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Spectrophotometric Determination of Trace Amounts of Sulfide by Formation of Iodide and Its Solvent Extraction with Methylene Green

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요오드이온 생성 및 Methylene Green과의 용매추출에 의한 미량 황이온의 분광광도법 정량

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Abstrcat : The iodide formed stoichiometrically for sulfide by its oxidation with iodate was extracted as an ion-pair with methylene green into 1, 2-dichloroethane and the extract was measured spectrophotometrically at 656nm for the determination of sulfide. Hydrogen sulfide separated from the sample matrix was introduced into a solution containing pH 3.5 acetate buffer and iodate, in which the hydrogen sulfide was completely converted into iodide. A linear calibration graph was obtained over the range 3×10^{-7}~1.2×10^{-5}M sulfide(0.0096~0.384μg of S^{2-}/m*l*) and the detection limit was 0.0032μg/m*l*. The apparent molar absorptivity and a correlation coefficient(r) were 6.7×10^{4} L mole^{-1} cm^{-1} and 0.999, respectively. When applied to the stream water samples, the proposed method gave a relative standard deviation of 1.59% at 5×10^{-6}M sulfide level.

요약 : 요오드산 이온의 황이온의 산화에 의해 화학양론적으로 형성되는 요오드이온과 methylene green과의 이온쌍을 1, 2-dichloroethane으로 추출하여 656nm에서 분광광도법에 의해 황이온의 정량법을 확립하였다. 시료기질로부터 분리되어지는 황화수소는 pH 3.5 초산완충용액과 요오드산 이온이 포함된 용액에 도입되어 완전히 전환되었다. 황이온의 정량범위는 3×10^{-7}~1.2×10^{-5}M (0.0096~0.384μg/m*l*) 였으며, 검출한계는 0.0032μg/m*l*였고, 몰흡광계수는 6.7×10^{4}L mole^{-1} cm^{-1}였다. 본 정량법을 하천수 중에 응용하였을 때 5×10^{-6}M 농도에서 상대표준편차는 1.59%로 미량에서 공존이온의 영향을 거의 받지 않고 재현성 있는 결과를 나타내므로 실시료 중에 효과적으로 응용할 수 있으리라 생각된다.

Key words : spectrophotometric determination of sulfide, the formation of iodide for

sulfide by its oxidation with iodate. methylene green, separation as hydrogen sulfide from sample matrix, solvent extraction.

1. Introduction

The determination of sulfide has been fraught with difficulty because of its instability, particularly when in aqueous solution. Sulfide is susceptible to air-oxidation to form sulfite, thiosulfate, and sulfate.[1] Various methods for the determination of sulfide has been proposed. In the sulfide ion selective method[2, 3] reported to accurately measure sulfide concentrations at 10ng/m*l* by using targeted calibration standards, the response is notably slow and interfering substances such as cyanide will produce a high background for low level determinations. Spectrofluorimetric methods using an Hg(Ⅱ)-PBI(2, 2′-pyridylbenzimidazole) complex[4, 5] and a Cu(Ⅱ)-HPB[o-(hydroxyphenyl) benzoxazole] complex[6, 7] have been proposed for the determination of sulfide, in which the fluorescence intensity of the PBI and HPB liberated by the reaction of the sulfide with the metal complexes is measured. These methods suffer from interference by anions such as cyanide, thiocyanate, and thiosulfate which react with the metals. Ion chromatographic methods using ultraviolet detector[8] and electrochemical detectors[9, 10] have been developed for the determination of sulfide. However, these procedures have been used not in practical applications but only with synthetic samples. Other analytical methods such as gas chromatographic method[11], polarographic and related electrochemical methods[12, 13], atomic absorption spectrophotometric method[14], and thermometric titrimetric method[15] have been published. Unfortunately, each method is subject to interference or sensitivity limitations. The spectrophotometric methods using methylene blue[16] and ethylene blue[17] are well known and widely used. But these methods suffer from the interferences of the reducing agents such as sulfite, thiosulfate, and iodide. Further, the reaction of sulfide with N, N-dimethyl-p-phenylenediamine or N, N-diethyl-p-phenylenediamine does not proceed to stoichiometric completion and the temperature has an effect on the measurement of the methylene blue or ethylene blue formed. Numerous indirect spectrophotometric methods using various metal complexes[18~22] have been developed for the determination of sulfide, which are based on a decrease in the absorbance of the metal complexes after their reaction with sulfide. These methods also suffer from interference by such anions as the thiocyanate, cyanide, and iodide, which react with the metals. Recently, the methods using thiocyanate formed from sulfide by its reaction by its oxidation with iodine[23] and hydrogen peroxide[24] in the presence of cyanide have been proposed. But these methods are subject to sensitivity limitation or the interference of cyanide by its oxidation. In this study, the follwing reaction :

