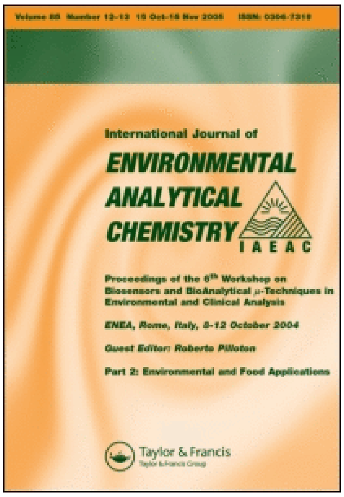

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Application of a Portable Ion Chromatograph for Field Site Measurements of the Ionic Composition of Fog Water and Atmospheric Aerosols

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For the analysis of selected organic and inorganic ions in atmospheric aerosol samples, Single Column Ion Chromatography was used. Atmospheric aerosol constituents were sampled with five-stage impactors, diffusion denuder trains and fog samplers. The concentrations of the components Cl^-, NO_2^-, NO_3^-, SO_4^{2-} and hydroxymethylsulfonate (HMSA) were determined by anion chromatography. Fluoride, formate, acetate, glycolate/lactate, propionate and butyrate were analyzed with ion exclusion chromatography, whereas monovalent cations Na^+, NH_4^+ and K^+ with cation chromatography. Resolution of HMSA-formate and HMSA-chloride pairs which were the most problematic cases were studied. Cross interferences and detection limits of all the ions of interest were determined. The methods were applied in a field sampling campaign in the Po Valley.

KEY WORDS: Single Column Ion Chromatography (SCIC), Ion Exclusion Chromatography (IEC), hydroxymethylsulfonate (HMSA), fog water, acidity of atmospheric aerosols.

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1. INTRODUCTION

Field campaigns to study acidifying atmospheric reactions usually involve sampling procedures for reactive compounds. In general, acidifying atmospheric compounds can be sampled in such a way, that ionic constituents of the samples can be analyzed by ion chromatographic methods.[1–3] For reactive compounds such as sulfite, nitrite and organic acids, problems concerning the stability of the samples are expected.[4–8] One possibility to stabilize the sample is to use preservatives (chloroform for organic acids)[7] or complexing agents (formaldehyde for sulfite).[6] Another possibility is to analyze the sample immediately after collection.

In this paper, we report about a portable "single column ion chromatograph' (SCIC), which was used at a field sampling campaign in the Po Valley. Ionic components were analyzed in samples obtained from different sampling procedures for acidic components in the atmosphere. Although detection limits may be slightly poorer in SCIC, as compared to suppressed ion chromatography, the methods used were adequate for the analytical problem.

The portability of the system and simplicity of operation enfavored the use of the SCIC for the field study. The ion chromatograph was used to analyze monovalent cations, inorganic and organic anions.

The major reasons to perform analysis at the field site were to have access to "fresh" samples and to obtain results during the field site activities which enhanced the motivation for the sampling programs.

2. EXPERIMENTAL

2.1. Apparatus

The ion chromatographic system used in the experiments consisted of a "Wescan" ion chromatographic module "ICM", an HPLC pump and a strip chart recorder. The "ICM" was equipped with an electrical conductivity detector (cell volume 0.5 μl), a "Rheodyne" Mod. 7125 sample injector (sample loop 100 μl) and an "active temperature controller" ("ATC") which was set for 30°C. The "ATC" controls the column compartment and the detector. Eluent flow was provided by an HPLC low pulsation pump (Kontron Mod. 414). The chromatograms were obtained by a strip chart recorder (Goerz Servogor Mod. RE 541). Remarkable advantages of the "ICM" were the favorable dimensions of 460 × 300 × 280 mm and the weight of 10 kg. The weight of the whole ion chromatographic system including the pump and the recorder was 20 kg.

