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Effects of Solvent Recycling on Radiolytic Degradation of 30% Tributyl Phosphate–*n*-Dodecane–HNO_3 System

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ABSTRACT

Samples of 30% tributyl phosphate (TBP)–*n*-dodecane–HNO_3 undergoing gamma radiolysis with and without solvent cleanup have been examined by GLC and IR spectrometry. In order to assess the rate of buildup of various radiolytic species in the solvent, their relative hydrophobicities with respect to alkaline wash have been determined. The differences in the Pu extraction and retention behaviors of the two solvent systems with increasing dose are explained in terms of the formation of derivatives of nitroparaffins and high molecular weight organophosphates.

INTRODUCTION

The strong radiolytic conditions prevailing in the first extraction cycle of the Purex process brings about severe radiation-chemical transformations in the solvent 30% tributyl phosphate (TBP)–*n*-dodecane (1). This is marked by the growth of many additional species as fingerprinted by gas liquid chromatography (2).

The radiolytic products can be broadly classified as 1) *hydrophilic* ones such as monobutyl phosphoric acid and dibutyl phosphoric acid, which are easily removed by alkaline wash, and 2) *hydrophobic* ones, generally known to be diluent degradation products (3, 4) as well as higher homologues and

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derivatives of TBP and DBP, which are referred to here as high molecular weight organophosphates (HMP's) (5).

Such species, in general, have metal complexing ability and poor solubility in the aqueous solution of sodium carbonate employed for solvent purification before its reuse. The presence of these hydrophobic species in the degraded solvent impairs its process performance by inhibiting the backextraction of actinides and creating problems of poor phase separation (6, 7). The deterioration in the quality of the solvent by radiation exposure becomes a recurring phenomenon upon successive recycling of the solvent in the Purex process and ultimately renders it unfit for reuse. Unlike many earlier reports (8, 9), special importance is given to the role of these lesser discussed hydrophobic degradation products in the present work.

Each extraction cycle in the Purex process may be considered as one batch of radiation-chemical degradation of the solvent during the extraction stage. The ideal situation in the Purex process envisages regular cleanup of the lean solvent before its recycling. However, economy and waste management considerations make it more appealing to recycle the solvent without washing it to the maximum extent, with the expectation of an overall satisfactory performance.

The Purex solvent is here termed "treated solvent" (TS) when after each batch of radiolytic degradation (equivalent to one recycling) it is subjected to alkaline cleanup followed by acidification in contrast to being subjected to continuous radiolytic degradation (during several extraction cycles) without involving alkaline cleanup and be termed "untreated solvent" (UTS).

A number of investigations reported earlier on the steady-state radiolytic degradation of the 30% TBP–*n*-paraffins–HNO_3 have been done under continuous irradiation conditions (10–12). Less attention has been paid to real process situations where the Purex solvent is recycled after alkaline cleanup followed by acidification, which is the focus of the present study. Consequently, the conclusions drawn from present investigations will better address the practical problems of solvent degradation in contrast to that from continuous gamma radiolysis studies.

This study aims at investigating the overall difference between the extraction performances of recycled treated and untreated solvents undergoing radiolytic degradation. A comparative examination of two such systems is rare in the literature.

The present report also describes a comparative examination of GLC and IR profiles of the radiolytic degradation products of 30% TBP–*n*-dodecane. This enabled us to evaluate the relative hydrophobicities of different degradation products with respect to the solvent scrub with 2% (w/v) Na_2CO_3 solution. A comparative examination of the extraction and stripping behaviors of Pu in the treated and the untreated 30% TBP–*n*-dodecane-HNO_3 (gamma irradiated) systems has also been carried out.

EXPERIMENTAL

Reagents and Materials. 30% Tri-*n*-butyl phosphate (Fluka AG) was prepared by diluting it with *n*-paraffin containing about 90% *n*-dodecane (Aldrich Inc.) and purifying by the procedure described elsewhere (2).

Plutonium Tracer Solution. Radiotracer solution containing predominantly ^{239}Pu of given specific activity was used. ^{239}Pu was chemically purified by the usual anion-exchange method reported elsewhere (2). Tracer ^{239}Pu solution for each experiment was taken from this stock and adjusted to the tetravalent state by the addition of sodium nitrite (0.03 mol/dm^3). All other reagents used were of AR grade.

Sample Preparation Procedure

In order to examine the differences in the compositions and the extraction performances, samples of 30% TBP–*n*-dodecane equilibrated with 1 M nitric acid were subjected to 4 days of gamma radiolysis with and without solvent-wash treatment after each 24 hours of radiolysis using a ^{60}Co source with a dose rate of 0.32 Mrad/h. In the case of TS, after every 24 hours of gamma radiolysis (absorbed dose, 7.6 Mrad) the solvent was subjected to alkaline cleanup (org/aq = 1, 20 minutes) using 2% (w/v) Na_2CO_3 solution followed by equilibration with 1 M HNO_3 under identical conditions. The samples were analyzed by GLC and IR techniques after each increment of radiolysis.

