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NEW DEVELOPMENTS IN ION CHROMATOGRAPHIC METHODS FOR ATMOSPHERIC ANALYSIS

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SUMMARY

Examples are given of the determination of inorganic anions, cations and organic acids in atmospheric samples. With amperometric detection, 2.7 ppb of bromide can be determined in the presence of 8 ppm of nitrate. With a column-switching technique, Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} can be determined within 8 min in a 50- μl sample using indirect fluorescence detection and a cerium(III) solution as eluent. A method of indirect amperometric detection after post-column derivatization with EDTA was developed for the determination of divalent transition metals, giving detection limits in the upper picogram range. With an enrichment technique involving solid-phase extraction, 0.28 ppb of monochloroacetate can be determined in rain-water samples.

INTRODUCTION

The complexity of methods used in atmospheric analysis is due to the heterogeneous composition of air. This requires careful sampling procedures in order to avoid any disturbance of the equilibrium when sampling and problems due to contamination. If a high resolution with respect to time is necessary and, for example, cloud drops are to be analysed, then even the analysis of matrix species is difficult because only a few microlitres are available for a single ion whereas several inorganic cations, anions and organic compounds may need to be analysed.

As is demonstrated in Fig. 1, the three different possible phases in the atmosphere can be easily reduced to one type of analysis in the aqueous phase. The problems with the different phases concern on the one hand the sampling procedure and on the other the requirements for enrichment.

In Table I, the inorganic anions, cations and organic acids that play an important role in atmospheric analysis and that can be analysed by using ion chromatography are listed. The reason for using ion chromatography is different for the three groups of species. For inorganic anions, the simultaneous determination of all important anions is much more advantageous than different spectrophotometric methods for each individual anion. In addition, there are fewer interferences and the detection limits are lower using ion chromatography. With inorganic cations, spectroscopic

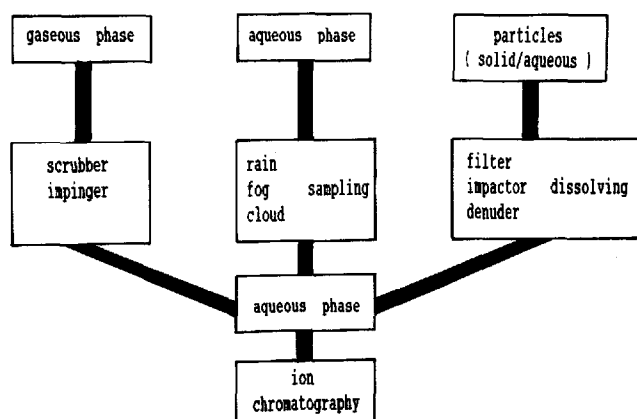


Fig. 1. Analytical pretreatment for atmospheric samples prior to ion chromatography. Problems: sampling, enrichment, contamination, storage (oxidation, bacterial degradation).

methods have lower detection limits, but the simultaneous determination of a number of elements in a small volume (*e.g.*, 10 μl) is only possible using a chromatographic method. In addition, the determination of NH_4^+ , which is important in air analysis, can be performed simultaneously with that of the alkali metal ions. The determination of organic acids is possible by derivatization and gas chromatography¹ or by

TABLE I

MEAN CONCENTRATIONS OF INORGANIC ANIONS, INORGANIC CATIONS AND ORGANIC ACIDS IN THE ATMOSPHERE

Type	Species	Aerosol (nmol/m^3)	Rain ($\mu\text{mol}/\text{l}$)	Fog ($\mu\text{mol}/\text{l}$)	Cloud ($\mu\text{mol}/\text{l}$)
Inorganic anions	Chloride	4.9	34	426	40
	Nitrate	15.4	145	700	170
	Sulphate	38.9	90	385	77
	Fluoride			130	
	Bromide	0.1	0.1		
	Nitrite		1.8	16	
	Sulphite		0.5	83	
Inorganic cations	Sodium	5.1	31	130	24
	Ammonium	82.3	150	1970	185
	Potassium	2.1	30	200	39
	Magnesium	1.5	9	30	13
	Calcium	3.7	23	160	40
	Manganese		0.2	0.7	
	Iron		0.9	7.2	
Organic acids	Formate	1400 ^a ; 1.10	18.5	56	6.0
	Acetate	1800 ^a ; 0.90	13.0	58	8.3
	Methanesulphonate	0.25	0.12		0.8
	Pyruvate	60 ^a ; 0.16	0.35	3.6	0.7
	Monochloroacetate	0.30	0.02		
	Dichloroacetate	0.03	0.01		

^a Gas phase (molar mixing ratios, ppt $\times 10^{12}$).

derivatization and reversed-phase chromatography². The drawbacks of these methods are that atmospheric samples are usually in the aqueous phase and that derivatization is easier in the organic phase. The determination of organic acids using ion-exchange or ion-exclusion chromatography can be carried out directly with acceptable detection limits.

