

ORNL  
**OAK RIDGE NATIONAL LABORATORY**  
operated by  
**UNION CARBIDE CORPORATION**  
for the  
**U.S. ATOMIC ENERGY COMMISSION**



ORNL - TM - 527 *slj*

COPY NO. - 172

DATE - March 21, 1963

**SURVEY OF RECENT DEVELOPMENTS IN SOLVENT EXTRACTION WITH  
TRIBUTYL PHOSPHATE**

R. E. Blanco, C. A. Blake, Jr., W. Davis, Jr., R. H. Rainey

**ABSTRACT**

Tributyl phosphate can be used for extraction in processing all current power reactor fuels. Nitric acid is the only salting agent required. Typical flowsheets are presented. In aluminum nitrate systems which are more than 0.1 M acid deficient, the uranium distribution coefficient is a function of pH and independent of aluminum concentration; the coefficient remains constant at one in fluoride systems when the nitrate to fluoride ratio is  $\sim 3.5$ . Many objectionable properties of degraded diluents are ascribed to nitroparaffins. Aliphatic diluents with the least branching are the most stable to nitration. The nitration stability of aromatic diluents varies with structure, e.g., stabilities of diethylbenzenes decrease as meta  $\gg$  ortho  $>$  para. Solvent purification by flash distillation appears superior to other methods. The stability of Amsco 125-82 was permanently improved by treatment with sulfuric acid. The radiation stability of TBP was  $\sim 2$  times higher in an aromatic diluent than in Amsco 125-82. The G decomposition value for 1 M TBP in Amsco alone was  $\sim 0.9$ , whereas in 1 to 3 M  $\text{HNO}_3$  it was 1 to 5 and G ( $-\text{HNO}_3$  org phase) was 3 to 20. Variation of uranium-thorium separation factors with structure of some neutral organophosphorus reagents is presented. Basic studies include measurement of activities in multicomponent solutions and description of aqueous activity coefficients by an extended Debye-Hückel equation.

---

To be presented at the Symposium on Aqueous Reprocessing Chemistry at Brussels, Belgium, April 23-26, 1963.

**NOTICE**

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

## INTRODUCTION

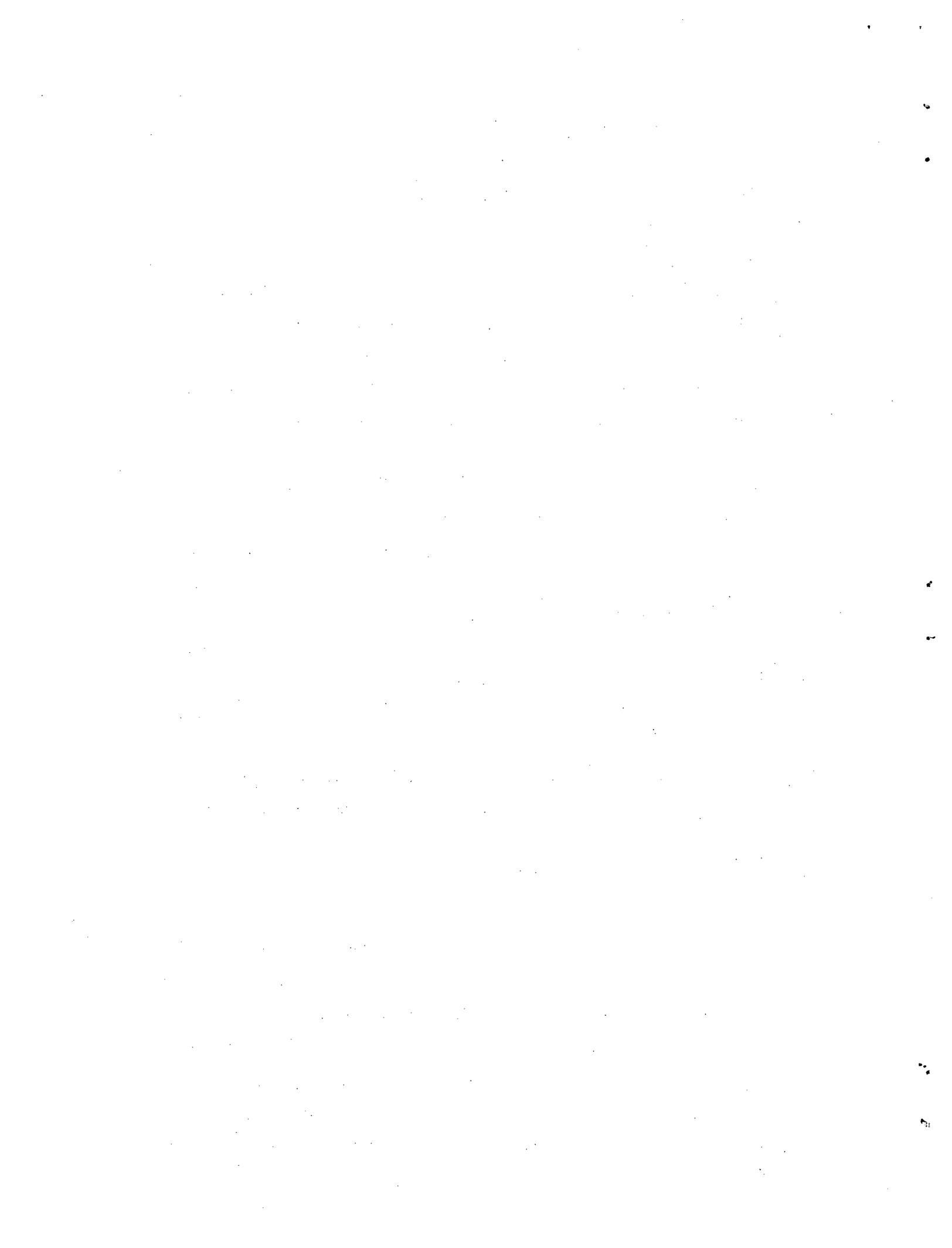
Tributyl phosphate is the most widely used solvent at atomic energy installations. Although large separation plants are successfully operated within existing knowledge limits, new processing techniques and variations of existing techniques are continually being developed as the need arises. The achievement of new economies in existing systems and the adaptation of the processes to new fuels will require a continuing vigorous search for basic chemical information. This report presents several new approaches to solvent extraction separation problems along with a discussion of factors influencing the choice of diluents and mechanisms of extraction.

## RECENT APPLICATIONS

### Extraction of Uranium and Thorium from Nitric Acid Solutions

"Acid" solvent extraction processes have been developed for the extraction of enriched uranium, uranium-233, or co-extraction of uranium and thorium from nitric acid solutions with tributyl phosphate (TBP) or di-sec-butyl phenyl phosphonate (DSBPP). For example, nitric acid replaces aluminum as the salting agent in the TBP-25,<sup>1</sup> Interim-23,<sup>2</sup> and Thorex<sup>3</sup> processes; the first two processes use 2.5 to 15% TBP and the last 30-40% TBP. Nitric acid salting of uranium extraction processes using 20-50% TBP are, of course, well known. Advantages of nitric acid salting include a large reduction in evaporated waste volumes because of elimination of non-volatile salting agents and a reduction of stage heights in extraction columns by factors of 2 to 4 due to the decrease in surface tension.<sup>4</sup> Decontamination factors and uranium or thorium recovery with the "Acid" processes are equal to those of the older techniques.

In previous processes for recovery of enriched uranium, aluminum clad or alloyed fuel was dissolved in nitric acid, and the aluminum nitrate provided salting strength for the first cycle of extraction.<sup>1</sup> The "Acid" processes are designed for use with headend processes where aluminum, stainless steel, or Zircaloy-2 fuel claddings are removed by dissolution or mechanically, as by the chop and leach technique.<sup>5</sup> An "Acid" process, which can be used for the second and third cycles in processing aluminum-uranium alloy fuels after the aluminum has been eliminated in the first cycle, was successfully demonstrated.



Laboratory experiments have demonstrated that in a given set of extraction equipment the increase in fission product extraction with increased TBP concentration can be counteracted by the increase in saturation of the solvent. Laboratory-scale tests showed that a 15% TBP, high-throughput system, resulted in the same decontamination and uranium recovery as a low-throughput 5% TBP system (Fig. 1). The tests were conducted in countercurrent equipment containing 5 extraction and 3 scrub stages with 5, 10, and 15% TBP, and a feed containing 20 g/l U and 3.0-4.0  $M$   $HNO_3$ . With each TBP concentration the flow ratio was varied to maintain a constant uranium loss when the nitric acid concentration in the extraction and scrub sections were 2 and 3  $M$ , respectively. Solvent saturation varied from 43% at 5% TBP to 57% at 15% TBP, but the gross gamma decontamination factor remained constant at  $\sim 10^5$ .

An "Acid" version of the Interim-23 process,<sup>6</sup> where uranium-233 is extracted from a thorium-nitric acid solution, was also successfully tested, producing a decontamination factor of  $\sim 10^5$  and a uranium loss of  $< 0.01\%$  (Fig. 2).

In the Acid Thorex process,<sup>7</sup> both uranium and thorium are extracted from the fission-product-bearing nitric acid solution (Fig. 3). The 0.1  $M$  aluminum was added as a complexing agent for fluoride in the dissolution step and is not effective as a salting agent for the solvent extraction. Decontamination factors obtained were 1000, 5000, 1000, and  $10^5$ , respectively, for ruthenium, zirconium-niobium, protactinium, and rare earths. Uranium and thorium losses were 0.01 and 0.3%, respectively. Thorium is less extractable than uranium, therefore an acid deficient feed was required to improve separation from fission products when the thorium is extracted. Acid is added to the extraction section below the feed plate to increase the salting strength in the lower part of the column so that thorium loss is minimized. Two scrub streams are provided to decrease the amount of acid extracted so that the product may be co-stripped by a minimum of dilute acid. The water scrub is not required if the thorium and uranium are to be selectively stripped from the solvent.

Variations of the Acid processes are possible to produce a special product or where existing non-critically safe equipment must be used. In the process to be used in reprocessing the uranium stored at ORNL before its use in fabrication of thoria fuel elements, the solvent concentration is limited to 2.5% to limit the concentration of uranium in

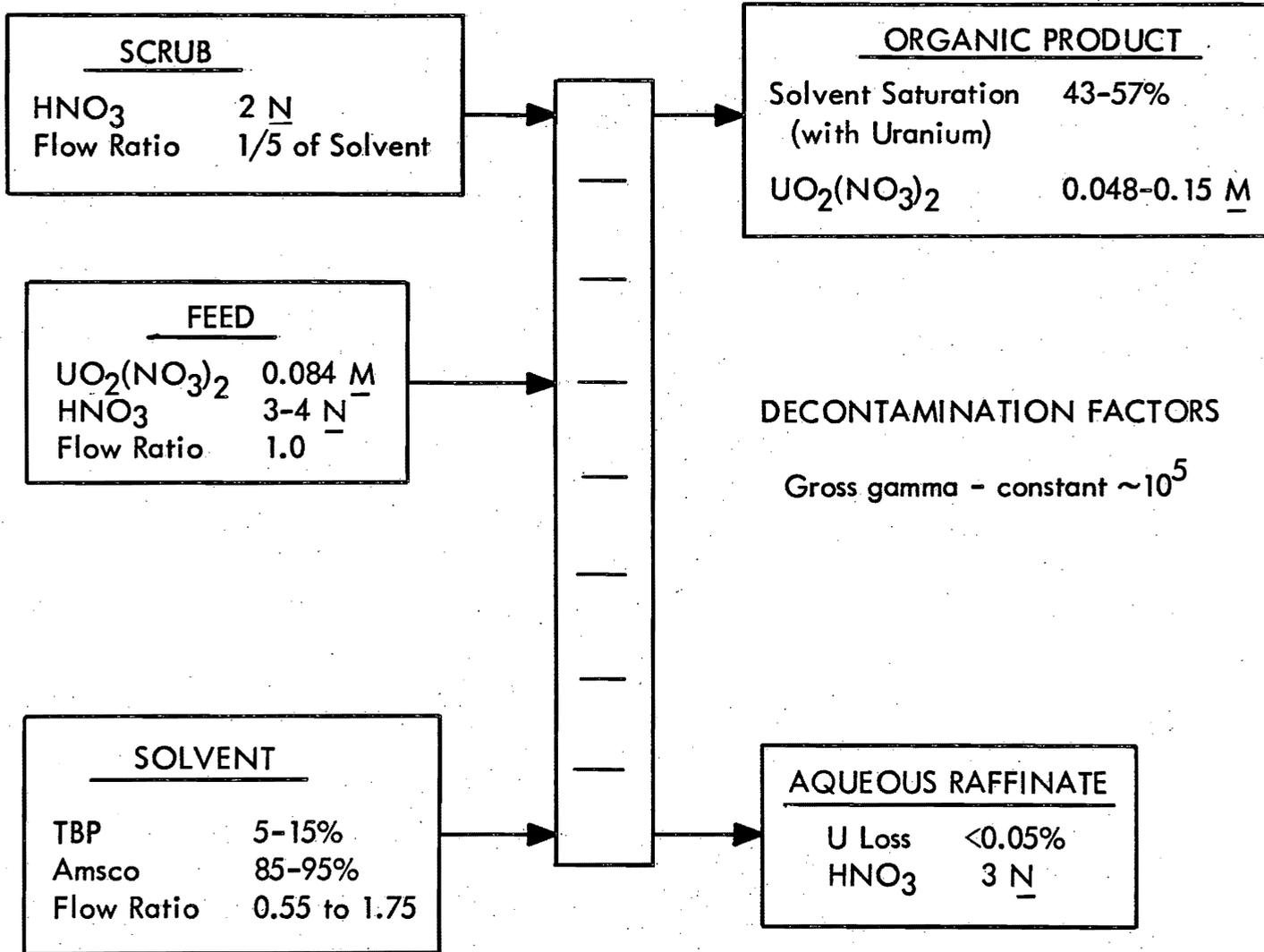


Fig. 1. Acid TBP-25 Process for Extraction of Uranium.

