

# Determination of Ammonium, Sodium, Potassium, Magnesium, and Calcium Cations in Rain Water by Column-Coupling Capillary Isotachopheresis

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Separation conditions suitable to the isotachopheretic determination of  $K^+$ ,  $Na^+$ ,  $NH_4^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  cations in rain water are described. The use of column-coupling ITP instrument with the electrolyte system enabling a complete resolution of the studied cations provided the limits of detection in the range of 0.4–2.1  $\mu\text{mol dm}^{-3}$  for a 30  $\text{mm}^3$  sample injection volume when the detection was carried out with the aid of a conductivity detector. Rapid (*ca.* 10 min analysis time) and reproducible determinations (typically 5 % relative standard deviations) were achieved. Recoveries of the analytes in rain water samples on  $\mu\text{mol dm}^{-3}$  concentration levels ranged from 94 to 120 % with the extreme values being typical for the analyte concentrations close to the limits of detection.

$K^+$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$  and  $NH_4^+$  cations are currently monitored in rain water. At present, ion chromatography (IC) [1–5], spectroscopy, and wet-chemistry methods [6, 7] are preferred for this purpose. A possibility to determine all these cations simultaneously makes IC a favourable alternative to these methods. However, concentration limits of detection (LOD) as achieved in a conventional IC arrangement need not be sufficient for some rain water samples and the use of a sample concentrator column with a purification of the eluent by a trap column may be necessary in such situations [5].

Recently, many papers dealing with capillary zone electrophoresis (CZE) separations of alkali and alkaline earth metal and ammonium cations have been published [8–16]. For example, it was shown that a complete group of these cations can be separated in one CZE run [12, 16]. From the point of view of the CZE quantitations of these cations in rain water, the main problems are associated probably with the use of the indirect detection. This is due to the fact that low LOD values (essential for rain water samples) require a low concentration of the visualization carrier ion [17, 18] in the carrier electrolyte solution. This restricts the sample load significantly so that the actual LOD values are only seldom lower than 0.1  $\text{mg dm}^{-3}$  [14]. The cations present in rain water samples can differ by a factor of  $10^2$ – $10^3$ . Such a concentration ratio may have a detrimental impact on the resolutions of the cations of close effective mobilities as, for example, illustrated for  $K^+$  and  $Na^+$  [11]. To solve these problems we enhanced the sample load capacity

by performing the CZE separations of the cations in a 300  $\mu\text{m}$  I.D. capillary tube in a combination with the concentrating electromigration injection [12]. Although significant improvements in the detectabilities of the cations were achieved and the concentration dynamic range enhanced, low reproducibilities of the quantitations linked with the electromigration injection may be considered to set the present limits of this very sensitive CZE approach.

Current limitations of CZE as outlined above led us to investigate the use of capillary isotachopheresis (ITP) in an instrument having an enhanced performance index [19]. We employed a column-coupling arrangement of the ITP separation unit [20, 21] as this is meeting best such a performance criterion. This work was aimed at finding separation conditions providing both low LOD values and adequate concentration dynamic ranges for the cations. Some basic performance parameters of the elaborated analytical procedure were assessed for model mixtures and rain water samples.

## EXPERIMENTAL

The chemicals used for the preparations of the leading and terminating electrolytes were obtained from Serva (Heidelberg, Germany), Janssen Chimica (Beerse, Belgium), and Lachema (Brno, Czech Republic). A 1 vol. % aqueous concentrate of hydroxyethylcellulose 4000 was obtained from Laboratory of Environmental Analytical Chemistry (Faculty of Science, Comenius University, Bratislava, Slovak Republic).

Water obtained from a RODEM-1 two-stage demineralization unit (Aqualabo, Brno, Czech Republic) was further purified by circulation through a pair of tandem coupled polytetrafluoroethylene columns packed with an Amberlite MB-1 mixed-bed ion exchanger (BDH, Poole, U.K.).

Ethylenediamine and acetic acid were purified by isothermal distillation into demineralized water kept in polyethylene vessels cleaned as described in the literature [23]. 18-Crown-6 ether contaminated with potassium salts was purified on a polypropylene column packed with a Serdolit MB mixed-bed ion exchanger (Serva).

Samples of rain water collected at various sampling sites in Slovak Republic were kindly provided by Slovak Hydrometeorological Institute (Bratislava, Slovak Republic).