EXPERIMENTAL

Sampling techniques

Sampling of rain water was carried out with a funnel made of stainless steel (area 1 m²) combined with a fraction collector (Sepafrac MFC-111 with a Sepacon TCU-211 time control unit; Labomatic, Sinsheim, F.R.G.).

Fog samples were taken with a fan collector. Fog droplets impact on PTFE strings (diameter 0.3 mm). The air flow-rate caused by the fan was 1080 m³/h. Cloud water samples were taken with a collector developed by Mohnen³. The collecting unit consists of ten slit PTFE rods (length 230 mm, slit width 1.5 mm, slit depth 2.5 mm, diameter 11 mm).

The material used for the sample bottles was polypropylene because of the low blank values for all the species analysed. All samples were filtered with Millex-GV filters (pore size 0.22 μm) before analysis.

Apparatus

Inorganic anions. The ions determined were Cl⁻, NO₃⁻, SO₄²⁻, SO₃²⁻, NO₂⁻, (COO)₂⁻ and Br⁻. An IC-2000i system (Dionex, Idstein, F.R.G.), including an HPIC-AG4 precolumn and an HPIC-AS4 analytical column, was used. The eluent was 1.2 mM Na₂CO₃-1.5 mM NaHCO₃ at a flow rate of 2 ml/min. For conductivity detection a micromembrane suppressor (AMMS-1, 12.5 mM sulphuric acid, 2.5 ml/min) was used. Amperometric detection of bromide was performed with a potentiostat (Dionex) with a silver working electrode and an Ag/AgCl reference electrode at +200 mV.

Inorganic cations. Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺ were determined with indirect fluorescence detection. The HPLC system included a Varian (Darmstadt, F.R.G.) Model 2510 pump, Rheodyne Model 7125 injection valve with a 50-μl sample loop and a Spectroflow 980 fluorescence detector (Applied Biosystems, Weiterstadt, F.R.G.). The excitation wavelength was set at 254 nm and an emission filter with a cut-off at 345 nm was used. The system included a GC 210 ion guard (ICT, Frankfurt/M, F.R.G.), an ION 210 separation column (ICT) for Na⁺, NH₄⁺ and K⁺ and an HPIC-CSI column (Dionex) for Mg²⁺ and Ca²⁺. The eluent was a 28 μM cerium(III)nitrate solution at a flow-rate of 1 ml/min.

Transition metals. The metal ions determined were Cu²⁺, Zn²⁺, Mn²⁺ and Ni²⁺. The HPLC system consisted of a Varian Model 2510 pump, a Rheodyne Model 7125 injection valve with a 20-μl sample loop and a Model 400 amperometric detector (Biotronik). Separation was effected on a Nucleosil SA (5 μm) column (250 × 4.6 mm I.D.) with 0.14 mM tartaric acid solution (pH 3, adjusted with sodium hydroxide) as eluent (1 ml/min). Post-column derivatization was carried out with 0.2 μM EDTA.

Organic acids. For the determination of organic acids (formate, acetate, pyruvate, methanesulphonate and monochloroacetate), the same ion chromatographic

system as for the detection of inorganic anions was used (conductivity detection) except that the eluent was 0.5 mM sodium hydrogencarbonate solution at 2 ml/min.

Materials

Standard solutions of the inorganic anions were prepared from their sodium salts (Suprapur; Merck, Darmstadt, F.R.G.). Standard solutions of the inorganic cations were prepared from their nitrates (analytical-reagent grade; Merck). Standard solutions of the organic acids (formate, acetate, pyruvate, methanesulphonate) were prepared from their sodium salts (analytical-reagent grade; Merck). Standard solutions of the dicarboxylic acids were prepared from their sodium salts or from the free acids. Standards solutions of monochloroacetate and dichloroacetate were prepared from the free acids (analytical-reagent grade; Fluka, Buchs, Switzerland; *ca.* 99%, Aldrich, Steinheim, F.R.G.).

