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

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Abstract

Single-column ion chromatography (SCIC) for cation determination in drainage water and soil solution was tested. Using a 100- μ l sample loop, the SCIC detection limits were 0.04 mg l⁻¹ for Na⁺, 0.02 mg l⁻¹ for NH₄-N, 0.06 mg l⁻¹ for K⁺, 0.05 mg l⁻¹ for Mg²⁺, and 0.085 mg l⁻¹ for Ca²⁺. Results were highly reproducible in wide ranges of concentrations. Results obtained by the SCIC method were compared with those by atomic emission spectrometry (Na⁺ and K⁺) and atomic absorption spectrometry (Mg²⁺ and Ca²⁺). Student's *t*-test and regression analysis showed that corresponding methods agree closely. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Currently, Na⁺, K⁺, Mg²⁺ and Ca²⁺ are usually determined using either atomic absorption spectrometry (AAS) or atomic emission spectrometry (AES) to measure metal concentrations one at a time, or inductively coupled plasma spectrometry (ICP) to measure the metals simultaneously. NH₄⁺ is typically determined using ion-selective electrode potentiometry, which measures the concentration of free ammonium. One of the principal advantages of ion chromatography is the possibility of determining these cations simultaneously, in a relatively short time [1,2]. Ion chromatography offers a nondestructive separation, a versatile, selective and sensitive analysis with minimal sample preparation, and relatively low costs. Ion chromatography is a multi-

species technique that has been applied to many problems in the environmental field involving ionic analysis [3–5].

For environmental control purposes, drainage water and soil solution samples have to be analysed regularly. Alkali, alkaline earth, and ammonium cations are often found together in such samples and the demand for determining these species is increasing. An effective isocratic separation of monovalent and divalent cations in one run by single-column ion chromatography (SCIC) was not achieved until recently. A cation-exchange stationary phase of polybutadiene–maleic acid (PBDMA) coated on silica allows the isocratic and simultaneous separation of monovalent and divalent cations by SCIC. The separation takes place due to ion-exchange and complex formation mechanisms, both of which reportedly have an important and sometimes opposing effect on the separation of cations. The elution of monovalent ions depends on the hydronium concentration, while the elution of divalent ions is

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greatly influenced by the type and concentration of the organic acid counter ion [6,7].

This paper focuses on applications of SCIC using a PBDMA-coated silica stationary phase as a method for the determination of major cations in soil solution and drainage water.

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 M Ω 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 to estimate total cation concentration and thereby ensure that the dilution fell within the range of the calibration graph ($\text{Cl}^- \leq 40$ mg/l). The resulting solution was passed through a Millipore membrane filter (HAWP, 0.45- μm) to remove particulate material.

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 NO₃-N; 18–120 mg l⁻¹ for SO₄-S; 9–560 mg l⁻¹ for Na⁺, 3–26 mg l⁻¹ for K⁺; 2–119 mg l⁻¹ for Mg²⁺ and 2–826 mg l⁻¹ for Ca²⁺.

2.2. Apparatus

The liquid chromatographic system used consisted of a low-capacity Waters IC-Pack C M/D column (silica base coated with polybutadiene–maleic acid copolymer of 1.5 \pm 0.2 $\mu\text{equiv. g}^{-1}$ capacity) with a thermostat column heater.

A Waters 430 electrical conductivity detector was placed immediately after the separation column for cation detection. 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 mobile phase solution of 0.1 mM H₂EDTA and 3.0 mM HNO₃ at a flow-rate of 1.0 ml min⁻¹ was used in this study. This eluent, which can be stored up to 1 month, was filtered (Millex HV 0.47 μm) and degassed before use, for optimum long-term performance of the column [8].

All solutions and eluents were prepared from analytical-reagent grade chemicals using deionized Milli-Q water (18.2 M Ω cm). Salts of ammonium and alkali metals were in the chloride form with the exception of lithium (hydroxide form). Salts of alkaline earth metals were in the nitrate form. One stock solution of 1000 mg l⁻¹ of each cation were used to prepare all the working solutions.

2.4. Other analytical methods

For comparative purposes, K⁺ and Na⁺ were determined by the AES method, and Mg²⁺ and Ca²⁺ by the AAS method.

2.5. Statistical procedures for comparison of methods

SCIC and spectrophotometry methods were compared using (i) Student's *t*-test for paired data, and (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 was used for the statistical analysis [9].

3. Results and discussion

3.1. Selectivity

The retention of ammonium, sodium, potassium, magnesium, and calcium cations by SCIC in the presence of a mobile phase containing H₂EDTA and HNO₃ followed the order Li⁺>Na⁺>NH₄⁺>K⁺>

$\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$, and separation was achieved within 22 min (Fig. 1).

The selectivity of the IC Pack C M/D column was evaluated by comparing elution order of the eight standard cations.