$$S^{2-} + IO_3^- + 6H^+ \longrightarrow S + I^- + 3H_2O \quad \text{(Eq. 1)}$$

was investigated in detail and the conditions under which the reaction proceeds to stoichiometric completion were established. The iodide formed stoichiometrically for sulfide according to Eq. (1) was extracted as an ion pair with methylene green (MG) similar to methylene blue in structure, into 1, 2-dichloroethane, an measured spectrophotometrically at 656nm. We found that sulfide at the 1×10^{-6} mole L^{-1} level and the hydrogen sulfide separated from the sample matrix are quantitatively converted into iodide. The proposed method has been successfully applied to the determination of sulfide in stream water samples.

2. Experimental

2.1. Chemicals and Apparatus

All of chemicals used were of analytical-reagent grade and were used without further purification. Doubly distilled water was used in all experiments. A sulfide solution was prepared from large crystals of sodium sulfide($Na_2S \cdot 9H_2O$) using oxyen-free water. In order to remove trace amounts of impurities from the surface of the crystals, they were rapidly washed with water and then dried by absorption of the water with filter paper. A sulfide solution(0.01M) was obtained by dissolving about 0.25g of the crystals in 100m*l* of water. The solutions was standardized by iodimetric back titration. Working standard sulfide solutions containing 2×10^{-4}M were prepared by appropriate dilution. The standard solutions must be used within 30 min of standardization, as the concentration of sulfide decreases after this time owing to oxidation by air. An iodide solution(1×10^{-3}M) was prepared by dissolving 0.166g of potassium iodide in 1L of water and working standards were used to ascertain the stoichiometric formation of iodide for both sulfide and hydrogen sulfide by their oxidation with iodate. An iodate solution(1×10^{-3}M) was prepared by dissolving 0.214g of potassium iodate in 1L of water. A MG solution(1×10^{-2}M) was prepared by dissolving 1.403g of MG($C_{16}H_{17}ClN_4O_2S$, 65%) in about 200m*l* of water, allowing the mixture to stand overnight and then diluting it to 250m*l*. Working solutions were prepared by appropriate dilution. Various pH solutions[solutions (pH 1.0~2.0) from fixed amounts of hydrochloric acid in 0.2M potassium chloride, acetate buffers(pH 2.5~5.5) from 1M acetic acid and 1M sodium acetate, phosphate buffers(pH 6.0~7.5) from 0.2M potassium dihydrogen phosphate and 0.2M sodium monohydrogen phosphate, and ammonium buffer (pH 0.8) from 1M ammonium hydroxide and 1M ammonium chloride] were prepared to study the effect of pH for the stoichiometric formation of iodide for both sulfide and hydrogen sulfide.

A Hewlett Packard Model 8452A recording spectrophotometer with 10mm quartz cells was used for all absorbance measurements and absorption spectra. A DMS Model DP-135M pH Meter was used for pH measurements. The flow rate of the nitrogen gas was regulated by a Kojima Model RK 1200 flow meter.

2.2. Procedures

Procedure I(Determination of soluble sulfide)

Place 3m*l* of pH 3.5 acetate buffer and 1m*l* of 1×10^{-3}M iodate in a 50m*l* separatory funnel. To this mixture add 10m*l* of a sample solution containing $3\times10^{-7}\sim1.2\times10^{-5}$M of sulfide and allow the mixture to stand for 5 min. After adding 1m*l* of 1×10^{-3}M MG and 10m*l* of 1, 2-dichloroethane, shake the funnel for 1 min to extract the ion pair between MG and iodide. After allowing the mixture for a given period of time, transfer the organic phase into a glass stoppered tube and add some anhydrous sodium sulfate in order to remove any water droplets present. Shake the mixture vigorously by hand untill it becomes transparent and then measure the absorbance at 656nm against 1, 2-dichloroethane using 10mm quartz cells.

