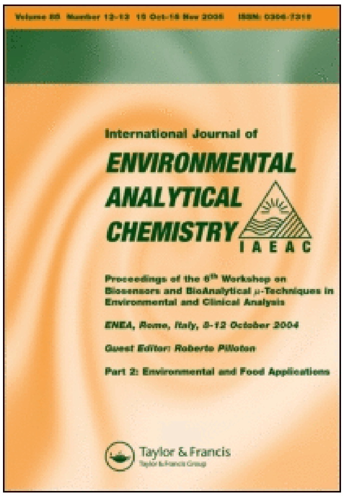

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The Determination of Common Anion Concentrations in Surface and Groundwater Samples by Eluent-Suppressed Ion Chromatography

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An automated ion chromatograph using hollow-fibre eluent suppression is shown to be a suitable instrument for continuous determination of F^-, Cl^-, PO_4^{-3}, NO_3^- and SO_4^{-2} at environmental concentrations in natural surface and ground water samples. Analytical precision for both standard anion solutions and samples, and the effect of NO_3^- sample concentration on NO_3^- retention time, is shown. Peak height and peak area quantification are compared and the effects of high Cl^- content, pH, storage and filtration on sample analysis are determined. The advantages of frequent automatic recalibration in maintaining reproducibility in continuous analysis are shown.

KEY WORDS: ion chromatography, environmental analysis, anions, groundwater, lakewaters.

INTRODUCTION

The use of ion chromatography with eluent suppression [ICES][1] is particularly suited to determining concentrations of F^-, Cl^-, PO_4^{-3}, NO_3^- and SO_4^{-2} in surface and groundwater samples. The principal advantages of ICES compared with the older wet-chemical methods of anion analysis are (a), smaller sample size (usually 100 μL); (b), multiple ion-analysis on a single 100 μL sample; (c) better sensitivity

(<μg/mL levels); (d), shorter analysis time (5–10 minutes per sample); and (e), lower cost. In addition the replacement of conventional ion-exchange resin suppressor columns by hollow fibre suppressors[2] makes continuous operation, without need of periodic regeneration, possible. Merriweather[3] has shown that comparison of data obtained from anion analysis by ion chromatography with that obtained from conventional EPA wet-chemical methods shows no appreciable difference in either precision or accuracy. An additional feature is ease of sample preparation: multi-component mixtures can be readily analysed at ultra-trace concentrations with the most likely sample pre-treatment being no more than simple dilution.[4]

Experimental section

The ion chromatograph used in this work consists of a modified Dionex 10 system with auto-sampler and reporting integrator capable of auto-recalibration (Figure 1). The original Dionex 10 eluent pump (Milton Roy, P/N920148-03) is used to deliver eluent to the columns. Samples are sequentially delivered to a 100μL sample injection loop by a Technicon sampler and proportioning pump. The column train consists of a 4 × 30 mm anion concentrator (Dionex P/N 030986) installed to protect the more expensive separator column from particulates, a 4 × 250 mm fast-run anion separator column (Dionex P/N 30985) followed by a hollow fibre suppressor unit (Dionex P/N 035691)[5]. The load/inject valve is an air-actuated Teflon slider type controlled by microswitches on the Technicon sampler. The eluted ions are detected by electrical conductance using the Dionex 10 conductivity meter followed by a Hewlett Packard 3390A reporting integrator. Recalibration of the integrator is achieved automatically by a sequential programming unit (5) coupled to the Technicon sampler. With this automated system, continuous sample analysis is limited only by the number of positions in the autosampler holding tray and not, as was formerly the case, by the ionic capacity of the suppressor column and manual sample injection.

Reagents and materials

All aqueous solutions and dilutions are prepared using double distilled deionised water obtained from a Corning "Megapure"

