Journal of Chromatography, 546 (1991) 221–228
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 2247

On-column matrix elimination of high levels of chloride and sulfate in non-suppressed ion chromatography

MARHENI, PAUL R. HADDAD* and ANDREW R. McTAGGART
Department of Analytical Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)

ABSTRACT

On-column matrix elimination, in which samples containing a very high level of a matrix anion are chromatographed using the same matrix anion as eluent, is evaluated for samples containing chloride or sulfate. The detection method employed must be selective, and direct UV absorbance at 210 nm is utilized. A mixture of ten UV-absorbing anions (iodate, bromate, nitrite, bromide, nitrate, molybdate, chromate, vanadate, iodide and thiocyanate) is separated on a Waters IC Pak A column using 15 m*M* sodium chloride containing 5 m*M* phosphate buffer at pH 6.5 as eluent. The chromatographic performance of this separation was virtually unaltered for sample chloride concentrations in the range 0–20 000 ppm. Detection limits are in the sub-ppm range for a 10-μl injection, but can be reduced substantially through the use of larger injection volumes. The same approach was applied to samples containing elevated levels of sulphate, and a mixture of eight anions (as above, except for molybdate and chromate) could be separated using 10 m*M* sodium sulphate containing 5 m*M* phosphate buffer at pH 6.5 as eluent. Again, chromatographic performance was maintained in samples containing up to 20 000 ppm sulphate.

INTRODUCTION

The determination of a trace component in the presence of very high levels of potentially interfering sample matrix components is a common problem in many areas of analytical chemistry. In ion chromatography (IC), this problem becomes particularly severe when the sample contains high levels of ionic species, as typified by the determination of trace ionic components in brine samples. Although it may be possible to separate chromatographically the ionic matrix components from the analyte ion(s), this separation becomes difficult to achieve when the concentrations of the matrix ions are high and they are eluted as very large peaks which may obscure the analyte peaks. Even when a selective detection method is employed with which the matrix ions give little or no detector signal, the matrix ions can still exert a major influence on the final chromatogram by inducing variable retention times and loss of chromatographic efficiency. For example, the peaks for 5 ppm nitrite and nitrate have been shown to be broadened by the presence of chloride at levels above 300 ppm [1]. These effects are the direct result of the presence of a high ionic concentration in the sample, leading to either self-elution by the sample itself, or to loss of the band-

0021-9673/91/$03.50

compression effect which occurs normally when a dilute sample is injected onto an ion-exchange IC column.

Several approaches have been suggested to overcome these adverse effects of matrix ions. First, the concentration of the matrix ion(s) in the sample can be reduced prior to the analysis, usually with the aid of a suitable pre-column. For example, chloride levels can be lowered by passage of the sample through a cation-exchange pre-column in the silver form [2–4]. However, this approach must be applied selectively because of the danger that some analyte ions may also be lost [5]. The same process of removal of an interfering matrix ion can also be accomplished using dialysis through membranes, rather than pre-columns [6–8]. A second general approach to the problem of matrix ions is the selective removal of the analyte ion(s) from the matrix, again using pre-columns [9] or membranes [10,11]. In all of these methods, sample contamination arising from the clean-up steps must be considered [12].

A third general approach, which may be described as on-column matrix elimination, has been suggested by Ito and Sunahara [13] and involves the use of the major matrix ion as the eluent. When this is done, the column is in the form of the major matrix ion before injection of the sample, so that the matrix ion shows little or no retention. Provided that the detection method used can discriminate against the matrix ion, a workable IC procedure results. As an example, the determination of anions in brine solutions can be considered. Here, an anion-exchange column can be used with a sodium chloride eluent and direct UV absorbance detection at 210 nm. At this wavelength, chloride does not absorb appreciably [14] and because chloride is present in the eluent, the method should also be resistant to high levels of chloride in the sample. This approach has been utilized for the determination of iodide and thiocyanate in concentrated salt solutions using UV absorbance and amperometric detection [15], and for iodide in sea water using amperometric detection [13].

