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GAS CHROMATOGRAPHIC DETERMINATION OF HYDROGEN SULPHIDE IN ANOXIC WATERS*

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SUMMARY

A gas chromatographic method has been studied for the determination of hydrogen sulphide in anoxic waters. To suppress the escape and the oxidation of hydrogen sulphide in the water sample, either acetone or ethanol was mixed with the sample, and a small amount of hydroxylamine hydrochloride was added. The hydrogen sulphide in this solution was determined by gas chromatography.

The proposed method is easy to perform and determination is possible for several days after the sampling. The limit of detection was about 0.1 ppm, the average of coefficients of detection was 9.2%.

INTRODUCTION

When the dissolved oxygen in natural waters is used up in summer and anoxic waters are formed, hydrogen sulphide occurs as a respiration product of sulphide reduction in the sediment and is eluted into the anoxic waters. The observation of the hydrogen sulphide content gives geochemically important information.

Hydrogen sulphide at low concentrations in natural waters has been determined spectrophotometrically by the methylene blue method since its introduction by Fischer[1], and Fonselius[2] used it for the determination of hydrogen sulphide in seawater. Recently, the diamine method, with which the colour is more sensitive and stable, was developed by Cline[3].

However, since hydrogen sulphide is easily oxidised to sulphur by oxygen in the air, analysis by the above method has to be performed within about an hour of sampling. Therefore, the determination is difficult if it takes a long time to take the

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water sample from the sampling station to the analytical apparatus. Moreover, there is a danger that hydrogen sulphide in a water sample from a great depth will escape because of a change in pressure.

To solve the problems described above, the present authors tried adding reducing agents to the organic solvents in which hydrogen sulphide is more soluble and stable than in water, and taking the water sample with a syringe containing these solvents. The determination was carried out by means of gas chromatography (GC) whose procedure is simpler than the usual spectrophotometrical method used.

Various reports of GC analysis of hydrogen sulphide in gas samples have appeared. Recently, Latif *et al.*[4] described an improved method for the determination of hydrogen sulphide using porous polymers as a column packing with direct injection of a gas sample into the gas chromatograph.

The present work deals with the stabilization of hydrogen sulphide and GC analysis in the case of direct injection of sample solution.

EXPERIMENTAL

Apparatus

Measurement was made by means of a Shimadzu Model 7A gas chromatograph equipped with a flame photometric detector connecting a Shimadzu Model C-R2A Chromatopac and a Hitachi Model 100-50 double-beam spectrophotometer with a 1-cm glass cell.

Reagents and standards

Mixed diamine reagent. 1.0 g of N,N-dimethyl-*p*-phenylenediamine sulphate and 1.5 g of ferric chloride ($FeCl_3 \cdot 6H_2O$) were dissolved in 250 ml of cool 50% (v/v) reagent-grade hydrochloric acid. This reagent is stable for several months, if kept in a dark bottle under refrigeration.

Standard sodium sulphide solution. Nitrogen is bubbled through 1 l of distilled water in a narrow-mouthed brown bottle for about 20 min to prepare oxygen-free water. Shielded from the air by a stream of nitrogen gas, about 5 mg-atoms of sodium sulphide ($Na_2S \cdot 9H_2O$), accurately weighed, were added to the water, and the bottle was sealed tightly.

Standard hydrogen sulphide solution. A syringe was used to extract 10 ml of hydrogen sulphide at room temperature from a cylinder through a rubber tube attached to the mouth of a reducing valve. This syringe was connected by means of a vinyl tube to another containing 10 ml of acetone and all the acetone was transferred into the syringe containing hydrogen sulphide. After removal of bubbles, the hydrogen sulphide–acetone solution was transferred to a small brown bottle with a pouring lip, sealed tightly and kept under an aluminium foil cover. Similarly, hydrogen sulphide–ethanol and hydrogen sulphide–water solutions were prepared.

Water sample

A sample of water was taken on the ocean bed in Lake Hamana in Japan. This water is brackish.

