Journal of Chromatography, 196 (1980) 133–141
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 12,854

QUANTITATIVE GAS CHROMATOGRAPHIC DETERMINATION OF TRIS-(2,3-DIBROMOPROPYL)PHOSPHATE IN THE 10-ng RANGE BY USING A 0.8-mm I.D. COLUMN PACKED WITH A HIGH LIQUID LOADED SUPPORT

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(First received February 26th, 1980; revised manuscript received March 21st, 1980)

SUMMARY

Tris(2,3-dibromopropyl)phosphate (TDP), a carcinogenic flame retardant, interacts with diatomaceous supports and decomposes in a gas chromatographic column packed with low OV-1 loaded Gas-Chrom Q. However, it is possible to determine amounts of TDP at the 10-ng level with negligible decomposition by using a 50 cm × 0.8 mm I.D. column packed with 15% OV-1 on Gas-Chrom Q (100–120 mesh) and a flame photometric detector. The calibration graph is linear at levels of 15–300 ng of TDP. The effects of column temperature and flow-rate of carrier gas on the calibration graph for TDP were also studied. It was found that eight typical flame-retardant phosphates can be well separated and determined simultaneously within 30 min by using this column.

INTRODUCTION

Tris(2,3-dibromopropyl)phosphate (TDP), the most widely used flame-retardant additive for polyester fabrics and polyurethane foams, has been shown to induce tumours in the kidneys of mice and rats and to exhibit mutagenicity to *Salmonella typhimurium*[1–5]. Because of such toxicity, the Consumer Products Safety Commission in the U.S.A., followed by other countries including Japan, banned its usage for children's sleepware. Moreover, TDP has been shown to be toxic to goldfish at concentrations of about 750 ppb in water[6]. Almost 300 tons/year of TDP were produced in 1977 in Japan[7]. Hence it is important to investigate the fate of this carcinogen and its metabolites in the environment.

Several methods for the determination of TDP have been reported. Thin-layer chromatography with a silver nitrate chromogenic spray for measuring TDP in a sewage sludge was reported by Gardner[8]. However, this method was not accurate enough for the determination of TDP even at levels of 100 ng, or for the separation of TDP from other related flame-retardant phosphates, *e.g.*, tris(1,3-dichloroisopropyl)phosphate. The liquid chromatographic determination of TDP in textiles by UV detection at 254 nm has also been reported[9], but this was neither sensitive (detection limit 6.25 μg) nor specific. Surprisingly, there are no reports on the gas

0021-9673/80/0000–0000/$02.25

chromatographic (GC) determination of TDP, except for that by Gardner[8]; he stated, "These GC techniques probably have not been recommended for the quantitative analysis of TDP because of their lack of reproducibility and the instability of TDP at high GC temperatures".

We also noticed this phenomenon and found it to be due mainly to solute–support interactions. These interactions cause adsorption and/or decomposition of the solute, especially in trace analysis with a non-polar liquid stationary phase[10]. The elimination of support activity has been effected in a number of ways, *e.g.*, vapour phase deposition of Carbowax 20M in the case of organophosphorus pesticides[11], and repeated injection of a small amount of water followed by repeated injection of Silyl-8 column conditioner in the case of abscisic acid methyl ester[12].

In this paper, we report a feasible means of determining TDP at the 10-ng level with negligible decomposition by using a 0.8-mm I.D. column packed with a high liquid loaded support.

EXPERIMENTAL

Materials

Tris(2,3-dibromopropyl)phosphate (TDP), tris(2-chloroethyl)phosphate, tris-(chloropropyl)phosphate, tris(1,3-dichloroisopropyl)phosphate and tris(*m*- and *p*-cresyl)phosphate were purchased from Tokyo Kasei (Tokyo, Japan). Triphenyl-phosphate and tris(*o*-cresyl)phosphate were obtained from Takeda (Osaka, Japan) and Daihachi (Osaka, Japan), respectively. These materials were of technical grade and were used without purification. Standard solutions were prepared by dissolving each phosphate in acetone and a 1-μl aliquot of the solution was injected into the gas chromatograph. Ethanol is not recommended as the solvent, because it accelerates the decomposition of TDP in the GC column.

