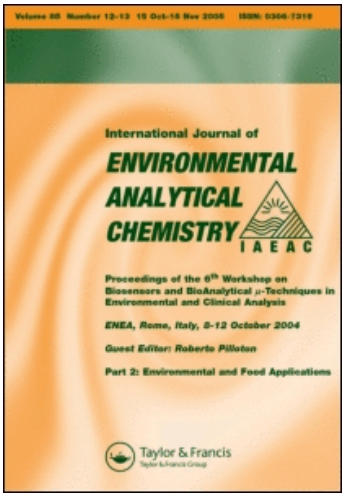

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Nüria Ferrer[a]; Juan J. Pérez[a]
[a] Dpt. de Química, Centre del Medi Ambient, ETS d'Enginyers Industrials (UPC), Barcelona, Spain

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Determining Inorganic Anions in the Atmosphere by Ion-Exchange Chromatography†

NÚRIA FERRER and JUAN J. PÉREZ

Dpt. de Química, Centre del Medi Ambient, ETS d'Enginyers Industrials (UPC), Av. Diagonal 647, 08028 Barcelona, Spain

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In the present paper we report on a sensitive technique for determining anions by means of ion exchange chromatography. The method is suitable for use in the analysis of anion content in atmospheric aerosols. Photometric detection, both direct and indirect is used. Although the direct photometry technique is more sensitive, it does not permit analysis of sulphates. Moreover, indirect photometry does not allow us to measure the levels of bromide in atmospheric aerosols due to its low concentration. These levels are successfully determined by direct photometry. Indirect photometry has the disadvantage that it presents a system peak which may overlap with the peaks of nitrate or sulphate, which do not appear in direct photometry. Nevertheless, if sulphates and bromides need to be analyzed simultaneously, both techniques seem to be complementary. Finally, the possible advantages which this kind of analysis may provide for the understanding and characterization of atmospheric aerosols are also considered.

KEY WORDS: Ion-exchange chromatography, atmospheric aerosols, anions in the atmosphere.

INTRODUCTION

Determining inorganic anions in atmospheric aerosols has become an area of growing interest with respect to the increase in pollution

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levels in large cities as well as the transportation of pollutants in the atmosphere.

Anions like nitrate and sulphate are responsible for the acidity of dry deposition. Others like bromide constitute a hazard for public health.

Anions travel as constituents of atmospheric aerosols and can be transported far from the place where they were released. Accurate knowledge of aerosol composition could be used to trace the sources of pollutants by means of receptor models.[1] Metals have been widely used for this purpose because they can be routinely determined in an easy and accurate way.

Knowledge of inorganic anion concentrations could also help us in our understanding of aerosol evolution as well as be used to trace fugitive emissions in receptor models.

Ion-exchange chromatography constitutes a reliable analytical method for easily and simultaneously determining inorganic anions with very high degree of accuracy, depending on the method of detection employed.

Although the use of ion-exchange chromatography for this purpose is not new, the papers published in the literature do not give a completely satisfactory method for determining anions in the atmosphere.

Among the detection methods employed, the conductimetric method, although it can be used for a simultaneous determination of anions, requires using either a suppressor column or resorting to preconcentration methods due to the poor level of sensitivity achieved for minority anions like bromides. Nevertheless, chlorides, nitrates and sulphates can be determined by this method without preconcentration or the use of a suppressor column if they are found in relatively high concentrations.[2]

The UV detection method offers two alternatives. On the one hand, the indirect photometry technique which can be used for the simultaneous determination of chlorides, nitrates and sulphates if they are found in concentrations higher than 1 ppm. On the other hand, direct photometry, which gives very high sensitivity,[3–6] excludes the possibility of a simultaneous determination of sulphates.

The aim of the present paper is to present a reliable method for simultaneous determination of majority as well as minority anions in atmospheric aerosols by means of the UV detection method, after

optimization of the direct and indirect techniques for these purposes.

The method we present has been developed over the last few years in our laboratory leading to a rapid, sensitive and easy determination of anions without any previous sample treatment. It consists of alternately using the direct and indirect photometry techniques depending on the concentration and kind of anions to be determined, and provides very accurate results.

