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# STUDIES ON THE IDENTIFICATION OF HARMFUL RADIOLYTIC PRODUCTS OF 30% TBP-n-DODECANE-$HNO_3$ BY GAS LIQUID CHROMATOGRAPHY. I. FORMATION OF DILUENT DEGRADATION PRODUCTS AND THEIR ROLE IN Pu RETENTION BEHAVIOR

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# STUDIES ON THE IDENTIFICATION OF HARMFUL RADIOLYTIC PRODUCTS OF 30% TBP-n-DODECANE-$HNO_3$ BY GAS LIQUID CHROMATOGRAPHY. I. FORMATION OF DILUENT DEGRADATION PRODUCTS AND THEIR ROLE IN Pu RETENTION BEHAVIOR

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The radiation-chemical transformations of Purex solvent, 30% TBP-n-dodecane-$HNO_3$, arising from radiolysis of nitric acid were examined by gas chromatographic fingerprinting of the radiolyzed system. The present study describes a procedure for identifying diluent degradation products by gas chromatographic, infrared and gas chromatographic—mass spectrographic assay. The identified gas chromatographic signatures can be used to monitor the growth of diluent degradation products (DDP) like nitroparaffins, long chain alcohols, and paraffins in the Purex solvent before its recycling. The increase in the concentration profiles of these species with absorbed dose parallels the increase in the retention of Ru, Zr, and

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Pu by the diluent phases resolved (by the phosphoric acid equilibration method) from the radiolyzed solvent under recycling conditions.

*Keywords:* TBP; Diluent degradation products; TBP, GC/MS; Gamma radiolysis; Gas chromatographic fingerprinting; Purex process.



## INTRODUCTION

In the reprocessing of spent nuclear fuel, a mixture of 30% TBP and n-paraffins is used as the extractant for plutonium and uranium from nitric acid solution containing a large number of fission products. During the extraction stage, nitric acid also gets extracted in the solvent, which upon exposure to radiation yields a number of degradation products with varying physicochemical properties. The degradation products of the 30% TBP-n-dodecane-$HNO_3$ could be broadly placed in two major categories:

1 Those of extractant TBP: for example, dibutyl phosphoric acid (HDBP), monobutyl phosphoric acid ($H_2MBP$), butanol, butyl nitrate, and high molecular weight organophosphates (HMPs), also described as oligomers of TBP, detectable only at higher absorbed doses [1–3].
2 Those of hydrocarbon diluent: This may comprise a nonpolar mixture of hydrocarbons and a number of nitroparaffins and subsequent derivatives [4–5]. A number of reports in the literature deal with the acidic degradation products of TBP, HDBP and $H_2MBP$, which can be removed by routine alkaline treatment before recycling [6–10]. It is known that the solvent wash becomes increasingly ineffective with successive recycling of the solvent in the Purex process [11]. This is due to incomplete removal of nitric acid-induced degradation products of the diluent, which is relatively more hydrophobic and constitutes the major impurities fraction in the radiolytically degraded solvent. Accumulation of such species in the solvent leads to increase in the viscosity and density as well as poor phase separation. Therefore, having removed the degradation products of TBP (e.g., HDBP and $H_2MBP$) by alkaline wash, the loss in the quality of the solvent should be a function of the concentration of these hydrophobic degradation products of n-paraffin diluent. Although there are some reports on the identification of these species in radiolyzed solvents [12–13], there is scarcely any report providing a standard

method for their qualitative and quantitative assay in the recycled Purex solvent. This is probably the reason behind the lack of any standard criteria based on compositional assay for the rejection of Purex solvent as "waste" after a certain number of extraction cycles.

Among the diluent degradation products, primarily formed nitroparaffins are reported to be the precursors of a deleterious species that is surface active and are emulsifiers formed as a result of secondary reactions [14]. The presence of such polymeric derivative species results in reduced mass transfer and poorer phase separation. Growing concentration of such surfactant-like species in the solvent leads to poor strippability of metal ions from the extraction system. Formation of emulsion also occurs during the solvent cleanup stage, thus reducing the efficiency of the solvent purification. Finally, the buildup of a small fraction of surfactant-like species in the extractant may ultimately lead to its rejection as waste after a certain number of extraction cycles [15].



Prior to the development of the chromatographic methods of analysis of degraded Purex solvent, titrimetric and potentiometric methods were employed. The liquid chromatographic methods reported in literature deal only with the estimation of HDBP and $H_2MBP$ in 30% TBP-n-paraffin mixture [16–17]. The ion chromatographic (IC) methods are known to be most sensitive with respect to the quantitative determination of HDBP and $H_2MBP$, which are removed by alkaline treatment of the degraded solvent [16]. However, both IC and HPLC methods have their inherent limitations with respect to resolving and detecting the multicomponent species of varying natures and boiling points, in radiolyzed solvent.

