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SURVEY OF METHODS FOR THE DETECTION OF H<sub>2</sub>S AND SO<sub>2</sub>

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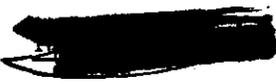
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ABSTRACT

Colorimetric, titration, mass analysis, combustion, electrolytic conductivity, thermal conductivity, ionization potential, ultraviolet absorption, infra-red absorption, and microwave absorption methods were evaluated on paper for use in a portable or semiportable instrument for the rapid, sensitive detection of both H<sub>2</sub>S and SO<sub>2</sub>. The ultraviolet absorption method appears to be the most promising for use in the development of a suitable detector.

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## SURVEY OF METHODS FOR THE DETECTION OF H<sub>2</sub>S AND SO<sub>2</sub>

### INTRODUCTION

For purposes of leak detecting and health monitoring, a portable or semiportable instrument is desired which is capable of rapid detection of H<sub>2</sub>S or SO<sub>2</sub> in concentrations below 10 ppm (by volume). The presence of D<sub>2</sub>S in the GS units makes it desirable that the instrument be sensitive to this gas as well.

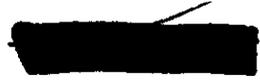
A portable instrument is arbitrarily defined for this report as being battery-operated and weighing less than 50 pounds. An instrument weighing between 50 and 200 pounds and/or requiring 110 v A.C. power is classed as semiportable.

### SUMMARY

For an immediate answer to the problem of detection of H<sub>2</sub>S and SO<sub>2</sub>, present chemical methods involving colorimetric or titration processes must be utilized. These methods have good sensitivity to either H<sub>2</sub>S or SO<sub>2</sub>, but not to both. Also, for the latter gas, the time required for analysis makes leak detecting difficult.

The Consolidated Titrilog, Model 26-103, is a semiportable device which has excellent sensitivity to H<sub>2</sub>S, D<sub>2</sub>S, and SO<sub>2</sub>, but requires 15 minutes for a spot analysis. It appears to be the best instrument available for H<sub>2</sub>S, D<sub>2</sub>S, or SO<sub>2</sub> monitoring. A less sensitive indication, but with a response time of only a few seconds, can be obtained using the Consolidated Leak Detector modified for detection of heavier ions. Its 470 pound weight is a severe handicap.

For a longer range program to meet the required standards, methods based on some physical property of the gases appear promising. The method of detection by ultraviolet absorption seems most promising to fulfill the requirements of short response time, portability, and high sensitivity to H<sub>2</sub>S, D<sub>2</sub>S, or SO<sub>2</sub>. Developmental work in the ultraviolet absorption method is being carried out at the Engineering Research Laboratory by the Applied Physics Section.





## DISCUSSION OF METHODS

### 1. Colorimetric

There are several extremely sensitive indicators for  $H_2S$ , the most common being lead acetate; the simplest device for detection of  $H_2S$  or  $D_2S$  operates on this principle. It is manufactured by the Mine Safety Appliances Company and consists of a tube of sensitized granules and a small aspirator bulb. When a known volume of air is aspirated through the tube, the length in which discoloration occurs depends on the  $H_2S$  concentration. A reading is obtained in a few seconds, and the minimum detectable concentration is 1-2 ppm. A serious disadvantage is the necessity of replacing the tubes after each determination. An obvious modification is the photometric measurement of the transmittance or reflectance of an impregnated tape or fiber.

The colorimetric method is excellent for simplicity, speed, and sensitivity to  $H_2S$  or  $D_2S$ . However, it is not applicable to the detection of  $SO_2$ .

### 2. Titration

The Consolidated Titrilog Analyzer is a titration apparatus which is extremely sensitive to  $H_2S$ ,  $D_2S$ , or  $SO_2$ ; it can detect concentrations below 1 ppm. A recent modification of the equipment (Model 26-103) is semiportable, and consists of three units, the largest of which weighs 50 pounds. Normally 110 v A.C. power is required, but a portable generator might be used. Unfortunately, the apparatus requires about 15 minutes for a spot analysis, making it unsatisfactory for leak detecting.

