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# Determination of sulfite in water samples by flow injection analysis with fluorescence detection

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## Abstract

A fast, sensitive, and reliable method for the determination of sulfite ( $\text{SO}_3^{2-}$ ) in fresh water and seawater samples was developed. The proposed method was based on the reaction of *o*-phthalaldehyde (OPA)–sulfite– $\text{NH}_3$  in alkaline solution, with flow injection analysis and fluorescence detection. The experimental parameters were investigated in pure water and seawater matrices. The detection limits ( $S/N = 3$ ) were  $0.006 \mu\text{mol/L}$  in pure water and  $0.018 \mu\text{mol/L}$  in seawater for  $\text{SO}_3^{2-}$ . The method was successfully applied to analyze  $\text{SO}_3^{2-}$  in the samples of rain water and flue gas desulfurization seawater.

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Sulfur dioxide ( $\text{SO}_2$ ) is a harmful gas that can result in acid rain and other environmental impairment.  $\text{SO}_2$  in atmosphere is discharged mostly from coal burning. The methods for  $\text{SO}_3^{2-}/\text{SO}_2$  determination are mostly in the field of food and air analysis. For example, formaldehyde absorbing-*o*-phthalaldehyde spectrophotometry method is widely applied in  $\text{SO}_3^{2-}/\text{SO}_2$  determination for air, water and food analysis [1,2]. However, the detection limits of existing methods are high and not suitable for samples of low  $\text{SO}_3^{2-}$  concentration analysis. On the other hand, the existing methods rarely consider the interference from complicated matrix samples such as seawater.

The technology for seawater flue gas desulfurization is widely adopted by coal-fired power plants in coastal areas.  $\text{SO}_2$  in the flue gas is absorbed by fresh seawater and transfers into aqueous phase as  $\text{SO}_3^{2-}$ . Therefore, it is necessary to determine the concentration of  $\text{SO}_3^{2-}$  in the seawater to evaluate the process of desulfurization, the efficiency of  $\text{SO}_3^{2-}/\text{SO}_4^{2-}$  conversion, and monitor the impact of waste seawater containing  $\text{SO}_3^{2-}$  on sea area. Thus, a method suitable for the determination of  $\text{SO}_3^{2-}$  in complicated seawater matrix is needed.

The method adopted in this research was based on the reaction of sulfite with *o*-phthalaldehyde (OPA) and ammonium. OPA reacts with molecules containing primary amino group in the presence of mercaptoethanol/thiol and in an alkaline medium to give a highly fluorescent product called isoindole [3]. Zhang and Dasgupta [4] modified the method by replacing mercaptoethanol with sulfite, and the OPA–sulfite– $\text{NH}_3$  reaction has been adopted for a variety of applications, such as determination of ammonium in seawater [5,6] and atmospheric ammonia [7] and amino acids in

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clinical samples [8]. The isoindole derived from OPA–sulfite–NH<sub>3</sub> reaction can be determined at  $\lambda_{\text{ex}} = 362.5$  nm and  $\lambda_{\text{em}} = 423.0$  nm with a fluorescence detector [5]. However, studies of sulfite determination on the basis of OPA–sulfite–NH<sub>3</sub> reaction are few. Tzanavaras et al. [9] determined total sulfite in wines based on the reaction of OPA and NH<sub>4</sub>Cl in basic medium with sequential injection technique.

In this work, the reaction of OPA–sulfite–NH<sub>3</sub> in alkaline solution was applied to determine SO<sub>3</sub><sup>2-</sup> in water samples. The reagents and instrumental parameters were investigated to suit the analyses of fresh water and seawater, respectively.

