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### The Use of Micro-HPLC and Capillary Zone Electrophoresis for the Analysis of Individual Raindrops

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# THE USE OF MICRO-HPLC AND CAPILLARY ZONE ELECTROPHORESIS FOR THE ANALYSIS OF INDIVIDUAL RAINDROPS

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A new sampling procedure for individual raindrops with volumes of 4 nl - 4  $\mu$ l is presented. It is demonstrated that analyte concentrations in small volumes can be analysed using micro-HPLC and capillary zone electrophoresis (CZE). Results for the analysis of cations such as  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and anions such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and organic acids are given and discussed.

**KEY WORDS :** micro-HPLC, CZE, individual rain drops, inorganic cations and anions

## INTRODUCTION

Theoretical studies of wet removal of atmospheric pollutants are only based on integral data of rain or fog and on laboratory experiments. For better understanding of atmospheric processes (cloud and fog physics and chemistry) the microanalysis of individual droplets is desirable. The analysis of the concentration of different species in droplets at different stages of growth should be the key to understand such processes. Furthermore, in the case of different chemical composition in individual droplets it is not possible to use an analysis of an integral rain sample for the interpretation of chemical reactions. Individual raindrops were collected by sampling and freezing them in liquid nitrogen<sup>1</sup>. Every individual raindrop was kept as an individual. Dimension and ionic concentration of each drop was determined.

Micro-HPLC and CZE have been developed mainly for the separation of organic compounds, while only few investigations were carried out for inorganic ions<sup>2-9</sup>. For the separation of cations, this is partly due to the lack of metal-free equipment and also due to the fact that for low limits of detection spectroscopic methods are used. In ion chromatography the determination of ions is usually carried out with conductivity detection<sup>10,11</sup>, although there exist very sensitive direct<sup>12</sup> and indirect photometric detection methods<sup>13-15</sup>. In our research using micro-HPLC and CZE indirect photometric detection was carried out.

Especially in micro-HPLC suppressed conductivity detection can not be used because micro suppressors are not commercially available.

## EXPERIMENTAL

### *Instrumentation*

**HPLC** The metalfree chromatographic system consists of an IRICA HPLC pump Sigma 871 ERC (Alteglöfshelm, Germany), and a 9125 injector Rheodyne (ERC, Alteglöfshelm, Germany). Connecting tubes were PEEK (polyetherether ketone) capillaries (I.D., 0.178 and 0.064 mm) from Upchurch Scientific (GAT, Bremerhaven, Germany). For the indirect fluorescence detection of the cations, we used a Spectroflow 980 fluorescence detector (Applied Biosystems, Weiterstadt, Germany) and, for the anions, a variable-wavelength Spectro Monitor 3100 detector (LDC/Milton Roy, Gelnhausen, Germany).

For conductivity detection we used a Dionex IC-2000i system including a polymer-type column PRP X-100 (Hamilton, Darmstadt, Germany) with a AMMS-1 Dionex micromembrane suppressor. For the analysis of cations we used an ION-210 Metals Column (560  $\mu\text{eq/g}$ ) (ICT, Frankfurt, Germany) and a Fast Cation I column (5  $\mu\text{eq/g}$ ) (Dionex, Idstein, Germany).

The separation of the anions was performed on a 3- $\mu\text{m}$  RP-18 Ultracarb Phenomenex (Amchro, Sulzbach, Germany). In micro-HPLC we used a micro sample injector (Rheodyne 7520 with an internal loop of 0.5  $\mu\text{l}$ ) and a SOMA S 3120 variable wavelength UV detector ERC (micro flow cell: 0.5  $\mu\text{l}$ ).

**Coating procedure** The columns were coated with 350 ml (micro-HPLC: 6 ml) of 1 mM dodecylamine in methanol-water (10:90) at a flow rate of 0.4 ml/min (micro-HPLC, 6  $\mu\text{l}/\text{min}$ ). The solution was adjusted to pH 4.0 ( $\text{H}_3\text{PO}_4$ ). After the coating procedure the columns were conditioned with the eluent.

**CZE** The electropherograms were performed on a Kapillar-Elektrophorese System 100 (GROM, Herrenberg, Germany). Indirect fluorescence detection was carried out with a Spectroflow 980 fluorescence detector (Applied Biosystems) which was modified for on column detection. To that end two holes were drilled through a home made detector cell housing which allowed to place a capillary at the surface of the 2  $\pi$  steradian mirror. The capillary was fixed with two screws after centring the capillary window exactly in the middle of the excitation beam. Capillaries were obtained from SGE (Weiterstadt, Germany).

### *Chemicals*

- Cerium (III) nitrate, 99.9% (Aldrich, Steinheim, Germany)
- Cerium (III) sulphate, 99.99% (Alfa, Karlsruhe, Germany)
- Dodecylamine, 99% (Fluka, Neu-Ulm, Germany)
- Acetonitrile HPLC grade (Baker, Gross-Gerau, Germany)

—2.5-Dihydroxybenzoic acid, 99% (Aldrich).

All other reagents were of p.a. quality (Merck, Darmstadt, Germany). All solutions were prepared using water generated by a Milli-Q purification system (Millipore) and were degassed under vacuum. For CZE all electrolytes were filtered through a 0.22  $\mu\text{m}$  membrane filter type GV (Millipore).

### *Sampling procedure*

In previous works a horizontal wind tunnel<sup>16</sup> and a disc<sup>17</sup> were used for sampling size classified rain drops. However, these methods cause errors due to, (e.g. evaporation and contamination) and they are not suitable for the sampling of individual droplets. The pH spectrum of individual rain drops<sup>18</sup> was determined with a pH sensitive filter paper. But with this method it is impossible to determine other components which are also important for the understanding of atmospheric processes. There are several requirements for the sampling of individual droplets: (a) the scavenging and release of gases should be stopped immediately; (b) chemical reactions should be stopped immediately; (c) any contamination during the sampling procedure has to be avoided; (d) for size classification, a simple separation should be possible; (e) the procedure should be suitable for field experiments.

For sampling and size classification of the droplets we used a Dewar container filled with liquid nitrogen and a set of 7 polyethylene sieves (Büttner, Wasserbrunn, Germany). The whole system is protected by a box of acrylic glass against moisture from the air which may cause condensation processes. Inside the box a copper pipe cooled with liquid nitrogen is used to freeze out all disturbing gaseous substances.

