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Note

Determination of trioctylphosphine oxide and its impurities by reversed-phase high-performance liquid chromatography

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Trioctylphosphine oxide (TOPO) always contains impurities from intermediary products used in its preparation or from secondary reactions occurring during this preparation. Most of these impurities are low-molecular-weight compounds which can be identified. They are basically on the one hand dioctylmonophosphinic acid (A1) and monooctyldiphosphonic acid (A2) and on the other hand Lewis bases such as dioctylphosphine oxide (DOPO) and dioctylphosphinate. The conditions are well known for the separation of these compounds by gas chromatography (GC) using a capillary column as mentioned by Gyllenhaal and Stuurman[1]. Although this technique is well adapted to the determination of TOPO, it is not suitable for the analysis of the two acids. Indeed, after silylation, a temperature of 300°C is required in order to separate these compounds and the results obtained are poorly reproducible because of the instability of the produced derivatives at such a temperature. A technique allowing the separation of the ionic compounds is isotachophoresis (ITP) as described by Boček *et al.*[2] for the separation of the degradation products of tributyl phosphate. We observed that it gave also good results for the separation of the A1 and A2 acids but could not be applied to separate the other non-ionic impurities or TOPO itself.

Ionizable compounds can be separated without derivatization by reversed-phase ion-pair chromatography systems which make possible the simultaneous separation of non-ionized compounds. This paper deals with the elaboration of simple high-performance liquid chromatographic (HPLC) systems which permit the separation and to determination of some of these compounds. We did not try to separate compounds of higher molecular weight which can also be identified, by liquid chromatography under modified conditions or by gel permeation chromatography (GPC), as impurities in some samples of trioctylphosphine oxide.

EXPERIMENTAL

Apparatus

The HPLC equipment was a Waters Model M740 liquid chromatograph

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equipped with a U6K injector and a R40 differential refractometer as detector. Stainless-steel chromatographic columns (4.6 mm I.D.) were laboratory made. Several column lengths and various packings of non-polar bonded silica were tested. The packing was carried out by the slurry-packing technique[3].

Reagents and samples

The compounds used for analysis were either reference compounds such as di-*n*-octylphosphinic acid (A1), *n*-octylphosphonic acid (A2), di-*n*-octylphosphine oxide (DOPO), di-*n*-octylphosphinate or a commercial sample, Merck trioctylphosphine oxide, and synthesized samples referred to as TOPO A, B and C.

Reference compounds were shown to be chromatographically pure according to the described chromatographic technique. A purified TOPO sample was obtained from a Merck commercial TOPO using the procedure described below.

The mobile phases were buffered solutions of $5 \cdot 10^{-3}$ *M* Na_2HPO_4 the pH of which was adjusted to 7.5 or 8 by addition of H_3PO_4 and to which quaternary ammonium counter ions were added. These ions were tetraoctylammonium (TOA), tetradecylammonium (TDA), tetradodecylammonium (TDDA) and cetrimide, in the form of bromides and obtained from Fluka. All solvents were HPLC grade and twice distilled water was prepared from a quartz apparatus. The mobile phases were filtered through 0.45-μm Millipore filters before use.

Selection of a detection technique

Several detection techniques were considered in order to select the one giving the best response for the whole group of compounds to be separated. UV spectra showed absorption for TOPO only at 230 nm; the absorption of other compounds was very weak even at wavelengths lower than 210 nm. Fluorescence spectra showed the existence of an excitation wavelength at 285 nm and an emission wavelength at 310 nm with all solutes, but the response was not better than the one from the UV detector. Voltamperometric curves showed that only dioctylphosphinic and monooctylphosphonic acids were reducible at about -0.8 and -0.9 V, within the limits of voltage which could be applied with the solvents used (water, methanol, acetonitrile).

Only refractometric detection could detect all the compounds for analysis and give acceptable responses, in spite of its relatively low sensitivity.

Elaboration of the chromatographic system

With the aim of separating the greatest number of compounds and considering the ionic nature of the acids to be analysed, a reversed-phase chromatographic system with a slightly basic pH and in the presence of a quaternary ammonium counter ion was chosen.

Stationary phase. Stationary phases made of bonded silica with C_{18} chains showed excessive retention for TOPO, and C_8 bonded packings were preferred. Several columns 10 and 12 cm long were packed with 5-μm particles of either LiChrosorb RP-8 or Hypersil C_8.

