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Chromatographic methods for the analysis of size-classified and individual raindrops

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ABSTRACT

The analysis of single and size-classified raindrops is expected to give new and interesting information about anthropogenic air pollution and its consequences. A principal strategy for chromatographic apparatus based on pressure-driven and electrokinetic systems is given. Three different methods are described that are of practical use for the analysis of single and size-classified raindrops. The main cations and anions (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, NO_3^-, $HCOO^-$ and CH_3COO^-) are measured in a single raindrop with a volume of more than 500 nl.

INTRODUCTION

The atmosphere is a chemical reaction system. Reactions take place as a result of anthropogenic pollution and natural emissions of substances. These reactions lead to consequences such as a decrease in the stratospheric ozone concentration, climatological changes {*e.g.*, anthropogenic pollution with NH_3 and SO_2 is followed by the formation of $(NH_4)_2SO_4$ and NH_4HSO_4 as cloud condensation nuclei and therefore by a change in cloud formation statistics [1]}, changes in radiation balances and negative influences on biological systems. The reactions, transport and deposition of pollutants are strongly influenced by heterogeneous processes at liquid and solid particles. Wet deposition and rain in particular are an important cleaning mechanism of the atmosphere.

Owing to the large number of physical and chemical parameters that influence these processes, a simulation in the laboratory and model calculations are hardly possible. Field measurements give data that show acceptable reliability.

Measurements concerning wet deposition are of-ten made in the bulk phase. Consequences such as clean-up of the atmosphere and influences on the ecosystem are estimated using average values of concentration.

Using a special collecting system, Georgii and Wötzel [2] and Turner [3] showed that raindrops of different size have different concentrations and these differences can often be greater than one order of magnitude. Esmen and Fergus [4] estimated pH values of single raindrops using pH paper without considering a correlation between pH and drop size.

It is impossible to give any interpretations using only average values. The aim of this work was to identify the main scavenging mechanism for each compound analysed. Typical relationships between concentration and drop radius are predicted by theoretical calculations and laboratory experiments (gas-scavenging [5] and aerosol scavenging [6,7]).

The size of raindrops has a strong influence on the scavenging coefficient [6]. Therefore, it is expected that a change in raindrop size distribution as a possible consequence of climatological changes and anthropogenic air pollution (e.g., a change in the number concentration of cloud condensation nuclei leads to a change in the cloud drop size distribution [1] and therefore to a change in raindrop size distribution), will lead to a difference in the overall scav-

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enging rate. Assuming a constant water deposition rate, a change in the composition of the atmosphere will be observed.

For calculations of these and other consequences, measurements of rain as a function of drop size and also of individual raindrops are necessary.

Analytical problem

Single raindrops have volumes ranging from 10^{-9} to 10^{-6} l. The concentrations of the main cations and anions are in the μmol/l range. As a consequence, low absolute amounts of ions have to be analysed. A further problem is the difficulty of collecting and handling single drops, owing to evaporation and contamination. Another serious task is the determination of the volumes without destroying the sample. Based on our own bulk measurements of rain, requirements for single raindrop analysis are given in Table I. The calculation is based on a drop volume of 0.5 μl. It was impossible to analyse drops of smaller volume until now. Raindrops having a volume of less than 0.5 μl (medium size raindrop) are only analysed as a size fraction.

Methods

Mainly chromatographic methods are used. Chromatographic micro systems such as micro-HPLC and capillary zone electrophoresis (CZE) usually show better absolute detection limits than larger systems such as HPLC. Hence HPLC systems are adapted to micro-HPLC and CZE. Absolute detection limits are improved by a factor of 100 or more (Table I).

Normally glass electrodes are used to measure the pH value. The volume needed for micro glass electrodes is at least 10 μl. For analysing small volumes we use a a flow-injection analysis (FIA) system with an injection volume of 0.5 μl.