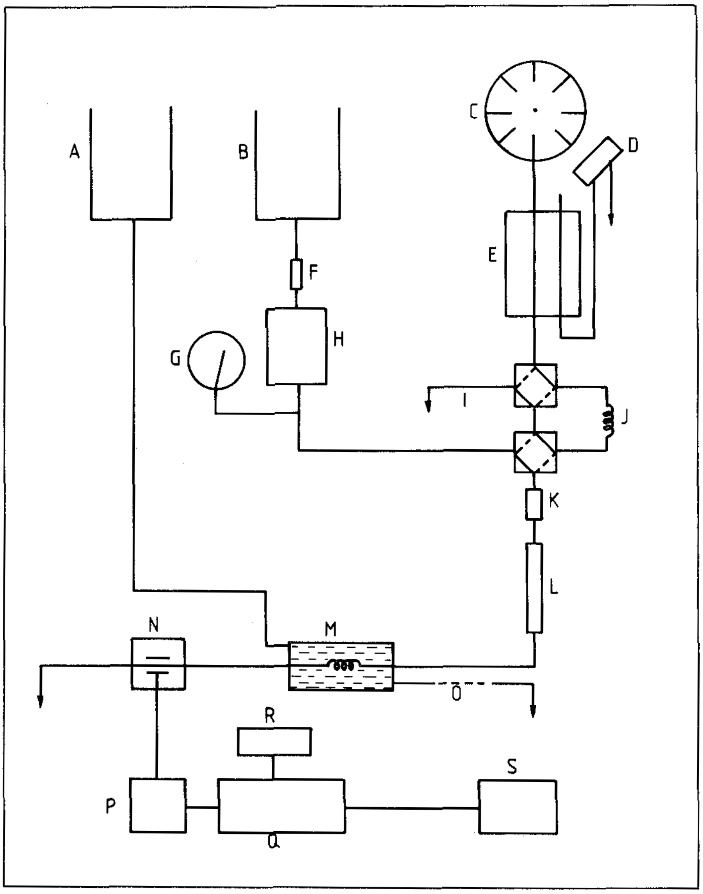

FIGURE 1 Block diagram of modified Dionex 10 ion chromatograph. (A) Regenerant carboy, (B) Eluent carboy, (C) Auto Analyzer Sampler II, (D) Wash cuvette on sampler, (E) Milton Roy pump, (F) Bubble trap, (G) Pressure gauge, (H) Proportioning pump, (I) Load/inject valve, (J) 100 μL injection loop, (K) Pre-column, (L) Separator column, (M) Hollow fibre assembly, (N) Conductivity cell, (O) Restrictor tubing, (P) Conductivity meter, (Q) HP3390A integrator, (R) Sequential Programming unit, (S) Printer (on integrator).

system with a LD2A demineralizer and a 3508A ultra-high purity cartridge. A mixed anion solution containing 1 μg/mL each of F^- and Cl^- and 10 μg/mL each of PO_4^{-3}, NO_3^- and SO_4^{-2} is used throughout as a calibration standard. The retention time (RT) of the

SO_4^{-2} peak in the calibration standard is used as the reference peak for identification of peaks on the sample chromatograms. Eluent is aqueous 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3 (pH 10.4) delivered at a flow rate of 2 mL/min. Pump pressure varied with individual separator columns but is generally in the 3.5 to 4 MPa range. The "water-dip"[2] on the chromatogram that has an RT between F^- and Cl^- with conventional packed resin suppressors occurs earlier when using hollow-fibre suppressors.[5] This earlier placement can interfere with F^- peak area integration and to overcome this an eluent addition is made to each sample. Other than dilution for high anion concentrations in samples this addition is the only pretreatment necessary and consists of adding 1 mL of a solution containing 2.77 g $NaHCO_3$/2.79 g Na_2CO_3/L deionised water to each 10 mL sample. An 0.025 N H_2SO_4 ion-exchange solution ("regenerant") flowing through the hollow fibre assembly counter current to the eluent is gravity fed through restrictor tubing at a rate of 3 mL/min. Background conductivity and suppressor membrane permeability to both H^+ and SO_4^{-2} ions depend on flow rate and concentration of the acid solution around the hollow fibre assembly. Flow rates below 1.3 mL/min produce unstable baselines, poor resolution and lowered sensitivity for a 20 μg SO_4^{-2}/mL standard solution using a 0.025 N H_2SO_4 ion-exchange solution. From 1.3 to 8.1 mL/min baseline stability, resolution and quantification are consistent (Figure 2). As

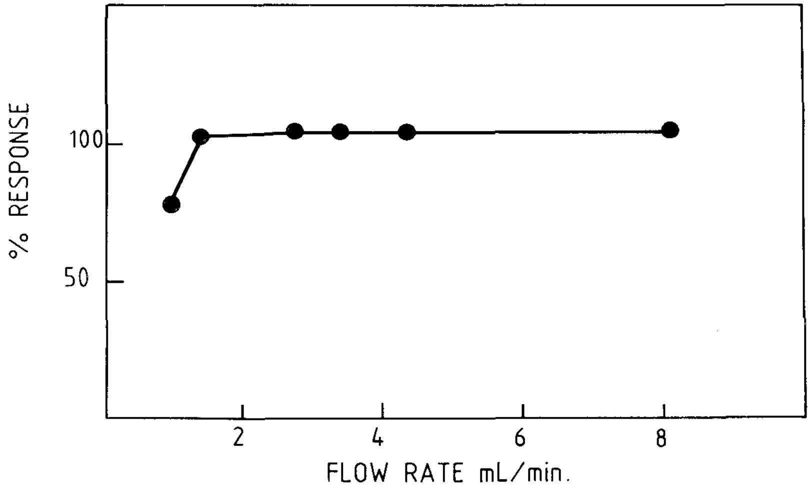

FIGURE 2 Effect of "regenerant" flow rate through a hollow fibre suppressor assembly on the response given by a 20 μg SO_4^{-2}/mL standard solution.

