

Note

Simultaneous determination of tributyl phosphate and dibutyl phosphate in spent fuel reprocessing streams by gas chromatography

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In Purex-type nuclear fuel reprocessing plants, dibutyl phosphate (DBP) is mainly formed as a degradation product resulting from the deterioration of the extractant, tributyl phosphate (TBP), in radiolytic and chemical processes [1–4]. The so-called “red-oil” is known to be formed during evaporation of the solution containing TBP under certain conditions [3,5]. It has been reported, on the other hand, that the concentration of DBP in the aqueous phase is of concern in the reformation of the organic phase [6]. The rapid and sensitive determination of TBP and DBP is therefore required in order to establish their concentrations in the aqueous phase of reprocessing streams.

Gas chromatography (GC) may be most suitable method to determine rapidly trace amounts of organic compounds. Brodda and Merz [7], Ladrielle *et al.* [8] and Lee and Ting [9] have reported the application of GC to the determination of DBP. Their methods, however, require derivatization of DBP by reactions such as esterification or silylation prior to the GC determination because of the poor volatility of DBP. These operations are so tedious and time consuming that they may not be appropriate for rapid determinations.

Recently, it was found that OV-17 stationary phase coated on Tenax GC was suitable for the direct determination of dicarboxylic acids and hydroxycarboxylic acids in their underivatized forms [10,11]. In this work, GC condition including column packing materials such as stationary phase-coated Tenax GC were investigated for the simultaneous determination of TBP and DBP without the derivatization of DBP. The recovery of TBP and DBP from the aqueous phase in reprocessing streams containing fission products (FPs) or plutonium was also examined.

EXPERIMENTAL

Reagents

Standard aqueous solutions of TBP (100 ppm) and DBP (1000 ppm) were prepared by dissolving TBP (>97%) and DBP (>95%) (Tokyo Kasei) in water. Other reagents were of analytical-reagent grade.

Extraction of TBP and DBP

A 3-ml volume of sodium hydroxide solution (10%) was added to 5 ml of the aqueous solution containing the FP elements (*ca.* 50 g/l, 2 *M* nitric acid). After the precipitate had been removed by filtration, the acidity of the supernatant was made 3 *M* in nitric acid. TBP and DBP contained in the supernatant were extracted by vigorous shaking with chloroform (1:1, v/v) for a few minutes. For the solutions from the aqueous product streams of plutonium, 2 ml of sodium hydroxide solution (30%) were added to 5 ml of the sample solution containing 50–100 mg of plutonium (1 *M* nitric acid) in order to precipitate the plutonium. The other operations were as already described. All operations were carried out in a glove-box or in a radioactively shielded space (hot cave).

Gas chromatography

A Shimadzu Model GC-14A gas chromatograph equipped with a hydrogen flame ionization detector and a flame photometric detector and a Chromatopac C-R4A data processor were used. A 1.0 m × 2.6 mm I.D. glass column was packed with 5% OV-101, 5% OV-17 or 5% OV-25, and 0.5 and 1.0 m × 2.6 mm I.D. columns with 1% PEG-20M. Tenax GC (80–100 mesh) was employed as a solid support. A solution coating technique [10] was used for the preparation of the packing and column conditioning was carried out for 10 h in a stream of nitrogen carrier gas at 260°C for PEG-20M and at 270°C for the other packings. The operating conditions were as follows: column temperature, 220°C, injection port and detector temperatures, 300°C; and carrier gas flow-rate, 50 ml/min. Certain amounts of TBP and DBP dissolved in *n*-hexane or chloroform were injected into the column with a 1- μ l syringe.

RESULTS AND DISCUSSION

Comparison of columns

Table I gives the numbers of theoretical plates and the separation factors of TBP/DBP in different columns. The separation factors obtained suggest that only OV-17 and PEG-20M are suitable for the simultaneous determination of TBP and DBP. Table I also indicates that the number of theoretical plates for TBP with OV-17 was greater than that with PEG-20M, whereas that for DBP with PEG-20M was greater than that with OV-17. The retention times of TBP and DBP with PEG-20M were 3.61 and 13.44 min, respectively, whereas those with OV-17 were 5.27 and 2.47 min, respectively. This implies a reverse order of elution of TBP and DBP in the two columns. The sensitivities of DBP relative to TBP were 0.035 and 0.128 with OV-17 and PEG-20M, respectively. It can be concluded that the PEG-20M column is the most appropriate for the simultaneous determination of TBP and DBP.

TABLE I
NUMBERS OF THEORETICAL PLATES AND SEPARATION FACTORS

Column	No. of theoretical plates		Separation factor, TBP/DBP
	TBP	DBP	
OV-101	9.73	9.11	0.01 ^a
OV-17	30.73	7.53	0.73
OV-25	14.66	15.15	0.02 ^a
PEG-20M	16.07	50.00	1.81

^a TBP and DBP were not separated.

Determination of TBP and DBP

The limits of determination of TBP and DBP with flame ionization detection (FID) were 1 and 5 ng, respectively, while those with flame photometric detection (FPD) were 0.2 and 1 ng, respectively. It was found that the FID response was consistently linear over a wide range up to 10^4 ng of both TBP and DBP, whereas the FPD response showed linearity within narrower ranges, between 0.2 and 10^3 ng for TBP and between 1 and 10^2 ng for DBP. The determination of DBP with FPD, however, can give a reproducible quadratic curve with a range of 10^3 , which is sufficient for the practical requirements for DBP determinations. The relative standard deviations for seven replicate measurements of TBP and DBP were, respectively, 4.1% at 10 ng and 5.3% at 50 ng when FID was employed, whereas those with FPD were 3.2% at 10 ng and 5.2% at 50 ng. Fig. 1 shows a typical chromatogram obtained with a 1.0-m PEG-20M column.

