

ANALYSIS OF ALKYL ESTERS OF PHOSPHORIC ACID BY GAS CHROMATOGRAPHY

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INTRODUCTION

Mono- and di-alkyl phosphoric acids are now widely used for the extraction of metal ions from aqueous solution¹. Mono- and di-*n*-butyl phosphoric acid (H₂MBP and HDBP respectively) are of importance² in commercial processes using tri-*n*-butyl phosphate (TBP) for the separation and purification of metals, because these acidic esters are formed by radiolysis and hydrolysis and lead to reduced separation factors, deposition of metal-complexes as solids, and emulsification problems.

A rapid paper-chromatographic method of analysis of H₃PO₄, H₂MBP and HDBP in TBP has been developed previously³. This method was essentially qualitative, but was later developed^{4,5} into a method suitable for the quantitative determination of these impurities in solutions of TBP in hydrocarbon diluents.

Gas chromatography should provide a more rapid and sensitive method of analysis but the main problem in the past has been the difficulty of making these compounds migrate through the gas-liquid column owing to their low volatility and their thermal decomposition. However, gas chromatography has been used to analyse butyl nitrate⁶ and water⁷ in TBP, and alkyl hydrogen *phosphites* have been analysed⁸ directly by gas chromatography. Diazomethane has been widely used for the conversion of fatty acids to their more volatile methyl esters (see references given in review⁹). It has now been shown that mixtures of alkyl esters of phosphoric acid can be converted into their more volatile methyl esters by diazomethane and that high separation factors can be obtained in simple gas-liquid columns. The method is applicable to the analysis of impurities in TBP and also to the analysis of alkyl phosphoric acids in general.

EXPERIMENTAL

The diazomethane was obtained by the reaction of nitrosomethylurea (NMU) (supplied by Dr. E. S. LANE, Chemistry Division, A.E.R.E.) in ether with an equal volume of 40 % w/v aqueous potassium hydroxide at room temperature, followed by drying the separated ether solution with pellets of solid KOH. The solid NMU is not very stable at room temperature and was stored at 0°. A more stable reagent for future work is *p*-tolyl-sulphonylnitrosamide (available from L. Light & Co. Ltd., Colnbrook, England); an ethereal solution of CH₂N₂ can be obtained by adding an ethereal solution of the nitrosamide to warm alcoholic alkali and distilling the ethereal CH₂N₂ as soon as it is formed¹⁰.

The ethereal solution of CH_2N_2 was added to a 0.05–0.1 ml sample of the mono- or di-alkyl phosphoric acid, with or without TBP present, until the yellow colour of CH_2N_2 just persisted, indicating that an excess was present; the reaction was fast at room temperature, *i.e.* complete in less than 1 min, with the evolution of nitrogen gas. The ether and excess CH_2N_2 were removed by warming the solution and bubbling dry air through it. A sample of the remaining methyl esters, alone or with TBP present, was taken up in a calibrated hypodermic syringe and 1–10 μl injected into the gas-chromatographic column through a rubber septum.

A standard Griffin and George Mark III A gas chromatograph was used with 3 ft. \times $\frac{1}{4}$ in. diameter glass columns containing (i) 13.6 g Perkin Elmer "C" material (Dow Corning silicone DC 200 on 80–100 mesh firebrick) at 188°, 2.3 l/h helium carrier gas; (ii) 1.5 g silicone E 301 (Griffin and George Ltd.) on 6.8 g 80–100 mesh celite at 197°, 1.7–2.5 l/h helium; and hot-wire thermal conductivity detectors at the column temperature.

Relative retention volumes (referred to TBP as internal standard) were calculated from retention distances measured on the recorder chart from the maximum of the air peak to the maxima of the solute peaks. Samples of H_2MBP and HDBP were separated from a commercially available mixture³; tributyl phosphate was purified¹¹ by steam-distillation of volatile impurities from its mixture with dilute aqueous alkali, separation from the aqueous phase (which contained the sodium salts of acidic impurities), and vacuum drying. A.R. ortho-phosphoric acid was used as received. Other alkyl phosphoric acids were obtained from Albright & Wilson Ltd., Oldbury, England.

RESULTS

Separation of H_3PO_4 , H_2MBP , HDBP and TBP

Retention volumes of the various esters were measured for 2 μl samples of solutions in TBP of the methyl esters of H_2MBP , HDBP and H_3PO_4 relative to TBP = 10 (see Table I).

TABLE I
RETENTION VOLUMES (RELATIVE TO TBP = 10) OF ALKYL PHOSPHATES

	<i>Liquid phase: silicone</i>	
	<i>DC 200, 188°</i>	<i>E 301, 197°</i>
Monomethyl di- <i>n</i> -butyl phosphate	4.1	4.4
Dimethyl mono- <i>n</i> -butyl phosphate	1.6	1.9
Trimethyl phosphate (2 peaks, see text)	~ 0.4 and 0.55	~ 0.4 and 0.6
Ether	~ 0.01	~ 0.01

The water present in the methyl esters after the diazomethane reaction was not completely removed by treatment with pellets of solid KOH for 15 min, and appeared on the chromatograms as a low tailing peak between relative retention volumes 0.5 and 3.