During sampling the box is opened at intervals of approx. 10 sec for 3 seconds depending on the rain intensity. The droplets fall into the liquid nitrogen and swim for a few seconds on a gaseous layer. Upon being frozen they sink due to their higher specific weight and are size classified by the sieves. For the precise size determination of large raindrops ( $> 0.5 \mu\text{l}$ ) a standard solution of  $\text{Li}^+$  is added. The volume of the smaller droplets is calculated by the mesh size of the sieves. The error in determining the volume of the droplets is size dependent and is in the same range as the analytical error (up to 15%).

During storage the droplets were kept frozen in a box under nitrogen gas until the analytical procedure started. For each drop a polypropylene conical vial (300  $\mu\text{l}$ ) (Neolab, Heidelberg, Germany) was used.

In laboratory experiments it was found that contamination during the freezing process can be excluded and that no loss of material occurred during the freezing process.

## RESULTS AND DISCUSSION

Theory shows that the three separation techniques HPLC, micro-HPLC and CZE have their optimum performance at different sample volumes,  $V_s$  (Figure 1). HPLC has the highest relative sensitivity,  $S_R$ , which is defined as

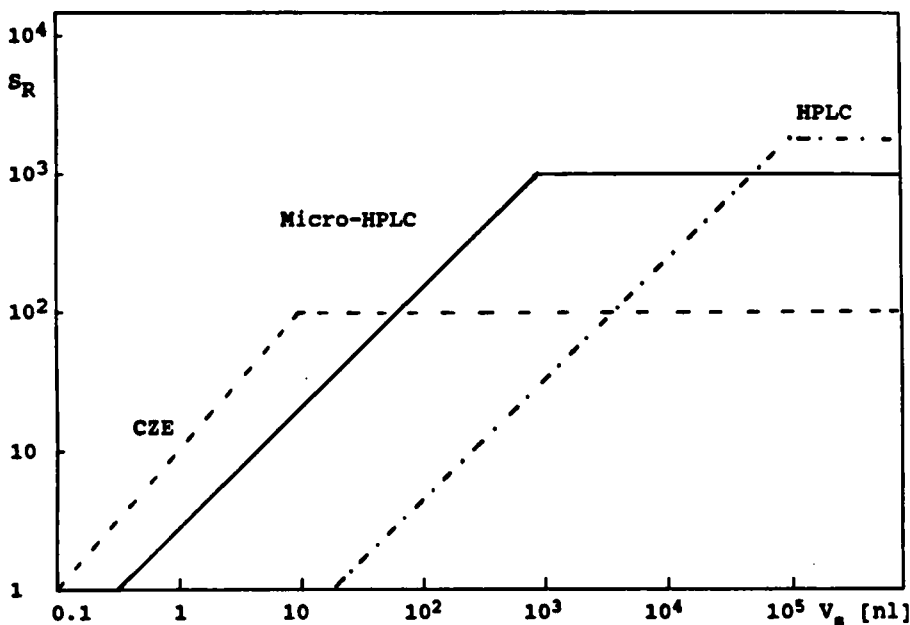


Figure 1 Comparison of the relative sensitivities,  $S_R$ , of HPLC, micro-HPLC and CZE.

$$S_R = \frac{V_s}{\text{LOD}} \quad (1)$$

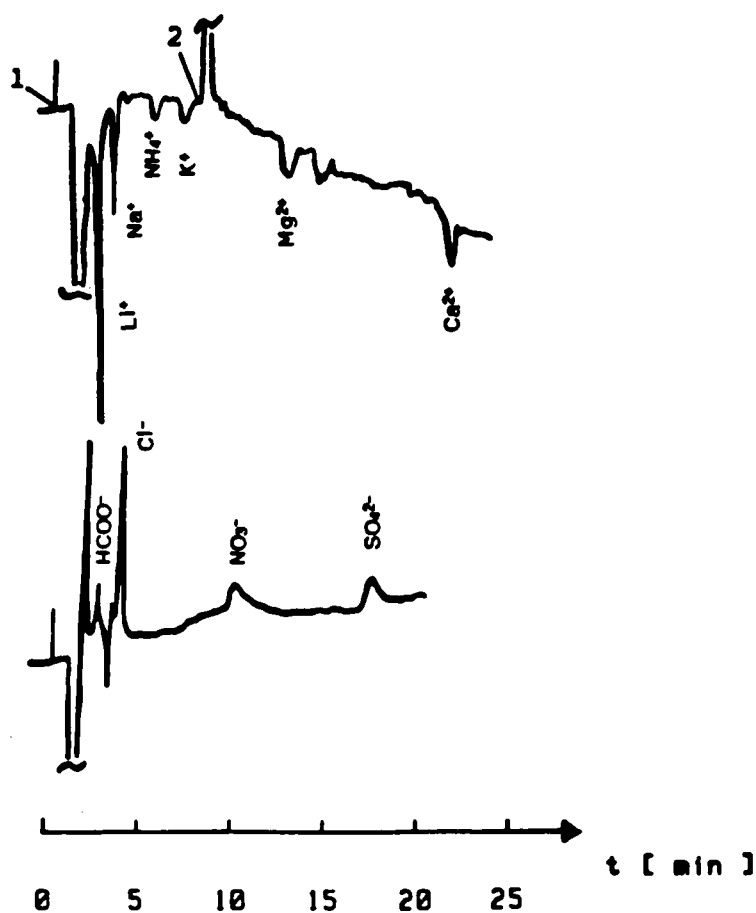
where  $S_R$  = relative sensitivity [ $\text{nl} \cdot \text{pg}^{-1}$ ],  $V_s$  = sample volume [ $\text{nl}$ ], and  $\text{LOD}$  = absolute limit of detection [ $\text{pg}$ ].

Assumptions for the calculation of the  $S_R$  values are as follows:

- HPLC:  $V_{s\text{max}} = 50 \mu\text{l}$ ,  $\text{LOD} = 25 \text{ pg}$
- Micro-HPLC:  $V_{s\text{max}} = 0.5 \mu\text{l}$ ,  $\text{LOD} = 0.5 \text{ pg}$
- CZE:  $V_{s\text{max}} = 0.01 \mu\text{l}$ ,  $\text{LOD} = 0.1 \text{ pg}$

For volumes of less than  $10 \mu\text{l}$  HPLC is not suitable any more (low mass sensitivity). If only limited sample volumes are available micro-HPLC should be used. Depending on the column I.D. sample volumes between  $10 \text{ nl}$  and  $1 \mu\text{l}$  can be injected. CZE shows the highest mass sensitivity of the three methods. As can be seen, the best relative sensitivity,  $S_R$ , with droplets of less than  $10 \text{ nl}$  can be reached with CZE.

