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Chromatographic determination of anions in industrial salt and sodium chloride brines used in chlor–alkali industry

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Abstract

An ion chromatographic method using an ion-exchange column for the simultaneous analysis of sulphate and chlorate in industrial salt and sodium chloride brines has been developed. A mixed eluent of 2.0 mM sodium carbonate and 0.75 mM sodium bicarbonate is used. The effects of various parameters have been reported and critically discussed. The results are precise and afford simultaneous determinations of sulphate and chlorate. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Brine is the life blood of all chlor–alkali electrolysis systems. The co-products chlorine, hydrogen and caustic are manufactured by the electrolysis of specially purified brine solution in a series of membrane cell frames. The electrolytic cell consists of anode (titanium) and cathode (nickel) compartments separated by an ion-exchange membrane. Each compartment has an electrolyte inlet at the bottom and gas–liquid outlet at the top. In the electrolytic process some of the hydroxyl ions are back-migrated into the anolyte. This increases the pH and oxygen is evolved which forms the chlorate in the anolyte brine [1,2]. The solar (industrial) salt used for the preparation of brine solution contains calcium sulphate and magnesium sulphate as impurities [3]. It has been reported that the less chlorate and sulphate content in the brine feed (anolyte), gives the less or nil concentrations of chlorate and sulphate in caustic lye

from membrane cell [4]. This pure grade caustic lye is called as rayon grade caustic. It has been also observed that chlorate present in the caustic lye corrodes nickel at an elevated temperatures [5] whereas sulphate at 10–20% concentration in acidic medium causes the corrosion of titanium [6]. Chlorate in contact with sparks or organic materials causes explosions in the industries [7]. In view of the above effects the monitoring of both the chlorate and sulphate in the brine feed is of great importance.

Suppressed ion chromatography (IC) provides a suitable way for the simultaneous determination of multiple anions in rain, lake, natural and environmental water samples [8–11]. In most of these analyses, the concentrations of anions are within an order of magnitude of each other. However, problems are encountered when dealing with samples in “complex” matrices such as sea-water, porewater, industrial brines, concentrated sodium hydroxide and sulphuric acid solutions [12–15]. Lash and Hill [16] have studied the simultaneous analysis of fluoride, bromide and sulphate in high salinity geothermal

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well water. They have observed the lower sulphate results as compared with other standard methods. The fluoride and bromide results are also affected due to lack of baseline resolution of respective peaks. Singh et al. [17] have reported the simultaneous analysis of bromide and sulphate in oilfield brines after 250-times dilution (low chloride matrix). However, the low recovery of sulphate is reported for the same oilfield brine after 50-times dilution (high chloride matrix). Marr [18] has also used suppressed IC for accurate determination of sulphate in oilwell brines.

In the above cited literature, the simultaneous analysis of chlorate and sulphate in industrial brine samples has not been studied. We have, therefore, undertaken the development of the suitable analytical method for simultaneous determination of chlorate and sulphate in saturated brine samples from chlor-alkali industry.

2. Experimental

2.1. Chromatographic system

All chromatography was performed on a Dionex (Sunnyvale, CA, USA) DX-500 ion chromatograph. The system consisted of a isocratic pump (IP 20), a liquid chromatography module (LC 10) and an electrochemical detector (ED 40). The data acquisition and integration of chromatograms were performed with a PC/AT-486 computer, WINCHROM software and an Epson LQ-1070+ printer. Table 1 summarises the details of the operating parameters.