Gas liquid chromatography with its relatively high resolution power for a variety of organic compounds of widely differing chemical natures is a potential tool for monitoring the growth of degradation products of the solvent [18]. Hyphenated techniques like GC-MS and GC-FTIR under optimal condition are the most suitable devices for the characterization of the individual species resolved by the gas chromatographic system.

Since identification and routine analysis of radiolytic species are challenging analytical problems, it would be more appropriate to focus attention on easily identifiable nitration products of the diluent as markers in the recycled solvent [19]. These considerations have prompted us to investigate the signatures of nitric acid induced radiolytic products of the diluent in the gas chromatographic fingerprinting of the 30% TBP-n-dodecane-$HNO_3$ system.

It may be emphasized that for practical applications in quality control tasks, packed column gas liquid chromatography, owing to rapidity and ruggedness, is a widely recommended technique. Hence, the present work stressed the use of packed column GLC assay for identification purpose.

Due to formation of a large number of degradation products by the ionizing gamma radiation packed column GLC analysis will not be able to offer perfect resolution of multicomponent mixture. Although the capillary columns offer very efficient resolution and precise identification (in tandem with MS) of such a multicomponent mixture, they cannot be used on a routine basis, where economy, rapidity, and ruggedness are important practical considerations. Hence, an analytical approach using packed column GLC was considered desirable.

The present report describes a procedure for identifying the degradation products of the diluent in a radiolyzed 30% TBP-n-dodecane-$HNO_3$ system under optimized GLC conditions used for routine analysis of Purex solvent. An attempt has been made to find a correlation between the growth of gas chromatographic signatures of nitric acid induced radiolytic degradation products of the diluent and their extraction performance towards radionuclides (Pu, Zr, and Ru) encountered in the Purex process.



## EXPERIMENTAL

### Reagents and Chemicals

Tri-n-butyl phosphate from Fluka AG ($>99\%$ pure) was used as such. n-Dodecane from Aldrich ($>99\%$ pure) was used. Samples of 30% TBP-n-dodecane were made by suitable mixing of TBP and n-dodecane followed by scrubbing the mixture with 2% (m/V) solution of sodium carbonate. All other reagents used, unless specified, were of AR grade.

### Sample Preparation Methods

#### Identification Method for Diluent Degradation Species

The samples of n-dodecane and 30% TBP-n-dodecane mixture before and after equilibration with nitric acid were subjected to gamma radiolysis ($^{60}$Cobalt source, dose rate $= 0.30 \pm 0.03$ Mrad/h) for 24 h. In order to recover the diluent component/phase from the gamma-irradiated 30%

TBP-n-dodecane mixtures the radiolyzed solvent samples were contacted (1:1 v/v, 20 min, 3 times) with concentrated phosphoric acid.

This resulted in the segregation of the radiolyzed solvent into a lighter diluent phase containing a small percentage of TBP and another denser and viscous fraction rich in organophosphate content. All of the samples were fingerprinted by GLC under standardized conditions [20] used for the quantitative assay of the Purex solvent. These samples were also fingerprinted by FTIR.

### Mixed Phase Irradiation

In order to confirm that the identified degradation species in the segregated diluent phases were originating from the diluent (n-dodecane) only, a sample of the n-dodecane in contact with nitric acid (two-phase system) was also kept for gamma irradiation (absorbed dose = 7.2 Mrads). The sample was periodically shaken (manually) in order to facilitate greater interaction between the two phases. This sample was also fingerprinted by GLC under identical conditions.

### Preparation of Diluent Samples Under Recycling Condition

The samples of 30% TBP-n-dodecane equilibrated with nitric acid (1 M) were subjected to steady state gamma radiolysis for periods of 5, 10, 15, and 20 h. These samples after each 5 h of irradiations were treated by 2% (w/v) $Na_2CO_3$ solution, followed by 1 M nitric acid, before further incremental exposure to gamma radiation. Each of these samples was subjected to the phosphoric acid equilibration method as above (1:1, v/v, 3 times) to give a low density "diluent phase." The samples were analyzed quantitatively by GLC (FID detection) and also subjected to IR fingerprinting.

## Extraction Behavior Studies

All of the diluent samples were equilibrated with an aqueous feed solution (2 M $HNO_3$) containing suitable amounts of major radionuclides as encountered in the Purex process, like Ru, Zr, and Pu. Samples of the diluent phases, after equilibration with the feed solution, were assayed radiometrically. Subsequently, the loaded samples were back-extracted (twice, 1:1, v/v, 20 min) with 0.1 N $HNO_3$ followed by radiometric assay of the organic phase. This value, expressed in $\mu$Ci/L (or mCi/L $\times 10^{-3}$) represents the extent of retention of the given radionuclide by the diluent phase component.

