Spectrophotometric Determination of Sulfide in the Presence of Sulfite and Thiosulfate *via* the Precipitation of Bismuth(III) Sulfide

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A photometric method has been developed for the determination of sulfide at 10^{-5} mol dm⁻³ levels, which is based on the reaction of sulfide with a given excess amount of bismuth(III) to form a precipitate of bismuth(III) sulfide and on the spectrophotometric measurement of the residual bismuth(III) at 335 nm after extracting with bismuthiol II reagent from an aqueous solution containing acetate buffer into benzene. The presence of sulfite and thiosulfate up to 0.002 mol dm⁻³ did not cause any interference in the determination of sulfide, because both sulfite and thiosulfate do not produce any precipitate with bismuth(III). A linear calibration plot with a negative slope was obtained for sulfide over the range of 5.00×10^{-7} – 3.00×10^{-5} mol dm⁻³ (16.0 – 960 ppb). An experimental calibration plot was in accord with the theoretical plot, taking into account the known excess of bismuth(III), showing that the reaction of sulfide with bismuth(III) proceeded to completion. The relative standard deviation of results from 10 replicate determinations of standard sulfide (2.00×10^{-5} mol dm⁻³) was 0.44%. The proposed method was successfully applied to the determination of sulfide in hot-spring water samples without any pretreatment.

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Introduction

Sulfide is susceptible to air-oxidation in an aqueous solution to form sulfite, sulfate and thiosulfate, and these sulfur anions are often found in ground and hot-spring water. Numerous analytical methods, such as titrimetric,^{1,2} amperometric,³ polarographic,^{4,5} potentiometric,^{6,7} catalytic,⁸⁻¹³ spectrophotometric¹⁴⁻²⁷ and chromatographic²⁸⁻³⁴ techniques, have been reported for the determination of sulfide in water samples. In most of these methods, the preparation of standard solutions of unstable sulfide causes difficulties. The Methylene Blue method¹⁴ has been widely used for the determination of sulfide, but suffers serious interferences from reducing agents, such as sulfite and thiosulfate, which react with *N,N* dimethyl-*p*-phenylene diamine to produce Methylene Blue. Several approaches^{17,19-25,27} have been investigated for the determination of sulfide in the presence of these interferents, such as the pre-separation of sulfide from the sample matrix by evolution as hydrogen sulfide from an acidic medium. This pre-separation technique, however, is tedious and moderately complex to perform. In view of this, there is a growing interest in a simple and selective method for the determination of sulfide, which does not suffer from interference by sulfite and thiosulfate. One approach to this is to utilize the fact that sulfide can react with bismuth(III) to form a precipitate of bismuth(III) sulfide, while both sulfite and thiosulfate ions do not react. If sulfide is added to a known excess amount of bismuth(III) and the residual

bismuth(III) measured photometrically, sulfide should be able to be determined in the presence of sulfite and thiosulfate. This approach has not been evaluated previously.

In this study, a bismuth(III) complex with bismuthiol II was found to be extractable from an aqueous solution containing acetate buffer into benzene, although this complex has previously been stated to be insoluble in benzene.³⁵ The conditions for the reaction of sulfide with bismuth(III) and a subsequent extraction of the residual bismuth(III) with bismuthiol II into benzene were studied. Compared with earlier photometric methods,^{17,19-25,27} the proposed method offers a simpler procedure for the determination of sulfide in the presence of sulfite and thiosulfate. This method has been successfully applied to the determination of sulfide in hot-spring waters, without any sample pretreatment.

Experimental

Reagents

All chemicals used were of analytical-reagent grade and were employed without further purification. Doubly distilled water was used in all experiments.

Large crystals of sodium sulfide (Na₂S·9H₂O) were washed rapidly with oxygen-free water in order to remove trace amounts of impurities from their surfaces, and then dried by the adsorption of the water with filter-paper. A sulfide solution (approximately 0.05 mol dm⁻³) was prepared by dissolving *ca.* 2.5 g of the crystals in 200 cm³ of oxygen-free water and standardized by iodimetric back-titration. Working solutions were obtained by appropriate dilution with oxygen-free water.