Usually an increase in relative detection limit for microsystems is observed. The dilution necessary for handling the sample, however, is decreased. The observed net effect is a decrease in the relative detection limit using micro systems for this special task. Because of the sample volume required for each analysis (0.5 μl in FIA and 5 μl in micro-HPLC or alternatively 10 μl in CZE) a dilution is still necessary. As a consequence of the needed connection between capillary and electrode the required volume fraction in CZE is much larger compared to the injection volume of at least 20 nl. Additionally, the volume of the size fractions has to be distributed into three fractions (micro-HPLC/FIA or CZE/FIA). Single raindrops and size fractions are diluted with 5–10 μl of internal standard solutions. The standard consists of LiClO$_4$ of known concentration. The dilution factor of Li$^+$ measured together with the analysed cations is used for volume calculation. The precision of the methods employed is

TABLE I

LIMITS OF DETECTION (ng/ml) DEFINED AS 3 · R.S.D.

R.S.D. = relative standard deviation of baseline noise.

Ion	Micro-HPLC	CZE
NH$_4^+$	1.3	25
K$^+$	1.3	70
Na$^+$	0.7	35
Ca^{2+}	3.0	40
Mg^{2+}	1.3	25
Li$^+$	0.2	12
Cl$^-$	8.0	35
SO$_4^{2-}$	22.0	180
NO$_3^-$	8.0	60
CO$_3^{2-}$	–	210
HCO$_2^-$	13.0	180
CH$_3$CO$_2^-$	20.0	450

TABLE II

RELATIVE STANDARD DEVIATIONS OF THE ANALYTICAL METHODS EMPLOYED AND FOR VOLUME CALCULATION (LiClO$_4$)

Species	CZE	Micro-HPLC	FIA
Cl$^-$	7	10	–
SO$_4^{2-}$	8	10	–
NO$_3^-$	10	15	–
HCOO$^-$	8	10	–
CH$_3$COO$^-$	10	10	–
NH$_4^+$	5	10	–
K$^+$	10	10	–
Na$^+$	7	10	–
Li$^+$	8	8	–
CA^{2+}	8	12	–
Mg^{2+}	10	12	–
pH	–	–	13

given in Table II. All the main cations and anions and the pH value are determined in size fractions. For single raindrops volume division is impossible and therefore the pH value is neglected.

The precision of the actual measurement is verified using the ion neutrality balance. Additionally, the measured concentrations weighted with the volume fractions are compared with the bulk concentrations. Volume fractions are calculated using drop size distributions measured with a dystrometer. The dystrometer is a rain spectrometer calculating drop size by impulse measurement. Usually good agreement is achieved.

Collection of rain samples

Single raindrops and size-classified raindrops are collected using the Guttalgor [8–10], which consists of a Dewar vessel filled with liquid nitrogen. Raindrops are allowed to fall into the liquid nitrogen and freeze in less than 1 s. They remain at the surface on a gas blanket until they have reached the evaporation temperature of liquid nitrogen. They then sink because of the higher density. The whole system is surrounded by an inert gas box to avoid contamination and condensation of water vapour. Depending on the rain rate, the Guttalgor is opened for several short periods. The opening time has to be limited because of the possible coalescence of two or more drops at the surface of the liquid nitrogen. Raindrops keep their spherical shape, so it is possible to separate them by seven sieves of different mesh widths in the range 0.1–1.0 mm. The collection methods allow the analysis of the bulk phase as both size fractions and individual raindrops. Experimental investigations with simulated rainwater sprayed by a scrubber system and subsequently collected show that the error based on the collection procedure is lower than the analytical detection limit.

EXPERIMENTAL

Micro-HPLC instrumentation

The analysis of alkali and alkaline earth metals was carried out with cerium(III) as eluent [11] on two laboratory-packed cation-exchange columns of different capacities [ION-210 metals column, ICT (100 × 0.5 mm I.D.) and Fast Cation 1, Dionex (150 × 0.5 mm I.D.)]. With column switching,

Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} were separated in one run [12]. For detection of cations a Spectroflow 980 fluorescence detector (Applied Biosystems, Weiterstadt, Germany) with a 1-μl flow cell (excitation, 251 nm; emission, 320-nm cut-off filter) was used.

The chromatographic system consisted of a metal-free IRICA Σ 871 HPLC pump (ERC, Alteglofsheim, Germany) and a Knaur metal-free injection valve. Usually 1-μl was injected for analysis.

