Scand J Work Environ Health 1979;5(1):31-34

<https://doi.org/10.5271/sjweh.2668>

Issue date: Mar 1979

**Hazards in the work environment--hydrogen sulfide.
Spectrophotometric determination of hydrogen sulfide.**

by [Waernbaum G](#), [Wallin I](#)

Key terms: [absorbtion](#); [air](#); [factory](#); [hazard](#); [hydrogen sulfide](#); [sewage plant](#); [silica gel](#); [spectrophotometric determination](#); [spectrophotometry](#); [work environment](#)

This article in PubMed: www.ncbi.nlm.nih.gov/pubmed/441707

This work is licensed under a [Creative Commons Attribution 4.0 International License](https://creativecommons.org/licenses/by/4.0/).

Hazards in the work environment — Hydrogen sulfide

Spectrophotometric determination of hydrogen sulfide

by GÖSTA WAERNBAUM, Ph.D., and INGA WALLIN¹

WAERNBAUM, G. and WALLIN, I. Hazards in the work environment — Hydrogen sulfide: Spectrophotometric determination of hydrogen sulfide. *Scand. j. work environ. & health* 5 (1979) 31—34. A convenient method for determining hydrogen sulfide in air has been developed in which the gas is first absorbed in silica gel and thereafter analyzed spectrophotometrically. The limit of detection is one part per billion when measured at a wavelength of 670 nm.

Key words: absorption, air, factories, hydrogen sulfide, sewage plants, silica gel, spectrophotometry.

Hydrogen sulfide is found in the atmosphere of a large number of workplaces not normally associated with the compound. A modified spectrophotometric method (1) has been developed for the analysis of hydrogen sulfide in air, and it has been applied in the present study to the estimation of concentrations of the gas in different industrial environments. The method appears specific for hydrogen sulfide since the presence of either dimethyl sulfide or other similar sulfides did not influence the measured results according to our experiments. Dimethyl sulfide was allowed to pass through silica gel tubes in a variety of concentrations without the detection of any colored products, neither in the tube nor in the reaction mixture. Furthermore, the

amount of gas absorbed did not change during the storage of collected samples for up to four weeks, and therefore it is not essential that analyses be performed immediately. After the treatment of the samples, the final colored reaction product was shown to be stable for several hours.

The method is simple and its limit of detection (one part per billion) compares favorably with a fluorimetric procedure [0.1—4.0 ppb (3)] and a gas chromatographic method [up to 5 ppb (2)].

MATERIALS AND METHODS

Chemicals

A total of 27.2 g of N,N-dimethyl-1,4-phenylenediammoniumdichloride is dissolved in 75 ml of icecold 9 M sulfuric acid (H₂SO₄) and diluted to 100 ml with

¹ Department of Occupational Health, National Board of Occupational Safety and Health, Stockholm, Sweden.

Reprint requests to: Dr. G. Waernbaum, National Board of Occupational Safety and Health, Fack, S-100 26 Stockholm, Sweden.

the same acid. An aliquot (2.5 ml) of this stock solution (I) is diluted to 100 ml with 9 M H_2SO_4 to give a working solution of the reagent containing 6.8 mg per milliliter (II). Solutions I and II are stable for up to three months and one month, respectively, when stored in a refrigerator. For solution III 100 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is dissolved in distilled water and diluted to 100 ml. In addition pure 100 % hydrogen sulfide (Matheson, East Rutherford, Georgia, U.S.A.) and silica gel, particle size up to 1 mm, were used in the analysis.

Apparatus

MSA portable pumps (model G) from the Mine Safety Appliances Company, a spectrophotometer from Hitachi (model 101, and glass tubes (inner dimensions 100 mm $\times$ 9 mm) with plastic screw caps were the apparatus used in the investigation.

Preparation of hydrogen sulfide collection tubes

Glass tubes were filled with approximately 2 g of silica gel coated with cadmium acetate (1 % m/m). This packing material was prepared by the soaking of silica gel in a breaker, air-dried at room temperature, with water containing the appropriate amount of cadmium acetate. After the tubes were filled, both ends were first plugged with glass wool and then sealed with plastic screw caps. These caps were replaced during the collection of samples by inlet screws into which a small glass tube (inner dimensions 50 mm $\times$ 4 mm) was fitted. The absorption of the hydrogen sulfide gas was complete unless the tube was overloaded, when a yellow staining of the packing material could be observed from one end of the column to the other. With this size of absorption tube, overloading could occur when more than 50 ppm of hydrogen sulfide was absorbed during a couple of minutes at an airflow of 1 l/min. One advantage of this type of sampling over our earlier method of sampling with an impinger containing sodium hydroxide and zinc acetate is its easier handling.

Air sampling

The air pump was calibrated against a flowmeter before and after the sampling procedure. An air flow of about 1 l/min was found to give satisfactory results. Depending upon the expected concentration of hydrogen sulfide in the air, different volumes were collected; 400 l of air was sampled when the amount of hydrogen sulfide was thought to be small.

