J. Flow Injection Anal., Vol. 23, No. 2 (2006) 107–111

Determination of Sulphate in Beverages by Spectrophotometric Flow Injection Analysis

Saisunee Liawruangrath* and Wilaiwan Phakthong

Department of Chemistry, Faculty of Science, Applied Chemistry and Environment Research Institute for Science and Technology Research and Development, Chiang Mai University, Chiang Mai 50200, Thailand.

Abstract

An inexpensive FI-manifold and a minicolumn packed with cation exchanger resin with spectrophotometric detection are described for the determination of sulphate ions. It is based on the competitive reaction of SO_4^{2-} and methythymol blue (MTB) with barium(II) in aqueous solution. Measurements were made at 610 nm. Conditions for the quantitation of sulphate ions were optimized using univariate and simplex methods. The cation exchange minicolumn was used to overcome some possible cationic inferences. Linear calibration graphs over the range of 5-25 mg/l SO_4^{2-} were established with the regression equation (n=5) Y=2.3172X-3.6798 (r=0.9963). The detection limit of 0.81 mg/l SO_4^{2-} respectively together with the RSD of 2.09 % for 10 mg/l SO_4^{2-} (N=10) were obtained. The proposed method has been applied satisfactorily to the determination of SO_4^{2-} in commercial beverages. Results obtained by the recommended method were in excellent agreement with those obtained by the reference method verified by using student t-test.

Keywords: Sulphate**;** spectrophotometry; flow injection analysis; simplex optimization; beverages

1. Introduction

Sulphate concentration can be affected by the technological use of sulphite. Sulphur and its compounds are remarkable use in agriculture due to their fairly good efficacy as pesticides. Sulphate is the anion usually determined as the final product of total oxidation of sulphur compounds, when it is necessary to quantify total amount of sulphur species. In comparison with other analytes, there are a few analytical procedures for sulphate. The gravimetric $BaSO_4$ method [1], indirect titration [2], or potentiometric back-titration [3], which are well-known procedures for the determination of sulphate accurately. However, due to the analytical characteristics of the time consuming and is not convenient for environmental studies, in which usually large numbers of samples of samples are involved. The most commonly used procedure is based on turbidimetric measurements of barium sulphate [4-6] or on spectrophotometric measurement using methylthymol blue [7-8], barium chloanilate [9-10]. Indirect method based on reduction of sulphate to hydrogen sulphide followed by its volatilization and absorption in alkaline solution [11]. During the last decade, ion chromatography [12, 13-15] has replaced turbidimetric and spectrophotometric techniques in many application areas and also superior selectivity. However, the sample throughput using ion chromatography is not sufficient if the number of sample is large. Methods currently in use include; spectrofluorimetric [16, 17], atomic absorption spectrometric [18], Ion-selective electrode [19, 20-23], Raman spectroscopy [24], flow injection analysis [25], capillary electrophoresis [26, 27] and sequential injection analysis methods [28, 29], HPLC [30], Flow injection analysis has recently been proposed to the determination of sulphate because of its simplicity of the instrumentation, low sample and reagent consumption, rapidity and high sampling rate. This paper describes, an inexpensive flow injection (FI) spectrophotometric procedure for determining sulphate ions based on the reaction between sulphate and MTB/Ba causing to a gradation of blue color measurements were made at 610 nm. Optimum conditions for the determination of sulphate ions were carried out using univariate and multivariate methods [32].

2. Experimental

2.1 Reagents

Most chemicals were of analytical-reagent grade (unless otherwise specified) and de-ionized distilled water was used throughout the whole experiment.

Standard sulphate stock solution (500 mg/l) was prepared by dissolving 0.1848 g sodium sulphate (E. Merck, Germany; preciously dried at 110°C for 1½ hrs.) in 250 ml water. Further dilute solutions (5-25 mg/l) were made by appropriate dilution of this stock solution with water.

