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DETERMINATION OF ANIONS AND CATIONS IN ATMOSPHERIC AEROSOLS BY SINGLE COLUMN ION CHROMATOGRAPHY*

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SUMMARY

In order to optimize accuracy in the determination of ammonium, chloride, nitrate, potassium, sodium and sulphate in airborne particulate matter, experimental conditions for the extraction were tested, possible sources for contamination were evaluated and the effect of sample storage was examined.

With the chosen parameters the method exhibits good repeatability and is well suited for the routine analysis of particulate matter collected on filters. It was applied to the analysis of cellulose and glass-fibre filters exposed in the city of Zürich. The charge balance of the water-soluble fraction is given, and artifact formation of sulphate as well as loss of ammonia due to volatilization has been estimated for the two filter materials.

INTRODUCTION

Water-soluble anions and cations, *i.e.* mainly nitrate, sulphate and ammonium ions, are important components of suspended particulate matter, and numerous methods have been developed for their determination. Sulphate has been the most intensively investigated[1]. During the past few years ion chromatography (IC) has become established as a powerful tool for the determination of anions in atmospheric aerosols, owing to its advantage of fast, sensitive and accurate determination of several ions in one run[2]. However, in spite of its wide application, only a few of the various problems that may lead to erroneous results have been reported. Even less experience exists concerning cation chromatography of atmospheric aerosols.

Besides the problems usually encountered in all kinds of high-performance liquid chromatographic methods, IC leads to some specific problems, which have to be taken into account when using the method. These problems fall into two categories: operational factors, which include instrumental parameters; and preanalysis factors, including contamination control and sample pretreatment. In this paper the emphasis will be on preanalysis factors; the former category has been discussed elsewhere[3].

TABLE I

EXPERIMENTAL PARAMETERS FOR ANION AND CATION ANALYSIS

	Anion analysis	Cation analysis
Column	Wescan High Speed 269-013, 100 × 4.6 mm I.D.	Wescan 269-004, 250 × 4.6 mm I.D.
Eluent	4 mM KHP (pH 3.6)	3.0 mM HNO$_3$ (pH 2.5)
Flow-rate	2.0 ml/min	1.0 ml/min

EXPERIMENTAL

Apparatus

The IC system consisted of the following instruments in series[4]: an eluent tank, thermostatted to 20.0 ± 0.05°C (the eluent was degassed by bubbling helium through the solution); a pump (Altex 110A); a pulse-dampening system (A. Portmann, Basel, Switzerland); an autosampling unit (Spark Holland Sp 125 fix) with a 100-μl sample loop; a precolumn and column, built into an insulating box made in our laboratory; a conductivity detector (Wescan 213A); and an integrator (Spectra-Physics SP 4270). The specific experimental parameters for the determination of anions and cations are given in Table I.

Chemicals

All reagents were of analytical grade (Merck p.A.). Deionized water cleaned by additional ion exchange and filtration through activated charcoal and a 0.45-μm filter (Millipore, Milli-Q) was used throughout.

For anion chromatography an eluent concentrate of pH 4.1 was prepared by dissolving 24.508 g of potassium hydrogen phthalate (KHP) in water, diluting to a final volume of 500 ml and freezing it in portions of 50 ml. To one of these portions 50 ml of 21.6 mM phthalic acid was added and made up to a final volume of 3 l to give an eluent of pH 3.6.

The eluent for cation analysis was prepared by appropriate dilution of 1.0 M nitric acid to give a concentration of 3.0 mM at pH 2.5.

Sampling

Air filters were obtained from the National Monitoring Network for Air Pol-

TABLE II

SAMPLING CONDITIONS FOR CELLULOSE AND GLASS-FIBRE FILTERS

Filter diameter means diameter of the coated area.

	Cellulose filters	Glass-fibre filters
Sample type	Low volume	High volume
Filter type	Whatman 40	Sartorius SM13400
Filter diameter	2.54 cm	14 cm
Sampled air volume	2.88 m^3	960 m^3

TABLE III

CONTAMINATION BY FILTERS

(A) Uncleaned filter; (B) after rinsing. Values in ppm.