The anions chloride, formate, acetate, nitrate and sulphate were separated on an Optisil ODS (5 μm) column (125 × 4.6 mm I.D.) (ERC) coated with dodecylamine [13] using a mixture of potassium hexacyanoferrate(II) and -(III) solutions (both 10 μM) as eluent with indirect UV detection. A Rheodyne Model 9125 metal-free injector (ERC) was used with a 5-μl sample loop. Usually 2.5 μl of sample were injected (Fig. 1).

CZE instrumentation

For the experimental studies two CZE systems were employed. One system was the CES I (Dionex, Sunnyville, CA, USA) with a positive and negative power supply and deuterium and tungsten lamps for UV detection. Polyimide-coated fused-silica capillaries (CS Chromatographie Service, Langerwehe, Germany) of 75 μm I.D. and 360 μm O.D. were used. The capillary dimensions were 60 cm total length with a 55-cm distance from the point of injection to the detector cell.

The other CZE system was laboratory built. The central part of this CZE system was a newly developed injection port for sample volumes between 0.5 and 5.0 μl (Fig. 2). The injection port consisted of a copper pin with a platinized funnel-shaped surface. This metal pin can be used as an electrode and as a sample vial [14,15]. The high voltage from a ±30 kV high-voltage power supply (F.u.G. Electronik, Rosenheim, Germany) was applied between both ends of the electrolyte vials and the copper pin respectively. For detection, the CES I (Dionex) was provided with a detector similar to that used in our laboratory-built system.

All electropherograms were recorded using an APEX data station (Autochrom, Milford, MA, USA).

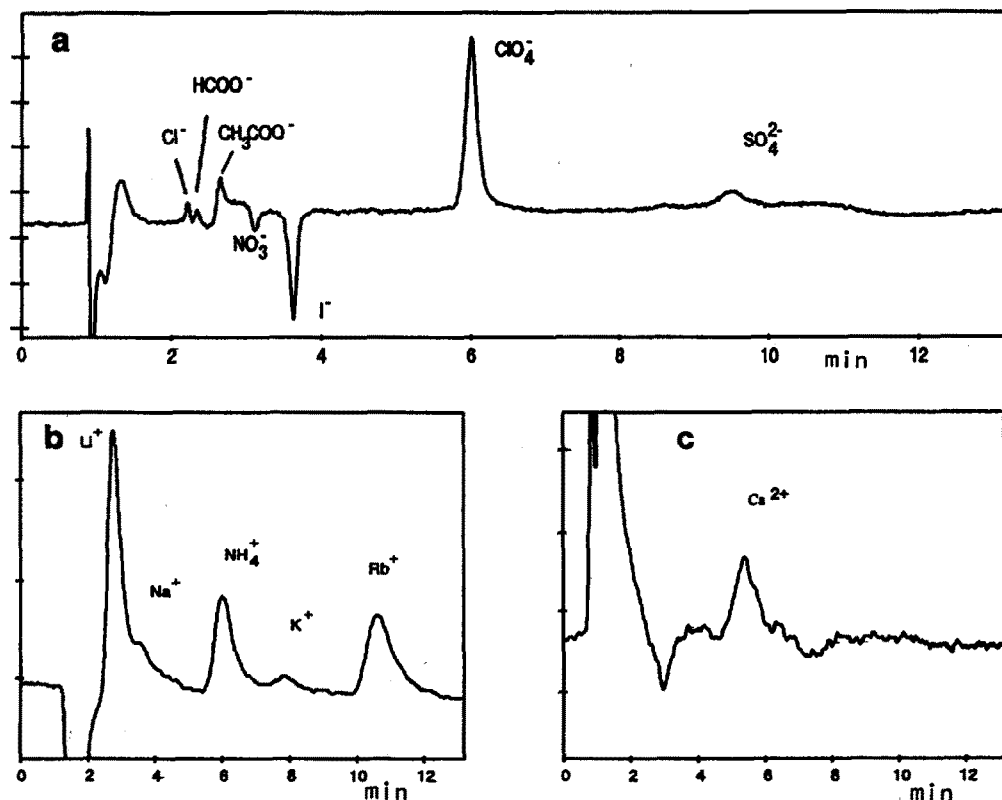All electrolytes were prepared fresh daily, filtered through a 0.22-μm filter (Millipore, Bedford, MA,