2.2. Reagents and solutions

High-purity deionized water with a specific resistance of $18.2 \text{ M}\Omega \text{ cm}^{-1}$ or higher was obtained from a ELGA UHQ system and used for preparing solutions, eluent and standards. This high purity water had minimal level of ionic impurities, organics, microorganisms and particulate matter (larger than $0.2 \mu\text{m}$). Analytical-grade sodium chloride (E. Merck), sodium sulphate (E. Merck) and sodium chlorate (Koch Light Labs.) were used to prepare the standard stock solutions. Standard stock solutions containing 1.0 g l^{-1} chlorate (ClO_3^-), 1.0 g l^{-1} of sulphate (SO_4^{2-}) and 30 g l^{-1} of sodium chloride were prepared. Various working standard solutions containing chlorate (ClO_3^-) and sulphate (SO_4^{2-}) in high-purity water, 600 and 3000 mg l^{-1} sodium chloride matrix were prepared by appropriately diluting the stock standard solutions with high purity water. Sodium carbonate, suprapure (E. Merck) and sodium bicarbonate, GR (E. Merck) were used for the eluent preparation. Eluent was prepared daily, filtered through a $0.22\text{-}\mu\text{m}$ filter and degassed.

2.3. Sample preparation

The brine samples obtained from chlor-alkali industry are clarified brine, pure brine and depleted brine. The brine samples from each of these streams were collected every 2 h, over a period of 24 h and individual composite sample mixtures were prepared. These composite brine samples were used for the determination of sodium chloride concentration as

Table 1
Operating parameters for the anion chromatography system

Analytical column	IonPac AS 9-SC (250×4 mm I.D.)
Guard column	IonPac AS 9-SC (50×4 mm I.D.)
Eluent	2.0 mM Na_2CO_3 +0.75 mM NaHCO_3
Eluent flow-rate	2.0 ml min^{-1}
Sample loop volume	50 μl
Regenerant flow-rate	$10\text{--}12 \text{ ml min}^{-1}$
Suppressor	Anion self regenerating suppressor (ASRS) external water mode
ASRS current	100 mA
Detection	Suppressed conductivity
Detector range	30 μS
Pump pressure	1100 p.s.i. (1 p.s.i.=6894.76 Pa)
Background conductivity	$10\text{--}12 \mu\text{S}$

per the standard method [19]. The chlorate and sulphate contents were determined after appropriate dilution of each composite brine sample with high-purity water and using IC as described above. The diluted brine sample contains approximately 600 mg l^{-1} of sodium chloride. The solar (industrial) salt used in chlor-alkali industry is stored in a salt shed in the form of heap. The salt samples were drawn from different heights, depths and intervals and mixed to prepare the composite salt sample. This composite salt sample was crushed and 30 g of sample was dissolved in 1 l of high-purity water. The chlorate and sulphate content were determined by IC using the matrix match technique as described above. The analysis of sulphate content was also carried out by the standard method [19].

3. Results and discussion

Preliminary analysis after 500-times diluted sodium chloride brine samples found to contain ap-

proximately 0.4 to 1.6 mg l^{-1} chlorate (ClO_3^-), 15 to 30 mg l^{-1} sulphate (SO_4^{2-}) and 600 mg l^{-1} sodium chloride. Ion chromatograms of standard solutions containing 1.6 mg l^{-1} chlorate (ClO_3^-) and 20 mg l^{-1} sulphate (SO_4^{2-}) in the presence of 0 (I), 600 (II) and 3000 mg l^{-1} (III) sodium chloride are shown in Fig. 1. The retention times of both chlorate and sulphate anions are increased with increase in 0 to 600 mg l^{-1} sodium chloride concentration (Fig. 1, I and II) whereas nearly equal retention times for both the anions are observed in 600 and 3000 mg l^{-1} sodium chloride concentration (Fig. 1, II and III). Although the sulphate peaks are well resolved up to the baseline (Fig. 1), about 28% lower peak heights as compared to the standard in water (Fig. 1, I) are observed in higher sodium chloride concentration (Fig. 1, II and III). This behaviour is in confirmation with the one observed by Singh et al. [17] for the determination of sulphate in chloride matrix. When chromatograms (Fig. 1) of increasing sodium chloride concentration (Fig. 1, I–III) are compared, a decrease in the peak area of chlorate is observed. At the same time, no change in the peak area of