Plutonium Retention Behavior Studies

The inability of the commonly used solvent cleanup reagent, sodium carbonate aqueous solution, to remove the highly hydrophobic and complexing radiolytic species leads to an increase in the plutonium retention behavior of the extractant. The quality of the solvent assessed with respect to its Pu retention behavior is known as P-test. In this test the irradiated sample, after two scrubbings with sodium carbonate solution followed by distilled water, is contacted with ^{239}Pu plutonium tracer (1 mg/L) at 2 M HNO_3 (1:1 contact, 20 minutes). After stripping the Pu-loaded solvent three times with equal volumes of 0.1 M HNO_3, the ^{239}Pu retained in the solvent is estimated radiometrically using an alpha proportional counter. Each time an unirradiated 30% TBP–*n*-dodecane stock sample was also checked to serve as reference. The plutonium retention of the solvent has been reported as alpha dpm for a fixed aliquot of organic phase planchetted. The organic samples after radiolysis were directly taken for a P-test as described above. In both cases the samples withdrawn at each 24-hour period of radiolysis (absorbed dose = 7.6 Mrad) were subjected to the P-test.

D Value Determination

Equal volumes of ^{239}Pu tracer (tetravalent form) in 2 M HNO_3 and the radiolyzed solvent samples were equilibrated for 20 minutes at room temperature (24 ± 1°C), followed by radiometric assay of Pu in both phases after centrifugation. The distribution ratio (D_m) of the metal ion, defined as the ratio of the concentration (activity) of the species in the organic phase to that in the aqueous phase, was thus calculated.

GLC Assay

A Shimadzu model GC-9A gas chromatograph with a C-R3A data processor was used for the resolution of the degradation products of the solvent under optimized temperature program conditions using a 10% XE60 (1.5 m × 0.32 cm) column in tandem with a thermal conductivity detector. Two different temperature programs were used; Condition 1 for assessment of the relative hydrophobicity as defined later, and Condition 2 for observing the qualitative changes under much higher resolution conditions.

Quantitative GLC assays of different radiolytic products of the extraction systems were done under Condition 1, using the area normalization method with a C-R3A data processor.

Operating GLC Parameters

Condition 1: Column temperature: 170°C → 230°C, with temperature holding times of 1 and 10 minutes, respectively, and a program rate of 10°C/min.
Condition 2: Column temperature: 120°C → 230°C, with temperature holding times of 0.2 and 10 minutes, respectively, and a program rate of 15°C/min.
An injection temperature of 240°C and a TCD temperature of 260°C, common for both the conditions.
A carrier gas (He) flow rate of 40 mL/min.

For a detailed qualitative examination of the GLC fingerprinting, the radiolyzed solvent samples were analyzed before and after esterification using diazomethane. The appearance of a peak only upon esterification indicates the presence of a weak acidic component in the solvent. Thus, it is possible to monitor the acidic and the nonacidic degradation products by GLC.

Assessment of Relative Hydrophobicity

For a given total absorbed dose the relative hydrophobicity of a radiolytic product with its characteristic retention time (GLC) is defined as “the ratio of the concentration of the species in the TS to that in the UTS samples.”

In the present case, for an absorbed dose equal to 31 Mrad, the relative hydrophobicities of the different degradation species were made from the quantitative GLC assay of the treated and untreated solvent samples under temperature program condition 1, standardized for assay of Purex solvent samples in our laboratory (22). The relative hydrophobicity values so derived for different peaks do not represent absolute values but are of practical importance in the present context. In other words, they provide a measure of buildup of radiolytic products in the solvent even after regular solvent cleanup. Due to the presence of a large number of unidentified radiolytic species formed, quantitative assay of various components by GLC will depend specifically on the chromatographic resolution for the peak and its detector response.

Infrared Absorbance Measurements

Qualitative IR fingerprints of the solvent at different stages of irradiation were taken with a Pye Unicam-9512 infrared spectrophotometer. For quantitative measurements, CaF_2 cell windows with 1 mm path lengths were used. The blank used in each case was the unradiolyzed solvent itself.

RESULTS AND DISCUSSION

Extraction Behavior of Plutonium

Figure 1 shows the distribution ratio (*D*) of plutonium(IV) from 2 M nitric acid solution for TS and UTS samples. The increase in *D* values in the case of

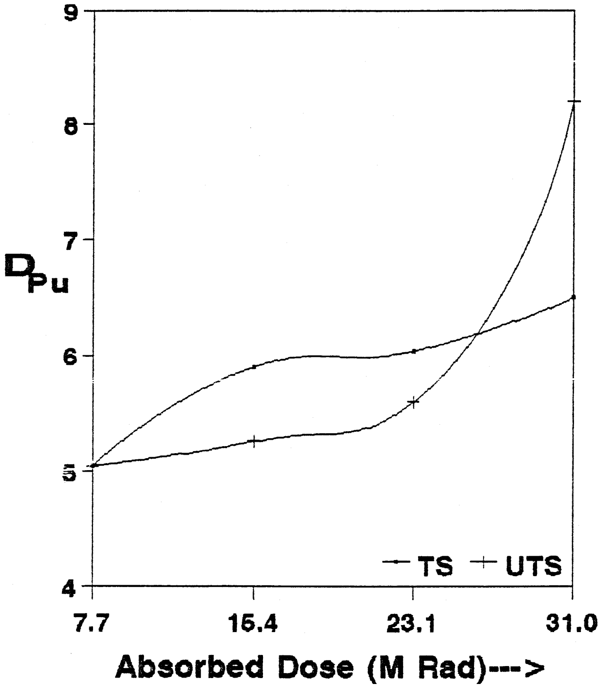

FIG. 1 Variation of D_{Pu} with absorbed dose.