It is interesting to note that the retention volume increases by an average factor of about 2.5 for each butyl group present. Three small sharp peaks appeared before

the trimethyl phosphate peak and were due to air, ether, and an unidentified impurity, in order of increasing retention volume. Two peaks were often obtained from the reaction of H_3PO_4 with CH_2N_2 . One was trimethyl phosphate and the other may have been dimethyl phosphoric acid or some impurity. The ratio of the two peaks obtained on treatment of a sample of H_3PO_4 with a slight excess of CH_2N_2 did not alter significantly on further treatment with CH_2N_2 . No products having low retention volumes were observed in a "blank" experiment in which a solution of CH_2N_2 in ether was (a) shaken with aqueous alkali, (b) the ether solution decanted off and dried with KOH, (c) the ether and CH_2N_2 evaporated off and (d) the residue taken up in pure TBP and a sample injected into the column. This indicates that volatile materials (which might be formed by the reaction of CH_2N_2 with CO_2 or impurities in the aqueous alkali) are not formed in the methylation of acidic phosphate esters by this method.

The feasibility of quantitative analysis of H_2MBP , $HDBP$ and H_3PO_4 in TBP

A sample of 2 μ l of a solution of $\approx 5\%$ w/w of H_2MBP and of $HDBP$ in TBP was injected into the silicone E 301 column at a temperature of 197° , a sensitivity $\times 3$, and a bridge-current of 200 mA. The areas of the peaks on the chromatogram were measured by counting squares and the weight percentage of the components calculated by the method of "internal normalisation", *i.e.* the percentage of a component is given by $100 \times$ the area of the peak for that component divided by the sum of the areas of the peaks for all the components:

Component	$\frac{\%}{w/w}$ present	$\frac{\%}{w/w}$ found
TBP	89.8	90.0
HDBP	4.9	4.9
H_2MBP	5.3	4.5
H_3PO_4		0.6

The H_2MBP contained about 10% of H_3PO_4 impurity, and the $HDBP$ a trace.

The injection of 5 μ l of a solution in TBP of 1% w/w of each of the components $HDBP$, H_2MBP , and H_3PO_4 is calculated to give peaks of the following heights (at a maximum sensitivity of $\times 1$ and 200 mA bridge current).

	TBP	HDBP	H_2MBP	H_3PO_4
Amount (%)	97	1	1	1
Peak-height (mm)	200	30	10	60

It therefore seems feasible with the present apparatus to determine 1% w/w of $HDBP$ and H_3PO_4 in TBP to about $\pm 5\%$ and of 1% H_2MBP to about $\pm 10\%$.

Experiments on other alkyl phosphoric acids and alkyl phosphates

Samples of impure mono-*n*-octyl phosphoric acid and di-*n*-octyl phosphoric acid were separately treated with diazomethane in ether and injected (with and without TBP

present) into the silicone DC200 column at 204°. The 2 μ l sample of impure mono-*n*-octyl phosphoric acid gave a main peak due to dimethyl mono-*n*-octyl phosphate and five small peaks at lower retention volumes due to unidentified impurities (one of which was probably trimethyl phosphate from phosphoric acid). The 2 μ l sample of di-*n*-octyl phosphoric acid gave one broad peak due to methyl di-*n*-octyl phosphate and a small sharp peak which could have been due to trimethyl-phosphate.

A 2 μ l sample of equal parts of tri-*n*-propyl phosphate (TPP) and TBP was chromatographed at 204° for comparison of their retention volumes and to test the pos-

TABLE II
RETENTION VOLUMES (RELATIVE TO TBP = 10) OF ALKYL PHOSPHATES

Tri- <i>n</i> -propyl phosphate (TPP)	3.7
Dimethyl mono- <i>n</i> -octyl phosphate	7.9
Methyl di- <i>n</i> -octyl phosphate	73

sible use of TPP as an internal standard for the analysis of mixtures of alkyl phosphoric acids which have components with retention volumes similar to that of TBP. The two phosphates were easily separated (see Table II).

CONCLUSIONS

Mono- and di-alkyl phosphoric acids can readily be converted to their methyl esters by treatment with diazomethane in ether. The diazomethane can be prepared from nitrosomethylurea but the use of *p*-tolyl-sulphonylnitrosamide is recommended for future work because of its greater stability. A high separation factor (2.5) can be obtained between the methyl butyl phosphates on a 3 ft. column containing silicone DC 200 at 188°, or silicone E301 at 197°.

Further work will be required to demonstrate that the diazomethane reaction is quantitative, and to obtain the optimum separation of the products by gas chromatography. The lower limit of detection will be set by the size of sample, the type of column and the type of detector employed. It is feasible to determine these impurities at the 1% level in TBP to about $\pm 5\%$ with the apparatus described, but a more sensitive detector should allow a considerable improvement on the accuracy at this level and the limit of detection.

SUMMARY

Mono- and di-alkyl phosphoric acids can be converted to volatile methyl esters by treatment with diazomethane in ether. The separation of the mixed methyl alkyl phosphates can readily be achieved by gas chromatography on a 3 ft. column of silicone DC200 on a firebrick support at 188° or silicone E301 on a celite support at 197°. The method is applicable to the quantitative analysis of mixtures of alkyl esters of phosphoric acid in TBP.

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