Apparatus and procedure

The gas chromatograph was a Shimadzu GC-4CM-PF equipped with a flame photometric detector (filter, at 526 nm). Unless stated otherwise, the conditions were as follows: injector and detector temperature, 260°C; column temperature, 225°C; carrier gas, nitrogen maintained at a flow-rate to give a retention time of TDP of 6.0 min; hydrogen flow-rate, 120 ml/min; air flow-rate, maintained so as to give the maximal sensitivity for TDP (in general, 80–90 ml/min). No special precautions were taken in connecting a U-shaped column of I.D. 0.8 mm (O.D. 4.9 mm) and length 50 cm to the chromatograph, and an ordinary glass insert tube of length 9 cm and I.D. 3 mm was used.

Various packings were prepared by standard solution coating method with dichloromethane. Glass columns of various lengths and diameters were packed with gentle vibration and a vacuum and conditioned overnight at 250°C with a slight flow of nitrogen. The columns tested are listed in Tables I and II.

RESULTS AND DISCUSSION

Choice of liquid phase

A high column temperature (above 200°C) is necessary for the GC of TDP

TABLE I

LIQUID PHASES AND RETENTION TIMES OF SOME FLAME-RETARDANT PHOSPHATES

Glass columns of 3 mm I.D. were used. Column length: 1.5 m for Nos. 1, 2, 3 and 1.0 m for No. 4. Support: Gas-Chrom Q (80–100 mesh).

Column No.	*Liquid stationary phase*	*Column temperature (°C) and programming rate*	*Flow-rate (N_2, ml/min)*	*Retention time (min)**			
				A	*B*	*C*	*D*
1	2% OV-1	120–270 (4°C/min)	60	9.8	11.0	21.8	34.0
2	3% QF-1	150	60	10.6	10.0 11.3 12.5		
3	1.5% OV-1 + 2% QF-1	150–215 (2°C/min)	200	6.0	5.7	21.9	58.6
4	2% Silar 5CP	165–230 (5°C/min)	80	7.2	4.3	14.9	—**

* Compounds: A = tris(2-chloroethyl)phosphate; B = tris(chloropropyl)phosphate; C = tris(1,3-dichloroisopropyl)phosphate; D = tris(2,3-dibromopropyl)phosphate (TDP).

** TDP was not eluted.

because of its low volatility; therefore several silicone polymers with different polarities were tested as liquid stationary phases. The results of preliminary tests on four flame retardants are summarized in Table I. Tris(2-chloroethyl)phosphate and tris(chloropropyl)phosphate had almost identical retention times on 3% QF-1. On 2% Silar 5CP, TDP was not eluted. Although the phosphates were well separated on both 2% OV-1 and 1.5% OV-17 + 2% QF-1, the retention time of TDP on the latter was too long in spite of the high flow-rate of the carrier gas. OV-1 was therefore selected as the liquid stationary phase for TDP.

Amounts of loading and packing and column performance

All of the columns listed in Table II were evaluated by comparing the peak shapes and their reproducibilities for TDP and constructing calibration graphs. Fig. 1a shows the poor shapes of the chromatograms obtained on long columns packed with the low liquid loaded support, such as column B (100 cm, 3%). In this column TDP, even in amounts as high as 790 ng, decomposed and showed no signif-

TABLE II

OV-1 COLUMNS TESTED

Column	*Amount of loading (%)*	*Support*	*Particle size (mesh)*	*I.D. (mm)*	*Length (cm)*
A	2	Chromosorb W AW DMCS	80–100	3	100
B	3	Gas-Chrom Q	80–100	3	100
C	3	Gas-Chrom Q	80–100	3	30
D	5	Gas-Chrom Q	80–100	3	100
E	10	Gas-Chrom Q	80–100	3	100
F	15	Gas-Chrom Q	80–100	3	50
G	15	Gas-Chrom Q	80–100	3	30
H	15	Gas-Chrom Q	100–120*	0.8	50

