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# STUDIES ON THE IDENTIFICATION OF HARMFUL RADIOLYTIC PRODUCTS OF 30% TBP-*N*-DODECANE-$HNO_3$ BY GAS-LIQUID CHROMATOGRAPHY. II. FORMATION AND CHARACTERIZATION OF HIGH MOLECULAR WEIGHT ORGANOPHOSPHATES

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Online publication date: 31 October 2001

**To cite this Article** Tripathi, S. C. , Ramanujam, A. , Gupta, K. K. and Bindu, P.(2001) 'STUDIES ON THE IDENTIFICATION OF HARMFUL RADIOLYTIC PRODUCTS OF 30% TBP-*N*-DODECANE-$HNO_3$ BY GAS-LIQUID CHROMATOGRAPHY. II. FORMATION AND CHARACTERIZATION OF HIGH MOLECULAR WEIGHT ORGANOPHOSPHATES', Separation Science and Technology, 36: 13, 2863 — 2883
**To link to this Article: DOI:** 10.1081/SS-100107634
**URL:** http://dx.doi.org/10.1081/SS-100107634

SEPARATION SCIENCE AND TECHNOLOGY, 36(13), 2863–2883 (2001)

# STUDIES ON THE IDENTIFICATION OF HARMFUL RADIOLYTIC PRODUCTS OF 30% TBP-*N*-DODECANE-$HNO_3$ BY GAS-LIQUID CHROMATOGRAPHY. II. FORMATION AND CHARACTERIZATION OF HIGH MOLECULAR WEIGHT ORGANOPHOSPHATES

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## ABSTRACT

Gamma radiolysis of Purex solvent, 30% tri-*n*-butylphosphate-*n*-dodecane-$HNO_3$ is observed to yield many undesirable metal complexing species. A method for identifying the gas-liquid chromatographic (GLC) signatures of high molecular weight organophosphates (HMPs) through a nitrogen- and phosphorous-selective detector is described. Fractionation of the radiolyzed solvent by vacuum distillation resulted in the enrichment of HMP species in the high boiling, viscous residue in the last fraction. This residue showed intense infrared signals characteristic of the presence of nitro, carbonyl, and phosphoryl groups, which implies the presence of multifunctional species. The study revealed a strong

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association among the components of radiolyzed solvent, which inhibits clean fractionation. Gas chromatography–mass spectrometry assay of the sample indicated that these HMPs consist of $(NO_2—C_4H_8)(C_4H_9O)_2PO$, $(OH—C_4H_8O)(C_4H_9O)_2PO$, and $(CH_3—C_4H_8)(C_4H_9O)_2PO$ species. The HMP-rich fraction exhibited very high plutonium-retention behavior, which was substantially lowered by efficient uptake of HMPs upon alumina treatment. Thus, the present study correlates the GLC signatures of HMPs, especially those of nitrated species, formed by radiolysis of 30% tri-*n*-butylphosphate-*n*-dodecane-$HNO_3$ and solvent quality deterioration with respect to Pu-retention behavior.

*Key Words*: Gamma radiolysis; TBP; GLC fingerprinting; Pu-retention behavior; HMP; Vacuum distillation

## INTRODUCTION

Tri-*n*-butyl phosphate (TBP) mixed with inert hydrocarbon diluent continues to be the most favored extractant in aqueous reprocessing of spent nuclear fuels based on the Purex process. The extraction selectivity of TBP for Pu and U is due to the presence of a polarizable phosphoryl group, which serves as electron donor in TBP bonds formed with $UO_2^{2+}$ and $Pu^{4+}$. The dilution of TBP with inert hydrocarbon (*n*-dodecane) imparts optimum extraction selectivity and favorable changes in density, viscosity, and interfacial tension to the extraction solvent (1).

During reprocessing, the extractant TBP undergoes gradual degradation by radiolysis and acidic hydrolysis. This degradation leads to the formation of a number of compounds of different hydrophobicities in addition to alkyl phosphoric acids, which are normally removed from the solvent by alkaline wash before recycling (2).

The targeted recovery and purity of the strategic product (fissile material) is very much dependent on the quality of the solvent. The quality of the feed as well as that of recycled Purex solvent is generally monitored in terms of alkyl phosphoric acid concentrations, such as mono- and di-*n*-butyl phosphoric acids (3).

Literature on solvent degradation studies contains numerous analytical methods designed to be used to monitor the quality of Purex solvent in terms of dibutyl phosphoric acid (HDBP) and monobutyl phosphoric acid ($H_2MBP$) (4–8). Because of its hydrophilic nature, $H_2MBP$ does not follow the organic phase, which makes it relatively innocuous. Thus, the analytical estimation of HDBP has become synonymous with the quality of the Purex solvent.

Due to waste management constraints, the solvent needs to be recycled a number of times; thus, some of the hydrophobic metal binders tend to accumulate in the used solvent even after alkaline treatment. These hydrophobic species may be classified as diluent degradation products (DDPs) and high molecular-weight organophosphates (HMPs). The primary effect of the radiolysis of solvent detectable at low absorbed doses is the formation of DDPs.

However, the formation of HMP species is very slow and HMPs become predominant only at high-absorbed doses (9). Because of the few stages of recycling (low absorbed doses), concentration of these species is too low to be quantified accurately. The scarcity of data in literature on characterization of these HMP species and their slow formation kinetics are probably the primary reasons that studies on HMP quantification and extraction behavior remained overlooked when researchers defined the quality of recycled Purex solvent.

The variety of radiolytic products accumulated in the solvent by successive solvent recycling is not easily analyzed by titrimetry, potentiometry, or even ion chromatographic methods (7). These species are believed to be metal binders. The quality assessment of solvent solely by HDBP-content analysis appears invalid for the final rejection of the Purex solvent after several recycling runs (6–10). It is the additional, lesser-known, and ill-defined species that cause the complexities in the extraction performance of solvent and lowers its quality after repeated subjection to recycling.

Recent studies have confirmed the formation and role of HMPs in the deteriorating quality of the Purex solvent after several recycling runs (3). This report presents qualitative identification of HMPs in radiolytically degraded 30% TBP-*n*-dodecane by GLC through flame photometric and N-P detectors. Data on Pu-retention behavior of 30% TBP-*n*-dodecane-$HNO_3$ as a function of absorbed dose is also presented.

