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RADIATION DAMAGE TO TBP AND DILUENTS
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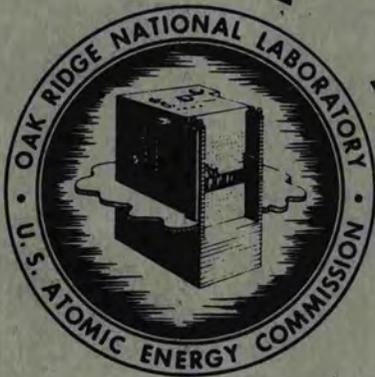
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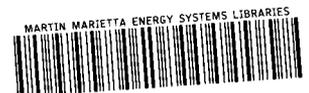
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1.0 ABSTRACT

Polymerization or other interaction between the radiation damage products of a hydrocarbon diluent and tributyl phosphate solvent, which is intensified by the presence of an aqueous phase and/or heat, results in the formation of emulsifiers, uranium complexing agents, and other deleterious materials in irradiated solvent. Vacuum distillation satisfactorily separates undamaged solvent from the higher boiling degradation products.

2.0 INTRODUCTION

Previous studies at ORNL on the effects of radiation damage to diluents and tributyl phosphate-diluent mixtures indicated that radiation doses as low as 0.5 watt-hr/liter can materially affect the performance of some solvent extraction processes and that doses of 10 watt-hr/liter may render other processes inoperable. Since the level of radiation to be encountered in the solvent extraction processing of power reactor fuels is expected to range from 2-4 watt-hr/liter, in contrast to 0.02 - 0.2 watt-hr/liter in present processes, these radiation effects will probably be one of the major factors in the design and operation of recovery plants. The principal effects of solvent damage include the extraction and retention of fission products, the retention of uranium, plutonium, or thorium in the organic phase, lowered decontamination factors, and the formation of emulsifiers that disrupt column operation. The studies reported here are qualitative and were made in an attempt to define some specific results of solvent or diluent irradiation and to develop methods for the removal of the deleterious products from the damaged solvent. Massive doses of Co^{60} γ radiation and of 1.5-2.0 Mev electrons from an ORNL Van de Graaff generator were used to produce quantities of the radiation damage products in solvent samples for the study of their effects on process operation.

The author wishes to acknowledge the work of the ORNL Analytical Chemistry Division, in particular P. F. Thomason, A. D. Horton, and R. M. Rush, for the gas chromatography, infrared spectra, and other analytical aids.

3.0 EFFECTS OF IRRADIATION ON DILUENTS

The principal TBP diluent currently in use at ORNL is Amsco 125-82, a saturated, branched-chain hydrocarbon (C_8-C_{12}) made from polymerized butenes and pentenes by the American Mineral Spirits Company. Table 1 lists some of the manufacturer's specifications plus data obtained at ORNL for Amsco 125-82.

Table 1. Properties of Amsco 125-82

Specific gravity: 0.7559	8.2 cp at -40°F
Acidity: neutral	Boiling point at 760 mm Hg:
Saybolt color: +30	Initial, $352^{\circ}\text{F}/177.8^{\circ}\text{C}$
Flash point: $128^{\circ}\text{F}/53.3^{\circ}\text{C}$	10%, $357^{\circ}\text{F}/180.5^{\circ}\text{C}$
Aromatics: none	20%, $359^{\circ}\text{F}/181.5^{\circ}\text{C}$
Paraffins: 99.4%	40%, $361^{\circ}\text{F}/182.7^{\circ}\text{C}$
Olefins: 0.6%	50%, $363^{\circ}\text{F}/183.9^{\circ}\text{C}$
Iodine no.: 2.0-2.4	70%, $368^{\circ}\text{F}/186.7^{\circ}\text{C}$
Freezing point: 55°F	80%, $373^{\circ}\text{F}/189.5^{\circ}\text{C}$
Viscosity: 1.4 cp at 75°F	End, $398^{\circ}\text{F}/203.3^{\circ}\text{C}$

Samples of two other diluents were also subjected to many of the tests that were applied to Amsco 125-82; these were Doebase, a sulfonated, odorless light-petroleum distillate manufactured by L. Sonneborn Sons, Inc., and Archer-Daniels-Midland n-dodecane, supplied by the Savannah River Laboratory research group.