TS is initially faster than that in the case of UTS, then it slows down. In the untreated samples, *D* of Pu(IV) remains lower up to a dose of about 21 Mrad, thereafter a sudden enhancement in the rate of increase of *D* as compared to that in the TS is noted. This implies a sudden enhancement in the generation of Pu complexants of greater relative hydrophobicities in the UTS.

Figure 2 shows the variation of plutonium retention of the radiolyzed solvent with absorbed dose. As compared to UTS, Pu retention was found to be greater in the case of TS up to 3 days of gamma radiolysis (dose = 23 Mrad). Thereafter, Pu retention in UTS becomes greater. This sudden reversal in the trend of Pu retention behavior of the radiolyzed UTS beyond an absorbed dose of 23 Mrad is an interesting observation explained by GLC and IR.

Gas Chromatographic Study

Figure 3 shows typical chromatograms of gamma irradiated (dose = 31 Mrad) 30% TBP–*n*-dodecane–HNO_3 samples with (A) and without (B) the cleanup treatment under GLC condition 1. Peaks (a) and (b) have been identified as nitric acid-induced radiolytic products of the diluent. Most species eluting after TBP (peaks c, d, e, f, g, and h) have been found to be radiolytically derivatized organophosphates of high molecular weight (HMP's) with respect to TBP by N-P detectors and flame photometric detection (13).

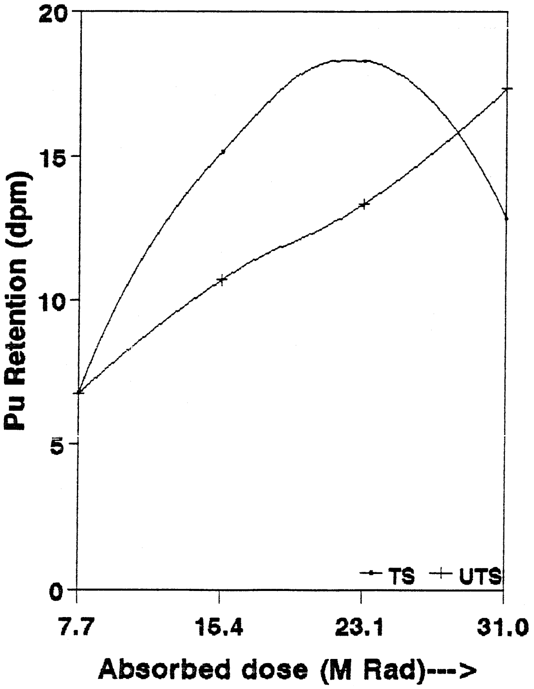

FIG. 2 Variation of Pu retention with absorbed dose.

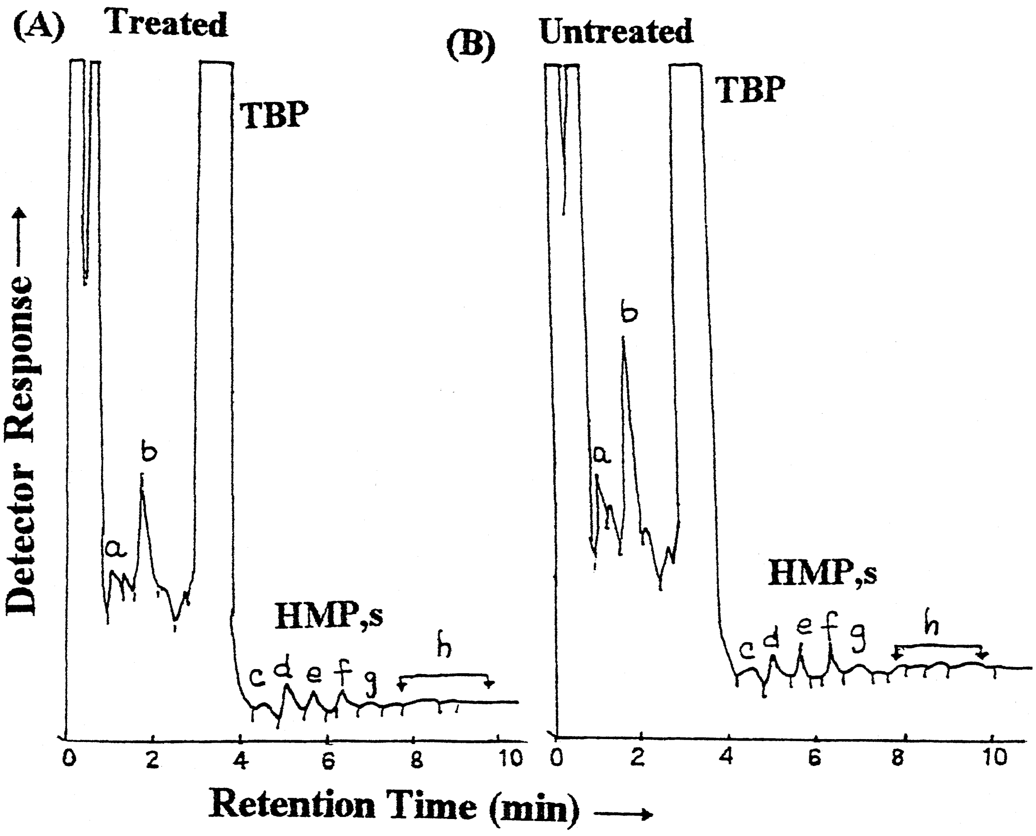

FIG. 3 A typical GLC profile of γ-irradiated (absorbed dose = 31 Mrad) 30% TBP–*n*-dodecane–HNO_3. (A) Treated (TS) and (B) untreated (UTS) systems under GLC conditions (1).

