



ELSEVIER

Journal of Chromatography A, 745 (1996) 209–215

JOURNAL OF
CHROMATOGRAPHY A

Analysis of single raindrops in the nl range by capillary electrophoresis

B. Tenberken, P. Ebert, M. Hartmann, M. Kibler, A. Mainka, T. Prokop, A. Röder,
K. Bächmann*

Fachbereich Chemie, Technische Hochschule Darmstadt, Petersenstr. 18, 64287 Darmstadt, Germany

Abstract

The analysis of single and size-classified rain- (volume: 10 μ l/3 nl), cloud- or fogdrops (volume: pl–fl) is expected to give new and interesting information about anthropogenic air pollution and drop formation processes in the atmosphere. This paper presents microanalytical investigations for the analysis of single rain- and fogdrops. Specially developed sampling procedures and methods to store and to handle single rain- and fogdrops are shown. The analysis is carried out by capillary zone electrophoresis (CZE). Sample injection is made using a new developed microinjection system. Raindrops are injected directly into the CZE capillary by applying a vacuum at the opposite end of the capillary. The main inorganic cations and anions (NH_4^+ , K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} , Cl^- , NO_3^- , NO_2^- , SO_3^{2-} , SO_4^{2-}), aldehydes, mono- and dicarboxylic acids occurring in rain are analysed using different detection methods like laser-induced fluorescence (LIF), amperometry, UV and fluorescence detection. The absolute limits of detection are in the fmol range.

Keywords: Rain water; Single raindrops; Environmental analysis; Anions; Inorganic cations; Aldehydes

1. Introduction

In the past many investigations about the determination of the chemical components in rain-, cloud and fogwater have been made. The analysis was always carried out on the assumption that individual drops forming the bulk phase have the same concentration of trace compounds as the bulk sample. This assumption may be justified considering average effects of rain- and cloudwater on the biosphere, soils, etc. The effects of drops which may have concentrations of trace elements (e.g. pH) which are much higher than the bulk sample are completely neglected by this assumption.

It is to be expected that different mechanisms are

responsible for the variation of the chemical content of raindrops:

1. condensation nuclei inside clouds
2. particle and gas scavenging
3. collision, coalescence and break up of falling raindrops
4. evaporation.

Bächmann et al. [1–8] have found a dependence of the concentration of trace elements on the radius of drops by analysing size-classified raindrops. More detailed information about the above mentioned processes can be obtained by the analysis of single raindrops as well as single fogdrops.

The analysis of single rain- and fogdrops is

*Corresponding author.

possible by using capillary zone electrophoresis (CZE). The high resolution and small sample requirement makes this method suitable for the quantitative, multicomponent chemical analysis of ultra-small volumes like single cells [9–19] and single rain- and fogdrops.

2. Experimental

2.1. Chemicals

All solutions were prepared daily using ultra-pure water purified with a Milli-Q system (Millipore Eschborn, Germany). The reagents used were of analytical reagent grade. 10 mM stock standard solutions of inorganic cations and inorganic and organic anions were prepared from their sodium, chloride and nitrate salts (Merck, Darmstadt, Germany). 1 M stock standard solutions of aldehydes were obtained by dilution of aldehydes (Fluka, Buchs, Switzerland). The derivatization of aldehydes occurred using 1-dimethylaminonaphthalene-5-sulfonyl hydrazine (DNSH) (Fluka, Buchs, Switzerland). All electrolytes were degassed under vacuum for 15 min. Tetradecyltrimethylammoniumhydroxide (TTAH) was produced by exchange of bromide in a solution of 50 mM tetradecyltrimethylammoniumbromide (TTAB) (Aldrich, Steinheim, Germany) using the ion-exchange material, Amberlite (IRA-904 Serva, Heidelberg, Germany). The paraffin oil, Uvasol (Merck), was purified by tenfold extraction with water. Barium hydroxide, 18-crown-6 and *p*-aminobenzoate were obtained from Merck, 4-N-methylaminophenol from Fluka.