2.2. Methods

2.2.1. Inorganic anions determination "Inorganic anions" were separated on a Wescan anion/R (resin type) column, dimension 250 × 4.6 mm. The objective of an optimization study was to determine the concentrations of Cl^-, Br^-, NO_2^-, NO_3^-, SO_3^{2-} and SO_4^{2-}, while no interference should be caused by fluoride, formate, acetate and other troublesome events such as injection, concentration or system peaks. The separation problem was to obtain a separation for certain early eluting components, while achieving a reasonable retention time for the stronger retained sulfate ion. The separation behavior of the mentioned ions was studied using various concentrations of the potassiumhydrogenphthalate (KHP) eluent (1 – 4 mM) and various pH values of the eluent (pH 4–8). Optimal conditions for the experiments were found with an eluent concentration of 4 mM KHP having a pH value of 4.9. The pH was adjusted by adding 0.1 M KOH. The eluent contained also 2.5% methanol as preservative. Eluent flow was 1.0 ml/min.

Adjusted retention times, relative to the retention time of chloride, are given in Table I. The ions are separated in approximately 10 minutes. Fluoride, formate, acetate and hydroxymethysulfonate (HMSA) are eluting with negative peaks. Oxalate is eluting shortly after sulfate. Quantitation of the peaks was carried out by peak height measurements. Relative sensitivities for the set of analyzed ions are given as the ratio of the peak height of 1 mg/l of the respective compound, compared to the peak height obtained for 1 mg/l chloride. For the described conditions and a 100 μl injection volume, reproducibilities for the determination of the standard ions at the concentrations C_s are given in Table I. Detection limits were calculated for the given conditions from results of repeated injections of 6 blank samples by taking 3 s of the signal at the position of the respective peak obtained by peak height evaluation.

Table I Detection limits, reproducibilities, adjusted relative retention times and relative sensitivities using anion chromatography with eluent KHP 4 mM, pH 4.9

Ion	D.L. (ppm)	C_s (ppm)	s (ppm)	T'/T'_{Cl}	R.H.S.
Fluoride	0.08	2	0.06	0.72	0.35
Formate	0.18	5	0.17	0.85	0.15
HMSA	0.10	5	0.12	0.90	0.19
Chloride	0.03	2	0.03	1.00	1.00
Acetate	0.20	5	0.17	1.17	0.10
Nitrite	0.04	2	0.05	1.23	0.49
Bromide	0.06	2	0.05	1.57	0.36
Nitrate	0.07	2	0.04	1.83	0.27
Sulfate	0.05	2	0.05	3.48	0.45
Oxalate	0.25	5	0.30	3.70	0.08

T_0 1.9 min, T_{Cl} 4.0 min, $\text{R.H.S.} = \frac{\text{mm(1 ppm X)}}{\text{mm(1 ppm Cl)}}$.

s = Standard deviation for 6 injections of standard samples,
C_s = Concentration of standard ion.

Experiments on the elution of diluted (0.5–2 mg/l) sulfite solutions, prepared from p.a. grade Na_2SO_3 in freshly degassed distilled water, gave the result, that sulfite in these concentrations is oxidized to sulfate during the analysis. However when a slight excess of formaldehyde is added to the sample, sulfite is eluting as the hydroxymethylsulfonate ion early in the chromatogram. For the components chloride, nitrite, nitrate, bromide and sulfate, the respective peaks were obtained with baseline- or near baseline-resolution. The peaks of formate and HMSA were separated with a resolution of 50%, when injecting equal concentrations (5 mg/l). In actual samples, formate concentrations were always in the same range or lower as compared to the HMSA concentrations. For such cases, peak height evaluation of HMSA was not significantly (<10% relative) interfered by the formate peak. A similar problem arose for the separation of HMSA and chloride. In fog water samples, the ratio of chloride to HMSA was typically between 1.5 and 5. For these conditions, the peak height of the chloride peak was not affected by the HMSA peak. However, a slight decrease of the HMSA response was observed. For the chloride/HMSA ratios

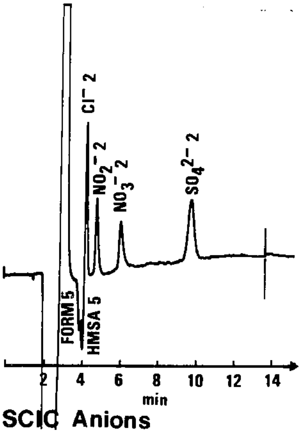

Figure 1 SCIC inorganic anions determination—standard chromatogram (5 mg/l Formate, HMSA, 2 mg/l Chloride, Nitrite, Nitrate and Sulphate). Chromatographic conditions: Wescan Anion/R column, 4 mM KHP, pH 4.9, 1 ml/min.

mentioned, the decrease of the HMSA peak was in the range of 7–10% relative and was considered for correction in the evaluation procedure.