## Gas Chromatographic Assay

A Shimadzu model GC-9A gas chromatograph equipped with dual column FID was used. A column of dimension (1.5 m × 0.32 cm) containing 10% XE60 [25% cyanoethyl and 75% methyl silicone] coated on Anakrom ABS (80–100 mesh) was used with heating rate as specified below along with other operating parameters.

Column temperature: 170°C → 230°C (Heating rate = 10°C/min.)
Hold time (1 min) (10 min)

Injection port temperature = 230°C, carrier gas (He) flow = 44.5 mL/min was used. Quantifications of the analyte GLC peaks were carried out using area normalization method of the C-R3A data processor. Each time 2.0 [$\mu$L] of the sample was injected. Inlet carrier gas pressure was 3 kg/cm$^2$. The estimated concentration values of the analyte (diluent degradation products) are the mean of 3 determinations with an RSD of ±2%.



## IR Assay

A Bomem model MB-101 FTIR equipment with an average resolution of 4 cm$^{-1}$ was used with $CaF_2$ windows of path length 1 mm, in the range of 1000–4000 cm$^{-1}$. The diluent phases of the samples of 30% TBP-n-dodecane, radiolyzed (absorbed dose = 7.2 Mrads) with and without equilibration with nitric acid (1 and 3 M) were fingerprinted by FTIR using KBr window of 1 mm path length.

## GC/MS Analysis

The diluent phase of radiolyzed solvent (total dose = 34 Mrad) samples was also assayed by GC/MS (Shimadzu, QP-5000) using DP-5 capillary column (50 m × 0.25 mm, film thickness = 0.25 $\mu$). Carrier flow rate was 1.0 mL/min. The EI was used as the ionization source with a Wiley library search device. It is mostly the polar and chemically active species that profoundly alters the extraction behavior of a pure solvent. Although the exact identification of the eluted species is not very obvious, it is worthwhile, especially from the solvent extraction point of view, to identify the most probable or suspected functional groups (from the suggested hit list compounds of the MS library) associated with the GLC peaks.

Temperature program condition for GC/MS studies:

Column Temperature: 80°C → 230°C[Program Rate = 10°C/min]
Hold time: (2 min) (25 min)

Injection port temp. = 250°C, carrier gas (He) flow rate = 44.5 mL/min; split ratio = 40; interface temp. = 260°C; mass range = 40–700 AMU.

## RESULTS AND DISCUSSION

### Gas Chromatographic Studies



Figure 1 shows the chromatograms of unirradiated and irradiated diluent (ndodecane). The radiolysis results in the formation of peaks represented as A, and a cluster of 5 small peaks represented as C1. Figure 2, (a) and 2(c), respectively, show the chromatograms of the radiolyzed samples of diluent phase of 30% TBP-n-dodecane of 30% TBP-n-dodecane-$HNO_3$, while Fig. 2(b) shows that of diluent (ndodecane)- $HNO_3$ two-phase system (radiolyzed with periodic manual agitations).

The peak A with retention time 1.41 min is common to gas chromatographic fingerprints of all of the samples; however, its radiolytic yield gets enhanced in the presence of $HNO_3$.Compound A is not produced exclusively in the radiolysis of nitric acid containing solutions. However, the peaks P1, P2, and P3 eluting between the peak A and the cluster C1 are observed only when the solvent samples are radiolyzed in the presence of $HNO_3$. The GLC signatures P1, P2, and P3, with characteristic retention times 1.99, 2.88, and 3.86 min, respectively, represent the major peaks (species) of their group associated with one or two minor peaks as shown in respective chromatograms. The elution profile of these species/peaks is generally observed to form a definite pattern, irrespective of its magnitude. Hence, these peaks represent the signatures of nitric acid induced radiolytic degradation products of the diluent (n-dodecane). The presence of these peaks grouped as P1, P2, and P3 in the chromatograms of the diluent (mixed-phase irradiation) as shown in Fig. 2b confirms that the identified species originate from the diluent. However, the observed difference in their quantitative profile is probably due to practical constraints of simulating identical radiation-chemical environment.