previously stated a regenerant flow rate of 3 mL/min is used throughout this work.

Results and discussion

Figure 3 shows chromatograms, processed by the integrator, obtained from a standard anion solution and a groundwater sample. F^-, Cl^-, and PO_4^{-3} retention times (RT's) are similar in samples and standards but RT's for NO_3^- and SO_4^{-2} are dependent on sample concentration with both anions showing an RT decrease as sample concentration increases over the range 1 to 20 μg anion/mL (Table I). These lower RT values are due to a change in peak shape: i.e. sharper leading edges and longer tailing were observed with the higher anion concentrations. As the HP 3390A reads RT as the time from injection to peak apex a change in peak shape can cause a shift in RT with subsequent failure on the part of the integrator to relate the peak to its proper anion. Even though NO_3^- has a shorter RT than SO_4^{-2}, its percentage RT change with concentration is greater than that of the sulphate ion (Table I).

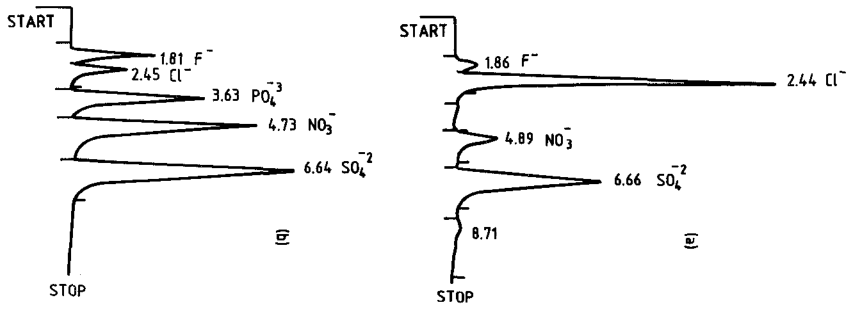

FIGURE 3 Integrator processed chromatograms obtained from a groundwater sample (a) and a standard anion solution (b). Integrator parameters were ZERO = 5, Att2 ↑ = 6, CHTSP = 0.5, PKWD = 0.16, THRSH = 6 and AR REJ = 0.

Linearity of response with increasing concentration and analytical precision were determined for a range of standard anion solutions containing 0.25 to 2.00 μg F^- and Cl^- and 2.5 to 20.00 μg PO_4^{-3},

TABLE I

Retention time vs. Concentration for nitrate and sulphate ions determined by Eluent Suppressed Ion Chromatography

	Retention time (RT) (minutes)								
	μg anion/mL								
Anion	1	2	4	8	10	12	14	16	20
NO_3^-	5.33	5.29	5.19	5.09	5.04	5.01	4.98	4.96	4.91
SO_4^{-2}	7.49	7.46	7.42	7.37	7.35	7.33	7.31	7.29	7.25

NO_3^- and SO_4^{-2} per mL eluent. As Table II shows all anions yield linear responses up to the highest concentrations and the relative standard deviation (RSD) is $<3\%$ in all determinations except the lowest F^- and Cl^- concentrations. Comparison of data in Table II with that in Table III, where the mean values ± standard deviation (SD) for the analysis of environmental water samples are shown, confirms that analytical precision is similar in both standard and environmental water samples.

Results reported in this work were obtained from chromatograms by using peak area integration but several workers[3,6,7] have used peak height rather than area in quantifying chromatograms. In Table IV, where the precision obtained using peak area is compared

TABLE II

Mean values for anion standards containing 0.25, 0.50, 1.00, 1.50 and 2.00 μg F^- and Cl^-/mL and 2.50, 5.00, 10.00, 15.00 and 20.00 μg PO_4^{-3}, NO_3^- and SO_4^{-2}/mL. Each mean and standard deviation [SD shown in parenthesis] is derived from peak area measurements of 15 replicate samples.

