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## Investigation of inorganic ions and organic acids in atmospheric aerosol by capillary electrophoresis

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### Abstract

In this paper capillary electrophoresis was applied for the analysis of inorganic cations and simultaneous investigation of inorganic anions and organic acids in atmospheric aerosol samples. Each method was developed for the characteristic matrix composition of atmospheric aerosol. Optimization of the composition of the background electrolytes, comparison of constant voltage and constant current separation modes, selection of the best detection wavelengths and investigation of the matrix effect of inorganic anions on the separation of organic acids were carried out. Simultaneous determination of inorganic anions and organic acids was achieved by using chromate as UV absorbing carrier ion in the running buffer. Reliability of the analysis of anions in the extracts of wide concentration range was improved by using constant current separation mode. Precision of the methods for migration time and peak area was found to be better than 0.5% and 2%, respectively. The results obtained by the analytical methods yield useful data for atmospheric physics and chemistry. © 1997 Elsevier Science B.V.

*Keywords:* Aerosols; Air analysis; Inorganic anions; Inorganic cations; Organic acids

### 1. Introduction

Since the early 1990s an increasing number of papers have been devoted to the application of capillary electrophoresis (CE) for the analysis of both inorganic cations [1–9] and low-molecular-mass anions [10–15]. These works include the study of different electrolyte compositions to achieve the best separation efficiency, optimization of indirect UV detection for the highest sensitivity etc. Several companies also offer routine-like application notes for the separation of these compounds [16,17]. However, if a new type of sample is to be analyzed these application notes have to be adopted to the

nature of the sample of interest and/or the objective of the analysis.

Ionic composition of atmospheric samples has usually been determined by ion chromatography [18–24]. Recently, however, CE has also been applied. Dabek-Zlotorzynska and Dlouhy [25] used CE for the determination of inorganic and also some organic anions in atmospheric aerosols. Their work was focused on the selection of the most useful background electrolyte. They recommended the use of two different buffers, one containing pyromellitate for the analysis of inorganic ions of high mobility and another containing 2,6-naphthalenedicarboxylate for the study of organic anions of medium mobility. Röder and Bächmann [26] investigated inorganic and organic anions in rain water by CE using *p*-amino-

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benzoate electrolyte with sample stacking for on-line sample enrichment.

In this work analytical methods based on CE were worked out for the investigation of inorganic cations and for the simultaneous analysis of inorganic anions and organic acids in urban atmospheric aerosols. The analytical methods had to fulfil the following criteria: (i) determination of inorganic anions and organic acids in a single run; (ii) baseline separation of all compounds in the concentration range occurring in aerosol extracts; (iii) reliable identification of the analytes and (iv) quantitative analysis with highest precision and sensitivity.

Results of these analyses can provide input data for the interpretation of physico-chemical processes (e.g., condensation, cloud formation, light scattering and absorption) in the atmosphere. Since the effect of the aerosol on these processes mainly depends on its chemical composition these data are essential for atmospheric research. Target components of our investigations are of particular interest because they are water soluble and their concentration is relatively high in the atmospheric aerosol. It should be noted, however, that another crucial parameter affecting the atmospheric behaviour of the aerosol is the size distribution of the different compounds. Therefore the developed methods were applied not only for the determination of the total concentrations of the species but also for the study of their size distributions in the aerosol samples.

## 2. Experimental

### 2.1. Instrumentation and analysis

Analysis was performed by a Quanta 4000 CE system (Waters, Milford, MA, USA) using fused-silica capillaries of 52 cm effective and 60 cm total length, of 75  $\mu\text{m}$  internal and 360  $\mu\text{m}$  outer diameter. Hydrostatic injection of the samples was carried out by lifting the sample vial 10 cm above the electrolyte level for 30 s. In potentiostatic mode the separation voltage was 20 kV for cation and  $-20$  kV for anion analysis. In constant current mode 5 and 30  $\mu\text{A}$  was applied for the separation of cations and anions, respectively. The components were detected by indirect UV detection at 185 and 254 nm using a mercury lamp and at 214 nm using a zinc lamp. The

capillaries were flushed with 0.5 M KOH for 15 min and then with the background electrolyte for 30–60 min prior to analysis. Between runs the capillaries were purged with the electrolyte for 2 min. In the case of anion analysis calibration for carbonate was performed separately because carbonate would produce carbon dioxide in its reaction with organic acids.

