Flow-Injection Spectrophotometric Determination of Micro
Amounts of Sulfate Ion in Surface- and Sea-Water Samples
with a Barium Chromate Reaction Column

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A rapid and simple flow-injection method using a reaction column packed with barium chromate powder is described for
the determination of micro amounts of sulfate ion in surface- and sea-water samples. An aqueous solution containing
4.5 mM sodium acetate and 4% ethanol was used as a carrier solution at a flow rate of 0.8 ml/min. The absorbance of
the chromate ion (which corresponds to the sulfate ion concentration) in the carrier solution from the reaction column was
measured using a photometric detector at 370 nm. Interference from some cations was eliminated by the use of a cation-
exchange resin column installed in front of the reaction column; interference from some anions was reduced by using the
carrier solution mentioned above. The concentration range from 0.5 to 5 ppm of the sulfate ion in practical water
samples can be determined by the proposed method with good reproducibility.

Keywords Flow injection analysis, barium chromate reaction column, sulfate ion, surface water, seawater

Various methods for determining the sulfate ion have
been suggested by many workers. They include
spectrophotometry1-3, ion chromatography4, indirect
atomic absorption spectrometry5 and a catalytic method
using a zirconium(IV)-Xylenol Orange reaction.6
Spectrophotometry using either barium chromate or
barium chloranilate, as well as ion chromatography, have
been well used for determining the sulfate ion con-
centration in surface- and sea-water samples. The principle of the sulfate ion determination using those
reagents is based on an exchange reaction between the
sulfate ion and solid barium chromate or barium
chloranilate; that is, solid barium sulfate is formed while liberating colored chromate or the chloranilate ion.
Such spectrophotometric methods, however, are con-
siderably time-consuming and are not suitable for
treating a large number of samples.

Flow injection analysis (FIA) has been applied to the
determination of several anions and cations.7 Toei
introduced the flow-injection method to a reaction
system in which the reaction of a solid reagent with a
liquid sample was proceeded in a stirred chamber
especially designed to meet with the flow system.8
Yakata et al. have described a FIA for the determination
of the sulfate ion in rain- and spring-water samples as a
very simple and highly sensitive method using the
reaction between a solid reagent and a liquid sample.9,10
These methods used a manifold in which a reaction
column packed with solid barium chloranilate or
cellulose beads containing barium chloranilate was
incorporated, and could determine down to 4 ppm of the
sulfate ion.

Utsumi et al. proposed some manual spectrophoto-
metric methods for the sulfate ion using solid barium
chromate or a suspension of barium chromate.9,11 In
this paper the authors report on the determination of the
sulfate ion in surface- and sea-water samples, using a
manifold in which a reaction column packed with solid
barium chromate is incorporated. The proposed proce-
dure is very simple; one sample per 2.5 min can be treated
in determining the sulfate ion down to 0.5 ppm. The
proposed method is superior to other methods9,10 from
the viewpoint of the determination limit, and has been
successfully applied to the determination of practical
samples. Since the reaction was greatly affected by the
presence of various cations, the interference was removed
by using a flow system incorporating a cation-exchange
resin column. Further, the interference from some
anions was reduced by using an aqueous solution
containing sodium acetate and ethanol, instead of pure
water as a carrier solution. The proposed method is
based on the following reaction:

\[
\text{SO}_4^{2-} + \text{BaCrO}_4 \rightarrow \text{BaSO}_4 + \text{CrO}_4^{2-}
\]

\[
\uparrow \quad \uparrow \quad \uparrow
\]

(solid) (solid) (dissolved in

carrier(yellow)).
Experimental

Reagents

All of the chemicals used were of guaranteed reagent grade, except for barium chromate. Barium chromate was obtained from Wako Pure Chemical Industries Ltd., and was used with further purification.

All of the solutions were prepared with ultra-pure water obtained by a Milli-Q SP Reagent Water System (Millipore Co.).

Standard sulfate solution (1000 ppm SO₄²⁻). Sodium sulfate (0.1479 g) was dissolved in water, and diluted to exactly 100 ml (=cm³). The working solution was diluted as required.

0.1 M sodium acetate stock solution. Sodium acetate anhydrous (8.202 g) was dissolved in 11 (=dm³) of water. Carrier solution (4.5 mM CH₃COONa and 4% ethanol). The carrier solution was prepared by mixing 45 ml of a 0.1 M sodium acetate stock solution and 40 ml of ethanol and diluting to 1 l with water.