## 1. Experimental

### 1.1. Reagents

OPA, NH<sub>4</sub>Cl, ethanol, Na<sub>2</sub>SO<sub>3</sub>, HCHO, Na<sub>2</sub>HPO<sub>4</sub>, borax and NaOH were purchased from Sinopharm Chemical Reagent Co., China. Pure water (18.2 M $\Omega$  cm) was obtained from a Milli-Q water purification system (Millipore Co., USA). Reagent 1 (R1), containing 10 mmol/L of OPA, was made by dissolving 1.34 g OPA in 75 mL ethanol and diluting to 1 L with pure water. Reagent 2 (R2), containing 2.5 mmol/L of NH<sub>4</sub>Cl, was made by dissolving 0.134 g NH<sub>4</sub>Cl in 1 L pure water, Na<sub>2</sub>HPO<sub>4</sub> was used as buffer at a concentration of 34.4 mmol/L, pH was adjusted with NaOH solution. R2 was used for freshwater measurement. Reagent 3 (R3), containing 2.5 mmol/L of NH<sub>4</sub>Cl, borax was used as buffer at a concentration of 13.5 g/L, pH was adjusted with NaOH solution. R3 was used for seawater measurement.

### 1.2. Standards

A 10 mmol/L SO<sub>3</sub><sup>2-</sup> stock solution was made daily by dissolving sodium sulfite solid (its purity was determined before use) in 100 mL of 10 mmol/L HCHO solution.

### 1.3. Sampling

The rain water sample was collected in Xiamen University campus, November 12, 2009. The seawater samples were obtained from the aeration tank of flue gas desulfurization waste seawater inside a power plant and sea area near to waste seawater discharging outlets. Samples were added with HCHO right after collection to reach a concentration of 1 mmol/L HCHO in samples, and filtrated through a filter membrane of 0.45  $\mu\text{m}$  pore diameter before analyzing. Samples with high SO<sub>3</sub><sup>2-</sup> concentration should be diluted before analysis.

### 1.4. Analytical equipments

HH-1 water bath device (Shunhua Instrument Inc., Jintan, China), a 4-channel LEAD-1 peristaltic pump (Longer Precision Pump Inc., Baoding, China), a 6-way Vici valve (Valco Co., USA), and a flow-through RF-10A XL fluorescence detector (Shimadzu Co., Japan).

The flow injection analysis (FIA) schematic diagram is shown in Fig. 1. Samples or standard solutions were pumped into sampling loop at filled position. Pure water or seawater was used as a carrier at injection position to put the sample zone forward. R1 merged with R2 in the connecting tube at first, and then mixed with sample stream in a heated mixing coil (65 °C). The sample throughput was 20 h<sup>-1</sup>, with triple determination for each. The final fluorescent product was detected with the fluorescence detector.

## 2. Results and discussion

### 2.1. Spectral characteristic

The maximum wavelengths of excitation and emission were located at 361.0 and 422.0 nm, respectively, determined with a scanning Varian Cary Eclipse fluorescence spectrophotometer (Varian Co., USA).

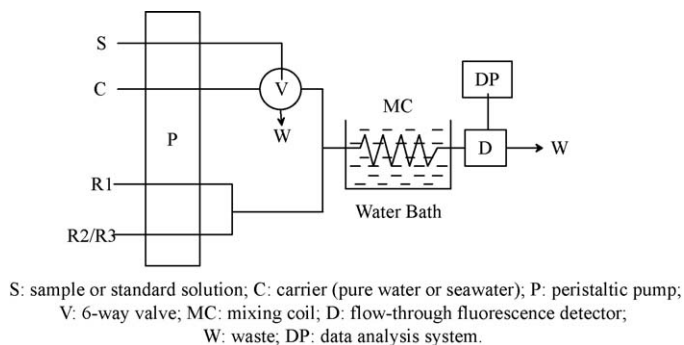


Fig. 1. Schematic diagram of FIA-fluorescence determination for  $\text{SO}_3^{2-}$  detection. S: sample or standard solution; C: carrier (pure water or seawater); P: peristaltic pump; V: 6-way valve; MC: mixing coil; D: flow-through fluorescence detector; W: waste; DP: data analysis system.