A CS Isotachophoretic Analyzer (Villa-Labeco, Spišská Nová Ves, Slovak Republic) was used in the column-coupling configuration of the separation unit. The separation unit was assembled from modules supplied by the manufacturer and others made in our laboratory. The sample was injected by a valve provided with a 30 mm<sup>3</sup> internal sample loop. The time-based lengths of the zones from the responses of the conductivity detectors were measured electronically [22]. Analytical data were processed by a CHEMSTAT program (Trilobyte, Prague, Czech Republic) which run on an IBM-PC.

## RESULTS AND DISCUSSION

### Separation Conditions

The ionic mobilities of some of the cations of our interest are close (Na<sup>+</sup>, Mg<sup>2+</sup>) or identical (K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>) in aqueous electrolyte solutions [24]. Currently, complex equilibria are used to differentiate their effective mobilities and hence optimize their ITP separations. Negatively charged ligands [21, 25–27] and electroneutral linear [28, 29] or cyclic polyethers [30, 31] are advantageously employed for this purpose. Of these, only linear polyethers (poly(ethylene glycols)) were shown to provide complete resolutions of alkali and alkaline earth metal cations and ammonium in one ITP run [29]. For obvious reasons, in this work we investigated the use of the electrolyte systems resolving the cations *via* differences in their complexations with the polyethers.

So far, ammonium was found to be the most mobile cation in the electrolyte system based on the use of the poly(ethylene glycol)—water solvent mixtures [28, 29]. However, a favourable ITP migration configuration requires that the analytes to be determined migrate with the effective mobilities which are intermediate to those of the leading and terminating ions [24]. Therefore, our main goal was to find the leading cation having a higher effective mobility than that of

ammonium. None of the cationic constituents studied in this context (dimethylamine, diethylamine, propylamine, and ethylenediamine) met this requirement.

In the electrolyte systems using complex equilibria of 18-crown-6 ether with the cations of our interest, H<sup>+</sup> and Cs<sup>+</sup> ions were already shown to be applicable as the leading cations [30, 31]. The former of them, however, is *a priori* less convenient as it requires the separations to be carried out in a non-buffered electrolyte system [24]. Cs<sup>+</sup> is not restrictive in this respect but our main problems were linked with lower purities of the available preparations of this constituent (hydroxide, acetate). ITP experiments showed their intolerable contaminations with K<sup>+</sup> and Na<sup>+</sup> cations. Attempts to reduce the contents of these interfering impurities using current laboratory purification procedures [33] were not effective. Therefore, our experimental search concerning the choice of the leading cation was focused on the above group of volatile amines. Of these, ethylenediamine (EDA) was the only constituent meeting the ionic mobility criteria. Its use, however, was restricted to the concentrations below 4 mmol dm<sup>-3</sup>. At higher concentrations of the leading electrolyte the ionic mobility of the corresponding ionic form (EDA<sup>2+</sup>) was lower than that of NH<sub>4</sub><sup>+</sup>. This was apparently due to a significant influence of electrophoretic and relaxation effects on the ionic mobility of the double-charged ionic form of EDA [34]. In our particular case this was not a disadvantage as a lower concentration of the leading cation gave lower steady-state concentrations in the analyte zones [24] and, hence, more favourable LOD values associated with the zonelength measurements.

The composition of the electrolyte system chosen as an optimum and used throughout is given in Ta-

Table 1. Operational System

Leading electrolyte	
Solvent	H <sub>2</sub> O
Leading cation	EDA <sup>2+</sup> <sup>a</sup>
Concentration/(mmol dm <sup>-3</sup> )	1.25
Counter ion	HAC <sup>b</sup>
Concentration/(mmol dm <sup>-3</sup> )	3.75
pH <sub>L</sub>	5.0
Additive	HEC <sup>c</sup>
Volume ratio (10 <sup>2</sup> φ <sub>r</sub> )	0.1
Complexing agent	18-crown-6 ether
Concentration/(mmol dm <sup>-3</sup> )	50
Terminating electrolyte	
Solvent	H <sub>2</sub> O
Termination cation	H <sup>+</sup> (HAC)
Concentration/(mmol dm <sup>-3</sup> )	3

a) EDA<sup>2+</sup> = ethylenediamine; b) HAC = acetic acid; c) HEC = hydroxyethylcellulose.

ble 1. Isotachophoreograms in Fig. 1 illustrate ITP separabilities of the cations of our interest using this electrolyte system.