Mobile phase. The chosen elution phase was first adjusted for a good separation of non-ionic compounds. Using a methanol–water mobile phase a variation of the water content by a few per cent altered retentions significantly. The addition of a

small amount of methylene chloride, which is a very good solvent for TOPO and its impurities, increased the sample solubility in the mobile phase, resulted in more symmetric peaks and decreased retention times without loss of resolution. A ternary mixture, methanol–water–methylene chloride, made possible an adequate separation of all non-ionic compounds within 13 min (Fig. 1). The proportions of this mixture can be altered slightly according to the packing and length of the columns used (Figs. 2 and 3).

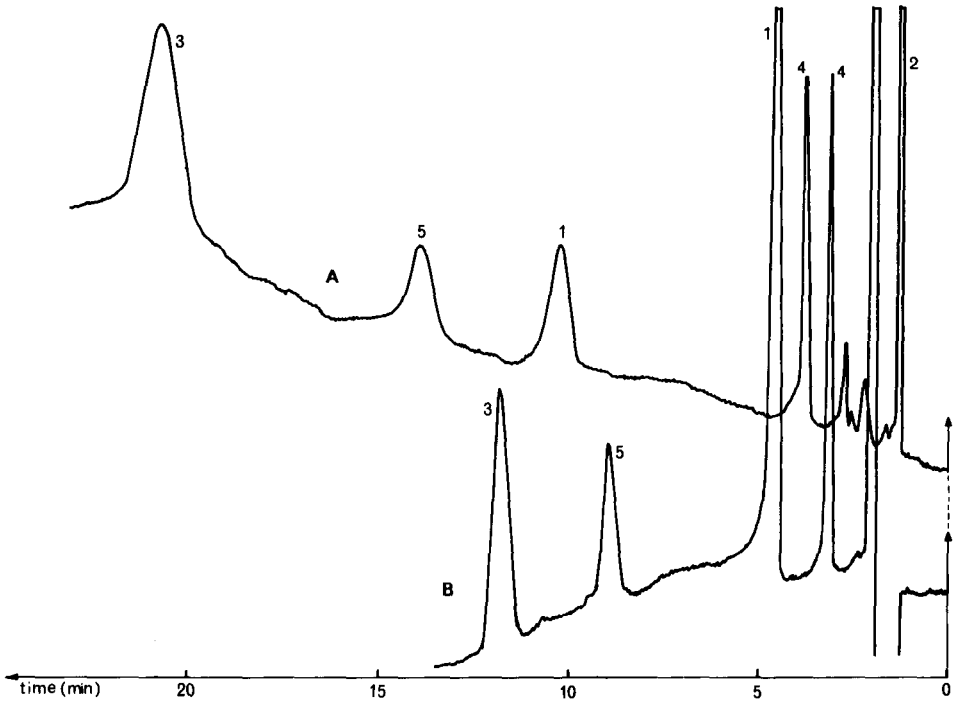

Fig. 1. Separation of a mixture of A1 acid (1), A2 acid (2), phosphinate (3), DOPO (4) and TOPO (5). Column: LiChrosorb RP-8, 5 μm, 12 cm × 4.6 mm I.D. Mobile phases: A, methanol–ammonia solution pH 8 (85:15) + TOA bromide (0.3 mg per 100 ml); B, methanol–ammonia solution pH 8–methylene chloride (85:15:10) + TOA bromide (0.3 g per 100 ml).

Selection of a counter ion. The counter ion was selected in order to achieve short enough retention times of the acids A1 and A2 without any interference from non-polar compounds. Using the mobile phase described above, quaternary ammonium counter ions with hydrocarbon chains shorter than C_8 did not enable the separation of the A2 peak from that due to the dead volume and those with C_{12} chains gave excessive retention times of the A1 acid. Counter ions with C_8 or C_{10} chains did result in separations of the different compounds, as shown in Table I and in Figs. 1–3.

However, in every case a disturbance showed up as a positive or negative peak at the retention time of the A2 acid, according to the nature and concentration of the injected solutes. This disturbance was all the more important as the injected