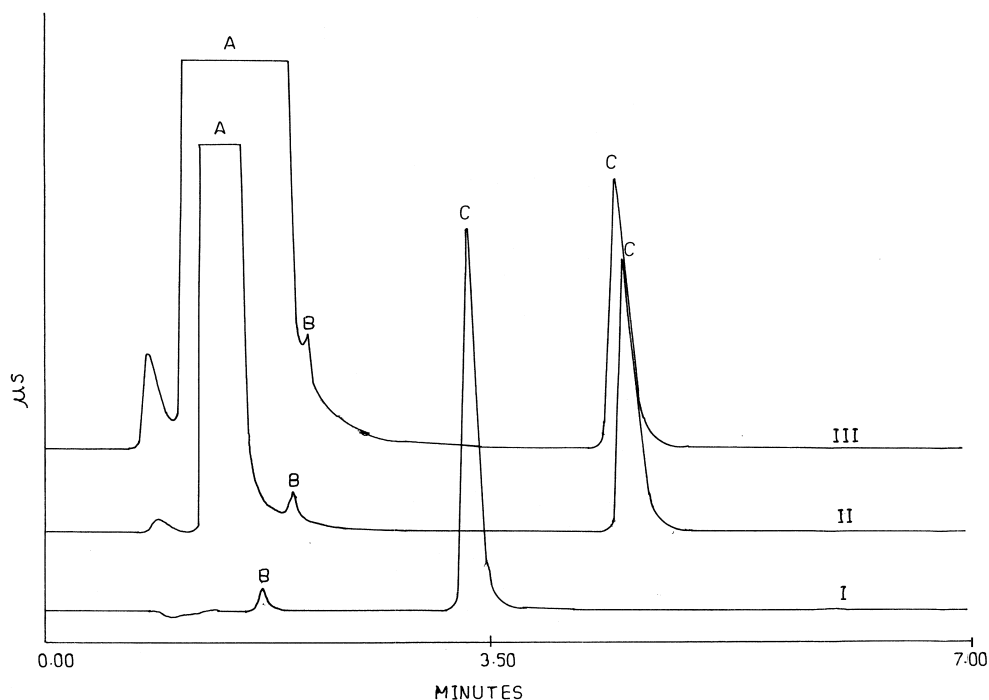


Fig. 1. Chromatograms of standard solutions containing 1.6 mg l^{-1} ClO_3^- (B) and 20 mg l^{-1} SO_4^{2-} (C) in a sodium chloride (A) matrix (I=0, II=600 and III=3000 mg l^{-1} NaCl).

sulphate occurred. However, a decrease in chlorate peak area is attributed to lack of baseline resolution.

3.1. Effect of sodium chloride concentration on the chlorate peak area

The effect of sodium chloride concentration on the peak areas of both anions has been studied by using three sets of calibration standards. The first and second sets of calibration standards contain 0.4, 0.8, 1.2, 1.6, 2.0, 2.4 mg l⁻¹ chlorate (ClO₃⁻) and 5, 10,

15, 20, 25, 30 mg l⁻¹ sulphate (SO₄²⁻) spiked into 0 (I) and 600 mg l⁻¹ (II) sodium chloride, respectively whereas the third set contains 1.6, 2.0, 2.4, 2.8 mg l⁻¹ chlorate (ClO₃⁻) and 20, 25, 30, 35 mg l⁻¹ sulphate (SO₄²⁻) spiked into 3000 mg l⁻¹ (III) sodium chloride. The individual peak areas were obtained for two replicate injections for each of standard solutions used in the calibration curve and mean values obtained were plotted against the corresponding concentrations. Since the mean values of sulphate areas were nearly equal for each standard