Ion	Cellulose nitrate		Cellulose acetate		PTFE		Durapore (Millex)	
	A	B	A	B	A	B	A	B
Na^+	3.4	1.3	1.0	0.6	0.8	0.8	1.6	1.1
NH_4^+	3.3	0.4	0.01	0.04	0.01	0.01	0.2	0.07
K^+	0.7	0.7	0.1	0.2	0.5	0.3	1.2	0.3
Cl^-	0.1	0.05	0.3	0.05	0.07	0.07	n.d.	n.d.
NO_3^-	0.3	0.05	0.2	0.05	0.05	0.05	n.d.	n.d.
SO_4^{2-}	1.5	0.2	5.0	0.4	0.3	0.1	n.d.	n.d.

lution (NABEL). The loading of the two filter types was carried out at the same time at the same place in the city of Zürich (Table II).

RESULTS AND DISCUSSION

Contamination

Contamination with chloride and sulphate can occur from various sources. For example, if containers and filter papers are touched with the fingers then chloride is transferred in microgram amounts. Many detergents contain appreciable amounts of sulphate, *e.g.* concentrations of up to 5 ppm have been found when using uncleaned 5-ml glass bottles. The first 2 ml of water passed through a new, uncleaned polycarbonate filter holder (*e.g.* Sartorius SM165 14 E) contained 0.1 ppm chloride, 0.1 ppm nitrate and 0.5 ppm sulphate. Special attention therefore has to be given to thorough cleaning of all materials that come into contact with the sample solution. Very pure water should be used for this purpose exclusively, and rinsing should be repeated several times. No leaching of anions from polyethylene, polystyrene, polycarbonate or glass containers could be observed after the cleaning procedure. Glass vials for the autosampler proved to be free of contamination by anions and could be used without cleaning.

In IC it is usually necessary to filter the samples prior to injection. Careful

TABLE IV

CONTAMINATION BY CONTAINER MATERIALS

Values are concentrations (ppm) in water after contact with the respective materials (A) immediatly after cleaning, (B) after contact time of 12 h; A' and B' are as A and B but using uncleaned vials.

Cation	Polyethylene		Plexiglass		Glass vials		Glass vials	
	A	B	A	B	A	B	A'	B'
Na^+	0.1	0.1	0.1	0.25	0.5	3.0	14.0	50.0
NH_4^+	0.01	0.01	0.1	0.4	0.3	0.2	0.2	2.0
K^+	0.05	0.05	0.05	0.05	0.05	0.05	0.4	8.0

attention is necessary to avoid contamination during this step. Table III shows the results of the examination of various filter materials. The values represent the concentration in 2 ml of water passed through (A) the uncleaned filter and (B) after rinsing with 10 ml of water. Except for potassium, the concentrations of all the impurities may be appreciably reduced by rinsing. Only PTFE filters exhibit low enough contamination that they can be used without cleaning; nevertheless, the high price reduces their applicability for routine analysis. If low cation concentrations have to be analysed, cellulose acetate is the material of choice, whereas for anion analysis cellulose nitrate filters show exceptionally low sulphate contamination; the latter (Sartorius SM 113 07) were chosen for all filtrations.

Table IV shows cation contamination by container materials. All materials have been rinsed with water before bringing them into contact with the sample solution. The respective contaminations are given under (A). If uncleaned glass bottles are used (A'), much higher contaminations are found, *i.e.* thorough rinsing with water reduces the contamination appreciably. Even then, prolonged storage leads to increased leaching, especially of Na^+ (B). When autosampling vials made from plexiglass were used, low Na^+ and K^+ but relatively high NH_4^+ contamination was found.

Because of the lack of availability of suitable polyethylene vials, it was impossible to use the autosampler for cation analysis.

Extraction

Appel *et al.*[5] thoroughly examined the efficiencies for various extraction methods currently in use by monitoring organizations. They found that a 30-min ultrasonic treatment and a 60-min reflux procedure yielded very similar results, whereas mechanical shaking for 60 min recovered *ca.* 3% more sulphate on average. In a similar study, Jenke[6] found no statistically significant difference between various extraction procedures, although boiling water extraction from teflon filters gave somewhat higher values for both sulphate and nitrate. Ultrasonic treatment seems to be the current method of choice and is also the procedure currently recommended by the United States Environmental Protection Agency[7]. Few data about the influence of temperature in ultrasonic extraction have been reported. Some authors start ultrasonication at room temperature[2], others extract at 40°C[8] or at even higher temperatures[6].