Stock sodium hydroxide solution (1 mg/l) was prepared by dissolving 40 g of sodium hydroxide (E. Merck, Germany) in 1,000 ml 40% v/v ethanol and standardized with standard potassium hydrogen phthalate using phenolphthalein as indicator [31]. The more dilute solutions were prepared by appropriate dilution of this solution with water.

Methylthymol blue/barium solution (2.00 mol/l MTB/Ba ratio) was prepared by dissolving 0.1478 g MTB sodium salt (Fluka Switzerland) in a solution containing 6.00 ml, mol/l HCl, 80 ml water and 14.00 ml of a 1 .526 g/l $BaCl_2.2H_2O$ (J.I. Baker Inc., Philipsberg, U.S.A.) solution. The solution was then diluted to 1,000 ml with water.

2.2 Apparatus

The proposed multi channel FI manifold is shown in Fig.1. Two EYELA peristaltic pumps, MP-3A (Tokyo Rikakikai Co., Ltd., Japan) were used. Tygon tubing (0.51 mm i.d. and 1.24 mm i.d.) were used as flow lines. A home-made injection valves (V_1) was used. A pre-column packed with Dowex 50 w–x8, 80-100 mesh (H^+) (BDH, U.K.) was used for removal of interfering cations. Two coiled reactors (R_1 and R_2) were used as a mixing coil. A spectrophotometer (Spectronic 21, Milton Roy Company, U.S.A.) equipped with a quartz flow-through cell (Hellma, 1 cm, Duprasil I window, tube 178, 711-GS) was used as a detector and a chart recorder model 135 A (National, Japan) was used to record the FI signals.

---

*Corresponding author: Tel: (66)053943341-5 Ext.126
Fax: (66)053892277
E-mail : scislwrn@chiangmai.ac.th

2. Procedure

The proposed method is based on the competitive reaction of sulphate and methylthymol blue (MTB) with Barium (Ba^{2+}) ions in aqueous solution. When SO_4^{2-} absent all Ba^{2+} ions are complexed with MTB giving rise to a deep blue colour. After a 100 µl sample or standard solution containing sulphate was injected via the injection valve (V_1). The sample stream was passed through an cation exchange column packed with Dowex 50 w–x8, 80-100 mesh (H^+), (BDH, U.K.) was used for removal of interfering cations which was then merged with a reagent stream containing bromothymol blue (MTB) and barium ions in a ratio of MTB:Ba^{2+} of 1.76 with a flow rate of 0.7 ml/min at coiled reactor R_1 (254 cm) the competitive reaction of sulphate and MTB/Ba was taken place, the reaction mixture was then merged with a 0.023 mol/l NaOH stream with a flow rate of 0.5 ml/min at the other coiled reactor R_2 (199 cm). A gradation of blue colour was taken place, which can be accomplished by measurement of the decreased absorbance due to MTB/Ba complex at 610 nm.

4. Results and discussion

4.1 Determination of sulphate by univariate method

The FI-spectrophotometric method for the determination of sulphate in beverages was developed. Preliminary investigations were carried out by determining sulphate using FI-manifold with spectrophotometric detection (Fig.1). Optimization of the experimental conditions was carried out based on the so-called univariate method. The optimum conditions for the quantitation of sulphate ions are shown in Table1.

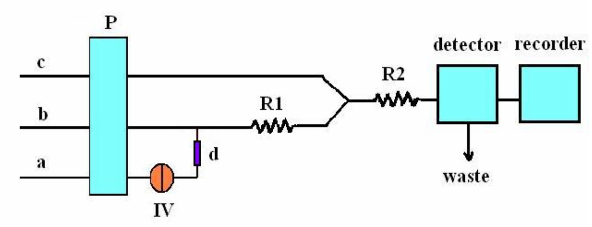

Fig. 1 Schematic diagram of flow system used for sulphate determination
(a) carrier (water), (b) MTB/Ba, (c) NaOH, (d) column, (IV) injection valve (R1) first mixing coil, (R2) second mixing coil, (P) peristaltic pump.