All chemicals used for the eluents were of analytical-reagent grade (Merck). Deionized water from a Milli-Q-System (Millipore, Eschborn, F.R.G.) was used. All solutions were degassed under vacuum.

RESULTS AND DISCUSSION

Determination of anions

The main anionic constituents of atmospheric samples are SO_4^{2-} , NO_3^- and Cl^- , the concentrations of other ions being relatively low. The determination of components of low concentration requires either an increase in selectivity or an enrichment procedure.

Fig. 2 shows a typical chromatogram for a rain sample with conductivity and UV detection. A number of substances with low concentrations are difficult to determine. Determination can be performed better with selective detection, *e.g.*, UV detection of NO_2^- . Another example is the determination of Br^- in air, which is difficult in the presence of high concentrations of NO_3^- . Zeissler⁴ found that with conductivity detection, only $\text{NO}_3^-/\text{Br}^-$ ratios of less than 1600 are acceptable. However, with amperometric detection, it is possible to determine 2.7 ppb^a of Br^- in the presence of 8 ppm of NO_3^- .

In some samples of fog water, a high concentration of SO_3^{2-} was found, which interferes with the amperometric detection of Br^- . This can be avoided by oxidation with oxygen in the presence of Co^{2+} as catalyst. Fig. 3 shows the different methods of detection for Br^- in rain water.

If the detection limit is higher than the concentration to be determined, then an enrichment step is necessary. In the determination of anions, most of the enrichment is carried out on precolumns without any selectivity. Therefore, the limitation is given by the total capacity of the column.

As the sum of the concentrations of SO_4^{2-} , NO_3^- and Cl^- in rain water was found to be *ca.* 3 μg on average (with the assumption of a 100- μl sample injection) and the column capacity is 50 μg , an enrichment factor of 20 is the limit in instances where no selectivity is obtained. The only possibility is to carry out a heart-cut of the analyte

^a Throughout this article, the American billion (10^9) and trillion (10^{12}) are meant.

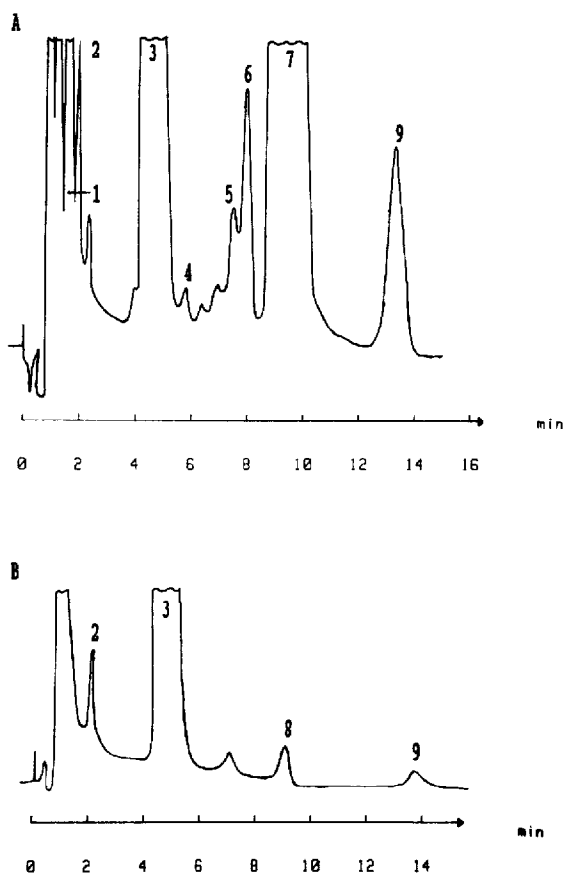


Fig. 2. Chromatograms of a rain-water sample. (A) Conductivity detection (range: $0.1 \mu\text{S}/\text{cm}$). (B) UV detection (range: 0.005). 1 = $0.760 \mu\text{g}/\text{ml Cl}^-$; 2 = $0.043 \mu\text{g}/\text{ml NO}_2^-$; 3 = $6.060 \mu\text{g}/\text{ml NO}_3^-$; 4 = $0.020 \mu\text{g}/\text{ml SO}_3^{2-}$; 5 = $0.138 \mu\text{g}/\text{ml succinate}$; 6 = $0.190 \mu\text{g}/\text{ml malonate}$; 7 = $9.600 \mu\text{g}/\text{ml SO}_4^{2-}$; 8 = $0.039 \mu\text{g}/\text{ml malate}$; 9 = $0.218 \mu\text{g}/\text{ml oxalate}$.

in question and to add up the fractions from several chromatographic separations. For some of the anions difficulties arise owing to their instability (SO_3^{2-} , NO_2^-) if the sample is not analysed immediately.