A chromatogram of a standard mixture of constituents typically found in fog samples is given in Figure 1. In Table I also the adjusted relative retention times for fluoride, formate, acetate, bromide and oxalic acid are reported. These components do not interfere in the analysis of the other ions of interest. The typical concentrations in the actual samples are however generally below the detection limits. Therefore, concentrations of fluoride and monovalent organic acids were determined by ion exclusion chromatography.

2.2.2. Organic anions determination Ion Exclusion Chromatography was performed on a Wescan ion exclusion column (300 × 8 mm) using 0.000125 M sulphuric acid as eluent with a flow rate of 0.6 ml/min. Included in the standard chromatogram were 5 carbonic acids and hydrofluoric acid. These acids showed linear response for peak height evaluation in the working range tested of 0.1–10 mg/l.

Adjusted retention times, relative to formate, are given in Table II.

Table II Detection limits, reproducibilities, adjusted relative retention times and relative sensitivities using ion exclusion chromatography with eluent 0.000125 M H_2SO_4

Ion	D.L. (ppm)	C_s (ppm)	s (ppm)	T'/T'_{Cl}	R.H.S.
Fluoride	0.002	0.1	0.003	0.40	4.10
Glycolate	0.006	0.5	0.025	0.88	0.59
Lactate	0.006	0.5	0.025	0.89	0.52
Formate	0.004	0.5	0.013	1.00	1.00
Acetate	0.07	5	0.15	1.68	0.064
Propionate	0.08	10	0.17	2.35	0.052
Butyrate	0.10	10	0.20	3.19	0.037

T_0 8.2 min, T_{Formiat} 15.6 min, $\text{R.H.S.} = \dfrac{\text{mm(1 ppm X)}}{\text{mm(1 ppm Formiat)}}$.

C_s,s, see Table I.

Also listed in Table II are relative sensitivities, reproducibilities and practical detection limits which were determined by the procedures mentioned under 2.2.1. Very good sensitivities were obtained for fluoride, formate and glycolate/lactate, whereas for acetate, propionate and butyrate, sensitivities were 15–25 times less as compared to formate, High amounts of carbonic acids (>50 mg/l) may also cause a peak which is occurring in the chromatogram between the peaks of acetate and propionate. Lactate and glycolate peaks are not resolved by IEC, a problem also encountered by other authors.[6,7] According to Guiang *et al.*,[6] the major fraction in the glycolate/lactate peak was found to be lactate in Minnesota rain. The relative sensitivities in IEC are similar for both ions (0.59 and 0.52 respectively). Because of the uncertainties of the identification of the respective compounds, the glycolate/lactate peak is reported as an unresolved pair and quantitative results have been estimated by using the mean value of the relative sensitivities for the quantification.

A standard chromatogram containing five organic acids and hydrofluoric acid is shown in Figure 2. Resolution of glycolate/lactate and formate is 80–90%. The other peaks are baseline separated. The stability of the response factors for all ions was very good also for time periods of several days.

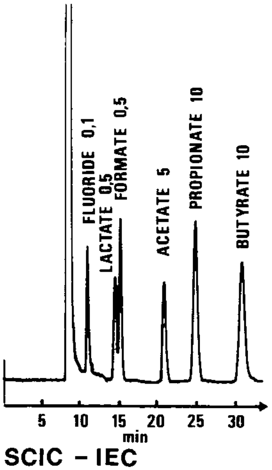

Figure 2 SCIC Ion Exclusion—standard chromatogram (0.1 mg/l Fluoride, 0.5 mg/l Lactate, Formate, 5 mg/l Acetate, 10 mg/l Propionate, Butyrate). Chromatographic conditions: Wescan Ion Exclusion Column, $1.25.10^{-4}$ M H_2SO_4, 0.6 ml/min.

Interference studies were performed with citrate, pyruvate, malate, sulfite, HMSA, nitrite and phosphate. The retention times for these substances, as compared to the respective compounds of interest (Table II), showed such significant differences, that no interferences are expected from these ions.