Qualitative GLC profiles of gamma-irradiated samples of 30% TBP–*n*-dodecane–HNO_3 with and without treatment did not show any significant difference. However, the quantitative profiles of the degradation species became more prominent at higher absorbed doses for UTS.

The adverse performance of 30% TBP–*n*-dodecane–HNO_3 is due to the accumulation of degradation products (other than DBP and MBP) in the solvent even after solvent cleanup. Therefore, the relative hydrophobicities of each prominent peak and groups of closely eluting peaks arising from radiolytic degradation have been derived. The higher retention time of a species on a polar GLC column implies lower volatility of the component, thereby suggesting higher molecular weight and/or higher polarity. This fact has been used to define the general nature of the radiolytic species formed.

The following observations were made:

(a) The relative hydrophobicity of radiolytic products for a given absorbed dose was found to be a function of their characteristic retention time, particularly for HMP's, as shown in Table 1.

TABLE 1
Relative Hydrophobicity Values of Different GLC Peaks as a Function of Their Respective Retention Times[a]

Retention time (min)	1.25 + 1.38 (a)	1.78 + 2.2 (b)	4.26 + 4.46 (c)	4.96 (d)	5.54 (e)	5.95 + 6.1 (f)	6.7 (g)	7.3 + All (h)	Mean value
Relative hydrophobicity	0.34	0.56	0.20	0.44	0.41	0.46	0.49	0.76	0.46

[a] Here, "+" refers to closely eluting peaks and "All" refers in the last but one column refers to summation of all the peaks with retention time greater than 7.3 minutes (a), (b), (c), (d), (e), (f) and (g) refers to the arbitrary labels for the peaks in Fig. 3.

(b) In general, the number of radiolytic species and their concentrations increase with the amount of absorbed dose and/or number of recyclings, as seen from Fig. 4.

(c) Certain species with higher retention times than that of TBP, called high molecular weight organophosphates (HMP's), exhibited a linear in-

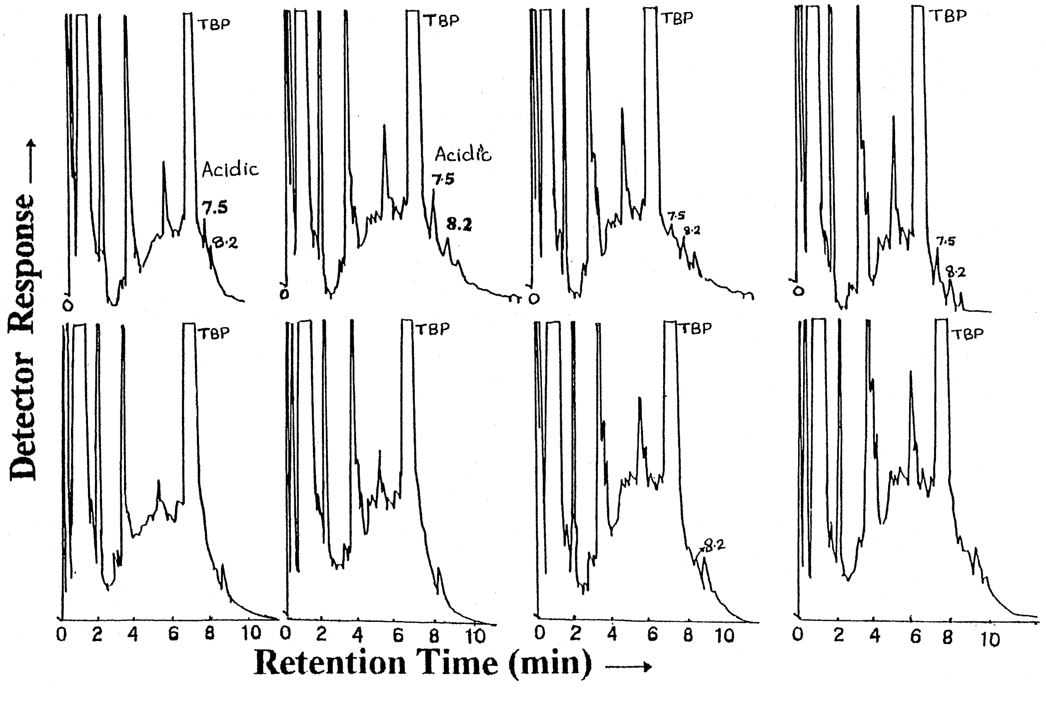

FIG. 4 Gas chromatograms of γ-radiolyzed 30% TBP–n-dodecane–HNO_3 with increasing periods of radiolysis (1, 2, 3, and 4 days, dose rate = 0.3 Mrad/h). (A) Unesterified (bottom) and (B) esterified (top) samples under GLC conditions (2).

