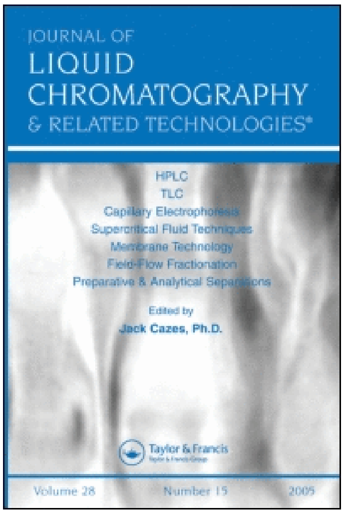

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Ion Chromatographic Determination of Dibutylphosphoric Acid in Nuclear Fuel Reprocessing Streams

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ION CHROMATOGRAPHIC DETERMINATION OF DIBUTYLPHOSPHORIC ACID IN NUCLEAR FUEL REPROCESSING STREAMS

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ABSTRACT

A rapid method has been developed for the determination of dibutylphosphoric acid (DBP), a degradation product of tributylphosphate (TBP), which is used in a solvent extraction process for recovery of uranium. DBP along with any monobutylphosphoric acid (MBP) and phosphoric acid are extracted from the organic phase into dilute sodium hydroxide. DBP is separated from MBP and phosphoric acid by ion chromatography and is determined on a peak height ratio basis. The method requires only 30 minutes per analysis as compared to the conventional alumina column separation-colorimetric determination procedure which requires 8 h to complete. DBP has been quantified to a lower limit of 1.5 mg/L. Relative standard deviations ranging from 5.7% to 0.4% were obtained for DBP concentrations ranging from 1.5 to 500 mg/L, respectively.

INTRODUCTION

Tributylphosphate (TBP) as a solution in kerosene is widely used in the nuclear fuel reprocessing industry as an extractant for the separation of uranium from reactor fuel cladding material and fission products. After separation, uranium is stripped from the TBP-kerosene phase with dilute nitric acid prior to further purification. During this process, TBP undergoes some degradation yielding mainly dibutylphosphoric acid (DBP) and lesser amounts of monobutylphosphoric acid (MBP) and phosphoric acid. DBP forms a stable complex with uranium which cannot be completely stripped from the TBP-kerosene phase with dilute nitric acid. It also forms stable complexes with fission products thus decreasing the efficiency of the uranium separation. It is therefore necessary to strip the TBP-kerosene extractant frequently with an aqueous sodium carbonate solution to minimize the build-up of DBP. A rapid, reliable method is needed to monitor the DBP content of the TBP-kerosene extractant and to evaluate the efficiency of the sodium carbonate stripping process.

Ewing et al. (1) extracted DBP from TBP-kerosene mixtures with aqueous sodium carbonate and determined inorganic phosphate after acid hydrolysis of the DBP. The method is not reliable for small amounts of DBP because of coextraction of small amounts of TBP. Wade and Yamamura (2) separated MBP and DBP from traces of TBP on an alumina column prior to colorimetric determination of the acid hydrolyzed DBP. MBP and DBP are not completely resolved by this procedure and the time required for a complete analysis is approximately 8 h. Pietri (3) determined DBP in TBP-kerosene solutions by contacting them with an aqueous uranyl nitrate solution to form the uranyl dibutylphosphate complex. The extracted uranium was then determined by fluorescence measurement. However, the uranium extraction is a function of the amount of both uranium and TBP and the method is not easily adaptable to samples containing varying amounts of these components. The separation of MBP and DBP by solvent extraction and paper chromatography was studied by Hardy and Scargill (4) and later developed into a quantitative procedure for determination of these components in TBP-hydrocarbon mixtures (5). This procedure involves determination by neutron activation analysis which is not readily available at our facility. Hardy (6) showed that alkyl phosphoric acids could be analyzed by gas chromatography of the corresponding methyl esters formed by reaction with diazomethane. Brignocchi *et al*. (7) developed the gas chromatographic method of Hardy into a quantitative procedure for the determination of MBP and DBP in various TBP-organic diluent samples. This approach appeared to be best suited for our purposes. However, the use of the potentially dangerous diazomethane led us to investigate an alternative method. More recently, MacDougall (8) reported the gas chromatographic analysis of the corresponding methyl esters formed by reaction with a dimethylformamide-dimethylacetal reagent. This procedure requires that the sample be vacuum dried overnight before reaction with the water-sensitive methylating reagent. In addition, the lower limit of detection is only 1×10^{-3} *M*.

