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Short Communication

Gas chromatographic determination of organobromine micropollutants in air and water

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ABSTRACT

A gas chromatographic method for the determination of organic halogen flame retardant compounds such as 1,1,3-tribromopropane (TBP) in the presence of bromoform and α-bromobutyric acid (BBA) in the presence of butyric acid in air and water was developed. The proposed method is appropriate; the determination limits for TBP are 0.5 $\mu g\ l^{-1}$ when sampling 20 l of air and 0.1 mg l^{-1} when sampling 100 ml of water and those for BBA are 0.2 $\mu g\ l^{-1}$ when sampling 120 l of air and 0.5 mg l^{-1} when sampling 100 ml of water.

INTRODUCTION

Organic halogen compounds (OHCs) are important chemicals in the manufacture of plastics, flame retardants, drugs, insecticides, etc. [1]. The allowable concentrations of some important OHCs such as 1,1,3-tribromopropane (TBP) and α-bromobutyric acid (BBA) have not been fixed and the determination of these compounds is not sufficiently described [2,3].

In this paper we describe a gas chromatographic method for the determination of TBP in the presence of bromoform and BBA in the presence of butyric acid in air and water. For sampling of air pollutants solid adsorbents were used and water samples were concentrated by liquid–liquid extraction.

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EXPERIMENTAL

Instruments

A Biochrom I Model 7 and a Tsvet 152 gas chromatograph equipped with a flame ionization detector were used. The columns used (glass) were as follows: (A) 3 m × 3 mm I.D. packed with 3% XE-60 on Chromaton N-Super, 100–120 mesh (Lachema, Brno, Czech Republic); (B) 3 m × 2 mm I.D. packed with 3.5% PDEAS on Chromaton N-Super, 100–120 mesh (Lachema).

Gas chromatographic conditions

For the determination of TBP column A was used. The temperatures were isothermal at 150°C for the column and 250°C for the injector and detector. The flow-rates were carrier gas (nitrogen) 30, hydrogen 30 and air 300 ml min^{-1}.

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For the determination of BBA column B was used. The temperatures were isothermal at 175°C for the column and 250°C for the injector and detector. The flow rates were carrier gas (nitrogen) 20, hydrogen 30 and air 300 ml min^{-1}. The volume injected was always 2 μl.

For the sampling of OHC air pollutants, a special glass collecting device containing solid adsorbents (silica gel, charcoal) was used, in which desorption with organic solvents also can be carried out [4].

Chemicals

Silica gel of 50–200 mesh (Lachema) and charcoal of 100–150 mesh (Reakhim, Russian Federation) were purified according to the procedure described by Paama *et al.* [4].

TBP, BBA, 1-decanol, bromoform, butyric acid and myristic acid were of analytical-reagent grade. Ethanol, diethyl ether and hexane were of pure grade and distilled before use. All chemicals were purchased from Reakhim.

The concentrations of the standard solutions (in ethanol) of TBP, 1-decanol, myristic acid were 100 μg ml^{-1} and those of BBA, bromoform and butyric acid were 10 μg ml^{-1}.

Air analysis

For the preparation of standard gas mixtures of OHC, dynamic methods developed earlier [4–7] were used. Air was drawn through the sampling device at a rate of 0.7–1.0 l min^{-1}. The micropollutants TBP and BBA were adsorbed on 150–200 mg of silica gel (in a tube). The subsequent desorption was carried out with 4 ml of ethanol. Then 1 ml of internal standard solution (100 μg ml^{-1}) was added to the solution of desorbed micropollutants and gas chromatographic analysis was carried out under the conditions described above.

Water analysis

For the determination of TBP in water, the samples (100 ml) were extracted with 4 ml of *n*-hexane, then 1 ml of internal standard (1-decanol) solution (100 μg ml^{-1}) was added and 2-μl volumes of the extracts were injected into the gas chromatograph.

For the determination of BBA in water, the samples (100 ml) were extracted (pH 2) with 4 ml of diethyl ether, then 1 ml of internal standard (myristic acid) solution (100 μg ml^{-1}) was added and the gas chromatographic analysis was carried out.

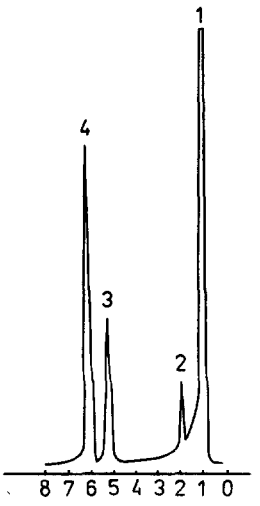

Fig. 1. Gas chromatographic separation of a solution of bromoform (2), TBP (3) and *n*-decanol (internal standard) (4) in ethanol (1). For conditions, see text. Time scale in min.

Calibration graphs for these analyses were obtained by co-injection of the analyte compounds and the internal standards.

RESULTS AND DISCUSSION

The retention times (t'_R) and separation factors (R_s) for the compounds investigated were calculated (see Figs. 1 and 2 and Table I). The results

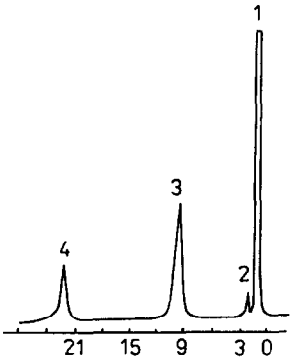

Fig. 2. Gas chromatographic separation of a solution of butyric acid (2), BBA (3) and myristic acid (internal standard) (4) in ethanol (1). For conditions see text. Time scale in min.