In this paper, we investigate the use of on-column matrix elimination with UV absorbance when chloride or sulphate is the major matrix anion. The utility of sodium chloride or sodium sulfate eluents for these situations is assessed.

EXPERIMENTAL

Instrumentation

The IC system consisted of a Millipore Waters (Milford, MA, U.S.A.) Model M 6000A pump and U6K injector, a Shimadzu (Kyoto, Japan) Model SPD-6AV UV–visible spectrophotometric detector operated at 210 nm and a Houston Instruments (Austin, TX, U.S.A.) Omniscribe recorder. The column used was a Waters IC Pak A, 50 × 4.6 mm I.D., packed with methacrylate-based anion exchanger of capacity 30 ± 3 μequiv./ml.

Reagents

All reagents were of analytical-reagent grade. Water used in this study was purified on a Millipore (Bedford, MA, U.S.A.) Milli-Q system and was filtered through a 0.45-μm membrane filter and degassed in an ultrasonic bath before use.

Stock solutions (1000 ppm) of the standard anions were prepared by dissolving appropriate amounts of sodium or potassium salts in purified water and were stored in glass containers. Working mixtures of these anions were prepared at the concentrations specified in the figure captions by dilution of the stock solutions. Sodium chloride eluents containing 5 m*M* phosphate buffer (pH 6.5) were prepared from stock solutions of 2 *M* analytical-reagent grade sodium chloride (Ajax, Sydney, Australia), 0.25 *M* disodium hydrogenphosphate and 0.25 *M* sodium dihydrogenphosphate. Sodium sulphate eluents containing 5 m*M* phosphate buffer (pH 6.5) were prepared in a similar manner. All eluents were operated at a flow-rate of 1.2 ml/min and separations were carried out at room temperature.

RESULTS AND DISCUSSION

Selection of chromatographic conditions

One of the first aims of this work was to investigate the utility of sodium chloride and sodium sulphate as eluents for the separation of anions. Since the ultimate purpose of these studies was to find chromatographic conditions which were tolerant towards very high levels of chloride and sulphate as matrix ion, it was necessary to employ a detection method which shows little response to these species.

Two suitable detection approaches are UV absorbance (at wavelengths greater than 200 nm) and amperometry at a suitable electrode surface. Of these two methods, we selected the former because of its more widespread applicability. Numerous common anions show substantial absorptivities in the wavelength range 200–220 nm, and Williams [14] has listed the wavelengths of maximum absorption for many of these species. In this study, we have considered only bromide, bromate, iodide, iodate, nitrite, nitrate, chromate, vanadate, molybdate and thiocyanate as solute anions.

Optimal eluent compositions were sought for the separation of the above anions. A buffered eluent was considered preferable because of the weakly acidic nature of some of the solute anions, especially nitrite. For this reason, a 5-m*M* phosphate buffer at pH 6.5 was included in each eluent. When the concentration of chloride ion in the eluent was increased, the capacity factors (k') for solute anions decreased in the manner shown in Fig. 1. The linear relationship observed between log [NaCl] and log k' is in accordance with theoretical predictions for ion-exchange separations [16] and the observed slopes of these plots are in the range -0.68 to -0.97 for the singly charged solutes and -1.25 to -1.53 for the doubly charged solutes. These values are less than the theoretical slopes and indicate that the phosphate ions present in the eluent make some contribution to the elution of solute anions. Retention plots were also prepared for sodium sulphate eluents, and similar results were obtained. These plots were then used for an empirical optimization of the separation of the test solutes. The optimal eluents were 15 m*M* sodium chloride and 10 m*M* sodium sulphate, both containing 5 m*M* phosphate buffer at pH 6.5. The chromatograms obtained with these eluents are shown in Figs. 2a and 3a. It is noteworthy that only eight of the ten anions in the sample mixture could be resolved with the sulphate eluent (chromate and molybdate could not be separated from the other ions), whereas all ten anions were resolvable with the chloride eluent.

