

Determination of Di-n-Butyl Phosphate in Organic Streams of FBTR Mixed Carbide Fuel Reprocessing Solution by Gas Chromatographic Technique

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ABSTRACT

The present work describes the amount of Di-n-butyl phosphate (DBP) produced when PUREX solvent (30% tri-n-butyl phosphate (TBP) mixed with 70% hydrocarbon diluent) is exposed to intensive radiolytic and chemical attack during the separation of uranium and plutonium from fission products of FBTR mixed carbide fuel reprocessing solution. DBP is the major degradation product of Tri-n-butyl phosphate (TBP). Amount of DBP formed in the lean organic streams of different fuel burn-up FBTR carbide fuel reprocessing solutions were analyzed by Gas Chromatographic technique. The method is based on the preparation of diazo methane and conversion of non-volatile Di-n-butyl phosphate in to volatile and stable derivatives by the action of diazomethane and then determined by Gas Chromatography (GC). A calibration graph was made for DBP over a concentration in the range from 200 to 1800 ppm with correlation coefficient of 0.99587 and RSD 1.2%. The degraded 30% TBP-NPH solvent loaded with heavy metal ions like uranium was analyzed after repeated use and results are compared with standard ion chromatographic technique. A column comparison study to select of proper gas chromatographic column for the separation of DBP from other components in a single aliquot of injection is also examined.

Keywords: Gas Chromatography, Flame Ionization Detector, Diazomethane, Di-n-Butyl Phosphate, PUREX Process, Degradation of TBP, Lean Organic Streams, Carbide Fuel

1. Introduction

Tributylphosphate (TBP) is the most popular reagent in liquid-liquid extraction. Di-n-butyl phosphate (DBP) is one of the degradation products of Tri-n-butyl phosphate (TBP) ($(C_4H_9O)_3P = O$), used in the well known PUREX (Plutonium Uranium Refining by Extraction) process [1] for the separation of uranium and plutonium from fission products in nuclear fuel reprocessing. During the solvent extraction process the solvent TBP undergoes degradation by hydrolysis and radiolysis yielding mainly Di-n-butyl phosphate (DBP) ($(C_4H_9O)_2P = O-(OH)$), to a lesser extent monobutylphosphate (MBP) ($(C_4H_9O)P = O-(OH)_2$), phosphoric acid and butanol [2]. The DBP complexes with Zr, Pu and other metal ions [3] which leads to loss of heavy metals to lean organic stream. Hence the quality of PUREX solvent is generally measured in terms of the concentration of DBP. Various analytical methods were reported in the literature for the determination of DBP. Bocek *et al.* [4] have used high-speed Isotachopheresis, a

form of capillary electrophoresis with conductivity detection, to analyze TBP for its degradation products in solutions containing nitrates and nitrites. Muller *et al.* [5] have determined trace amounts of DBP and TBP in nuclear fuel reprocessing solutions by Liquid Chromatography [6] while Wilkinson and Williams [7] determined DBP and MBP by direct titration of irradiated TBP samples. The latter method fails in presence of nitric acid. Krishnamurthy and Sampathkumar [8] have used titrimetry to determine DBP and MBP as degradation products in the two component TBP-nitric acid system. Grant *et al.* [9] have performed the separation and measurement of TBP, DBP and MBP by Ion-pair Chromatography with refractive index detection. Infra Red Spectroscopy is used [10] for determination of DBP concentration in the solvent based on the P=O absorption at 1230 cm^{-1} with a poor detection limit due to interferences from the TBP. Techniques [11] of ionization at atmospheric pressure, *i.e.*, electrospray (ESI) or atmospheric pressure chemical ionization (APCI) with Mass Spectrometry (MS) have been used