## EXPERIMENTAL

### Reagents

Commercial TBP was purified by washing with a 2% (wt/vol) solution of sodium carbonate and then by distilled water. The purity of TBP was found to be better than 99% by GLC assay. The *n*-paraffin mixture (C-10 to C-16 chain lengths) from Aldrich Inc (USA) containing 90% *n*-dodecane was used for dilution of TBP to 30% (vol/vol). Finely divided alumina (neutral) of chromatography grade was used. All other reagents used were of analytical reagent (AR) grade.

A radiotracer Pu solution, containing predominantly $^{239}Pu$, of a specific activity was used. $^{239}Pu$ was chemically purified by the anion exchange method as reported by (11). Tracer $^{239}Pu$ for each experiment was taken from this stock and adjusted to a tetravalent state by the addition of sodium nitrite (0.03 mol/L).





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## Gamma Irradiation Source

A $^{60}$Co source of γ radiation with a dose rate of 0.5 MRad/h was used for the irradiation of 30% TBP-*n*-dodecane samples after they were equilibrated with $HNO_3$. The measurements of absorbed dose were carried out using Fricke dosimetry that employed a freshly prepared air-saturated solution of ferrous ammonium sulfate (1 mmol/L) in 0.47 mol/L sulfuric acid that also contained sodium chloride (1 mmol/L).

To determine the absorbed dose using the Fricke dosimeter solution in a glass container (i.d. ≈ 8 mm), we placed the sample in a radiation field of $^{60}$Co gamma rays and measured the yield of ferric ions spectrophotometrically at 304 nm by using an extinction coefficient of 2204 (25°C). $G_{Fe}^{3+} = 15.5$ for $^{60}$Co gamma rays.

$$D_D = 2.76 \times 10^4 \left(\frac{\Delta A}{l}\right)$$

where $D_D$ is the dose (rads) in the dosimeter container; $\Delta A$ is change in the absorbance; and $l$ is the optical path length. The molar changes in the concentration of $Fe^{3+}$ over time gives the dose rate of the irradiation source.

## Gas-Liquid Chromatography

A Shimadzu model GC-9A gas chromatograph with a C-R3A data processor was used. For the preliminary investigation, the resolution of a multicomponent mixture of solvent degradation products was performed with a temperature-programmed 10% XE-60 column (1.5 m × 0.32 cm) with thermal conductivity detection.

170°C → 230°C (hold time = 10 minutes) Condition (1)

(1 minute) Program rate = 10°C/min

120°C → 230°C (hold time = 10 minutes) Condition (2)

(0.2 minutes) Program rate = 15°C/min

An injection temperature of 240°C and carrier (helium) flow of 50 mL/min was used.

### Flame Photometric Detection

The vacuum distilled fractions were analyzed by GLC (Shimadzu model) with flame photometric detection. The sample was first diluted with *n*-dodecane, and a fixed attenuation was reached.





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N-P Detection

The radiolyzed solvent was analyzed by GLC (Chemito model 5000) in N-P mode (combined) as well as P selective mode employing suitable attenuation. The sample was also analyzed under identical conditions as under flame-ionization detection mode.

## Gas Chromatography–Mass Spectrometry Analysis

A Shimadzu model QP-5050A gas chromatography–mass spectrometry (GC/MS) system with chemical ionization (CI) source was used. Because CI data are identified through a library search device, but the source did not have a library search engine. Therefore, the only means of obtaining the identity of the eluted component is through the presence of an intense molecular ion peak. Because the radiolysis mechanism was quite predictable in the samples studied, we could derive the identity of the components based on the molecular weight/ion peaks. The chosen mass spectral range was between 70 and 800 atomic mass units (AMU). A split capillary injection was performed on a DB-5 column (30 m $\times$ 0.2 mm of 0.25 $\mu$m thickness). The injection temperature was 250°C, and helium was used as carrier gas with a total flow rate of 62 mL/min and a split ratio of 75. The interface temperature was 300°C.

Initial column temperature of 80°C was maintained for 2 minutes, then raised to 120°C and finally to 250°C at rates of 10°C/min and 15°C/min, respectively. The hold times at 120°C and 250°C were 1 minute and 15 minutes, respectively. Carrier gas pressure was 50.4 kPa.

## Infrared Spectrophotometer

A Perkin Elmer model 783 infrared (IR) spectrophotometer, with a sodium chloride disc as the sample window, was used for qualitative IR fingerprinting of the sample. Quantitative IR absorbances of test samples were measured on IR spectrophotometer model PU-9512, with a $CaF_2$ window and a 0.1-mm path, against 30% TBP-*n*-dodecane.

## Plutonium Retention Test

The inefficacy of the solvent cleanup by sodium carbonate scrub in removing the highly hydrophobic and metal-complexing radiolytic products led to an increase in the plutonium- retention behavior of the extractant TBP. The quality of the solvent was checked by a Pu retention test. After three scrubbings with sodium





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carbonate and distilled water, the irradiated sample was contacted with a plutonium (IV) tracer (200 mg/L) at 2 mol/L $HNO_3$ to allow maximum loading (1:1 contact for 20 minutes) of the solvent. The plutonium retained in the solvent after stripping four times with equal volumes of 0.1 mol/L $HNO_3$ was estimated by planchetting a 50-μL aliquot for radiometric measurements with an alpha proportional counter. For each sample, the unirradiated 30% TBP-*n*-dodecane stock was used as a reference blank. The plutonium retention of the solvent has been reported as alpha disintegrations per minute (dpm) for a fixed aliquot of organic phase.

## Alumina Treatment

The samples of 30%TBP-*n*-dodecane-$HNO_3$ spiked with 3 vacuum-distilled fractions were subjected to treatment with neutral alumina (200 mg/3 mL, 20 minutes). The samples of 30% TBP-*n*-dodecane-$HNO_3$ subjected to increasing periods of radiolysis were also treated in a similar manner. Alpha counting was conducted using a proportional counter with efficiency of 49.55%.

## Procedure

### Sample Irradiation

The sample of pure TBP (>99.5% by GLC assay) was gamma radiolyzed for an absorbed dose of 24 MRads for use in monitoring the GLC signatures of HMP species. In addition, the samples of 30% TBP-*n*-dodecane-$HNO_3$ were radiolyzed for an absorbed dose of 43.5 MRads to enhance the yield of degradation products, which were further enriched by vacuum distillation and subsequently subjected to GC/MS assay and Pu retention tests.