## 2.2. Reagent composition

Optimal parameters for fresh water analysis were studied by analyzing  $\text{SO}_3^{2-}$  at a concentration of  $1 \mu\text{mol/L}$  in pure water matrix. Carrier was pure water. The results showed that the fluorescence intensity increased with OPA concentration in the range of 1–20 mmol/L, the chosen concentration was 10 mmol/L for it was satisfactory enough for sensitivity. The optimal concentration of  $\text{NH}_4\text{Cl}$  in R2 was 2.5 mmol/L. Solution pH had a significant effect on the signal. The sensitivity of the detection would be substantially decreased when the pH of R2 was outside the range of 10.3–11.2. Final pH of R2 was adjusted to 10.70 with NaOH solution. Since  $\text{SO}_3^{2-}$  is easy to be reduced, HCHO was chosen as a protective agent for  $\text{SO}_3^{2-}$ . The fluorescence intensity decreased slowly as the concentration of HCHO increased in the range of 1–1500  $\mu\text{mol/L}$ . Considering the amount of  $\text{SO}_3^{2-}$  in real samples, concentration of HCHO was chosen at 1000  $\mu\text{mol/L}$  for its acceptable influence on sensitivity and adequate amount for protection.

Temperature, loop/coil length, and flow rate: Increasing the reaction temperature was effective in accelerating the desired reaction in the range of 30–75 °C. 65 °C was chosen as the water bath temperature for bubbles would form inside the system and cause erroneous signals under higher temperature. Optimal length of the sampling loop and mixing coil were found to be 73 cm and 257 cm, corresponding to 0.66 mL and 2.31 mL, respectively. The optimal flow rates were 0.45 mL/min for R1, R2, R3 and carrier, 0.47 mL/min for sample and standard, respectively.

## 2.3. Performance in pure water analysis

Under the optimum conditions, there was a good linear relationship between  $\text{SO}_3^{2-}$  concentration and signal for pure water matrix. The linear range, linear equation and detection limit ( $S/N = 3$ ) were 0.1–20  $\mu\text{mol/L}$ ,  $F = 22.9404C + 0.5121$  ( $n = 6$ ,  $R^2 = 0.99998$ ), 0.006  $\mu\text{mol/L}$ , respectively. Precision of this method was also examined, pure water spiked at 1  $\mu\text{mol/L}$  and 10  $\mu\text{mol/L}$   $\text{SO}_3^{2-}$  was determined continuously for 7 times, the RSDs were 1.65% and 1.02%, respectively.

## 2.4. Interference study

The potential interference existing in real water samples was studied. The permission concentrations of coexisting ions for the determination of 1  $\mu\text{mol/L}$   $\text{SO}_3^{2-}$  with deviation less than  $\pm 5\%$  was listed in Table 1. It can be also seen from Table 1 that the interference of  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$  was significant (deviation over  $\pm 5\%$ ), therefore, it is highly recommended to use the real water, which has similar characteristics with samples and is free of  $\text{SO}_3^{2-}$ , as the

Table 1  
Coexisting and interference ions and the interference level.

Coexisting and interference ions	$\text{K}^+$	$\text{Na}^+$	$\text{Al}^{3+}$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{NO}_2^-$	$\text{F}^-$	$\text{I}^-$	$\text{S}^{2-}$	$\text{Ca}^{2+}$	$\text{SO}_4^{2-}$	$\text{CO}_3^{2-}$
Added concentration ( $\mu\text{mol/L}$ )	10,000	20,000	3.7	10,000	10,000	10	50	80	1	1800	10,000	1700
Interference level (%)	$< \pm 5$	$< \pm 5$	$< \pm 5$	$< \pm 5$	$< \pm 5$	$< \pm 5$	$< \pm 5$	$< \pm 5$	$< \pm 5$	-12.9	+21.8	+10.3

matrix to prepare standard solutions and as the carrier solution. The  $\text{SO}_3^{2-}$  free water could be obtained by exposing the water in the air for several days.

In previous studies, mercaptoethanol was used with OPA as the reagent for the determination of ammonia and amino acid [3], so that the interference of mercaptoethanol was studied. It was found that the signal produced by  $10 \mu\text{mol/L}$  mercaptoethanol was equal to  $0.05 \mu\text{mol/L}$   $\text{SO}_3^{2-}$ . Thus the interference of mercaptoethanol can be ignored for it rarely exists in natural waters and it has little influence on  $\text{SO}_3^{2-}$  determination.

### 2.5. Application in rain water analysis

The method described above was applied in analyzing the rain water sample. In order to eliminate the interference in rain water matrix, the determination was carried out with standard addition method, and the  $\text{SO}_3^{2-}$  concentration was  $1.26 \mu\text{mol/L}$ .

