

Coulometric determination of sulfur speciation in natural waters^{*}

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Abstract—A systematic analytical method for the species of trace sulfur in water has been developed by using electrochemically coulometric titration in combination with several separation and concentration techniques. Based on the reaction of iodine with sodium azide, the studies were carried out on the catalytically coulometric determination of ppb levels of ionic or molecular sulfides, thiosulfates and hydrogen sulfide in water; constant current coulometric determination of sulfites; and indirect coulometric determination of sulfate salts and esters. Coupled with the determination of the content of total sulfur, the scope of distribution of the species of inorganic sulfur (including trace sulfur compounds in labile state) and organic sulfur in water was given. The method thus developed was found to be featured by being easy and reliable to operate with a higher sensitivity and reproducibility and to be applicable to the analysis of sulfur species in water.

Keywords, sulfur; analysis of species; electrochemical technique; catalytically coulometric titration; indirect coulometric titration.

1 Introduction

The total amount of an element in a water body is a sum of all chemical species of the element present in the water body. The ability of transportation of an element and its biological effects in an aqueous environment are usually not dependent on its total amount, but rather closely related to its chemical species and the respective levels of these species. Sulfur is a widely distributed element in nature and has a number of species present in water bodies. These different species are extremely easy to be converted into each other, and even some of them are very labile and at an extremely low concentration so that they are difficult to be detected.

Because of the importance in the formation of acidic precipitation, the accurate information about sulfur species in water is necessary to understand the sulfur cycle. In comparison to oceans, lakes tend to have lower dissolved solid and higher particulate loads, with higher

* This study was supported by the National Natural Sciences Foundation of China

biological activity, greater ratio of sediment to water surface areas, and very transient transport and mixing features, and may be influenced more by inputs from rivers and industrial sources. This report presents the first systematic investigation of the distribution and speciation of sulfur in the Fuhai Lake in Beijing.

In view of the obvious differences in the chemical behavior of sulfur in different oxidation states, numerous methods have been tried in a continuing effort to quantify the sulfur species in natural water. At present, the spectrophotometry (Lander, 1983), complex titration (Berner, 1964) and polarography (Luther, 1985) are still used as major methods for the analysis of some sulfur species.

The interest in the development of a new analytical system for sulfur speciation stimulated us to investigate the coulometric behavior of sulfur compounds. With the catalytically coulometric titration to determine trace sulfides, thiosulfates and dissolved hydrogen sulfide the indirect coulometric titration for sulfate salts and esters and total sulfur, and the constant current coulometric titration for sulfite, seven sulfur species in lake water and their speciation distribution had been well detected by the coulometric analytical system. And some separation and preconcentration techniques were studied.

2 Experiment

2.1 Instruments

A coulometric titration apparatus (Fig. 1), and a SJP-1A oscilopolarography (DME, Pt, Ag/AgCl) were used in this study.

2.2 Reagents

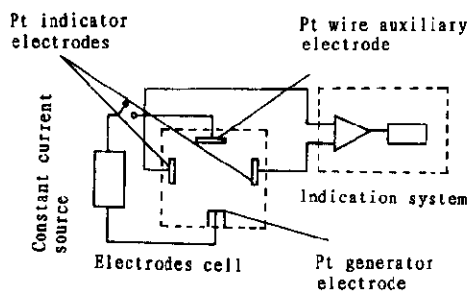


Fig. 1 Schematic diagram of coulometric titration
Reagents

All chemicals used were of analytical reagent grade, and redistilled water, a standard sulfate solution (0.010mg/ml), and an element sulfur solution (5.000mg/ml), a 50% aqueous alcohol solution were used. Heparin-S was taken as a representative of sulfate ester; stock sulfide solution (5mg/ml), stock thiosulfate solution (1mg/ml) and stock sulfite solution (1mg/ml) were all standardized in iodometrically before use. Working solutions were prepared by dilution of stock solutions before use. An acidic barium chromate solution (2.5mg/ml), a sodium

azide solution (3.1mol/L), a zinc acetate (0.4mol/L)-sodium acetate (0.15mol/L) solution a potassium iodide solution (1mol/L), and a zinc nitrate solution (0.1mol/L) were also used.

2.3 Analytical procedures

The fresh natural water samples to be tested were collected from the Fuhai Lake in the Yuan Ming Yuan (the Burnt Palace), Beijing, in April 1993 and taken from a depth below the water-air interface in the lake. After collected, each of the water samples was immedi-

ately divided into two portions as follows:

A: a turbid fresh water sample;

B: a fresh water sample filtered through a 0.45 μm microporous membrane, with the resulting filtrate used to be tested for dissolved sulfur species.

