B; U.S. National Institute of Occupational Safety and Health (NIOSH): Cincinnati, OH, 1977; Vol. 2, p S4-1-S4-10.

[2] Wilczek, T.; Hydrogen Sulfide in Workplace Atmospheres. http://www.osha.gov/dts/sltc/methods/inorganic/id141/id141.html (accessed 2005), OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1983.

[3] Cassinelli, M. E.; Hydrogen Sulfide. *NIOSH Manual of Analytical Methods (NMAM)*, 4th ed.; U.S. National Institute of Occupational Safety and Health: Cincinnati, OH, 1994; Vol. 2.

sulfide ion formed is then converted to sulfate with hydrogen peroxide and analyzed by ion chromatography using a conductivity detector.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)[4]

Symptoms observed from exposure between 5 and 2000 ppm are as follows:

1000 – 2000 ppm: Breathing stops due to paralysis of the respiratory system.

500 – 1000 ppm: Breathing rates speed up followed by temporary suspension of breathing at higher concentrations.

50 – 500 ppm: Respiratory tract and eye irritation. Prolonged exposures to concentrations between 50 and 600 ppm can cause pulmonary edema (swelling and accumulation of fluid in the lungs). Olfactory fatigue occurs at concentrations between 150 and 200 ppm.

5 - 50 ppm: Irritation of the eyes.

Long term effects from repeated hydrogen sulfide exposure have not been established but symptoms may include dizziness, headaches and fatigue. Hydrogen sulfide is not regarded as a cumulative toxin as it is quickly oxidized to sulfate and then excreted by the kidneys.

1.1.3 Workplace exposure[5]

Workplace exposure of hydrogen sulfide has been reported "in the gas, oil chemical, geothermal energy, and viscose rayon industries and workers in sewer systems, tanneries, mining, drilling, smelting, animal waste disposal, and on fishing boats".

1.1.4 Physical properties and other descriptive information[6, 7]

synonyms:	sulfuretted hydrogen
IMIS[8]:	1480
CAS number:	7783-06-4
boiling point:	-60.4 °C (-76.7 °F)
melting point:	-85.5 °C (-122 °F)
molecular weight:	34.08
vapor pressure:	20 atm @ 25.5 °C
appearance:	colorless gas
vapor density:	1.189 (air = 1.0)
molecular formula:	H_2S
odor:	offensive rotten egg smell
odor threshold:	0.02 ppm (olfactory fatigue at high concn)
solubility:	soluble in alcohol and water

autoignition

[4] Hydrogen Sulfide. *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 7th ed.; American Conference of Governmental Industrial Hygienists, Inc.: Cincinnati, OH, 2001; Vol. 2.

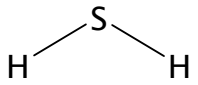
[5] *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Kroschwitz, J. I., Ex. Ed.; John Wiley: New York, 1991; Vol. 23, p 282.

[6] *The Merck Index*, 13th ed.; Budavari, S., Ed.; Merck & Co. Inc.: Whitehouse Station, NJ, 2001; p 859.

[7] Lewis, R. J. Sr.; *Hazardous Chemicals Desk Reference*, 4th ed.; Van Nostrand Reinhold Co.: New York, 1997, p 597.

[8] Hydrogen Sulfide. OSHA Chemical Sampling Information. http://www.osha.gov/dts/chemicalsampling/ data/CH_246800.html (accessed 2005).

temperature: 260 °C (500 °F)
structural formula:



This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"[9]. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations and acceptance criteria. The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations in ppm are referenced to 25 °C and 101.3 kPa (760 mmHg).

1.2 Limit defining parameters

1.2.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure is 0.568 ng hydrogen sulfide (1.60 ng sulfate). This is the amount of sulfate that will give a detector response that is significantly different from the response of a calibration blank. (Section 4.1)

1.2.2 Detection limit of the overall procedure

The detection limit of the overall procedure is 7.48 µg hydrogen sulfide per sample (0.448 ppm or 0.623 mg/m^3 for a TWA sample, 0.715 ppm or 0.997 mg/m^3 for a ceiling sample, 1.07 ppm or 1.50 mg/m^3 for a peak sample). This is the amount of hydrogen sulfide on the sampler that will give a detector response that is significantly different from the response of a sampler blank. (Section 4.2)

1.2.3 Reliable quantitation limit

The reliable quantitation limit is 8.69 µg hydrogen sulfide per sample (0.520 ppm or 0.724 mg/m^3 for a TWA sample, 0.831 ppm or 1.16 mg/m^3 for a ceiling sample, 1.25 ppm or 1.74 mg/m^3 for a peak sample). This is the amount of hydrogen sulfide on the sampler that will give a detector response that is considered the lower limit for precise quantitative measurements. (Section 4.2)

1.2.4 Instrument calibration

The standard error of estimate is 3.51 µg/mL sulfate over the range of 7 µg/mL to 59 µg/mL. This range corresponds to approximately 0.25 to 2 times the target concentration. (Section 4.3)

1.2.5 Precision

The precision of the overall procedure at the 95% confidence level for the ambient temperature 17-day storage test for samples collected from a dynamically generated

[9] Burright, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C.; *Evaluation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis*. http://www.osha.gov/dts/sltc/methods/chromguide/index.html (accessed 2005), OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1999.

atmosphere of 20.1 ppm (28.0 mg/m^3) is ± 9.94%. This includes an additional 5% for sampling pump variability. (Section 4.4)

1.2.6 Recovery

The recovery of hydrogen sulfide from samples used in a 17-day storage test remained above 96.6% when the samples were stored at ambient temperature. (Section 4.5)

1.2.7 Reproducibility

Six samples were collected from a controlled test atmosphere and submitted for analysis by the OSHA Salt Lake Technical Center. The samples were analyzed according to a draft copy of this procedure after 9 days of storage at ambient temperature. No individual sample result deviated from its theoretical value by more than the precision reported in Section 1.2.5. (Section 4.6)

2. Sampling Procedure

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.1 Apparatus

Samples are collected using a specially made sampler described in detail in Appendix A.

Samples are collected using a personal sampling pump calibrated, with the sampling device attached, to within ±5% of the recommended flow rate. When sampling at 0.5 L/min use a sampling pump that can maintain flow with a back pressure of approximately 15 inches of water.

2.2 Reagents

None required

2.3 Technique

All samplers should be from the same lot.

Attach the sampler to the sampling pump with flexible tubing so that the sampler is in an approximately vertical position with the inlet (large end) facing down in the worker's breathing zone during sampling. Position the sampling pump, sampler and tubing so they do not impede work performance or safety.

Draw air directly into the inlet of the sampler. The air being sampled should not pass through any hose or tubing before entering the sampler.

After sampling for the appropriate time, remove the sample and seal it with plastic end caps. Seal each sample end-to end with a Form OSHA-21.

Submit at least one blank sample with each set of samples. Handle the blank sample in the same manner as the other samples except draw no air through it.

Record sample air volume (L), sampling time (min) and sampling rate (L/min) for each sample, along with any potential interferences on the Form OSHA-91A.

Submit the samples to the laboratory for analysis as soon as possible after sampling. If a delay is unavoidable, store the samples in a refrigerator. Ship any bulk samples separate from the air samples.

2.4 Sampler capacity (Section 4.7)

The sampling capacity of the front section of the sampler was tested by sampling a dynamically generated test atmosphere of hydrogen sulfide (28.8 mg/m^3 or 20.7 ppm) with an average relative humidity of 81% at 21 °C. The samples were collected at a sampling rate of approximately 0.05 L/min for 450 min. No breakthrough from the front section was observed.

The sampling capacity of the front section of the sampler was also tested by sampling a dynamically generated test atmosphere of hydrogen sulfide (64.9 mg/m^3 or 46.6 ppm) with an average relative humidity of 81% at 21 °C. The samples were collected at a sampling rate of 0.5 L/min for 15 min. No breakthrough from the front section was observed for two of the three samplers tested, however, a 1.2% (0.78 mg/m^3) breakthrough from the front section was observed on the third sampler.

The sampler was found to have adequate capacity for sampling workplaces with concentrations of hydrogen sulfide at the TWA, ceiling and peak levels.

2.5 Extraction efficiency (Section 4.8)

It is the responsibility of each analytical laboratory to determine the extraction efficiency because the adsorbent material, reagents and laboratory techniques may be different than those listed in this evaluation and influence the results.

The mean extraction efficiency for hydrogen sulfide over the range of RQL to 2 times the target concentration (8.41 to 408 µg per sample) was 95.1%. The extraction efficiency was not affected by the presence of water (average recovery of 95.2%).

Extracted samples remain stable for at least 24 h.

2.6 Recommended sampling time and sampling rate

Sample for up to 240 min at 0.05 L/min (12 L) to collect TWA (long-term) samples.