To study the plutonium retention behavior of the solvent as a function of absorbed dose, suitable aliquots of the sample undergoing γ radiolysis were withdrawn after 7 hours of radiolysis.

### Fractionation of Radiolyzed Solvent: Vacuum Distillation

To establish the precise nature of the radiolytic degradation products, a sample with an absorbed dose of 43.5 MRads was vacuum distilled. The process yielded 3 products: One reached a boiling point at 46–48°C under vacuum of 0.1 mm Hg; another had a boiling point of 98–105°C under vacuum at 0.05 mm Hg; and the last fraction was a brown residue.

Each of these sample fractions was fingerprinted by GLC and IR, and the corresponding plutonium retention values were determined before and after alumina treatment.





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Phosphoric Acid Equilibration Method

Phosphoric acid equilibration is another method of resolving the radiolyzed solvent for ascertaining the identity of the species formed from DDPs and TBP degradation products, especially the more hydrophobic HMP species.

To assess the nature of chemical modifications in the solvent, the radiolyzed sample (absorbed dose = 35 MRads) was fractionated into a diluent-rich layer and a middle phase containing organophosphate-rich fractions. This was accomplished by equilibrating the radiolyzed solvent with concentrated phosphoric acid to obtain a lighter diluent phase fraction and a relatively dense phase, the middle layer/phase, that is the adduct of organophosphate with concentrated $H_3PO_4$ (12–13). The organic component obtained by breaking the middle phase/layer adduct through dilution with excess water was named "the middle phase."

## RESULTS AND DISCUSSION

### Gas-Liquid Chromatography Study

Results of GLC fingerprinting of the unirradiated and γ-irradiated samples of pure TBP without any derivatization under condition no. 1 (esterification with diazomethane) are shown in Figs. 1a and 1b, respectively. The retention time of the individual species (GLC peaks) is, in general, a function of its boiling point, which is related to its molecular weight. We observe several distinct peaks characterized by retention times greater than that of TBP, which would presumably correspond to formation of HMP species.

Figures 2a, 2b, and 2c show the GLC fingerprinting of the γ-irradiated 30% TBP-*n*-dodecane-$HNO_3$ using a flame ionization detector (FID) and nitrogen-phosphorous detectors in N + P and P selective modes under identical conditions using suitable attenuation. The N + P mode of GLC detection signifies the presence of species containing nitro, nitro and phosphoryl groups together, or phosphoryl groups alone. Special attention is drawn to the peaks with retention times higher than that of TBP in these chromatograms. Several peaks (no. 1, 2, and 4) are common to the chromatograms in N + P and P mode of detection. However, in P mode of detection, many additional peaks (HMP species) of retention times higher than that signified by peak no. 5 were not detected by FID.

Figure 3 shows typical gas chromatogram obtained from a flame photometric detector of radiolytic degradation products of 30% TBP-*n*-dodecane-$HNO_3$ (esterified sample, absorbed dose = 43.5 MRads) enriched by vacuum distillation (last residue) under GLC condition no. 1. Arrows indicate peaks of HDBP, TBP, and HMP species. Even under high signal attenuation and sample dilution (100





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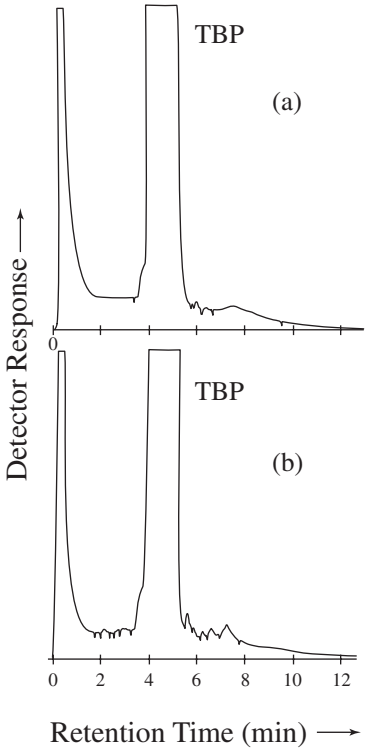


***Figure 1.*** Gas chromatographic fingerprint of (a) unirradiated and (b) γ-irradiated undiluted TBP; absorbed dose = $2.4 \times 10^5$ Gy.

times), several gas chromatographic signatures of HMP species of varying intensities were similar to those seen in Fig. 3. This experimental observation provides additional evidence to radiolytic formation of HMP species in the studied system.

## Study of Vacuum Distilled Fractions

### Gas Chromatography

Figs. 4a, 4b, and 4c show the typical GLC composition profiles under condition no. 2 of radiolyzed solvent (absorbed dose = 43.5 MRads), the second distilled fraction and the third fraction, i.e. last residue left (at 98°C and $10^{-2}$ mm Hg) of the solvent. The XE-60 column is a moderately polar column, where order of

elution also follows the order of the polarity of species. The first distillate (at boiling point = 38°C and $10^{-3}$ mm Hg) predominantly containing nonpolar diluent components (retention times of 0.0 to 1.6 minutes) of negligible Pu retention is not shown. Figure 4b, representing the composition profile of the second distillate (boiling point of 98°C), reflects a high level of TBP enrichment (86%) as well as radiolytic products of hydrocarbon diluent (DDPs formed in the presence of nitric acid) (14). The higher intensities of DDP species observed in the chromatograms

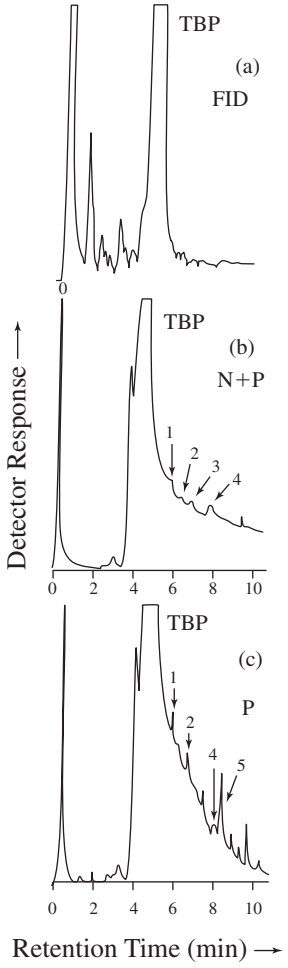


***Figure 2.*** Gas chromatographic fingerprint of γ-irradiated 30% TBP-*n*-dodecane-$HNO_3$ using (a) a flame ionization detector (FID) (b) N-P detector in N + P selective mode, (c) in P selective mode; absorbed dose = $2.4 \times 10^5$ Gy.





