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Short communication

## Determination of organic anions in waste liquid of sodium hydrosulfite production by ion chromatography

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### Abstract

An ion chromatographic method for simultaneous determination of formate, hydroxyethyl sulfonate (HES), hydroxyethyl thiosulfate (HET), and coexisting anions in the industrial waste liquid of sodium hydrosulfite production was developed. The mixture of 1.6 mmol/l of phthalic acid and 1.2 mmol/l tri-(hydroxyethyl) aminomethane was used as eluent. The interference of coexisting sulfite anion with HES was avoided by selective oxidation with hydrogen peroxide as oxidizer. The other coexisting inorganic anions,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  can be determined simultaneously. The linear range of the peak area calibration curves for all analytes was up to two or three orders of magnitude. The detection limits ( $S/N=3$ ) for formate, HES and HET were 2.4, 1.0 and 0.5 mg/l, respectively. The recoveries for all analytes were 91.61–100.6%. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Sodium hydrosulfite; Formate; Hydroxyethyl sulfonate; Hydroxyethyl thiosulfate

### 1. Introduction

Sodium hydroxyethyl sulfonate (SHES,  $\text{HOC}_2\text{H}_4\text{SO}_3\text{Na}$ ), sodium hydroxyethyl thiosulfate (SHET,  $\text{HOC}_2\text{H}_4\text{S}_2\text{O}_3\text{Na}$ ) and sodium formate (SF,  $\text{HCOONa}$ ) which hold a great proportion in final waste liquid are the main by-products of sodium hydrosulfite ( $\text{SHS}$ ,  $\text{Na}_2\text{S}_2\text{O}_4$ ) production. In order to regenerate the resource and reduce the pollution of the waste liquid to the environment, the best way is to reclaim these by-products from the waste liquid. SF is a common chemical reagent, and its reclaiming process from the waste liquid of SHS production is running at Guangdong Zhongcheng Chemicals Co. Ltd. in China. SHES and SHET have been confirmed

to be useful as additives of detergents, but no application examples of reclaiming SHES and SHET from the waste liquid of SHS production were reported. The feasibility of the technological process of reclaiming SHES and SHET is currently being investigated.

In order to estimate the value of the reclaiming project, design the technological process and control the quality of the reclaimed products, it is important to determine the concentration of the by-product such as SHES, SHET and SF in the waste liquid. However, it seems very difficult because there are several kinds of coexisting inorganic anions in the industrial waste liquid. Ion chromatography (IC) is the best method for the simultaneous analysis of ionic analytes [1,2], but the simultaneous determination of SHES, SHET and SF by IC has not been

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reported up to now. In our study, an IC method for the simultaneous determination of SHES, SHET, SF and coexisting inorganic anions in industrial waste liquid was developed.

## 2. Experimental

### 2.1. Apparatus and chemicals

The ion chromatograph HIC-6A (Shimadzu, Japan) was used in our study. It consists of an LP-6A liquid delivery pump, a CTO-6AS column oven, a CCD-6A conductivity detector and a Shimadzu data system (C-R4A).

All chemicals used were of analytical–reagent grade, and deionized water was used throughout the experiment. SHES and SHET were synthesized in Guangdong Zhongcheng Chemicals Co. Ltd. (China). The stock solution of anions (1000 mg/l) was prepared by dissolving its sodium salt in water and was diluted to suitable concentration before use. The eluent used in this study was a mixture of 1.6 mmol/l of phthalic acid (PA) and 1.2 mmol/l tri-(hydroxyethyl) aminomethane (TRIS), and it was prepared by dissolving 0.42 g PA and 0.145 g TRIS in 1000 ml of deionized water.

### 2.2. Chromatographic conditions

An anion exchange column Shimpak IC-A1 (4.6 mm I.D.×100 mm) was used. The mobile phase was a mixture of 1.6 mmol/l PA and 1.2 mmol/l TRIS. The flow-rate was 1.2 ml/min. The temperature of the column oven was set at 40°C. Samples were injected by a 20 µl loop injector. The sensitivity of the conductivity detector was 1 µs/cm.