Figure 3 shows the dependence of the GLC concentration profiles of the nitric acid induced radiolytic products (identified as peak groups P1,

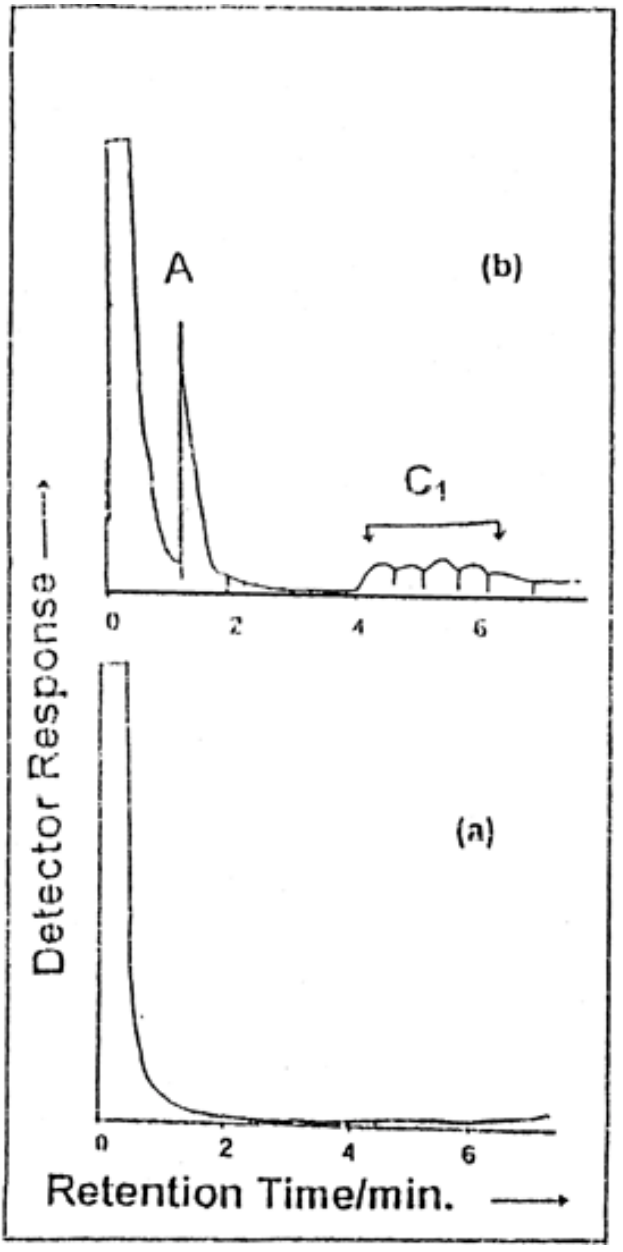


*Figure 1.* Gas chromatographic fingerprints of (a) unirradiated and (b) irradiated n-dodecane (absorbed dose = 14.5 Mrads).

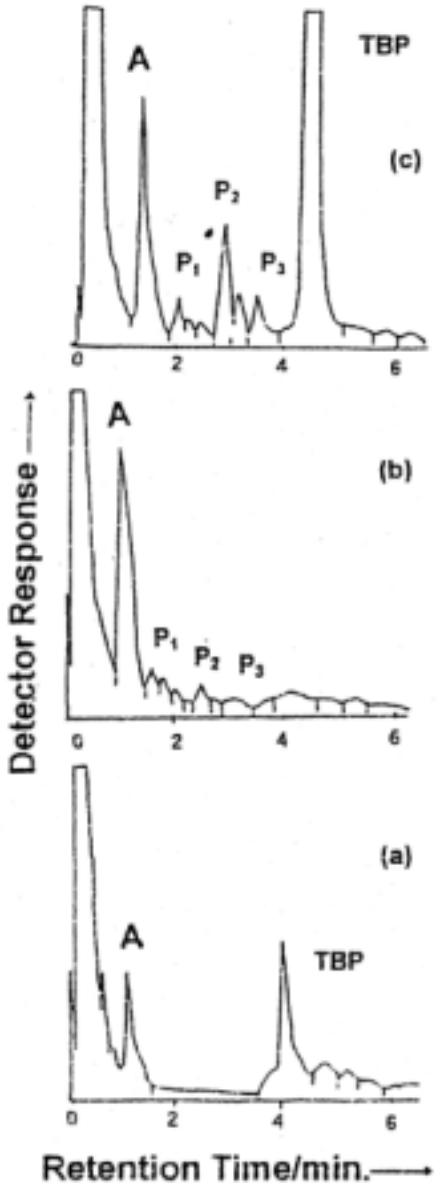


*Figure 2.* Gas chromatographic fingerprints of diluent phases of radiolyzed samples of (a) 30% TBP-n-dodecane, (b) irradiated n-dodecane of mixed phase radiolysis experiment, and (c) 30% TBP-n-dodecane-$HNO_3$ (absorbed dose = 14.5 Mrads).

