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THE LABORATORY DEVELOPMENT OF A CONTINUOUS SOLVENT EXTRACTION PROCESS FOR THE RECOVERY OF U^{235}

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THE LABORATORY DEVELOPMENT OF A CONTINUOUS SOLVENT EXTRACTION PROCESS FOR THE RECOVERY OF U^{235}

F. R. Bruce

Experimental Work By:

W. H. Baldwin
R. E. Blanco
F. R. Bruce
A. DeHaan
C. V. Ellison
D. E. Ferguson
A. T. Gresky
W. A. Horne
W. B. Lanham
R. E. Leuze
L. E. Morse
D. C. Overholt
M. R. Poston
T. C. Runion
J. E. Savolainen

DATE ISSUED

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Union Carbide and Carbon Corporation
Post Office Box P
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1.0 Abstract

This report describes the laboratory development of a continuous solvent extraction process for the separation of enriched uranium from fission products. The need for such a chemical process arises from the proposed operation of the Materials Testing Reactor which employs U-235 as fuel.

NOTE: In this report hexone refers to methyl isobutyl ketone produced by Shell, unless otherwise indicated.

2.0 Introduction

The operation of nuclear reactors requires an attendant chemical process for the separation of fissionable material from associated, neutron absorbing fission products. Such a chemical process has been developed at Oak Ridge National Laboratory for the recovery of the U-235 which is to be employed as fuel in the Materials Testing Reactor[1].

The requirements of this chemical process are that uranium recovery be at least 99.9% and that fission products be decontaminated by a factor of 10^8. However, the removal of fission products by a factor of 10^5 is sufficient to permit further purification of the uranium behind light shielding in laboratory equipment and this degree of separation has been the minimum requirement in the development of a remotely controlled process.

A number of batch processes were previously conceived for the separation of reactor fuels from fission products[2] [3] [4]. In these processes, repeated application of solvent extraction; scavenging, by-product precipitations; and product precipitation ultimately yielded a product which was sufficiently purged from fission products. The number of steps required, however, was always large and product losses were high, necessitating uranium recovery operations on a large number of waste solutions. In the interest of obtaining a simplified process,

Introduction (continued)

which would give high yields and adequate decontamination, the development of a continuous solvent extraction recovery scheme was undertaken.

In the process which has been chosen, the irradiated fuel rods, in the form of an aluminum - U-235 alloy, are dissolved in nitric acid containing mercury catalyst. The solution is then filtered and the feed solution containing U-235, fission products, and aluminum nitrate salting agent enter a packed tower at a point near the middle and flow countercurrently to an organic solvent which is introduced at the bottom of the tower. In this section, uranium transfers to the organic phase while the bulk of the fission products remains in the aqueous stream. In the top section of the column, the hexone phase containing uranium and some fission products, flows countercurrently to a fresh aluminum nitrate solution. Additional fission products are removed from the solvent phase in this stage. The organic phase then flows to a second tower where the uranium is removed by equilibration of the solvent with a dilute nitric acid solution. This solution is next salted with aluminum nitrate and put through a second extraction cycle.

Such a scheme for separating the heavy metals from fission products underwent extensive development and demonstration in the Redox process

Introduction (continued)

at Argonne National Laboratories, where hexone was found to be a satisfactory solvent. Although batch data which were obtained at Oak Ridge National Laboratory indicated the choice of dibutyl cellosolve as solvent, it was decided that the major effort should be devoted to utilizing hexone since this solvent had been proved.

In addition to the establishment of a high neutron flux, the Materials Testing Reactor offers a unique source of heretofore relatively unavailable transuranics Np^{237}, Pu^{238}, and Pu^{241}. The recovery and decontamination of these materials is also desired; with the provision, however, that they be obtained with little additional expense and with no sacrifice in process effectiveness.

Throughout this report the term distribution ratio is employed to indicate the ratio of the concentration of extractable material in solvent phase to that in the aqueous phase.

3.0 Summary

A continuous solvent extraction process has been developed for the recovery and decontamination of the U-235 which is employed as fuel in the Materials Testing Reactor. The process consists of the following steps: dissolution of the U-235-aluminum alloy in nitric acid; filtration of the solution to remove solid foreign matter; and finally, effecting the separation of uranium from aluminum and fission products by continuous solvent extraction, using hexone as solvent.

The optimum conditions for obtaining the maximum separation of uranium from fission products were found to be hexone extraction from a 0.2 M acid deficient solution and the employment of sufficiently strong aluminum nitrate (1.6 M) in the feed to permit column operation with equal volumes of aqueous and extractant solutions. A dilute solution of aluminum nitrate (1.0 M), one-fourth the volume of the feed solution, was found most effective for scrubbing. Dilute nitric acid (0.05 M) satisfactorily stripped the uranium from the solvent. Neptunium and plutonium are associated with the fission products in the waste stream.

The second solvent extraction cycle is similar to the first except that ferrous sulfamate (0.05 M) is included.

Laboratory batch tests of this process, employing irradiated U-235 as starting material, indicated a decontamination factor of 5×10^5 for

Summary (continued)

gamma activity on a level about 10% of that anticipated in the final process.

On pilot plant scale verification runs, this process separated uranium from gross gamma emitting fission products by a factor of 1.5×10^6 in two solvent extraction cycles. A uranium loss of 0.1% in filtration and 0.01% in the solvent extraction cycles was obtained.

A batch extraction process employing di-isopropyl ether as solvent was used for final product concentration and isolation. This reduced the concentration of residual fission products to an undetectably low level. Only barely detectable traces of other contaminants were associated with the product.

4.0 Solvent Chemistry

Hexone and dibutyl cellosolve are the two solvents which have been investigated most thoroughly for the solvent extraction recovery of U-235. Methyl isobutyl ketone, commonly called hexone, is an organic solvent with a boiling point of 116.8°C at 760 mm. pressure and has a density of 0.8017 gms./cm^3. It is soluble to the extent of 1.9% by volume in water. Dibutyl cellosolve, ethylene glycol dibutyl ether, has a boiling point of 203°C at 760 mm. and a density of 0.838 gms./cm^3. Water dissolves 0.2% dibutyl cellosolve by volume.

Solvent Chemistry (continued)

Hexone was originally used as a solvent in Redox development work at Argonne National Laboratory and exhibited good operating characteristics and adequate decontaminating ability in fission product separations. Early in the development work at Oak Ridge National Laboratory, it was found that dibutyl cellosolve was inherently capable of accomplishing higher separations of uranium from fission products than was hexone. However, laboratory investigations which were conducted in small, packed columns disclosed the fact that emulsion formation and cruds were often associated with the utilization of this solvent. The height of packed section equivalent to a theoretical stage in the dibutyl cellosolve system also proved to be substantially greater than that in the hexone system. Hexone was readily available and inexpensive, was not unusually hazardous and toxic, and was stable with respect to radiation. For these reasons, and because hexone operability had been proved and the decontamination obtainable with it appeared adequate, the decision was made to concentrate development work on the hexone system. In the light of experience which has been gained in the use of larger packing in solvent extraction processes, it now appears that the dibutyl cellosolve system could be made operable. The advantages of employing this solvent rather than hexone, however, are envisioned as being slight, if existent

Solvent Chemistry (continued)

at all, and it is the present belief that hexone is the preferred material for achieving the separation of uranium from fission products.

Both hexone and dibutyl cellosolve are obtainable as commercial products and their purity, as obtained from the vendor, is often questionable. The presence of oxidizable substances, materials which influence the distribution ratios of uranium and fission products in extraction, methods for treating new solvent and recovering used material, and the reactions of solvent with nitric acid are questions which bear on the utilization of the material in a process. A more complete description of hexone chemistry investigations at ORNL is given in separate reports(5) (6).

4.1 Hexone

4.11 Effect of Impurities on Yield and Decontamination

Mesityl oxide, methyl isobutyl carbinol, and an aromatic, possibly mesitylene, were found to be the most detrimental impurities which are present in commerical hexone. Table 4.1-1 summarizes data on the purity of commercial hexone. All of these materials in concentrations as high as 2% had a negligible effect on the distribution ratios of either macro or micro concentrations of uranium. The effect of these contaminants on the fission product distribution ratio was investigated

Effect of Impurities on Yield and Decontamination (continued)

in two systems: one containing aluminum nitrate, nitric acid, water and hexone; the other containing the above reagents plus sodium dichromate. In a system containing no sodium dichromate, the presence of as much as 1% mesityl oxide, methyl isobutyl carbinol or mesitylene did not increase the extraction of radio cerium, radio zirconium, and gross beta activity. In the presence of sodium dichromate, these materials increased markedly the extraction of cerium and zirconium. Organic acids, possibly present because of hexone decomposition, lowered gross beta decontamination by a factor of about two. It is not believed, however, that organic acids in sufficient concentration to cause such an effect occur in either virgin hexone or in hexone which has been used and recovered.

4.12 Hexone Pretreatment

Since it was found that impurities which are capable of effecting the efficiency of solvent extraction processes occur in new and used solvent, the need arose for a method of removing these materials. Also, from time to time, various agents were added to the process to aid in accomplishing either specific yield or decontamination objectives. These materials included: hydrazine and its reaction products with hexone,

Hexone Pretreatment (continued)

2-hexyl pyridine, and di-phenyl thiourea. Thus, solvent treatment has three problems: (1) the removal of naturally occurring impurities, (2) the removal of fission product activity which is associated with used solvent, and (3) the elimination of solvent soluble process additives.

The impurities which occur in new hexone are all mild reducing agents and may be destroyed by agitating the hexone with an oxidizing aqueous phase. This procedure consists of the following steps: (1) stirring the hexone in contact with a 1/10 volume of 1 M $Na_2Cr_2O_7$-1 M HNO_3 solution for two hours; (2) separating the phases; (3) stirring 30 minutes with a 1/10 volume of 0.5 M NaOH; (4) separating the phases; (5) steam distillation of the hexone from a 0.5 M NaOH heel. This pretreatment accomplishes three objectives: (1) it removes reducing substances, (2) it removes acids, and (3) it improves the color of the hexone. This procedure is also adequate for removing fission product contamination from hexone which has been employed in an extraction process. It was not proved that so extensive a treatment is necessary when a virgin solvent is to be used in a process not employing an oxidized feed. It is believed, however, that a more consistent, higher quality solvent is obtained for experimental purposes by pretreating before use.

Hexone Pretreatment (continued)

The separation of hexone from its ketazine, a reaction product of hexone and hydrazine, may be accomplished by either of two methods: washing with two 1/2 volume passes of 0.5 M $K_2Cr_2O_7$-0.5 M HNO_3 followed by a water wash; or by washing with two 1/2 volume passes of 6 N H_2SO_4, followed by a water wash. In the latter method a white precipitate forms.

Hexone containing 2% by volume of 2-hexyl pyridine may be purified by washing with two 1/10 volume passes of 8 M nitric acid. The solvent is then washed with two 1/10 volume passes of water and finally distilled from a 0.5 M sodium hydroxide heel. A simple steam distillation does not effectively separate 2-hexyl pyridine from hexone.

Di-phenyl thiourea is a hexone soluble complexing agent for ruthenium. Both diphenyl thiourea and ruthenium activity may be removed from hexone by a steam distillation followed by a 1 M $Na_2Cr_2O_7$-1 M HNO_3 wash and a water wash. At this point, the hexone contains a slight coloring which is removed by subsequent steam distillation.

4.13 Analytical

The principle criterion of hexone purity is its reducing normality, since the presence of either methyl isobutyl carbinol or mesityl oxide is reflected in this value. The reducing normality of

Analytical (continued)

hexone may be determined in the following manner: (1) adding 5 ml of 0.1 N potassium dichromate to a 20 ml aliquot of solvent; (2) adding 25 ml of 5 N nitric acid; (3) shaking for 15 seconds and allowing to stand 5 minutes; (4) adding 15 ml of sulfuric acid and one drop of ferroin indicator; and (5) titrating to the reddish-orange end point with 0.1 N ferrous ammonium sulfate solution.

4.14 Reaction of Hexone with HNO_3

In order to operate a continuous extraction column under conditions where there is no transfer of nitric acid, it is frequently necessary to acidify the organic phase. When appreciably high nitric acid concentrations are required in the hexone phase, there is a possibility of an uncontrollable reaction ensuing.

It was found that hexone as much as 12 N in nitric acid did not explode at room temperatures. Heating resulted, however, in the copious evolution of nitrogen oxides and the residue ignited when dryness was reached. For each nitric acid concentration in hexone, there was a minimum temperature at which a visible reaction characterized by boiling and the evolution of brown fumes was observed. This temperature was, in general, inversely proportional to the nitric acid normality (Table 4.1-2).

4.15 Radiation Stability of Hexone

The radiation stability of hexone was investigated under the high acid, Argonne National Laboratory Redox flowsheet conditions and full Hanford fission product radiation level[7]. These chemical conditions specified higher concentrations of uranium and nitric acid than those of the proposed 25 process. The radiation levels, on a volume basis, are approximately equivalent in the two processes. The conditions of this test were undoubtedly more condusive to solvent decomposition than those of the proposed 25 recovery process because of the high concentrations of nitric acid and uranium employed. Therefore, it is felt that the data which were obtained present a more pessimistic picture of hexone decomposition by radiation than will prevail under the proposed low nitric acid conditions of the 25 process.

The radiation stability of hexone was studied by equilibrating organic solvent with an aqueous phase containing full Hanford radiation level. The contact time of the two phases was varied and the distribution ratios prevailing in these steps was employed as a criterion of solvent decomposition. Since gas evolution may influence the mechanical operability of a continuous solvent extraction process, this aspect of the problem was also investigated.

Radiation Stability of Hexone (continued)

The investigation proved that hexone, exposed to W chemical conditions and radiation levels for more than 50 times longer than the contact anticipated in the proposed 25 Process, did not exhibit any change in extractive properties for uranium and fission products in extraction, scrubbing and stripping steps.

Under Redox chemical conditions and radiation levels, no gas was evolved from hexone decomposition during an induction period of about 70 hours, or 430 times the contact anticipated in the 25 Process. On further exposure, gas was evolved, reaching a constant maximum rate after a total of 120 hours exposure, or 720 times longer than the anticipated plant contact time. This maximum gas evolution rate was about 0.02 ml/sec/curie of beta radiation absorbed in the hexone. Since the induction times necessary for gas evolution to occur were so much longer than the anticipated plant contact times, it is concluded that gas evolution will not present a problem in the 25 Process. Furthermore, it is felt that even after a long induction period has elapsed, the amount of gas evolving is not sufficient to impair the operation of a continuous extraction process.

4.2 Dibutyl Cellosolve

The reducing normality of dibutyl cellosolve, as obtained from the manufacturer, was found to be higher than that of hexone. Several methods, outlined in Table 4.2-1, decreased the reducing normality of 0.028 N, as received, to about 0.003 N. The principle impurities in dibutyl cellosolve were tentatively identified as ethylene glycol monomethyl ether and ethyl glycol mono-n-butyl ether.

The effect of these materials on the dibutyl cellosolve extraction of uranium was negligible. Their effect on fission product extraction is not known.

The reaction of dibutyl cellosolve with nitric acid was qualitatively similar to that of hexone, except for the fact that oxalic acid was produced in appreciable quantities when 70% nitric acid and dibutyl cellosolve were mixed. On adding an equal volume of 70% nitric acid to cellosolve at room temperature and allowing the mixture to stand several hours, a reaction occurred which yielded 20% or more of oxalic acid crystals. The minimum reaction temperatures of mixtures of dibutyl cellosolve and nitric acid are summarized in Table 4.2-2.

4.3 Tertiary Alcohols

A homologous series of tertiary alcohols was investigated as extractants for uranium in separations involving ruthenium activity[8].

Tertiary Alcohols (continued)

It was found that the solubility of both uranium and ruthenium acitvity in the organic phase decreased as the length of the normal chain increased. The alcohols studied may be arranged as follows, in order of decreasing effectiveness in ability to achieve the separation of uranium from ruthenium activity: 2-methyl 2-pentanol, 2-methyl 2-heptanol, 2-methyl 2-hexanol, tertiary amyl alcohol (Table 4.3-1). However, none of the alcohols showed as good selectivity in the extraction of uranium from ruthenium activity as either hexone or dibutyl cellosolve. On the basis of these results, the use of tertiary alcohols as extractants for uranium did not appear promising.

5.0 The Chemistry of Specific Elements

5.1 Neptunium

Neptunium with the mass assignment 237 will be formed in the proposed pile by the following reaction:

$$U^{235}\ (n,\gamma)\ U^{236}\ (n,\gamma)\ U^{237} \xrightarrow[6.8\ d]{\beta^-} Np^{237}$$

It is estimated that the yearly production of Np^{237} at steady state will be about 37 grams. This isotope is an alpha emitter with a half life of 2.25×10^6 years. Because of its relative nuclear stability, Np^{237} is of considerable interest for studies of the transuranics.

Neptunium (continued)

Neptunium exhibits valence states of 3, 4, 5, and 6. In general, its chemistry is similar to that of uranium, but it has a tendency towards greater stability of the lower valence states, particularly the pentavalent. Hexavalent neptunium is soluble in certain organic solvents and an attempt was made to utilize this property as a basis for a recovery process. The oxidation of neptunium by dichromate ion may be represented by the following equation:

$$6\ NpO_2^{+} + 14\ H^{+} + Cr_2O_7^{=} \rightleftarrows 6\ NpO_2^{++} + 2\ Cr^{+++} + 7\ H_2O$$

This shows that the fraction of oxidized neptunium is markedly dependent on the hydrogen ion concentration. Early work indicated the desirability of operating a process under low acidity to obtain the optimum separation of uranium from fission products. At that time, it appeared that neptunium could not be effectively oxidized with $Cr_2O_7^{=}$ and the major recovery effort was subsequently devoted to a separations scheme based on the complexing of Np^{IV}. It should be emphasized that the oxidation of neptunium in an acid deficient system is not considered hopeless, but rather that recovery of this material was not believed sufficiently important to justify the expenditure of a major development effort. On the other hand, enough was known about the complexing action of neptunium to make a process based on this effect appear

Neptunium (continued)

immediately feasible. Should the reclaiming of neptunium be emphasized in the future, it is felt that the possibility of employing an ozidized system should be reinvestigated.

5.11 Preparation of Neptunium Tracer

In all of the work to be described, Np^{239} formed by an (n,γ) reaction from U^{238} was employed. Fission product activity in the pile irradiated uranium was minimized by utilizing uranium peroxide which was depleted in U^{235} to the extent of 1 part of U^{235} to 1250 parts of U^{238}. Irradiation and cooling times of about 16 hours each were found to provide satisfactory yields of Np^{239} having little short lived contamination. After the cooling period elapsed, the sample was dissolved in nitric acid and a neptunium separation effected. Two processes were employed for the preparation of neptunium tracer: one based on precipitation of lanthanum fluoride, alternately from oxidized and reduced solutions; and the other on hexone extraction of alternately reduced and complexed systems containing aluminum nitrate salting agent.

The former method for preparing neptunium tracer was based on the fact that tetravalent neptunium carried on lanthanum fluoride, while hexavalent neptunium did not carry. After the dissolution of neutron

Preparation of Neptunium Tracer (continued)

irradiated uranium peroxide in nitric acid, the solution was oxidized with sodium dichromate and three lanthanum fluoride scavenging precipitations made. These steps removed chiefly rare earth activities. The neptunium was next reduced with hydroxylamine hydrochloride and carried on lanthanum fluoride. This step served to separate neptunium from uranium.

If the presence of macro amounts of fluoride ion were objectionable in subsequent operations, the lanthanum fluoride was metathesized with sodium hydroxide and the neptunium found associated with the lanthanum hydroxide precipitate.

A solvent extraction method was adopted in preference to that previously described in order to obtain greater operational simplicity in the preparation of tracer. After dissolution of uranium peroxide in nitric acid, neptunium was reduced by adding urea and ferrous ion to the solution. After a thirty minute reduction period at room temperature, the solution was made 1.2 M in aluminum nitrate and the pH adjusted to 0.3. Uranium and solvent extractable fission products were subsequently removed by equilibrating the solution twice with equal volume passes of hexone. The aqueous phase, containing neptunium, was next made 0.1 M in hydrazine and digested for thirty minutes at 80°C. An equal volume extraction was then made with hexone which was 0.1 M in

Preparation of Neptunium Tracer (continued)

hydrazine nitrate. Finally, the neptunium was stripped from the hexone with water. Although this method yielded a product of satisfactory radiochemical purity, uranium removal was incomplete, even when as many as five hexone extractions of the uncomplexed solution were made. For the purposes for which this tracer was employed, however, the presence of uranium was not objectionable.

5.12 Variables Affecting the Neptunium Distribution Coefficient in Extraction Utilizing Hydrazine

It has been found that the extraction of heavy metals by organic solvents is markedly dependent on the concentration of nitrate ion in the solvent and that the nitrate salts of hexone soluble bases may be added to the solvent to enhance the extraction of neptunium. Hydrazine, which forms mono and dinitrates, both preferentially soluble in the hexone phase, is such a material. Thus, it became possible to base neptunium recovery on the extraction of the complexed, reduced state and at the same time, take advantage of the lower hexone solubility of the reduced states of fission products. The distribution ratio of neptunium in the system hexone-aluminum nitrate-ferrous ammonium sulfate-hydrazine-water was effected by the following variables: nitric acid concentration, hydrazine concentration, equilibration time, and the

Variables Affecting the Neptunium Distribution Coefficient in Extraction Utilizing Hydrazine (continued)

digestion time of the hydrazine-hexone phase before use.

The distribution ratio of neptunium in hexone extractions employing hydrazine was independent of pH in the range between 0.1 and 0.9 pH units. At pH's greater than 0.9, however, the neptunium distribution ratio fell off rapidly, until, at a pH of 1.2, it was only one-ninetieth that observed at a pH of 0.9. In 1.0 M aluminum nitrate containing 0.05 M ferrous ammonium sulfate and 0.5 M hydrazine, a neptunium distribution ratio of 28 was obtained at a pH of 0.9 in equal volume extraction with hexone (Figure 5.1-1).

Increasing the total hydrazine concentration in a solution containing 1.0 M aluminum nitrate and 0.05 M ferrous ammonium sulfate, enhanced the distribution ratio of neptunium in hexone extraction. On increasing the hydrazine concentration from 0.043 M to 0.43 M, the neptunium distribution ratio was increased from 7.7×10^{-2} to 11. In the same system containing ferrous ion, but no hydrazine, a neptunium distribution ratio of 1.7×10^{-2} was observed (Table 5.1-1).

Increasing the agitation time of the aqueous and organic phases increased the neptunium distribution ratio in hexone extraction from aluminum nitrate solutions containing hydrazine. In general, extending

Variables Affecting the Neptunium Distribution Coefficient in Extraction Utilizing Hydrazine (continued)

the agitation time from 2.5 minutes to 5 minutes approximately doubled the neptunium distribution ratio (Table 5.1-2).

When hydrazine was added to hexone, and the digestion time before use varied, it was observed that the neptunium distribution ratio in subsequent extraction increased with increasing hydrazine-hexone digestion times. Although the magnitude of this variation was slight, it nevertheless indicated the desirability of allowing the hexone to stand for at least an hour after hydrazine addition before use. For example, hexone which was allowed to digest for 15 minutes after hydrazine addition gave a neptunium ditribution ratio of 88 on extraction while solvent which was digested for 1 hour yielded a neptunium distribution ratio of 103 (Table 5.1-3).

5.13 Oxidation of Neptunium

Preliminary data indicated that dichromate ion would not oxidize neptunium to the solvent soluble, hexavalent state in solutions of low acidity because of the high pH dependence of the $Cr_2O_7^{=}$ - Cr^{+3} couple. The oxidation potential of BrO_3^-, on the other hand, should be sufficiently negative to effect the oxidation of NpO_2^+ to NpO_2^{++} at the proposed acidities. An attempt was made to utilize this reagent.

Oxidation of Neptunium (continued)

In 1.3 M aluminum nitrate containing 0.1 M potassium bromate, the neptunium distribution ratio in hexone extraction fell to less than unity at a pH between 0.6 and 1.0, and at a pH between 0.4 and 0.6, the distribution ratio became less than that of uranium in the same system. At pH's below 0.4, however, the neptunium distribution ratio was greater than that of uranium under the same conditions (Table 5.1-4). These data are interpreted as being indicative of incomplete neptunium oxidation, probably because of the short oxidation time, at room temperature, which was employed.

5.2 Ruthenium

Two ruthenium isotopes, Ru^{103} and Ru^{106}, result from the fission of U^{235}. Ru^{103} has a 43 day half life and 0.3 Mev beta and 0.55 Mev gamma radiations. Ru^{106} has a 1 year half life and a 3.6 Mev beta radiation stemming from its 30 second rhodium daughter. Ruthenium activity constitutes 4-5% of the gross beta radiation in irradiated uranium which has cooled 3-6 months.

In its solution chemistry, ruthenium is known to occur in all valence states from zero to eight. However, in acid solutions such as those attendant to a uranium separation process, the 3, 4, and 8 valence states are the only stable ones. It might reasonably be felt

Ruthenium (continued)

that the octavalent state would not be stable at all in the presence of an organic solvent such as hexone. While this is undoubtedly true in the case of macro quantities of ruthenium tetroxide, too little is known at present about the behavior of trace amounts of ruthenium to rule out the presence of this state in process solutions containing an oxidizing agent.

Ruthenium is obtained commercially as a mixture of the tri and tetravalent chlorides. In hydrochloric acid solution, chlorine oxidizes the material to ruthenium tetrachloride, while iodide, hydroxylamine, hydrazine and sulfites reduce it to ruthenium trichloride. Treatment of either Ru^{+3} or Ru^{+4} with strong oxidizing agents such as perchloric acid, sodium bismuthate and potassium permanganate yields volatile ruthenium tetroxide which may be collected in cold water, alkaline solution, or a mixture of peroxide and nitric acid. In acid solution ruthenium tetroxide decomposes to give a mixture of Ru^{+3} and Ru^{+4}. In addition to the multiple valence states which ruthenium exhibits, its chemistry is further complicated by the fact that the element forms a great number of complexes with common anions and the behavior of particular valence states is undoubtedly influenced by complex formation in the solutions with which we are concerned.

5.21 Observations on the Behavior of Ruthenium in Hexone Extraction

Ruthenium proved to be one of the most difficult fission products to separate from uranium by a continuous solvent extraction process. At the end of a single solvent extraction cycle, under acid conditions, ruthenium activity comprised between 70 and 98% of the gross beta activity remaining with the product. When reducing agents were present, the separation from ruthenium was more complete, and it then constituted from 40 to 70% of the gross beta activity associated with the product solution. The importance of ruthenium as a contaminant may be decreased by the inclusion of specific reagents aimed at the elimination of this element. However, the overall effectiveness of the acid deficient solvent extraction process which has been developed was sufficient to make such an expedient unnecessary.

The difficulty encountered in separating ruthenium from uranium results from the fact that once it has entered the solvent phase, it does not scrub out on equilibration with fresh aqueous phase. For example: an aqueous phase containing 1.3 M $Al(NO_3)_3$, 0.05 M $Fe(NH_2SO_3)_2$, 0.05 M nitric acid deficiency and ruthenium tracer was contacted with an equal volume of hexone. In this initial contact, a ruthenium distribution ratio of 0.040 was obtained. The organic extract was then contacted five times with equal volumes of fresh aqueous phase of the same

Observations on the Behavior of Ruthenium in Hexone Extraction (continued)

composition as the above feed, except that ruthenium tracer was absent. In these scrubbings, ruthenium distribution ratios of 0.65, 0.83, 1.5, 0.9, and 1.8 were observed. After the third scrubbing, the hexone phase was allowed to stand for fifty hours before the fourth and fifth contacts were made (Table 5.2-1). The results of this experiment, which are typical of the behavior of ruthenium in solvent extraction, indicate that on scrubbing a hexone phase, containing ruthenium, with fresh aqueous, the ruthenium activity shows increasing organic solubility as more scrubbing stages are added. Furthermore, there is evidence that the organic soluble form of ruthenium reverts to a more aqueous soluble form on long standing. The anamolous behavior of ruthenium is generally consistent with the assumption that either the material exists in multiple, irreversible chemical forms which fractionate on solvent extraction, or that it is partially present as a radiocolloid which does not exhibit normal behavior. Since the extraction characteristics of ruthenium in several other solvents resemble those shown in hexone, it must be assumed that this unusual behavior may not be explained in total by postulating a reaction between hexone, or its decomposition products, and ruthenium.

5.211 Proposed Explanation of Ruthenium Extraction

In order to explain the conduct of radio-ruthenium in solvent extraction, the Chemistry Division at Oak Ridge National Laboratory postulated the presence of four forms: Ru_A, Ru_B, Ru_C, and Ru_D, each acting in a characteristic manner(9). Colloidal properties of ruthenium appeared to play a prominent part in explaining the observed data on ruthenium extraction.

The proposed theory postulates that the distribution ratios of Ru_A, Ru_B, Ru_C, and Ru_D in hexone extraction are about 7.4, 0.05, 0.001, and 15, respectively. When ruthenium tetroxide is allowed to stand in dilute nitric acid for several days, it is believed that Ru_C is obtained. Ruthenium tetroxide decomposed in dilute nitric acid containing potassium permanganate forms Ru_D. Strong oxidation of Ru_C yields a material possessing the extraction properties of Ru_D: conversely, the strong reduction of Ru_D yields a form which resembles Ru_C. From this it was inferred that Ru_D represents a higher oxidation state than Ru_C. On either long standing in aluminum nitrate solutions containing nitric acid or by treatment with nitrous acid, Ru_C is converted to Ru_A or Ru_B. Ru_A and Ru_B, in turn, may be reverted to Ru_C by treatment with urea. Since urea reacts with nitrous acid according to the following reaction,

$$CO(NH_2)_2 + 2\ HNO_2 \longrightarrow 2\ N_2 + 3\ H_2O + CO_2$$

it was concluded that Ru_A and Ru_B are nitrosyl complexes of Ru_C.

Proposed Explanation of Ruthenium Extraction (continued)

Ru_C was tentatively identified as trivalent ruthenium and Ru_D as tetravalent ruthenium. By assuming ruthenium to be present in these four forms, it became possible to explain quite satisfactorily the solvent extraction of ruthenium. The original work on this subject assigned equilibrium constants and reaction half times for the various rutheniums present in both hexone and aqueous aluminum nitrate solutions.

5.212 Variables Affecting the Ruthenium Distribution Coefficient in Extraction and Scrubbing

The concentrations of aluminum nitrate and nitric acid were found to be important factors influencing the ruthenium distribution ratio in the extraction and scrubbing steps. Increasing the concentration of either of these materials enhanced the ruthenium distribution in favor of the organic phase. In general, changes in the concentration of nitric acid influenced the ruthenium distribution ratio more than changes in the concentration of aluminum nitrate.

Aqueous phases 0.2 M in nitric acid, 0.1 M in potassium dichromate and containing varying amounts of aluminum nitrate were contacted with hexone in batch equilibrations simulating the extraction step in a column process. The data show that the ruthenium distribution ratio varied from 0.17 when the aqueous phase was 0.5 M in aluminum nitrate

Variables Affecting the Ruthenium Distribution Coefficient in Extraction and Scrubbing (continued)

to 2.3 when the aluminum nitrate concentration was 2.0 M. When the aqueous phase contained no aluminum nitrate, a ruthenium distribution ratio of 0.078 was observed (Figure 5.2-1).

The ruthenium distribution ratio in scrubbing was studied by equilibrating hexone with an aluminum nitrate solution containing ruthenium tracer. This hexone was then used to study the effect of aluminum nitrate concentration on the scrubbing of ruthenium. Ruthenium distribution ratios varied from 0.068 when the extract was equilibrated with 0.5 M aluminum nitrate to 0.26 when 2.0 M aluminum nitrate was employed (Figure 5.2-1).