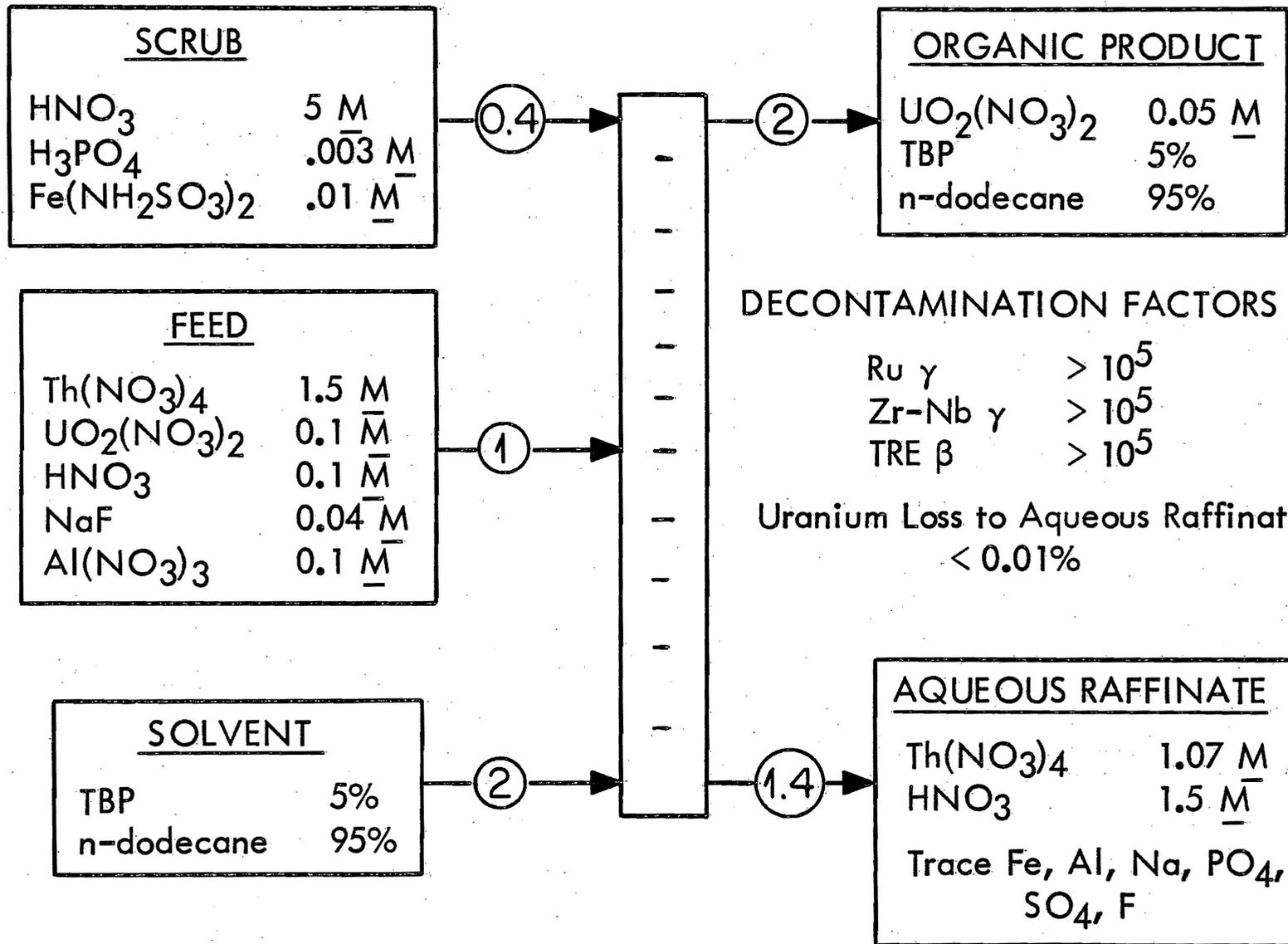


Fig. 2. Acid Interim-23 Process for Extraction of Uranium from Irradiated Thorium.

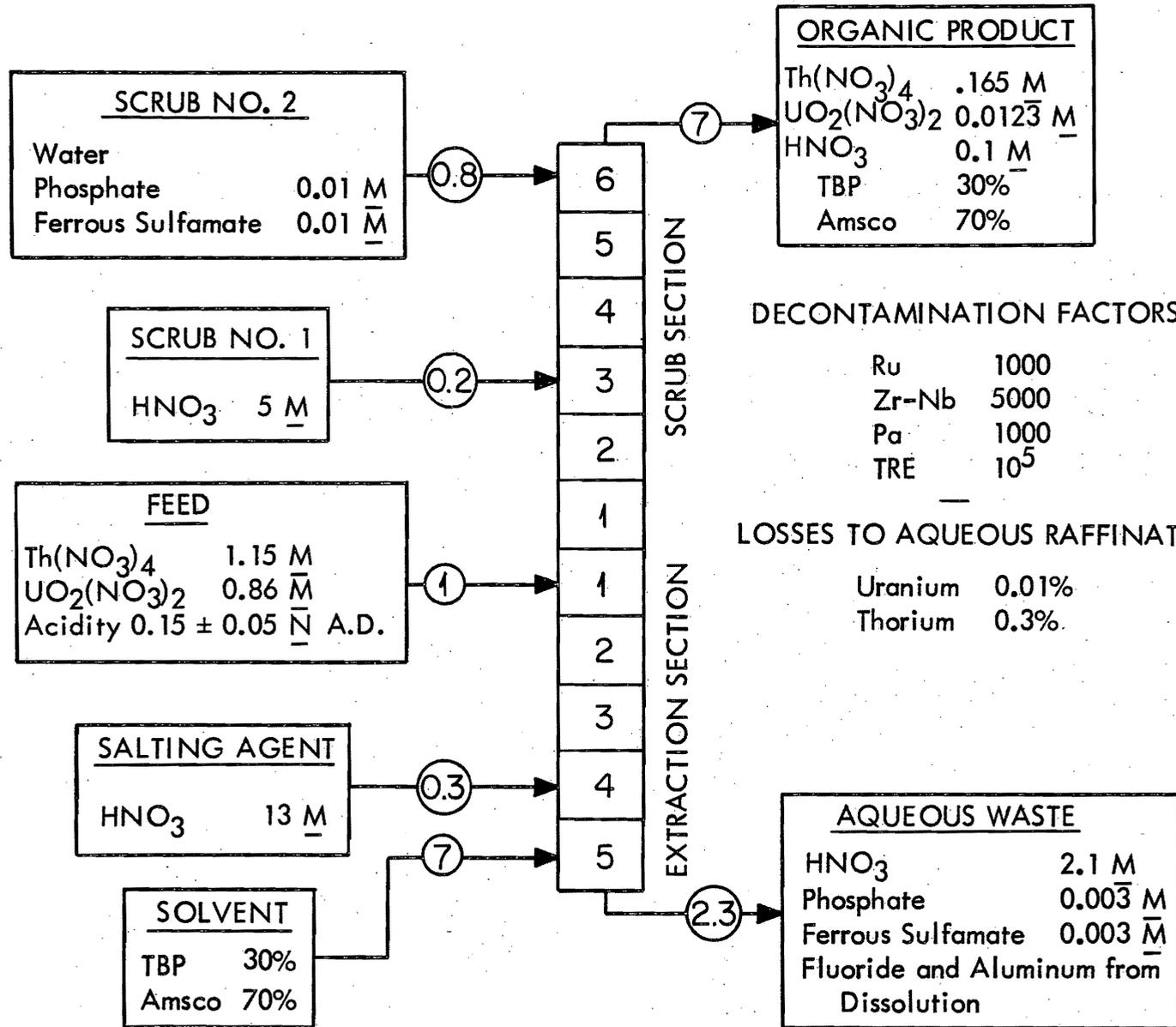


Fig. 3. Acid Thorex Process for Co-Extraction of Uranium and Thorium.

non-critically safe equipment (Fig. 4). Thorium is used both as a nuclear poison and as a salting agent for the 2.5% solvent system. Di-sec-butyl phenyl phosphonate (DSBPP) is used rather than TBP because the separation factors for U/Th are higher by a factor of four in the DSBPP system at thorium concentrations less than 100 g/l. The acid deficient aluminum nitrate scrub produces a product with nitrate-to-uranium ratio of less than 2.3 as required by the Sol-Gel fuel preparation process.<sup>8</sup> Decontamination from thorium-228 and its' daughters is  $\sim 10^4$ .

#### Extraction of Uranium from Nitric Acid-Hydrofluoric Acid Solutions

The advent of nuclear fuels containing zirconium has increased interest in systems in which both uranium and zirconium are soluble. The simple nitric acid-hydrofluoric acid-uranium system was studied to determine the effect of fluoride on uranium extraction from nitric acid solutions (Fig. 5). The uranium distribution coefficient for the HF-HNO<sub>3</sub>-30% TBP system increased with about the 1.8th power of the nitric acid concentration at constant fluoride concentration. The complexing effect of fluoride and uranium was illustrated by a decrease in uranium distribution coefficient with about the 1.6th power of fluoride concentration. Nitric acid therefore compensates on approximately a mole-for-mole basis for the complexing action of the fluoride. Over the range 0.5-4 M HF, the uranium distribution coefficient remains constant at 1 when the nitrate to fluoride ratio is about 3.5. The effect of zirconium on the system has not been determined but is expected to have little effect other than the essentially complete removal from the system of 4 moles of fluoride per mole of zirconium by the strong zirconium-fluoride complexing action.

#### Extraction of Uranium from Acid Deficient Aluminum Nitrate Solutions

The uranium distribution coefficient between dilute TBP in n-dodecane and less than 0.1 N acid deficient aluminum nitrate may be expressed solely as a function of the pH of the aqueous solution and when thus expressed is independent of aluminum nitrate concentration (Fig. 6). A plot of the log of the distribution coefficient vs pH gives a straight line in the acid deficient range, with a slope of about -2. When the  $\log \frac{DC}{(NO_3)^2}$  is plotted vs pH, the slope is -1. This decrease in distribution coefficient is attributed to uranium hydrolysis and is qualitatively in agreement with the hydrolysis as reported by Rush et al.<sup>9</sup> The plot shows that the hydrolysis of uranium

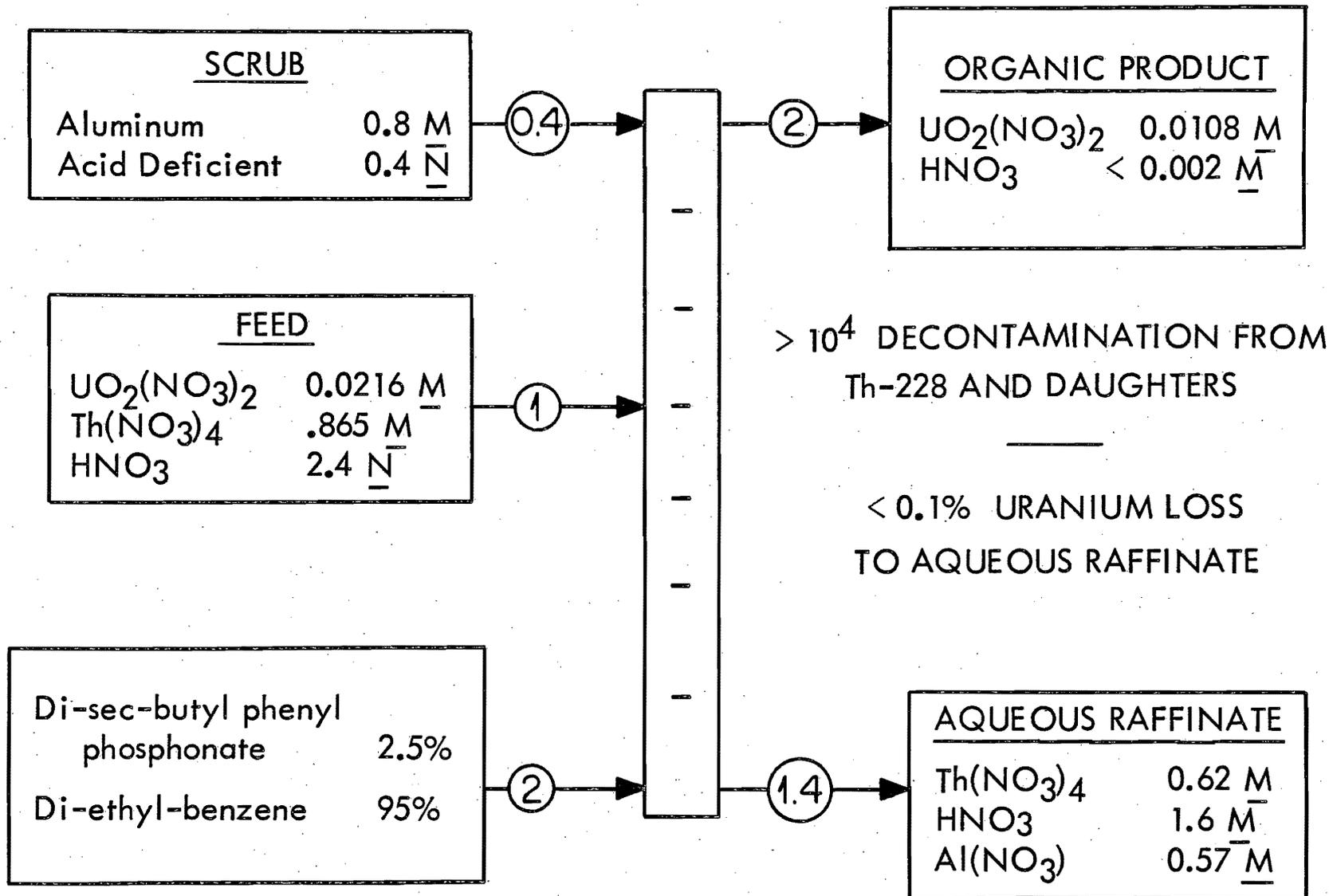


Fig. 4. Extraction of U-233 from Daughters of U-232.

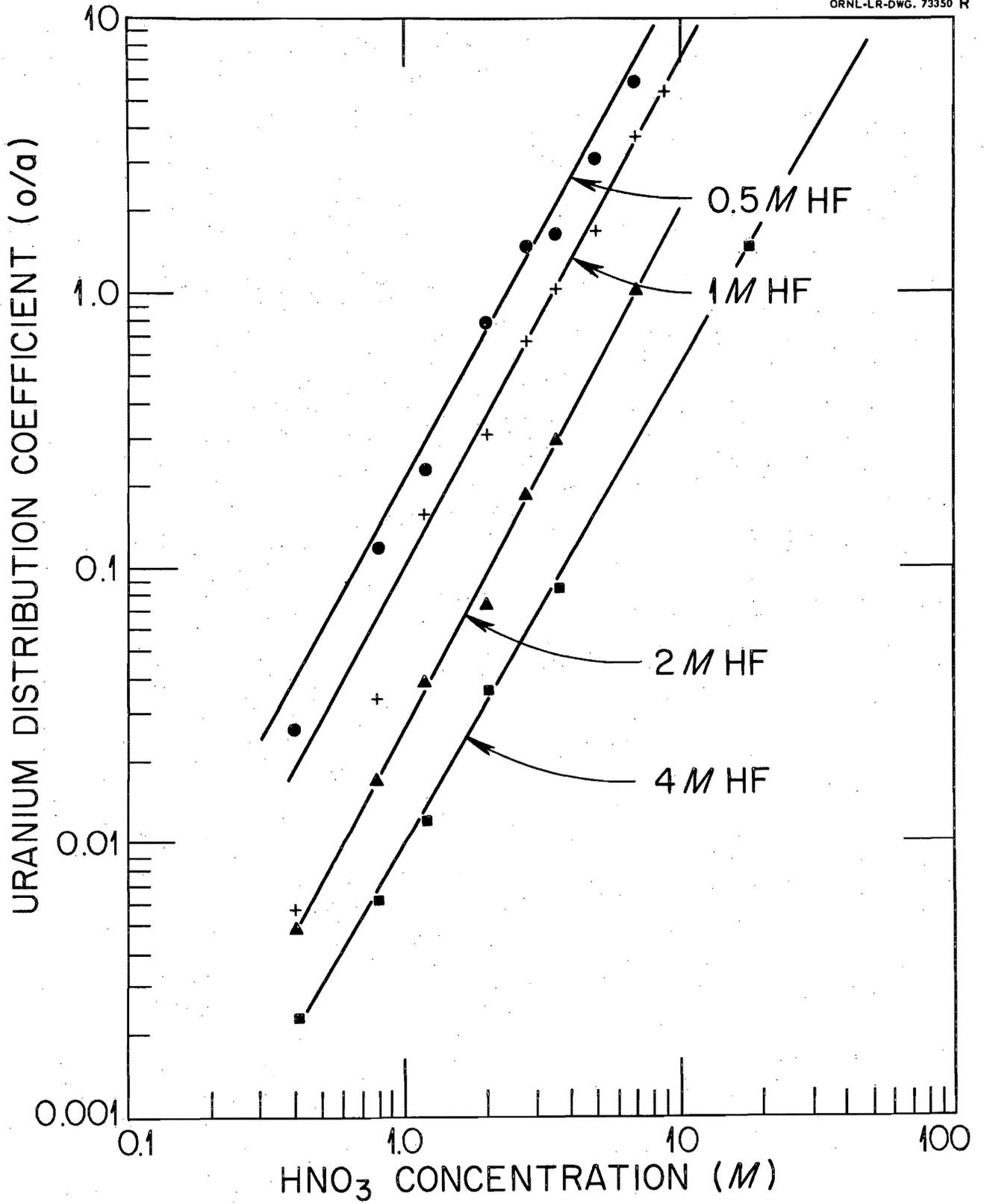


Fig. 5. Extraction of Uranium with 30% TBP from HNO<sub>3</sub>-HF Solutions.