In Table I the limits of detection which are required and which we have obtained for the analysis of individual rain droplets are summarized. As can be seen in table I it is possible to carry out an analysis of the main cations and anions for the larger droplets. The small droplets could not be analysed as individual drops and had to be measured as size fractions.



**Figure 2** Chromatogram of a 400 nl raindrop.

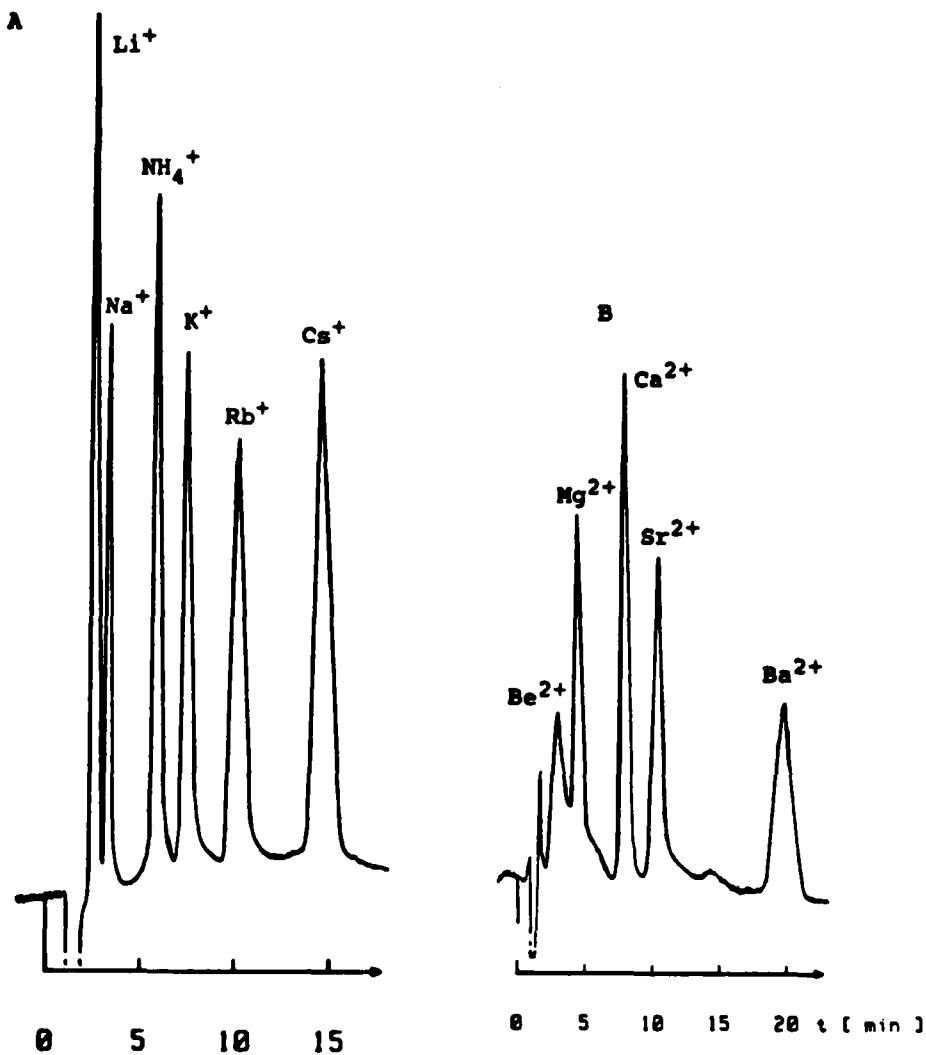
Cations: Li<sup>+</sup>: internal standard, Na<sup>+</sup>: 130 ng/ml, NH<sub>4</sub><sup>+</sup>: 50 ng/ml, K<sup>+</sup>: 31 ng/ml, Mg<sup>2+</sup>: 26 ng/ml, Ca<sup>2+</sup>: 94 ng/ml.

(1) column: ION-210 Metals Column (ICT), 100 \* 3.2 mm.  
 (2) column: Fast Cation I (DIONEX), 250 \* 4 mm I.D.

Eluent: 10 μM Ce(NO<sub>3</sub>)<sub>3</sub>, 1 ml/min;  
 detection: fluorescence, range: 0.01;  
 injection volume: 4.5 μl.

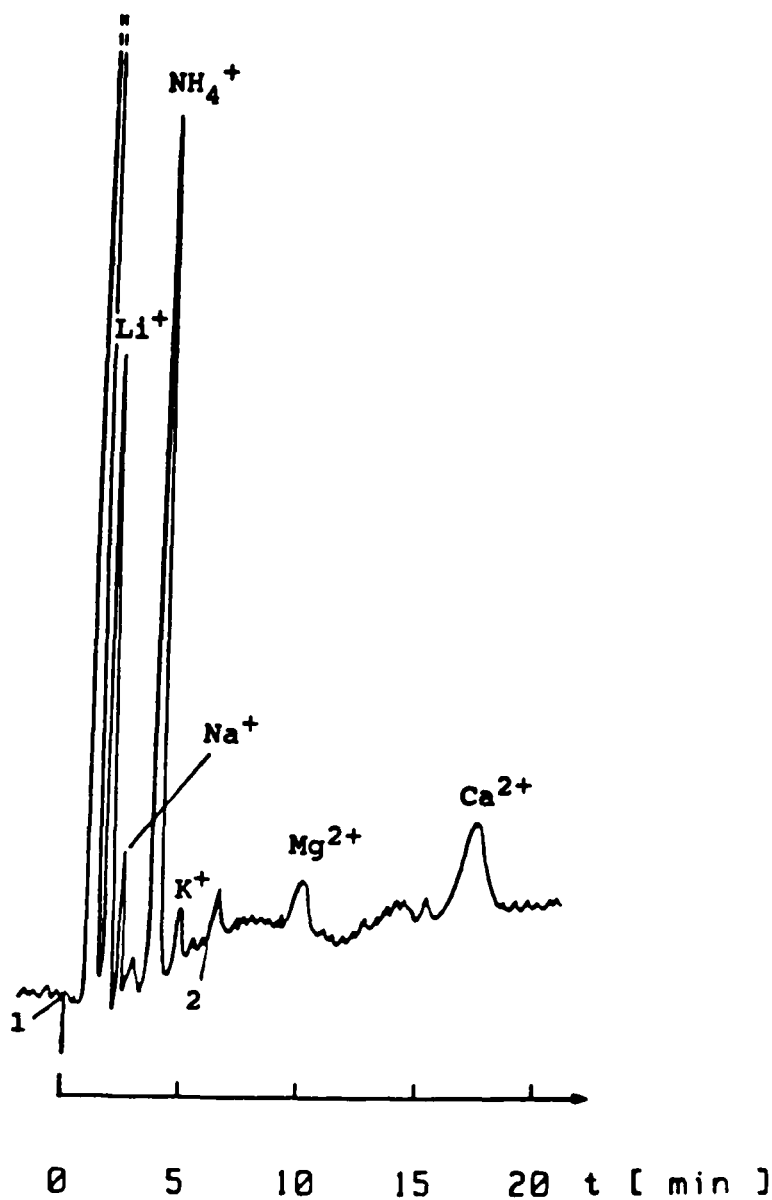
Anions: HCOO<sup>-</sup>: 94 ng/ml, Cl<sup>-</sup>: 195 ng/ml, NO<sub>3</sub><sup>-</sup>: 230 ng/ml, SO<sub>4</sub><sup>2-</sup>: 310 ng/ml.