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The standards need to be used within 30 min of the standardization, as the concentration of sulfide decreases after this time owing to oxidation by air.

Bismuth metal was washed with a small volume of nitric acid, rinsed with water and then dried by air. The bismuth (0.4180 g) was dissolved in 1 cm³ of nitric acid with heating and the heating was continued until most of the nitric acid had evaporated. After cooling, the residue was dissolved in 32.6 cm³ of 60% perchloric acid (9.2 mol dm⁻³) and diluted to 1 dm³ with water to obtain a standard solution of 2.00×10^{-3} mol dm⁻³ bismuth(III)-0.3 mol dm⁻³ perchloric acid. A standard solution of 1.20×10^{-4} mol dm⁻³ bismuth(III)-0.02 mol dm⁻³ perchloric acid was prepared by adding 6.0 cm³ of the 2.00×10^{-3} mol dm⁻³ bismuth(III) solution to water containing 2.0 cm³ of 0.1 mol dm⁻³ perchloric acid and diluting to 100 cm³ with water. The 1.20×10^{-4} mol dm⁻³ bismuth(III) solution proved to be stable for up to three months after preparation.

A bismuthiol II solution (0.1 mol dm⁻³) was obtained by dissolving 2.83 g of bismuthiol II (5-mercapto-3-phenyl-1,3,4-thiadiazole-2-thione potassium salt, obtained from Dojindo Laboratories, Kumamoto, Japan) in water and diluting to 100 cm³.

A buffer solution (pH 5.6) was prepared by mixing 25 cm³ of 1 mol dm⁻³ acetic acid with 200 cm³ of a 1 mol dm⁻³ sodium acetate solution.

Apparatus

A Shimadzu (Kyoto, Japan) Model UV-240 recording spectrophotometer with 10-mm quartz cells was used for all absorbance measurements. pH measurements were made with a Hitachi-Horiba (Tokyo, Japan) Model M-7 pH meter. An Iwaki (Tokyo, Japan) Model KM shaker was used for extraction.

Procedure

A 2-cm³ aliquot of the 1.20×10^{-4} mol dm⁻³ bismuth(III) in 0.02 mol dm⁻³ perchloric acid standard solution and 1 cm³ of 0.01 mol dm⁻³ bismuthiol II solution were put into a 50-cm³ separatory funnel. To this solution, 10-cm³ of a sample solution containing sulfide up to 3.00×10^{-5} mol dm⁻³ was added. The pH of the mixture was thereby brought to 2.6, and sulfide reacted with bismuth(III) to precipitate quantitatively bismuth(III) sulfide after the mixture was allowed to stand for 15 min at room temperature. To this mixture, 2 cm³ of acetate buffer solution (pH 5.6) was added to adjust the pH to 5.5 (optimal range of 4.8–5.9), and 10 cm³ of benzene was added. The funnel was shaken for 3 min to extract the residual bismuth(III) as a bismuth(III)-bismuthiol II complex. After standing for 15 min, the absorbance of the organic phase was measured at 335 nm against benzene.

In order to obtain a calibration line for bismuth(III), the standard bismuth(III) solution was used. The absorbance of bismuth(III) solutions was obtained by using 2 cm³ of water and 10 cm³ of 0.004 mol dm⁻³ perchloric acid containing $(2.4 - 0) \times 10^{-5}$ mol dm⁻³ bismuth(III) equivalent to $(0 - 3.6) \times 10^{-5}$ mol dm⁻³ sulfide, in the place of 2 cm³ of the solution of 1.20×10^{-4} mol dm⁻³ bismuth(III) in 0.02 mol dm⁻³ perchloric acid and 10 cm³ of the sample solution, respectively, in the procedure described above.