for the direct quantification of MBP and DBP in a TBP matrix, without any prior separation. Recently use of ligand-sensitized Fluorescence Spectroscopy [12] is reported for the determination of DBP in TBP/dodecane solutions with Tb^{3+} as the fluorescent. This method is suitable for the determination of DBP over the concentration of 0.1% - 10% DBP in TBP. Among the various methods of analysis, application of chromatographic methods has gained wider acceptance owing to their high sensitivity and greater resolving power [13] Gas Chromatography (GC) is the most widely used technique for the determination of DBP, mainly in the organic phase. Hardy *et al.* [14] showed that DBP could be analyzed by gas chromatography of the corresponding methyl esters formed by reaction with diazomethane. Brignocchi *et al.* [15] developed the gas chromatographic method of Hardy [16,17] into a quantitative procedure for the determination of DBP and MBP in various organic streams [18,19]. Experimental details and results obtained by this method are described in this paper

2. Experimental

2.1. Reagents

Tri-n-butyl phosphate (Merck) and Di-n-butyl phosphate (Fluka). All other chemicals used were of AR or GR grade. Diazomethane was prepared immediately before use from a precursor in the laboratory fume hood and stored in refrigerator. The precursor used in the present study is N-methyl-N-nitroso-p-toluenesulfonamide (Diazald)

2.2. Instrumentation

A Shimadzu Gas chromatograph model 14 B equipped with a Flame Ionization Detector (FID) was used to detect the eluted components. Metrom IC Net 2.3 software is used for data acquisition. A stainless steel column of 4 meters long and 1/8" dia packed with 10% XE-60 was used for the separation of components. Nitrogen gas with a flow rate of 30ml/min was used as carrier gas. Hydrogen gas and zero air with a flow rate of 30 and 300ml/min were respectively used to generate flame. Column, Injector and detector temperatures were 230°C, 260°C and 260°C respectively.

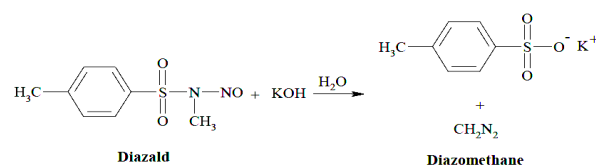
3. Gas Chromatographic Condition

Gas chromatograph:	Shimadzu GC model 14 B
Analytical Column:	Stainless steel packed column
Liquid phase:	10% XE-60
Nature of the column:	Polar
Length:	4 meters
Diameter:	1/8"
Solid:	Anakrom-ABS
Mesh range:	60/80

Maximum column operating temperature:	250°C
Column temperature :	230°C
Injector temperature:	260°C
Detector temperature:	260°C
Fuel gas:	Hydrogen
Supporting gas:	Zero air
Carrier gas:	Nitrogen
Carrier gas flow rate:	30 ml/min
Hydrogen gas flow rate:	30 ml/min
Zero Air flow rate:	300 ml/min
Detector:	Flame Ionization Detector
Detector range:	2
Detector polarity:	1
Analytical mode:	Isothermal
Injection volume:	5 μ L
Run time:	15 min
Quantitation:	Peak area

3.1. Preparation of Diazomethane

Diazomethane (CH_2N_2) is the most common methylating reagent for carboxylic acid and has found wide application in the methylation of phenols, enols, and heteroatoms such as nitrogen and sulfur. Diazomethane is easy to prepare and use. It is prepared immediately before use from a precursor, after addition of base. The precursor used in the present study is N-methyl-N-nitroso-p-toluenesulfonamide.

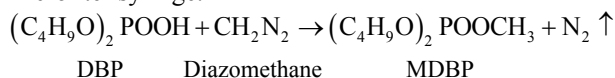


Preparation and handling of diazomethane requires special precautions because it is a highly explosive gas at room temperature. Diazomethane gas may explode violently even if it is diluted with nitrogen (OSHA, US Department of Labor). Contact with sharp or rough surfaces, or heat may cause diazomethane to explode. Diazomethane is a severe pulmonary irritant and causes coughing, fever, fulminating pneumonia, and death on humans. High velocity ventilation in the working area involving diazomethane is needed to guarantee minimum exposure to diazomethane. Diazomethane was prepared by the use of specially designed glassware kit (Aldrich Diazald Apparatus) in order to avoid accidental explosion of CH_2N_2 with sharp or rough surfaces. A safety shield was placed in the highly ventilated reaction hood to provide maximum isolation from exposure to diazomethane and possible explosion. The receiving flask was surrounded by a NaCl-ice bath (33% NaCl by weight) giving a cool environment at about $-20^\circ C$ because diazomethane is a gas at

