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Comparative studies on the determination of di-*n*-butyl phosphate in degraded solvent of PUREX process by ion chromatography and gas chromatography methods

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ABSTRACT

This paper describes comparative studies on the determination of di-*n*-butyl phosphate (DBP) by ion chromatography (IC) and gas chromatography (GC) techniques in spent solvent of PUREX process used for the reprocessing of spent nuclear fuels. The ion chromatography method involves the separation of DBP from 30% TBP–NPH (tri-*n*-butylphosphate diluted in normal paraffin hydrocarbon) containing heavy metal ion like uranium and nitric acid by extraction of DBP into alkaline medium. DBP was subsequently eluted by ion-exchange separation in ion chromatography column and followed by suppressed conductivity detection. DBP is quantified to a lower limit of about 1 ppm with 3% RSD. However, in order to determine DBP by gas chromatography technique DBP is first quantitatively converted into its volatile and stable derivatives by using diazomethane prior to analysis by GC. Results obtained with ion chromatographic technique are compared with those of obtained by standard gas chromatographic technique. It was observed that IC technique involves minimum steps and is much faster than GC analysis. The effect of mobile phase flow rate on the detector response, retention time, and column pressure are also investigated.

Keywords: Di-*n*-butyl phosphate; Ion chromatography; Gas chromatography; Suppressed conductivity; Flame ionization detector; Diazomethane; PUREX process

1. Introduction

To recover uranium and plutonium from spent nuclear fuel, tri-*n*-butyl phosphate (TBP) diluted with *n*-dodecane (hydrocarbon diluent) is used as a solvent in the PUREX (plutonium–uranium extraction) process [1] of nuclear fuel reprocessing plant. TBP though very stable, is prone to hydrolysis or dealkylation under the influence of acid attack and radiation effect leading to the formation of di-*n*-butyl phosphate (DBP), monobutyl phosphate (MBP), phosphoric acid, and butanol [2]. These degradation products decrease the fission product decontamination efficiency and can prevent complete uranium and plutonium stripping, resulting in their losses to solvent wash waste. Therefore, its detection has attracted considerable analytical interest.

Various analytical methods were reported in the literature for the determination of DBP in organic medium. Bocek et al. [3] have used high-speed isotachophoresis, a form of capillary electrophoresis with conductivity detection, to analyze TBP and its degradation products in solutions containing nitrates and nitrites. Muller et al. [4] have determined trace

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amounts of DBP and TBP in nuclear fuel reprocessing solutions by liquid chromatography [5]. Wilkinson and Williams [6] determined DBP and MBP by direct titration of irradiated TBP samples. This method fails in the presence of nitric acid. Krishnamurthy and Sampathkumar [7] have used titrimetry to determine DBP and MBP as degradation products in the two component TBP–nitric acid systems. Grant et al. [8] have performed the separation and measurement of TBP, DBP, and MBP by ion-pair chromatography with refractive index detection. Stieglitz et al. have used infra red spectroscopy [9] for the determination of DBP in solvent based on the P=O absorption at $1230\,\mathrm{cm}^{-1}$ with a poor detection limit (150 mg/L) due to interferences from the TBP. Techniques 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 [10]. Recently, use of ligand-sensitized fluorescence spectroscopy [11] 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 range of 0.1–10% DBP in TBP.

Gas chromatography is the most widely used technique for the determination of DBP, mainly in the organic phase. Hardy et al. [12] showed that DBP can be analyzed by gas chromatography method by converting into corresponding methyl esters formed by reaction with diazomethane. Brignocchi et al. [13] developed the gas chromatographic method of Hardy [14] into a quantitative procedure for the determination of DBP and MBP in various organic streams. The advantage of gas chromatographic method is that concurrently all components MBP, DBP, and TBP in the matrix of hydrocarbons can be determined without any interference from hydrocarbons peaks using 10% XE-60 column. However, the drawback of GC method for the determination of TBP degradation products is the need of conversion of acidic groups into their methyl esters to improve their volatility. This preliminary step is time-consuming and may rise to many problems of incomplete reaction or by-products formation [12,13,15]. The method employs diazomethane (highly explosive gas) for derivatization [16,17]. Diazomethane gas may explode violently even if it is diluted with nitrogen (OSHA, U.S. Department of Labor). Contact with sharp or rough surfaces, or heat may cause diazomethane to explode. Diazomethane is a severe pulmonary irritant [18] 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. The precursor used in the present study is *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide. Freshly prepared diazomethane should be used as it can otherwise give rise to spurious peaks in the chromatogram [19]. The precursor (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) used for the preparation of diazomethane is not currently available commercially in the international market [20]. This leads to the development of an alternate and simple ion chromatographic method for the quantitative estimation of DBP in the spent solvent of PUREX process. The present method described here is an improved version of the earlier reported procedure [21,22].