### 2.6. pH and buffer for seawater analysis

High pH in the test solution or sample, for example, seawater, would cause precipitation. Thus, R2 was substituted by R3. The optimal pH of R3 and buffer were investigated. It was found that pH 9.52 was the best for R3. The precipitation of hydroxide was found, when mixing  $\text{Na}_2\text{HPO}_4$  with sea water. For the analysis of seawater, the buffer in R3 was borax and its optimal concentration was  $13.5 \text{ g/L}$ . Carrier was seawater. Other experimental parameters were the same as those in fresh water analysis.

### 2.7. Performance in seawater analysis

The developed method was applied in analyzing the waste seawater of flue gas desulfurization. A typical calibration series was shown in Fig. 2. The linear range, linear equation and detection limit were  $0.1\text{--}20 \mu\text{mol/L}$ ,  $F = 7.9031C + 0.0549$  ( $n = 7$ ,  $R^2 = 0.99999$ ),  $0.018 \mu\text{mol/L}$ , respectively. Seawater spiked at  $10 \mu\text{mol/L}$   $\text{SO}_3^{2-}$  was determined continuously for 5 times, the RSD was 0.73%. Recoveries from seawater matrix were 93.5–103.9%, which were acceptable.

### 2.8. Comparison with reference method

The two samples were collected from the aeration tank of a flue gas desulfurization waste seawater. Comparison of the analytical results of the proposed method and reference method (pararosaniline spectrophotometric method) [10] was shown as Table 2. There was no significant statistical difference between the two methods with the paired Student's *t*-test at 95% confidence level.

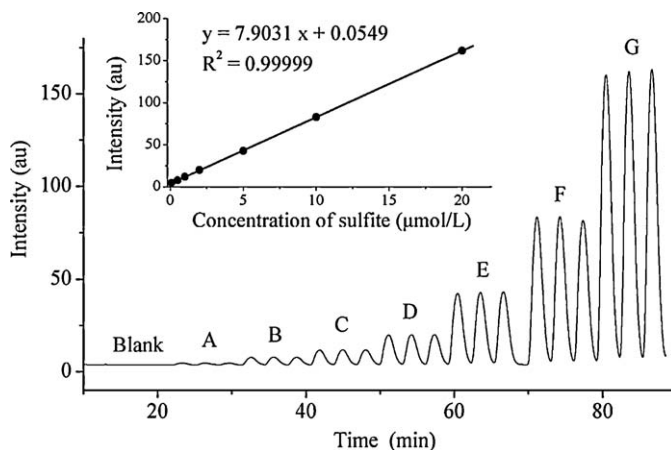


Fig. 2. Typical signal output and calibration curve of seawater spiked at  $0.1\text{--}20 \mu\text{mol/L}$   $\text{SO}_3^{2-}$ . (A)  $0.1 \mu\text{mol/L}$ ; (B)  $0.5 \mu\text{mol/L}$ ; (C)  $1 \mu\text{mol/L}$ ; (D)  $2 \mu\text{mol/L}$ ; (E)  $5 \mu\text{mol/L}$ ; (F)  $10 \mu\text{mol/L}$ ; (G)  $20 \mu\text{mol/L}$ .

Table 2  
Comparison of analytical results of the proposed method and a reference method [10].

Sample	Cp ± S.D. (n = 4, μmol/L)		Calculated t-value	Critical t-value (P = 0.95)
	Proposed method	Reference method		
1	10.56 ± 0.16	10.61 ± 2.42	0.03	2.45
2	15.05 ± 0.13	15.30 ± 1.29	0.32	2.45

### 3. Conclusion

A sensitive, fast and reliable method was developed for the determination of  $\text{SO}_3^{2-}$  in fresh water and seawater samples. It showed no significant difference with the classical pararosaniline spectrophotometry method. This method was suitable for the analysis of  $\text{SO}_3^{2-}$  in acid rain, the evaluation of flue gas desulfurization and aeration efficiency through  $\text{SO}_3^{2-}$  determination, as well as the analysis of other water samples with complicated matrix.

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