* The 100–120-mesh fraction was obtained by sieving 80–100-mesh Gas-Chrom Q coated with 15% of OV-1. This is not unusual, because the specified mesh-size ranges of commercial supports are smaller than those obtained after sieving, as stated by Cramers *et al.*[14].

icant peak, but in larger amounts (>3000 ng) TDP gave an asymmetrically leading peak. The calibration graph obtained with column B was not linear and far from the ideal line, as shown in Fig. 2. Sometimes one can prepare low loaded supports that give a performance such as that of column A (2%), which gave reasonable chromatograms, as shown in Fig. 1b; however, further conditioning of column A (at 290°C overnight) resulted in considerable deterioration of the column efficiency (Fig. 1c). On the other hand, TDP showed a symmetrical peak on the chromatogram and good reproducibility on repeated injections on columns with a higher liquid loading than 5% (Fig. 1d). On comparing the calibration graph obtained with column C (3%, 30 cm) with those obtained with columns B (100 cm, 3%) and G (30 cm, 15%) in Fig. 2, it is evident that the decomposition of TDP decreases with increasing

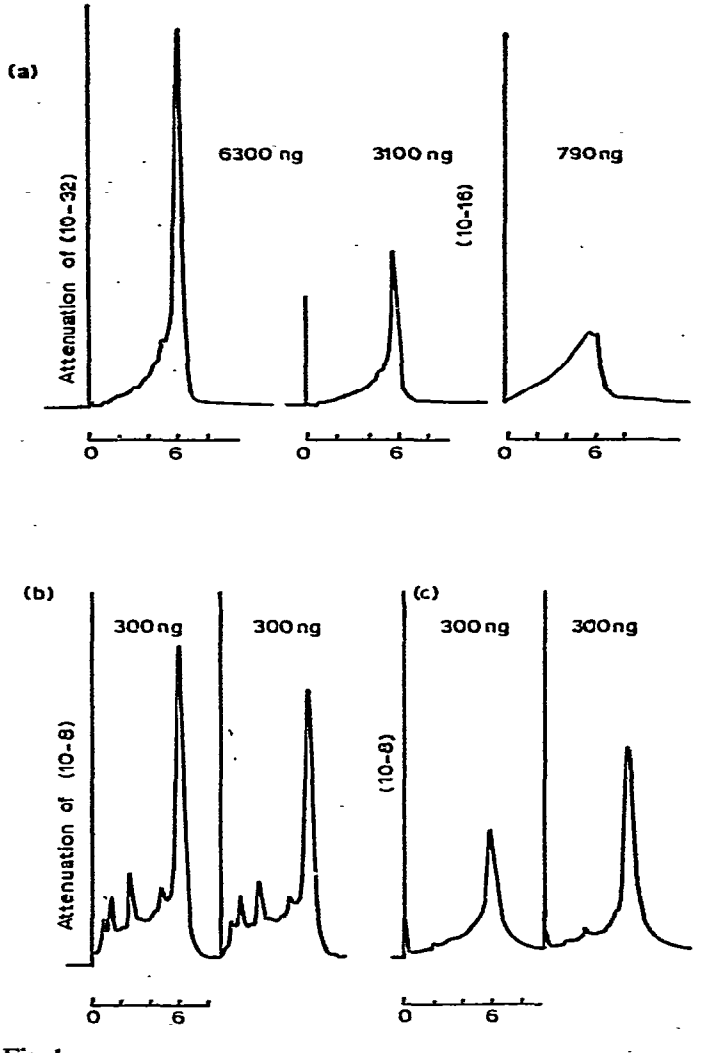

Fig. 1.