The present paper describes that a rapid method has been developed for determination of DBP concentration in organic phase using the ion chromatography system and the results have been compared with standard gas chromatographic technique. Ion chromatography technique [23] uses the anionic properties of DBP in basic media and separation on anion exchange resins followed by suppressed conductivity detection.

2. Experimental

2.1. Reagents

Uranyl nitrate hexahydrate (Analytical reagent) obtained from BDH Chemicals Ltd. was used. An amount of 30% tri-*n*-butyl phosphate of purity >99% (Fluka AG) was prepared by diluting it with *n*-paraffin hydrocarbons supplied by M/s. Tamilnadu Petrochemicals Ltd., Chennai. Di-*n*-butyl phosphate (Fluka) of purity >97% is used for preparing DBP standards. All other chemicals used were of analytical grade reagent. The mobile phase was filtered through a 0.45 μm nylon membrane filter. Milli-Q water was used for all solution preparations.

2.2. Instrumentation

Metrohm make modular ion chromatography system equipped with 819 IC conductivity detector, 820 IC separation center, 818 IC isocratic pump, 833 IC liquid handling unit and 830 IC interface were employed for the analysis. The eluent was aqueous solution of mixture of 3.2 mM $\mathrm{Na_2CO_3}$ and 1.0 mM $\mathrm{NaHCO_3}$ used at flow rate of 0.7 mL/min. The separation was carried out using an anion exchange column Metrosep A Supp 5-250 [250 mm (L) × 4.0 mm (ID)] containing carrier material polyvinyl alcohol with quaternary ammonium groups and guard column Metrosep A Supp 4/5. The pH range of the analytical column is between 3 and 12 and operated at ambient temperature. Sample was injected manually through a 20 μL PEEK loop fitted with injector. Run time for each sample is 15 min and quantified by using peak area measurement. IC net 2.3 Metrohm software was used for instrument control and data acquisition.

2.3. Procedure

The method was standardized by preparing known concentrations of DBP in normal paraffin hydrocarbon. DBP was weighed using Sartorius semimicro balance model CP 225D. The standard solution was treated with 1% sodium carbonate and sodium hydroxide mixture and mixed well using Heidolph multi reax vortex mixture (2,000 rpm). The contents were allowed to settle, aqueous phase was separated, a known aliquot of which was then taken in a 100 mL standard flask and made up to the mark with high-purity Milli-Q water. Aqueous phase samples were injected through 20 μL PEEK loop manually and subsequent ion-exchange separation in anionic column followed by suppressed conductivity detection chromatograms were obtained. A calibration graph for DBP in the concentration range of 1–1000 ppm was made by dissolving known concentration of DBP in Milli-Q water and analyzed directly in IC.

2.4. Preparation and determination of DBP in synthetic organic solvent

Synthetic organic solutions were prepared by adding known concentration of DBP in 30% TBP–NPH mixture. These were then equilibrated with uranyl nitrate solution of known concentration of uranium prepared in 4 M nitric acid. The aqueous phase was removed and the organic phase was equilibrated twice with 0.01 M nitric acid and subsequently washed twice with 2 N sulfuric acid to remove heavy metal ions. Known aliquot of organic phase which contains metal–DBP complex was then taken in a centrifuge tube and followed the above-described procedure to determine concentration of DBP. The experiment was repeated with changing concentrations of DBP and uranium.

3. Gas chromatographic method of determination of DBP

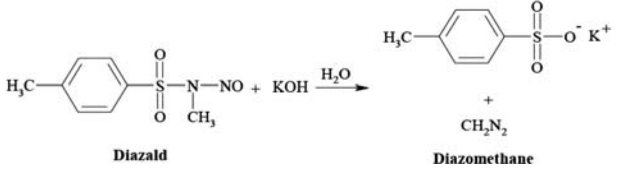
Gas chromatography (GC) is one of the sensitive and dominant methods for determination of TBP, HDBP, H_2MBP, and other species derived from the radiation or thermal decomposition of TBP–diluent–HNO_3–H_2O solutions. DBP and MBP cannot be determined directly by GC as they are nonvolatile and thermally unstable. However, in order to determine these compounds by GC they are first quantitatively converted into their volatile and stable derivatives by using diazomethane prior to analysis by GC.