Fig. 1. Chromatograms of an individual raindrop. (a) Anions. Column, Optisil ODS (150 mm × 4.5 mm I.D.), permanently coated with dodecylamine; eluent, 2.5 μg/ml Fe(CN)$_6^{3-}$–Fe(CN)$_6^{4-}$; flow-rate, 1 ml/min; detection, indirect UV (205 nm). (b) Alkalin metal cations. Column, ION-210 metals column (120 mm × 0.75 mm I.D.); eluent, 3 μM cerium(III) nitrate; flow-rate, 43 μl/min; detection, fluorescence (254 nm). (c) Alkaline earth metal cations, column, Fast Cation 1 (150 mm × 0.50 mm I.D.); eluent, 14 μM cerium(III) nitrate; flow-rate, 36 μl/min; detection, fluorescence (254 nm).

USA) and degassed under vacuum for 5 min. For cations the electrolyte consisted of 4 mM 4-methyl-aminophenol sulphate (Fluka, Buchs, Switzerland) and 2.5 mM 18-crown-6 (Merck, Darmstadt, Germany) [16]. The electrolyte for anions consisted of 5 mM K$_2$CrO$_4$ (Merck) and 0.5 mM tetradecyltrimethylammonium bromide (Aldrich, Steinheim, Germany).

All standard mixtures were prepared by dilution of 10 mM stock solutions containing a single cation or anion. Water purified with a Milli-Q system (Millipore) was used throughout.

Before each electrophoresis the capillary was rinsed for 3 min with electrolyte solution by vacuum applied at the end of the capillary outlet. All injections during the measurement were performed in the hydrostatic mode where the capillary was immersed in the sample at a height 10 cm above the running electrolyte for 30 s. On lowering the sample to the 0 cm level the capillary was removed from the sample and the loaded capillary was immersed in the running electrolyte with a voltage of up to 30 kV.

FIA system instrumentation

Flow-injection analysis with UV detection was used for the determination of pH values [17]. A mixture of two pH indicators, Methyl Red and Methyl Orange (Merck), is used as a UV-absorbing reagent. Aqeuous solutions (40 mM) of the sodium salts of the pH-sensitive dyes were prepared and mixed in a ratio of 1:1. Therefore, pH values in the
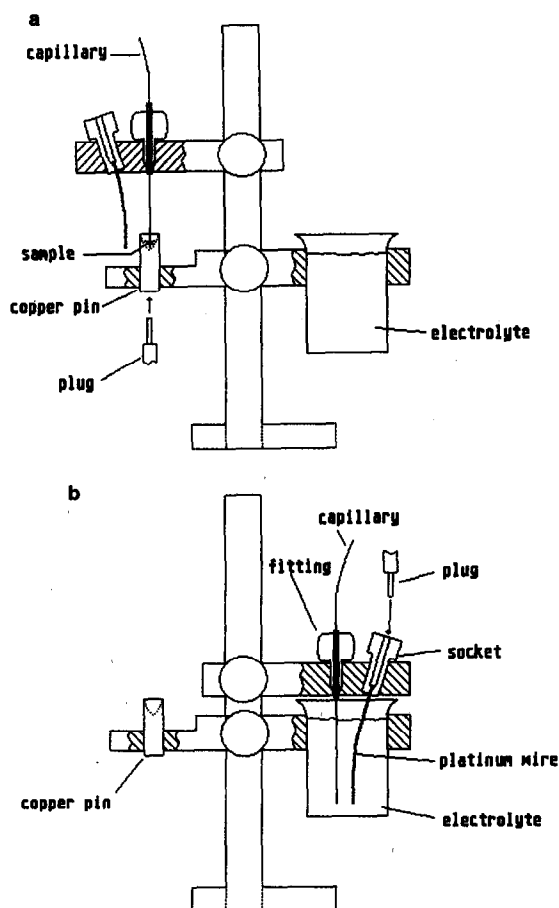
Fig. 2. CZE injection port for small volumes. (a) Injection of a sample; (b) electrophoresis.