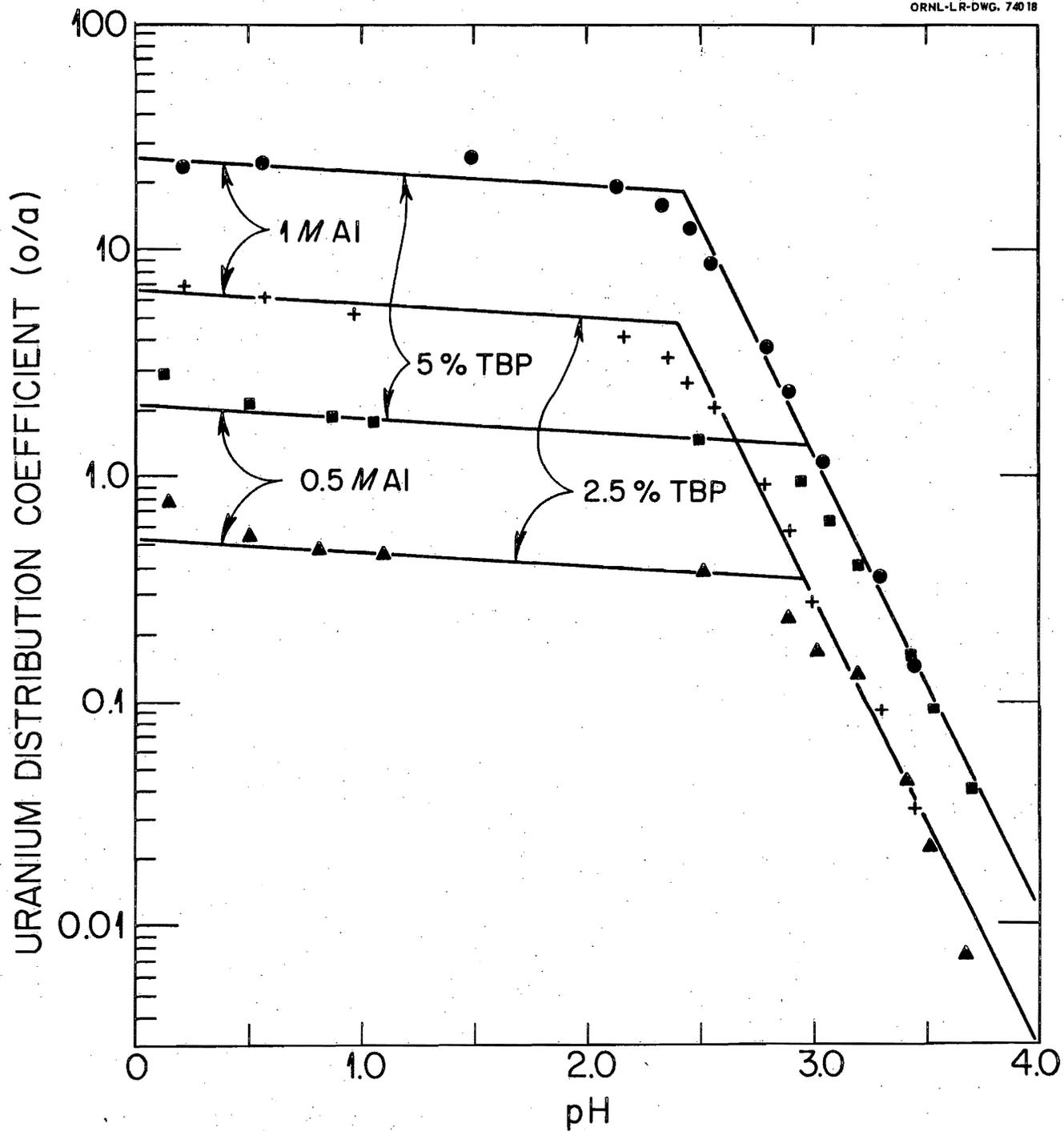


Fig. 6. Extraction of Uranium from Acid Deficient Solutions.

becomes a controlling factor at pH 2.4 in 1 M  $\text{Al}(\text{NO}_3)_3$  and at pH 3.0 in 0.5 M  $\text{Al}(\text{NO}_3)_3$ . This corresponds to about 0.1 N acid deficiency in each system.

In fuel recovery processes, uranium reflux in the scrub section of the extraction column increases decontamination as the result of an increase in uranium concentration. A strict control of uranium concentration is required in non-geometrically safe equipment, however. In the past, due to variations in routine analyses, the careful balance between these two requirements has been difficult when acid deficient aluminum nitrate was used in the scrub. A pH measurement of the scrub solution simplifies this control.

### DILUENT STUDIES

Until a few years ago most solvent studies were concerned with the extractant, i.e., TBP stability, DBP extraction properties, etc. More recently, the prospect of fuel processing at much higher activity levels and at consequently greater degradations, coupled with some difficult operating experiences, brought an awareness that diluent performance was important, and emphasis shifted to studies of chemical properties of diluents.<sup>10</sup> Effects caused by degradation products include low decontamination factors, poor phase separations, loss of metal values to waste streams, and increased activity levels in the recycled organic extractant. Diluents were previously selected for use on the basis of expense, availability, flash point and other physical properties. Operators hesitated to pay more than 35¢ per gallon, and because of equipment design, flash points of 140°F or higher were required in many cases.

Because nearly all the processing sites use different supporting diluents, it is difficult to correlate solvent degradation and cleanup data. Although all the diluents are primarily saturated aliphatic hydrocarbon mixtures, some contain substantial quantities of cyclic paraffins, aromatic hydrocarbons or compounds with high degrees of unsaturation, and all have differing chain lengths and type of branching. Further, solvent degradation during processing is frequently blamed for poor process results in cases where improper operation is probably the true offender, e.g., improper feed preparation, unusual column operating conditions, introduction of contaminants by recycle of waste streams during periods of high metal value losses, and subjection of the extractant to severe degradation by improper operation of equipment such as intercycle evaporators.

Present solvent purification procedures, generally alkaline and acid washing, are ineffective where degradation is significant, because they do not remove diluent degradation products from the organic stream. As a result, more stable, pure diluents are being tested whose structures offer few sites for nitric acid attack, or alternatively, diluents prepared from a relatively stable commercial hydrocarbon by chemical pre-treatment to destroy those sites most active to nitric acid. Plant-scale demonstrations are now being made<sup>11</sup> to establish whether savings resulting from improved operation with relatively pure and stable diluents can offset their higher initial cost.

### Diluent Degradation

The extraction of zirconium-niobium fission products by degraded solvent occurs as a result of the introduction of nitro groups on the diluent molecule. The mechanism of extraction is difficult to establish because of the low concentrations usually involved, but extraction has been ascribed to the nitroparaffins themselves (or specifically, to their enolic acidic forms)<sup>12</sup> or to hydroxamic acids subsequently formed from the nitroparaffins.<sup>13</sup>

Concentrations of nitroparaffin in degraded Amsco 125-82 have been estimated by ultraviolet spectrophotometry and by total organic nitrogen determinations.<sup>12</sup> The ultraviolet spectra of simple nitroparaffins give an intense band at around 200  $\mu$ , as did also a number of samples of Amsco and TBP-Amsco exposed for varying times to boiling nitric acid or to gamma irradiation in the presence of nitric acid (Fig. 7). The absorbance, attributed to nitroparaffin concentration, increased linearly with exposure time. Since 100 watt hr/liter irradiation, while being stirred with 2 M  $\text{HNO}_3$ , appeared essentially equivalent to 11 hr refluxing with 2 M  $\text{HNO}_3$ , the irradiation dose scale at the top of Fig. 7 was arbitrarily adjusted to make the slope for the diluent radiation damage match that for the diluent chemical damage. This resulted in good agreement of the single TBP-diluent chemical damage point with the TBP-diluent radiation damage. The slopes indicate that nitration was at least twice as fast in the presence of TBP, probably because of nitrate and nitrite extraction by the TBP, and perhaps also from stabilization of the nitroparaffins by complexing with the TBP.

The ratio of total nitrogen (determined by chemical analysis) to nitro groups (determined by spectrophotometry) in the organic phase was almost constant in degraded

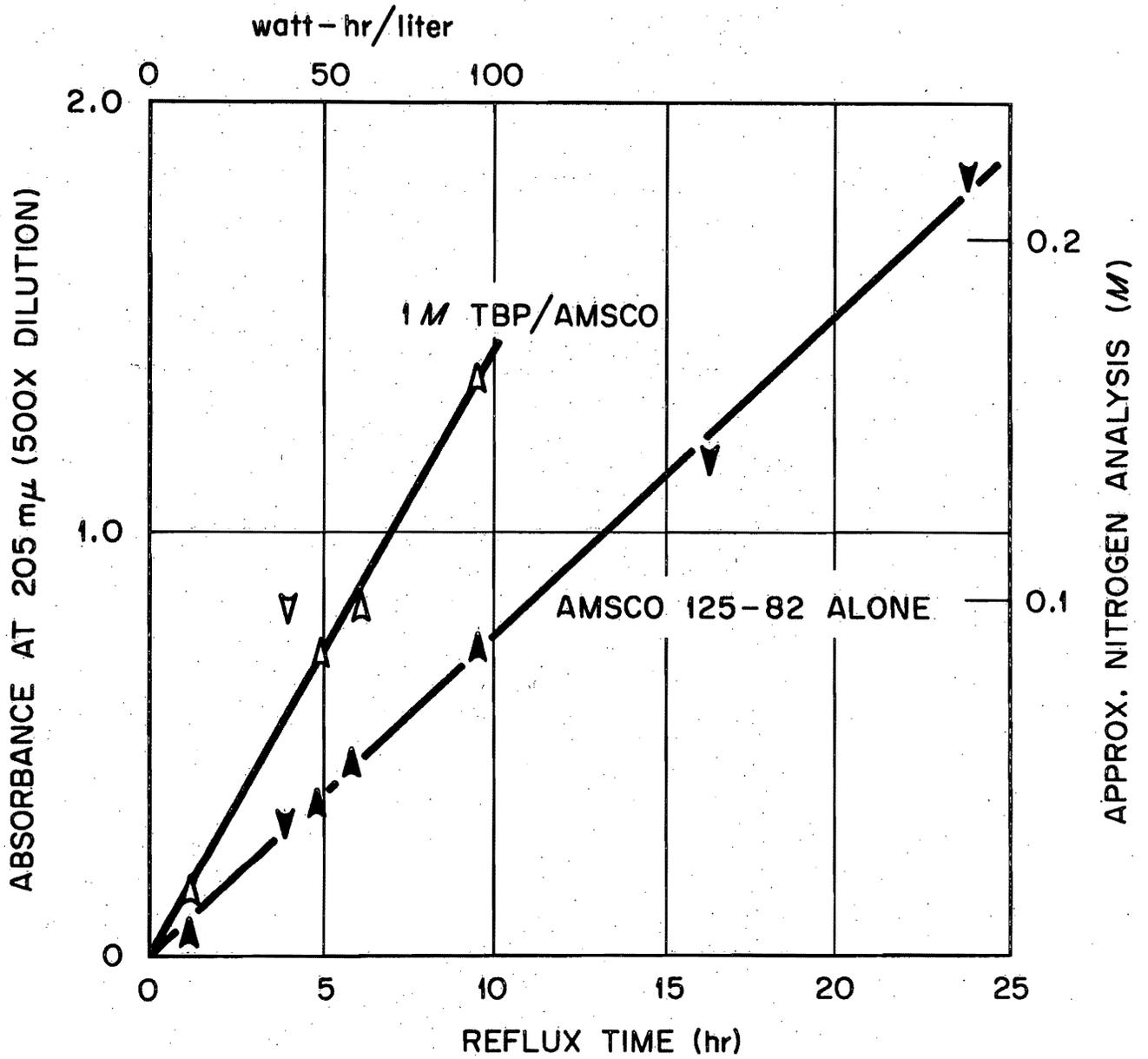


Fig. 7. Correlation of Type of Degradation with Absorbance.

solutions. These include about half of the test points in Fig. 7. The right-hand scale, Approx. Nitrogen Analysis, was fitted smoothly to these points for general comparison.

Approximate zirconium extraction coefficients with degraded Amsco 125-82 have been plotted as a function of the concentration of nitro groups determined by UV absorption spectra. In the log-log plot (Fig. 8), a line through the points has a slope of 4, signifying a combining ratio of 4 for extractant to extracted zirconium. This conclusion may be tenuous since (1) the concentration of extracting agent need not be a linear function with total nitration products, (2) the zirconium extraction coefficients were not determined with great accuracy, and (3) the slope for high combining ratios is difficult to establish from limited data. A combining ratio of 4 between tetravalent zirconium and monobasic acids is a logical conclusion, however. These tests were made without TBP in the extractant phase. No calculations were made with TBP present, but TBP causes a large synergistic enhancement of Zr-Nb extraction by degraded diluent.

#### Diluent Purification

Whether the extraction and retention of fission products in degraded solvents is caused by enol nitroparaffins, by hydroxamic acids derived therefrom, or by other related components, such extraction correlates with the concentration of nitroparaffin present, and elimination of nitroparaffin also eliminates the objectionable extraction. Accordingly, nitroparaffin concentration is used in the present study as a measure of diluent degradation, and solvent purification is defined as removal of the nitroparaffins. While this definition of purification may be oversimplified it is still in strong contrast to the mere stripping out of the extracted and retained metals. That operation may reduce solvent activity levels, but it does not generally remove the extractants which remain to extract fission products again and recontaminate the solvent on recycle.