Standardization

Standard sodium sulphide solutions (0.1, 0.2, 0.3, ... ml) were added to several measuring flasks (volume: 50 ml) to which 40 ml of distilled water and 4 ml of mixed diamine reagent were added. The solutions were shaken and diluted to the mark with water. After 20 min the absorbance was measured spectrophotometrically at 670 nm. A calibration curve of sodium sulphide was prepared by plotting absorbances against the concentration sodium sulphide.

The absorbance of standard hydrogen sulphide solution was measured as described above. The concentration (ppm as S) was calculated from the calibration curve of sodium sulphide.

Procedure

An adequate amount of organic solvent was taken into a syringe (volume: 10 ml), and bubbles were removed. This syringe was now used to extract a water sample through a rubber tube from the water bottle. Some of the mixed solution was transferred to a small brown plastic bottle equipped with a pouring lip (volume: 7 ml). When it was full, it was sealed tightly and kept under an aluminium foil cover.

A 2-μl volume of the solution was analysed by GC and the concentration of hydrogen sulphide was calculated from the calibration curves of hydrogen sulphide by GC. The conditions for the GC analysis are shown in Table I.

TABLE I

ANALYTICAL CONDITIONS FOR THE DETERMINATION OF HYDROGEN SULPHIDE BY GC

Column temperature	110°C
Injection temperature	150°C
H_2 pressure	0.75 kg/cm^2
Air pressure	1.30 kg/cm^2
Carrier gas	Nitrogen, 90 ml/min
Injection volume	2 μl
Glass column	1.1 m × 3.2 mm I.D.
Packing material	Porapak N (50–80 mesh)

RESULTS AND DISCUSSION

Packing materials of GC

Porous polymer beads have been used as a column-packing material in GC for the analysis of hydrogen sulphide[5,6]. Since the present sample used for GC analysis contains an appreciable quantity of water, two types of Porapak (50–80 mesh, Waters Assoc.) which are made of porous polymer beads and are suitable for direct injection of the aqueous solution were examined as packing materials on the basis of the above reports.

The results are shown in Fig. 1. Using Porapak Q, it was impossible to measure peak height accurately because the peak of hydrogen sulphide and the quenching by water overlapped. Porapak N was therefore used in subsequent experiments.

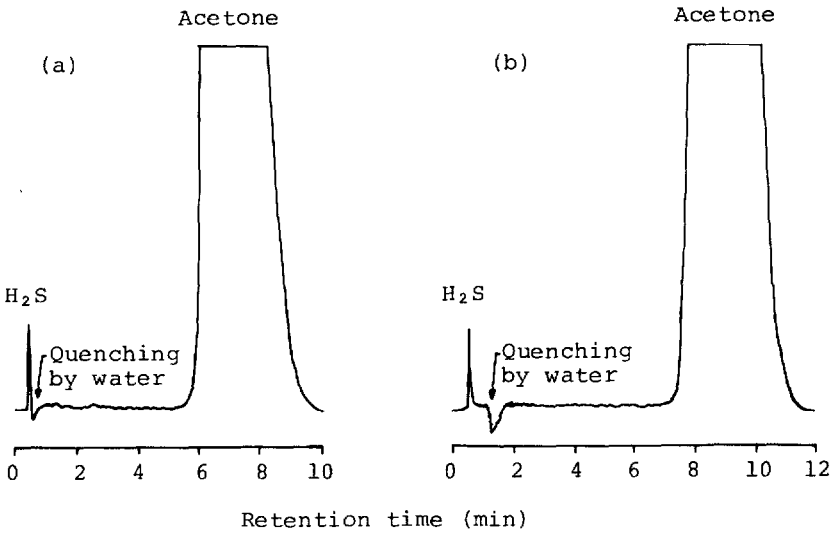

Fig. 1. Gas chromatograms of hydrogen sulphide in acetone–water (1:1) using (a) Porapak Q and (b) Porapak N.