3.1 Chemical Changes

Exploratory work by Flanary, Tweedie, and Kibbey⁽³⁾ indicated that formation of unsaturates was the primary result of irradiation of highly purified diluents. Nitrite formation in nitrate solutions on irradiation was studied by Mahlman,⁽⁷⁾ and nitrite has been found to be one of the principal agents in chemical attack on diluents.^{8, 9}

Dry Irradiation. When Amsco 125-82 was irradiated dry in a Co^{60} source, the rate of unsaturates formation was almost linear with increasing irradiation dosage up to 68.2 watt-hr/liter (Table 2, Fig. 1). The rate gradually decreased

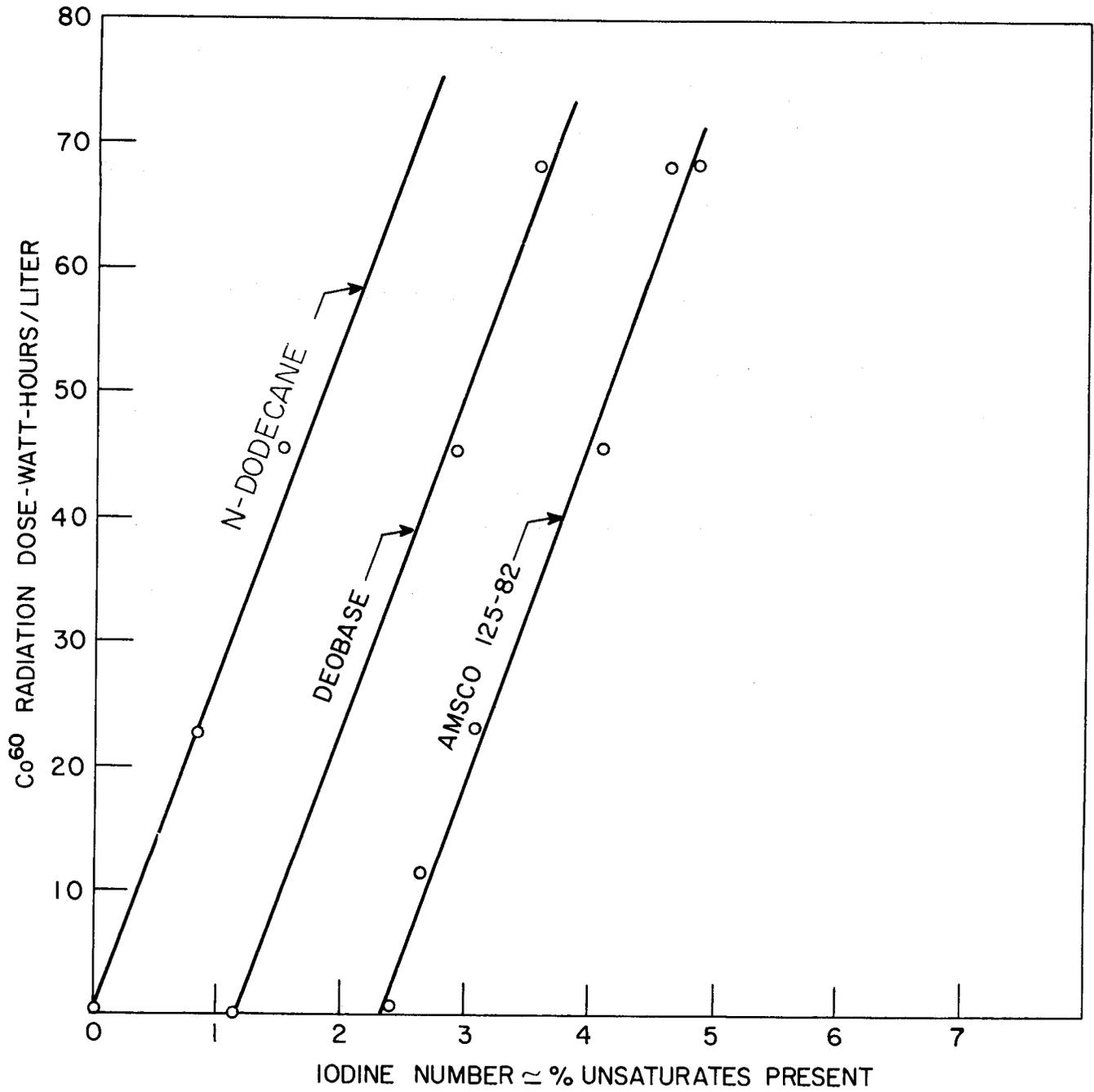


Fig. 1. Formation of Unsaturates in Hydrocarbon Diluents as a Function of Irradiation Dosage.

at higher irradiation levels as the unsaturates polymerized and re-formed the structure of the Amsco. A probable maximum iodine number for Amsco 125-82 is about 15 (Fig. 2).*

Wet Irradiation. Irradiation of Amsco in static contact with 0.1 vol of 1 M HNO₃-1 M Al(NO₃)₃, i.e., wet irradiation, showed increasing nitration of the solvent with increasing irradiation (Table 2). The nitration of the solvent was shown by the gradual yellowing of the diluent and the pronounced odor change as well as by chemical analysis.