Several studies of solvent cleanup methods have been made at ORNL<sup>12,14</sup> and elsewhere,<sup>13,15-17</sup> but only three approaches will be discussed here: (1) sorption of nitroparaffins on activated solids; (2) partitioning the nitroparaffins into liquid scrubbing reagents; (3) distillation of the pure TBP-Amsco mixture away from the nitroparaffin.

Solid Sorption. Current solvent purification in processing plants using TBP involves combinations of washings with acidic solutions, alkaline solutions, and occasionally, alkaline permanganate solutions.<sup>17</sup> While each of these acts to remove degradation

UNCLASSIFIED  
ORNL-LR-DWG. 76340

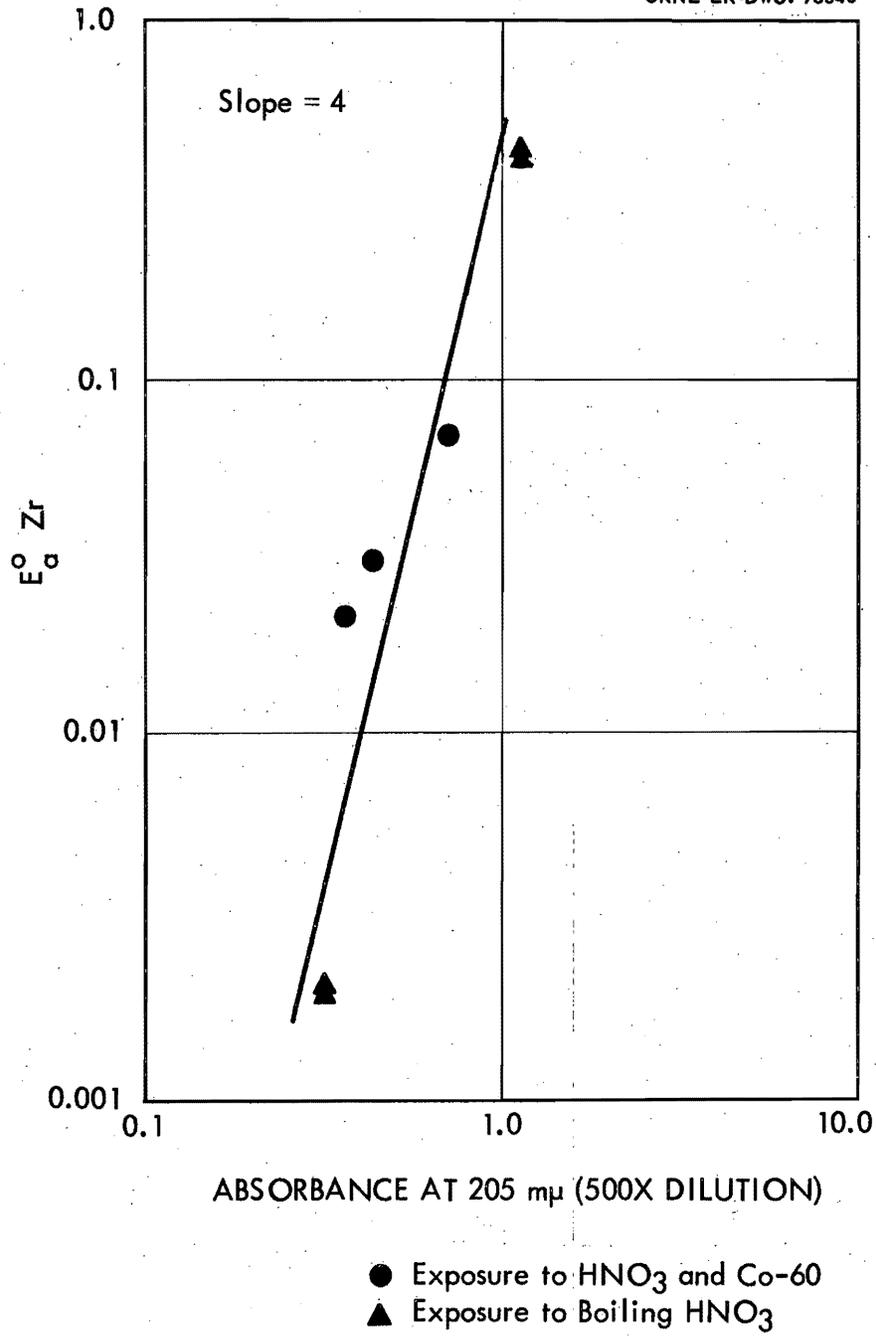


Fig. 8. Correlation of Zr<sup>95</sup> Extraction Coefficient of Degraded Amsco 125-82 with Absorbance.

products of the TBP, only the alkaline permanganate treatment removes significant amounts of diluent degradation products from the organic phase. Absorption of these on the solid manganese dioxide formed during the scrubbing accounts for the cleanup, and the effectiveness of the treatment depends on temperature, amount of solid, alkalinity and degree of degradation. Activated alumina also sorbs diluent degradation products. The two sorbents were tested on a 1 M TBP-Amsco solution which had been exposed in the presence of nitric acid to 45 watt-hr/liter irradiation. Principal interest was in the ability of the solids to decrease Zr-Nb extraction by the irradiated solvent.

The two solids showed similar sorption patterns at room temperature. Impurities causing 50-60% of the Zr-Nb extraction by the irradiated, carbonate-scrubbed solvent were easily sorbed by 2 g MnO<sub>2</sub>/liter or 20 g Al<sub>2</sub>O<sub>3</sub>/liter. Removal of another fraction causing 20-25% of the Zr-Nb extraction was achieved by further relatively large additions of solid (10 g MnO<sub>2</sub>/l, 200 g Al<sub>2</sub>O<sub>3</sub>/l), but, even at the highest solids levels used, the solvent retained 20-25% of its Zr-Nb extraction power. To achieve equivalent performance, it was necessary to use 10-20 times more alumina than manganese dioxide (Fig. 9).

Liquid Scrubbing. Solvent cleanup with a liquid scrub rather than with a solid has operational advantages. In studies involving nearly one hundred liquids, or liquid-solid combinations, most effective cleanup was achieved by ethanolamine.<sup>18,19</sup> The amine and nitroparaffins form salts which are soluble in the amine.

A principal disadvantage of solvent cleanup with ethanolamine is the high reagent cost. Ethanolamine and 1 M TBP-Amsco cost ~\$2.00 and ~\$1.50 per gallon, respectively. If each gallon of TBP-Amsco requires 1 gallon of ethanolamine for cleanup, the cost for the scrub solution would be ~\$2.00 or ~50 cents more than if the 1 M TBP were discarded without cleanup. The cost would be reduced if cleanup of the total solvent stream during each cycle was not necessary, or if the amine solution could be recovered. Recovery methods, such as distillation, have not been studied. If a greater than equal volume of scrub phase is required the costs will increase. In addition, TBP is lost to the ethanolamine and a significant amount of amine is soluble in the TBP phase. When contacting an equal volume of 0.5-1.0 M TBP in Amsco 125-82, the TBP distribution appeared to be solubility-limited at ~0.05 M TBP (~13 g/liter) in the ethanolamine. This loss of TBP is equivalent to about 6 cents per gallon of ethanolamine used.

UNCLASSIFIED  
ORNL-LR-DWG 73844

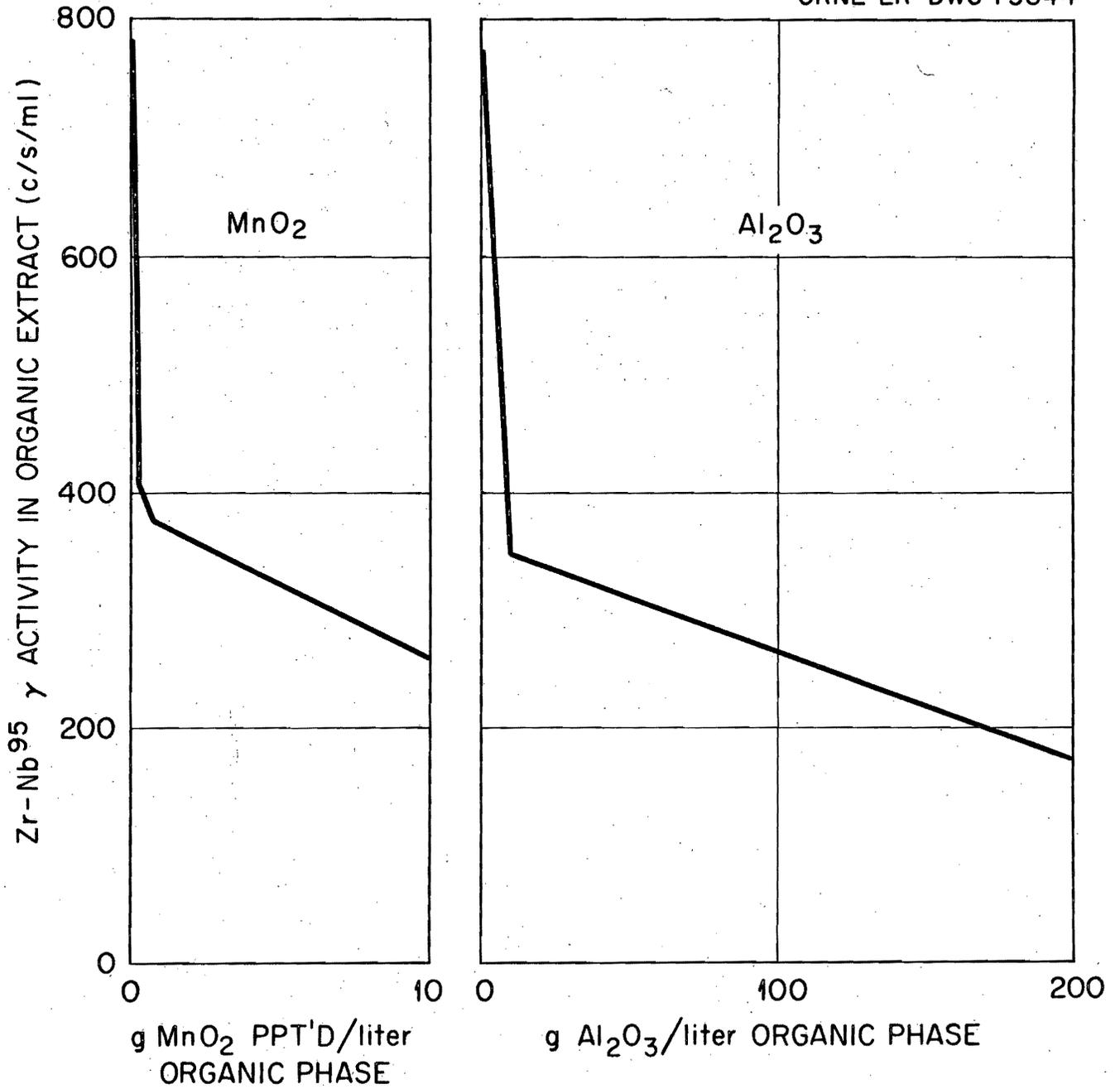


Fig. 9. Comparison of Cleanup of Amsco 125-82 by Alkaline Permanganate Solutions and by Activated Alumina.

Distillation. Low-pressure flash distillation appears at present to be the best, and possibly the cheapest, method for repurification of TBP-Amsco 125-82 solutions that have been decomposed by radiation in systems containing  $\text{H}_2\text{O}$ ,  $\text{HNO}_3$ , and  $\text{UO}_2(\text{NO}_3)_2$ . This statement is based on laboratory studies of molecular and rapid (not flash) distillation of 30% TBP-Amsco 125-82 solutions degraded by (1) irradiation to the 122 watt-hr/liter level in a nominal 10,000 curie cobalt-60 source while being agitated with an aqueous phase containing 1.84 M  $\text{HNO}_3$  and 310 g U/liter in the ratio 2.7 vols organic per volume of aqueous solution; and (2) in processing irradiated reactor fuels in the ORNL solvent extraction (Thorex) pilot plant. Both molecular distillation at  $\sim 70^\circ\text{C}$ , which corresponds to  $\sim 10^2$  microns TBP vapor pressure, and rapid pot-to-pot distillation at  $110\text{--}120^\circ\text{C}$ , corresponding to  $\sim 5 \times 10^2$  microns TBP vapor pressure, showed that the degradation products detectable as nitro or similar compounds by fission product extraction-scrub-strip tests remained as a pot residue. Extraction tests showed essentially no distillation of materials that affect the Zr, Nb, Ru, or U extraction properties of the 30% TBP-Amsco 125-82 organic solution.

On the basis of these tests a specially designed flash distillation unit has been proposed by Weinrich and Associates, Fig. 10, to handle 150 liters of TBP-diluent solution/hr. This unit provides for heating the solution to  $160^\circ\text{C}$ , preferably after contacting with dilute  $\text{Na}_2\text{CO}_3$  solution to remove  $\text{HNO}_3$  and uranium, feeding the solution to a packed column at a pressure of 55-60 mm Hg, and flashing the diluent and TBP into two separate fractions. TBP, removed as a side stream, will contain some diluent, perhaps 10% diluent-90% TBP. The remaining diluent will be taken off the top of the still.

Costs of building and operating the flash distillation unit are estimated to be \$0.11-0.15 per gallon of solvent, including taxes, insurance, amortization, and general overhead, or \$0.078 per gallon exclusive of these costs. For comparison, and at purchase costs of \$0.34/gal Amsco 125-82 and \$4.29/gal technical grade TBP, the initial cost of 30% TBP in Amsco 125-82 is  $\sim$ \$1.50/gal.