Procedure II (Determination of the hydrogen sulfide liberated from the sample matrix).

Place 3m*l* of pH 3.5 acetate buffer, 1m*l* of 1×10^{-3}M iodate, and 8m*l* of water in a 50m*l* separatory funnel. Then pipet 10m*l* of a sample solution containing 3×10^{-7}M~1.2×10^{-5}M of sulfide into a 30m*l* glass stoppered vessel(D in *Fig.* 1) and connect the syringe containing 2m*l* of 2×10^{-3}M sulfuric acid to the gas dispenser(E in *Fig.* 1) with silicon-rubber tubing(C in *Fig.* 1). Immediately after adding the sulfuric acid in the syringe to the sample in the 30m*l* vessel, remove the syringe from the dispenser and bubble nitrogen gas through the solution for 5 min at a flow rate of 250m*l* min^{-1}. This facilitates the complete introduction of the hydrogen sulfide evolved into the absorption

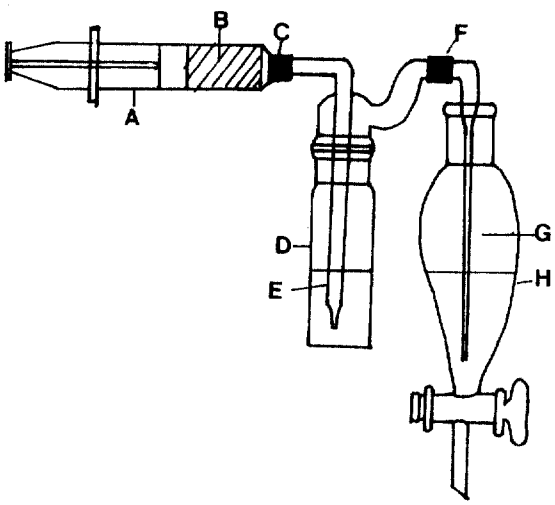

Fig. 1. Evolution-absorption apparatus.
A, 5m*l* syringe; B, 2m*l* of 2×10^{-3}M sulfuric acid C and F, silicone-rubber tubing; D, 30m*l* glass stoppered vessel; F and G, gas dispenser; H, absorption vessel(50m*l* separating funnel)

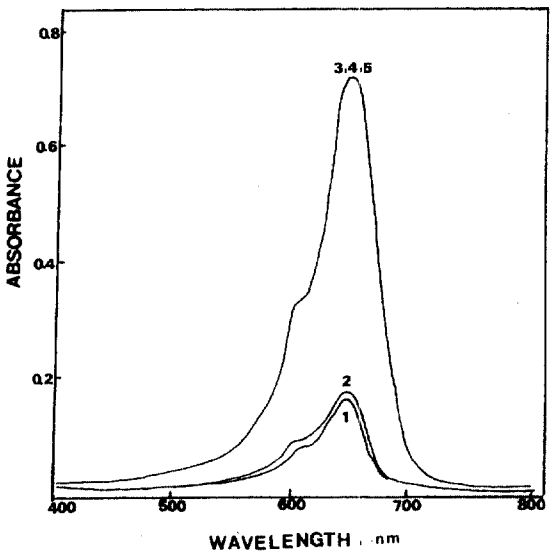

Fig. 2. Absorption spectra of ion pair between MG and iodide formed by procedure Ⅰ and Ⅱ. No. 1, 2, 3, 4, and 5 are from MG, MG and sulfide, MG and iodide formed for sulfide by procedure Ⅰ and Ⅱ, and MG and iodide by procedure Ⅰ, respectively.

vessel(H in *Fig.* 1). Then wash the gas dispenser(G in *Fig.* 1) using 2m*l* of water and allow the mixture to stand for 5 min for the stoichiometric formation of iodide from the absorbed hydrogen sulfide. To this mixture, add 1m*l* of 1×10^{-3}M MG and 10m*l* of 1, 2-dichloroethane. Shake the funnel for 1 min to extract the ion pair between MG and iodide. After allowing the mixture to stand for a given period of time, transfer the organic phase into a glass-stoppered tube, remove any water droplets and measure the absorbance at 656nm against 1, 2-dichloroethane.

