Short communication

Development of new methods for the analysis of single cloud-, fog- and raindrops by capillary electrophoresis

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Abstract

A new electrolyte system for the analysis of inorganic and organic anions by capillary electrophoresis (CE) in single raindrops (nl–µl) and single fog- or clouddrops (fl–pl) is developed. It is possible to separate the main anions occurring in rain, fogs and clouds (chloride, nitrate, sulphate, oxalate, malonate, formate, maleinate, adipinate, acetate, azelate, propionate, butyrate, valerate, pelargonate) in a single run. The analysis time is 5 min. Absolute limits of detection are in the range 30–70 fmol using indirect UV-detection. The applicability of the newly developed electrolyte system is demonstrated for the analysis of single fogdrops and raindrops.   © 1997 Elsevier Science B.V.

Keywords: Raindrops; Clouddrops; Fogdrops; Anions

1. Introduction

The analysis of single raindrops, fog- and clouddrops is of vital interest for the understanding of atmospheric processes, especially for the formation and development of clouds and rain as fundamental components of global biogeochemical cycles. Many investigations have been carried out to determine the chemical species in rain-, cloud- and fogwater. These analyses were always carried out assuming that single drops forming the bulk phase have the same concentrations of chemical species as the bulk sample. However the concentration of chemical species in rain, fog and clouds is influenced by many parameters, e.g. by the condensation nucleii inside the cloud, particle and gas scavenging, evaporation, collision, coalescence and break up of falling drops etc. Hence the chemical content of rain-, cloud- and

fogdrops cannot be independent of the size of the drops.

Investigations by Bächmann and coworkers (e.g. [1–4]) indicate a dependence of the chemical content of rain on the size of raindrops. These results are obtained by analysing size fractions of raindrops. The dependence of the chemical content of raindrops on the size of raindrops is called c/r-dependence.

More detailed information can be derived by the analysis of single raindrops. Tenberken et al. [5,6] analysed inorganic cations by CE in single raindrops. The obtained results show concentration distributions for single raindrops with a definite radius, i.e. even in one rain event drops of the same size have different concentrations. These distributions give information about parameters that influence raindrops during the falling process (e.g. break up).

Cloud- and fogwater is usually sampled by impactors (counterflow virtual impactors, aerosol impactors etc.) [7,8] and analysed by ion chromatography. A

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problem of this sampling procedure is the simultaneous impaction of aerosol particles. Hence Tenberken et al. [5] developed an electrostatic precipitator for sampling single cloud- and fogdrops and analysed inorganic cations in single fogdrops by CE.

Absolute amounts of inorganic and organic anions in single rain-, cloud- and fogdrops are in fmol range. Therefore it is necessary to develop analytical methods with absolute detection limits in this range. Analysis of inorganic and organic anions in one run is usually carried out by ion chromatography [9] due to low concentration limits of detection. However for the analysis of volumes in the fl–nl range ion chromatography is not suitable. In order to analyse volumes in the range of fl–nl, CE in particular is well suited because of low absolute LODs, low sample requirement, high resolution and fast separations. The applicability of CE for the analysis of small volumes was shown by analysing single cells (e.g. [10–13]) (fl–pl) and nl volumes handled in chip-based microvials [14,15]. Further numerous applications of CE have been reported for the determination of inorganic and organic ions (e.g. [16–18]).

This paper presents a new electrolyte system for the analysis of inorganic and organic anions in fl–nl samples (single rain-, cloud- and fogdrops) by CE with absolute LOD in the range of fmol.

2. Experimental

2.1. Instrumentation

All experiments were performed using a laboratory-built CE-equipment [9,10]. Detection was by indirect UV detection using an on-column detector (Dionex, Idstein, Germany). High voltage was obtained from a 30 kV high-voltage power supply (F. u G. Elektronik, Rosenheim, Germany). The injection of rain- and fogdrops was observed under a microscope and was performed by application of a vacuum with a syringe at the outlet vessel. The capillary was fixed at an angle of 30°. Separations were carried out using conventional fused-silica capillaries (64 cm total length×50 μm I.D.) from CS-Chromatographie Service (Langerwehe, Germany). All separations were performed at room temperature. All elec-

tropherograms were recorded by an A/D board from ERC (Altglofsheim, Germany) using APEX chromatography software (Autochrome, Milford, MA, USA). The signal output is in units of μV (19 V=1 AU).