The fraction of the total plant throughput of TBP-diluent requiring distillation depends on plant operating and radiation dose conditions. At high doses, for example 0.1 watt-hr/liter per pass, as in the first cycle of the Thorex pilot plant,<sup>21</sup> and if only one extractant stream is used for all cycles, it would be necessary to distill 100% of the organic solution on each pass through the plant. On the other hand, if separate

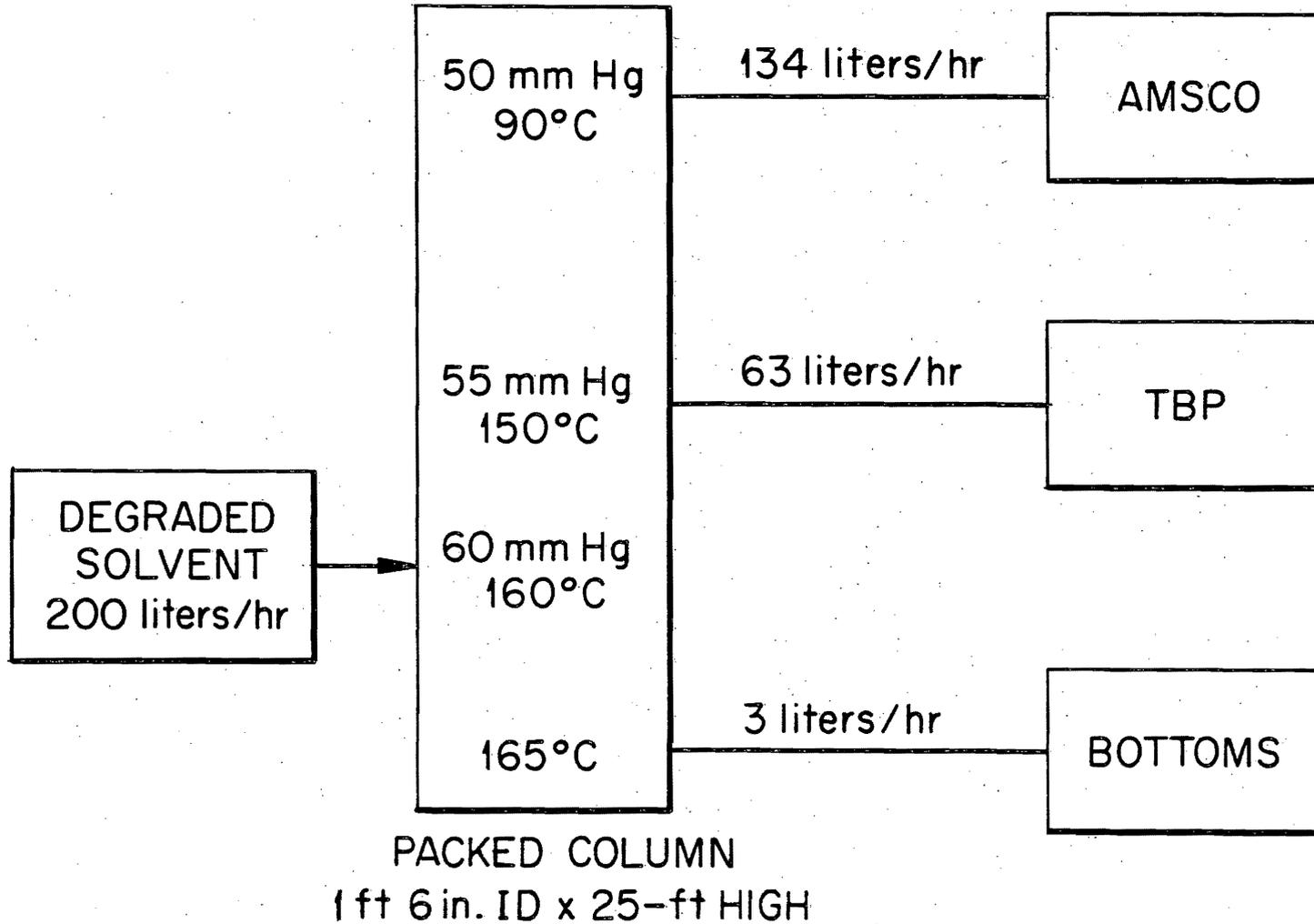


Fig. 10. Flash Distillation System for TBP-Amsco (Excluding Reflux Streams).

extractant streams for the two cycles were used, only the first cycle would require continuous purification. Only one still would be needed to produce high-quality TBP and diluent.

At the American Atomic Energy Commission's request, Mallinckrodt Chemical Company is considering recovery of both TBP and kerosene from 170,000 gal of degraded 30% TBP solution. Preliminary calculations show that, if a new facility is built capable of processing 100 l/hr of the solvent by flash distillation, the TBP and kerosene may be recovered at costs below their original levels.

#### Pretreatment to Improve Diluent Stability

Amsco 125-82 is a specially prepared aviation naphtha, a solvent considered to be among the most stable of the commercial aliphatic hydrocarbons. Yet, Amsco can be degraded severely under several different conditions. This is not surprising, since Amsco 125-82 is composed of 17 or more compounds in the  $C_{12}$ - $C_{14}$  range, many of which are highly branched.<sup>20</sup>

Amsco can be improved by destroying, prior to process use, some of the sites which are reactive to nitric acid. Experimentally this has been done by (1) pretreating with concentrated sulfuric acid and (2) by preliminary nitric acid degradation followed by treatment with sulfuric acid.

Sulfuric acid scrubbing is more effective when Amsco is warmed while contacting with the concentrated acid (>95%), or when oleum is added to the concentrated acid for use at room temperature. In Fig. 11 the Amsco treated with sulfuric acid and untreated Amsco were made 1 M in fresh TBP and then degraded up to 24 hr by boiling with 2 M nitric acid. Degradation was followed by conversion of nitroparaffins to the enol form, through sodium carbonate and calcium hydroxide treatment, and extraction of tracer ( $Hf^{181}$ ). Whereas the solution in untreated Amsco, after 8 hr nitric acid degradation, showed a hafnium extraction coefficient of  $E = 16$ , those in Amsco pretreated with 96%, 98%, or 100% sulfuric acid showed coefficients of 0.3, 0.15, and 0.03, respectively. Solutions in Amsco pretreated with 100% and 105% acid at room temperature and with 95.6% acid at 50°C for 30 min all had extraction coefficients of but  $\sim 0.15$  even after 24 hr degradation. The sulfuric acid apparently acts to destroy the active

sites by sulfonation to sulfuric acid-soluble byproducts or by rearrangement of the molecule to a more stable configuration. No sulfur has been detected in the diluent after treatment. Oleum (120-130%  $H_2SO_4$ ) cannot be used since it causes severe solvent degradation.

Amsco degraded with nitric acid, scrubbed with concentrated sulfuric acid at room temperature, made to 1 M TBP and then boiled for 24 hr with 2 M nitric acid was as stable as Amsco pretreated with 100 and 105% sulfuric acid at room temperature or with 95.6% acid at elevated temperatures. This treatment makes use of the fact that sulfuric acid will partition nitroparaffins away from the bulk Amsco. (Such scrubbing is not practical on the 1 M TBP solution containing nitroparaffin, for the TBP also distributes to the sulfuric acid.)

The limit to cleanup suggested by the data of Fig. 11 is apparently real. Amsco was recovered from the 24-hr degraded 1 M TBP solutions by extracting the TBP and nitroparaffin with concentrated sulfuric acid. The recovered Amsco was again made 1 M in fresh TBP and subjected to an additional 24-hr degradation with 2 M nitric acid, and subsequent testing again gave a hafnium extraction coefficient of  $\sim 0.15$ . Repetition of the cycle four additional times produced the same amount of extractants during each 24-hr degradation. Apparently after the initial treatments to remove or deactivate the sites susceptible to easy nitration, the bulk of the Amsco degraded at a consistently low rate. The final rate of degradation is close to that of n-dodecane (Table 1).

This behavior also has significance with respect to the distillation method of cleanup, for such treatment could constitute not only "cleanup" but gradual "purification" of the Amsco diluent. Thus, Amsco which has been degraded and distilled several times should be much less susceptible to degradation than the original stock.

#### Comparison of Diluents

Many diluents now in use have structures as complicated as Amsco 125-82 (and apparently less stable), so it is difficult to compare data between various operating sites. Further, different lots of the same diluent frequently have different compositions. The trend toward use of simple, relatively pure, more stable, normal hydrocarbons, e.g., n-dodecane, is encouraging, as is the effort of the petroleum industry to supply these at more reasonable prices.

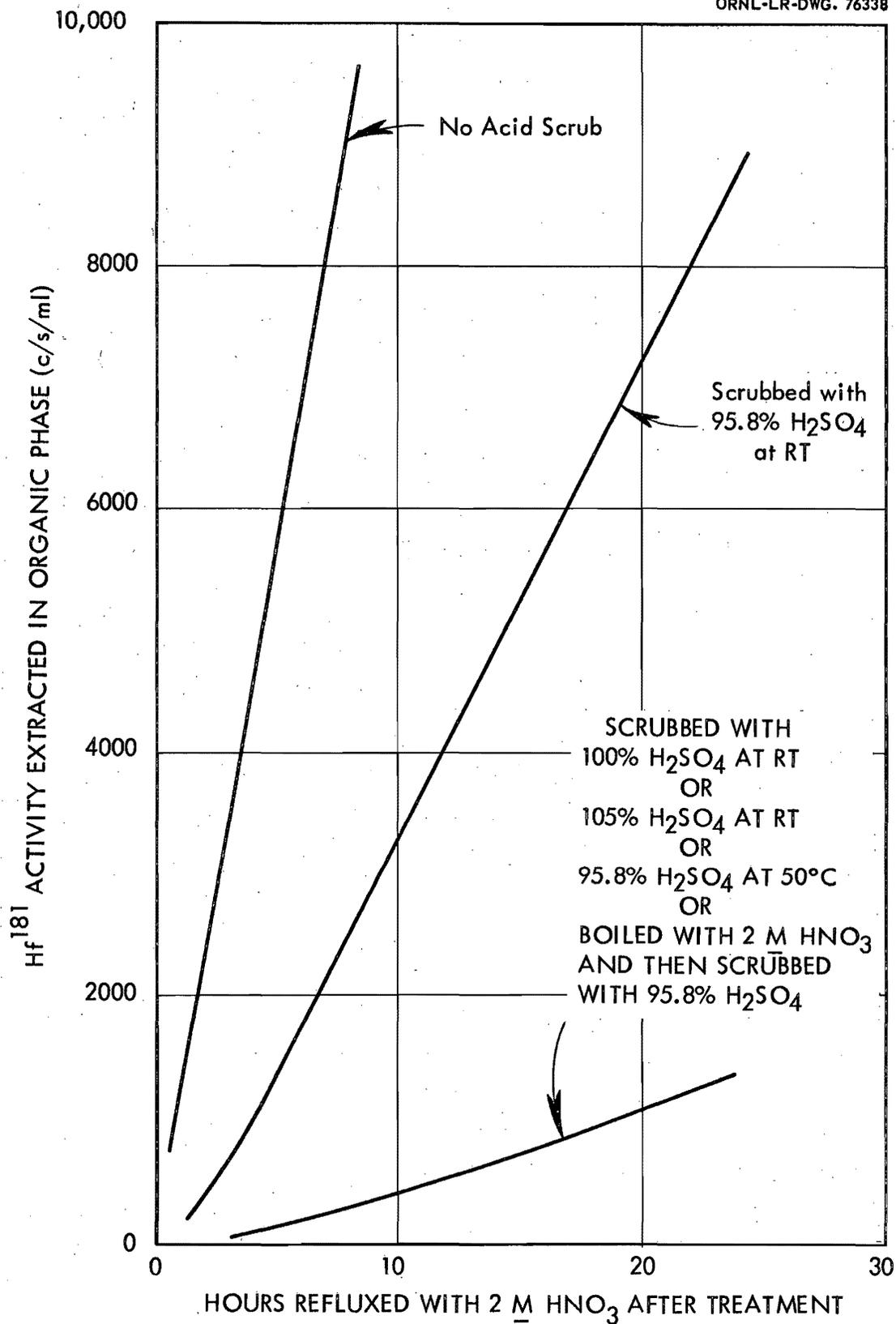


Fig. 11. Purification of Amsco 125-82 by Treatment with Sulfuric Acid.

A program of systematic testing of alternative diluents is in progress at Oak Ridge National Laboratory. Both aliphatic and aromatic compounds have been examined. Aromatic diluents increase the solubility of metal-aromatic extraction reagent complexes (for example uranium and thorium di-*sec*-butyl phenylphosphonate), increase the extraction ability of reagents such as TBP, impart greater radiation stability to the extracting reagent, and improve the ability of reagents such as TBP to separate uranium from fission products. Nitric acid attacks the aromatic diluents at points along the aliphatic side chain and, under some conditions, at points on the benzene ring itself. As with the aliphatic diluents, the calcium hydroxide, used in evaluating degradation, reacts only with those nitro groups which can enolize. Thus, nitro groups on the ring should not form calcium salts nor lead to fission product extraction. Tests with pure compounds confirmed this assumption. Consequently, "stability" of the aromatics as it is used in this paper refers to the formation of primary and secondary nitro groups on the alkyl side chains, not to nitration on the benzene ring itself.

Table 1 shows the performance of a number of diluents after degrading a solution 1 M in TBP for 4 hr in boiling nitric acid. All the simple aliphatic hydrocarbons tested were more stable than untreated Amsco 125-82, but the sulfuric-acid-scrubbed Amsco was of comparable stability. The stability of the aromatic diluents tested varied widely with structure. Benzene, the various methylbenzenes, the monoalkylbenzenes, 1,3-diethylbenzene, and triethylbenzene usually had stabilities comparable to that of *n*-dodecane. Stability of alkylbenzenes with two side chains apparently depended upon the particular isomer or purity, e.g., 1,3-diethylbenzene is much more stable than its two other isomers, and the commercial mixture of diisopropyl benzenes (~70% *meta* isomer) was very unstable. Benzenes with single but cyclic side chains (tetrahydronaphthalene and cyclohexylbenzene) were also unstable. The indication that iso-branching in monoalkylbenzenes may be favorable needs further substantiation. Triisopropylbenzene was very unstable.

The commercial mixture of diethylbenzene (Table 1) is being used for separation of thorium from uranium in the ORNL fuel recycle pilot plant (Fig. 4). An aromatic diluent was required to achieve adequate solubility of metal complexes of di-*sec*-butyl phenylphosphonate in the solvent phase and the commercial mixture with a flash point

Table 1. Performance of Degraded Diluents

Diluent	Flash Point (Closed Cup) °F	Zr-Nb <sup>95</sup> $\gamma$ (c/s/ml) (Calcium Test)**
<u>ALKYL BENZENES</u>		
1,2,4-Trimethyl (pseudocumene)	125	100
1,2,3,4-Tetramethyl (prehnitene)	163*	200
Ethyl	59	500
1,2-Diethyl	138*	4000
1,3-Diethyl		100
1,4-Diethyl		>6000
Diethyl benzene (mixture)		4000
Triethyl (mixture)		140
Propyl	86	80:450
Isopropyl (cumene)	102	30:4000
Diisopropyl (mixture)	170	>6000
Triisopropyl (mixture)		>6000
n-Butyl	160*	125
sec-Butyl	126	130
tert-Butyl	140*	120
iso-Butyl		45
Tetralin	171	decomposes
1-Methyl-4-isopropyl (paracymene)	138	4000
n-Hexyl	210	120
Cyclohexyl		>6000
n-Nonyl		180
Dodecyl (branched)		220
Solvesso-100	118	>6000
Solvesso-150	150	>6000
<u>ALIPHATIC HYDROCARBONS</u>		
Amsco 125-82	128	4000
Amsco 125-82 (H <sub>2</sub> SO <sub>4</sub> scrubbed)	128	100
n-Decane	115	1000
2,2,5-Trimethylhexane		80
n-Dodecane	165	125
n-Hexadecane		140

\* Open cup.

\*\* Calcium test: (1) Boil, under reflux, 1 M TBP solution with equal volume 2 M HNO<sub>3</sub>.  
 (2) Scrub twice with equal volume of 0.2 M aqueous Na<sub>2</sub>CO<sub>3</sub>.  
 (3) Contact 30 min with solid calcium hydroxide, ~50 g solid/liter.  
 (4) Contact with Zr-Nb<sup>95</sup> tracer solution in 2 M HNO<sub>3</sub>, 10<sup>4</sup> c/s/ml  $\gamma$ .

of 140°F was available from Dow Chemical Company at \$1.40/gallon. A diluent with high chemical and radiation stability is not required in this particular case. Where higher stability is required, a diluent comparable to pure meta-diethylbenzene would be selected.