### 2.3. Sample preparation

A 1.0 g amount of industrial waste liquid was dissolved in about 20 ml deionized water in a beaker, 2–3 drops 30% H<sub>2</sub>O<sub>2</sub> was added, and then diluted to 100 ml with deionized water. It was filtered through

a 0.45 µm membrane filter and diluted to suitable concentration before injection.

## 3. Results and discussion

### 3.1. Selection of eluent

The main anions in the industrial waste liquid of SHS production include formate, HES, HET, Cl<sup>-</sup>, SO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>. In our work, a non-suppressed IC was used to separate the above anions. The common eluents of non-suppressed IC are electrolyte solution with lower conductance, such as carboxylic acid and carboxylate. Several kinds of eluent such as potassium hydrogenphthalate, oxalic acid, tartaric acid, pyromellitate, PA/TRIS were investigated. The mixture of PA and TRIS was found to be the most suitable eluent for the above anions. TRIS was employed to adjust the pH of the eluent and the concentration of eluent ion (phthalate). When PA and TRIS were mixed, PA would be neutralized partly by TRIS, and the pH of the eluent and the concentration of phthalate were increased. Thus, the elution capability of the mixed eluent would be increased as the ratio of TRIS increased in the eluent. The separation efficiency of the anions was low when the capability of the eluent was too strong, however thiosulfate anion would be difficult to be eluted when the elution capability of the eluent was too weak. By comparing several different ratios of PA and TRIS, a better separation was obtained when the ratio of PA and TRIS was 1.6 to 1.2 mmol/l. In addition, the mixed eluent PA/TRIS had two other advantages. The first, the mixed eluent could provide a higher buffering capacity, and the second, a higher detection sensitivity could be obtained because TRIS lowered the background conductance of the eluent. The chromatogram of a standard mixture is shown in Fig. 1. Under this condition, the peak of sulfite anion was overlapped with the peak of HES. It was necessary to avoid the interference of sulfite anion for the quantitative determination of HES. A pretreatment procedure of oxidizing sulfite anion to sulfate anion selectively was used in order to eliminate the interference of sulfite anion. 2-Thioethanol (HOC<sub>2</sub>H<sub>4</sub>SH) was also retained on the column under the same conditions. It eluted faster than all other anions.

