Gas-chromatographic analysis of tri-*n*-butyl phosphate

A gas-chromatographic method was found to be applicable for the quantitative analysis of dilute mixtures of tri-*n*-butyl phosphate (TBP), containing water and other impurities.

Normally, indirect methods[1] are used to determine the TBP content in mixtures. Mono- and di-*n*-butyl phosphates (MBP, DBP) are determined by potentiometric titration[2] or by paper chromatography[3]. Butyl alcohol is measured by its reaction with dichromate in sulphuric acid[4]. For water, either Karl-Fisher reagent is used or the weight loss is determined after evaporation under vacuum[5]. These methods are inconvenient and time consuming because each component has to be analyzed separately. The method described below (which is a programmed temperature gas-chromatographic analysis) is simple and rapid.

While this work was in preparation, BERLIN *et al.*[6] published results of isothermal gas-chromatographic analyses of several classes of organophosphorus compounds.

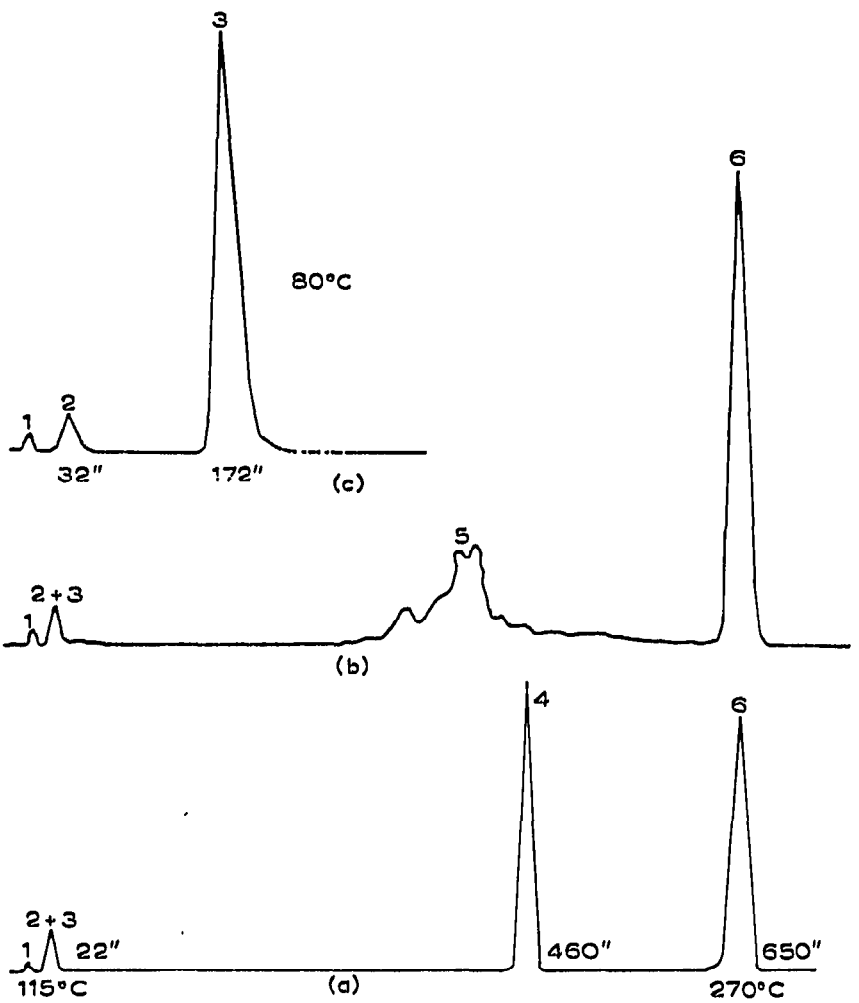


Fig. 1. Chromatographic analyses of TBP–diluent mixtures. (a) 60% v/v TBP + 40% v/v dodecane, saturated with water, 1.5 μl; (b) TBP + kerosene, saturated with water, 3 μl; (c) butyl alcohol + water, 1 μl. 1 = air; 2 = water; 3 = butanol; 4 = dodecane; 5 = kerosene; 6 = tri-*n*-butyl phosphate.

They found that TBP gave a clean, well defined peak with little or no decomposition. The conditions under which they worked differ from those described here.

Experimental

The gas chromatograph used was an F & M Scientific Corp., Model 810, with a dual thermal conductivity detector. The output signal was recorded by a 1 mV Honeywell Electronik-15 recorder, which was equipped with a Disc Chart Integrator, Model 201-B (Disc Instruments Inc.).