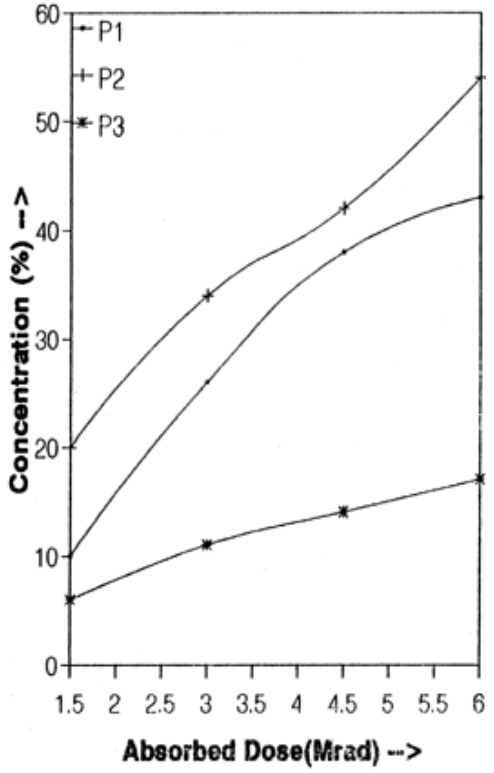


*Figure 3.* Dependence of GLC concentration profiles of nitric acid induced radiolytic products of the 30% TBP-n-dodecane-HNO3 denoted as (i) P1 (ii) P2 and (iii) P3, with absorbed dose.

P2, and P3) corresponding to Fig. 2c. The order of increase in the concentration with a given absorbed dose is: P2 > P1 > P3. Figure 4 shows the chromatograms of 30% TBPn-dodecane-$HNO_3$ (gamma radiolyzed) and that of actual process sample. The pattern of the eluted peaks qualitatively corresponds to the identified signatures P1, P2, and P3; however, the quantitative profiles, in particular that of P2 is very low in the case of the actual process solvent.

A typical capillary GC/MS spectrum of the diluent phase of radiolyzed solvent (total dose = 34 MRad) is presented in Fig. 5. Due to difference in the columns used in gas chromatographic study (using packed column) and GC/MS (capillary) assay, it is appropriate to look for relative position of the identified peaks, rather than the absolute retention

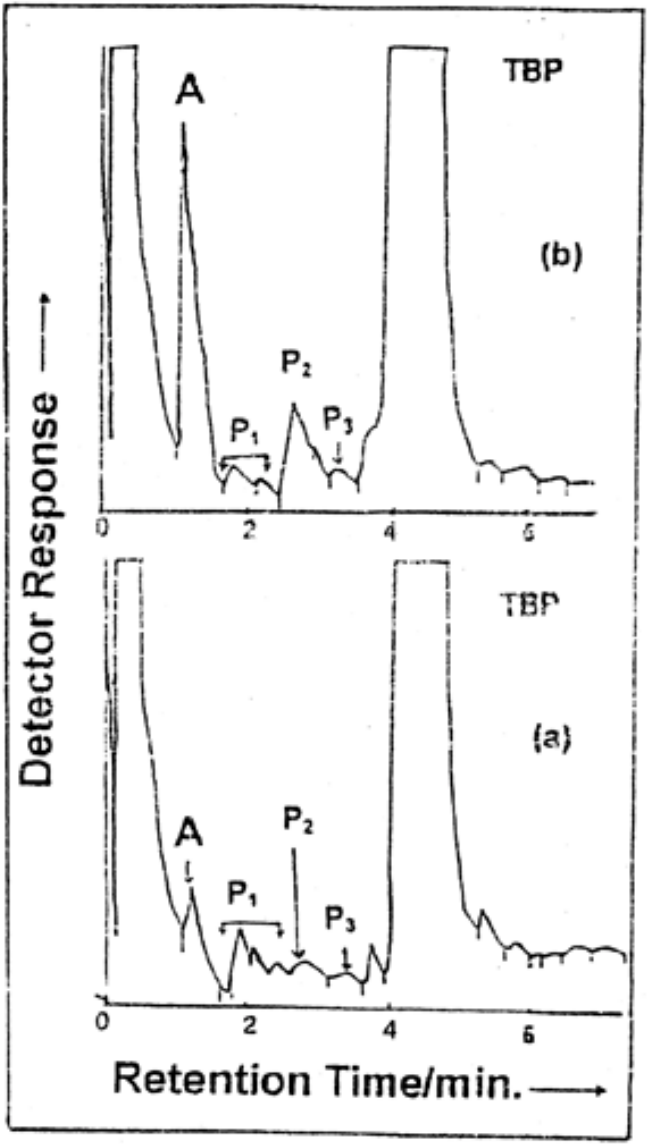


*Figure 4.* Gas chromatographic fingerprints of radiolyzed samples of (a) degraded process solvent and (b) 30% TBP-n-dodecane-$HNO_3$ (absorbed dose = 14.5 Mrads).

