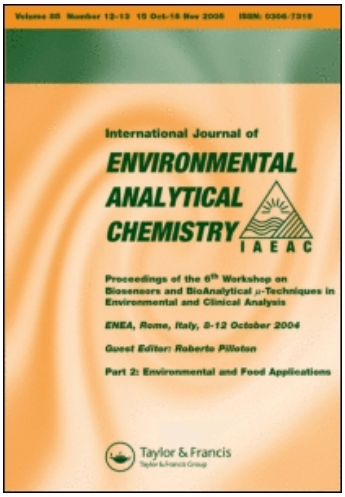

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Matrix Effects in the Determination of Low Anion Concentrations using Suppressed IC

Jos Neele[a]; Rob Cleven[a]; Henk Van de Wiel[a]
[a] Laboratory of Inorganic-Analytical Chemistry, National Institute of Public Health and the Environment (RIVM), Bilthoven, The Netherlands

Online publication date: 17 September 2010

To cite this Article Neele, Jos , Cleven, Rob and Van de Wiel, Henk(2002) 'Matrix Effects in the Determination of Low Anion Concentrations using Suppressed IC', International Journal of Environmental Analytical Chemistry, 82: 1, 13 — 22
To link to this Article: DOI: 10.1080/03067310290024058
URL: http://dx.doi.org/10.1080/03067310290024058

Intern. J. Environ. Anal. Chem., Vol. 82, No. 1, pp. 13–22

Taylor & Francis
Taylor & Francis Group

MATRIX EFFECTS IN THE DETERMINATION OF LOW ANION CONCENTRATIONS USING SUPPRESSED IC

JOS NEELE, ROB F.M.J. CLEVEN* and HENK J. VAN DE WIEL

Laboratory of Inorganic-Analytical Chemistry, National Institute of Public Health and the Environment (RIVM), P.O. Box 1, 3720 BA, Bilthoven, The Netherlands

(Received 25 February 2001 ; In final form 10 July 2001)

Concentrations of anions in environmental water samples such as chloride, nitrate and sulphate, may differ orders of magnitude. Conditions have been investigated under which the quality of ion chromatographic data for series of environmental water samples, comprising samples with low anion concentrations, can be affected by the matrix of previous samples in the series. Effects of a high ionic sample matrix on the elution and retention processes of analytes have also been studied by repeated analyses of standards and blanks. The study was performed using a Dionex 2000i chromatograph and an AS4ASC column. Additionally, a Dionex DX500 chromatograph, equipped with a sodium hydroxide eluent generator and a AS15 column, was applied to investigate effects of low anion concentrations in the (bi)carbonate eluent used in the Dionex 2000i system. The effects are explained by distortions of the distribution of anions over eluent and stationary phase. Simultaneous analyses of major and minor components in routine measurements in a single series is still possible using suppressed ion chromatography, even in cases where the matrices are also divergent. Remedial tools to reduce undesired effects are described.

Keywords: Matrix effects; Anions; Ion chromatography

INTRODUCTION

Chemically suppressed ion chromatography (IC) with conductivity detection has developed into a precise and reliable technique for quantification of common anionic species, and is nowadays an important analytical tool in routine analyses of environmental water samples[1]. Concentrations of anions of environmental samples, for example chloride, nitrate and sulphate, may differ orders of magnitude in such samples. In ground water in The Netherlands, chloride concentrations occur in the range from $10–10^5$ μmol/l. Still, different types of samples, including rainwater, drinking water, ground water, extracts of air filters, surface water and stemflow, comprising widely diverging matrices, are being analysed in our laboratory in a single series, in which both chloride, nitrate and sulphate are simultaneously determined at the μmol/l level.

It is well known that IC determinations of anions are highly matrix independent[2, 3]. However, it has been observed that under certain conditions, undesired matrix effects

*Corresponding author. Fax: +31-30-274 4455; E-mail: rob.cleven@rivm.nl

ISSN 0306-7319 print © 2002 Taylor & Francis Ltd
DOI: 10.1080/03067310290024058

may arise, hampering correct quantification and identification of these components in routine measurements, especially when their concentrations are low[4]. Many conventionally applied anion exchange columns have low capacities, which allows only the use of low concentrations of eluents. The rate of migration of the anions through the column is directly dependent upon the type and concentrations of the constituents in the eluent. With the low ion exchange capacities and low eluent concentrations inorganic, and high molecular mass organic anions injected with the sample may be retained on the column, and contamination of columns may result.

