Analysis of inorganic anions in drainage water and soil solution by single-column ion chromatography

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Abstract

Single-column ion chromatography (SCIC) for anion determination in drainage water and soil solution was tested. The SCIC minimum detection limits (100-μl sample loop) were 0.75 mg l^{-1} for Cl$^-$, 0.2 mg l^{-1} for NO$_2$-N, 0.02 mg l^{-1} for NO$_3$-N, 1.25 mg l^{-1} for HPO$_4$-P, and 0.5 mg l^{-1} for SO$_4$-S. The results showed a high reproducibility. Results for Cl$^-$, NO$_3$-N and SO$_4$-S obtained by the SCIC method were compared with those obtained by traditional methods; Student's t-test and regression analysis showed that the methods agree closely.   © 1998 Published by Elsevier Science B.V.

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1. Introduction

The inorganic anions in drainage water and soil solution are commonly analysed by separate analytical methods [1–5]. Many of these methods are laborious, time consuming, and require analytical skills. Moreover, these environmental samples typically present low concentrations of many anions of interest; low detection limits are required to measure analytes with acceptable precision [6].

Several characteristics of ionic chromatography (IC), such as its speed, simple operation and easily obtainable reagents, together with its versatility and high sensitivity [7], make it attractive for environmental sample analyses. IC has become a rapid and sensitive technique for analysing complex mixtures of ions [8,9]. It is an analytical technique that can separate ionic species, in discrete bands in a liquid moving phase, using different separation modes and different detection technology [10]. In addition, it is relatively inexpensive, and in many cases the sample preparation required is minimal so that the 'dilute-and-shoot' approach is all that is needed for an analysis [11]. IC has been applied successfully to the determination of ions in diverse types of environmental sample [7,10,12] and it is widely accepted and recommended by the US Environmental Protection Agency (EPA) and by the American Public Health Association [13].

At present, two types of IC are in practical use: the suppressor-based system and single-column ion chromatography (SCIC). In the second type, the capacity of several columns to operate without suppressor column devices simplifies equipment requirements and enhances ease of use. In SCIC, a poly(methylmethacrylate)-based anion-exchanger stationary phase dominates. Although favourable chromatographic performance has been demonstrated with very strong eluents such as naphthalenetrisul-

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phonate, the most common eluents used in SCIC are phthalate or a borate–gluconate mixture [13,14].

The aim of this study was to evaluate SCIC as an analytical technique for the determination of chloride, nitrite, nitrate, phosphate, and sulphate in drainage water and soil solution. Results for chloride, nitrate, and sulphate were compared with those obtained by traditional methods.

2. Experimental

2.1. Samples

Drainage water samples were collected from two monolith lysimeters containing undisturbed soil. Soil solution samples were extracted from the soil with suction cups installed at 30, 60 and 90 cm depth in an experimental field. Samples were collected on different sampling dates.

Samples were diluted, whenever necessary, using deionized water (18.2 MΩ cm) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). The required dilution factor was determined by a routine measurement of electrical conductivity (EC) to estimate total anion concentration and thereby ensure that the dilution fell within the range of the calibration graph (Cl$^-\leq$40 mg/l). The resulting solution was passed through a Millipore membrane filter (HAWP, 0.45 μm) to remove particulate material.

Main anion and cation contents were analysed in samples of drainage water and soil solution. The concentration ranges were 100–2500 mg l^{-1} for Cl$^-$, 2–160 mg l^{-1} for NO$_3$-N; 18–120 mg l^{-1} for SO$_4$-S; 9–560 mg l^{-1} for Na$^+$, 3–26 mg l^{-1} for K$^+$; 2–119 mg l^{-1} for Mg^{2+} and 2–826 mg l^{-1} for Ca^{2+}.

2.2. Apparatus

The liquid chromatographic system used consisted of a low-capacity Waters IC-Pack A column (polymethacrylate resin with a quaternary ammonium functional group of 30$\pm$3 μequiv. ml^{-1} capacity) with a thermostat column heater preceded by an IC Pack Anion Guard.

A Waters 430 conductivity detector and a Waters 486 ultraviolet–visible variable-wavelength detector were placed in series immediately after the separation column, the former for detection of Cl$^-$, NO$_2^-$, NO$_3^-$, HPO$_4^{2-}$ and SO$_4^{2-}$, and the latter for a more selective and sensitive detection of NO$_3^-$ and NO$_2^-$.