The M.S.A. "SO<sub>2</sub> Impinger" is another titration device which is sensitive to less than 5 ppm of  $SO_2$ . It weighs about 12 pounds. A disadvantage is the photosensitivity of the iodine starch solution used in the titration. It requires about 30 seconds for a determination.

The titration method is applicable for detecting  $H_2S$ ,  $D_2S$ , or  $SO_2$ , but has the disadvantage of a slow response time.

### 3. Ultraviolet Absorption

A portable instrument utilizing the principle of ultraviolet absorption has been constructed for detection of Hg vapor and organic vapors which have strong absorption around 2537 A (1).



For the detection of Hg vapor the device is sensitive to a few ppm. The method should be adaptable to SO<sub>2</sub> which has strong absorption bands around 3000 A (2). For detection of H<sub>2</sub>S, developmental work in the vacuum ultraviolet (below 2000 A) is being carried out at the Engineering Research Laboratory by the Applied Physics section (3). Their results indicate that a portable instrument of the required sensitivity can likely be built. However, before undertaking the construction of a prototype analyzer, they anticipate a research program of some 12 months.

Detection by the measurement of ultraviolet absorption promises to fulfill best the requirements of short response time, portability, and high sensitivity to H<sub>2</sub>S, D<sub>2</sub>S, or SO<sub>2</sub>.

#### 4. Infrared Absorption

In theory all heteroatomic gases are amenable to measurement by infrared analyzers. These analyzers fall into two classes: the positive-filter and the negative-filter types. A brief description of their operation is given in Appendix II. Of the two types, the positive-filter analyzer appears to be inherently more sensitive. (4) Models of this type are available from the Mine Safety Appliances Company and Liston-Becker Instrument Company in this country and from Sir Howard Grubb Parsons and Company and the Infrared Development Co. Ltd. in England. Manufacturers of the negative-filter analyzer include Leeds and Northrup, and Baird Associates, Inc.

Unfortunately, the infrared absorption method is not well suited for the detection of H<sub>2</sub>S which is a very weak absorber of radiation. An extremely long absorption path would be required to achieve the required sensitivity with the usual detecting system. Even with multiple reflection techniques no compact instrument seems possible. (See Appendix III) An alternative method of increasing sensitivity might utilize the principle of the pneumatic detector developed by Golay. (5)

Another disadvantage of this method is the fact that the strongest absorption bands of both H<sub>2</sub>S and SO<sub>2</sub> lie in the spectral region beyond 7μ where it is necessary to use window materials such as NaCl or CaF<sub>2</sub> and such sources as a Nernst glower or globar. These require 50 to 200 watts so that a high-capacity battery would be required. In addition, a light-chopper, rectifier, and amplifier system would probably be necessary, so that a portable instrument would be impossible.

Although the method of infrared absorption is technically feasible for the rapid sensitive detection of H<sub>2</sub>S, D<sub>2</sub>S, or SO<sub>2</sub>, much developmental work would be required for even a semiportable device.





## 5. Mass Spectrometer

### a. Magnetic Analyzer

The Consolidated Leak Detector utilizes a permanent magnet and analyzer tube for detecting helium. A sensitivity to 5 ppm is claimed. By using the Diatron 20 analyzer tube, it is adaptable to the detection of heavier ions, resolving those up to mass 40 which differ by 2 mass units. Somewhat lower sensitivity is obtained with heavier ions. The principle masses encountered would be at 16, 18, 32, 34, 36, 44, and 64 mass units, due to  $O^{++}$ ,  $H_2O^+$ ,  $O_2^+$ ,  $H_2S^+$ ,  $D_2S^+$ ,  $CO_2^+$ , and  $SO_2^+$  ions, respectively. Hence, this instrument should be applicable for rapid detection of  $H_2S$ ,  $D_2S$ , and  $SO_2$ . However, the requirement of a high vacuum system precludes the use of this method in a portable instrument. The Consolidated model weighs 470 pounds and is 42" x 25" x 22".

### b. Time-of-flight Analyzer

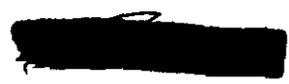
No magnet is required for mass analysis with the Bennett rf spectrometer tube (6). A light and compact adaptation for rocket installation has been recently described (7). This should also be adaptable to rapid analysis of  $H_2S$ ,  $D_2S$ , or  $SO_2$ . Again, however, a high vacuum system would be necessary, making this a semiportable instrument at best.