3.1. Instrumentation

Analysis was performed on a Shimadzu gas chromatograph (model 14 B) equipped with flame ionization detector (FID). The gas chromatograph contained 10% XE-60 stainless steel packed column (4 m × 1/8″ ID). Nitrogen was used as the carrier gas with a flow rate of 30 mL/min. The column oven, injector and detector temperatures were maintained at 230°C, 260° C, and 260°C, respectively. Hydrogen gas was used as fuel gas and zero air was used as supporting gas with a flow rate of 30 and 300 mL/min, respectively. FID detector range was kept at 2 and running time for each sample is 15 min. DBP was quantified by using peak area measurement. IC net 2.3 Metrohm software was used for data acquisition.

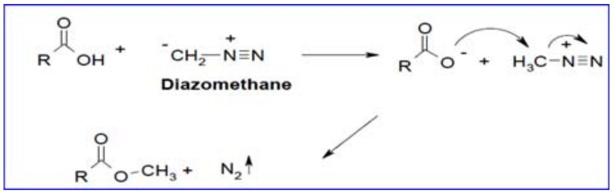
3.2. Preparation of diazomethane

Preparation and handling of diazomethane requires special precautions. Diazomethane is prepared by the action of alkali on precursor *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in the presence of diethyl ether and the product was distilled using hot water bath. Precursor (10 g) is added to a round bottom flask containing 100 mL of diethyl ether and kept in a water bath. An amount of 5% KOH prepared in 95% alcohol was carefully added to the reaction vessel and the temperature was raised from 30°C to 65°C. A yellow colored diazomethane was collected in the round bottom flask contains diethyl ether and flask cooled in ice bath. This phenomenon is described by the following reaction.



3.3. Conversion of DBP in to methyl ester

Diazomethane is an ideal derivatization reagent. Diazomethane is added at least 100-fold excess to convert organic acids to their methyl derivatives. The reaction is fast and often proceeds to completion in seconds. The by-product is nitrogen. The reaction for the conversion of DBP to methyl ester is outlined below:



Two of the protons in the resulting methyl ester originate from the diazomethane. The other one is the donated acidic proton from the DBP.

$$(C_4H_9O)_2POOH + CH_2N_2 \rightarrow (C_4H_9O)_2POOCH_3 + N_2\uparrow$$

DBP Diazomethane MDBP

Standard DBP solution was taken in a 15 mL graduated centrifuge tube, added diazomethane till the yellow color of diazomethane appeared and solution was warmed at 60°C using a water bath. Ether and excess diazomethane present in the sample were evaporated. Five microliters of MDBP was injected into the GC.

3.4. Analysis of degraded organic solvent

Organic solvent after repeated use containing 30% TBP–NPH loaded with uranium was analyzed for DBP content. Organic phase was equilibrated twice with 0.01 M nitric acid and subsequently washed twice with 2 N sulfuric acid to remove heavy metals. Then the resultant organic phase was taken into a 5 mL standard flask and diluted with *n*-paraffin hydrocarbon (NPH). Around 0.2 mL of the above-treated organic solution was taken into a 15 mL centrifuge tube, followed the esterification procedure and converted DBP into MDBP before injection into GC to determine the concentration of DBP.

4. Results and discussion

Table 1 summarizes the amount of DBP determined by ion chromatographic method after the extraction in an alkaline medium. The average recovery in a single extraction is 99.50%. These results have confirmed that 1% sodium carbonate and sodium hydroxide mixture is adequate to transfer DBP concentrations normally encountered in the actual PUREX process (200–2,000 ppm). Table 2 refers the ion chromatographic results obtained by direct injection of simulated solvent (30% TBP–NPH) containing DBP. The result shows that the average recovery of DBP is 85.8% only. This is due to the presence of hydrocarbons and TBP in the organic solvent which deteriorates ion chromatographic column separation resulting to lower recovery of DBP. It was observed that they interfere only during direct injection of organic solvent. The results obtained with 30% TBP–NPH simulated organic solvent loaded with uranium are summarized in Table 3. The table data also indicate the effect of change of concentration of DBP and uranium on the stripping behavior of the latter and the extent of degradation that has occurred over a period of time.

Table 4 shows the comparison of results of estimated values of DBP by IC and GC methods in 30% TBP–NPH–uranium-loaded degraded organic solvent. The peak area thus obtained was compared with standard calibration graph of DBP obtained by injecting DBP standards every day for both IC and GC. The obtained results from both the methods were found to be in good agreement .The relative standard deviations were 2 and 1.2% for repeated nine injections for GC and IC, respectively. Table 5 refers the ion chromatography results of kinetic study on the transfer of di-*n*-butyl phosphate from 30% TBP–NPH simulated organic solvent to aqueous alkaline medium. The result confirms that two minutes contact time at 2,000 rpm is adequate to transfer entire DBP from 30% TBP–NPH organic solvent to aqueous alkaline medium.