### 2.2. Chemicals

For the analysis of cations 4-methylbenzylamine (Fluka, Buchs, Switzerland) was used as a visualizing reagent and 18-crown-6 (Merck-Schuchardt, Hohenbrunn bei München, Germany) and  $\alpha$ -hydroxyisobutyric acid (HIBA) (Fluka) used as complexing agents. For the investigation of anions sodium chromate (Fluka) and potassium hydrogen phthalate (Fluka) were applied as UV absorbing materials. The electroosmotic flow modifier was Anion BT at a concentration of 2.5  $\text{cm}^3$  in 100  $\text{cm}^3$  electrolyte solution (Waters). Standard solutions of cations and anions were prepared from the appropriate standard materials of analytical grade. High purity Milli-Q water was used for preparing each solution and background electrolyte. The pH of the background electrolyte was 3.5–3.6 for cation and 8.0–8.1 for anion analysis.

### 2.3. Samples and sample preparation

Aerosol samples were collected in Veszprém on glass fibre filters (Whatman, Maidstone, UK) and on aluminium foils in a 9-stage Berner-type cascade impactor for size distribution analysis. Sampling time was about 60 h, the sampled volume of air was about 120  $\text{m}^3$ . The samples were extracted in ultrasonic bath with 10  $\text{cm}^3$  Milli-Q water for 30 min. The extracts were filtered with Millex GV membrane filter of 0.22  $\mu\text{m}$  pore size (Millipore, Bedford, MA, USA) before analysis.

## 3. Results and discussion

### 3.1. Optimization of the composition of background electrolytes

Besides the visualizing reagent (4-methylbenzyl-

amine in our experiments) used for indirect UV detection, the background electrolyte for the analysis of inorganic cations should usually contain complexing reagent(s) in order to control the selectivity and improve the resolution of the separation. If the mobilities of several ions are very similar appropriate separation can be achieved by partial complexation of the ions according to their complex-forming equilibrium constants. In this case the mobility of the zone containing the ion is the sum of the mobilities of the free ion and the complex weighted by their mole fractions.

The predominant cations in atmospheric aerosol are ammonium, potassium, calcium, sodium and magnesium. The electrophoretic mobilities of ammonium and potassium and those of sodium and magnesium are very close to each other and without selective complexation these ions co-migrate. Separation of ammonium and potassium is usually achieved by adding 18-crown-6 to the carrier electrolyte [9]. For the separation of calcium, sodium and magnesium several organic acids of medium strength were tested as complexing reagents, among them the most frequently used one was HIBA [2–8]. Waters suggest the use of 1.89 mM 18-crown-6 and 6.53 mM HIBA in their application note [16].

Since preliminary experiments showed that aerosol extract might contain ammonium and potassium up to 10–12 ppm while calcium, sodium and magnesium up to 0.5–2 ppm, standard solutions of 16 ppm and 4 ppm concentrations were tested for the separation of ammonium–potassium and calcium–sodium–magnesium, respectively. The electropherograms of these two standard solutions using background electrolyte in which the concentrations of the complexing reagents were as suggested by Waters can be seen in Fig. 1. The separation of ammonium and potassium in the 4 ppm standard is still good but neither the separation of these two ions in the 16 ppm standard nor the separation of calcium, sodium and magnesium in either standard can be achieved under these experimental conditions.

One possible way to improve resolution would be to dilute the extracts but in this case the ions at lower concentration (primarily magnesium) might not be determined in the same run. Instead, the concentrations of both complexing reagents were doubled. The resulting electropherograms of the same standard solutions are shown in Fig. 2. It can be seen that