Column: Hamilton PRP X-100;  
 eluent: 2.5 mM Na<sub>2</sub>CO<sub>3</sub>, 0.17 mM p-cyanophenol,  
 6% acetonitrile, 1 ml/min;  
 detection: conductivity with suppressor;  
 injection volume: 4.5 μl.



**Figure 3** Chromatogram of a standard.

- (A)  $\text{Li}^+$ : 100 ng/ml,  $\text{Na}^+$ : 240 ng/ml,  $\text{NH}_4^+$ : 245 ng/ml,  
 $\text{K}^+$ : 500 ng/ml,  $\text{Rb}^+$ : 1200 ng/ml,  $\text{Cs}^+$ : 3000 ng/ml.  
 Column: ION-210 Metals Column (ICT), 90  $\times$  0.5 mm I.D.;  
 eluent: 4.7  $\mu\text{M}$  cerium (III) sulfate, 13  $\mu\text{l}/\text{min}$ ;  
 detection: fluorescence (1  $\mu\text{l}$  cell), range: 0.02;  
 injection volume: 0.5  $\mu\text{l}$ .
- (B)  $\text{Be}^{2+}$ : 100 ng/ml,  $\text{Mg}^{2+}$ : 100 ng/ml,  $\text{Ca}^{2+}$ : 400 ng/ml,  
 $\text{Sr}^{2+}$ : 600 ng/ml,  $\text{Ba}^{2+}$ : 1000 ng/ml.  
 Column: Fast Cation I (DIONEX), 250  $\times$  0.75 mm I.D.;  
 eluent: 21  $\mu\text{M}$   $\text{Ce}(\text{NO}_3)_3$ , 60  $\mu\text{l}/\text{min}$ ;  
 detection: fluorescence (5  $\mu\text{l}$  cell), range: 0.015; injection volume: 2.5  $\mu\text{l}$ .



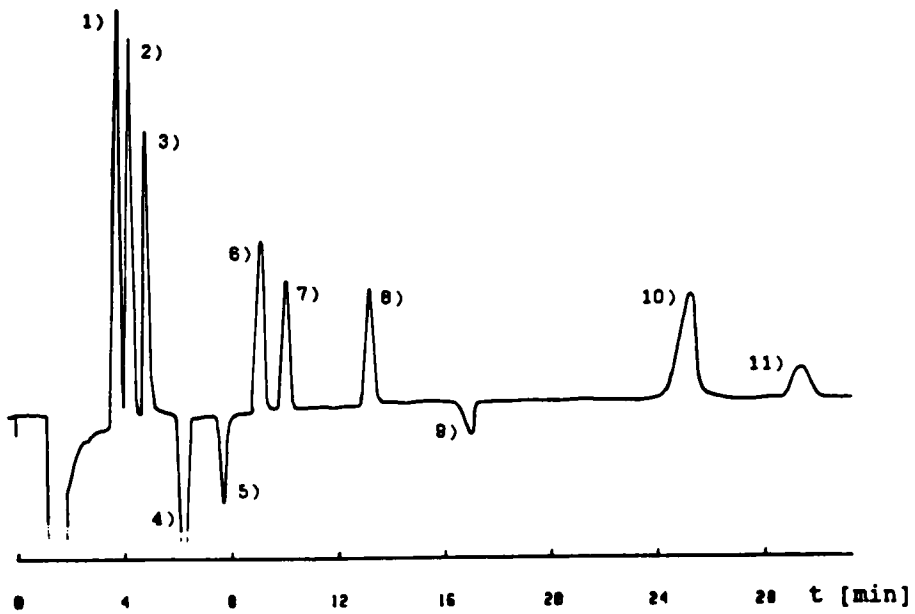
**Figure 4** Chromatogram of a 3 µl raindrop (Darmstadt, 28.10.90).

- $\text{Li}^+$ : internal standard,  $\text{Na}^+$ : 22 ng/ml,  $\text{NH}_4^+$ : 73 ng/ml,  $\text{K}^+$ : 18 ng/ml,  $\text{Mg}^{2+}$ : 15 ng/ml,  $\text{Ca}^{2+}$ : 75 ng/ml.
- (1) column: ION-210 Metals Column (ICT), 110 × 0.75 mm I.D.; eluent: 14 µM  $\text{Ce}(\text{NO}_3)_3$ , 48.3 µl/min; detection: fluorescence, range: 0.01; injection volume: 1.6 µl.
- (2) column: Fast Cation I (DIONEX), 250 × 0.75 mm I.D.; eluent: 14 µM  $\text{Ce}(\text{NO}_3)_3$ , 27.3 µl/min; detection: fluorescence, range: 0.01; injection volume: 0.9 µl.



