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CHEMICAL TECHNOLOGY DIVISION
CHEMICAL DEVELOPMENT SECTION C
PROGRESS REPORT FOR
AUGUST-SEPTEMBER 1961

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CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section C
Progress Report for
August-September 1961

Date Issued

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ABSTRACT

Final Cycle Plutonium Recovery by Amine Extraction

In development of final cycle plutonium recovery by extraction with amines, batch countercurrent testing of a proposed chemical flowsheet with simulated Purex 1BP solution confirmed the phase stability of the loaded extractant, the validity of the previously-reported extraction isotherm data, the operability of the acetic acid stripping system, and overall good physical behavior in phase mixing and disengagement. Zr-Nb⁹⁵ tracer at 7×10^5 γ counts/min ml in the feed could not be measured directly in the product; radiochemical zirconium analysis indicated a decontamination factor from zirconium of 5×10^4 .

Extraction Performance of Degraded Process Extractants: Effect of TBP on Degradation of Amsco 125-82 with Nitric Acid

Degradation of Amsco 125-82 by irradiating or by heating in the presence of HNO₃ was more severe when TBP was present than when it was not. This is presumed to be a consequence principally of complexing by TBP and extraction into the solvent of HNO₃ and possibly HNO₂. The same degradation products (nitro-paraffins) were found to result from either irradiation or heating as determined by Zr-Nb⁹⁵ extraction tests, measurements of nitrogen content of the organic phase, and examination of ultraviolet spectra of the solvents. The degradation varied linearly with exposure. When no TBP was present equivalent degradation was achieved at 90 watt hr/liter irradiation or 9 hours' contact with boiling 2 M HNO₃. The irradiation tests also provided estimates of the radiation-induced decomposition of HNO₃ ($G_{\text{HNO}_3} \sim 5$), the formation of DBP ($G_{\text{DBP}} \sim 2$) and the formation of HNO₂.

Fission Product (Cesium) Recovery

Sodium dinonylnaphthalenesulfonate (0.5 M in hexone) selectively extracts cesium ($E_{\alpha}^0 \approx 0.5$) from simulated low nitric acid (formaldehyde treated) Purex 1WW waste which has been complexed with tartrate and neutralized to pH ~ 12 . Dilute nitric acid readily strips the cesium and sodium from the solvent.

Monoheptadecylphosphoric acid extracts cesium in preference to sodium from acidic cesium - sodium nitrate solutions. Single stage separation factors may be as high as 40. Application of this reagent to direct cesium recovery from Purex 1WW has not been promising owing to low coefficients at low pH and formation of stable emulsions at high pH.

Cursory tests show that p-dodecylphenol in xylene extracts cesium (E_{α}^0 1-3) from tartrate-complexed, formaldehyde-treated

Purex 1WW at high pH with an indicated Cs-Na separation factor of ~5. Good separation is obtained from aluminum and iron.

Interface Mechanism for Uranium Extraction by Amine Sulfate

Kinetic studies of the transfer of $S^{35}O_4$ from an organic phase containing di-n-decylamine sulfate to an aqueous phase containing Na_2SO_4 and/or H_2SO_4 were done in such a way as to detect the transfer of anionic uranium species across the interface from aqueous to organic phase. No evidence for such transfer of anionic uranium species was obtained. This negative evidence plus other evidence obtained previously suggests that transfer across the interface is effected by a neutral or possibly a cationic uranium species.

Alkaline Earth Extraction by D2EHPA and NaD2EHP

Continued work on strontium extraction from 4 M sodium nitrate by di(2-ethylhexyl)phosphoric acid in benzene has resulted in a series of curves at various total reagent concentrations each showing E_{Sr} as a function of pH or $[H^+]$; pH and $[H^+]$ are related in simple manner in this system. From this set of extraction curves, plots of $\log E_{Sr}$ vs \log total reagent concentration at various sodium form-hydrogen form ratios have been constructed. All gave slopes of 1 within experimental error. Plots of E vs fraction of reagent in the Na form have shown a maximum extraction at 25% Na form at all total reagent concentrations.

