CHROM. 11,755

Note

Determination of bromide in water by gas chromatography

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(Received February 6th, 1979)

The determination of trace amounts of bromide in water is a considerable problem, the removal of several interfering agents is often necessary. It is well known that the phenol red method[1] for the determination of Br⁻ in drinkable water can be applied to coloured or/and turbid samples only if preliminary treatments are carried out. Similar difficulties also arise when selective electrodes are used in a complex aqueous solution.

In this work, a simple and sensitive method for the determination of trace amounts (down to 0.05 ppm) of Br⁻ in water is reported. The procedure consists of two stages. The first is described by the well known reaction

$$Br^- + 2Cl_2 + 2CN^- \rightarrow BrCN + ClCN + 3Cl^-$$
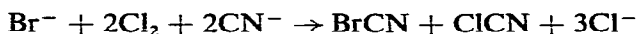
recommended by Schulek and Pungor[2]. In the second stage, cyanogen bromide (BrCN) is separated by gas chromatography and selectively detected with an electron-capture detector.

EXPERIMENTAL

Reagents

Potassium bromide, thiocyanate and cyanide and nitromethane were Carlo Erba (Milan, Italy) products of analytical-reagent grade. Chlorine water was prepared by passing through water the chlorine gas produced by reaction between hydrochloric acid and manganese dioxide (Carlo Erba).

Gas chromatograph

A Fractovap Model GI gas chromatograph (Carlo Erba) equipped with an electron-capture detector (nickel-63 source) was used. The column was made oi

borosilicate glass (1 m × 0.3 cm I.D.) and was packed with Porapak Q (80–100 mesh) (Waters Assoc., Milford, Mass., U.S.A.). Nitrogen was used as the carrier gas at a flow-rate of 50 ml/min. The injector and detector temperatures were kept at 120° and 150°, respectively. The retention times of cyanogen bromide and nitromethane (internal standard) were about 4 and 7 min, respectively. The oven temperature was 100°.

Preparation of sample

A known volume of sample, not exceeding 5 ml and containing not less than 0.5 and not more than 10 μg of Br$^-$, was placed in a 10-ml measuring flask. A 0.5-ml volume of 85% (w/w) orthophosphoric acid was added, together with 0.5 ml of freshly prepared chlorine water. After standing for a few minutes, 0.5 ml of 1 M KCN potassium cyanide solution was added. The solution was shaken throughly and then 1 ml of 5% (w/w) aqueous nitromethane solution, which served as the internal standard, was added. Finally, the mixture was diluted to 10 ml with water.

A 1-μl volume of solution was sampled with a 10-μl Hamilton syringe and immediately injected into the gas chromatograph.

Calibration graphs

A calibration graph for Br$^-$ concentrations between 0.08 and 1.0 ppm was obtained by treating, as described above, samples prepared by diluting stock solutions of potassium bromide.

As the peaks of cyanogen bromide and nitromethane are symmetrical, peak heights can conveniently be adopted in the calculations instead of the peak areas.

The calibration graph is obtained by plotting the ratio of the peak height of cyanogen bromide to that of the internal standard (nitromethane) *versus* the amount of Br$^-$.

RESULTS AND DISCUSSION

In Fig. 1 a typical gas chromatogram is shown, which was obtained by injecting a 1-μl sample of a 0.16 ppm Br$^-$ solution previously oxidized to cyanogen bromide and containing nitromethane, prepared as described under *Preparation of sample*. A calibration graph is shown in Fig. 2.

Table I gives the results of a series of measurements. The precision and accuracy of the method are illustrated by the results in the last two columns.

It should be noted that the internal standard (nitromethane) must always be introduced after the addition of CN$^-$ in order to prevent rapid darkening of the solutions, which causes non-reproducible results.

With the present method no interferences are caused by oxidizing or reducing substances or by mercury or cadmium at concentrations below 200 ppm. Mercury and cadmium are, among the metals, the strongest complex-forming agents with Br$^-$.

On the other hand, even small amounts of aromatic compounds are likely to produce some interferences owing to their tendency to bind bromine, which is formed by reaction with chlorine water.
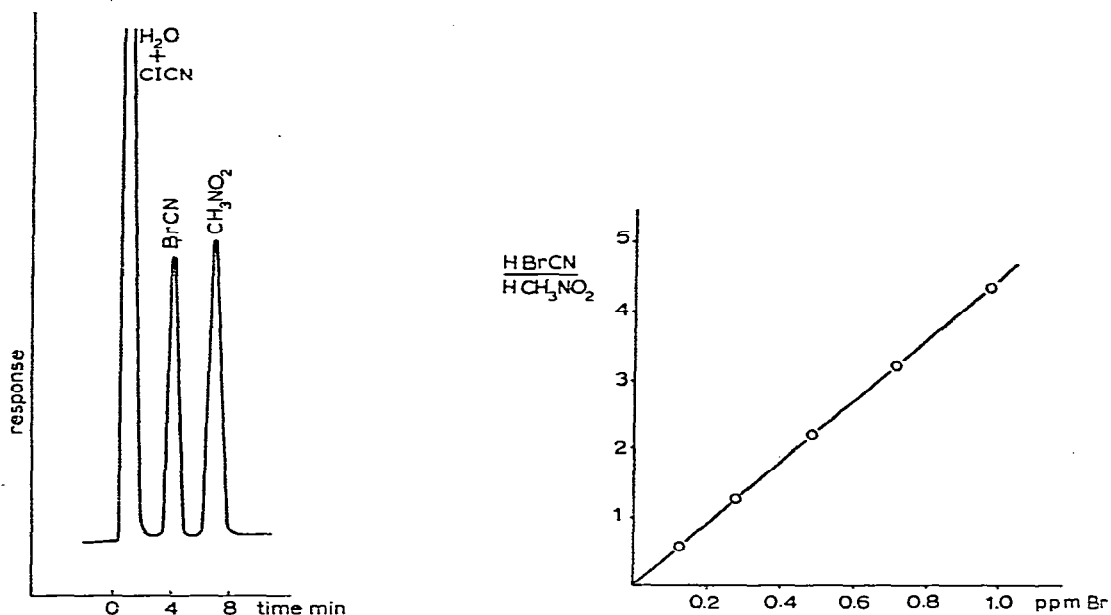
Fig. 1. Gas chromatogram obtained by injecting 1 μl of a water sample treated as described under Experimental.

Fig. 2. Calibration graph obtained by plotting peak-height ratio of BrCN to CH_3NO_2 against amount of Br$^-$.

TABLE I

RESULTS OF SOME TEST MEASUREMENTS

Amount of Br$^-$ (ppm)	No. of measurements	Average peak-height ratio ($BrCN/CH_3NO_2$)	S*	S$_r$** (%)
0.163	9	0.760	0.012	1.6
0.652	9	2.38	0.033	1.2
1.650	9	4.31	0.050	1.1

* S = absolute deviation.
** S_r = percentage relative deviation.

ACKNOWLEDGEMENT

REFERENCES

1 *Standard Methods for the Examination of Water and Waste-Water*, American Public Health Association, American Water Works Association and Water Pollution Control Federation, New York. 13th ed., 1971, p. 75.
2 E. Schulek and E. Pungor, *Anal. Chim. Acta*, 5 (1951) 137.