In batch extractions of aqueous phases containing 0.1 M $Na_2Cr_2O_7$, 1.2 M $Al(NO_3)_3$ and 8 grams of U/liter, increasing the nitric acid concentration from 0.2 M nitric acid deficient to 0.9 M increased the ruthenium distribution ratio from 1.5×10^{-3} to 660×10^{-3} (Figure 5.2-2). The importance of maintaining a low nitric acid concentration in order to obtain high ruthenium decontamination is clearly indicated.

Simulated scrubbing experiments employing 0.75 M aluminum nitrate and an organic extract containing ruthenium tracer showed a ruthenium distribution ratio of 0.49 at a nitric acid concentration of 2.0 molar.

Variables Affecting the Ruthenium Distribution Coefficient in Extraction and Scrubbing (continued)

When the acidity of the scrub solution was reduced to 0.3 molar, a distribution ratio of 0.43 for ruthenium acidity was observed. Employing a scrub solution that was 0.2 molar deficient in nitric acid lowered the ruthenium distribution ratio to 0.049 (Figure 5.2-2).

For further information on the solvent extraction behavior of ruthenium, see Section 6.3.

5.22 Ruthenium Complexing Agents

5.221 Diphenylthiourea

The use of s-diphenylthiourea to improve the separation of uranium from ruthenium was investigated by Chemistry Division at Oak Ridge National Laboratory[10].

Diphenylthiourea forms a stable complex with ruthenium. This complex is soluble in hexone and only very slightly soluble in aqueous solutions. Consequently, it was suggested that diphenylthiourea, in hexone solution, be added to the organic phase leaving the extraction column to form the ruthenium complex, thereby providing further decontamination of uranium from ruthenium in the stripping column. Diphenylthiourea does not form stable complexes with uranium, neptunium, columbium, or zirconium.

Diphenylthiourea (continued)

The time and temperature of reaction and the concentration of diphenylthiourea were found to be important factors in the formation of the ruthenium-diphenylthiourea complex. At a diphenylthiourea concentration of 10 grams per liter, the complex formation had a reaction half time of about 30 minutes at 25°C and a half time of about 1 minute at 60°C. Therefore, the satisfactory utilization of diphenylthiourea required heating the organic extract at 60°C for about 10 minutes before stripping. In the stripping step, a ruthenium distribution ratio of about 50 was obtained under simulated process conditions utilizing diphenylthiourea.

5.222 Thiourea

Thiourea is a reagent which is employed in the colorimetric determination of ruthenium. Since it is insoluble in hexone and soluble in aqueous aluminum nitrate solutions, it presented the possibility of rendering the ruthenium aqueous soluble and achieving enhanced decontamination of uranium from ruthenium in the extraction section of a continuous extraction column.

The utilization of thiourea was explored using ruthenium as tracer in the hexone extraction of a 1.3 M aluminum nitrate solution which was 0.05 M nitric acid deficient. Temperature and time of digestion

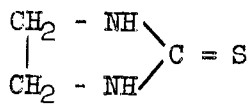
Thiourea (continued)

were found to be important factors in forming the thiourea-ruthenium complex. In 1.3 M aluminum nitrate at a pH of 1.85, a ruthenium distribution ratio of 3×10^{-2} was observed. A solution of 1.3 M aluminum nitrate at a pH of 0.1, containing 0.05 M thiourea and ruthenium tracer was digested for one hour at 85°C, the pH adjusted to 1.85 and the solution equilibrated with hexone. A ruthenium distribution ratio of 4×10^{-4} was obtained, indicating the presence of an aqueous soluble ruthenium-thiourea complex (Figure 5.2-3). Thiourea did not effect uranium extraction.

Although this work suggested that thiourea should be a valuable reagent for effecting the elimination of ruthenium, subsequent experimentation employing the solution of an irradiated slug as tracer exhibited both poor reproducibility in ruthenium decontamination and the occurrence of a precipitate on extraction. Scrubbing the hexone extract resulting from the equilibration of an aqueous phase containing thiourea showed that the material which extracted possessed a very high distribution ratio. It was, therefore, concluded that thiourea was not sufficiently promising to justify continuance of further development work (Table 5.2-2 and 5.2-3).

5.223 Ethylene Thiourea

Ethylene thiourea is a heterocyclic compound with the structure:



It is soluble in water to the extent of 2% at 30°C and 9% at 60°C and is insoluble in hexone. It was considered concurrently with thiourea as a means of aiding ruthenium decontamination. As in the case of thiourea, time and temperature of digestion of the aqueous phase containing ethylene thiourea were found to be important factors influencing the effectiveness of the reagent. Because of the limited solubility of ethylene thiourea, the concentration of the material was not investigated as a variable. Like thiourea, this material had no effect on uranium extraction.

In a 1.3 M aluminum nitrate solution at a pH of 1.85 and containing ruthenium tracer, a ruthenium distribution coefficient of $19.\times10^{-3}$ was obtained in hexone extraction. When this solution was made 0.1 M in ehtylene thiourea and digested for 1 hour at 55°C, a ruthenium distribution coefficient of 2.7×10^{-3} was obtained. Increasing the digestion temperature to 75°C lowered the ruthenium distribution coefficient to 1.0×10^{-3}. The results are summarized in Table 5.2-4. The use of ethylene thiourea was investigated in solutions containing sodium dichromate and similar results were obtained, although a darkening during the oxidation step indicated that a side reaction occurred.

Ethylene Thioruea (continued)

Ethylene thiourea was equally effective in complexing ruthenium in the solution of an irradiated uranium slug. Results for extraction and subsequent scrubbing steps are shown in Table 5.2-5.

While the preceeding data indicated considerable promise for ethylene thiourea as a aid for achieving ruthenium decontamination, it was not found operable. Laboratory extraction column runs employing ethylene thiourea showed poor reproducibility in ruthenium decontamination and, in many cases, the formation of white amorphous precipitates was observed. Although work on both thiourea and ethylene thiourea was abandoned, it is felt that they may be profitable fields for future investigation.

5.224 Sulfanilamide

The mechanism of ruthenium extraction previously proposed[9] postulates that hexone soluble ruthenium is present as a nitrosyl complex. The possibility of employing a hexone soluble material which reacts with nitrites, thereby destroying this complex and decreasing the organic solubility of ruthenium, presented itself. Sulfanilamide was investigated with this in mind. Experimental results showed no significant lowering in the distribution ratio for ruthenium in extraction and scrubbing steps when sulfanilamide was present in the

Sulfanilamide (continued)

extracting solvent. Therefore, it was concluded that either nitrosyl complexes are not entirely responsible for the hexone solubility of ruthenium or that the nitrosyl complexes react very slowly, or not at all, with sulfanilamide.

5.3 Zirconium and Columbium

Zirconium, with the mass assignment of 95, occurs with a 6% yield from the fission of uranium. Zr^{95} has a half life of 65 days and possesses 0.42 Mev beta and 0.8 Mev gamma radiations. Columbium with a mass of 95 occurs both from fission and by the decay of Zr^{95}. It has a 35 day half life and 0.15 Mev beta and 0.8 Mev gamma radiations. Zirconium and columbium are well known for their ease of colloid formation and for their complexes with fluoride, oxalate, tartrate and sulfate ions.

While ruthenium contributes the major portion of the beta activity associated with uranium at the end of a solvent extraction cycle, zirconium and columbium are responsible for a significant part of the gamma activity.

The concentrations of aluminum nitrate and nitric acid are the chief variables which were investigated in the hexone extraction of zirconium and columbium. Some attempts were made to decrease the hexone solubility of zirconium and columbium by formation of the oxalate complexes of these elements.

Zirconium and Columbium (continued)

The results indicated, however, that the addition of oxalate ion to solvent extraction systems was deleterious to the recovery of uranium and did not aid appreciably in the decontamination of zirconium and columbium.

The distribution ratio of an equilibrium mixture of zirconium and columbium was studied as a function of aluminum nitrate concentration in the system hexone, 0.25 M HNO_3, 0.1 M $K_2Cr_2O_7$. The distribution ratios of zirconium and columbium ranged from 0.16 in a solution 2.0 M in aluminum nitrate to less than 10^{-3} in a solution 0.25 M in aluminum nitrate (Table 5.3-1). When the aluminum nitrate was held at 1.2 M and the nitric acid concentration varied, the zirconium and columbium distribution ratios varied from 1.3×10^{-4} for a 0.1 M nitric acid deficient solution to 2.25 for a solution 0.9 M in nitric acid (Table 5.3-2).

5.4 Cerium

Two cerium isotopes with mass assignments of 141 and 144 arise from uranium fission. Ce^{141} with a fission yield of 5.7% has a 28 day half life and 0.6 Mev beta and 0.22 Mev gamma radiations. Ce^{144}, appearing in 5% fission yield, has a 275 day half life and a 0.35 Mev beta radiation. Trivalent cerium, behaving like the other rare earths in solvent extraction processes, presents no problem. In the presence of

Cerium (continued)

dichromate ion, small amounts of tetravalent cerium are formed and this material has an appreciable solubility in organic solvents. It is believed that the intermediate valence states of chromium play an important role as catalysts in the oxidation of cerium. Cerium is a much less important contaminant in U^{235} solvent extraction product solutions than ruthenium, zirconium, and columbium.

The hexone extraction of cerium as a function of aluminum nitrate and nitric acid concentration was investigated. The cerium distribution ratio in a solution containing 0.2 M nitric acid and 0.1 M potassium dichromate was found to be 1.8×10^{-3} when the aluminum nitrate concentration was 0.25 molar. In the same system, increasing the aluminum nitrate concentration to 2.0 molar increased the cerium distribution ratio to 0.25 (Figure 5.4-1). At an aluminum nitrate concentration of 1.0 molar, the cerium distribution ratio varied from 0.09 at 0.6 M nitric acid to 1.0 at a concentration of 2.2 M nitric acid (Table 5.4-1).

5.5 Plutonium

Plutonium presents a serious hazard in the metallurgical processing of uranium. Consequently, development effort was expended to assure the elimination of this element with the fission products in the process waste streams.

Plutonium (continued)

In salt solutions containing appreciable quantities of nitric acid, tetravalent plutonium extracts into hexone to about the same degree as uranium, while hexavalent plutonium extracts more readily than uranium. Trivalent plutonium does not extract appreciably into hexone under these conditions. In very low acid, or acid deficient solutions, hexavalent plutonium only is extractable. Therefore, in order to obtain the maximum separation of uranium from plutonium, it was clear that the solvent extraction process should be operated under conditions favoring the lower plutonium valence states.

Ferrous sulfamate is the only reducing agent which was investigated in this program to improve plutonium elimination. In the system 1.4 M $Al(NO_3)_3$-0.05 M HNO_3 deficiency - 20 grams of uranium per liter, plutonium, added as tetravalent plutonium and digested for one hour at room temperature, exhibited a distribution ratio of 5×10^{-2}. The same system with the addition of 0.05 M ferrous sulfamate yielded a plutonium distribution ratio of 6.5×10^{-4}. The fact that ferrous sulfamate inclusion enables the attainment of high separation of uranium from plutonium was verified by semi-works and pilot plant runs which yielded plutonium decontamination factors of greater than 1000 in a single cycle.

6.0 Investigations of Process Steps

6.1 Crud Removal

Early development work on a liquid-liquid extraction process, performed in packed columns, was aimed at employing small Fenske packing in order to obtain optimum column performance. It was apparent that the successful utilization of small packing required that all solutions entering the column should contain an absolute minimum of solid material in order to prevent column plugging. Filtration was selected as the most satisfactory way of removing extraneous material from the feed solutions. Since all solutions of aluminum nitrate contain significant quantities of silicious matter, it was felt necessary to employ a filter aid to obtain adequate filtration rates. Manganese dioxide was selected for this purpose. The choice of manganese dioxide was based, first on its ready solubility in common reagents, thereby eliminating the disposal of solid waste and, secondly, on the fact that the uranium associated with this filter aid may be readily recovered. In addition, manganese dioxide was shown to be an effective scavenger for colloidal zirconium, columbium, and ruthenium[11] [12]. This work on the utilization of manganese dioxide as filter aid in the 25 Process has been described in detail elsewhere[13]. Both preformed and co-formed manganese dioxide were investigated.

Crud Removal (continued)

Co-formed manganese dioxide filter aid was found to give lower filtration rates than preformed material. For this reason, preformed manganese dioxide was recommended over co-formed material. In pilot plant practice, only filtration through a stainless steel element, without filter aid was found necessary.

6.11 Preformed Manganese Dioxide as a Filter Aid

Preformed manganese dioxide was found to be the more satisfactory filter aid for the 25 Process. Optimum filtration characteristics were obtained using commercial manganese dioxide in the 40-170 micron particle size range. The filter aid gave best results when added both to the solution to be filtered and as a thin precoat on the filter. The filtration rate was observed to be a function of the number of small size particles of manganese dioxide present, indicating the necessity of eliminating particles of less than 40 microns in diameter.

E grade Micro Metallic filter plate was found to be the preferred support for the cake. This grade filter has a pore size of 40 microns.

The holdup of uranium on preformed manganese dioxide was investigated by the filtration of a solution of 1.3 M aluminum nitrate at a pH of 1.1 containing 5 grams of uranium per liter. 14.8 grams of preformed manganese dioxide was used as a filter bed. After solution

Preformed Manganese Dioxide As a Filter Aid (continued)

filtration, the cake was washed with five passes of hot 1.3 M aluminum nitrate at a pH of 1.1. Each wash volume was equal to the volume of cake. At this point, the cake contained 0.16 milligrams of uranium per gram of manganese dioxide. From this it was concluded that a reasonable amount of washing of the filter cake reduced the uranium content to a satisfactorily low level.

6.12 Co-formed Manganese Dioxide As a Filter Aid

It was found that the effectiveness of co-formed manganese dioxide filter aid depended on the following factors: the pH of the solution before the manganese dioxide precipitation; the amount of manganous oxide formed; and the digestion time. The most satisfactory filter aid was obtained when the precipitation was made at 90°C from a solution having a pH between 0.5 and 1.9, and by adding potassium permanganate to the solution containing manganous nitrate. 4 moles of potassium permanganate were required per 11 moles of manganous nitrate. After digesting, with agitation, for 1/2 hour at 90°C, the solution was filtered at this temperature.

6.2 The Extraction Step

The laboratory work which was performed was aimed primarily at obtaining the optimum solvent extraction process for the separation of uranium from fission products. It might be well at this point to

The Extraction Step (continued)

consider the variables which influence this separation and to define the conditions which are necessary to obtain the required uranium recovery. In a continuous extraction system, the loss of extractable material is given by the expression, $L = \frac{R-1}{R^{n+1}-1}$, where L = the ratio of the weight of extractable material in the aqueous waste to the weight in the feed stream, R = the distribution coefficient of the extractable material times the ratio of the organic extractant and aqueous phase volumes; and n = the number of theoretical extraction stages in the extraction section of the column. The distribution coefficient is defined as the ratio of the concentration of material in the oragnic phase to that in the aqueous phase at equilibrium. In the case of uranium extraction, in which R is >1, it is clear that L may be made as small as possible, if n is sufficiently large. Knowing the permissible values of product loss, the magnitude of R and n may be established. From work which is to be described later, it develops that a satisfactory value for n in this process is about 10. If a uranium loss ratio of 10^{-4} (0.01% loss) is sought, then R must equal 2.5. In other words, the product of the uranium distribution coefficient and the ratio of the organic and aqueous phase volumes must equal 2.5. It is apparent that any number of conditions exist which give the required value of R.

The Extraction Step (continued)

In the case of fission products, R is considerably less than 1 and the expression for L shows that the separation of uranium from fission products is independent of the extraction column length. This conclusion has been verified experimentally. Thus, the decontamination which is obtained in the extraction section of a column may be approximated by measuring the distribution ratio of fission products in a single batch equilibration of an aqueous and organic phase. It is clear that the maximum separation of uranium from fission products is obtained when the uranium distribution ratio and fission product distribution ratio differ by a large amount. Process modifications which either decrease the distribution ratio of fission products or increase the distribution ratio or uranium thus enhance the separation of the two materials. The development of this process included, therefore, determining that set of circumstances which yielded the greatest separation of uranium from fission products. This separation is influenced by the concentrations of salting agent and nitric acid; by temperature; by the presence of reducing agents or complexing agents; and by the volumes of the organic and aqueous phases.

In order to simplify the problem of comparing various sets of conditions, the following convention was used. Since the purpose of the process is to obtain both uranium yield and decontamination, the

The Extraction Step (continued)

effectiveness of a particular condition may be evaluated by inspection of the ratio of the uranium distribution coefficient and the fission product distribution coefficient. This ratio is called the separation factor, S, and is numerically related in the following way to the decontamination predicted in the extraction section of a continuous extraction column: decontamination factor = $(S+1)\frac{1}{R}$. The term decontamination factor, in turn, is defined as

$$\frac{\text{fission product activity/unit of uranium in feed stream}}{\text{fission product activity/unit of uranium in product stream.}}$$

6.21 Variables Affecting the Distribution Ratio of Uranium and Fission Products

The discussion which follows is taken from more complete reports on the effects of variables on the hexone extraction of uranium and fission products[14] [15].

6.211 Nitric Acid and Aluminum Nitrate Concentrations

Nitric acid and aluminum nitrate were both used as salting agents in aqueous phases to increase the extraction of uranium into hexone. The concentration of these two materials was found to be the most important variable influencing the effectiveness of solvent

Nitric Acid and Aluminum Nitrate Concentrations (continued)

extraction as a means of separating uranium from fission products. Qualitatively, uranium and fission products responded similarily to variations in the concentrations of nitric acid and aluminum nitrate in hexone extraction. However, it was found that the distributive behavior of uranium into hexone was much less sensitive to changes in nitric acid concentration than that of fission products. This effect is attributed to the fact that fission products possess larger hydrolysis constants than uranium and, consequently, at higher pH's they are present as non-extractable, hydrolyzed species. In the case of varying the concentration of aluminum nitrate, it was found that the uranium extraction exhibited a greater dependence than fission product extraction. These two characteristics provided extremely effective tools for obtaining high separation of uranium from fission products by hexone extraction. For example, an early semi-works column run employing 1.06 M aluminum nitrate and 0.3 M nitric acid, in the feed solution, and hexone 0.5 M in nitric acid as solvent yielded a gross gamma decontamination factor of 40. A later run made with a feed solution 1.55 M aluminum nitrate and 0.2 M deficient in nitric acid and employing neutral hexone as solvent showed a decontamination factor of 2×10^4[16].

The logarithm of the distribution ratios of uranium and gross gamma activity are plotted in Figure 6.2-1, as a function of aluminum nitrate concentration, for various nitric acid concentrations. Figure 6.2-2 shows the separation factor obtainable, at various nitric acid

Nitric Acid and Aluminum Nitrate Concentrations (continued)

concentrations, as a function of aluminum nitrate concentration. These results indicate clearly that a continuous hexone extraction process should employ a very low nitric acid concentration and a reasonably high aluminum nitrate concentration in extraction in order to achieve maximum efficiency. It must be borne in mind that lowering the nitric acid concentration, to obtain improved decontamination, requires the addition of aluminum nitrate in order to maintain the uranium distribution ratio which is required for realizing the desired product yield. Similarly, enhancing decontamination by raising the aluminum nitrate concentration requires that the volume of organic extractant employed be decreased to maintain a constant uranium extraction factor.

The data of Figure 6.2-1 have been put in the form of line coordinate charts, Figures 6.2-3 and 6.2-4, which are useful for predicting the distribution ratios of uranium and gross gamma emitting fission products in hexone extraction. The empirical equations which describe the effect of aluminum nitrate concentration on the distribution ratios of uranium and fission products, at various nitric acid concentrations, are shown in Table 6.2-1.

6.212 Temperature

The effect of temperature on the distribution ratios of uranium and fission products was investigated in the system: 1.25 M $Al(NO_3)_3$-0.1 M $Na_2Cr_2O_7$ - 0.45 M HNO_3 - 0.021 M $UO_2(NO_3)_2$ - hexone (Figure 6.2-5). Within the temperature range of 15°C to 55°C the distribution ratio of uranium was described empirically by the equation, $7.58\ (10^{-0.011t})$, and the distribution ratio of gross gamma activity by the equation, $0.020\ (10^{-0.012t})$. The results indicated that both uranium and gross gamma fission product activity were influenced to the same extent by temperature changes. Consequently, the degree of separation of uranium from fission products which is achieved in hexone extraction is appreciably affected by temperature. However, if a constant uranium distribution ratio is desired in a solvent extraction process, then temperature must be controlled. Thus, if a 5% variation in uranium distribution ratio is permissible, temperature must be controlled to within 6%. In order to avoid the necessity of close temperature control, it is recommended that the extraction conditions be chosen to yield the desired uranium distribution ratio under the highest temperatures anticipated. It is apparent that the effect of temperature on decontamination is slight.

6.213 Uranium Concentration

Since a uranium concentration gradient exists in a continuous solvent extraction column, the effect of concentration on the uranium distribution ratio was investigated. It was found that

Uranium Concentration (continued)

the uranium distribution ratio in hexone extraction was independent of uranium concentration in the range between 2 and 5 grams of uranium per liter. At uranium concentrations below 2 grams per liter, there was evidence that the distribution ratio increased significantly (Figure 6.2-6).

6.214 Phase Contact Time

In continuous, liquid-liquid, extraction column operation, the aqueous phase, saturated with hexone and containing fission products, is in contact for a relatively long time with the extracting solvent. It was felt that under these conditions, solvent decomposition, which might impair decontamination, could occur. In order to investigate this possibility, an aqueous phase containing 1.1 M $Al(NO_3)_3$, 0.03 M HNO_3, 0.1 M $Na_2Cr_2O_7$, 5 grams of uranium per liter and fission products was contacted with an equal volume of hexone and samples removed after agitation times varying from five minutes to seventeen hours. This study showed that the extraction of fission products is independent of phase contact time.

6.22 Column Studies

6.221 Variables Affecting the HETS in Extraction

In determining the optimum conditions for the separation of uranium from fission products by solvent extraction, consideration must be given not only to the distribution ratios of uranium and fission products prevailing under a given set of conditions, but also to the height of a theoretical stage (HETS) which is obtained in a packed column run under these conditions. The magnitude of the HETS determines the number of theoretical stages in a given length of packed section and accordingly determines the uranium loss obtained under these conditions. It is known that the efficiency of a packed column depends on such factors as the size and type of packing employed, the viscosity and interfacial tension of the solutions, flow rates, position of the interface, temperature and properties of the material which is transferring. The most important variables: aluminum nitrate concentration, flow rates, interface position and temperature were investigated. These data were obtained in a one inch diameter glass column, packed with 3/16 inch Fenske rings. Extraction and scrub section packed heights were 46 and 13 inches, respectively. This work has been covered more completely in a separate report(17).

6.2211 Aluminum Nitrate and Nitric Acid Concentration

The HETS varied directly with aluminum nitrate and nitric acid concentration. At an aluminum nitrate concentration of 1.24 molar, an HETS of 0.87 feet was observed with 3/16 inch Fenske rings. Increasing the aluminum nitrate concentration to 1.8 molar, raised the HETS to 5.3 feet (Figure 6.2-7).

6.2212 Flow Rates

The HETS was found to vary directly with flow rate. Thus, at a flowrate of 50 milliliters per minute, an HETS of 0.87 feet was observed, while at a flow rate of 90 milliliters per minute, the HETS was 2.1 feet. This effect was observed at both aluminum nitrate concentrations studied and was independent of the position of the interface and phase flow rate ratio (Figure 6.2-8).

6.2213 Phase Flow Ratio

With the interface at the top, increasing the phase flow rate ratio (organic/aqueous) decreased the HETS. With the interface at the bottom, increasing the phase flow ratio increased the HETS. This was true at both aluminum nitrate concentrations investigated (Figure 6.2-9).

6.2214 Interface Position

The effect of interface position on the HETS varied with the phase flow rate ratio. In general, if the phase flow rate ratio (organic/aqueous) was greater than 1, then the HETS was less with the interface at the top of the column than with the interface at the bottom. Conversely, when the flow rate ratio was less than 1, the smaller HETS was obtained with the interface at the bottom of the column. These results indicate that maximum column efficiency is obtained when the phase having the lower flow rate is continuous and occupies the bulk of the column volume.

6.2215 Temperature

The effect of temperature on the efficiency of continuous extraction was investigated in the system 1.2 M $Al(NO_3)_3$-0.1 M $Na_2Cr_2O_7$-0.1 M HNO_3- 0.02 M $UO_2(NO_3)_2$-H_2O-hexone. A 1 inch diameter, jacketed column having a four foot section packed with 3/16 inch Fenske rings was employed. This study showed the HETS to vary inversely with temperature and the uranium loss to vary directly with temperature (Figure 6.2-10). The data obtained in these runs were used to calculate the column height necessary to acheive 99.9% recovery of uranium in this system and it was found that the required column height was relatively independent of temperature within the range of 7.5°C to 20°C. Above this range the column height required to obtain the desired uranium recovery increased from 12 feet at 20°C to

Temperature (continued)

14.5 feet at 31°C. This increase in column height required to obtain the desired uranium yield is small and it is proposed that a factor of safety be provided in column height rather than including temperature control equipment in the process.

6.222 Determination of Optimum Extraction Section Length

Employing the data previously presented, it became possible to make a recommendation concerning the number of extraction stages, and, therefore, extraction section length, required to obtain the most effective separation of uranium from fission products. It was shown that the decontamination factor obtained in the extraction section of a column was independent of the number of theoretical stages, n, other conditions being held constant. However, when the uranium loss was held constant and the combinations of n and uranium distribution ratios which satisfy this condition were examined, it was found that the decontamination factor varied directly with n. This follows from the fact that when n was made small, the uranium distribution ratio had to be large in order to attain the desired yield. All of the methods known for increasing the uranium distribution ratio also increase the fission product distribution ratio, thereby decreasing

Determination of Optimum Extraction Section Length (continued)

the decontamination factor. Conversely, increasing n permits column operation in regions where the uranium and fission product distribution ratios are smaller.

Table 6.2-2 shows the decontamination factors which are predicted for various values of n, assuming that a uranium loss of 0.01% is desired. This study showed that decontamination increased with n until a value of 9 stages was reached. Beyond this point, the decontamination factor became relatively independent of n. From these considerations, it was concluded that this process may be operated effectively in a column containing 9 theoretical extraction stages. The following restrictions were applied in making this analysis: the uranium loss was fixed at 0.01%; the organic and aqueous flow rates were equal; uranium distribution ratios were altered by changing the aluminum nitrate concentration; the aqueous phase was 0.05 M deficient in nitric acid.

A nomograph, Figure 6.2-11, was drawn up to facilitate repeated solution of the loss ratio equation.

6.223 The Extraction of Nitric Acid

It is known that nitric acid, when it is present to the extent of greater than 0.1 molar in the aqueous feed, transfers to the organic phase in about the same degree as uranium. This transfer

The Extraction of Nitric Acid (continued)

leaves the aqueous phase at the bottom of the extraction column less highly salted than that at the feed plate. Under these conditions, the uranium distribution ratio at the bottom of the column is significantly less than it is at the feed plate, unless nitric acid is added in the equilibrium amount to the solvent to correct for this transfer.

An investigation was initiated to determine the extraction behavior of nitric acid in continuous extraction columns employing acid deficient feed solutions. The effect of aluminum nitrate concentration and nitric acid concentration on nitric acid extraction were studied. It was found that the amount of nitric acid extracted from neutral solutions increased with increasing aluminum nitrate concentration. Increasing the acid deficiency of the feed solution decreased the amount of nitric acid transferred to the organic phase and it was found that no nitric acid transferred to the organic phase when the acid deficiency was 0.05 molar or greater (Table 6.2-3). From this study it was concluded that it was not necessary to add nitric acid to the organic extractant employed with aqueous feeds having 0.05 molar or greater acid deficiency.

6.3 The Scrubbing Step

In the scrubbing section of a continuous extraction column, the transfer of material is opposite that in the extraction section, and in defining the extraction factor, distribution ratios are written as the ratio of the concentration of material in the aqueous phase to that in the organic. The amount of uranium refluxed to the scrubbing section is independent of the number of stages, while the fission product reflux is dependent on the number of stages. The true behavior of fission product activity in scrubbing is, however, anomalous and the distribution coefficients increase as the organic phase approaches the top of the column. As a result, the amount of decontamination effected in the scrubbing section is very modest compared to that which is calculated employing the distribution ratios prevailing in the extraction section. Nevertheless, it is possible to employ the scrubbing section both effectively and efficiently.

6.31 Countercurrent Batch Extraction Analysis of the Scrubbing Step

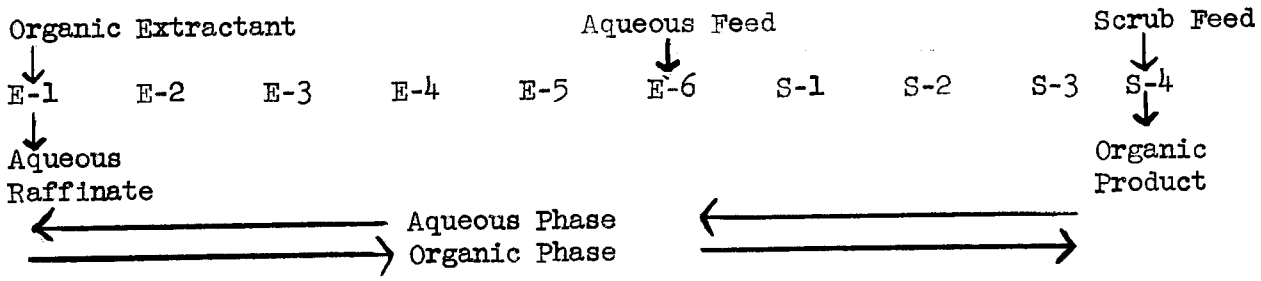
The use of a countercurrent batch extraction apparatus has proved very useful in laboratory studies of liquid-liquid extraction systems. Although not a truly continuous countercurrent operation, a close correlation exists between results obtained with this apparatus

Countercurrent Batch Extraction Analysis of the Scrubbing Step (continued)

and those obtained using pilot plant and semi-works scale extraction columns. This technique has several obvious advantages over columns for laboratory investigations: simplicity of construction and operation; a run may be made in 3-4 hours; the whole assembly is small enough to fit on a laboratory bench or in a hood; relatively small volumes of feed solutions are required, and at the end of a run, it is possible to obtain samples from either liquid phase in any or all stages.

The two liquid phases are equilibrated in a series of cylinders made by cutting off the top of cylindrical separatory funnels. Equilibration is accomplished by interface stirrers driven by either electric or air motors. Each cylinder then corresponds to a theoretical stage in a column. Any reasonable number of stages may be used and chemical conditions and phase flows varied at will. The equipment is shown in Figure 6.3-1.

The assembly most often used in the laboratory consists of six extraction and four scrub stages to simulate the first column of the 25 Process. For purposes of illustration, the cylinders may be indicated diagramatically from left to right as follows:



Countercurrent Batch Extraction Anlaysis of the Scrubbing Step (continued)

The organic extractant is introduced at E-1 and flows to the right, countercurrently to the aqueous feed which is introduced at E-6. The organic extract passes into the scrub section where it flows countercurrently to the scrub solution which is introduced into S-4. Since each phase in all stages may be sampled at the end of a run, it is possible to calculate distribution coefficients in each stage, fraction of material refluxed in the scrub section, and extraction and scrub decontamination factors.

6.32 The Effect of Aluminum Nitrate Concentration on Decontamination

It was shown previously that the distribution ratios of both uranium and fission products varied directly with aluminum nitrate concentration. Therefore, in order to obtain optimum removal of fission products from the solvent in the scrub section, it was apparent that a low aluminum nitrate concentration should be employed. Under these conditions, the transfer of uranium to the aqueous phase was also increased. The refluxed uranium was returned to the extraction section where its extraction factor was greater than unity and it was then reextracted into the solvent.