Determination of cations in air samples

When sampling cloud or fog water with a high time resolution, the available volumes are small⁵ and a large number of substances need to be identified. Therefore, it is necessary to develop a method for the determination of several cations requiring only a few microlitres of one sample and permitting absolute detection limits at the picogram level. These requirements are usually not fulfilled by spectroscopic methods.

Ion chromatography combined with indirect fluorescence detection^{6,7} allows the determination of alkali metal, ammonium and alkaline earth metal ions in the desired concentration range. Elution and simultaneous detection are carried out with

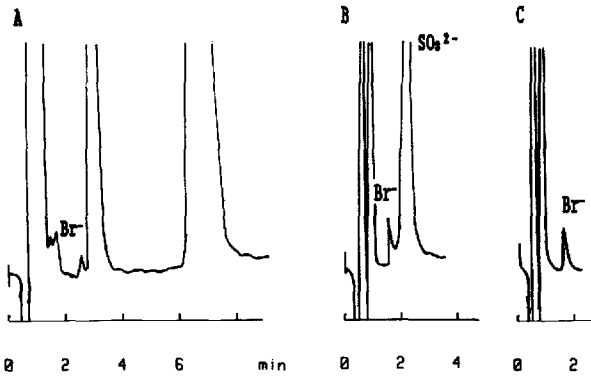


Fig. 3. Determination of bromide. (A) Conductivity detection [rain sample, 16 ng/ml Br^- ; range: 0.1 $\mu\text{S}/\text{cm}$]. (B) Amperometric detection [rain sample, 13 ng/ml Br^- , before oxidation of sulphite; range: 30 nA]. (C) Amperometric detection (after oxidation of sulphite).

cerium(III) nitrate⁸. In order to perform analyses with high sensitivity, it is necessary to work with very low cerium(III) concentrations (12 mg/l). However, under these conditions, the alkaline earth metal ions cannot be eluted from the column (ION 210 metal column; ICT). The use of a CS-1 cation-exchange column (Dionex) permits the

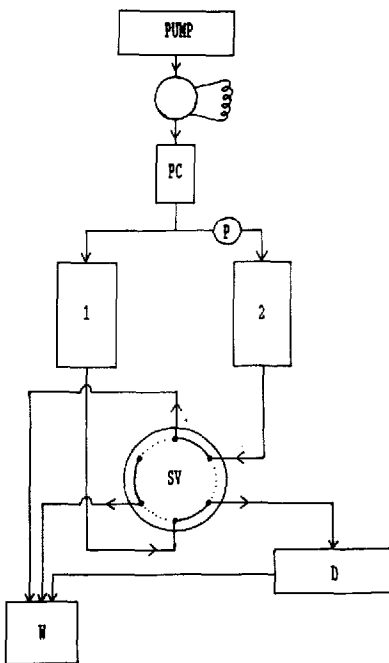


Fig. 4. Column switching. PC = Pre-column; P = pressure relief valve; 1 = ION 210 column (ICT); 2 = CS-1 column (Dionex); SV = switching valve; D = detector; W = waste.

