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DETERMINATION OF MONO- AND DIVALENT CATIONS AND ANIONS IN SMALL FOG SAMPLES BY ION CHROMATOGRAPHY

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SUMMARY

The application of ion chromatography to the determination of inorganic and organic anions and mono- and divalent cations in fog samples with a total volume of 1 ml is described. After filtration, the samples were split for four different ion chromatographic injections, all by autosampler. Detection limits were below 20 ppb for all ions. The pH was determined by means of a micro pH meter. The calculated ion balances agreed to within 16% or better in all instances. Adding glycerine did not enhance the stability of sulphite during sampling but enhanced the stability of sulphite in fog samples against oxidation by hydrogen peroxide in laboratory experiments.

INTRODUCTION

Fog droplets are efficient collectors of airborne species close to the earth's surface and therefore can contain high concentrations of critical pollutants[1]. These fog droplets can be deposited on trees and plants and may be one reason for forest disease[2]. Therefore, under the auspices of the Swiss National Science Foundation (National Programme on Forest Disease and Air Pollution NFP-14+), fog impactors were installed at four measuring towers up to 70 m high on the Lägeren mountain, Switzerland [416–844 m above sea level (a.s.l.)]. This fog sampling programme is part of a wide gas chemistry measurement programme[3]. The installed impactor types[4] allow a rapid resolution, but normally yield fog samples of 1 ml or less. Therefore, based on string collector samples obtained on the same mountain by the Swiss Federal Institute for Forestry Research (EAFV), an analytical procedure was outlined to proceed to an ion balance as complete as possible for these small samples. The method of choice for this purpose was ion chromatography.

EXPERIMENTAL

Sampling

Fog samples were obtained by a string collector with an air sampling rate of 370 m^3/h and a 50% collection efficiency for droplets of about 5 μm[5]. Fog water was sampled simultaneously into two collecting bottles, placed side by side in the sampler.

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One string collector was operated stationarily on the Lägeren mountain at Zindelen (685 m a.s.l.). Another string collector was mobile and was operated either on the Lägeren mountain near Hochwacht (820 m a.s.l.) for sampling of hill fogs (stratus) or at Birmensdorf near Zürich (550 m a.s.l.) for sampling of ground fogs. Cloud water and hill and ground fogs were sampled from August 4th to October 5th, 1987. Glycerine has been found to be a reasonable stabilizing agent in standard solutions when used in excess[6]. To test its stabilizing ability in fog samples, 25–100 μl of glycerine (85% glycerine, diluted 2:1 with water) was added to one of the two collecting bottles of the string samplers, resulting in a glycerine concentration of at least 0.05%. Formaldehyde would be a stronger stabilizer, but the hydroxymethylsulphonic acid formed interferes with sulphate in ion chromatography.

Apparatus

A Sykam ion chromatography system consisting of a pump (S 3110), various columns, a unit for chemical suppression and a detector (S 1000 A, with a cell constant of 0.4) was used, coupled to an autosampler designed for small sample volumes (Kontron MSI 660) and an integrator (Shimadzu C-R3A). Precolumns and analytical columns were placed in an Isothermer, a thermostated cabinet that allows switching between three different columns. Hence, owing to temperature equilibration of all the columns, determinations on a different column were possible 30 min after column switching. Chemical suppression was applied for the anions (column system, Sykam) and for the divalent cations (membrane system, Dionex), whereas the monovalent cations were determined without chemical suppression.

Analytical procedure

Samples were filtered either immediately after sampling at the sampling site or within the first hour after arriving at the laboratory. Millipore poly(vinylidene difluoride) (PVDF) filters (pore size 0.45 μm) with a small dead volume and very low contamination levels were used. After filtering, samples were transferred to autosampler vials (Semadeni, polypropylene, 1.2 ml), which, after prewashing proved to produce contamination levels below 20 ppb* for all ions determined. Samples were diluted 5–10-fold for inorganic anions and monovalent cations and up to 2-fold for organic anions.

The parameters of the four different ion chromatographic separations are shown in Table I. For the standard anions and the monovalent cations, routine analytical procedures were used. Oxalate, having a slightly higher retention time than sulphate, was determined together with the standard anions. For the determination of F^- and some organic acids, according to Weiss[7], 1–1.5 mM tetraborate was used as the eluent. For divalent cations, the lower ion-exchange capacity of the column used for this work yielded considerably shorter retention times for Mg^{2+} and Ca^{2+}, compared with the results of Hill and Lieser[8], in spite of the use of a more dilute eluent. Mixing of the samples with highly concentrated eluent was necessary only for the hydrogencarbonate–carbonate eluent, whereas for the other determinations the water dip did not interfere. Eluents were degassed with helium before use. With the tetraborate eluent, continuous degassing was applied, as uptake of carbon dioxide

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* Throughout this article the American billion (10^9) is meant.