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1.0 SOLVENT EXTRACTION TECHNOLOGY

1.1 Final Cycle Plutonium Recovery by Amine Extraction (C. F.

Coleman, F. A. Kappelmann, J. P. Eubanks

The amine extraction of plutonium nitrate is being examined to develop one or more flowsheets suitable for final cycle plutonium recovery and purification, after typical Purex extraction and partition from uranium. To compete successfully with TBP extraction-anion exchange cycles already designed, an amine extraction flowsheet must provide high decontamination and should provide reasonably high concentration in a single cycle, besides fulfilling its apparent promise of simplicity and much lower nitric acid consumption.

The proposed chemical flowsheet¹ (Figure 1) was tested* in batch countercurrent extraction from simulated LBP solution containing 1 g Pu/liter. With 0.3 M trilaurylamine (TLA) in diethylbenzene, at flow ratio A/O = 4/1 in four extraction stages, plutonium was not detected in the raffinate. The organic flow rate was decreased to give significantly measurable plutonium in the raffinate (7% of feed at A/O = 12/1) before the run was ended to measure the complete profile, which proved to agree well with previously-measured extraction isotherms.¹ Subsequent runs in progress are testing 0.1 and 0.15 M TLA.

Zirconium-niobium⁹⁵ tracer added to the feed at 7×10^5 γ counts/min ml could not be detected above gamma background in the product. Radiochemical analysis indicated that the decontamination factor from zirconium was 5×10^5 (niobium not yet reported).

This first completed countercurrent test of plutonium purification in the present investigation confirmed the phase stability of the loaded extractant, the validity of the generalized extraction isotherm data, the operability of the dilute nitric acid scrub and the acetic acid strip systems, and overall good physical behavior in phase mixing and disengagement. The information will be used in continued batch countercurrent tests, and also in hot-cell mixer settler tests with actual Purex LBP solution which should provide decontamination data and answer questions about stage efficiency, rate of equilibration, and possible effects from any constituent in the actual process solution.

1.1.1 Materials and Flowsheet. The plutonium used was pretreated by anion exchange sorption on Permutit SK resin from 7.5 M HNO₃ and elution in 0.7 M HNO₃. Subsequent analyses gave α_{Am}/α_{Pu} ratios in the range $(4 - 9) \times 10^{-4}$. Simulated LBP solution was made up from this plutonium stock (Table 1) at ~ 1.5 M HNO₃, ~ 1 g Pu/liter reduced with 0.03 M Fe(NH₂SO₃)₂ then reoxidized to Pu(IV) with 0.2 M NaNO₃, and $\sim 7 \times 10^5$ Zr-Nb γ counts/min ml.

*These tests were carried out in the Chemical Isolation Laboratory with the cooperation of R. E. Leuze and coworkers.