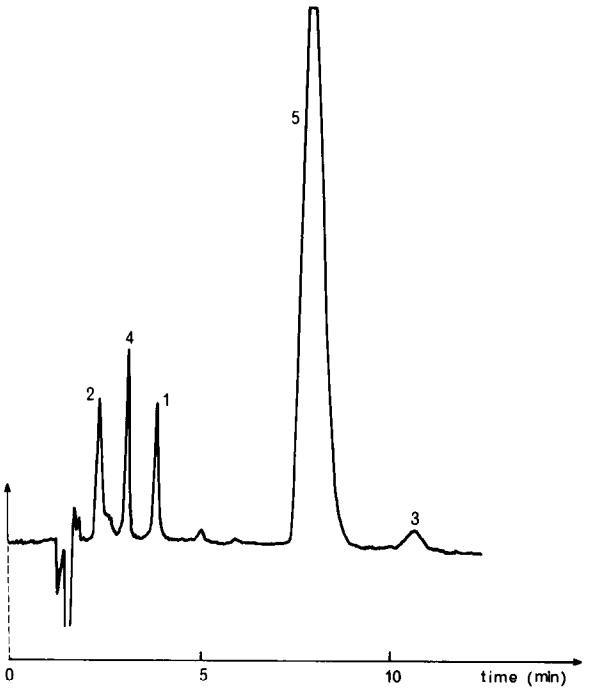

Fig. 2. Analysis of a TOPO B sample. Column: Hypersil C_8, 5 μm, 10 cm × 4.6 mm I.D. Mobile phase: methanol–phosphate buffer pH 8–methylene chloride (85:14:9) + TOA bromide (0.3 g per 100 ml). Peaks: 1 = A1 acid; 2 = A2 acid; 3 = phosphinate; 4 = DOPO; 5 = TOPO.

amount of sample was more important and prevented the determination of the A2 acid. In the presence of a counter ion with a C_{10} chain this interference extended as far as the DOPO peak (Fig. 3). Therefore the counter ion with a C_8 chain which gives sharper peaks and a better resolution was selected for the determination of DOPO, TOPO and of the A1 acid.

Influence of the ionic strength. The elution of basic compounds such as DOPO, TOPO, etc., can be improved by the use of a slightly basic pH, obtained by addition of ammonia or by means of a phosphate buffer. This increased also the ionic strength of the solution, the effect of which was to eliminate the peak tailing of acids and to decrease their retention while maintaining a good resolution. A similar effect was also observed, for the A1 monoacid at least, by maintaining the ionic strength by means of potassium bromide (Table I). These results are in agreement with the observations of Bidlingmeyer and co-workers[4,5] in regard to the influence of ionic compounds on the separation of charged species. However, in the case of the A2 acid which is very dissociated, an increase of the ionic strength by addition of KBr failed to reduce the retention.

Preparation of pure trioctylphosphine oxide

The analysis of all TOPO samples by chromatography showed that they always contained significant amounts of impurities (Figs. 2 and 3). The preparation of a purified TOPO sample which could be used as a reference compound for calibration

Fig. 3. Analysis of a TOPO A sample. Column: LiChrosorb RP-8, 5 μm, 10 cm × 4.6 mm I.D. Mobile phase: methanol–phosphate buffer pH 7.5–methylene chloride (85:15:9) + TDA bromide (0.15 g per 100 ml). Peaks as in Fig. 2.

TABLE I

INFLUENCE OF THE COUNTER ION NATURE AND OF THE IONIC STRENGTH ON RETENTION OF COMPOUNDS FOR ANALYSIS

Mobile phase: methanol–water–methylene chloride (85:15:9).

Column	*Counter ion*	*pH*	*Ionic strength (M)*	*k'*				
				A2	*A1*	*DOPO*	*TOPO*	*Phosphinate*
LiChrosorb RP-8, 5 μm, 12 cm	C_8	8.0 (NH_4OH)	–	0.64	3.03	1.13	4.72	
		8.0 (NH_4OH)	KBr, 10^{-2}	0.65	2.65	1.17	5.00	
	C_{10}	8.0 (NH_4OH)	–	1.87	6.64	1.21	5.33	
		8.0 (NH_4OH)	KBr, 10^{-2}	2.48	4.13	1.19	5.26	
	C_{12}	8.0 (NH_4OH)	–	3.74	> 10	1.03	4.43	
LiChrosorb RP-8, 5 μm, 10 cm	C_8	7.5 ($5 \cdot 10^{-3}$ *M* $Na_2HPO_4 + H_3PO_4$)		0.35	1.12	0.76	3.31	5.75
	C_{10}	7.5 ($5 \cdot 10^{-3}$ *M* $Na_2HPO_4 + H_3PO_4$)		1.30	2.42	0.95	3.65	

was carried out by preparative chromatography using a Waters PREP LC 500 apparatus provided with a radially compressed Prep-Pak cartridge with C_{18} bonded silica packing. The separation was carried out with the eluent mixture described above without counter ion and buffer in order to obtain a pure product. After evaporating the eluent, the residue gave a product in which no impurity could be detected by chromatographic analysis and mass spectrometry.