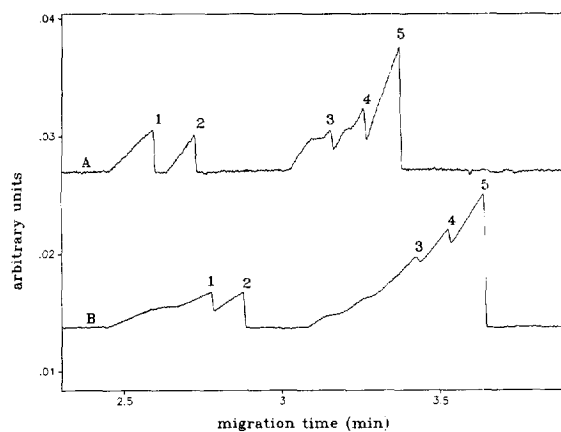


Fig. 1. Separation of cations in standard solutions of (A) 4 ppm, (B) 16 ppm concentration. Background electrolyte: 5.05 mM 4-methylbenzylamine, 1.89 mM 18-crown-6 and 6.53 mM HIBA. Capillary: 60 cm  $\times$  75  $\mu$ m I.D. fused-silica. Applied voltage: 20 kV (positive). Hydrostatic injection: 10 cm for 30 s. UV detection at 185 nm. Peaks: 1=ammonium; 2=potassium; 3=calcium; 4=sodium; 5=magnesium.

practically baseline separation can be achieved both for ammonium–potassium at both concentrations and for calcium–sodium–magnesium at the concentration of 4 ppm. Therefore, the background electrolyte containing 3.78 mM 18-crown-6 and 13.06 mM HIBA was used for the single-run analysis of the inorganic cations in our aerosol samples. Later we intend to perform complex-forming equilibrium calculations to find the optimum concentrations of

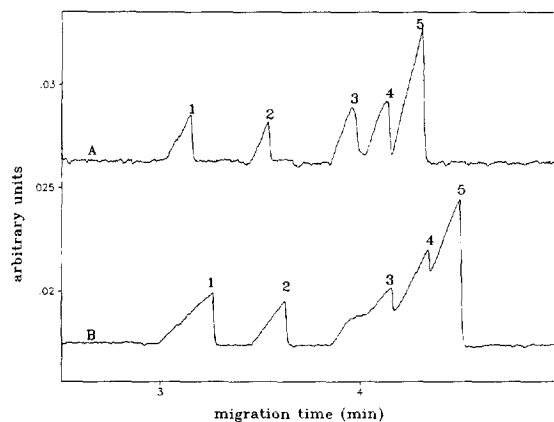


Fig. 2. Separation of cations in standard solutions of (A) 4 ppm, (B) 16 ppm concentration. Experimental conditions as in Fig. 1, except background electrolyte contained 3.78 mM 18-crown-6 and 13.06 mM HIBA.

the complexing agents for the best separation. It is still worth noting that an additional benefit of the increased concentrations of the complexing reagents was the decrease of the mobilities of the ions and consequently, the reduction of the peak distortion effect of electrophoretic dispersion (compare the electropherograms in Figs. 1 and 2).

The background electrolyte for anion analysis should contain an electroosmotic flow modifier (Anion BT in our case) and also a visualizing ion for indirect UV detection. To maintain a good separation efficiency the mobility of the visualizing ion and those of the analytes should be similar in order to minimize the effect of electrophoretic dispersion. Therefore, for the separation of the inorganic anions of high mobility chromate is usually recommended [10,12,13,16] but for the separation of the organic acid anions of medium mobility phthalate is suggested [10,17]. Since our goal was to analyse these two groups of ions simultaneously standard samples were run both in chromate and phthalate electrolyte. The electropherograms are shown in Fig. 3. In the phthalate electrolyte separation of inorganic anions failed with a negative-to-positive going peak at the front of the electropherogram (curve A) while in the chromate electrolyte both inorganic and organic ions

were well resolved (curve B). Consequently, the background electrolyte containing 6 mM chromate was applied for the simultaneous determination of inorganic anions and organic acids in aerosol samples.

It should also be mentioned that separation efficiency expressed in theoretical plate numbers ( $N$ ) for the two most mobile organic anions (oxalate and malonate) were higher in the chromate than in the phthalate electrolyte and opposite results were only obtained for the less mobile organic anions (formiate, succinate).

### 3.2. Application of constant current separation

During the analysis of ions of high mobility migration time of the analyte can considerably change by altering the concentration of the sample even if the experimental conditions are well controlled. This change in migration time is due to the difference in the conductivities of the samples containing the same ions at different concentrations. For the reduction of the effect of the sample conductivity on the migration time Waters suggest applying constant current instead of constant voltage in the first part of the separation [27]. The magnitude of the current should be about the same as that under the constant voltage conditions and the duration of the constant current should be optimized by means of standard solutions.