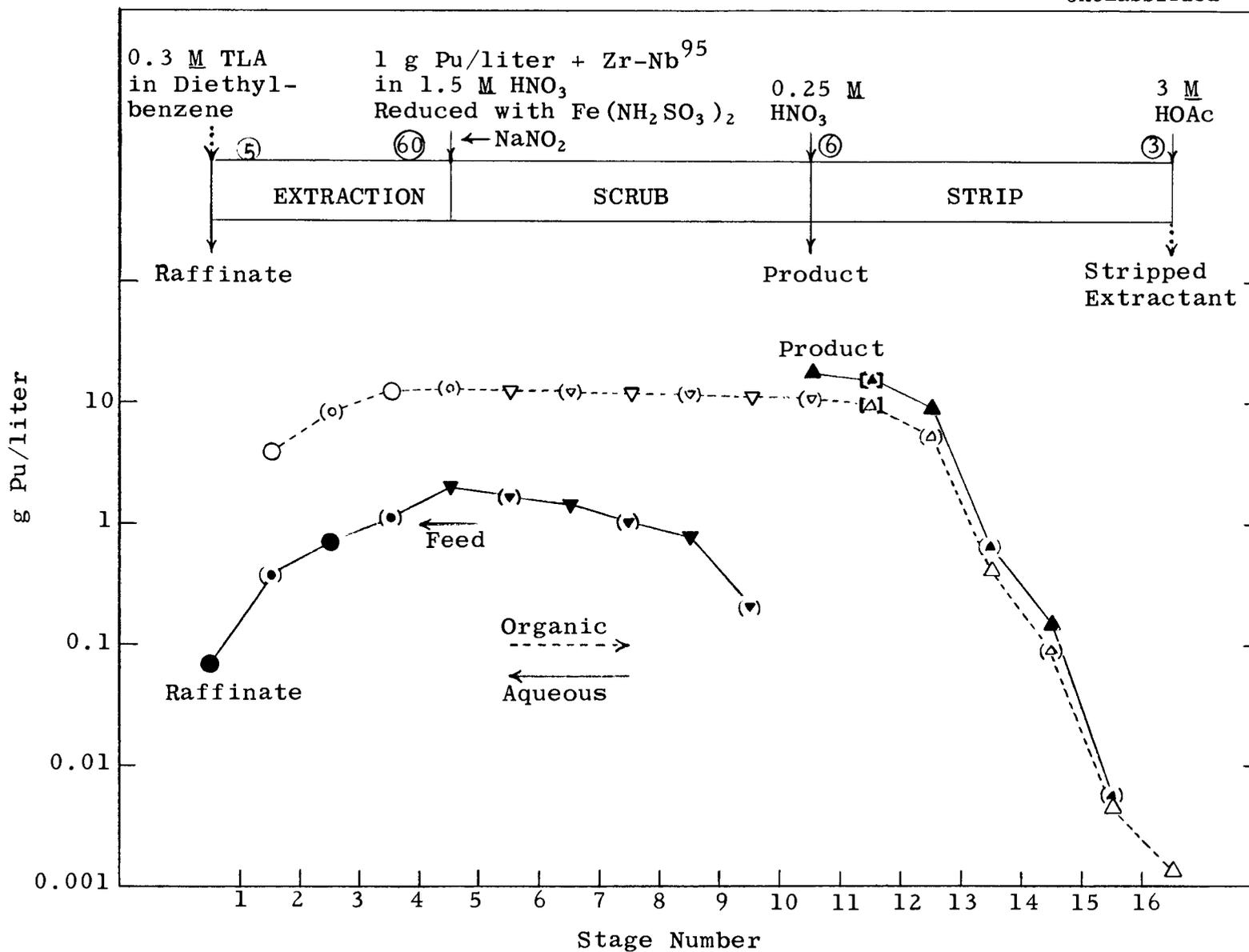


Fig. 1. Flowsheet and Profile, Plutonium Purification Cycle.

Table 1. Feed Solution Analyses
Simulated IBP

| Batch No. | Used in Cycles | H ⁺ M | Pu α | | Am α | Gross γ |
|-----------|----------------|------------------|----------------------|----------------------|----------------------|----------------------|
| | | | Total | (IV) | | |
| 1 | 1-14 | 1.65 | 6.03x10 ⁷ | 6.19x10 ⁷ | 2.53x10 ⁴ | - |
| 2 | 15-30 | 1.49 | 7.08x10 ⁷ | 7.01x10 ⁷ | 5.90x10 ⁴ | 7.26x10 ⁵ |
| 3 | 31-46 | 1.48 | 6.86x10 ⁷ | 6.93x10 ⁷ | 5.8x10 ⁴ | 7.45x10 ⁵ |
| 4 | 47-62 | 1.35 | 6.85x10 ⁷ | 6.95x10 ⁷ | 6.3x10 ⁴ | 7.78x10 ⁵ |

Preparation: Plutonium nitrate solution reduced with ferrous sulfamate (quantity equivalent to 0.03 M Fe(NH₂SO₃)₂ in final volume), reoxidized with nitrite (NaNO₂:Fe = 7/1 mole ratio), and spiked with Zr⁹⁵-Nb⁹⁵ tracer at ~7x10⁵ γ counts/min ml in the final solution.

The Zr⁹⁵-Nb⁹⁵ was obtained from the ORNL Isotopes Division and separated from oxalate by W. E. Oxendine. Its activity was ~60% Nb, 40% Zr.

Trilaurylamine (General Mills Alamine 304, ORNL Batch No. 86J) and diethylbenzene (Dow) were obtained from A. D. Ryon. The amine assayed 543 neutral equivalent (theoretical 522), 93% tertiary, 7% secondary, <1% primary amine. The diluted solution assayed 0.302 M titratable amine.