Sample for 15 min at 0.5 L/min (7.5 L) to collect ceiling samples.

Sample for 10 min at 0.5 L/min (5 L) to collect peak samples.

2.7 Interferences (sampling) (Section 4.9)

Retention

The retention efficiency for all samples was above 102.8% of theoretical, when samplers containing approximately 72 µg of hydrogen sulfide were allowed to sample 9 L of contaminant-free air having an average relative humidity of 78% at 22 °C. The samples were collected at a sampling rate of 0.05 L/min for 180 min.

Low humidity

Sampler capacity at various low humidities was tested using test atmospheres containing two times the target concentration of hydrogen sulfide (40 ppm), and the 0.5 L/min sampling rate that is required for ceiling samples. This extreme combination of parameters was used to provide a "worst case" scenario for this sampler. These tests show that the combination of high hydrogen sulfide levels, high sampling rate, and low relative humidity results in reduced sampling capacity of the front section. This situation requires use of the back section to obtain quantitative results as shown in Table 2.7.1.

Table 2.7.1
Capacity of Sampler at Low Humidity
for Hydrogen Sulfide at 2X Target

relative humidity (%)	front section (% recovery)	back section (% recovery)	total (% recovery)
6	94.5	7.03	101.5
20	69.2	26.7	95.9
35	79.5	19.1	98.6

It was not determined why the front section of the sampler had a larger capacity at 6% relative humidity than at 20% and 35%. (See Section 4.9 for more information regarding humidity.)

Light

The collection efficiency for all samples was above 102.0% of theoretical, when the sampler was exposed to sunlight for seven days, and then used to sample a test atmosphere containing 2 times the target concentration of hydrogen sulfide with an average relative humidity of 32% at 21 °C. The samples were collected at a sampling rate of 0.5 L/min for 15 min.

The collection efficiency for all samples was above 103.2% of theoretical, when the sampler was exposed to sunlight for seven days and then used to sample a test atmosphere containing 2 times the target concentration of hydrogen sulfide with an average relative humidity of 81% at 21 °C. The samples were collected at a sampling rate of 0.5 L/min for 15 min.

Low concentration

The collection efficiency for all samples was above 96.7% of theoretical, when the sampler was used to sample a test atmosphere containing approximately 0.1 times the target concentration of hydrogen sulfide with an average relative humidity of 80% at 21 °C. Samples were collected at a sampling rate of 0.5 L/min for 15 min.

Interference

The following interferences were selected for testing because they may be found in the same workplace as hydrogen sulfide.

The ability of the sampler to collect hydrogen sulfide in the presence of sulfur dioxide was determined from a test atmosphere containing 27.5 mg/m^3 (19.7 ppm) of hydrogen sulfide, 8.63 mg/m^3 (3.29 ppm) of sulfur dioxide, with an average relative humidity of 80% at 21 °C. The samples were collected at a sampling rate of 0.5 L/min for 15 min. The collection efficiency of hydrogen sulfide for all samples was between 100.4% and 104.0% of theoretical. Samplers that had the coated GFF removed had recoveries at 127% demonstrating the need to scrub sulfur dioxide. (See Section 4.9 for more information on sulfur dioxide.)

Methanethiol (methyl mercaptan) was tested as a potential interferent by injecting 42.5 µg of methanethiol gas (42.5 µg / 7.5 L = 5.67 mg/m^3 or 2.88 ppm) directly upstream of three samples that where sampling contaminant-free air, with an average relative humidity of 80% at

21 ℃, at 0.5 L/min. After injection of the methanethiol sampling continued an additional 15 min at a rate of 0.5 L/min. Samples collected 0.85 µg or less of methanethiol, or an equivalent 0.6 µg hydrogen sulfide or less, on the front section demonstrating that methanethiol is not a significant interferent.

See Section 4.9 for other possible potential interference that were investigated including, carbonyl sulfide, ethanethiol, 1-butanethiol, thiophenol, carbon disulfide and ozone.

3. Analytical Procedure

Adhere to the rules set down in your Chemical Hygiene Plan[10]. Avoid skin contact and inhalation of all chemicals and review all appropriate MSDS. Dispose of cyanide solutions in an appropriate manner.

3.1 Apparatus

Ion chromatograph with a conductivity detector and autosampler. A Dionex DX-500 ion chromatograph with a GP40 gradient pump, an ED40 electrochemical detector with a conductivity cell, an ASRS-ULTRA II 4-mm anion suppressor and a Waters 717plus autosampler was used in this evaluation.

IC column and guard column that can separate sulfate from potential interferences. A Dionex IonPac AS14 analytical column (250-mm × 4-mm i.d.) and a Dionex IonPac AG14 guard column (50-mm × 4-mm i.d.) were used in this evaluation.

A means to integrate chromatograms. Dionex Peaknet 5.1 software was used in this evaluation.

Autosampler Vials. Waters 4-mL clear glass vials with plastic cap were used in this evaluation.

Water purifier. A Barnstead NANOpure Diamond system was used to produce 18.0 MΩ-cm DI water in this evaluation.

Glass 20-mL scintillation vials were used to prepare samples. Wheaton glass liquid scintillation vials were used in this evaluation.

Scintillation vial racks. Polypropylene Scienceware scintillation racks were used in this evaluation.

Static control device. A Milty Zerostat 3 anti-static gun and a Staticmaster ionizing unit were used in this evaluation.

A means to dispense and dilute solutions. A Hamilton Microlab 540B dual syringe diluter/dispenser and an Eppendorf Series 2100 Research pipette (100 – 1000 µL) were used in this evaluation.

Water bath. A Precision Scientific model 66643 (5 – 100 ℃ range) water bath was used in this evaluation.

A mechanical shaker. An Eberbach heavy-duty mechanical shaker was used in this evaluation.

Analytical balance capable of weighing at least 0.01 mg. An Ohaus Galaxy 160D balance was used in this evaluation.

[10] Occupational Exposure to Hazardous Chemicals in Laboratories. *Code of Federal Regulations*, Part 1910.1450, Title 29, 2003.

Class A 2-L and 500-mL volumetric flasks.

Class A 20-mL volumetric pipets.

3.2 Reagents and Standards

Note: Some reagents used in this method contain trace amounts of sulfide and sulfate; to keep background levels of sulfate low use the highest grade of reagents available.

DI water, 18.0 MΩ-cm.

Sodium Cyanide (NaCN), [CAS no. 143-33-9], containing ≤ 0.01% sulfate and ≤ 0.001% sulfide. The sodium cyanide used in this evaluation was Fluka BioChemika Ultra, ≥97.0% (AT) (lot no. 1183988) purchased from Sigma-Aldrich.

Sodium Hydroxide (NaOH), [CAS no. 1310-73-2], ≥ 99.9% purity. The sodium hydroxide used in this evaluation was 99.998% pellets (lot no. 06603LC) purchased from Sigma-Aldrich.

30% Hydrogen Peroxide (H_2O_2), [CAS no. 7722-84-1], A.C.S. grade or higher. The hydrogen peroxide used in this evaluation was 30% ULTREX II Ultrapure Reagent (lot no. B17467) purchased from J.T. Baker.

Sulfate (SO_4^{2-}) 1000 mg/L standard solution. The 1000 mg/L sulfate standard used in this evaluation was (lot no. 041007) purchased from Dionex Corporation.

AS14 Eluent Concentrate, containing 350 mM sodium carbonate (Na_2CO_3) [CAS no. 497-19-8] and 100 mM sodium bicarbonate ($NaHCO_3$) [CAS no. 144-55-8]. AS14 Eluent Concentrate was purchased from Dionex Corporation.

Eluent [3.5 mM Na_2CO_3 / 1.0 mM $NaHCO_3$]: Add approximately 500 mL of DI water to a 2-L volumetric flask, followed by 20 mL of AS14 Eluent Concentrate, and then dilute to mark with DI water and mix well. Degas the solution and transfer to appropriate container(s). It is recommended that fresh eluent be prepared for each sample set analyzed.

Extraction solution [0.5 M NaCN / 0.1 M NaOH]: Add approximately 100 mL of DI water to a 500-mL volumetric flask. Weigh out 12.25 g of NaCN and 2 g of NaOH and carefully add them to the volumetric flask. Dilute to the mark with DI water, mix well, and transfer to an appropriate storage bottle. It is recommended that the solution be stored and used for no longer than one year.

3.3 Standard preparation

Prepare a concentrated stock standard, using a 1000 mg/L sulfate standard, of 100 mg/L using the eluent as the diluent. From the stock standard prepare 3 or more working standards also using the eluent as the diluent. It is recommended that working range standards be prepared in the range of 1 - 40 mg/L (20 – 800 µg/sample).

