Journal of Chromatography, 248 (1982) 109–114
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 15,085

DETERMINATION OF TRI-*n*-OCTYLPHOSPHINE OXIDE BY CAPILLARY COLUMN GAS CHROMATOGRAPHY

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(Received June 3rd, 1982)

SUMMARY

The determination of tri-*n*-octylphosphine oxide by gas chromatography has been studied. Packed columns gave irreproducible results, probably owing to the thermolability of the compound. Moreover, tailing was observed in most systems, which might be due to adsorption. Good results have been obtained with a glass capillary column (7 m × 0.26 mm I.D.) coated with Carbowax 20M and with temperature programming starting at 140°C until 1 min after injection, then increased at 30°C/min to 240°C. Tri-*n*-nonylphosphine oxide was used as an internal standard. A coefficient of variation of 1.8% was obtained (flame-ionization detector). Less than 1 ng/ml can be determined by the use of a thermionic detector.

INTRODUCTION

Tri-*n*-octylphosphine oxide (TOPO) is a strong electron donor and proton acceptor and is therefore used as a complex-forming agent for metals and carboxylic acids, in batch extraction[1,2] and in liquid chromatography[3,4]. TOPO, dissolved in an alkane, has been applied as a liquid stationary phase in reversed-phase liquid–liquid chromatography[4]. The retention behaviour of organic acids in these systems can be described qualitatively by their complex formation with TOPO[4]. Strong indications were found, however, that the concentration of TOPO in the chromatographic system is much lower than was assumed[5]. The quantitation of TOPO was therefore of interest.

TOPO has been determined by non-aqueous titrimetry[6] and by spectrophotometry of the complex with titanium(IV) and thiocyanate after extraction into an organic phase[7]. The molar ratio between TOPO and bis(2-ethylhexyl)phosphoric acid has been estimated by electron spectroscopy (ESCA), nuclear magnetic resonance spectroscopy and mass spectrometry[8]. For the determination of TOPO in aqueous and organic solutions none of these methods is suitable. Some gas chromatographic

0021-9673/82/0000–0000/$02.75

investigations have been reported[9–13], mostly of arylphosphine oxides. Organophosphorus compounds can also be determined as phosphine by flame photometry after reduction with hydrogen and gas chromatographic separation from by-products[14].

TOPO has no chromophoric groups and is not electrochemically active. It contains, however, a phosphorus atom, which could be suitable for phosphorus-sensitive detection, *e.g.*, in combination with gas chromatography. Preliminary experiments with packed columns and various stationary phases gave unsatisfactory results, however. We found a spread of up to 10% between consecutive injections of microgram amounts of TOPO (9,10-dibromoanthracene as internal standard and flame-ionization detection). Non-polar, medium polar and many polar stationary phases gave tailing peaks. Almost symmetrical peaks were obtained only with 5% Carbowax 20M–2% potassium hydroxide. The column temperature, however, had to be kept at 250°C, owing to the high molecular weight (386) and polarity of TOPO, and the column packing rapidly deteriorated. The better chromatographic behaviour on Carbowax–potassium hydroxide might be explained by the slight basicity of the oxygen atom of TOPO.

Other experiments showed that TOPO decomposed before its boiling point was reached. The colourless liquid (melting point *ca.* 52°C) turned light yellow after 6 min at 250°C. The bad reproducibility in our preliminary experiments might be due to uncontrollable decomposition of TOPO in the gas chromatographic system.

In this paper we present conditions for the determination of TOPO by gas chromatography, using a Carbowax 20M glass capillary column and flame-ionization or thermionic detection. The use of tri-*n*-nonylphosphine oxide (TNPO) as an internal standard greatly improved the quantitation.

EXPERIMENTAL

Gas chromatographic conditions

A Varian 3700 gas chromatograph with flame-ionization and thermionic (nitrogen–phosphorus) detectors was used. It was modified with adaptors for capillary column gas chromatography[15] for split flow and make-up connections. The inlet pressure of the carrier gas (helium) was 150 kPa, giving a column flow-rate of 7 ml/min at 150°C. The make-up gas (helium) flow-rate was 20 ml/min. The detector and the injector were kept at 300 and 240°C, respectively. Air and hydrogen flow-rates for the thermionic detector were 175 and 5 ml/min, respectively.

The capillary column (soda glass) had an inner diameter of 0.26 mm. A 7 m long piece was etched twice with hydrogen chloride gas at 350°C for 3 h and was then filled with a 1% solution of Carbowax 20M in methylene chloride and left overnight. The column was subsequently rinsed with methylene chloride and coated dynamically with the same solution as above. The column ends were closed after drying and the column was baked at 250°C[16] and finally rinsed with methylene chloride.