In this study, conditions have been investigated under which the quality of ion chromatographic data for series of environmental water samples, notably samples with low anion concentrations, can be affected by the matrix of previous samples in a series. Effects of a high ionic sample matrix on the elution and retention processes in the ion chromatographic column have also been studied, by repeated analyses of samples, to investigate the influence on the analytical response of chloride and of low levels of nitrate, sulphate, and oxalate. Those sample matrices have been effectuated by additions of potassium chloride, hydrochloric acid or sodium hydroxide to mixed standard solutions and blanks. Additionally, effects of low anion concentrations present in the (bi)carbonate eluent used, have been separately investigated.

EXPERIMENTAL

Instrumentation

A Dionex Model 2000i ion chromatographic system has been used, equipped with Dionex Ion Pac AG4ASC and AS4ASC columns (Dionex) with a capacity of 20 μeq/1. Isocratic elution with an eluent composed of mixtures of 1.7 mmol/l $NaHCO_3$ and 1.8 mmol/l Na_2CO_3 in water has been applied at a flow rate of 1.0 ml/min. The separator column, inserted in a column holder, and the regenerant supply have been thermostatted at $31 \pm 0.1°C$. The suppressor was an ASRS, depending on the application, either in the chemical mode or in the water mode. An AMMSII suppressor has also been used in some experiments. Detection was carried out with a Pulsed Electrochemical Detector in the conductivity mode (Model PEDII) and a UV-VIS spectrophotometer Milton Roy type SM 4000 with UV detection at 198 nm. Data acquisition and peak integration have been performed with a Pentium linked 486 PC with Dionex AI 450 software, release 3.31. Sample injections were carried out with an inert slider valve with a 50 μl sample loop, unless stated otherwise. PTFE tubings have been used throughout, the connections being as short as possible. Additionally, a Dionex Model DX500 ion chromatographic system has been used, equipped with AG11HC/AG15/AS15 columns (Dionex), and an eluent generator EG 40, generating ultrapure potassium hydroxide solution. Detection was carried out with a Pulsed Electrochemical Detector in the conductivity mode (Model PE40). The two guard columns with the AS15 seperation column in combination with gradient elution (20–40 mmol/l) resulted in excellent resolution between low and high concentrations of anions.

Reagents

High purity deionized Milli Q water (Millipore) has been used, after a distillation trap, resulting in a specific resistance of 18 $M\Omega.cm^{-1}$, for preparing eluent, standard and

blank solutions. Eluents have been degassed by purging with helium. The quality of the chemicals (all: Merck) was *suprapure* for sodium carbonate, potassium chloride, potassium nitrate and sodium hydroxide, whereas the quality of hydrochloric acid, sodium hydrogen carbonate, sodium oxalate and potassium sulphate was *pro analyse*.

Procedure

Standard Operation Procedures M302[5] and M276[6] have generally been adopted as basis procedures in the study for the chromatographic systems 2000i and DX500, respectively, The quantification of the anion concentrations was carried out using external standard calibration with mixed standard solutions. Performance characteristics of both procedures are: detection limits of 2–4 μmol/l and repeatablities better than 3% for the components studied in the concentration ranges involved.