3. Results and Discussion

3.1. Absorption spectra

To study the absorption spectra of the ion-pair between MG and iodide formed for sulfide and hydrogen sulfide by their oxidation with iodate, each aliquot(10m*l*) of both sulfide and iodide solution (8×10^{-6}M) was added to a solution containing 3m*l* of pH 3.5 acetate buffer and 1m*l* of 1×10^{-3}M iodate. Then the mixture was treated as described in procedure I and 10m*l* of sulfide(8×10^{-6}M) was added into a 30m*l* glass stoppered vessel and that was treated as described in procedure Ⅱ. As shown in *Fig.* 2, the absorption spectra of ion pair between MG and iodide formed for sulfide and hydrogen sulfide by their oxidation with iodate in procedure Ⅰ and Ⅱ were identical with that for standard iodide. Hence the sulfide or hydrogen sulfide evolved from the sample soultion was converted stoichiometrically into iodide according Eq. (1).

3.2. Calibration graphs

A series of standard solutions(10ml) of sulfide and iodide were treated as described in procedure I. If sulfide is converted stoichiometrically into iodide according to Eq. (1), the calibration graph for sulfide should coincide with that for iodide when plotted in terms of molar concentrations. As shown in *Fig.* 3, the formation of iodide for sulfide

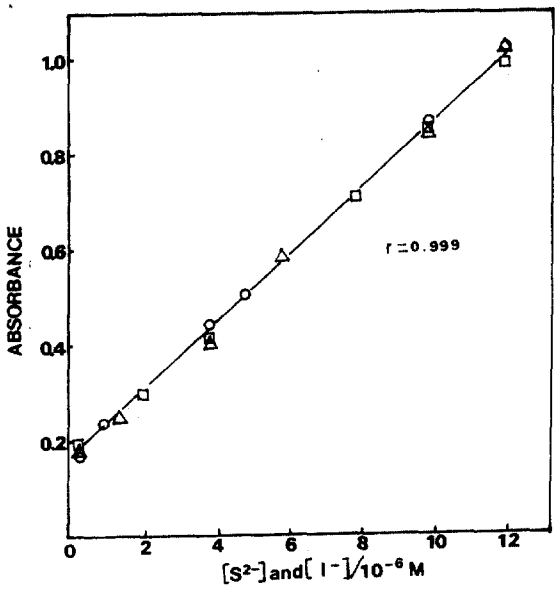

Fig. 3. Calibration graphs for sulfide and iodide. ○, S^{2-} by procedure Ⅰ ; △, S^{2-} by procedure Ⅱ ; □, I^- by procedure Ⅰ.

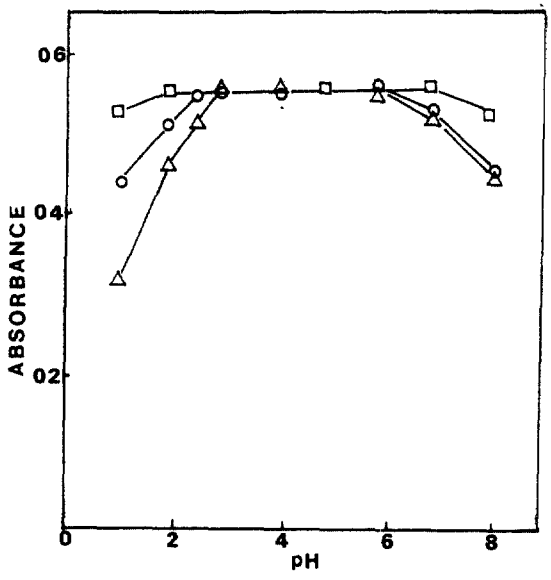

Fig. 4. Effect of pH on the formation of iodide for sulfide or hydrogen sulfide (8×10^{-6}M) by its oxidation with iodate. Each reagent blank was subtracted from all of the absorbances measured. ○, S^{2-} by procedure Ⅰ ; △, S^{2-} by procedure Ⅱ ; □, 8×10^{-6}M I^- by procedure Ⅰ.