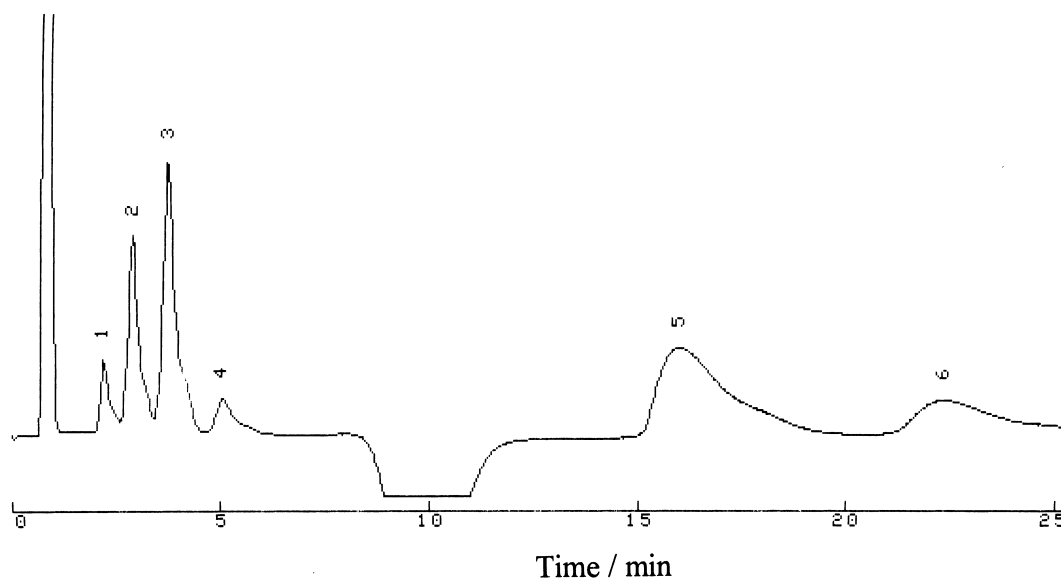


Fig. 1. Chromatograms of a standard mixture. Column: Shimpak IC-AI; Eluent: 1.6 mmol/l PA+1.2 mmol/l TRIS; Flow rate: 1.2 ml/min. Sample size: 20  $\mu$ l; Peaks (mg/l): 1=formate (40), 2=HES (90), 3= $\text{Cl}^-$  (20), 4=HET (40), 5= $\text{SO}_4^{2-}$  (80), 6= $\text{S}_2\text{O}_3^{2-}$  (50).

2-Thioethanol was oxidized partly and the reproducibility of its oxidizing reaction was not good, so it was not contained in the standard mixture in Fig. 1.

### 3.2. The selective oxidation of sulfite anion

It was difficult to separate HES from sulfite anion under the above selected conditions, so it was important to eliminate the interference of sulfite anion. A pretreatment method of oxidizing sulfite anion to sulfate anion was considered. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was used in this method.

A series of experiments were done to find the amount of  $\text{H}_2\text{O}_2$  for oxidizing the sulfite anion. The effects of  $\text{H}_2\text{O}_2$  on the oxidation of HES, HET and 2-thioethanol were studied. Sulfite anion could be oxidized completely when the molar amount of  $\text{H}_2\text{O}_2$  was four times of it and at the same time HES and HET were not nearly oxidized with a lower relative deviation (about  $\pm 0.8\%$ ). The content of sodium sulfite in real samples was under 5%, which meant at most 50 mg (about 0.4 mmol) of sodium sulfite in 1 g sample, so that it could be oxidized completely when 2–3 drops of 30%  $\text{H}_2\text{O}_2$  (about 2.3–3.5 mmol) were added. 2-Thioethanol was oxi-

dized partly and the reproducibility of its oxidizing reaction was not good.

### 3.3. Detection limits and linear range

The peak area calibration curves were used for the quantitative analysis of the anions in our work. The detection limits and the linear range of calibration curves for formate, HES, HET and main coexisting inorganic anions are listed in Table 1. The detection limits were calculated from the peak height of analytes diluted appropriately and the noise height at a signal-to-noise ratio of three. The calibration curves of formate, HES and HET had the linear range up to two or three orders of magnitude. The detection limits of formate, HES and HET were 2.4,

Table 1  
Linear range and detection limit ( $S/N=3$ ) of several analytes

Ion	Linear range (mg/l)	Detection limit (mg/l)
$\text{HCOO}^-$	4.0–1000	2.4
$\text{HOC}_2\text{H}_4\text{SO}_3^-$	1.0–1000	1.0
$\text{HOC}_2\text{H}_4\text{S}_2\text{O}_3^{2-}$	1.0–000	0.5
$\text{Cl}^-$	2.0–4000	0.2
$\text{SO}_4^{2-}$	4.0–2000	2.0
$\text{S}_2\text{O}_3^{2-}$	10–2000	5.4