### Some Analytical Performance Characteristics

External calibrations served for the evaluations of the lengths of the analyte zones. The parameters of the corresponding regression equations describing the calibration graphs are summarized in Table 2. The concentration spans for which the calibration data were measured covered the concentrations of the cations as currently found in the precipitation samples. The highest concentrations corresponded to 20–30 % of the maximum concentrations loadable into the separation compartment. This indicates a wide dynamic concentration range attainable under our working conditions.

In blank ITP runs (water demineralized in the way described in Experimental served as a sample) the zones of the cations were always detected (see also Fig. 1A). Experiments carried out with 300 mm<sup>3</sup> volumes of the demineralized water revealed that their origin

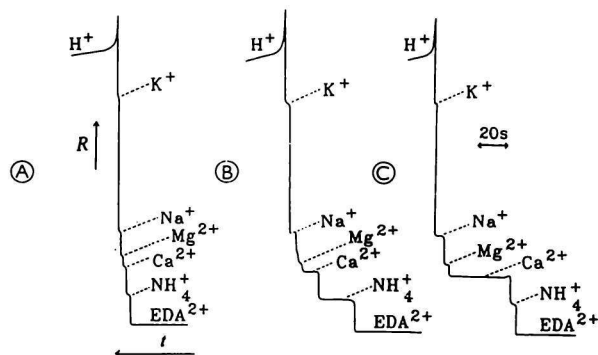


Fig. 1. Isotachophoreograms from the analysis of  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  in rain water. A = blank run; B = sample of rain water; C = model mixture of the cations ( $[\text{NH}_4^+] = 2 \mu\text{mol dm}^{-3}$ ;  $[\text{Ca}^{2+}] = 40 \mu\text{mol dm}^{-3}$ ;  $[\text{Mg}^{2+}] = 2 \mu\text{mol dm}^{-3}$ ;  $[\text{Na}^+] = 10 \mu\text{mol dm}^{-3}$ ;  $[\text{K}^+] = 2 \mu\text{mol dm}^{-3}$ ). The separations were carried out in the operational system given in Table 1. The driving currents were 75  $\mu\text{A}$  and 15  $\mu\text{A}$  in the pre-separation and analytical column, respectively. Only the records from the detector in the analytical column are given. A total analysis time was 10 min.  $R$ ,  $t$  = increasing resistance and time, respectively.

Table 2. Regression Equations for Calibration Lines of the Cations in the Concentration Range 2–60  $\mu\text{mol dm}^{-3}$  and Detection Limits ( $n = 15$ )

Cation	A s	B s $\text{dm}^3 \text{mol}^{-1}$	C. C.	$c_{\text{LOD}}$ $\mu\text{mol dm}^{-3}$
$\text{NH}_4^+$	2.6	$4.48 \times 10^5$	0.9998	1.7
$\text{Na}^+$	1.7	$4.78 \times 10^5$	0.9970	2.1
$\text{K}^+$	0.3	$6.39 \times 10^5$	0.9982	1.6
$\text{Mg}^{2+}$	1.07	$8.64 \times 10^5$	0.9999	0.4
$\text{Ca}^{2+}$	1.61	$8.81 \times 10^5$	0.9998	1.1

A = intercept; B = slope;  $n$  = number of data points;  $c_{\text{LOD}}$  = limit of detection (30 mm<sup>3</sup> sample volume); C.C. = correlation coefficient.

Table 3. Reproducibilities of ITP Determinations of  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  in Rain Water

Sample	Parameter	Cation				
		$\text{NH}_4^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$
1	$c/(\mu\text{mol dm}^{-3})$	4.2	7.8	6.8	2.2	10.8
	C.I./( $\mu\text{mol dm}^{-3}$ )	3.7–4.8	7.5–8.1	6.5–7.0	1.7–2.8	10.6–10.9
2	$c/(\mu\text{mol dm}^{-3})$	21.6	13.7	9.8	13.8	42.2
	C.I./( $\mu\text{mol dm}^{-3}$ )	21.1–22.0	13.3–14.1	9.6–10.1	13.4–14.1	41.8–42.5
3	$c/(\mu\text{mol dm}^{-3})$	41.1	4.2	5.3	2.9	9.8
	C.I./( $\mu\text{mol dm}^{-3}$ )	40.6–41.7	3.8–4.6	5.0–5.6	2.3–3.4	9.7–10.0
4	$c/(\mu\text{mol dm}^{-3})$	46.5	4.5	4.6	4.8	23.3
	C.I./( $\mu\text{mol dm}^{-3}$ )	45.9–47.1	4.1–4.9	4.3–4.9	4.3–5.2	23.1–23.5
5	$c/(\mu\text{mol dm}^{-3})$	74.8	6.4	6.4	10.6	34.7
	C.I./( $\mu\text{mol dm}^{-3}$ )	73.8–76.0	6.2–6.6	6.2–6.6	10.2–10.9	34.4–35.0
6	$c/(\mu\text{mol dm}^{-3})$	36.0	7.5	5.9	3.0	11.5
	C.I./( $\mu\text{mol dm}^{-3}$ )	35.7–36.8	7.2–7.8	5.6–6.2	2.4–3.5	11.3–11.6