Ion chromatography is a relatively new analytical technique which has been applied to the analysis of organic acids in solution (9). This contribution describes an ion chromatographic procedure for separation of DBP from MBP and phosphate and rapid determination of DBP in TBP-kerosene reprocessing solutions down to a lower limit of 7.1 x 10^{-6}<u>M</u>.

EXPERIMENTAL

Apparatus

The ion chromatograph used was a Model 10 unit equipped with a 3 x 150 mm pre-column, a 3 x 500 mm separating column and a 6 x 250 mm suppressor column, all available from Dionex Corp., 1228 Titan Way, Sunnyvale, California 94086.

Reagents

All chemicals were analytical reagent grade. The DBP was purified from a commercial mixture of DBP and MBP (50% DBP, 50% MBP available from Eastman Kodak) according to the method of Hardy and Scargill (4). Purity was determined by potentiometric titration (7). Kerosene was obtained from Union Oil Co., Vancouver, Washington (AMSCO Odorless Mineral Spirits P-1) and used as received. Water from a Milli Q water purification system (Millipore Corp.) was used throughout.

Preparation of Standard Synthetic Fuel Reprocessing Solutions

560 mL of a solution containing the diverse ions listed in Table 1 was extracted for five minutes with 400 mL of a 5% v/v solution of TBP in kerosene. The resulting organic phase was

TABLE 1

Diverse Ion Solution

Ion	Concentration mg/ml
U^{+6}	0.32
Zr^{+4}	58.4
Al^{+3}	16.7
B^{+3}	2.6
Cr^{+6}	0.5
F^-	81.5
NO_3^-	173.6

scrubbed with 52 mL of a solution 0.4 M in ammonium hydroxide and 0.75 M in aluminum nitrate. The organic phase was further scrubbed with 176 mL of 0.005 M nitric acid to yield Matrix A. A portion of Matrix A was further scrubbed with 28 mL of 0.04 M nitric acid to yield Matrix B. Purified DBP was then added to portions of both matrices to yield synthetic reprocessing solutions ranging from 1.5 to 500 mg/L. These solutions closely represent typical fuel reprocessing solutions that are routinely analyzed.

Procedure

Calibration standards were prepared by dissolving DBP in 0.005 M sodium hydroxide to yield concentrations ranging from 1.5 to 500 mg/L. A 5 mL aliquot of the synthetic reprocessing solution was placed in a 25 mL test tube and extracted for 1 minute with a 10 mL aliquot of 0.005 M sodium hydroxide. The tube was centrifuged to facilitate separation of the phases and after removal of the organic phase, a portion of the aqueous phase was injected into the ion chromatograph. Chromatographic conditions were as shown in Table 2. The appropriate calibration standard was then injected into the chromatograph and results were calculated by peak height ratio.

RESULTS AND DISCUSSION

The success of an ion chromatographic method for determination of DBP rests mainly on the ability to separate DBP from other base extractable components such as MBP and phosphate.

TABLE 2

Chromatographic Conditions

Eluent	0.003 M NaOH
Flow Rate	92 ml/h
Analytical Columns	3 x 150 mm Anion Precolumn
	3 x 500 mm Anion Separator
Suppressor Column	6 x 250 mm
Detector Sensitivity	Variable from 1 to 30 MHO FS depending on DBP content
Injection Volume	100 L
Regenerant	1 M H_2SO_4

Figure 1 shows an ion chromatogram of a mixture of DBP, MBP and phosphate in which the peaks are well resolved. DBP is eluted very close to the void volume and is likely to encounter interference from very weak organic acids which might be extracted from the TBP-kerosene mixtures. Conditions were changed to those shown in Table 2, which are the conditions used for the analysis of samples. As shown in Figure 2, the DBP peak is now eluted in approximately 6 minutes. MBP and phosphate elute as