Our investigations have shown that varying the extraction time from 5 to 120 min as well as changing the temperature between 20 and 70°C does not significantly alter the extraction efficiency. Nevertheless, if oily residues are present on the filters, the wetting is much slower and higher extraction times may be necessary[5]. For glass-fibre filters the following extraction procedure was used: the filter (15 cm in diameter) was folded once and cut radially with a scalpel and a ruler into sixteen pieces of equal area with the help of a pattern designed on the back of a glass plate. One of these pieces was then extracted with 10 ml of water by ultrasonic treatment at 40°C for 15 min. The extract was then filtered through a 0.2-μm cellulose nitrate filter and injected into the system. For anion analysis no dilution was necessary, but for the determination of cations the solution was diluted ten-fold. The same procedure, but without dividing, was applied to cellulose filters.

Storage

Depending on the type and duration of sample storage, ion concentrations may undergo appreciable alteration. We have found that it is very important to keep the sample solutions completely free of particulate contamination. If, for example, the extract is stored with the filter, irreproducible losses of Na^+, Cl^-, NO_3^- and SO_4^{2-} and gain of NH_4^+ occur. The same is true if the filtration is not carried out properly or if air dust is allowed to enter into the sample vials.

Correctly prepared sample solutions may be kept at $-20°C$ for at least several weeks without changing the mean of the ions under consideration, with the exception of NH_4^+. The concentration of the latter increases by *ca.* 10% each time it is frozen and thawed. The reason for this increase is still not known and needs further investigation. For all ions the repeatability decreases after storage and sometimes outliers are found, but this is still acceptable for refrigerated samples even for the case of ammonium (Table V). For these reasons, analysis immediately after extraction is recommended whenever possible.

Analytical performance

Fig. 1 shows typical chromatograms for the determinations of anions and cations. The choice of a relatively low pH for anion analysis prolongs the lifetime of the analytical column to over 1000 injections. This low pH, however, increases the retention times to such an extent that reasonable analysis times are achieved only with a short column.

The cation column suffers from being loaded with polyvalent cations, resulting in a tremendous reduction of the separation ability within a few days. Repeated injection of 0.2 *M* EDTA re-establishes the original performance, so it is highly recommended that this procedure be carried out daily.

The repeatability has been determined by successive analysis of all sixteen parts of one air filter. Whereas anions were determined in freshly prepared as well as in frozen samples, cation analysis was performed only in stored solutions. The results are shown in Table V. The repeatability for nitrate and sulphate in fresh solutions is excellent, which means that the filter loading is very homogeneous and the cutting procedure may be applied. The repeatability for the stored cations and anions is of the same order of magnitude and is appreciably lower than in the fresh samples.