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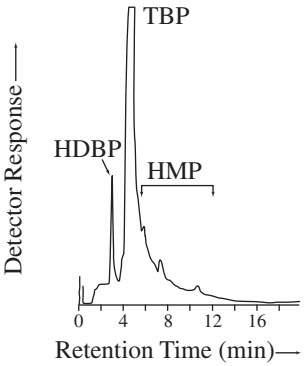


***Figure 3.*** Gas chromatogram obtained by phosphorous selective flame photometric detection of the third fraction obtained by vacuum distillation (0.05 mm Hg; boiling point = 98°C) of radiolyzed 30% TBP-*n*-dodecane-$HNO_3$ (absorbed dose = $4.35 \times 10^5$ Gy); dilution factor = 100; attenuation = 128 using GLC condition no. 1.

of the second fraction imply that their enrichment was achieved by removal of nonpolar diluent components through vacuum distillation. The codistillation of DDP species along with TBP implies some kind of physicochemical association between them, possibly through hydrogen bonding, as suggested in our separate communication (15). Had no such association been established, the DDPs would have distilled out as a separate fraction (TBP-free) at much lower temperature than that of TBP. This fraction possessed substantially high plutonium-retention behavior (Table 1).

Similar logic can be extended to the chromatograms of the third fraction (vacuum distilled residue) as shown in the Fig. 4c. This sample is essentially an HMP-enriched fraction as indicated by the presence of several intense peaks of higher retention times (refer to N-P fingerprint in Fig. 2b) than that of TBP. The presence of some peaks in the retention-time zone of DDPs indicates some existing associations between DDPs, TBP, and HMPs. The physicochemical association between DDPs, HMPs, and TBP resulted in a brown viscous residue that would undergo thermochemical transformation rather than boiling at relatively high temperature. In the case of the colored residue, the occurrence of some thermochemical alteration (98°C) in the composition of radiolyzed solvent cannot be ruled out.

Table 1 shows that the third fraction possessed the extremely high plutonium retention behavior indicative of preferential enrichment of Pu complexants. These HMP species with their high retention times exhibit strongly hydrophobic character, especially with respect to the alkaline scrub normally employed as solvent in the wash procedure. Thus, the HMP species tend to accumulate in the solvent upon each recycling, and more so, when a solvent wash is not a regular step during solvent recycling in the Purex process (Table 2). Table 2 also shows that

regular solvent cleanup of radiolyzed solvent slows down the accumulation of HMP species in the recycled Purex solvent.

Infrared Fingerprinting

Figure 5 shows that the most conspicuous IR signals of radiolytic products are in the regions of 1) 1520–1570 $cm^{-1}$ with absorption maxima = 1554 $cm^{-1}$

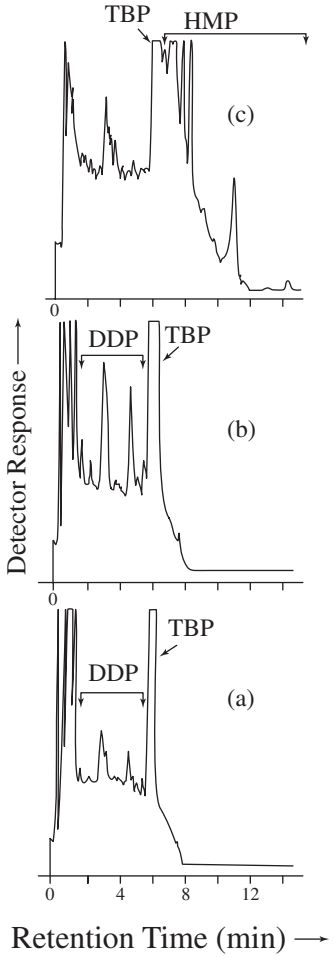


***Figure 4.*** Gas chromatographic profiles of unesterified samples of (a) radiolyzed solvent, absorbed dose = $4.35 \times 10^5$ Gy, and its vacuum distilled fractions; (b) second fraction, boiling point = 98°C; (c) third fraction, brownish-yellow residue.





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***Table 1.*** Plutonium Retention Behavior of Vacuum Distilled Fractions of 30% TBP-*n*-dodecane-$HNO_3$ with Absorbed Dose

| Fraction No. | Boiling Point (°C) | Vacuum mm of Hg | Aliquot Spiked to 30% TBP (10 mL) | Pu-Retention (dpm) | |
|---|---|---|---|---|---|
| | | | | Initial | After $Al_2O_3$ Treatment |
| 1 | 46–48 | 0.1 | 0.25 mL | 1065 | 28 |
| 2 | 98–105 | 0.05 | 0.25 mL | 6228 | 54 |
| 3 | > 105 | 0.05 | 0.10 mL | 260 110 | 2123 |

for nitro compounds, 2) 1620–1680 $cm^{-1}$ with absorption maxima ≈ 1645 $cm^{-1}$ for alkyl nitrates $RONO_2$/olefinic compound, and 3) 1700–1740 $cm^{-1}$ with absorption maxima = 1726 $cm^{-1}$ for carbonyl compounds (RCO/RCHO).

Semiquantitative IR absorbance measurements of Table 3 show that the intensities (yield) of these radiolytically generated nitro compounds in a 30% TBP-*n*-dodecane-$HNO_3$ system are much higher than those of the carbonyl species. The yields of these nitro and carbonyl species are dependent on the nitric acid content of the extraction system and the absorbed dose.

Finally, the first fraction of vacuum distillation was rich in *n*-paraffin only and lacked any of the typical IR bands that mark harmful radiolytic products as described above (fingerprint not shown). The second product had noticeable IR absorption in the region of interest and plutonium retention of high magnitude. The last, highly colored residue showed great intensification of alkyl nitrates/olefinic and carbonyl species.