The flowsheet conditions used for the last 30 cycles are shown in Fig. 1. The initial conditions and the changes made during the run are summarized in Table 2. Briefly, the feed/extractant ratio was changed from 4/1 to 12/1, the strip acetic acid from 2 to 3 M and the scrub nitric acid from 0.5 to 0.25 M. Phases were mixed by hollow stirrers in cylindrical separatory funnels for 5 minutes. Separations were usually rapid, although occasionally slow (<3min) in one of the strip-section contactors.

Table 2. Flowsheet Conditions
(cf. Fig. 1)

| Cycle Nos. | Volume, ml | | | | Scrub, M HNO ₃ | Strip | |
|------------|------------|------|-------|-------|---------------------------|--------|--------------------|
| | Extract | Feed | Scrub | Strip | | M HOAc | M HNO ₃ |
| 1-22 | 15 | 60 | 6 | 3 | 0.5 | 2 | 0.1 |
| 23-28 | 15 | 60 | 6 | 4 | 0.5 | 2 | 0.1 |
| 29-62 | 5 | 60 | 6 | 3 | 0.25 | 3 | 0 |

Eight contactors were used, each for two stages, in single-diamond contact pattern divided 4 stages in extraction, 6 in scrub, and 6 in stripping. Samples of raffinate, product, and stripped extractant from about one-fifth of the cycles were analyzed, usually for gross α and gross γ (Table 3). Corresponding samples from the other cycles have been held for possible rechecks or further analysis.

1.1.2 Run Samples. Under the initial conditions of A/O = 4/1 the 0.3 M amine provided more extraction power than was needed even with only four extraction stages. The total alpha activity found in the raffinate (Table 3, cycles 8-26) was within the range of americium α found in the feed and expected to report in the raffinate. Thus, while $\Sigma \alpha$ in the raffinate approached 0.1% of that in the feed, the plutonium loss to the raffinate was indicated to be <0.01%.

The initial acetic acid concentration in the strip solution (2 M) was too low for 0.3 M amine nitrate at A/O = 5/1, resulting in fractional stripping, reflux, and increasing plutonium concentration in the stripped extractant (Table 3, cycles 8-20). About 1/6 of the plutonium was stripped and up to ~5% was carried out in the extractant; hence, 80-85% was refluxed. It is noteworthy that this increasing reflux burden of plutonium did not produce detectable plutonium in the raffinate.

Stripping capacity was increased slightly for cycles 21-27, by increasing the aqueous phase volume to raise the phase ratio A/O from 3/15 to 4/15. This and/or the increasing reflux burden increased the fraction stripped to ~30%, while the stripped extractant still carried ~5%.

At cycle 30 the extraction capacity was decreased considerably by decrease of the extractant volume, changing the phase ratio A/O from 4/1 to 12/1. The stripping capacity was increased by increasing the acetic acid concentration to 3 M, although the strip volume was at the same time decreased to the initial 3 ml, giving a new phase ratio A/O = 3/5. These conditions were maintained for the remainder of the run. The $\Sigma \alpha$ in the stripped extractant dropped rapidly (after organic phase at the new volume reached the end of the system) to <0.01%. The product rose to well over 100% of the feed as the reflux burden was discharged, then dropped back toward 100%. The run was terminated after cycle 62, as the raffinate and stripped-organic analyses appeared to indicate steady state and the raffinate loss level (7%) promised accurate stage calculations. The product analyses subsequently showed that discharge of the excess reflux burden had not been quite completed, so that the reflux level shown in the profile (below) is a little higher than it would be for true steady state.

Table 3. Plutonium Distribution in Run Samples
(cf. Fig. 1)