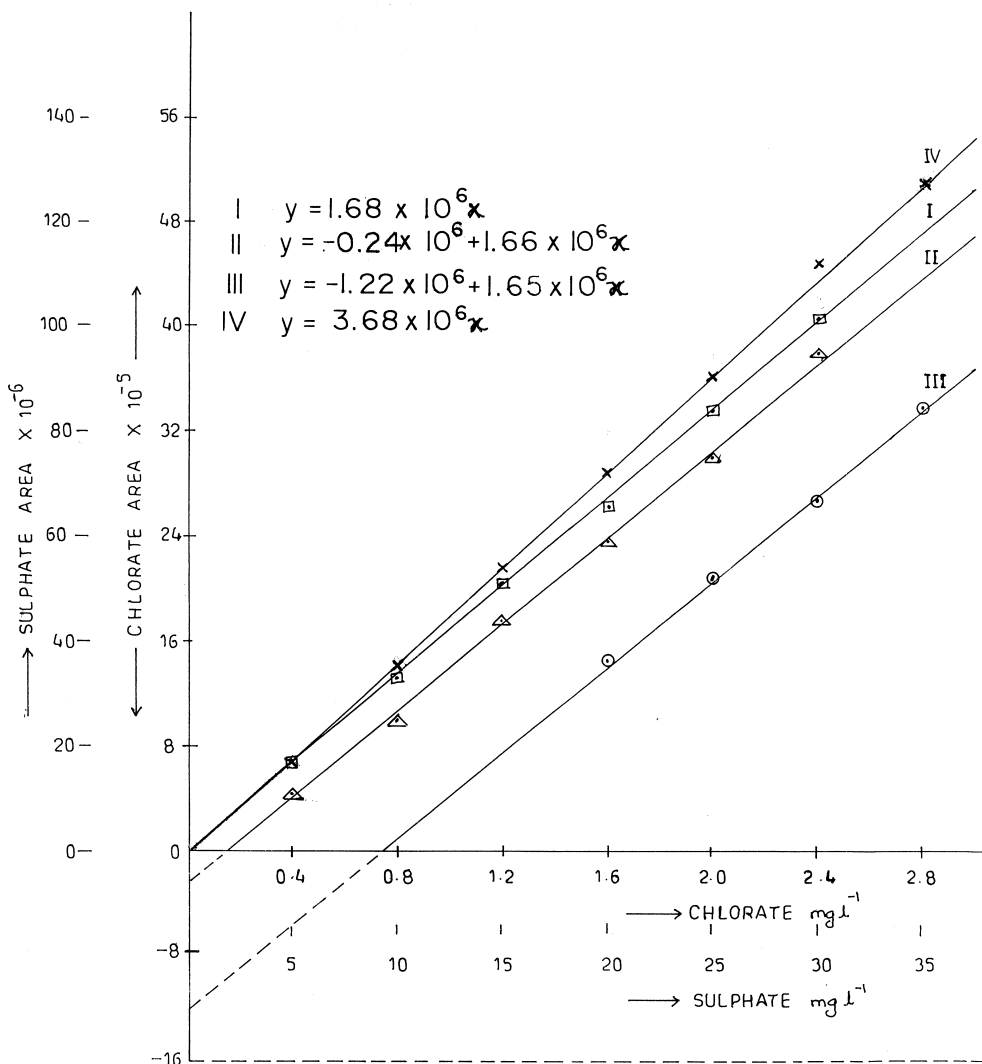


Fig. 2. Influence of sodium chloride concentration on the chlorate (ClO₃⁻) I, II, III and sulphate (SO₄²⁻) IV calibration curves (I=0, II=600, III=3000 mg l⁻¹ NaCl and IV=0, 600 and 3000 mg l⁻¹ NaCl). Calibration equation: y =peak area, x =concentration (mg l⁻¹).

from the first, second and/or third set of calibration standards, mean of mean values were plotted against the corresponding concentrations. Fig. 2 shows the influence of sodium chloride concentration on the chlorate I, II, III and sulphate IV calibration curves. Equations of calibration curves for chlorate and sulphate anions, spiked into the 0, 600, 3000 mg l⁻¹ sodium chloride, are also shown in Fig. 2. These calibration curves are linear with correlation coefficients greater than 0.997. Under the fixed efficiency of analytical column, as the sodium chloride concentration increases from 0, 600 to 3000 mg l⁻¹, the y-intercept values of chlorate calibration curves (Fig. 2, I–III) decrease gradually from 0, -0.24·10⁶ to -1.24·10⁶, respectively whereas slope values are nearly equal. However, using similar conditions of sodium chloride concentration, a single calibration curve with 0 y-intercept value is obtained for the sulphate anion. This indicates that the chlorate determination is directly affected due to co-elution of chlorate and chloride in the presence of sodium chloride whereas the sulphate determination is not

affected in the above studies. Therefore, matrix match technique using 600 mg l⁻¹ sodium chloride matrix provides the suitable method for simultaneous determination of chlorate and sulphate in industrial brine samples.