All the samples were stored at 4°C and isolated from air to prevent any oxidation reaction until their use for an analysis. The determinations were carried out within 24 h after sampling.

2.3.1 Determination of sulfide and thiosulfate (electroactive) with the catalytic coulometric method developed in our lab

To 200 ml of each fresh sample (A or B) 10 ml of 0.1 mol/L zinc acetate and 2.5 ml of 1 mol/L NaOH were added. The mixture was stirred completely, then the resulting precipitate was filtered off through a 0.45 μm filter, and transferred into an electrolytic cell (20°C) containing 10 ml of 0.02 mol/L sodium azide and 0.1 mol/L KI (pH 6.0), then the amount of sulfide was measured with the catalytic coulometric method (Li, 1993). 5 ml of the resulting solution (pH 7.0) was pipetted into an electrolytic cell (22°C) containing 5 ml of 0.06 mol/L sodium azide and 0.1 mol/L KI and was determined (pH 6.0) for the amount of thiosulfate by using the catalytic coulometric method.

2.3.2 Determination of sulfate, sulfate ester (non-electroactive) and total sulfur with the indirect coulometric method developed in our lab. (the water samples had to be pretreated for determining sulfate ester and total sulfur)

2.0 ml of fresh sample (A or B) was pipetted into a 25 ml volumetric flask, to which 2.0 ml of barium chromate solution, 4 ml of 6 mol/L ammonia water and 8 ml of anhydrous alcohol were added and the content was made up to the mark. The solution was filtered through a 0.45 μm filter. 7 ml of 4 mol/L HCl and 4 ml of 1 mol/L KI added to the filtrate and the mixture was allowed to stand for 20 min in the dark. After adding the standard thiosulfate solution, the excess of thiosulfate was titrated coulometrically with a blank being determined simultaneously.

2.3.3 Determination of sulfite (electroactive) with the constant current coulometric method developed in our lab

50 ml of each fresh sample (A or B) were adjusted with 0.2 mol/L NaOH to pH 13, then acidified with 0.5 mol/L sulfuric acid to liberate sulfur dioxide (Sullivan, 1990). The solution was bubbled with a stream of nitrogen for 40 min and the sulfur dioxide evolved was absorbed in 5 ml of 0.1 mol/L sodium tetrachloromercurate-0.5 mol/L KBr (pH 6.0). Sulfite was determined by using the method of Yan *et al.* (Yan, 1982).

3 Results and discussion

3.1 Determination of total sulfur by preoxidation

To oxidize all forms of sulfur compounds into sulfate, Nriagu *et al.* (Nriagu, 1985) used hydrogen peroxide and boiled the analyze for 1h, and Shan *et al.* (Shan, 1992) used NaOH to trap hydrogen sulfide which was then oxidized with hydrogen peroxide. However,

our results in this study show that 2 ml of turbid water sample(A) was oxidized by adding 2 drops of 30% hydrogen peroxide and then adding 1 ml 1 mol/L HCl and then boiled and evaporated on a water-bath to remove the excess hydrogen peroxide completely. Then the concentration of total sulfur was determined with the indirect coulometric method developed in our lab. The recovery in the method was 92.0–97.6%.

The relative standard deviation for the determination of 50 μ g sulfate in water under the optimized conditions was 1.9% ($n=9$). The recovery was from 95.3% to 102.8%.

3.2 Effect of saponification time on sulfate ester (represented by Heparin-S)

The amount of sulfate in sulfate ester was determined with method (2) indirectly. Through a saponification the sulfate was liberated from the sulfate ester at pH 13. The saponification was found to have an optimized time of 4 h and a recovery of 96.0% (Table 1).

Table 1 Effect of saponification time on sulfate ester

Reaction time, h	1	2	3	4
	17.5	21.7	23.8	24.2
SO ₄ ²⁻ , μ g	17.0	22.0	23.5	24.1
	17.2	22.2	23.7	23.9

Heparin-S sample containing 25.0 μ g sulfate

Table 2 Application of several pretreatment techniques to determining sulfur compounds

No.	Methods(theory)	Separation techniques	Determination methods	Ions
1	Physical-mechanical separation	Filtration	Coulometric analysis	SO ₄ ²⁻
2	Catalytic effect	Coprecipitation and distillation	Catalytic coulometry	H ₂ S, S ²⁻ S ₂ O ₃ ²⁻
3	Auxiliary balance	Solvent extraction	Polarography	S ⁰

3.3 Preconcentration of sulfide using distillation

The effect of pretreatment techniques on sulfur species was studied and shown in Table 2.