$c$  = concentration; C.I. = confidence interval for 95 % probability (3 determinations).

**Table 4.** Recoveries of the Cations in Rain Water Samples at Low Concentrations

Sample	Parameter	Cation				
		NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>
1	Added					
	<i>c</i> /(μmol dm <sup>-3</sup> )	2.3	5.9	3.7	5.6	3.7
	C.I./ (μmol dm <sup>-3</sup> )	2.2—2.3	5.6—6.2	3.5—3.9	5.4—5.9	3.2—4.2
	Found					
	<i>c</i> /(μmol dm <sup>-3</sup> )	2.7	6.0	3.6	5.7	3.5
	C.I./ (μmol dm <sup>-3</sup> )	2.7—2.8	5.7—6.3	3.4—3.8	5.5—5.9	2.9—3.9
Recovery/%	112.9	101.7	96.8	100.7	93.8	
2	Added					
	<i>c</i> /(μmol dm <sup>-3</sup> )	5.5	1.2	8.0	1.1	6.8
	C.I./ (μmol dm <sup>-3</sup> )	5.2—5.8	1.1—1.3	7.8—8.1	1.0—1.1	6.3—7.2
	Found					
	<i>c</i> /(μmol dm <sup>-3</sup> )	5.4	1.2	7.6	1.1	7.5
	C.I./ (μmol dm <sup>-3</sup> )	5.1—5.7	1.1—1.2	7.5—7.8	1.1—1.2	7.1—8.0
Recovery/%	98.6	97.5	95.9	100.9	111.5	

C.I. = confidence interval for 95 % probability from 3 determinations.

was in the leading and terminating electrolyte solutions. Nevertheless, the zonelengths of these impurities were constant (also when the electrolyte solutions were prepared repeatedly) so that long term validities of the calibration graphs were preserved. Run-to-run fluctuations in the zonelengths of the cations in the blank runs in fact determined their LODs. The values of these fluctuations expressed *via* standard deviations provided basic data related to the LODs. The actual values given in Table 2 were estimated by taking the signal-to-noise ratio of three while the standard deviations of the zonelengths of the analytes in the blank runs served as the noise values. They agree favourably with those typically reported for IC and for similar sample matrices [1—5] and they are significantly lower than those attainable by CZE [14]. In this context it seems appropriate to stress that the LOD values do not represent ultimate limits as the available load capacity of the separation compartment employed in this work was exploited only by 20—30 % for practical rain water samples. Here, only the use of the sample injection device with a larger sample loop (not available for this work) is in fact the only requirement.

Six samples of rain water (see Experimental) were taken to assess the reproducibilities of the ITP determination of the cations. The relevant data are summarized in Table 3. From these data we can see that the confidence interval spans for the cations were almost constant and did not depend on their concentrations in the samples. They also suggest that an increased sample injection volume (assuming the use of the separation unit of the same performance index [19]) can be expected to provide a convenient way in increasing the precision in the determination of the cations present in the rain water samples at very low concentrations.

To demonstrate the accuracy of the elaborated method [35], we spiked a pair of the rain water samples

(the samples with minimum and maximum concentrations of ammonium served for this purpose) with the cations at known concentrations. The data from these measurements (Table 4) show that in both instances good recoveries were achieved and no indications of systematic errors were detected.

Experiments with model samples revealed that ITP in the column-coupling configuration of the separation compartment is applicable for samples of extreme cationic compositions. For example, a 10<sup>3</sup>-fold excess of ammonium present in the injected sample did not influence the quantitations of the rest of the cations.

A short analysis time (*ca.* 10 min) and low running costs are attributes of the elaborated ITP procedure to be also mentioned in outlining its application features.

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