EXPERIMENTAL

Instrumentation

The apparatus used for determining the anions consisted of a Spectra-Physics 8700 liquid chromatograph, a Spectra-Physics SP8440 variable wavelength spectrophotometer and a Shimadzu UV-240 spectrophotometer. The integration was carried out on the Spectra-Physics SP4270.

The column used was the low capacity Vydac 302 IC 4.6 (250×4.6 mm ID), with a 100 μl sample loop.

Particulate matter was collected on a MCV High Volume sampler on fibre-glass filters GFA (15 cm in diameter).

Reagents and eluents

The standard solutions of the anions (1000 ppm) were prepared by dissolving appropriate amounts of analytical grade (Merck) sodium or potassium salts in water previously purified by a Millipore Milli-Q system.

Working standards were prepared daily by dilution of the stock solutions.

Eluents were prepared using analytical grade (Merck) sodium perchlorate, methanesulphonic acid and potassium hydrogen phthalate dissolved in water purified by the Millipore Milli-Q system. The pH of eluents was adjusted by dropwise addition of 1 M sodium hydroxide.

The eluents were then filtered through a 0.45 μm filter (Millipore HAWP04700) and degassed with helium.

Sampling

The aerosol samples were collected over a 24 hr period on the MCV High Volume sampler. The particulate matter was extracted from the fibre-glass filters by using 15 ml of water purified on the Milli-Q system and by means of an ultrasonic bath at 40°C for 15 min. For the reference sample a blank filter was used to which 15 ml of water had been added.

The solution was filtered through a Black ribbon Schleicher Schull filter paper in order to separate the paper from the solution and made up to 250 ml with water. Prior to injection into the column, the samples were filtered through a 0.45 μm filter (Millipore HATF01300).

Finally, in order to obtain a reliable standard for our purposes, all the experimental work was carried out using concentrations of inorganic anions similar to those found in the atmosphere.

RESULTS AND DISCUSSION

From the analytical point of view, there are a large number of error sources to be taken into account in order to obtain significant data from the aerosol sample analysis. These problems may fall into two categories. On the one hand, the sample treatment, including precautions to prevent any contamination, the extraction procedure and in general, the sample preparation prior to injection. On the other hand, the operational factors, which are related to the instrumental parameters involved. In the present paper we have evaluated only the latter, while the former have been widely discussed by Baltensperger *et al.*[2]

The contamination due to the blank filter was previously determined. 1.5 ppm was found as a mean for chloride, which must be subtracted from each analysis. Nitrate was also found in the blank filters but the amounts were low enough to fall outside the range of analysis.

Indirect photometry

Potassium hydrogen phthalate was used as eluent. The effects of the

eluent concentration on the separation of the anions studied are shown in Figure 1.

Eluent concentrations greater than 0.003 M cannot be used due to the absorption range of the detector. As can be seen from Figure 1, good resolution within reasonable analysis times is achieved using a concentration of 0.003 M.

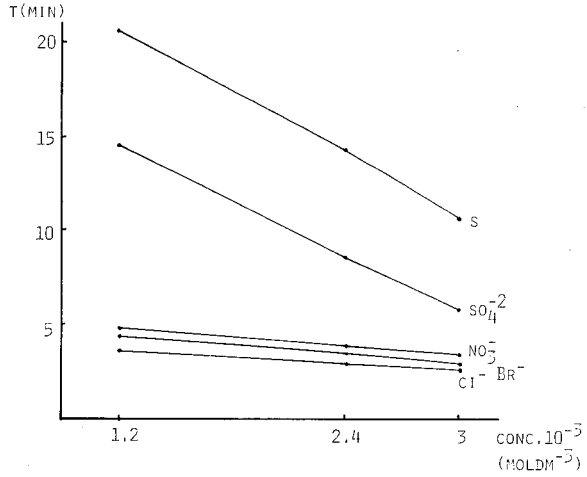

FIGURE 1 Effect of eluent concentration on retention time. Eluent: potassium hydrogen phthalate; pH = 5.0; wavelength: 280 nm; flow-rate: 2 ml/min.