An acceptable general-use aromatic diluent, comparable to n-dodecane in the aliphatic series, has not been commercially available, and, in fact, testing beyond that shown in Table 1 has not progressed to a stage which would justify specification of one particular structure. In further studies of aromatic diluents, continued consideration is being given to flash point, metal-salt solubility properties, separation factors, nitration of the side chains and of the aromatic ring itself during nitric acid attack in and out of a radiation field, and any of these features which relate to safety of operation.

The improvement in uranium extraction with TBP which results when aromatic rather than aliphatic diluents are used is shown in Table 2. A potential for greater uranium purification is also indicated (hafnium is here used to typify Zr-Nb fission product).

Aromatic diluents also impart greater radiation stability to TBP (Table 3).

Table 2. Effect of Diluent Type on Uranium Extraction and Decontamination

Diluent	1 M TBP Extraction Coefficients, $E_a^o$		Calculated Separation Factor $SF = E_U/E_{Hf}$
	Uranium	Hafnium	
Amsco 125-82	50	0.12	400
n-Dodecane	40	0.12	350
Diethylbenzenes	65	0.07	950
Trimethylbenzene (1,2,3)	65	0.09	700
n-Butylbenzene	60	0.09	650
Solvesso-100	55	0.08	700

2 M  $HNO_3$  initially, with 0.08 g U(VI)/l or  $10^4$  c sec<sup>-1</sup> ml<sup>-1</sup> Hf<sup>181</sup>.  
Equal volumes aqueous and organic phases.

Table 3. Radiation Degradation of Three Extraction Systems Under "Ideal" and "Process" Conditions  
 1 M Solutions of Extractant in Diluent\*  
 ( $\text{Co}^{60}$  Gamma and/or 1-Mev Electron Radiation)

	TBP in Amsco 125-82	TBP in Solvesso-100	DSBPP in Solvesso-100
Dry System G (-Extractant)	0.8 - 1.	0.3	0.2 - 0.6
H <sub>2</sub> O Sat'd System G (-Extractant)	0.8 - 1.	0.3	0.2 - 0.3
Equilib. with 1 M HNO <sub>3</sub>			
G (-Extractant)	0.6 - 1.3 <sup>a</sup>		0.2 - 0.8
G (-HNO <sub>3</sub> )	3.5 - 5.6		1 - 3
G (Organic Acid) <sup>b</sup>	0.75 <sup>b</sup>	0.3	0.2
Equilib. with 3 M HNO <sub>3</sub>			
G (-Extractant)	1.7 - 5.5		
G (-HNO <sub>3</sub> )	6 - 20		

\* Dose Rates: 2 to 200 watts/liter.  
 Dose Densities: 10 to 400 watt-hr/liter.  
 Generally the higher value in a range of G values (molecules/100 ev) was observed at the lower dose densities.

<sup>a</sup> 1-Mev electrons. Organic and aqueous phases not in contact during irradiation.

<sup>b</sup>  $\text{Co}^{60}$   $\gamma$  radiation. Organic and aqueous phases in contact during irradiation.

## RADIATION STABILITY OF EXTRACTANTS

It is not the purpose of this paper to review the large literature on radiation degradation of extractants, but we would like to summarize some of the work performed at Oak Ridge National Laboratory<sup>22,23</sup> and at the Stanford Research Institute<sup>24</sup> during the past several years, particularly concerning the effects of process constituents, such as nitric acid, and the nature of the diluent. First (Table 3), nitric acid in TBP-Amsco solutions can increase the G value of TBP decomposition (determined from organic acid formation) by several-fold, depending on the acid concentration. The acid itself extensively decomposed,  $G(-\text{HNO}_3)$  values ranging up to 20 molecules per 100 ev. Second, if an aromatic rather than paraffinic diluent is used, the stability of TBP is increased by a factor of 2 to 3. In fact, the aromatic diluent renders TBP nearly as resistant to radiation degradation as is di-sec-butyl phenylphosphonate (DSBPP), which is one of the most radiation-stable extractants known.

Available data are not adequate for a quantitatively mechanistic interpretation of the radiolysis process, but some qualitative conclusions may be drawn. Nitric acid decomposition in these organic solutions is larger than that in aqueous solutions,<sup>25</sup> which for 1 and 3 M  $\text{HNO}_3$  correspond to  $G(-\text{HNO}_3)$  of 0.34 and 1.02, respectively. In aqueous solution considerable recombination of the primary products  $\text{OH} + \text{NO}_2$  or  $\text{HNO}_2 + 1/2 \text{O}_2$  may occur. If recombination is much less important in TBP solutions, then the result is greater acid decomposition and more reaction of acid decomposition products with TBP and diluent.

Qualitatively the low G value for decomposition of TBP in an aromatic diluent (Solvesso-100) as contrasted with its value in the naphtha Amsco 125-82 is explained by the frequently mentioned stabilizing, or "energy sink," action of the benzene ring. The fact that DSBPP is not appreciably more stable in an aromatic diluent than in an aliphatic implies that there is a maximum effectiveness to the sink action of the benzene structure and that the phenyl group of DSBPP is adequate to provide maximum stability to the extractant.

Attempts were also made to study the radiolysis products of solutions of TBP-Amsco- $\text{H}_2\text{O}-\text{HNO}_3-\text{UO}_2(\text{NO}_3)_2$ . Unfortunately, the analytical difficulties were not completely resolved.

## MECHANISMS OF EXTRACTION

Although solvent extraction is the most widely used chemical process in the atomic energy field, many of the basic mechanisms involved are not completely understood. Work is now proceeding at many installations not only to define the effect of solvent structure on extraction but to develop true thermodynamic interpretations of the systems. This should permit prediction of optimum solvents and conditions.

One phase of more basic studies of the mechanisms of extraction being pursued at Oak Ridge National Laboratory involves the development of mathematical equations to describe the extraction of nitrates, such as nitric acid and uranyl nitrate, by TBP-diluent solutions. Both existing and new data are being used to obtain a more exact description of the thermodynamic properties of the aqueous and organic phases.

New data<sup>26-28</sup> are being obtained as follows:

1. From measurements of the partial pressures of TBP, H<sub>2</sub>O, and HNO<sub>3</sub> over solutions containing combinations of TBP, H<sub>2</sub>O, HNO<sub>3</sub>, and UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>.
2. Calculation of activities of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> for the mixed system using the measured partial pressures of TBP, H<sub>2</sub>O, and HNO<sub>3</sub>.
3. From extraction experiments to obtain activity coefficient ratios and thermodynamic equilibrium constants.

The extraction data do not provide values of individual activity coefficients or thermodynamic constants. Instead, they provide values of combinations of these quantities. In the case of extraction by TBP-Amsco solutions of HNO<sub>3</sub> from aqueous solution,<sup>26</sup> the term  $K_1^C y_T / y_{TN}$  is obtained (Fig. 12), where  $K_1^C$  is the thermodynamic equilibrium constant for extraction of nitric acid by TBP,  $y_T$  and  $y_{TN}$  are activity coefficients of "free" TBP and the complex TBP·HNO<sub>3</sub>, respectively. Measurements of the vapor pressure of anhydrous TBP, of water saturated TBP, and of TBP over TBP-H<sub>2</sub>O-HNO<sub>3</sub> two-phase systems were performed to obtain the quantity  $y_T$ . Results of the vapor pressure measurements, from which  $y_T$  was obtained, are shown in Fig. 13 in terms of activities of TBP, H<sub>2</sub>O, and HNO<sub>3</sub> versus the loading of the organic phase. Thus, from the combination of extraction and vapor pressure experiments, the quantity  $K_1^C / y_{TN}^W$ , where  $y_{TN}^W$  is the activity coefficient of TBP·HNO<sub>3</sub> infinitely dilute in water-saturated TBP, was obtained.  $K_1^C / y_{TN}^W$  has a numerical value of 1.754 (std. dev.

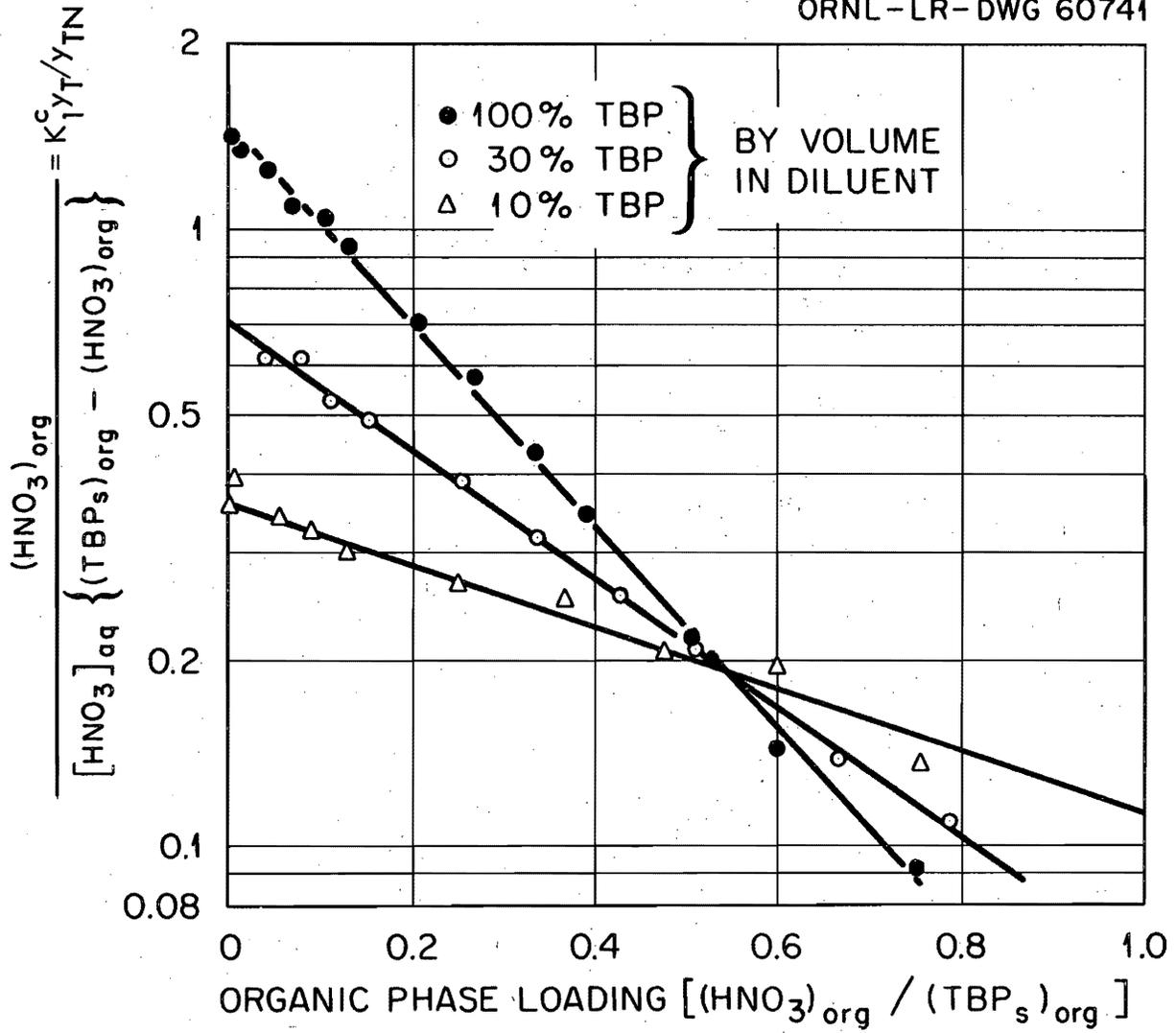
UNCLASSIFIED  
ORNL-LR-DWG 60741

Fig. 12. Correlation of HNO<sub>3</sub> Extraction into TBP-Amsco 125-82 Solutions with Organic Phase Loading.

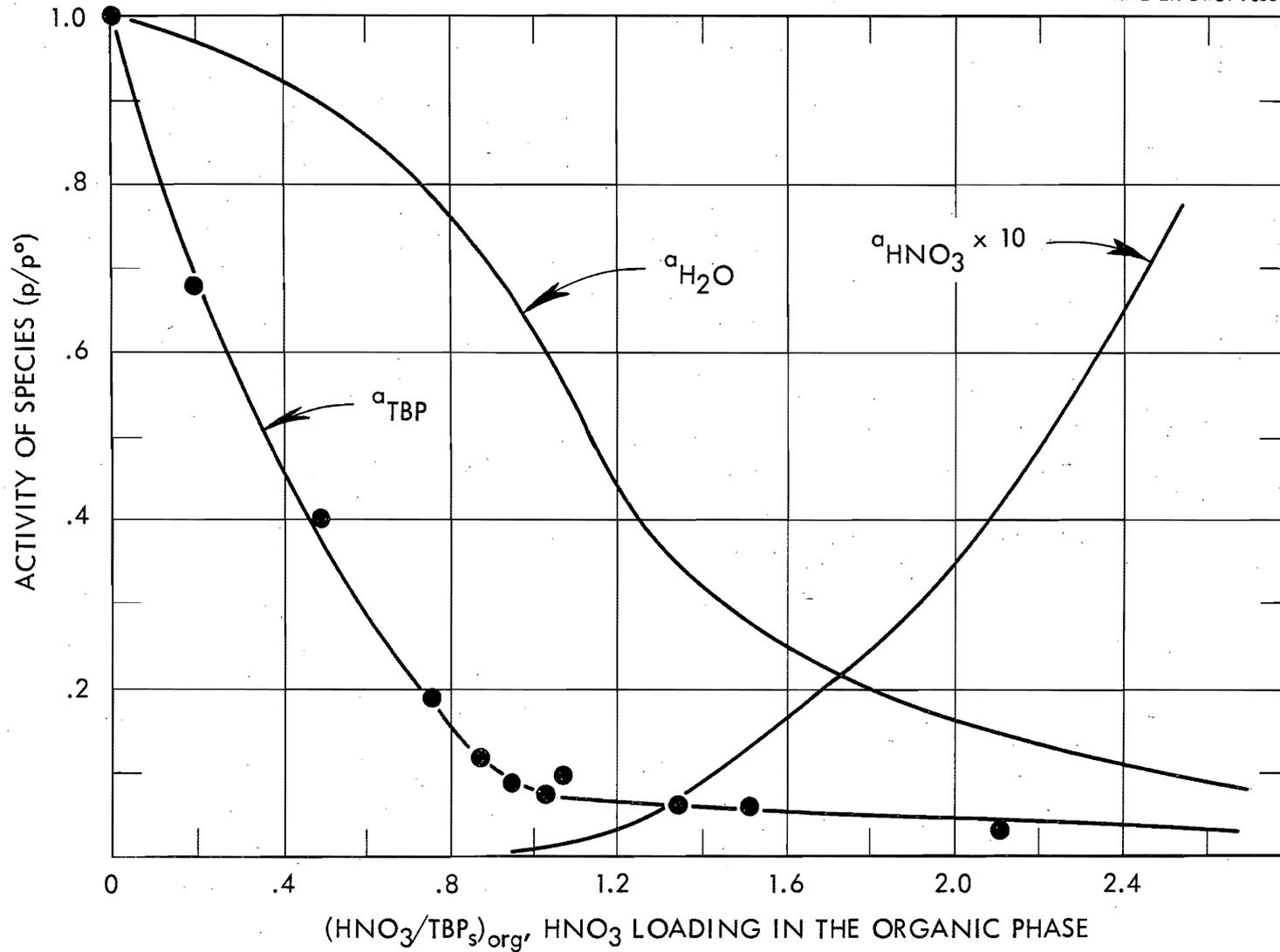


Fig. 13. Activities of TBP, HNO<sub>3</sub>, and H<sub>2</sub>O Over the Two Phase System. Water Saturated TBP is Taken as the Standard State for TBP.

of 0.086). We do not yet know  $y_{\text{TN}}^{\text{W}}$ , and hence  $K_1^{\text{C}}$ , since  $y_{\text{TN}}^{\text{W}}$  refers to a water-saturated system, and we cannot assign it a value of 1 since the reference state is  $y_{\text{TN}}^{\text{O}} = 1$  for TBP·HNO<sub>3</sub> infinitely dilute in anhydrous TBP.

