Hydrogen Sulfide

Analyte:	Hydrogen Sulfide	Method No.: S4
Matrix:	Air	Range: 8.5-63 mg/cu m
OSHA Standard:	20 ppm (30 mg/cu m) - Ceiling 50 ppm (70 mg/cu m) - Peak	Precision $(\overline{CV}_T)$: 0.121
Procedure:	Absorption - Methylene Blue Spectrophotometric	Validation Date: 9/13/74

1. Principle of the Method

1.1 Hydrogen sulfide is collected by aspirating a measured volume of air through an alkaline suspension of cadmium hydroxide (Reference 11.1). The sulfide is precipitated as cadmium sulfide to prevent air oxidation of the sulfide which occurs rapidly in an aqueous alkaline solution. STRactan 10® is added to the cadmium hydroxide slurry to minimize photo-decomposition of the precipitated cadmium sulfide (Reference 11.2). The collected sulfide is subsequently determined by spectrophotometric measurement of the methylene blue produced by the reaction of the sulfide with an acid solution of N,N-dimethyl-p-phenylenediamine and ferric chloride (References 11.3, 11.4, 11.5).

1.2 Collection efficiency is variable below 10 µg/cu m and 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 (References 11.6, 11.7, 11.8).

2. Range and Sensitivity

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

3. Interferences

3.1 The methylene blue reaction is highly specific for sulfide at the low concentrations usually encountered in ambient air. Strong reducing agents (e.g. SO_2) inhibit color development. Even sulfide solutions containing several micrograms sulfite per 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 µg/ml color formation is retarded. The use of 0.5 ml of ferric chloride solution during analysis eliminates the SO_2 interference up to 40 µg/ml.

3.2 Nitrogen dioxide gives a pale yellow color with the sulfide reagents at 0.5 µg/ml or more. No interference is encountered when 0.3 ppm NO_2 is aspirated through a midget impinger containing a slurry of cadmium hydroxide-cadmium sulfide-STRactan 10®. If H_2S and NO_2 are simultaneously aspirated through cadmium hydroxide-STRactan 10® slurry, lower H_2S results are obtained, probably because of gas phase oxidation of the H_2S prior to precipitation as CdS (Reference 11.8).

3.3 Ozone at 57 ppb reduced the recovery of sulfide previously precipitated as CdS by 15 per cent (Reference 11.8).

3.4 Substitution of other cation precipitants for the cadmium in the absorbent (i.e. zinc, mercury, etc.) will shift or eliminate the absorbance maximum of the solution upon addition of the acid-amine reagent.

3.5 Cadmium sulfide decomposes significantly when exposed to light unless protected by the addition of 1 per cent STRactan® to the absorbing solution prior to sampling (Reference 11.2).

3.6 The choice of impinger used to trap H_2S with the $Cd(OH)_2$ slurry is very important when measuring concentration in the range 5-100 mg/cu m. Impingers or bubblers having fritted-end gas delivery tubes are a problem source 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 sample through the system. One way of avoiding this problem is to use a midget impinger with standard glass-tapered tips.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 8.5-63 mg/cu m was 0.121. This value corresponds to a 3.6 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.9.

4.2 On the average the values obtained using the overall sampling and analytical method were 10% higher than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 Effect of Light and Storage - Disadvantage

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

5.1.2 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 photo-decomposition. Losses of 50-90 per cent of added sulfide have been routinely reported by a number of laboratories. Even though the addition of STRactan 10® to the absorbing solution controls the photo-decomposition (Reference 11.2), 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 an aluminum foil wrapping.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the impinger collection method consists of the following components:

6.1.1 A graduated 25-ml midget impinger with a standard glass-tapered gas delivery tube containing the absorbing solution or reagent. The impinger should be wrapped in aluminum foil to protect the sample from exposure to light.

6.1.2 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. 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.

6.1.3 An integrating volume meter such as a dry gas or wet test meter or rotameter capable of measuring 2 liters of air at 0.2 liter per minute with an accuracy of ±5%. Instead of these, calibrated hypodermic needles may be used as critical orifices if the pump is capable of maintaining greater than 0.7 atmospheric pressure differential across the needle (Reference 11.10).

6.1.4 Thermometer.

6.1.5 Manometer.

6.1.6 Stopwatch.

6.2 Associated laboratory glassware.

6.3 Colorimeter with red filter or spectrophotometer at 670 nm.

6.4 Matched cells, 1-cm path length.

7. 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.

7.1 Amine-sulfuric Acid Stock Solution. Add 50 ml concentrated sulfuric acid to 30 ml water and cool. Dissolve 12 g of N,N-dimethyl-p-phenylene-diamine dihydrochloride* (para-aminodimethylaniline) (redistilled if necessary) in the acid. Do not dilute. The stock solution may be stored indefinitely under refrigeration.