3.2. Calibration curves

Calibration curves covering the concentration ranges shown in Fig. 1 and Table 1 were prepared injecting 50- μl aliquots. Linear relationships between peak area and concentration were experimentally verified for Na^+ , $\text{NH}_4\text{-N}$, K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} . Table 1 shows high values of correlation coefficient for all the assayed curves.

Detection limits (Table 1) based on the classical signal-to-noise ratio of 2 [10] were calculated from

the standard solution chromatograms using a 100- μl loop.

3.3. Reproducibility

To test reproducibility (precision), nine 100- μl samples with a known concentration of each assayed cation (Na^+ , $\text{NH}_4\text{-N}$, K^+ , Mg^{2+} and Ca^{2+}) were injected into the eluent stream at a flow-rate of 1.0 ml min^{-1} with the exception of the two higher concentration for Na^+ in which 50 μl were injected. For nine replicates, the experimental standard deviation is less than 1.5 times the value of the population standard deviation (97.5% certainty) [11]. For each cation, five different concentrations were used (Table 2). Table 2 shows that for all the cations, even for the lowest concentration of K^+ (0.05 mg l^{-1} ; lower

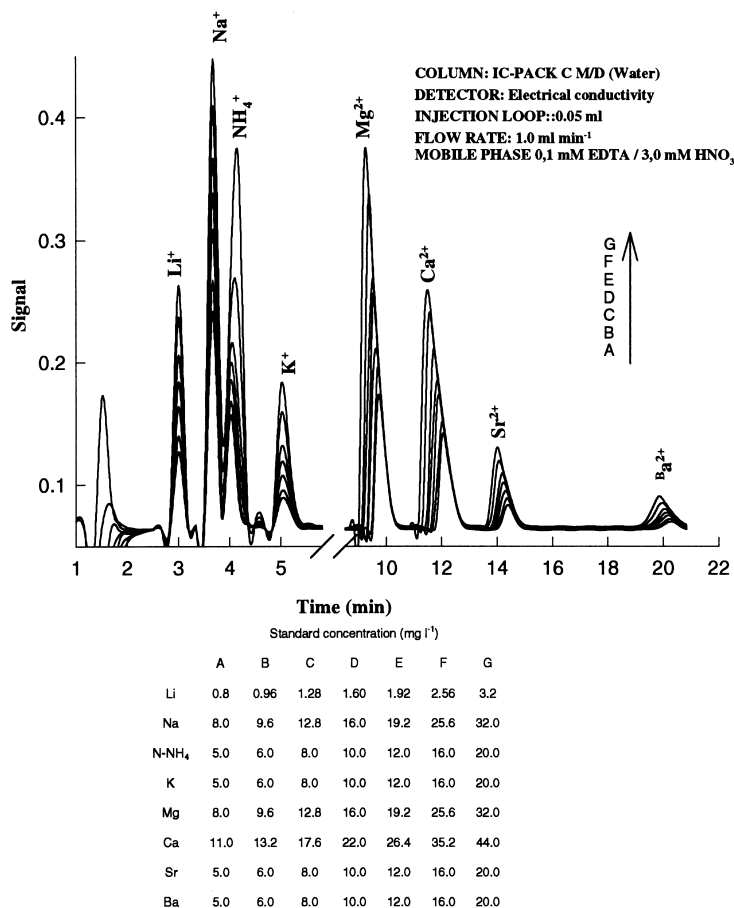


Fig. 1. Sensitivity diagrams for inorganic cations.

Table 1

Standard concentration ranges, regression equation of the cations calibration plots, peak signal (y , relative unit) vs. concentration (x , mg l^{-1}), coefficients of correlation (r), and detection limits for Na^+ , $\text{NH}_4^+\text{-N}$, K^+ , Mg^{2+} , Ca^{2+} by SCIC

Cation	Concentration range (mg l^{-1})	Equations of the calibration plots	Coefficient of correlation (r)	Detection limit 100- μl loop (mg l^{-1})
Na^+	2.0–10.0	$y=0.64+1.72x$	0.9998	0.04
$\text{NH}_4^+\text{-N}$	0.04–2.0	$y=-0.47+2.71x$	0.9999	0.02
K^+	0.05–8.0	$y=-0.008+0.084x$	0.9998	0.06
Mg^{2+}	0.10–20.0	$y=-0.12+3.35x$	0.9999	0.05
Ca^{2+}	1.0–17.5	$y=1.19+1.94x$	0.9998	0.08

than the detection limit), the R.S.D.s were less than 6%.

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 potassium peak at the beginning and end of a column life. The maximum value ($N=2241$) was calculated for the early injections, while the minimum value ($N=1727$) was calculated at the end of the column life (after approximately 1000 injections).

With groups of 40 chromatograms at the beginning and end of the column life, R.S.D.s of the retention times after 1000 injections were $\leq 5\%$. Nevertheless, it was observed that the column was progressively losing efficiency of separation and showing poor peak shapes.