2.2. Instrumentation

All experiments were carried out on laboratory-built capillary electrophoresis (CE) systems. The capillary was fixed at an angle of 30° in order to observe the injection of drops by a microscope (Leica, Bensheim, Germany). The injection of drops was achieved by applying a vacuum with a syringe at the opposite end of the capillary. Indirect UV detection was carried out using a capillary on-column detector (Dionex, Idstein, Germany). Laser-induced fluorescence detection (LIF) was made by

the application of an on-column He–Cd laser-based fluorescence detector ($\lambda_{\text{exc}}=325$ nm, 5 mW; $\lambda_{\text{exc}}=442$ nm, 30 mW) (SOPRA, Büttelborn, Germany). Amperometric detection occurred using a laboratory built off-column detection cell and an amperometric detector (EG&G 400, Princeton, USA). A high-voltage power supply HCN6M-30000 (F. u. G. Elektronik, Rosenheim, Germany) delivering 0–30 kV was used. The separations were carried out in conventional fused-silica capillaries from CS-Chromatographie Service (Langerwehe, Germany). Electropherograms were recorded by an A/D board from ERC (Altglofsheim, Germany) using APEX chromatography software (Autochrom, Milford, MA, USA).

2.3. Sampling and handling of single raindrops

Owing to the small volumes of single raindrops (volume: 10^{-5} – 10^{-9} l), there are difficulties concerning the sampling procedure and the handling of single raindrops because of contamination and evaporation. Sampling of size-classified and single raindrops occurred using the 'Guttalgor' method [1,4,5] developed in our group. The Guttalgor [gutta (lat.)=drop; algor (lat.)=frost] mainly consists of a dewar vessel filled with liquid nitrogen. Raindrops falling into the liquid nitrogen freeze and sink down. The drops remain their spherical shape during the freezing process and therefore it is possible to separate the frozen drops by polyethylene sieves of different mesh widths (0.1–1.4 mm). After sampling, the single raindrops are kept under water-extracted paraffin oil in petri dishes of polystyrol in order to exclude evaporation. The concentrations of the main trace elements occurring in rain are in the μ molar range. Hence the analysis depends upon methods with low absolute limits of detection. Therefore CZE in particular is suitable because this method is designed for the analysis of smallest volumes. Analysis is performed with a modified CZE apparatus. The capillary is fixed at an angle of 30° in order to observe the injection of the drop by a microscope. Sample injection occurs by moving the petri dish and connecting a drop to the capillary tip. By applying a vacuum at the opposite end of the capillary the drop is introduced into the capillary. This process is demonstrated in Fig. 1 photographically.

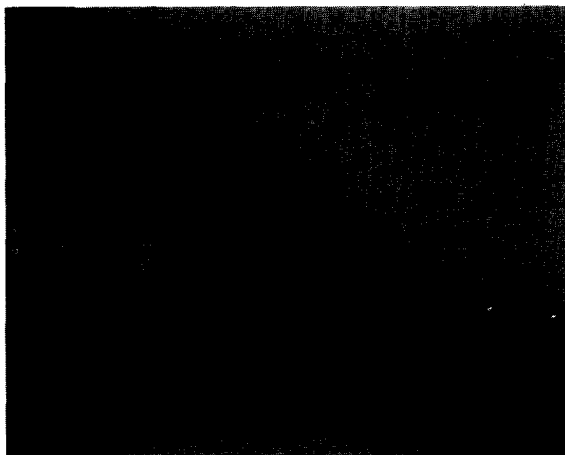


Fig. 1. Injection of a raindrop.

3. Results and discussion

3.1. Determination of the raindrop volume

The analysis of single raindrops requires an accurate measurement of the drop volume in order to determine exactly the concentration of trace elements. Below three techniques are described to ascertain the volume of single raindrops.