A column (2 m length, $^1/_4$ in. O.D.) was filled with a packing material containing 20% by wt. Apiezon-L on 60–80 mesh Diaport-S (both supplied by F & M, Scientific Corp.). The flow rate was 50 ml of helium per min, as measured by a soap flowmeter. The injector port was maintained at 250° and the detector at 265° (175 mA). The liquid samples (0.5–3.0 μl) were injected with a 5 μl Hamilton microsyringe. The column temperature was programmed from 115° (1 min) to 270° (4 min) at the rate of 20° per min.

All materials were used without further purification. TBP of different degrees of purity was obtained from J. T. Baker Chemical Co., Merck, Eastman-Kodak and Prolabo; together with TBP technical MBP and DBP were supplied by Bios Laboratories Inc., and *n*-butanol A.R. by British Drug Houses, Ltd.

Results and discussion

Typical analyses of synthetic mixtures of TBP, dodecane (or kerosene) and butyl alcohol are presented in Figs. 1a and b. A retention time of 22 sec was found

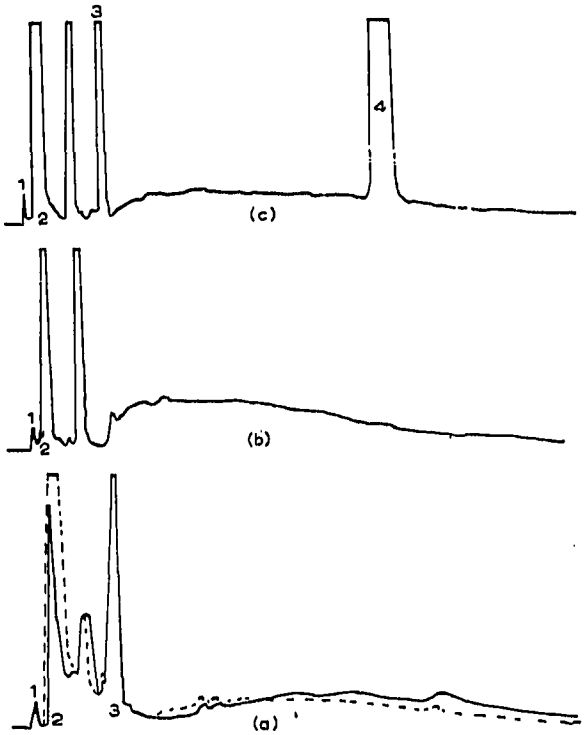


Fig. 2. Thermal decomposition of MBP and DBP. (a) DBP (1 μl), injection port at 240°, and DBP (1 μl), injection port at 290° (dashed lines); (b) MBP (1 μl); (c) 1.5 μl MBP + 1.5 μl DBP + 7 μl TBP. 1 = air; 2 = butanol; 3 = amyl alcohol; 4 = TBP.

for butanol and water, 650 sec for TBP and 460 sec for dodecane. In standard analyses where only the concentrations of TBP and the diluent are of interest, the peaks of butanol and water may remain unresolved. If the water content has to be determined, the programming should be started early, beginning at 80° (other conditions as above). This results in complete resolution of the peaks (Fig. 1c).

Thermal decomposition and very low vapour pressures do not permit the appearance of MBP and DBP peaks. Degradation products like butanol, dibutyl ether, butenes[7] and probably high-boiling hydrocarbons, are presented in Figs. 2a–c. At present the identification of all the peaks, obtained by thermal decomposition, is not quite certain. The problem is complicated by the fact that it is very difficult to obtain MBP and DBP of a high degree of purity[8]. Thermal decomposition strongly depends on the temperature of the injection port (Fig. 2a). This presents a possibility of controlling the pyrolysis by temperature programming of the injection port or by on-column injection.

The diffused and overlapping peaks of high-boiling hydrocarbons have probably little practical value for analytical purposes, but give an indication on TBP purity.