Since the concentrations of the ions in the aerosol extracts varied by more than an order of magnitude (especially if size distribution analysis was carried out) significant shift of the migration time with the changing conductivity of the sample was in fact observed under constant voltage conditions. Therefore constant current separation mode was also applied for both cation and anion analysis. During the model experiments two standards containing the same ions in a concentration ratio of 1:8 were tested. For anions 1 and 8 ppm standards, while for cations 0.5 and 4 ppm standards were used. Migration times of the same ions in the two standards were determined and their difference was plotted against the duration of the constant current applied at the beginning of the separation. As the mobilities of the anions are smaller, but the mobilities of the cations greater than those of the corresponding background

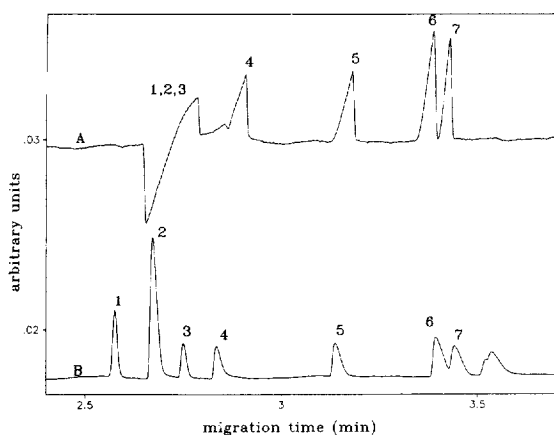


Fig. 3. Simultaneous separation of inorganic anions and organic acids in (A) 5 mM phthalate and (B) 6 mM chromate electrolyte. Both background electrolytes contained 2.5 cm<sup>3</sup> Anion BT in 100 cm<sup>3</sup> solution. Capillary: 60 cm × 75 μm I.D. fused-silica. Applied voltage: 20 kV (negative). Hydrostatic injection: 10 cm for 30 s. UV detection at 254 nm. Peaks: 1=chloride; 2=sulphate; 3=nitrate; 4=oxalate; 5=malonate; 6=formiate; 7=succinate.

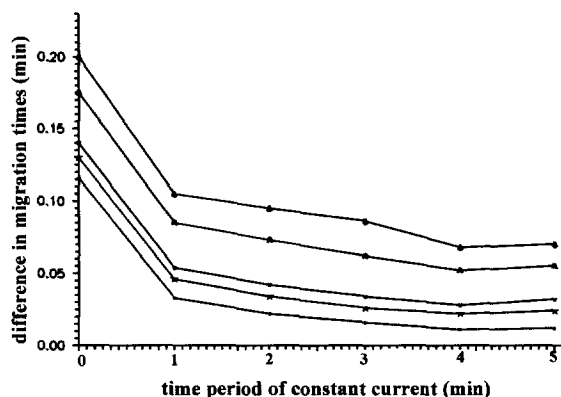


Fig. 4. Difference of the migration times measured for the same anions in 1 ppm and 8 ppm standard solutions as a function of the duration of the constant current at the beginning of the separation. Magnitude of current: 30  $\mu$ A. Other experimental conditions as in Fig. 3 for chromate background electrolyte. Curves: 1 = acetate; 2 = formiate; 3 = oxalate; 4 = sulphate; 5 = chloride.

electrolytes, migration times were found to be greater for the 1 ppm standard for anions, but greater for the 4 ppm standard for cations. Consequently difference in migration times was calculated as  $t_m(1 \text{ ppm}) - t_m(8 \text{ ppm})$  for anions and  $t_m(4 \text{ ppm}) - t_m(0.5 \text{ ppm})$  for cations. The plots are shown in Figs. 4 and 5, respectively.

For anions, as indicated by Waters [16], the difference in the migration times has been signifi-