Results and Discussion

Calibration plots

A series of standard solutions (10.0 cm³) of sulfide was treated exactly as described in the procedure. The calibration

Fig. 1 Calibration plots. (a) Calibration plot for sulfide standards using the recommended experimental procedure; (b) calibration plot for bismuth(III) standards; (c) a standard-addition plot for hot-spring water sample to which various amounts of sulfide were added. A 10-cm³ aliquot of sample solution was used.

plot obtained is shown in Fig. 1(a). In addition, a plot of the bismuth(III) calibration is shown in Fig. 1(b); this was prepared to confirm the completion of the reaction of sulfide with bismuth(III). If 3 moles of sulfide react with 2 moles of bismuth(III) to produce quantitatively a precipitate of bismuth(III) sulfide, the calibration plot for sulfide should coincide with that for bismuth(III) when the molar concentration scales for sulfide and bismuth(III) are shown as in Fig. 1. Figure 1 shows that the calibration plot for sulfide up to 3.00×10^{-5} mol dm⁻³ was in good agreement with that of bismuth(III), indicating that the reaction of sulfide with bismuth(III) reached completion under the procedure conditions. Thereby, sulfide may be determined by using the calibration plot for standard bismuth(III) instead of using a sulfide calibration plot prepared from very unstable sulfide.

The proposed method is applicable to the determination of sulfide in the concentration range from 0.06×10^{-5} to 3.00×10^{-5} mol dm⁻³ (1.92 to 960 ppb). The precision was estimated from 10 measurements of 10 cm³ portions of 2.00×10^{-5} mol dm⁻³ sulfide solution (6.40 µg of S²⁻); the mean value of sulfide found was 6.40 µg with a standard deviation of 0.028 µg of sulfide and a relative standard deviation of 0.44%.

Absorption spectra

Although chloroform has been used for the extraction of bismuth(III) with bismuthiol II agent,³⁶ in the present study, benzene was used because the benzene phase separated from the aqueous phase in a shorter standing time after being shaken according to the procedure, and benzene was also less expensive than chloroform. Absorption spectra showed that the absorbance for bismuth(III) reached a maximum at 335 nm and the difference between the bismuth(III) standard and bismuth(III)-free solutions was also maximal at 335 nm. The wavelength of the maximum absorbance (335 nm) did not alter with any change in the experimental conditions. The apparent molar absorptivity of the extract at 335 nm was 46700 mol⁻¹ dm³ cm⁻¹, which was slightly higher than that obtained using

Fig. 2 Effect of the pH on the extraction of bismuth(III) with bismuthiol II. (a) 1.07×10^{-5} mol dm $^{-3}$ bismuth(III) solution (the absorbance against that for bismuth(III)-free solution); (b) bismuth(III)-free solution.

Fig. 3 Effect of the pH on the precipitation of sulfide with bismuth(III). (a) 2.00×10^{-5} mol dm $^{-3}$ sulfide solution; (b) 1.07×10^{-5} mol dm $^{-3}$ bismuth(III) solution.

chloroform³⁶ as a solvent. All measurements of the absorbance, therefore, were made at 335 nm.

Optimization of extraction of bismuth(III)-bismuthiol II complex into benzene

The effects of a range of experimental conditions (pH, amount of bismuthiol II and shaking time) on the extraction of bismuth(III) were investigated as described in the procedure, except that 2 cm 3 of water and a 10-cm 3 aliquot of 0.004 mol dm $^{-3}$ perchloric acid containing various amounts of bismuth(III) were used instead of the bismuth(III) reagent and the sample solutions, respectively.

In order to measure the effect of the pH on the extraction, the aqueous solution was adjusted to various pH values by using 2 cm 3 of various acetate buffers (1 mol dm $^{-3}$) in the place of the pH 5.6 buffer solution. The results are shown in Fig. 2. The

Table 1 Effects of sulfite and thiosulfate on the determination of 2.00×10^{-5} mol dm $^{-3}$ sulfide

Ion	Added/mol dm $^{-3}$	S $^{2-}$ found/ 10^{-5} mol dm $^{-3}$
None	—	2.00
SO $_3^{2-}$	2.00×10^{-5}	1.99
	2.00×10^{-4}	2.00
	2.00×10^{-3}	1.99
	2.00×10^{-2}	1.48
S $_2$ O $_3^{2-}$	2.00×10^{-5}	1.99
	2.00×10^{-4}	1.99
	2.00×10^{-3}	2.03
	2.00×10^{-2}	2.71

absorbance for the bismuth(III)-free solution (Fig. 2(b)) was increased at low pH values because of extraction of protonated bismuthiol II species into benzene. Figure 2(a) shows that the difference in absorbance between the bismuth(III) standard solution and the bismuth(III)-free solution reached a maximum in the range of pH 4.8–5.9. At pH above 5.9, the absorbance for bismuth(III) decreased due to hydrolysis. Therefore, the pH of the aqueous solution was adjusted to 5.5 in further experiments.