room temperature and liquifies at -23°C (density 1.45), and freezes at -145°C . Ethanol (10 ml) was added into KOH solution in the reaction flask, which was prepared by dissolving potassium hydroxide (5 g) in water (8 ml). The solution of Diazald (5.0 g Diazald in 45 ml ether) was added in the reaction flask, and was heated to 65°C . The rate of addition of Diazald solution was approximately the rate of distillation. Some extra ether was added in the reaction flask after the Diazald solution was used up in order to trap the entire diazomethane in the receiving flask. The reaction was terminated when the distillate become colorless. The strength of diazomethane was determined Spectrophotometrically at 410 nm where its extinction coefficient, ϵ , is 7.2.

3.2. Procedure

Stock solution of DBP was prepared in n-dodecane and from this stock solution various concentration of DBP was diluted in n-dodecane and treated with diazomethane solution which was prepared immediately before use from a precursor. Solution was warmed at 60°C using a water bath. The ether and the excess diazomethane were evaporated by the flow of nitrogen gas through the solution. After the conversion of DBP into its methyl ester, solution was injected into Gas chromatograph using Hamilton microliter syringe.



Radioactive lean organic solutions of various burn-up of FBTR mixed carbide fuel reprocessing solution was washed with 2N sulphuric acid to remove any heavy metal ions and then subsequently treated with diazomethane before injection in to Gas chromatograph.

In another experiment degraded solvent of repeatedly used 30% TBP-NPH phase loaded with 70 g/L concentration of uranium was analyzed for its DBP content by this procedure. 3 ml of organic phase was equilibrated twice with 0.01 M nitric acid and subsequently washed twice with 2N sulphuric acid to remove heavy metals. Then 0.25 ml of organic phase was taken in a 5 ml standard flask and made up to the mark with n-dodecane. From this 0.2 ml of aliquot was taken in a 15 ml centrifuge tube and followed the above procedure to determine the concentration of DBP.

3.3. Studies on the Selection of Gas Chromatographic Column for DBP Separation

Studies were carried out to find best gas chromatographic column for the separation of DBP from hydrocarbon peaks (C10 to C14) and TBP in a single aliquot of inject-

tion. Columns of different stationary phases SE-30 and XE-60 were taken for studies. Detailed column parameters were described in **Table 1**

4. Results and Discussion

Diazomethane is an ideal derivatization reagent. The reaction is fast, the yield is high, side reactions are minimal, the by-product is nitrogen gas and reaction conditions are very mild. Diazomethane is a yellow gas so the progress of the reaction can be easily followed. The reaction for the conversion of DBP to methyl ester is outlined below:

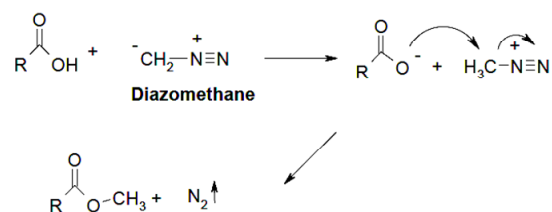


Table 1. Comparison of Column parameters used for the separation of DBP from other components.