RESULTS AND DISCUSSION

Repeatability and 'System Blank'

As this study is aimed at matrix effects on the performance of ion chromatographic routine analyses of low anion concentrations, the repeatability of the adopted method was first reconfirmed under well-defined conditions. Relative standard deviations of repeated analyses (with $n = 5$) of mixed standard solutions of nitrate, sulphate and oxalate have been determined with respect to the integrated peak area and the observed retention times. The results, presented in Table I, are in good agreement with the expected values. Nevertheless, during operational management of the method, incidentally small peaks sometimes appeared in blank solutions, violating, in the case of low analyte levels, the generally good performance. In initial experiments to investigate these unexpected peaks, a number of series of four successive blanks were analyzed that had been preceded by three runs with standard solutions of potassium sulphate. A composition of eight chromatograms of the blank solutions are presented in Fig. 1. The lower four chromatograms, from bottom to top in the figure, refer to blanks that have been successively analyzed after the analysis of three standard solutions of potassium sulphate of 5 mmol/l. The upper four chromatograms, from bottom to top in the figure, refer to blanks, successively analyzed after analysis of three standard solutions of potassium sulphate of 100 mmol/l. In nearly all the chromatograms small peaks can be observed. In the composition of chromatograms, the small peaks in the blanks

TABLE I Relative Standard Deviations (RSD) of the peak area and of the retention time for repeated ion chromatographic determinations ($n = 5$) of low concentrations of nitrate, sulphate and oxalate in mixed standard solutions

Concentration (μmol/l)	*RSD (peak area) (%)*			*RSD (retention time) (%)*		
	Nitrate	*Sulphate*	*Oxalate*	*Nitrate*	*Sulphate*	*Oxalate*
2.0	2.4	1.4	2.0	0.2	0.0	0.0
5.0	2.5	0.8	0.8	0.0	0.0	0.0
10.0	2.1	1.1	1.2	0.0	0.2	0.2

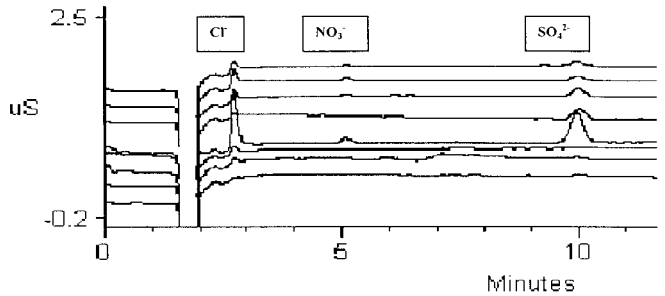

FIGURE 1 A composition of eight chromatograms, all of them referring to determinations of blank solutions. The lower four chromatograms refer to blanks that have been successively analyzed after the analysis of three standard solutions of K_2SO_4 of 5 mmol/l; the upper four refer to blanks, successively analyzed after analysis of three standard solutions of K_2SO_4 of 100 mmol/l.

occur at retention times of 3.8, 5.0 and 10.0 min, and are to be assigned to chloride, nitrate and sulphate, respectively. In the fourth blank of the lower four chromatograms, the 'highest' concentrations chloride, nitrate and sulphate, of 8.0, 0.9 and 4.4 μmol/l respectively, occur. It is noted, as different concentrations potassium sulphate had been added to samples preceding both series of blanks, that the sulphate concentrations in the blanks are not higher after the highest addition. As it has been verified that carry-over could be excluded, it is concluded that the observed concentrations of chloride, nitrate and sulphate in the blanks will not be dependent on the specific composition of the preceding samples. In continuation of the analysis of the blanks after these series presented, the peaks disappear. These experiments have been confirmed by a number of comparable series of analyses, also using different valves, suppressor modes, sample loops and tubing material. It is noted that carrying out the experiments with an addition of concentrated eluent in the samples (blanks and standards), so that the concentrations of eluent components in the 'sample' are nearly equal to the concentrations in the eluent, the peaks of chloride, nitrate and sulphate in blanks remain much smaller than those described in Fig. 1.

The results suggest a more general effect of the applied potassium sulphate solutions on the results for the subsequently following blank samples, notably a delivery of traces 'column-bound' anions. With an injected blank, differing strongly from the eluent with respect to anion concentrations, trace amounts from the column will be mobilized. The injected matrix disrupts the equilibration distribution of the trace anion contaminants between the eluent and the stationary phase. In these cases the concentration of anions in the blank injections may incidentally be increased, giving rise to a 'system blank', caused by differences in ionic strength between 'sample' and 'eluent'[4].