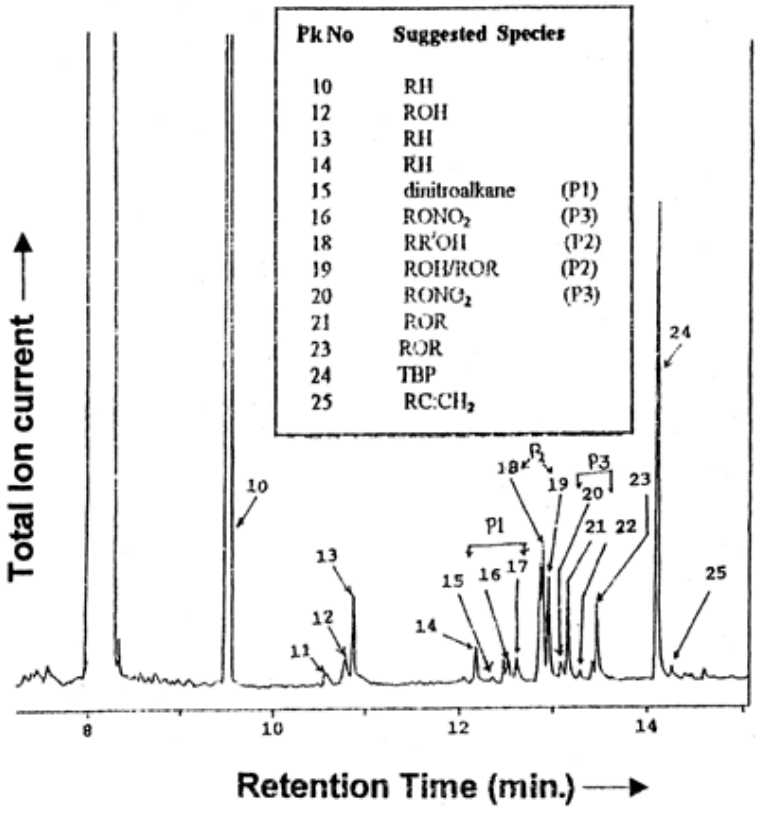


*Figure 5.* GC/MS Chromatograms of the diluent phase of radiolyzed (absorbed dose = 34 Mrad) 30% TBP-n-dodecane-$HNO_3$. The tentative identity of the numbered GLC peaks is given in the inset. The groups of GC/MS peaks corresponding to P1, P2, and P3 are identified by their typical elution pattern and with the TBP peak as reference, shown as enclosed regions. Different RH species typify alkanes of different boiling points.

times of the identified signatures. The tentative identities of the numbered GLC peaks are given in the inset. The groups of GC/MS peaks corresponding to P1, P2, and P3 are identified by their typical elution pattern and with the TBP peak as a reference, shown as enclosed regions. Different RH species typify alkanes of different boiling points. As usual, the higher the retention time of a species, the higher would be its molecular weight.

In spite of this, it has been observed that the pattern of peaks identified as gas chromatographic markers of radiolytic degradation (qualita-

tive and qualitative profiles) remains identical in GC and GC/MS studies. So the relative positions of the peaks have served as important references or indicators in the final stage of identifying components using capillary GC-MS data. Peak P2 is the most visible key marker of DDP species. Some of the DDP components elute before it and some after it. Besides, a hump (a small peak) always precedes that of TBP in all TBP samples (a manufacturing process impurity but not a radiolytic product). Hence, the peaks eluting after P2 and this "hump" has been used for tracing the origin of capillary column peaks corresponding to that obtained with packed column GC assay (P3).

Also, it is not claimed that peaks P1, P2, and P3 are pure peaks. Instead, they represent the group of peaks corresponding to the markers of harmful radiolytic species.

It should also be remembered the mass spectral data of eluted peaks (capillary column) did not correspond well with the hit list compounds suggested by the Wiley library search engine; for example, n-paraffins elute in the order of their boiling points and the library search did not strictly follow this fact. The only point that got confirmed was that a species under investigation is mostly an n-paraffinic one. The logic for identifying other species (ROR and $RONO_2$) was similar for other peaks in Fig. 5. In addition, the identifications based on library search (with a high confidence index) were found quite in contradiction to the derivatives (radiolytic) expected of the starting material (hydrocarbon diluent + TBP + $HNO_3$) for some of the peaks. Hence, our peak assignment ignored such identifications and mentioned only (appropriately) the functionality or nature of the species common to different alternatives species, irrespective of the associated confidence index.

It is equally noteworthy here that the species formed by gamma radiolysis of the solvent components does not necessarily deserve a place among the list of the mass spectral data of useful compounds in the Wiley standard library. The commercial nonavailability of the major radiolytic products (nitroparaffins) to be used as primary standards for more precise identification was a major practical limitation in the present study. Hence, insight from radiation chemistry of the studied system is carefully applied before making any confirmatory assignments.