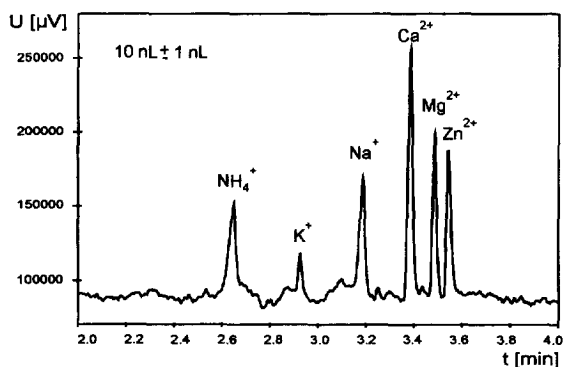


Fig. 2. Electropherogram of a simulated raindrop. Sample: 10 nl (NH_4^+ : 40 μM ; K^+ : 13 μM ; Na^+ : 41 μM ; Ca^{2+} : 37 μM ; Mg^{2+} : 22 μM ; Zn^{2+} : 20 μM); electrolyte: 4 mM 4-N-methylaminophenol, 4 mM 18-crown-6, pH 6.5; capillary: 50 μm I.D., 74 cm total length, 60 cm to detector; voltage: 25 kV; detection: indirect UV detection (220 nm).

3.1.1. Determination of the drop volume directly from the electropherogram

Using several standard solutions (NH_4^+ , K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} ; 10–100 μM), drops of different volumes in the range from 10–140 nl were produced and inserted into paraffin oil (for analysis see Section 3.3). A ratio of the half width of the EOF peak and the retention time of the EOF was established. From this follows a linear dependence of the drop volume on the EOF.

3.1.2. Determination of the drop volume by the measurement of the length of the sample in a capillary

Simulated raindrops of definite volumes (Section 3.1.1) were injected into a capillary (I.D.=75±5 μm). Clear deviations of the drop volume are obtained by this inaccuracy of about 7%. A further disadvantage of this technique is that in order to analyse the drop it has to be injected a second time into the separation capillary. As this procedure requires a lot of time it is not useable for the analysis of single raindrops.

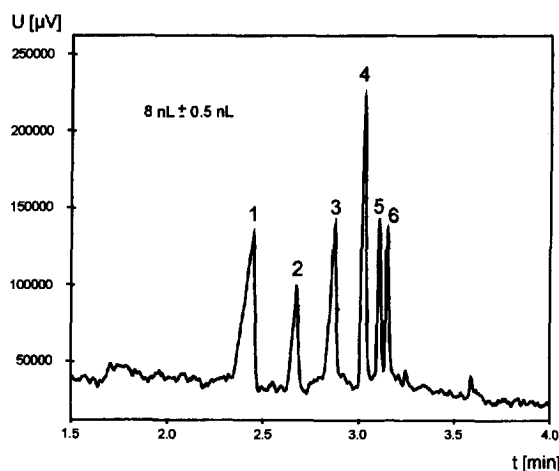


Fig. 3. Electropherogram of a single raindrop. Sample: 8 nl (1, NH_4^+ : 108 μM ; 2, K^+ : 57 μM ; 3, Na^+ : 70 μM ; 4, Ca^{2+} : 56 μM ; 5, Mg^{2+} : 25 μM ; 6, Zn^{2+} : 21 μM); electrolyte: 4 mM 4-N-methylaminophenol, 4 mM 18-crown-6, pH 6.5; capillary: 50 μm I.D., 74 cm total length, 60 cm to detector; voltage: 25 kV; detection: indirect UV detection (220 nm).

3.1.3. Calculation of the drop volume by measuring the diameter of drops

The diameter of drops is measured using a scaled microscope. This method can be used to determine the volume of raindrops because water drops remain their spherical shape in paraffin oil. A deviation of the drop volume of 4–10% is caused by an error in reading of ± 0.5 graduations of scale. This technique is the simplest way to determine the volume of a drop because the diameter of a drop can be determined simultaneously when sample injection occurs. In the following, this method is used for the determination of the drop volume.

3.2. Calibration

A difficulty in the analysis of single raindrops is the different sample volumes. This requires cali-

bration graphs for each drop size because the complete raindrops are injected into the capillary. Simulated raindrops are therefore produced by a sprayer system and introduced into paraffin oil. After the diameter of a drop has been determined, the drop is injected into the capillary. The capillary is then reinserted into the electrolyte vessel and the separation is started. Fig. 2 shows an electropherogram of a simulated raindrop.