Blanks with hydrochloric acid

A further investigation of the presumed mobilization of traces of 'column-bound' anions is performed by addition of hydrochloric acid to blanks. The results are presented in Fig. 2, consisting of a composition of seven ion chromatograms of the analytical response of additions of 0.5, 1.0, 5.0, 10, 20, 50 and 100 mmol/l HCl respectively, to blank solutions. In the upper chromatograms of that composition, small peaks at the retention time for sulphate, at 8.8–9.0 min, can be observed. The highest

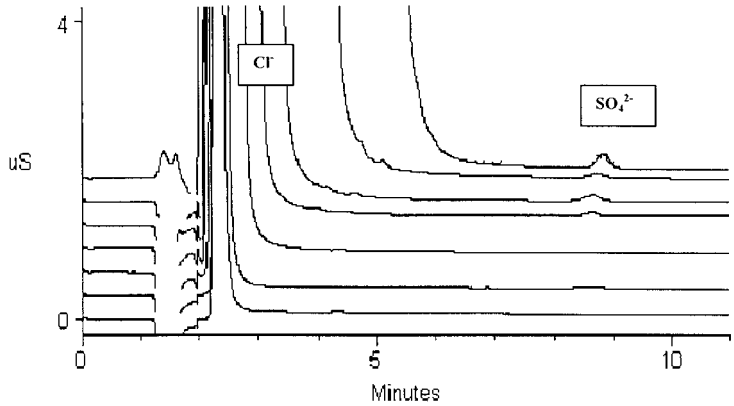

FIGURE 2 A composition of seven ion chromatograms of the (from bottom to top) analytical response of additions of 0.5, 1.0, 5.0, 10, 20, 50 and 100 mmol/l HCl respectively, to blank solutions.

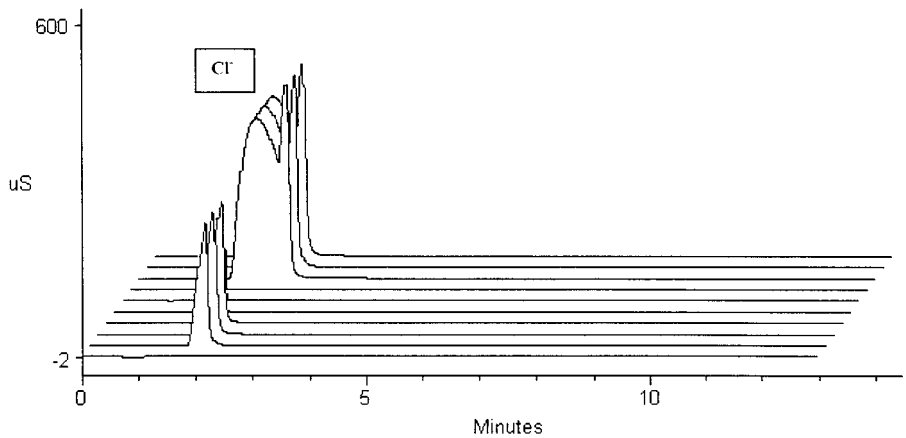

FIGURE 3 A composition of ten ion chromatograms of successive runs of (from bottom to top) a blank, three blanks with an addition of 10 mmol/l HCl, three blanks, and three blanks with an addition of 50 mmol/l HCl.

peak represents a sulphate concentration of 3.9 μmol/l. As for high hydrochloric acid concentrations, low concentrations of the bromide, nitrate can also be distinguished, and moreover, a shift of the retention time of sulphate can be observed; it is not likely that impurities in the acid exclusively account for the additional small peaks. The capacity of the Dionex analytical column applied, type AS4ASC, is sufficient to deal with the injected amounts of hydrochloric acid. Overload of the column cannot be the origin of the shift of the retention time of sulphate at this level.