If upon analysis, sample concentrations fall outside the range of prepared standards, prepare and analyze additional standards to confirm instrument response, or dilute high samples with eluent and reanalyze the diluted samples.

3.4 Sample preparation

Note: When hydrogen sulfide reacts with the silver nitrate coated on the silica gel, silver sulfide is formed, causing the color of the coated silica gel to change from white to a grayish-black metallic color. If the front section of the coated silica gel is less than 50% consumed and if no color change is seen on the back section then the back section does not need to be analyzed.

Note: It is recommended that scintillation vials be placed on top of an ionizing unit and that an anti-static gun be used during transfer of the silica gel to reduce the possible loss of sample due to static charge.

Carefully remove the quartz wool plug from the backend (small end) of the sampler. Transfer the back section of silica gel to a 20-mL scintillation vial or dispose if it does not need to be analyzed as determined above. The sampler may need to be discharged using an anti-static gun and/or gently tapped against the scintillation vial in order to remove all the silica gel. If necessary, gently tap the scintillation vial ensuring that all silica gel settles to the bottom of the vial.

Use a separate 20-mL scintillation vial for the front section.

Carefully remove the next quartz wool plug and transfer the front section of silica gel to a 20-mL scintillation vial. The foam plug should be carefully inspected and any silica gel attached removed and placed in the scintillation vial.

Do not analyze the glass fiber filters for hydrogen sulfide.

Add 2 mL of extraction solution to each scintillation vial and cap tightly.

Place scintillation vials in a scintillation rack and place rack in a boiling water bath (100 ℃). Water in the bath should cover at least the bottom third of the scintillation vials. The purpose of the water bath is to extract the silver sulfide from the silica gel.

Remove the scintillation rack from the water bath after 20 min, or transfer scintillation vials to a dry rack, and secure on a mechanical shaker. Shake samples for 1 hour allowing the cyanide to react with the silver sulfide forming a silver cyanide complex and releasing the sulfide.

Next remove the scintillation rack from the shaker. To each scintillation vial add 100 µL of hydrogen peroxide by opening the scintillation vial, adding the solution, and then quickly recapping the vial. The hydrogen peroxide will react with the sulfide forming sulfate.

Return the samples to the scintillation rack and shake for 15 min.

Remove the samples from the shaker after shaking for 15 min. Add 17.9 mL of eluent to each sample and mix well (for a final solution volume of 20 mL). Let samples sit for 2 hours to insure that all sulfide reacts with the hydrogen peroxide.

Finally, transfer approximately 3 mL of the sample solution to a 4-mL autosampler vial and cap. Puncture the cap of each vial using a small needle to reduce pressure buildup in the vial prior to analysis. Failure to puncture the cap could cause results to be low.

Analyze samples.

3.5 Analysis

It is necessary that all samples be injected twice to insure that a pressure buildup in the vial did not occur due to the hydrogen peroxide. Analytical results from the second injection should agree with the first to within ±10%. The calculated final result should then be an average of the two injections. If the analytical results of the two injections do not agree to within ±10%, discard the initial injections and reinject the sample twice more.

3.5.1 Analytical Conditions

IC conditions

columns:	IonPac AS14 column (250-mm x 4-mm i.d.) and AG14 guard column (50-mm x 4-mm i.d.)
flow rate:	1.2 mL/min
eluent:	3.5 mM Na_2CO_3 / 1.0 mM $NaHCO_3$
pump pressure:	~1600 psi
injection volume:	50 µL
retention time:	10.7 min (each column varies slightly)

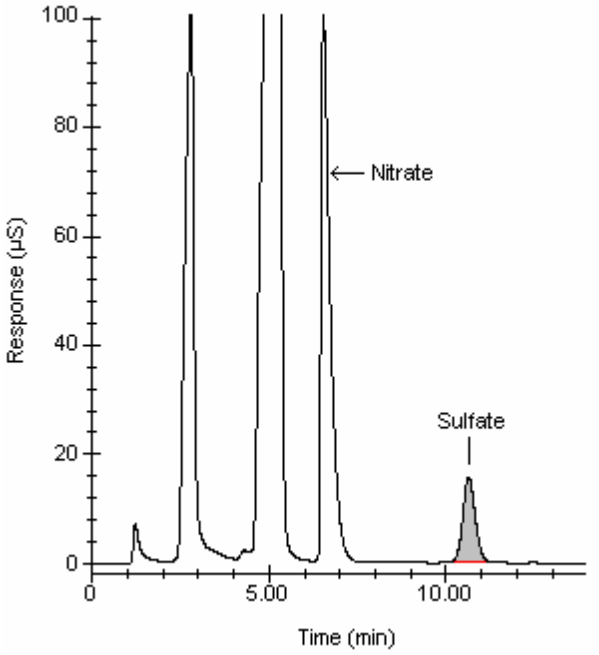


Figure 3.5.1. Chromatogram obtained at target concentration with recommended conditions.

3.5.2 Calibration

An external standard calibration method is used. A calibration curve can be constructed by plotting response of standard injections versus µg/mL of sulfate per sample. Bracket the samples with freshly prepared analytical standards over the range of concentrations.

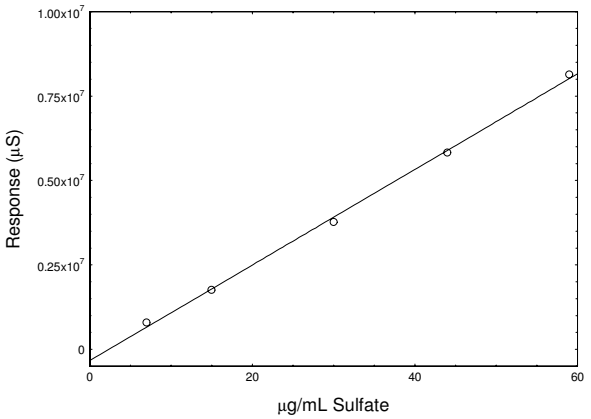


Figure 3.5.2. Calibration curve of sulfate. (Y = 141486X – 332515)

3.6 Interferences (analytical)

Any compound that produces a response and has a similar retention time as sulfate is a potential interference. If any potential interferences were reported, they should be considered before samples are extracted. Generally, chromatographic conditions can be altered to separate an interference from the analyte.

When necessary, the identity or purity of an analyte peak may be confirmed by additional analytical techniques or alternate columns such as a Dionex IonPac AS4 analytical column.

3.7 Calculations

The air concentration is calculated using the following formulas.

Micrograms of hydrogen sulfide per sample is:

$$M = [((F_S) \times (D_F) - B) + ((B_S) \times (D_B) - B)] \times SV \times GF$$

where:

M is µg of hydrogen sulfide per sample
F_S is the mean of two injections of sulfate (µg/mL) found on front section
D_F is dilution factor applied to front section (if appropriate)
B_S is the mean of two injections of sulfate (µg/mL) found on back section
D_B is dilution factor applied to back section (if appropriate)
B is the mean of two injections of sulfate (µg/mL) found on a section of a blank sampler
SV is solution volume of sample (20 mL)
GF is the gravimetric factor (0.3548 H_2S/SO_4^{2-})

Concentration by weight of hydrogen sulfide (mg/m^3) is:

$$C_M = \frac{M}{E_E V}$$

where:

C_M is concentration by weight of hydrogen sulfide (mg/m^3)
M is µg of hydrogen sulfide per sample
E_E is extraction efficiency in decimal form
V is L of air sampled

Concentration by volume of hydrogen sulfide (ppm) is:

$$C_V = \frac{V_M C_M}{M_r}$$

where:

C_V is concentration by volume of hydrogen sulfide (ppm)
C_M is concentration by weight of hydrogen sulfide (mg/m^3)
V_M is molar volume at NTP (24.46)
M_r is molecular weight of hydrogen sulfide (34.082)

4. Backup data

General background information about the determination of detection limits and precision of the overall procedure is found in the "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatography Analysis"[11]. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations and acceptance criteria.

4.1 Detection limit of the analytical procedure (DLAP)

DLAP is measured as mass of analyte introduced onto the chromatographic column. Ten analytical standards were prepared with equal increments with the highest standard containing 0.403 µg/mL sulfate. This is the concentration that would produce a peak approximately 10 times the response of a calibration blank near the elution time of the analyte. These standards, and the calibration blank were analyzed with the recommended analytical parameters (50-µL injection), and the data obtained were used to determine the required parameters (standard error of estimate and slope) for the calculation of the DLAP. Values of 2293 and 1226 were obtained for the slope and standard error of estimate respectively. DLAP was calculated to be 0.568 ng hydrogen sulfide (1.60 ng sulfate).