Another important parameter is the pH of the eluent. In Figure 2 the effects of the pH of the eluent on the retention time for the anions at 0.003 M for eluent concentration are shown. The lowest pH considered, 4.2, is that of a solution of 0.003 M of potassium hydrogen phthalate. The highest pH values are obtained by adding sodium hydroxide prior to the dilution.

It is necessary to note that the ultraviolet spectrum of the potassium hydrogen phthalate presents a maximum of between 270 and 280 nm (Figure 3). The value of the absorption for this maximum decreases by increasing the pH. Thus, when the pH is between 4.2 and 4.5, it is not possible to work at 280 nm due to the limited range of absorption in the spectrophotometer detector. Because of this, it is necessary to work at 288 nm or higher wavelengths. At pH 5.0 and above, the maximum absorption can be reached at 280 nm.

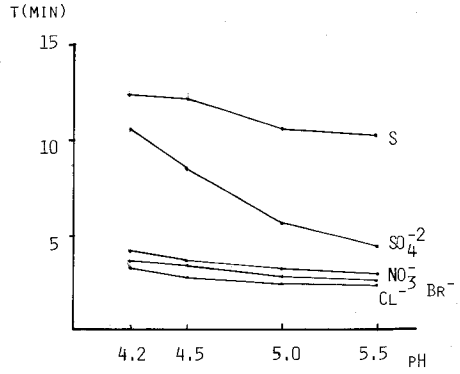

FIGURE 2 Effect of the eluent pH on retention time. Eluent: potassium hydrogen phthalate 0.003 M; wavelength: 280 nm; flow-rate: 2 ml/min.

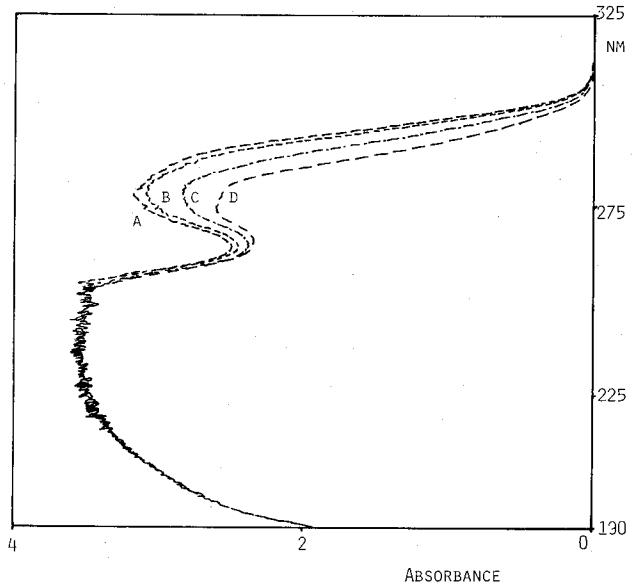

FIGURE 3 Ultraviolet spectra for potassium hydrogen phthalate 0.003 M. (A) pH = 4.2; (B) pH = 4.5; (C) pH = 5.0; (D) pH = 5.5.

Determination of inorganic anions using non-supressed ion chromatography with indirect UV absorption detection, shows a system peak which also appears when water is injected.[7] This peak displays a great dependence on the pH of the eluent and it can cause some problems when sulphate anions must be determined.

Working with a pH near 4 the resolution between sulphate and the system peak is poor. By increasing the pH, the retention time for sulphates decreases considerably with respect to the system peak and the other anions. Finally, at high values of pH—around 6—the peak of the sulphate anion overlaps with the peak of the nitrate anion. Thus, by keeping the pH between 4.5 and 5.5 good resolution and reasonable analysis times are achieved. Nevertheless, as stated before, the absorption maximum decreases and consequently the sensitivity of the analysis decreases. Thus, a compromise must be sought. Experimentally, it was found that by working at pH = 5.0 good resolution for the sulphate anion, relatively short time of analysis and good sensitivity are achieved, including the advantage of working at maximum of absorption.

Figure 4 shows a chromatogram corresponding to a mixture of chloride, nitrate and sulphate at the optimum conditions of concentration and pH.

Concentrations of chloride, nitrate and sulphate present in the atmosphere are high enough for them to be determined with good sensitivity by working with indirect photometry. Nevertheless, the concentration of bromide in the atmosphere is very low and falls near the detection limits with this technique. Thus, its determination could be feasible but would include a relatively large degree of uncertainty.