| Cycle No. ^a | $\Sigma \alpha$ /min ml | | | % of $\Sigma \alpha$ in Feed ^b | | | g Pu/liter in Product ^e |
|------------------------|-------------------------|--------------------|--------------------|---|---------|-------------------|------------------------------------|
| | Raffinate ^c | Product | Org. ^d | Raffinate ^c | Product | Org. ^d | |
| 2 | 8.56×10^4 | | | 0.13 | | | |
| 8 | 3.73×10^4 | 2.06×10^8 | | 0.06 | 15 | | 2.9 |
| 10 | | 4.88×10^8 | | | 36 | | 7.0 |
| 12-13 | | 2.12×10^8 | 1.55×10^5 | | 16 | 0.06 | 3.0 |
| 14-15 | 3.44×10^4 | 2.21×10^8 | 7.68×10^6 | 0.05 | 16 | .28 | 3.2 |
| 17 | | | 5.35×10^7 | | | 2.0 | |
| 19 | | | 1.24×10^8 | | | 4.6 | |
| 20 | 3.99×10^4 | 2.33×10^8 | | 0.06 | 17 | | 3.3 |
| 23 | | | 1.48×10^8 | | | 5.5 | |
| 25 | | | 1.00×10^8 | | | 3.7 | |
| 26-27 | 4.31×10^4 | 3.05×10^8 | 1.35×10^8 | 0.06 | 29 | 5.0 | 4.4 |
| 29 | | | 9.58×10^7 | | | 1.2 | |
| 36-37 | 6.07×10^4 | 1.01×10^9 | 1.02×10^8 | 0.09 | 75 | 1.2 | 14 |
| 40-41 | 1.90×10^5 | 1.41×10^9 | 8.79×10^7 | 0.28 | 104 | 1.1 | 20 |
| 44-45 | 2.81×10^5 | 9.84×10^8 | 8.87×10^7 | 0.42 | 73 | 1.1 | 14 |
| 47 | | | 2.02×10^6 | | | 0.02 | |
| 49 | | | 6.49×10^5 | | | 0.008 | |
| 50 | 1.92×10^6 | 1.78×10^9 | | 2.8 | 131 | | 25 |
| 58-59 | 3.97×10^6 | 1.46×10^9 | 1.92×10^5 | 5.9 | 145 | 0.002 | 21 |
| 60-61 | 4.76×10^6 | 1.6×10^9 | 1.01×10^5 | 7.0 | 118 | 0.001 | 23 |
| 62 | 4.98×10^6 | 1.45×10^9 | | 7.3 | 107 | | 21 |

^aRaffinate and product discharged only after even-numbered cycles, stripped extractant only after odd-numbered.

^b 6.77×10^7 α /min ml, mean of four batches (Table 1).

^cNot corrected for Am α , which was reported at $(2-6) \times 10^4$ counts/min ml in feed batches and in the same range in raffinate from cycles 50, 58, 60, and 62.

^d"Org." = stripped extractant.

^eg Pu/liter from $\Sigma \alpha$, assuming all non-Pu α negligible in the product.

1.1.3 Profiles. All solutions were analyzed after cycle 62, giving the $\Sigma \alpha$ profiles shown in Table 4 and Fig. 1. Only the odd-numbered stages contained solutions at this point. This included raffinate (Stage 1) and product (Stage 11) but not stripped extractant (Stage 16); the stripped extractant analysis from cycle 61 was used. Concentrations for the other even-numbered stages were calculated by material balance from the corresponding opposite phases, and are marked by parentheses in both table and graph. One missing analysis (repeat analysis in progress) was filled in by interpolation in the profile curve, in order to allow complete examination of the McCabe-Thiele diagram.

Extraction. The profile data are replotted as extraction, scrub, and stripping isotherms in Fig. 2. The equilibrium curve for the extraction was drawn according to the empirical equations previously derived from semi-micro extractions,¹

$$E(\text{Pu}) \approx E_1 [\underline{M}_{\text{amine}} - 3 \underline{M}_{\text{Pu}}]^2 \text{ and } \log E_1 \approx 3.5 - 2.5 \sqrt{\underline{M}_{\text{SO}_4}}$$

for extraction from $\sim 1.5 \text{ M HNO}_3$ with trilaurylamine in diethylbenzene. The proximity of the stage points to this curve is a gratifying confirmation of the previous measurements.

The calculation of every second stage concentration by means of material balance, if all from the same starting point, would in itself assure exact agreement of the McCabe-Thiele step intersections with the operating line. However, it was possible to start the material balance calculations from both ends of this profile. Concentrations indicated for stage 4 based on the raffinate end and on the product end were similar but not identical. The latter were plotted for stage 4 in Fig. 2, while stage 2 concentrations were calculated from the raffinate end. The small discrepancy between them is indicated by the small deviation of the step intersections from the operating line.

Scrub. The calculated aqueous concentration, 0.2 g Pu/liter, for the last scrub stage (10) was subject to more error than the other calculated concentrations, involving a smaller difference between larger numbers. Its location so far to the left (i.e., with so high an extraction coefficient) is surprising, and is probably not valid.