proceeded to quantitative completion. The calibration graph obatined for sulfide by procedure Ⅱ also coincided with that obtained with procedure Ⅰ for iodide. These experimental results indicate that under the conditions of procedure Ⅱ, the sulfide separated as hydrogen sulfide from the sample matrix is completely converted into iodide, and that sulfide can be selectively determined. The proposed method showed a linear calibration graph over the range of concentration from 3×10^{-7} to 1.2×10^{-5}M(0.0096~0.384μg/m*l*) of sulfide and the minimum detectable amount was found to be 0.0032μg/m*l* of sulfide. The apparent molar absorptivity for sulfide at 656nm and a correlation coefficitent(r) are 6.7×10^4L mole^{-1} cm^{-1} and 0.999, respectively.

3.3. Effect of pH

The formation of iodide by the oxidation of sulfide with iodate was found to be affected by the pH of the reaction solution. To study this effect, each aliquot(10m*l*) of both sulfide and iodide solution(8×10^{-6}M) was added to a solution containing 3m*l* of various buffers and 1m*l* of 1×10^{-3}M iodate. The mixture was treated as described in procedure Ⅰ. As shown in *Fig.* 4, the absorbance obtained for sulfide coincided with that for standard iodide over the pH range 2.5~6.0; the sulfide was converted stoichiometrically into iodide according to Eq. (1). A decrease in absorbance below pH 2.5 can be attributed to both a partial evoution of hydrogen sulfide and excess chloride present on this pH range. which forms an ion-pair with MG. A decrease in absornance above pH 6.0 is probably due to the incomplete oxidation of sulfide. The hydrogen sulfide evolved from the sample solution in procedure Ⅱ was found to be converted quantitatively into iodide over the pH range 3.0~6.0. Hence the pH of the reaction solution was adjusted to pH 3.5 under the conditions described in both pro-

cedure Ⅰ and Ⅱ.

3.4. Effect of the amount of iodate

Iodate was used as an oxidizing agent for sulfide, when the iodide was obtained stoichiometrically for sulfide by its oxidation with iodate. To establish the optimum amount of iodate required for the stoichiometric formation of iodide for sulfide, each aliquot(10m*l*) of both sulfide and iodide(1.2×10^{-5}M) was added to a solution containing 1m*l* aliquot of 10^{-4}, 2×10^{-4}, 5×10^{-4} and 1×10^{-3}M iodated solutions was used to oxidize sulfide in the solutions over the pH range 2.5~6.0 and the mixture was treated as described in procedure I. As shown in *Fig.* 5, when 1m*l* solution of 1×10^{-4}M iodate was employed, the formation of iodide for sulfide did not proceed to completion, even after 60 min, owing to the insufficient amount of iodate being available. However, the absorbance for sulfide using 1m*l* each of 2×10^{-4}, 5×10^{-4} and 1×10^{-3}M iodate reached that for iodide in 20, 10 and 3 min, respectively. Hence a 1m*l* volume of 1×10^{-3}M iodate was used and the formation reaction of iodide for sulfide was run for 5 min as described in procedure I.

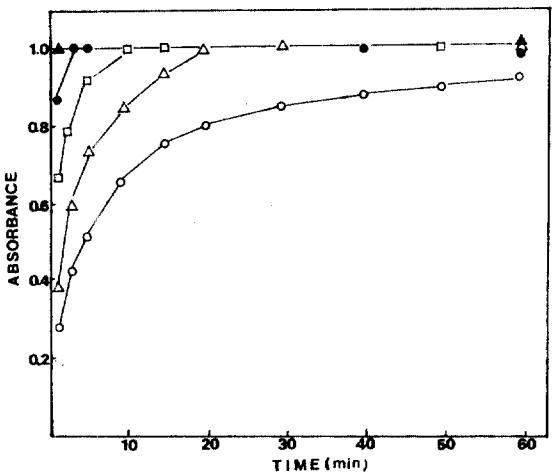

Fig. 5. Effect of the amount of iodate on the formation of iodide for sulfide (1.2×10^{-5}M) by its oxidation with iodate.