3.3. Analysis of single raindrops

Single raindrops are sampled by the 'Guttalgor' method (see Section 2.3). The frozen drops are introduced directly in paraffin oil and thaw spontaneously. The analysis occurs as described in Section 3.2. In Fig. 3 an electropherogram of a real raindrop is demonstrated.

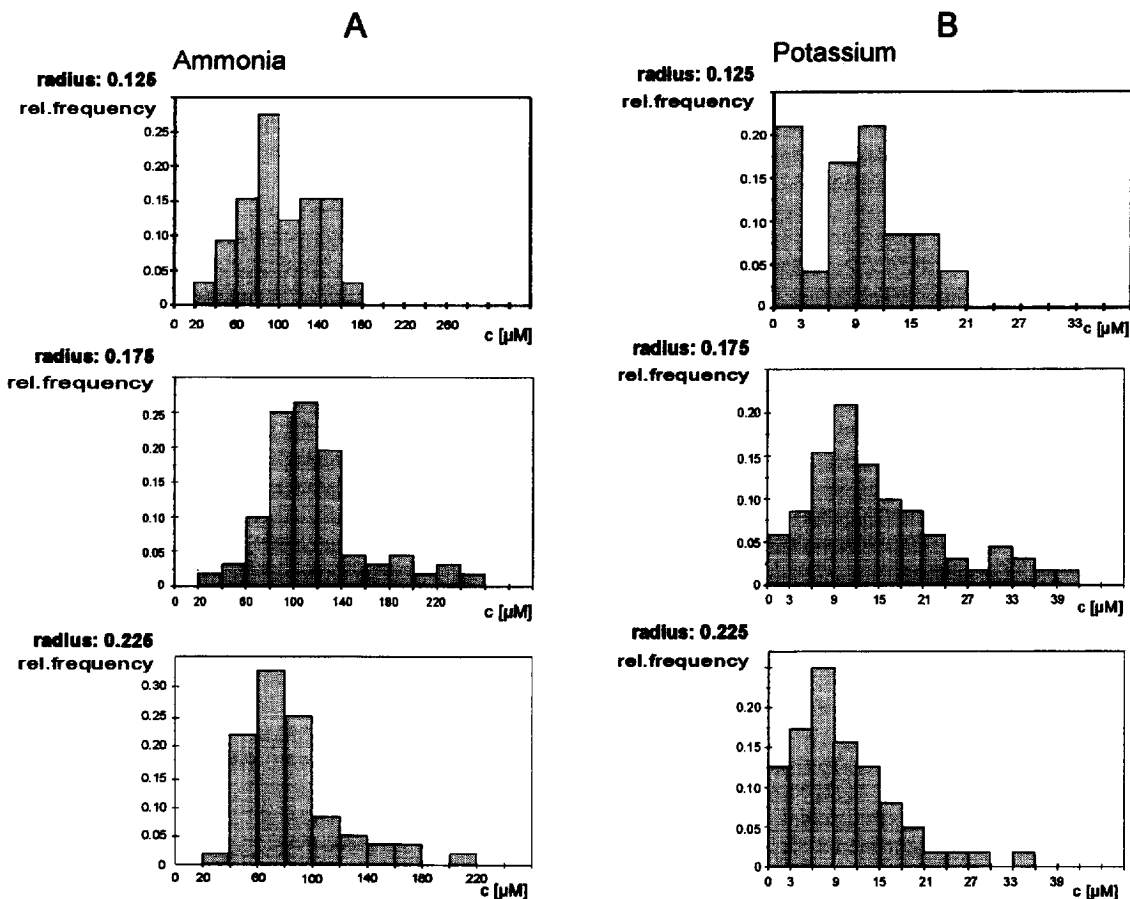


Fig. 4. Concentration distributions of trace elements in single raindrops. (A) ammonia; (B) potassium.