TABLE I

SEPARATION PARAMETERS FOR THE FOUR DIFFERENT DETERMINATIONS

Parameter	*1*	*2*	*3*	*4*
Ions determined	Cl^-, NO_2^-, NO_3^-, SO_3^{2-}, SO_4^{2-}, oxalate	F^-, acetate, formate	Na^+, NH_4^+, K^+	Ca^{2+}, Mg^{2+}
Pre-column	Dionex AG4A	Dionex AG4A	Sykam macroporous neutral absorption material	Sykam macroporous neutral absorption material
Column	Dionex HPIC AS4A	Dionex HPIC AS4A	Sykam LCA K01	Sykam LCA K01
Eluent	0.5 m*M* $NaHCO_3$–1.3 m*M* Na_2CO_3	1.5 m*M* $Na_2B_4O_7$	4.5 m*M* HNO_3	1 m*M* histidine–1 m*M* diaminopropionic acid–12 m*M* HCl
Flow-rate (ml/min)	2	1	1	1
Chemical suppression	Sykam column, 1 *M* H_2SO_4	Sykam column, 1 *M* H_2SO_4	–	Dionex membrane, 20 mM tetramethyl ammonium hydroxide
Conductance (μS/cm)	12.5	3.0	1090	1.8
Sample dilution	Up to 1:9	–	Up to 1:9	Up to 1:1
Sample loop (μl)	50	50	50	50

from the atmosphere resulted in substantial shifts in retention times. With this weak eluent, other anions did not elute from the column or only very late. To eliminate these interferences, 0.2 *M* sodium hydroxide solution was injected by the autosampler after every run. Equilibrium conditions on the column were re-established 30 min after the injections of sodium hydroxide solution. When the tetraborate eluent had been standing in the column overnight, the retention times were reduced by about 25% next morning. After a single injection of 0.2 *M* sodium hydroxide solution the original retention times were obtained again. The pH was determined by means of a micro pH meter (Nanolab, Model 136), which consumed about 50 μl per determination.

RESULTS

Fig. 1 shows the chromatograms for 100-ppb standards and for fog samples obtained with the four different injections. Using a 50-μl loop, detection limits were below 20 ppb for all ions mentioned. The chromatogram of the divalent cations shows that ion chromatography can be a powerful alternative to atomic absorption spectrometry, at least for small samples (20 ppb in samples of 200 μl represents 4 ng of Ca^{2+} and Mg^{2+} within 10 min, injected by an autosampler).

A first set of results is shown in Table II, including cloud water, hill and ground fogs. Average values for the two individual collecting bottles of the string sampler (with and without glycerine) are shown, because large discrepancies in the ion concentrations could be found owing to non-symmetrical collecting in the two bottles.