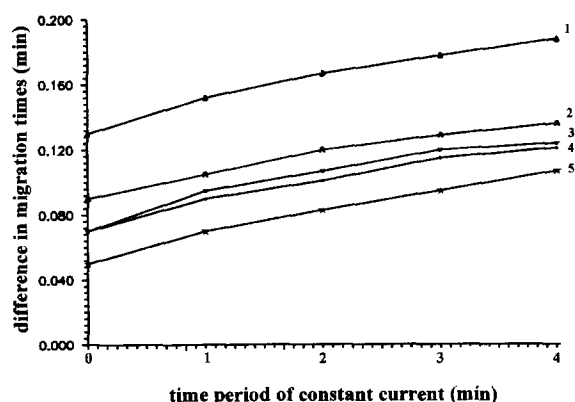


Fig. 5. Difference of the migration times measured for the same cations in 4 ppm and 0.5 ppm standard solutions as a function of the duration of the constant current at the beginning of the separation. Magnitude of current: 5  $\mu$ A. Other experimental conditions as in Fig. 2. Curves: 1 = magnesium; 2 = sodium; 3 = calcium; 4 = ammonium; 5 = potassium.

cantly reduced by applying a constant current even only for 1 min. The difference in the migration times could be reduced further by increasing the duration of the constant current. The best results were obtained when the duration of the amperostatic separation was 4 min. In this case the difference of the migration times has been found to be one third to one fifth of that obtained at constant voltage separation. Therefore during the analysis of anions constant current separation (30  $\mu$ A for 4 min) followed by constant voltage separation (20 kV for 1 min) was used. In this case the uncertainty of the identification of the co-migrating ions, e.g. formiate and succinate, could be reduced considerably without the need of an internal standard.

For cations, however, opposite tendency was observed (Fig. 5). The difference of the migration times was increased by applying constant current (5  $\mu$ A) instead of constant voltage and it increased continuously with the increasing duration of the constant current. As a result the subsequent separation of cations was carried out in potentiostatic (20 kV) separation mode.

Nevertheless the explanation for the opposite tendency observed for anions and cations is still incomplete. This phenomenon calls for further studies.

### 3.3. Selection of detection wavelength

The instrument used in this work is capable of single wavelength photometric detection at 185, 214 and 254 nm. For the analysis of anions in chromate electrolyte a detection wavelength of 254 nm is used in every case, but for cations both 185 [4,5,16] and 214 nm [2–6,8] has been recommended. Therefore detection sensitivity and detection limit of the indirect UV detection of cations at 185 and 214 nm was compared. The results are summarized in Table 1. It can be seen that the detection sensitivity at 185 nm is 1.7–2.4 times higher than that at 214 nm. However, the detection limits are about the same at both wavelengths. This may be explained by the increased baseline noise at the 185 nm (about 100  $\mu$ V) compared to the 214 nm wavelength (about 70  $\mu$ V).

The limit of detection expressed in molar con-

Table 1

Detection sensitivity (detection signal/ppm) and detection limit (ppb at signal-to-noise ratio 2) of cations at 185 and 214 nm wavelength

Component	Sensitivity of detection (detection signal/ppm)		Limit of detection (ppb) at signal-to-noise ratio 2	
	at 185 nm	at 214 nm	at 185 nm	at 214 nm
Ammonium	1057	616	67	76
Potassium	684	342	74	78
Calcium	969	529	30	37
Sodium	1326	556	32	38
Magnesium	2150	1256	25	27

Composition of the background electrolyte: 5.05 mM 4-methylbenzilamine, 3.78 mM 18-crown-6 and 13.06 mM HIBA (pH=3.6).

centration (CLOD) in indirect UV detection can be calculated as follows [9,17]:

$$\text{CLOD} = \frac{c_{\text{VR}}}{D_r R_d} \quad (1)$$

where  $c_{\text{VR}}$  is the concentration of the visualizing reagent,  $R_d$  is the displacement ratio, i.e., the portion of the visualizing ions replaced by the analyte and  $D_r$  is the dynamic reserve of the system, i.e., the signal of the visualizing reagent divided by the baseline noise.

Since detection limits were found to be about the same at the two wavelengths values of  $D_r$  should also be similar in the two cases. As the detection noise was 1.5 times higher at 185 than at 214 nm the ratio of the absorptivities of the visualizing reagent should also be about the same at these wavelengths.

The detection limits for the three less mobile cations are about 2 to 3 times lower than those of ammonium and potassium. This is because the mobilities of these ions are closer to the mobility of the visualizing ion and  $R_d$  is higher, consequently CLOD is lower for these ions. The mobility of the visualizing ion is closest to the mobility of magnesium resulting in the most symmetrical peak shape and lowest detection limit for this ion.

In summary, though the detection limit is practically the same at 185 and at 214 nm because of higher detection sensitivity indirect UV detection of the cations were performed at 185 nm wavelength.

