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Note

Electron-capture gas chromatographic determination of sulphide as a new pentafluorobenzyl derivative

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Sulphide is a significant environmental pollutant derived partly from industrial effluents. It contaminates water supplies and results in distressing odours.

Several methods, including titrimetric[1–3], colorimetric[4], fluorimetric[5,6], ultraviolet spectrophotometric[7,8], coulometric[9] and electrode[10,11] techniques, have been used for the determination of sulphide in water. In addition, direct gas chromatography (GC) with β-ionization detection[12] has been used to analyze hydrogen sulphide in air at ppm levels. However, there is still a need for a specific and more sensitive method for quantitation of sulphide in complicated matrices.

In this paper, a new approach based on detector-oriented derivatization of sulphide, as bis(pentafluorobenzyl) sulphide, is described for quantitative analysis of inorganic sulphide (S^{2-}) down to ppb* levels. The method has been applied to the analysis of S^{2-} in spring-water. The results indicate that the method is specific and highly sensitive.

EXPERIMENTAL

GC conditions

A Yanaco (Kyoto, Japan) Model G2800EN gas chromatograph equipped with an electron-capture detector (ECD) of non-radioactive type (Kyoto, Japan) was used. The column was a coiled glass tube (3.0 m × 3 mm I.D.) packed with 3% silicone gum SE-30 on Chromosorb W AW DMCS (60–80 mesh). The injection port and detector temperatures were kept at 250°C and that of the column was isothermally set at 180°C. Helium was used as the carrier gas at a flow-rate of 30 ml/min. A Yanaco VR-101 recorder with a chart speed of 5 mm/min was used. The peak area ratios were computed by a Shimadzu (Kyoto, Japan) Chromatopac E1A digital integrator.

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* Throughout this article, the American billion (10^9) is meant.

Materials

Pentafluorobenzyl phenyl thioether, pentafluorobenzyl *n*-butyl thioether and bis(pentafluorobenzyl) sulphide (BPFBS) were synthesized at this laboratory and their structures were confirmed by mass spectrometry (MS). Pentafluorobenzyl bromide (PFBBr or α-bromo-2,3,4,5,6-pentafluorotoluene) (Aldrich, Milwaukee, WI, U.S.A.) and 3% silicone gum SE-30 on Chromosorb W AW DMCS (60–80 mesh) (Nishio, Tokyo, Japan) were used without further treatment. Sodium sulphide nonahydrate ($Na_2S \cdot 9H_2O$), toluene and other reagents were of analytical grade. Deionized and distilled water was used to prepare aqueous solutions.

Solutions of the internal standard (I.S.), 0.5 μM, and of the reference standard were separately prepared by dissolving pentafluorobenzyl phenyl thioether in toluene and a suitable amount of $Na_2S \cdot 9H_2O$ in 0.01 N sodium hydroxide (NaOH). The sample solution was prepared by dilution of an equal volume spring-water in 0.02 N NaOH solution, and further dilution in 0.01 N NaOH if necessary. The PFBBr solution, 0.4 μM, was prepared by dissolving PFBBr in acetone.

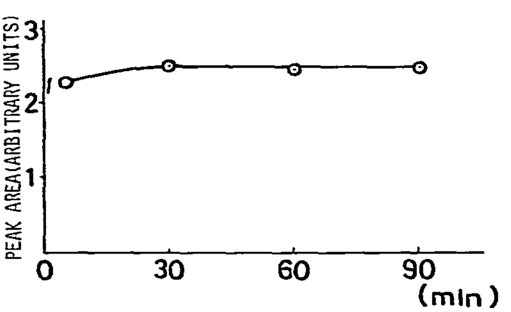
Procedure

A 0.5-ml volume of PFBBr solution was added to a 15-ml glass-stoppered flask containing 0.1 ml of the reference standard or sample solution. The reaction mixture was magnetically stirred for 1 h at room temperature and then evaporated under a nitrogen stream for 2 min at room temperature. To the concentrated solution, 1.0 ml of I.S. solution was added and mixed well, followed by a small pinch of anhydrous sodium sulphate. The GC determination was performed by injecting about 0.4 μl of the clear toluene layer.

