

A Continuous flow system for the simple rapid and sensitive determination of sulfate in various salts

Takeshi Yamane^a, Nobuhiro Aoyama^a and Keiro Higuchi^b

^a Department of Chemistry, Faculty of Education and Human Sciences, Yamanashi University, Takeda-4, Kofu 400-8510, Japan

^b Tokyo Kasei Kogyo Co.Ltd., Toshima 6-15-9 Tokyo 114-0003, Japan

A flow injection analysis (FIA) system is presented for the simple, rapid, and sensitive determination of sulphate in purified and common salts. The preconcentration/separation of sulphate ions with an activated aluminium oxide column (2 mm i.d., 5 cm long) is directly inline coupled with photometric detection using barium complex of 1,8-Dihydroxy-2,7-bis(2sulfophenylazo)-3,6-naphthalenedisulfonic acid (DMS) as chromogenic reagent in a continuous flow system. In order to improve the rate of reaction between sulfate and the barium complex of DMS, a small column reactor (3 mm i.d., 12 cm long) with immobilized barium sulphate on glass beads was in-line incorporated prior to the photometric detection. The absorbance change due to the reaction was monitored at 662 nm and recorded automatically. Most ions commonly found in the salts did not interfere with the determination. A linear calibration with a 1.0-m sample loop injection was obtained for 0–10 µg/ml sulphate ion even in the presence of 2.0 M sodium chloride. The detection limit is 1.7 µg/g in solid samples, which is about 6 times more sensitive than the conventional method. The time needed for analysis is reduced to about 6 min/sample. The proposed FIA system was successfully applied to various salt samples.

1. INTRODUCTION

Salt is one of the most important foodstuffs for human life and nowadays it is also an essential base material for the chemical industry. There is, therefore, a significant need for the analysis of salt. Sulfate, one of the impurities in salt that have received much attention, has usually been determined by gravimetry or titrimetry. However, such method is only applicable to samples containing more than 0.03% sulphate [1] and thus more sensitive methods are needed for the analysis of purified salts and salts produced by the electrodialysis technique using an ion exchange membrane. Spectrophotometry [1,2,3] utilising methylenblue formation and liberation of chromate ion has sometimes been employed for sulphate concentrations as low as 0.001% and 0.01%, respectively, which is still unsatisfactory for the purified salts. The time-consuming, laborious and complicated operations required for analysis are shortcomings of such methods. Ion chromatography, has also been applied [4], however, has a limitation with respect to the determination of trace sulphate in salt since the matrix sodium in excess concentration affects the sulphate peak [5,6]. Flow Injection Analysis (FIA), an analytical system rapidly

becoming popular is expected to promote the automation of chemical analysis. FIA methods based on the turbidimetric measurements of barium sulphate were reported for determination of sulphate at a level of ten ppm or more [7,8] in river water, but are not sensitive enough for the present purpose. Kondo, et al [9] have reported a more sensitive FIA method for determining sulphate in river water using the barium complex with 2,7-bis(4-methyl 2-sulfo-phenylazo)-1,8-dihydroxy-3,6-naphthalene-disulfonic acid (DMS). The method is based on the formation of barium sulphate precipitation and the measurement of the absorbance change due to liberated DMS in a continuous flow system. Our preliminary experiments, however, showed that the sensitivity of this method was significantly decreased with increase in the concentration of sodium chloride present. This is probably due to the increase in the solubility of barium sulphate in presence of an excess of sodium chloride. Many cations can cause interference by complexation with the DMS. In addition, a blank peak effect due to refractive index perturbation which occurred when samples containing a large excess of salt were injected into the carrier was found to become another problem for trace sulphate

determination. In considering such situation, incorporation of in-line separation and preconcentration of sulphate, directly coupled with the detection using barium complex of DMS (Ba-DMS) in a FIA system, seems to become an attractive means to develop a new methodology for determining micro amounts of sulphate in the salt.

In the present work, we studied this approach which made use of an aluminium oxide column for in-line preconcentration/ separation of sulphate and an immobilised barium sulphate column for promoting the formation of barium sulphate in the photometric detection using Ba-DMS. Detailed investigations were made to establish the optimal conditions for developing a novel FIA system for determining micro amounts of sulphate in salts.