Performance characteristics and interference effects

Detection limits (for a 10-μl injection volume) obtainable in both eluents are listed in Table I, from which it can be seen that most of the test anions were detectable in the sub-ppm range. Peak height precision values for ten replicate injections of a

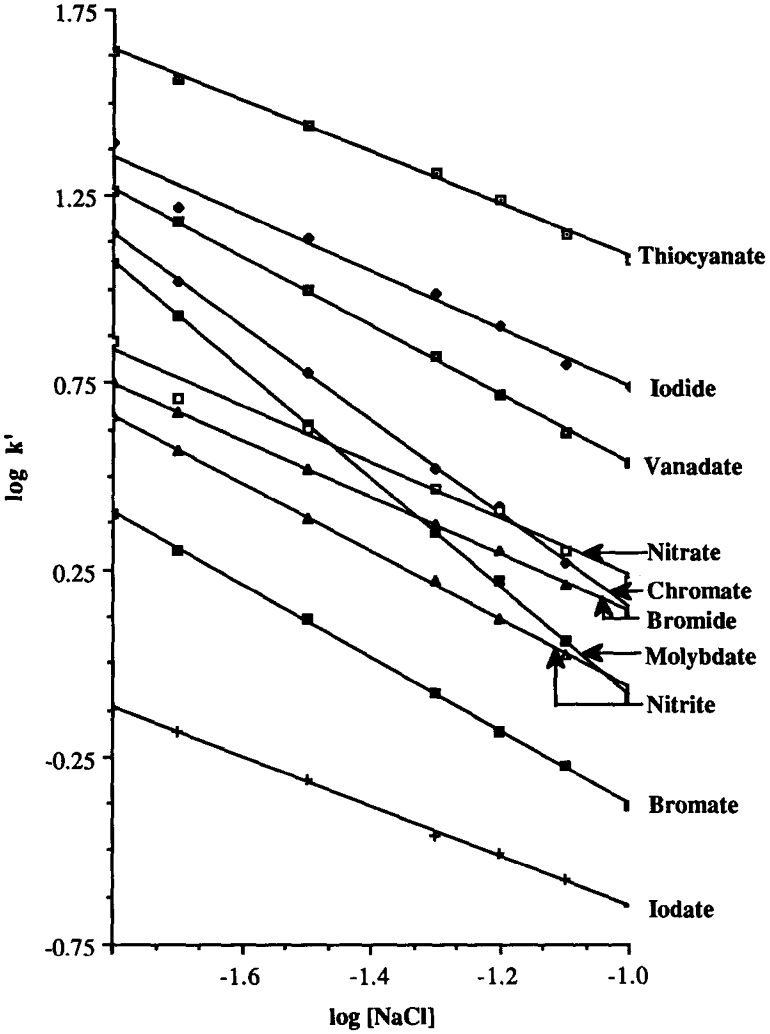

Fig. 1. Variation of solute retention with the concentration of chloride in the eluent.

standard mixture of anions were in the range 0.2–1.2% relative standard deviation (R.S.D.) for the chloride eluent and 1.6–3.1% R.S.D. for the sulphate eluent.

The tolerance of the separation shown in Fig. 2a to high levels of chloride present in the sample was studied using standards containing chloride in the range 0–30 000 ppm. The peak heights, detection limits, peak shapes and resolution of adjacent peaks were noted for each injection. Virtually no changes were observed up to 20 000 ppm, as evidenced by comparison of the chromatograms shown in Fig. 2a and b. The only exception to this was that the peak heights for some solutes (especially bromate) showed decreases; however, the areas of these peaks were not altered significantly. For samples containing more than 20 000 ppm of chloride, the negative peak which was eluted prior to nitrite became slightly more pronounced and some