Table 4.1
Detection Limit of the Analytical Procedure

concentration (µg/mL SO_4^{2-})	mass on column (ng)	area counts (µS)
0	0	0
0.040	2.02	7473
0.081	4.03	12442
0.121	6.05	16594
0.161	8.06	19852
0.202	10.1	24489
0.242	12.1	27854
0.282	14.1	35842
0.323	16.1	38457
0.363	18.1	43605
0.403	20.2	47864

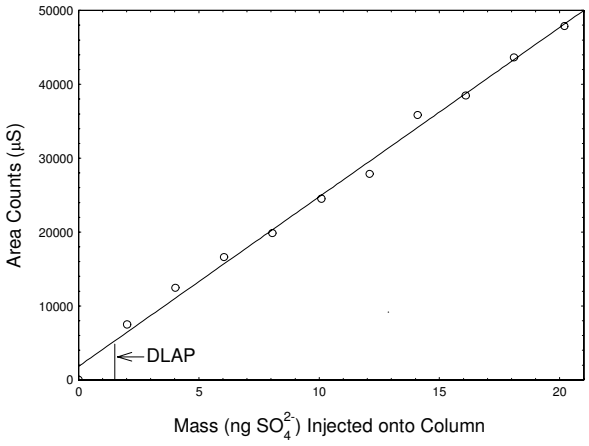


Figure 4.1. Plot of data to determine the DLAP. (Y = 2293X + 1839)

4.2 Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL)

DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten blank samples were prepared and analyzed with the recommended analytical parameters, and the data obtained used to calculate the mean mass and standard deviation of the samples for the calculation of the DLOP (see Table 4.2). Values of 6.96 µg H_2S and 0.173 µg H_2S were obtained for the mean mass and standard deviation, respectively. The DLOP, calculated as the mean mass plus 3 times the standard deviation, was determined to be 7.48 µg hydrogen sulfide per sample (0.448 ppm or 0.623 mg/m^3 for a TWA sample, 0.715 ppm or 0.997 mg/m^3 for a ceiling sample, 1.07 ppm or 1.50 mg/m^3 for a peak sample).

[11] Burright, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C.; *Evaluation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis*. http://www.osha.gov/dts/sltc/methods/chromguide/index.html (accessed 2005), OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1999.

Table 4.2
Detection Limit of the Overall Procedure

sample no.	mass per sample (µg SO_4^{2-})	equivalent µg H_2S
1	20.2	7.17
2	20.2	7.17
3	19.5	6.92
4	19.4	6.88
5	20.1	7.13
6	19.8	7.02
7	19.6	6.95
8	18.7	6.63
9	19.1	6.78
10	19.6	6.95
mean =	19.6	6.96
σ =	0.460	0.173

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the mean mass and standard deviation obtained for the calculation of the DLOP. The RQL, calculated as the mean mass plus 10 times the standard deviation, was determined to be 8.69 µg hydrogen sulfide per sample (0.520 ppm or 0.724 mg/m^3 for a TWA sample, 0.831 ppm or 1.16 mg/m^3 for a ceiling sample, 1.25 ppm or 1.74 mg/m^3 for a peak sample).

Note: The DLOP and RQL are mostly a function of the quality of the reagents used, particularly the sodium cyanide, which contained small amounts of sulfate and sulfide.

Normally the DLOP and RQL are determined from a series of spiked samplers, similar to how the DLOP was determined in Section 4.1. However, for this evaluation the normal procedure was not used due to the difficulty and error associated with gas spiking low levels of hydrogen sulfide.

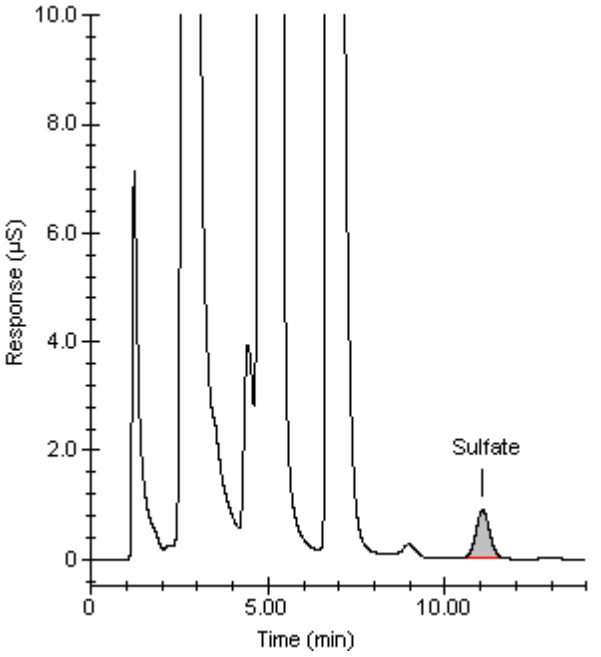


Figure 4.2. Chromatogram of the RQL.

4.3 Instrument calibration

The standard error of estimate was determined from the linear regression of data points from standards over a range that covers 0.25 to 2 times the TWA target concentration. A calibration curve was constructed and shown in Section 3.5.2 from the six injections of five standards. The standard error of estimate is 3.15 µg/mL sulfate.

Table 4.3
Instrument Calibration

standard concn ($\mu g/mL\ SO_4^{2-}$)	area counts (μS)					
7	789182	791441	788961	790097	792821	788196
15	1755949	1761060	1752928	1752893	1749453	1746778
30	3775728	3762262	3762589	3756467	3769679	3775118
44	5843452	5798744	5830182	5809790	5838468	5813324
59	8141640	8125568	8125702	8149930	8091286	8176779

4.4 Precision (overall procedure)

The precision at the 95% confidence level is obtained by multiplying the standard error of estimate by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). In Section 4.5, 95% confidence intervals are drawn about their respective regression lines in the storage graph figures. The precision of the overall procedure of ± 9.94% was obtained from the standard error of estimate of 5.07% in Figure 4.5.1. The precision includes an additional 5% for sampling error.

4.5 Storage test

Storage samples for hydrogen sulfide were prepared by collecting samples from a controlled test atmosphere using the recommended sampling conditions. The concentration of hydrogen sulfide was at the target concentration (20.1 ppm) and having an average relative humidity of 80% at 21 °C. Thirty-three storage samples were prepared. Three samples were analyzed on the day of generation. Fifteen of the tubes were stored at reduced temperature (1 °C) and the other fifteen were stored in a closed drawer at ambient temperature (about 21 °C). At 3-5 day intervals, three samples were selected from each of the two storage sets and analyzed. Sample results were not corrected for extraction efficiency.

Table 4.5
Storage Test for Hydrogen Sulfide

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	98.0	97.0	98.0			
3	96.0	96.4	96.0	96.8	97.2	97.2
7	97.9	98.6	98.3	98.3	99.4	98.7
10	96.8	96.3	96.5	95.0	95.5	94.9
14	96.1	96.4	96.2	97.0	97.6	96.5
17	97.0	97.0	96.8	97.3	97.2	97.8

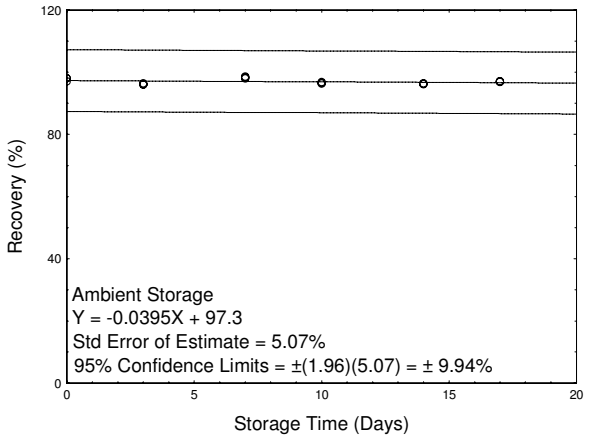


Figure 4.5.1. Ambient storage test for hydrogen sulfide.

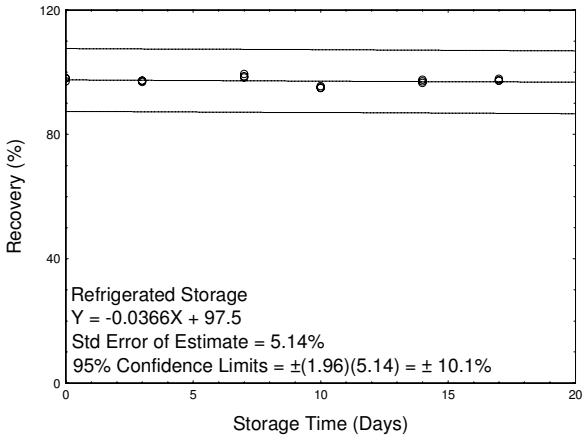


Figure 4.5.2. Refrigerated storage test for hydrogen sulfide.

