

## IX. APPENDIX I

### AIR SAMPLING METHOD FOR HYDROGEN SULFIDE

The sampling method for hydrogen sulfide is a validated NIOSH method [168].

Collect breathing-zone samples representative of the individual employee's exposure. Collect enough samples to permit calculation of a representative ceiling concentration for every operation or location in which there is exposure to hydrogen sulfide. At the time of the sample collection, record a description of sampling location and conditions, equipment used, time and rate of sampling, and any other pertinent information.

#### Equipment

The sampling unit for the impinger collection method consists of the following components:

(a) A graduated 25-ml midget impinger with a standard glass-tapered gas delivery tube containing 10 ml of cadmium hydroxide absorbing solution. Petticoat bubblers may be used, but not fritted bubblers. The impinger should be wrapped in metal-foil to protect the sample from exposure to light.

(b) A personal sampling pump whose flow can be determined within 5% at 0.20 liter/minute through the impinger. The sampling pump is protected from splashover or water condensation by an adsorption tube

loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

(c) An integrating gas volume meter such as a dry gas or wet-test meter or a rotameter, capable of measuring 2 liters of air at 0.2 liter/minute with an accuracy of  $\pm 5\%$ . Collection efficiency is 100% at this rate.

### Calibration

The accurate calibration of a sampling pump is essential to the correct interpretation of the volume sampled. The frequency of calibration depends on the use, care, and handling to which the pump is subjected. Pumps should also be recalibrated if they have been misused or if they have just been repaired or received from a manufacturer. If the pump receives hard use, more frequent calibration may be necessary. Maintenance and calibration records should be maintained.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. The accuracy of calibration depends on the type of instrument used as a reference. The choice of calibration instrument will depend largely upon where the calibration is to be performed. For laboratory testing, a soapbubble meter is recommended, although other standard calibrating instruments can be used. The actual setups will be similar for all instruments.

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

- (a) Check the voltage of the pump battery with a voltmeter to ensure adequate voltage for calibration. Charge the battery if necessary.
- (b) Plan to sample for 10 minutes at 0.2 liter/minute.
- (c) Assemble the sampling train as shown in Figure XIV-1.
- (d) Turn on the pump and moisten the inside of the soapbubble meter by immersing the buret in the soap solution. Draw bubbles up the inside until they are able to travel the entire buret length without bursting.
- (e) Adjust the pump flowmeter to provide the desired flow rate.
- (f) Check the water manometer to ensure that the pressure drop across the sampling train does not exceed 2.5 inches of water at 0.2 liter/minute.
- (g) Start a soapbubble up the buret and measure with a stopwatch the time it takes the bubble to move from one calibration mark to another.
- (h) Repeat the procedure in (g) at least three times, average the results, and calculate the flow rate by dividing the volume between the preselected marks by the time required for the soapbubble to traverse the distance. If, for the pump being calibrated, the volume of air sampled is calculated as the product of the number of strokes times a stroke factor (given in units of volume/stroke), the stroke factor is the quotient of the volume between two preselected marks divided by the number of strokes.
- (i) Data for the calibration should include the volume measured, elapsed time or number of strokes of the pump, pressure drop, air temperature, atmospheric pressure, serial number of the pump, date, and the name of the person performing the calibration.

### Sampling Procedure

(a) Prepare absorbing solution as described in Appendix II. Pipet 5 ml of cadmium sulfate-arabinogalactan solution directly into the midget impinger and mix with 5 ml of the sodium hydroxide solution. The addition of 5 ml of 95% ethanol to the absorbing solution just prior to aspiration controls foaming for 2 hours.

(b) Connect the impinger (via the absorption tube) to the sampling pump with a short piece of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and the impinger should be used. Air being sampled should not be passed through any other tubing or other equipment before it enters the impinger.

(c) Set the flowrate as accurately as possible using the manufacturer's directions. Record the temperature and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. Sample air at 0.2 liter/minute for 10 minutes.

(d) Do not remove the impinger stem after sampling since it contains cadmium sulfide deposits. Cadmium sulfide may decompose if exposed to light, so the impinger should be wrapped in metal foil to protect the light.

(e) Seal the outlets of the stem with Parafilm or other nonrubber covers, and seal the ground glass joints by taping to secure the top tightly.

(f) Treat at least one impinger in the same manner as the other samples (fill, seal, and transport), but do not draw air through this impinger. This impinger serves as a blank.

(g) Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day. Strong reducing agents (eg, sulfur dioxide) inhibit color development in the analysis step; they should be excluded if possible during sampling. Nitrogen dioxide and ozone may also interfere and should be excluded. Cadmium sulfide may be decomposed if exposed to light; the collected sample should be protected from light as described above.