The vapor pressure approach to activities of solutes is also being used with solutions of H<sub>2</sub>O-HNO<sub>3</sub>-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>. As a result of our finding that the experimental activity of water over this three component solution is equal to the product of water activities over the two 2-component solutions (H<sub>2</sub>O-HNO<sub>3</sub> and H<sub>2</sub>O-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>), the integrated Gibbs-Duhem equation provides not only the variation of nitric acid activity with uranyl nitrate concentration but also the variation of uranyl nitrate activity with nitric acid concentration.

In addition to using vapor pressure measurements to obtain activities of volatile species in the more complex solutions, this technique was used<sup>27</sup> to obtain partial pressures of nitric acid over its aqueous solutions (Fig. 14). By combining these new data with literature data,<sup>29-31</sup> new values of the activity coefficients and of some of the other thermodynamic properties of this acid were obtained. Although the results of this study provide numbers that differ from those of McKay<sup>32</sup> (because McKay used activity coefficients from the Landolt-Bornstein tables), they provide an excellent confirmation of his mathematical model.

Other work directed towards obtaining a mathematical description of the extraction of nitric acid and uranyl nitrate from aqueous nitrate solutions by TBP-diluent solutions involves use of available data and the assumption that activity coefficients in the aqueous phase can be described by an extended Debye-Huckel equation. By this technique, and by means of a high speed computer, Lietzke and Stoughton<sup>33</sup> derived thermodynamic equilibrium constants for nitric acid and uranyl nitrate extraction. An example of the results is shown in Fig. 15 for extraction of uranyl nitrate from an ammonium-nitrate-salted aqueous phase by 5.4% TBP in Amsco 125-82. It should be noted that the method of Lietzke and Stoughton also provides estimates of aqueous-phase activity coefficients of those species that are extractable into the organic phase. Thus, while differing in detail, this use of extraction data to obtain aqueous-phase activity coefficients is similar to that of Jenkins and McKay.<sup>34</sup> Both methods are capable of yielding more accurate aqueous-phase activity coefficients when more complete chemical analyses of the organic phase are used.

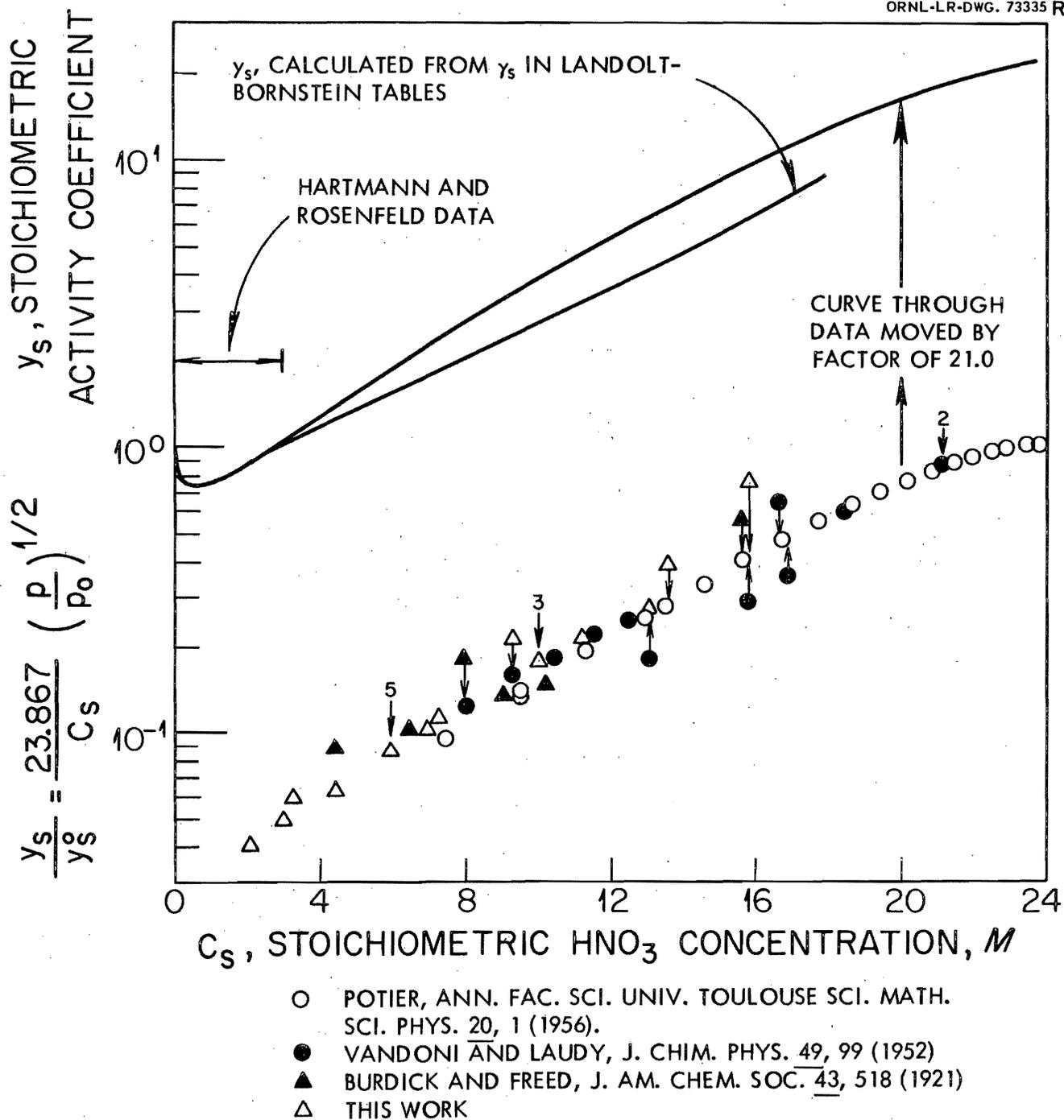


Fig. 14. Nitric Acid Activity Coefficients at 25°C.

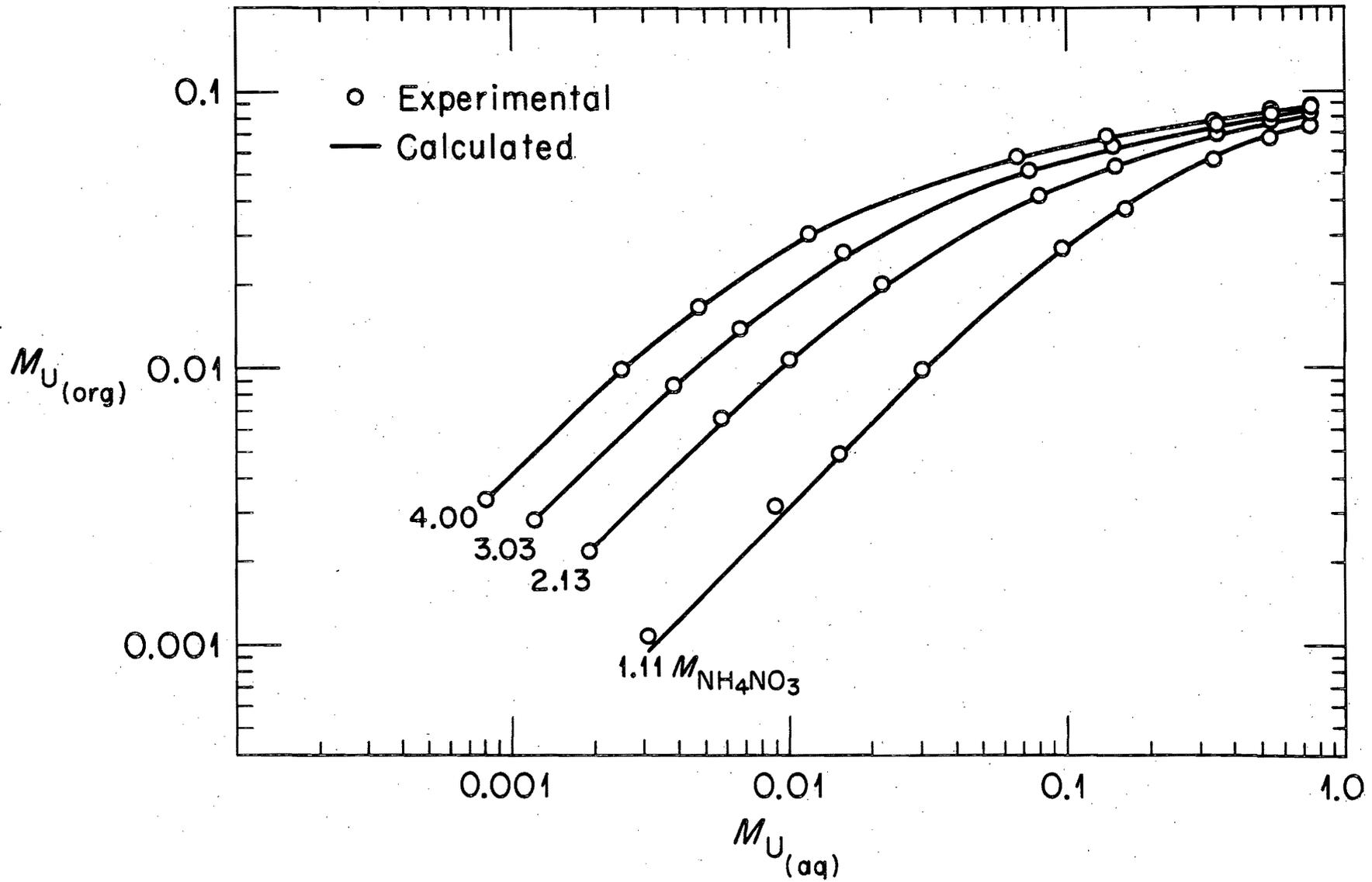


Fig. 15. Extraction of Uranium from  $\text{NH}_4\text{NO}_3$  with 5.4% TBP.

Additional work has been done to describe the combining ratio of TBP with thorium for aqueous solutions containing 0.5, 1.0, or 2.0 M Al(NO<sub>3</sub>)<sub>3</sub>, and 6 M NaNO<sub>3</sub> and 0.1 N HNO<sub>3</sub> and organic solutions containing 0.2 to 16% TBP in n-dodecane. Duplicate experiments using thorium-234 tracer in one series and 0.002 M Th-232 in the other are in close agreement. The combining ratio, N, of TBP to thorium was calculated by means of the equation

$$\log \left( \frac{DC_1}{DC_2} \right) = N \log \left( \frac{TBP_1}{TBP_2} \right),$$

which is applicable because the thorium concentration in the aqueous phase was so low that its activity coefficients in aqueous and organic phases changed but slightly during the extraction while the amount of nitric acid plus thorium nitrate extracted was so small as to leave the concentration and activity coefficient of TBP nearly unchanged<sup>26</sup> (Fig. 16). At less than 1% TBP the calculated combining ratio scattered between 2.5 and 4.0 with an average value of 3.15. This is close to the value of 3.0 as determined by Peppard<sup>35</sup> and Siddall<sup>36</sup> but does not agree with the ratio of 2.0 as determined by Hesford.<sup>37</sup> At higher TBP concentrations, the activity coefficients do not cancel, and the apparent combining ratio decreases to 2.5 for the 8-16% TBP range. The combining ratio obtained by extrapolation of the ratios calculated from TBP concentrations greater than 1% indicate a value of approximately 4.0, in agreement with Gresky.<sup>38</sup> This value would be in agreement with a coordination number of 8 as indicated by the work of Stoughton, Fry, and Barney.<sup>39</sup>

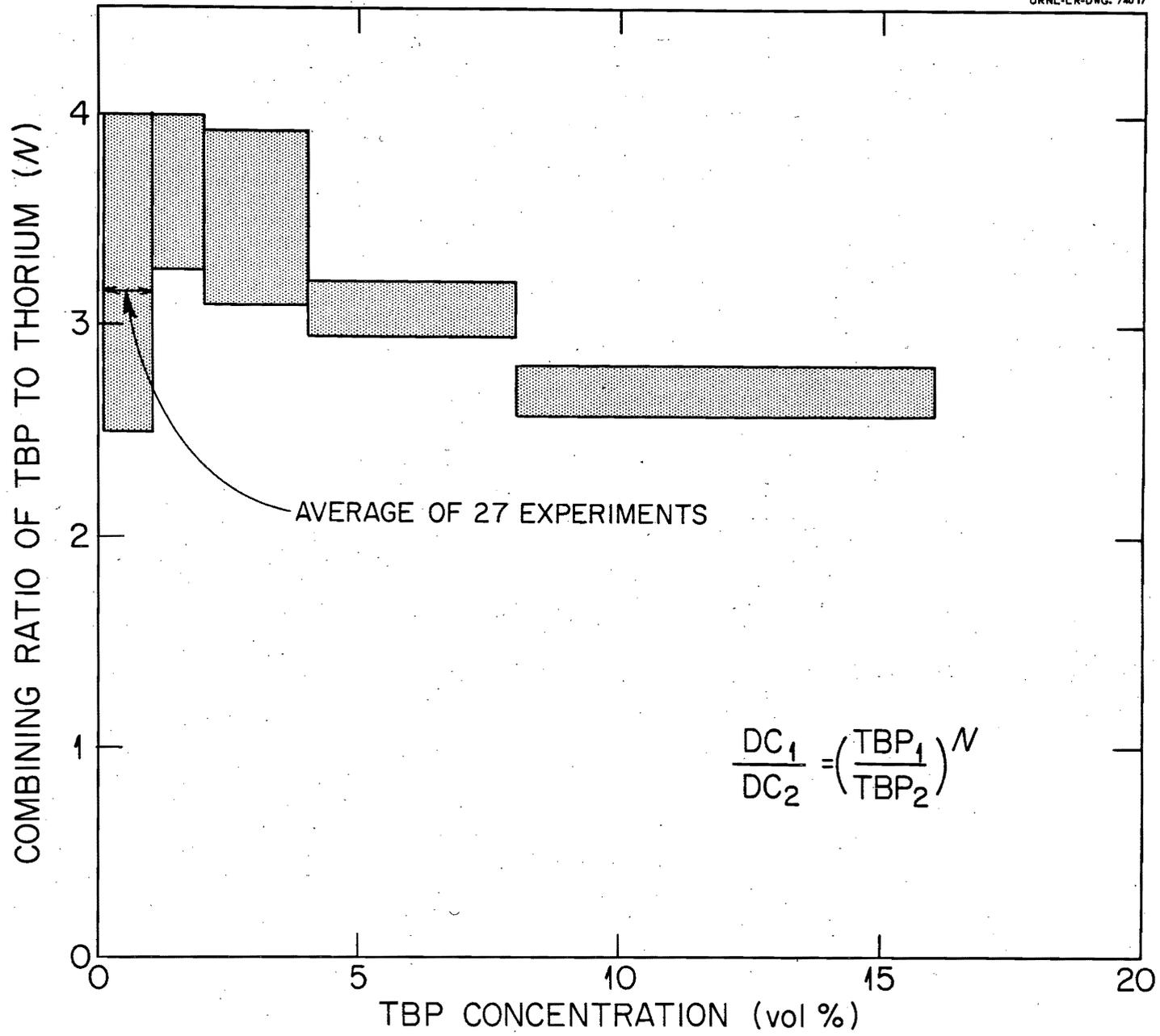


Fig. 16. Combining Ratio of  $Th(NO_3)_4$  and TBP in n-dodecane (TBP conc., 0-17 vol %).