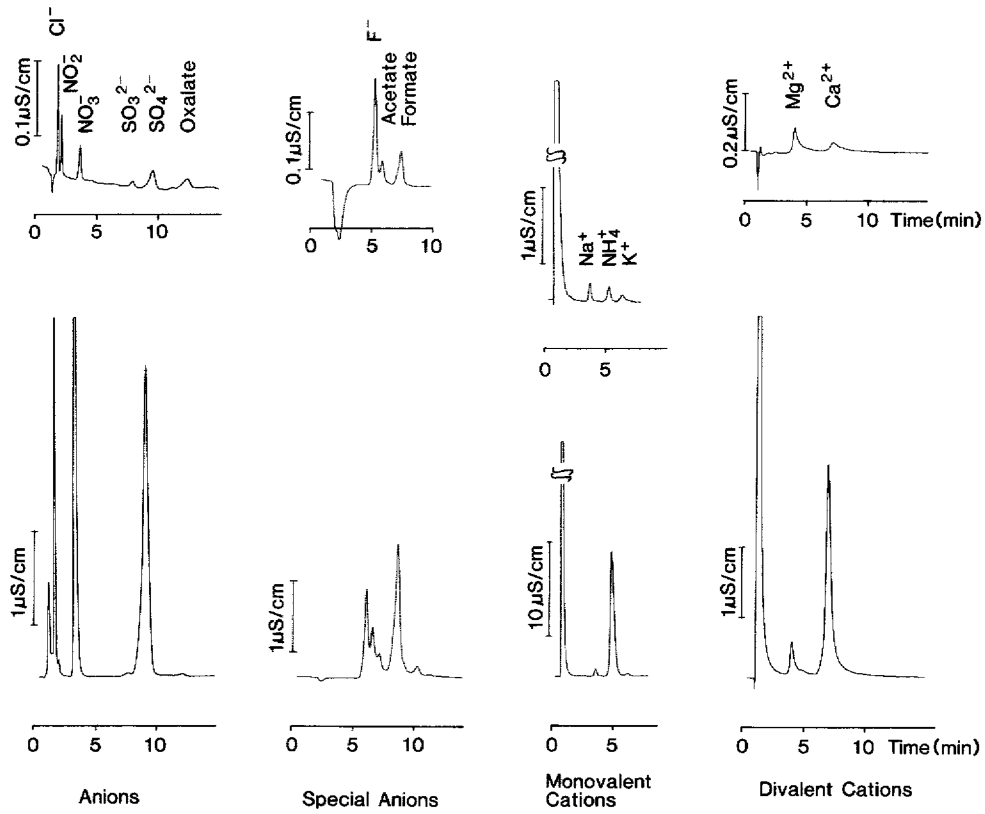

Fig. 1. Top: chromatograms of standard solutions (100 ppb each). Bottom: chromatograms of the fog samples, with (from left to right) 4.1 ppm Cl^-, 0.23 ppm NO_2^-, 22.6 ppm NO_3^-, 0.29 ppm SO_3^{2-}, 14.3 ppm SO_4^{2-} and 0.23 ppm oxalate; 0.6 ppm F^-, 2.4 ppm acetate and 3.0 ppm formate; 0.33 ppm Na^+, 7.22 ppm NH_4^+ and 0.36 ppm K^+; and 0.36 ppm Mg^{2+} and 4.6 ppm Ca^{2+}.

There are large concentration variations for the different fog types. The ratio of the sum of anions to the sum of cations varied from 0.84 to 1.12, which means that the ion balance was complete to within 16% in all instances.

Organic anions, especially formate and acetate, are mainly produced by gas-phase reactions and may be present in comparable concentrations as sulphate and nitrate in urban areas on clear summer days[9]. As can be seen in Fig. 1, the fog samples may contain other organic anions, such as propionate, which have not yet been identified. However, in these samples, formate and acetate normally represented the highest concentrations of organic anions, as found also by Keene *et al.*[10]. The sum of these organic anions considered in all instances in less than 15% of the total anion concentration. To determine ion balances it must additionally be taken into account that at a lower pH only a fraction of these organic anions are dissociated.

As shown recently[11], high variations can be found in sequential fog samples. This is also true for the sequential samples 6 and 7. Sample 7 shows generally higher concentrations owing to a lower liquid water content (LWC), and substantially higher

TABLE II

CONCENTRATIONS OF ANIONS AND CATIONS IN FOG SAMPLES (μequiv./l)

Samples: 1 = cloud water, Zindelen, 4.8.87, 13.30–16.10; 2 = cloud water, Zindelen, 18.8.87, 07.30–10.00; 3 = hill fog, Hochwacht, 1.10.87, 10.20–11.50; 4 = hill fog, Hochwacht, 1.10.87, 12.00–12.55; 5 = ground fog, Zindelen, 5.10.87, 05.40–11.10; 6 = ground fog, Birmensdorf, 5.10.87, 08.00–09.30; 7 = ground fog, Birmensdorf, 5.10.87, 09.35–11.25.

Ion	*1*	*2*	*3*	*4*	*5*	*6*	*7*
F^-*	24	4	18	16	16	29	33
Cl^-	146	228	343	589	114	212	2141
NO_2^-	–**	–	17	24	9	24	N.D.**
NO_3^-	347	269	1203	1662	564	1579	2731
HSO_3^-	–	6	13	16	30	129	140
SO_4^{2-}	535	245	488	680	312	1046	1807
Oxalate*	10	5	15	24	11	21	28
Acetate*	4	N.D.	58	51	90	41	64
Formate*	12	18	50	73	22	72	93
Total anions	1077	768	2120	3028	1108	3126	6866
H^+	8	66	169	251	28	16	659
NH_4^+	806	489	1976	2482	806	3021	4676
Na^+	119	11	82	86	83	54	75
K^+	55	23	49	57	56	24	32
Mg^{2+}	N.D.	6	29	53	8	16	63
Ca^{2+}	N.D.	90	214	316	88	176	782
Total cations	988	685	2519	3245	1069	3307	6287
Anions/cations	1.09	1.12	0.84	0.93	1.04	0.95	1.09

* Oxalate considered as bivalent anion, the other marked anions considered as monovalent. However, for determination of the ion balance, only the free portion was taken into consideration, according to the pH of the sample and the pK_a of the acid.