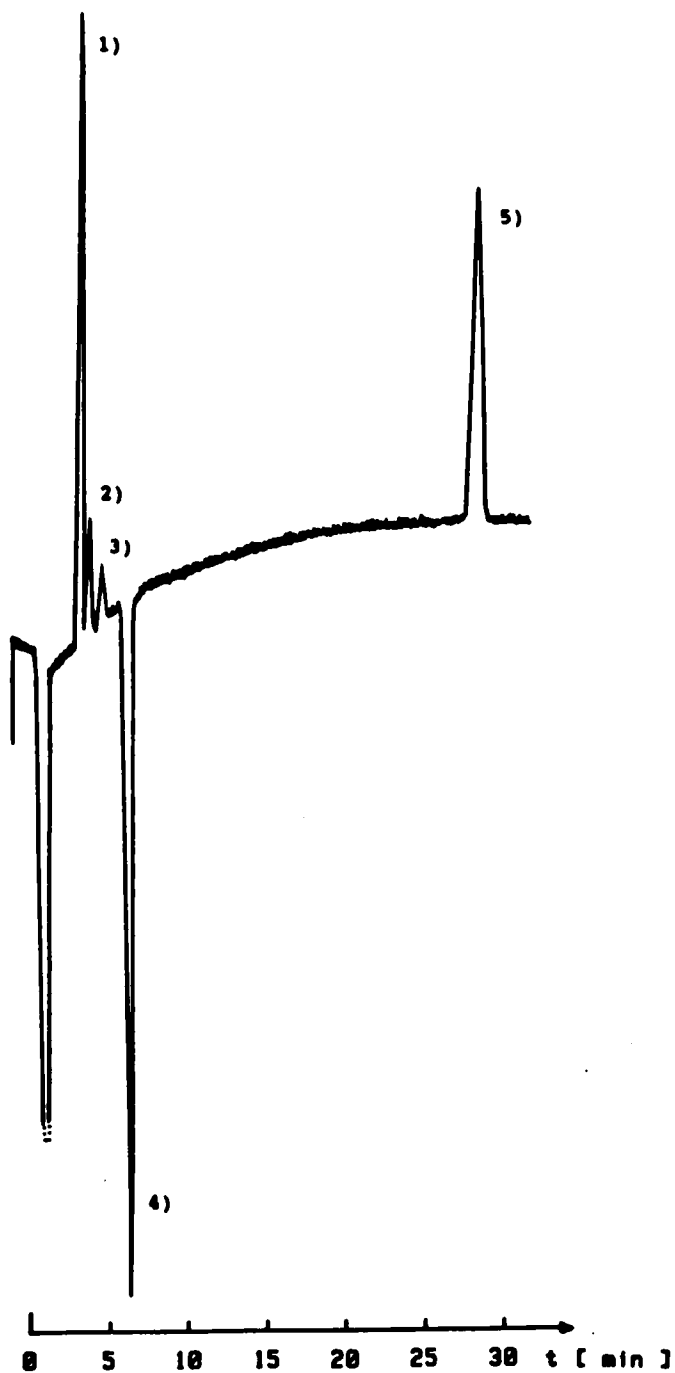
**Table 1** Requirements for individual raindrop analysis

Species	Rain <sup>1</sup> [pg]	LOD <sup>2</sup> [pg]	Volume <sup>3</sup> [μl]	Method <sup>4,5</sup>
Na <sup>+</sup>	30	0.2	0.01	CZE
NH <sub>4</sub> <sup>+</sup>	30	0.4	0.01	CZE
K <sup>+</sup>	30	0.4	0.01	CZE
Mg <sup>2+</sup>	5	0.8	0.01	CZE
Ca <sup>2+</sup>	30	2	0.01	CZE
Cl <sup>-</sup>	50	13	0.5	micro-HPLC
NO <sub>3</sub> <sup>-</sup>	80	15	0.5	micro-HPLC
SO <sub>4</sub> <sup>2-</sup>	120	40	0.5	micro-HPLC
HCOO <sup>-</sup>	90	25	0.5	micro-HPLC
CH <sub>3</sub> COO <sup>-</sup>	120	35	0.5	micro-HPLC

**Figure 5** Chromatogram of an anion standard.

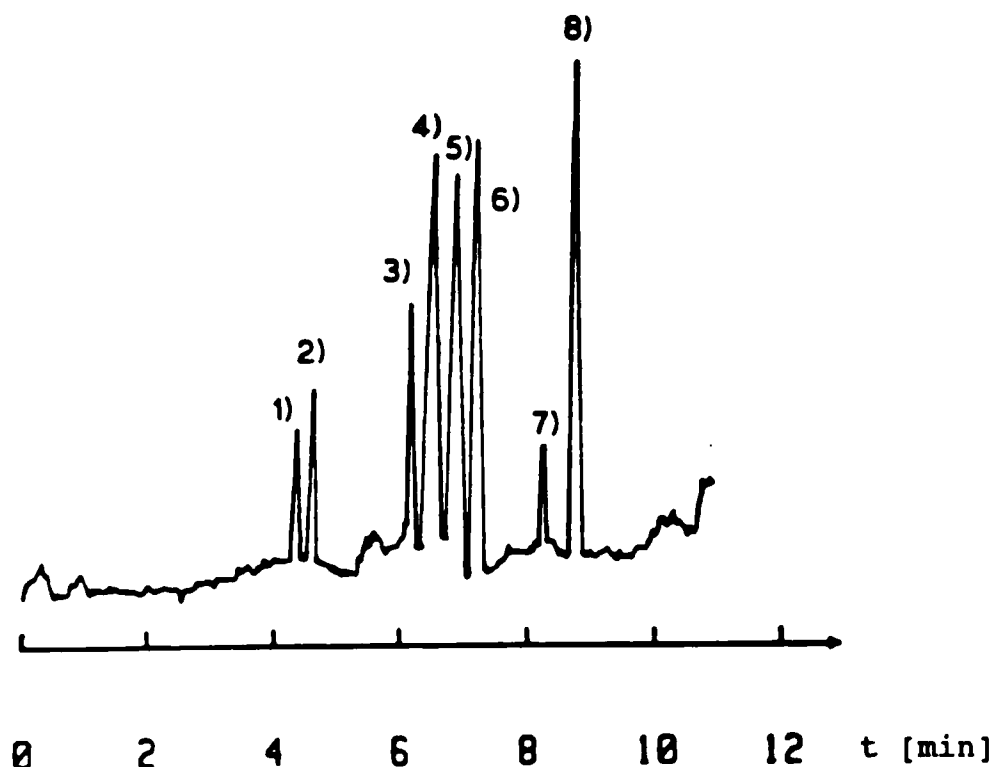
- (1) Cl<sup>-</sup>: 4 μg/ml; (7) ClCH<sub>2</sub>CO<sub>2</sub><sup>-</sup>: 5 μg/ml;  
 (2) HCO<sub>2</sub><sup>-</sup>: 5 μg/ml; (8) ClO<sub>4</sub><sup>-</sup>: 5 μg/ml;  
 (3) CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>: 5 μg/ml; (9) SCN<sup>-</sup>: 10 μg/ml;  
 (4) NO<sub>3</sub><sup>-</sup>: 4 μg/ml; (10) Cl<sub>2</sub>CHCO<sub>2</sub><sup>-</sup>: 5 μg/ml;  
 (5) I<sup>-</sup>: 5 μg/ml; (11) SO<sub>4</sub><sup>2-</sup>: 5 μg/ml;  
 (6) ClO<sub>3</sub><sup>-</sup>: 5 μg/ml