For the detection of the anions all the three detection wavelengths were tested. The results showed, as expected, that 254 nm is the most suitable wavelength for the detection. The reason for that is not only the highest absorptivity of chromate but also the lowest detection noise at this wavelength

compared to the others. The detection noise at 254 nm was around 25 mV, 3 and 8 times lower than at 214 and 185 nm, respectively. The detection limits for the anions at 254 nm are listed in Table 2. In this case the two ions of highest mobility have the lowest detection limits because their mobilities best match the mobility of chromate and the value of  $R_d$  is the highest for these ions.

#### 3.4. Study of the matrix effect of inorganic anions on the separation of organic acids

Concentration of inorganic compounds in the aerosol samples is usually two to three orders of magnitude higher than those of the organic acids. Consequently, separation of organic acids is to be carried out in a solution containing inorganic salts at much higher concentrations and the matrix effect of these salts might not be neglected. Matrix effect of the inorganic compounds was studied by performing separation of organic acids in standard samples

Table 2

Detection limit (ppb at signal-to-noise ratio 2) of anions at 254 nm wavelength

Component	Detection limit (ppb) at signal-to-noise ratio 2
Chloride	33
Sulphate	48
Nitrate	90
Oxalate	104
Malonate	98
Formiate	95
Succinate	119
Acetate	88

Composition of the background electrolyte: 6 mM sodium chromate and 2.5 cm<sup>3</sup> Anion BT in 100 cm<sup>3</sup> solution (pH=8.0).

where the concentrations of the acids were constant (0.5 ppm—average concentration found in aerosol samples) but the concentrations of sulphate and nitrate varied from 1 to 32 ppm. Plate numbers ( $N$ ) for the acids were calculated by:  $N = 5.54(t_m/w_h)^2$  ( $t_m$  is the migration time of the compound,  $w_h$  is the peak width at half height) and the results as a function of the concentrations of the inorganic ions are plotted in Fig. 6. It is obvious that the separation of the less mobile organic anions (e.g., formiate and acetate) has not been affected by the concentrations of the inorganic ions. For malonate a slight decrease of the separation efficiency was observed. Matrix effect of the inorganic salts was most pronounced for oxalate, whose migration behaviour is the most similar to those of the inorganic anions. Nevertheless matrix effect was significant only if the concentration of the inorganics was increased to 32 ppm. In this case the value of  $N$  for oxalate was reduced to one-third of its original value. This may also imply that in practice the detection limit of oxalate may be slightly higher than that listed in Table 2 when this matrix effect was not considered. Based upon the results, however, it can be concluded that the overall matrix effect of the inorganic anions on the sepa-

ration of organic acids in aerosol extract is not significant.

### 3.5. Precision of the methods and investigation of aerosol samples

Precision of the developed methods was determined by 5 consecutive runs of the same standards of 2 ppm concentration. Both for cation and anion analysis the relative standard deviation for migration time and corrected peak area was in the range of 0.2–0.4% and 0.9–1.9%, respectively.

Typical electropherograms of the aerosol extracts are shown in Fig. 7 for cations and in Fig. 8 for anions. The predominant ions are ammonium, sulphate and nitrate. Higher concentrations of potassium and chloride were found in the aerosol in winter (the electropherograms shown are for a winter sample). Concentration of the organic acids were about two orders of magnitude lower than those of the inorganic anions. In this selected sample their concentration is relatively high. As it can be seen in Fig. 8 formiate and succinate migrated quite close to each other and in this selected sample their peaks were not entirely resolved. However, concentrations of these two acids were usually smaller in the aerosol samples than in this selected sample shown in Fig. 8 and in most cases baseline separation of the two compounds could be achieved. Anyway, concentrations of the organic anions were frequently close or below