A quite different matrix effect, in this case evoked by hydrochloric acid levels in blanks, that also incidentally can be observed, is presented in Fig. 3. This figure shows a composition of 10 ion chromatograms of successive runs of series of blanks with and without different levels of added hydrochloric acid. It is noted that the concentration levels of hydrochloric acid in the blanks exceed the total concentration of carbonate and hydrogen carbonate in the eluent. For the relatively high concentrations

of chloride, peak splitting occurs, and thus correct peak integration is hampered. It is assumed that in these cases, chloride is temporarily absorbed within the micromembrane suppressor surface, causing both broadening and splitting of the peak. As the retention time for chloride also increases, correct identification is also hampered. In this case chloride itself acts as the eluent, a phenomenon called 'on column eluent change'[7]. In addition to the phenomena described in this experiment, a lowering of the baseline has been observed, due to chemical reactions of hydrochloric acid, being a strong acid, with the basic components in the applied eluent[8], because of a decrease in the total conductivity as a result of these reactions. This effect may hamper computerized peak processing and thus correct calculations of analyte concentrations.

Different ionic strength sample matrices

Effects of the sample matrix have been further investigated by determining trace concentrations of nitrate, sulphate and oxalate in the presence of either 50 mmol/l sodium hydoxide, or hydrochloric acid or potassium chloride. Series of three samples, being mixed standard solutions of sodium nitrate, potassium sulphate and sodium oxalate, have been analyzed. For each trio applies: the concentration of (all) the anions to be determined is 2.0, 5.0 or 10.0 µmol/l. In Fig. 4, two corresponding compositions of several trios of chromatograms are shown, all of them (except the additional bottom ones for blanks) referring to the mixed standard solutions, with and without the abovementioned 'matrices'. The mode of detection is different for the two compositions. For the composition on top, UV detection, whereas for the bottom one conductivity detection has been applied. The difference in retention times between the responses of the conductivity and UV detector is only 0.1 min.

In the mixed standard solution without additions, and in the presence of sodium hydroxide, the retention times of nitrate, sulphate and oxalate are 4.5, 8.6 and 11 min, respectively. It can be observed in Fig. 4, that the retention time of nitrate is shifted from 4.5 to 5.0 min in the hydrochloric acid matrix and for sulphate from 8.6 to 8.8 min, whereas there is no shift in the case of oxalate. The composition on top also shows that the impact of the hydrochloric acid matrix on the retention times for nitrate is more pronounced than in the case of the potassium chloride matrix, retention times for nitrate being 5.2 and 4.8 min, respectively. It also can be observed that bromide is eluting just before the nitrate. Bromide is here to be considered as an impurity in hydrochloric acid and in potassium chloride, because the bromide peak heights are proportional to the acid and salt concentrations.

Additional peaks occur in the high ionic matrices, for example at a retention time of about 1.4 min, in the chromatograms with UV detection. If the anions comprising the sample matrix act as an eluent, weakly retained ions, such as sodium and potassium ions, can be eluted from the column. Additional peaks, also at about 1.4 min, in those chromatograms with conductivity detection that refer to additional amounts of sodium hydroxide, will be caused by a temporary excess of protons due as a result of the interactions of the relatively high sodium hydroxide in the suppressor. This phenomenon also results in a distortion of the base line in the range of 1.2–3 min (in the case of added sodium hydroxide), excluding that range for correct determinations. However, applying UV detection (see the upper composition in Fig. 4), no distortion of the base line occurs in that range of retention times, supporting the hypothesis of reactions of an excess sodium hydroxide within the suppressor.