3.2. Analytical performance and applications

The recoveries of chlorate (ClO₃⁻) and sulphate (SO₄²⁻) from synthetic mixtures in the 600 mg l⁻¹ sodium chloride are given in Table 2. The observed error of the method is less than ±5.0%. The statistical evaluation of the method is given in Table 3. The reproducibility of the quantitative measurement is quite good as indicated by the relative standard deviation (RSD) ranging from 0.4 to 2.9% for the three sets containing different levels of chlorate and sulphate. This method has been proved to be accurate and rapid; the total analysis time being less than 7 min.

The proposed method was applied to the analysis of sodium chloride brines and solar (industrial) salt

Table 2
Recovery of chlorate (ClO₃⁻) and sulphate (SO₄²⁻) spiked into synthetic sodium chloride brine (600 mg l⁻¹)

Set		Amount taken (mg l ⁻¹)	Amount found (mg l ⁻¹) ^a	% Error
1	Chlorate	0.24	0.23	-4.2
	Sulphate	3.00	3.10	+3.3
2	Chlorate	0.40	0.39	-2.5
	Sulphate	5.00	5.01	+0.2
3	Chlorate	0.50	0.48	-4.0
	Sulphate	6.00	5.70	-5.0
4	Chlorate	0.70	0.68	-2.8
	Sulphate	9.00	8.84	-1.8
5	Chlorate	0.80	0.78	-2.5
	Sulphate	10.00	9.60	-4.0
6	Chlorate	0.90	0.88	-2.2
	Sulphate	12.00	11.40	-5.0
7	Chlorate	1.20	1.23	+2.5
	Sulphate	15.00	15.20	+1.3
8	Chlorate	1.60	1.58	-1.2
	Sulphate	20.00	20.07	+0.4
9	Chlorate	2.00	2.07	+3.5
	Sulphate	25.00	24.20	-3.2
10	Chlorate	2.40	2.50	+4.2
	Sulphate	30.00	30.80	+2.7

^a Average of two determinations.

Table 3
Reproducibility study of chlorate (ClO_3^-) and sulphate (SO_4^{2-}) spiked into synthetic sodium chloride brine (600 mg l^{-1})

Set		Amount taken (mg l^{-1})	Amount found (mg l^{-1}) ^a	SD	RSD (%)
I	Chlorate	0.4	0.39	0.01	2.6
	Sulphate	5.0	5.02	0.02	0.4
II	Chlorate	1.2	1.23	0.03	2.4
	Sulphate	15.0	15.40	0.20	1.3
III	Chlorate	2.4	2.44	0.07	2.9
	Sulphate	30.0	30.35	0.33	1.1

^a Average of five determinations.

samples. Fig. 3 shows chromatograms of solar (industrial) salt (I), clarified brine (II), pure brine (III) and depleted brine (IV) samples from chlor-alkali industry. Table 4 shows the levels of chlorate, sulphate (by the IC method) and sodium chloride concentration (by the standard method) in the above samples. In the electrolytic process pure brine and depleted brine are the inlet and outlet of the anolyte, respectively. It is observed that the anolyte sodium chloride concentration decreases from 304 g l^{-1}