2. EXPERIMENTAL

2.1. Chemicals and solutions

All reagents were of analytical-reagent grade, unless otherwise noted. DMS solution ($5.0 \cdot 10^{-3}$ M) was prepared by dissolving the reagent (Tokyo Kasei, Tokyo) in water and filtering the solution through a membrane filter (0.45 μ m). A indicator solution mixture (Ba-DMS) was prepared according to the previous work [9] with a minor modification by using acetic acid in place of trichloroacetic acid; 5.6ml of $5.0 \cdot 10^{-3}$ M DMS solution, 2.5ml of 0.5 M potassium nitrate solution, 5.0ml of $4.0 \cdot 10^{-3}$ M barium chloride solution, 2.5ml of 2.0 M acetic acid solution and 170ml of ethanol were mixed and then diluted to 250 ml with water. Standard solutions of sulphate (1000ppm) were prepared by dissolving potassium sulphate in water and diluting. More dilute solutions were prepared by suitable dilution of this stock standard solution.

2.2. Apparatus and preparation of columns

Fig.1 shows a schematic diagram of the FIA manifold established in this study.

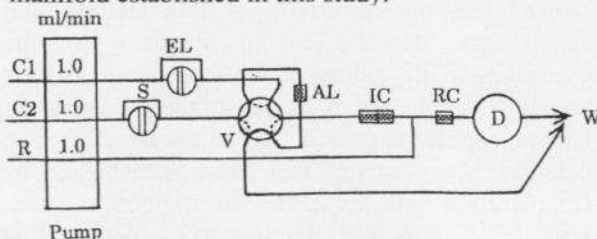


Fig.1 Schematic diagram of FIA system for determination of sulphate in salts.

C1,C2: Carrier(water), R: Ba-DMS solution, S: sample injection valve with a loop(1-m, 0.5 mm.i.d.), EL: elution valve with a loop(1-m, 0.5 mm. i.d.), AL: separation column(5cm long 2mm.i.d.), IC: suppressor column(12 cm long, 3 mm i.d.) or Nafion membrane tubing, RC: reactor column(12 an, 3 mm i.d.), D: spectrophotometer(at 662 nm), W: waste

All components in contact with solution (tubing valves, and connectors) were made of Teflon, Daiflon, ceramics or glass. Nihon Seimitsu Model NSP-800-6u, and NPFX-3 pumps (metal-free type) were used. A Jasco Model Uvidec-320 spectrophotometer equipped with a flow-through cell was used for absorbance measurement at 662 nm. The separation column (AL) was prepared by slurry packing the activated aluminium oxide (acid, activity I, purchased from Merck, Germany) into a borosilicate glass column (2 mm i.d., 5 cm long). The reactor (RC) consisted of immobilised barium sulphate on glass beads (0.4 mm diameter) packed into a borosilicate glass column (3mm i.d., 12 cm long). The suppressor column (IC) was prepared by slurry packing the strongly acidic cation-exchange resin (DiaionSK-1, H⁺ form) into a borosilicate glass column (3mm i.d., 12 cm long).

2.3. Procedure

The sample solution injected through a injection valve S in a 1 m sample loop (0.5 mm, i.d. tubing) is carried through the column AL and drained to waste with the 6-way valve V (solid line in V, Fig. 1). After preconcentration/separation for 13 min, V is switched to the elution position (broken line in V) and a 0.20 M ammonia solution is injected via injection valve E with a 1m loop (0.5 mm i.d. tubing) to elute the sulphate into the suppressor column IC. The sulphate ion eluted from IC reacts with the indicator mixture (Ba-DMS) in the reactor (RC) and the absorbance change is monitored at 662 nm. The peak height from the baseline is linearly related to the sulphate concentration.

2.4. Sample preparation

A salt sample (5.8g) was accurately weighed and dissolved in water, followed by dilution to 100 ml with water. The resultant solution was filtered through a membrane filter (0.45 μ m) and an aliquote of this solution was injected into FIA system. Sample weight should be varied within 12g of the upper limit

depending on the sulphate contents so that the concentrations of the sample solution would fit into the linear range of the calibration graphs (1-10 ppm). The calibration graph is prepared by using same concentration of sodium chloride as in the sample solution.