2.2. Chemicals

All solutions were prepared using ultra-pure water purified with a Milli-Q system (Millipore, Eschborn, Germany). Stock solutions of organic and inorganic anions (10 mM) were made of analytical grade reagents from Merck (Darmstadt, Germany). The following chemicals of analytical reagent grade were obtained from Fluka (Buchs, Switzerland): salicylic acid, tris-(hydroxymethyl)aminomethane, poly-(N,N,N′,N′-tetramethyl -N-trimethylene-hexamethylene-diammonium)dibromide (polybrene, hexadimethrin bromide, HDB), paraffin oil.

3. Results and discussion

3.1. Separation conditions

In order to achieve optimal peak symmetries in CE separations the mobility of the electrolyte co-ion has to be comparable to the mobilities of the analyte ions. If inorganic anions with high electrophoretic mobility and organic anions with low electrophoretic mobility should be analysed in one run the electrolyte co-ion should have an average mobility. For the use of indirect UV detection [19] the electrolyte co-ion should have a high molar absorptivity. Salicylic acid was chosen as electrolyte because of its average mobility [20,21] and of its molar absorptivity of 1259 l mol^{-1} cm^{-1} ($\lambda=233$ nm) [22]. Salicylate as buffer additive is mentioned in several papers for the analysis of bicarbonate and iodate [17], chloride, nitrate, perchlorate, permanganate, chromate, iodate and phosphate [23] using laser-induced fluorescence detection, for indirect UV detection of amino acids [24], for the separation of alkylsulfonates and alkylsulfates [25,26] and for the analysis of cyclodextrins [27].

Analysis of inorganic and organic anions in one run by CE has already been performed by Mainka et
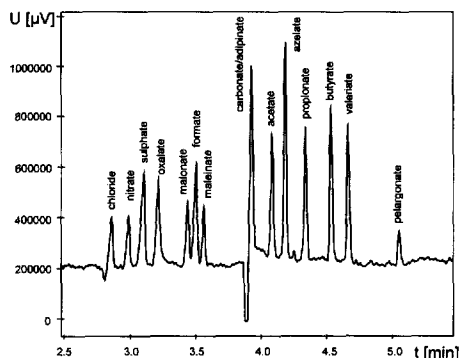
Fig. 1. Electropherogram of a standard of inorganic and organic anions. Electrolyte: 20 mM salicylic acid, 32 mM tris-(hydroxymethyl)aminomethane, 0.001% HDB (pH 8.1); capillary: 64 cm total length×50 μm I.D., 50 cm to detector; voltage: −25 kV; detection: indirect UV detection (220 nm); injection: 10 cm, 45 s; separation temperature: room temperature.

al. [20]. Absolute limits of detection of this system are in the fmol range. In order to analyse even the slow mobile analytes (e.g. pelargonate) the mobility of the electroosmotic flow (EOF) is decreased using dodecyltrimethylammoniumhydroxide (DoTAH). The use of decreased EOF allows a simultaneous enrichment of the analytes from larger sample volumes (200–300 nl) by sample stacking. However, this system is not applicable for the analysis of single

rain-, cloud- and fogdrops because it is performed in fused-silica capillaries with inner diameters of 75 μm, whereas for the injection of single cloud- and fogdrops (diameters of 5–50 μm) it is necessary to use capillaries with inner diameters of 50 μm or even smaller. Furthermore it is possible to use a reversed EOF for the analysis of single drops as the whole drop is injected into the capillary and it is not possible to enrich analytes by sample stacking. The use of reversed EOF would decrease analysis time because it is possible to separate the anions coelectroosmotically. As EOF modifier we use HDB. This modifier reverses the EOF at concentrations of about 0.001% [28,29].

Fig. 1 shows an electropherogram of a standard of inorganic and organic anions. The concentration of each anion is 50–100 μM. As can be seen from this electropherogram, peaks are well separated within 5 min.