RESULTS AND DISCUSSION

Detector response and calibration

The compounds which were determined under the conditions described above are DOPO, TOPO and dioctylphosphinic acid. Calibration curves were drawn using as ordinate either the peak areas or peak heights. Actually TOPO was by far the major constituent in the sample for analysis; the amounts injected had to be large enough to enable the detection of the impurities contained therein. TOPO was then

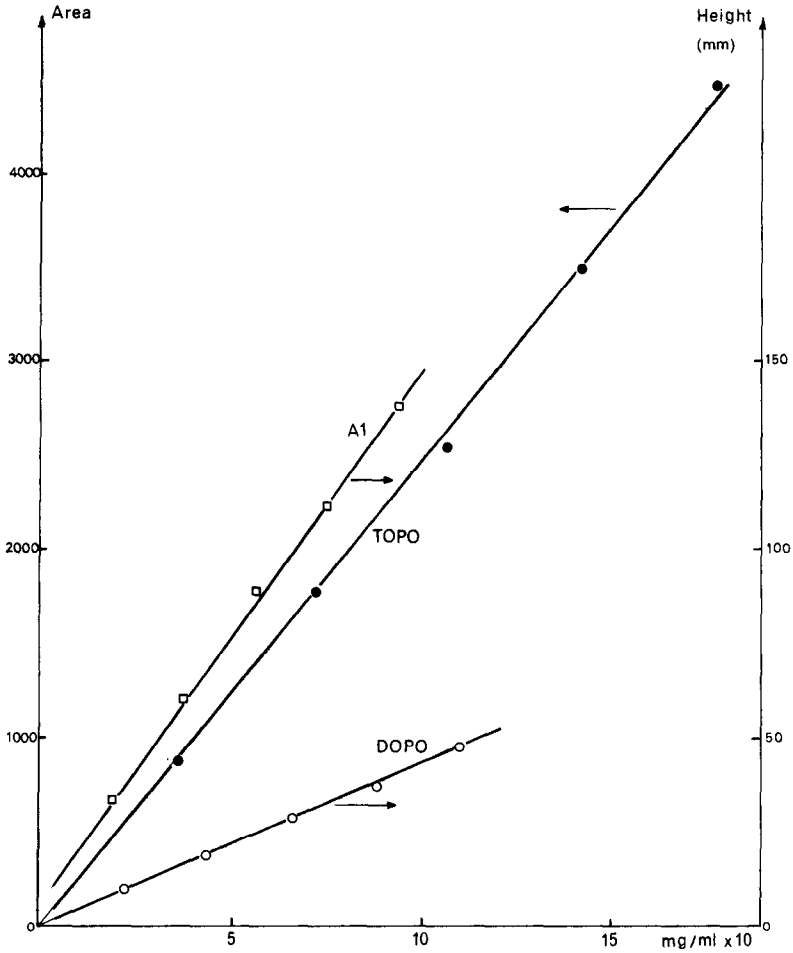

Fig. 4. Calibration curves for A1 acid, DOPO and TOPO.

eluted as a broad peak of which only the area was a linear function of TOPO concentration. For minor compounds, DOPO and monoacid A1, the dispersion of results was lower if peak heights instead of peak areas were measured. Under the above conditions the calibration curves were always straight lines and the correlation coefficients were greater than 0.99 for injected amounts varying from 0 to 25 μg for DOPO and phosphinic acid and from 0 to 0.5 mg for TOPO. Some calibration lines are shown in Fig. 4.

Reproducibility of results

Table II shows results concerning four different TOPO samples; six analytical samples were taken of each and injected twice. The table shows the mean content of each component and the corresponding standard deviation as a percentage of the mean content is 2.6% at most for TOPO and about 1% generally; even in the case of low amounts of impurities, such as a few percent, the analytical results are reproducible on the whole to within $\pm 5\%$. Considering this good reproducibility, a high value of the standard deviation suggests a lack of homogeneity of the sample.