○, S^{2-} with 1m*l* of 10^{-4}M IO_3^- ; △, S^{2-} with 1m*l* of 2×10^{-4}M IO_3^- ; □, S^{2-} with 1m*l* of 5×10^{-4}M IO_3^- ; ●, S^{2-} with 1m*l* of 10^{-3} ; ▲, 1.2×10^{-5}M I^- with 1m*l* of IO_3^-.

3.5. Evolution of hydrogen sulfide

In procedure Ⅱ, it was attempted to separate from the sample matrix in the form of hydrogen sulfide and then to convert into iodide according to Eq. (1). various amounts of sulfuric acid were added to a 30m*l* glass stoppered vessel (D in *Fig.* 1) containing to 10m*l* of sulfide solution(1.2×10^{-5}M) using a syringe (A in *Fig.* 1). Nitrogen gas was then bubbled through the solution at a flow rate of 250m*l* min^{-1}. This facilitated both the evolution of hydrogen sulfide from the mixture and its subsequent introduction into the solution in the 50m*l* separating funnel (H in *Fig.* 1). which contained 3m*l* of pH 3.5 acetate buffer, 1m*l* of 1×10^{-3}M iodate, and 8m*l* of water.

The complete formation of iodide for the hydrogen sulfide evolved was not achieved, even after

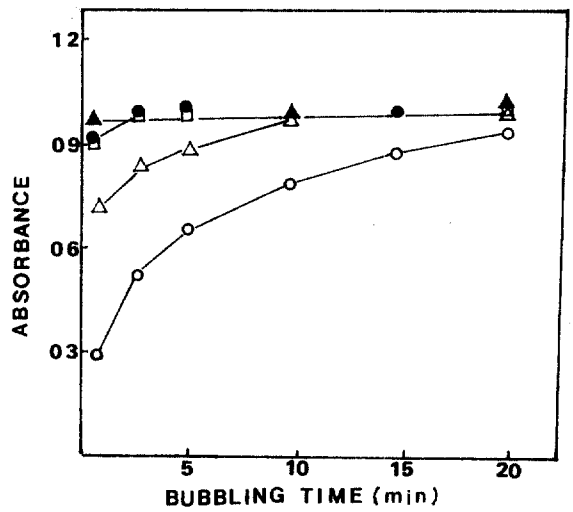

Fig. 6. Effect of the amount of sulfuric acid on the evolution of hydrogen sulfide from the sulfide solution(1.2×1^{-5}M).

○, 2m*l* addition of 2×10^{-4}M) ; △, 2m*l* addition of 5×10^{-4}M ; □, 2m*l* addition of 10^{-3}M ; ●, 2m*l* addition of 2×10^{-3}M ; ▲, expected value(1. 2×10^{-5}M I^-) by procedure Ⅰ.

20min, when 2m*l* of 2×10^{-4}M sulfuric acid solution was employed. But the complete formation was achieved in 10, 3 and 3min, respectively when each 2m*l* aliquot of 5×10^{-4}M, 1×10^{-3}M, and 2×10^{-3}M sulfuric acid solutions was added. Hence a 2m*l* volume of 2×10^{-3}M sulfuric acid was used and nitrogen gas was bubbled through the solution for 5min at a flow rate of 250m*l* min^{-1}, as described in procedure Ⅱ.