Column: LiChrospher RP 18-5 (Merck) 200 • 4.6 mm I.D. coated with dodecylamine;  
 eluent: 23 μM [Fe(CN)<sub>6</sub>]<sup>3-</sup>, 1 ml/min;  
 detection: UV (205 nm), range: 0.01 AU;



**Figure 6** Chromatogram of a rain sample.

(1)  $\text{Cl}^-$ : 580 ng/ml, (2)  $\text{HCO}_2^-$ : 210 ng/ml, (3)  $\text{CH}_3\text{CO}_2^-$ : 150 ng/ml, (4)  $\text{NO}_3^-$ : 750 ng/ml, 5)  $\text{SO}_4^{2-}$ : 920 ng/ml  
Column: Ultracarb RP 18-3  $\mu\text{m}$  (Phenomenex), 150  $\times$  0.5 mm I.D. coated with dodecylamine; eluent: 9.4  $\mu\text{M}$   $\text{K}_3$   $[\text{Fe}(\text{CN})_6]$ , 13  $\mu\text{l}/\text{min}$ ; detection: UV (205 nm), range: 0.001 0:001 AU; injection volume: 0.5  $\mu\text{l}$ .



**Figure 7** Electropherogram of a standard. (1)  $\text{Rb}^+$ : 1.7  $\mu\text{g/ml}$ , (2)  $\text{K}^+$ : 0.8  $\mu\text{g/ml}$ , (3)  $\text{Ba}^{2+}$ : 2.7  $\mu\text{g/ml}$ , (4)  $\text{Ca}^{2+}$ : 0.8  $\mu\text{g/ml}$ , (5)  $\text{Na}^+$ : 0.5  $\mu\text{g/ml}$ , (6)  $\text{Mg}^{2+}$ : 0.5  $\mu\text{g/ml}$ , (7)  $\text{Be}^{2+}$ : 0.2  $\mu\text{g/ml}$ , (8)  $\text{Li}^+$ : 0.1  $\mu\text{g/ml}$ .

Capillary: fused silica, 70 cm  $\times$  75  $\mu\text{m}$  I.D.;

electrolyte: 350  $\mu\text{M}$  cerium (III) sulfate;

voltage: 30 kV;

detection: fluorescence fluorescence, range: 0.05;

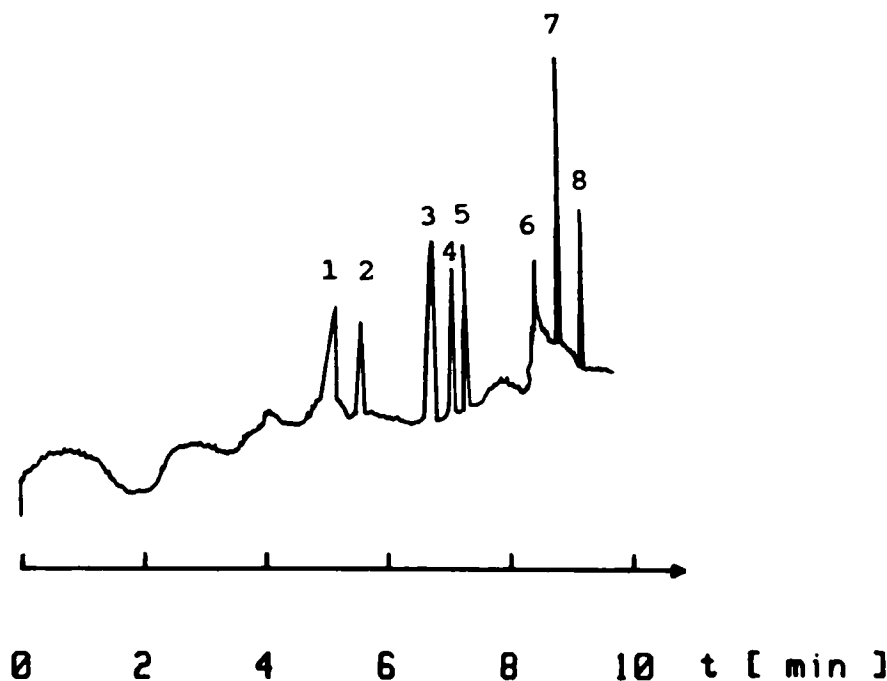
injection: hydrostatic 30 s, 10 cm.

The cut between large and small droplets depends on the number of species which have to be analyzed in one event and on the limit of detection.

For indirect fluorescence detection of the cations Ce (III) was added to the HPLC eluent<sup>19</sup>. Metal-free equipment is advantageous because of a more stable baseline, less system peaks and a better background signal<sup>20</sup>. In order to determine the alkali and the alkaline earth ions in the same chromatogram we used a column switching set-up with two different cation exchangers<sup>21</sup>.

The anions were separated on a PRP X-100 column<sup>1</sup>. To prevent contamination the sample volume (4.5  $\mu\text{l}$ ) is not injected by a syringe but sucked through a short PEEK capillary. Figure 2 shows the chromatograms of the cation and anion analysis of a 400 nl raindrop. It can be seen that the system has to be improved for smaller droplets.

We therefore started our investigations in micro-HPLC in order to achieve a lower absolute mass sensitivity. As columns homepacked PEEK capillaries with I.D.s. from 0.75 to 0.25 mm were used<sup>21</sup>. Figure 3 shows the chromatograms of an alkali and an alkaline earth