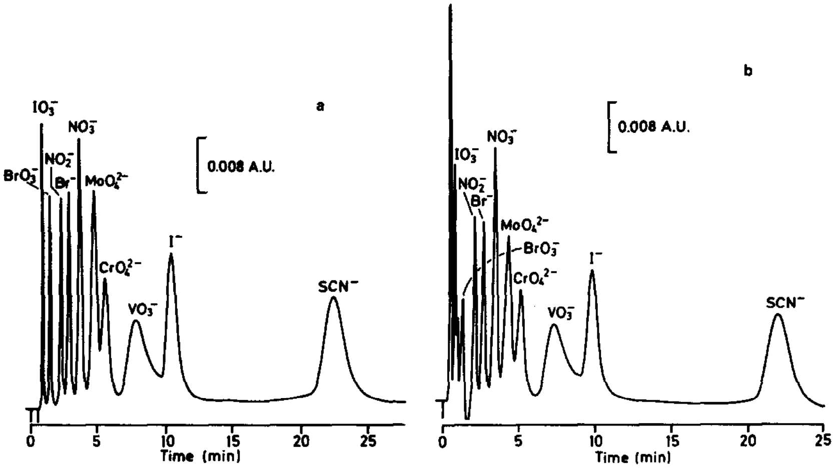

Fig. 2. Separation of ten anions in (a) water and (b) 20 000 ppm chloride. A Waters IC Pak A column was used and the eluent was 15 m*M* sodium chloride containing 5 m*M* phosphate buffer at pH 6.5, operated at a flow-rate of 1.2 ml/min. Detection was by UV absorbance at 210 nm. Solute concentrations are 5 ppm for nitrite, 10 ppm for nitrate and iodide, 25 ppm for iodate, bromide and molybdate, and 50 ppm for the remainder. The injection volume was 10 μl.

band broadening was observed. The identity of this negative peak is unknown. These effects are summarized in Table II, which shows the effect of chloride levels in the sample on some indicative performance characteristics. Data given in Table I show that there was a moderate increase in detection limits with increased chloride content in the sample. These results suggest that the chromatographic performance of the method is constant up to the approximate levels of chloride present in sea water, and

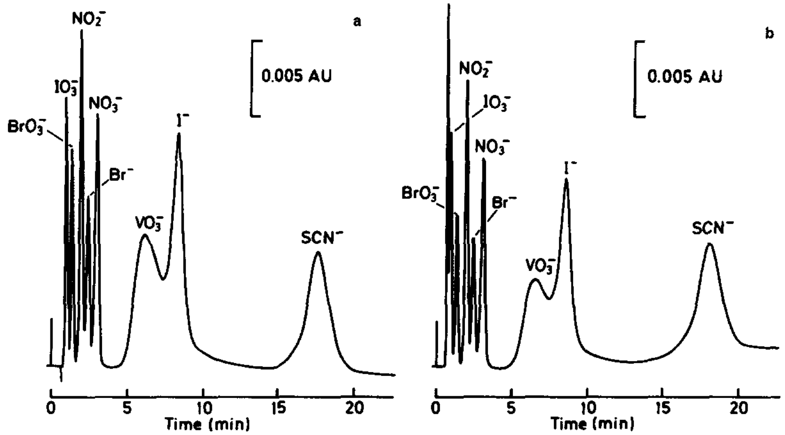

Fig. 3. Separation of eight anions in (a) water and (b) 20 000 ppm sulphate. A Waters IC Pak A column was used and the eluent was 10 m*M* sodium sulphate containing 5 m*M* phosphate buffer at pH 6.5, operated at a flow-rate of 1.2 ml/min. All other conditions as in Fig. 2.