RESULTS AND DISCUSSION

Derivatization

Alkylation of S^{2-} with PFBBr in an alkaline medium proceeds quickly at room temperature and the reaction equilibrium can be attained in 30 min as shown in Fig. 1. GC analysis could be run after this time, but the analytical data presented here were obtained after 1 h unless otherwise indicated. Derivatization of S^{2-} in neutral water instead of 0.01 N NaOH solution resulted in slower formation of the derivative, and in stronger alkali (0.06 N NaOH) a complicated reagent background is formed.



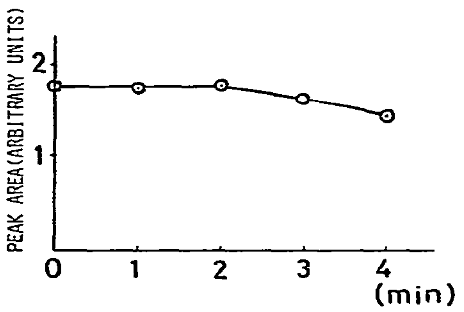


Fig. 1. Effect of reaction time on the formation of the sulphide derivative.

Fig. 2. Effect of evaporation time on loss of the sulphide derivative.

This background interferes with the analysis of the S^{2-} derivative and stems probably from the products of hydrolysis of PFBBr. Concentration of the reaction solution by evaporation under a nitrogen stream can lessen the reagent tailing in the chromatogram, but a concentration period longer than 2 min as shown in Fig. 2 results in lower analyses for the S^{2-} derivative. The same phenomenon is found in the case of evaporation of the reaction solution with a rotary evaporator under reduced pressure, and is due probably to loss of the volatile S^{2-} derivative. The I.S. is also volatile, so it was added to the reaction solution after the concentration step.

Interference

Several anions were investigated for interference with 0.3 ppm of S^{2-}, as shown in Table I. The method does not seem to suffer interference from acetate, sulphite, sulphate, chloride, carbonate, thiosulphate, cyanide, nitrate and nitrite at the levels found in environmental samples. Thus the method is quite specific for S^{2-} analysis in the presence of these anions.

Aliphatic and aromatic mercaptans, such as *n*-butanethiol and thiophenol, could also be converted into their pentafluorobenzyl derivatives[13], but the S^{2-} derivative can be well separated from these derivatives, the elution order under the present GC conditions being as follows: pentafluorobenzyl *n*-butyl thioether; pentafluorobenzyl phenyl thioether; the S^{2-} derivative. Pentafluorobenzyl phenyl thioether, which is structurally similar to BPFBS, is used as I.S. in this work. If a water sample contains thiophenol, the S^{2-} value measured will be lower than the real value. The presence of thiophenol in a sample can be corrected for by running a chromatogram without addition of I.S.

Analytical calibration

Seven samples containing the reference standard at about 0.8–65 ng of S^{2-} were analyzed to construct a calibration graph of the amount of S^{2-} against peak-area ratios of the S^{2-} derivative to I.S. A linear regression equation ($y = 0.05871\,x +$

TABLE I

INTERFERENCE STUDY

Concentration of sulphide investigated: 0.3 ppm.

Anion spiked	*Concentration spiked (ppm)*	*Recovery (%)**
None	–	100.0 ± 2.3
CH_3COO^-	100	99.1 ± 2.7
SO_3^{2-}	100	101.9 ± 2.5
SO_4^{2-}	100	101.6 ± 1.2
Cl^-	100	99.7 ± 3.4
CO_3^{2-}	100	98.0 ± 1.0
$S_2O_3^{2-}$	50	102.2 ± 2.2
CN^-	50	102.8 ± 0.6
NO_3^-	20	102.0 ± 2.3
NO_2^-	20	100.8 ± 2.4

* Mean of triplicate analyses.

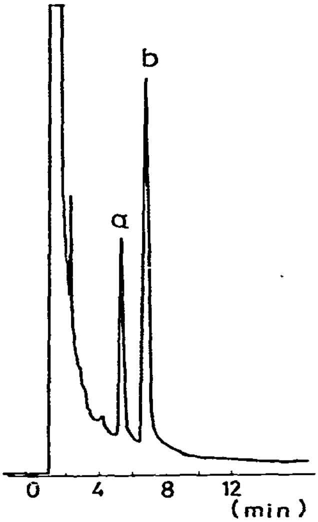


Fig. 3. Typical gas chromatogram of pentafluorobenzyl phenyl thioether (a, I.S.) and bis(pentafluorobenzyl) sulphide (b).