The GC/MS analysis confirms the presence of a nitroalkanes corresponding to the GLC peak P1 and P3. However, the middle peak P2 corresponds to alkyl alcohols (ROH) and other derivatives ($ROR^{/}$) of diluent. The nitro compounds are present in smaller concentration as compared to the other species in the diluent phase component. It has been reported that the nitroparaffins associate themselves with TBP; hence possibly they would tend to remain with the TBP rich phase

obtained by phosphoric acid equilibration method. This explains the low concentration of nitroparaffins in the diluent phase. Formation of radiation-induced diluent degradation products may be explained in terms of following equations:

Direct Radiolysis of Hydrocarbon Diluent (RH):

$$RH \rightarrow [RH^*] \rightarrow [R\cdot + H] \text{or} [R^{/\cdot} + H_2] \tag{1}$$

$$H + RH \rightarrow H_2 + R\cdot; 2R\cdot \rightarrow R - R \quad \text{or} \quad RH + R^{/\cdot} \tag{2}$$

where $R^{/\cdot}$ is an unsaturated hydrocarbon radical. Nitric acid induced radiolytic products of the diluent may arise predominantly from the radiolysis of nitric acid, which dissociates into OH and $NO_2$ radicals.

$$HNO_3 \rightarrow OH\cdot + NO_2 \tag{3}$$

Nitration of the hydrocarbon diluent:

$$RH + NO_2 \rightarrow R\cdot + HNO_2 \tag{4}$$

$NO_2$ radicals react with n-paraffin to give nitroparaffin as follows:

$$R\cdot + NO_2 \rightarrow RNO_2 \text{ (nitro)} \qquad \text{(peak Pl)} \tag{5}$$

$$2R\cdot + O_{2(\text{dissolved})} \rightarrow 2RO + NO_2 \rightarrow RONO_2 \text{ (peak P3)} \tag{6}$$

or

$$R\cdot + HNO_{3(\text{undissociated})} \rightarrow RH + NO_3 \tag{7}$$

$$R\cdot + NO_3 \rightarrow \qquad RONO_2 \qquad \text{(peak P3)} \tag{8}$$

$$R\cdot + OH\cdot \rightarrow \qquad ROH \qquad \text{(peak P2)} \tag{9}$$

$$R\cdot + R\cdot R^{/\cdot} \rightarrow R - R \quad \text{or} \quad R - R^{/\cdot} \qquad \text{(polymerization) (peak P2)} \tag{10}$$

It should be remembered that routine assay of these products is normally performed on a packed column and hence, such gas chromato-

grams (using packed column) *only* should be able to provide correlation between the GLC peaks with deterioration in the solvent quality with each recycling. Therefore, each time capillary column GC/MS is not desirable, although it would be an ideal but impractical solution to the problem.

## Infrared Fingerprinting

Figure 6 shows the FTIR spectra of the samples of diluent phases of 30% TBP-n-dodecane radiolyzed with and without equilibration with nitric acid (1 and 3 M). The spectra show the absorption peaks of nitroparaffins (weak absorption at 1556 $cm^{-1}$) and that of alkyl nitrates ($RONO_2$, at 1650 $cm^{-1}$). The intensity of these peaks (nitro compounds) is observed to get enhanced with higher nitric acid content of the solvent prior to radiolysis. This observation supports the method of identification of nitric acid-induced radiolytic products of the diluent phase.



## Correlation of GLC Signatures with Extraction Behavior

Figure 7 shows the amounts of Pu/Zr/Ru species retained by the radiolyzed diluent phase components as a function of absorbed dose (1.5 to 6.0 Mrad) after back-extraction with 0.1 N nitric acid. It is observed that the amount of radionuclides retained by the solvent increases with absorbed dose. The relative order of retention is Pu > Zr > Ru.

This increases in the retention of radionuclides (Pu, Ru, and Zr) with absorbed dose parallels the increase in the GLC concentration profiles of diluent degradation products (DDP), especially the nitro alkanes. Here, the tentative chemical identity of the peak P2 revealed by GC-MS assay as ROH or long chain alkane (R-R/ R-$R^{/\cdot}$) does not impart it with metal complexing or retaining ability. Hence, the only GLC signatures P1 and P3 identified as $RNO_2$, $RONO_2$ may under favorable conditions be the cause of retention of radionuclides [19].