***Table 2.*** GLC Concentration Profile of High Molecular Weight Organophosphates with Absorbed Dose

| Adsorbed Dose Gy | Concentration of all Radiolyzed Solvent Samples | |
|---|---|---|
| | Washed | Unwashed |
| $7.6 \times 10^4$ | 0.08 | 0.08 |
| $1.52 \times 10^5$ | 0.18 | 0.23 |
| $3.0 \times 10^5$ | 0.27 | 0.57 |

Washing/no washing refers to the radiolyzed sample with sodium carbonate solution before successive exposure to gamma radiation.





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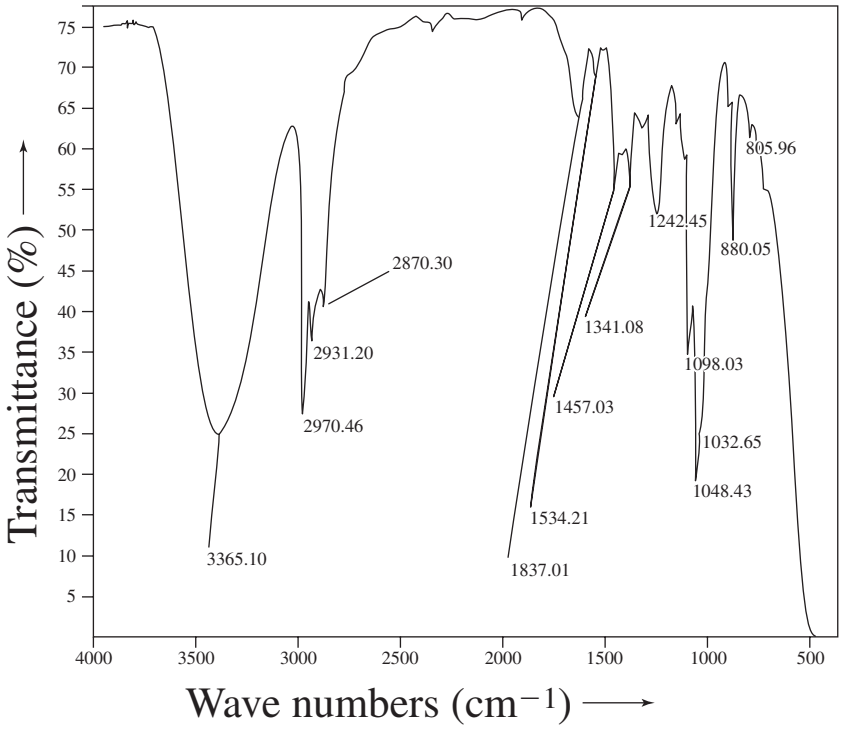


***Figure 5.*** IR fingerprint of the vacuum-distilled third fraction of 30% TBP-*n*-dodecane-$HNO_3$ (absorbed dose = $4.35 \times 10^5$ Gy) in methanol.

***Table 3.*** Dependence of Infrared Absorbance of 30% TBP-*n*-dodecane-$HNO_3$ System with Absorbed Dose and $[HNO_3]_{TBP}$

| | IR Absorbance (Area unit) at Absorbed Dose (× 100) | | | |
|---|---|---|---|---|
| | $2.4 \times 10^5$ Gy | | $4.85 \times 10^5$ Gy | |
| $[HNO_3]_{TBP}$ (mol) | [1510–1580] $cm^{-1}$ | [1700–1750] $cm^{-1}$ | [1510–1580] $cm^{-1}$ | [1700–1750] $cm^{-1}$ |
| 0.18 | 1.9 | 0.63 | 3.1 | 1.43 |
| 0.57 | 2.8 | 0.90 | 5.0 | 2.56 |

Cell: $CaF_2$ Path length = 0.1 mm.
Blank = 30% TBP-*n*-dodecane.





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## Study of Fractions Resolved by Phosphoric Acid Equilibration

Gas Chromatography

Figures 6a and 6c show the chromatograms of the diluent phase and the middle phase (TBP-rich fraction), while Fig. 6b represents that of the radiolyzed solvent (starting material, absorbed dose = 35 MRads). The chromatogram depicted in Fig. 6a shows intensification of the signals corresponding to DDP species and reduced intensity of those peaks associated with TBP and HMP species. We observed that the concentration of DDP species in 30% TBP-*n*-dodecane-$HNO_3$ increases with absorbed dose; the efficacy of TBP removal by phosphoric acid equi-

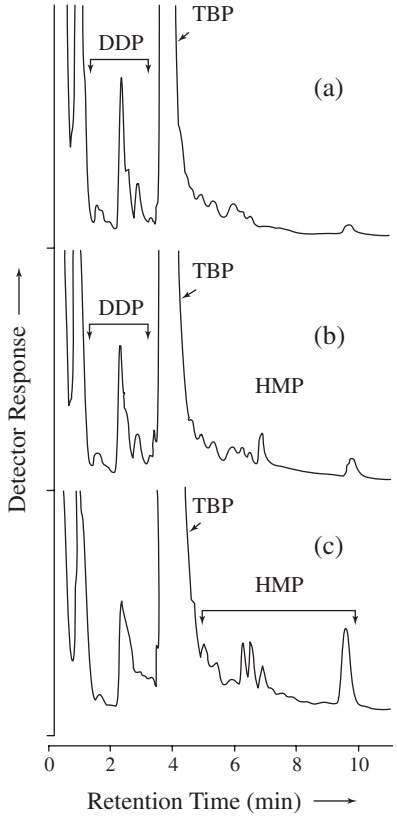


***Figure 6.*** Typical gas chromatograms of (a) diluent phase, (b) the radiolyzed solvent (absorbed dose = $3.5 \times 10^5$ Gy), and (c) middle phase; the diluent and middle phase were obtained by phosphoric acid equilibration method.





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libration was reduced. This phenomenon may be attributable to the increasing extent of H bonding between TBP and DDPs.