Table 1. Effect of foreign ions on the determination of sulfide

Ions	Amount, μg	Procedure Ⅰ (S^{2-}, μg)			Procedure Ⅱ (S^{2-}, μg)		
		Added	Found	Error(%)	Added	Found	Error(%)
NH_4^+	10,000	3.20	3.10	−3.1	3.20	3.25	+1.6
Na^+	10,000	3.20	3.08	−3.7	3.20	3.28	+2.5
K^+	10,000	3.20	3.15	−1.6	3.20	3.26	+1.9
Mg^{2+}	10,000	3.20	3.08	−3.7	3.20	3.25	+1.6
Ca^{2+}	10,000	3.20	3.12	−2.5	3.20	3.18	−0.6
Ba^{2+}	10,000	3.20	3.15	−1.6	3.20	3.25	+1.6
Zn^{2+}	100	3.20	3.05	−4.7	3.20	3.15	−1.6
	1,000	3.20	3.15@	−2.5	3.20	2.93	−8.4
Ni^{2+}	100	3.20	3.00	−6.2	3.20	3.02	−5.6
	1,000	3.20	3.15@	−1.6	3.20	2.88	−10.0
Al^{3+}	1,000	3.20	2.88	−10.0	−	−	−
	10,000	3.20	3.12@	−2.5	3.20	3.15	−1.6
Mn^{2+}	100	3.20	3.15	−1.6	−	−	−
	1,000	3.20	2.98	−6.9	3.20	3.12	−2.5
Fe^{3+}	100	3.20	3.05	−4.7	3.20	3.12	−2.5
Cu^{2+}	10	3.20	0.75	−76.6	3.20	0.88	−72.5
	1,000	3.20	3.05@	−4.7	3.20	−	−
Cl^-	1,000	3.20	3.28	+2.5	−	−	−
	10,000	3.20	4.38	+36.9	3.20	3.30	+3.1
Br^-	100	3.20	3.45	+7.8	−	−	−
	10,000	3.20	−	−	3.20	3.18	−0.6
I^-	10	3.20	4.58	+51.6	−	−	−
	1,000	3.20	−	−	3.20	3.15	−1.6
SO_4^{2-}	10,000	3.20	3.15	−1.6	3.20	3.18	−0.6
NO_3^-	100	3.20	3.58	+11.9	−	−	−
	10,000	−	−	−	3.20	3.15	−1.6
$S_2O_3^{2-}$	10	3.20	4.25	+32.2	−	−	−
	10,000	−	−	−	3.20	3.24	+1.3
HSO_3^-	10	3.20	3.95	+23.4	−	−	−
	10,000	−	−	−	3.20	3.25	+1.6
SCN^-	10	3.20	5.25	+64.1	−	−	−
	10,000	3.20	−	−	3.20	3.15	−1.6
HCO_3^-	10,000	3.20	3.18	0.6	3.20	3.15	−1.6
CO_3^{2-}	10,000	3.20	3.26	+1.9	3.20	3.12	−2.5
$H_2PO_4^-$	10,000	3.20	3.28	+2.5	3.20	3.18	−0.6
$C_2O_4^{2-}$	10,000	3.20	3.30	+3.1	3.20	3.26	+1.9
CN^-	10,000	3.20	3.28	+2.5	3.20	3.25	+1.6

@ : A 2m*l* solution of 0.2M EDTA was added.

3.6. Effect of foreign ions

A 10m*l* solution containing 3.2μg of sulfide (1×10^{-5}) and various amounts of foreign ions was treated as described in procedure Ⅰ and Ⅱ. The results are given in *Tabel* 1. The interferences from anions such as chloride, bromide, iodide, nitrate, thiosulfate, bisulfite, and thiocyanates in procedure Ⅰ could be eliminated by separating the sulfide off as hydrogen sulfide, as in procedure Ⅱ. However, Cu(Ⅱ) that forms extremely insoluble sulfide gave strong interference, even in procedure Ⅱ. In procedure Ⅰ, the interferences of Zn(Ⅱ), Ni(Ⅱ), Fe(Ⅲ) and Cu(Ⅱ) could be eliminated to a certain extent by masking them with EDTA.

3.7. Application to stream water samples

The proposed method was applied to the determination of sulfide in stream water samples. Potential matrix interference from unknown species in real samples were investigated by adding amount of sulfide to stream water samples and then treating the mixtures as described in procedure Ⅰ and Ⅱ. The results are given in *Table* 2. The sulfide contents in the original samples A, B, C and D were determined as being 0.84, 1.3, 3.75, 5.25 ppm (by procedure Ⅰ), and 0.75, 0.96, 1.9 and 4.1 ppm (by procedure Ⅱ), respectively, using the standard addition method. The higher sulfide contents obtained by procedure Ⅰ can probably be caused by nitrate, chloride, iodide, or thiocyanate which forms the ion-pair with MG. Procedure Ⅰ gave much lower recoveries for samples B, C and D due to serious matrix interferences. However, the recoveries obtained by procedure Ⅱ, in which the sulfide was separated as hydrogen sulfide, ranged from 89.1 to 102.5 with an average of 94.7%. The precision of the proposed method(procedure Ⅱ) was based on 9 replicate analyses of 10m*l* ali-

Table 2. Recovery of sulfide in stream water samples by standard addition method.

