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Chemistry

AEC Research and Development Report

THE IODIMETRIC DETERMINATION OF HYDROGEN SULFIDE IN GAS SAMPLES

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Analytical Chemisty Division

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ABSTRACT

An iodimetric method was developed for the determination of hydrogen sulfide in gas mixtures. The maximum standard deviation of the method was 0.2 per cent in the range from 2 to 100 per cent hydrogen sulfide.

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INTRODUCTION

An accurate and rapid method was required for determining hydrogen sulfide in gas mixtures which contained from 40 to 99 per cent hydrogen sulfide, the principal impurities being carbon dioxide, oxygen, and nitrogen. All samples were water saturated and were contained in steel cylinders at 20 atmospheres pressure.

Four possible approaches were considered: (a) a photometric method(1) in which hydrogen sulfide is absorbed in zinc acetate solution and treated with dimethyl p-phenylenediamine and ferric alum to produce methylene blue; (b) a turbidimetric method(2) in which the sulfide is oxidized to sulfate and barium sulfate is precipitated in glycerol; (c) a gravimetric method(3) in which the sulfide is oxidized and contacted with silver gauze to form silver sulfate; and (d) an iodimetric method(4) in which the hydrogen sulfide is titrated with iodine.

The last method, modified for gaseous samples, was selected for development.

SUMMARY

A method was developed for the determination of hydrogen sulfide in gas samples. The maximum standard deviation was 0.2 per cent in the range from 2 to 100 per cent hydrogen sulfide.

A vessel was designed to permit the titration of a measured amount of gas sample. Since samples were contained in steel cylinders at 20 atmospheres pressure, a low-pressure manifold was used for filling the evacuated titration vessel. Excess iodine was added to the vessel containing the sample, and the excess was determined by titration with sodium thiosulfate. The time required for a single analysis was fifteen minutes.

To insure the decomposition of any solid or liquid hydrogen sulfide hydrate, the cylinder was warmed to 40°C before delivery of gas to the titration vessel.

DISCUSSION

The iodimetric method for hydrogen sulfide determination usually involves the precipitation of cadmium sulfide, dissolution of the precipitate in dilute acid, and titration of the hydrogen sulfide with standard iodine. In the method described here, the precipitation step was eliminated and the gaseous sample was titrated directly.

APPARATUS

A manifold, Figure 1, was provided for filling the titration vessel. This manifold consisted of two mercury bubblers connected by a three-way stopcock. In one position, the stopcock allowed complete flushing of the manifold with sample gas. When the stopcock was rotated 180 degrees, the sample gas flowed into the evacuated titration vessel, Figure 2. A pair of grooves that were cut into the plug of the stopcock near the capillary leading to the titration vessel allowed a closer control of the flow from the manifold into the vessel.

Representative sampling would have been impossible in the presence of hydrogen sulfide hydrate which exists at room temperature under 20 atmospheres pressure. A phase diagram of the hydrogen sulfide - water system is shown in Figure 3(5). The presence of hydrate was eliminated by maintaining the sample cylinder in a water bath at 40°C.

The remainder of the apparatus included a 150-ml gas titration vessel, Figure 2, an open-end manometer, and a vacuum pump. The titration vessel was maintained in a water bath at 25°C. The manometer by which the pressure was measured also served as a safety valve to prevent the pressure inside the vessel from exceeding one atmosphere.

Tygon tubing was used because it is less reactive to hydrogen sulfide than is rubber tubing.

PROCEDURE

The sample cylinder is placed in the 40°C water bath for 30 minutes prior to sampling. With the stopcock in the position for flushing, the cylinder valve is opened and the manifold is flushed for five minutes. Meanwhile, the cell is evacuated and the height of mercury in the manometer is recorded. The three-way stopcock is then rotated to allow the gas sample to flow slowly into the titration vessel with an excess flow from the sample cylinder continuously discharging from the first bubbler. After the vessel is filled to a pressure of about 600 mm Hg absolute, the flow is stopped and the new mercury level is recorded. The vessel is filled to slightly less than atmospheric pressure to permit the reagents to flow without venting. The vessel is removed from the apparatus and a measured volume of standard 0.1N iodine, in excess of that required to react with the hydrogen sulfide, is added directly from a burette. As the reaction proceeds, the pressure inside the vessel decreases and several 1M hydrochloric acid funnel rinses are drawn into the vessel. The reaction is rapid and complete; however, thorough shaking is necessary to bring the liquid and gas into good contact. Starch indicator is then added and the excess iodine is titrated with sodium thiosulfate.