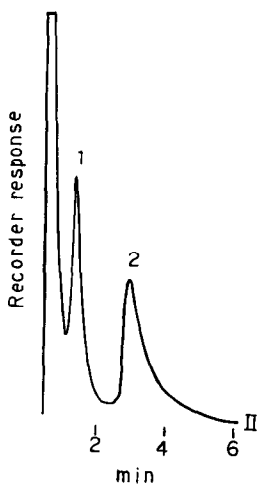


Fig. 1. Separations of TBP and DBP. Column: 1% PEG-20M on Tenax GC (1.0 m \times 2.6 mm I.D.); column temperature, 220°C; injection port temperature, 300°C; detector temperature, 300°C; carrier gas flow-rate, nitrogen 50 ml/min; hydrogen, 0.6 kg/cm²; air, 0.5 kg/cm². Peaks: 1 = TBP (10 ng); 2 = DBP (50 ng).

TABLE II
DETERMINATION OF TBP AND DBP RECOVERED FROM PRACTICAL SAMPLES

Sample	TBP added (ppm)	TBP found (ppm) ^a	DBP added (ppm)	DBP found (ppm) ^a
HALW ^{b,c} (ca. 50 g FPS/l 2 M HNO ₃)	100	94 ± 5	100	90 ± 5
Plutonium nitrate ^c (30 g/l, 2 M HNO ₃)	100	93 ± 5	100	86 ± 7

^a Mean ± average deviation for five results.

^b HALW = highly active liquid waste.

^c TBP and DBP levels originally present in the solutions were negligible.

Recovery of TBP and DBP from aqueous solutions

Previous studies suggested that the separation of DBP from TBP with chloroform was satisfactory after DBP had been back-extracted into the aqueous phase [9]. This implies that TBP and DBP dissolved in an aqueous phase may be simultaneously extracted with chloroform with high recovery. The recoveries of TBP and DBP in nitric acid solutions with a wide range of concentrations (1–6 M) were examined by the procedure given. The average recoveries for TBP and DBP within the above range were 96 ± 3% and 92 ± 6%, respectively. It was observed in the solutions

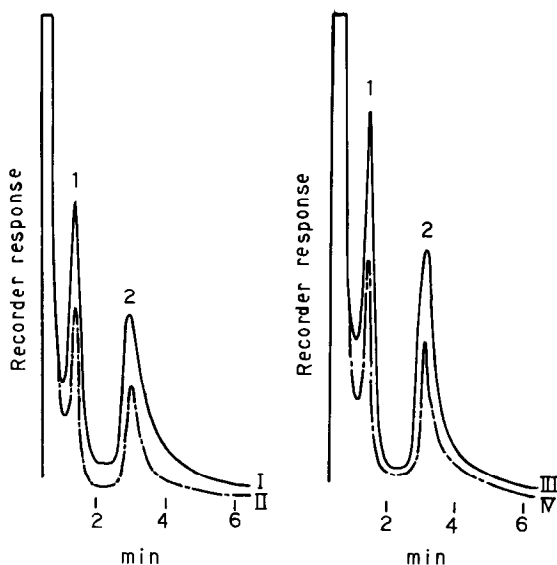


Fig. 2. Gas chromatograms of TBP and DBP recovered from practical samples. TBP and DBP were recovered from standard TBP- and DBP-added samples of HALW (I, II) and plutonium nitrate (III, IV). (I) 1 = TBP (20 ppm), 2 = DBP 100(ppm); (II) 1 = TBP (10 ppm), 2 = DBP (50 ppm); (III) 1 = TBP (30 ppm), 2 = DBP (150 ppm); (IV) 1 = TBP (15 ppm), 2 = DBP (75 ppm). Column, 1% PEG-20M on Tenax GC (1.0 m × 2.6 mm I.D.). Conditions as in Fig. 1.

from the reprocessing streams that a large portion of DBP, mainly generated as a radioactive degradation product or as a hydrolysis product of TBP, was converted into a precipitate of DBP metal complexes. This type of precipitate could also be a source of the third phase [6] during evaporation. Therefore, it is important to determine DBP contained in both the supernatant and the precipitate. The recoveries of TBP and DBP were examined in solutions including FP elements. It was confirmed that more than 95% and 86% of TBP (100 ppm) and DBP (500 ppm), respectively, were recovered from solutions including 500 ppm of Fe, Zr, Ru, Cr, Y, Se, Sr, Mo, Pd, Ag, Cs, La, Ce, Sm, Eu, Gd, Ni, Cd, Rb, Nd and Ba. This implies that good recoveries of not only TBP and DBP freely contained in aqueous solutions but also DBP contained in the precipitate of DBP metal complexes from the solutions containing various metal ions can be achieved using the proposed procedures. The results suggest that DBP present in a precipitate as a complex may be converted into free DBP by making the solutions alkaline.

Determination of TBP and DBP in practical samples

The accuracy of the method was examined by analysing practical samples to which known amounts of TBP and DBP had been added. The results are given in Table II. The values found agreed well with the amounts added. Fig. 2 shows the chromatograms of TBP and DBP including a precipitate recovered from a practical samples. The times required for one determination of TBP and DBP in aqueous solutions from highly radioactive liquid waste streams and plutonium streams were *ca.* 1 h and 40 min, respectively. It is concluded that TBP and DBP in the aqueous phase of reprocessing streams can be determined by GC without any interferences.

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