Reagents and chemicals

Tri-*n*-octylphosphine oxide (TOPO) of zur Extraktionsanalyse grade, *n*-decane of zur Synthese grade and ethyl acetate of analytical-reagent grade were obtained from E. Merck (Darmstadt, G.F.R.), *n*-Hexane of HPLC grade from Rathburn Chemicals (Walkerburn, Great Britain) and *n*-dotriacontane from Fluka (Buchs, Switzerland).

The internal standard tri-*n*-nonylphosphine oxide (TNPO) was synthesized from *n*-nonylmagnesium bromide and phosphorus oxychloride[17]. The structure and purity were confirmed by ^{13}C NMR spectroscopy. The melting point was 41.5–42.5°C, as determined with a Büchi melting point apparatus and a temperature gradient of 2°C/min.

Determination of TOPO content of liquid chromatographic columns

The liquid stationary phases, containing TOPO, were stripped from the columns with ethanol[5] and 1 ml of the eluate was diluted with ethanol (1–5 ml) to give an expected concentration of TOPO in the range 55–175 μg/ml. A 1-ml volume of this solution was mixed with 200 μl of TNPO in ethanol (1 mg/ml) and analysed by capillary column gas chromatography with flame-ionization detection. A volume of 1 μl was injected with the split valve closed. The valve was opened after 0.8 min. The column temperature was held at 140°C for 1 min after the injection, then increased to 240°C at a rate of 30°C/min. The peak heights of the phosphine oxides were measured. The amount of TOPO in the sample was calculated from the peak-height ratio and a calibration graph. Standards were prepared from solutions of known amounts of TOPO in ethanol: 1 ml was mixed with 200 μl of the internal standard solution. They were then gas chromatographed as above.

Determination of TOPO in aqueous solutions

An aqueous phosphate buffer solution of pH 6.4 ($\mu = 0.1$) was equilibrated with a solution of TOPO in *n*-decane. After centrifugation the organic phase was discarded. A 20-ml volume of the aqueous phase was extracted with 2 ml of *n*-hexane and 100 μl of the internal standard TNPO in ethanol (2.09 μg/ml) for 30 min. A volume of 1 ml of the organic phase was evaporated to dryness using a stream of nitrogen at room temperature. The residue was dissolved in 20 μl of ethyl acetate, 1 μl of which was analysed by gas chromatography with phosphorus-selective detection. Standard samples were prepared by spiking 20-ml aliquots of phosphate buffer solution with 0–100 μl of TOPO in ethanol (2.09 μg/ml) and then treated as above.

RESULTS AND DISCUSSION

Choice of chromatographic method

Determination of TOPO using packed columns was not successful. A system with Carbowax–potassium hydroxide gave symmetrical peaks (see above), but had a short lifetime. A 30-cm short glass column with only 5 cm of chromatographic packing and a high carrier gas flow-rate gave no improvement.

The use of a short capillary column with a polar character was then investigated. A relatively high temperature and a high carrier gas flow-rate were required to elute TOPO within 10 min. The samples were introduced by splitless injections at a low column temperature, although this was only required for the determination of small amounts of TOPO, *e.g.*, in aqueous samples.

As the preliminary studies showed that TOPO might decompose at high temperatures, a solution of TOPO and *n*-dotriacontane was injected at different column temperatures. The hold-up time of TOPO was kept constant by adjusting the inlet pressure. The area ratios are presented in Table I and indicate that TOPO does not

TABLE I

INFLUENCE OF COLUMN TEMPERATURE ON PEAK-AREA RATIO

Sample: 177 μg/ml of TOPO and 117 μg/ml of *n*-dotriacontane in ethyl acetate. Volume injected: 1 μl, 3–4 times at each temperature. Splitting ratio: *ca.* 1:10.

Column temperature (°C)	*Peak-area ratio* (± S.D.)*	*t_R (TOPO)** (min)*	*Inlet pressure (kPa)*
200	0.97 ± 0.07	2.8	210
210	1.20 ± 0.05	2.6	135
220	1.03 ± 0.01	2.4	100
230	1.16 ± 0.06	2.3	65

* Peak-area ratio TOPO/*n*-dotriacontane.
** Relative retention of *n*-dotriacontane/TOPO = 0.53.

decompose under these conditions. Temperature-related decomposition would have given a lower peak-area ratio of TOPO to the hydrocarbon at 230°C compared with 200°.