Table 2. Effect of Co⁶⁰ Irradiation on Amsco 125-82

Dry: irradiated as delivered

Wet: irradiated in presence of 0.1 vol of 1 M HNO₃-1M Al(NO₃)₃; no stirring

Time (hr)	Dose		Dry			Wet			
	(r)	(watt-hr/liter)	I ₂ No.	Color	Odor ^a	I ₂ No.	N(ppm)	Color	Odor ^a
0	0	0	2.2	clear	W	2.2	5	clear	W
4	4.4 x 10 ⁶	11.36	2.67	clear	W	2.67	8	clear	M
8	8.8 x 10 ⁶	22.72	3.10	clear	M	3.01	16	clear	S
16	1.76 x 10 ⁷	45.44	4.12	clear	-	-----	-	-----	-
24	2.64 x 10 ⁷	68.16	4.64	clear	S	4.85	40	Lt.Yel.	VS

^a weak, medium, strong, or very strong.

3.2 Physical Changes

Possible Mechanism of Irradiation Damage. It is proposed that simple cleavage by high-energy particles, R-CH₂-CH₂-R' $\xrightarrow{\beta-\gamma}$ R-H + H₂C=CH-R', where

* The irradiation was carried out in a 1.1 x 10⁶ r/hr Co⁶⁰ source. The radiation doses were calculated on the basis of 1 r/hr = 2.58 x 10⁻⁶ watt/liter. Another useful conversion factor for Co⁶⁰ irradiation is 5.35 x 10¹³ ev/g
H₂O = 1r.