Apparatus and analytical procedure

The flow system used for determining the sulfate ion is shown in Fig. 1. The carrier solution was pumped into a flow system of stainless-steel tubing (0.5 mm i.d.) with an Intelligent HPLC pump (JASCO 880-PU) at a flow rate of 0.80 ml/min. A sample solution (50 µl) was injected through a Rheodyne 7125 syringe loading sample injector valve (50 µl loop) into the stream of the carrier solution. A cation-exchange resin column (4.0 mm i.d. x 50 mm) packed with Dowex 50W-X4 (100 - 200 mesh) cation-exchange resin (prepared for sodium form type) and a reaction column (the same size as the cation-exchange column) packed with a purified barium chromate powder (0.5 g) are located in series behind the injector valve. The chromate ion concentration (which corresponds to the sulfate ion concentration) in the carrier solution from the reaction column was monitored by an Intelligent photometric detector (JASCO 870-UV; equipped with a flow cell of 8 µl) at 370 nm, and was then recorded on a Nippon Denshi Kagaku (Model u-228) chart recorder as a peak height. The peak height was used for quantification of the sulfate ion.

Results and discussion

Calibration curve

The proposed method gave a linear calibration curve in the concentration range of 0.5 to 5 ppm sulfate ion; thus, the sensitivity is approximately 10-fold as good as that of the methods reported by Yakata et al. The relative standard deviation of ten measurements was 0.75% for a 3 ppm sulfate ion standard solution.

Composition of the carrier solution

When pure water was used as a carrier solution, there was no problem regarding the stability of the base line and the sensitivity. However, the water carrier resulted in the influence of some co-existing anions. We examined carrier solutions of various compositions in order to develop an useful method for determining small amounts of sulfate ions. The influence of some anions could be considerably lowered by using an aqueous solution containing sodium acetate and ethanol. Various concentrations of sodium acetate, ranging from 1 mM to 7 mM in the carrier solution, were tested. The results are shown in Fig. 2. Both peak heights for 1 and 5 ppm sulfate ion increased with an increase in the concentration of sodium acetate; the peak heights then remained constant over the sodium acetate concentration in the range of 4 mM - 7 mM. Further, the difference in the peak heights between 1 and 5 ppm sulfate ion almost became constant in that region.

On the other hand, the solubility of barium chromate is depressed in the presence of organic solvents. It was reported that the reaction with sulfate ion could be carried out in 40% ethanol. After examining carrier solutions of various ethanol concentrations, 4% ethanol

![Fig. 1: FIA system: C, carrier solution (4.5 mM CH₃COONa-4% C₂H₅OH); P, pump (flow rate, 0.80 ml/min); S, sample injector (50 µl) IEC, cation-exchange resin column; RC, reaction column; D, detector; Rec., recorder and W, waste.](image1)

![Fig. 2: Effect of the sodium acetate concentration on the peak height. Each solution contains 4% C₂H₅OH. Flow rate, 0.8 ml/min; sample volume, 50 µl; wavelength, 370 nm; O, sulfate ion 1 ppm; Δ, sulfate ion 5 ppm.](image2)
was chosen after considering the sensitivity, the durability of the reaction column and the stability of the base line. Consequently, an aqueous solution containing 4.5 mM sodium acetate and 4% ethanol was found to be suitable as a carrier solution.

When an FIA system with a single stream as a carrier was used and pure water as a sample solution was injected into the carrier stream, a positive peak occurred in the FIA chart. This was due to the dissolution of solid barium chromate, which was caused by the dilution of ethanol in the carrier solution with the injected sample solution.

**Packing of the reaction column**

In case a reaction column packed with a solid reagent is handled, it is important to prepare reaction columns with uniform sensitivity, as pointed out by Yakata et al.9 After trying some methods to prepare such a reaction column, we introduced a dry packing method because the procedure gave the most desirable result.