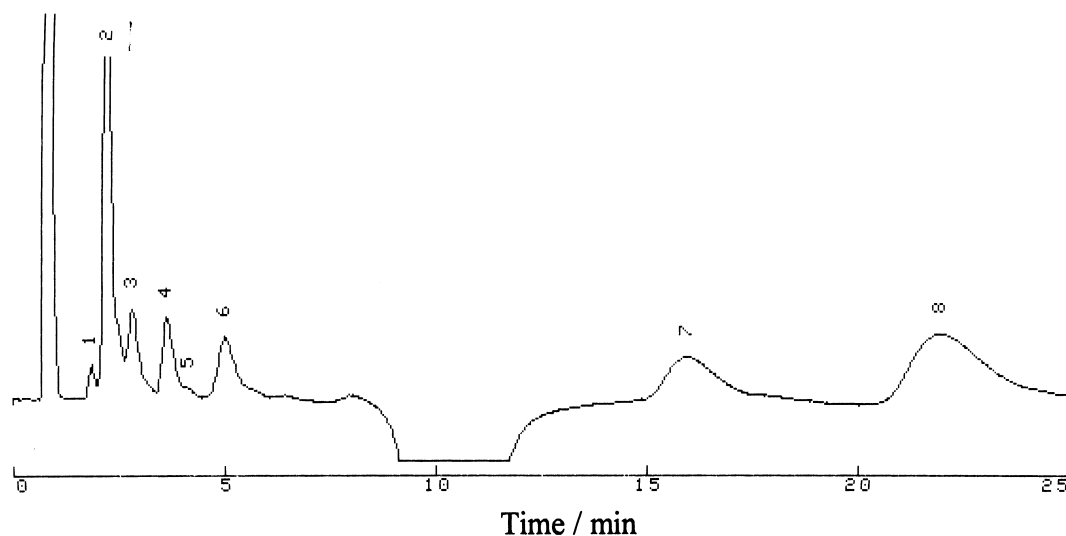


Fig. 2. Chromatogram of an industrial waste liquid. Conditions were the same as in Fig. 1. Peaks: 1=2-thioethanol, 2=formate, 3=HES, 4=Cl<sup>-</sup>, 5=unknown, 6=HET, 7=SO<sub>4</sub><sup>2-</sup>, 8=S<sub>2</sub>O<sub>3</sub><sup>2-</sup>.

1.0 and 0.5 mg/l, respectively, which approached the sensitivity of inorganic anions.

### 3.3.1. Analysis of real samples

The IC method developed in our work was applied to determine formate, HES, HET, and coexisting inorganic anions in industrial waste liquid of SHS production. The chromatogram of a real sample is shown in Fig. 2. A good separation was obtained. The interferences from other common anions were investigated. SO<sub>3</sub><sup>2-</sup> interfered HES, and other common anions such as acetic acid, NO<sub>3</sub><sup>-</sup>, Br<sup>-</sup> could be separated simultaneously, but these anions were not detected in the waste liquid. The determination

results of a real sample are listed in Table 2. The waste liquid in the vessel was not well-distributed. The upper solution in the vessel was dilute and some salt crystal was at the bottom of the vessel. The upper part was determined in this work. As shown in Table 2, the recovery for S<sub>2</sub>O<sub>3</sub><sup>2-</sup> was lower (91.61%), but for other ions was good (96.65–100.6%). The relative standard deviations (RSD) were 0.46–4.2% for the ions determined.

It is difficult to determine 2-thioethanol by this method because it was oxidized partly by H<sub>2</sub>O<sub>2</sub>. The content of sulphate anion listed in Table 2 was the total value of sulphate anion and sulfite anion in the original sample.

Table 2  
The determination results and recoveries of the ions in a waste liquid sample

Analyte	Content in sample (g/l)	RSD (%)	Added (mg/l)	Found (mg/l)	Recovery (%)
HCOONa	74.21	0.46	20.00	19.45	97.25
HOC <sub>2</sub> H <sub>4</sub> SO <sub>3</sub> Na	12.95	3.18	45.00	45.23	100.1
HOC <sub>2</sub> H <sub>4</sub> S <sub>2</sub> O <sub>3</sub> Na	21.36	1.44	20.00	19.56	96.65
Cl <sup>-</sup>	1.36	0.75	8.50	8.52	100.2
SO <sub>4</sub> <sup>2-</sup>	7.88	2.54	40.00	40.24	100.6
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	23.86	4.20	25.50	23.36	91.61

#### **4. Conclusion**

The method developed in this work can be used for the simultaneous determination of formate, HES, HET and other coexisting inorganic anions in industrial waste liquid. This method is useful for the design of technological processes of reclaiming formate, HES and HET, and the quality control of the products of formate, HES and HET.

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