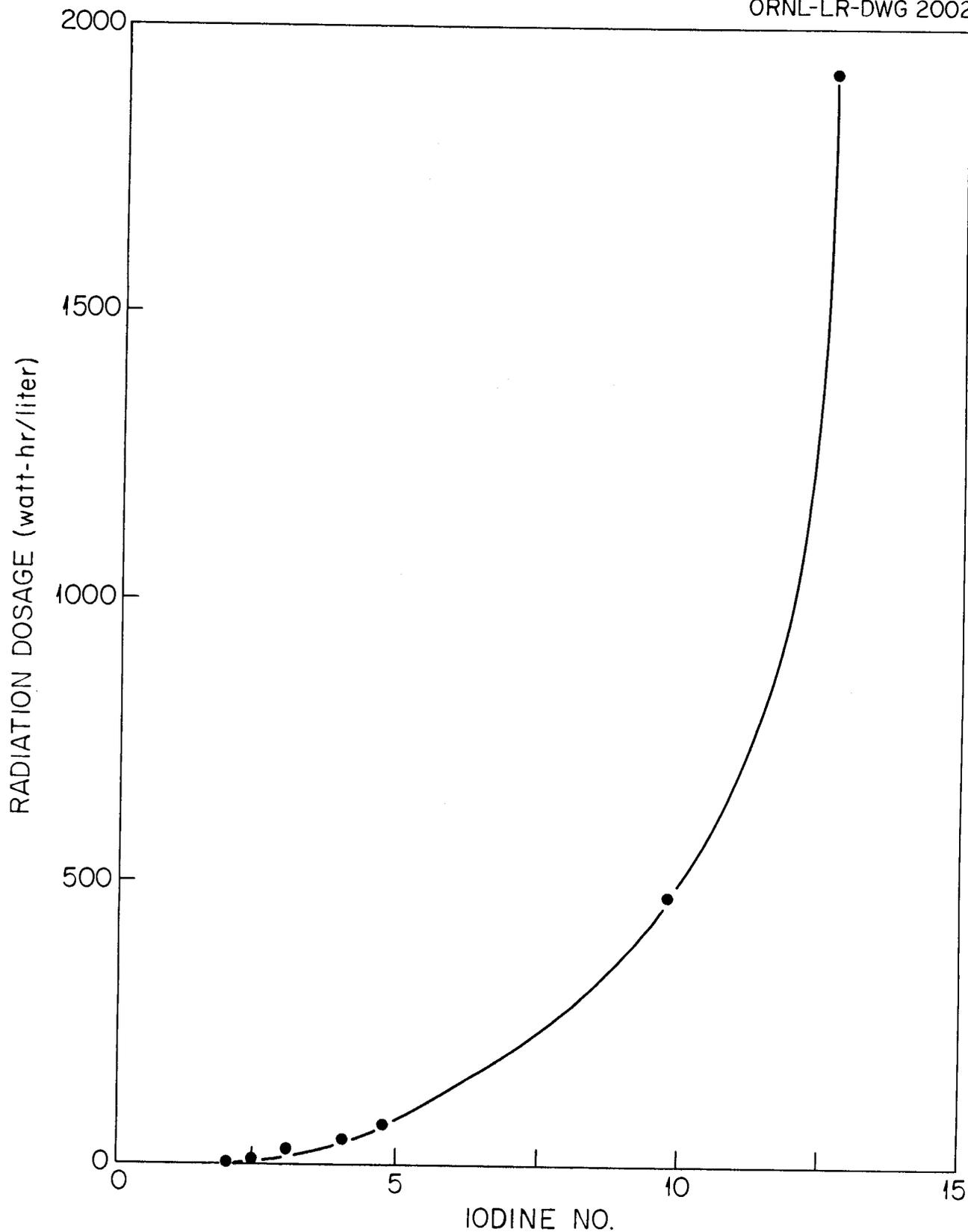


Fig. 2. Effect of Irradiation on Iodine Number of Amsco 125-82 Diluent.

R' is lighter than R, is responsible for the formation of double bonds and the subsequent increase in iodine number. These conclusions were reached by examination of vapor-phase chromatograms of virgin and irradiated Amsco 125-82 (Fig. 3) and by infrared analysis (Fig. 4). Figure 3 shows a shift from higher to lower boiling isomers or new compounds on irradiation. The shift appeared much greater than the few percent change in iodine number, and suggested that the rest of the radiation damage mechanism to the diluent might be due to the formation of free radicals by the high-energy particles, thus creating additional sites for rearrangement, polymerization, addition of fission products, and nitration. The increases in the peak heights at 6.1 and 11.3 μ in Fig. 4 were assigned* to the formation of double bonds. The small peaks of low-boiling components between 0 and 5 on the time scale of the 68.18 watt-hr/liter trace are indications of cleavage or cracking.

These speculations were confirmed by work of Silverman.^(10, 11) Irradiation of dry Amsco 125-02 in the Van de Graaff generator for 3.7×10^{22} ev/ml, or about 1920 watt-hr/liter, at room temperature increased the viscosity at 75°F from 1.4 to 1.5 cp and that at -40°F from 8.2 to 12.5 cp, indicating possible polymerization. A material balance on the irradiated material showed that 77.3% of the distillate had the same boiling range as unirradiated Amsco, 15.6% was "polymer", a dark yellow, viscous distillation residue, and 7.2% was lost as gases and light fractions that had been cracked by the irradiation. The iodine number of the irradiated Amsco was 12.55, its color medium yellow, and its odor strong. At the boiling point of Amsco, 55% of the distillate had a slightly lower boiling point than the original, 30% was "polymer", and 15% was cracked and lost as gases and light fractions. The iodine number of the irradiated Amsco was 10.70 and its viscosity at -40°F was 38 cp.⁽¹¹⁾ The experiments showed a pronounced temperature effect on the formation of polymer and light fractions for the same radiation dosage, which was also evidenced by a decrease in iodine number as the unsaturates recombined at the higher temperature. The "lost" materials in the material balances are probably the low-boiling components represented by the small peaks between 0 and 5 on the time scale of the 68.18 watt-hr/liter trace in Fig. 4.

Fission Product Retention. There was no correlation between the retention of long-lived fission products and the radiation dosage up to 68.18 watt-hr/liter (Table 3), indicating that the diluent is not responsible for the

* By R. M. Rush of the ORNL Analytical Chemistry Division.