Procedure for the assay of total hydrogen sulfide

The silica gel from the sample collection tubes was transferred to a 100-ml glass flask with a glass stopper. Ten milliliters of dilute hydrochloric acid (1:2) was added and, after careful and thorough mixing, 5 ml of the solution was pipetted into a 10-ml volumetric flask. Two milliliters of the N,N -dimethyl-1,4-phenylenediammoniumdichloride (II) and 0.2 ml of the ferric chloride solution (III) were then added and followed by distilled water to the mark. The solution was allowed to stand for 30 min at room temperature before its absorption was estimated at a wavelength of 670 nm in a 1-cm glass cuvette. A hydrogen sulfide-free sample of air treated in exactly the same way acted as a reagent blank. All samples were compared in the spectrophotometer with a distilled water blank. If any dilution of the final solutions was found to be necessary, it was performed with hydrochloric acid (1:2); the reagent blank sample was treated in the same way.

The amount of the absorbed hydrogen sulfide was calculated with reference to a standard curve.

Preparation of the standard curve

Twenty-milliliter plastic sacks (aluminum foil coated with polyester on the inside) were filled with about 10 l of air. Pure hydrogen sulfide was allowed to pass through a plastic rubber tube before a gas-tight syringe was filled with an appropriate amount of the gas. After the injection of this gas into the half-filled plastic sack, the contents were mixed,

more air (up to a total of 20 l) was added, and the components were again mixed. Gas samples were taken from this sack with an air pump, and the air/hydrogen sulfide mixture was passed through the previously mentioned silica gel-filled absorption tubes. The gas flow was at all times 1 l/min, and various gas mixtures in the range of 0.1 to 10 ppm were analyzed. The arrows on the standard curve in fig. 1 indicate the highest and lowest values from three different analyses with the same concentration of the gas mixture.

Effect of storage on hydrogen sulfide absorbed in cadmium acetate-coated silica gel tubes

Hydrogen sulfide (10 l, 5 ppm) was absorbed in a series of coated silica gel tubes with a gas flow of 1 l/min, and the tubes were then sealed with caps. Two tubes were analyzed immediately, two were analyzed after a period of two weeks stored at room temperature, and another two were analyzed after four weeks of storage. No significant difference could be detected between the levels of the hydrogen sulfide found in those tubes which were stored and those which were analyzed immediately (table 1).

RESULTS AND DISCUSSION

Depending upon the expected amount of hydrogen sulfide in the air examined, suitable sample volumes were allowed to pass through the absorption tubes. Thus in a sewage treatment plant where levels were assumed to be very low about 400 l of air was sampled. The same volume was used for samples obtained from non-restricted areas of steel works and pulp plants, but smaller volumes (5–20 l) were sampled elsewhere. The results obtained following the analysis of hydrogen sulfide in air samples collected from various work environments are presented in table 2, but only those which gave a positive

Fig. 1. Standard curve for the spectrophotometric determinations of hydrogen sulfide at 670 nm (1-cm cuvette). The arrows indicate the highest and lowest values of three determinations.

Table 1. Effect of storage on samples of hydrogen sulfide^a absorbed in coated silica tubes.

Time of storage	Level (ppm) ^b
Determined immediately	4.97
After 2 weeks	5.45
After 4 weeks	5.43

^a Five parts per million of hydrogen sulfide, 10 l of air/hydrogen sulfide.

^b Given as the average of two analyses.

reaction to the reagents. Although the parts-per-million levels were generally low, it was occasionally found that the threshold limit value for the gas (in Sweden 10 ppm) was exceeded. However, those places where the levels of hydrogen sulfide were found to be dangerously high were, in most cases, restricted areas even for plant personnel, although in one nonrestricted area of a pulp plant used for a resin distilling process the amount of hydrogen sulfide was found to be high (12 ppm).

Table 2. Concentration of hydrogen sulfide in air samples collected from different work environments.

Type of factory and locations of taken samples (nonrestricted areas)	Environmental conditions of the workplace	Amount of hydrogen sulfide found (ppm) ^b
Rayon plant		
At a desk	Huge room with a spinning machine; no obvious fumes or odors; the spinning machine was enclosed	0.25
At a spinning machine		0.07
Spinning machine (inside) ^a		161
Plants for sewage treatment		
1. Coarse treatment	Very airy conditions, fast air circulating but still smelly	0.36
Grit chamber		0.47
Aeration tank		0.007
2. Aeration tank (at the wall)		0.03
» » (in the middle)		0.03
Steel works		
Heat treatment department (at the floor)	Smokey, nasty smelling and very warm	0.10
Heat treatment department (at the ceiling)		1.21
Scrubber ^a		87
Pulp plants		
1. Resin distilling area	Narrow spaces and nasty smelling	1.22
2. Resin distilling area		12
Control room for personnel		0.03
Outside the control room		0.11

^a Restricted area.

^b Given as an average value of two analyses.

REFERENCES

1. MAIER, H. G. and DIEMAIR, W. Zur colorimetrischen Bestimmung flüchtiger Schwefelverbindungen in Lebensmitteln. *Fresenius Z. Anal. Chem.* (1966): 227, 187—197.
2. TAKAHASHI, T., NAKAJIMA, S., KONISHI, I., MIEDANER, H. and NARZISS, L. Gas chromatographic determination of H₂S and DMS in beer. *Brauwissenschaft* 31 (1978): 1, 1—4.
3. TANAKA, S., HAHSIMOTO, Y. and NAKAMURA, K. Fluorometric method using fluorescein mercuric acetate reagent for determination of hydrogen sulfide in the atmosphere. *Bunseki kagaku* 26 (1977): 4, 241—246.

Received for publication: 20 September 1978