The dependence of the mobilities μ_{eff} of the anions is shown in Fig. 2. The mobilities of all anions increase slightly with increasing pH value. Fig. 3 shows a diagram of the resolution between malonate and formate as well as between formate and maleinate. The resolution of malonate and formate increases with increasing pH whereas resolution between formate and maleinate decreases. This can be explained by different dissociation steps
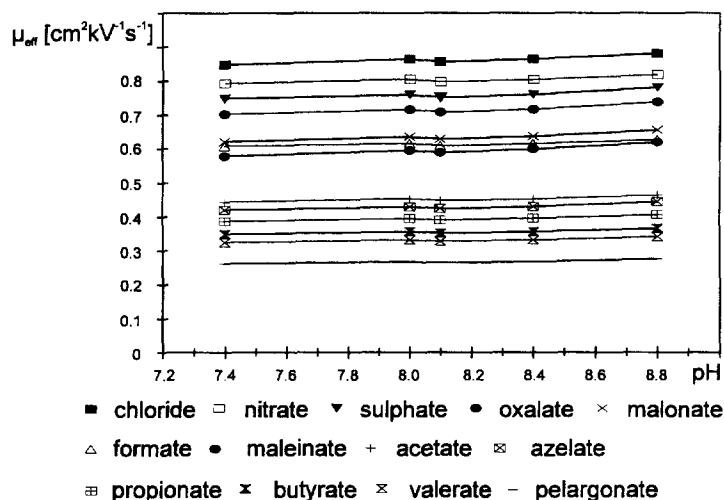

Fig. 2. Influence of pH on the electrophoretic mobilities of the main anions occurring in rain (conditions see Fig. 1).
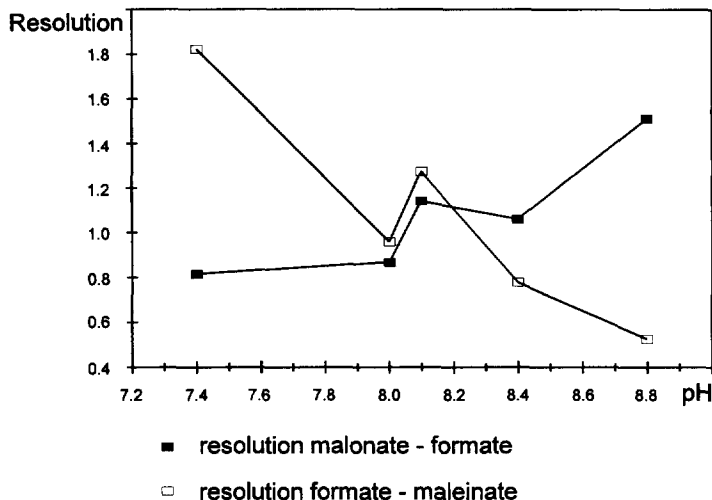
Fig. 3. Influence of pH on the resolution of malonate, formate and maleinate (conditions see Fig. 1).

of single-charged and double-charged anions. As can be seen from Fig. 2, the effective mobilities of the double-charged anions malonate and maleinate increase more than the effective mobility of the single-charged formate. At pH 7.4 the effective mobilities of malonate and formate are nearly the same. With increasing pH the mobility of malonate increases more than the mobility of formate, resulting in an improvement of resolution. As the effective mobility of maleinate also increases more than the mobility of formate resolution decreases with increasing pH value. Optimal separation conditions for the main anions occurring in rain are obtained at pH 8.1.

Absolute detection limits are in the fmol range (Table 1). Relative standard deviations of corrected peak areas ($n=10$) are 4–9%. The reproducibility of migrations times ($n=10$) is 0.61–0.87%.

3.2. Application to raindrops and fogdrops

Single raindrops are sampled using the Guttalgor and handled under paraffin oil as described by Bächmann et al. [5,6].

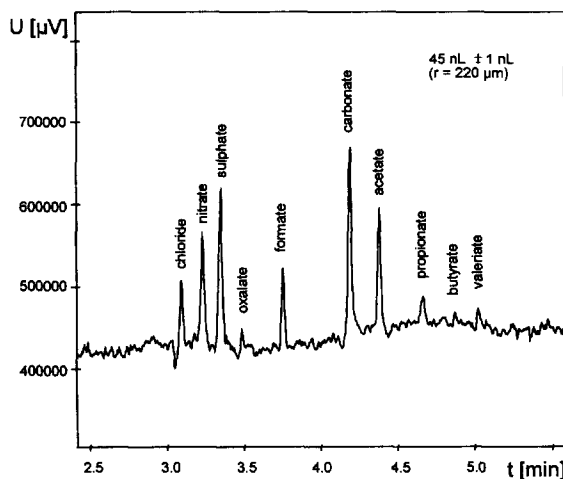Fig. 4 shows an electropherogram of a single

Fig. 4. Electropherogram of a single raindrop (conditions see Fig. 1). Cl^-: 5.8 μM, NO_3^-: 15 μM, SO_4^{2-}: 10 μM, $C_2O_4^{2-}$: 1.2 μM, $HCOO^-$: 4.1 μM, $C_2H_3O_2^-$: 8.7 μM, $C_3H_7O_2^-$: 1.5 μM ($r=$drop radius).