The chromatogram of the middle phase shows a strong TBP peak and enhanced peaks of HMP species. In addition, the middle phase also contains a relatively low amount of DDPs. This observation further supports the possibility of association between TBP, HMPs, and DDPs. The existence of strong associations (hydrogen bonding) between TBP, nitro-alkanes ($RNO_2$), hydroxy species (ROH), and HMP species may be responsible for the undesirable changes in the physicochemical behavior of the radiolyzed solvent (15). This reason explains why the formation of even small amounts of radiolytic species has been reported to cause relatively large increases in the viscosity of the solvent. Because HMP species include several nitro TBP species, the degree of association is expected to be enhanced between various radiolytic species.



### Infrared Study

Figures 7a and 7c respectively show IR fingerprints of the diluent phase and the middle phase respectively, while Fig. 7b shows that of the radiolyzed 30%TBP-*n*-dodecane-$HNO_3$ (the starting material with absorbed dose = 35 MRads).

Apart from the diluent component, the middle phase (a relatively dense organophosphate-rich fraction including HMP) of the radiolyzed solvent exhibits strong signals of nitro compounds, indicating the presence of nitrated TBP species. In addition to this result, a peak of approximately 1729 $cm^{-1}$, due to the existence of carbonyl species, is also present in this fraction. These observations are valuable guides in the identification of peaks by the GC/MS-library search method. The IR spectra of the last residue (vacuum distilled) suggest the presence of nitro and carbonyl groups, which are quite likely to be associated with HMPs.

## Gas Chromatography–Mass Spectroscopy Studies

Figure 8 shows the total ion current versus retention time of the GC/MS spectrum for the third fraction (the last, high-boiling residue) obtained by vacuum distillation of the radiolytically degraded 30% TBP-*n*-dodecane-$HNO_3$. Because isobutane gas is the mode of ionization, and no library search facility is available for chemical ionization results, the identification of a given species was based on the molecular ion peak that had the highest intensity. Besides, the mechanism of radiolytic transformation is fairly well understood; it is easier to predict the species corresponding to a given molecular ion peak. The peak with retention time 13.18 minutes was identified as TBP because of the characteristic molecular ion peak 266. Results from gas chromatographic fingerprinting (with packed column) has already suggested the possibility of nitro and phosphorous compounds corresponding to



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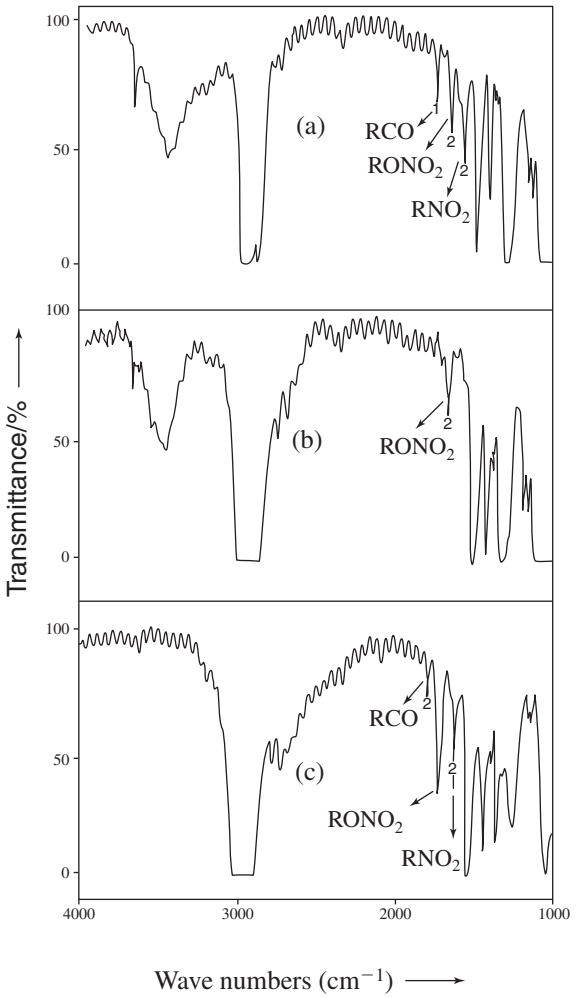


***Figure 7.*** IR fingerprint of the (a) diluent phase, (b) the radiolyzed solvent, absorbed dose $= 3.5 \times 10^5$ Gy, and (c) middle phase; the diluent and middle phase were obtained by the phosphoric acid equilibration method.

several peaks eluting after TBP. Owing to inherently greater resolution power, the capillary column of the GC/MS system yielded more HMP peaks for the same sample than were obtained with the packed-column gas chromatographic assay. Based on the intense molecular-ion peak of the typical GC/MS profile in chemical ionization mode, the HMP peaks designated as 1, 2, 3, 4, 5, and 6 are respectively $CH_3$—TBP, OH—TBP, $O_2N$—TBP; $O_2N$—TBP; $O_2N$—TBP; $O_2N$—TBP. The

peaks identified as $O_2N$—TBP and denoted with 1, 2, 3, and 4 may be TBP nitrated at different carbon atoms of the butoxy groups each with molecular ion peaks at 312. The increasing order of the retention times of these peaks is also suggestive of the relative order of their polarities. Because the sample subjected to the GC/MS assay had been preconcentrated by vacuum distillation and subsequently diluted to facilitate injection into the GC; hence, the exact concentration factor is not available. If these qualifying factors are ignored, we can state that the relative percentages of the HMP species in the sample subjected to GC/MS assay is in following order: HMP1 (MeTBP, m/z = 281) = 0.43; HMP2 (OH—TBP, m/z = 283) = 2.36; and the 4 nitrated TBP species identified with molecular ion peaks of 312 were HMP3 = 0.5, HMP4 = 0.26, HMP5 = 2.09, and HMP6 = 0.98. TBP in this enriched fraction was shown to be 85.09%.Thus, the GC/MS assay led to a precise identification of HMP species as suggested by the results from nitrogen and phosphorous selective detectors and those from the packed-column gas chromatographic study.

## Probable Mechanism

Although the extent of C—C bond scission is relatively less with straight chain hydrocarbons, a smaller yield of methyl radicals along with corresponding low carbon-chain hydrocarbon radicals is also formed. This alkyl radical may undergo substitution to either the diluent (*n*-dodecane) or the butoxy groups of TBP.