Sample aliquots were introduced by a Waters Wisp 712 automatic injector (injection loop 25–100 μl). Data collection and evaluation were done with Waters BASELINE 810 software.

2.3. Reagents and standards

A low-conductivity mobile phase [solution of 0.0013 *M* sodium borate–0.0013 *M* sodium gluconate in 12% acetonitrile (v/v) pH 8.5, and conductivity about 270 μS cm^{-1}] at a flow-rate of 1.2 ml min^{-1} was used in this study. This eluent was prepared as a stock standard solution (50-fold concentrated) that was adequately diluted and filtered (Millex HV 0.47 μm) prior to use (12% acetonitrile was added during the dilution step of the stock solution) [15–17]. Following Saari-Nordhaus et al. [18], the presence of acetonitrile in a borate–gluconate eluent facilitates phase transfer and produces sharper peaks and shorter retention times.

All standard solutions and eluents were prepared from analytical-reagent grade chemicals using deionized Milli-Q water (18.2 MΩ cm). All salts were in the sodium form with the exception of phosphate (potassium form). Five stock standard solutions, each having an anion concentration of 1000 mg l^{-1}, were used and all the working solutions were prepared from them.

2.4. Other analytical methods

For comparative purposes, Cl$^-$ was determined by the ferric nitrate–mercuric thiocyanate colorimetric method [19], NO$_3^-$-N by the sodium salicylate colorimetric method [20], and SO$_4^{2-}$-S by the barium chloride turbidimetric method [21].

2.5. Statistical procedures for comparison of methods

SCIC and traditional methods were compared

using (i) Student's *t*-test for paired data; (ii) linear regression analysis studying coefficient of correlation (*r*), slope (test of hypothesis $\beta=1$), intercept (test of hypothesis $\alpha=0$), and residuals (Durbin–Watson statistics). The SIGMASTAT statistical analysis system program of Jandel Corporation [22] was used in all these statistical applications.

3. Results and discussion

3.1. Selectivity

Chloride, nitrite, nitrate, phosphate and sulphate in drainage water and soil were analysed using SCIC with low conductivity eluent and two modes of detection: EC and direct UV detection. The retention time of these inorganic anions by SCIC in the presence of borate–gluconate eluent (pH 8.5) were 2.63 min for Cl^-, 3.30 min for NO_2^-, 5.11 min for NO_3^-, 6.07 min for HPO_4^{2-}, 8.86 min for SO_4^{2-}, and separation was achieved within 10 min. These results agree with those reported by Walter and Cox [16].

The selectivity of the IC Pack A column was evaluated by comparing the elution order of the five standard anions. The selectivity is so favourable that mixtures of closely eluting anions such as Cl^-, NO_2^- and NO_3^- are readily separated. For direct UV-detection of ionic compounds, sufficient absorption in the UV region is required. Some anions, such as SO_4^{2-}, HPO_4^{2-} or Cl^-, show no, or only a negligible, UV absorption [23]. Such anions were eliminated from the analysis. At 214 nm, NO_2^- and NO_3^- show a maximum of absorption (retention times 3.09 min for NO_2^- and 4.84 min for NO_3^-), and it is useful to

detect them at this wavelength. There were no unresolved or overlapping chromatographic peaks — a commonly encountered practical problem [24] — so it was not necessary to calculate resolution between critical peak pairs.

3.2. Calibration curves

Calibration curves covering the concentration ranges shown in Table 1 were prepared injecting 50-μl aliquots. Linear relationships between peak area and concentration were experimentally verified for Cl^-, NO_2^-, NO_3^- and HPO_4^{2-} (EC detection), and for NO_2^- and NO_3^- (UV detection). For SO_4^{2-} peaks, the calibration was made between peak height and concentration because the correlation coefficient was higher than using peak area. Table 1 shows high values of correlation coefficient for all the assayed curves. The equation slope of the calibration curves (Table 1) indicate that for NO_2^- and NO_3^-, direct UV detection is much more sensitive than EC detection.

Detection limits (Table 1) based on the classical signal-to-noise ratio [25] were calculated from the standard solution chromatograms using a 100-μl loop. Detection limits for NO_2-N and NO_3-N with the UV detector (0.2 and 0.02 mg l^{-1} respectively) were lower than those determined with the EC detector (1.0 mg l^{-1} for NO_2-N and 0.9 mg l^{-1} for NO_3-N).