3.4. Concentration distributions of trace elements in single raindrops

Until now concentration distributions of trace compounds in rain could only be drawn up for size-classified rain samples [5,8]. A disadvantage of this method is that it is not possible to determine the precise volumes of the analysed drops. Concerning the size fraction, only the average volume of the analysed drops can be determined. Using the new developed method shown in this paper it is possible to determine concentration distributions for raindrops of the same volume. Inorganic cations were analysed (requirements see Section 3.3). The distributions of the concentrations measured in single raindroplets show Gaussian curves for dropsizes in the range of 20–50 nl (e.g. sodium and ammonia, Fig. 4). These distributions are caused by evaporation of raindrops and aerosol particle scavenging during the falling process. The concentrations of the main cations are 10–100 μM .

For the smallest raindroplets (volume: 3 nl–14 nl; average diameter: 0.25 mm) a second maximum at low concentrations (0–3 μM) for the cations potassium, sodium, calcium, magnesium and zinc is found. This second maximum at low concentrations is the result of coalescence and breakup of large raindrops which have low concentrations. Evidence for this conclusion is the agreement of the concentration of the second maximum and the concentration measured for the fraction of large raindrops ($d=1$ mm).

For ammonia there is no second maximum at low concentrations. This effect is due to gas scavenging.

3.5. Analysis of carbonyl compounds, organic anions and sulfite in size-classified rainsamples

The analysis of carbonyl compounds by CE–LIF (Fig. 5), organic anions by CE–indirect UV detection (Fig. 6) and sulfite by CE combined with amperometric detection (Fig. 7) occurs until now in size-classified and bulk rainsamples [20,21]. Results show a dependence of the concentration of organic compounds in rain on the radius of raindrops. These investigations give information on the influences of organic compounds in the atmosphere. But in order to get more detailed information it is necessary to analyse single raindrops. Hence these techniques will

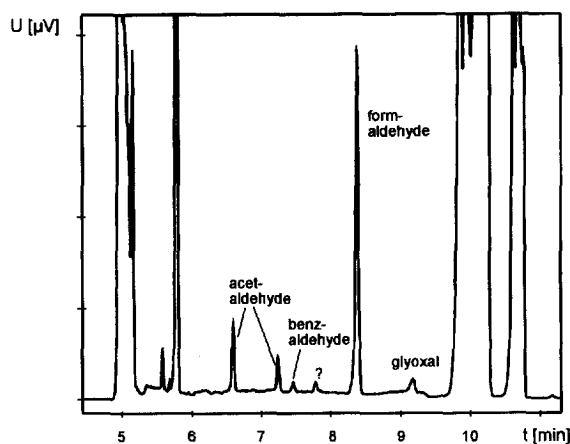


Fig. 5. Laser-induced fluorescence detection of carbonyl compounds derivatized by DNSH in a size-classified rain sample. Electrolyte: 5 mM Na_3PO_4 , 10 mM $\text{Na}_2\text{B}_4\text{O}_7$, 20% acetonitrile, pH 8; detection: laser-induced fluorescence detection, $\lambda_{\text{exc}}=325$ nm; injection mode: stacking of 200 nl of a rainsample.

be applied in future works for the analysis of single raindrops.

3.6. Sampling and analysis of single fogdrops

The sampling of fogdrops occurs by corona dis-

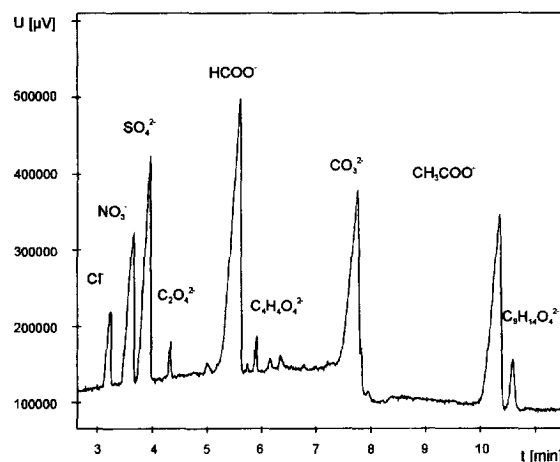


Fig. 6. Electropherogram of organic and inorganic anions in a size-classified rain sample. Electrolyte: 7.5 mM *p*-aminobenzoate, 750 μM barium hydroxide, 100 μM TTAH, pH 9.4; capillary: 75 μm I.D., 70 cm total length, 63 cm to detector; detection: indirect UV detection (264); voltage: -28 kV; injection: 30 s, 1.5 p.s.i. (1 p.s.i.=6894.76 Pa).