Table I shows the relative standard deviation for chloride, nitrate and sulphate anions in the concentration range found in the atmosphere.

Regression parameters are shown in Table II. It must be observed that the sensitivity of this method decreases in the chloride > nitrate > sulphate sequence.

Direct photometry

For direct photometry, the non-absorbent eluents sodium perchlorate and methanesulphonic acid were used.

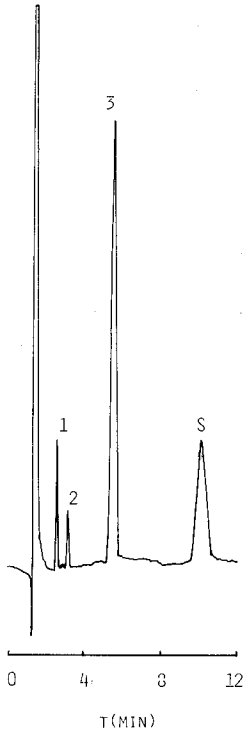

FIGURE 4 Chromatogram of a mixed standard. (1) chloride 5 ppm, (2) nitrate 5 ppm, (3) sulphate 50 ppm, (4) system peak. Eluent: potassium hydrogen phthalate 0.003 M; pH = 5.0; flow-rate: 2 ml/min; sample size: 100 μl; sensitivity: 0.0025 a.u.; wavelength: 280 nm.

TABLE I

Relative standard deviation.

Anion	Concentration ppm	n	Peak height precision % RSD
Eluent: potassium hydrogen phthalate 0.003 M *Wavelength: 280 nm*			
chloride	5	10	1.5
nitrate	10	10	1.6
sulphate	20	10	0.3

TABLE II

Regression parameters.

Anion	Number of levels	Range ppm	Slope	Intercept	Correlation coefficient
Eluent: potassium hydrogen phthalate 0.003 M Wavelength: 280 nm					
chloride	5	1–10	51.9	11.8	0.9999
nitrate	5	2–20	27.8	8.1	0.9999
sulphate	5	4–40	24.2	21.5	0.9999

In Figure 5 the effects of the eluent concentration on the separation of the anions are shown. The sulphate anion cannot be detected by direct photometry due to its low absorption.

Concentrations of 0.02 M and 0.002 M for methanesulphonic acid and sodium perchlorate, respectively, seem to give good resolution and reasonable times of analysis.

In this case, that of direct photometry, the system peak is not observed, and moreover, changes in the pH do not affect the retention time.

Figure 6 shows a chromatogram corresponding to a mixture of chloride, bromide and nitrate using the optimum concentration of methanesulphonic acid and sodium perchlorate. As can be seen, the bromide anion is determined with a good degree of sensitivity.[4]

In Table III the relative standard deviations for chloride, bromide and nitrate anions are shown.

Regression parameters are shown in Table IV. In this case the sensitivity of the method decreases in the bromide > nitrate > chloride sequence.

In the case of direct photometry the wavelength is an important parameter to consider. Figure 7 shows a plot of peak height versus wavelength. For simultaneous determination of chloride, bromide and nitrate, the optimum wavelength must be situated between 186 nm (which is the lowest limit for the UV detector) and 191 nm. Higher wavelengths give low sensitivity for the chloride anion.