2.2.3. Cations determination Monovalent cations (Na^+, K^+, NH_4^+) were separated on a Wescan cation column (250 × 2 mm) using 0.002 M HNO_3 as eluent with a flow rate of 0.5 ml/min. The practical detection limits were determined with the same procedure as described in the inorganic anions determination section. The detection limits were for Na^+ 0.02 mg/l, for NH_4^+ 0.02 mg/l and for K^+ 0.04 mg/l.

Polyvalent ions are not eluted by the eluent used for monovalent ions. The enrichment of these strongly retained ions on the separation column leads to a steady change of the retention behaviour and of the peaks height response factors of the analyzed ions. For this reason, a standard sample is injected always after a set of five samples for analysis. The bias originating from the change of the response factors is depending on the amount of strongly retained ions (in the case of aerosol and fog water mainly of calcium and magnesium). By intrapolating the response factors for each set of five samples, the change of the response factor from one sample to the following is in the range of 0.05–0.2% relative. Thus, the relative error introduced by the change of the response factors is <0.2%. After a set of 100–200 samples, the separation column was regenerated by flushing with 20 ml of 0.05 N HNO_3 with a flow of 1 ml/min. Analysis time for one sample was 12 min.

2.3. Sampling and sample preparation

Atmospheric samples (fog water, denuder and impactor aerosol samples) were collected at a field site at San Pietro Capofiume (south-eastern part of the Po Valley, between the cities of Bologna and Ferrara, Italy). The station was equipped in addition to the routine micrometeorological instrumentation, with a network of instruments for fog microphysics investigations (for a more detailed description see ref. 5).

Sampling was performed during a study programme on fog measurements, organized by the "Institute for studies of physical and chemical phenomena of the lower and higher atmosphere" (FISBAT) of the National Research Council (CNR) in cooperation with participants from USA, Germany and Austria.

Fog water was sampled during fog events from two collectors, operated by a group from the "center for environmental protection", University of Frankfurt and a "FISBAT" fog collector.

Constituents of the atmospheric aerosols were sampled with five stages low pressure impactors (LPI 80/0.04) as well as with a multistage "high efficiency" denuder train designed at the TU Vienna. For the impactors, aluminium foils were used as substrates for the deposition of the aerosol particles. The performance of the impactors is described elsewhere.[9] A description of the denuder sampling unit is in preparation.[10] The denuder tubes were constructed from 10 × 12 mm pyrex glass tubes with an inner core part made from a 4 mm glass rod. The "annular" designed tubes were coated with selective reagents for the collections of gaseous constituents. The coating solutions in the various tubes were of NaF (for strong acidic compounds), NaOH (for organic acids and SO_2) and H_3PO_4

(for NH_3). Sampling rates were $80\,\mathrm{l\,min}^{-1}$ for the impactors and $10\,\mathrm{l\,min}^{-1}$ for the denuder trains. Sampling intervals were 4 h for impactors and denuder trains, 0.5–1 h for fog samples.

Fog water samples were analyzed immediately after collection for inorganic anions, followed by the organic acids and cations determination after changing the system and operating it with the corresponding columns without any sample preparation. The impactor samples were analyzed after extracting aliquots of the Al-foils with 3 ml distilled water in an ultrasonic bath for 5 min.

All chemicals used were analytical reagent grade. All the standard solutions, used to obtain standard chromatograms, including the eluents, were prepared by direct weighing of their salts and dilution with distilled water.

3. RESULTS AND DISCUSSION

During the field sampling campaign, approximately 400 samples from the various collection methods have been analyzed by SCIC. The ranges of the observed concentrations in fog water samples, denuder and impactor sample extracts are presented in Table III.

Table III Concentration ranges of ions in fog water and aerosol extracts. Number of samples: fog 25, denuder tubes 140, impactors 68, data in mg/l, N.A. not analysed, D.L. detection limit

Ion	D.L.	Fog	Denuder	Impactor (5-stage)
Chloride	0.09	0.8 –20	0.1–1.5	D.L.–7.5
Nitrite	0.15	D.L.–1.0	D.L.–0.2	D.L.
Nitrate	0.13	4.0 –60	0.3–4.0	0.6–74
Sulphate	0.15	5.0–45	0.2–18	0.2–77
HMSA	0.35	D.L.–15	N.A.	D.L.
Fluoride	0.01	0.05–1.2	N.A.	N.A.
Formate	0.04	0.4 –3.2	0.2–4.5	N.A.
Acetate	0.44	0.6 –5.5	D.L.–3.5	N.A.
Glycolate/ Lactate	0.07	0.2 –2.0	D.L.–2.0	N.A.
Sodium	0.02	0.05–2.7	0.2– 0.9	0.05–2.1
Potassium	0.04	D.L.–0.9	0.1– 0.5	D.L.–1.3
Ammonium	0.02	1.9 –18	0.2– 3.1	0.07–15