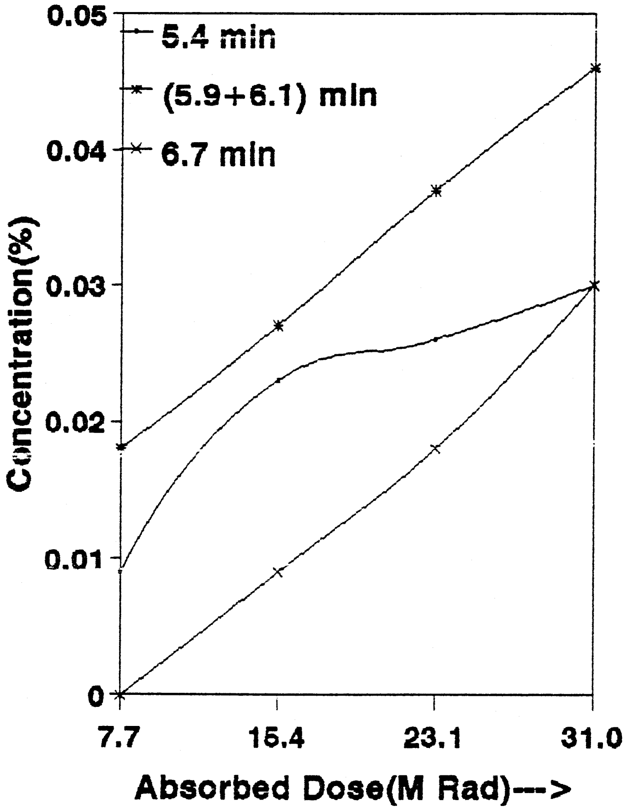

FIG. 5 Variation of GLC concentration profiles of HMP's [identified with retention times of 5.4 minutes (5.9 + 6.1) minutes and 6.7 minutes under GLC conditions (1)] in the treated (TS) and untreated solvent samples (UTS).

crease in their concentration with absorbed dose (Figs. 5 and 6). A significant concentration of these species is usually observed only at a higher absorbed dose.

(d) However, certain components, especially those with a higher retention time than that of TBP, exhibited drastic growth beyond a dose of 23 Mrad (after 3 days of radiolysis) as seen from Fig. 6, particularly in the case of UTS. Figure 4 shows chromatograms of the radiolyzed 30% TBP–*n*-dodecane–HNO_3 samples before (bottom) and after (top) esterification under treated-recycling conditions for increasing absorbed dose.

(e) The appearance of a distinct peak with a retention time of 7.5 minutes after that of the TBP peak (Fig. 4) and the enhanced intensity of the 8.2 minute peak upon esterification (with respect to that in its unesterified chromatogram) suggests their acidic nature. Such acidic compounds may be taken as higher homologues of DBP and therefore would be strong metal complexants of greater hydrophobicity owing to the presence of a longer alkyl chain with respect to DBP.

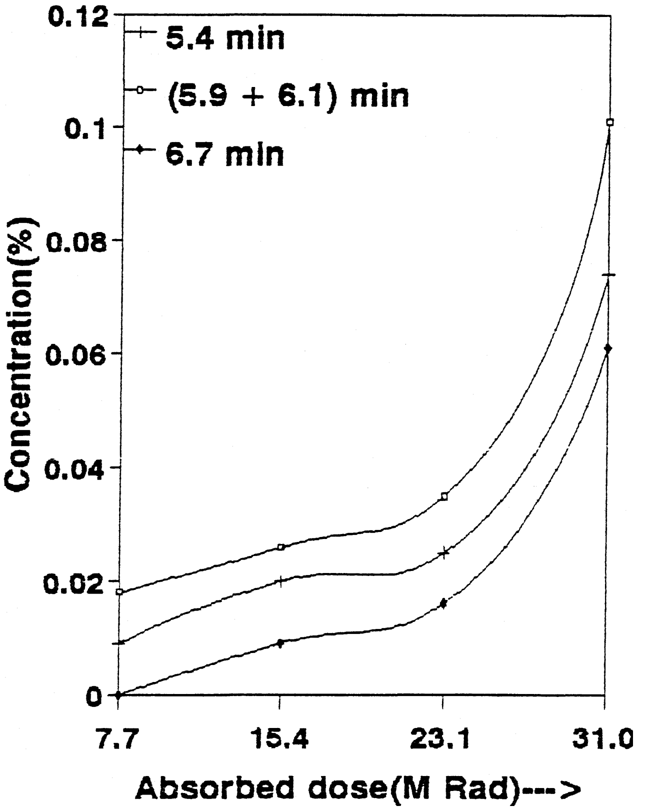

FIG. 6 Variation of GLC concentration profiles of HMP's in the TS [identified with retention times of 5.4 minutes (5.9 + 6.1) minutes, and 6.7 minutes under GLC conditions (1)] with absorbed dose.