3. RESULTS AND DISCUSSION

3.1. Detection of sulphate with DMS in a continuous flow system

In the FIA method based on the formation of barium sulphate on and turbidimetric measurement, it was shown that the increase in turbidity was observed during the nucleation process which in some cases was remarkably slow [7,8]. This slow nucleation is considered to become a limiting factor in the sensitivity, reproducibility and sample throughput. In the photometric detection of sulphate ion with Ba-DMS, the reaction conditions and wavelength for absorbance measurement were similar to earlier work [9] but significant modifications of the manifold were made in the present study. Specifically an immobilised barium sulphate column was employed in order to promote the formation of barium sulphate (consequently liberation of DMS) instead of using the solution saturated with barium sulphate as carrier in the earlier work [9]. Fig. 2 shows that the sensitivity and reproducibility for sulphate detection by Ba-DW were remarkably improved by placing the immobilised barium sulphate column (RC in Fig.1) in the stream of reaction mixture, probably due to the provision of nuclei and hence to the acceleration on barium sulphate formation. This can provide an additional advantage by eliminating a reaction coil in contrast to conventional FIA methods requiring a long reaction coil for the promotion of the reaction.

The column efficiency for the detection reaction (formation of barium sulphate and therefore liberation of DMS) was studied by changing the flow rate. A constant and maximum peak height was observed for total flow rates of carrier and reagent solutions between 1.5 and 3.0 ml/min, which were kept in a 1: 1 ratio. A flow rate in each channel of 1.0 ml/min provided satisfactory reproducibility and sensitivity.

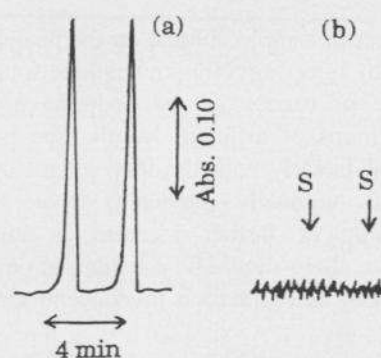


Fig.2 Signal profile for detection of sulphate with Ba-DMS reagent in a FIA system (a) with and (b) without immobilised barium sulphate reactor.

3.2. Preconcentration and separation by aluminium oxide column

In order to achieve the preconcentration and separation of sulphate from a sodium chloride matrix, an aluminium oxide column was introduced and coupled in-line with the photometric detection with Ba-DMS reagent. The effect of pH on the adsorption of sulphate ion on the aluminium oxide column was studied by injecting 5.0 ppm sulphate solutions adjusted to different pH values and then by desorbing with 0.20M ammonia solution. The resultant peak height (corresponding to a signal readout for sulphate detection) showed that the adsorption of sulphate ion was maximal and quantitative for a pH ranging from 2.0 to 7.9 and decreased sharply outside of this pH range, especially at the higher pH region.

The effect of sodium chloride added to the sample solution on the peak height (adsorption efficiency for the sulphate ion) was studied for sulphate ion concentration of 5.0 ppm. The peak height has a tendency to decrease slightly with increasing sodium chloride concentration, for instance, the peak height in the presence of 1.0 M sodium chloride solution was about 10% lower than that in the absence of sodium chloride. However, there found little difference in the peak heights at sodium chloride concentrations between 1.0 and 3.0 M. As a linear relationship was confirmed between the peak height and sulphate ion concentration in the range 0-10 ppm even in the presence of excess sodium chloride as shown later, it has been suggested that the limit of determination of sulfate ion can be improved by taking a larger sample weight for preparation of the sample solution.

The effect of sample volume on the peak height was studied by injecting 5.0 ppm sulphate solution in the presence of excess 2.0 M sodium chloride with sample loops of different length. The peak height increased linearly with the loop length up to up to 2m and gradually deviated from the linear relationship at further increase in loop length. Therefore, there should be a limitation on improving the limit of determination preconcentration a larger sample.