To preconcentrate and separate trace amount of sulfide from natural water, the water was pretreated by using distillation and coprecipitation. The conditions for recovering different amounts of sulfide from samples were optimized by distilling 100 ml of water sample with 30 ml of 4 mol/L HCl for 15 min at 50–60°C and bubbling with nitrogen. Evolved hydrogen sulfide was adsorbed in 5ml of zinc acetate-sodium acetate, then determined with catalytic coulometric titration. The results are listed in Table 3. The recovery was ranged from 72% to 88%. Therefore, the distillation method is not satisfactory.

Table 3 Results of distilling different concentration of sulfide

Taken S ²⁻ , ng	Distilling soln., ml	Absorbing soln., ml	Found S ²⁻ , ng	Recovery, %
50	100	5	42	80
50	100	5	36	72
100	100	5	88	88
100	100	5	85	85
250	100	5	215	86
250	100	5	205	82

3.4 Separation of sulfide and thiosulfide by coprecipitation

Sakuragawa *et al.* (Sakuragawa, 1980) used zinc nitrate-sodium carbonate coprecipitant in UV-VIS to determine sulfide. However, it was found to be unsuitable for an electroanalysis. Because carbonate was at a higher level in the water sample, the hydrogen sulfide produced from acidified precipitate was easy to evolve while producing carbon dioxide, and the carbon dioxide gas would be absorbed onto the surface of platinum electrodes and affected the assay results. Instead, satisfactory results can be obtained by using 10 ml of 0.1 mol/L zinc nitrate and 2.5 ml of 1 mol/L NaOH as coprecipitator in the determination of 200 ml sample. The effect of the amount of NaOH on the recovery is shown in Table 4.

Table 4 Effect of sodium hydroxide concentration on the recovery

Added S ²⁻ , ng	Volume of soln., ml	Coprecipitant, ml Zn(NO ₃) ₂ -NaOH		Recovery*, %
		0.1mol/L	1mol/L	
200	200	10	2.5	98
200	200	10	2.0	95
200	200	10	1.5	73
200	200	10	1.0	73

* Average value of three replicate determinations

The recovery was below 88% by using centrifugation (30min) to separate the precipitate, but it was increased to over 95% by filtering through a 0.45µm filter.

After prepreparing sulfide and thiosulfate by coprecipitation, the RSD of 9 replicate samples were 2.6% for 250ng of sulfide added and 1.1% for 100ng of thiosulfate added with a recovery of 97.5%–106.1% and 95.0%–100.5% respectively.

Studies on the conditions required to optimize the determination of dissolved sulfite, such as sodium tetrachloromercurate, KBr and NaOH concentrations, have been well investigated (Yan, 1982; Sullivan, 1990). These results have been confirmed through our experiments in our experimental system.

3.5 Extraction of dissolved hydrogen sulfide

To trap the dissolved hydrogen sulfide, 1000 ml of fresh sample was filled in a sealed flask and bubbled with a stream of nitrogen for 2 h and the evolved hydrogen sulfide gas was absorbed in 5 ml 0.4 mol/L zinc acetate-0.15 mol/L sodium acetate, then determined by method (1). The pre-separation method was applied to determining dissolved sulfide a level of 0.1 ng/L.

3.6 Application to lake water

Sulfur occurs in a wide range of species in water, which can be divided into five groups. They are closely related to pH in natural water. The dominant forms and species which are possible to exist are listed in Table 5.

Table 5 Dominant sulfur forms and species

No.	Oxidation No.	Molecules	Ions	Others
1	+6	H_2SO_4	HSO_4^- , SO_4^{2-}	Polysulfur
2	+4	H_2SO_3	HSO_3^- , SO_3^{2-}	Organic sulfur
3	+2		$\text{HS}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_3^{2-}$	
4	0	S^0		
5	-2	H_2S	HS^- , S^{2-}	