7.2 Amine Test Solution. Dilute 25 ml of the Stock Solution to 1 liter with 1:1 sulfuric acid.

7.3 Ferric Chloride Solution. Dissolve 100 g of ferric chloride, $FeCl_3 \cdot 6H_2O$ in water and dilute to 100 ml.

7.4 Ethanol, 95%.

7.5 STRactan 10®. (Arabinogalactan) Available from Stein-Hall and Company, Inc., 385 Madison Avenue, New York, New York. Arabinogalactan sold under other brand names may be used.

7.6 Cadmium Sulfate-STRactan® Solution. Dissolve 8.6 g of $3CdSO_4 \cdot 8H_2O$ in approximately 600 ml of water. Add 20 g STRactan 10® and dilute to 1 liter.

7.7 Sodium Hydroxide Solution. Dissolve 0.6 g sodium hydroxide in approximately 600 ml of water and dilute to 1 liter.

7.8 Cadmium Hydroxide-STRactan® Absorbing Solution. This absorbing solution is prepared by pipeting 5 ml of cadmium sulfate-STRactan® solution (7.6) and 5 ml of sodium hydroxide solution (7.7) directly into the midget impinger and mixing. This solution is stable for 3 to 5 days.

7.9 Stock Sodium Sulfide Standard. Place 35.28 g of $Na_2S \cdot 9H_2O$ 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 4700 μg sulfide/ml of solution. The exact concentration must be determined by iodine-thiosulfate standardization immediately prior to dilution.

* 10.5 g N,N-dimethyl-p-phenylenediamine oxalate may be used.

7.10 Working Sodium Sulfide Solution. Dilute 25 ml of stock solution (7.9) with oxygen free water to 250 ml. This solution contains the sulfide equivalent of approximately 500 µg/ml of H_2S. 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 (7.9).

For the most accurate results in the iodometric determination of sulfide in aqueous solution, the following general procedure is recommended:

1. Replace the oxygen from the flask by flushing with an inert gas such as carbon dioxide or nitrogen.

2. Add an excess of standard iodine, acidify, and back titrate with standard thiosulfate and starch indicator (Reference 11.14).

8. Procedure

8.1 Cleaning of Equipment. All glassware should be thoroughly cleaned; the following procedure is recommended:

8.1.1 Wash with a detergent and tap water solution followed by tap water and distilled water rinses.

8.1.2 Soak in 1:1 or concentrated nitric acid for 30 minutes and then follow with tap, distilled, and double distilled water rinses.

8.2 Collection and Shipping of Samples

8.2.1 Prepare 10 ml of absorbing solution as described in Section 7.8 directly in the midget impinger. The addition of 5 ml of 95% ethanol to the absorbing solution just prior to aspiration controls foaming for 2 hours (induced by the presence of STRactan 10®). In addition, 1 or 2 Teflon demister discs may be slipped up over the impinger air inlet tube to a height approximately 1 to 2" from the top of the tube. Wrap the impinger with aluminum foil.

8.2.2 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 impinger should be used.

8.2.3 Air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

8.2.4 At the ceiling and peak concentrations, a sample size of 2 liters is recommended. Sample for 10 minutes at a flow of 0.20 liter per minute. The flow rate should be known with an accuracy of at least ±5%.

8.2.5 Turn on the pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible.

8.2.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available, record the elevation.

8.2.7 After sampling, the impinger stem must not be removed since it contains CdS deposits. It is necessary to ship the impingers with the stems in so the outlets of the stem should be sealed with Parafilm or other non-rubber covers, and the ground glass joints should be sealed (i.e. taped) to secure the top tightly.

8.2.8 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

8.2.9 Whenever possible, hand delivery of the samples is recommended. Otherwise, special impinger shipping cases designed by NIOSH should be used to ship the samples.

8.2.10 A "blank" impinger should be handled as the other samples (fill, seal, and transport) except that no air is sampled through this impinger.

8.3 Analysis

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

8.3.2 Add 15 ml of amine test solution through the impinger inlet tube into the volumetric flask. This is necessary to dissolve the CdS deposited inside the inlet tube. Mix gently to avoid loss of H_2S.

8.3.3 Add 0.5 ml of ferric chloride solution and mix. Bring to volume with distilled water. Allow to stand 20 minutes.

8.3.4 Prepare a zero reference solution in the same manner using a 10-ml volume of absorbing solution, through which no air has been aspirated.

8.3.5 Measure the absorbance of the color at 670 nm in a spectrophotometer or colorimeter set at 100 per cent transmission against the zero reference.

9. Calibration and Standards

9.1 Aqueous Sulfide

9.1.1 Place 5 ml of each of the absorbing solutions (Sections 7.6 and 7.7) into each of a series of 250 ml volumetric flasks. Add standard sulfide solution equivalent to 0, 20, 40, 80, 120, 160 μg of hydrogen sulfide to the different flasks.