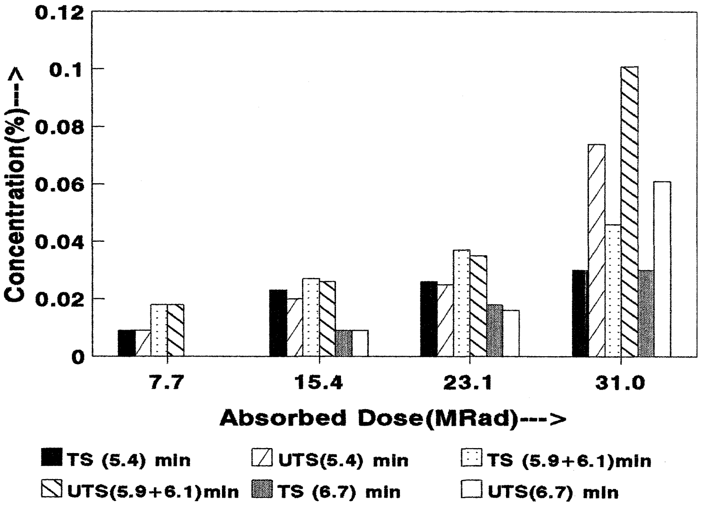

FIG. 7 Comparative changes in the concentration profiles of HMP's [identified with retention times of 5.4 minutes, (5.9 + 6.1) minutes, and 6.7 minutes] in the TS and UTS with absorbed dose.

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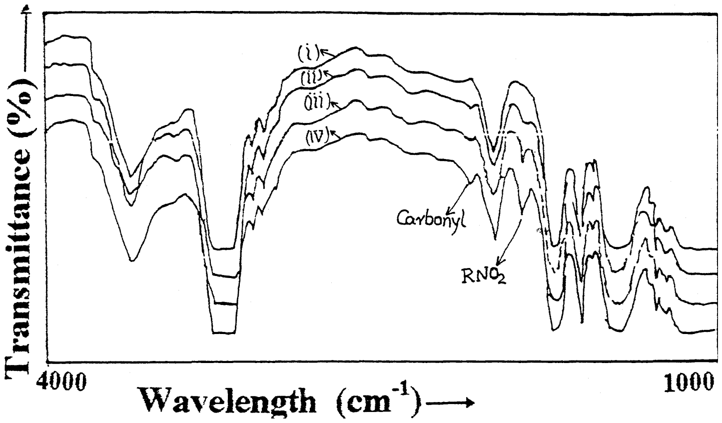


FIG. 8 Variation in the IR profiles of γ-irradiated 30% TBP–*n*-dodecane–HNO_3 with absorbed dose for treated solvent: (1) 7.6 Mrad, (2) 15.2 Mrad, (3) 23 Mrad, and (4) 31 Mrad.

(f) The growth and decay of the 7.5 minute peaks with absorbed dose points to the occurrence of secondary reactions in both systems.

IR Absorbance Measurements

Figure 8 shows a typical IR fingerprint of the gamma radiolyzed 30% TBP–*n*-dodecane–HNO_3 system as a function of period of radiolysis. Figure 9 shows the IR spectra of the 30% TBP–*n*-dodecane and the 30% TBP–*n*-dodecane–HNO_3 before and after irradiation for recycled TS and UTS undergoing gamma radiolysis. This enabled us to identify the functional groups associated with the radiolytic products formed.

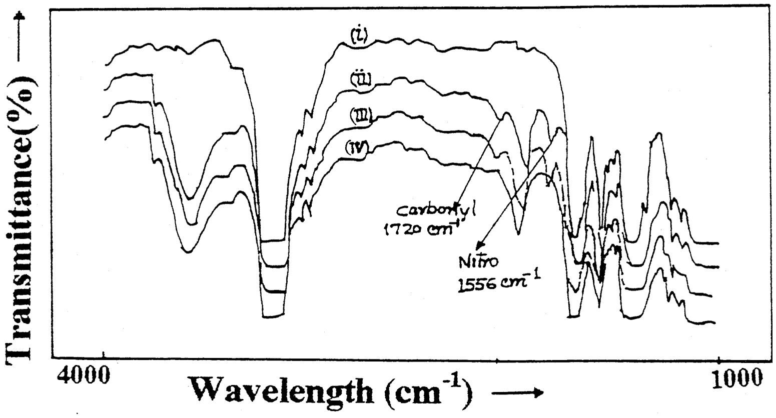


FIG. 9 IR spectra of (i) unirradiated 30% TBP–*n*-dodecane, (ii) γ-irradiated untreated 30% TBP–*n*-dodecane–HNO_3 [UTS, dose = 31 Mrad], (iii) γ-irradiated treated 30% TBP–*n*-dodecane–HNO_3 [TS, dose = 31 Mrad], and (iv) unirradiated 30% TBP–*n*-dodecane–HNO_3.

TABLE 2

IR Absorbance of Treated and Untreated Solvent Samples with Absorbed Dose

	Absorbances (peak area) at			
	$1556\ cm^{-1}$		$1720\ cm^{-1}$	
Absorbed dose (Mrad)	Treated	Untreated	Treated	Untreated
7.7	0.4	0.4	0.0	0.0
15.4	1.0	0.9	0.5	0.3
23.0	1.5	1.4	0.5	0.5
31.0	2.0	1.8	1.0	0.8

(1) There was no significant difference in the qualitative IR profile of the degraded sample with and without recycling treatment of the solvent.