range 3.0–7.0 appropriate to the acidity of rainwater could be measured by using this reagent [15]. The sample was injected directly into the reagent flow by a Rheodyne type 7520 valve and reacts in the connecting tube between injector and detector cell based on dispersion. The indicator solution was pumped at 0.15 ml/min with a Irica Σ 871 pump. A Spectroflow 757 UV detector (Applied Biosystems), measured the absorbance at 430 nm. The volume of the loop of the injection valve was 0.5 μl but a sample volume of 2 μl was required to guarantee a contamination-free injection. The system was calibrated with unbuffered standards prepared from 1 M hydrochloric acid (Merck) and 1 M sodium hydroxide solution (Merck) by dilution with water. These

standards showed a low ionic strength comparable to that of rainwater. For each analysis it was necessary to record a calibration graph for the complete pH range.

RESULTS AND DISCUSSION

Advantages and disadvantages of the applied methods are outlined below.

CZE

The main advantage of the CZE for rain analysis is the small injection volume, usually *ca.* 10 nl. Therefore, it is possible to analyse small samples several times without using the whole sample volume. The main disadvantage is the large volume needed for the analytical procedure. For an automatic injection at least 10 μl are needed, which means a three orders of magnitude higher volume than the injection volume. This disadvantage is caused by the fact that an electrical current is needed for CZE and therefore the capillary and the electrode have to be connected by the liquid, which requires at least 10 μl. A new experimental set-up was used to overcome this problem. The pin (Fig. 2), as an alternative for sample injection, needs a volume of only 0.5–1.0 μl but no automatic version can be envisaged in the near future. CZE shows higher detection limits than Micro-HPLC, so its use for single raindrop analyses is limited at present. However, owing to the possibility of automation and the large numbers of measurements needed for rain analysis, CZE is used when possible. A typical chromatogram is shown in Fig. 3.

Micro-HPLC

Micro-HPLC is a powerful analytical method. The detection limits are usually lower than those in CZE, owing to the possible employment of off-column detection techniques. However, no automatic sample injection is possible. To avoid contamination, metals have to be excluded in the experimental set-up.