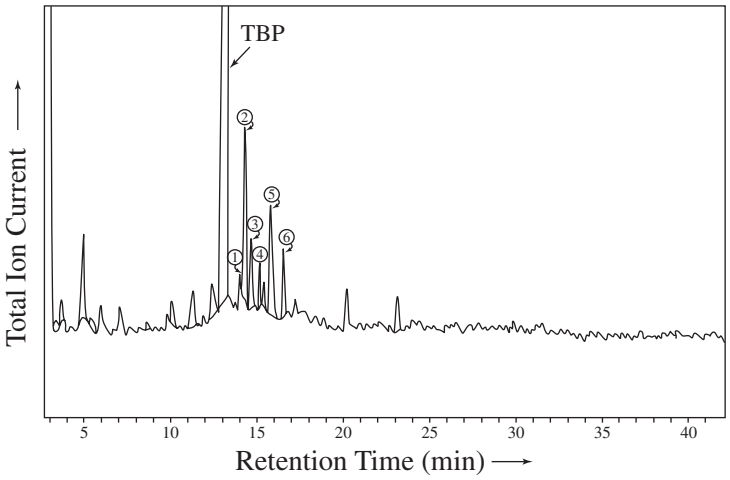


***Figure 8.*** GC/MS spectra of radiolyzed 30% TBP-*n*-dodecane-$HNO_3$ (absorbed dose = $3.5 \times 10^5$ Gy) obtained from a chemical ionization detector set in the range of 70–700 AMU. The HMP peak labels correspond to species identified on the basis of molecular ion peak (CI source) as 1 = $CH_3$—TBP; 2 = OH—TBP; 3 = [$NO_2$—TBP]1; 4 = [$NO_2$—TBP]2; 5 = [$NO_2$—TBP]3; and 6 = [$NO_2$—TBP]4.





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In addition, these radicals may undergo interaction with other radicals that will lead to the formation of new species.

However, a likely mechanism is one in which the hydrogen-deficient butoxy groups of TBP give rise to an alkyl-substituted TBP. Formation of nitrated TBP may also arise from the action of $NO_2$ and $NO_3$ radicals as described in subsequently presented equations.

Generation of derivatized radicals may arise from the radiolysis of water as well as nitric acid extracted in the solvent (Eqs. 1–3).

$$HNO_3 \;\sim\!\!\rightarrow\; OH\cdot + NO_2\cdot \tag{1}$$

$$H_2O \;\sim\!\!\rightarrow\; OH\cdot + H\cdot \tag{2}$$

$$HNO_3 + OH \rightarrow H_2O + NO_3\cdot \tag{3}$$

Generation of alkyl radicals may arise of the hydrocarbon diluent, which is represented as $R_1H$, as depicted in Eqs. (4–7).

$$R_1H \;\sim\!\!\rightarrow\; [R_1H^*, R_1^+\cdot, e] + e \tag{4}$$

$$R_1H^* \rightarrow R_1\cdot + H\cdot \tag{5}$$

$$\rightarrow R_1\cdot'\cdot + H_2 \tag{6}$$

$$R_1H + OH\cdot/H\cdot/NO_2/NO_3\cdot \rightarrow R_1\cdot + H_2O/H_2/HNO_3 \tag{7}$$

Similarly, generated TBP radicals may arise from reactions depicted in Eqs. (10) and (11):

$$[(RO)_3P=O] \;\sim\!\!\rightarrow\; [(RO)_3P=O^* \rightarrow [(RO)_3P=O]^+\cdot + e \tag{8}$$

$$[(C_4H_9O)_3P=O] + OH\cdot/H\cdot/NO_2/NO_3\cdot \rightarrow \cdot C_4H_8O(C_4H_9O)_2P=O + H_2O/H_2/HNO_3/HNO_3 \tag{9}$$

Formation of HMPs may result predominantly from the recombination of alkyl radicals and TBP (hydrogen deficient) radicals as follows:

$$\cdot C_4H_8O(C_4H_9O)_2P=O + R_1\cdot \text{ or } R_1'\cdot \rightarrow (R_1' \text{ or } R_1\text{—}C_4H_8O)(C_4H_9O)_2P=O \tag{10}$$

$$+NO_2\cdot \rightarrow (O_2N\text{—}C_4H_8O)(C_4H_9O)_2P=O \tag{11}$$

$$+NO_3\cdot \rightarrow (O_2NO\text{—}Cs_4H_8O)(C_4H_9O)_2P=O \tag{12}$$

$$+OH\cdot \rightarrow (OH\text{—}C_4H_8O)(C_4H_9O)_2P=O \tag{13}$$

## Plutonium Retention Behavior and Alumina Treatment

The plutonium retention by the solvent after sodium carbonate wash was found to increase with the absorbed dose and gets restored almost to original value by the treatment of the solvent with alumina.





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Table 1 shows the plutonium retention behavior of the 3 vacuum distilled fractions before and after alumina treatment. For a comparative study of the Pu retention test, small aliquots (0.25 mL) of the first and second fractions and 0.1 mL to the third fraction were spiked to 10 mL of unirradiated solution of 30% TBP-*n*-dodecane-$HNO_3$ and the corresponding Pu amount retained was determined. The retention of Pu by the first fraction was the same as that of fresh 30% TBP-*n*-dodecane (control). However, amounts of Pu retained in second and third fraction were in exponentially increasing order. The vacuum-distilled third fraction obtained from the γ-irradiated 30% TBP-*n*-dodecane-$HNO_3$ contains strong plutonium complexants. The data of Table 1 also suggest that alumina treatment of the third fraction significantly reduces the extremely high Pu retention behavior of the HMP rich fraction. Correspondingly, a comparative examination of its quantitative GLC profile revealed near quantitative and selective removal of most of the HMP species, especially the nitrated TBP. Also, we observed substantial reduction in the intensities of IR bands (semiquantitative data not shown here) in the region of 1556, 1650, and 1726 $cm^{-1}$. Based on these observations, we believed that identified GLC markers of HMP species, associated with characteristic infrared features, are among the suspected Pu-retaining species. However, other complexing species capable of plutonium retention proposed by several other authors (7,8) cannot be ruled altogether because the system under study was a multicomponent mixture.



## Infrared Studies

Semiquantitative measurements of the intensities of characteristic IR fingerprints corresponding to nitro compounds and carbonyl species (Table 3) suggest that the yield of nitro compounds is much greater than that of the carbonyl species. Also, the absorbance of nitro and carbonyl species are dependent on absorbed dose as well as nitric acid content of the solvent prior to gamma radiolysis.