4.6 Reproducibility

Six samples were prepared by collecting them from a controlled test atmosphere similar to that which was used in the collection of the storage samples. The samples were submitted to the OSHA Salt Lake Technical Center for analysis, along with a draft copy of this method. The samples were analyzed after being stored for 9 days at ambient temperature (about 21 °C). Sample results were corrected for extraction efficiency. No sample result for hydrogen sulfide had a deviation greater than the precision of the overall procedure determined in Section 4.4.

Table 4.6
Reproducibility
Data for Hydrogen Sulfide

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
192	187	97.4	-2.6
195	193	98.9	-1.1
194	193	99.5	-0.5
190	195	102.6	+2.6
195	201	103.1	+3.1
193	197	102.1	+2.1

4.7 Sampler capacity

The sampling capacity of the front section of the sampler was tested by sampling from a dynamically generated test atmosphere of hydrogen sulfide at 2 times the TWA (28.8 mg/m^3 or 20.7 ppm) with an average relative humidity of 81% at 21 °C. The samples were collected at a sampling rate of 0.05 L/min. All samplers in this test had the back section of silver nitrate coated silica gel removed. Backup samplers were placed in-line behind the front sampler and they were changed every 30 min after the initial collection of 330 min. No breakthrough from front section was observed; even after sampling for 450 min. (Results are shown in Table 4.7.)

Table 4.7
Breakthrough of Hydrogen Sulfide

test no.	air vol (L)	sampling time (min)	downstream concn (mg/m^3)	breakthrough (%)
1	16.4	330	0	0
	17.9	360	0	0
	19.4	390	0	0
	20.9	420	0	0
	22.4	450	0	0
2	17.1	330	0	0
	18.7	360	0	0
	20.2	390	0	0
	21.8	420	0	0
	23.4	450	0	0
3	16.2	330	0	0
	17.7	360	0	0
	19.1	390	0	0
	20.6	420	0	0
	22.1	450	0	0

The sampling capacity of the front section of the sampler was also tested by sampling a dynamically generated test atmosphere of hydrogen sulfide at 2.3 times the target concentration (64.9 mg/m^3 or 46.6 ppm) with an average relative humidity of 81% at 21 °C. The samples were collected at a sampling rate of 0.5 L/min for 15 min. No breakthrough from the front section was observed for two of the three samplers tested, however, a 1.2% (0.78 mg/m^3) breakthrough from the front section was observed on the third sampler.

The sampler was found to have adequate capacity for sampling workplaces with concentrations of hydrogen sulfide at the TWA, ceiling and peak levels.

4.8 Extraction efficiency and stability of extracted samples

Extraction efficiency

The extraction efficiency of hydrogen sulfide was determined by gas spiking four samplers, at each concentration level, with hydrogen sulfide from the RQL to 2 times the target

concentration. These samples were stored overnight at ambient temperature and then analyzed. The mean extraction efficiency over the working range of the RQL to 2 times the target concentration is 95.1%. The extraction efficiency for the wet samplers was not included in the overall mean because it would bias the results.

Table 4.8.1
Extraction Efficiency of Hydrogen Sulfide

level		sample number				
x target concn	µg H_2S per sample	1	2	3	4	mean
RQL	8.41	81.6	90.1	90.9	89.0	87.9
0.25	50.4	94.7	95.4	95.5	94.7	95.1
0.5	101	94.6	93.5	94.3	94.2	94.2
1.0	192	96.8	97.7	97.3	97.8	97.4
1.5	312	98.0	97.2	98.0	98.4	97.9
2.0	408	97.5	97.9	98.3	98.4	98.0
1.0 (wet)	192	94.4	97.0	94.4	95.2	95.2

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. The average percent change was +0.20% for samples that were resealed with new septa and +0.90% for those that retained their punctured septa. The test was performed at room temperature (about 21 °C).

Table 4.8.2
Stability of Extracted Samples for Hydrogen Sulfide

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
97.3	97.3	0.0	96.8	98.0	+1.2
97.8	98.2 (mean)	+0.4	97.7	98.3 (mean)	+0.6
97.6	97.8	+0.2	97.2	98.2	+0.9

4.9 Interferences (sampling)

Retention

The ability of the sampler to retain hydrogen sulfide was tested by sampling from a dynamically generated test atmosphere of hydrogen sulfide (24.2 mg/m^3 or 17.4 ppm) with an average relative humidity of 78% at 22 °C. Six samplers had contaminated air drawn through them at 0.05 L/min for 60 min. Sampling was discontinued and three samples set aside. The generation system was flushed with contaminant-free air. Sampling resumed with the other three samples having contaminant-free air drawn through them at 0.05 L/min for 180 min and then all six samplers were analyzed. The mean of the samples in the second set had retained more than 101% of the mean collected by the first three samples.

Table 4.9.1
Retention Efficiency (%) of Hydrogen Sulfide

set no.	1	2	3	mean
first	100.8	103.9	102.7	102.5
second	103.9	102.8	104.4	103.7
second/first				101

Low humidity

Sampler capacity at various low humidities was tested using test atmospheres containing two times the target concentration of hydrogen sulfide (40 ppm), and the 0.5 L/min sampling rate that is required for ceiling samples. This extreme combination of parameters was used to provide a "worst case" scenario for this sampler. These tests show that the combination of high hydrogen sulfide levels, high sampling rate, and low relative humidity results in reduced sampling capacity of the front section. This situation requires use of the back section to obtain quantitative results.

The ability of the sampler to collect hydrogen sulfide from a dry atmosphere was tested by sampling from a dynamically generated test atmosphere of hydrogen sulfide (55.5 mg/m^3 or 39.8 ppm) with an average relative humidity of 6% at 21 ℃. Samples were collected at a sampling rate of 0.5 L/min for 15 min. The samples collected 94.5% on the front section, 7.03% on the back section for a total of 101.5% of theoretical.

Table 4.9.2
Capacity of Sampler at a Relative Humidity of 6% for Hydrogen Sulfide at 2X Target

sample no.	front section (% recovery)	back section (% recovery)	total (% recovery)
1	92.1	9.22	101.4
2	97.0	4.84	101.8
3	94.4	7.02	101.4
mean	94.5	7.03	101.5

The capacity of the sampler was also tested using a dynamically generated test atmosphere of hydrogen sulfide (55.8 mg/m^3 or 40.0 ppm) with an average relative humidity of 20% at 21 ℃. Samples were collected at a sampling rate of 0.5 L/min for 15 min. The samples collected 69.2% on the front section, 26.7% on the back section for a total of 95.9% of theoretical.

Table 4.9.3
Capacity of Sampler at a Relative Humidity of 20% for Hydrogen Sulfide at 2X Target

sample no.	front section (% recovery)	back section (% recovery)	total (% recovery)
1	74.6	21.0	95.6
2	66.2	29.5	95.7
3	66.7	29.7	96.4
mean	69.2	26.7	95.9

The capacity of the sampler was further tested using a dynamically generated test atmosphere of hydrogen sulfide (55.8 mg/m^3 or 40.0 ppm) with an average relative humidity of 35% at 19 ℃. Samples were collected at a sampling rate of 0.5 L/min for 15 min. The samples collected 79.5% on the front section, 19.1% on the back section for a total of 98.6% of theoretical.

Table 4.9.4
Capacity of Sampler at a Relative Humidity of 35% for Hydrogen Sulfide at 2X Target

sample no.	front section (% recovery)	back section (% recovery)	total (% recovery)
1	76.0	22.9	98.9
2	83.6	14.2	97.8
3	78.8	20.1	98.9
mean	79.5	19.1	98.6

It was not clear why the front section of the sampler had a higher capacity at 6% relative humidity than at 20% and 35% but the observation was confirmed with additional data. Replication of the test at 6% relative humidity resulted in nearly identical results as to those shown in Table 4.9.2. Comparison of the data shown in Table 4.9.4 (35% relative humidity) and Table 4.9.5 (32% relative humidity) show similar mass being collected on the front section, further confirming the data shown in this section (55.8 mg/m^3 X 7.5 L X .795 = 333 µg vs. 51.4 mg/m^3 X 7.5 L X .918 = 354 µg).

The "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatography Analysis"[12] require that 90% of the analyte be collected on the front section of the sampler when sampling at two times the target concentration at a relative humidity of 20%. However, in this case the back section of the hydrogen sulfide sampler is not completely analogous to the backup section of adsorbent tubes. The backup section of adsorbent tubes is often used to indicate when the capacity of the front section is exceeded (breakthrough). Capacity in that instance is related to the ability of the front section to collect a certain mass of the analyte. Sampling capacity of the hydrogen sulfide sampler is more complicated and is more limited by the derivatization reaction than by the mass of sampled analyte. The back section of the sampler in this case is intended to be used mainly for reserve capacity. Detection of a significant amount of hydrogen sulfide on the back section of the sampler is not desirable from a technical standpoint, but it was the preferred option as opposed to decreasing the ceiling sampling flow rate or increasing the mass of coated silica gel of the front section.