## REFERENCES

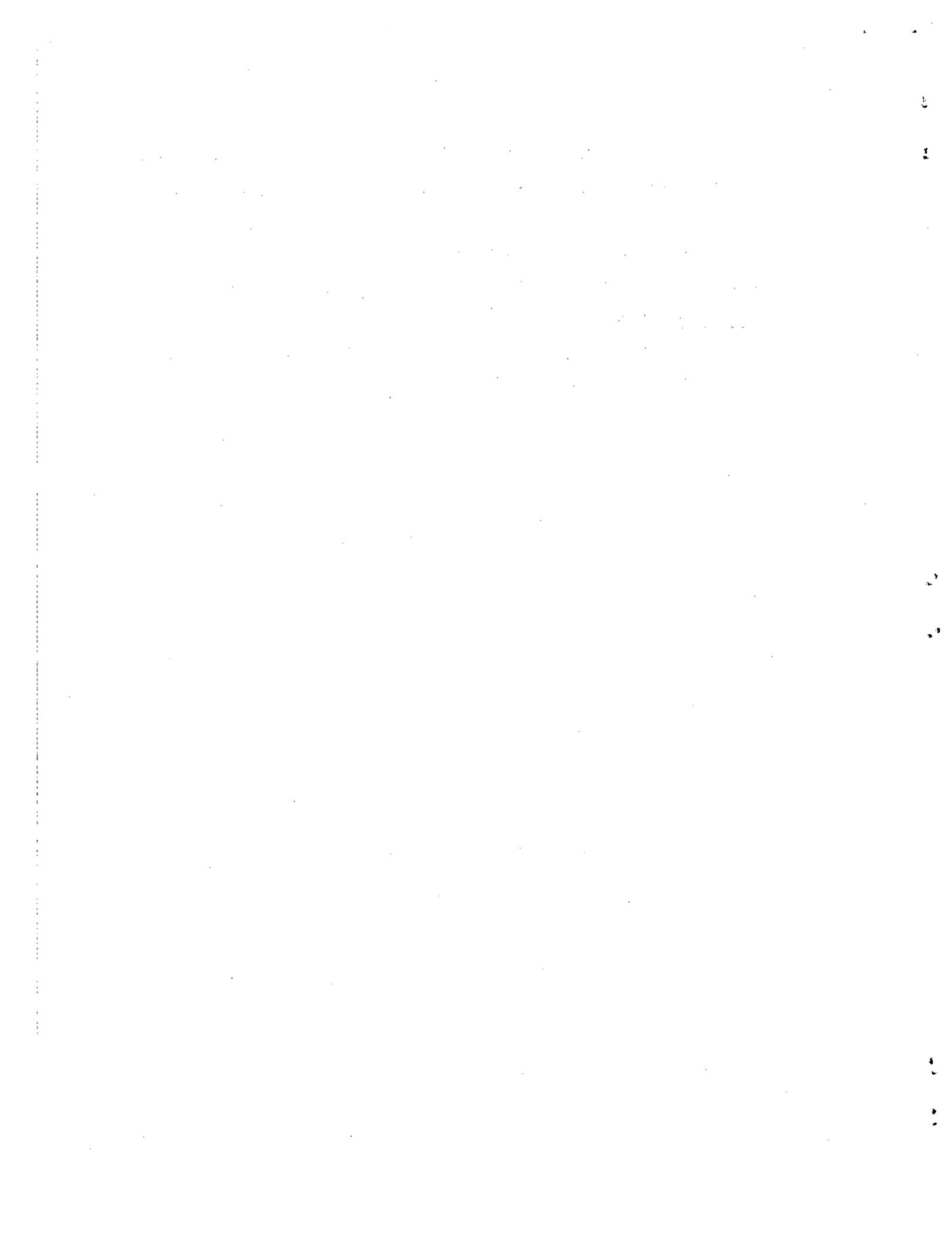
1. J. R. Flanary et al., Chemical Development of 25-TBP Process, ORNL-1993 (April 1957) Revised, Deleted.
2. A. T. Gresky, Progress Report, Laboratory Development of the Thorex Process, ORNL-1367 (1952) Classified. Summarized in Reactor Handbook, Vol. II Fuel Reprocessing, p 211, Interscience, New York, 1961.
3. A. T. Gresky, "Solvent Extraction Separation of U-233 and Thorium from Fission Products by Means of Tributyl Phosphate," Proc. 2nd Internat'l Conf. Peaceful Uses of Atomic Energy, Vol. 9, p 505 (1956).
4. A. D. Ryon, "Solvent Extraction Studies" in Chemical Technology Division Unit Operations Section Monthly Progress Report, ORNL-CF-60-10-49, p 33 (1960).
5. C. D. Watson, et al., "Mechanical Processing of Spent Power Reactor Fuel at Oak Ridge National Laboratory," pp 307-400 in Chemical Processing of Irradiated Fuels, TID-7583 (1959).
6. R. H. Rainey and J. G. Moore, "Acid Interim-23 Process," in Chemical Technology Division Monthly Progress Report for Chemical Development Section B, July 1959, ORNL-CF-59-10-113, p 28 (1959).
7. R. H. Rainey and J. G. Moore, "Laboratory Development of the Acid Thorex Process for Recovery of Thorium Reactor Fuel," Nucl. Sci. and Eng. Vol. 10, No. 4, pp 367-371 (1961), U. S. Patent 3,049,400.
8. D. E. Ferguson, E. D. Arnold, W. S. Ernst, and O. C. Dean, Preparation and Fabrication of ThO<sub>2</sub> Fuels, ORNL-3225 (1962).
9. R. M. Rush, J. S. Johnson and K. A. Kraus, "Hydrolysis of Uranium VI: Ultracentrifugation and Acidity Measurements in Chloride Solutions," Inorganic Chemistry, Vol. 1, 378-383 (1962).
10. Solvent Extraction Chemistry Symposium, Session 7, Solvent Degradation and Clean-up, Gatlinburg, Tennessee, October 23-26, 1962. Sponsored by Oak Ridge National Laboratory. The papers in this session summarized U. S. and U. K. studies, contained complete references to earlier work, and are to be published in Nucl. Sci. and Eng. The papers were: (a) D. A. Orth and T. W. Olcott, "Purex Process Performance vs Solvent Exposure and Treatment," E. I. Du Pont de Nemours and Company, Savannah River Plant, Aiken, South Carolina; (b) H. T. Hahn and E. M.

Vanderwall, "Tributyl Phosphate Decomposition Product Behavior in Postextraction Operations," Phillips Petroleum Company, Idaho Falls, Idaho; (c) E. S. Lane, "Performance and Degradation of Diluents for TBP and the Cleanup of Degraded Solvents," United Kingdom Atomic Energy Authority, Harwell, Great Britain; (d) C. A. Blake, Jr., W. Davis, Jr., and J. M. Schmitt, "Extraction Behavior of Degraded TBP-Amsco Solutions and Alternative Extractant-Diluent Systems," Oak Ridge National Laboratory, Oak Ridge, Tennessee; (e) A. J. Huggard and B. F. Warner, "Studies at Windscale on the Extent and Causes of TBP Solvent Degradation and Methods for Solvent Cleanup," United Kingdom Atomic Energy Authority, Windscale, Great Britain.

11. P. J. P. Chastagner, Evaluation of Adakane 12 for Purex Use, DP-601 (October 1961).
12. Reference 10, paper (d).
13. Reference 10, papers (c) and (e).
14. R. H. Rainey, J. G. Moore, Solvent Recovery: Filtration with Filter Paper and Fritted Glass Filters, ORNL-CF-59-10-113 (Jan. 14, 1960).
15. R. H. Ellerhorst, Studies of the Behavior of the TBP-Kerosene Solvent in Uranium Refining: Recovery of Discarded Refinery Solvent, NLCO-714 (Jan. 17, 1958).
16. T. H. Siddall III, and H. Pollock, Decontamination and Purification of Degraded Purex Solvent, DP-290 (May 1958).
17. G. L. Richardson, Purex Solvent Washing with Basic Potassium Permanganate, HW-50379 (May 29, 1957).
18. C. A. Blake, J. M. Schmitt, W. E. Oxendine, Extraction Performance and Cleanup of Degraded Process Extractants: TBP-Amsco 125-82 Cleanup with Alkanolamines and Other Scrubbing Agents, ORNL-TM-265, p 47 (Aug. 10, 1962).
19. E. S. Lane, Degraded TBP-Kerosene Cleanup Using the Alkanolamines and Related Compounds, AERE-M-809, Harwell (January 1961).
20. J. A. Knight, Radiation Chemistry of Organic Substances, Final Report, Subcontract between Engineering Experiment Station, Georgia Institute of Technology, Atlanta and Oak Ridge National Laboratory (Jan. 31, 1959).
21. W. Davis, Jr., Radiation Densities and TBP Radiolysis During Thorex Short Decay Runs, ORNL-2764 (Aug. 6, 1959).

22. C. A. Blake, Jr., A. T. Gresky, J. M. Schmitt, and R. G. Mansfield, Comparison Dialkyl Phenylphosphonates with Tri-n-Butyl Phosphate in Nitrate Systems: Extraction Properties, Stability and Effect of Diluent on the Recovery of Uranium and Thorium from Spent Fuels, ORNL-3374 (Jan. 8, 1963).
23. K. B. Brown, et al., Chemical Technology Division Chemical Development Section C Monthly Progress Report for November 1959, ORNL-CF-59-11-132 (Jan. 12, 1960).
24. E. M. Kinderman and A. H. Samuel, Radiation Stability of Organic Liquid, Final Summary Report, Stanford Research Institute, SRIA-101 (Feb. 15, 1963).
25. H. A. Mahlman, J. Chem. Phys. 35, 936 (1961).
26. W. Davis, Jr., Thermodynamics of Extraction of Nitric Acid by Tri-n-Butyl Phosphate-Hydrocarbon Diluent Solutions. I. Distribution Studies with TBP in Amsco 125-82 at Intermediate and Low Acidities. Nucl. Sci. and Eng. 14, 159 (1962). II. Densities, Molar Volumes, and Water Solubilities of TBP-Amsco 125-82-HNO<sub>3</sub>-H<sub>2</sub>O Solutions, Nucl. Sci. and Eng. 14, 169 (1962). III. Comparison of Literature Data, Nucl. Sci. and Eng. 14, 174 (1962).
27. W. Davis, Jr. and H. J. de Bruin, New Activity Coefficients of 0-100% Aqueous Nitric Acid Based on a Relation Between Two Thermodynamic Standard States, (in press).
28. W. Davis, Jr. and P. S. Lawson, Vapor Pressures of Tri-n-Butyl Phosphate over Tri-n-Butyl Phosphate-Nitric Acid-Water Solutions, (in press).
29. A. Potier, Ann. Fac. Sci. Univ. Toulouse Sci. Math. Sci. Phys. 20, 1 (1956).
30. M. R. Vandoni and M. Laudy, J. Chimie Physique: 49, 99 (1952).
31. C. L. Burdick and E. S. Freed, J. Am. Chem. Soc.: 43, 518 (1921).
32. H.A.C. McKay, Trans. Faraday Soc.: 52, 1568 (1956).
33. M. H. Lietzke and R. W. Stoughton, "A Mathematical Model for the Solvent Extraction of Uranyl Nitrate and Nitric Acid," Nucl. Sci. and Eng., (in press).
34. I. L. Jenkins and H.A.C. McKay, Trans. Faraday Soc.: 50, 107 (1954).
35. D. F. Peppard, G. W. Mason and J. L. Maier, "Interrelationships in the Solvent Extraction Behavior of Scandium, Thorium and Zirconium in Certain Tributyl Phosphate-Mineral Acid Systems," J. Inorg. Nucl. Chem. 3, 223-4 (1956).
36. T. H. Siddall III, "Solvent Extraction Processes Based on Tri-n-butyl Phosphate," in Chemical Processing of Reactor Fuels, Academic Press (1961).

37. E. Hesford, H.A.C. McKay and D. Scargill, "Tri-n-Butyl Phosphate as an Extracting Solvent for Inorganic Nitrates - IV Thorium Nitrate," J. Inorg. Nucl. Chem., 4:321 (1957).
38. A. T. Gresky, "Solvent Extraction Separation of U-233 and Thorium from Fission Products by Means of Tributyl Phosphate," Proc. 2nd Internat'l Conf. Peaceful Uses of Atomic Energy, Vol. 9, p 505 (1956).
39. R. W. Stoughton, A. J. Fry, and J. E. Barney, II, "A Study of Thorium-Iodate Complexing in Aqueous Solutions," J. Inorg. Nucl. Chem., Vol. 19, pp 286-297 (1961).



## DISTRIBUTION

- 1-150. R.O.R. Brooks, Scientific Secretary,  
Eurochemic Co., Mol, Belgium
- 151. C. A. Blake, Jr.
- 152-153. R. E. Blanco
- 154. J. C. Bresee
- 155. R. E. Brooksbank
- 156. K. B. Brown
- 157. F. L. Culler
- 158. W. Davis, Jr.
- 159. D. E. Ferguson
- 160. H. E. Goeller
- 161. A. T. Gresky
- 162-163. E. J. Murphy
- 164. R. H. Rainey
- 165. J. W. Ullmann
- 166. M. E. Whatley
- 167. E. L. Anderson, AEC, Wash.
- 168-169. C. R. Library, Doc. Ref. Sec.
- 170. Y-12 Technical Library, Doc. Ref. Sec.
- 171. Laboratory Records
- 172. Laboratory Records (RC)
- 173-187. DTIE
- 188. Division of Research and Development, ORO