The Effect of Aluminum Nitrate Concentration on Decontamination (continued)

A series of column runs was made in order to determine the optimum salting agent concentration in the scrub section of the 25 Process. In this study, the aluminum nitrate concentration in the scrub solution was varied and its effect on uranium reflux and gross beta decontamination was noted. In each case, the aluminum nitrate concentration in the feed solution was adjusted to maintain a constant value in the extraction section.

This investigation showed that the gross beta decontamination obtained in the scrub section of a continuous extraction column was increased two fold by lowering the aluminum nitrate concentration from 1.3 M to 0.75 M (Table 6.3-1). As a result of this work, 1.0 M aluminum nitrate is recommended as the scrub solution in the 25 Process. This is the lowest aluminum nitrate concentration at which the uranium reflux is independent of scrub section length.

6.33 The Effect of Scrub Section Length on Decontamination

The number of scrub section stages, which is proportional to the scrub section length, enters as a power in the expression which yields the decontamination factor attainable in scrubbing. Scrub section length is, therefore, a very important variable influencing the effectiveness

The Effect of Scrub Section Length on Decontamination (continued)

of continuous solvent extraction processes. This variable would be more important but for the fact that certain fission species, particularly ruthenium, exhibit irreversible extractibility in the scrubbing step. Consequently, after a certain amount of contacting in the scrub section, the fission products remaining in the extractant display distribution ratios approaching those of uranium and further separation is no longer possible on subsequent scrubbing. The following investigation had the goal of determining just how much of the scrub section is utilized effectively.

A countercurrent batch extraction, consisting of one extraction stage and five scrubbing stages, was made to study the distribution of fission products in scrubbing. This study showed that ruthenium was the predominant fission product remaining in the solvent after a very few scrubbing stages (Table 6.3-2). These data proposed a simple method for determining the height of a theoretical stage in the scrubbing section of a packed column; namely, by comparing the decontamination effected in a known scrub section length with that obtained in a given number of batch extraction stages. When this was done, the height of a theoretical stage in scrubbing was found to be approximately the same as that determined by conventional methods for the extraction section.

The Effect of Scrub Section Length on Decontamination (continued)

Thus, a given packed length of scrub section contains roughly the same number of theoretical stages as the same length of extraction section.

Column runs were made, varying the scrub section length, in order to establish the proper conditions for optimum decontamination. This study showed that the gross decontamination factors obtained in scrubbing and stripping were functions of the scrub section length. On going from zero to three feet of scrub section, the decontamination achieved in stripping increased by a factor of about 1.5, and remained constant for scrub section lengths greater than three feet. This implied that the scrubbing operation removed a small amount of activity which otherwise would transfer with uranium in the stripping step. The decontamination effected in the scrubbing step, and overall decontamination, increased with increasing scrub section length until 12 feet of scrub section were employed. Beyond this point decontamination was independent of scrub section length. These data are shown in Figure 6.3-2. Figure 6.3-3 shows the behavior of specific fission products in scrubbing.

On the basis of this work, between 10 and 15 feet of scrub section was selected as the maximum length which was effective in increasing decontamination.

6.34 The Effect of Scrub Volume on Decontamination

Examination of the equation which defines the effectiveness of the scrub section for separating uranium from fission products shows that increasing the ratio of scrub to organic extractant should result in enhanced decontamination. Three studies were made in a packed column run under conditions where the organic to scrub flow rate ratio was 10, 6, and 3 (Table 6.3-3). No significant difference was noted in decontamination.

On the basis of these results, a small scrub volume is recommended in order to minimize the waste problem associated with the process.

6.35 Alternate Salting Agents in Scrubbing

It was reported by Argonne National Laboratories that replacing ammonium nitrate with aluminum nitrate as a salting agent in the Redox process resulted in five to ten fold increased decontamination. This fact suggested the possible application of salts other than aluminum nitrate in the scrubbing operation of the 25 Process. Aluminum nitrate, ammonium nitrate, calcium nitrate and sodium nitrate were compared in scrubbing efficiency. All salts were employed at reagent acidity and under concentration conditions selected to give comparable uranium distribution ratios in hexone extraction. Ammonium nitrate was found to be about twice as effective as aluminum nitrate. Calcium nitrate

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INVENTORY 1953

The following equation,

$\log y = 0.31Z - 1.9X - 0.44XZ - 0.49$,

appearing on page 67 is incorrect and the following two equations should be substituted for it:

$\log y = 0.0124X(1-Z) + 2.54Z - 3.13$,

which applies in the range from 0.0 to 0.4 M HNO_3;

and,

$\log y = X(0.0090 - 0.41Z) + 0.81Z - 2.42$, which applies in the form 0.40 to 0.90 M HNO_3.

Notice

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Alternate Salting Agents in Scrubbing (continued)

and sodium nitrate were about equal in effectiveness, and intermediate between ammonium nitrate and aluminum nitrate (Table 6.3-4). None of these materials appeared to be sufficiently attractive to warrant their substitution in place of aluminum nitrate in the 25 Process.

6.4 The Stripping Step

In the packed column in which the stripping step was performed, hexone containing uranium was introduced at the bottom and flowed countercurrently to a dilute nitric acid solution which was introduced at the top. In this tower, the distribution of uranium favored the aqueous phase. The distribution ratio of uranium was found to vary directly with uranium concentration and nitric acid concentration and was described by the following expression:

$$\log y = 0.31\, z - 1.9\, x - 0.44\, xz - 0.49$$

where:

y = the uranium distribution ratio (organic/aqueous)

x = the uranium concentration (total uranium expressed as grams per liter of aqueous phase)

z = the nitric acid molarity (total nitric acid expressed as moles per liter of aqueous phase)

The Stripping Step (continued)

This expression was valid for uranium concentrations between 10 and 110 grams/liter and for nitric acid molarities between 0 and 0.9 molar. The experimental data from which this expression was derived were obtained by equilibrating five volumes of organic phase with two volumes of aqueous. It was found to be fairly accurate for phase ratios (organic/aqueous) ranging from 0.5 to 10.

While both the extraction and scrubbing operations accomplish sizeable separation of uranium from fission products, little or no decontamination is achieved in the stripping step. The reason for this is that stripping is performed under conditions which favor fission product concentration in the aqueous phase. This step then appears to be a relatively unexplored field, subject to future development aimed at improving the effectiveness of solvent extraction processes.

6.5 Final Product Purification

A batch solvent extraction process, developed originally for the concentration and purification of U^{233}, proved to be equally adaptable to the final purification of U^{235}[19]. This process consists of the following steps:

(1) The second cycle strip product is evaporated to dryness and dissolved in 2.5 M aluminum nitrate.

Final Product Purification (continued)

(2) Eight to ten successive, equal volume batch extractions are made at 20°C using diisopropyl ether as solvent.

(3) The aqueous and organic phases are drawn through a coarse sintered glass filter, settled, and separated.

(4) The diisopropyl ether extract is stripped of 25 using four one-quarter volume passes of 2% nitric acid.

(5) The material is calcined. Calcination is carried out by either of two methods (a) precipitation of ammonium diuranate and firing at 1000°C to U_3O_8, with a loss of 0.1% or (b) by heating the uranyl nitrate at 250°C for one hour, converting to UO_3 anc finally firing at 1000°C to U_3O_8 with a loss of 0.05%.

Processing of U^{233} by this procedure demonstrated an average uranium loss of 0.03% and beta and gamma decontamination factors of 10^2 and 10^3, respectively. Salts other than uranium were reduced to a level just barely detectable by spectrographic techniques.

6.6 Irradiated U-235 Demonstration Runs

A series of batch extractions were made on U^{235} which had been irradiated in the Oak Ridge National Laboratory pile[14]. The purpose of these experiments was to demonstrate consistency between the

Irradiated U-235 Demonstration Runs (continued)

the decontamination data obtained at tracer levels and the results obtained on highly radioactive solutions.

Foils of U^{235} aluminum alloy containing about 17% U^{235} were irradiated in the ORNL pile for 30 days at 90% of the maximum pile flux. The total average irradiation was about $2x10^6$ kilowatt hours. After 30 day cooling, the samples contained about 10% of the fission product concentration anticipated in the high flux pile. These samples were placed in glass vessels behind shielding, dissolved in nitric acid and the solutions employed in the following extraction study. About 35 milliliters of aqueous feed containing 250 mgs of U^{235} were employed in each experiment. Gross beta and gamma disentigrations per minute per gram of uranium in the feed solution were about $3x10^{11}$ and $1x10^{10}$, respectively. Table 6.6-1 shows the chemical conditions employed in these runs.

These laboratory batch studies indicated that a two cycle gamma decontamination factor of about $5x10^5$ may be expected in the hexone extraction of irradiated U^{235} (Table 6.6-2). Gross beta decontamination factors averaged two to three fold higher. These values are, in general, slightly higher than the separation predicted from low level work. This difference may be attributed to higher analytical accuracy at the increased activity level. Of all the fission elements, only ruthenium,

Irradiated U^{235} Demonstration Runs (continued)

zirconium, columbium, and the total rare earths were found in appreciable amounts in the final product (Table 6.6-3). Ruthenium was the most important contaminant, contributing from 49-85% of the gross beta activity (Table 6.6-4). While appreciable amounts of iodine were found to extract, this element, because of its short half life, does not present a serious problem in dealing with material which has been cooled for longer periods.

7.0 Process Additives

7.1 Ferrous Sulfamate

Ferrous sulfamate, $Fe(NH_2SO_3)_2$, was suggested as a reducing agent for inclusion in the 25 Process. This reagent is especially valuable because of its stability in process solutions and because the sulfamate ion does not complex uranium or fission products.

Ferrous sulfamate may be prepared by the reaction between iron and sulfamic acid.

$$Fe + 2\ NH_2SO_3H \rightarrow Fe(NH_2SO_3)_2 + H_2$$

Sulfamate ion, which reacts with nitrites as follows,

$$SO_3NH_2^- + NO_2^- \rightarrow N_2 + H_2O + SO_4^=$$

serves to stabilize ferrous ion in aluminum nitrate solutions.

Ferrous Sulfamate (continued)

Ferrous sulfamate decomposes on heating, with resulting oxidation of iron by air or nitrites present in process solutions.

The concentration of ferrous sulfamate, reduction time, and reduction temperature were investigated as variables affecting the distribution ratio of fission products in subsequent hexone extraction. The effectiveness of this reagent was found to be relatively insensitive to concentration and reduction time. Arbitrarily, a concentration of 0.05 molar and a reduction time of one hour were arrived at for process utilization. Under these conditions, the use of ferrous sulfamate increased gross beta and gamma decontamination two fold. By performing the reduction with ferrous sulfamate at 85°C instead of room temperature, a slightly greater effect was obtained. However, because of the instability of the reagent, this was not considered practicable. Heating with ammonium sulfamate, rather than ferrous sulfamate, produced an effect of the same magnitude, suggesting that the predominant mechanism of this reaction is nitrite destruction rather than reduction of fission products to inextractible valence states. Additional evidence of this rests in the fact that ferrous sulfamate was found to influence primarily the distribution ratio of ruthenium and affected the extraction of the other fission products little or not at all. The ability of ruthenium to form solvent soluble nitrite complexes is well known.

Ferrous Sulfamate (continued)

The beneficial influence of ferrous sulfamate was observed only in the extraction step and was not reflected in the behavior of fission products in subsequent scrubbing.

The distribution ratio of ferrous sulfamate was found to be $2x10^{-4}$ (organic/aqueous) in the system 1.3 M $Al(NO_3)_3$-0.05 M HNO_3 deficiency-0.04 M $Fe(NH_2SO_3)$-H_2O-hexone. There was evidence that the presence of 5 grams of uranium per liter increased this value about three fold.

In the proposed 25 recovery process, the addition of 0.05 M ferrous sulfamate lowered the plutonium distribution ratio from $5x10^{-2}$ to $6.5x10^{-4}$.

Ferrous sulfamate forms an insoluble compound with mercury and, consequently, may be employed only in the second cycle of the 25 Process.

7.2 Complexing Agents

Since hydrazine and certain organic bases which are soluble in hexone have the ability of increasing the distribution ratio of uranium in favor of the solvent, the possibility of employing them to obtain increased decontamination was recognized. The realization of this hope depended upon the selection of conditions under which the process additive increased the extraction of uranium into the solvent more than it increased the extraction of fission products. Then, the

Complexing Agents (continued)

volume of organic extractant required to attain the desired recovery of uranium could be decreased with a corresponding increase in decontamination. None of the complexing agents investigated, however, yielded appreciably increased decontamination under acid deficient conditions in solutions more than 1.0 molar in aluminum nitrate. The advantages to be gained from employing complexing agents were found to be:

(1) Fission product decontamination became relatively independent of nitric acid concentration.

(2) An appreciable saving in organic extractant volume was effected.

(3) If it were desired to operate a process at low aluminum nitrate concentrations, there was some advantage to be gained by the utilization of complexing agents.

In this work, hydrazine, tri-n-butylamine, 2-hexylpyridine, and dibenzoyl-methane were studied as possible complexing agents for uranium. Figure 7.2-1 shows the relative effectiveness of these three complexing agents to be hydrazine, tri-n-butylamine, and 2-hexylpyridine in order of decreasing effectiveness. Dibenzoylmethane provided no measurable increase in the separation of uranium from fission products.

7.21 Hydrazine

Hydrazine, in conjunction with ferrous ammonium sulfate, was considered as a possible reducing agent in the feed for the second cycle of the 25 recovery process. It was discarded in favor of ferrous sulfamate because of the fact that hydrazine forms hexone soluble complexes with uranium and fission products, is toxic and relatively unstable. The following studies evaluated the use of hydrazine as a uranium complexing agent.

7.211 The Stability of Hydrazine

The stability of hydrazine in the contemplated second cycle feed system 1.0 M $Al(NO_3)_3$-0.2 M HNO_3-0.05 M $Fe(NH_4)_2(SO_4)_2$-0.1 M $N_2H_4 \cdot HNO_3$-0.2 M $NH_4NO_3^-$ 10 gms. U/liter was investigated at room temperature, at 75°C; and at the boiling point. Hydrazine solutions proved to be moderately stable at room temperature, only 8% of the original material decomposing in 15 days. At 75°C, 9% of the hydrazine decomposed on two hours standing. Boiling the simulated second cycle feed resulted in an uncontrolled reaction taking place after about 30 minutes. Analysis of the residual solution at this point showed that no hydrazine remained. Table 7.2-1 summarizes the data on hydrazine stability.

7.212 The Distribution Coefficients of Uranium and Fission Products in Extractions Employing Hydrazine

The distribution ratio of uranium as a function of aluminum nitrate and nitric acid concentration in hexone extraction of solutions containing hydrazine is represented by a line coordinate chart in Figure 7.2-2. These data show that the log of the uranium distribution ratio is linear with respect to aluminum nitrate concentration at all of the acidities investigated.

Reduction time and temperature, hydrazine concentration and equilibration time were found to be the most important variables affecting the separation of uranium from fission products in hexone extraction utilizing hydrazine. Increasing the digestion time in the presence of hydrazine lowered the gross gamma distribution ratio. The presence of ferrous ion and digestion at elevated temperature accelerated the reaction by which the fission product distribution was decreased (Figure 7.2-3).

Fission product analysis indicated that heating with hydrazine lowered the ruthenium and columbium distribution ratios ten fold and the zirconium distribution ratios five fold under those prevailing in an unheated system. Since zirconium and columbium have only one valence state, the reason for hydrazine's influence on them is not understood. On the basis of these results, subsequent work with hydrazine was accompanied by digestion of the feed for one hour at 85°C.

The Distribution Coefficients of Uranium and Fission Products in Extraction Employing Hydrazine (continued)

The addition of hydrazine to 0.3 molar to the system 1.3 M $Al(NO_3)_3$-10 gms. U/liter-0.05 M deficient in HNO_3-0.05 M Fe(II), followed by digestion at 85°C for 1 hour, increased the uranium distribution ratio in subsequent hexone extraction nine fold while the gross gamma distribution ratio remained essentially unchanged. The separation factor was increased ten fold, suggesting that the addition of hydrazine to the 25 process should yield approximately ten fold improvement in decontamination (Table 7.2-2).

The chief determent to the use of hydrazine in a continuous solvent extraction process was the fact that the uranium distribution ratio prevailing in hexone extractions containing hydrazine is time dependent. This may be explained in part by the fact that the reaction between hexone and hydrazine to form ketazine is time dependent. In a continuous solvent extraction process, one has very little control over the time of contact between the organic and aqueous phases, and these times are, in general, too short to fully utilize the effect of hydrazine predicted in batch tests. Table 7.2-3 summarizes this data, indicating that increasing the phase equilibration time from 5 to 60 minutes enhanced the uranium distribution ratio 150 fold. Because of this effect, hydrazine was not used in the process.

7.22 Tri-n-Butylamine

Tri-n-butylamine, $(C_4H_9)_3\ \underline{N}$, and its salt with nitric acid are soluble in hexone, resulting in increased distribution ratios for uranium and fission products. Under conditions of low aluminum nitrate and high nitric acid concentration the utilization of tri-n-butylamine offered promise of substantially increasing the separation of uranium from fission products in hexone extraction. Under acid deficient process conditions, however, the inclusion of tri-n-butylamine did not result in significantly improved decontamination (Table 7.2-4).

Although the use of tri-n-butylamine did not improve the separation of uranium from fission products, it offered the possibility of operating a continuous extraction process with very small organic extractant volumes. Countercurrent batch extraction runs were made to test the feasibility of this and to compare the decontamination achieved under these conditions with that obtained with the basic flowsheet. The results (Table 7.2-5) show that the use of tri-n-butylamine is actually deleterious to the extraction process.

7.23 2-Hexyl Pyridine

2-Hexyl pyridine was investigated less thoroughly than hydrazine and tri-n-butylamine as a uranium complexing agent because preliminary work indicated it to be the least effective of the three (Table 7.2-6).

7.24 Dibenzoylmethane

Dibenzoylmethane forms an organic solvent soluble complex with uranyl ion. A study was made of the extraction of uranium and fission products by hexone containing dibenzoylmethane and it was found that this material complexed uranium and fission products to about the same extent. Consequently, no further effort was made to utilize it.

8.0 Appendix

8.1 Physical State of Dissolver Solution

The amount of radio colloids in a solution of irradiated uranium was determined by dialysing the solution and counting the dialysate, the residue, and the dissolved membrane for beta and gamma activity and analysing for uranium.

The solution was placed in a dialysis cell having a cellophane membrane about one inch in diameter. Water was passed over the other side of the membrane at about 2.5 ml. per hour. At the end of the experiment,

Physical State of Dissolver Solution (continued)

the solution was drained from the cell and the membrane dissolved in sulfuric acid and nitric acid.

The dissolved membrane contained 13.5% of the beta activity, 47.6% of the gamma activity and 0.8% of the uranium. The dialysis residue contained 4.1% of the beta activity, 19.2% of the gamma activity and 5.4% of the uranium (Table 8.1-1).

Assuming that all activity in the ionic state followed the uranium in the dialysis, then 16.5% of the beta and 62% of the gamma activities appeared to be in a colloidal state. However, a large portion of this may be ions adsorbed on the surface of the membrane. This may be particularly true of the ruthenium activity.

A feed solution was dialysed through a cellophane membrane into a simulated feed not containing fission products. Each 24 hours the simulated feed was replaced by new solution until four changes were effected. Equal volume hexone extractions were made on both the dialysate and the residue. The decontamination factors using the two solutions indicated the presence of colloidal gamma activity which lowered decontamination in hexone extraction (Table 8.1-2).

8.2 Nitric Acid Neutralization by Urea Hydrolysis

In the 25 process the first cycle product solution, which is 0.07 M in nitric acid and contains 30 gms. of uranium per liter, is reduced in volume by a factor of five before being introduced into the second cycle. During this volume reduction, the acidity of the solution increased to 0.35 M nitric acid while a neutral solution was desired for introduction to the second cycle. This acid could be neutralized by the addition of base; however, if this was done, a uranium precipitate formed which redissolved very slowly. In order to circumvent this difficulty, it was suggested that the acid be neutralized by hydrolyzing urea during the volume reduction step.

The reaction between urea and nitric acid is given by the equation,

$$CO(NH_2)_2+2HNO_3+H_2O \longrightarrow 2\ NH_4NO_3+CO_2.$$

In dilute nitric acid solutions, the reaction is first order having a velocity constant, k, equal to 0.00133 min.$^{-1}$ in 0.06 M nitric acid. From this value of k, it develops that the hydrolysis of urea should proceed to approximately 99% completion in the 24 hour boil down employed. A laboratory run was made in which a solution 0.07 M in nitric acid and containing 30 grams of uranium per liter was volume reduced five fold in the presence of urea. This run indicated k to have a value of 0.00122 min.$^{-1}$ and the hydrolysis of urea to be 95% complete at the end of 24 hours. In this and subsequent work there was no indication that precipitation of uranium occurred during the hydrolysis of urea.

8.3 Crud Formation in Solvent Extraction

8.31 Hexone System

In early semi-works runs, where sodium dichromate was included in the feed solutions, foreign matter often deposited on the column packing or at the interface. In general this solid matter fell into one of two qualitative classifications, according to color: black material and orange material. The black crud was the more serious and capable of rendering a column process inoperable, while the orange crud did not interfere with column operation (Table 8.3-1).

Several samples of black crud were obtained from the packing of laboratory and semi-works columns. This material proved to be insoluble in water and nitric acid and only slightly soluble in hydrochloric acid. Spectrographic analysis showed the samples to contain gross amounts of aluminum, calcium and iron; appreciable amounts of chromium, magnesium, manganese and silicon and a moderate amount of uranium. The analyses of several samples differed widely and attempts to duplicate this crud in the laboratory were unsuccessful. Wet crud samples were examined miscroscopically and found to be hexone-aqueous emulsions with the hexone phase discontinuous. It is believed that this type of crud entered the system as dirt, rather than as a result of chemical reaction and was deleterious chiefly through its ability to stabilize emulsions in the process. It was found subsequently that systems employing scrupulously clean feed solutions did not develop this type of crudding.

Hexone System (continued)

The second crud, the yellow type, was slightly soluble in water and readily soluble in dilute nitric acid. This material was found both in the feed tanks and in the packing. It has been identified as $(NH_4)_2(UO_2)_2(CrO_4)_3 \cdot 6\ H_2O$, a crystalline solid which forms in solutions of high pH. The formation of this compound is effectively prevented by neutralizing feed solutions with sodium hydroxide rather than with ammonium hydroxide or urea. Since the use of sodium dichromate was discontinued in the 25 process, this crud is of no importance.

8.32 Dibutyl Cellosolve System

Dibutyl cellosolve was investigated as an alternate solvent for the continuous extraction of uranium. However, it was shown that after several hours operation, the column became inoperable because of a grey emulsion which formed and plugged the column. This condition persisted even when filtered feeds and solvent which was purified by passage through an alumina absorption column were employed. This emulsion was not successfully duplicated in the laboratory nor its cause determined.

8.4 The Extraction of Uranium and Fission Products by Dibutyl Cellosolve

The effects of nitric acid concentration, aluminum nitrate concentration, uranium concentration and temperature on the extraction of uranium and fission products were investigated employing dibutyl cellosolve as solvent. For a given set of conditions in the aqueous phase, the distribution ratio of uranium and fission products in extraction was considerably lower when dibutyl cellosolve was employed than when hexone was employed.

Increasing the nitric acid concentration caused the fission product distribution ratio to increase rapidly at about 0.1 M higher acid concentration for dibutyl cellosolve than for hexone (Figure 8.4-1).

With dibutyl cellosolve, the uranium distribution ratio displayed the predicted behavior as the aluminum nitrate concentration was increased, but the fission product distribution ratio increased only until a strength of 1 M aluminum nitrate was reached. In the salting range between 1 M and 2.75 M, the gamma activity distribution coefficient was almost constant (Figure 8.4-2). These data indicate that solvent extractions employing dibutyl cellosolve should permit appreciable volume reduction in solvent, with a corresponding increase in decontamination.

Within the uranium concentration range between one and five grams per liter, the uranium distribution ratio exhibited a dependence very similar to that reported for hexone (Figure 8.4-3).

The Extraction of Uranium and Fission Products by Dibutyl Cellosolve (continued)

The effect of temperature on the distribution ratio of uranium was found to be more marked than was the case with hexone; a temperature increase from 15°C to 55°C decreasing the distribution ratio by a factor of about 5. This is shown in Figure 8.4-4.

8.5 The Determination of Aluminum Nitrate and Nitric Acid by Measurement of Specific Gravity and pH

Previous work indicated the dependence of uranium and fission product distribution ratios on the concentrations of aluminum nitrate and nitric acid salting agents. In order to make close control of these variables possible, a program was initiated to establish a correlation between aluminum nitrate concentration, nitric acid concentration, specific gravity, and pH. This resulted in a simple and accurate method for establishing the concentration of these constituents.[20]

8.51 Aluminum Nitrate Determination

Aluminum nitrate concentration was studied as a function of specific gravity and temperature in the system $Al(NO_3)_3$-HNO_3(or NH_4OH)-$UO_2(NO_3)_2$-NH_4NO_3-H_2O, by observing the effect produced on the specific gravity by a single variable at several values of each of the other variables.

Aluminum Nitrate Determination (continued)

As one would expect, a linear relationship was found between specific gravity and the concentration of each of the variables. The slope of the expression representing the effect of a single variable was independent of the other variables and it was found that the aluminum nitrate molarity could be represented by the following expressions:

$Al(NO_3)_3$ Molarity = 6.592X - 0.00834y + 0.00322 +- 0.171A - 0.165C- 6.672, for solutions containing nitric acid; and,

$Al(NO_3)_3$ Molarity = 6.592X - 0.00834y + 0.00322t + 0.040b - 0.165C- 6.672 for solutions containing an acid deficiency.

In these equations, X = the observed specific gravity referred to water at 25°C, with an assumed density of 1.000.

y = the uranium concentration in grams/liter

t = the temperature in °C

a = the nitric acid concentration in moles/liter

b = the acid deficiency in moles/liter

and c = the ammonium nitrate concentration in moles/liter.

For all practical purposes, the effect of acid deficiency is so small that it may be neglected and the first equation, for solutions containing nitric acid, employed by setting the nitric acid concentration equal to zero. In Figure 8.5-1, a nomograph is shown which facilitates

Aluminum Nitrate Determination (continued)

the solution of this equation. When the concentration of $UO_2(NO_3)_2$, HNO_3, and NH_4NO_3 are sufficiently low, Figure 8.5-2 may be employed to determine the $Al(NO_3)_3$ molarity.

8.52 Nitric Acid Determination

In the system $Al(NO_3)_3$-$UO_2(NO_3)_2$-HNO_3 (or HNO_3 deficiency) NH_4NO_3-H_2O, the pH was found to be a function of the concentrations of aluminum nitrate, uranyl nitrate and nitric acid (or nitric acid deficiency). While the mathematical relationship between these variables is not known at present, sufficient data were obtained to construct line coordinate charts which correlate these variables. These charts, Figures 8.5-3 and 8.5-4, yield an accurate value for the nitric acid concentration in process solutions whose aluminum nitrate and uranyl nitrate concentration are known. Two examples of the use of these charts follow.

Nitric Acid Determination (continued)

Example A. A solution containing 20 grams of uranium per liter is 1.55 M in $Al(NO_3)_3$ and has a pH of 1.42. What is the nitric acid molarity?

1. Neglecting the uranium in the solution, Figure 9.5-3, indicates that the nitric acid concentration should be -0.03 M. By employing this approximate nitric acid concentration, Figure 8.5-4 shows that 20 grams of uranium/liter lowers the pH by approximately 0.15 pH units. The approximate pH, corrected for 20 grams of uranium/liter, then is obtained by subtracting 0.15 pH units from the originally observed value. This corrected pH is 1.27.

2. From Figure 8.5-3, the corrected pH value predicts a nitric acid concentration of -0.018 M. Using this value, a more accurate correction of 0.16 pH units is ascribed to the presence of uranium. The observed pH less 0.16 pH units corresponds to a nitric acid concentration of -0.017 M, which is very close to the second approximation and accurate enough for general use.

Example B. A solution is to be made up 1.2 M in $Al(NO_3)_3$, 0.05 M in HNO_3, and to contain 30 grams of uranium per liter. What will the pH of the final solution be?

Nitric Acid Determination (continued)

1. From Figure 8.5-3, a 1.2 M aluminum nitrate solution which is 0.05 M in nitric acid is found to have a pH of 0.51.

2. From Figure 8.5-4, the presence of 30 grams of uranium per liter in a solution which is 0.05 M in nitric acid is seen to lower the pH by 0.06 pH units. The pH of a 1.2 M aluminum nitrate solution which contains 30 grams of uranium per liter will then be 0.45.

The longevity of electrode life in simulated process solutions was studied. It was found that the life of a Beckman #1190 glass electrode immersed continuously in a highly salted, simulated process solution was about 20 hours. The life of a Beckman #1170 calomel electrode under the same conditions was about 50 hours. Electrode deterioration was evidenced by drifting of the indicating needle.

8.6 The Effect of Solvents and Decontaminating Solutions on Plastic Gasketing Materials (21)(22)

Plastics are valuable materials of construction for plants processing radioactive materials. Many, however, decompose on prolonged contact with organic solvents; absorb excessive amounts of fission product activity from the contacting solvent; or decompose in the presence of the solutions which are employed to decontaminate them. This study was aimed at determining the effect of various solvents of process significance on

The Effect of Solvents and Decontaminating Solutions on Plastic Gasketing Materials[21][22]

several plastics; the amount of activity absorbed from the solvent by the plastic; and the effectiveness of several washing procedures for removing contamination. The solvents which were investigated were of interest in the chemical processing of U-235, U-233 and protoactinium.

These tests were conducted by contacting samples of plastics for nine days with solvent containing uranium and fission products. The sample was then removed, washed with water and counted for beta activity. This was followed by another water wash and finally by a 1 M nitric acid wash. Decontamination factors were calculated as the ratio of activity on one face of the sample, before washing, to the activity on that face after washing. The samples of plastics were approximately 2.0 centimeters in diameter and ranged from 0.5 to 2.2 cubic centimeters in volume The average surface exposed to the solvent was about 6.5 square centimeters.

The results of these experiments may be summarized as follows:

1. In hexone, dibutyl cellosolve, di-isopropyl carbinol, and di-isopropyl ether solutions; teflon, polythene, and saran showed excellent resistance to the decomposing action of the solvent.

The Effect of Solvents and Decontaminating Solutions on Plastic Gasketing Materials[21][22]

2. In the four solvent solutions used: neoprene, ankorite, blue african, and the two types of koroseal were decomposed by the solvents to the extent that they were very easily broken. They also adsorbed so much activity that no accurate determination of the amount could be made.
3. Teflon, polythene, and saran adsorbed radioactivity in amounts varying from 0.03% of the original activity in contact with the material for teflon in di-isopropyl carbinol to 6.2% for saran in hexone. The average percent of original activity adsorbed for these three was 2%-3%. Decontamination factors for these three materials ran from 2-4, in general; one notable exception being a decontamination factor of 18 for saran in dibutyl cellosolve (Tables 8.6-1, 2, 3, and 4).

In addition, the decontaminatability of polythene, teflon and saran which were contacted with hexone containing fission products was further studied using special decontaminating solutions. The decontaminating solutions employed were: H_2O at 100°C, 20% HNO_3 at 104°C, 6% HNO_3 at 100°C, 20% HNO_3 - 1% HF at 60°C-70°C, and 50% NaOH at 100°C.

The Effects of Solvents and Decontaminating Solutions on Plastic Gasketing Materials [21][22] (continued)

15 to 20 minute digestion was used for decontaminating in each case. From these experiments, the following conclusions were drawn:

1. Decontamination with 20% HNO_3 or 20% HNO_3-1% HF gave the best results of the solutions used.
2. Polythene was decontaminated better by these solutions than either teflon or saran (Table 8.6-5).
3. None of the gasketing material showed any change in physical appearance or volume in the solutions at elevated temperatures.