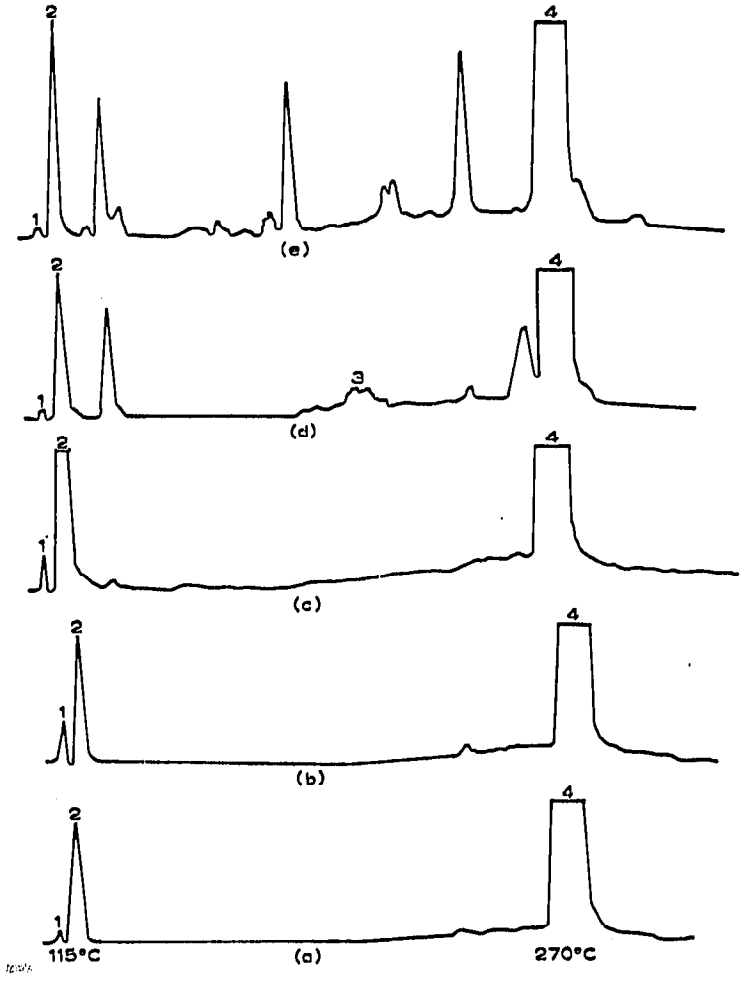
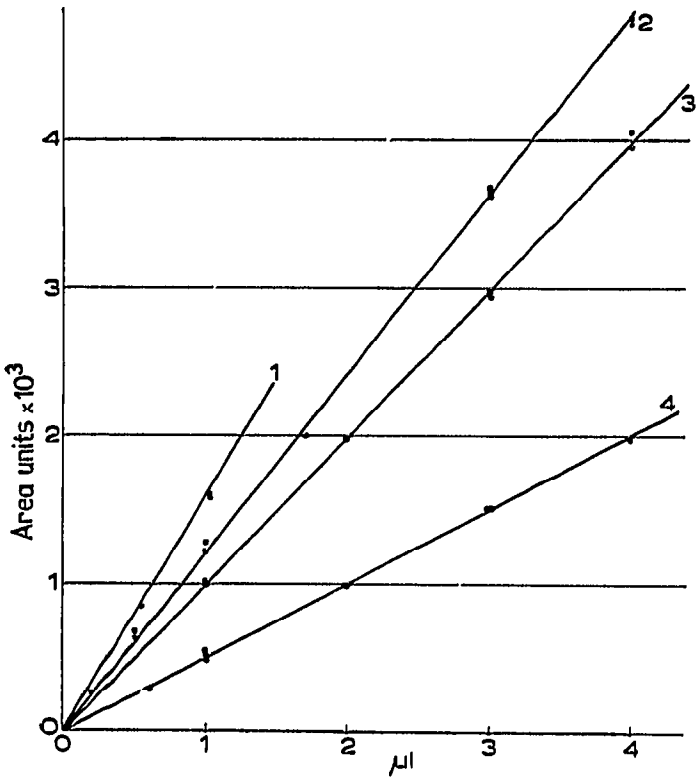


Fig. 3. Chromatograms of TBP (3 μl) obtained from several sources. (a) Baker, lot 4-170; (b) Eastman-Kodak, lot 2957; (c) Merck lot 6835, T 61823; (d) "technical"; (e) Prolabo, lot N-28726. 1 = air; 2 = butanol (+ water); 3 = kerosene; 4 = tri-*n*-butyl phosphate.

The relative purity of TBP obtained from several sources and analysed under identical conditions is presented in Figs. 3a–e.

Calibration curves (Fig. 4) for TBP, dodecane, butanol and water were prepared from synthetic mixtures. The straight lines were obtained for 0–4 μl samples. In order to present all the curves in one figure, arbitrary units of area were chosen.

Our results for solubility of TBP in water (0.39 g TBP/l at 22°) were found to be in agreement with the data compiled by McKAY AND HEALY[9] (0.39 g TBP/l at 25°, obtained by BURGER AND FORSMANN, 0.41 g TBP/l by ALCOCK and co-workers) and with those of HIGGINS, BALDWIN AND SOLDANO[10] (0.414 g TBP/l). The solubility of water in TBP–dodecane mixtures is presented in Fig. 5 and compared with data from the literature. The small discrepancies can be explained by temperature effects and by the nature of the diluents.