TABLE V

REPEATABILITY FOR FRESH AND STORED SAMPLES

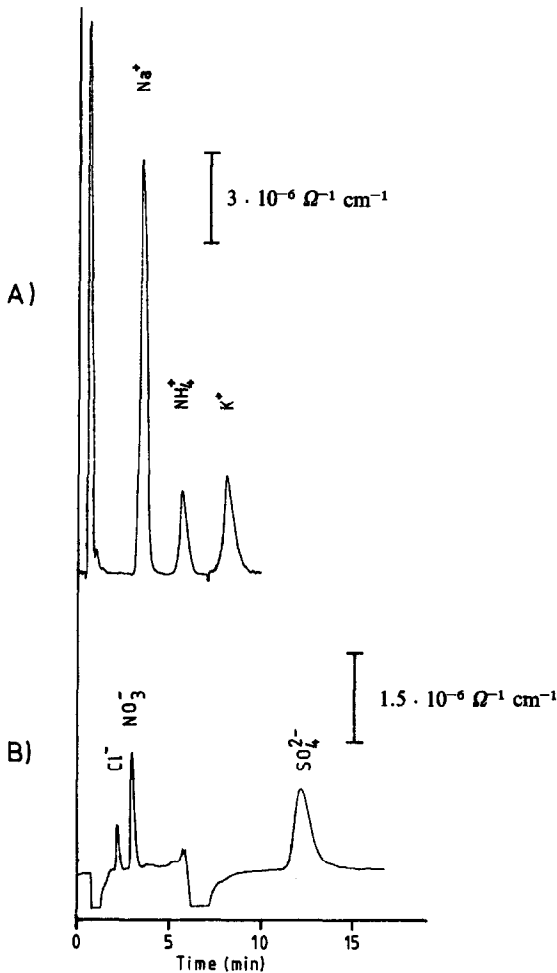| Ion	Standard deviation (%), n = 16	
	Fresh	*Stored*
Cl^+	6.0	8.6
NO_3^-	1.8	4.9
SO_4^{2-}	2.3	4.8
Na^+	n.d.	5.6
NH_4^+	n.d.	5.1 (two outliers)
K^+	n.d.	7.8

Fig. 1. Chromatograms of air filters. (A) Cation chromatogram; concentrations: 5, 2 and 2 ppm for Na^+, NH_4^+ and K^+, respectively. (Attenuation changed by a factor of four for K^+). (B) Anion chromatogram (after 1000 injections on column); concentrations: 2, 14 and 21 ppm for Cl^-, NO_3^- and SO_4^{2-}, respectively.

Real samples

Figs. 2 and 3 show the results for cation and anion determination on glass-fibre and cellulose filters. Only the data for nitrate, sulphate, ammonium and potassium are listed, although also sodium and chloride were determined. Since the cellulose filters were touched by fingers during collection, chloride and sodium contamination was introduced; therefore, the respective results were discarded. Blank values for sodium on glass-fibre filters were appreciably high, so the low ambient Na^+ concentration could not be evaluated.

For better comparability the Cl^- values on glass-fibre filters were discarded as well. At our sampling location, which is normally not affected by sea spray, the mean concentrations for these two ions are low (*e.g.* 1.4 $\mu g/m^3$ = 40 nequiv./m^3 for Cl^-),
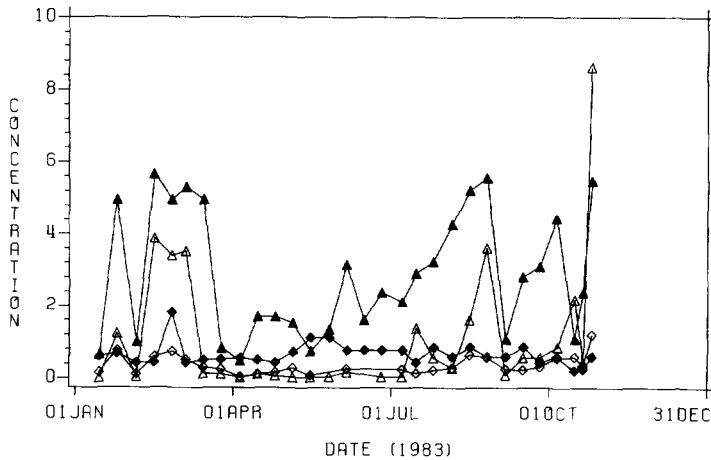
Fig. 2. Concentrations (μg/m^3) of NH_4^+ and K^+ in air: $\triangle$ = NH_4^+ on glass-fibre filters; $\blacktriangle$ = NH_4^+ on cellulose filters; $\diamondsuit$ = K^+ on glass-fibre filters; $\blacklozenge$ = K^+ on cellulose filters.

so the mass balance is not significantly affected by the omission. The charge balance (Fig. 4) shows a good correlation for cations and anions on cellulose filters, whereas on glass-fibre filters the mean equivalents for anions are much higher than those for cations. Several artifacts are responsible for these differences. Owing to the high pH on glass-fibre filters, ammonium is deprotonated and the ammonia is volatilized during sampling. About 80% of the collected ammonium is lost during the summer months whereas in winter the loss is only *ca.* 35%. On cellulose filters no artifact of this kind is observed. This is confirmed by the fact that cellulose filters that were stored at room temperature for 3 years prior to analysis still exhibited a good correlation in charge balance ($n = 30$).