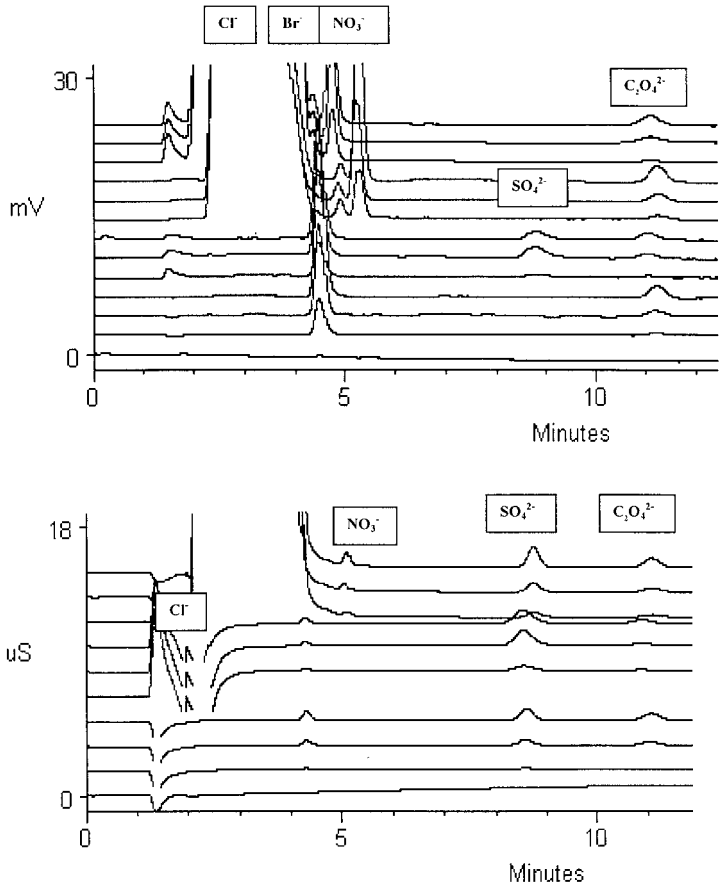

FIGURE 4 Two corresponding compositions of several trios of chromatograms, all of them (except the additional bottom ones for blanks) referring to determinations of standard solutions of mixtures of KNO_3, K_2SO_4 and $Na_2C_2O_4$. For each trio applies: the levels are 2.0, 5.0 or 10 μmol/l, respectively, for these components. Except for the first trio, 50 mmol/l of NaOH, or HCl, or KCl (only in top composition) is additionally present. The mode of detection differs: top composition, UV detection; bottom composition, conductivity detection.

Peak broadening also occurs, due to the 'matrix', as the anions at a high concentration temporarily will occupy exchange sites on the column. This 'on-column' elution by the matrix anions results in enhanced elution of trace anions from the column. It is clear from the overview of the chromatograms in Fig. 4 that due to the matrix, the identifications of nitrate and/or bromide are seriously hampered. A remedial tool is the simultaneous application of both conductivity and UV detection. The ratio of the analytical responses of both detectors should be matrix independent. This ratio provides an additional confirmation of the identity of an analyte. In the lower composition in Fig. 4, the chromatograms referring to the sodium hydroxide matrix (nrs. 4–7 from the bottom) also show peak broadening for sulphate and oxalate, at retention times of 8.8 and 11 min, respectively. The corresponding chromatograms in the upper composition, where UV detection applies, show a peak at a retention time of 8.5 min, that is *nearly* the retention time of sulphate. This peak cannot be a response for sulphate

because this substance gives no absorption in the UV at 198 nm, at low sulphate concentrations. Novič *et al.*, reported on-column inter-eluent neutralization in acid matrices[9], whereas Singh *et al.*, reported this effect in salt matrices[10]. The effect has been explained as the result of anion–proton interactions within the suppressor. Large amounts of H^+ react with SO_4^{2-} resulting in the formation of HSO_4^-. This type of interaction is equally applicable to $C_2O_4^{2-}$ (oxalate) yielding $HC_2O_4^-$. The effect is more pronounced for sulphate than for oxalate.

Additional investigations of anion concentrations in the eluent used in SOP M302 (eluent 302) have been peformed using a DX500 chromatographic system with potassium hydroxide solution as eluent, generated by Eluent generator EG 40. The results are given in Table II and Fig. 5. It is clear that in eluent 302, consisting of a pure carbonate/bicarbonate solution, if it is measured as a sample on the DX500 system,

TABLE II Average anion concentrations ($n = 5$), in μmol/l in eluent 302, and, for comparison, in Milli Q water and in a diluted standard solution, using a ion chromatographic system DX500, equipped with an eluent generator producing an ultrapure potassium hydroxide solution

Matrix	*Chloride*	*Sulphate*	*Bromide*	*Nitrate*
Eluent 302	1.4	~0.3	~0.3	~0.3
Diluted standard	22.5	2.2	0.6	0.4
Milli Q water	0.3			