TABLE I

RETENTION TIMES AND SEPARATION FACTORS FOR GAS CHROMATOGRAPHIC DETERMINATION OF TBP IN PRESENCE OF BROMOFORM AND BBA IN PRESENCE OF BUTYRIC ACID

Column	Substance	Retention time, t'_R (min)	Separation factor, R_s [a]
A	(1) TBP	5.5	5.8 (1–2)
	(2) Bromoform	2.3	7.3 (2–3)
	(3) *n*-Decanol (internal standard)	6.5	1.6 (1–3)
B	(4) BBA	11.3	6.3 (4–5)
	(5) Butyric acid	1.8	9.3 (5–6)
	(6) Myristic acid (internal standard)	21.3	1.9 (4–6)

[a] Compound numbers in parentheses.

in Table I show that the separation of TBP in the presence of bromoform and BBA in the presence of butyric acid was satisfactory.

A dynamic method was developed for the preparation of a standard gas mixture of TBP, bromoform, BBA and butyric acid [4]. The diffusion tubes contained the pure compounds that were used to prepare the standards. The gas mixing system was maintained at a constant temperature (±0.02°C) for the diffusion tubes and carrier gas. Measurement of the actual diffusion rate was easily achieved. The basic principle of operation is the gravimetric measurement of the mass loss from the device. The volumetric flow through the gas mixing system was monitored using flow meters.

The concentration of TBP in the standard gas mixture was 0.44–29.48 $\mu g\ l^{-1}$ and that of BBA

TABLE II

RESULTS OF GAS CHROMATOGRAPHIC DETERMINATION OF TBP IN AIR AND WATER

Sample	Concentration of TBP in standard gas mixture ($\mu g\ l^{-1}$) or in water ($mg\ l^{-1}$)	Sample volume of air (l) or water (ml)	Measured concentration ($P = 0.95$, $n = 5$) [a]			
			$\bar{C}$	S_c	S_r (%)	$\pm\frac{tS}{\sqrt{n}}$ [b]
Air ($\mu g\ l^{-1}$)	0.44	20	0.45	0.09	0.20	0.11
	3.25	10	3.30	0.41	0.13	0.52
	7.78	10	7.72	0.83	0.11	1.03
	14.08	10	14.40	1.49	0.10	1.86
	29.48	5	29.32	2.80	0.09	3.48
Water ($mg\ l^{-1}$)	0.10	100	0.09	0.017	0.19	0.021
	0.25	100	0.24	0.03	0.13	0.040
	0.50	100	0.51	0.06	0.11	0.072
	1.00	100	1.02	0.10	0.10	0.13
	2.00	100	1.98	0.16	0.08	0.20

[a] $\bar{C}$ = Mean result ($n = 5$); C_c = standard deviation; S_r = relative standard deviation.
[b] Confidence limit.
[c] Concentration of bromoform = 5.5–10.0 $\mu g\ l^{-1}$.
[d] Concentration of bromoform = 10 $mg\ l^{-1}$.

TABLE III

RESULTS OF GAS CHROMATOGRAPHIC DETERMINATION OF BBA IN AIR AND WATER

Sample	Concentration of TBP in standard gas mixture ($\mu g\ l^{-1}$) or in water ($mg\ l^{-1}$)	Sample volume of air (l) or water (ml)	Measured concentration ($P = 0.95$, $n = 5$) [a]			
			$\bar{C}$	S_c	S_r (%)	$\pm\frac{tS}{\sqrt{n}}$ [b]
Air ($\mu g\ l^{-1}$)	0.42	100	0.40	0.048	0.12	0.06
	2.10	100	2.20	0.28	0.13	0.35
	9.20	10	9.0	0.81	0.09	1.08
	16.40	10	15.8	1.51	0.10	1.87
Water ($mg\ l^{-1}$)	0.25	100	0.24	0.034	0.14	0.04
	0.50	100	0.52	0.062	0.12	0.08
	1.0	100	0.98	0.108	0.11	0.01
	2.0	100	2.02	0.20	0.10	0.02
	4.0	100	3.90	0.35	0.09	0.04

[a,b] See Table II.
[c] Concentration of butyric acid = 5 $\mu g\ l^{-1}$.
[d] Concentration of butyric acid = 2 $mg\ l^{-1}$.

was 0.42–16.40 $\mu g\ l^{-1}$. The concentration of bromoform was 5.5–10 $\mu g\ l^{-1}$ and that of butyric acid 5.0 $\mu g\ l^{-1}$.

Satisfactory results were obtained for the determination of TBP and BBA in air (Tables II and III). The relative standard deviation was 0.09–0.20% [8].

The concentration of TBP in the water samples was 0.10–2.00 $mg\ l^{-1}$ and that of BBA was 0.25–0.40 $mg\ l^{-1}$. The concentration of bromoform in the water was 10 $mg\ l^{-1}$ and that of butyric acid was 2 $mg\ l^{-1}$ (Tables II and III). The relative standard deviation for the determination of TBP and BBA in water samples was 0.09–0.19%.

CONCLUSIONS

The proposed gas chromatographic method is appropriate for the determination of the micropollutants TBP and BBA in air and water. The determination limits for the gas chromatographic determination of TBP in the presence of bromoform are 0.5 $\mu g\ l^{-1}$ when sampling 20 l of air and 0.1 $mg\ l^{-1}$ when sampling 100 ml of water. The determination limits for the gas chromatographic determination of BBA in the presence of butyric acid are 0.2 $\mu g\ l^{-1}$ when sampling 120 l of air and 0.50 $mg\ l^{-1}$ when sampling 100 ml of water.

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