The effect of the concentration of the bismuthiol II was investigated over the range of 0.008–0.03 mol dm $^{-3}$, and it was found that absorbance remained essentially constant under these conditions. Thus, 1 cm 3 of 0.01 mol dm $^{-3}$ bismuthiol II solution was used in all subsequent experiments.

The effect of the shaking time was studied over the range from 30 s to 5 min, and it was found that adequate extraction of the bismuth(III)-bismuthiol II complex into benzene was achieved for extraction times in excess of 2 min. The shaking time was therefore fixed at 3 min in further experiments. In addition, the use of successive 10-cm 3 portions of benzene for extraction showed that the bismuth(III)-bismuthiol II complex was extracted quantitatively by the first extraction. Therefore, a single extraction was carried out in the experimental procedure. The extract in benzene was very stable, with no measurable change in the absorbance being observed after standing for 3 h in a glass-stoppered tube at room temperature.

Conditions for precipitation of sulfide with bismuth(III)

The effect of the reaction time on the precipitation of bismuth(III) sulfide was studied. The absorbance for 2.10×10^{-5} mol dm $^{-3}$ sulfide reached that for 1.00×10^{-5} mol dm $^{-3}$ bismuth(III) in 5 min and remained constant for 30 min, while the reagent blank did not show any change in the absorbance for 0.5–30 min. The reaction was therefore carried out for 15 min in order to form quantitatively the precipitation of the bismuth(III) sulfide.

The effect of pH on the precipitation reaction is shown in Fig. 3. The absorbance for a 2.00×10^{-5} mol dm $^{-3}$ sulfide reached that for 1.07×10^{-5} mol dm $^{-3}$ bismuth(III) over the range of pH 2.4–3.0. Increased absorbance at lower pH was attributed to a decrease in the concentration of sulfide owing to conversion into hydrogen sulfide. Adjustment of the pH above 3.0 was difficult because perchloric acid in the 1.20×10^{-4} mol dm $^{-3}$ bismuth(III) reagent solution was fixed at 0.02 mol dm $^{-3}$. The optimal pH range of solution on the reaction of sulfide with bismuth(III) was found to be 2.4–3.0, with a pH of 2.6 being used in the experimental procedure.

Effect of foreign ions

Solutions containing various amounts of foreign ions, both in

Table 2 Effect of foreign ions

Ion	Added/ μg	S ²⁻ found/ μg	Error, %	Ion	Added/ μg	S ²⁻ found/ μg	Error, %
None	—	0.640	—	None	—	0.640	—
Na ⁺	10000	0.645	0.8	F ⁻	10000	0.651	1.7
K ⁺	10000	0.645	0.8	Cl ⁻	10000	0.651	1.7
NH ₄ ⁺	10000	0.641	0.1	Br ⁻	10000	0.635	-0.8
Mg ²⁺	10000	0.643	1.3	I ⁻	10000	0.664	3.8
Ca ²⁺	10000	0.635	-0.8	NO ₃ ⁻	10000	0.645	0.8
Mn ²⁺	100	0.423	-33.9	Borate	10000 ^a	0.651	1.7
	10	0.638	-0.3	HCO ₃ ⁻	10000	0.715	11.7
Zn ²⁺	10000	0.654	1.7		1000	0.650	1.5
Cd ²⁺	100	0.970	51.6	CN ⁻	1000	0.685	7.0
	1	0.639	-0.1		500	0.639	-0.2
Co ²⁺	10000	0.564	-11.9	SCN ⁻	10000	0.646	0.9
	5000	0.636	-0.6	HPO ₄ ²⁻	10000	0.725	13.3
Ni ²⁺	10000	0.636	-0.6		5000	0.630	-1.6
Cu ²⁺	10	0.926	44.7	HAsO ₄ ²⁻	10000	0.733	14.5
	1	0.658	2.8		5000	0.630	-1.6
Pb ²⁺	100	0.738	15.3	Oxalate	10000	0.796	24.4
	50	0.671	4.8		5000	0.664	3.8
Fe ²⁺	10000	0.515	-19.5	Tartrate	10000	0.713	11.4
	1000	0.646	0.9		5000	0.641	0.1
Fe ³⁺	100	0.738	15.3	Citrate	10000	0.947	48.0
	50	0.671	4.8		1000	0.760	4.7