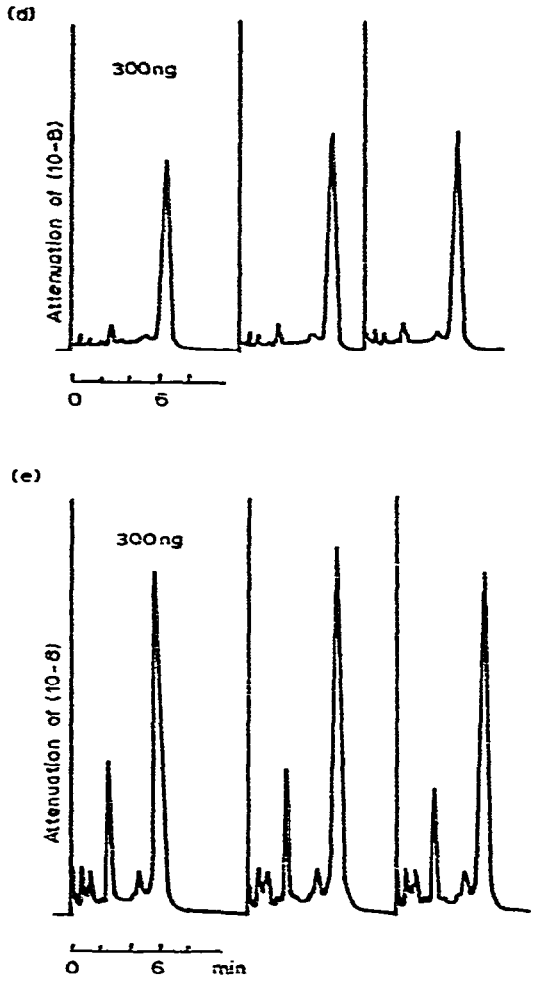

Fig. 1. Peak shapes of TDP obtained on (a) column B, (b) column A, (c) column A further conditioned at 290°C overnight, (d) column D and (e) column H (*cf.*, Table II).

amounts of liquid stationary phase and with decreasing amounts of support. These results can be explained by solute–support interactions. TDP decomposed at the active sites of the diatomaceous support, which were deactivated by the liquid stationary phase, particularly at high liquid loadings. This effect of high liquid loadings has been found to be greater with non-polar than with polar liquid stationary phases[10]. Cremer and Huber[13] also studied solute–support interactions for Chromosorb P coated with various amounts of PEG 400, using ethanol as the test material, and reported that the interaction could still be measured at 15% loading[13]. This is consistent with our finding that the calibration graph obtained with column G, as shown in Fig. 2, approached the ideal line, but is still not entirely linear.

Usefulness of 0.8-mm I.D. column packed with a high liquid loaded support

The requirement that the decomposition of TDP must be minimized by using

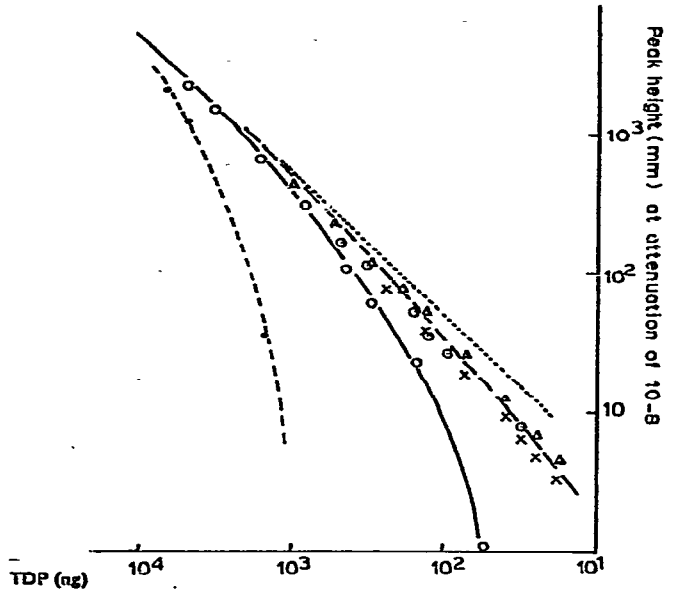

Fig. 2. Calibration graphs for TDP obtained with various columns. ----------, Ideal calibration graph; ●, column B; ○, column C; △, column D; ×, column E; ⊙, column G.