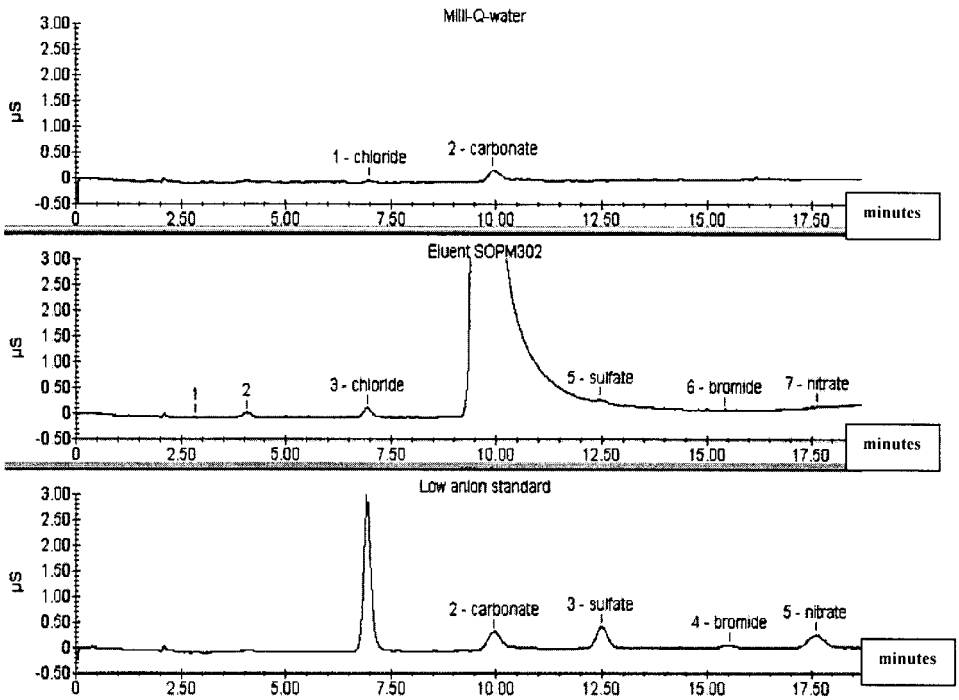

FIGURE 5 Ion chromatograms of anion determinations with the DX500 system, in Milli Q water, in eluent 302 and in a diluted standard solution. Concentrations are given in Table II.

traces chloride and sulphate show up. For comparison, Milli Q water and a (diluted) standard solution of chloride, sulphate, bromide and nitrate, have also been measured with the DX500 system, to support the significance of the results for eluent 302. The remedy to avoid misinterpretations of peaks in system 2000i, is to spike samples with the eluent.

Reducing the impact of high ionic strength matrices

As reduction or elimination of high ionic strength matrices can be important in suppressed ion chromatography to prevent erroneous results, sample dilution may be effective. For some of the matrix effects, the application of a smaller injection loop can be sufficient. Nowadays, 'clean-up' methods are also available to reduce high salt levels or extreme pH values in samples[11, 12]. Several *on-line* sample preparation techniques have been recently described[13, 14]. In this study, two *off-line* clean-up methods, to reduce a 200 mmol/l sodium hydroxide matrix, have been tested. Effects of different clean-up techniques on the determinations of chloride, nitrate and oxalate, all present in this matrix at a concentration of 10 μmol/l, and sulphate, present at 5 μmol/l, have been investigated. The techniques included: the use of an OnGuard-H pretreatment cartridge (Dionex, 39596), and a Milli Trap H^+ membrane cartridge (Waters, 35662). The OnGuard-H cartridge contains a styrene-based strong acid resin in the H^+ form[11]. In the Milli Trap H^+ device, a fiber-constructed cation exchange membrane in the hydrogen form is applied to eliminate the excess of hydroxide, cations and carbonate in the samples[12]. Both techniques have been used under optimum operational conditions. Conductivity detection has been applied in these experiments. The Milli Trap H^+ device was not able to reduce completely the initially high hydroxide level sufficiently, and hence peaks for sulphate and oxalate are virtually absent. The excess of hydroxyl ions in the samples is efficiently and easily removed by the OnGuard-H pretreatment cartridge. Results for the OnGuard-H pretreated samples are comparable to the results of the analyte concentrations in the original mixed standard solution (without matrix addition).