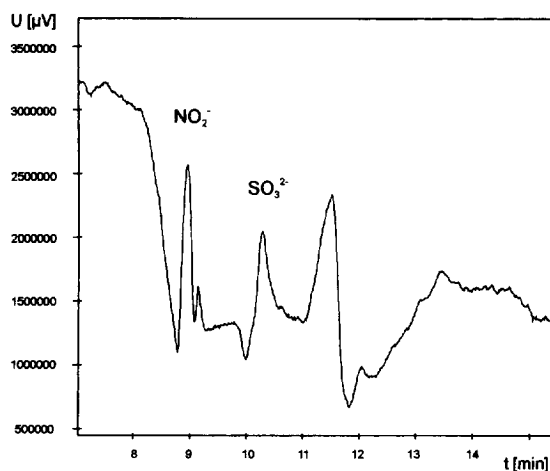


Fig. 7. Amperometric detection of sulfite and nitrite in a bulk rainsample. Sample: nitrite: $0.28 \mu\text{M}$, sulfite: $0.14 \mu\text{M}$; electrolyte: $5 \text{ mM Na}_2\text{HPO}_4$, $5 \text{ mM NaH}_2\text{PO}_4$, pH 6.7; capillary: $50 \mu\text{m}$ I.D., 80 cm total length; voltage: -10 kV (110 mbar); detection: $U=900 \text{ mV}$, $I_{\text{max}}=2 \text{ nA}$, Au electrode, $d=0.5 \text{ mm}$; injection: 5 min , 110 mbar , sample stacking.

charge. A copper electrode serving as discharge electrode is positioned at a distance of 10 cm above a precipitation electrode consisting of aluminium (Fig. 8). The corona electrode is given a sufficiently high voltage ($25\text{--}30 \text{ kV}$) to spray off negative charges, i.e. electrons. Owing to the strong field around the copper electrode further charges by ionizing the surrounding gas molecules are generated. The charges are transferred to droplets $\geq 2 \mu\text{m}$ by the action of the electric field. For droplets $< 2 \mu\text{m}$ the transfer of charge occurs by diffusion [22]. The charged droplets move to the precipitation electrode and are collected in a petri dish

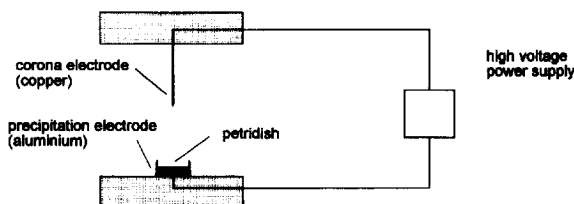


Fig. 8. Schematic of an electrostatic precipitator for the sampling of single fogdrops.

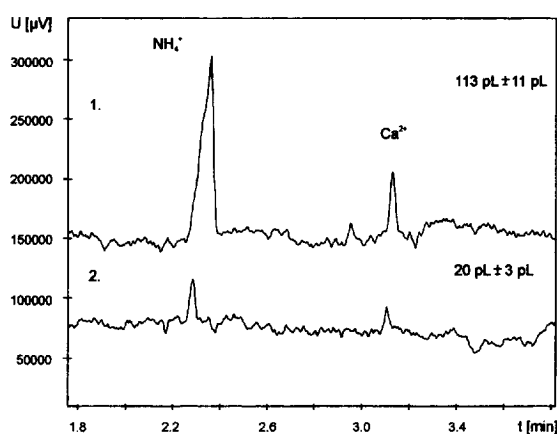


Fig. 9. Electropherograms of fogdrops. Electrolyte: 4 mM 4-N-methylaminophenol, 4 mM 18-crown-6, pH 6.5; capillary: $50 \mu\text{m}$ I.D., 64 cm total length, 50 cm to detector (capillary tip etched with HF); voltage: 25 kV ; detection: indirect UV detection (220 nm); sample: (1) $113 \pm 11 \text{ pl}$ (NH_4^+ : 21 mM , Ca^{2+} : 0.9 mM), (2) $20 \pm 3 \text{ pl}$ (NH_4^+ : 14 mM , Ca^{2+} : 1.3 mM).