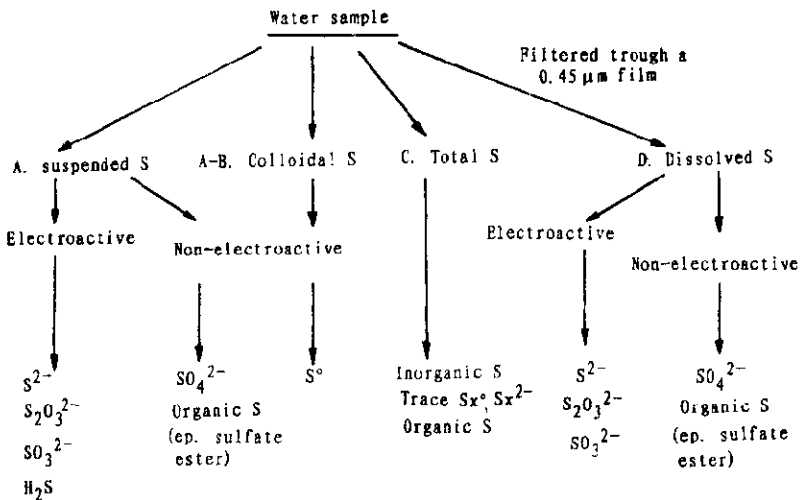


Fig. 2 Distribution scheme of major sulfur species

Jasiniski (Jasiniski, 1974) divided metal species into two groups: electroactive and non-electroactive species. For this reason and based on the electrical properties of sulfur ions, sulfur species was described by us as above scheme (Fig. 2) to describe the major sulfur species found in the Fuhai Lake in the Yuan Ming Yuan Park, Beijing. With the electrical properties of sulfur ions (or molecules) and coulometric titration methods, it was possible to directly and quantitatively measure all species, and to obtain the distribution of sulfur species

in dissolved, suspended and colloidal forms and total amount in natural water. The details are shown in Table 6.

Table 6 Assay results of sulfur speciation in the Fuhai Lake, Yuan Ming Yuan, Beijing

	No.	Dissolved S found, $\mu\text{g/ml}$	Suspended S found, $\mu\text{g/ml}$	Colloidal S found, $\mu\text{g/ml}$	Total amount found, $\mu\text{g/ml}$
SO_4^{2-}	1	58.5	7.0		65.5
	2	58.2	7.7		65.9
	3	58.7	6.5		65.2
S^{2-}	1	0.3×10^{-3}	2.7×10^{-3}		3.0×10^{-3}
	2	0.3×10^{-3}	4.2×10^{-3}		4.5×10^{-3}
	3	0.2×10^{-3}	3.0×10^{-3}		3.2×10^{-3}
H_2S					$< 0.2 \times 10^{-3}$
$\text{S}_2\text{O}_3^{2-}$	1	1.3×10^{-3}			1.3×10^{-3}
	2	1.9×10^{-3}			2.0×10^{-3}
	3	2.0×10^{-3}			2.0×10^{-3}
SO_3^{2-}	1	0.03			0.03
	2	0.04			0.04
	3	0.05			0.05
Colloidal S ^{**}				0.7×10^{-3}	0.7×10^{-3}
$\text{S}_x^0, \text{S}_x^{2-}$		—	—	—	—
Sulfate ester	1	2.1	0.3		2.4
	2	2.0	0.5		2.5
	3	2.2	0.4		2.6
Inorganic S*		58.4	7.1		65.5
Organic S*		8.8	0.9		9.7
Total S	1	67.5	7.6		75.1
	2	65.2	9.2		74.1
	3	68.9	7.2		76.1

* Average value of three replicate determinations; # The elemental colloidal S (non-electroactive) in 100ml water sample was extracted with CHCl_3 and then determined with the oscillcololar polarography developed by Zhao(Zhao, 1982)

Samples were taken in April 1993 with a pH value of 7.2 at a temperature of 7°C. The concentrations of all species were expressed as sulfate amount. Trace S_x^0 and S_x^{2-} were not detected. Suspended S was the difference between total sulfur and dissolved S.

Inorganic S = sulfate + sulfide + thiosulfate + sulfite + element sulfur

Organic S = total sulfur - inorganic S.

Comparative experiments were carried out and results are listed in Table 7.

Table 7 Assay results of sulfur species using comparative methods

Species	Assay result, $\mu\text{g/ml}$	Comparative method	Comparative experiment result, $\mu\text{g/ml}$
SO_4^{2-}	65.5	IC	64.2
S^{2-}	3.0×10^{-3}	Ocilopolar	1.6×10^{-3}
$\text{S}_2\text{O}_3^{2-}$	1.3×10^{-3}	Ocilopolar.	*
SO_3^{2-}	0.03	Ocilopolar	*
Total S	75.1	ICP	73.8

* Below the detection limit

4 Conclusion

The analysis results confirm the availability and reliability of the electroanalytical method and the speciation scheme for the determination and distribution of diverse sulfur species in natural water.

The application of the sensitive and accurate analytical procedures for the determination of dominant inorganic sulfur (including the transportation of some sulfur compound species) and organic sulfur in natural water has been demonstrated.

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(Received November 15, 1995)