Application to atmospheric aerosol analysis

This study was applied to the analysis of filters exposed on an

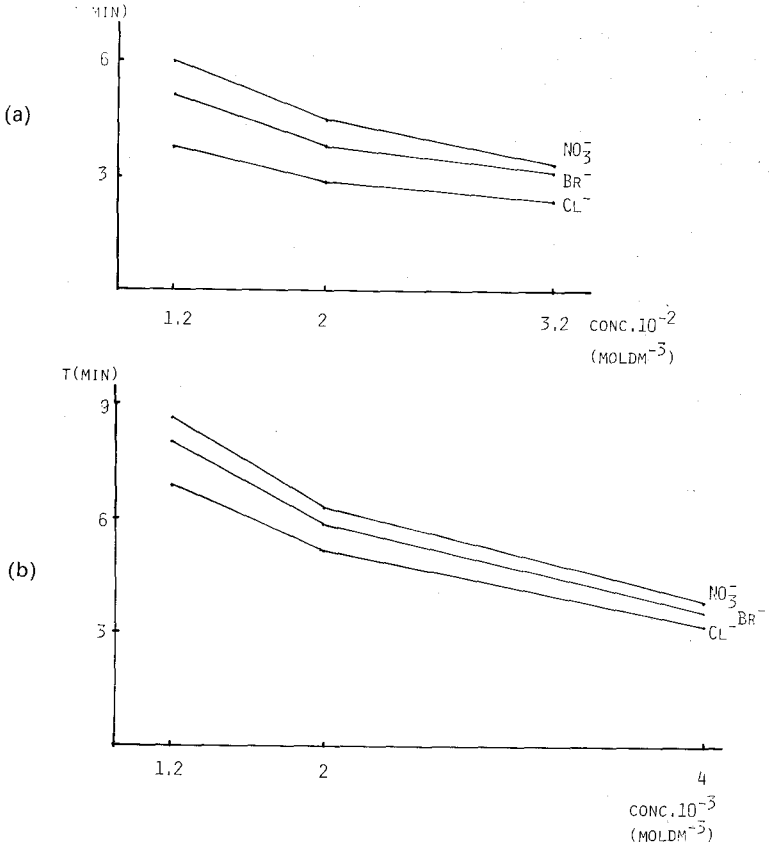

FIGURE 5 Effect of eluent concentration on retention time. (a) eluent: methanesulphonic acid; pH = 4.5; wavelength: 190 nm; flow-rate: 2 ml/min. (b) eluent: sodium perchlorate; pH = 5.4; wavelength: 190 nm; flow-rate: 2 ml/min.

industrial site 15 km from the city of Barcelona. This area lies beside the sea, which will contribute as a natural source of anions.

Both kinds of photometric detection must be used if the simultaneous evaluation of bromides and sulphates is required. If not, either of the methods can be used, since chloride and nitrate are well determined using both direct and indirect photometry.

Figure 8 shows two chromatograms which correspond to the same sample of atmospheric aerosol using (a) direct and (b) indirect

TABLE III

Relative standard deviation.

Anion	Concentration ppm	n	Peak height precision % RSD
Eluent: methanesulphonic acid 0.02 M *Wavelength: 190 nm*			
chloride	5	10	1.5
bromide	0.5	10	1.6
nitrate	10	10	0.3
Eluent: sodium perchlorate 0.0012 M *Wavelength: 190 nm*			
chloride	5	10	2.9
bromide	0.5	10	3.6
nitrate	10	10	0.4

TABLE IV

Regression parameters.

Anion	Number of levels	Range ppm	Slope	Intercept	Correlation coefficient
Eluent: methanesulphonic acid 0.02 M *Wavelength: 190 nm*					
chloride	5	1–10	41.7	10.9	0.9999
bromide	5	0.1–1	265.5	2.3	0.9999
nitrate	5	2–20	210.0	5.5	0.9999
Eluent: sodium perchlorate 0.002 M *Wavelength: 190 nm*					
chloride	5	1–10	35.0	12.7	0.9988
bromide	5	0.1–1	290.3	−5.1	0.9997
nitrate	5	2–20	321.9	−70.0	0.9992