9.1.2 Add 90 ml of distilled water.

9.1.3 Add 15 ml of amine-acid test solution to each flask and mix gently.

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

9.1.5 Determine the absorbance in a spectrophotometer at 670 nm against the sulfide-free reference solution.

9.1.6 Prepare a standard curve of absorbance versus μg H_2S.

9.2 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 levels. Nitrogen containing hydrogen sulfide in the 450-600 mg/cu m range 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 chemical procedure. This calibration curve includes the important correction for collection efficiency at various concentrations of hydrogen sulfide.

9.2.1 Prepare or obtain a cylinder of nitrogen containing hydrogen sulfide in the range of 450-600 mg/cu m.

9.2.2 To obtain standard concentrations of hydrogen sulfide, assemble the apparatus consisting of appropriate pressure regulators, needle valves and flow meters for the nitrogen and for a dry air diluent stream. All 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 previously calibrated flow meter in the range of 0.2 to 2.0 liters per minute. Diluent dry air from a cylinder is controlled by a similar needle valve-flow meter combination in the range of 1 to 20 liters per minute. The hydrogen sulfide in nitrogen and the diluent air are combined in a mixing chamber at atmospheric pressure, from which they flow through a baffle tube in which mixing takes place into a 1 liter sampling flask which is 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.

9.2.3 Procedure for Preparing Simulated Calibration Curves. The following description represents a typical procedure for air sampling of short duration.

1. The system is designed to provide an accurate measure of hydrogen sulfide in the 10-60 mg/cu m range. It can be easily modified to meet special needs.

2. The dynamic range of the colorimetric procedure fixes the total volume of the sample at 2 liters; then, to obtain linearity between the absorbance of the solution and the concentration of hydrogen sulfide in mg/cu m, 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 per minute. The concentration of standard H_2S in air is computed as follows:

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

where:

C = concentration of H_2S in mg/cu m

c = concentration of H_2S in nitrogen, before dilution

F = flow of diluent air, as measured by calibrated flow meter

f = flow of H_2S in nitrogen, as measured by calibrated flow meter.

9.2.4 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, 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.

9.2.5 If hydrogen sulfide is present at much lower concentrations (1.5 to 140 μg/cu m), commercially available permeation tubes containing liquified hydrogen sulfide may be used to prepare calibration tubes (Reference 11.8, 11.11, 11.12, 11.13, 11.14).

10. Calculations

10.1 Gaseous Sulfide

10.1.1 Using the Beers-Law Standard curve of absorbance versus μg H_2S determine μg H_2S in the sampling impinger corresponding to its absorbance reading at 670 nm.

10.1.2 The concentration of H_2S in the air sampled can be expressed in mg/cu m which is numerically equal to μg/liter.

$$\text{mg/cu m} = \mu\text{g/liter} = \frac{\mu\text{g } H_2S \text{ (Section 10.1)}}{\text{Air volume sampled (liter)}}$$

10.1.3 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

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NIOSH Analytical Methods for Set A
Standards Completion Program

October 1975

U.S. Department for Health, Education, and Welfare
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
Division of Laboratories and Criteria Development
Cincinnati, Ohio

NIOSH Analytical Methods for Set A

A joint National Institute for Occupational Safety and Health (NIOSH)/Occupational Safety and Health Administration (OSHA) Standards Completion Program will complete standards for approximately 400 air contaminants presently listed in Tables Z-1, Z-2, and Z-3 of 29 CFR Part 1910.1000 by adding other requirements of a standard required under Section 6(b)(7) and 8(c)(3) of the Occupational Safety and Health Act of 1970 (PL 91-596). These completed standards will then contain, in addition to the permissible exposure limit given in 1910.93, appropriate provisions requiring monitoring of worker exposure, engineering control, personal protection, employee training, medical surveillance, and record keeping.

As a part of the Standards Completion Program, NIOSH is engaged in a two-year study under contract CDC-99-74-45 to validate sampling and analytical procedures for use in monitoring worker exposure to substances listed in Tables Z-1, Z-2, and Z-3. These methods have been validated and are suitable for measuring airborne concentrations of these substances and thus may be used for determining compliance with the standard or the need for control, for research, or whenever there is a need to measure airborne concentrations in the workplace. These analytical methods should not be considered the only methods which may be used to evaluate worker exposure. Other methods meeting the accuracy requirements in the standard may also be used.

These analytical methods will be periodically modified as new developments in science and technology require.

Set A

Acetone
2-Butanone
Cyclohexanone
Hexone
Hydrogen sulfide
Manganese
2-Pentanone

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
Division of Laboratories and Criteria Development
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