Dry barium chromate powder (about 0.5 g) previously purified and grained by an agate mortar was packed into an empty stainless-steel column (4.0 mm i.d. X 50 mm) with one end plugged with a glass-wool ball. After filling the column with barium chromate powder, it was subjected to centrifugation at 2000 rpm for 1 min in order to pack the reagent particles into the column uniformly. Then, the open end was plugged with another glass-wool ball. Since the grain size of barium chromate packed scarcely affected the sensitivity or reproducibility for determining the sulfate ion, the reagent without dry sieving was packed into the column. The columns prepared by the above-mentioned procedure gave reproducible results after the injection of 150 samples (3 ppm standard sulfate ion solution).

**Injection volume**

The effect of the sample volume over the 25 - 150 µl range was investigated by injecting a 3 ppm sulfate ion solution. The results are summarized in Fig. 3. Although the absorbance increased with an increase in the sample volume, 50 µl was chosen for subsequent experiments by considering the sensitivity, durability of the reaction column and reproducibility of the peak heights.

**Flow rate**

To establish the optimum flow rate, experiments were carried out over a range of 0.6 - 1.4 ml/min by injecting a 3 ppm sulfate ion solution. The results are shown in Fig. 4. The maximum peak height was obtained at 0.8 ml/min. Flow rates of less than 0.8 ml/min resulted in a higher dispersion, giving lower peak heights. When the flow rate was higher than 0.8 ml/min, the peak height was lower because of an insufficient contact period of the sample plug with barium chromate. Consequently, a flow rate of 0.8 ml/min was found to be most effective for high sensitivity.

**Effect of temperature**

The effect of the temperature on the exchange reaction was examined by varying the temperature from 15 to 35°C. The reaction proceeded at almost a constant rate over that temperature range. Therefore, temperature control was not performed throughout this work.

**Effect of foreign ions**

The main defect of the photometric methods using barium salts involves a severe interference from multivalent cations which form precipitates with counter...
Sample solutions containing some cations, such as calcium(II), magnesium(II) and iron(III), were injected into the flow system both without and with the cation-exchange resin column. The results are shown in Fig. 5. Extreme interference caused by these cations could be effectively eliminated by introducing a cation-exchange resin column.

Then, the effect of foreign anions which are usually found in surface- and sea-water, which contain 0.5-5 ppm of sulfate ion, was examined. The experimental results are given in Table 1. If an aqueous solution containing sodium acetate and ethanol was used as a carrier solution, there was no interference from the anions in those samples. Figure 6-1 shows the absorption spectra for carrier solutions of various compositions which flowed out of the barium chromate reaction column. Further, model sample solutions which contained sodium acetate, sulfate ion and carbonate ion as a foreign ion were injected into the stream of a carrier solution containing only 4% ethanol; typical results are shown in Fig. 6-2. Sodium acetate in a carrier solution accelerates the dissolution of solid barium chromate, which is more than that caused by the interfering anions. Since the effects of some anions were behind the base line using a solution containing sodium acetate and ethanol as a carrier solution, the

<table>
<thead>
<tr>
<th>Ion (added as)</th>
<th>Amounts, ppm</th>
<th>Recovery, %</th>
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<tbody>
<tr>
<td></td>
<td>C1</td>
<td>C2</td>
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<tr>
<td>Cl⁻ (NaCl)</td>
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<td>Br⁻ (NaBr)</td>
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<td></td>
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<td></td>
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<td>PO₄³⁻ (Na₃H₂PO₄·12H₂O)</td>
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<tr>
<td></td>
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<tr>
<td>CO₃²⁻ (Na₂CO₃)</td>
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<td>Ca²⁺ (Ca(NO₃)₂·4H₂O)</td>
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<td>103.2</td>
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<td>Mg²⁺ (MgCl₂·6H₂O)</td>
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<tr>
<td>Fe³⁺ (FeCl₃·6H₂O)</td>
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</table>

Sample, SO₄²⁻: 3 ppm; C1, H₂O; C2, 4.5 mM CH₃COONa–4(v/v)% C₂H₅OH solution.

**Table 1** Effect of foreign ions
interference was apparently reduced when sodium acetate was contained in the carrier.

**Determination of sulfate ion in water samples**

Sulfate ion in sea-, well-, and rain-water samples were determined by the proposed method. After suspended matter was removed by using a 0.45 µm membrane filter (47 mm i.d.), a sample was introduced into the FIA system. The obtained results are listed in Table 2, together with the results of a recovery test.

In conclusion, the proposed method was found to be a rapid and simple determination method for micro amounts of the sulfate ion in surface- and sea-water samples.

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**References**


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