(2) Table 2 shows that IR absorbance at $1556\ cm^{-1}$ (nitroparaffins) are greater than those at $1720\ cm^{-1}$ (carbonyl group). This implies that nitroparaffins are the primary radiolytic degradation products and that carbonyl species are generated subsequently through their derivatization.

(3) However, IR absorbances at $1556\ cm^{-1}$ (nitroparaffins) and at $1720\ cm^{-1}$ (carbonyl group) were found to be greater in the case of TS. This is due to the uptake of fresh nitric acid during each treatment followed by its radiolysis, resulting in a relatively greater yield of nitration products of greater hydrophobicities in the solvent. Consequently, we observe a higher absorbance in TS at $1720\ cm^{-1}$ due to carbonyl species which are secondary degradation products.

Alkaline treatment followed by acidification is known to generate hydroxamic acids, RCONHOH, from primarily formed nitroparaffins, as secondary products which contain the carbonyl group as well (19). This seems to be a plausible reason for the observed IR data and may be explained in terms of the following mechanism.

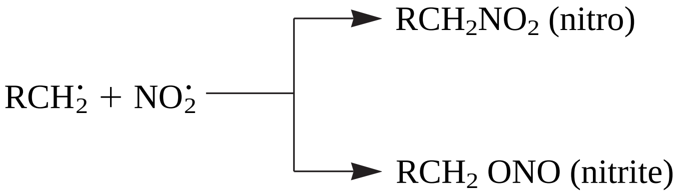
1. Formation of primary derivatizing radical NO_2:

$$HNO_3 \rightsquigarrow OH^{\bullet} + NO_2^{\bullet} \tag{1}$$

$$NO_2^{\bullet} + NO_2^{\bullet} \xrightarrow[(H^+/H_2O)]{} HNO_2 + HNO_3 \tag{2}$$

2. Nitration of the hydrocarbon diluent:

$$RCH_3 + NO_2^{\bullet} \rightsquigarrow RCH_2^{\bullet} + HNO_2 \tag{3}$$



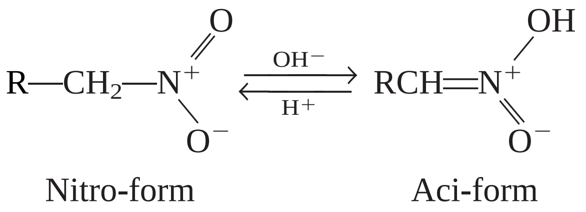
$$RCH_2^{\bullet} + NO_2^{\bullet} \rightarrow RCH_2NO_2 \text{ (nitro)} \quad (4)$$

$$RCH_2^{\bullet} + NO_2^{\bullet} \rightarrow RCH_2\,ONO \text{ (nitrite)} \quad (5)$$

The generation of carbonyl species may result from equations given in the next section.

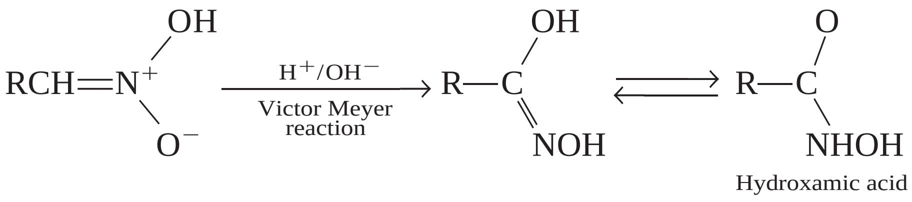
Secondary Reactions Resulting in Ligand Formation

Plutonium complexing hydrophobic ligands in the radiolyzed solvent are known to be generated from primarily formed nitroparaffins. A number of side reaction may also take place simultaneously, generating metal complexing ligands as well as noncomplexing species depending on the chemical conditions. According to Lane's hypothesis, solvent treatment results in tautomeric conversion of RNO_2 into the enol form, the species known as nitronic acid (19):



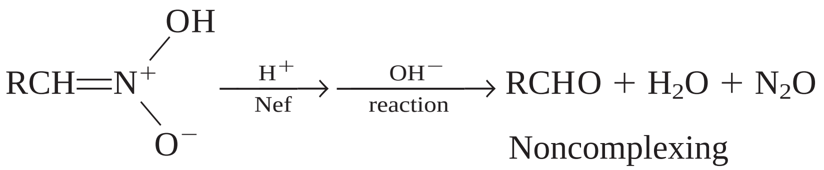
(6)

According to Blake, the aci-form is a metal complexant and its formation is favored by alkaline treatment and acidification normally employed in the case of a treated solvent (20). Nitronic acid formed via Reaction (6) may produce strong metal complexants like hydroxamic acid and carboxylic acid by undergoing a Victor Meyer rearrangement reaction.



(7)

Nitronic acid may also yield a noncomplexing species like a carbonyl compound by undergoing a nef reaction as follows:



(8)

Explanation for Pu Retention Behavior from Study of the GLC Profile

The fall in Pu retention behavior in the case of TS after an extended period of radiolysis can be better explained by quantitative GLC assay. Figures 5 and Fig. 6 show the variation of the concentration of HMP's with absorbed dose for TS and UTS, respectively.