#### Shipping Instruction

Hand deliver the samples if possible. Otherwise, ship samples in appropriate impinger shipping cases.

#### Alternative Method

NIOSH-certified hydrogen sulfide detector tubes [169] may be used to supplement or replace this sampling method for determining compliance with the ceiling concentration limit. The manufacturer's directions should be followed in using such tables.

## X. APPENDIX II

### ANALYTICAL METHOD FOR HYDROGEN SULFIDE

This analytical method for hydrogen sulfide is a validated NIOSH method [170].

#### Principle of the Method

Hydrogen sulfide is collected by drawing a measured volume of air through an alkaline suspension of cadmium hydroxide. The sulfide is precipitated as cadmium sulfide to prevent air oxidation of the sulfide which occurs rapidly in an aqueous alkaline solution. Arabinogalactan is added to the cadmium hydroxide slurry to minimize photodecomposition of the precipitated cadmium sulfide. The collected sulfide is subsequently determined by spectrophotometric measurement of the methylene blue produced by the reaction of the sulfide with a strongly acid solution of N,N-dimethyl-p-phenylenediamine and ferric chloride.

#### Range and Sensitivity

This method was validated over the range of 8.5-63 mg/cu m (6-45 ppm), at atmospheric temperature and pressure of 25 C and 760 mmHg, using a 2-liter sample. Under the conditions of sample size (2 liters), the probable range of the method is 5-100 mg/cu m (3-72 ppm). For sample concentrations outside this range, the sampling volume should be modified.

### Interferences

The methylene blue reaction is highly specific for sulfide at the low concentrations usually encountered in air. Strong reducing agents, eg, sulfur dioxide, inhibit color development. Even sulfide solutions containing several milligrams of sulfite/ml show this effect and must be diluted to eliminate color inhibition. If sulfur dioxide is absorbed to give a sulfite concentration in excess of 10  $\mu\text{g/ml}$ , color formation is retarded. The use of 0.5 ml of ferric chloride solution during analysis eliminates the sulfur dioxide interference up to 40  $\mu\text{g/ml}$ .

Nitrogen dioxide gives a pale yellow color with the sulfide reagents at 0.5  $\mu\text{g/ml}$  or more. No interference is encountered when 0.3 ppm nitrogen dioxide is aspirated through a midget impinger containing a slurry of cadmium hydroxide-cadmium sulfide arabinogalactan. If hydrogen sulfide and nitrogen dioxide are simultaneously aspirated through the cadmium-arabinogalactan slurry, lower hydrogen sulfide results are obtained, probably because of gas-phase oxidation of the hydrogen sulfide prior to precipitation as cadmium sulfide.

Ozone at 57 ppb reduced the recovery of sulfide previously precipitated as cadmium sulfide by 15%. Substitution of other cation precipitants, eg, zinc or mercury, for the cadmium on the absorbent will shift or eliminate the absorbance maximum of the solution upon addition of the acid-amine reagent.

Cadmium sulfide decomposes significantly when exposed to light unless protected by the addition of 1% arabinogalactan to the absorbing solution prior to sampling.

The choice of the impinger used to trap hydrogen sulfide with the cadmium hydroxide slurry is very important when measuring concentration in the range of 5-100 mg/cu m (3,072 ppm). Impingers or bubblers with fritted-end gas delivery tubes are a source of error if the sulfide in solution is oxidized to free sulfur by oxygen from the atmosphere. The sulfur collects on the fritted-glass membrane and may significantly change the flow rate of the air sampled through the system. One way to avoid this problem is to use a midget impinger with standard glass-tapered tips.

#### Precision and Accuracy

The coefficient of variation (standard deviation/mean x 100) for the total analytical and sampling method in the range of 8.5-63 mg/cu m (6-45 ppm) is 0.121. The standard deviation at 20 ppm is 8%.

The average agreement between the true values and found values was 10% for the total analytical and sampling method at 20 ppm.

#### Advantages and Disadvantages of the Method

Collection efficiency is variable below 0.0007 ppm, but this is inconsequential. It is affected by the type of scrubber, the size of the gas bubbles, and the contact time with the absorbing solution and the concentration of hydrogen sulfide. The collection efficiency is 100% at the recommended flow rate.

Hydrogen sulfide is readily volatilized from aqueous solution when the pH is below 7.0. Alkaline aqueous sulfide solutions are very unstable, because the sulfide ion is rapidly oxidized by exposure to the air.