CONCLUSION

Under a number of conditions, the ion chromatographic determination of trace anions in routine analyses, may lead to erroneous results, even in cases where the repeatability of the methods according to standard test procedures, appears to be good. When the composition of the eluent, which is a compromise between sufficient peak resolution and satisfactory peak quality, is very different from the injected sample matrix, the delicate distribution of (small) anion concentrations between the eluent and stationary phase of the ion chromatographic column may be disrupted. Small impurities in the eluent will, under the mentioned conditions, result in an over-estimation of the concentration of analytes in samples. Moreover, high concentrations of ions in the sample matrices, in routine analysis of trace anions, may temporarily affect the elution and retention processes in the column. Analyte peaks may show up in blanks, low concentrations determined for analytes in samples may differ from the correct values, and retention time can be shifted, usually to longer retention times. This causes problems in peak identification and peak quality. With simultaneously applied conductivity

and UV detection, identification as well as quantification of detectable anions can be confirmed and errors can be eliminated. If an analyte is present in a high concentration, attention should be paid to the performance of the suppressor, as its capacity may be limited. Peak splitting may occur and peaks from intermediates in the chemical reactions in the suppressor arise, thus hampering correct determinations of analyte concentrations. An appropriate clean-up method will in a number of cases reduce problems. Reducing the differences in matrices between the sample and eluent concentration, has a remedial effect. Such a reduction is easily performed by spiking concentrated eluent to the sample, or by dilution of the sample. It is concluded that although matrix effects may occur in routine analysis of low concentrations of anions (at the μmol/l level), highly reproducible determinations are still possible in environmental samples series, if adequate precautions are adopted.

References

[1] P. Papoff, A. Giacomelli and M. Onor, *Microchemical J.*, **46**, 385–389 (1992).
[2] M.N. Bynum, S.Y. Tyree and W.E. Weiser, *Anal. Chem.*, **53**, 1936–1938 (1981).
[3] P.L. Buldini, J.L. Sharma and S. Sharma, *Analyst*, **119**, 121–124 (1994).
[4] A. Siriraks, C.A. Pohl and M. Toofan, *J. Chromatogr.*, **602**, 89–95 (1992).
[5] Standard Operation Procedure M302, Laboratory of Inorganic Analytical Chemistry, National Institute of Public Health and the Environment, Bilthoven (1997).
[6] Standard Operation Procedure M276, Laboratory of Inorganic Analytical Chemistry, National Institute of Public Health and the Environment, Bilthoven (1999).
[7] M. Novic, B. Divjak, B. Pihlar and V. Hudnik, *J. Chromatogr. A*, **739**, 35–42 (1996).
[8] J. Slanina, F.P. Bakker, P.A.C. Jongejan, L. van Lamoen and J.J. Möls, *Anal. Chim. Acta*, **130**, 1 (1981).
[9] M. Novič, B. Divjak and B. Pihlar, *J. Chromatogr. A*, **827**, 83–89 (1998).
[10] R.P. Singh, N.M. Abbas and S.A. Smesko, *J. Chromatogr. A*, **733**, 73 (1996).
[11] Installations Instructions and Trouble Shooting Guide for OnGuard Cartridges, Document 032934, Revision 07, Dionex Corporation, USA (1995).
[12] Waters, *Care and Use Manual.* Waters Milli Trap H^+ Membrane Cartridge, Document 35663 Revision 0 (1969).
[13] R.M. Montgomery, R. Saari-Nordhaus, L.M. Nair and J.M. Anderson, Jr., *J. Chromatogr. A*, **804**, 55 (1998).
[14] E. Kaiser, R. Kiser, J. Riviello and A. Siriraks, *LC-GC*, **13**, 888 (1995).