**Figure 8** Electropherogram of a standard.

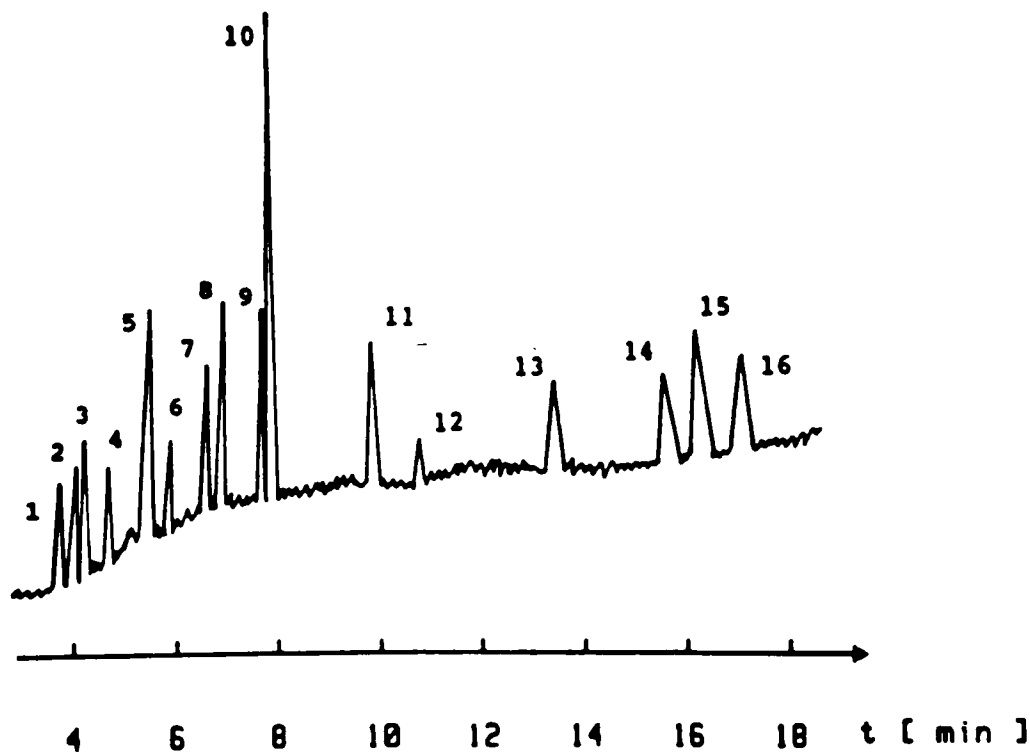
(1)  $\text{NH}_4^+$ : 1.8  $\mu\text{g/ml}$ , (2)  $\text{K}^+$ : 3.9  $\mu\text{g/ml}$ , (3)  $\text{Ca}^{2+}$ : 4.0  $\mu\text{g/ml}$ ,  
 (4)  $\text{Na}^+$ : 2.3  $\mu\text{g/ml}$ , (5)  $\text{Mg}^{2+}$ : 2.4  $\mu\text{g/ml}$ , (6)  $\text{Be}^{2+}$ : 0.9  $\mu\text{g/ml}$ ,  
 (7)  $\text{Li}^+$ : 0.7  $\mu\text{g/ml}$ , (8)  $\text{Ba}^{2+}$ : 13.7  $\mu\text{g/ml}$ .

Capillary: fused silica, 75 cm  $\times$  75  $\mu\text{m}$  I.D.;

electrolyte: 250  $\mu\text{M}$  cerium (III) sulfate, 1 mM Dicyclohexyl-18-crown-6

ion standard. In order to analyze the alkali and alkaline earth ions in one run a micro column switching set-up with 0.75 mm I.D. columns was developed. After injection (Rheodyne 9125 valve with 2.5  $\mu\text{l}$  sample loop) the sample passes through a micro filter (PEEK union with a 0.5 mm thru-hole containing a 2  $\mu\text{m}$  polyethylene frit (Upchurch Scientific) is inserted). Then the sample is split in a T-piece. Chromatography takes place simultaneously on two columns. Due to the different operating pressure of the columns the flow rate has to be regulated mechanically by reducing the I.D. of the connecting tube with a screw. Figure 4 shows the separation of the alkali and alkaline earth ions and ammonia in an individual rain drop. In comparison to the conventional column switching the limits of detection could be improved by a factor of 20.

Anion micro columns and micro suppressors are not commercially available. We therefore developed a new method with indirect UV detection using hexacyanoferrate (III),  $[\text{Fe}(\text{CN})_6]^{3-}$ , as eluent additive for the determination of organic and inorganic anions (Figure 5).  $\text{NO}_3^-$ ,  $\text{I}^-$  and  $\text{SCN}^-$  appear as positive signals because these anions show stronger UV absorbance than the eluent at 205 nm. As stationary phase a C-18-bonded silica column was coated with dodecylamine. For the determination of the anions in individual raindrops it is also necessary to use micro-HPLC. As column, a homepacked PEEK capillary with an I.D. of 0.5 mm was used. Figure 6 shows a chromatogram of the main anions ( $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,



**Figure 9** Electropherogram of an anion standard.

(1) sulfate 3  $\mu\text{g/ml}$ ; (9) oxalate 3  $\mu\text{g/ml}$ ;  
 (2) iodate 3  $\mu\text{g/ml}$ ; (10) formate 6  $\mu\text{g/ml}$ ;  
 (3) bromate 3  $\mu\text{g/ml}$ ; (11) pyruvate 3  $\mu\text{g/ml}$ ;  
 (4) perchlorate 3  $\mu\text{g/ml}$ ; (12) glycolate 3  $\mu\text{g/ml}$ ;  
 (5) methanesulfonate 3  $\mu\text{g/ml}$ ; (13) succinate 3  $\mu\text{g/ml}$ ;  
 (6) chlorate 3  $\mu\text{g/ml}$ ; (14) acetate 6  $\mu\text{g/ml}$ ;  
 (7) hydrogenphosphate 3  $\mu\text{g/ml}$ ; (15) propionate 3  $\mu\text{g/ml}$ ;  
 (8) malonate 3  $\mu\text{g/ml}$ ; (16) adipate 3  $\mu\text{g/ml}$ .  
 Capillary: fused silica, 66 cm \* 75  $\mu\text{m}$  I.D.;  
 buffer: 1.4 mM 2.5-dihydroxybenzoic acid;  
 voltage: 30 kV;  
 detection: fluorescence, range: 0.05;  
 injection: hydrostatic 30 s, 10 cm.

$\text{CH}_3\text{CO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) in a rain sample. Limits of detection in the pg range (from 15 to 40 pg depending on the anion) were obtained.

If CZE instead of micro-HPLC is used for volumes of less than 1  $\mu\text{l}$  two problems arise: injection and detection. For injection from volumes of less than 1  $\mu\text{l}$  no really satisfactory solution exists until now. To analyze such small samples like individual raindrops new micro injection systems will have to be developed. Using an indirect method for detection in CZE it is necessary to optimize the electrolyte solution for both detection and separation.