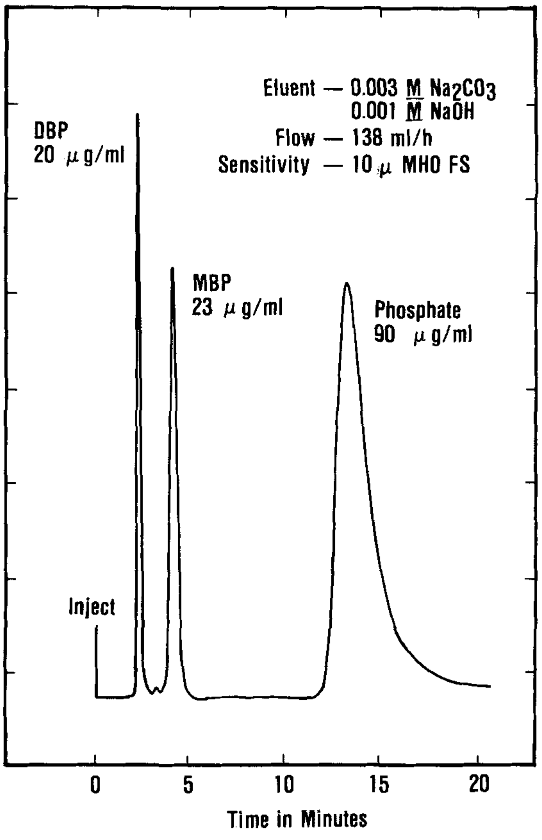

Figure 1. Separation of DBP from MBP and Phosphate

very low, wide peaks under these conditions and are detectable only as a minor baseline drift. They therefore do not interfere with later determinations. Two small side peaks can also be seen in Figure 2. The one on the trailing edge of the DBP peak was not identified. However, the one on the leading edge was tentatively identified as butyric acid resulting from the decomposition of TBP.