μg anion/mL [±SD]				
F^-	Cl^-	PO_4^{-3}	NO_3^-	SO_4^{-2}
0.24[0.01]	0.27[0.01]	2.18[0.06]	2.37[0.04]	2.49[0.06]
0.49[0.01]	0.52[0.01]	4.69[0.10]	4.90[0.06]	5.03[0.06]
1.01[0.02]	1.00[0.02]	10.03[0.02]	10.01[0.12]	10.03[0.12]
1.54[0.02]	1.57[0.02]	15.09[0.21]	15.01[0.14]	15.14[0.19]
2.04[0.05]	2.01[0.05]	20.54[0.29]	20.09[0.21]	20.18[0.24]

TABLE III

Mean values for some surface and groundwater samples. Each mean and standard deviation [SD shown in parenthesis] is derived from peak area measurements of 15 replicate samples.

Sample Source	μg anion/mL [$\pm$SD]				
	F^-	Cl^-	PO_4^{-3}	NO_3^-	SO_4^{-2}
Stemflow (10a)	0.21[0.04]	0.74[0.01]	3.90[0.12]	—	4.54[0.07]
Stream (army culvert)	0.06[0.004]	4.45[0.06]	—	—	10.26[0.12]
Stream (PLS-14)	—	0.64[0.01]	—	0.90[0.02]	13.05[0.15]
Lake water (PL)	0.05[0.04]	4.26[0.06]	—	—	5.10[0.06]
Rain	—	0.16[0.01]	—	0.68[0.04]	0.64[0.05]
Groundwater	0.26[0.005]	15.86[0.50]	—	—	9.61[0.11]
Standard	1.00[0.02]	0.99[0.03]	10.01[0.12]	9.98[0.16]	9.99[0.12]

$F^-, Cl^- = 1\,\mu g/mL$

$PO_4^{-3}, NO_3^-, SO_4^{-2} = 10\,\mu g/mL$

TABLE IV

Relative standard deviation [RSD] obtained using peak area integration and peak height measurement. Each RSD is obtained from 30 or more samples for each anion. RSD = SD/Mean × 100.

	RSD%				
Measurement used	F^-	Cl^-	PO_4^{-3}	NO_3^-	SO_4^{-2}
Peak area	2.6	2.1	1.2	1.3	1.1
Peak height	2.6	3.0	1.4	3.1	2.0

with that obtained from peak height, the data indicate that area measurement is preferable because of a generally lower RSD than when height is used.

Several factors in the analysis of water samples—some intrinsic, others brought about by sample handling and storage—may result in the production of inaccurate data. High Cl^- content, sample pH, filtration, storage and calibration frequency are some of the factors investigated during the course of this work.

High Cl content

Environmental water samples may contain high Cl^- concentrations from run-off contamination with salts used for de-icing roads and the possibility exists that high Cl^- content may interfere with the resolution of other anion peaks in the chromatogram. Cl^- additions of 120, 240 and 500 μg/mL were made to a stem-flow sample (SF8) and the anion concentrations were then determined. There was no significant difference in either the mean values or the SD's for PO_4^{-3}, NO_3^- and SO_4^{-2} from the sample without addition. An increase in F^- content as the Cl^- concentration was increased was caused by impurities in the reagent-grade NaCl used to make the Cl^- addition.

Sample pH

The pH of samples analyzed in this work varied from approx. 4.0 (acid rain) to >6.0 (some lake and ground waters). As the 100 μL sample is injected directly into the eluent stream any change in eluent ionic strength brought about by sample pH could produce varied and misleading chromatograms. Ten samples of a standard anion mixture containing 1 μg F^-, Cl^- and 10 μg PO_4^{-3}, NO_3^- and SO_4^{-2}/mL were adjusted with either HCl or NaOH to cover a pH range from 3.9 to 10.3 and their anion concentrations were determined. There was no indication that sample pH had any effect on the analysis of F^-, PO_4^{-3}, NO_3^- and SO_4^{-2} and in all cases the values obtained were within the variance limits. Addition of HCl in that part of the range below pH 7.0 precluded assessment of pH effect on Cl^- determination but from pH 7.8 to 10.6 (NaOH addition only) no effect was observed.