Stabilizers

Various reducing agents and a chelating agent were added to the solutions to stabilize hydrogen sulphide, and its stability was examined. The residual hydrogen sulphide concentration after any arbitrary interval expressed as a percentage of its initial concentration was taken as a measure of stability. Each solution was poured into a brown plastic bottle, sealed tightly and kept under an aluminium foil cover. Table II shows that, after a day, the residual hydrogen sulphide is approximately 80% when the reagents investigated, except hydroquinone, are added.

The stability of hydrogen sulphide in distilled water and lake water was examined, using various concentrations of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) which gave the best stability in the above preliminary experiments. As shown in Table III, when the $NH_2OH \cdot HCl$ concentration was above 0.1 g/l in distilled water and above 0.5 g/l in lake water, the residual hydrogen sulphide after a day is nearly

TABLE II

EFFECT OF DIFFERENT STABILIZERS IN ACETONE–DISTILLED WATER (7:3)

Initial H_2S concn.: 1.0 ppm, stabilizer: 2.0 g/l.

Stabilizer	*Residual H_2S after a day (%)*
L-Ascorbic acid	78.0
Hydroxylamine hydrochloride	88.5
Hydrazine sulfate	85.4
Hydroquinone	17.1
EDTA	85.7
Nothing added (in acetone)	97.4
Nothing added (in acetone–distilled water (7:3))	73.0

TABLE III

DEPENDENCE OF STABILITY OF HYDROGEN SULPHIDE IN VARIOUS SOLUTIONS ON HYDROXYLAMINE HYDROCHLORIDE CONCENTRATION

Initial H_2S concn.: 1.0 ppm.

Solvent	*$NH_2OH \cdot HCl$ concn. added (g/l)*	*Residual H_2S after a day (%)*	
		Distilled water	*Lake water*
Acetone–water (7:3)	0	73.0	34.7
	0.1	88.4	50.4
	0.5	90.2	80.5
	1.0	91.4	86.1
	2.0	84.0	78.0
Ethanol–water (7:3)	0	75.1	35.7
	0.1	91.2	47.6
	0.5	87.0	87.6
	1.0	91.9	92.2
	2.0	88.5	85.0

constant, about 80–90%. For the following analysis, therefore, a concentration of 1.0 g/l was used.

The results in Fig. 2 show how the hydrogen sulphide concentration in both distilled water and lake water decreased with time. The relationship between time and the logarithm of residual hydrogen sulphide was linear, which suggests that the hydrogen sulphide decrease was a first-order reaction. Without $NH_2OH \cdot HCl$, the