## 6. Thermal Conductivity

A simple low-cost method of analysis for many applications is by measurement of thermal conductivity. Units for this purpose are available from the Gow-Mac Instrument Company. The method is especially useful for analysis of  $H_2$ ; this is apparent from its high conductivity coefficient shown in Table I (8). For the commercial models, the highest sensitivity (for  $H_2$  in  $O_2$ ) is about 20 ppm with a minimum time response of 30 seconds. Hence it appears that the method would be very insensitive to  $H_2S$ . Another serious limitation is that the method is not specific for any one gas: an  $H_2S$  detector would be sensitive to  $CO_2$  as well.

## 7. Microwave Absorption

Resonance absorption at microwave frequencies due to molecular rotational transitions should be a sensitive method of detection. Rather elaborate instrumentation is required for studies in this region of the spectrum, so that the method has as yet very restricted use as an analytical tool. An additional





restriction is that many molecules do not absorb radiation strongly in the accessible spectral region. This is true for  $H_2S$  (10), whose strongest absorption lines are predicted to lie at wave-lengths below 2 mm. (11). Sulfur dioxide, on the other hand, has five absorption lines which have been mapped (12). It appears that several years of developmental work would be required to use this method.

#### 8. Ionization Potential

Hydrogen sulfide is unique in that its first ionization potential is lower than that of  $O_2$ ,  $H_2$ ,  $H_2O$ , or  $CO_2$ . (See Table II) This property might be utilized to construct a detecting instrument. Unfortunately  $SO_2$  occupies an intermediate position, so that some additional analyzer such as a mass spectrometer would be necessary for the desired selectivity.

#### 9. Combustion

The heat released by the burning of  $H_2S$  to form  $H_2O$  and  $SO_2$  might be measured to give a quantitative indication of  $H_2S$ . At  $18^\circ C$ , a one liter volume of air containing 10 ppm of  $H_2S$  would release about 0.05 calories. This would be difficult to measure with portable apparatus. In addition, the method is not applicable to the detection of  $SO_2$ .

#### 10. Electrolytic Conductivity

The Davis Instrument Company manufactures apparatus which catalytically oxidizes  $H_2S$  to  $SO_2$  and measures changes in the conductivity of an aqueous solution of the  $SO_2$ . The sensitivity and response time are reported to be comparable to those of the Consolidated Titrilog. The Thomas Autometer operates on the same principle; it is manufactured by the Leeds and Northrup Company.

This method can be utilized in an analyzer which has high sensitivity to either  $H_2S$  or  $SO_2$ . However, the response time and the size of the required components are not well-suited for a portable, high-speed detector.

#### CONCLUSIONS

No completely portable instrument is available having the required speed and sensitivity to both  $H_2S$  and  $SO_2$ . The purpose of this study was to explore and evaluate methods which might be





utilized for construction of such a device.

Table III summarizes several methods, both those which are now used and those which seem most promising for development of a portable detector. For immediate application, the use of the Consolidated Titrilog appears preferable because of its high sensitivity to  $H_2S$ ,  $D_2S$ , or  $SO_2$ ; however, its use requires about 15 minutes for a spot analysis. For future development, an ultraviolet analyzer offers most promise for rapid, sensitive detection.

T. F. Parkinson  
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Instrument Development Section

John Wilson

APPENDIX I

TABLE I

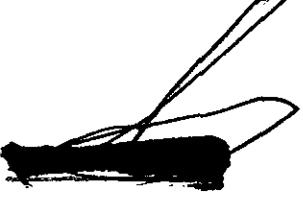
<u>Gas</u>	<u>Thermal Conductivity at 0°C</u> <u>(10<sup>-5</sup> cal sec<sup>-1</sup> cm<sup>-2</sup> °C<sup>-1</sup>)</u>
Air	5.83
CO <sub>2</sub>	3.52
N <sub>2</sub>	5.81
H <sub>2</sub>	41.6
O <sub>2</sub>	5.89
H <sub>2</sub> S	3.14
SO <sub>2</sub>	2.04

