

## Note

### Determination of nitrate and sulphate in rain-water by capillary isotachopheresis

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(First received February 28th, 1986; revised manuscript received June 9th, 1986)

The presence of nitrate and sulphate in precipitation in densely populated regions is due to a fairly large extent to human activity<sup>1,2</sup>. Both anions are closely associated with "acid rain" and, therefore, their determination in rain-water is routinely carried out in laboratories involved in environmental control.

Of the wet-chemistry methods suitable for the determination of sulphate (see, e.g., refs. 3-5) few meet the required detection limit of *ca.* 1 ppm in rain-water. In practice, photometric titrations using barium chloride as a titrant (ref. 1, Part 1, p. 16) or turbidimetric determinations<sup>4</sup> are used for this purpose. In both instances a sample pretreatment is necessary before the final analytical step (removal of  $\text{Ca}^{2+}$ , evaporation of the sample). The decreased reproducibilities of these methods for 0-5 ppm sulphate concentrations led to the indirect determination by flame emission spectroscopy<sup>6</sup>.

Nitrate in rain-water is determined, after reduction to nitrite, by a photometric Griess-Ilosvay method<sup>3-5</sup>. The World Meteorological Organization (WMO) recommends another photometric method in which nitrate is reduced to ammonia before the determination (ref. 1, Part 1, p. 17).

Particle-induced ionization mass spectrometry enables simultaneous determination of both anions with detection limits of less than 1 ppm<sup>7</sup>. Both anions can be simultaneously determined in rain-water also by ion chromatography<sup>8-12</sup>. Detection limits of 10 pmol were claimed for the determination of sulphate, nitrate and chloride in drinking water by capillary zone electrophoresis<sup>13</sup>.

The potential of capillary isotachopheresis (ITP) in the analysis of inorganic anions present in surface and drinking water has recently been demonstrated<sup>14,15</sup>. From the point of view of the routine analysis of sulphate and nitrate in rain-water, however, the separation conditions used in those studies have certain disadvantages

(see Results and Discussion). The aim of this work was to devise a more suitable system for this analytical problem and to assess the analytical performance of ITP in comparison to the approved wet-chemistry procedures (see above).

## EXPERIMENTAL

A CS Isotachophoretic Analyzer (VVZ PJT, Spišská Nová Ves, Czechoslovakia) was used. The separation unit was assembled in a coupled-column configuration<sup>16,17</sup> with a 40 mm × 0.85 mm pre-separation column coupled to a 150 mm × 0.30 mm analytical column. Samples were injected with the aid of a valve provided with a 50- $\mu$ l sample loop. The lengths of the zones recorded by the conductivity detector of the analytical column were measured electronically<sup>18</sup>.

Triply distilled water was used for preparation of the solutions. Histidine (Reanal, Budapest, Hungary) was purified by a repeated precipitation of its aqueous solution with deionized ethanol. Magnesium chloride and acetic acid (Lachema, Brno, Czechoslovakia) of analytical grade purities were used as received. Hydroxyethylcellulose (HEC) was obtained from Polysciences (Warrington, PA, U.S.A.) and its stock solution was purified on a mixed-bed ion exchanger.

## RESULTS AND DISCUSSION

Nitrate and sulphate are present in rain-water in similar concentrations, generally within the range 1–10 ppm. Anions of fatty acids, appearing in precipitation at lower concentrations<sup>19,20</sup>, are probably the only constituents which need to be considered as potential interferents in the ITP analysis. The effective mobilities of this group of anions are lower than those of sulphate and nitrate under the working conditions of ITP (see, *e.g.*, refs. 21–23). Therefore, our choice of the separation conditions was restricted to the systems differentiating the latter anions.

Sulphate and nitrate can be separated at pH 6.0 using histidine<sup>24–26</sup> or 1,3-bis[tris(hydroxymethyl)methyl]aminopropane<sup>27</sup> as buffering agents. Also complex-forming cations, Ca<sup>2+</sup> (refs. 15, 32, 29) or Mg<sup>2+</sup> (ref. 14) are suitable for the optimization of the separating conditions. A strong retardation of sulphate relative to nitrate is possible using triethylenetetramine as a co-counter ion in the leading electrolyte<sup>18</sup>.

From the viewpoint of the analysis time, the applied charge must be used efficiently<sup>28</sup>. In this respect, a low pH of the leading electrolyte (*e.g.*, refs. 14, 29), should not be used when only the separation of sulphate and nitrate is required. For the same reason a lower effective mobility of Mg<sup>2+</sup>, in comparison to Ca<sup>2+</sup> (ref. 21), favours the use of the former co-counter ion since these cations form complexes with sulphate which have very similar stability constants<sup>30</sup>. The low solubility product of calcium sulphate in water<sup>30,31</sup> is another reason to use Mg<sup>2+</sup>.

The separation at a high pH<sup>15,32</sup> seems less convenient as a practically carbonate-free solution of the leading electrolyte should be employed so as to avoid disturbance of the quantitation of sulphate and nitrate (for an analogous situation see ref. 33, Fig. 9).

With these facts in mind we used the system described in Table I. The composition of the leading electrolyte is such as to combine the complexation effect of

TABLE I  
OPERATIONAL SYSTEM

HIS<sup>+</sup> = Histidine; Ac<sup>-</sup> = acetate; HEC = hydroxyethyl cellulose.

Parameter	Electrolyte	
	Leading	Terminating
Anion	Cl <sup>-</sup>	Ac <sup>-</sup>
Concentration (mM)	10	5
Co-counter ion	2 mM Mg <sup>2+</sup>	—
Counter ion	HIS <sup>+</sup>	HIS <sup>+</sup>
pH	6.0	5.0
Additive	0.2% HEC	—

Mg<sup>2+</sup> with the retardation of sulphate via the electrophoretic and relaxation effects of both counter ionic constituents<sup>34</sup>. As the effective mobilities of the separands were high under these conditions, a mobile terminating anion (acetate) could be employed. Consequently, the analysis times were less than 10 min. Isotachopherograms of the analysis of anions in a rain-water sample under the described conditions are given in Fig. 1.