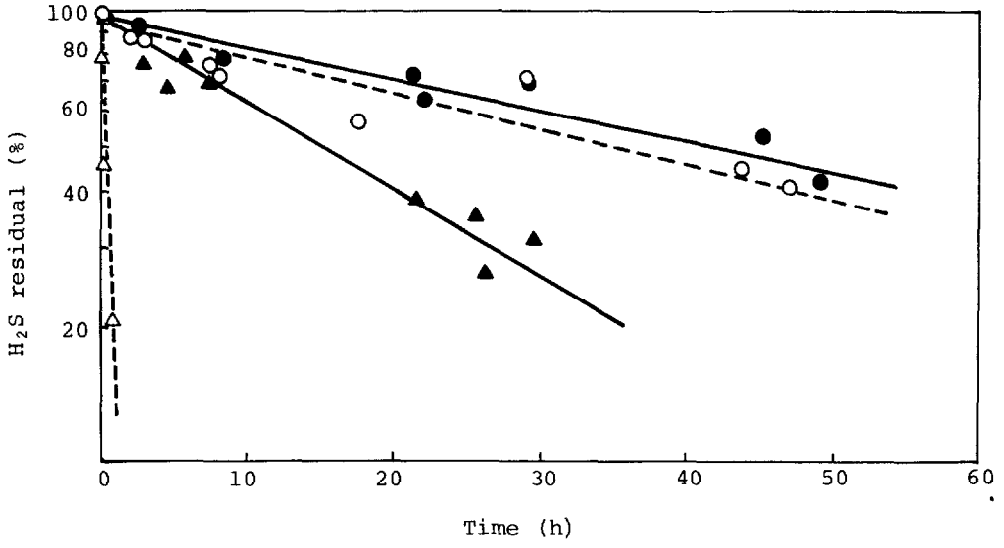

Fig. 2. Residual hydrogen sulphide in water. ▲—▲ = Distilled water; ●—● = distilled water + $NH_2OH \cdot HCl$ 1.0 g/l; △---△ = lake water; ○---○ = lake water + $NH_2OH \cdot HCl$ 1.0 g/l, initial H_2S concn.: 1.0 ppm.

TABLE IV

STABILITY OF HYDROGEN SULPHIDE IN VARIOUS SOLVENTS

Initial H_2S concn.: 1.0 ppm.

Organic solvent	*Retention time (min)*	*Residual H_2S after a day (%)*	
		Organic solvent	*Organic solvent distilled water (7:3) + $NH_2OH \cdot HCl$ 1.0 g/l*
Methanol	2.1	79.4	87.5
Ethanol	5.0	84.8	91.6
Methyl formate	3.1	84.8	87.6
Acetone	8.9	97.4	89.3

hydrogen sulphide concentration in lake water decreased much more rapidly than in distilled water. The reason may be that various metals in lake water catalyse the oxidation of hydrogen sulphide. Adding $NH_2OH \cdot HCl$ to a concentration of 1.0 g/l resulted in increased, approximately, equal values for the residual hydrogen sulphide in distilled water and lake water.

Solvent

The influence of the solvent on the stability of hydrogen sulphide was investigated. Its stability in organic solvents whose retention times for GC are relatively short is given in Table IV. In the absence of a reducing agent, the stability in the pure organic solvents was higher than in distilled water, acetone producing the highest value. When $NH_2OH \cdot HCl$ was added to organic solvent–distilled water (7:3) solutions, the residual hydrogen sulphide values after a day of all the organic solvents

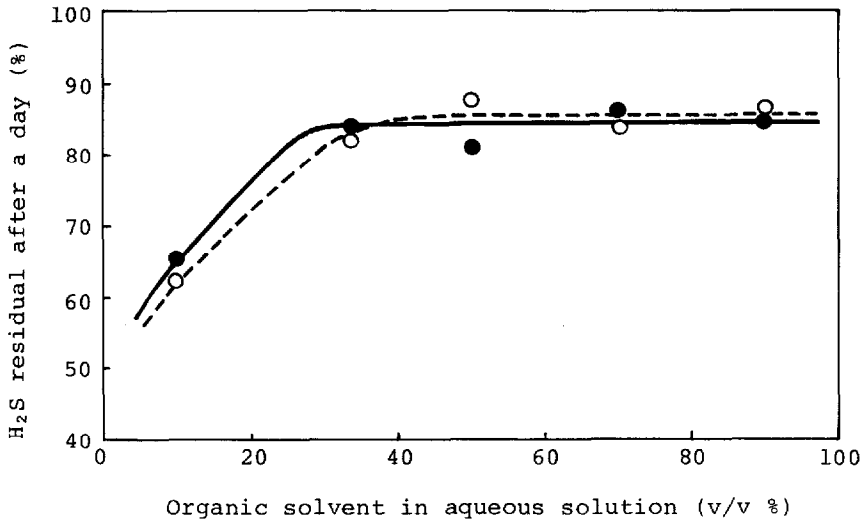

Fig. 3. Dependence of stability of hydrogen sulphide on organic solvent–lake water ratio. ●—● = Acetone; ○---○ = ethanol, initial H_2S concn.: 1.0 ppm, $NH_2OH \cdot HCl$: 1.0 g/l.