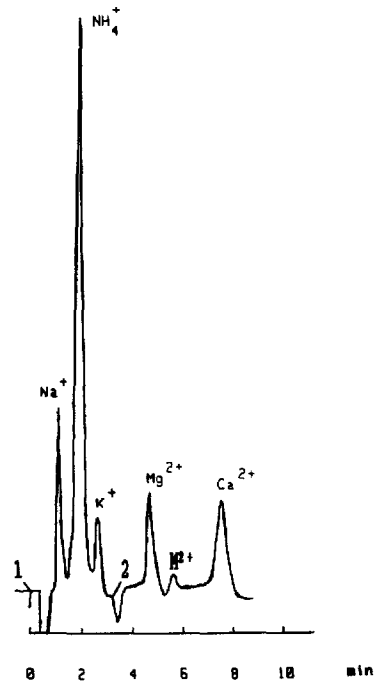


Fig. 5. Chromatogram of a fog sample (diluted 1:50) containing 0.52 $\mu\text{g}/\text{ml}$ Na^+ , 1.32 $\mu\text{g}/\text{ml}$ NH_4^+ , 0.53 $\mu\text{g}/\text{ml}$ K^+ , 0.09 $\mu\text{g}/\text{ml}$ Mg^{2+} , 0.26 $\mu\text{g}/\text{ml}$ Ca^{2+} . M^{2+} = divalent transition metals. (1) ION 210 metal column (range: 0.01). (2) CS-1 column (range: 0.002).

separation of these ions. The detection limits for the alkali metal ions lie between 0.25 ng/ml for lithium and 10 ng/ml for cesium and for the alkaline earth metal ions between 1 ng/ml for magnesium and 100 ng/ml for barium. A system in which both columns are combined was developed that permits the determination of Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} in a 50- μl sample within 8 min (Fig. 4). Chromatography takes place simultaneously on both columns by a splitting technique. With a switching valve one can choose the effluent to be detected. After elution of the alkali metal ions from the ICT column, the valve has to be switched to detect the alkaline earth metal ions from the CS-1 column. Owing to the very different pressures of the two columns, a back-pressure is necessary to regulate the flow-rate at 1 ml/min for each column. Fig. 5 shows a chromatogram of a fog sample obtained with this column-switching technique.

In the chromatogram of the alkaline earth metal cations, the sum of the divalent transition metals can be determined between the Mg^{2+} and Ca^{2+} peaks (Fig. 5). So far we have not succeeded in separating and determining transition metals with cerium(III) as the eluent. Therefore, an ion chromatographic separation followed by

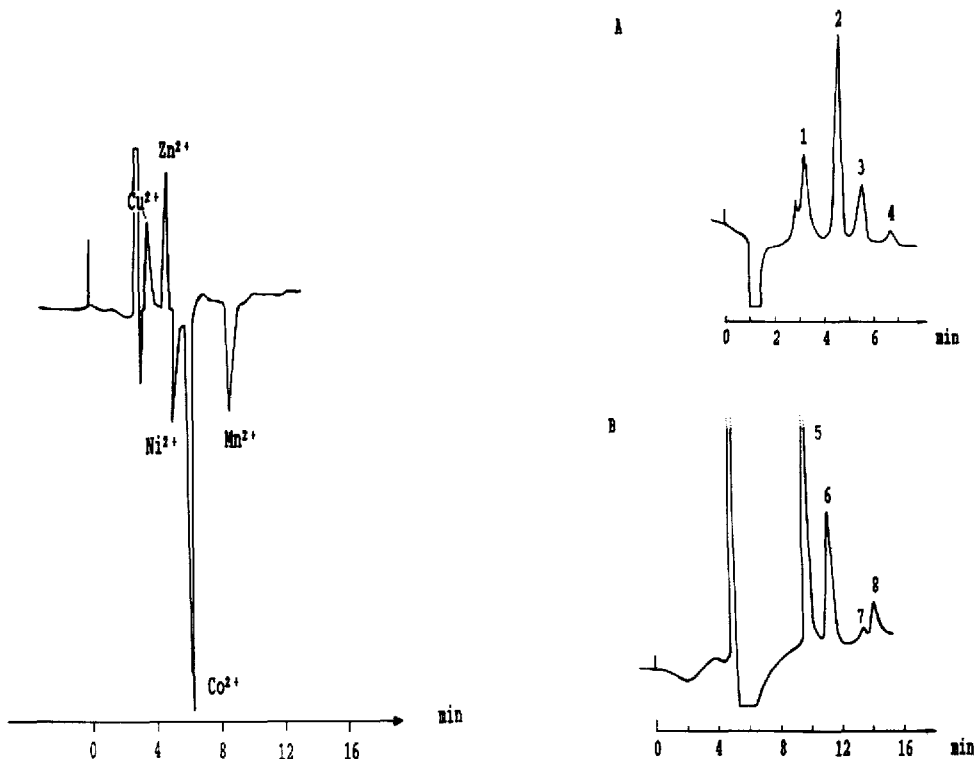


Fig. 6. Indirect amperometric detection of the transition metals Co, Zn and Cu (20 $\mu\text{g}/\text{ml}$ each), Ni (35 $\mu\text{g}/\text{ml}$ and Mn (0.05 $\mu\text{g}/\text{ml}$). Detection: 1100 mV Pt vs. Ag/AgCl. Range: 20 nA.