Table 1
Absolute LODs for anions (conditions see Fig. 1)

Anion	LOD (fmol)	Anion	LOD (fmol)	Anion	LOD (fmol)
Chloride	70	Formate	51	Propionate	45
Nitrate	69	Maleinate	50	Butyrate	46
Sulphate	43	Acetate	65	Valerate	50
Oxalate	42	Azelate	32	Pelargonate	72
Malonate	41				

Table 2
Equations of regression lines and correlation coefficients ($y=$ corrected peak area, $x=$moles)

Anion	Equations of regression lines	r^2
Chloride	$y=1.47 \cdot 10^{15}x+296,659$	0.958
Nitrate	$y=9.44 \cdot 10^{14}x+533.716$	0.989
Sulphate	$y=2.60 \cdot 10^{15}x+366.037$	0.998
Oxalate	$y=1.99 \cdot 10^{15}x+452,835$	0.995
Formate	$y=9.45 \cdot 10^{14}x+485.411$	0.985
Acetate	$y=1.80 \cdot 10^{15}x+186.112$	0.999
Propionate	$y=1.76 \cdot 10^{15}x+328.514$	0.969

Table 3
Equations of regression lines and correlation coefficients ($y=$ corrected peak area, $x=$moles)

Anion	Equations of regression lines	r^2
Nitrate	$y=1.16 \cdot 10^{15}x+69.443$	0.995
Sulphate	$y=2.58 \cdot 10^{15}x+73.467$	0.985

raindrop. The anions chloride, nitrate, sulphate, oxalate, formate, acetate, propionate, butyrate and valerate are separated. Equations of regression lines as well as correlation coefficients are given in Table 2.

The fogdrops are sampled by an electrostatic precipitator and also handled under paraffin oil [5]. In Fig. 5 an electropherogram of a single fogdrop is shown. Nitrate and sulphate are the only components. Correlation coefficients and equations of regression lines are presented in Table 3.

Interpretations of results obtained by the analysis of single rain-, cloud- and fogdrops will be discussed in further publications.
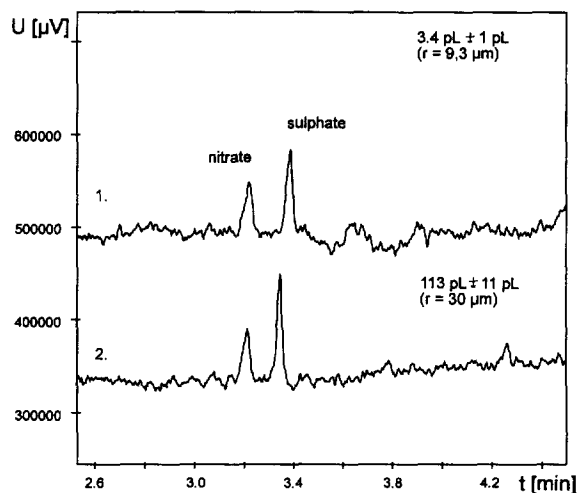
4. Conclusion

We have demonstrated a newly developed electrolyte system for the analysis of organic and inorganic anions in single rain-, cloud- and fogdrops. The absolute limits of detection are in the fmol range. The applicability of the electrolyte system to real rain- and fogdrops is shown. Combined with the analysis of inorganic cations in single rain-, cloud- and fogdrops [5,6] this system makes it possible to give more exact interpretations about processes that influence the formation and development of clouds and rain.

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Fig. 5. Electropherogram of a single fogdrop (conditions see Fig. 1). 1, NO_3^-: 110 mM, SO_4^{2-}: 54 mM; 2, NO_3^-: 4 mM, SO_4^{2-}: 3 mM.

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