TABLE I

DETECTION LIMITS (ppm) FOR THE PROPOSED METHODS, USING A 10-μl INJECTION VOLUME

Anion	Eluent 15 m*M* NaCl		Eluent 10 m*M* Na_2SO_4	
	Sample in H_2O	Sample in 20 000 ppm Cl^-	Sample in H_2O	Sample in 20 000 ppm SO_4^{2-}
IO_3^-	0.12	0.26	0.56	0.63
BrO_3^-	0.32	1.2	1.36	1.94
NO_2^-	0.03	0.06	0.07	0.08
Br^-	0.16	0.29	1.75	2.3
NO_3^-	0.08	0.12	0.17	0.21
MoO_4^{2-}	0.18	0.40	–	–
CrO_4^{2-}	0.70	1.32	–	–
VO_3^-	1.70	2.6	1.9	3.4
I^-	0.57	0.82	0.25	0.3
SCN^-	0.60	1.0	1.2	1.3

this behaviour is in marked contrast to previously reported results with a tetraborate–carbonate eluent, wherein a maximum of 300 ppm of chloride could be tolerated [1].

A similar study was conducted by determining the tolerance of buffered sodium sulphate eluents towards concentrations of sulphate in the sample within the range

TABLE II

PERFORMANCE PARAMETERS FOR THE DEVELOPED SEPARATIONS IN THE PRESENCE OF HIGH LEVELS OF MATRIX ANIONS

The values shown for each parameter are percentages normalized to the value of that parameter for samples containing no matrix anion.

Performance parameter	Eluent 15 m*M* NaCl			Eluent 10 m*M* Na_2SO_4		
	ppm Cl^- in sample			ppm SO_4^{2-} in sample		
	10 000	20 000	30 000	10 000	20 000	30 000
Peak height BrO_3^-	92	65	38	83	79	75
Peak height IO_3^-	94	88	76	99	96	94
Peak height NO_2^-	96	95	88	97	92	71
Peak height Br^-	91	85	84	88	84	81
Peak height NO_3^-	97	95	95	99	98	94
Peak height MoO_4^{2-}	86	80	70	–	–	–
Peak height CrO_4^{2-}	89	83	75	–	–	–
Peak height VO_3^-	99	96	95	92	87	82
Peak height I^-	92	86	86	98	95	95
Peak height SCN^-	90	85	85	99	96	95
R_s IO_3^-/BrO_3^-	100	100	98	100	98	96
R_s NO_2^-/Br^-	100	98	97	100	99	99
R_s Br^-/NO_3^-	100	99	95	99	97	95
R_s VO_3^-/I^-	100	97	96	100	98	95
N for NO_3^-	100	96	96	100	99	97
N for SCN^-	99	99	98	100	98	98

0–30 000 ppm. Again, indicative performance characteristics are summarized in Table II, which shows that the presence of 20 000 ppm of sulfate produced little effect. Above this level, some changes in performance (especially on peak heights) were observed, but these were relatively slight. Comparison of Fig. 3a and b illustrates these effects. Again, detection limits increased slightly as sulphate was added to the sample (Table I), but the changes were relatively small.

Determination of trace levels of iodide

In view of the apparent ruggedness of the methods when used for samples containing ppm levels of solute anions, the application of the technique to trace level determinations was also studied. In particular, we wished to investigate the effects produced by varying the ratio of the matrix ion concentration in the sample to that in the eluent. These effects could be most clearly demonstrated using a solute anion with strong retention, since high eluent concentrations could be employed. For this reason, the determination of iodide in high-chloride matrices was selected as a model system.

Fig. 4 shows chromatograms obtained for 100-μl injections of 100 ppb (10^9) of iodide in a matrix of 20 000 ppm of chloride, using eluents containing 15, 50 and 100 m*M* of sodium chloride. As expected, the retention time of iodide decreased with increasing eluent concentration, leading to sharper peaks, but the chromatographic efficiency (as determined by calculation of the number of theoretical plates for each peak) was approximately constant for all injections. This suggests that the concentration ratio of the matrix anion in the sample and the eluent does not play a significant effect in the matrix elimination technique. That is, provided the eluent contains sufficient concentration of the matrix anion to saturate all of the ion-exchange sites on the stationary phase, then effective on-column matrix elimination will occur.