Table 4.1-1

Impurities in Commercial Hexone*

Impurity	% by Wt.	B.P. (°C)	% Impurity in water Azeotrope	Azeotrope B.P. (°C)
MIBC**	0.2-0.3	131.8	55.6	94.3
Mesityl Oxide	0.2-0.7	130.	65.2	91.8
Water	0.03-0.08	100.	-	-
Aromatic***	ca. 0.05	164.8	-	-

* Data received for Shell hexone from Shell Chemical Corporation.
** Methyl Isobutyl Carbinol
*** An aromatic hydrocarbon - possibly mesitylene

Table 4.1-2

Minimum Reaction Temperatures of Hexone-HNO_3 Mixtures

HNO_3 Normality	Reaction Temperature (°C)
1	125.
2	83.
3	84.
5	82.
7	80
9	74.
11	76.
13	78.
15	74.

Table 4.2-1

Effect of Various Treatments on the Reducing Normality of Dibutyl Cellosolve

Treatment	Reducing Normality
None-Untreated cellosolve	0.028
Fractionation - 1st 2% of distillate	>0.10
Fractionation-residue after 5% distilled off	0.011
6 hr. agitation with 1/10 volume of 0.1M $K_2Cr_2O_7$-1M HNO_3 plus water wash	0.006
Passed through alumina absorption column	0.002
Eight 1/2 volume washes with water at 50-60°C	0.002

Table 4.2-2

Minimum Reaction Temperature of Dibutyl Cellosolve - HNO_3 Mixtures

Acid Normality	Reaction Temperature (°C)
1	110.
3	99.
5	84.
7	79.
9	74.
11	69.
13	62.
15	56.

Table 4.3-1

The Extraction of Uranium and Radio-Ruthenium by Tertiary Alcohols

Aqueous: $Al(NO_3)_3$, 0.2 M HNO_3, 10 gms. U/liter, Ru tracer
Solvents: As indicated (Volume equal to aqueous phase volume)

Solvent	$Al(NO_3)_3$ Concentration (moles/liter)	U Distribution Ratio (organic/aqueous)	Ru Distribution Ratio (organic/aqueous)	Separation* Factor
Tertiary Amyl Alcohol	0.5	0.19	0.46	0.41
	1.0	1.2	1.4	0.86
	1.5	8.5	2.4	3.5
	2.0	35.	3.6	9.7
2-Methyl 2-Pentanol	0.5	0.050	0.14	0.36
	1.0	0.55	0.56	0.98
	1.5	5.4	1.3	4.2
	2.0	22.	2.7	8.2
2-Methyl 2-Hexanol	0.5	0.028	0.084	0.33
	1.0	0.32	0.33	0.97
	1.5	2.9	0.8	3.6
	2.0	16.	2.0	8.0
2-Methyl 2-Heptanol	0.5	0.026	0.055	0.47
	1.0	0.29	0.22	1.3
	1.5	1.3	0.68	1.9
	2.0	14.	2.1	6.7
Hexone	0.5	0.10	0.049	2.0
	1.0	1.0	0.088	11.
	1.5	8.5	-	-
	2.0	35.	-	-
Dibutyl Cellosolve	0.5	0.014	-	-
	1.0	0.13	-	-
	1.5	1.1	-	-
	2.0	4.9	-	-

*The separation factor is the uranium distribution ratio divided by the fission product distribution ratio. It equals the decontamination predicted in the extraction section of a continuous, countercurrent column operated with an extraction factor of one.

Table 5.1-1

The Effect of N_2H_4 Concentration on the Neptunium Distribution Coefficient in Hexone Extraction

Aqueous: 1.0 M $Al(NO_3)_3$, 0.05 M $Fe(NH_4)_2(SO_4)_2$
Solvent: Hexone (Volume equal to aqueous phase volume)
Equilibration Time: 5 minutes

The pH of the aqueous phase after equilibration was 1.03.

Total N_2H_4 Molarity (Aqueous + Organic)	Neptunium Distribution Ratio (Organic/Aqueous)
0.00	1.7×10^{-2}
0.004	1.7×10^{-2}
0.043	7.7×10^{-2}
0.43	11.

[redacted]

Table 5.1-2

The Effect of Equilibration Time on the Neptunium Distribution Ratio in Hexone Extractions Containing Hydrazine

Aqueous: 1.0 M $Al(NO_3)_3$, 0.05 M $Fe(NH_4)_2(SO_4)_2$
Organic: Hexone (Volume equal to aqueous volume)

Total N_2H_4 Concentration: 0.48 M

Equilibration Time (Minutes)	pH of Aqueous Phase After Equilibration	Neptunium Distribution Ratio (Organic/Aqueous)
2.5	0.67	26.
5	0.67	57.
10.	0.70	79.
2.5	0.84	7.
5	0.84	17.
10.	0.88	108.
10.	1.0	43.
20	1.0	102.

Table 5.1-3

The Effect of Hexone-Hydrazine Digestion Time on the Neptunium Distribution Ratio in Subsequent Extraction

Aqueous: 1.0 M $Al(NO_3)_3$, 0.05 M $Fe(NH_4)_2(SO_4)_2$, 0.1 M N_2H_4, pH of 0.87 after equilibration
Organic: Hexone 0.38 M N_2H_4 (Volume equal to aqueous phase volume)
Agitation time: 10 minutes

Disgestion Time Hours	Neptunium Distribution Ratio (organic/aqueous)
0.25	88.
0.5	92.
1	103.
3	103
5	103.
24	117.
46	116.

Table 5.1-4

The Distribution of Neptunium as a Function of pH

Aqueous: 1.3 M $Al(NO_3)_3$, 0.1 M $KBrO_3$, 5 gms. U/liter, oxidized 1/2 hour at room temperature at the indicated pH.
Organic: Hexone (Volume equal to aqueous phase volume)

pH	HNO_3 Conc.* M	Neptunium Distribution Ratio (Organic/Aqueous)	U Distribution Ratio (Organic/Aqueous
0.36	0.10	7.1	2.9
0.57	0.05	1.4	2.5
0.97	0.00	0.37	1.0
1.73	-0.05	0.15	1.4
1.92	-0.10	0.06	1.2

* Negative HNO_3 concentrations indicate a solution which is deficient in acid.

[redacted]

Table 5.2-1

The Distribution Ratio of Ruthenium Activity in Successive Batch Extraction and Scrubbing

Aqueous Feed: 1.3 M $Al(NO_3)_3$, 0.05 M $Fe(NH_2SO_3)_2$, 0.05 M nitric acid deficient, ruthenium tracer. Reduced 1 hour at room temperature.

Solvent: Hexone (Volume equal to aqueous phase volume)

Scrub Solution: 1.3 M $Al(NO_3)_3$, 0.05 M $Fe(NH_2SO_3)_2$, 0.05 M nitric acid deficient.

Operation	Distribution Ratio (Organic/Aqueous)			
	1	2	3	4
*Extraction	0.040	0.027	0.020	0.016
	0.65	0.84	0.81	0.77
	0.83	1.10	1.10	1.37
	1.5	1.90	2.5	3.1
**Scrubbing	(A 50 hour period elapsed)			
	0.9	1.1	1.7	1.9
	1.8	1.0	1.0	2.0

* The extraction values shown represent the distribution ratio obtained on successive equilibrations of the same aqueous phase with fresh hexone.

**The scrubbing values shown in column 1 are the ruthenium distribution ratios obtained when the hexone phase from the extraction step of column 1 was equilibrated successively with fresh portions of scrub solution. The same applies to columns 2, 3, and 4 except that the hexone phase which was scrubbed came from the extraction equilibration of the column in question.

Table 5.2-2

The Effect of Digestion Time on Gross Fission Product Distribution Ratios In the Presence of Thiourea

Aqueous: 1.3 M $Al(NO_3)_3$, 5 gms. U/liter, 0.05 M $(NH_2)_2$ CS, solution of irradiated slug, digested at 65°C at a pH of 1.0. The pH was adjusted to 1.85 before equilibration.

Organic: Hexone (Volume equal to aqueous phase volume)

Thiourea Concentration	Digestion Time	Gross Beta Distribution Ratio (Organic/Aqueous) ($x10^3$)	Gross Gamma Distribution Ratio (Organic/Aqueous) ($x10^3$)
None	60 min.	13.	-
	15 min.	3.2	1.8
	30 min.	2.7	1.7
	45 min.	1.8	1.2
	60 min.	1.9	1.0
	120 min.	2.5	0.5

Table 5.2-3

The Effect of Thiourea Concentration on Gross Fission Product Activity Distribution Ratios

Aqueous: 1.3 M $Al(NO_3)_3$, 5 gms. U/liter, $(NH_2)_2$ CS, digested at 65°C for 1 hour at a pH of 1.0. The pH was adjusted to 1.85 before equilibration.

Organic: Hexone (Volume equal to aqueous phase volume)

Thiourea Concentration	Gross Beta Distribution Ratio (Organic/Aqueous) ($x10^3$)
None	13.
0.05 M	1.9
0.10 M	0.5
0.25 M	0.6
0.50 M	0.5
1.0 M	0.6

Table 5.2-4

The Effect of Disgestion Time and Temperature on the Ruthenium Distribution Ratio in a Solution Containing Ethylene Thiourea

Aqueous: 1.3 M $Al(NO_3)_3$, 0.1 M ethylene thiourea, ruthenium tracer, digested at pH 1.0. The pH was adjusted to 1.85 before equilibration.

Organic: Hexone (Volume equal to aqueous phase volume)

Digestion Time (Hours)	Digestion Temperature (°C)	Ruthenium Distribution Ratio (Organic/Aqueous) ($x10^3$)
No Ethylene Thiourea		19.
1/2	55	5.6
1		2.7
2		1.6
4		0.90
1/2	75	1.9
1		1.0
2		0.90
4		0.85

[redacted]

Table 5.2-5

The Effect of Ethylene Thiourea on Gross Beta Decontamination Extraction and Scrubbing

Aqueous: 1.3 M $Al(NO_3)_3$, 5 gms. U/liter, solution of an irradiated slug, digested 2 hours at 75°C.

Solvent: Hexone (Volume equal to aqueous phase volume)

Feed	Extraction	Gross Beta Decontamination Factor			
		First Scrub		Second Scrub	
		No Ethylene Thiourea	0.1 M Ethylene Thiourea	No Ethylene Thiourea	0.1 M Ethylene Thiourea
No Ethylene Thiourea	222.	1.4	1.6	1.1	1.2
0.1 M Ethylene Thiourea	593.	3.9	4.3	1.4	1.9

Table 5.3-1

The Effect of $Al(NO_3)_3$ Concentration on the Distribution Ratios of Zirconium and Columbium

Aqueous: 0.1 M $K_2Cr_2O_7$, 0.25 M HNO_3, Zr-Cb spike. Digested 1 hour at room temperature.

Organic: Hexone (Volume equal to aqueous phase volume)

$Al(NO_3)_3$ Molarity	Zirconium-Columbium Distribution Ratio (Organic/Aqueous) ($x10^4$)
2.0	1600.
1.5	560.
1.0	180.
0.5	11.
0.25	5.2

[redacted]

Table 5.3-2

The Effect of HNO_3 Concentration on the Zirconium-Columbium Distribution in Solvent Extraction

Aqueous: 0.1 M $Na_2Cr_2O_7$, 1.2 M $Al(NO_3)_3$, 8 gms. U/liter, irradiated slug solution. Oxidized 1 hour at room temperature.

Solvent: Hexone (Volume equal to aqueous phase volume.)

HNO_3 Molarity*	Distribution Ratio (Organic/Aqueous) ($x10^4$)
-0.1	1.3
0.0	2.2
0.1	22.
0.2	111.
0.3	236.
0.5	1180.
0.7	3660.
0.9	22500.

* Negative HNO_3 concentrations indicate the solution to be deficient in HNO_3.

[redacted]

Table 5.4-1

The Effect of HNO_3 Concentration on the Hexone Extraction of Cerium

Aqueous: 1.0 M $Al(NO_3)_3$, 0.1 M $K_2Cr_2O_7$, HNO_3 cerium tracer. Digested 1 hour at room temperature.

Organic: Hexone (Volume equal to aqueous phase volume)

HNO_3 Molarity	Distribution Ratio (Organic/Aqueous) ($x10^2$)
0.6	8.8
1.2	38.
1.7	67.
2.2	100.

Table 6.2-1

Expression of the $Al(NO_3)_3$ Concentration Effect on the Uranium and Fission Product Distribution Ratio in Hexone Extraction at Various HNO_3 Concentrations

Total HNO_3 Concentration (Moles/Liter)*	Empirical Equation ***	
	Uranium	Gross Gamma Activity
** - 0.20	$y = 1.78 \times 10^{-3}(10^{2.17x})$	$y = 6.1 \times 10^{-5}(10^{0.79x})$
** - 0.10	$y = 2.42 \times 10^{-3}(10^{2.10x})$	$y = 8.7 \times 10^{-5}(10^{0.75x})$
0.00	$y = 8.77 \times 10^{-3}(10^{1.80x})$	$y = 8.6 \times 10^{-4}(10^{0.59x})$
0.10	$y = 1.63 \times 10^{-2}(10^{1.74x})$	$y = 4.6 \times 10^{-3}(10^{0.62x})$
0.20	$y = 2.41 \times 10^{-2}(10^{1.70x})$	$y = 2.8 \times 10^{-3}(10^{0.90x})$
0.30	$y = 2.92 \times 10^{-2}(10^{1.66x})$	$y = 4.4 \times 10^{-3}(10^{0.85x})$
0.40	$y = 2.36 \times 10^{-2}(10^{1.78x})$	$y = 2.5 \times 10^{-3}(10^{1.17x})$

* Arbitrarily, all the HNO_3 is considered as located in the aqueous phase. The total HNO_3 is the sum of that in the aqueous phase plus that in the organic and is expressed as moles of HNO_3 per liter of aqueous phase.

** This represents a solution which is deficient in HNO_3. However, because of $Al(NO_3)_3$ hydrolysis, it has a pH of less than 7.

*** y is the uranium (or fission product) distribution ratio, organic/aqueous and x is the molar concentration of $Al(NO_3)_3$.

[redacted]

Table 6.2-2

The Effect of Number of Extraction Stages on Fission Product Decontamination Under Conditions of 99.99% Uranium Recovery

Number of Extraction Stages	Uranium Distribution Ratio (Organic/Aqueous)	*$Al(NO_3)_3$ Molarity	*Gross Gamma Decontamination Factor
5	6.1	1.67	330
7	3.6	1.51	430.
9	2.7	1.46	480.
11	2.2	1.41	490.
13	1.9	1.38	500.
15	1.7	1.35	510.

* These values were obtained from Figures 6.2-3 and 6.2-4.

Table 6.2-3

The Distribution of Nitric Acid in the Extraction of Acid Deficient Aluminum Nitrate

Feed: $Al(NO_3)_3$
Organic: Hexone
Scrub: Same composition as feed: scrub flow rate = 1/4 the feed flow rate
Column: 1 inch diameter glass column packed with 3/16 inch Fenske rings: extraction height 46 inches, scrub height 13 inches

Feed		Flow Ratio (organic/aqueous)	HNO_3 Conc. (M) in the Aqueous Phase at		
HNO_3 Molarity*	$Al(NO_3)_3$ Molarity		Feed Plate	Raffinate Outlet	Top of Scrub Section
-0.008	1.0	0.5	-0.009	-0.010	-0.008
-0.008		1.0	-0.008	-0.010	-0.008
-0.009		2.0	-0.008	-0.012	-0.009
-0.008	1.3	0.5	-0.012	-0.016	-0.012
-0.008		1.0	-0.013	-0.020	-0.012
-0.008		2.0	-0.012	-0.022	-0.012
-0.014	1.8	0.5	-0.010	-0.018	-0.009
-0.009		1.0	-0.012	-0.024	-0.011
-0.009		2.0	-0.015	-0.041	-0.012
-0.10	1.2	0.5	-0.10	-0.10	-0.10
-0.10		1.0	-0.10	-0.10	-0.10
-0.10		2.0	-0.10	-0.10	-0.10

* Negative acid concentrations indicate nitric acid deficiency.

[redacted]

Table 6.3-1

The Effect of $Al(NO_3)_3$ Concentration On Decontamination In Scrubbing

Feed: 5 gms U/liter, 0.05 M HNO_3 deficient, $Al(NO_3)_3$ concentration as indicated.
Scrub: 0.05 M HNO_3 deficient, $Al(NO_3)_3$ concentration as indicated.
Extractant: Hexone
Column: 1" diameter glass pipe packed with 3/16" Fenske rings. 4' extraction section, 2 scrub section.

$Al(NO_3)_3$ Molarity		Relative Phase Volume			U Reflux (%)	Gross β Decontamination		
Scrub	Feed	Scrub	Feed	Extractant		Extraction (x10-2)	Scrub	Overall (x10-3)
1.30	1.30	1.	4.	10.	2.	3.6	4.	1.5
1.02	1.36	1.	4.	10.	12.	2.7	8.	2.2
0.75	1.48	1.	4.	10.	63.	3.8	9.	3.4
1.22	1.36	2.5	2.5	10.	8.	3.3	5.	1.7
1.02	1.56	2.5	2.5	10.	29.	2.0	10.	2.0
0.86	1.75	2.5	2.5	10.	80.	4.3	9.	3.8

Table 6.3-2

The Distribution Of Fission Products In Extraction And Scrubbing

Feed: (4 volumes): 1.3 M $Al(NO_3)_3$, 0.05 M HNO_3 deficient, 6.5 grams U/liter
Scrub (1 volume): 1.3 M $Al(NO_3)_3$, 0.05 M HNO_3 deficient
Solvent (10 volumes): Hexone

	Extraction Stage	Scrub Stage				
		1	2	3	4	5
Gross β Distribution Ratio (Organic/Aqueous)	0.001	0.035	0.047	0.057	0.076	0.10
Ruthenium Distribution Ratio (Organic/Aqueous)	0.017	0.034	0.034	0.048	0.074	0.09
Overall Decontamination Factor	215.	607.	1.3×10^3	3.1×10^3	5.5×10^3	10.9×10^3

Table 6.3-3

The Effect Of Scrub Volume On Decontamination

Feed: 1.3 M $Al(NO_3)_3$, 0.05 M HNO_3 deficient, 5.4 gms. U/liter
Scrub: 1.3 M $Al(NO_3)_3$, 0.05 M HNO_3 deficient
Solvent: Hexone
Column: 1" diameter glass pipe packed with 3/16" Fenske rings, 4 feet of extraction and 2 feet of scrub

Relative Flow Rate			Gross β Decontamination Factor		
Scrub	Feed	Solvent	Extraction	Scrubbing	Overall
1.0	4.0	10	510.	3.0	1530.
1.7	3.3	10	535.	3.5	1870.
3.3	1.7	10	450.	3.6	1610.

Table 6.3-4

The Use of Alternate Salting Agents In Scrubbing

Feed (4 volumes): 1.3 M $Al(NO_3)_3$, 0.05 M HNO_3 deficient, 5 gms. U/liter
Scrub (1 volume): as indicated
Solvent (10 volumes): Hexone
Countercurrent batch extraction 2 extraction and 3 scrub stages

Scrub Solution	pH	Uranium Distribution Ratio in Scrubbing (Organic/Aqueous)	Gross β Decontamination Factor		
			Extraction	Scrubbing	Overall
0.8 M $Al(NO_3)_3$	1.6	0.3	720.	5.1	3700.
3.1 M $NaNO_3$	5.3	0.3	850.	5.4	4600.
1.7 M $Ca(NO_3)_2$	5.3	0.4	400.	11.	4500.
4 M NH_4NO_3	5.1	0.3	1200.	7.3	7700.

[redacted]

Table 6.6-1

Chemical Conditions for Irradiated U-235 Extractions

Run No.		1		2		3		4	
		Ext.	Scrub	Ext.	Scrub	Ext.	Scrub	Ext.	Scrub
First Cycle	HNO_3 Molarity	0.2	0.2	0.32	0.2	0.23	0.2	0.09	0.05
	$Al(NO_3)_3$ Molarity	1.25	1.25	1.0	1.0	1.1	1.0	1.2	0.84
Second Cycle	HNO_3 Molarity	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.17
	$Al(NO_3)_3$ Molarity	1.25	1.25	1.0	1.0	1.0	1.0	0.8	0.5
	NH_4NO_3 Molarity	0.9	-	0.9	-	0.9	-	0.1	-

Table 6.6-2

Gross Decontamination Factors In Irradiated U-235 Extraction

Run No.		1	2	3	4
First Cycle	Beta	120.	1200.	1400.	9200.
	Gamma	210.	440.	500.	3300.
Second Cycle	Beta	750.	320.	960.	460.
	Gamma	150.	240.	1200.	260.
Overall	Beta	9.4×10^4	3.8×10^5	1.3×10^6	4.3×10^6
	Gamma	3.5×10^4	1.1×10^5	6.0×10^5	8.6×10^5

Table 6.6-3

Two Cycle, Fission Product Decontamination Factors In Irradiated U-235 Extractions

Run	Decontamination Factor				
	Ru	Zr	Cb	Total Rare Earths	I
1	3×10^3	$1. \times 10^5$	$7. \times 10^4$	$3. \times 10^6$	$4. \times 10^3$
2	5×10^3	$9. \times 10^4$	$5. \times 10^5$	$7. \times 10^7$	$8. \times 10^3$
3	4×10^4	$8. \times 10^5$	$2. \times 10^5$	$3. \times 10^6$	$3. \times 10^4$
4	8×10^4	$5. \times 10^6$	$3. \times 10^5$	$2. \times 10^7$	-

Table 6.6-4

Beta Radiochemical Composition of Final Product From Irradiated U-235 Extractions

Run	% of Gross Beta Contributed By				
	Ru	Zr	Cb	Total Rare Earths	I
1	62.	3.4	0.9	2.1	6.0
2	85.	6.8	0.4	0.3	18.
3	49.	3.4	4.0	23.	12.
4	31.	7.0	17.	12.	-

Table 7.2-1

The Stability of Hydrazine in Simulated Second Cycle Feed Solutions

Composition: 1.0 M $Al(NO_3)_3$, 0.2 M HNO_3
0.05 M $Fe(NH_4)_2(SO_4)_2$, 0.1 M $N_2H_4 \cdot HNO_3$,
0.2 M NH_4NO_3, 10 gms. U/liter

Time	Temperature	Hydrazine Decomposed (%)
0.7 days	25°C	0.
4.4 "	25°C	8.
5.7 "	25°C	9.
6.8 "	25°C	9.
15. "	25°C	8.
1.1 hours	75°C	0.
2.2 "	75°C	9.
3.4 "	75°C	10.
4.4 "	75°C	14.
5.8 "	75°C	24.
6.8 "	75°C	29.
5. minutes	110°C	7.
10. "	110°C	13.
15. "	110°C	19.
20. "	110°C	28.
30. "	110°C	58.
33. "	110°C	100.*

* A vigorous reaction, evolving the oxides of nitrogen occurred at this point.

[redacted]

Table 7.2-2

The Distribution Coefficients of Uranium and Gross Gamma Activity as Functions of $N_2H_4 \cdot HNO_3$ Concentration

Aqueous: 1.3M $Al(NO_3)_3$, 10 gms. U/l; 0.05M deficient in HNO_3
0.05M Fe(2) - Digested 1 hour at 85°C.

Solvent: Hexone (equal volume extraction, 10 min. equilibration)
Extraction made at room temperature

$N_2H_4 \cdot HNO_3$ Concentration (M)	Uranium Distribution Ratio (Organic/Aqueous)	Fission Product Distribution Ratio (Organic/Aqueous)x10^3	*Separation Factor
0.00	2.0	2.0	980.
0.05	1.7	1.8	983.
0.10	2.3	1.7	1340.
0.20	6.0	1.5	4080.
0.30	18.0	1.8	10,040.

* The separation factor is the uranium distribution ratio divided by the fission product distribution ratio. It equals the decontamination predicted in the extraction section of a continuous, countercurrent extraction column operated with an extraction factor of one.

[redacted]

Table 7.2-3

Effect of Equilibration Time on the Uranium Distribution Ratio In Hexone Extraction Containing N_2H_4

Aqueous: 1.1M $Al(NO_3)_3$; 10 grams U/liter; 0.05M acid deficient total N_2H_4 - 0.39M (added to aqueous phase)

Solvent: Hexone (volume equal to aqueous volume)

Equilibration Time	Uranium Distribution Ratio	
	No Hydrazine	Hydrazine Present
5 minutes	0.82	0.90
15 minutes	0.75	3.1
30 minutes	0.78	13.
60 minutes	0.81	138.

Table 7.2-4

The Effect of Tri-n-Butylamine on the Hexone Extraction of Uranium and Fission Products

Solvent: Hexone (Volume equal to aqueous phase volume)

Aqueous	Tri-n-Butylamine Concentration	Distribution Ratio $\frac{\text{organic}}{\text{(aqueous)}}$		Separation Factor
		Uranium	Gross Gamma($\times 10^3$)	
	0.00M	0.20	6.0	33.
0.8M $Al(NO_3)_3$	0.02M	0.96	14.	70.
0.02M HNO_3	0.05M	2.0	26.	77.
10 grams U/1	0.10M	6.5	39.	170.
	0.20M	17.	52.	330.
	0.40M	39.	71.	550.
	0.60M	77.	79.	980.
	0.80M	110.	91.	1200.
	0.00M	1.9	1.3	1400.
1.3M $Al(NO_3)_3$	0.05M	8.3	5.3	1600.
0.05M HNO_3 Deficient	0.10M	25.	14.	1800.
10 grams U/1	0.20M	100.	30.	3200.
	0.30M	190.	48.	4000.

[redacted]

Table 7.2-5

The Effect of Tri-n-Butylamine on Decontamination Under Basic Flowsheet Conditions

Aqueous Feed: 1.3M $Al(NO_3)_3$; 0.05M deficient in HNO_3; 10 grams of U/liter
Scrub: 1.3M $Al(NO_3)_3$, 0.05M deficient in HNO_3
Solvent: A-Hexone
B-Hexone, 0.5M in $(C_4H_9)_3N \cdot HNO_3$
Phase Volumes: A-Feed:Scrub:Hexone = 4:1:10
B-Feed:Scrub:Hexone = 10:5:1

Stage Number	Distribution Ratio (Organic/Aqueous)				Decontamination Factor	
	Uranium		Gross Gamma			
	A	B	A	B	A	B
Extraction					320.	130.
1*	2.8	7.2	2.3×10^{-3}	8×10^{-2}		
2	3.0	11.	8.3×10^{-4}	6.8×10^{-2}		
Scrubbing					3.8	2.7
1	5.8	15.	5.8×10^{-3}	1.6		
2	6.1	23.	2.0×10^{-2}	2.3		
3*	13.	30.	2.5×10^{-2}	1.7		
Overall Decontamination					1200	350

*Feed point

Table 7.2-6

The Effect of 2-Hexyl Pyridine on the Hexone Extraction of Uranium and Fission Products

Solvent: Hexone (Volume equal to aqueous phase volume).

Aqueous	2-Hexyl Pyridine Concentration	Distribution Ratio $\left(\frac{\text{organic}}{\text{aqueous}}\right)$		Separation Factor
		Uranium	Gross Gamma ($\times 10^3$)	
0.8M $Al(NO_3)_3$ 0.02M HNO_3 10 grams U/l	0.0M	0.20	6.0	33.
	0.05M	1.4	18.	75.
	0.10M	2.9	29.	100.
	0.15M	4.4	35.	130.
	0.20M	6.6	44.	150.
	0.30M	12.	58.	200.
	0.40M	16.	67.	250.
1.3M $Al(NO_3)_3$ 0.05M deficient in HNO_3 10 grams U/l	0.0M	1.8	2.0	900
	0.05M	4.4	11.	400
	0.10M	8.4	21.	400
	0.20M	20.	41.	490
	0.30M	38.	61.	610

[redacted]

Table 8.1-1

The Composition of Dialysate from the Dialysis of a Uranium Solution Containing Fission Products

Aqueous: 3 gms. U/liter, 0.6 M HNO_3

Volume (ml.)	% Beta Activity	% Gamma Activity	% U
7.6	29.4	6.8	28.3
15.0	57.6	14.6	52.4
34.4	70.0	27.1	81.6
49.3	80.3	31.9	92.4
53.1	82.4	33.2	93.8

Table 8.1-2

The Hexone Extraction of a Dialyzed Solution

Aqueous: 1M $Al(NO_3)_3$, 0.6M HNO_3, 3 gms. U/liter

Organic: Hexone, 0.5M in HNO_3 (Volume equal to aqueous phase volume)

	Dialysate	Residue
Beta Decontamination Factor	54	103
Gamma Decontamination Factor	16	8

Table 8.3-1

Spectrographic Analysis of Column Cruds

Aqueous: 1.1 M $Al(NO_3)_3$, 0.1 M $Na_2Cr_2O_7$, 10 grams U/liter, 0.05 M HNO_3 deficient except where noted

Solvent: Hexone

Crud Source	Constituent*						
	Fe	Cr	Al	Si	Ca	Mg	Mn
(1) Removed from interphase and packing of run made 0.1 M HNO_3 deficient	*	*	*	*	*	*	*
(2) As in (1) except 0.07 M HNO_3 deficient	*	*					
(3) Removed from bottom of aqueous feed tank	*	*					
(4) Removed from bottom of hexone feed tank	*	*		*		*	*
(5) Removed from interphase of column after run 0.04 M HNO_3 deficient		*	*				

* Elements whose presence was indicated strong by spectrographic analysis.

Table 8.6-1

The Effect of Hexone Containing Fission Products on Plastic Gasketing Materials

Conditions - Hexone; 3 g. U/liter, 0.5M HNO_3, 1.3×10^4 β c/m/ml.
9 days contact

Plastic	% Vol. Increase	% Original Activity Absorbed	Decontamination Factor			Remarks
			H_2O Wash	1M HNO_3 Wash	Overall	
Teflon	4.1	2.8	1.4	1.2	1.8	Excellent Resistance to solvent action.
Saran	2.3	6.2	1.2	1.5	1.9	" " " " "
Polythene	1.2	1.4	1.2	1.6	2.0	" " " " "
Neoprene	221.1	-	-	-	-	Very poor resistance to solvent action.
Ankorite	-	-	-	-	-	Very poor resistance to solvent action.
Garlock	86.2	14.8	1.3	1.0	1.0	HNO_3 wash apparently brought more activity to the surface. Poor resistance to solvent action.
Blue African	-	-	-	-	-	Very poor resistance to solvent action. High activity absorption.
Amber Koroseal	-	-	-	-	-	Split apart into 4 pieces.
Black Koroseal	-	-	-	-	-	Split apart into 2 pieces.

Table 8.6-2

The Effect of Dibutyl Cellosolve Containing Fission Products on Plastic Gasketing Materials

Conditions: Dibutyl Cellosolve; 3 gms. U/liter.; 0.1 M HNO_3, 2.5×10^4 β c/m/ml
9 days contacts

Plastic	% Vol. Increase	% Original Activity Absorbed	Decontamination Factor			Remarks
			H_2O Wash	1M HNO_3 Wash	Overall	
Teflon	4.9	1.3	1.1	1.8	2.3	Excellent Resistance to solvent action.
Saran	2.9	2.3	1.8	10.0	18.0	Excellent resistance to solvent action.
Polythene	9.7	0.2	1.9	1.9	3.6	Excellent resistance to solvent action.
Neoprene	139.2	-	-	-	-	Badly decomposed by solvent Activity too great for accurate count.
Ankorite	115.2	-	-	-	-	Badly decomposed by solvent. Activity too great for accurate count.
Garlock	72.4	8.0	1.1	1.3	1.4	Poor resistance solvent action.
Blue African	-	-	-	-	-	Almost completely dissolved in the solvent
Amber Koroseal	7.9% vol. decrease	-	-	-	-	Solvent causes shrinkage. Activity too high to count accurately.
Black Koroseal	11.6% vol. decrease	-	-	-	-	Solvent causes shrinkage. Activity too high to count accurately.