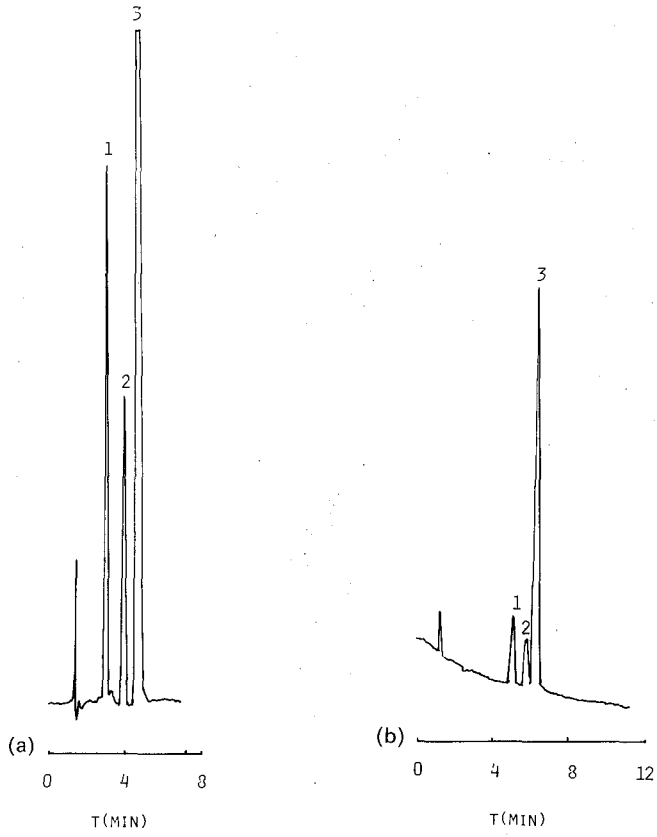

FIGURE 6 Chromatograms of a mixed standard. (1) chloride 5 ppm, (2) bromide 0.5 ppm, (3) nitrate 5 ppm. (a) eluent: methanesulphonic acid 0.02 M; pH = 4.5. (b) eluent: sodium perchlorate 0.002 M; pH = 5.4. Flow-rate: 2 ml/min; sample size: 100 μl; sensitivity: 0.0025 a.u.; wavelength: 190 nm.

photometry. The concentrations mentioned in these chromatograms correspond to 2.96, 0.59, 1.50 and 15.71 $\mu g\,Nm^{-3}$ for chloride, bromide, nitrate and sulphate respectively.

Similar concentrations of chloride and nitrate were found in both methods, as can be seen in Table V. This table includes the differences in using direct and indirect photometry with samples collected during the same week.

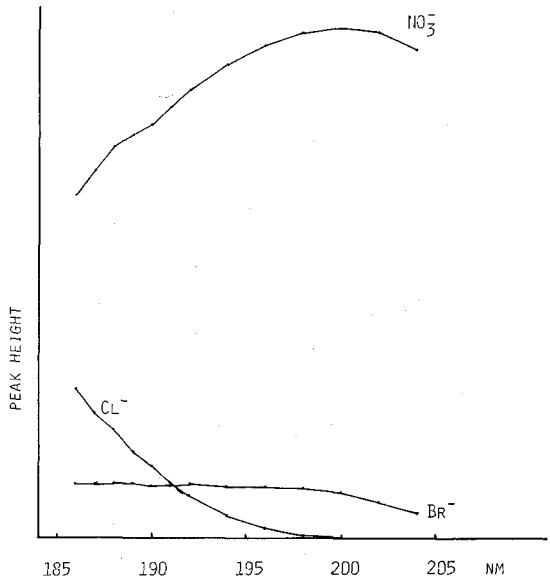

FIGURE 7 Plot of peak high versus wavelength. (1) chloride 5 ppm, (2) bromide 0.5 ppm, (3) nitrate 5 ppm.

TABLE V

Determination of chloride and nitrate anions.

	Chloride (ppm)		Nitrate (ppm)	
Sample	Direct	Indirect	Direct	Indirect
Direct photometry—eluent: methanesulphonic acid 0.02 M *Indirect photometry—eluent: sodium hydrogen phthalate 0.003 M*				
1	1.44 ± 0.02	1.41 ± 0.02	5.60 ± 0.02	5.75 ± 0.09
2	3.41 ± 0.05	3.64 ± 0.05	3.29 ± 0.01	3.12 ± 0.05
3	5.47 ± 0.08	5.63 ± 0.08	8.97 ± 0.03	9.08 ± 0.15
4	2.06 ± 0.03	1.89 ± 0.03	4.48 ± 0.01	4.24 ± 0.07