Light

The effect of light on the sampler was tested by placing six capped samplers in a west facing window for seven days from April 25 through May 2, 2006 with the samplers exposed to over 5 hours of direct sunlight each day. After seven days no visible color change of the silver nitrate coated silica gel could be seen.

Three of the samplers were then used to collect hydrogen sulfide from a relatively dry atmosphere by sampling from a dynamically generated test atmosphere of hydrogen sulfide (51.4 mg/m^3 or 36.9 ppm) with an average relative humidity of 32% at 21 ºC. Samples were collected at a sampling rate of 0.5 L/min for 15 min. The samples collected 91.8% on the front section, 10.3% on the back section for a total of 102.1% of theoretical.

Table 4.9.5
Capacity of Sampler at a Relative Humidity of 32% for Hydrogen Sulfide at 2X Target after Light Exposure

sample no.	front section (% recovery)	back section (% recovery)	total (% recovery)
1	92.0	9.99	102.0
2	91.5	10.7	102.2
3*			
mean	91.8	10.3	102.1

* sample lost in analysis

The other three samplers were used to collect hydrogen sulfide from a dynamically generated test atmosphere of hydrogen sulfide (51.4 mg/m^3 or 36.9 ppm) with an average relative humidity of 81% at 21 ºC. Samples were collected at a sampling rate of 0.5 L/min for 15 min. The samples collected 103.5% of theoretical on the front section, with no hydrogen sulfide seen or detected on the back section. Exposure to light was shown not to have any effect on the sampler.

Table 4.9.6
Capacity of Sampler at a Relative Humidity of 81% for Hydrogen Sulfide at 2X Target after Light Exposure

sample no.	front section (% recovery)	back section (% recovery)	total (% recovery)
1	103.2	0	103.2
2	103.3	0	103.3
3	104.0	0	104.0
mean	103.5	0	103.5

Low concentration

The ability of the sampler to collect hydrogen sulfide at low concentrations was tested by sampling from a dynamically generated test atmosphere of 0.081 times the target concentration of hydrogen sulfide (2.26 mg/m^3 or 1.62 ppm) with an average relative humidity of 80% at 21

[12] Burright, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C.; *Evaluation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis*. http://www.osha.gov/dts/sltc/methods/chromguide/index.html (accessed 2005), OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1999.

°C. Three samplers had contaminated air drawn through them at 0.5 L/min for 15 min. All of the samples were immediately analyzed. The samplers had collected 101.1%, 104.5% and 96.7% of theoretical.

Sulfur dioxide

The ability of the sampler to scrub sulfur dioxide from a dry atmosphere of over two times the OSHA PEL (36.2 mg/m^3 or 13.8 ppm) of sulfur dioxide was tested by sampling from a dynamically generated test atmosphere with an average relative humidity of 80% at 21 °C. Samples were collected at a sampling rate of 0.05 L/min. All samplers in this test had the silver nitrate coated silica gel removed. Backup samplers were placed in-line behind the front sampler and they were changed every 30 min after the initial collection of 270 min. No breakthrough of sulfur dioxide was observed even after 420 min of sampling. (Results are shown in Table 4.9.7.)

Table 4.9.7
Breakthrough of Sulfur Dioxide

test no.	air vol. (L)	sampling time (min)	downstream concn (mg/m^3)	break-through (%)
1	13.4	270	0	0
	14.9	300	0	0
	16.4	330	0	0
	17.9	360	0	0
	19.4	390	0	0
	20.9	420	0	0
2	13.3	270	0	0
	14.7	300	0	0
	16.2	330	0	0
	17.7	360	0	0
	19.2	390	0	0
	20.6	420	0	0
3	13.5	270	0	0
	15.0	300	0	0
	16.5	330	0	0
	18.0	360	0	0
	19.5	390	0	0
	21.0	420	0	0

Samples were prepared for analysis by placing each filter in a 20 mL scintillation vial. Ten mL of eluent was added along with 100 µL of hydrogen peroxide. Samples were placed on a shaker and shaken for 30 min, allowed to settle for 1 hour, and then analyzed.

The ability of the sampler to scrub sulfur dioxide from a dry atmosphere of over two times the OSHA PEL (30.2 mg/m^3 or 11.5 ppm) of sulfur dioxide was tested by sampling from a dynamically generated test atmosphere with an average relative humidity of 20% at 22 °C. Three samplers had contaminated air drawn through them at 0.5 L/min for 15 min. All of the samples were immediately analyzed. The samplers scrubbed 105%, 105% and 105% of theoretical with no sulfur dioxide found on a downstream filter.

The ability of the sampler to collect hydrogen sulfide in the presence of sulfur dioxide was tested by sampling an atmosphere containing 27.5 mg/m^3 (19.7 ppm) of hydrogen sulfide and 8.63 mg/m^3 (3.29 ppm) of sulfur dioxide with an average relative humidity of 80% at 21 °C. Three samplers had contaminated air drawn through them at 0.5 L/min for 15 min. All of the samples were immediately analyzed. The samples collected 100.4%, 104.0% and 101.2% of theoretical of hydrogen sulfide. An additional three samplers, that had the sodium carbonate impregnated filter removed, also had contaminated air drawn through them at 0.5 L/min for 15 min. All of the samples were immediately analyzed. The analytical results were 127%, 127% and 127% of theoretical for hydrogen sulfide demonstrating that sulfur dioxide is a positive interference and that the sodium carbonate filter eliminates the potential interference.

Other interferences

Methanethiol was tested as a potential interferent. Three samplers, with Gastec total mercaptan detector tubes (SKC Inc., cat. no. 810-70L) attached in series downstream, having contaminant-free air drawn through them at 0.5 L/min (RH of 80% at 21 °C), had 42.5 µg of methanethiol gas (42.5 µg / 7.5 L = 5.67 mg/m^3 or 2.88 ppm) injected directly upstream of the sampler. Contaminant-free air continued to be drawn through the sampler for an additional 15 min at a rate of 0.5 L/min. After injection of the methanethiol the detector tube quickly changed color providing a visual demonstration that the compound was passing though the sampler. The samples were stored overnight and then the front section of each sample was prepared and analyzed using the recommended analytical parameters. The samples collected 0.60, 0.11 and 0.28 equivalent µg of hydrogen sulfide demonstrating that methanethiol is not a significant interferent. A similar amount would be expected to be found on the back section.

Table 4.9.8
Methanethiol

sample no.	theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	equivalent µg H_2S
1	42.5	0.85	2.00	0.60
2	42.5	0.15	0.35	0.11
3	42.5	0.40	0.94	0.28

Carbonyl sulfide was tested as a potential interferent. Three samplers having contaminant-free air drawn through them at 0.5 L/min (RH of 80% at 21 °C), had 63.0 µg of carbonyl sulfide gas (63.0 µg / 7.5 L = 8.4 mg/m^3 or 3.42 ppm) injected directly upstream of the sampler. Contaminant-free air continued to be drawn through the sampler for an additional 15 min at a rate of 0.5 L/min. The samples were stored overnight and then both the front and back sections were prepared and analyzed using the recommended analytical parameters. Results for the three samples were zero demonstrating that carbonyl sulfide is not an interferent.

Ethanethiol, 1-butanethiol, thiophenol, and carbon disulfide were also tested as potential interferents, with each compound being tested separately (4 separate tests for a total of 12 samples). A sampling train consisting of an 8-cm long glass tube (6-mm i.d. x 8-mm o.d.) containing a quartz wool plug followed by a sampler, and in the case of ethanethiol, 1-butanethiol and thiophenol, followed by a total mercaptan detector tube was used. Thirty µL of the neat compound (as a liquid) was injected into the quartz wool plug and then contaminant-free air (RH of 80% at 21 °C) was drawn through the samples at 0.05 L/min for 240 min. In the case of ethanethiol, 1-butanethiol and thiophenol the detector tube changed color providing a visual demonstration that the compound was passing through the sampler. The samples were stored overnight and then the front section of each sample was prepared and analyzed using the recommended analytical parameters. Results are shown in Table 4.9.9. For 1-butanethiol the back section was also analyzed with 12.7, 11.6, and 10.0 equivalent µg of hydrogen sulfide found indicating that the front and back section collect approximately the same amount.