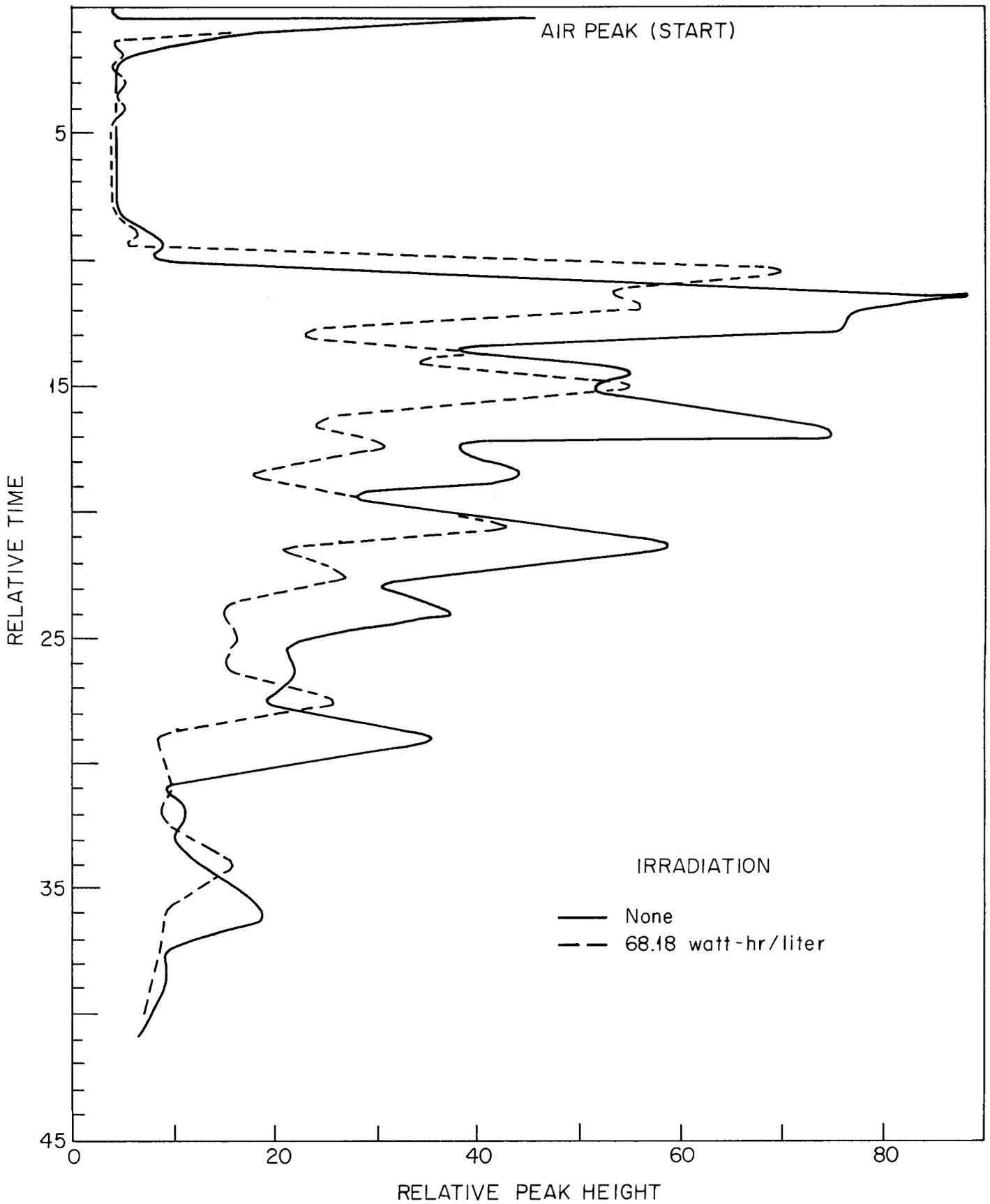


Fig. 3 . Vapor-phase Chromatograms of Amsco 125-82 Diluent.