The calibration graph obtained for IC and GC are linear with R^2 (correlation coefficient) value 0.99998

Table 1
Ion chromatography results after the extraction of DBP in alkaline medium

S. No.	DBP content taken (ppm)	DBP content found (ppm)	Recovery (%)
1	2,086	2,062	98.85
2	2,086	2,046	98.10
3	2,086	2,078	99.62
4	2,086	2,076	99.52
5	2,086	2,062	98.85
6	2,086	2,081	99.76
7	2,086	2,083	99.86
8	2,086	2,084	99.90
9	1,658.8	1,650	99.47
10	1,658.8	1,649	99.41
11	1,658.8	1,660	100.07
12	1,658.8	1,652	99.59
13	1,658.8	1,658	99.95

Vortex mixer: 2,000 rpm, A/O: 5:1, aqueous: 1% Na_2CO_3 + NaOH mixture, column: Metrosep A Supp 5-250 [250 mm (L) × 4.0 mm (ID)]. Guard column: Metrosep A Supp 4/5, mobile phase: 3.2 mM Na_2CO_3 + 1.0 mM $NaHCO_3$, Volume of injection: 20 μL, pump: isocratic, detector: suppressed conductivity.

Table 2
Ion chromatography results from direct analysis of degraded (30 vol.% TBP in NPH)-DBP-simulated solvent

S. No.	DBP content taken (g/L)	DBP content found (g/L)	Recovery (%)
1	1.82	1.61	88.3
2	1.82	1.58	86.8
3	1.82	1.57	86.5
4	1.82	1.55	85.2
5	1.82	1.49	82.1

Volume of injection = 20 µL.

Table 3
Ion chromatography results from 30% TBP–NPH–Uranium and DBP-simulated organic solvent after stripping/extraction in alkaline medium

Amount of uranium added (mg)	DBP content added (ppm)	DBP content obtained after 16 days (ppm)
Saturated	0	91
131.056	4,688	5,283
131.056	4,688	5,307
131.056	4,688	5,230
Saturated	4,688	6,098
Saturated	4,688	6,151
Saturated	4,688	6,006
Saturated	4,688	6,035
Saturated	7,032	8,615
Saturated	7,032	8,676
Saturated	7,032	8,637

Vortex mixer: 2,000 rpm, A/O: 5:1, aqueous: 1% Na_2CO_3+NaOH mixture, volume of injection: 20 µL, strip acid: HNO_3: 0.01 M and H_2SO_4: 2 N, background DBP estimated in 30%TBP–NPH is 31 ppm.

Table 4
Estimated values of DBP by GC and IC techniques in 30% TBP–NPH uranium-loaded degraded solvent

Sample No.	Concentration of DBP (g/L) estimated by	
	Gas chromatography[a]	Ion chromatography[b]
1	14.71	14.42
2	7.82	7.45
3	2.63	2.41

[a] Errors in the estimates by gas chromatographic method is about 5%.

[b] Errors in the estimates by ion chromatographic method is about 3%.

Table 5
Ion chromatography results of kinetic study on the recovery of di-*n*-butylphosphate from 30% TBP–NPH organic solvent

Time (min)	Conc. of DBP in 30% TBP–NPH (g/L) added	Conc. of DBP estimated (g/L)	Recovery (%)
1	2.14	2.10	98.1
2	2.14	2.143	100.1
5	2.14	2.15	100.4

Vortex mixer: 2,000 rpm, A/O: 5:1, aqueous: 1% Na_2CO_3 + NaOH mixture, column: Metrosep A Supp 5-250 [250 mm (L) × 4.0 mm (ID)]. Guard column: Metrosep A Supp 4/5, mobile phase: 3.2 mM Na_2CO_3 + 1.0 mM $NaHCO_3$, volume of injection: 20 µL, pump: isocratic, detector: suppressed conductivity.

and 0.99843, respectively. The effect of mobile phase flow rate on the detector response, retention time, and column pressure with respect to DBP determination is studied. When flow rate of mobile phase increase from 0.4 to 0.8 mL/min the detector response decreases (R^2: 0.99309). At a lower flow rate (0.4 mL/min) the detector response is better and column pressure is less except that time taken for analysis of DBP is longer (retention time 14.8 min), hence an optimum flow rate of 0.7 mL/min was chosen. Figs. 1 and 2 describe the typical chromatograms of standard DBP for IC and GC, respectively. In ion chromatographic method DBP peak is well separated (retention time 8.7 min) from the water peak which elutes in about 3.5 min (Fig. 1) The relative standard deviation was 0.506% for retention time and 0.502% for peak area for the repeated ten injections of standard DBP (5.6 ppm) in IC and the average retention time of DBP is