Table 4.9.9
Ethanethiol, 1-Butanethiol, Thiophenol and Carbon Disulfide

sample no.	ethanethiol equivalent µg H_2S	1-butanethiol equivalent µg H_2S	thiophenol equivalent µg H_2S	carbon disulfide equivalent µg H_2S
1	8.37	13.5	0	1.03
2	8.86	9.22	0	1.67
3	8.98	10.8	0	0.99

The compounds listed in Table 4.9.9 represent an extreme challenge to the sampler. For example, ethanethiol has a density of 0.839 g/mL at 25 °C, that would mean 30 µL would be equivalent to approximately 25170 µg as follows:

$$30uL \times \frac{mL}{1000uL} \times \frac{0.839g}{mL} \times \frac{1000mg}{1g} \times \frac{1000ug}{1mg} = 25170ug$$

This would give an equivalent air concentration of 2098 mg/m^3 (25170 µg / 12 L = 2098 mg/m^3 or 825 ppm) which is obviously not an amount that would be expected in a workplace environment. However, these tests show that even when the sampler is exposed to extreme amounts of potential interferences, that the sampler and/or analytical method do not have much capacity to collect and detect these compounds and that they do not create significant interferences.

Ozone was tested as an interferent because it has been reported to blacken silver[13]. Three samplers were used to collect ozone (0.3 ppm) from a dynamically generated test atmosphere with an average relative humidity of 80% at 22 °C. Samples were collected at a sampling rate of 0.5 L/min for 15 min. No visible color change of the silver nitrate coated silica gel was seen. The samples then had hydrogen sulfide (52.9 mg/m^3 or 37.9 ppm) drawn through them using a dynamically generated test atmosphere with an average relative humidity of 35% at 22 °C. Samples were collected at a sampling rate of 0.5 L/min for 15 min. Finally, the samples were again used to sample from a dynamically generated test atmosphere of ozone (0.3 ppm), with an average relative humidity of 80% at 22 °C, at a sampling rate of 0.5 L/min for 15 min. The samples collected 102.7% of theoretical hydrogen sulfide on the front section with none detected on the back section demonstrating that ozone is not an interferent.

Table 4.9.10
Ozone

sample no.	front section (% recovery)	back section (% recovery)	total (% recovery)
1	101.4	0	101.4
2	104.1	0	104.1
3	102.6	0	102.6
mean	102.7	0	102.7

4.10 Matrix effect

The sulfate standards are prepared in a slightly different matrix than the samples. The possibility of a matrix effect between the samples and standards was tested by comparing peak area counts for standards (Table 4.10.1) and samples (Table 4.10.2) spiked with sulfate. Two standards at three different levels were compared to two samples at the same three levels, along with a calibration and sample blank. After correcting for background no matrix effect was found and %RSD's were less than 1.6 for the three levels investigated as shown in Table 4.10.3.

Table 4.10.1
Peak Area of Standards

	7 µg/mL	7 µg/mL	30 µg/mL	30 µg/mL	59 µg/mL	59 µg/mL	blank	blank
peak area	784211	777757	3762125	3747530	8103054	8151728	0	0
	793123	785415	3767270	3762502	8145011	8177057	0	0
	800968	791782	3843963	3797059	8356486	8160080	0	0
mean		788876		3780075		8182236		0

Table 4.10.2
Peak Area of Samples

	7 µg/mL	7 µg/mL	30 µg/mL	30 µg/mL	59 µg/mL	59 µg/mL	blank	blank
peak area	896443	893637	3856684	3894719	8246092	8221945	96134	96626
	896283	905211	3893382	3905876	8261325	8291430	100508	100017
	915475	923874	3971618	3963801	8293148	8439175	97463	99786
mean		905154		3914346		8292186		98422

[13] *The Merck Index*, 13th ed.; Budavari, S., Ed.; Merck & Co. Inc.: Whitehouse Station, NJ, 2001; p 1525.

Table 4.10.3
Comparison of Standards to Samples
After Correcting for Background

concn	mean sample peak area	mean standard peak area	%RSD
7 µg/mL	806732	788876	1.58
30 µg/mL	3815924	3780075	0.67
59 µg/mL	8193764	8182236	0.10

4.11 Generation of test atmospheres

A test atmosphere generator, as diagramed in Figure 4.11, was set up in a walk-in hood. House air was dried, purified and then regulated using a Miller Nelson Model 401 Flow-Temperature-Humidity Control System. A measured flow of 5% hydrogen sulfide gas, flowing through stainless steel lines from a gas cylinder, was introduced into a measured flow of dilution air coming from the Miller Nelson control system. The hydrogen sulfide gas and dilution air flowed into a mixing chamber (76-cm X 15-cm) and then into a sampling chamber (56-cm X 9.5-cm). Samples were collected through sampling ports on the sampling chamber. Temperature and humidity were measured near the exit of the sampling chamber using an Omega Digital Thermo-hygrometer model RH411. The outgas was scrubbed using activated charcoal before sending it up the hood vent.

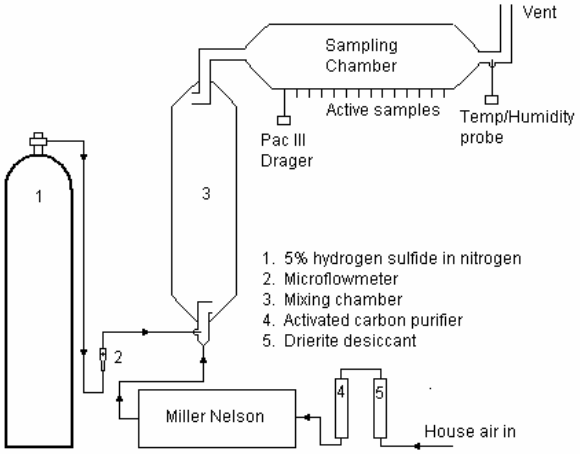


Figure 4.11. Diagram of apparatus used to generate test atmospheres.

A direct reading PAC III Dräger meter with a hydrogen sulfide sensor, that was calibrated using an independent source of hydrogen sulfide, was attached to a sampling port on the sampling chamber. The PAC III was used to monitor the concentration of the test atmosphere during generation. The PAC III was also used as a check on the calculated theoretical concentration of the test atmosphere generator (the calculated concentration was used as the theoretical value for all test performed in this evaluation).

Appendix A

A.1 Sampler description and preparation

The glass tube, shown in Figure A.1, is similar to a glass tube proposed in OSHA ID-200[14], but never used for sampling sulfur dioxide. The sampler works by first passing the sample air stream through an uncoated glass fiber depth filter (GFF) to collect particulates. Next, the air stream passes through a sodium carbonate / glycerol coated GFF scrubbing any sulfur dioxide. The preparation of the sodium carbonate coated GFF is similar, although modified, to a procedure described in NIOSH 6004[15]. Finally, the air stream passes though the 5% silver nitrate coated silica gel used to collect hydrogen sulfide. The preparation of the silver nitrate coated silica gel is based on, although modified, a procedure described in a Japanese Ministry of the Environment document titled *Manual on Determination of Dioxins in Ambient Air*[16].

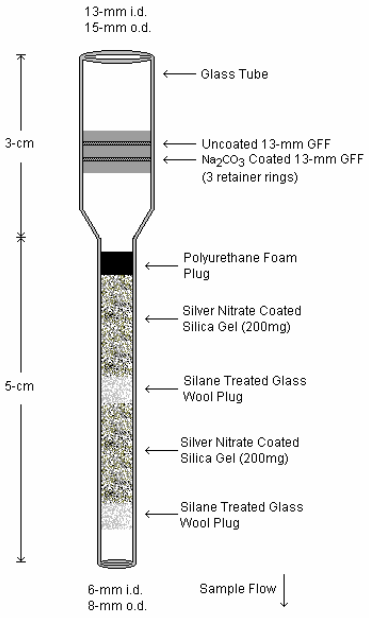


Figure A.1. Hydrogen sulfide sampler.

The polyurethane foam plug on the upstream side of the silica nitrate coated silica gel was used mainly for convenience of getting a quantitative transfer of the first section of medium. The use of the uncoated GFF is not necessary in regards to the collection of hydrogen sulfide but was added for possible use of the sampler for sulfur dioxide. The use of the coated GFF is necessary, however, otherwise sulfur dioxide would collect on the silver nitrate coated silica gel giving a positive interference for hydrogen sulfide. The reason for using 13-mm GFF, instead of smaller 6-mm GFF, was to increase the capacity of the coated filter to scrub sulfur dioxide without having to use a second coated filter. Also, using the larger 13-mm filters reduces back pressure of the sampler when sampling at 0.5 L/min. The back pressure of the sampler is around 14 inches of water when sampling at 0.5 L/min.

Below are instructions on how the sampler in this evaluation was constructed including equipment, reagents, and supplies used.

A.1.1 Apparatus

Binder free 13-mm (1.0 µm pore size) glass fiber depth filters (GFF). The GFF used in this evaluation (lot no. 4170403) were purchased from SKC, Inc. (cat. no. 225-16).

Saint-Gobain Performance Plastics Chemfluor PFA fluoropolymer tubing 0.437-in i.d. × 0.5-in o.d. (lot no. 5952471) purchased from VWR (cat. no. 63014-861) and cut into 3-mm retainer rings (ring dimension is 0.437-in i.d. × 0.5-in o.d. × 3-mm height).