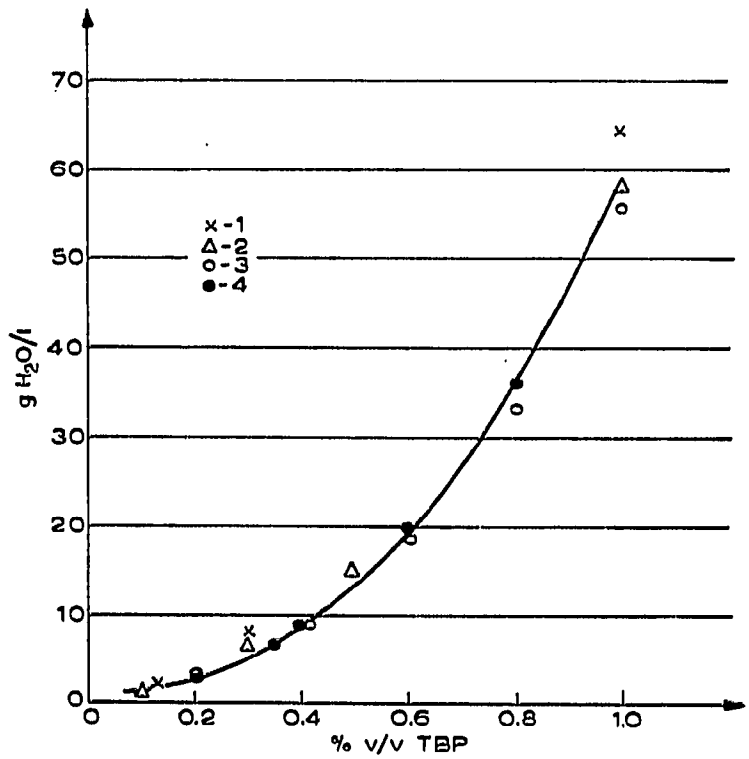


Fig. 4. Calibration curves for (1) butanol, (2) water, (3) TBP, and (4) dodecane.

Fig. 5. Solubility of water in TBP–dodecane mixtures. (1) and (2) data compiled by McKAY AND HEALY[8]; (3) ROZEN's data[12]; (4) this work.

The Apiezon-L column gives good results for analyses of TBP–diluent mixtures (TBP can be diluted not only by hydrocarbons). In addition, a TBP purification procedure[11] can be rapidly controlled by the relative indication of impurities present.

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Gas-chromatographic characterization of the electrophoretically separated fractions of acid mucopolysaccharides

Acid mucopolysaccharides can be separated by elution of columns of cellulose[1] (after precipitation with cetylpyridinium chloride), Dowex-1[2] or DEAE-Sephadex[3] with magnesium chloride or sodium chloride solutions of increasing concentration. Relatively large (about 10 mg) quantities of mucopolysaccharides are required for these methods.

Very small (5–10 μg) samples of mucopolysaccharides can be analyzed by means of cellulose acetate electrophoresis[4,5], but it has been difficult to characterize the fractions chemically.

Materials and methods

Materials. D-Glucosamine and D-galactosamine, homogenous in paper chromatography, were obtained from Mann Research Laboratories Inc., New York, N.Y., D(+)-glucose, analytical reagent grade, from B.D.H., Poole, Great Britain; galactose, *puriss.* from E. Merck A.G., Darmstadt, Germany; D(+)-glucuronic acid lactone, *puriss.* from Fluka AG, Buchs, S.G., Switzerland; hexamethyldisilazane, *purum* 98 %, and trimethylchlorosilane, *puriss.* 99 %, from Fluka AG, Buchs, S.G., Switzerland; pyridine, reagent grade, redistilled, anhydrous, J. T. Baker Chem. Co., Phillipsburg, N.J.; cetylpyridinium chloride, Recip AB, Stockholm, Sweden; oxoid electrophoretic strips, The Oxoid Division, OXO Ltd., London; Dowex-50, J. T. Baker Chem. Co., Phillipsburg, N.J.; and alcian blue, Gurr Ltd., London.

Iduronic acid was prepared from chondroitin sulphate B and was a gift from K. VON BERLEPSCH, F. Hoffman-La Roche Ltd., Basel, Switzerland.

Samples of keratosulphate and heparitin sulphate were obtained from Dr. M. B. MATHEWS, University of Chicago, Chicago, Ill., and from Prof. K. MEYER, Columbia University College of Physicians and Surgeons, New York, N.Y.

Extraction of mucopolysaccharides. The acid mucopolysaccharides were liber-