From Fig. 3 we observe that the growth of all the HMP species of retention times 5.4, 5.9 + 6.1, and 6.7 minutes show an unusually higher increase in the UTS. This may be due to slow buildup of unsaturation in the alkyl chain of TBP which would have catalyzed its interaction with the different transients and reactive intermediates species radiolytically formed in the solvent. This phenomenon appears to be passivated by alkaline treatment in the TS samples. The concentration of different HMP species either increases at the same rate or begin to slow down beyond an absorbed dose of 23 Mrad. Thus the growth of HMP's in the UTS overtakes the growth in the TS samples (Fig. 7).

Correspondingly, if we look at Fig. 1, which shows the variation of the *D* value of Pu with absorbed dose, we find a trend identical to that of the growth for HMP's in both systems as reflected in Fig. 6. This clearly suggests the formation of hydrophobic plutonium complexing ligands is greater in UTS than that in TS above an absorbed dose of 23 Mrad.

It is therefore obvious that radiolytically formed HMP's in the solvent is very difficult to remove by alkaline cleanup. However, regular solvent wash appears to be beneficial for long-term use of Purex solvent because it appears to check the factors responsible for enhancing the growth of HMP's. The fall in Pu retention behavior beyond an absorbed dose of 23 Mrad by the solvent is clearly explainable by the GLC profiles of HMP's.

Yongin, Stieglitz, and Adamov reported the formation of long-chain acidic and nonacidic organophosphates as possible metal complexants (3, 14–18). Such compounds may be formed by the interaction of DBP and alkyl radicals identified by ESR studies (7). However, they were not solely responsible, and some other unidentifiable radiolytic products with much stronger complexing abilities must be involved. There is now good evidence that the principal metal-retaining ligands in the solvents are long-chain alkyl phosphoric acids (8).

Explanation Based on Quantitative IR Data

The higher Pu retention behavior in TS up to an absorbed dose of 23 Mrad may be explained by the relatively higher IR absorbances at 1555 cm^{-1} (nitro group) and the corresponding generation of carbonyl species absorbing at 1720 cm^{-1}. A species similar to hydroxamic acid (RCONHOH) is probably the hydrophobic ligand for Pu in the treated recycled solvent.

It has been reported (1, 20) that as compared to acidic condition, basic media favors enol form and equilibrium is moderately fast. Change to an acid medium, however, produces free enol in much larger amounts via Reaction (1), and hydroxamic acid may in turn form metal complexes. A similar situation is observed in the case of treated solvent where, after each batch of gamma radiolysis, the solvent is subjected to alkaline contact followed by equilibration with nitric acid. Hence, as compared to a continuously irradiated UTS, Pu retention was observed to be greater in the treated solvent. This explains the extraction behavior up to an absorbed dose of 23 Mrad (3 days of radiolysis).

The subsequent drop in Pu retention of the treated system may be attributed to the destruction of hydroxamic acid into nonligand species. However, continuously greater IR absorbances due to nitroparaffins in a treated recycled system may be taken as the sum of complexing nitro compounds (usually bifunctional ligands) and noncomplexing ones like primary nitroparaffins. This absorbance is higher because after each solvent cleanup the TS was equilibrated with nitric acid unlike the case of UTS. The fall in Pu retention behavior may be attributed to the fall in the concentration of complexing nitroparaffins by hydrolysis and other radiation-chemical processes.

CONCLUSIONS

By making a comparative study between treated and untreated solvent under the influence of radiation-chemical degradation, the present investigation has revealed some interesting aspects of the phenomenon of solvent degradation. The results of present study can be summarized as follows.

(1) The deterioration in the quality of 30% TBP–*n*-dodecane is due to the buildup of several hydrophobic radiolytic products upon successive recyclings. In the case of treated solvent, additional species like hydroxamic acids or nitronic acid have a role in enhancing Pu retention as compared to untreated solvent samples, at least during the initial stages of solvent radiolysis (recycle).

(2) The decrease in Pu retention of the treated solvent beyond an absorbed dose of 23 Mrad is possibly due to derivatization of nitrogenous ligands into noncomplexing species through side reactions, in addition to a relatively controlled rate of formation of HMP's which behave as stronger ligands owing to their multifunctional and acidic nature.

(3) Formation of longer chain alkyl phosphoric acids is observed but found to gradually transform into higher homologues. The major cause of impaired extraction performance of the solvent may be ascribed to these HMP's.

(4) Regular solvent wash appears to be beneficial for long-term use of Purex solvent by way of checking the radiolytic yield of more harmful HMP species in the solvent.

(5) It is not just one species but several species of different hydrophobicities and metal complexing abilities that are formed at different levels of doses absorbed by the solvent. Hence, a direct (linear) correlation between the GLC signature of a degradation product and the corresponding deviation in extraction performance will remain valid only over a limited range of absorbed gamma dose.

(6) With increasing doses absorbed by the solvent upon recycling, the formation of various metal complexing species in the solvent is likely to be in the following order. HDBP $<$ hydroxamic acid or enol form of nitroparaffins $<$ long-chain alkyl phosphoric acid $<$ bifunctional organophosphates. At very high doses (above 23 Mrad), an enhanced increase in the concentration of some of these polyfunctional species (oligomeric organophosphate) is observed, especially in the case of an untreated system, which explains the greater retention of Pu by the solvent because such species not only behave as ligands but also acts like surfactants and emulsifying agents which significantly minimize the mass transfer coefficient of metal ions. This may also cause the difficulty in the backextraction of the metal ions.

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