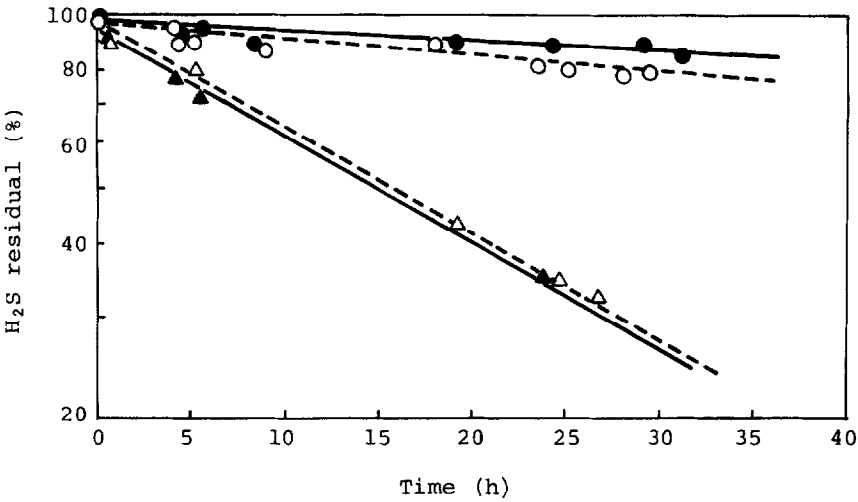

Fig. 4. Residual hydrogen sulfide in organic solvent–lake water (7:3) solutions. ▲—▲ = Ethanol–lake water (7:3); ●—● = ethanol–lake water (7:3) + $NH_2OH \cdot HCl$ 1.0 g/l; △---△ = acetone–lake water (7:3); ○---○ = acetone–lake water (7:3) + $NH_2OH \cdot HCl$ 1.0 g/l, initial H_2S concn.: 1.0 ppm.

were approximated equal, *ca.* 90%. Since the solubility of largely hydrogen sulphide is greater in acetone and ethanol, it was decided to use these solvents.

The dependence of the stability of hydrogen sulphide on the organic solvent–lake water ratio is shown in Fig. 3. When the organic solvent–lake water solution contained more than 40% organic solvent, a constant value of above 80% for the residual hydrogen sulphide after a day was obtained. This means that it is possible to vary the ratio between the actual sample water and organic solvent in order to produce a suitable concentration of hydrogen sulphide for this GC analysis.

Fig. 4 shows the stability in organic solvent–lake water (7:3) solutions. The hydrogen sulphide decrease was a first-order reaction as it was when only water was involved. From the slope of the straight lines in Figs. 2 and 4, the rate constants for the disappearance of hydrogen sulphide in the various solutions were calculated (Table V). The initial hydrogen sulphide concentration in the lake water can be also estimated from the time elapsed since sampling.

TABLE V

RATE CONSTANTS FOR THE DISAPPEARANCE OF HYDROGEN SULPHIDE IN VARIOUS SOLUTIONS

Solvent	*Rate constant* (sec^{-1})	
	Nothing added	*1.0 g/l of* $NH_2OH \cdot HCl$ *added*
Distilled water	$1.6 \cdot 10^{-5}$	$0.62 \cdot 10^{-5}$
Lake water	$76 \cdot 10^{-5}$	$0.63 \cdot 10^{-5}$
Acetone–lake water (7:3)	$1.7 \cdot 10^{-5}$	$0.28 \cdot 10^{-5}$
Ethanol–lake water (7:3)	$1.7 \cdot 10^{-5}$	$0.14 \cdot 10^{-5}$

TABLE VI

DEPENDENCE OF STABILITY OF HYDROGEN SULPHIDE ON INITIAL CONCENTRATION

$NH_2OH \cdot HCl$: 1.0 g/l.

Initial H_2S concentration (ppm)	*Residual H_2S after a day (%)*	
	Acetone–lake water (7:3)	*Ethanol–lake water (7:3)*
0.1	78.2	84.6
0.3	80.2	92.7
0.7	79.9	91.5
1.0	82.2	86.8
3.0	92.4	91.6
Calculated*	78.5	88.6

* These values were calculated from the rate constant in Table V.