minimal amounts of high liquid loaded support results in an appreciable decrease in column performance. This paradoxical requirement led us to use a column of I.D. 0.8 mm and length 50 cm, which was called a "micro-packed column" by Cramers

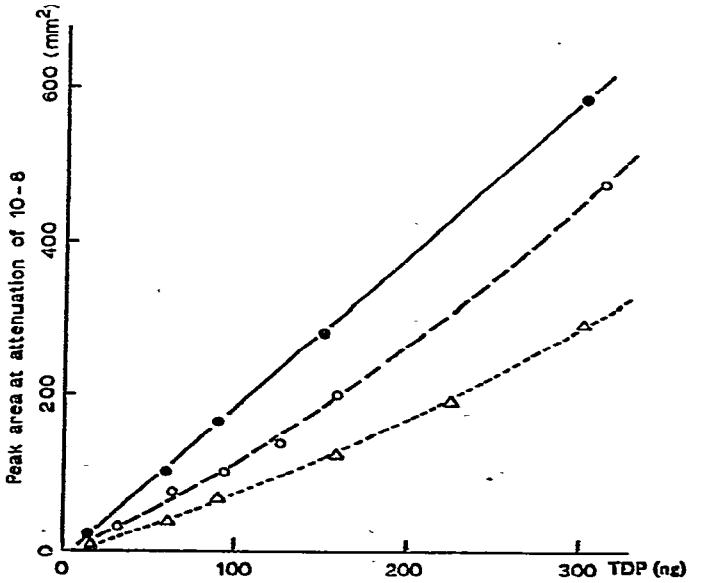

Fig. 3. Caiibration graphs for TDP obtained with 15% OV-1 columns of various sizes. ●, Column H, 50 cm × 0.8 mm I.D. (HETP 0.058 cm); ○, column G, 30 cm × 3 mm I.D. (HETP 0.12 cm); △, column F, 50 cm × 3 mm I.D. (HETP 0.15 cm).

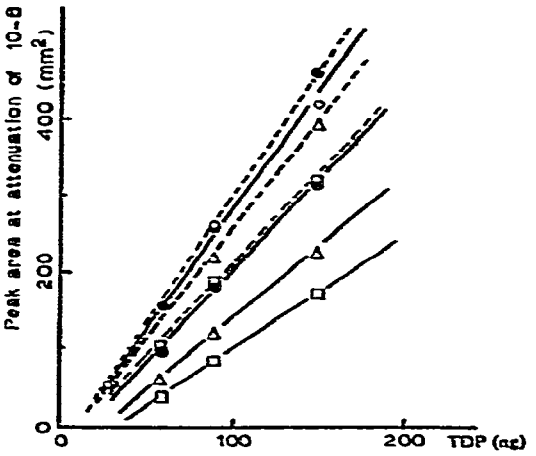

Fig. 4. Influence of column temperature and retention time on calibration graph for TDP obtained with column H. Nitrogen was maintained at a flow-rate allowing a retention time of TDP of 6.0 min (solid lines) or 3.0 min (broken lines). Column temperature: ●, 220; △, 230; □, 240; ○, 210°C.

et al.[14]. Fig. 1e shows the chromatograms of TDP obtained with column H, the micro-packed column with 15% OV-1 on Gas-Chrom Q (100–120 mesh, sieved after coating). TDP gave a sharp, symmetrical peak with good reproducibility on repeated injections. The height equivalent to a theoretical plate (HETP) with respect to TDP under the conditions used, *i.e.*, column temperature 225°C, nitrogen flow-rate 10 ml/min (retention time of TDP = 6 min), was 0.058 cm. This is a good value by normal GLC standards. The relation between the slope of the calibration graph and the volume of the column clearly shows that the decomposition of TDP decreases with decreasing amounts of support, even at the high loading of 15% (Fig. 3). The calibration graph obtained with column H is linear at levels of 15–300 ng of TDP (intersecting the abscissa at the 3–5 ng level). The minimum detectable amount was 8 ng.