Table 1. Optimum conditions for sulphate determination using univariate method and their analytical characteristics

Parameters studied	**Optimum conditions**
Wavelength (nm)	610
MTB/Ba molar ratio	2.00
NaOH concentration (M)	0.02
Injection volume (µl)	100
MTB/Ba solution flow rate (ml/min)	0.7
NaOH flow rate (ml/min)	0.5
Inner diameter of mixing coil (cm)	0.05
Length of mixing coil (cm) R_1, R_2	300 and 200
Linear range of the calibration curve (ppm)	5-25
Slope of calibration curve (mV/ppm)	0.85
Precision (% RSD)	2.61
Detection limit (mg/l)	0.81
Sample throughput (hr^{-1})	33

As mentioned earlier in the experimental section, an indirect determination of sulphate based on competitive reaction of sulphate and MTB with barium(II) in the basic solution which was then accomplished by measurement of the absorbance due to either uncomplex MTB to the MTB-barium complex according to the following chemical reactions.

$$Ba^{2+} + MTB \rightleftharpoons BaMTB^{4-} \; (\lambda_{max} = 610 \text{ nm}) \qquad (1)$$

$$BaMTB^{4-} + SO_4^{2-} \longleftarrow BaSO_4 + MTB^{6-} \; (\lambda_{max} = 460 \text{ nm}) \qquad (2)$$

The absorption maximum of the barium-MTB complex is at 610 nm and that of the free MTB so at 460. The absorbance at 460 nm due to uncomplex MTB will increase while the absorbance due to the MTB-barium complex will decrease as sulphate concentration increases.

4.2 Determination of sulphate by simplex optimization method

The procedure for determining sulphate was adapted for the development of a procedure for determining sulphate in beverages collected from supermarkets in Chiang Mai Province. A novel inexpensive FI manifold is shown in Fig.1. Optimization of the chemical and the flow parameters were carried out by simplex optimization method or the so-called multivariate method [32].

The parameters optimized were concentrations of NaOH, molar ratio of MTB/Ba, mixing tubing (R1 and R2) lengths. The sulphate determinations were performed according to the reported procedure [32, 33]. In each case the responses as peak heights were considered. Optimum experimental conditions for sulphate determination are summarized in Table 2.

Table 2. Optimum conditions for determination sulphate by simplex method and their analytical characteristics

Parameter studied	Optimum conditions
Molar ratio of MTB/Ba	1.76
NaOH concentration (mol/l)	0.023
Length of mixing part (R1 and R2) (cm)	254 and 199
Pump flow rate of MTB/Ba (ml/min)	0.7
Pump flow rate of NaOH (ml/min)	0.5
Injection volume (μL)	100
Wavelength (nm)	610
Linear range of the calibration curve (mg/l)	5-25
Slope of calibration (mV/ mg/l)	0.85
Precision (%RSD)	2.09
Detection limit (mg/l)	0.81
Sample throughput (hr^{-1})	33

Simplex optimization was carried out to confirm the results obtained from univariate method for determination of sulphate by selecting some optimum parameters from those obtained by the univariate method namely flow rates of reagents, inner diameter of the mixing tubing for mixing coil and mixing coil length. The simplex-optimized parameters chosen for sulphate determination were concentrations of NaOH, molar ratio of MTB/Ba and mixing tubings (R1 and R2). Table 3 indicated that the results obtained by the simplex optimization method for sulphate determinations were in good agreement with those obtained using the univariate one.

Table 3. Comparison of optimized conditions obtained by univariate and simplex optimization methods for sulphate determinations

Parameter	Method	
	Univariate	Simplex
MTB/Ba (molar ratio)	2.00	1.76
Concentration of NaOH (mol/l)	0.020	0.023
Mixing tubing R1 (cm)	300	254
Mixing tubing R2 (cm)	200	199

Optimum experimental conditions for determination of sulphate are summarized in Table 2. These optimum conditions were then used throughout this research work.