Ammonia solutions varying from 0.05M to 1.0 M were examined by eluting 5.0 ppm of sulphate ions adsorbed on the aluminium oxide column using a 1 m elution loop. Results showed that the peak height reached a maximum when a 0.1 M ammonia solution was used and then leveled off at larger ammonia concentrations. It was also found that adsorbed sulphate ion was desorbed quantitatively with recovery > 96% by a single elution run with 0.2M ammonia solution and a 1m elution loop. On the other hand, this ammonia solution proved to deteriorate the sensitivity for sulphate detection because it changed the H^+ concentration in the reaction mixture, which resulted in the increase in the solubility of barium sulphate. In order to overcome this problem, a H^+ form cation-exchange column (IC in Fig.1) was incorporated in-line after separation column (AL). The principle suppressing for the effect of ammonia can be explained as follows: H^+ on ion-exchange resins is liberated by exchanging NH_4^+ in the eluate and reacts with OH^- from ammonia, which results in the formation of H_2O . This ion-exchange suppressor column must be regenerated every ca. 20 sample injections because the ion-exchange capacity is not very high. Nafion membrane tubing suppressor can be used alternatively and is desirable to avoid complications as regeneration. It should be noted that the sample plug passed through the separation column should not enter into this suppressor column because excess Na^+ in the sample deteriorates the suppression efficiency of the cation-exchange column. Therefore, a switching valve (V) has been mounted above the suppressor column so as to discard the sample effluent from the separation column directly to the waste. The AL column provided efficient operation for as many as 100 runs without significant deterioration.

3.3. Calibration graph

Based on the experiments described above, a FIA system was constructed and a procedure was designed as shown in Fig.1 and Section 2. Calibration graphs made by the standard solutions containing sulphate ions and sodium chloride a mixture showed a linear response of the peak height vs. sulphate concentration in the 0 - 10 ppm range in the presence of 0.2M, 1.0 M and 2.0 M sodium chloride. The slope of the graphs has a tendency to gradually decrease with increasing sodium chloride concentration; for instance, the slope in the presence of 1.0 M sodium chloride solution was about 10% lower than that in the absence of sodium chloride.

Therefore it is recommended to prepare the calibration graph using the same concentration of sodium chloride, as in the sample solution. For sample injections with a 1 m sample loop, the relative standard deviation for 5.0 ppm sulphate ion in the presence of 2.0 M sodium chloride was 3.0% ($n=5$). The limit of determination was estimated (signal six times the standard deviation of the blank peak) to be as low as 0.2 ppm which corresponds to 1.7 ppm based on a solid sample, when a 2.0 M sample solution is prepared. This limit of determination is about 6 times lower than that for the most sensitive photometric method based on the formation of methyleneblue [2]. The sensitivity can be further improved by using a larger sample volume injection.

3.4. Interferences

The effect of coexisting ions on the determination of 5.0 ppm sulphate in the sample solution was studied according to Section 2.3. No significant interference was observed by the following ions ($\mu g/ml$), $Ca(II)(30)$, $Mg(II)(30)$, $Fe(II,III)(1)$, $Cu(II)(1)$, $Mn(II)(1)$, $Ni(II)(1)$, $I^-(30)$, $Br^-(30)$, $F^-(30)$, $H_2PO_4(1)$. Relative errors less than $\pm 5\%$ were considered tolerable. It is noteworthy that this good selectivity in comparison to the earlier work [9] should be due to the selective separation of sulphate from other associated metal ions by the aluminium oxide column. Thus the method is free from interference by most coexisting ions commonly found in common salts and purified salts.

3.5. Analysis of salt samples

The proposed method was applied to the determination of sulphate in various salts. In order to evaluate possible effects from other coexisting components, the recovery of known amounts of sulphate spiked to the sample solutions was also studied. These results summarised in Table 1 and show good reproducibility with relative standard deviations less than 3% and satisfactory recoveries larger than 96%.

4. CONCLUSION

As shown in this work, in-line separation/preconcentration using the aluminium oxide column directly combined with photometric detection utilising the immobilised barium sulphate column as reactor for Ba-DMS reagent has shown to provide a sensitive simple and rapid method for the determination of sulphate in purified and common salts. The advantage of the present FIA system over conventional photometric methods is that the analysis is achieved in a continuous and nearly closed system without instrumental and operational complexity, which can minimise the manual operation and offer possible way to automation of chemical analysis for sulphate. The short analysis time of about 6 min/sample and the good reproducibility with r.s.d. < 3.0 % are additional appealing features of the present FIA system.

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