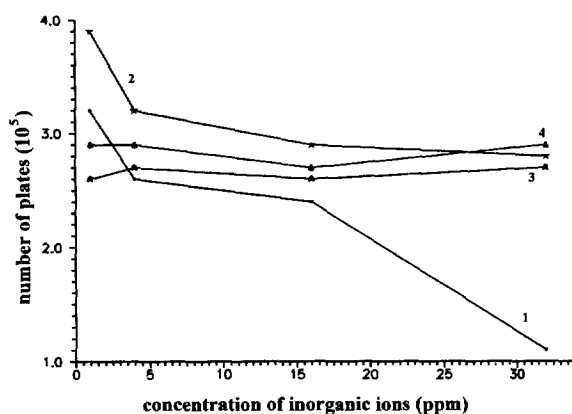


Fig. 6. Theoretical plate numbers for organic acids as a function of the concentration of sulphate and nitrate in the sample. Concentration of organic acids: 0.5 ppm. Experimental conditions as in Fig. 3 for chromate electrolyte, except separation procedure: constant current separation at 30  $\mu$ A for 4 min followed by constant voltage separation at 20 kV for 1 min. Curves: 1 = oxalate; 2 = malonate; 3 = formiate; 4 = acetate. (Since the curve for succinate was practically the same as that of formiate it was not involved in the figure).

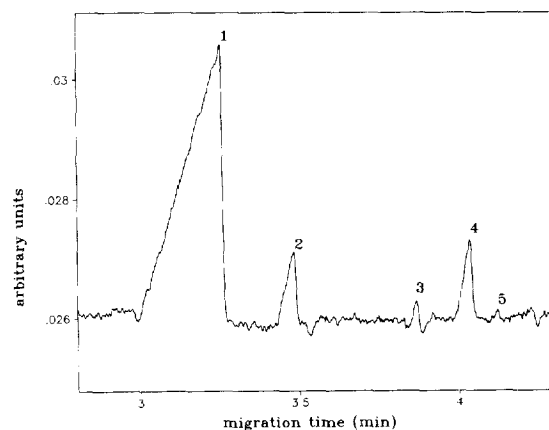


Fig. 7. Electropherogram of an aerosol extract for cation separation. Experimental conditions as in Fig. 2. The peaks are as in Fig. 1.

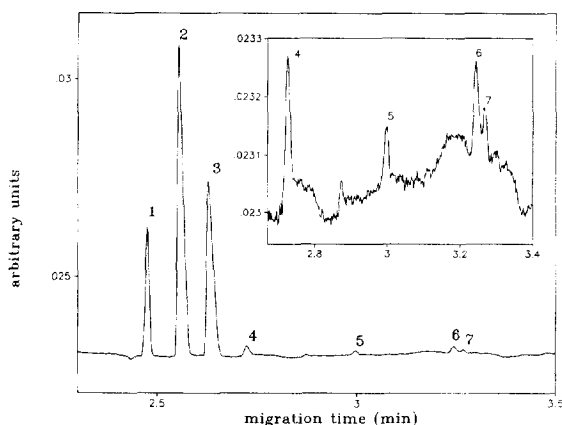


Fig. 8. Electropherogram of an aerosol extract for anion separation. Experimental conditions as in Fig. 3 for chromate electrolyte, except separation procedure: constant current separation at 30  $\mu$ A for 4 min followed by constant voltage separation at 20 kV for 1 min.

the detection limit of the analytical procedure. Therefore, studying the methods for on line preconcentration of these compounds (e.g., electrokinetic injection, sample stacking) is in progress.

The predominant ions as well as the organic acids were found in the fine aerosol ( $d < 2 \mu\text{m}$ ). The highest concentrations of these species were observed in the size range of  $0.5 \mu\text{m} < d < 1 \mu\text{m}$ . Potassium and chloride were uniformly distributed in the whole size range, while calcium, sodium, magnesium and carbonate were mostly found on coarse particles ( $d > 2 \mu\text{m}$ ). These results will be published elsewhere in more detail [28].

#### 4. Conclusions

CE proved to be a useful technique for the study of inorganic ions and organic acids in atmospheric aerosol samples. By adding 3.78 mM 18-crown-6 and 13.06 mM HIBA to the background electrolyte ammonium and potassium could be well resolved up to a concentration of 16 ppm while calcium, sodium and magnesium up to a concentration of 4 ppm. Application of chromate as the UV absorbing carrier ion allowed simultaneous determination of inorganic anions and organic acids. Reliability of the analysis of anions in the extracts of wide concentration range was improved by using constant current separation

mode. The precision of the methods were better than 0.5% and 2% for migration time and corrected peak area, respectively. The optimized methods were applied for the determination of the total concentration and size distribution of the species in urban atmospheric aerosol. The results of the analyses can be used for the interpretation of physical and chemical processes in the atmosphere.

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