Fig.1 shows the FI gram for the determination of sulphate at various concentrations monitored at 610 nm. Calibration curves, which were the plot of peak heights against various concentrations of sulphate at 610 nm have been established over the ranges 1-50 mg/l. The calibration curve was linear cover the ranges 1-25 mg/l sulphate, with the correlation coefficients of 0.9963. The regression equations for sulphate are as follows:

$$Y = 2.3172x - 3.678, (r^2 = 0.9963)$$

Where Y is signal as peak height in mV
X is concentration of sulphate in mg/l

4.3 Manifold design

The FI manifold is shown in Fig.1, Two EYELA peristaltic pumps MP-3A (Tokyo Rikakikai Co., Ltd., Japan) were used for propelling the reagent and carrier streams. Tygon tubings (0.51 mm i.d. and 1.24 mm i.d.) were used as flow lines. The sample solution was injected via a home-made injection valve (V_1) passed through a pre-column packed with Dowex 50 w-×8, 80-100 mesh (H^+) (BDH, U.K.). When sulphate is absent, all the Ba^{2+} ions are complex with MTB producing a deep blue colour. After the sample was introduced and mixed with MTB/Ba, NaOH respectively, the competitive reaction of sulphate and MTB/Ba was taken place resulting in a gradation of blue colour. The chemical reactions are shown by reactions (1) and (2) respectively:

The turbidity measured as absorbance unit due to sulphate produced can be monitored at 610 nm of a spectrophotometer (spectronic 21, Milton Roy Company U.S.A.) and the FIA grams were recorded by a chart recorder model 135A (National, Japan.) as shown in Fig.2.

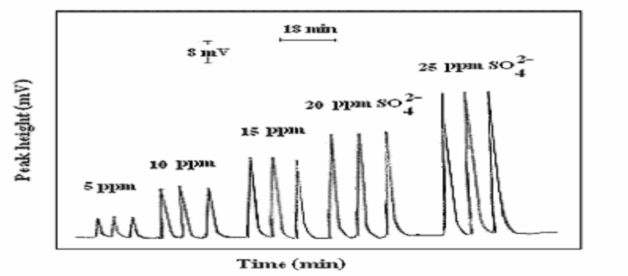

Fig. 2 Calibration signal output of sulphate determination.

4.4 Reproducibility and recovery

The precision of the proposed method have been determined with 10 replicates determination of 10 mg/l sulphate (express as the relative standard deviation), which is 2.09%. The limit of detection (LOD), calculated from linear regression of the calibration curve using Miller and Miller's [34] method, were found to be 0.81 mg/l sulphate at 610 nm as shown in Table 2. The percentage recoveries of added sulphate were found in the range of 94-119 %.

4.5 Interferences

In any analytical procedure, it is necessary to determine some possible interferences before any quantitative analysis is carried out. Table 4 summarized the results obtained by investigation of some possible interfering species prior to determination of 10 mg/l sulphate. It was found that many cations interfere with the MTB dye in the same way, as does barium(II) calcium(II) and magnesium(II) are the most frequently encountered interferences. Thus the use of a cation exchange resin column (in the H^+ form) incorporated with the FIA system provides efficient ability for the removal of these cations and any other cationic interferences. However, the tolerable ratio of Ca^{2+} and Mg^{2+} are still unsatisfactory (31 and 10) respectively. The reason why the interference has not been removed efficiently by the cation exchange column can be due to the fact that the ion exchange process depends on pH of the sample solution and the column capacity. Effect of pH over the range 1-7 on the elution of some selected interfering cations was studied. It was found that hydrogen ion (pH) exhibited no effect on the sulphate determination at pH range 2-7. This is due to the fact that when the interfering cations passed through the cation exchange column (hydrogen form), hydrogen ions are eluted from the column and the interfering cations were retained on the column. If the H^+ concentration is too high (low pH<2) the ion exchange efficiency is poor because the H^+ on the resin can not be completely eluted as soon as the interfering ions passed through the column. With respect to effect of column capacity, it noticed that the removal of any cationic interferences depends on the capacity of column and hence, the column length and inner diameter. In case of on-line removal of cations by a mini- or micro- column, the inner diameter of the column was restricted to fit with the optimum size of the flow line tubing. Therefore, the length of column is important factor to be studied for the quantitative tolerable ration of SO_4^{2-} to Mg^{2+} and SO_4^{2-} to Ca^{2+}. The effect of the length of column on the removal of Mg^{2+} and Ca^{2+} was examined in the range of 10-50 cm. The results demonstrated that, the tolerable ration increases, from 0 up to 40 and 0 up to 110 for Mg^{2+} and Ca^{2+} respectively, with increasing in column length (Table 5).