The volume of sample at STP is calculated from the observed temperature and pressure and the calibrated volume of the vessel. The volume of hydrogen sulfide at STP is calculated from the equivalents of iodine consumed in the reaction. The ratio of these volumes is the mol fraction of hydrogen sulfide.

Colloidal sulfur that is formed on the walls of the titration vessel may be removed by soaking in a 25 per cent sodium sulfide solution for two hours at 35°C.

RESULTS

The results from the analysis of five samples are given in the following table. Cylinder 1 contained Matheson hydrogen sulfide specified to be 99.9 per cent pure. Cylinders 2, 3, 4, and 5 contained plant samples.

HYDROGEN SULFIDE ANALYSES

	Cylinder 1	Cylinder 2	Cylinder 3	Cylinder 4	Cylinder 5
	99.5%	96.4%	97.1%	22.6%	1.5%
	100.1	96.5	97.1	22.6	1.9
	99.8	96.7	97.1	22.5	
	99.6	96.3	97.4	22.8	
		96.5	97.1		
Average	99.8%	96.5%	97.2%	22.6%	1.7%
Absolute Standard Deviation	0.3%	0.1%	0.1%	0.1%	0.3%

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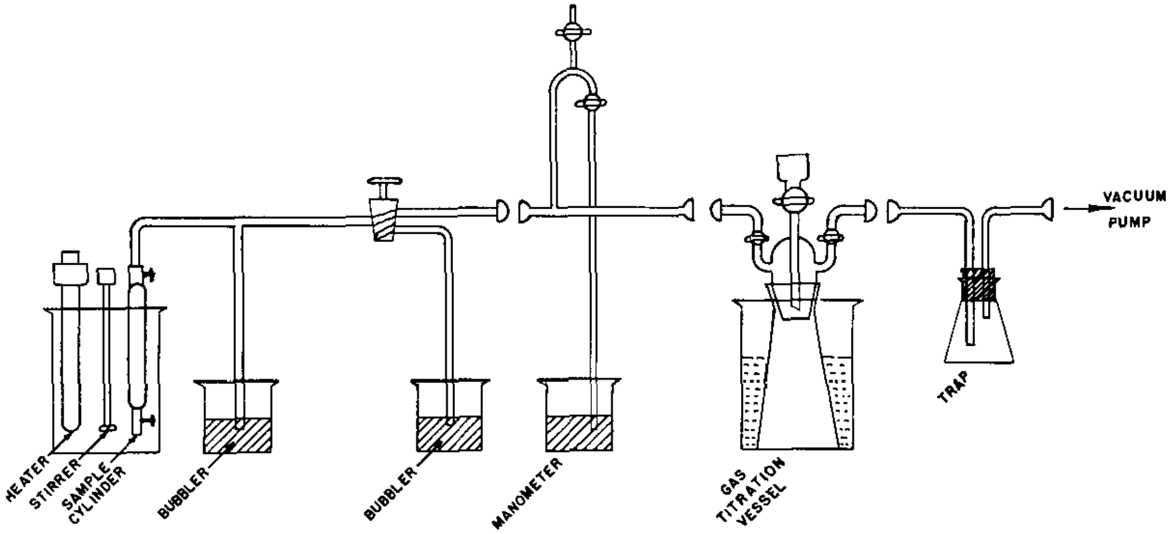
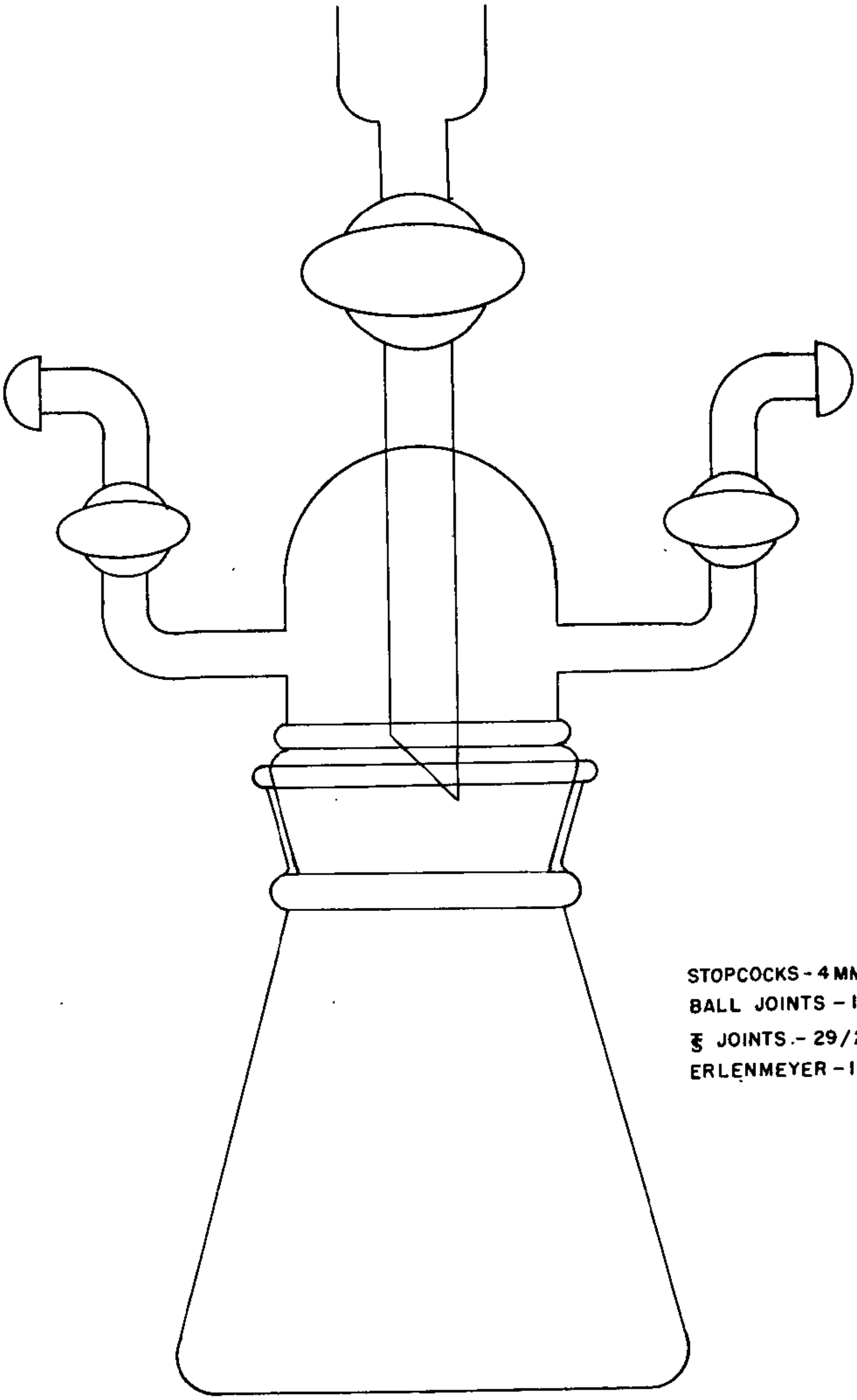
FIGURE 1