Properties of Column	XE-60	SE-30
Material	S.S packed column	S.S packed column
Liquid phase	10% XE-60	10% SE-30
Nature	Polar	Non-Polar
Length	4 meters	4 meters
Diameter	1/8"	1/8"
Solid	Anakrom-ABS	ChW/HP
Mesh range	60/80	60/80
Maximum Temperature	250°C	300°C
Column temperature	230°C	230°C
Injector temperature	260°C	260°C
Detector temperature	260°C	260°C
Fuel gas	Hydrogen	Hydrogen
Supporting gas	Zero air	Zero air
Carrier gas	Nitrogen	Nitrogen
Carrier Gas flow rate	30 ml/min	30 ml/min
Hydrogen gas flow rate	30 ml/min	30 ml/min
Zero Air flow rate	300 ml/min	300 ml/min
Detector	FID	FID
Detector range	2	2
Detector polarity	1	1
Analytical mode	Isothermal	Isothermal
Injection volume	5 μL	5 μL
Run time	15 min	15 min
Quantitation	Peak area	Peak area

Two of the protons in the resulting methyl ester originate from the diazomethane. The other one is the donated acidic proton from the DBP. A calibration graph (**Figure 1**) was made for DBP concentration in the range from 200 to 1800 ppm in n-dodecane with correlation coefficient of 0.99587 and RSD 1.2% and each standard was esterified using diazomethane procedure as described above. By using this calibration graph the concentration of DBP present in the unknown samples were calculated. **Table 2** gives results of gas chromatographic determination of DBP and TBP in radioactive lean organic streams of various fuel burn-up of FBTR carbide fuel reprocessing solution. The table confirms that the TBP percentage remains more or close to 30% and the concentration of DBP is fairly high, its concentration depends on strength of the nitric acid, concentration of plutonium and contact time during the solvent extraction process. The higher DBP concentration in the low burn-up fuel is probably due to delayed stripping of heavy metal ions during the commissioning of the reprocessing plant with low burn-up fuel. **Figure 2**

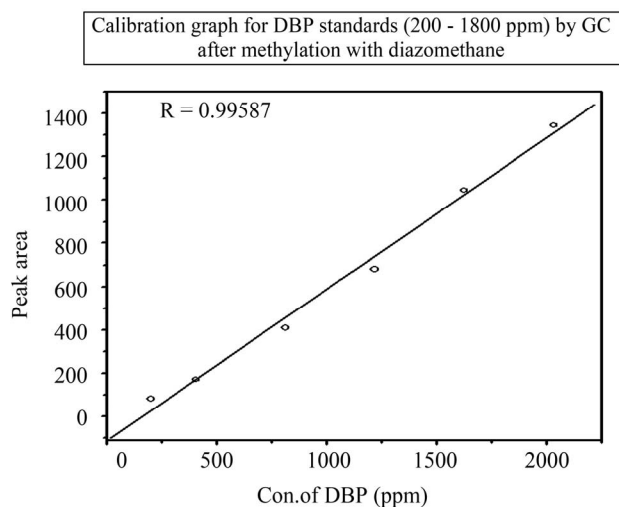


Figure 1. Typical calibration graph for the determination of DBP by gas chromatographic technique after methylation using diazomethane.

Table 2. Results of gas chromatographic determination of DBP and TBP in lean organic streams of various fuel burn-up of FBTR mixed carbide fuel reprocessing solution.

S.No	Fuel Burn-up (MWd/T)	Nature of the sample	% of TBP determined	Conc. of DBP (g/L)
1	Low burn-up	Lean Organic	29.971	2.654
2	25000-1	Lean Organic	29.508	1.664
3	25000-2	Lean Organic	29.383	2.387

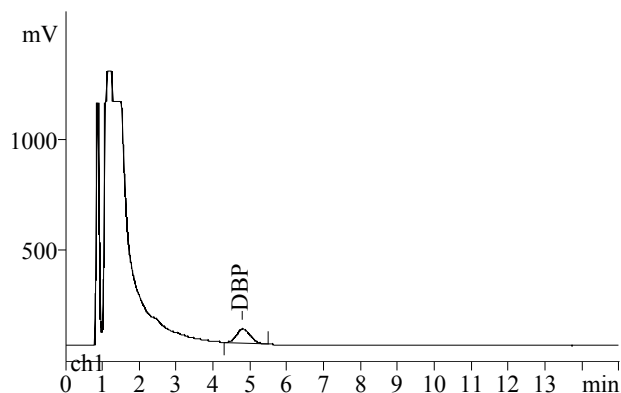


Figure 2. Typical Gas chromatogram of standard Di-n-butyl phosphate (1.659 g/L).