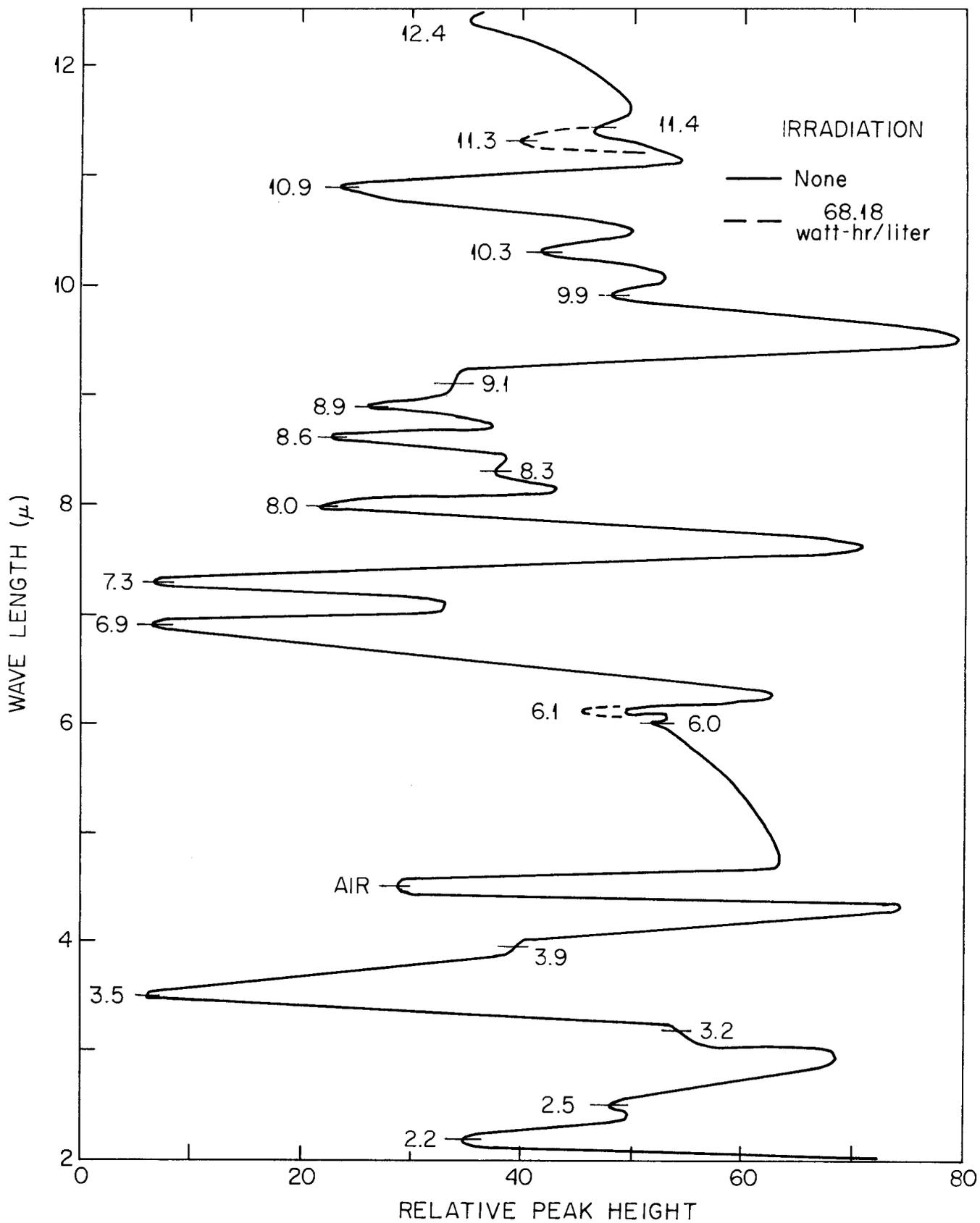


Fig. 4. Infrared Spectrum of Amsco125-82 Diluent

retention of fission product activity. Similar experiments with tracer I^{131} did not establish any relation between I^{131} retention, iodine number, and the radiation dose; in all cases about $4 \times 10^6 I^{131} \gamma$ c/m/ml was retained by the diluent after being contacted with a 10^7 c/m/ml aqueous phase and washed with sodium carbonate solution; the γ activity was probably due to simple addition. The tests were conducted by contacting the diluents, some of which had been irradiated both wet and dry, with an equal volume of 1 M HNO_3 -1 M $Al(NO_3)_3$ solution spiked to $10^6 \beta$ and $10^6 \gamma$ c/m/ml, separating the phases, and counting samples of the diluent.

Table 3. Retention of Fission Products by Irradiated Diluents

Dose (watt-hr/ liter)	Amsco 125-82		Deobase		n-dodecane	
	Gr β	Gr γ	Gr β	Gr γ	Gr β	Gr γ
0.00	34	318	30	326	27	439
11.36	33	330	--	--	--	--
22.72	37	453	--	--	54	424
45.44	24	263	53	703	19	295
68.16	36	318	56	441	--	--

Samples of Amsco which had been irradiated to 477 and 1920 watt-hr/liter in the Co^{60} source and Van de Graaff, respectively, were contacted with the same fission product solution used above, washed with 0.1 M Na_2CO_3 , and counted. The results showed that the 477 watt-hr/liter material retained 876 β and 9440 γ c/m/ml, while the 1920 watt-hr/liter solution held 236 β and 2150 γ c/m/ml. These amounts are insignificant compared to the activity held by TBP-Amsco mixtures (Sec. 4.0).

4.0 RADIATION DAMAGE TO TBP-AMSCO MIXTURES

4.1 Uranium Retention

Prior work on the effects of radiation on TBP and TBP-diluent mixtures was primarily concerned with the hydrolysis products of tri-, di-, and

monobutyl phosphates. Cathers⁽²⁾ determined a G value (molecules formed per 100 ev) of 0.24 for the formation of DBP by low doses of Co⁶⁰ irradiation. Both of these acidic degradation products may be removed by washing the solvent with sodium carbonate or hydroxide solutions.