***Table 4.*** Pu Retention Behavior of Radiolytically Degraded Solvent

| | System: 30% TBP-*n*-dodecane-$HNO_3$ | |
|---|---|---|
| | Pu-retention (dpm) | |
| Dose Gy | Initial | After $Al_2O_3$ Treatment |
| 03.4 × 103 | 705 | 26 |
| 0.68 | 2083 | 40 |
| 1.03 | 9987 | 197 |
| 1.37 | 15936 | 316 |



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## CONCLUSIONS

The present investigation enabled us to identify the GLC signatures of HMP species. Nitric acid induced radiolytic degradation of 30% TBP-*n*-dodecane also results in the nitration of TBP, of course, to a lesser extent than that of the hydrocarbon diluent.

The HMP species tend to remain associated with polar DDPs. Such an association is difficult to break despite phosphoric acid equilibration of radiolyzed solvent. The enrichment of HMPs in the last fraction achieved by vacuum distillation showed that the HMP species possess color and high viscosity. These HMP species are reported to be hydrophobic and resistant to removal by alkaline scrub and enhance the plutonium retention behavior after several stages of Purex solvent recycling. They are likely to behave like surfactants and cause phase separation problems during extraction.

The gas chromatographic signatures suggest that the HMP species (the $NO_2$ derivatives of TBP) are the most likely to enhance Pu retention of radiolytically degraded solvent. Hence, the dose-dependant deterioration in the quality of the recycled Purex solvent can be evaluated by systematically monitoring the concentration profiles of these HMP species by GLC.



## ACKNOWLEDGMENTS

The authors thank Shri K. Balu, Director, Nuclear Recycle Group (NRG) and Shri V. P. Kansara, Associate Director, NRG, for their encouragement during the course of the present investigation. The authors thank Dr. M. S. Nagar, Radiochemistry Division, Dr. L. P. Badheka, and Dr. Subroto Chattopadhyay, Head, Bioorganic Division for their kind support in the experimental work. Authors also thank Shri N. K. Rikhari for providing the quality scans of the figures.

## REFERENCES

1. Schulz, W.W.; Navratil, J.D. *Science and Technology of Tributyl Phosphate*; CRC Press Inc: Boca Raton, FL, 1984; Vol. 1, 9–10.
2. Tahraqui, A.; Morris, H. Decomposition of Solvent Extraction Media During Nuclear Reprocessing. Sep. Sci. Technol. **1995,** *30* (12), 2603.
3. Tripathi, S.C.; Ramanujam, A.; Nadkarni, M.N.; Bandyopadhyay, C. Thin Layer Chromatographic Separation and Spectrophotometric Determination of Dibutyl Phosphate in a Mixture of Monobutyl Phosphoric Acid and Tri-*n*-Butyl Phosphate. Analyst **1986,** *111,* 239.
4. Kuo, C.H.; Shih, J.S.; Yeh, Y.C. Determination of Dibutyl Phosphate and Monobutyl Phosphate in Mixtures of Kerosene and Tributyl Phosphate. Analyst **1982,** *107,* 1190.



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5. Bocek, P.; Dolnik, V.; Deml, M.; Janice, J. Separation and Determination of Degradation Products of Tributyl Phosphate by High Speed Analytical Isotachophoresis. J. Chromatog. **1980,** *195,* 303.
6. Lee, Y.C.; Ting, G. Determination of Dibutyl and Monobutyl Phosphate in Tributyl Phosphate Kerosene Mixture by Solvent Extraction and Gas Chromatography. Anal. Chim. Acta **1979,** *106,* 373.
7. Lash, R.P.; Hill, C.J. Ion Chromatographic Determination of Dibutyl Phosphoric Acid in Nuclear Fuel Reprocessing Streams. J. Liq. Chromatogr. **1979,** *4,* 417.
8. Tripathi, S.C.; Sumathi, S.; Ramanujam, A. Effects of Solvent Recycling on Radiolytic Degradation of 30% TBP-*n*-Dodecane-$HNO_3$. Sep. Sci. Technol. **1998,** *34* (14), 2887.
9. Brodda, B.G.; Heinen, D. Solvent Performance in Nuclear Fuel Reprocessing II. On the Formation of Dibutyl Phosphoric Acid by Radiolytic and Hydrolytic Degradation of TBP-*n*-Paraffin Extractant. Nucl. Technol. **1977,** *4,* 428.
10. Shankar, R.; Venkateswarulu, K.S. Estimation of Substituted Phosphates Such as Dibutyl and Monobutyl Phosphates Based on Their Reaction with Lanthanum-Xylenol Orange Complex. Talanta **1972,** *19,*1207.
11. Ryan, E.; Wheelwright, A.W. The Recovery, Purification and Concentration of Plutonium by Anion Exchange in Nitric Acid. US-AEC Rep HW-55983, 1959.
12. Adamov, V.M.; Andreev, V.I.; Belayaev, B.N.; Polyakov, G.S.; Ritari, A.E.; Yu.Shipol'nikov, A. Identification and Mechanism of Formation of Decomposition Products of Extraction Systems on the Basis of Tri-*n*-Butyl Phosphate Solutions in Aliphatic Hydrocarbons. Radiokhimiya **1992,** *34,* 189.
13. Desingker, D.S.; Ramaswamy, M.; Kartha, P.K.S.; Kutty, P.V.E.; Ramanujam, A. Treatment of Tributylphosphate Wastes by Extraction Cum Pyrolysis Process. Government of India, BARC Report, BARC-1480, 1989.
14. Tripathi, S.C.; Bindu, P.; Ramanujam, A. Studies on the Indentification of Harmful Radiolytic Products of 30% TBP-*n*-Dodecane-$HNO_3$ by Gas Liquid Chromatography. Part I: Formation of Diluent Degradation Products and Their Role in Pu Retention Behavior. Sep. Sci. Technol. **2001,** *36* (7), 1463–1478.
15. Tripathi, S.C.; Ramanujam, A. Effect of Radiation-Induced Physicochemical Transformations on Density and Viscosity of 30% TBP-*n*-Dodecane-$HNO_3$ System. Sep. Sci. Technol. in press.

Received August 1999
Revised October 2000

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