Journal of Chromatography, 356 (1986) 464–467
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 18 448

Note

Sensitive method for bromide determination in atmospheric aerosols

NURIA FERRER* and JUAN J. PEREZ
Dpto. de Quimica & Centro del Medio Ambiente, ETS d'Enginyers Industrials, Av. Diagonal 647, 08028 Barcelona (Spain)
(First received October 28th, 1985; revised manuscript received December 30th, 1985)

An easy and accurate determination of bromides is of great importance as this ion represents a dangerous hazard to public health. Bromides are present in the atmosphere as constituents of particulate matter, being released mainly by motor vehicles. Consequently, they usually have to be determined in the presence of nitrates, sulphates or chlorides. For this reason it is desirable to have a reliable analytical method which would facilitate the routine determination of bromide, in addition to the other ions mentioned.

Kamiura *et al.*[1] have published a sensitive HPLC method with UV detection, which provides good results. However, the method is not as precise as one might desire for bromides at very low concentrations; it can measure up to 100 ppb, and the use of an activated charcoal column to remove organic compounds adds an element of uncertainty with respect to bromide recovery.

One of us has recently developed a very sensitive method for determination of nitrites and nitrates[2] by means of ion-exchange chromatography, which yields very reliable results. The present report describes the extension of this procedure to bromide determination. It will be shown that very accurate results can be obtained, the method being simple enough to use routinely. In addition, the use of different columns and eluents has also been investigated.

EXPERIMENTAL

Ions were analyzed on an Spectra Physics 8700 chromatograph using a Spectra Physics 8440 variable-wavelength UV detector. Absorptions were measured on a Shimadzu UV-240 spectrometer. The columns used were an Ionosphere tmA (250 × 4.6 mm I.D.) (Chrompack), a Nucleosil 10 anion (250 × 4 mm I.D.) (Macherey-Nagel) and a Vydac 302 (250 × 4.6 mm I.D.). The mobile phases were sodium perchlorate (0.004–0.040 mol dm^{-3}, pH = 5.5), potassium hydrogenphthalate (0.003 mol dm^{-3}, pH 4.1) and methanesulphonic acid (0.020 mol dm^{-3}, pH = 4.4). These solutions were made up using analytical grade chemicals (Merck) dissolved in water purified by a Millipore Milli-Q system. Each solution was filtered through a 0.45-μm filter and degassed with helium.

The aerosol samples were collected over a 24-h period on a MVC high volume sampler on fibre-glass filters. The particulate matter was extracted from the filters by

0021-9673/86/$03.50

means of an ultrasonic bath using twice distilled water as solvent. The solutions were then filtered and made up to 250 cm^3 with twice distilled water. Finally, prior to injection into the column, the solutions were filtered through a 0.45-μm filter. Care must be taken during the sample preparation to prevent any contamination, given the low concentrations of bromide to be analyzed.

RESULTS AND DISCUSSION

Initially, potassium hydrogen phthalate was used as the eluent, as well as sodium perchlorate and methanesulphonic acid. Both potassium hydrogen phthalate[3–7] and methanesulphonic acid[8–11] are widely employed as eluents. Sodium perchlorate[2] has been introduced only recently into the framework of ion-exchange liquid chromatography without a suppressor column.

The eluent concentrations were varied, depending on the column. The Ionosphere and Nucleosil columns have high capacities, requiring about ten times more concentrated solutions than the Vydac column, which has a low capacity.

Phthalate was soon discarded as eluent for the present investigation as it has the drawback of strong absorption in the region where the anions absorb, about 190–210 nm. By means of indirect photometric detection, we showed that whilst the separation achieved is good, the sensitivity attainable is inadequate for the analysis of bromide in aerosols. On the other hand, this procedure allows the determination of sulphates, not attainable by direct photometry due to their lack of absorption in the range mentioned.

By using sodium perchlorate and methanesulphonic acid, which have low absorbence in the region where the anions absorb, with the exception of sulphate, the analysis could be done by direct photometric detection, at the absorption maximum of bromide at 190 nm, where the highest sensitivity is achieved (Fig. 1).

We shall now discuss the results for the different eluents employed.

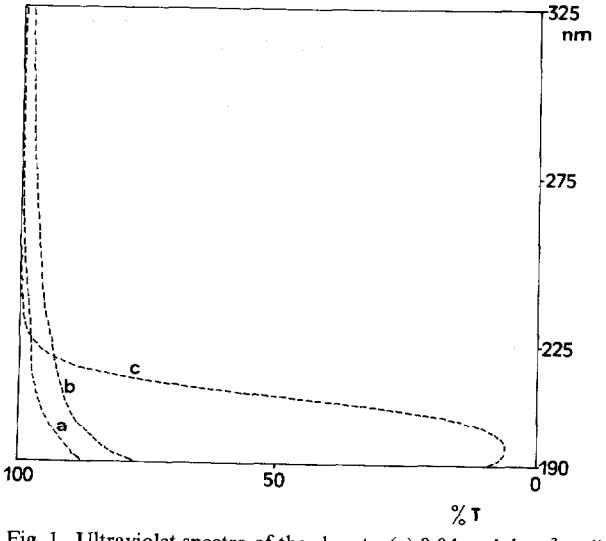

Fig. 1. Ultraviolet spectra of the eluents: (a) 0.04 mol dm^{-3} sodium perchlorate; (b) 0.2 mol dm^{-3} methanesulphonic acid (pH = 4.4 with sodium hydroxide); (c) 10 ppm potassium bromide.