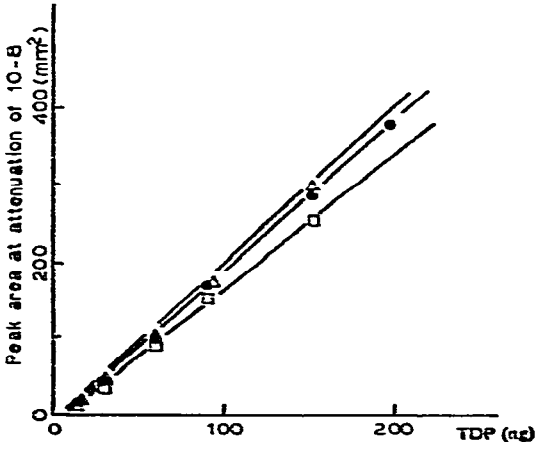

Fig. 5. Influence of column temperature on calibration graph for TDP at a constant flow-rate of nitrogen (10 ml/min) obtained with column H. Column temperature: ●, 220; △, 230; □, 240°C.

Hence it is concluded that column H is the best for determining trace amounts of TDP.

As shown in Fig. 4, the peak areas decreased with increasing column temperature and retention time, indicating that the decomposition of TDP is dependent on temperature and heating time (retention time in column). At a constant flow-rate of nitrogen (10 ml/min), as shown in Fig. 5, the calibration graphs were almost identical between 220 and 230°C because the opposing effects of temperature and retention time cancel each other.

Therefore, the recommended chromatographic conditions for the determination of TDP are as follows: 15% OV-1 on Gas-Chrom Q (100–120 mesh), 50 cm × 0.8 mm I.D. glass column, nitrogen flow-rate 10 ml/min, column temperature 225°C, injector and detector temperature 260°C, hydrogen flow-rate 120 ml/min and air flow-rate 90 ml/min.

Finally, Fig. 6 illustrates the separation of several flame-retardant phosphates using column H. They are well separated and can be determined simultaneously within 30 min under the conditions described for Fig. 6.

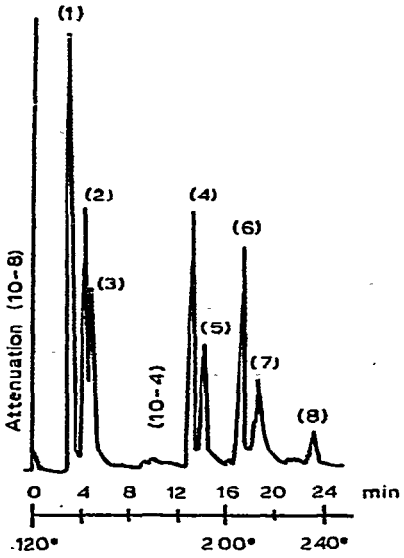

Fig. 6. Separation of a mixture of the typical flame-retardant phosphates using column H. Column temperature, 120–240°C (programmed at 5°C/min); nitrogen flow-rate, 10 ml/min; other conditions as in Experimental. Compounds: 1 = tributylphosphate (23.3 ng); 2 = tris(2-chloroethyl)phosphate (21.0 ng); 3 = tris(chloropropyl)phosphate (16.1 ng); 4 = tris(1,3-dichloroisopropyl)phosphate (18.9 ng); 5 = triphenylphosphate (9.9 ng); 6 = tris(*o*-cresyl)phosphate (21.1 ng); 7 = tris(*m*- and *p*-cresyl)phosphate (27.7 ng); 8 = tris(2,3-dibromopropyl)phosphate (TDP) (30.2 ng).

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