** –, Lower than detection limit; N.D., not determined.

concentrations of Cl^-, H^+, Ca^{2+} and Mg^{2+}, which may be due to an input from a local source.

The present data were obtained during late summer and early autumn, with relatively low ambient sulphur dioxide concentrations. Even higher sulphur concentrations can be found during late autumn and winter[12]. Many investigations were carried out on the oxidation rates of SO_2 to SO_4^{2-} (see, *e.g.*, ref. 13 and references cited therein), and it was found that the oxidation rates were of the order of a few percent per hour[13]. We therefore tried to stabilize sulphite by adding glycerine before sampling directly to the collecting bottles. However, the concentration ratio of sulphite to sulphate was virtually the same in the samples with and without glycerine. Repeated determinations 2 weeks later still showed the original sulphite concentrations, even in the samples without glycerine. Therefore, some experiments concerning sulphite stability were carried out. First, the oxidation rates in standard solutions were investigated, for which kinetic data were given by Lind *et al.*[14]. Standard solutions containing 1 ppm of sulphite, with and without 0.1% of glycerine, were prepared at pH 4 and 6. Hydrogen peroxide was added to these solutions so that they contained 1 mM of hydrogen peroxide and immediately subjected to ion chromato-

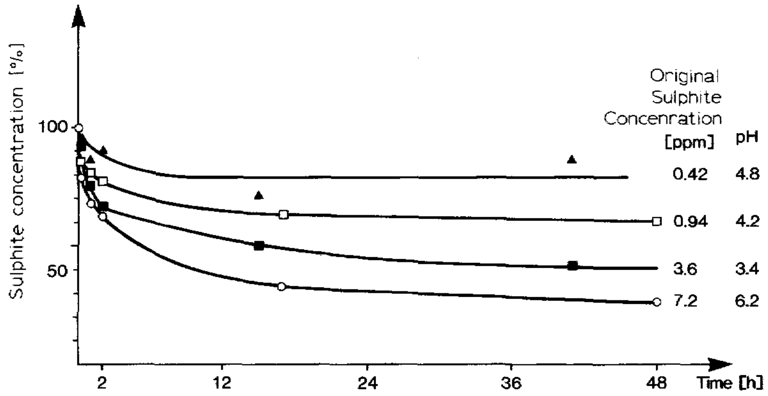

Fig. 2. Fractional decrease in sulphite concentrations in 1 m*M* hydrogen peroxide in different fog samples, stabilized with 0.05% glycerine. Note that for the lowest sulphite concentration the relative error is about 10%, whereas for the other determinations it is less than 5%.

graphy. In all instances, virtually all of the sulphite was immediately oxidized to sulphate, *i.e.*, glycerine was not able to stabilize sulphite under these conditions. In the fog samples, however, the oxidation with 1 m*M* hydrogen peroxide proceeded much more slowly, as shown in Fig. 2. With the exception of the measurements after 2 days, all points were determined for separately prepared solutions, in order to prevent effects of air oxygen. The presence of sulphite before oxidation was additionally verified by a corresponding increase in the sulphate peak after oxidation. The pH of the fog samples had no influence on the oxidation rate, but, the oxidation rate seemed to be faster for higher original sulphite concentrations. Oxidation rates without glycerine were about twice as fast, but still much slower than those with standard solutions. Alkalinization to pH > 10 with sodium hydroxide and repeated addition of hydrogen peroxide oxidized 95% of the sulphite within 1 h and 100% by the next day. More investigations have to be carried out with such fog samples, but it can be tentatively concluded that there are some additional agents with different stabilizing powers for sulphite in fog samples.

CONCLUSIONS

With the ion chromatographic system described it is possible to determine all major organic and inorganic ions in fog samples as small as 1 ml with four different injections. In all instances the calculated ion balances agreed to within 16% or better. Adding glycerine did not enhance the sulphite stability during sampling but enhanced the stability of sulphite in fog samples against oxidation by hydrogen peroxide in laboratory experiments.

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