Table 4. Influence of some possible interfering ions on the determination of sulphate (10mg/l) by combine a 20 cm column length.

Interfering ion studied	Tolerable ratio
NO_3^-	240
K^+	160
$S_2O_3^{2-}$, NO_2^-, CO_3^{2-}	100
Na^+	80
PO_4^{3-}	60
Ca^{2+}	31
SO_3^{2-}	30
Mg^{2+}	10

Table 5 The effect of the length of column for removal interfering ions.

Length of column(cm)	Tolerable ratio	
	Mg^{2+}	Ca^{2+}
10	0	0
20	10	30
30	15	50
50	40	110

4.6 Application

The proposed FI procedure has been satisfactorily applied to the determination of sulphate in 10 commercial beverage samples. The comparative results of the recommended FIA method with the turbidimetric methods were performed. They were in good agreements between the proposed and turbidimetric method (verified by student's t-test).

Table 6. Application of FI method for the determination of sulphate in various beverages

Sample	Concentration (mg/l) of Sulphate	
	FIA	Std. Method**
Coconut juice (Olig)	155	157
Apple juice (Ivy)	12	12
Apple juice (Tipco)	12	11
Thai white wine	175	182
Coconut juice (Coco)	154	156
Tipco (cool mix)	18	18
Cooler club (apple)	94	93
Coconut juice (Seaside)	24	26
Cooler club (passion)	79	79
Cooler club (rose)	85	85

**Turbidimetric method

5. Conclusion

The FI-spectrophotometric method has been developed for the determination of sulphate in beverages. Optimum conditions were investigated by univariate method which was agreed well with those obtained by the simplex optimization method. Simplex optimization method was preferable because less number of experiments were performed. The working calibration curve was linear over the range 5-25 mg/l sulphate, with the correlation coefficients of 0.9963. A detection limit of 0.81 mg/l sulphate with precision of 2.09% was obtained. Phosphate and colored samples interfere with sulphate determination. Therefore, the presence of those interfering ions in the samples must be avoided. The comparative results of the proposed FIA method with the turbidimetric method were in good agreement. The advantages of the proposed method are simple, rapid highly sensitive and precise.

Acknowledgements

The authors would like to express their sincere thanks to Postgraduate Education and Research in Chemistry (PERCH) and the Royal Golden Jubilee project for their very kind financial support. We also would like to express our sincere thanks to the Graduate School and the Department of chemistry Faculty of Science Chiang Mai University for their partial support.