(pure brine) to 202 g l^{-1} in the depleted brine. Hence, the sulphate concentration is expected to increase from 6965 mg l^{-1} (pure brine) to 10482 mg l^{-1} ($6965 \times 304/202$) in depleted brine. Similarly chlorate concentration is expected to increase from 210 mg l^{-1} (pure brine) to 316 mg l^{-1} ($210 \times 304/202$) in depleted brine. It is evident from Table 4 that the expected 10482 mg l^{-1} of sulphate concentration correlates well with the 10400 mg l^{-1} of sulphate determined by the IC method. However, the

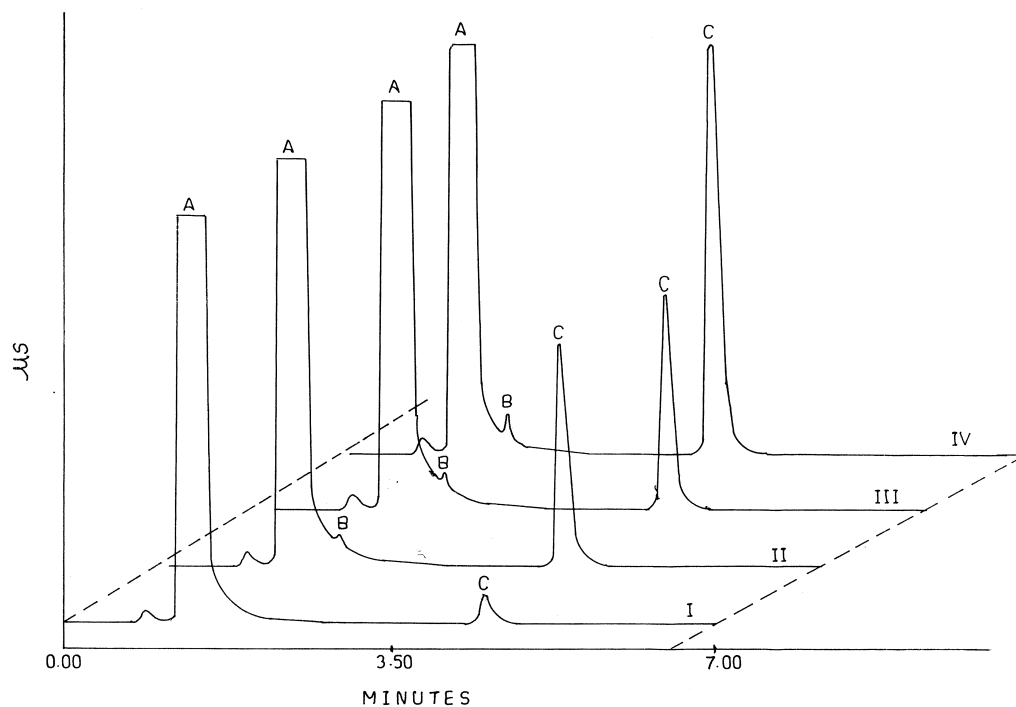


Fig. 3. Chromatograms of industrial salt and sodium chloride (A) brine samples (from chlor-alkali industry) containing ClO_3^- (B) and SO_4^{2-} (C). I=Industrial salt (600 mg l^{-1}), II=clarified brine (at 500-times dilution), III=pure brine (at 500-times dilution) and IV=depleted brine (at 333-times dilution).

Table 4
Analysis of industrial salt, clarified brine, pure brine and depleted brine samples from chlor-alkali industry

Sample	Dilution of brine (times)	Chlorates ^a (as ClO ₃ ⁻) (mg l ⁻¹)	Sulphate ^a (as SO ₄ ²⁻) (mg l ⁻¹)	Sodium chloride ^b (g l ⁻¹)
Solar (industrial) salt	1666	Nil	2.10 (3500) ^c	–
Clarified brine	500	0.45 (225)	14.47 (7235)	310
Pure brine	500	0.42 (210)	13.93 (6965)	304
Depleted brine	333	1.12 (373)	31.23 (10 400)	202

^a Numbers in parentheses represent the concentration in undiluted sample.

^b Sodium chloride concentration by silver nitrate titration method.

^c Sulphate concentration in solar salt by standard method gives 3450 mg l⁻¹.