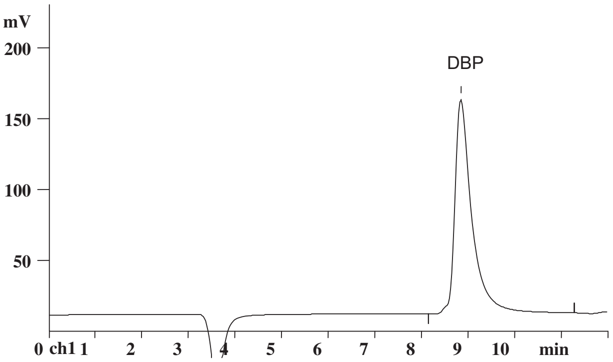


Fig. 1. Ion chromatogram of DBP standard (5.6 ppm), Metrosep A Supp 5-250 Column: [250 mm (L) × 4.0 mm (ID)]. Guard column: Metrosep A Supp 4/5, eluent: 3.2 mM Na_2CO_3 + 1.0 mM $NaHCO_3$, flow rate: 0.7 mL/min, injection volume was 20 µL, pump: isocratic, detector: suppressed conductivity.

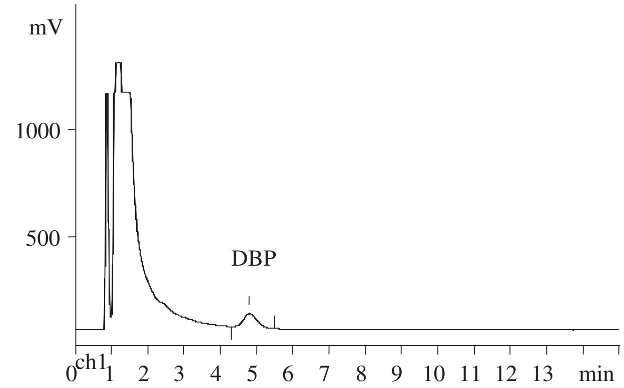


Fig. 2. Gas chromatogram of DBP standard (1.659 g/L), Column: 10% XE-60 (4 M × 1/8″ ID), mobile phase: nitrogen, flow rate: 30 mL/min, injection volume was 5 μL, detector: FID.

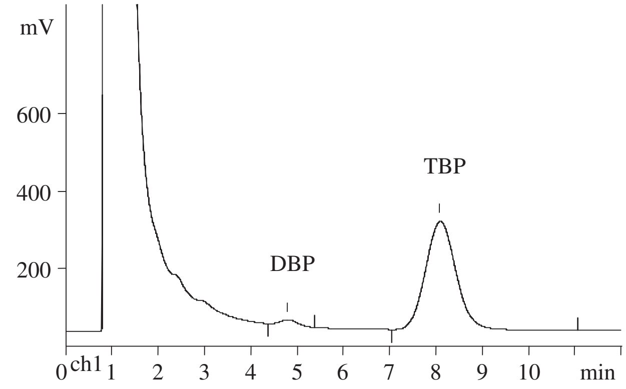


Fig. 3. Gas chromatogram of DBP (14.71 g/L) & TBP in uranium loaded 30% TBP–NPH degraded solvent after methylation using diazomethane. Column: 10% XE-60 (4 M × 1/8″ ID), mobile phase: nitrogen, flow rate: 30 mL/min, injection volume: 5 μL, detector: FID.

8.7 min. Fig. 3 is the typical gas chromatogram of 30% TBP–NPH–uranium-loaded degraded solvent after methylation using diazomethane. DBP and TBP are well separated with selectivity factor (α) greater than one.

5. Conclusions

A comparative study on the determination of DBP using IC and GC in the spent solvent of PUREX process has been described in the present investigation. Determination of DBP by ion chromatography method is simple, accurate, and precise when compared to conventionally used GC. DBP being ionic in nature is amenable for direct analysis. It involves minimum steps and is much faster than GC. The reproducibility and linearity of the IC method suggest that it is well suited for the determination of DBP over a concentration range of above 1 ppm in TBP compared to above 200 ppm in GC method. The advantage of gas chromatographic method is all together MBP, DBP, and TBP can be determined from hydrocarbon matrix without any interference from hydrocarbon peaks (C-10 to C-14) by using gas chromatographic column XE-60. On the other hand using ion chromatographic method only MBP and DBP can be determined. TBP and hydrocarbons cannot be determined directly by IC as they are nonionic in nature and interfere only during direct analysis of DBP by ion chromatographic method.

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