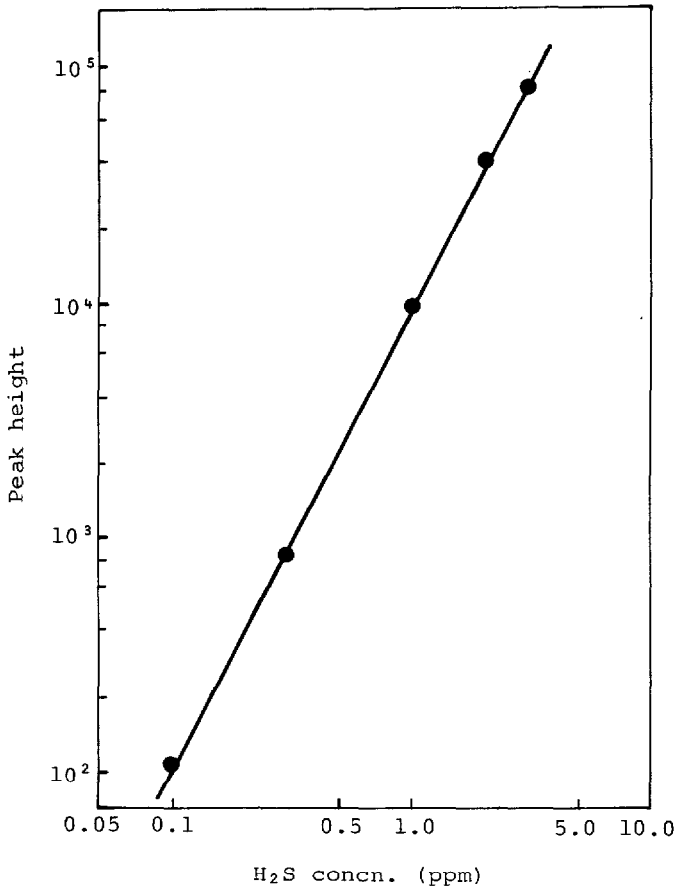

Fig. 5. Calibration curve of H_2S concentration by GC.

TABLE VII

PRECISION AND ACCURACY OF DETERMINATION OF HYDROGEN SULPHIDE IN LAKE WATER

Proposed GC method					*Spectro-photometry (ppm)*	*Difference (ppm)*
Solvent	*Sample taken (ml)*	*Number of runs*	*H_2S found (ppm)*	*Coefficient of variation* (%)*		
Acetone	4	8	0.42	9.2	0.43	−0.01
	4	9	0.93	9.7	0.95	−0.02
	2	7	2.47	8.5	2.24	+0.23
Ethanol	4	9	0.37	5.7	0.41	−0.04
	4	7	0.77	11.2	0.75	+0.02
	2	8	1.18	11.0	1.26	−0.08

* The average of coefficients of variation is 9.2%.

Whether the disappearance rate constants obtained for acetone and ethanol were applicable to the initial hydrogen sulphide concentration range 0.1–3.0 ppm was tested, as shown in Table VI. The residual values obtained were nearly constant and agreed with the calculated values from Table V at the above range.

These results also suggest that acetone and ethanol have a similar effect on the stabilization of hydrogen sulphide and either is a suitable choice as solvent.

Calibration curve

Fig. 5 shows that the logarithmic calibration curve for this GC analysis was linear with a gradient of 2 in the range 0.1–3.0 ppm. The calibration curve was virtually the same for all the solvents. The limit of detection was estimated at 0.1 ppm, since the background variation in peak height was about 30.

Precision and accuracy

The precision and accuracy of the proposed method were tested for various concentrations of hydrogen sulphide in acetone–lake water (7:3) solutions and ethanol–lake water (7:3) solutions. As can be seen from Table VII, the precision and the accuracy obtained compare well with the ordinary spectrophotometric method and were satisfactory for the required purpose.

In conclusion, the proposed method, by which the disappearance of hydrogen sulphide after sampling is suppressed, can be widely applied to the determination of hydrogen sulphide in anoxic waters, and is considered to be useful for geochemical survey.

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