Dry 50% TBP--50% Amsco 125-82 was irradiated for one week in the Co⁶⁰ source to 477 watt-hr/liter and then contacted with 0.5 vol of aqueous uranyl nitrate (320 mg U/ml) containing 2 M HNO₃. After the uranium-bearing organic phase had been stripped six times with double volumes of 0.01 M HNO₃, the solvent uranium concentration was 38.1 mg/ml. The aqueous stripping solution was colorless. The solvent was then washed twice with triple volumes of 1 M Na₂CO₃ and twice with triple volumes of dilute HNO₃ to break the emulsion formed in carbonate washing; the "clean" solvent still retained 0.93 mg U/ml. Direct titration of the solvent showed that 0.17 meq/ml of a single monobasic acid was present, which was assumed to be DBP. Since two moles of DBP is required per mole of uranium in the UO₂(DBP)₂(HNO₃)_x complex, there was roughly half enough DBP (0.17 M) in the solvent to tie up the 0.16 M (38 mg/ml) uranium that was retained after stripping. This fact and the retention of about 1 mg U/ml after procedures that would strip U-DBP complexes suggested that long-chain phosphates or other uranium-complexing compounds had been formed by interaction between the diluent and TBP under irradiation.

Burger states¹² that in addition to hydrogen and small amounts of hydrocarbons, butyl alcohol, dibutyl ether, and acid phosphates are formed by radiolysis of TBP; the principal product, however, is DBP. He found the DBP that was produced at γ dosages of 10⁴, 10⁶, and 10⁸ r to be 0.016, 0.32, and 32 g/liter, respectively, from pure TBP and 0.0058, 0.099, and 12.2 g/liter from 30% TBP in an isoparaffin hydrocarbon diluent. At levels above 10⁷ r (~ 25 watt-hr/liter), he also found small amounts of an unknown material that complexed uranium very strongly. The amounts of DBP found in the present experiments at levels of 477 watt-hr/liter, or roughly 1.4 x 10⁸ r, are of the same magnitude as those obtained by Burger.

Another quantity of wet 50% TBP--50% Amsco, irradiated to 477 watt-hr/liter in the presence of 1 M Al(NO₃)₃--1 M HNO₃ aqueous phase, retained about the same quantity of uranium, 0.14-0.16 M, but the titrated acidity was 0.32 M. Of this acid, 0.12 M was stripped by water and was assumed due to a

nitric acid complex with the TBP; the remaining 0.20 M was DBP. The increase in DBP formation from 0.17 to 0.20 M in the presence of the aqueous phase may be due to analytical error. Titration of 100% TBP which had been irradiated dry for the same length of time showed that about the same amount of acid had been formed per gram of TBP as in the irradiation of dry 50% TBP. Since an aqueous phase appears to intensify the radiation damage effects by forming more DBP in addition to emulsifiers, it is suggested that future work incorporate this parameter as soon as the products of a dry irradiation are identified.

4.2 Fission Product Retention

When 30% TBP in *n*-dodecane was contacted with a radioactive feed solution providing 10 watt-hr/liter dosage, cleaned by the normal carbonate and acid solvent recovery procedure, and analyzed for retained activity, a maximum of 200 β c/ml was retained, with no ruthenium activity.⁽¹³⁾

Samples of 50% TBP in Amsco, which had been irradiated for 477 watt-hr/liter both wet and dry, were contacted with 1 M HNO₃—1 M Al(NO₃)₃ solutions containing mixed aged fission products, and then washed with sodium carbonate and nitric acid solutions. Both samples retained about 10 times (10⁵ β c/ml) as much activity as an unirradiated control.

4.3 Settling Time

Settling time determinations and solvent recovery tests with 477 watt-hr/liter irradiated Amsco, TBP, and mixtures of the two indicated that emulsification is acid-dependent and that feed acidities below 2 M would probably result in emulsions after large radiation doses. A 30% solvent made from 477 watt-hr/liter irradiated Amsco and unirradiated TBP settled to a sharp interface in 45 sec after contact with dilute sodium carbonate solution; solvent made from irradiated TBP and unirradiated Amsco settled in about 100 sec, leaving a cloudy organic phase. Solvent made from irradiated (dry) 50% TBP—50% Amsco required over 2 min to disengage, leaving an emulsified organic phase; substitution of the wet 50% TBP, irradiated in the presence of aluminum nitrate and nitric acid, intensified emulsification and further increased settling time. In addition, the solvent made from the wet or nitrated 50% TBP formed interfacial solids, an emulsified interface, and a hazy organic phase upon contact with a 2 M HNO₃—0.75 M Al(NO₃)₃ simulated aqueous process feed solution. None of the other samples of solvent produced

these effects.

Sodium carbonate appeared to precipitate a sodium salt of the radiation-produced compounds in the organic phase. Subsequent water washes then emulsified both phases, but nitric acid redissolved the compounds and broke the emulsions. This phenomenon could be reproduced as long as the normal solvent recovery procedure was used, and indicates why the present solvent recovery systems are not effective for the removal of the emulsifiers and many of the radiation damage products. During pulsed-column operation of flowsheets in which the extraction of the column is at low acidities, emulsification has been minimized or eliminated by addition of small amounts of nitric acid to the scrub section.