[redacted]

Table 8.6-3

The Effect of Di-isopropyl Carbinol Containing Fission Products on Plastic Gasketing Materials

Conditions: Di-isopropyl Carbinol; 2.73M HNO_3, 2.25×10^4 β c/m/ml.
9 day contact.

Plastic	% Vol. Increase	% Original Activity Absorbed	Decontamination Factor			Remarks
			H_2O Wash	1M HNO_3 Wash	Overall	
Teflon	11.0	0.03	1.0	1.3	1.3	Excellent resistance to solvent action.
Saran	Vol. decreased 2.2%	0.05	1.1	1.2	1.3	Excellent resistance to solvent action.
Polythene	Vol. decreased 5.5%	0.05	1.8	1.8	3.3	Excellent resistance to solvent action.
Neoprene	-	-	-	-	-	Badly decomposed
Ankorite	75.3	-	-	-	-	" "
Garlock	47.2	2.5	-	-	-	Hardened
Blue African	-	-	-	-	-	Badly decomposed
Amber Koroseal	18.2	0.5	-	-	-	Hardened and blistered.
Black Koroseal	3.9	1.0	-	-	-	Hardened and blistered.

[redacted]

Table 8.6-4

Effect of Di-Isopropyl Ether Containing Fission Products On Plastic Gasketing Materials

Conditions: Di-Isopropyl Ether; 0.1M HNO_3; 2 x 10^3 beta c/m/ml. 9 days contact

Plastic	% Vol. Increase	% Original Activity Absorbed	Decontamination Factor			Remarks
			H_2O Wash	1M HNO_3 Wash	Overall	
Teflon	1.5	2.7	1.7	1.2	2.0	Excellent resistance to solvent action.
Saran	3.1	2.2	1.2	3.2	4.0	" " " " "
Polythene	12.7	1.9	1.7	1.2	2.0	" " " " "
Neoprene	7.9	-	-	-	-	Poor " " "
Ankorite	7.8	28.5	-	-	-	Became soft and spongy. Poor resistance to solvent action. Became soft and spongy.
Garlock	17.8	-	-	-	-	Poor resistance to solvent action. Became soft and spongy.
Blue African	-	-	-	-	-	Split apart into two pieces. Badly decomposed.
Amber Koroseal	-	9.2	-	-	-	Hardened and blistered.
Black "	-	12.1	-	-	-	Hardened and blistered.

Table 8.6-5

Effect of Decontaminating Solutions at Elevated Temperatures on Plastic Gasketing Materials

Conditions: Contaminating Solution - Hexone containing 3 gms. U/liter, 1.5×10^4 beta c/m/ml.; 8 days contact. Decontaminating time - 15 - 20 min. Diameter of piece - 2 cm.; Area - 10 cm^2.; Volume - 1.9 cm^3.

Plastic	Decontaminating Solution	Temperature °C	% of Original Activity Absorbed*	Decontamination Factor	Residual Activity Beta c/m/ml
Teflon	H_2O	100	3.3	1.9	5.2×10^3**
	6% HNO_3	100.5	4.3	1.4	9.2×10^3**
	20% HNO_3	104	9.0	15.0	1.8×10^3**
	20% HNO_3 - 1% HF	65	4.0	60.0	2.0×10^3**
	50% NaOH	100	7.7	8.0	2.9×10^3**
Saran	H_2O	100	3.0	1.1	3.0×10^3
	6% HNO_3	100.5	2.4	8.5	0.34×10^3
	20% HNO_3	104	4.5	28.0	0.2×10^3
	20% HNO_3 - 1% HF	65	4.6	16.0	0.3×10^3
	50% NaOH	100	4.5	2.8	0.2×10^3
Polythene	H_2O	100	3.5	1.0	2.9×10^3
	5% HNO_3	100	2.7	52.0	100
	20% HNO_3	104	5.3	250	17.0
	20% HNO_3 - 1% HF	65	3.8	130	100
	50% NaOH	100	3.8	5.0	1.3×10^3

* Ratio of second shelf beta count as determined on one surface to the total in the 20 ml. of test solution.
** Samples were thicker and were closer to counter window, thereby increasing the geometry. [redacted]

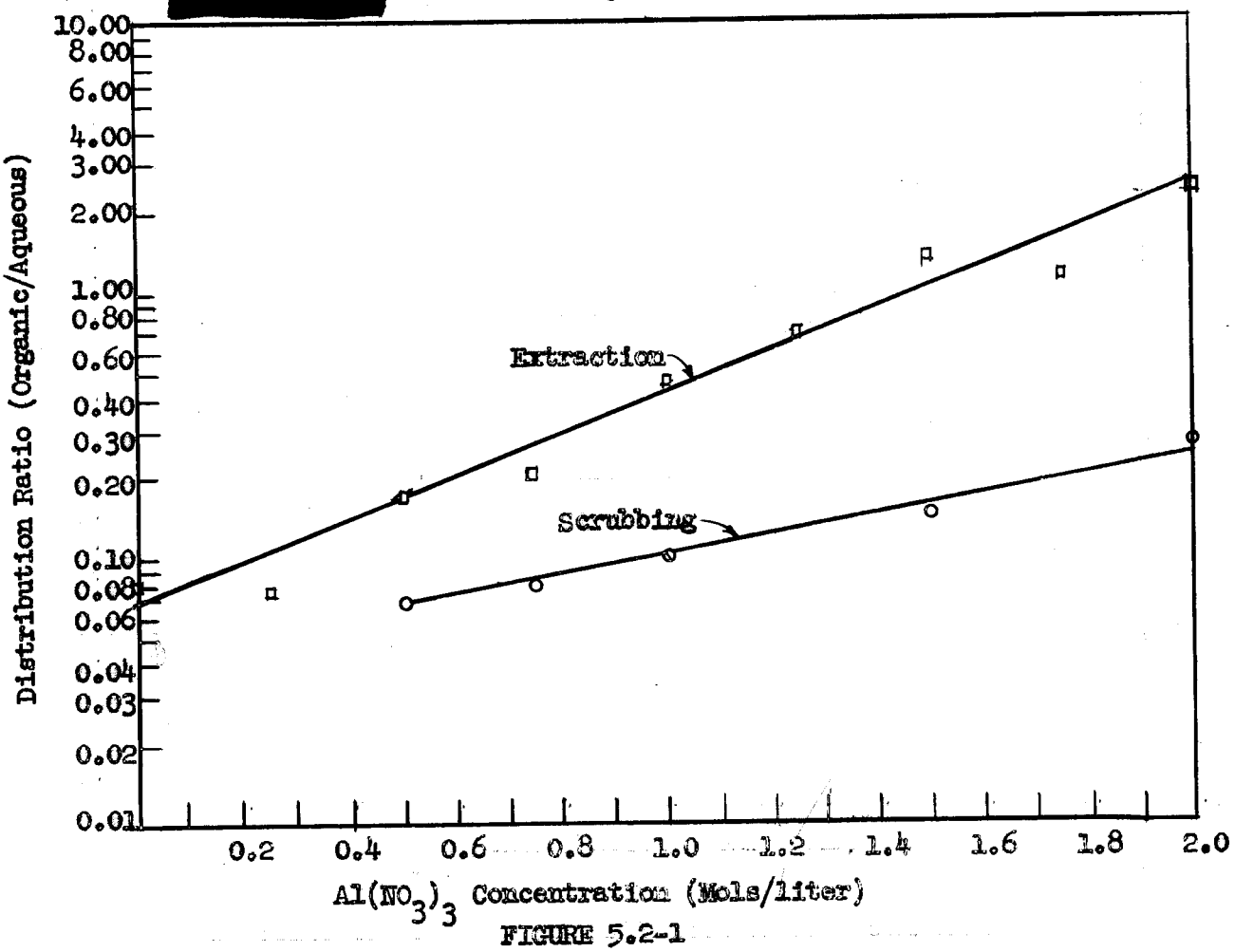


FIGURE 5.2-1

The Effect of $Al(NO_3)_3$ Concentration on the Ruthenium Distribution Ratio in Extraction and Scrubbing

Extraction:

Aqueous: 0.1 M $K_2Cr_2O_7$, 0.2 M HNO_3, $Al(NO_3)_3$, ruthenium tracer

Organic: Hexone (Volume equal to aqueous phase volume)

Scrubbing:

Aqueous: Fresh $Al(NO_3)_3$, 0.1 N in HNO_3

Organic: Hexone which had previously been equilibrated with aqueous $Al(NO_3)_3$ containing ruthenium tracer

$Al(NO_3)_3$ Molarity	Distribution Ratio (Organic/Aqueous)	
	Extraction	Scrubbing
0.0	0.078	---
0.25	0.071	---
0.50	0.17	0.068
0.75	0.20	0.077
1.0	0.46	0.095
1.25	0.69	---
1.50	1.3	0.14
1.75	1.1	---
2.0	2.3	0.26

[redacted]

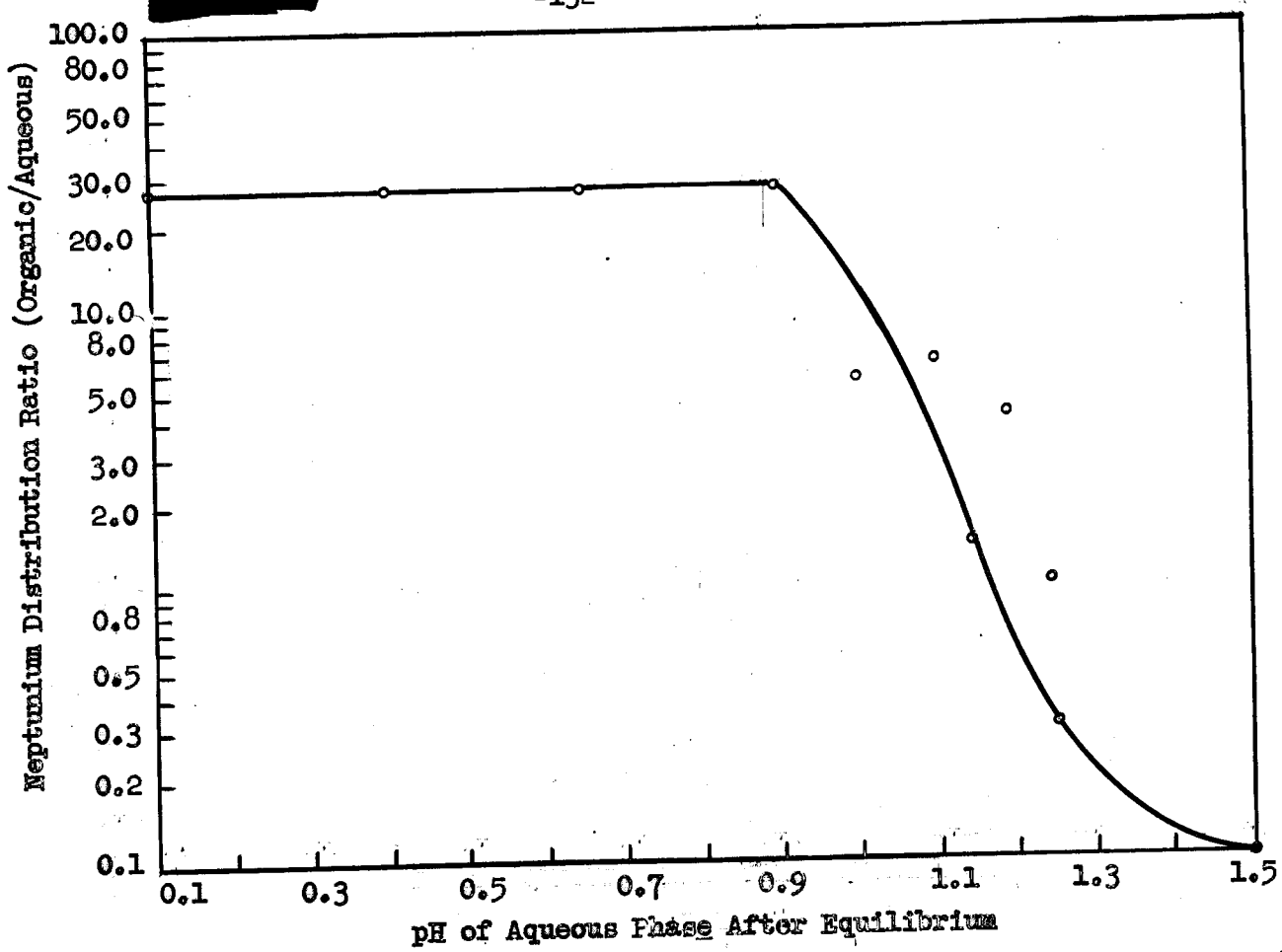


FIGURE 5.1-1

The Effect of pH on the Distribution Ratio of Neptunium in Hexone Extraction

Aqueous: 1.0 M $Al(NO_3)_3$, 0.05 M $Fe(NH_4)_2(SO_4)_2$

Solvent: Hexone (Volume equal to aqueous phase volume)

Total N_2H_4 Concentration: 0.5 M

Equlibration time: 5 minutes

pH of Aqueous Phase After Equilibration	Neptunium Distribution Ratio (organic/aqueous)
0.10	27.5
0.40	27.5
0.65	27.5
0.90	27.5
1.00	5.5
1.10	6.2
1.13	1.4
1.19	4.0
1.24	1.0
1.25	0.3
1.50	0.1

[redacted]

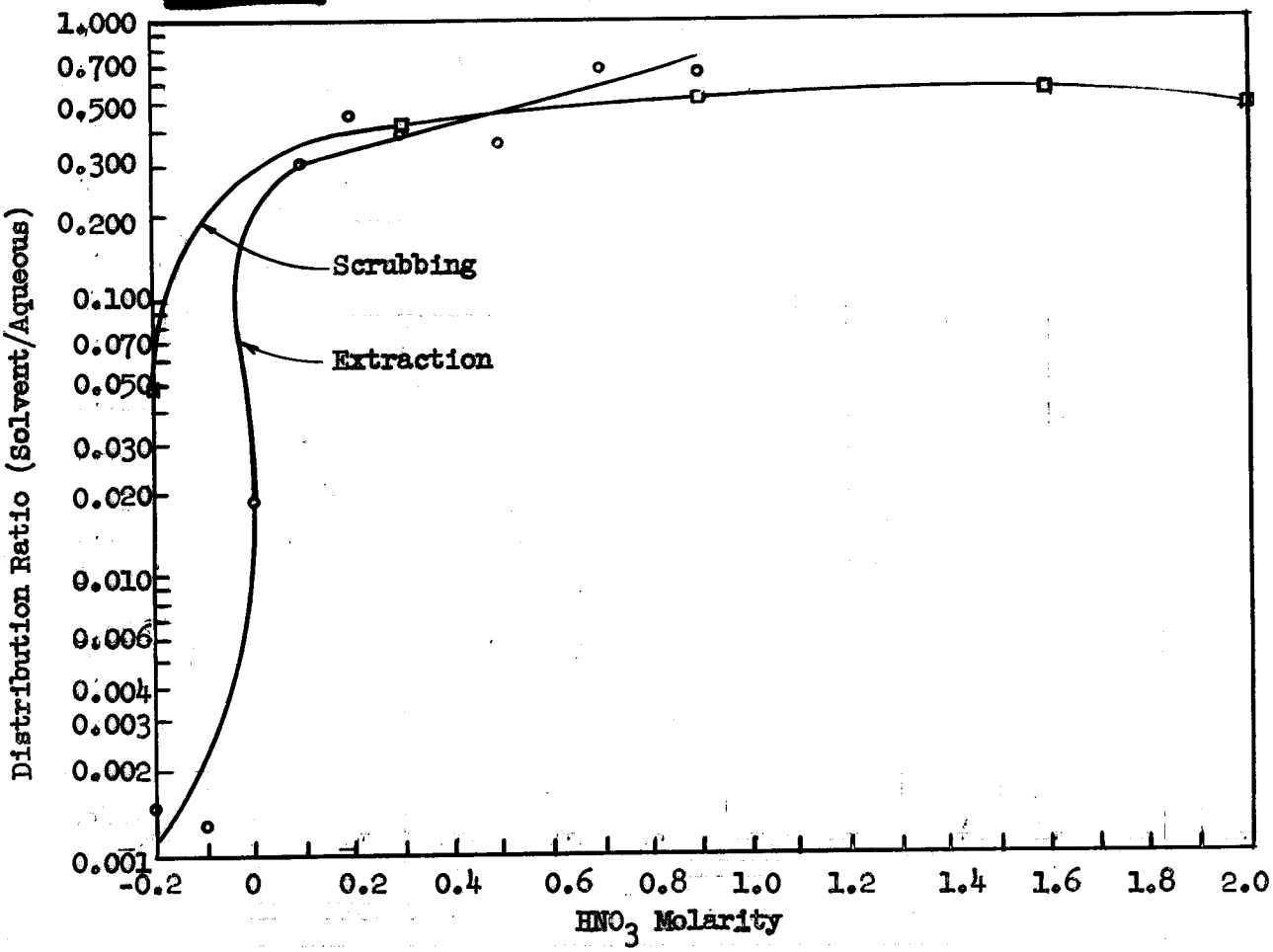


FIGURE 5.2-2

The Effect of HNO_3 Concentration on the Distribution Ratio of Ruthenium in Extraction and Scrubbing

Extraction

Aqueous: 0.1 M $Na_2Cr_2O_7$, 1.2 M $Al(NO_3)_3$, 8 gms. U/liter irradiated slug solution oxidized 1 hr. at room temp.

Solvent: Hexone (volume equal to aqueous phase volume).

Scrubbing

Aqueous: 0.75 M $Al(NO_3)_3$

Solvent: Hexone which had previously been equilibrated with aqueous $Al(NO_3)_3$ containing ruthenium tracer.

HNO_3 Molarity	Distribution Ratio (Organic/Aqueous) (x 10^3) Extraction	Distribution Ratio (Organic/Aqueous) Scrubbing
*-0.2	1.5	0.049
-0.1	1.3	---
0.0	19	---
0.1	310	---
0.2	460	---
0.3	390	0.43
0.5	370	---
0.7	690	---
0.9	660	0.53
1.6	---	0.56
2.0	---	0.49

* Negative HNO_3 concentrations indicate a deficiency of HNO_3

[redacted]

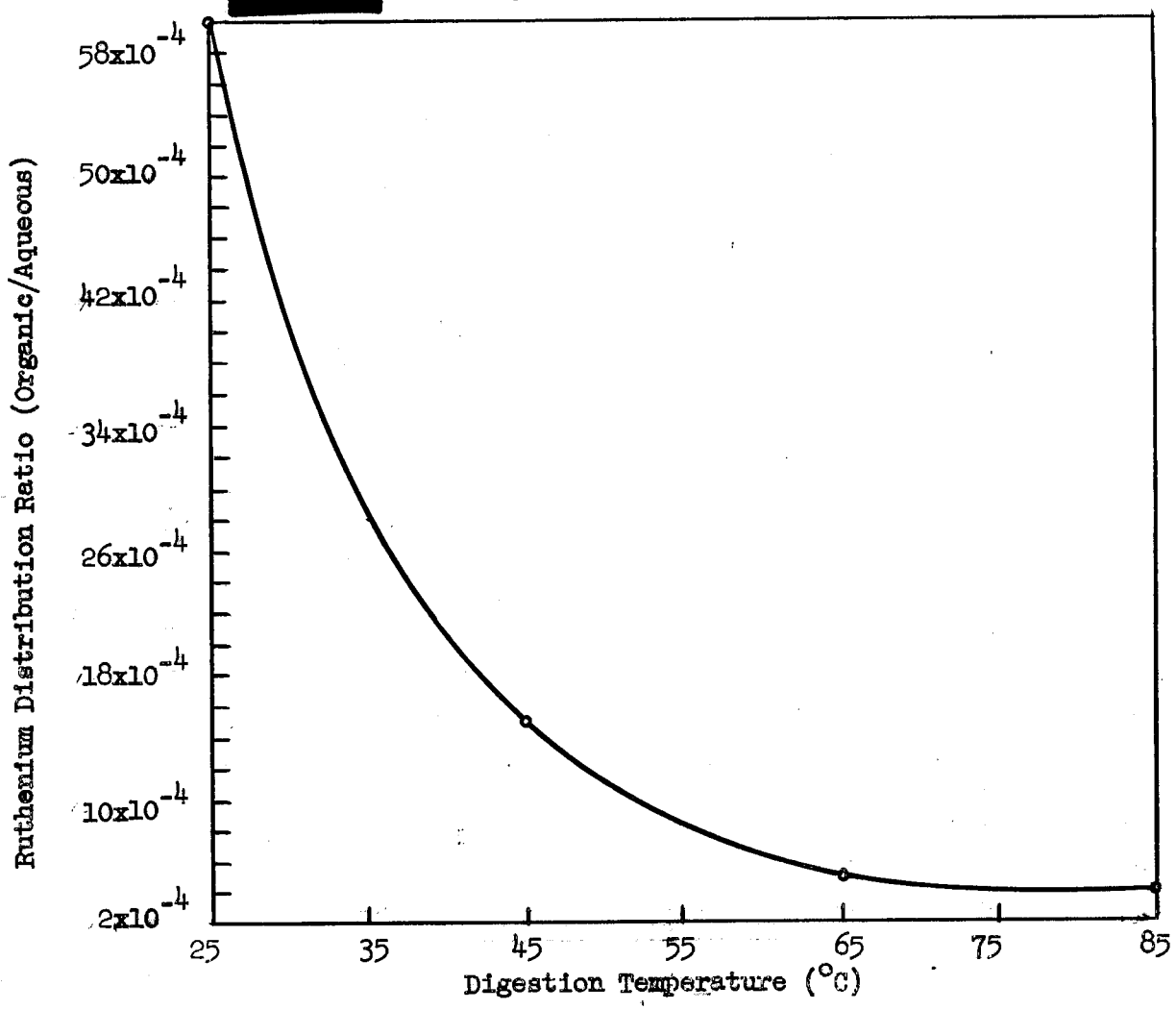


FIGURE 5.2-3

The Effect of Digestion Temperature on the Ruthenium Distribution Ratio in the Presence of Thiourea

Aqueous: 1.3 $Al(NO_3)_3$, pH 0.1, 0.05 M $(NH_2)_2$ CS, Ru^{106} tracer - digested for 1 hour at indicated temperature. pH adjusted to 1.8 and extracted.

Solvent: Hexone (volume equal to aqueous phase volume)

Digestion Temperature (°C)	Ruthenium Distribution Ratio (Organic/Aqueous) (X 10^4)
25	60
45	15
65	5
85	4

[redacted]

[redacted]

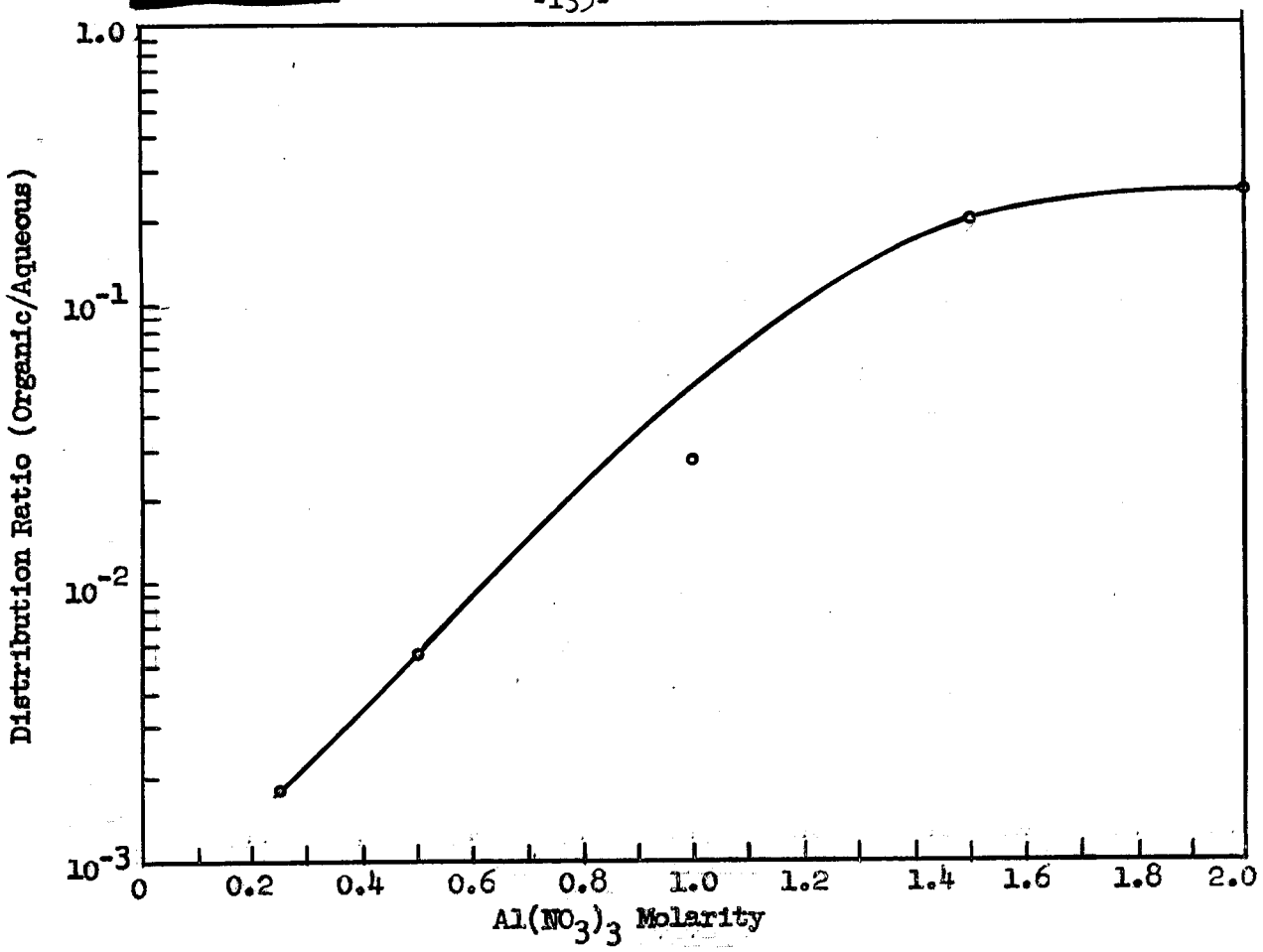


FIGURE 5.4-1

The Effect of $Al(NO_3)_3$ Concentration on the Hexone Extraction of Cerium

Aqueous: 0.2 M HNO_3, 0.1 M $K_2Cr_2O_7$, $Al(NO_3)_3$, cerium tracer. Digested 1 hour at room temperature.

Organic: Hexone (Volume equal to aqueous phase volume)

$Al(NO_3)_3$ Molarity	Distribution Ratio (Organic/Aqueous) (x 10^3)
0.25	1.8
0.50	5.5
1.0	27.
1.5	200.
2.0	250.

[redacted]

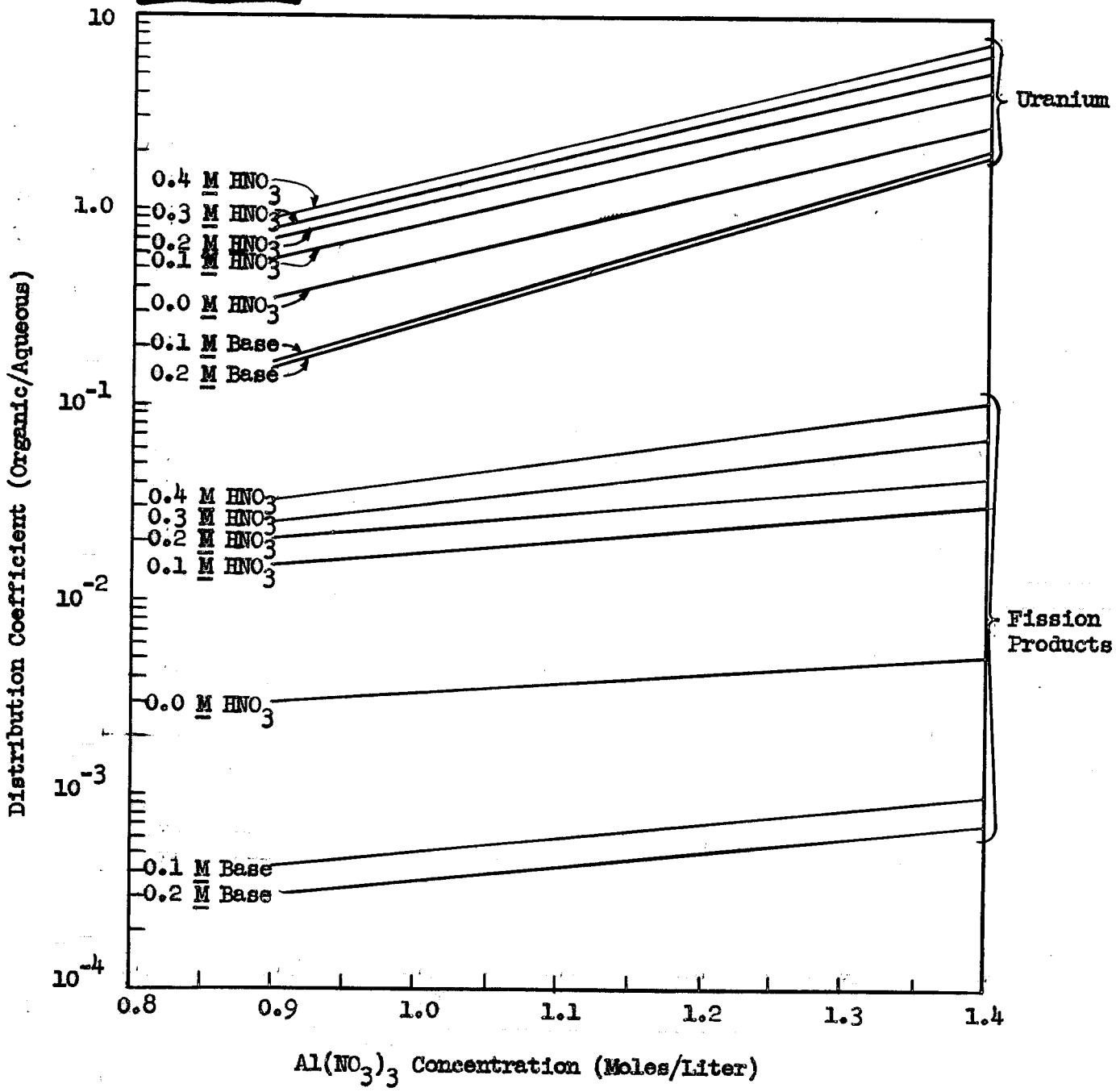


FIGURE 6.2-1

The Effect of $Al(NO_3)_3$ Concentration on the Distribution Coefficients of Uranium and Fission Products in Hexone Extraction at Various HNO_3 Concentrations