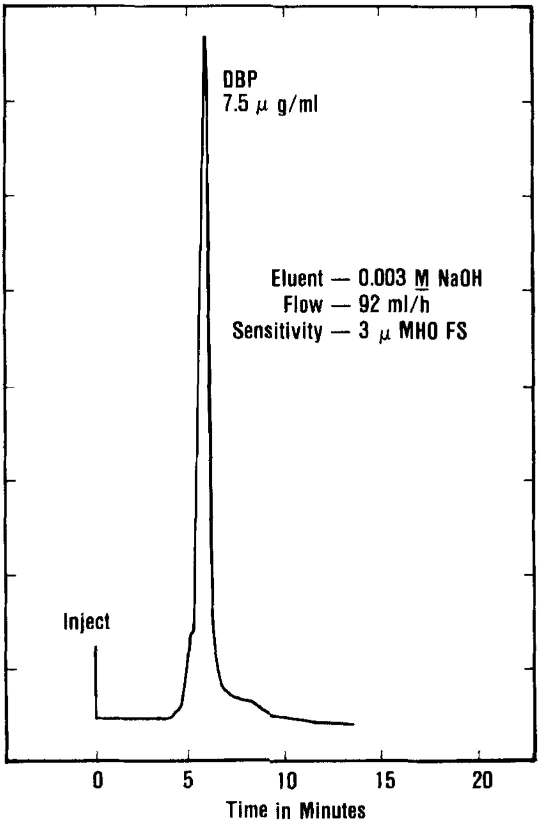

Figure 2. Typical Ion Chromatogram of 0.005M NaOH Extract

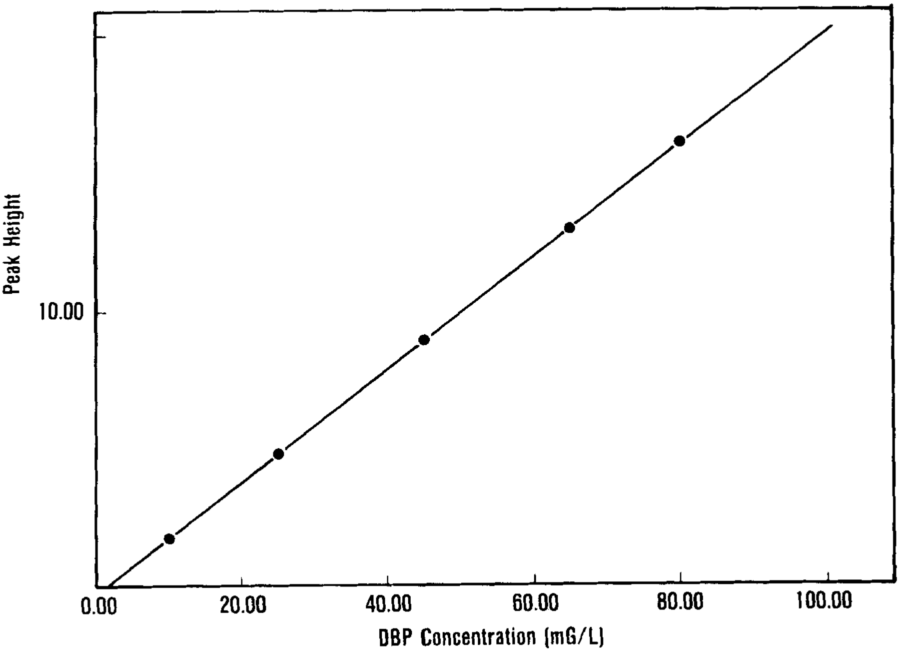

Figure 3. Calibration Curve for DBP

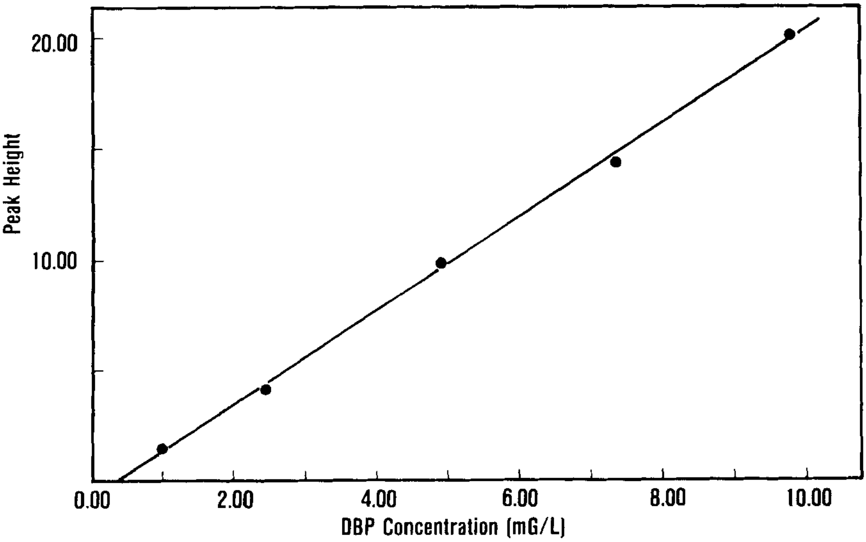

Figure 4. Calibration Curve for DBP

TABLE 3

Repeatability of IC Measurement for Dibutylphosphoric Acid (80 mg/L level)[a]

Peak Height, mm		
130.5	130.0	
130.5	130.5	
130.5	130.5	% Relative Standard Deviation = 0.49%
131.0	129.0	
131.0	129.5	

[a] Data was obtained over a five hour period

TABLE 4

Analysis of Synthetic Fuel Reprocessing Solutions

	DBP, mg/L		Percent	Relative Std.
Matrix	Added	Found	Recovery	Deviation, %
A	499.2	485.0	97.2	0.4
A	144.4	136.7	94.7	1.1
A	14.4	14.0	97.2	3.1
A	1.50	1.55	103.3	5.7
B	149.5	147.8	98.9	0.2
B	15.2	14.6	96.1	1.0

[a] Average of 10 Determinations at each level

Figures 3 and 4 show standard curves obtained by plotting peak height response vs DBP concentration for two different levels of DBP.

The repeatability of the IC measurement is shown in Table 3. The data were the average of 10 analyses at the 80 mg/L level and yielded a relative standard deviation of 0.49%.

The results of the analysis of the synthetic fuel reprocessing solutions are shown in Table 4. The data show that DBP can be determined with good precision and accuracy over the range of 1.5 to 500 mg/L.

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