The fogdrops are handled like single raindrops under by water extracted paraffin oil in a petri dish of polystyrol

In order to inject a single fogdrop into a capillary, the tip of the capillary has to be modified because the diameters of fogdrops are in the range of $1\text{--}50 \mu\text{m}$. The modification occurs by etching the capillary tip in $40\% \text{ HF}$. During the etching process a uniform N_2 flow is passed through the capillary to keep the inner diameter of the capillary constant. Injection and analysis of the fogdrops is similar to injection and analysis of single raindrops. Fig. 9 shows electropherograms of two fogdrops. The cations ammonia and calcium are detected.

4. Conclusion

We have demonstrated a new technique to handle and to analyse nanoliter and picoliter samples. The absolute limits of detection are in the fmol range. The applicability of the new developed method was exemplary shown for the analysis of single rain- and fogdrops. Results obtained by these measurements give explanations about atmospheric processes.

References

- [1] K. Bächmann, I. Haag, U. Sprenger, K.-H. Steeg, K. Steigerwald, B. Bastian and A. Röder, *Fresenius' J. Anal. Chem.*, 340 (1991) 548–552.
- [2] K. Bächmann, A. Röder and I. Haag, *Atmos. Environ.*, 26A (1992) 1795–1797.
- [3] K. Bächmann, I. Haag, T. Prokop, A. Röder and P. Wagner, *J. Aerosol. Sci.*, 24 (1993) S421–S422.
- [4] K. Bächmann, I. Haag and A. Röder, *Atmos. Environ.*, 27A (1993) 1951–1958.
- [5] K. Bächmann, I. Haag, T. Prokop, A. Röder and P. Wagner, *J. Chromatogr.*, 643 (1993) 181–188.
- [6] K. Bächmann, P. Ebert, I. Haag, T. Prokop, A. Röder and K. Steigerwald, *Proceedings of EUROTRAC Symposium '94*, 1994, p. 1101–1104.
- [7] K. Bächmann, P. Ebert, I. Haag, T. Prokop and K. Steigerwald, *Final report: tropospheric oxidation mechanisms*, Leipzig, September 1994, p. 403–408.
- [8] K. Bächmann, I. Haag and K. Steigerwald, *Atmos. Environ.*, 29A (1995) 175–177.
- [9] R.A. Wallingford and A.G. Ewing, *Anal. Chem.*, 59 (1987) 1762–1766.
- [10] R.A. Wallingford and A.G. Ewing, *Anal. Chem.*, 60 (1988) 1972–1975.
- [11] R.T. Kennedy, M.O. Oates, B.R. Cooper, B. Nickerson and J.W. Jorgenson, *Science*, 246 (1989) 57–63.
- [12] T.M. Olefirowicz and A.G. Ewing, *Anal. Chem.*, 62 (1990) 1872–1876.
- [13] T.M. Olefirowicz and A.G. Ewing, *Chimica*, 45 (1991) 106–108.
- [14] B.L. Hogan and E.S. Yeung, *Anal. Chem.*, 64 (1992) 2841–2845.
- [15] T.T. Lee and E.S. Yeung, *Anal. Chem.*, 64 (1992) 3045–3051.
- [16] S.D. Gilman and A.G. Ewing, *Anal. Chem.*, 67 (1995) 58–64.
- [17] H.T. Chang and E.S. Yeung, *Anal. Chem.*, 67 (1995) 1079–1083.
- [18] F.E. Regnier, D.H. Patterson and B.J. Harmon, *Trends Anal. Chem.*, 14 (1995) 177–181.
- [19] J.A. Janowski, S. Tracht and J.V. Sweedler, *Trends Anal. Chem.*, 14 (1995) 170–76.
- [20] A. Mainka and K. Bächmann, unpublished results.
- [21] M. Hartmann and K. Bächmann, unpublished results.
- [22] A. Bürkholz, *Droplet Separations*, VCH, Weinheim, 1989, p. 17–25.