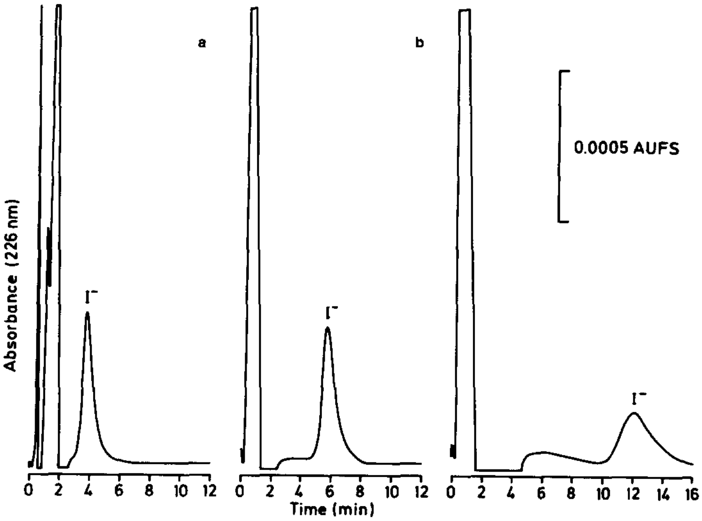

Fig. 4. Elution of trace iodide with eluents comprising (a) 100, (b) 50 and (c) 15 m*M* sodium chloride with 5 m*M* phosphate buffer at pH 6.7. The sample was 100 μl of 100 ppb (10^9) iodide in 20 000 ppm chloride. A Waters IC Pak A column was used, but the particular column employed was a different one than that used for Fig. 2.

CONCLUSIONS

On-column matrix elimination, wherein the major matrix anion is utilized as the eluent anion, has been shown to be an effective method for dealing with samples containing very high levels of chloride and sulphate. Under the conditions described, the method is restricted to the separation and detection of UV-absorbing anions, but would be equally applicable to other selective detection methods, such as amperometry and potentiometry. The method provides a viable approach to the ubiquitous problem of determining anionic species in saline samples.

REFERENCES

1 H. Saitoh and K. Oikawa, *Bunseki Kagaku*, 33 (1984) E441.
2 K. Oikawa, H. Sato, S. Sakazume and M. Fujii, *Bunseki Kagaku*, 31 (1982) E251.
3 F. A. Buytenhuys, *J. Chromatogr.*, 218 (1981) 57.
4 R. Bagchi and P. R. Haddad, *Proc. 9th Aust. Symp. Anal. Chem., Sydney, May, 1987*, Royal Australian Chemical Institute, Analytical Chemistry Division, Sydney, 1987, p. 147.
5 P. R. Haddad, *J. Chromatogr.*, 482 (1989) 267.
6 J. A. Cox and N. Tanaka, *Anal. Chem.*, 57 (1985) 385.
7 W. R. Jones and P. Jandik, *J. Chromatogr. Sci.*, 27 (1989) 449.
8 J. M. Pettersen, H. G. Johnsen and W. Lund, *Talanta*, 35 (1988) 245.
9 W. Buchberger and K. Winsauer, *J. Chromatogr.*, 482 (1989) 401.
10 J. A. Cox, E. Dabek-Zlotorzynskaya, R. Saari and N. Tanaka, *Analyst (London)*, 113 (1988) 1401.
11 F.R. Nordmeyer and L. D. Hansen, *Anal. Chem.*, 54 (1982) 2605.
12 P. R. Haddad and P. E. Jackson, *Ion Chromatography –Principles and Applications*, Elsevier, Amsterdam, 1990, p. 435.
13 K. Ito and H. Sunahara, *Bunseki Kagaku*, 37 (1988) 292.
14 R. J. Williams, *Anal. Chem.*, 55 (1983) 851.
15 K. Ito and H. Sunahara, *J. Chromatogr.*, 502 (1990) 121.
16 P. R. Haddad and C. E. Cowie, *J. Chromatogr.*, 303 (1984) 321.