a. The value was calculated as a H₃BO₃.

Table 3 Determination of sulfide in hot-spring water samples

Sample	Dilution, fold	S ²⁻ added/ 10 ⁻⁵ mol dm ⁻³	Found/ 10 ⁻⁵ mol dm ⁻³	Content in sample	Recovery, %
A	0	0	0.18 ^a	0.18	—
	0	0	0.17 ^{a,b}	0.17	—
	2	0	0.09	0.18	—
	2	0.50	0.60	0.20	102
	2	1.50	1.60	0.20	101
B	0	0	0.11 ^a	0.11	—
	0	0	0.12 ^{a,b}	0.12	—
	2	0	0.06	0.12	—
	2	1.00	1.06	0.12	100
	2	1.50	1.56	0.12	100
C	0	0	1.06 ^a	1.06	—
	0	0	1.05 ^{a,b}	1.05	—
	2	0	0.53	1.06	—
	2	1.00	1.54	1.18	101
	2	1.50	2.07	1.14	103
D	2	2.00	2.53	1.06	100
	250	0	0.10 ^a	25.0	—
	250	0.50	0.59	22.5	98.0
	250	1.00	1.10	25.0	100

a. Mean was obtained from three replicate results.

b. Sulfide was calculated from the consumption of bismuth(III) estimated by using the calibration plot for standard bismuth(III) instead of sulfide calibration plot.

the presence of 2.00×10^{-5} mol dm⁻³ sulfide (6.40 μg) and in its absence, were treated as described in the experimental procedure. Sulfite and thiosulfate were found to give no interference, even when present at concentrations as high as 2.00×10^{-3} mol dm⁻³, as can be seen in Table 1. Sulfate up to 0.02 mol dm⁻³ did not interfere. The effects of other common ions are listed in Table 2. Cations such as Mn²⁺ (100 μg), Cd²⁺

(100 μg), Cu²⁺ (10 μg), Pb²⁺ (100 μg) and Fe³⁺ (100 μg) interfered owing to formation of their sulfides, which were present as insoluble compounds in aqueous solution. However, in a real sample these species would have already formed such precipitates prior to analysis, and would therefore not affect the concentration of free sulfide ion.

Determination of sulfide in water samples

The proposed method was applied to the determination of sulfide in hot-spring water. The results are given in Table 3, which also includes recovery values (98 to 103%) for sulfide added to the samples. In addition, Fig. 1(c) shows a standard addition plot for sulfide added to the hot-spring water diluted twice. The plot in Fig. 1(c) is displaced vertically from those of Figs. 1(a) and (b) because a trace amount of sulfide was present in the hot-spring water. Three replicate analyses for the hot-spring water C in Table 3 gave a mean value of 1.06×10^{-5} mol dm⁻³ sulfide and a relative standard deviation (RSD) of 1.5% using the sulfide calibration plot, and a mean value of 1.05×10^{-5} mol dm⁻³ and RSD of 1.7% using the bismuth(III) calibration plot. This demonstrated that the matrix in the hot-springs did not show any interference in the determination of sulfide. The calibration line for bismuth(III) can therefore be used instead of that for sulfide, which removes the need to prepare a sulfide standard.