No metal-free microlitre syringe is commercially available. Therefore, the sample is sucked from the rearside through a short PEEK cappillary. Additionally, partial filling of the sample loop is necessary for cases of limited sample volume. Raindrops are limited in volume by nature and dilution has to
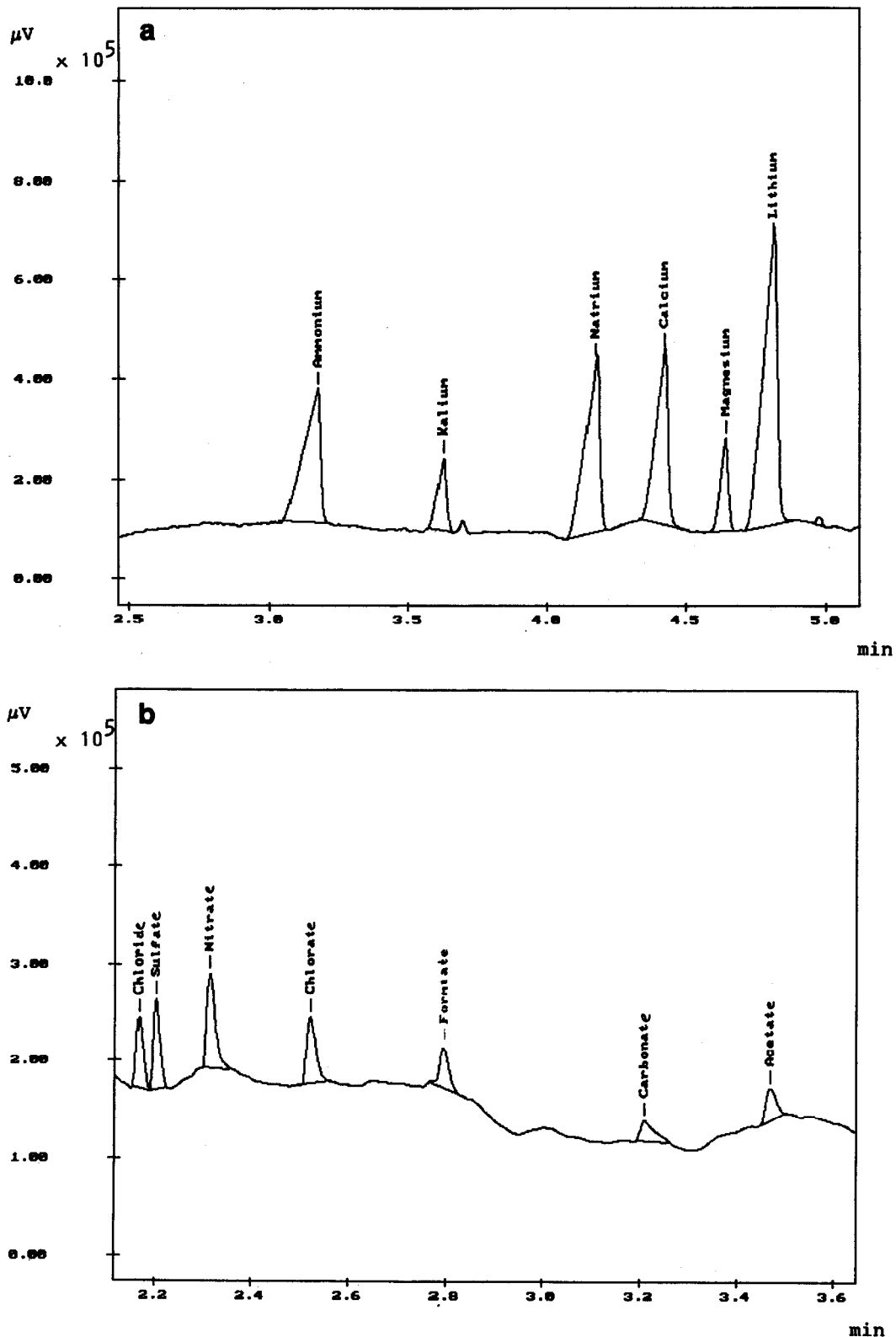
Fig. 3. Electropherogram of rain samples of (a) cations and (b) anions. (a) Electrolyte: 4 mM methylaminophenol sulfate and 4 mM 18-crown-6; 55 cm effective capillary length; injection: hydrostatic, 10 cm for 30 s; migration voltage: 22 kV; detection: indirect UV (220 nm). (b) Electrolyte: 5 mM potassium chromate and 0.2 mM tetradecyltrimethylammonium bromide; 55 cm effective capillary length; injection: hydrostatic, 10 cm for 30 s; migration voltage: 22 kV; detection: indirect UV (276 nm).

be minimized in order to avoid contamination and decreases in concentration. Often for size fractions only small volumes are collected as a consequence of the low volume of the smallest drops (< 10 nl). Therefore, the sieves with the smallest mesh width (0.2 and 0.3 mm) often showed volumes of 1 μl or less.

Micro-HPLC usually works with an analytical volume close to 1 μl. However the sample loop and all the dead volume in front of the loop are rinsed five times to obtain high reproducibility. This would lead to an unacceptable loss of sample which is not used for the analysis, so the sample plug has to be transported in the sample loop using an internal standard solution consisting of 35 μM rubidium iodide. The fraction of the volume introduced in the sample loop is calculated by measuring the decrease in internal standard concentration. The sample loop employed is compatible with the sample plug, so usually the whole sample volume is used for analysis. About 2.5 μl of the whole sample volume are injected.

For determination, not only standards of different concentrations but also with different volumes have to be measured. However, calibration is very time consuming. Therefore, micro-HPLC is used if the detection limits needed cannot be achieved by CZE.

FIA

Traditionally, a flow-injection system is distinguished by rapid sample analysis and high reproducibility. In addition, it is possible to handle small injection volumes using the applied system. The flow velocity is limited to 0.15 ml/min to achieve a maximum reaction rate by a minimum dilution factor. Therefore, about 5 min are required for each measurement. Only for size fractions with a volume larger than 2.5 μl can the pH value be determined because 2 μl of the undiluted sample are taken for the pH determination.