Determination of TOPO content in liquid chromatographic columns

The calibration graph was linear with a small intercept (Fig. 1), which may be due to the presence of a small amount of TOPO in the internal standard. Each point

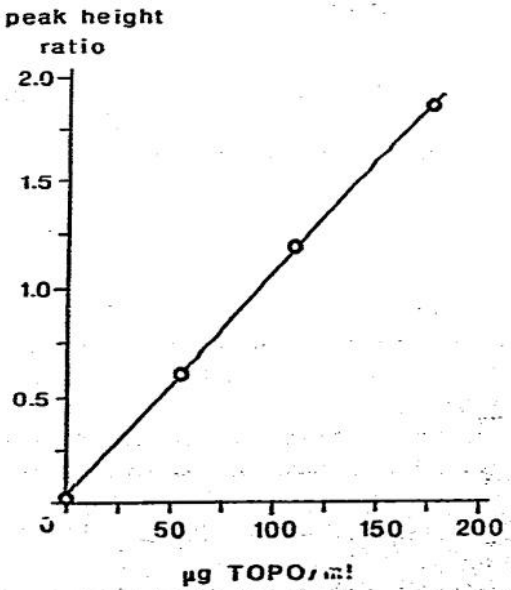

Fig. 1. Calibration graph for the determination of TOPO. Internal standard: TNPO. Column: 7 m × 0.26 mm I.D. glass capillary, coated with Carbowax 20M. Carrier gas (helium) flow-rate: 7 ml/min (at 150°C). Temperature: 140°C for 1 min after injection, then increased at 30°C/min to 240°C. Intercept: 0.039 ± 0.009, slope 0.01042 ± $8 \cdot 10^{-5}$.

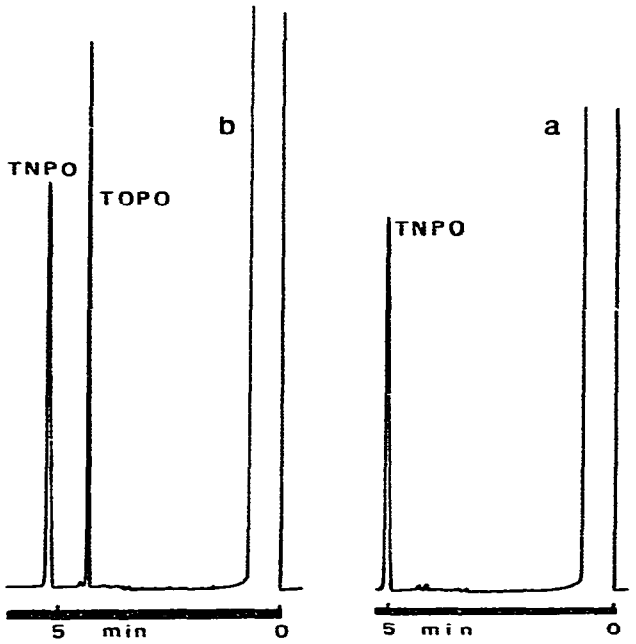

Fig. 2. Capillary column gas chromatograms of TOPO and TNPO (internal standard). (a) Blank; (b) eluate from liquid chromatographic column. Conditions as in Fig. 1.

on the graph was the mean value of eight or nine injections, except at [TOPO] = 0 (three injections). The regression coefficient was 0.999.

A sample containing approximately 25 mg of TOPO per 100 ml of ethanol was analysed five times. The coefficient of variation, including an initial 1 + 2 dilution, was 1.8%. The use of TNPO as an internal standard probably contributes to this low value. The two chromatograms in Fig. 2 illustrate a blank with only TNPO added (a) and a sample found to contain 127 μg/ml of TOPO (b). The chromatograms and the data above show that this system is well suited for the chromatographic determination of TOPO and TNPO. About 20 samples have been analysed by this method[5].

Determination of TOPO in aqueous solutions

The detection limit could be lowered by the use of a thermionic detector. Less than 1 ng/ml of TOPO could be determined in aqueous solutions after extraction into *n*-hexane and evaporation of the organic solvent. A new injection could be made every 8 min. It has not yet been possible to use this method for the determination of the partition of TOPO between an alkane, such as *n*-decane, and an aqueous buffer solution. High and varying concentrations of TOPO were measured in the aqueous phase, which might be due to the presence of small droplets of the organic phase in the aqueous solution, as a cause of difficulties in separating the phases.

ACKNOWLEDGEMENTS

We are grateful to Dr. K.-E. Karlsson and Dr. N.-O. Ahnfelt for their valuable assistance during the early stage of this work, to Dr. A. Arfwidsson for the synthesis

of TNPO, to Mr. L. Johansson for the preparation of the capillary column and to Professor J. Vessman for valuable discussions and encouragement.

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