373 mg l⁻¹ of chlorate concentration obtained by the IC method appears to be higher than the expected 316 mg l⁻¹ of chlorate. This high chlorate concentration (57 mg l⁻¹) observed may be due to the formation of sodium chlorate by back migration of OH⁻ ions in the anolyte system [2]. The proposed IC method can be satisfactorily applied to the determination of sulphate in solar (industrial) salt, as confirmed by the analysis using standard method (Table 4).

4. Conclusions

(i) On the basis of peak area evaluation, the determination of 5 to 35 mg l⁻¹ of sulphate (SO₄²⁻) is not affected in 3000 mg l⁻¹ of sodium chloride. (ii) Chlorate determination is affected due to co-elution of chlorate and chloride in the presence of sodium chloride matrix. (iii) A matrix match method for the simultaneous determination of chlorate and sulphate in industrial salt and sodium chloride brines is reported. This method has been proved to be practicable, accurate and rapid and applicable for monitoring the electrolysis system in chlor-alkali industry.

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References

- [1] Kirk-Othmer Encyclopedia of Chemical Technology, A Wiley-Interscience Publication, John Wiley and Son, New York, 4th ed., Vol. 1, 4th ed., 1991, pp. 948, 972.
- [2] Ullmann's Encyclopedia of Industrial Chemistry, VCH Publishers, D-6940 Weinheim (Fed. Rep. of Germany), 5th ed., Vol. A6, 5th ed., 1986, p. 438.
- [3] Encyclopedia of Chemical Processing and Design, MARCEL DEKKER, New York, Vol. 7, 1978, p. 391.
- [4] Ullmann's Encyclopedia of Industrial Chemistry, VCH Publishers, D-6940 Weinheim (Fed. Rep. of Germany), 5th ed., Vol. A24, 5th ed., 1993, p. 348.
- [5] Kirk-Othmer Encyclopedia of Chemical Technology, A Wiley-Interscience Publication, John Wiley and Son, New York, 4th ed., Vol. 1, 3rd ed., 1978, p. 858.
- [6] Encyclopedia of Chemical Processing and Design, MARCEL DEKKER, New York, Vol. 7, 1978, p. 453.
- [7] R.J. Lewis Sr. (Ed.), 8th ed, Sax's Dangerous Properties of Industrial Materials, Vol. III, Van Nostrand Reinhold, New York, 1992, p. 3070.
- [8] J. Weiss, Handbook of Ion Chromatography, Dionex, Sunnyvale, CA, 1986.
- [9] H. Small, Ion Chromatography, Plenum Press, New York, 1989.
- [10] V. Cheam, A.S.Y. Chau, Analyst (London) 112 (1987) 993.
- [11] K. Punning, T. Somer, J. Veisserik, Symp. Biol. Hung. 34 (1986) 541.
- [12] R.E. Smith, Anal. Chem. 55 (1983) 1427.
- [13] R.P. Singh, N.M. Abbas, presented at the Pittsburgh Analytical Conference '93, Atlanta, GA, 1993.

- [14] R.P. Singh, presented at the 28th Middle Atlantic Regional Meeting, The American Chemical Society, Baltimore, MD, 1994.
- [15] G.S. Pyen, M.J. Fishman, in: J.D. Mulik, E. Sawicki (Eds.), *Ion Chromatographic Analysis of Environmental Pollutants*, Vol. 2, Ann Arbor Science Publishers Inc, Ann Arbor, MI, 1979, pp. 235–244.
- [16] R.P. Lash, C.J. Hill, *Anal. Chim. Acta* 108 (1979) 405.
- [17] R.P. Singh, E.R. Pambid, N.M. Abbas, *Anal. Chem.* 63 (1991) 1897.
- [18] I.L. Marr, *Anal. Proc. (London)* 29 (1992) 153.
- [19] *Standard Methods for the Examination of Water and Wastewater*, 15th ed., APHA–AWWA–WPCF, Washington, DC, 1980, pp. 271, 439.