0.0610) was obtained with a correlation coefficient of 0.9997. This indicates high linearity over the range examined. The equation was then used to calculate the S^{2-} content in samples.

A typical chromatogram presented in Fig. 3 demonstrates the good resolution and high symmetry of the peak of the S^{2-} derivative. The retention time of peak b is identical to that of BPFBS, synthesized by scaling up the amounts of S^{2-} in 0.01 *N* NaOH and PFBBr in acetone and allowing them to react at room temperature for 1 h. The crystals obtained were examined by MS using a Hitachi RMU-6E mass spectrometer with an ionization source temperature of 200°C, an electron energy of 70 eV and an acceleration energy of 1.8 kV. The mass spectrum obtained exhibits a parent ion at $m/e = 394$, representing the formation of BPFBS, and some other peaks are tentatively assigned as in Fig. 4.

Further comparison of the retention time of peak b in Fig. 3 and that of BPFBS was carried out using a Yanaco G180 flame-ionization gas chromatograph

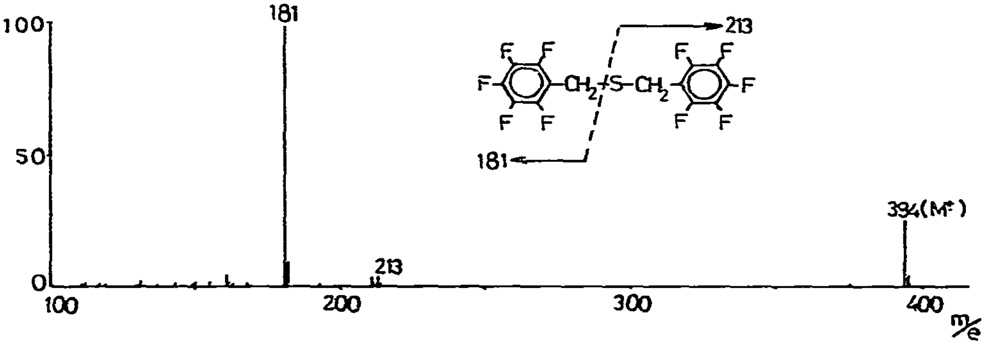


Fig. 4. Mass spectrum of bis(pentafluorobenzyl) sulphide.

TABLE II

COMPARISON OF THE ANALYSIS OF SULPHIDE CONTENT IN SPRING-WATER BY THE TWO METHODS

Sample	*GC–ECD**	*Colorimetry (ppm)*
A	2.55 ± 0.02 ppm	2.52
B	1.71 ± 0.09 ppm	1.76
C	1.04 ± 0.02 ppm	1.05
D	5.50 ± 0.17 ppb	**
E	**	**

* Average of triplicate analyses.
** Below detection limit.

with: (1) a coiled glass column (2 m × 3 mm I.D.) of 10% silicone OV-17 on Shimalite W AW DMCS (60–80 mesh), carrier gas (nitrogen) flow-rate 55 ml/min; and (2) a stainless-steel column (2 m × 3 mm I.D.) of 5% PEG-HT on Uniport HT (60–80 mesh), carrier gas (nitrogen) flow-rate 31 ml/min. In both cases the injection temperature was 275°C and the column temperature was 170°C. The results of these chromatographic separations based on stationary phases of weak and strong polarity gave the same retention times for peak b and BPFBS. Therefore, peak b in Fig. 3 can be assigned as BPFBS.

The method was applied to the analysis of S^{2-} in spring-water and the results compared to those obtained by a colorimetric method[4] based on methylene blue formation. The results in Table II reveal good agreement between the two methods, and the reliability of the proposed method. The high sensitivity of our method is reflected in the analysis of sample D. The S^{2-} content in sample E is below the detection limit of both methods, and is estimated to be less than 0.5 ppb based on the detection limit of the proposed GC–ECD method.

Possible applications of this method to other anions, such as nitrite and cyanide, using pentafluorophenyl-type reagents are being investigated.

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