Cadmium sulfide is not appreciably oxidized even when aspirated with pure oxygen in the dark. However, exposure of an impinger containing cadmium sulfide to laboratory or to more intense light sources produces an immediate and variable photodecomposition. Losses of 50-90% of added sulfide have been routinely reported by a number of laboratories. Even though the addition of arabinogalactan to the absorbing solution controls the photodecomposition, it is necessary to protect the impinger from light at all times. This is achieved by the use of low actinic glass impingers, paint on the exterior of the impingers, or a metal-foil wrapping.

#### Apparatus

Colorimeter with red filter or spectrophotometer at 670 nm. Matched cells, 1-cm path length.

Volumetric flasks: 20, 50, 100, 250, 1,000 ml.

Graduated cylinders or volumetric flasks: 20, 50, 100, 1,000 ml.

Pipets: 5 ml.

Pipeting bulb.

Clean rubber policeman.

#### Reagents

All reagents must be ACS analytical reagent quality. Distilled water should conform to the ASTM Standards for Referee Reagent Water. All reagents should be refrigerated when not in use.

(a) Amine-sulfuric acid stock solution: Add 50 ml of concentrated sulfuric acid to 30 ml of water and cool. Dissolve in the acid 12 g of

N,N-dimethyl-p-phenylene-diamine dihydrochloride (p-aminodimethylaniline, redistilled if necessary) or 10.5 g of N,N-dimethyl-p-phenylenediamine oxalate. Do not dilute. The stock solution may be stored indefinitely under refrigeration.

(b) Amine test solution: Dilute 25 ml of the stock solution to 1 liter with 1:1 sulfuric acid.

(c) Ferric chloride solution: Dissolve 100 g of ferric chloride,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , in water and dilute to 100 ml.

(d) Ethanol, 95%.

(e) Arabinogalactan: Stractan 10, available from Stein-Hall and Company Inc, New York, or arabinogalactan sold under other brand names may be used.

(f) Cadmium sulfate-arabinogalactan solution: Dissolve 8.6 g of cadmium sulfate,  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ , in approximately 600 ml of water. Add 20 g arabinogalactan and dilute to 1 liter.

(g) Sodium hydroxide solution: Dissolve 0.6 g of sodium hydroxide in approximately 600 ml of water and dilute to 1 liter.

(h) Standard sulfide solution: Place 35.28 g of sodium sulfide,  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , into a 1-liter volumetric flask and add enough oxygen-free distilled water to bring the volume to 1 liter. Store under nitrogen and refrigerate. Standardize with standard iodine and thiosulfate solution in an iodine flask under a nitrogen atmosphere to minimize air oxidation. The approximate concentration of the sulfide solution will be 4,700  $\mu\text{g}$  sulfide/ml of solution. The exact concentration must be determined by iodine-thiosulfate standardization immediately prior to dilution.

(i) Working sulfide solution: Dilute 25 ml of stock solution to 250 ml with oxygen-free water. This solution contains the sulfide equivalent of approximately 500  $\mu\text{g}$  of hydrogen sulfide/ml. Make fresh working sulfide solution daily. The actual concentration of this solution can be determined from the titration results on the stock sodium sulfide standard.

#### Analysis of Samples

All glassware should be thoroughly cleaned. Wash the glassware with a detergent and tap water solution followed by tap water and distilled water rinses; then soak in 1:1 or concentrated nitric acid for 30 minutes. Follow with tap water, distilled water, and double-distilled water rinses.

(a) Remove the impinger top and drain it thoroughly into the impinger flask. Set top aside. Transfer the solution and deposit in the impinger flask to a 250-ml volumetric flask. Using 50 ml of distilled water, rinse the bottom twice with a clean rubber policeman on a glass stirring rod. Add the rinse solutions to the contents of the volumetric flask. With the rubber policeman, wash the outside of the impinger stem with 20 ml of distilled water and the washings to the flask. Drain 20 ml of distilled water through the impinger into the flask. The total wash-water volume should be 90 ml.

(b) Add 15 ml of amine test solution through the impinger inlet tube into the volumetric flask. This is necessary to dissolve the cadmium sulfide deposited inside the inlet tube. Mix gently to avoid loss of hydrogen sulfide.

(c) Add 0.5 ml of ferric chloride solution to the mixture within

the volumetric flask and mix. Bring to volume with distilled water. Allow to stand 20 minutes.

(d) Measure the absorbance of the color at 670 nm in a spectrophotometer or colorimeter set at 100% transmission against the zero reference.

#### Calibration and Standards

(a) Aqueous sulfide

(1) Place 5 ml of cadmium sulfate-arabinogalactose solution and 5 ml of sodium hydroxide solution into each of a series of 250-ml volumetric flasks.

(2) Add standard sulfide solution equivalent to 0, 20, 40, 80, 120, and 160  $\mu\text{g}$  of hydrogen sulfide to the different flasks.