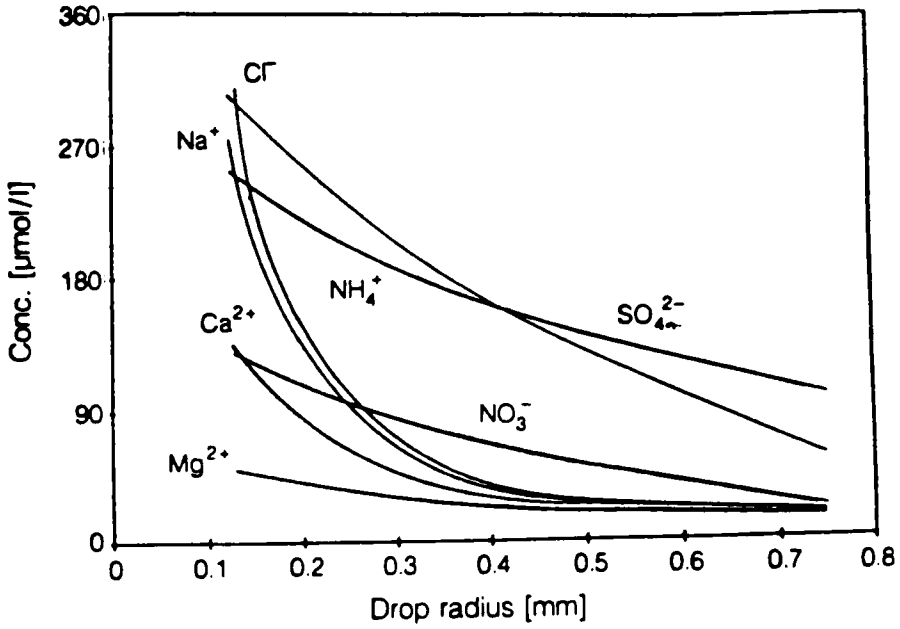


Figure 10 Characteristic concentrations as a function of the drop radius from the examination of size-classified raindrops.

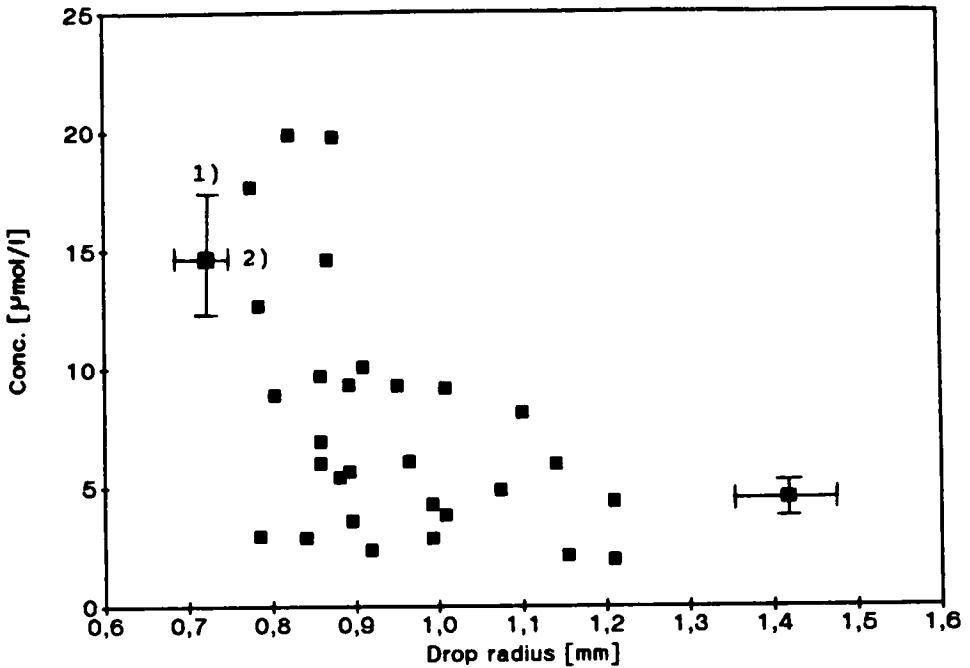


Figure 11 Sodium concentration of individual raindrops.

= range of analytical error;

(1) error in sodium concentration; (2) error in determination of the radius.

According to the investigations of Yeung<sup>22</sup> one has to use low eluent concentrations in order to get low limits of detection. Furthermore, high resolution is achieved when analyte and electrolyte ions have rather similar ion mobilities<sup>23</sup>.

For the separation of alkali and alkaline earth ions we used  $\text{Ce}^{3+}$ . Figure 7 shows an electropherogram of a standard with indirect fluorescence detection. Using the  $\text{Ce}^{3+}$ -based electrolyte system it is not possible to work at  $\text{pH} > 5$  because of the formation of cerous hydroxides. At  $\text{pH} < 5$ ,  $\text{NH}_4^+$  and  $\text{K}^+$  have the same retention times. However, separation of these cations is possible by adding 18-crown-6 [1,4,7,10,13,16-hexaoxacyclooctadecan] to the  $\text{Ce}^{3+}$  electrolyte (Figure 8). Variable ring sizes and the type, the number and position of the donor atoms in the ether ring permit selective adaptation to a certain cation. Because of the selective interaction between 18-crown-6 and  $\text{K}^+$  and  $\text{Ba}^{2+}$ , the retention times of these two ions change.

For the separation of organic and inorganic anions we used 2,5-dihydroxybenzoic acid with indirect fluorescence detection (Figure 9). This electrolyte shows the highest fluorescence intensity from among several mono- and dihydroxybenzoic acids compared by Van Duuren<sup>24</sup>. With this electrolyte it is possible to separate inorganic anions with high ion mobilities as well as low-molecular-weight organic anions. With 2 mM 2,5-dihydroxybenzoic acid as electrolyte and a longer capillary (75 cm \* 75  $\mu\text{m}$  I.D.) the highly mobile ions  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  could be separated.

### *Results of field experiments*

Typical results for the analysis of size classified rain droplets are given in Fig. 10. As the ratio of e.g.  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  changes with the radius of the droplets they must be scavenged by different mechanisms (gases or aerosols). Fig. 11 shows results from the analysis of large individual raindrops. It can be seen that drops of equal radius differ considerably in concentration. The reason for this result is the different history of each drop (e.g. 'in cloud scavenging' and 'below cloud scavenging').

## CONCLUSIONS

A new sampling procedure for individual rain drops was developed. The rain drops were collected in liquid nitrogen and kept as an individual or size-classified. The main cations and anions in rain samples were determined with micro-HPLC and indirect detection. The concentration of the ions depends on the drop size. Another powerful system for the analysis of inorganic and organic ions, especially in the case of samples with very small volumes, is CZE. Here it will be necessary to develop a new micro injection system to handle with individual rain drops smaller than 1  $\mu\text{l}$ .

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