5.0 SOLVENT RECOVERY SYSTEMS

5.1 Chemical Washes

Standard solvent recovery techniques of washing solvent successively with dilute sodium carbonate or sodium hydroxide, nitric acid, and water reduced the retained activity in degraded 42% TBP by a factor of 2, leaving 3×10^5 γ c/m/ml in the TBP mixture. Earlier work by Wischow⁽⁵⁾ showed increases in the oxidizing normality of the solvent as a function of radiation dose; aqueous oxidizing and reducing agents, such as SnCl_2 , FeSO_4 , H_2O_2 , NH_2OH , KMnO_4 , had essentially no effect on removal of the fission product activity or the degradation products from the organic phase.

5.2 Steam Distillation

Samples of orange-colored radioactive 42% TBP, damaged in plant use, were steam distilled from a 1 M NaOH aqueous heel to recover the diluent free of TBP. The TBP is hydrolyzed and lost in this type of distillation. The recovered diluent, Amsco 125-82, was water-white, entirely free of fission product activity, and had an iodine number of 2.2, comparable to that of virgin diluent. The colored degradation products and fission products remained in the still pot with the TBP. Infrared examination of the distillate showed that essentially no structural changes had occurred. The experiment indicated that the major portion of the diluent was undamaged by the radiation which had made the solvent mixture almost useless for plant use, and that steam distillation could be used as a recovery method for the diluent.

5.3 Vacuum Distillation

The use of the technique of steam distillation as a solvent recovery method would be uneconomical because of destruction of TBP; therefore vacuum distillation was investigated as a means of recovering both the Amsco and the TBP from irradiated solvent. In a series of quantitative experiments conducted by Vaughen and Maak⁽¹⁴⁾, MIT Practice School, 90% recoveries of a colorless, decontaminated solvent were possible. These studies were made with 42% TBP in Amsco severely damaged by radiation in pilot plant use.

A sample of the same solvent was distilled at 2 mm pressure, and 88% was recovered and reconstituted into solvent; the remainder was lost as light fractions and the colored radioactive still residue. The uranium retention of the recovered solvent, as distilled, was 0.002 mg/ml, which may be satisfactory for processes recovering large quantities of normal or depleted uranium. A solvent-washing technique may reduce this retention.

A crude fractional distillation was made of a 25-ml sample of the 477 watt-ht/liter dry 50% TBP, which had a uranium retention of 38.1 mg/ml, in order to determine which fraction was responsible for uranium and fission product retention and emulsification during solvent extraction. The materials responsible for the retention of the uranium (and fission products) are held largely in the high-boiling still residue (Table 4), and the distillation could be controlled so that compounds boiling higher than TBP are left in the still. The clean distillates (fractions 1-7 and 9, Table 4) were recombined, washed with sodium carbonate and nitric acid, and then contacted with uranyl nitrate (320 mg U/ml) in 2 M HNO₃. The organic phase was stripped then with triple volumes of 0.01 M HNO₃ until the strip was colorless. The uranium retention was 0.014 mg/ml, which represents a "decontamination factor" of 2.72×10^3 from the uranium retention agents through vacuum distillation. Minute traces of the still residue, when added to clean solvent, formed organic-in-aqueous emulsions, held uranium in an organic phase, and retained fission product activity.

Table 4. Fractional Vacuum Distillation of Irradiated TBP-Amsco

Fraction No.	Pressure (mm Hg)	Still Temp. (°C)	Dist. Vol. (ml)	U Retention (mg/ml)
1	5	65-70	3	0.013
2	3	70-80	3	0.005
3	2	80-120	0.75	-----
4	2	120-142	0.75	0.026
5	2	142-150	4	0.086
6	2	150-170	2	1.198
7	2	> 170	3	1.238
8	2	Residue	3	94.2
9	2	Cold trap	1	-----

6.0 CONCLUSIONS

The results of recent experiments on the effects of radiation on diluents and TBP-diluent mixtures suggest that the agents responsible for emulsification, uranium, plutonium, or thorium retention and fission product extraction are long-chain phosphates or other compounds formed by interaction between the damage products of the TBP and the diluent. The presence of a nitric acid--metal nitrate aqueous phase during irradiation intensifies the deleterious effects of the agents and/or forms additional degradation products. The usual solvent recovery procedure does not remove these materials, and as a result, a gradual buildup occurs that finally necessitates discard of the solvent. Laboratory-scale work has indicated that vacuum distillation may be used to recover 90% of the solvent, free of fission products, heavy metal complexing agents, and emulsifiers.

In addition to identification of the degradation products and possible methods of minimizing the damage due to radiation, some future effort might well be spent on an economic evaluation of a vacuum distillation solvent recovery system.

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