## CONCLUSIONS

The present study clearly reveals the identity of nitric acid-induced radiolytic products of diluent (n-dodecane), present in the diluent phase, as the typical gas chromatographic signatures. The identified species correspond to nitro alkanes, alcohols, and long chain hydrocarbons. However, the precise characterizations of these species will need detailed

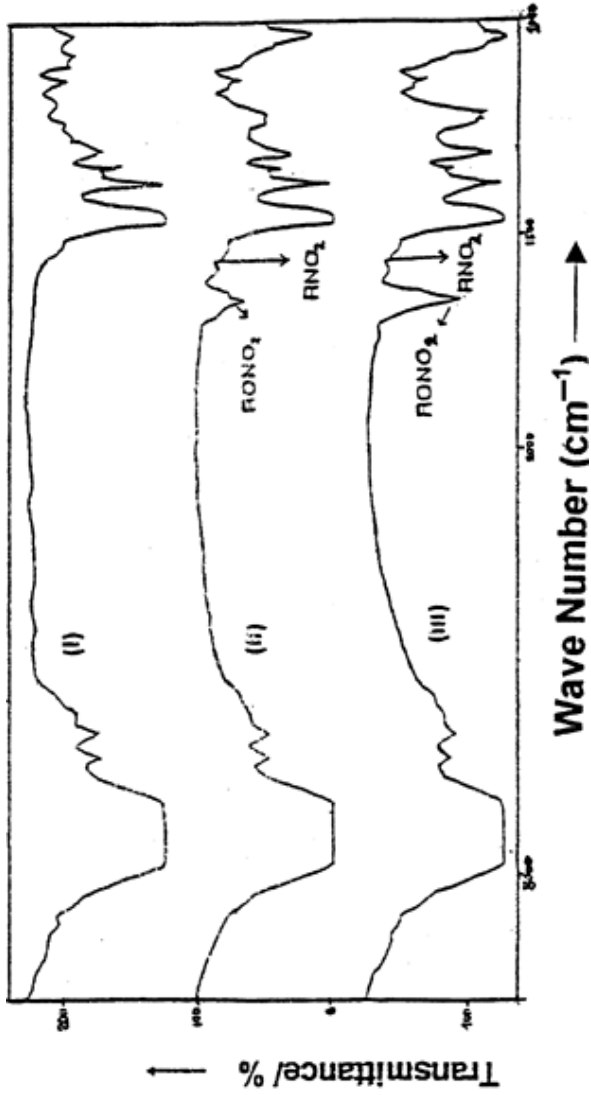


***Figure 6.*** FTIR fingerprint of the samples of diluent phases recovered from radiolyzed solvent (absorbed dose = 14.5 MRad) [i] 30% TBP-n-dodecane-$H_2O$, [ii] sample (i) equilibrated with $HNO_3$ (1M), and (iii) sample (i) equilibrated with $HNO_3$ (3M).

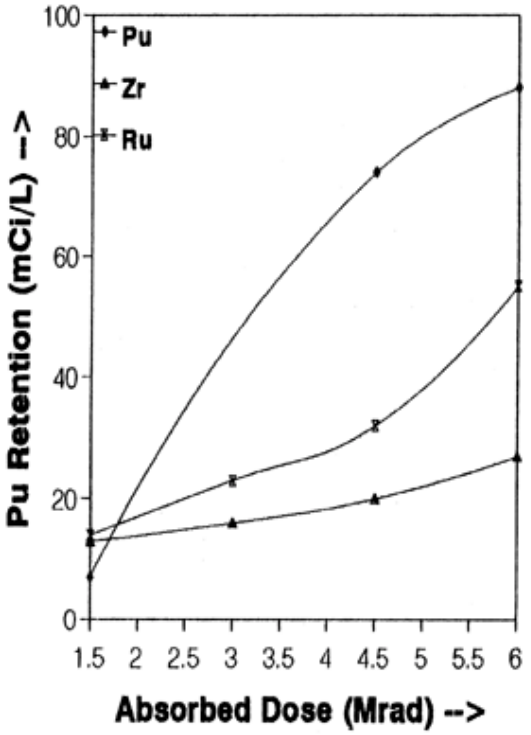


*Figure 7.* Dependence of retention [(mCi/L) $\times$ $10^{-3}$] of Pu, Ru, and Zr with absorbed dose.

analytical investigation. The concentration of these species is found to increase with absorbed dose. Their concentration profiles can be used to monitor the quality of the recycled Purex solvent in terms of the growth of diluent degradation products marked as peaks of nitroparaffins, long chain alcohols, and paraffins. Although the long chain alcohols and paraffins do not contribute to the retention of radionuclides, they are reported to cause undesirable changes in the physicochemical behavior of the solvent.

Observation of similar peaks in actual Purex solvent (upon successive recycling) has been found to cause increasing adversities (retention of radionuclides) in the overall extraction behavior [21]. The present study thus justifies the importance of monitoring the gas chromatographic markers of diluent degradation products for assessment of the quality of recycled Purex solvent.

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