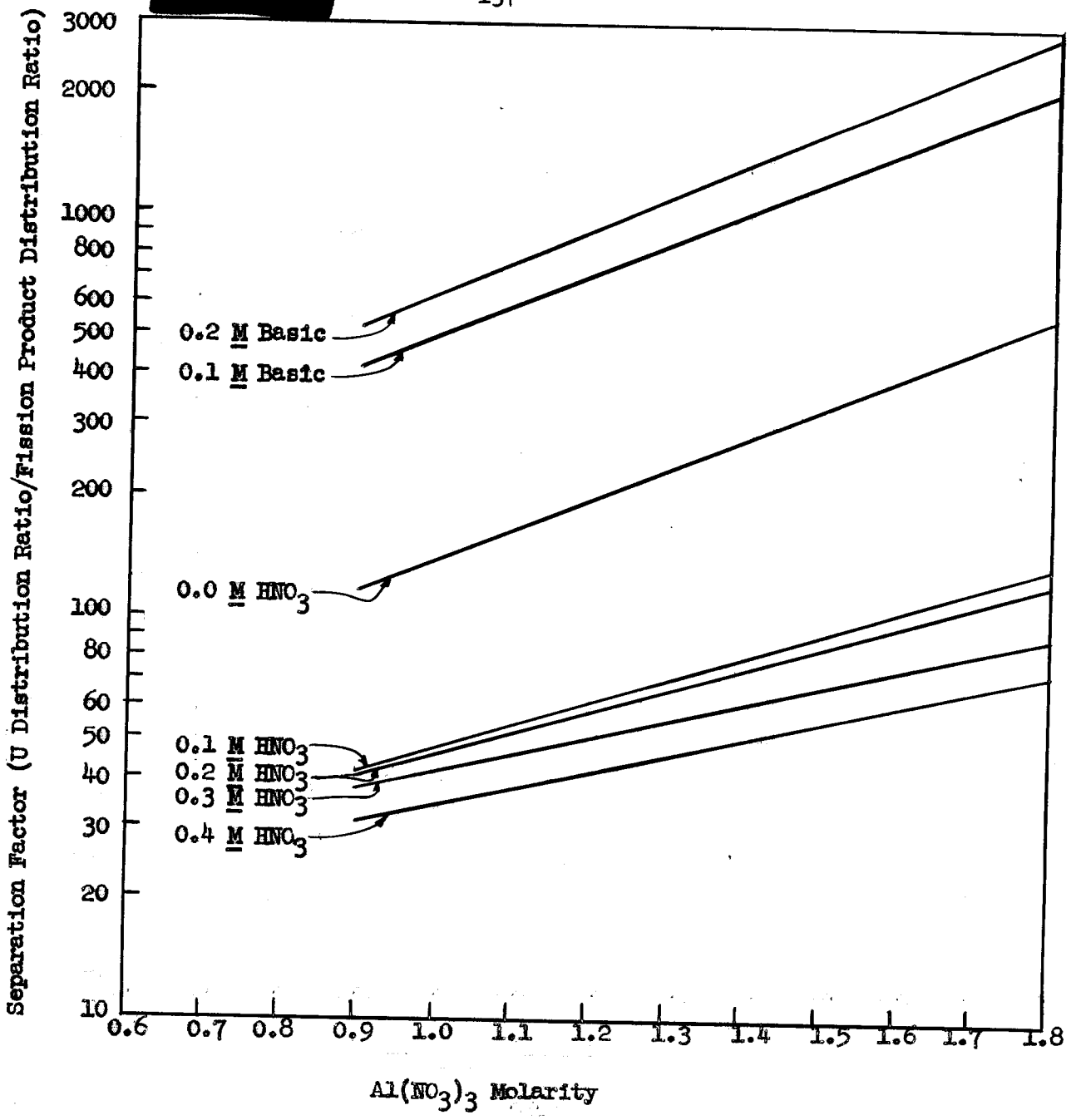
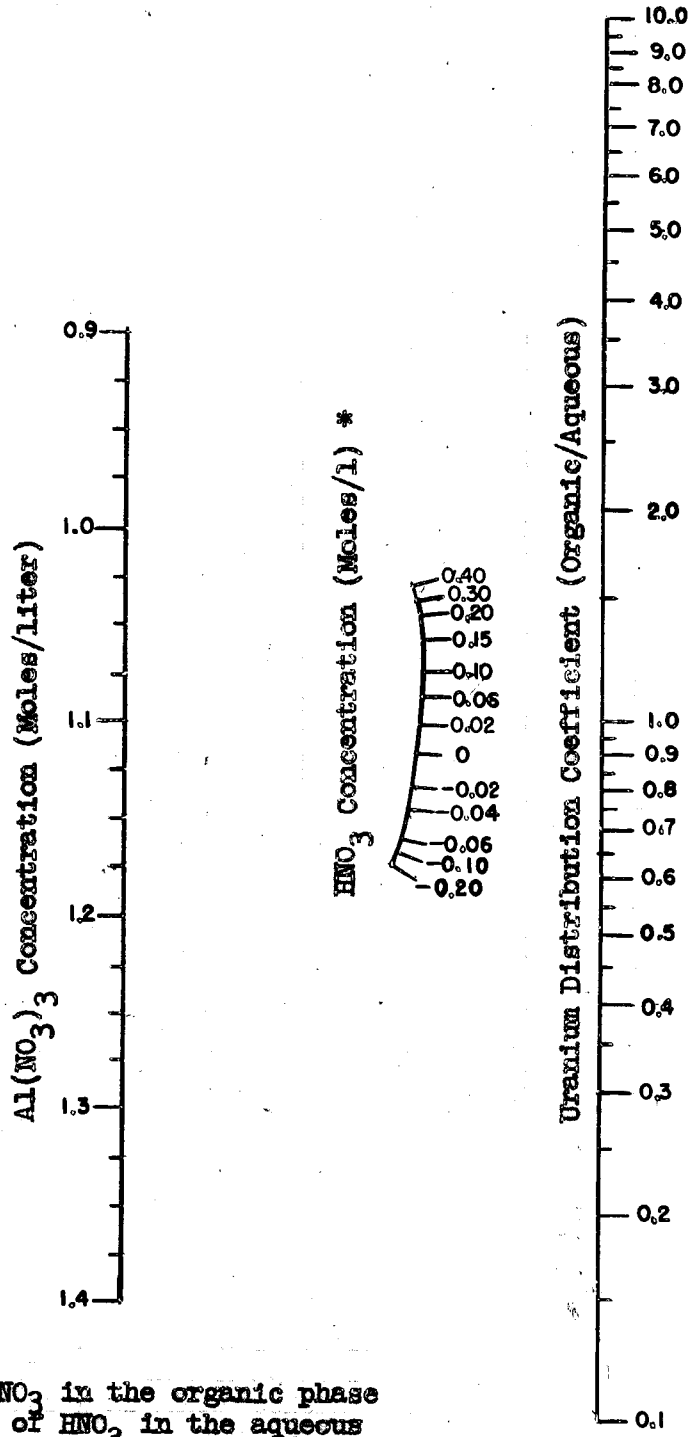


FIGURE 6.2-2

The Effect of $Al(NO_3)_3$ Concentration on the Separation Factor at Various HNO_3 Concentrations

[redacted]



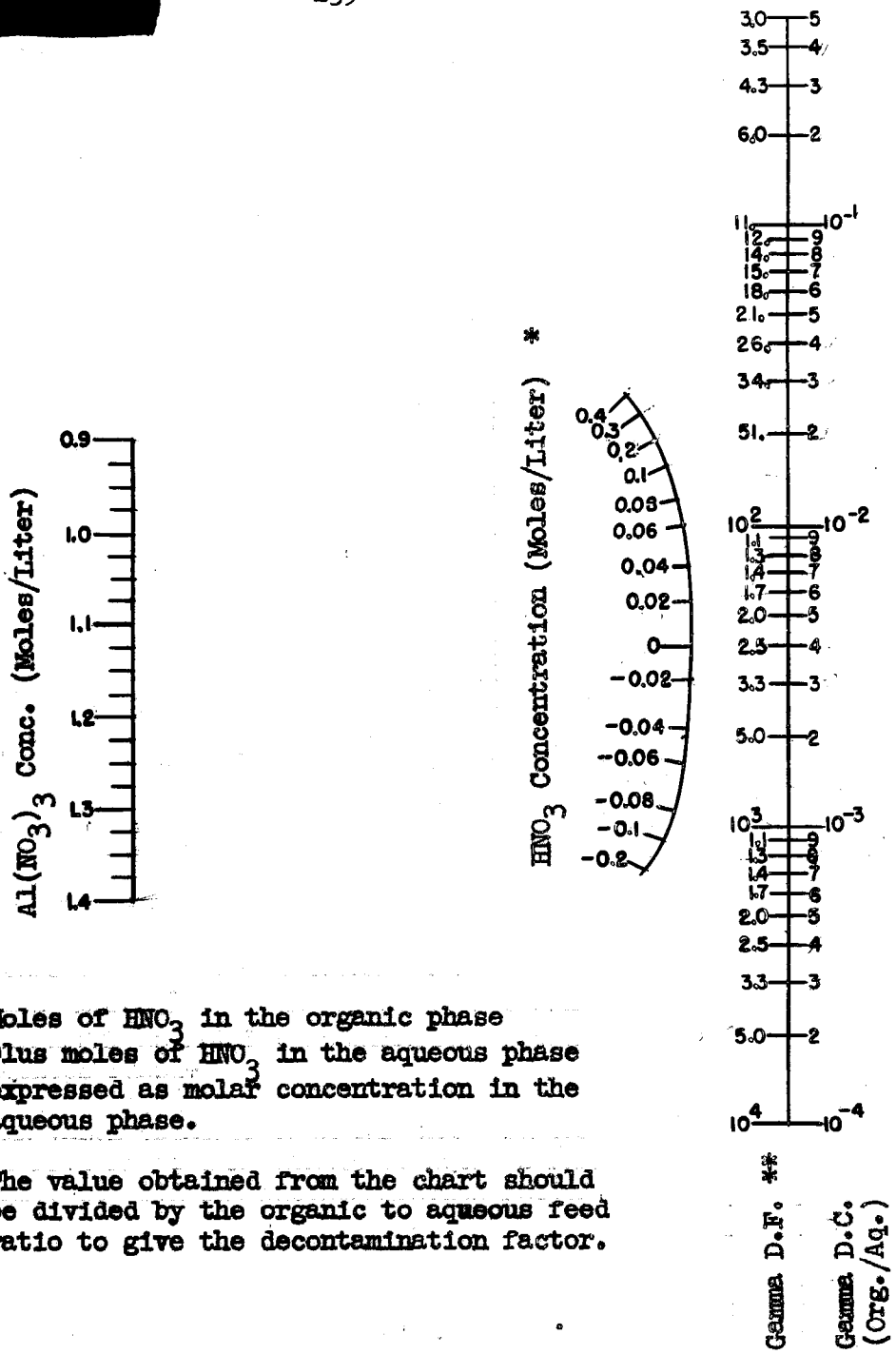
* Moles of HNO_3 in the organic phase plus moles of HNO_3 in the aqueous phase, expressed as molar concentration in the aqueous phase.

FIGURE 6.2-3

The Uranium Distribution Coefficient in Hexone Extraction as A function of $Al(NO_3)_3$ and HNO_3 Concentration

[redacted]

[redacted]



* Moles of HNO_3 in the organic phase plus moles of HNO_3 in the aqueous phase expressed as molar concentration in the aqueous phase.

** The value obtained from the chart should be divided by the organic to aqueous feed ratio to give the decontamination factor.

FIGURE 6.2-4

The Gamma Emitting Fission Product Distribution Coefficient in Hexone Extraction As A Function of $Al(NO_3)_3$ and HNO_3 Concentrations

[redacted]

[redacted]

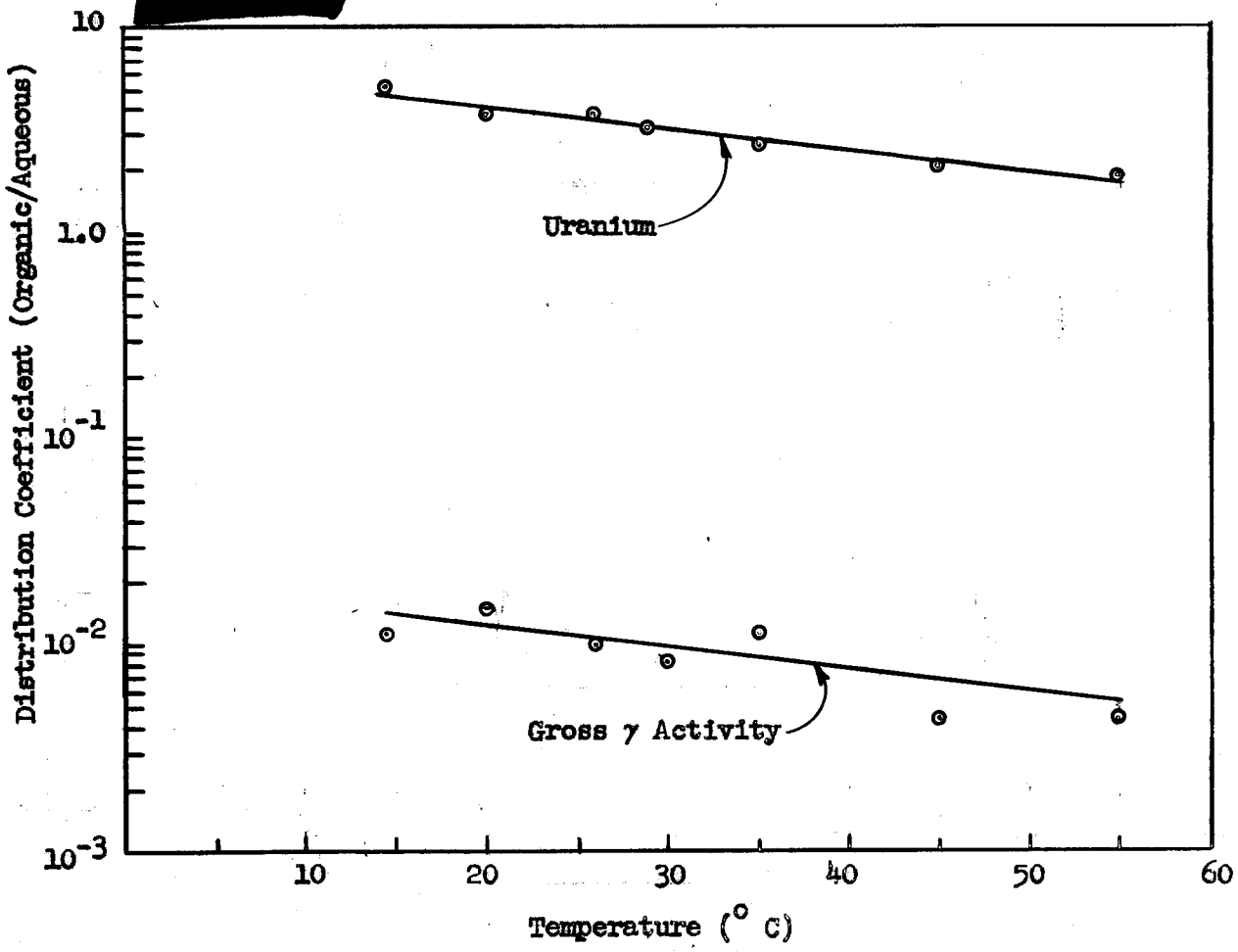


FIGURE 6.2-5

The Effect of Temperature on the Distribution Coefficients of Uranium and Fission Products

Aqueous: 1.25 M $Al(NO_3)_3$, 0.1 M $Na_2Cr_2O_7$, 0.45 M HNO_3, 5 Gms. U/Liter.

Organic: Hexone

Oxidized 1 hr. at Room Temperature, 6 Wk. Old Activity Source

[redacted]

[redacted]

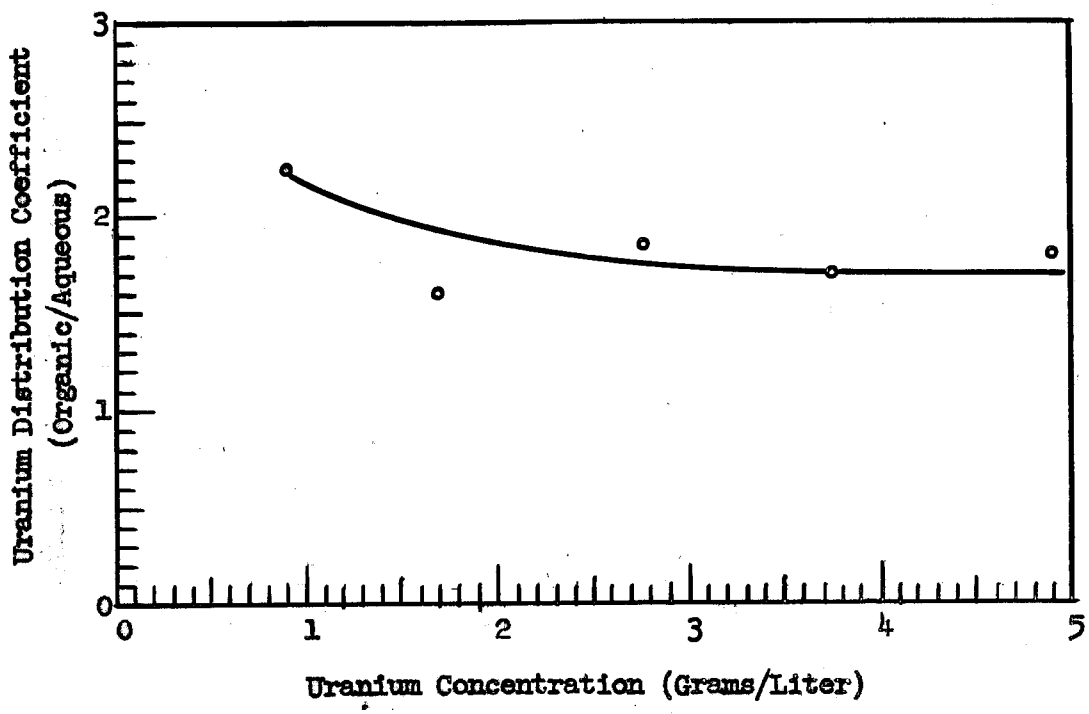


FIGURE 6.2-6

Effect of Uranium Concentration on
the Uranium Distribution Coefficient
In Equal Volume Hexone Extraction at 30°C

Aqueous: 1 M $Al(NO_3)_3$, 0.2 M HNO_3

Organic: Hexone, 0.25 M in HNO_3

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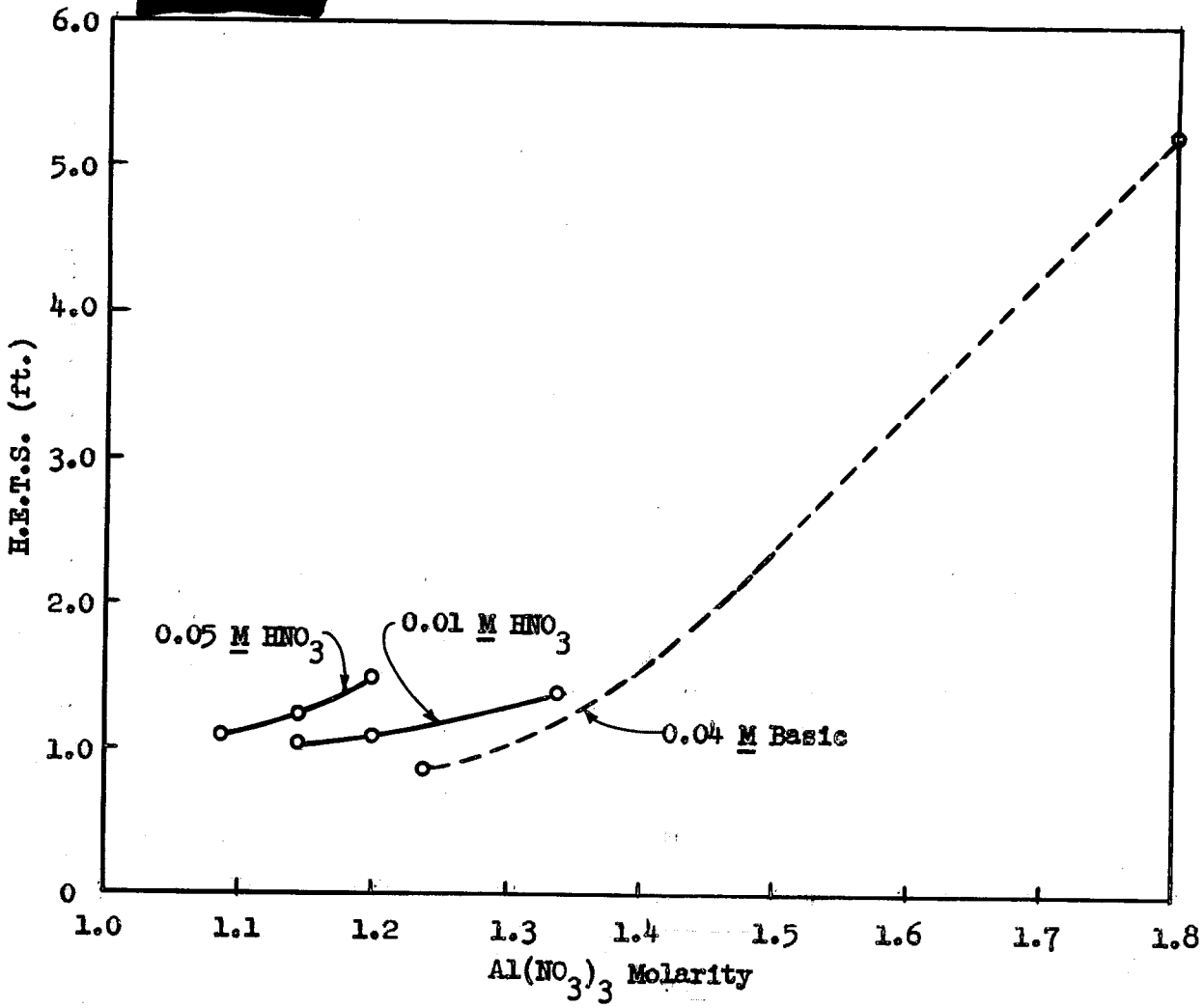


FIGURE 6.2-7

The Effect of $Al(NO_3)_3$ Concentration and Acidity On H.E.T.S. In First Cycle Extraction

Conditions:

Aqueous Feed: $Al(NO_3)_3$ (variable conc.)
HNO_3 (variable), 0.1 M $Na_2Cr_2O_7$

Organic Feed: Hexone - Pretreated

Flow Rates: 25 cc/min for each phase

Temperature: 20° C

Column: Glass, 1 inch in diameter, packed with 3/16-inch Fenske rings.
Interface at top

[redacted]

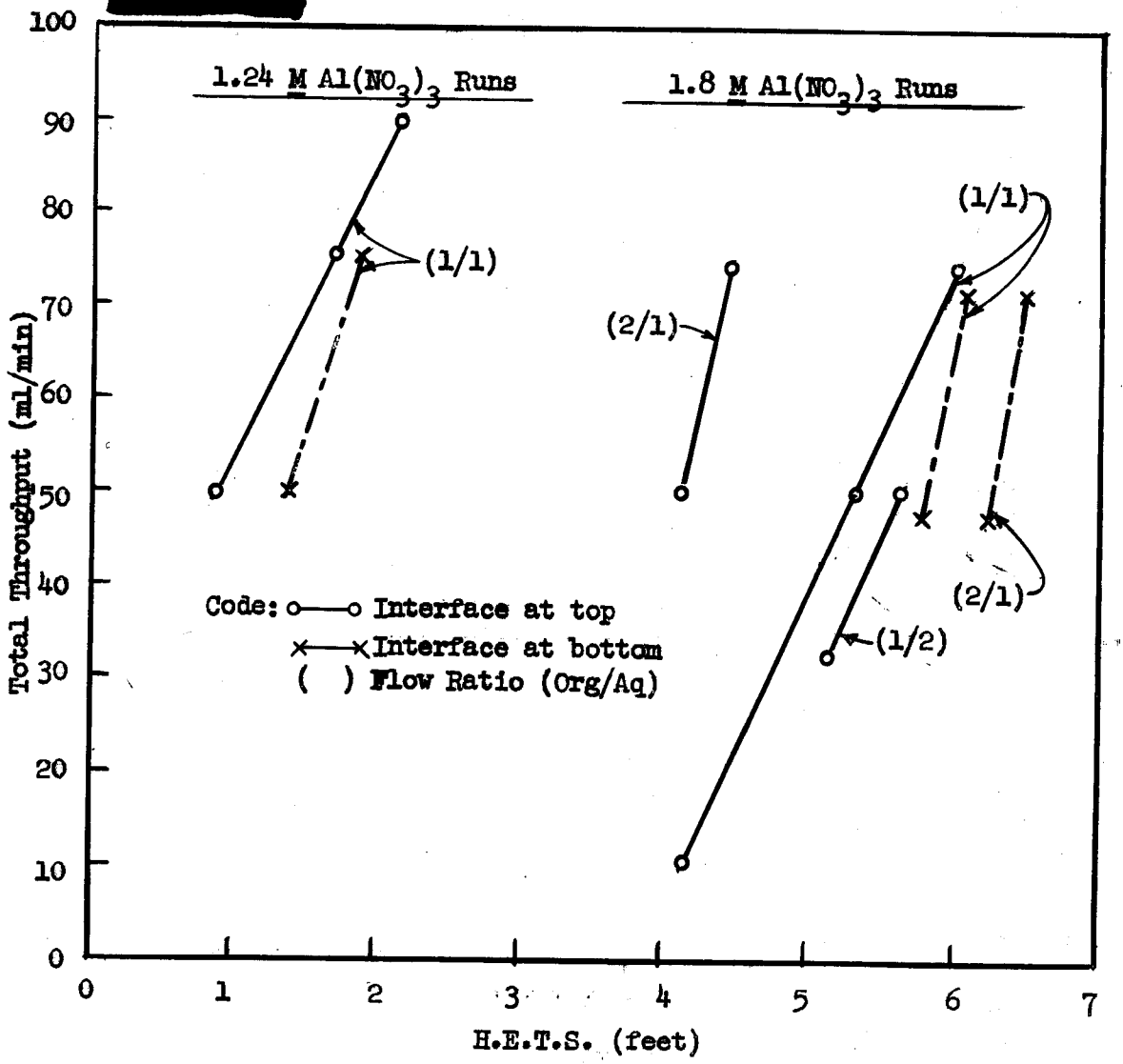


FIGURE 6.2-8

H.E.T.S. Versus Total Throughput at Various Flow Ratios

Aqueous Feed: 1.24 or 1.8 M $Al(NO_3)_3$, 0.1 M $Na_2Cr_2O_7$, 0.04 M acid deficient.

Organic Feed: Hexone -- (Pretreated and neutral)

Temperature: 20° C

Column: Glass, 1 inch in diameter, packed with 3/16-inch Fenske rings

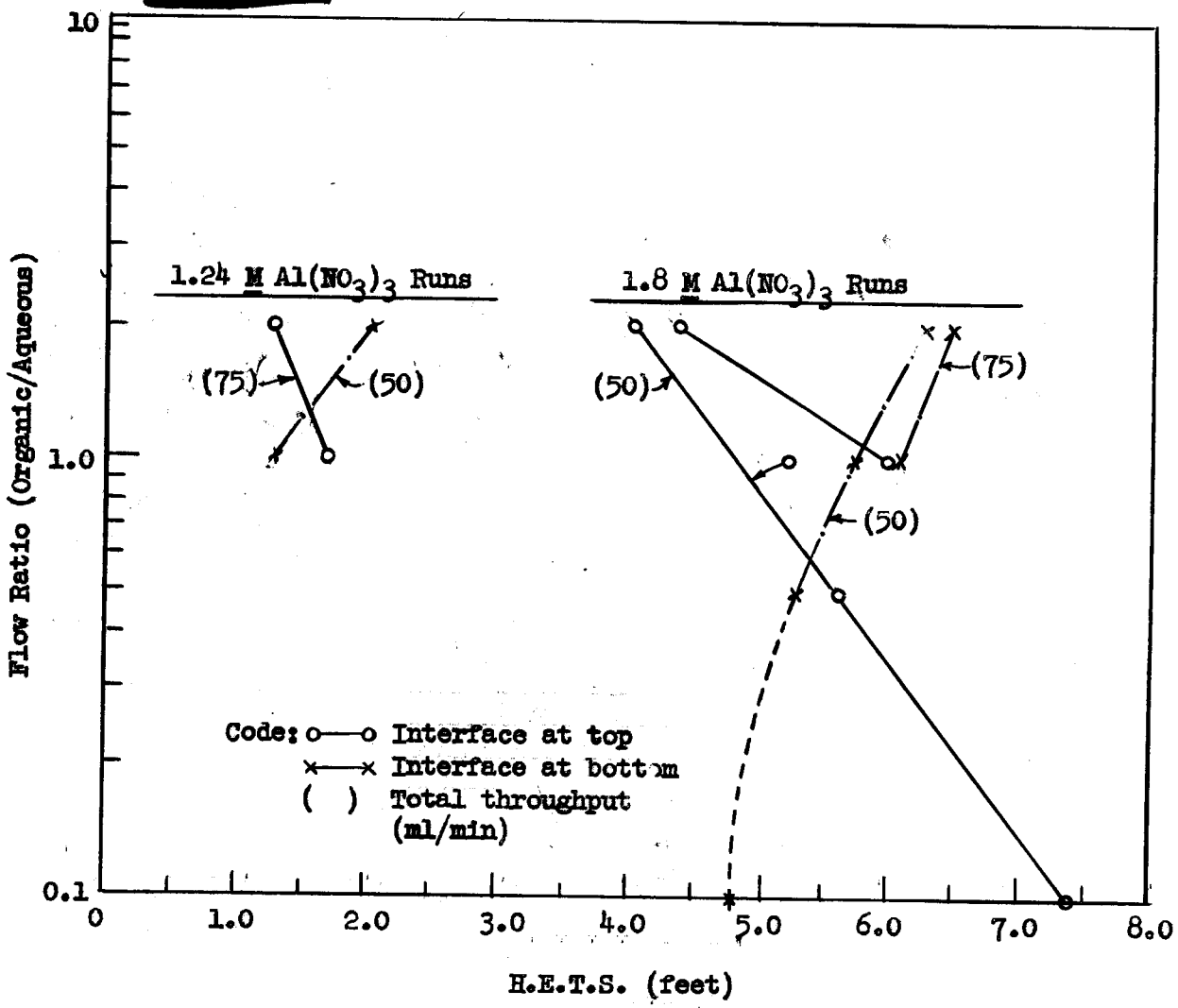


FIGURE 6.2-9

The Effect on the H.E.T.S. of Flow Ratio and Interface Position at Various Total Throughputs

Conditions (First Cycle Extraction):

Aqueous Feed: 1.24 or 1.8 M $Al(NO_3)$, 0.1 M $Na_2Cr_2O_7$, 0.04 M basic

Organic Feed: Hexone -- (Pretreated and Neutral)

Temperature: 20° C

Column: Glass, 1 inch in diameter, packed with 3/16-inch Fenske rings

[redacted]