Eight cm sampling glass tubes consisting of a 3-cm × 13-mm i.d. × 15-mm o.d section and a 5-cm × 6-mm i.d. × 8-mm o.d. section. The glass tubes used in this evaluation were specially made by Dependable Glass & Lab Supply, Salt Lake City, UT.

[14] Ku, J. C.; Sulfur Dioxide in Workplace Atmospheres. http://www.osha.gov/dts/sltc/methods/inorganic/id200/id200.html (accessed 2005), OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1992.

[15] Eller, P. M., Cassinelli, M. E.; Sulfur Dioxide. *NIOSH Manual of Analytical Methods (NMAM)*, 4th ed.; U.S. National Institute of Occupational Safety and Health: Cincinnati, OH, 1994; Vol. 3.

[16] Determination of Dioxins in Ambient Air. http://www.env.go.jp/en/chemi/dioxins/manual.pdf (accessed December 2005), Ministry of the Environment, Government of Japan: p 32.

Glass wool-silane treated. The glass wool used in this evaluation (lot. No. V0168) was purchased from Supelco (cat. no. 20410).

Polyurethane 6-mm foam plugs. The foam plugs used in this evaluation were purchased from SKC, Inc.

Glass 20-mL scintillation vials. Wheaton glass liquid scintillation vials were used in this evaluation.

10-mL disposable transfer pipettes.

Petri dishes.

Rotary evaporator, heating bath, vacuum pump and evaporation flask. The rotary evaporator used in this evaluation was a Buchi Rotavapor R-205S, with a Buchi B-490 heating bath, a model no. 8805 DirecTorr vaccum pump and a 250 mL flat bottom evaporation flask.

Water purifier. A Barnstead NANOpure Diamond system was used to produce 18.0 MΩ-cm DI water in this evaluation.

Analytical balance capable of weighing at least 0.01 mg and weighing paper. An Ohaus Galaxy 160D balance was used in this evaluation.

Glass 50-mL beaker.

Class-A 50-mL volumetric flask.

A means to dispense solutions. A Hamilton Microlab 540B dual syringe diluter/dispenser and an Eppendorf Series 2100 Research pipette (100 – 1000 µL) were used in this evaluation.

Tube furnace and quartz process tube. A Lindberg model 55035 tube furnace and 1-inch diameter quartz process tube were used in this evaluation.

Stainless steel #45 sieve (355 µm opening) with pan and cover.

Static control device. A Milty Zerostat 3 anti-static gun and a Staticmaster ionizing unit were used in this evaluation.

Desiccator. A Plas-Labs amber acrylic desiccator cabinet model 860-CGA was used in this evaluation.

PTFE coated forceps.

Forty place polypropylene 15-mm tube rack with 10-mm diameter holes on the bottom.

Nitrogen gas.

A.1.2 Reagents

Washed 20/40 mesh silica gel with 30 angstrom pore size. The washed silica gel used in this evaluation was purchased from SKC, Inc.[17] (lot no. 3722). A description of a washing procedure for silica gel can be found in the appendix of NIOSH 7903[18].

Silver nitrate ($AgNO_3$), [CAS no. 7761-88-8]. The silver nitrate used in this evaluation was 99.9999% (lot no. 03017ED) purchased from Sigma Aldrich.

Sodium carbonate anhydrous (Na_2CO_3), [CAS no. 497-19-8]. The sodium carbonate used in this evaluation was granular sodium carbonate anhydrous (lot no. 7527 KHEJ) purchased from Mallinckrodt.

Ethanol anhydrous (C_2H_6O), [CAS no 64-17-5]. The ethanol used in this evaluation was ethanol anhydrous, 200 proof, 99.5+% (lot no. 05548PC) purchased from Sigma Aldrich.

Glycerol ($C_3H_8O_3$) [CAS no. 56-81-5]. The glycerol used in this evaluation was 99.5+% A.C.S. reagent grade (lot no. 02210HZ) purchased from Aldrich Chemical Company.

GFF coating solution: Add approximately 10 mL of DI water to a 50-mL volumetric flask. Weigh out 2.5 g of sodium carbonate and carefully add to the volumetric flask. Next add 10 mL of ethanol and 1 mL of glycerol, dilute to the mark with DI water, mix well, and transfer to an appropriate storage bottle. It is recommended that the solution be stored and used for no longer than six months.

A.1.3 Preparation of coated filters

Place a GFF over each of the forty 10-mm wide holes on the bottom of an overturned polypropylene 15-mm tube rack.

Pipette 100 µL of coating solution onto each filter.

Place rack in a desiccator, purge desiccator with nitrogen and allow filters to dry overnight.

Place coated filters in a Petri dish and store in desiccator.

A.1.4 Preparation of silica gel

Insert a quartz wool plug in a 1-inch diameter quartz process tube, followed by 22 g of washed silica gel and a second quartz wool plug to hold silica gel in place.

Place the process tube in a tube furnace and set temperature to 180 °C. Continually purge the process tube with nitrogen at a rate of about 0.5 L/min. Allow the silica gel to dry in the tube furnace for 4 hours.

Allow the process tube to cool, remove one of the quartz wool plugs, and transfer silica gel to two 20-mL scintillation vials.

Store scintillation vials in desiccator.

[17] Personal communication from Cindy Kuhlman in regards to pore size, SKC Inc., 12/16/2005.
[18] Cassinelli, M. E.; Acids, Inorganic. *NIOSH Manual of Analytical Methods (NMAM)*, 4th ed.; U.S. National Institute of Occupational Safety and Health: Cincinnati, OH, 1994; Vol. 1.

A.1.5 Preparation of 5% silver nitrate coated silica gel

Set the temperature of the rotary evaporator water bath to 95 °C.

Place 10 g of the silica gel, prepared following the procedure in A.1.4, into a 250-mL flat bottom evaporation flask. Gently shake the flask so as to evenly spread the silica gel on the bottom of the flask.

Weigh out 0.526 grams of silver nitrate and place in a cleaned 50-mL beaker and then add 7.5 mL of DI water. Carefully mix until all the silver nitrate is dissolved. (Use 0.0526 g silver nitrate and 0.75 mL of DI water per 1 gram of silica gel.)

Pipette the silver nitrate solution into a transfer pipette, insert the pipette into the evaporation flask, and evenly dispense the solution onto the silica gel.

Attach the evaporating flask to the rotary evaporator, partially submerging flask in the water bath, and apply a vacuum. Rotate the flask at 100 rpm for approximately 10 sec and then set at 20 rpm for the remainder of the drying process. Once the coated silica gel is dry and free flowing allow it to continue drying for an additional 10 min.

Remove the evaporating flask from the rotary evaporator and dry the bottom of the flask. Transfer the coated silica gel to a #45 stainless steel sieve to remove any fine particulates.

Place the 10 g of 5% silver nitrate coated silica gel in a 20-mL scintillation vial and store in desiccator.

A.1.6 Assembling the sampler

Insert a 6-mm polyurethane foam plug into the wide end of an 8-cm sampling glass tube. Using a thin glass rod position the plug into place as shown in Figure A.1.

Crease a piece of weighing paper down the middle and place on balance. Weigh out 200 mg of the 5% silver nitrate coated silica gel and then carefully pour the coated silica gel into the narrow end of the tube. Gently tap the tube several times to settle the coated silica gel. An anti-static gun and/or Staticmaster ionizing unit may be needed to help control static.

Place a small glass wool plug into the narrow end of the tube and using a thin glass rod position the plug so that it firmly holds the silica gel in place. Avoid putting to much pressure on the silica gel so as not to crush the media.

Note: Use the minimum amount of glass wool as possible, especially for the center plug. Using too much glass wool can increase the back pressure of the sampler when sampling.

Again crease a piece of weighing paper down the middle and place on balance. Weigh out 200 mg of the 5% silver nitrate coated silica gel and then carefully pour the coated silica gel into the narrow end of the tube. Gently tap the tube to settle the coated silica gel.

Place a small glass wool plug into the narrow end of the tube and using a thin glass rod position the plug so that it firmly holds the silica gel in place.

Insert a 3-mm Chemfluor PFA fluoropolymer retainer ring into the wide end of the sampler. Using a thin glass rod or forceps position the ring into a horizontal position as shown in Figure A.1.

Next, insert a coated GFF and position it on top of the first retaining ring.

Then, insert the middle retaining ring and firmly press against the coated filter so that the filter is held in place between the two rings.

Next, insert a non-coated GFF and position it on top of the second retaining ring.

Finally, insert the third retaining ring and firmly press against the non-coated filter so that the filter is held in place between the two rings.

Store samplers in a small air tight container that has been flushed with nitrogen.