APPARATUS FOR ANALYSIS OF HYDROGEN SULFIDE

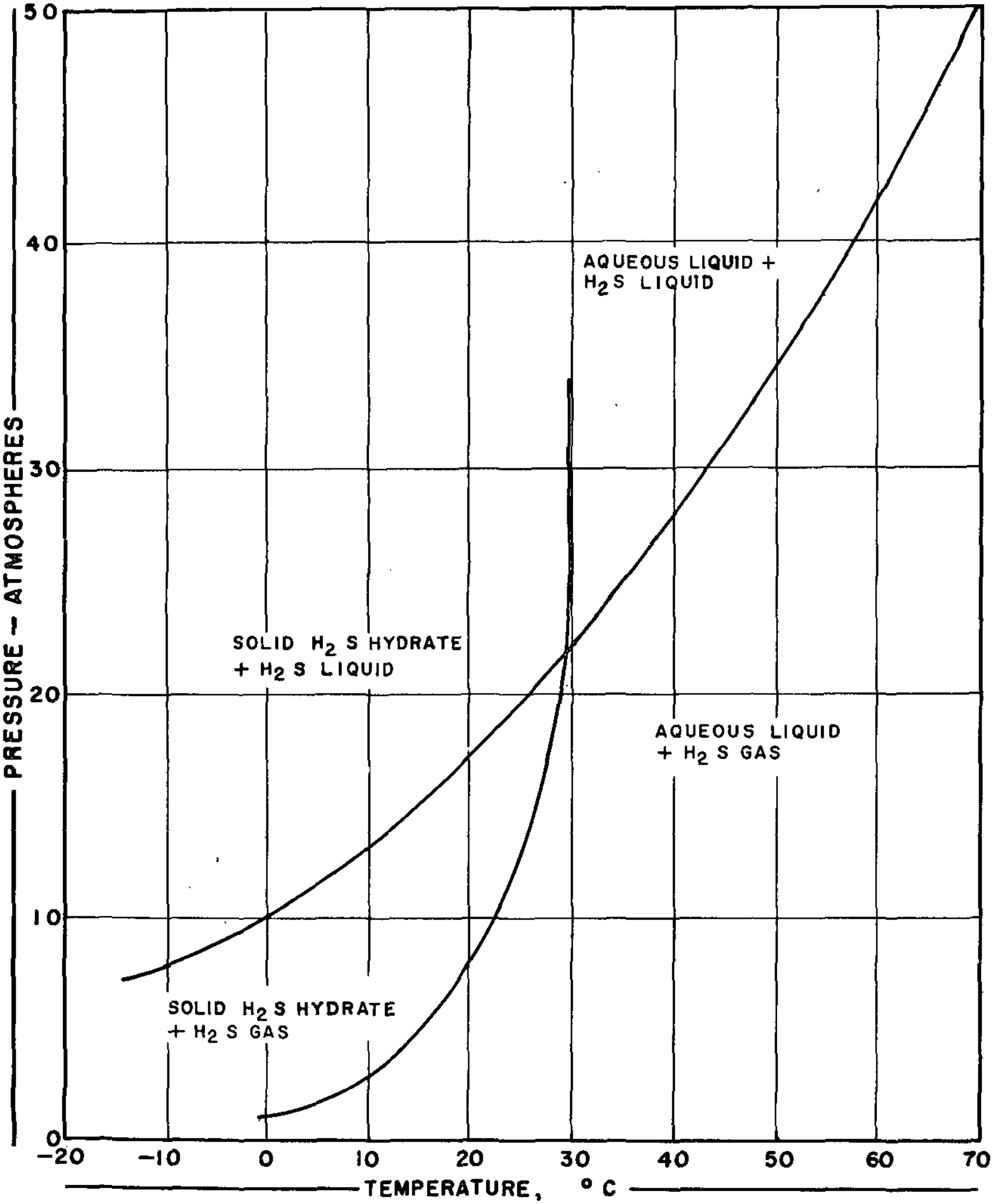
FIGURE 2



STOPCOCKS - 4 MM BORE
BALL JOINTS - 12/5
₮ JOINTS - 29/26
ERLENMEYER - 150 ML

GAS TITRATION VESSEL

FIGURE 3



PRESSURE– TEMPERATURE DIAGRAM $H_2S + H_2O$