3.3. Reproducibility

To test reproducibility (precision), nine 50 μl samples with a known concentration of each assayed anion (Cl^-, NO_2^-, NO_3^-, HPO_4^{2-} and SO_4^{2-}) were

Table 1
Standard concentration ranges, regression equation of the inorganic anion calibration plots, peak signal (*y*, relative unit) vs. concentration (*x*, mg l^{-1}), coefficients of correlation (*r*), and detection limits for Cl^-, NO_2-N, NO_3-N, HPO_4-P and SO_4-S by SCIC

Anion (detection)	Concentration range (mg l^{-1})	Regression equation	Coefficient of correlation (*r*)	Detection limit (mg l^{-1})
Cl^- (EC)	1.0–60	$y=0.006+0.021x$	0.9999	0.75
NO_2-N (UV)	0.5–30	$y=0.430+0.724x$	0.9996	0.20
NO_2-N (EC)	0.5–30	$y=0.009+0.043x$	0.9999	1.00
NO_3-N (UV)	1.0–60	$y=0.441+1.146x$	0.9995	0.02
NO_3-N (EC)	1.0–30	$y=-0.050+0.058x$	0.9997	0.90
HPO_4-P (EC)	0.5–60	$y=-0.022+0.022x$	0.9994	1.25
SO_4-S (EC)	1.0–30	$y=0.001+0.001x$	0.9998	0.50

injected into the eluent stream. For nine replicates, the experimental standard deviation was less than 1.5 times the value of the population standard deviation (97.5% certainty) [26]. For each anion and detection method, six different concentrations were used (Table 2). Table 2 shows that for all the anions, except HPO_4^{2-}, the R.S.D.s ranged from 0.11 to 5.50% and are smaller than those reported by Nieto and Frankenberger [27] for solutions containing 10 mg ion l^{-1} (R.S.D. 5.4–8.4%) using a column containing a polymethacrylate resin with quaternary ammonium functional groups.

For HPO_4^{2-}, R.S.D.s were higher than for the other anions, ranging from 4.56 to 10.1%. Phosphate is not a frequent anion in drainage water and soil solution at a depth >30 cm, so we have not insisted on optimising its determination.

3.4. Efficiency and column life

Efficiency, calculated as the number of theoretical plates [$N=16$(retention time/width of the peak)^2], was measured for the sulphate peak at the beginning and end of a column life. The maximum value ($N=740$) was calculated for the early injections, while the minimum value ($N=610$) was calculated at the end of the column life (after approximately 1500 injections).

With groups of 40 chromatograms at the beginning and end of the column life, R.S.D.s of the
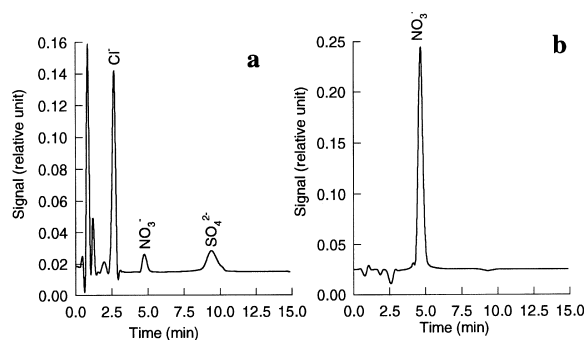

Fig. 1. Chromatogram of the separation of anions in a typical drainage water or soil solution sample with (a) conductivity detection and (b) direct UV detection.

retention times after 1500 injections were ≤5%. Nevertheless, it was observed that the column was progressively losing efficiency of separation and showing poor peak shapes. Cox et al. [28] reported that polymethacrylate-based IC columns have an expected lifetime of 500 or more injections.

3.5. Chromatograms of drainage water and soil solution

Typical drainage water or soil solution chromatograms using EC and UV detectors are shown in Fig. 1. The main components of these samples were Cl$^-$, NO_3^- and SO_4^{2-}, with Cl$^-$ being especially abundant. For the nitrate peak, greater sensitivity was achieved

Table 2
R.S.D.s for determination of Cl$^-$, NO_2-N, NO_3-N, HPO_4-P and SO_4-S (nine replicates per concentration) by SCIC