The results of the quantitative analyses were derived from the electronically measured residence times of the zones in the conductivity detector of the analytical column. The calibration curves (time-based zone lengths vs. the concentrations) employed for the evaluation of the results were characterized by the following regression equations:

$$t_{\text{NO}_3} = 1.22 + 154.27c_{\text{NO}_3} \quad (r = 0.99985, n = 15)$$

$$t_{\text{SO}_4} = 0.98 + 341.53c_{\text{SO}_4} \quad (r = 0.99997, n = 15)$$

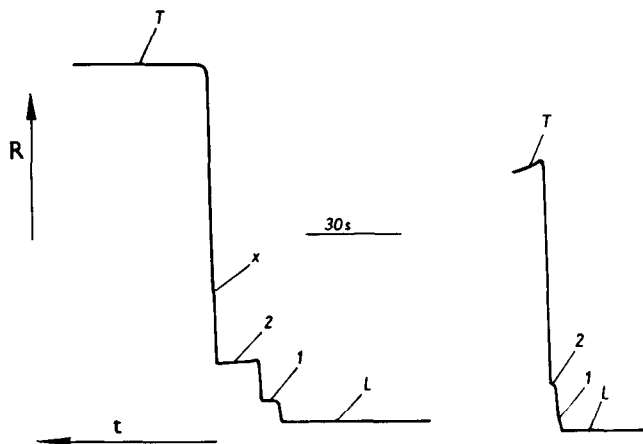


Fig. 1. Isotachopherograms from the analysis of nitrate (1) and sulphate (2) in rain-water (left, analytical column; right, pre-separation column). The separation was carried out using the system described in Table I. The driving currents were 350 and 40  $\mu\text{A}$  in the pre-separation and analytical columns, respectively. L = Chloride; T = acetate; x = impurity from the operational system; R = resistance; t = time.

TABLE II

## RESULTS OF THE DETERMINATIONS OF SULPHATE AND NITRATE IN RAIN-WATER SAMPLES

PT = Photometric titration; T = turbidimetry; G-I = Griess-Ilosvay method (the subscripts indicate the different laboratories).

Sample No.	Sulphate (ppm)			Nitrate (ppm)		
	ITP	PT	T	ITP	G-I <sub>a</sub>	G-I <sub>b</sub>
1	6.11	4.92	5.69	2.84	2.87	2.97
2	4.71	3.30	5.39	2.41	2.45	2.26
3	5.61	4.32	5.39	2.98	3.09	2.96
4	2.64	2.01	3.29	1.08	1.19	1.11
5	6.52	6.67	7.49	2.35	2.70	2.57
6	7.02	6.77	6.89	2.74	2.10	2.12
7	8.30	8.10	8.69	2.89	2.93	2.83
8	6.19	5.91	5.99	2.69	2.62	2.66
9	3.86	3.40	4.19	1.63	1.62	1.90
10	8.39	8.41	8.39	3.53	3.49	3.54

Under the experimental conditions described, we could quantitate with confidence samples containing nitrate and sulphate concentrations of 0.35 and 0.25 ppm, respectively. These are 2-3 times lower than the lowest concentrations actually found in a series of several hundred samples.

Ten samples of rain-water collected at different sampling profiles in Slovakia were taken to assess the analytical performance of the ITP method. They were simultaneously analyzed in two laboratories by use of the approved wet-chemistry

TABLE III

## REPRODUCIBILITIES OF ITP DETERMINATIONS OF NITRATE AND SULPHATE IN RAIN-WATER

$\bar{x}$  = Mean value of the zone length as determined from three experiments;  $s$  = standard deviation; C.V. = coefficient of variation.

Sample No.	Nitrate			Sulphate		
	$\bar{x}$ (s)	$s$ (s)	C.V. (%)	$\bar{x}$ (s)	$s$ (s)	C.V. (%)
1	8.32	0.15	1.8	22.71	0.23	1.0
2	7.06	0.19	2.7	15.51	0.37	2.1
3	8.74	0.19	2.2	20.87	0.40	1.9
4	3.17	0.08	2.7	9.80	0.12	1.2
5	6.88	0.09	1.2	24.22	0.13	0.6
6	8.04	0.10	1.2	26.11	0.05	0.2
7	8.47	0.19	2.2	30.84	0.05	0.2
8	7.90	0.11	1.4	23.02	0.05	0.2
9	4.79	0.01	0.1	14.34	0.08	0.6
10	10.35	0.14	1.4	31.19	0.14	0.5

methods (see Introduction). The results of the comparative analyses are given in Table II.

Deviations found in the determinations of nitrate by different methods were evaluated as statistically insignificant by the *t*-test, when the sets of the results were compared as previously proposed (ref. 35, p. 43). However, the results of the determinations of sulphate obtained by the different methods deviated with a high statistical significance. The same conclusions were drawn from the comparison of ITP with photometric titration, while the results obtained by turbidimetry deviated from those of ITP with a low statistical significance. Incomplete precipitation of sulphate in the titration can provide an explanation for these deviations<sup>5,6</sup>.

The within-day reproducibilities (Table III) as well as a high day-to-day precision of the analyses (relative deviations less than 3% for nitrate and 2% for sulphate) also indicate a very good analytical performance of ITP in this application. As economic aspects of this method are favourable (short analysis time, no sample pretreatment, low running cost), its use in the routine analyses of sulphate and nitrate in rain-water seems very promising.

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