shows the typical gas chromatogram of standard DBP (1.659 g/L) after methylation using diazomethane. **Figure 3** refers the typical gas chromatogram of DBP and TBP in radioactive lean organic solvent of FBTR carbide fuel (25,000 MWD/T burn-up) reprocessing solution. In **Figures 2** and **3** the DBP peak was well separated from hydrocarbon and TBP peaks respectively with the separation factor (α) greater than 1. **Table 3** shows the results of comparison of Gas Chromatographic and Ion chromatographic methods from repeatedly used degraded 30% TBP-NPH solvent loaded with uranium. Errors estimated in the present gas chromatographic method is about 5%. All the estimated values of different concentration range of DBP were higher in GC than the estimated values of DBP by IC. This positive error in GC estimation of DBP may be due to pre-concentration of the solution during the conversion of DBP into its methyl ester under hot condition. The peak area obtained was compared with standard calibration graph of DBP obtained by injecting DBP standards every day after methylation using diazomethane. The relative standard deviation was 1.2% for the repeated nine injections. **Table 1** refers the comparison of column parameters used for the separation of DBP from other components. The column selection studies carried out for the separation of DBP is reveal that the best column is XE-60 than SE-30. This is due to the polar nature of column XE-60 separates the non polar hydrocarbon (C-10 to C-14) peaks as a single peak from DBP and TBP (**Figure 2** and **3**), hence there is no interference of hydrocarbon peak for the separation, identification and quantitative estimation of DBP in the degraded solvent using XE-60. Whereas non polar nature of column SE-30, hydrocarbons C10 to C14 (non polar) peaks were individually well separated. It was found that use of column SE-30 the retention time of peak C-14 (tetradecane, retention time 4.5 min) and the retention time of DBP peak were same. Therefore SE-30 column is not suitable for the

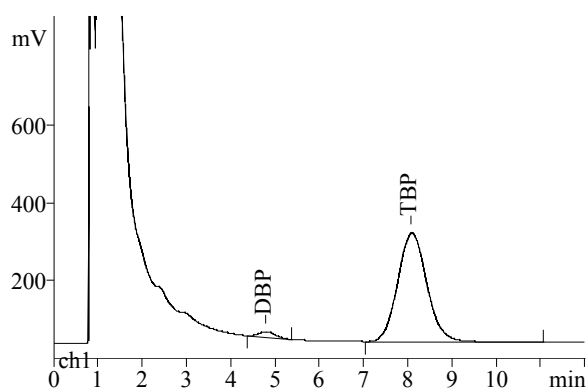


Figure 3. Typical Gas chromatogram of DBP (1.664 g/L) & TBP (29.51%) in lean organic solution of FBTR mixed carbide (25,000 MWD/T Burn-up) reprocessing solution.

Table 3. Estimated values of DBP by present method and Ion chromatographic method.

Sample no	Concentration of DBP(g/L) estimated by	
	Gas chromatography method ^a (described in this work)	Ion-chromatography method
1	14.71	14.42
2	7.82	7.45
3	2.63	2.41

^aErrors in the estimates by Gas chromatographic method is about 5%.

qualitative and quantitative estimation of DBP in presence of various hydrocarbons particularly diluent NPH (Normal Paraffin Hydrocarbon) in the degraded solvent of reprocessing plants.

5. Conclusions

Analysis of DBP content in the radioactive lean organic streams of FBTR mixed carbide fuel reprocessing solutions by gas chromatography method was demonstrated. It is simple, only needs the conversion of DBP into its methyl ester prior to injection. The major advantage of GC method is the simultaneous determination of MBP, DBP and TBP and hydrocarbons in a single aliquot without any interference using 10% XE-60 column. The reproducibility and linearity of the method suggest that it is well suitable for the determination of DBP over a concentration in the range from 200 to 1800 ppm and relevant to organic streams of purex process.

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