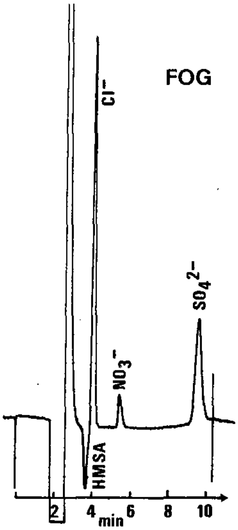

Figure 3 SCIC inorganic anions determination—fog sample from Po Valley (24.11.1985) Ion concentrations in mg/l: HMSA 11, Cl 14, NO_3 3.1 SO_4 10.

Inorganic anions Typical chromatograms of fog water samples show peaks of HMSA, Cl^{-1}, NO_2^-, NO_3^- and SO_4^{2-} (Figure 3), whereas aerosol extracts from impactor samples usually gave no NO_2^- and HMSA peaks.

Whereas detection limits of SCIC are less for the anion detection as compared to suppressed IC, the SCIC gave satisfactory results for the analysis of the mentioned samples. It should be stressed also, that an increase of the detection power is possible by using sample enrichment techniques or larger sampling loops.

Organic anions Also for the organic anions analysis, fog water samples gave the most complex chromatograms (Figure 4). Generally, up to seven peaks were observed including fluoride, formate, acetate, the unresolved glycolate/lactate peak and three further peaks which were not identified. Surprisingly, for some fog water samples, the glycolate/lactate concentration was higher as compared to formate and acetate concentrations.

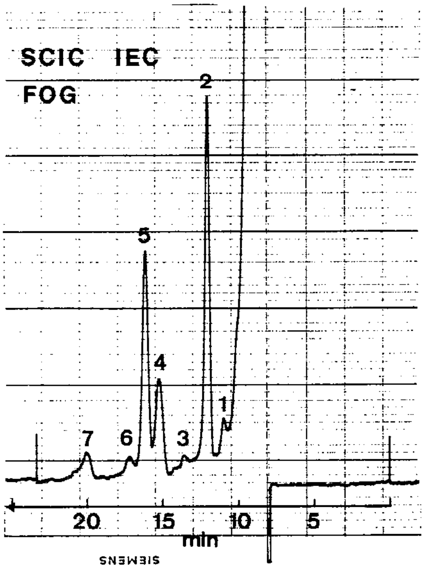

Figure 4 SCIC Ion Exclusion—fog sample from Po Valley (24.11.1985) Ion concentrations in mg/l: Peak 2 Fluoride 0.7, Peak 4 Glycolate/Lactate 0.37, Peak 5 Formate 1.6, Peak 7 Acetate 2.1. Peaks 1, 3, and 6 unknown.

Very favourable D.L. for fluoride, formate and the glycolate lactate pair allowed the quantitation of these compounds in all fog samples. Despite of the poorer D.L. for acetate, also quantitative determinations were possible in all samples observed during the fog sampling. In aerosol extracts from impactor samples, organic acids were generally under the D.L., except formate. The atmospheric concentrations for "particulate" formate was found to be around 1% or less of the gas phase concentration.

Volatile organic acids were sampled from the atmosphere with NaOH coated denuder tubes. IEC chromatograms from the denuder tube extracts showed also seven peaks as observed for fog samples. In a similar way as for fog samples, some denuder extracts gave very intensive peaks of glycolate/lactate.

Monovalent cations Monovalent cations were determined with the common standard procedure for SCIC. Large sets of samples could be analyzed without problems. The excellent D.L. could be achieved throughout the experiments.

4. CONCLUSIONS

SCIC proved to be a useful tool for the analysis of the main compounds responsible for the acidity of the atmospheric aerosols. Because of light weight instrumentation and ease of operation, the SCIC system described is especially useful for performing analysis at field sites or in mobile laboratories.

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