Filtration

Water samples reported here were filtered using a pre-column before the main anion separator column. Use of this precolumn was largely determined by the fact that most membrane-type filters contain sufficient quantities of common anions to seriously contaminate water samples when they are filtered through them without careful pre-washing. Others have reported that filters based on cellulose esters (Millipore type) may contain as much as 1 μg Cl^-/cm^2 as a contaminent as well as variable concentrations of many cations. (9)

Leachable anion content of a range of 47 mm diameter filters [Millipore SSWP, RAWP, HAWP, and VCWP, GSWP, SCWP and Gelman GA-1, GA-3, GA-6, GA-8, Glass fibre, TUFFRYN HT100, GN6 and Nucleopor membra-fil and Polycarbonates] were determined by soaking filter discs in 10 mL demineralised water for 24 h. Apart from Polycarbonate filters all leachates contained sufficient concentrations ($>\mu$g per disc) of F^-, Cl^-, PO_4^{-3}, NO_3^- and SO_4^{-2} to seriously alter anion concentrations encountered in environmental water samples. Unwashed polycarbonate filters contained leachable anions at $<\mu$g per disc but would still require washing to prevent errors due to contamination from occurring in low-level samples (e.g. precipitation samples).[9]

Storage

Water samples were stored at 4°C in high density polyethylene (HDPE) bottles with no additions being made to reduce surface adsorption. Polyethylene was chosen because others have reported that no significant adsorption or leaching takes place with most aqueous solutions.[10] Table V shows that apart from F^- content there is good agreement between the two time-separated analyses indicating that storage had made little difference to the original anion contents. In all cases F^- concentration has increased by 0.02

TABLE V

Comparison of F^-, Cl^- NO_3^- and SO_4^{-2} content of surface water samples stored at 4°C for approximately 7 months. 1st value measured in Oct. 1982, 2nd value (shown in parenthesis) measured in May 1983.

	μg anion/mL			
Sample source	F^-	Cl^-	NO_3^-	SO_4^{-2}
Main stream	0.09(0.15)	18.19(18.30)	<0.2(<0.2)	6.82 (7.41)
East Swamp Stream	0.10(0.12)	2.99 (2.95)	<0.2(<0.2)	9.60 (9.68)
Perch Lake Weir	0.09(0.15)	4.08 (4.07)	<0.2(<0.2)	13.76(13.75)
Perch Lake Outlet	0.10(0.14)	5.61 (5.47)	<0.2(<0.2)	7.11 (7.45)
H1 Inlet	0.08(0.13)	10.35(10.28)	<0.2(<0.2)	22.10(22.14)
H2 Inlet	0.09(0.13)	15.95(14.45)	<0.2(<0.2)	7.07 (7.37)
H4 Inlet	0.06(0.09)	0.76 (0.77)	<0.2(<0.2)	6.38 (6.61)

to 0.06 μg/mL during storage presumably due to leaching from the polyethylene container. Increase of F^- content has also been noticed in anion standard solutions stored in polyethylene.

Recalibration

The results of analysis using unrecalibrated and recalibrated data are given in Table VI.

TABLE VI

Comparison of relative standard deviation [RSD] obtained from recalibrated and unrecalibrated data. *Calibration occurred after every 4th sample. †Calibration occurred at beginning of run only. Each RSD is derived from analysis of 30 replicate samples.

		RSD%	
Anion	μg/mL	Recalibrated*	Unrecalibrated†
F^-	0.5	3.0	5.3
Cl^-	1.0	1.9	8.1
PO_4^{-3}	10.0	1.4	4.2
NO_3^-	10.0	1.2	4.5
SO_4^{-2}	10.0	1.2	4.2

Recalibration, using a standard anion solution inserted at every fifth position on the auto sampler holding tray, improves and maintains analytical precision. Comparison of data with those of other workers[11] where RSD's for common anions at similar concentrations are given as 5% (SO_4^{-2}) to 42% (Cl^-) indicates that recalibration is essential if high precision is sought in ICES analysis. Recalibration also avoids the necessity for close control of the conductivity detector's temperature which, according to Jenke *et al.*,[12] is necessary if reproducibility is to be maximized. His data, however, using a thermally insulated detector, column and support tubing showed lower sensitivity (factor of 10) for Cl^-, NO_3^- and SO_4^{-2} analysis and poorer reproducibility (factor of 2) than reported here.

Without reference samples of known anion content accuracy of a method cannot be evaluated. The only reference sample available for this work was a standard water sample used in the U.S. Geological Survey's international interlaboratory analytical comparison study.[13] Table VII shows the standard reference sample values obtained by the method described here compared to the average values from laboratories in the U.S.A.

TABLE VII

Comparison of analysis of a Standard Reference Water Sample by U.S.A. laboratories and the method described in this report

	Mean concentration μg/mL[SD]	
Anion	U.S.A. Laboratories	This work
F^-	0.57[0.08]	0.55[0.01]
Cl^-	2.77[0.83]	2.61[0.03]
SO_4^{-2}	27.5[3.1]	29.7[1.3]

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