(3) Add 90 ml of distilled water.

(4) Add 15 ml of amine test solution to each flask and mix gently.

(5) Add 0.5 ml of ferric chloride solution to each flask. Mix, make up to volume, and allow to stand for 20 minutes.

(6) Determine the absorbance in a spectrophotometer or colorimeter at 670 nm against the sulfide-free reference solution.

(7) Prepare a standard curve of absorbance versus  $\mu\text{g}$  of hydrogen sulfide.

(b) Gaseous sulfide

Cylinders of hydrogen sulfide in dry nitrogen in the range desired are available commercially and may be used to prepare calibration curves for use at the 10-60 mg/cu m (7-43 ppm) levels. Nitrogen containing

hydrogen sulfide in the range of 322.6-430.2 ppm can be diluted to the desired concentrations. Analyses of these known concentrations give calibration curves which simulate all of the operational conditions performed during the sampling and analytical procedure. This calibration curve includes the important correction for collection efficiency at various concentrations of hydrogen sulfide. Prepare or obtain a cylinder of nitrogen containing hydrogen sulfide in the range of 450-600 mg/cu m (322-430 ppm). To obtain standard concentrations of hydrogen sulfide, assemble the apparatus consisting of appropriate pressure regulators, needle valves, and flowmeters for the nitrogen and for a dry air diluent stream. Stainless steel, glass, or rubber tubing must be used for the hydrogen sulfide mixture. Flow of hydrogen sulfide in nitrogen is controlled by a needle valve operated in conjunction with a flowmeter previously at 0.2 liter/minute. Diluent dry air from a cylinder is controlled by a similar needle valve-flowmeter combination in the range of 1-20 liters/minute. The hydrogen sulfide in nitrogen and the diluent air are combined in a mixing chamber at atmospheric pressure. They flow through a baffle tube in which mixing takes place into a 1-liter sampling flask provided with one or more nipples from which samples can be taken. Sampling is done by connecting a midget impinger to the nipple and drawing a known volume of the mixture through the impinger for a measured length of time, using a critical orifice to control flow at a constant known rate.

The dynamic range of the colorimetric procedure fixes the total volume of the sample at 2 liters; to obtain linearity between the absorbance of the solution and the concentration of hydrogen sulfide in ppm, select a constant sampling time. This fixing of the sampling time is

desirable also from a practical standpoint. In this case, select a sampling time of 10 minutes. To obtain a 2-liter sample of air requires a flow rate of 0.2 liter/minute. The concentration of standard hydrogen sulfide is computed as follows:

$$C = \frac{cf}{F + f}$$

where:

- C = concentration of H<sub>2</sub>S in mg/cu m
- c = concentration of H<sub>2</sub>S in nitrogen, before dilution
- F = flow of diluent air, as measured by calibrated flowmeter
- f = flow of hydrogen sulfide in nitrogen, as measured by calibrated flowmeter

Commercially prepared hydrogen sulfide in nitrogen can be obtained with a known concentration, as analyzed by the laboratory preparing the gas. If it is desired to check this concentration, a measured volume of the gas can be bubbled through the absorbing solutions, and the collected sulfide titrated against iodine-thiosulfate. The volume of gas can be measured using a wet-test meter.

If hydrogen sulfide is present at much lower concentrations (0.001-0.1 ppm), commercially available permeation tubes containing liquified hydrogen sulfide may be used to prepare calibration tubes.

### Calculations

(a) Determine the sample volume, in liters, from the gas meter or flowmeter readings and the time of sampling. Adjust volume to 760 mmHg and 25 C.

$$V_n = V \times \frac{P}{760} \times \frac{298}{(T+273)}$$

where:

V<sub>n</sub> = Volume of air (liters) at standard conditions  
V = Volume of air samples (liters)  
P = Barometric pressure (mmHg)  
T = Temperature of sample air (C)

(b) Use the Beers-Law standard curve of absorbance versus  $\mu\text{g}$  of hydrogen sulfide to determine  $\mu\text{g}$  of hydrogen sulfide in the sampling impinger corresponding to its absorbance reading at 670 nm.

(c) To determine the concentration of hydrogen sulfide in ppm:

$$\text{ppm H}_2\text{S} = 0.717 \times \mu\text{g H}_2\text{S}/V_n$$

where:

$\mu\text{g H}_2\text{S}$  = micrograms of hydrogen sulfide  
determined in paragraph (b)

#### Alternative Method

NIOSH-certified hydrogen sulfide detector tubes [169] may be used to supplement or replace this method of analysis for determining compliance with the ceiling workplace environmental concentration limit. The manufacturer's directions should be followed in using such tubes.