References

[1] APHA, *Standard Methods for the Examination of Water and Wastewater*, 18thed., Anerican Public Healt Association, 1992, p.4-134.
[2] S.M. Prada, M.G. Guekezian, M.E.V. Suárez-Iha, *Anal. Chim. Acta,* **329**, 197 (1996).
[3] T. Masadome, Y. Asano, *Talanta,* **48**, 669 (1999).
[4] J.A. Vieira, B. F. Reis, E.A.M. Kronka, A.P.S. Paim, M.F. Giné,*Anal. Chim. Acta,* **366,** 255 (1998).
[5] R.E. Santelli, P.R.S. Loes, R.C.L. Santelli, D.L.R. Wagener, *Anal. Chim Acta*, **300,** 146 (1995).
[6] R.L. Coleman, W.D. Shults, M.T. Kelley, J.A. Dean, *Anal. Chem.*, **44,** 1013 (1972).
[7] B.C. Madsen, R.J. Murphy, *Anal. Chem.*, **53,** 1924 (1981).
[8] G. Colovos, M.R. Panesar, E.P. Parry, *Anal. Chem.*, **48,** 1693 (1976).
[9] H.N.S. Schafer, *Anal. Chem.*, **39,** 1719 (1967).
[10] R.J. Bertolacini, J.E. Barney, *Anal. Chem.*, **63,** 1897 (1991).
[11] A.L. Molinero, R. Batlle, A. Villareal, J.R. Castillo, *Talanta,* **43,** 1565 (1996).
[12] G. Dugo, L. La Pera, T.M. pellicanó, G. Di Bella, M. D'Imperio, *Food Chemistry,* **91,** 355 (2005).
[13] M. Zhou, D. Guo, *Microchemical Journal*, **65,** 221 (2000).
[14] C. Mongay, A. Pastor, C. Olmos, *J. Chromatogr. A*, **736,** 351 (1996).
[15] M. Novič, A. Dovžan, B. Pihlar, V. Hudnik, *J. Chromatogr. A*, **704,** 530 (1995).
[16] P. Singh, E.R. Pambid, N.M. Abbas, *Anal. Chem.*, **63,** 1897 (1991).
[17] L.H. Tan, T.S. West, *Analyst*, **96,** 281 (1971).
[18] B. Fernandez-Band, P. Linares, M.D. Luque de Castro, M. Valcarcel, *Analyst*, **116,** 305 (1991).
[19] A.M. Othman, M.S. El-Shahawi, M. Abdel-Azeem, *Anal.Chim. Acta,* **555,** 322 (2006).

[20] S.R.P. Meneses, N. Maniasso, E.A.G. Zagatto, *Talanta,* **65,** 1313 (2005).

[21] Y.G. Mourzina, T.E. Ermolenko, T. Yoshinobu, Y. Vlasov, H. Iwasaki, M.J. Schöning, *Sensors and Actuators,* **91,** 32 (2003).

[22] M.R. Ganjali L. Naji, T. Poursaberi, M. Taghizadeh, H. Pirelahi, M. Yousefi, A. Yeganeh-Faal, M. Shamsipur, *Talanta,* **58,** 359 (2002).

[23] M. Morigi, E. Scavetta, M. Berettoni, M. Giorgetti, D.Tonelli, *Anal. Chim. Acta,* **439,** 265 (2001).

[24] K. Murata, K. Kawakami, Y. Matsunaga, S. Yamashita, *Anal.Chim.Acta,* **344,** 153 (1997).

[25] K. Sonne, P.K. Dasgupta, *Anal.Chem.,* **63,** 427 (1991).

[26] J. Sullivan, M. Douek, *J. Chromatogr. A*, **1039,** 215 (2004).

[27] R. Kokkonen, H. Sirén, S. Kauliomäki, S. Rovio, K. Luomanperä, *J. Chromatogr. A*, **1032,** 243 (2004).

[28] I.P.A. Morais, M.R.S. Souto, T.I.M.S. Lopes, A.O.S.S. Lopes, *Water Research,* **37**, 4243 (2003).

[29] A. Rius, M.P. Callao, F.X. Rius, *Analyst*, **122**, 737 (1997).

[30] Y. Zuo, H. Chen, *Talanta,* **59**, 875 (2003).

[31] R. belcherand, A.J. Nutten, *Quantative Inorganic Analysis*, 3rd de., Butterworth and Co., (publishers), Ltd., 1970.

[32] F.H. Walters, L.R. Parker, S.L. Morgan and S.N. Deming, *Sequential Simplex Optimization*, CRC Press, Boca Raton, 1991.

[33] B. Purachat, S. Liawrungrath, P. Sooksamiti, S, Rattanaphani, D. Bubbhasukh, *Anal. Sci*, **17,** 443 (2001).

[34] J.C. Miller, J.N. Miller, *Statistics for analysis Chemistry*, 3rd ed., Ellis Horwood, New York, 1993, p.58-59, 110-117.

(Received 23, July 2006)
(Accepted 19, October 2006)