TABLE II (9)

<u>Gas</u>	<u>Ionization Potential (ev)</u>
H <sub>2</sub> S	10.42
O <sub>2</sub>	12.5
H <sub>2</sub> O	12.56
SO <sub>2</sub>	13.1
CO <sub>2</sub>	14.4
N <sub>2</sub>	15.51

TABLE III

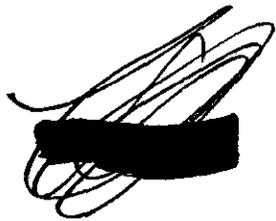
Method	Time for Procurement	Weight	Response time	Min. detectable conc.		Remarks
				H <sub>2</sub> S ppm	SO <sub>2</sub> ppm	
Colorimetric-visual (MSA Aspirator)	Immediate	<1 lb.	<10 sec.	1-2	-	One-shot indicator
Titration (Consol. Titrilog)	"	<100 lb.	15 min. for spot test	<1	<1	
(SO <sub>2</sub> Impinger)	"	<20 lb.	<1 min.	-	2	Photosensitive titration soln.
Mass Analysis (Consol. Leak Detector)	"	470 lb.	<1 min.	~10	~10	Detects 5 ppm He; somewhat less sensitive to heavier ions.
Electrolytic Conductivity	"	~100 lb.	<1 min.	<10	<10	
Colorimetric-Photometric	3 mo.	~20 lb.	<10 sec.	<10	-	
Ultraviolet Absorption	6-12 mo.	<50 lb.	<10 sec.	~10	~10	
Infrared Absorption	12-24 mo.	~100 lb.	<10 sec.	~10	~10	Would require multiple reflection cell and development of more sensitive detector.



APPENDIX II

Operation of Infrared Gas Analyzers

In the positive-filter analyzer, a beam of radiation passes through a sample cell filled with the unknown gas mixture and the absorbed energy is measured. This is accomplished by comparing the transmitted energy to that of a reference beam. The detector consists of a pair of cells filled with the appropriate component of the mixture, e.g.  $H_2S$ , the two cells being separated by a thin diaphragm. An energy differential in the two beams is thus converted into a pressure differential which is indicated by the movement of the diaphragm. In the negative-filter analyzer, all the radiation of wave-lengths absorbed by the component to be analyzed is removed from one beam. Then this beam and a reference beam are passed through the sample cell containing the unknown mixture. The energy differential is then measured by a bolometer or thermocouple. Excellent selectivity for either type of analyzer can be achieved by the use of filter cells.



APPENDIX III

Cell Length For H<sub>2</sub>S Detection

The performance of most commercial detectors is given for CO<sub>2</sub> but not for H<sub>2</sub>S. Knowing the minimum detectable concentration of CO<sub>2</sub>, the cell length used, and the absorption coefficients of CO<sub>2</sub> and H<sub>2</sub>S, it is possible to estimate the cell length required to measure the same concentration of H<sub>2</sub>S.

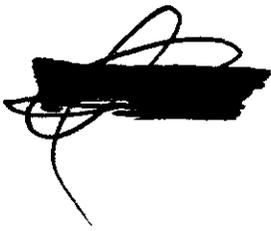
From the Lambert-Beer's law, the per cent absorption is as follows:

$$\% \text{ Abs.} = 100 \left( 1 - \frac{I}{I_0} \right) = 100 (1 - e^{-kcl}) \approx 100 kcl,$$

where I and I<sub>0</sub> are the transmitted and incident intensities, respectively, k is the absorption coefficient at a given wavelength, c is the concentration, and l is the path length. The approximation is valid for small absorptions. Available analyzers are said to be able to detect about 2 ppm of CO<sub>2</sub> with 20 cm cells. To give the same absorption for 2 ppm of H<sub>2</sub>S, a cell length of 20 cm  $\left( \frac{k_1}{k_2} \right)$  is required, where k<sub>1</sub> and k<sub>2</sub> refer to CO<sub>2</sub> and H<sub>2</sub>S,

respectively. Evaluating these for the strongest absorption bands of the two gases (13) (14) gives a length of about 300 m for 2 ppm of H<sub>2</sub>S, or about 60 m for 10 ppm.





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