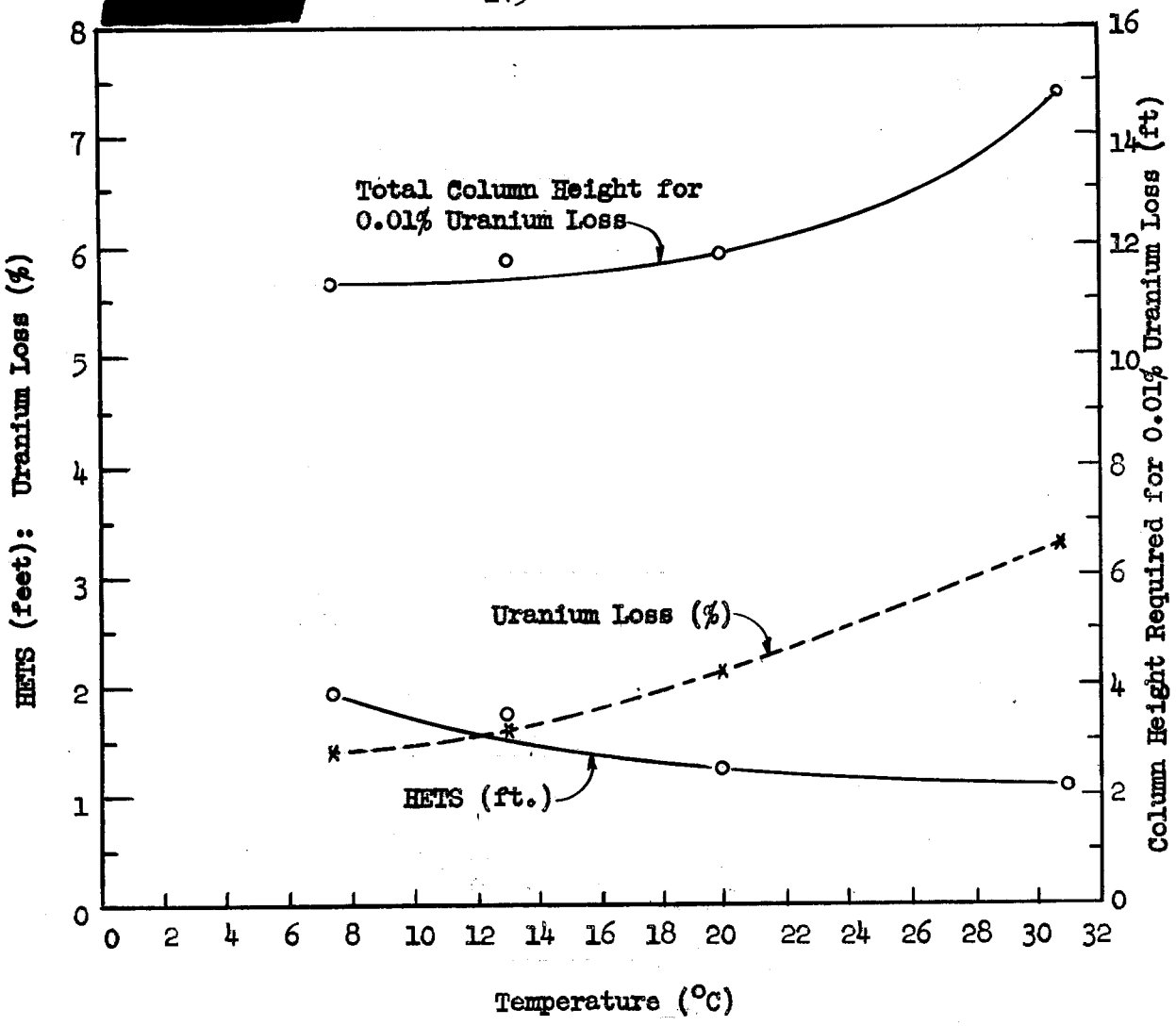


FIGURE 6.2-10

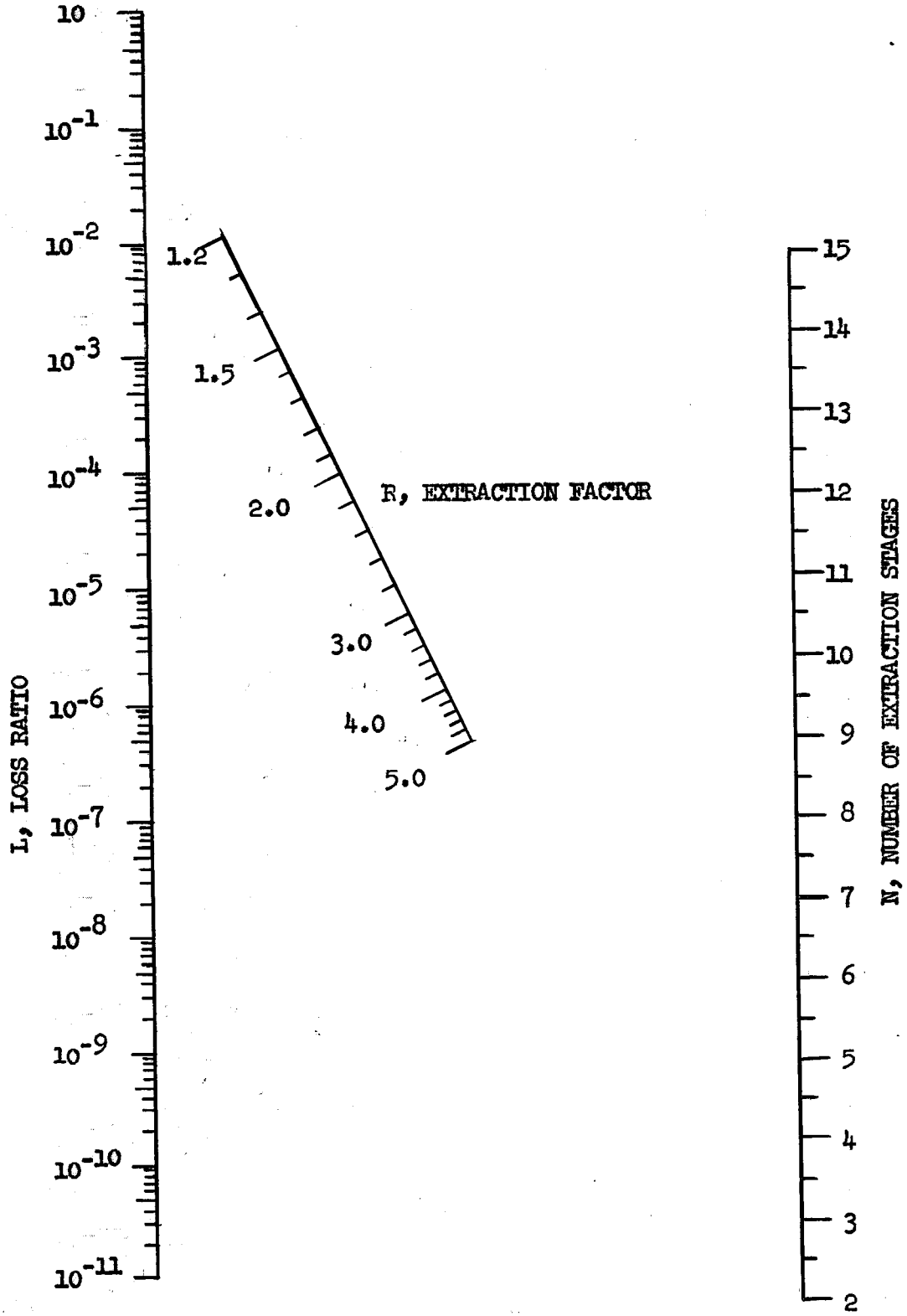
The Effect of Temperature on Column Extraction

Aqueous Feed: 1.2 M $Al(NO_3)_3$
0.1 M $Na_2Cr_2O_7$
0.1 M HNO_3

Organic Feed: Pretreated hexone, made 0.1 M in HNO_3

Column: Glass, 1 inch in diameter, packed with 3/16 inch Fenske rings to a height of 4 ft.

[redacted]



$$L = \frac{R - 1}{R^{n+1} - 1}$$

FIGURE 6.2-11

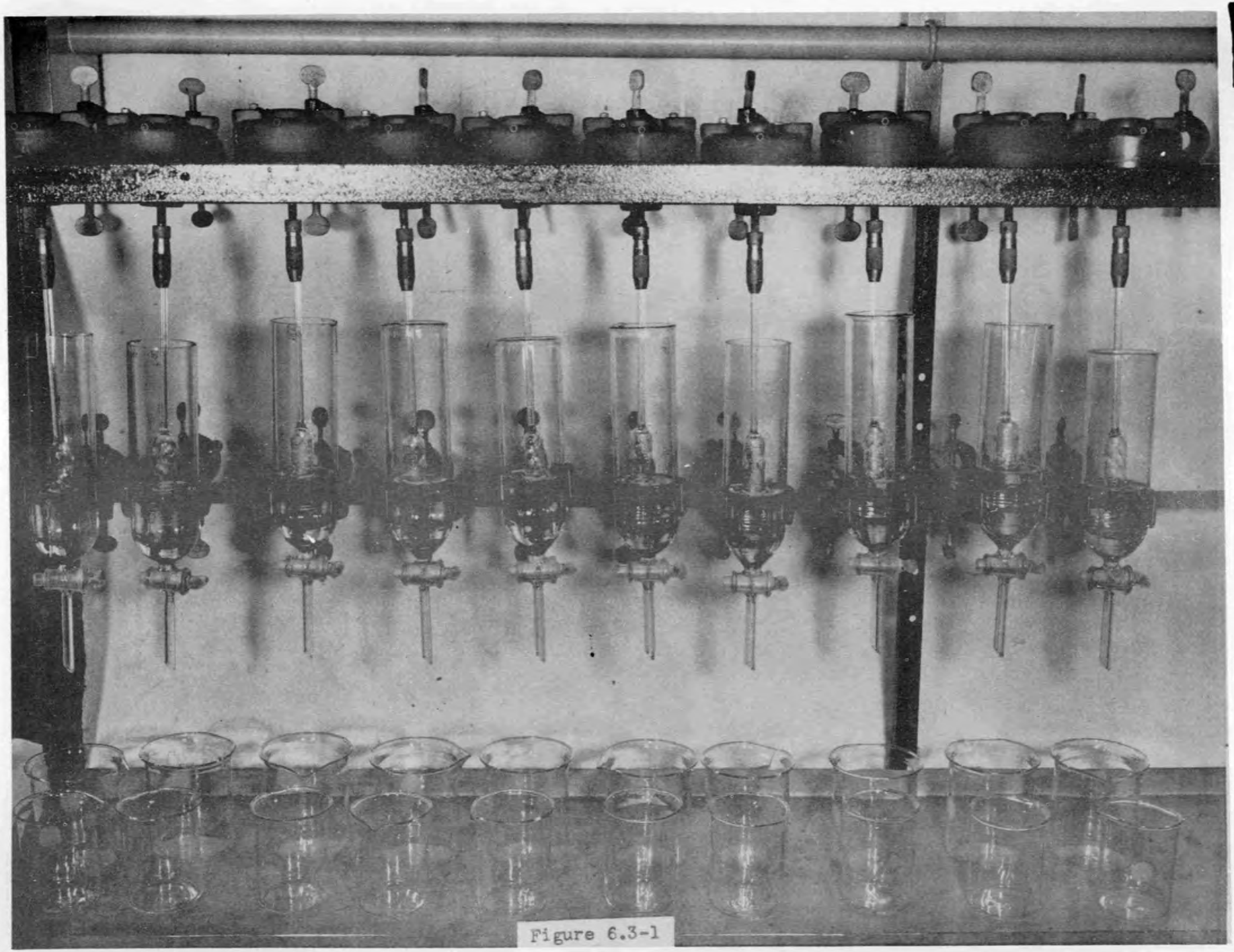


Figure 6.3-1

Photo #3925

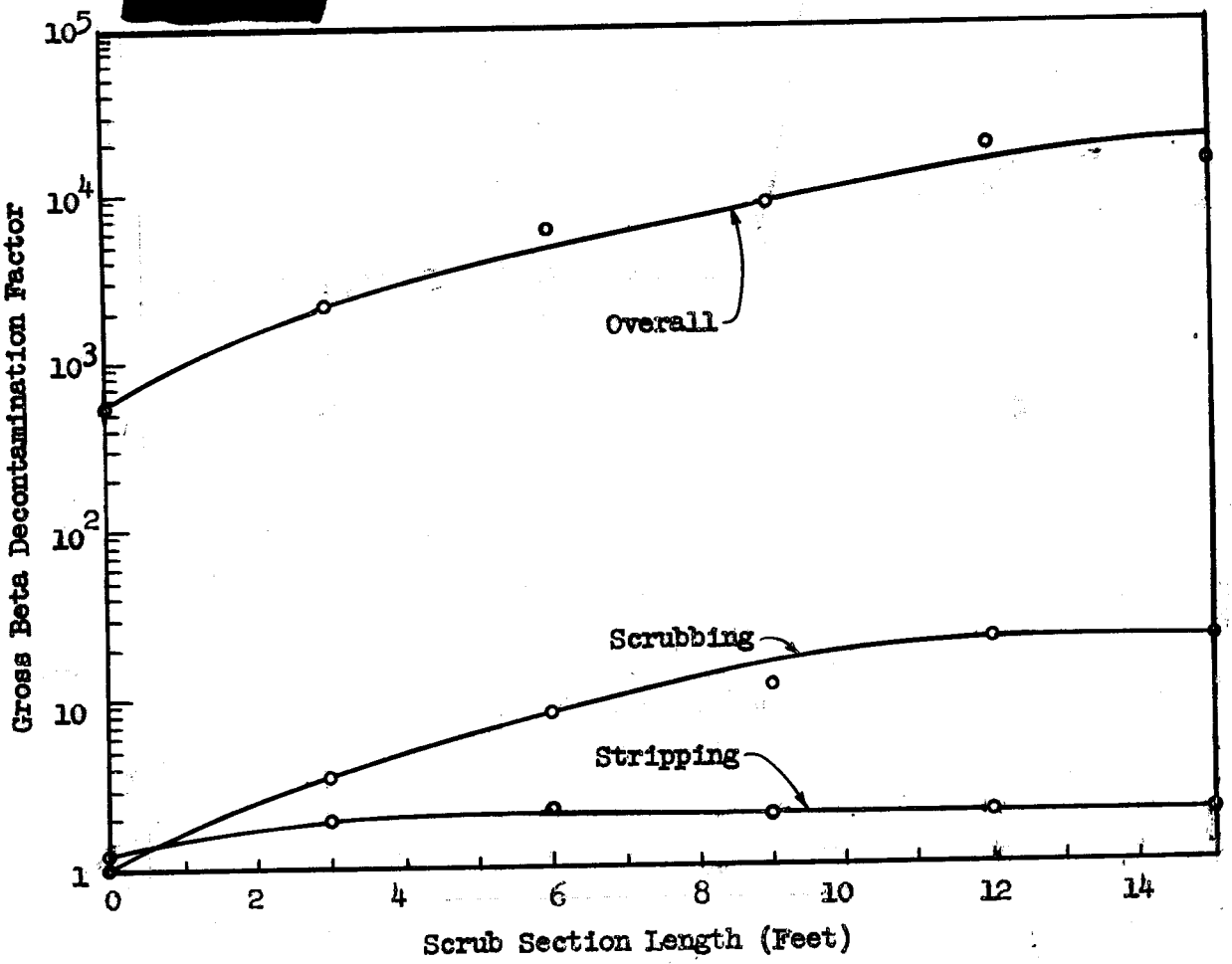


FIGURE 6.3-2

Gross Beta Decontamination As A Function of Scrub Section Length

Feed (4 volumes): 1.3 M $Al(NO_3)_3$, 0.05 M HNO_3 deficient, 7 gms. U/liter

Scrub (1 volume): 1.3 M $Al(NO_3)_3$, 0.05 M HNO_3, deficient

Solvent (10 volumes): Hexone

Column: 1" diameter glass pipe packed with 3/16" diameter. Fenske rings, 10 feet of extraction.

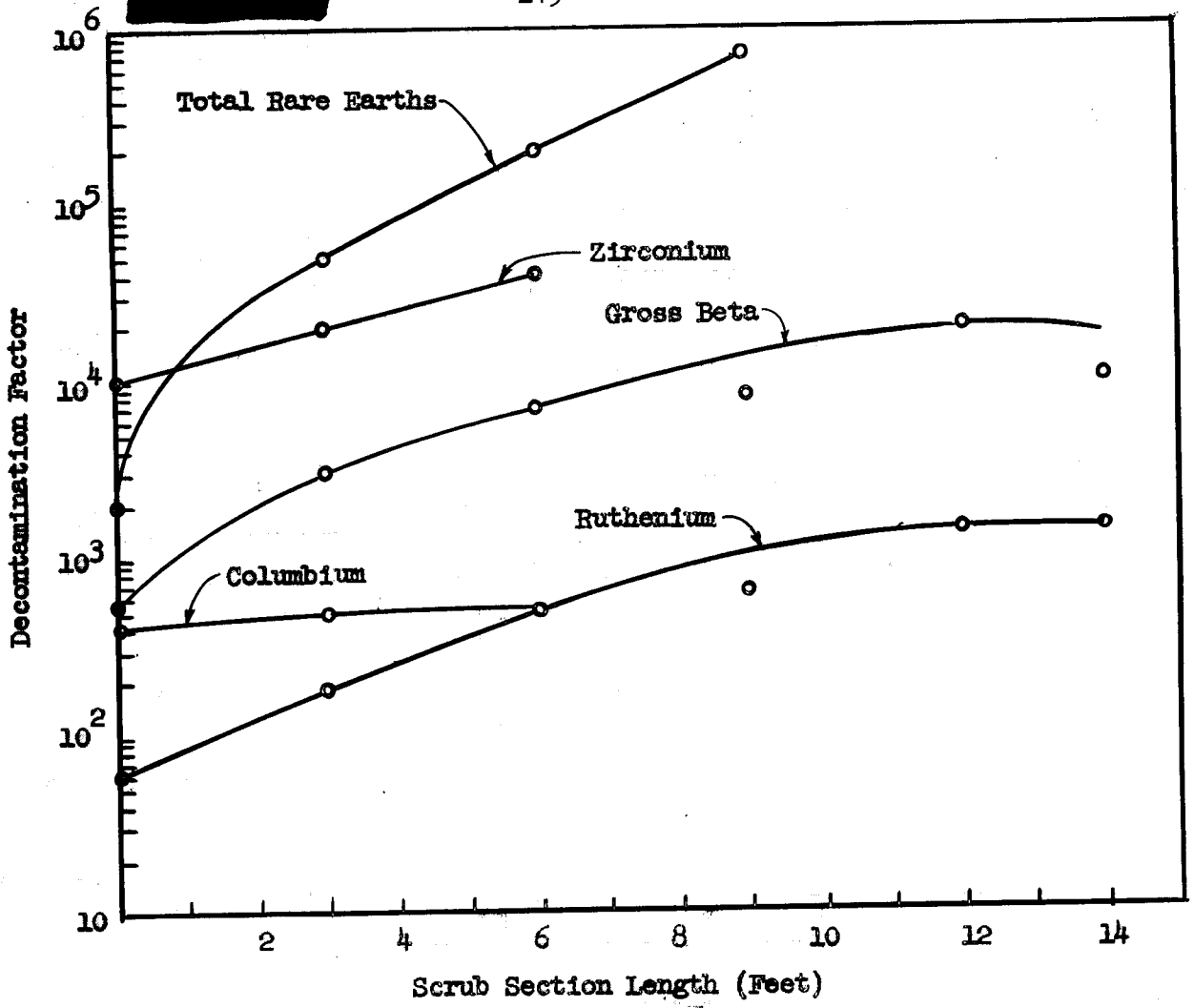


FIGURE 6.3-3

The Overall Decontamination of Specific Fission Products as a Function of Scrub Section Length

Feed (4 volumes): 1.3 M $Al(NO_3)_3$, 0.05 M HNO_3 deficient, 7 gms. U/liter

Scrub (1 volume): 1.3 M $Al(NO_3)_3$, 0.05 M HNO_3 deficient

Column: 1" diameter glass pipe packed with 3/16" diameter Fenske rings; 10 feet of extraction.

Solvent (10 volumes): Hexone

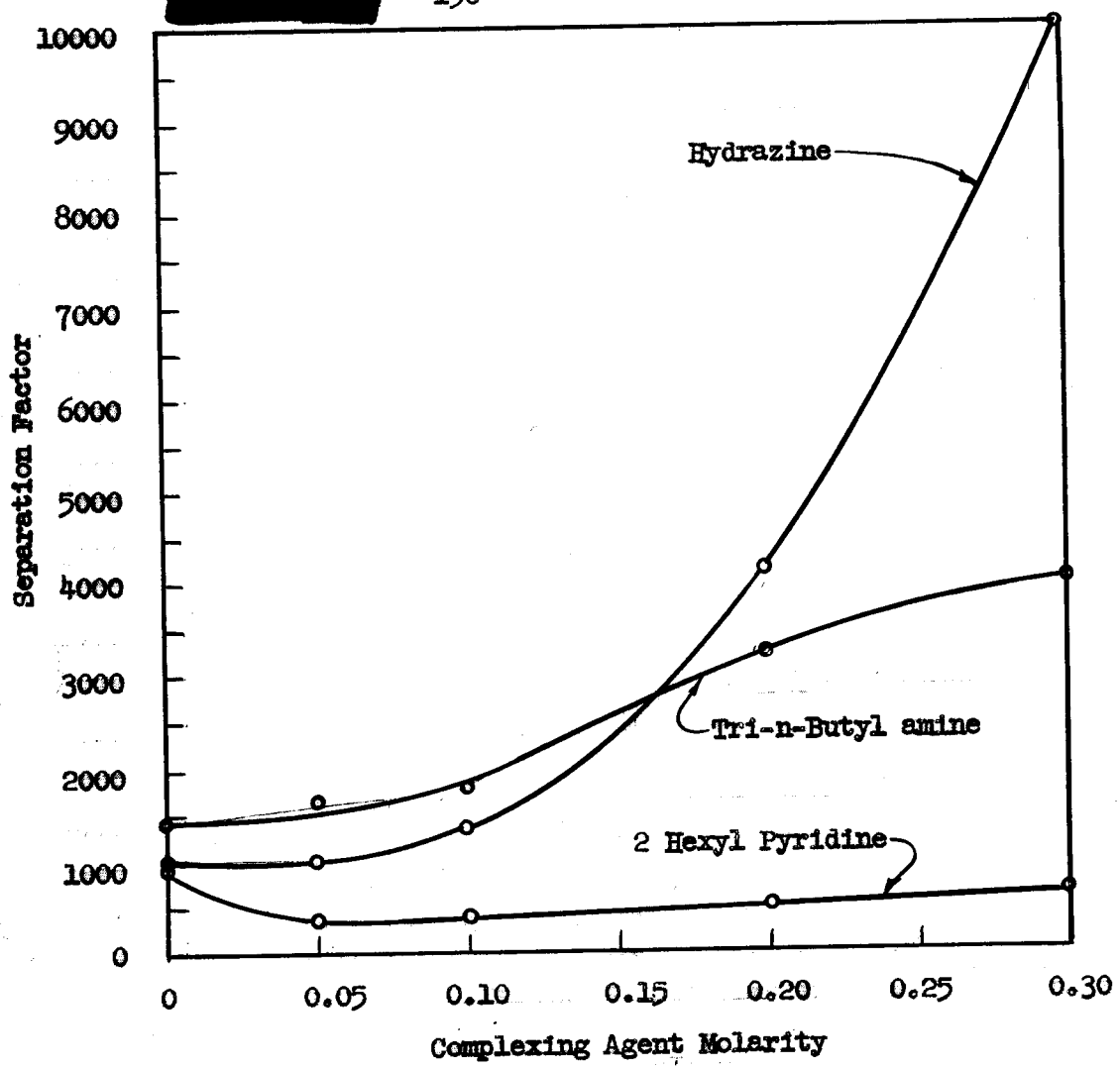


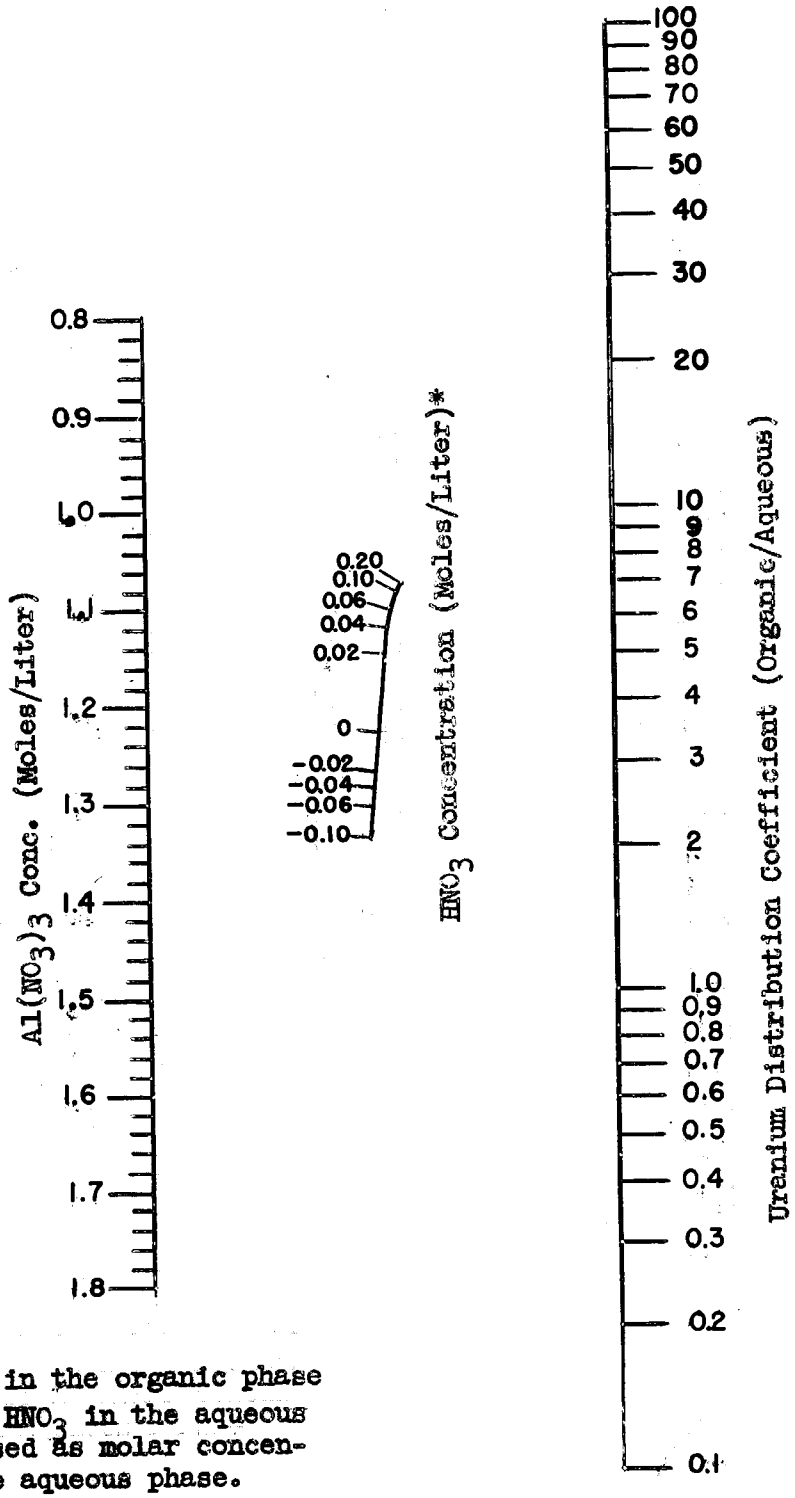
FIGURE 7.2-1

The Separation Factor as a Function of Complexing Agent Concentration

Aqueous: 1.3 M $Al(NO_3)_3$; 0.05 M HNO_3 deficient

Solvent: Hexone (Volume equal to aqueous phase volume)

[redacted]



* Moles of HNO_3 in the organic phase plus moles of HNO_3 in the aqueous phase, expressed as molar concentration in the aqueous phase.

FIGURE 7.2-2

The Distribution Coefficients of Uranium in the System $Al(NO_3)_3$-H_2O-HNO_3-0.1 M N_2H_4-Hexone

[redacted]

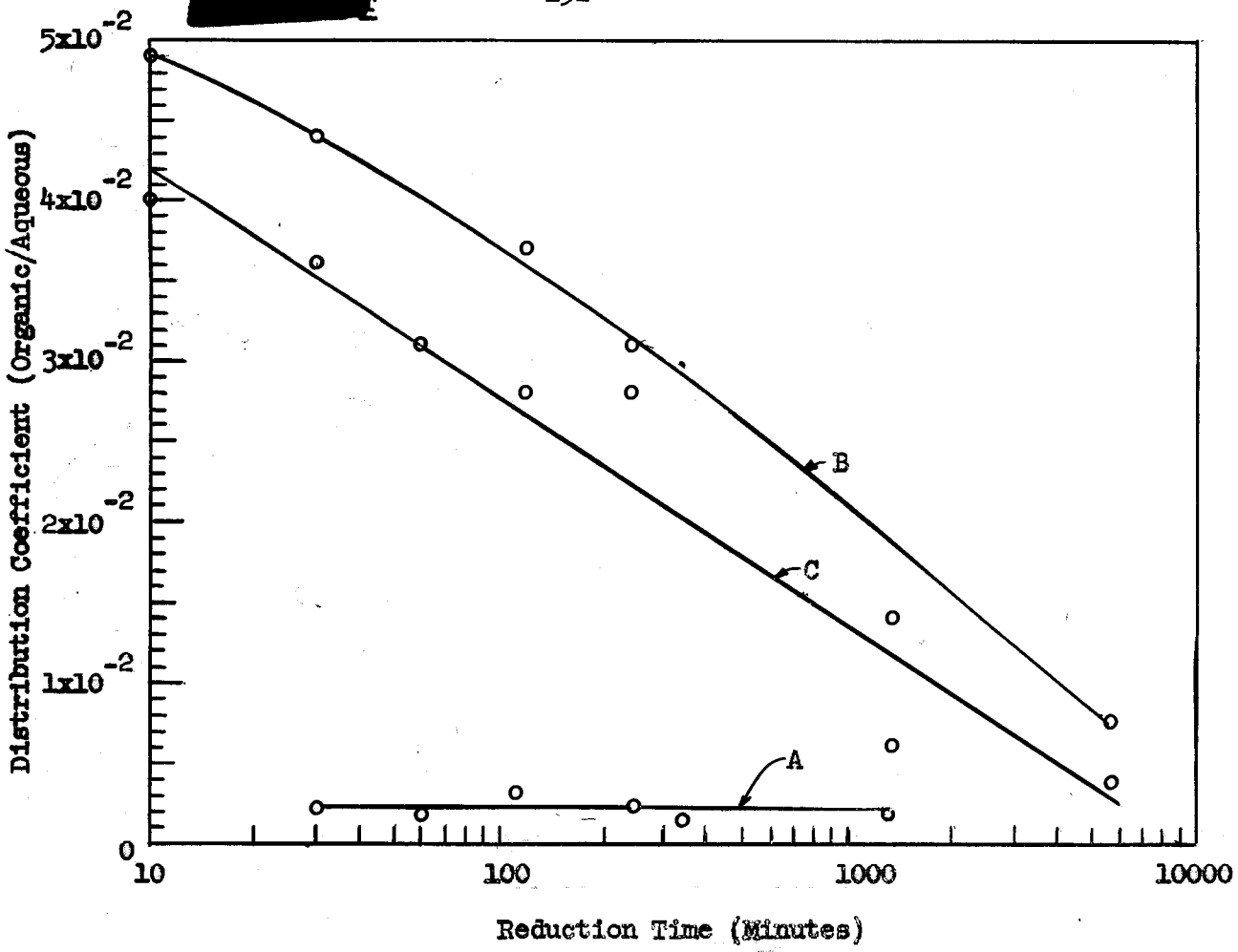


FIGURE 7.2-3

The Effect of Reduction Time on the Distribution Ratio of Fission Products in the Hexone Extraction of Solutions Containing Hydrazine

Aqueous: A - 1.3 M $Al(NO_3)_3$*; 10 gms. U/liter; 0.5 M $N_2H_4 \cdot HNO_3$; 0.05 M HNO_3 deficient. Digested at 85° C.

B - 1.0 M $Al(NO_3)_3$; 10 gms. U/liter; 0.5 M $N_2H_4 \cdot HNO_3$; 0.05 M HNO_3 deficient; Digestion at Room Temperature

C - Same as in B except 0.05 M in Fe (2)

Solvent: Hexone (Equal volume extraction, 10 minutes equilibration)

Digestion Time	Gross Gamma Distribution (org/aq) x 10^3		
	Reduction at Room Temperature		Reduction at 85° C*
	No Fe (2)	0.05 M Fe (2)	
10 minutes	49	40	---
30 minutes	44	36	2.1
1 hour	50	31	1.8
2 hours	37	28	3.1
4 hours	31	28	2.2
6 hours	---	---	1.4
24 hours	14	6.0	1.4
96 hours	7.7	4.1	---

* It is estimated that the fission product distribution ratio is increased by about 30% in going from 1.0 M $Al(NO_3)_3$ to 1.3 M $Al(NO_3)_3$.