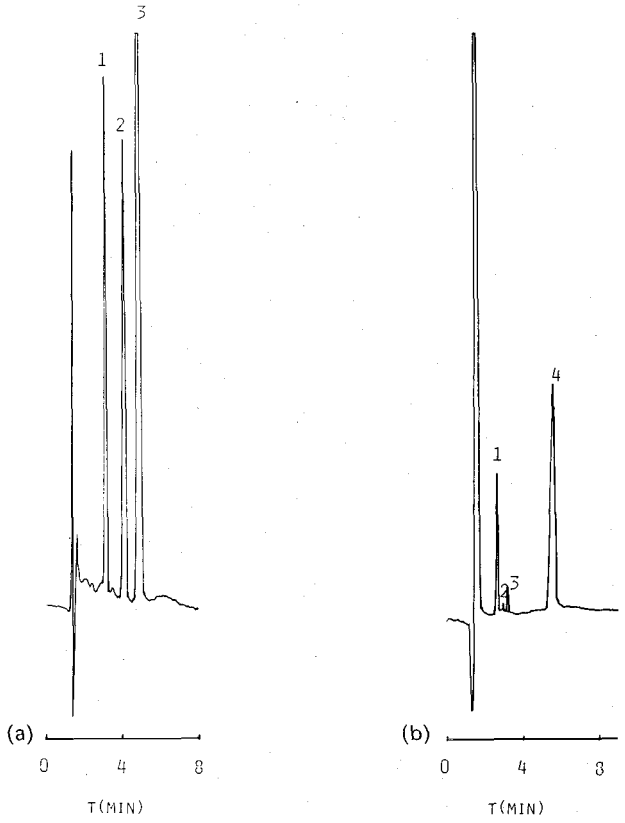

FIGURE 8 Chromatograms of a sample of atmospheric aerosol. (1) chloride 5.67 ppm, (2) bromide 0.85 ppm, (3) nitrate 2.15 ppm, (4) sulphate 22.5 ppm. Eluent: (a) methanesulphonic acid 0.02 M, (b) potassium hydrogen phthalate 0.003 M. pH: (a) 4.5, (b) 5.0. Flow-rate: 2 ml/min; sample size: 100 μl; sensitivity: 0.0025 a.u.; wavelength: (a) 190 nm, (b) 280 nm.

Figure 9 shows a typical pattern for weekly concentrations of chloride, bromide, nitrate and sulphate in particulate matter collected during the week from the 9th to the 14th December 1985. Values for total suspended particles are also presented at the top of the figure.

One final remark is that one of the major applications of the method of analysis outlined above will be found in the analysis of

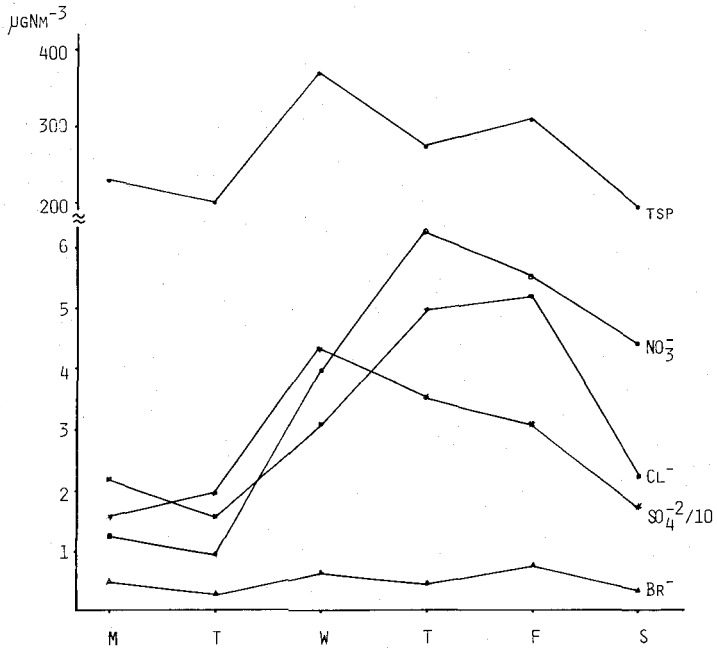

FIGURE 9 Concentrations of total suspended particulates, chloride, bromide, nitrate and sulphate collected during a week. (Note that concentration of sulphates is ten times greater than represented.)

the aerosol fractions collected from a cascade sampler. Further research is being carried out in this direction in our laboratory at the present time.

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