References

1. P. O. Bethge, *Anal. Chim. Acta*, **1954**, *10*, 113.
2. W. P. Kilroy, *Talanta*, **1983**, *30*, 419.
3. J. Kurzawa, *Anal. Chim. Acta*, **1985**, *173*, 343.
4. D. R. Canterfold, *Anal. Chem.*, **1975**, *47*, 88.
5. L. K. Leung and D. E. Bartak, *Anal. Chim. Acta*, **1981**, *131*, 167.
6. H. Glysters, F. Adams, and F. Verbeck, *Anal. Chim. Acta*, **1976**, *83*, 27.

7. M. G. Glaister, G. J. Moody, and J. D. R. Thomas, *Analyst*, **1985**, *110*, 113.
 8. P. Kokkonen and H. Hyvarinen, *Anal. Chim. Acta*, **1988**, *207*, 301.
 9. T. Togawa, M. Ogawa, M. Nawata, Y. Ogasawara, K. Kawanabe, and S. Tanabe, *Chem. Pharm. Bull.*, **1992**, *40*, 3000.
 10. Y. Miura, M. Tsubamoto, and T. Koh, *Anal. Sci.*, **1994**, *10*, 595.
 11. Y. Miura, T. Maruyama, and T. Koh, *Anal. Sci.*, **1995**, *11*, 617.
 12. Y. Miura, K. Fukasawa, and T. Koh, *J. Chromatogr. A*, **1998**, *804*, 143.
 13. J. L. Burguera and A. Townshend, *Anal. Chim. Acta*, **1980**, *114*, 209.
 14. A. Safavi and M. A. Karimi, *Talanta*, **2002**, *57*, 491.
 15. T. J. Hurse and W. P. P. Abeydeere, *J. Chromatogr. A*, **2002**, *942*, 201.
 16. O. F. Kamson, *Anal. Chim. Acta*, **1988**, *211*, 299.
 17. M. F. Mousavi and M. Shamsipur, *Bull. Chem. Soc. Jpn.*, **1992**, *65*, 2770.
 18. A. A. Ensafi, *Anal. Lett.*, **1992**, *25*, 1525.
 19. A. A. Ensafi and M. Samimifar, *Anal. Lett.*, **1994**, *27*, 157.
 20. M. F. Mousavi and N. Sarlark, *Anal. Lett.*, **1997**, *30*, 1567.
 21. S. A. Rahim, A. Y. Salim, and M. S. Shereef, *Analyst*, **1973**, *98*, 851.
 22. A. Safavi and Z. Ramezani, *Talanta*, **1997**, *44*, 1225.
 23. T. Koh and Y. Miura, *Anal. Sci.*, **1987**, *3*, 543.
 24. P. Selvapathy, T. V. Ramakrishna, and R. Pitchai, *Mikrochim. Acta*, **1989**, *II*, 23.
 25. A. Punta, F. J. Barragon, M. Ternero, and A. Guiraum, *Analyst*, **1990**, *115*, 1499.
 26. T. Koh, Y. Miura, N. Yamamuro, and T. Takaki, *Analyst*, **1990**, *115*, 1133.
 27. K. Sonne and P. K. Dasgupta, *Anal. Chem.*, **1991**, *63*, 427.
 28. V. Kuban, P. K. Dasgupta, and J. N. Marx, *Anal. Chem.*, **1992**, *64*, 36.
 29. T. Koh and N. Takahashi, *Anal. Sci.*, **1992**, *8*, 219.
 30. T. Koh and K. Okabe, *Anal. Sci.*, **1992**, *8*, 285.
 31. T. Koh, N. Takahashi, N. Yamamuro, and Y. Miura, *Anal. Sci.*, **1993**, *9*, 487.
 32. T. Koh, K. Okabe, and Y. Miura, *Analyst*, **1993**, *118*, 669.
 33. M. S. P. Silva, I. S. Silva, G. Abate, and J. C. Masini, *Talanta*, **2001**, *53*, 843.
 34. K. C. Bowles, M. J. Ernste, and J. R. Kramer, *Anal. Chim. Acta*, **2003**, *477*, 113.
 35. A. K. Majumdar, *J. Indian Chem. Soc.*, **1944**, *21*, 347.
 36. K. Watanabe, M. Awano, T. Nishiyama, and K. Kawagaki, *Bunseki Kagaku*, **1981**, *30*, 800.
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