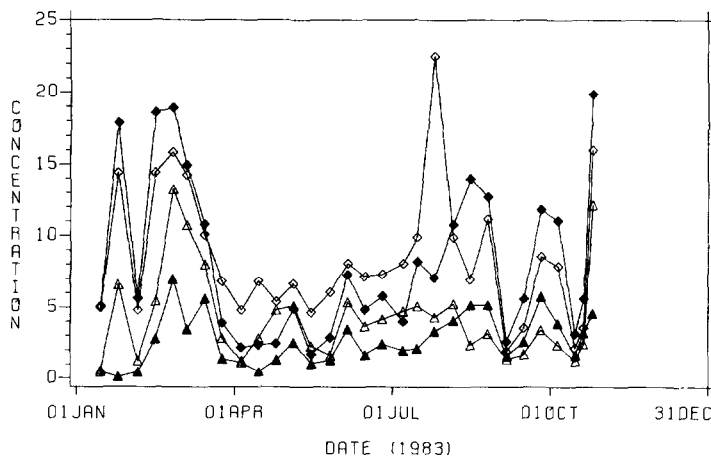Extensive investigations of artifact formation of sulphate and nitrate on glass-

Fig. 3. Concentrations (μg/m^3) of NO_3^- and SO_4^{2-} in air: $\triangle$ = NO_3^- on glass-fibre filters; $\blacktriangle$ = NO_3^- on cellulose filters; $\diamondsuit$ = SO_4^{2-} on glass-fibre filters; $\blacklozenge$ = SO_4^{2-} on cellulose filters.
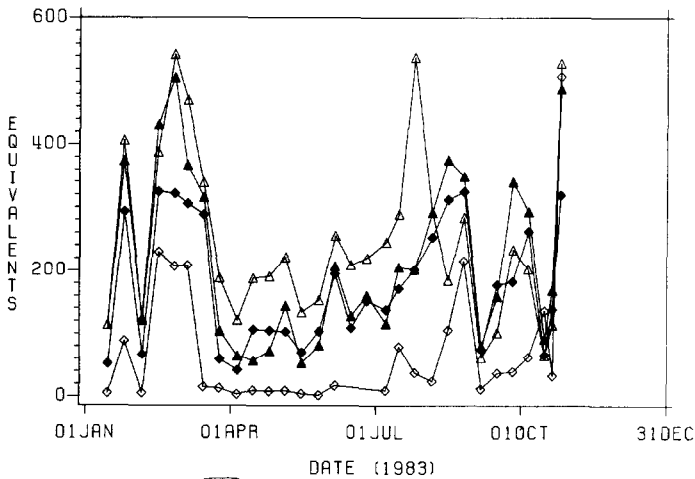
nequiv/m3

Fig. 4. Charge balance (NH_4^+ and K^+ for cations, NO_3^- and SO_4^{2-} for anions): ◇ = cations on glass-fibre filters; ◆ = cations on cellulose filters; △ = anions on glass-fibre filters; ▲ = anions on cellulose filters.

fibre filters have been reported[9,10]. This is confirmed by our results of the summer months. In wintertime, however, the SO_4^{2-} concentrations are lower on glass-fibre than on cellulose filters. According to the Coutant model[11], artifact formation should be more pronounced at high humidity and high SO_2 concentrations. This contradicts our findings and leads to the assumption that positive artifacts form on cellulose filters in wintertime.

CONCLUSIONS

Very often the quality of an analytical method is measured by the attainable detection limit, which is appreciably lower in suppressed than in single column IC. The present paper, however, shows that for the analysis of air filters pre-analysis factors determine the accuracy and reproducibility of the analytical procedure. If contamination precautions are followed and samples are stored as described, anions in air filters can be detected fast and reliably by single column IC. In cation determination there still remain some unsolved problems concerning contamination and storage.

In spite of these drawbacks, which are encountered in other analytical methods as well, single column IC is the method of choice for the determination of water-soluble anions and cations in ambient air particles.

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