Smaple	S^{2-} added, μg	Procedure Ⅰ (S^{2-}, μg)		Procedure Ⅱ (S^{2-}, μg)	
		Found	Recovery(%)	Found	Recovery(%)
Sapmle A[a]	–	1.68	–	1.50	–
	0.64	2.37	102.2	2.19	102.3
	1.60	3.21	97.9	3.03	97.7
	3.20	4.93	101.0	4.82	102.6
Sapmle A[b]	–	0.65	–	0.48	–
	0.64	1.10	85.3	1.04	92.9
	1.60	1.82	80.9	2.00	96.1
	3.20	3.19	82.9	3.37	91.6
Sapmle C[c]	–	0.75	–	0.38	–
	0.64	1.22	87.8	0.94	92.2
	1.60	1.93	82.1	1.81	91.4
	3.20	3.12	79.0	3.19	89.1
Sapmle D[c]	–	1.05	–	0.82	–
	0.64	1.39	82.2	1.34	91.8
	1.60	2.33	87.9	2.27	93.8
	3.20	3.81	89.6	3.82	95.0

The a, b and c were diluted to 5-fold, 20-fold and 50-fold the original vollume, respectively.
Sample A, Ongpo stream ; Sample B, Han stream ; Sample C, Byungmun stream ; Sample D, Sanji stream.

quot of sample A diluted to 5-fold, to which a known amount of sulfide (1.6μg) has been added. The mean value of the sulfide found was 1.57μg with a standard deviation of 0.025μg and a relative standard deviation of 1.59%.

4. References

1. J. D. Cline and F. A. Richards, *Environ. Sci. Technol.*, **3**, 838(1969).
2. E. W. Baumann, *Anal. Chem.*, **46**, 1345(1974).
3. H. Guterman, S. Ben-Yaakov and A. Abelovich, *ibid.*, **55**, 1731(1983).
4. Y. Arikawa and H. Kawai, *Bunseki Kagaku*, **35**, 720(1986).
5. L. S. Bark and A. Rixon, *Analyst*, **95**, 786(1990).
6. F. Vernon and P. Whithan, *Anal. Chim. Acta.*, **59**, 155(1972).
7. Y. Hong, K. Yamaya and M. Yoshida, *Anal. Sci.*, **3**, 337(1987).
8. R. J. Williams, *Aanl. Chem.*, **55**, 851(1983).
9. K. Han and W. F. Koch, *ibid*, **59**, 1016(1987).
10. L, R. Goodwin, D. Francom, A. Urso and F. P. Dieken, *ibid.*, **60**, 216(1988).
11. K. Funazo, T. Hirashima, M. Tanaka and T. shono, *Fresenius' Z. Anal Chem.*, **311**, 27(1982).
12. D. R. Canterford, *Anal. Chem.*, **45**, 2414(1973).
13. T. M. Florence, *Anal. Lett.*, **B11**, 913(1978).
14. A. Kovastis and M. Tsougas, *Bull. Environ. Contam. Toxicol.*, **15**, 412(1976).
15. R. Bin Ahmad, J. O. Hill and R. J. Magee, *Thermochim. Acta.*, **98**, 127(1986).
16. L. Gustafsson, *Talanta*, **4**, 227(1960).
17. C. F. Wood and I. L. Marr, *Analyst*, **113**, 1635 (1988).
18. M. Deguchi and A. Kitamura, *Bunseki Kagaku*, **27**, 527(1978); *Chem. Abster.*, **90**, 96946v(1979).
19. S. R. Bhat, J. M. Eckert, R. Geyer and N. A. Gibson, *Anal. Chim. Acta*, **108**, 293(1979)
20. F. Wei, Y. Zhu, F. Yin and N. Shen, *Talanta*, **28**, 853(1981).
21. M. R. Ceba, F. V. Jara and J. A. M. Leyva, *Analyst*, **107**, 781(1982).
22. I. Singh and P. S. Kadyan, *ibid.*, **110**, 309(1985).
23. T. Koh, Y. Miura, N. Yamamuro and T. Takaki, *ibid.*, **115**, 1133(1990).
24. T. Koh, N. Takahashi, N. Yamamuro and Y. Mimura, *Anal. Sci.*, **9**, 487(1993).