Fig. 7. (A) Ion-exchange chromatography (cloud sample; range 0.3 $\mu\text{S}/\text{cm}$). 1 = 0.35 $\mu\text{g}/\text{ml}$ acetate; 2 = 0.23 $\mu\text{g}/\text{ml}$ formate; 3 = 0.18 $\mu\text{g}/\text{ml}$ pyruvate; 4 = 0.02 $\mu\text{g}/\text{ml}$ methanesulphonate. (B) Ion-exclusion chromatography (rain sample; range 0.3 $\mu\text{S}/\text{cm}$). 5 = 0.72 $\mu\text{g}/\text{ml}$ formic acid; 6 = 0.28 $\mu\text{g}/\text{ml}$ acetic acid; 7 = 0.15 $\mu\text{g}/\text{ml}$ propionic acid; 8 = carbonate.

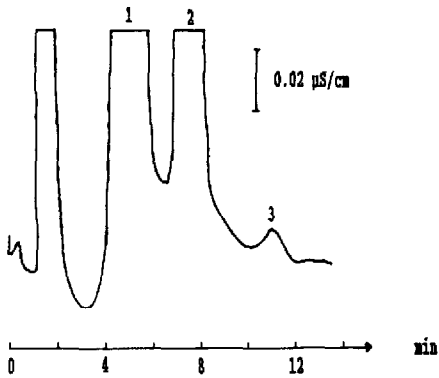


Fig. 8. Determination of monochloroacetate after pre-concentration (1:50) of rain water. 1 = Acetate; 2 = formate; 3 = 0.28 ng/ml monochloroacetate.

TABLE II

RESULTS OF FIELD MEASUREMENTS (MEAN VALUES, $\mu\text{mol/l}$)

<i>Species</i>	<i>Rain</i> (<i>Kolmbach/Odenwald,</i> <i>May 27th, 1988</i>)	<i>Fog</i> (<i>Beedenkirchen/Oden-</i> <i>wald, August 2nd, 1989;</i> <i>Kolmbach/Odenwald,</i> <i>November 24th, 1988</i>)	<i>Cloud</i> (<i>Frankfurt/Main, August</i> <i>23rd, 1986; Sylt, August 23rd,</i> <i>1987; Whiteface Mountain,</i> <i>September 30th, 1987</i>)
Chloride	34.0	612.0	40.0
Nitrate	145.0	805.0	170.0
Nitrite	1.8	16.0	0.9
Bromide	0.1		
Sulphite	5.0	103.0	
Sulphate	99.0	410.0	77.0
Formate	20.0	22.0	9.0
Acetate	14.0	82.0	6.4
Pyruvate		7.6	0.8
Methane- sulphonate			1.7 ^a
			0.2 ^b
Monochloro- acetate	0.02 ^c		
Dichloro- acetate	0.01 ^c		
Sodium	43.0	110.0	24.0
Ammonium	148.0	1507.0	185.0
Potassium	30.0	293.0	39.0
Magnesium	9.0	31.0	13.0
Calcium	23.0	82.0	40.0

^a Maritime.

^b Continental.

^c Rain sample taken in Darmstadt (1987).