Table 2

R.S.D.s for determination of Na^+ , $\text{NH}_4\text{-N}$, K^+ , Mg^{2+} and Ca^{2+} (nine replicates per concentration) by SCIC

Na^+ (mg l^{-1})	2.00	6.00	10.00	20.0 ^a	30.0 ^a
R.S.D. (%)	2.2	1.1	1.7	1.0	0.9
$\text{NH}_4\text{-N}$ (mg l^{-1})		0.04	0.06	0.10	2.00
R.S.D. (%)		5.8	5.7	3.2	3.4
K^+ (mg l^{-1})	0.05	0.20	0.50	4.00	8.00
R.S.D. (%)	5.9	5.3	3.9	2.3	1.6
Mg^{2+} (mg l^{-1})	0.10	0.40	1.00	5.00	20.0
R.S.D. (%)	4.7	4.1	2.4	1.2	0.8
Ca^{2+} (mg l^{-1})	1.00	3.00	5.00	10.00	17.50
R.S.D. (%)	4.4	2.4	2.1	2.0	1.5

Injection volume; 50 μl .

3.5. Chromatograms of drainage water and soil solution

Typical drainage water and soil solution chromatograms using electrical conductivity detector are shown in Fig. 2a–b. The main components of these samples were Na^+ , K^+ , Mg^{2+} and Ca^{2+} , Na^+ and Ca^{2+} being especially abundant.

3.6. Comparing results from SCIC and traditional methods

Results for Na^+ , K^+ , Mg^{2+} and Ca^{2+} obtained by the SCIC method were compared with those by atomic spectrophotometry 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.

Results obtained for Na^+ , K^+ , Mg^{2+} and Ca^{2+} by the SCIC and the atomic spectrophotometry methods were compared analysing samples of drainage water and soil solution covering the concentration ranges

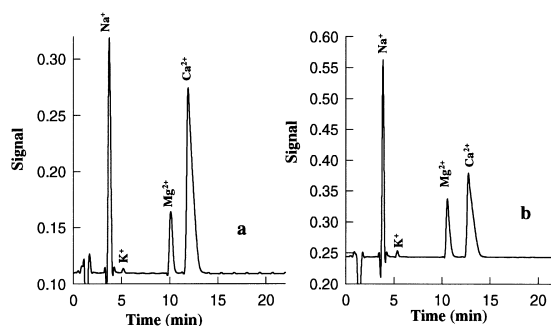


Fig. 2. Chromatogram of the separation of cations in (a) a typical drainage water sample and (b) a soil solution sample.

Table 3

Paired *t*-tests parameters; linear regression analysis and Durbin–Watson statistic for the comparison of SCIC (*y*) and atomic spectrophotometry method (*x*) results for Na⁺, K⁺, Mg²⁺, and Ca²⁺ determination (mg l⁻¹) (±S.E.)

Anion	Paired <i>t</i> -test			Linear regression analysis		Durbin–Watson statistic
	<i>t</i>	<i>N</i>	<i>P</i>	Equation	<i>r</i>	
Na ⁺	-1.691	31	0.101	$y=6.92(\pm 6.97)+0.98(\pm 0.02)x$	0.991	1.9052
K ⁺	-1.928	22	0.067	$y=0.74(\pm 0.84)+0.99(\pm 0.07)x$	0.955	1.6491
Mg ²⁺	1.872	28	0.072	$y=1.60(\pm 2.37)+0.94(\pm 0.04)x$	0.982	1.8640
Ca ²⁺	1.282	34	0.209	$y=5.54(\pm 4.37)+0.97(\pm 0.01)x$	0.998	1.7824

of 9–560 mg Na⁺ l⁻¹, 3–26 mg K⁺ l⁻¹, 2–119 mg Mg²⁺ l⁻¹ and 2–826 mg Ca²⁺ l⁻¹. Paired *t*-tests indicated that there was no significant difference between the different methods ($P>0.05$) (Table 3). Linear regression analysis (Table 3) showed that for each cation, SCIC and atomic spectrophotometry method results were highly correlated ($P<0.001$). The distribution of the residuals, plotted against the independent (Table 3), showed that the residuals were independent and their averages were close to zero. Accordingly, values of the Durbin–Watson statistic were close to 2. In the four comparisons, the tests of hypothesis $\alpha=0$ and $\beta=1$ [12] were fulfilled, therefore the values 0 and 1 were within the confidence intervals for slope and intercept respectively. Thus SCIC results for Na⁺, K⁺, Mg²⁺ and Ca²⁺ are comparable to those obtained by atomic spectrophotometry 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 cations simultaneously in one assay in 13 min instead of in separate assays as with traditional methods.

4. Conclusions

The method of single-column ion chromatography is a valuable technique for the analysis of inorganic cations in drainage water and soil solution samples. Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺ can be determined simultaneously in one assay with high reproducibility

(R.S.D.<5.9%). The results obtained by SCIC were in good agreement with those obtained by traditional methods.

Acknowledgements

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