Analytical strategy

The following strategy is used for measurements on real rain samples. Single raindrops are always analysed by micro-HPLC, owing to the better detection limit for the available volume. It is impossible to divide such small volumes into two fractions, so it is not practicable to measure anions and

cations in addition to the pH value in a single raindrop. Therefore, the pH is neglected, but for size fractions H^+ concentration, as an important cation for ion balance, is always measured. For anions and cations two different procedures are used. The decision as to whether micro-HPLC or CZE should be used is accomplished by bulk analysis. With highly concentrated rain the automatic CZE system is used. When the relative detection limits are expected to be sufficient for the manual CZE system, this experimental set-up is used because of the faster standardization. For the lowest concentrations micro-HPLC is preferred. The latter system is often used for rain events showing volumes of 500 nl–3.0 μl leading to a high dilution factor. Small volumes are observed for short rain events such as thunder storms or rain events with a low precipitation intensity.

Significance of results for the atmospheric system

Typical relationships between concentration and radius as a function of time were found. These fundamental connections were observed for several rain events independent of the meteorological conditions. Interpretations based on physical and chemical models are given elsewhere [10]. Results for ammonia concentration in single raindrops are shown in Fig. 4.

At the beginning of a rain event a continuous increase in concentration with decreasing drop radius is observed. This function changes during the rain event and maximum concentration is found for raindrops of medium size. Single raindrops also vary in concentration. These differences are significantly higher than the error of measurement.

A change in raindrop size distribution towards smaller drops as a possible consequence of anthropogenic pollution will lead to an increase in the number of highly concentrated drops with a corresponding danger potential. The bulk concentration of rain as a whole increases especially at the beginning of the rain event. A high concentration, with a decrease in pH value for instance, results in increasing environmental consequences.

A positive effect is expected for the balance of radiation. The increasing scavenging coefficient of smaller drops has the consequence that an increasing number of aerosols are scanvenged and therefore light scattering at aerosol particles decreases.
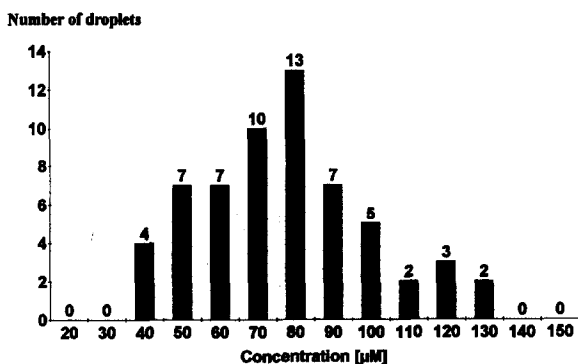
Number of droplets

Fig. 4. Distribution of ammonia concentration for individual raindrops. Concentration intervals of 10 μM; sieve fraction, 0.4 mm; drop radii, 0.4–0.5 mm.

This phenomenon will have a positive influence on the temperature increase discussed as a consequence of CO_2 emission. Chemical reactions are a function of drop size. For example, SO_2 oxidation shows two different reaction mechanisms depending on the pH: at pH < 5.0 H_2O_2 and at pH > 5.0 ozone are the main oxidants.

Therefore, a change in dropsize distribution may lead to a change in reaction mechanism. At present it is impossible to draw any conclusions about the consequences on the change in lifetimes of atmospheric pollutants resulting from alterations to the drop size distribution. In the future it will be necessary to use these results for model calculations. Further measurements are required at different locations to give a more detailed picture.

CONCLUSIONS

Single raindrop analysis and the analysis of size-classified rain can be achieved using micro-HPLC, FIA and CZE. The main cations and anions but neglecting the pH value can be determined in a single raindrop. The drop volume is available in addition. Analysing size fractions, a volume division is

possible so the pH value can be measured. The concentration variations in single drops and size fractions show a significant tendency.

In the future, enrichment systems for small volumes will be needed to obtain information about the less concentrated components in the microsystem described.

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