TABLE II

PRECISION OF THE DETERMINATION OF TOPO, DOPO AND DIOCTYLPHOSPHINIC ACID (A1) IN DIFFERENT SYNTHESIZED TOPO SAMPLES

Lot	*TOPO*		*DOPO*		*Acid A1*	
	% (w/w)	*S.D. (%) (n = 6)*	*% (w/w)*	*S.D. (%) (n = 6)*	*% (w/w)*	*S.D. (%) (n = 6)*
Merck	93.8	1.1	1.80	3.3	1.08	1.85
A	83.3	1.0	5.27	1.5	2.62	7.6
B	81.8	2.6	0.71	15.5	6.5	3.8
C	94.1	1.2	2.49	2.0	1.14	5.3

Separation of monooctyldiphosphonic acid

Interfering peaks such as the one which interferes with the A2 peak are often observed and have been called ghost peaks[6], vacant peaks[7–9], induced peaks[10] or system peaks[11,12]. They have been studied extensively by Schill and co-workers[11,12] and Bidlingmeyer and co-workers[4,5]. Such a disturbance can be observed each time the mobile phase contains a compound which can give rise to an equilibrium distribution between the stationary phase and the mobile phase, so as to compete with solutes, and be detected by the detector used. This occurs generally in ion-pair chromatography with refractometric detection. Thus the observed disturbance with the same retention time as that of the TOA counter ion resulted from the displacement of the distribution equilibrium of TOA on the stationary phase. This phenomenon was most completely described by Bidlingmeyer and Warren[5] within the pattern of ionic interaction which they used to explain ion pairing. We found positive or negative peaks depending on whether the injected solutes were not very polar such as TOPO or DOPO or ionic such as phosphinic acid. It was all the more important as the amount of injected solute was important. Such a case was the analysis of

TOPO samples which required a significant amount of solute to be injected in order to obtain an adequate response for minor compounds.

As a rule it was possible to change the retention time of such a peak by altering the ionic strength[5] but the resulting variations in k' values for TOA were not great enough to obtain a better resolution between TOA and A2 acid even with 10^{-2} M KBr in the mobile phase. The use of quaternary ammonium ions with long hydrocarbon chains made it possible to increase the capacity factors (k') of acids but the retention times of such ions varies in the same way whatever the composition of the mobile phase. Among the ions tested, only cetrimide gave a proper peak sufficiently separated from the A2 peak provided the mobile phase had a low methylene chloride content. The chromatogram in Fig. 5 shows the separation obtained: the A2 peak is fully separated from the S peak of the system. The acids and TOPO were also well separated but the elution of TOPO required more than 18 min and showed significant tailing which made its determination quite uncertain.

Thus it was impossible to improve the separation of phosphonic acid and to separate distinctly the other sample components for their simultaneous analysis.

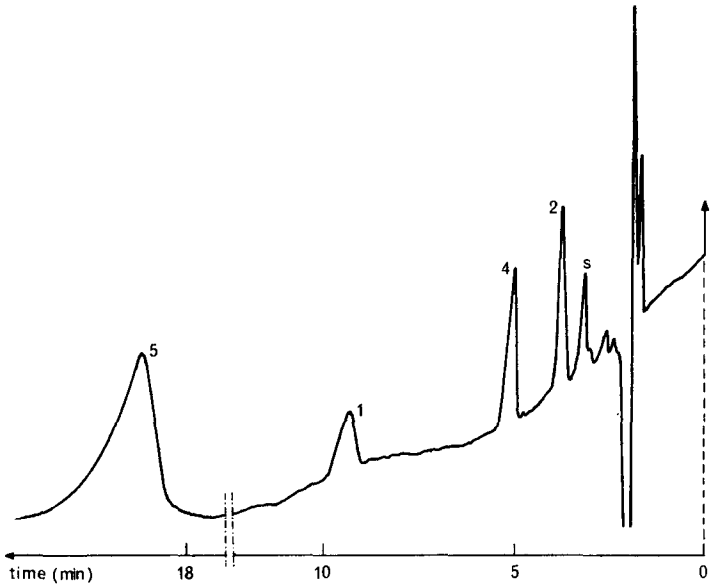

Fig. 5. Optimized separation of diphosphonic acid (A2). Column: LiChrosorb RP-8, 5 μm, 12 cm × 4.6 mm I.D. Mobile phase: methanol–phosphate buffer pH 7.5–methylene chloride (85:15:3) + cetrimide (0.5 g per 100 ml). Peaks: 1 = A1 acid; 2 = A2 acid; 4 = DOPO; 5 = TOPO.

CONCLUSIONS

The separation of TOPO and of the different impurities it contains is possible through the use of a quite simple chromatographic system and in the presence of a quaternary ammonium counter ion. However, disturbances resulting from the counter ion desorption interfere with the elution of monooctyldiphosphonic acid and make it impossible to analyse simultaneously all the sample constituents. A modifi-

cation of the eluent is necessary in order to isolate this acid completely, but this results in excessive retention times and distorsion of the TOPO peak.

As it is necessary to use a refractometric detector which alone can give convenient responses for all compounds to be analysed, one cannot employ a composition gradient of the mobile phase on a single injection for a complete analysis.

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