[redacted]

[redacted]

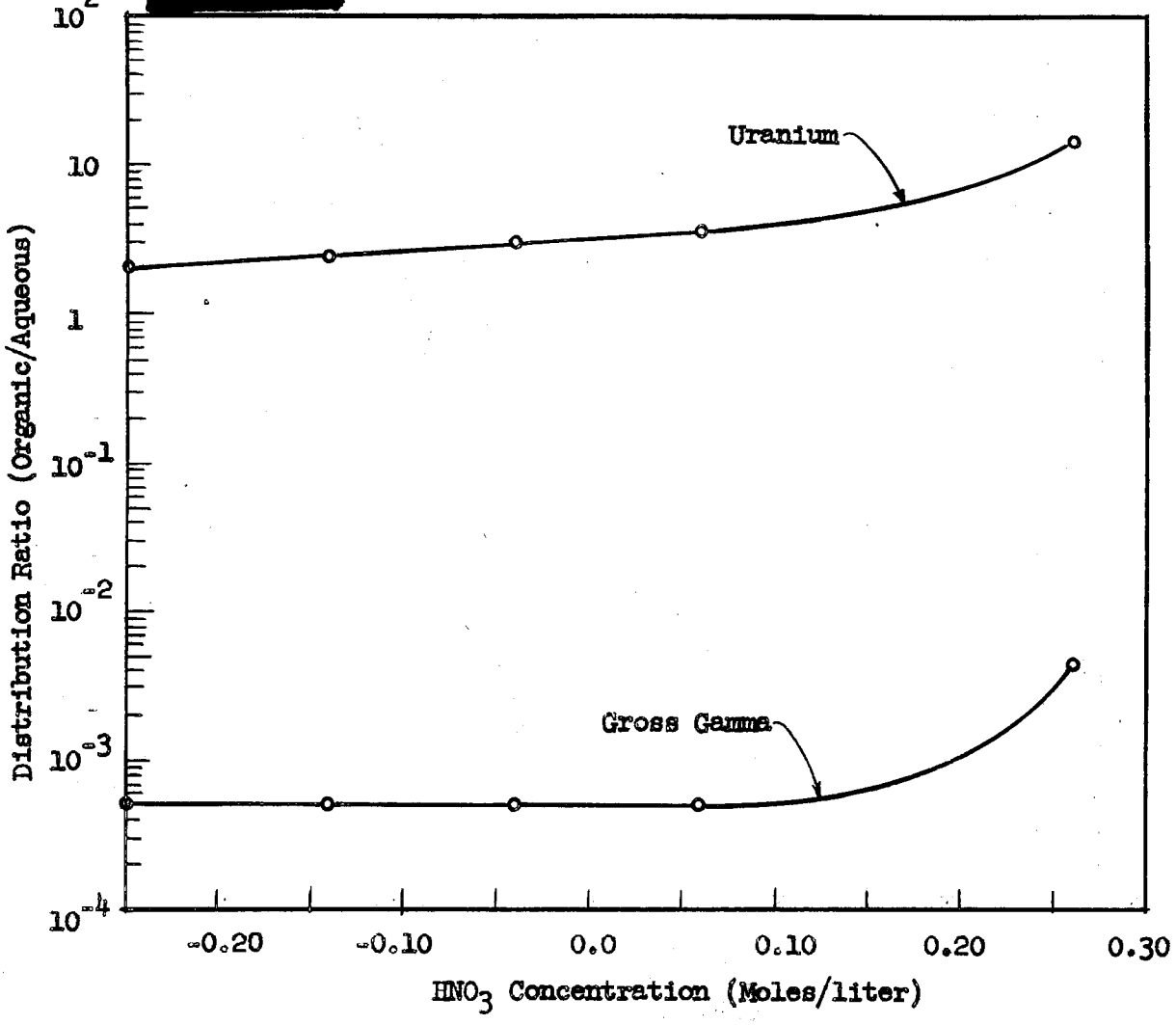


FIGURE 8.4-1

The Effect of HNO_3 Concentration on the Uranium and Gross Gamma Distribution Ratio in Dibutyl Cellosolve Extraction

Aqueous: 2 M $Al(NO_3)_3$, 0.1 M $Na_2Cr_2O_7$, 5 gms. U/liter.
One hour oxidation at 25° C.

[redacted]

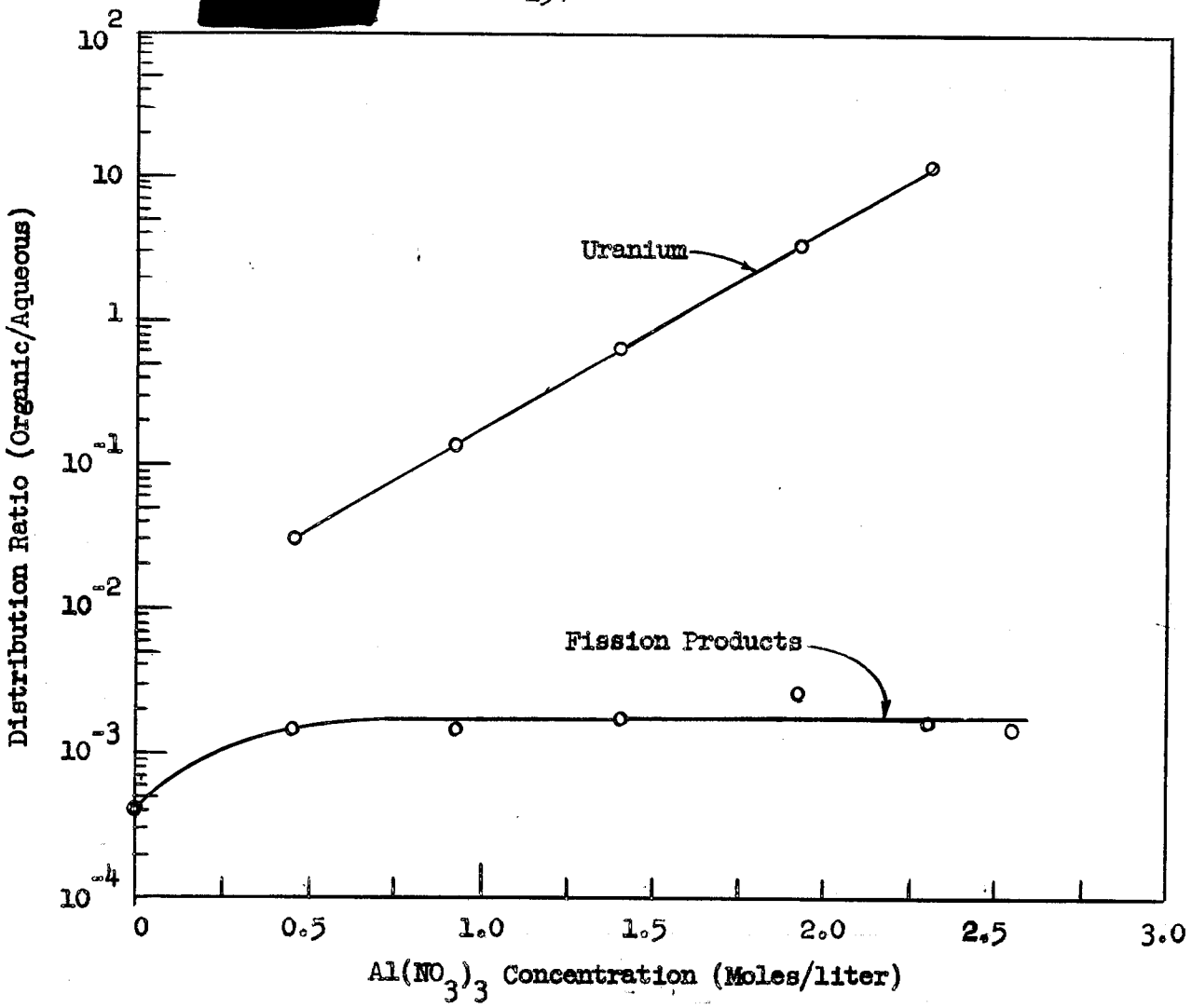


FIGURE 8.4-2

The Effect of $Al(NO_3)_3$ Concentration on the Uranium and Fission Product Distribution Ratios in Dibutyl Cellosolve Extraction

Aqueous: 0.2 M HNO_3, 0.1 M $Na_2Cr_2O_7$, 5 gms. U/liter. Oxidized 1 hour at room temperature.

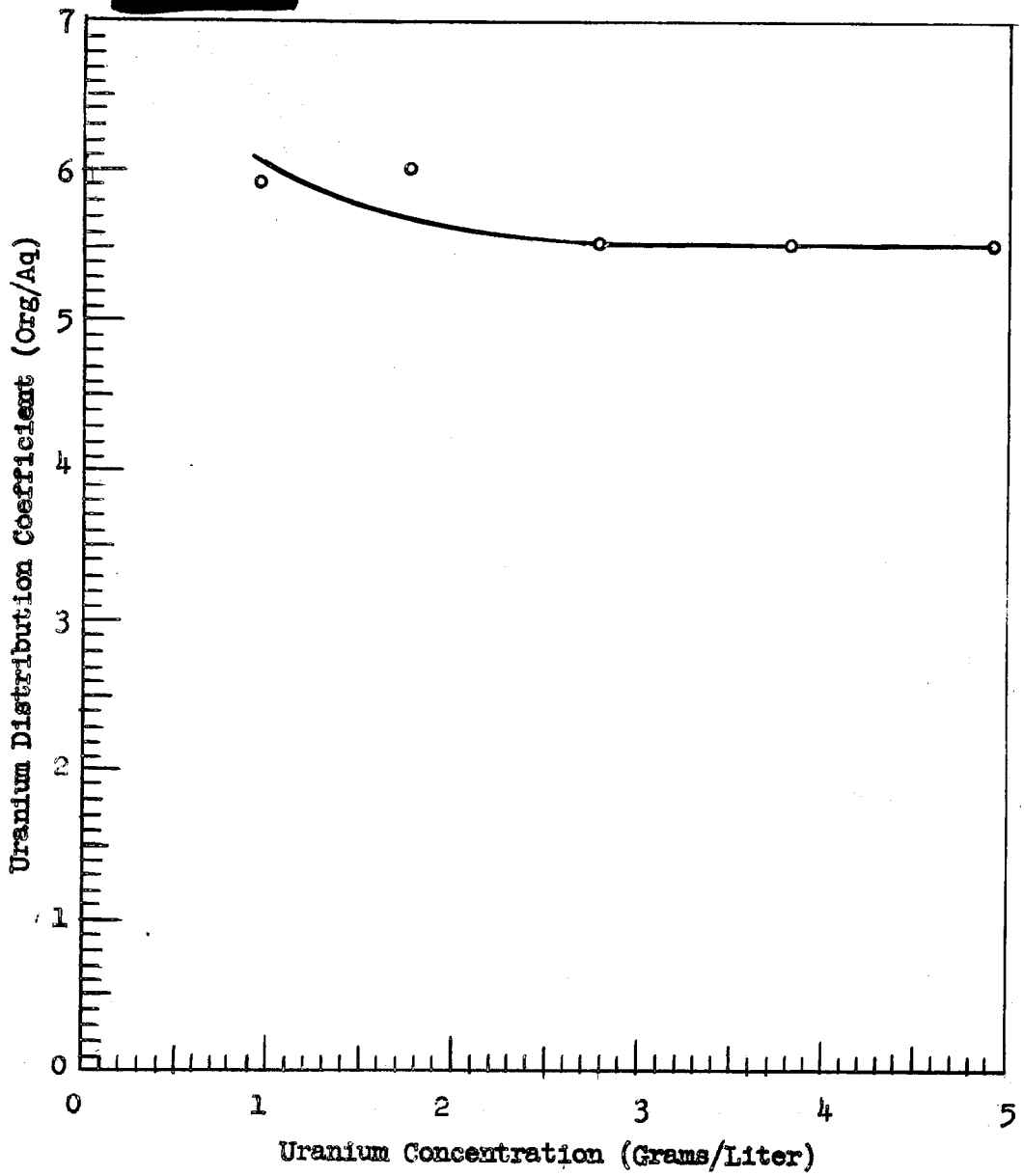


FIGURE 8.4-3

The Effect of Uranium Concentration on Uranium Distribution Coefficient in Dibutyl Cellosolve Extraction

Aqueous: 2 M $Al(NO_3)_3$
0.1 M HNO_3

Solvent: Dibutyl Cellosolve, 0.17 M in HNO_3

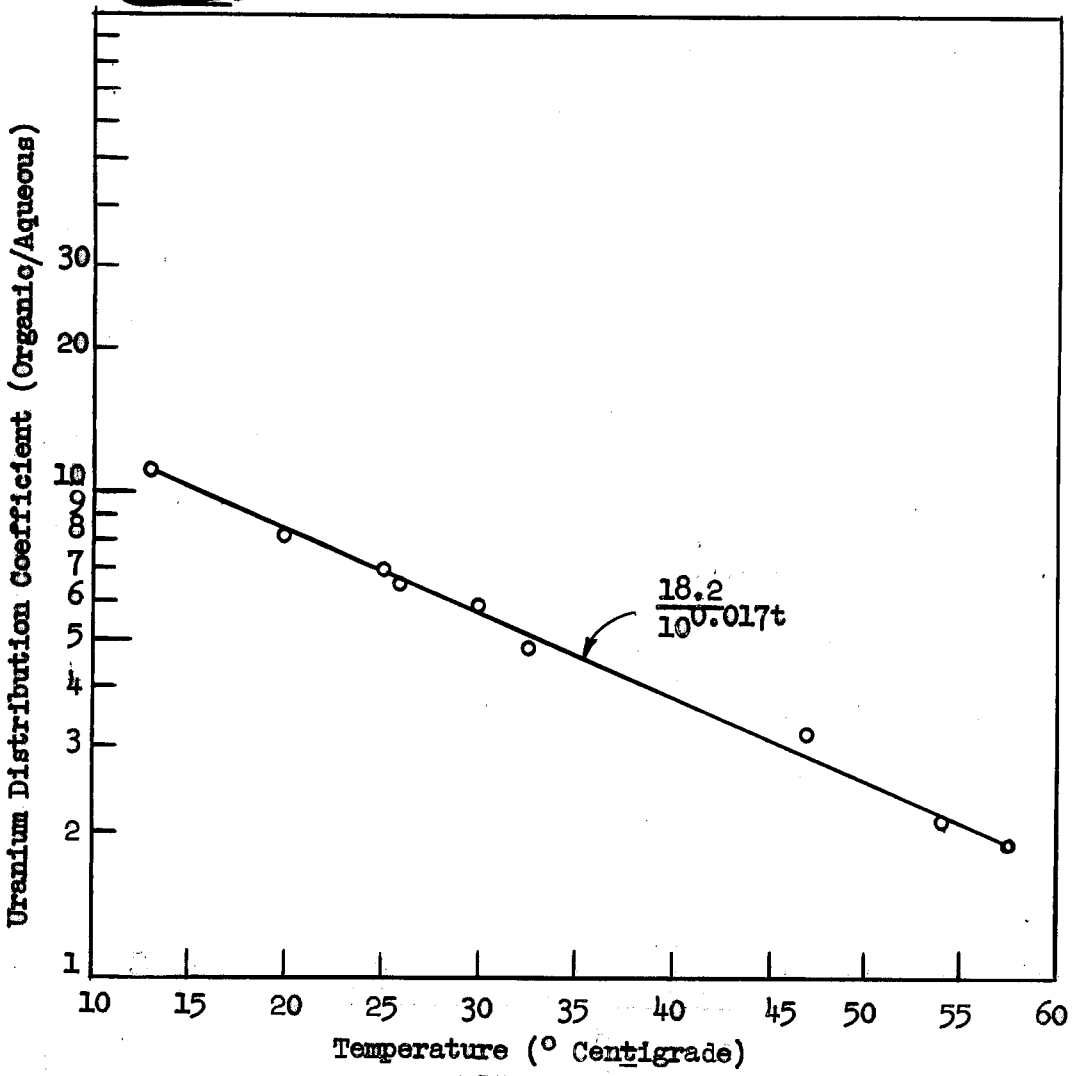


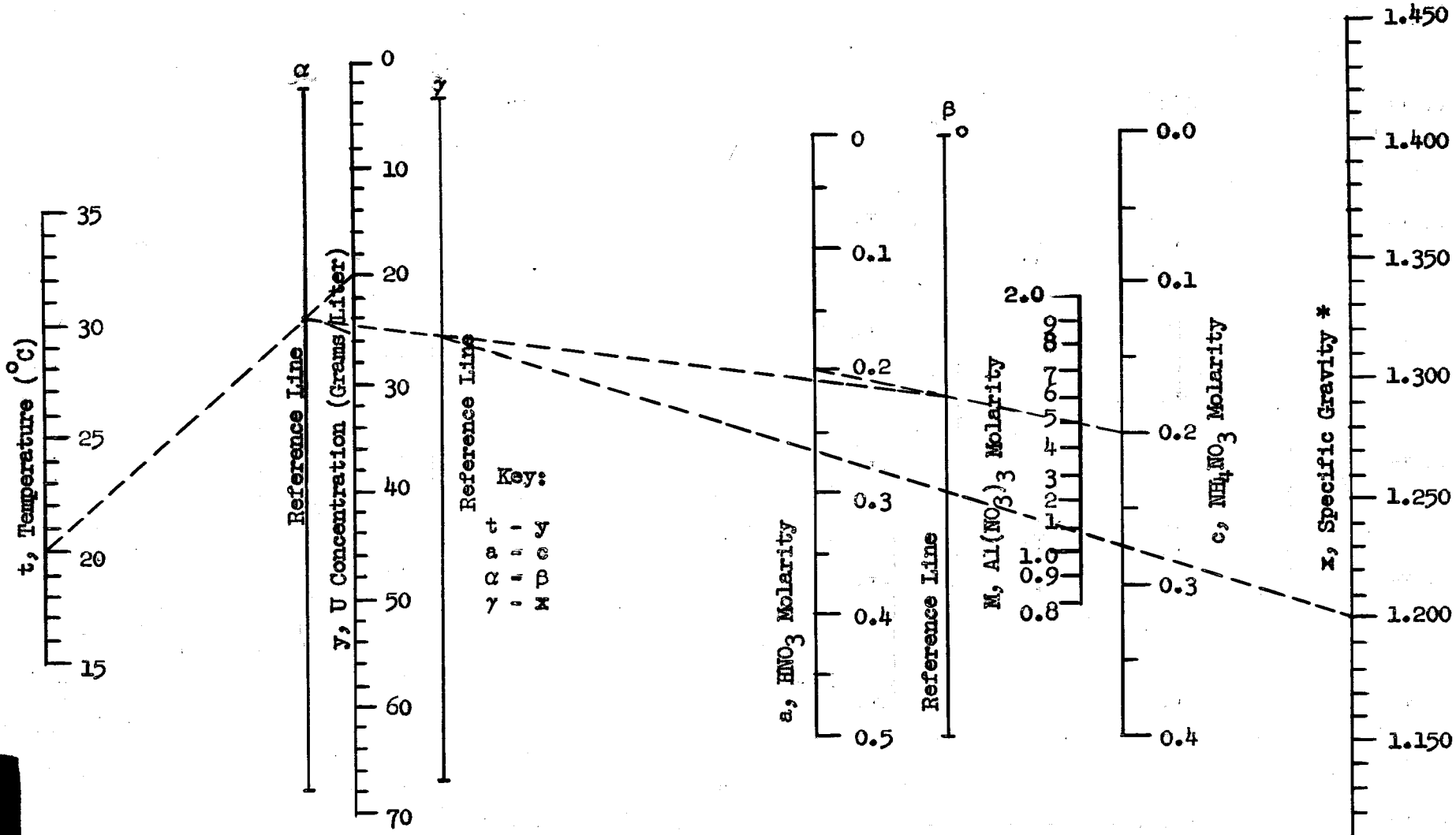
FIGURE 8.4-4

Effect of Temperature on the Uranium Distribution Coefficient in Equal Volume DiButyl Cellosolve Extraction

Aqueous: 2 M $Al(NO_3)_3$, 0.1 M HNO_3

Solvent: DiButyl Cellosolve 0.17 M in HNO_3

[redacted]



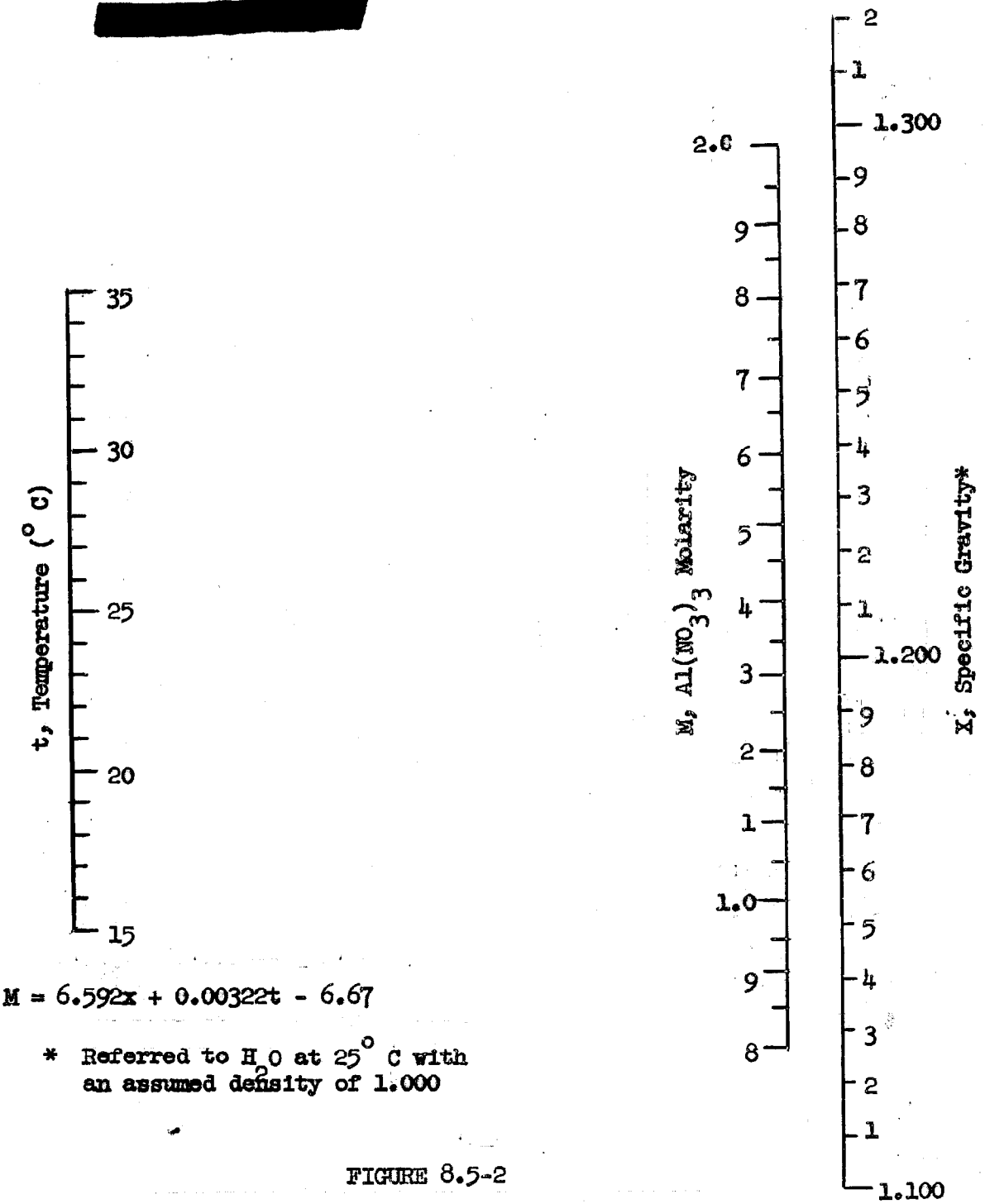
* Referred to H_2O at 25° C with an assumed density of 1.000

$$M = 6.592x - 0.00834y + 0.00322t - 0.171a - 0.165c - 6.672$$

FIGURE 8.5-1

Nomograph for Determining $Al(NO_3)_3$ Molarity in the System $Al(NO_3)_3 - UO_2(NO_3)_2 - HNO_3 - NH_4NO_3 - H_2O$

[redacted]



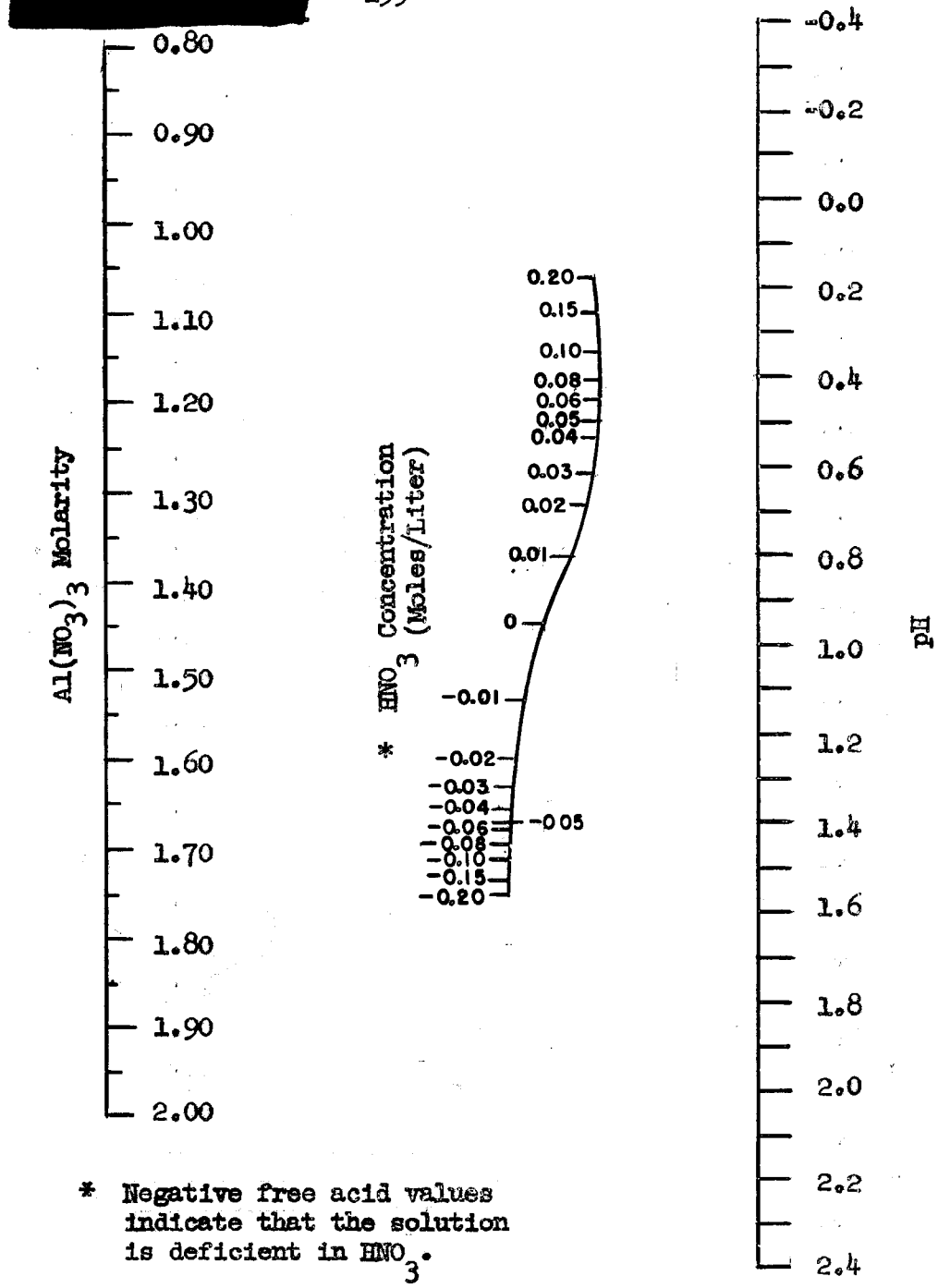
$M = 6.592x + 0.00322t - 6.67$

* Referred to H_2O at 25° C with an assumed density of 1.000

FIGURE 8.5-2

Nomograph for determining $Al(NO_3)_3$ Molarity in the System $Al(NO_3)_3 - H_2O$

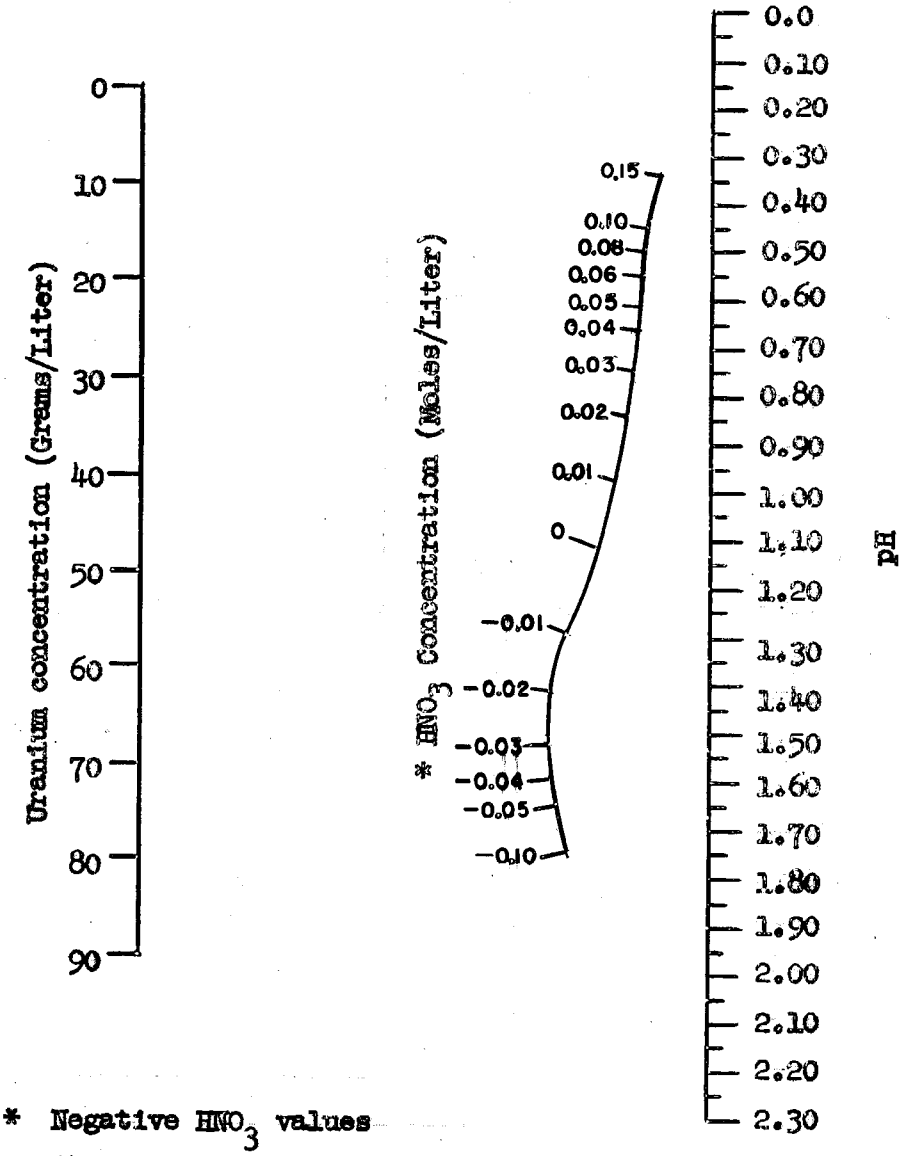
[redacted]



* Negative free acid values indicate that the solution is deficient in HNO_3.

FIGURE 8.5-3

Free HNO_3 as a function of $Al(NO_3)_3$ Concentration and pH in the System $Al(NO_3)_3$ - HNO_3 (or NaOH) - H_2O. Temperature 25° C



* Negative HNO_3 values indicate that the solution is deficient in HNO_3.

FIGURE 8.5-4

pH as a function of $UO_2(NO_3)_2$ and HNO_3 Concentration in the System $Al(NO_3)_3$ - HNO_3 (or NH_4OH) - H_2O. Temperature 52° C

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F. R. Bruce

F. R. Bruce

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