Methanesulphonic acid

The Ionosphere and Nucleosil columns require high eluent concentrations (0.2 mol dm^{-3}) to separate the anions in a relatively short time, and although their detection with good resolution and sensitivity is possible, the use of relatively concentrated eluents considerably decreases the life time of the columns. In the case of the Vydac column, the optimum eluent concentration is 0.02 mol dm^{-3}. The resolution and sensitivity are very good in this case. Table I shows the retention times for the different anions on a Vydac column. The detection limit is 1 ppb* with a relative standard deviation of 1.7% for 100 ppb and $n = 10$.

TABLE I

EFFECT OF THE ELUENT CONCENTRATION ON THE RETENTION TIME USING DIFFERENT COLUMNS

The flow-rate was 2 cm^3 min^{-1} for all columns except Nucleosil, for which it was 1.5 cm^3 min^{-1}. pH was 4.1 for potassium phthalate, 5.5 for sodium perchlorate. For methanesulphonic acid the pH was kept at 4.4 using sodium hydroxide.

Eluent	*Column*	t_R *(min)*				*Detection limit (ppb)*
		Cl^-	NO_2^-	Br^-	NO_3^-	
Methanesulphonic acid (0.020 mol dm^{-3})	Vydac	4.4	6.6	7.2	9.9	1
Sodium perchlorate (0.040 mol dm^{-3})	Ionosphere	3.5	4.0	4.5	4.8	1
(0.020 mol dm^{-3})	Nucleosil	5.3	6.3	6.8	7.3	1
(0.004 mol dm^{-3})	Vydac	4.4	5.5	5.5	6.3	

Sodium perchlorate

The nitrite and bromide ions cannot be separated by using the Vydac column. This could be done by using lower eluent concentrations but the analysis times would increase considerably. The Ionosphere and Nucleosil columns gave better resolution and good sensitivity. Nevertheless, poorer resolution than with methanesulphonic acid as eluent is observed. These results are shown in Table I. The detection limit achieved in this case is 1 ppb with a relative standard deviation of 1.4% for 100 ppb and $n = 10$.

Application to the determination of bromides in particulate matter

Bromide from several samples of particulate matter, collected over a 24-h period, was analyzed. As stated above, the extraction was carried out, using an ultrasonic bath, for 15 min using twice distilled water as solvent. The mean ion concentrations found were 1.5 $\mu g\ m^{-3}$ for chlorides, 0.01 $\mu g\ m^{-3}$ for nitrites, 0.3 $\mu g\ m^{-3}$ for bromides and 6 $\mu g\ m^{-3}$ for nitrates.

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

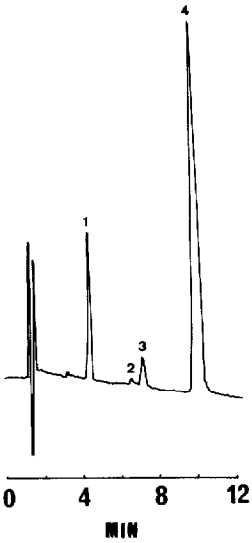

Fig. 2. Chromatogram of particulate matter extracted from a fibre-glass filter by means of an ultrasonic bath. Mobile phase: 0.02 mol dm^{-3} methanesulphonic acid. Column: Vydac. pH: 4.4 (with sodium hydroxide). Flow-rate: 2 cm^3 min^{-1}. Sensitivity: 0.0025 u.a.f.s.; attenuation, 1024. Sample size: 100 mm^3. Wavelength: 190 nm. Peaks: 1 = chloride (5 ppm); 2 = nitrite (0.02 ppm); 3 = bromide (0.3 ppm); 4 = nitrate (6 ppm).

As discussed above, due to the low bromide concentrations in comparison with the other anions, only the direct photometric technique can be used. Fig. 2 shows a typical chromatogram for particulate matter using methanesulphonic acid as eluent on a Vydac column; these conditions correspond to the best found, as shown in Table I.

REFERENCES

1 T. Kamiura, Y. Mori and M. Tanaka, *Anal. Chim. Acta*, 154 (1985) 319–322.
2 L. Eek and N. Ferrer, *J. Chromatogr.*, 322 (1985) 491–497.
3 K. O. Heisz, *GIT Fachz. Lab.*, 27 (1983) 596–600.
4 R. A. Cochrane and D. E. Hillman, *J. Chromatogr.*, 241 (1982) 392–394.
5 J. A. Hern, G. K. Rutherford and G. W. VanLoon, *Talanta*, 30 (1983) 677–682.
6 D. R. Jenke, P. K. Mitchell and G. K. Pagenkopf, *Anal. Chim. Acta*, 155 (1983) 279–285.
7 A. L. Heckenberg and P. R. Haddad, *J. Chromatogr.*, 299 (1984) 301–305.
8 J. P. Ivey, *J. Chromatogr.*, 267 (1983) 218–221.
9 G. P. Ayers and R. W. Gillett, *J. Chromatogr.*, 284 (1984) 510–514.
10 P. E. Jackson, P. R. Haddad and S. Dilli, *J. Chromatogr.*, 295 (1984) 471–478.
11 P. R. Haddad and A. L. Heckenberg, *J. Chromatogr.*, 318 (1985) 279–288.