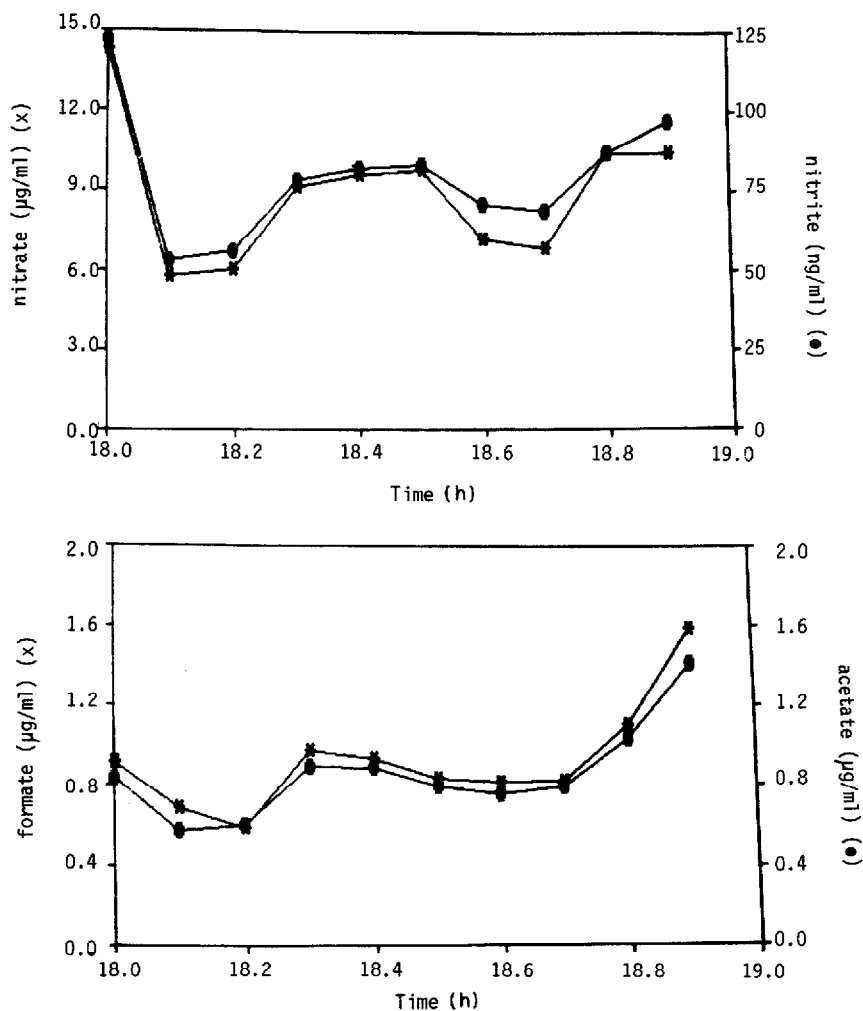


Fig. 9. Correlation of nitrate/nitrite and formate/acetate ratios during a rain sampling (Kolmbach/Odenwald, May 27th, 1988).

indirect amperometric detection was developed. The post-column complexation of the metal ions with an oxidizable organic ligand (EDTA) is measured and the change in concentration of the reagent is detected (Fig. 6). The detection limits of this method are in the upper picogram range⁹.

Determination of organic acids in air samples

The main acids found in atmospheric samples are formate, acetate, dicarboxylic acids, methanesulphonic acid, pyruvic acid and monochloroacetate. In other analytical methods such as esterification and gas chromatographic separation, enrichment steps and extraction are necessary, whereas for these main components such procedures are not required when using liquid chromatography.

Chromatographic separation is possible with either ion-exchange or ion-exclusion chromatography. Using ion-exchange chromatography, the weak acids elute before the strong acids, whereas with ion-exclusion chromatography, the sequence is reversed. Fig. 7 shows typical chromatograms for cloud and rain water. The amount of methanesulphonic acid depends on the maritime contribution (sea spray) in the atmosphere.

When very low concentrations (1 ppb) of mono- or dichloroacetate have to be determined together with formate (>1 ppm), a direct determination is impossible. Fuchs and Bächmann¹⁰ have demonstrated how heart-cutting of monochloroacetate from many samples leads to enrichment and to a partial separation from formate, but this was a very time-consuming procedure. An enrichment procedure using solid-phase extraction was developed in which there was no appreciable selectivity in the adsorption but the enrichment factor of 50 was high enough to allow the direct determination of monochloroacetate (Fig. 8). The main difficulties arise from impurities in the solid-phase column¹¹.

Results of field measurements

In Table II, results for cloud, fog and rain water are summarized. The interpretation of these results will be restricted to some general comments: (1) the concentrations in the fog samples are much higher (by a factor of 10) than those in rain samples; (2) during a rain event there are dramatic changes in the concentrations of the different substances; (3) in rain and cloud water samples the concentrations of the different ions are in comparable ranges; (4) the ratios of nitrate to nitrite and formate to acetate concentrations, for example, correlate during this rain event (Fig. 9).

ACKNOWLEDGEMENT

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