Cl$^-$ (CE) mg l^{-1}	1	2	5	16	24	40
R.S.D. (%)	4.93	2.97	3.30	2.48	0.34	0.28
NO_2-N (UV) mg l^{-1}	0.5	1	2.5	8	12	20
R.S.D. (%)	0.52	1.08	0.27	0.11	1.87	0.01
NO_2-N (EC) mg l^{-1}	0.5	1	2.5	8	12	20
R.S.D. (%)	3.75	2.35	3.98	2.39	0.15	0.55
NO_3-N (UV) mg l^{-1}	1	2	5	16	24	40
R.S.D. (%)	1.43	1.10	0.42	0.16	0.12	0.15
NO_3-N (EC) mg l^{-1}	1	2	5	16	24	40
R.S.D. (%)	3.08	1.55	2.24	2.08	0.87	0.89
HPO_4-P (EC) mg l^{-1}	0.5	1	2.5	8	12	20
R.S.D. (%)	8.80	9.20	4.56	6.46	9.15	10.10
SO_4-S (EC) mg l^{-1}	1	2	5	16	24	40
R.S.D. (%)	5.50	1.6	1.17	0.56	0.53	0.78

Table 3
Analysis of representative samples of drainage water and soil solution

	Sampling date	Cl^- (mg l^{-1})	NO_3-N (mg l^{-1})	SO_4-S (mg l^{-1})
Soil solution (30 cm depth)	March 1994	599.3	21.8	61.7
Soil solution (60 cm depth)	July 1994	1242.1	40.5	75.0
Soil solution (90 cm depth)	June 1993	526.3	15.8	97.9
Drainage water (lysimeter 1)	November 1993	1680.5	56.8	104.9
Drainage water (lysimeter 2)	January 1994	1436.5	37.3	117.1

by direct UV detection (Fig. 1b) than by EC detection (Fig. 1a).

There are same peaks which elute before Cl^-. These peaks are probably due to the presence of carbonate in the samples, apart from the pseudo peak.

3.6. Comparing results from SCIC and traditional methods

Results for Cl^-, NO_3^- and SO_4^{2-} obtained by SCIC method were compared with those obtained by traditional methods. On some occasions, samples were diluted as many as 100 times, so that results are affected not only by methodological differences but also by accidental errors. Usually, one dilution was adequate for all analytes. The proportion of different anions in the soil solution and drainage water samples was quite constant during the experiment depending on the climatic conditions. Higher salt concentrations were found after the dry season. Table 3 shows some examples of the anionic composition of samples of soil solution and drainage water during the experimental period.

Results obtained for Cl^-, NO_3-N and SO_4-S by the SCIC and the traditional methods were compared analysing samples of drainage water and soil solution covering the concentration ranges of 100–2500 mg l^{-1} Cl^-, 2–160 mg l^{-1} NO_3-N and 18–120

mg l^{-1} SO_4-S. Paired t-tests indicated that there was no significant difference between the two methods ($P>0.05$) (Table 3). Linear regression analysis (Table 4) showed that for each anion, SCIC and the traditional method results were highly correlated ($P<0.001$). The distribution of the residuals, plotted against the independent variable, showed that the residuals were independent and their averages were close to zero. Accordingly, values of the Durbin–Watson statistic were close to 2 (Table 4). In the three comparisons, the tests of hypothesis $\alpha=0$ and $\beta=1$ [29] were fulfilled, therefore the values 0 and 1 were within the confidence intervals for slope and intercept respectively. Thus, SCIC results for chloride, nitrate, and sulphate are comparable with those obtained by traditional methods. SCIC has the added advantage of being a rapid and sensitive method, requiring microliter-sized samples. At the same time, using SCIC it is possible to determine several anions simultaneously in one assay in 10 min, instead of in separate assays as traditionally.

4. Conclusions

SCIC is a valuable technique for the analysis of inorganic anions in drainage water and soil solution samples. Chloride, nitrite, nitrate and sulphate can be determined simultaneously in one assay with high

Table 4
Paired t-tests parameters; linear regression analysis and Durbin–Watson statistic for the comparison of SCIC (y) and traditional method (x) results for Cl^-; NO_3-N and SO_4-S determination (mg l^{-1}) ($\pm$S.E.)

Anion	Paired t-test			Linear regression analysis		Durbin–Watson statistic
	t	N	P	Equation	r	
Cl^-	1.992	26	0.057	$y=-8.08(\pm18.16)+0.98(\pm0.02)x$	0.996	2.3393
NO_3-N	2.063	17	0.056	$y=0.38(\pm3.80)+0.89(\pm0.05)x$	0.978	1.5362
SO_4-S	0.233	39	0.817	$y=2.75(\pm1.49)+0.96(\pm0.02)x$	0.993	1.5216

reproducibility (R.S.D.<5.6%). The results obtained by SCIC were in good agreement with those obtained by traditional methods.

Acknowledgements

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