Even with stage 10 discounted, the scrub shows higher extraction coefficients, giving less net reflux and maintaining more nearly constant organic phase plutonium concentrations, than were expected on basis of the available information on

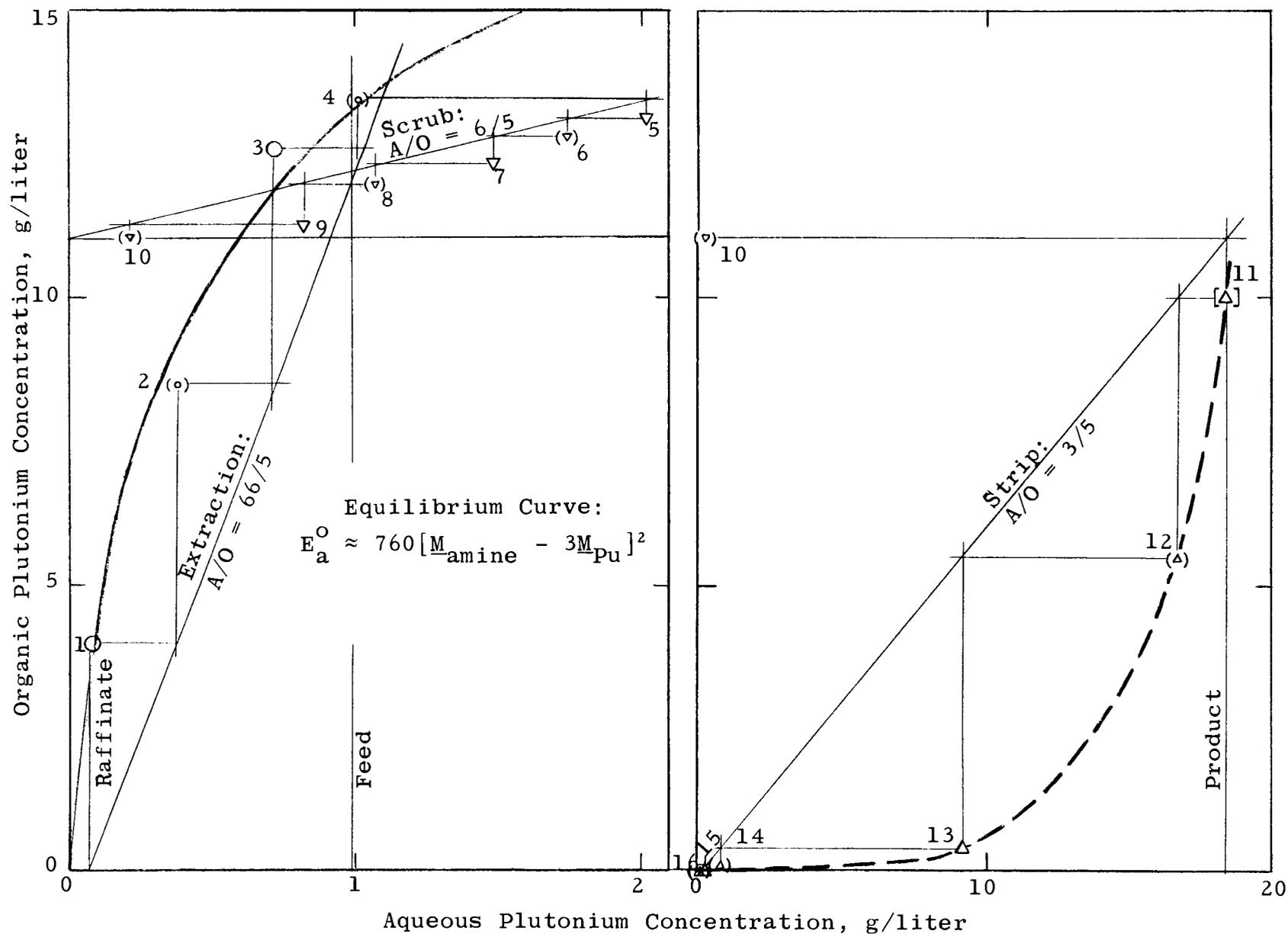
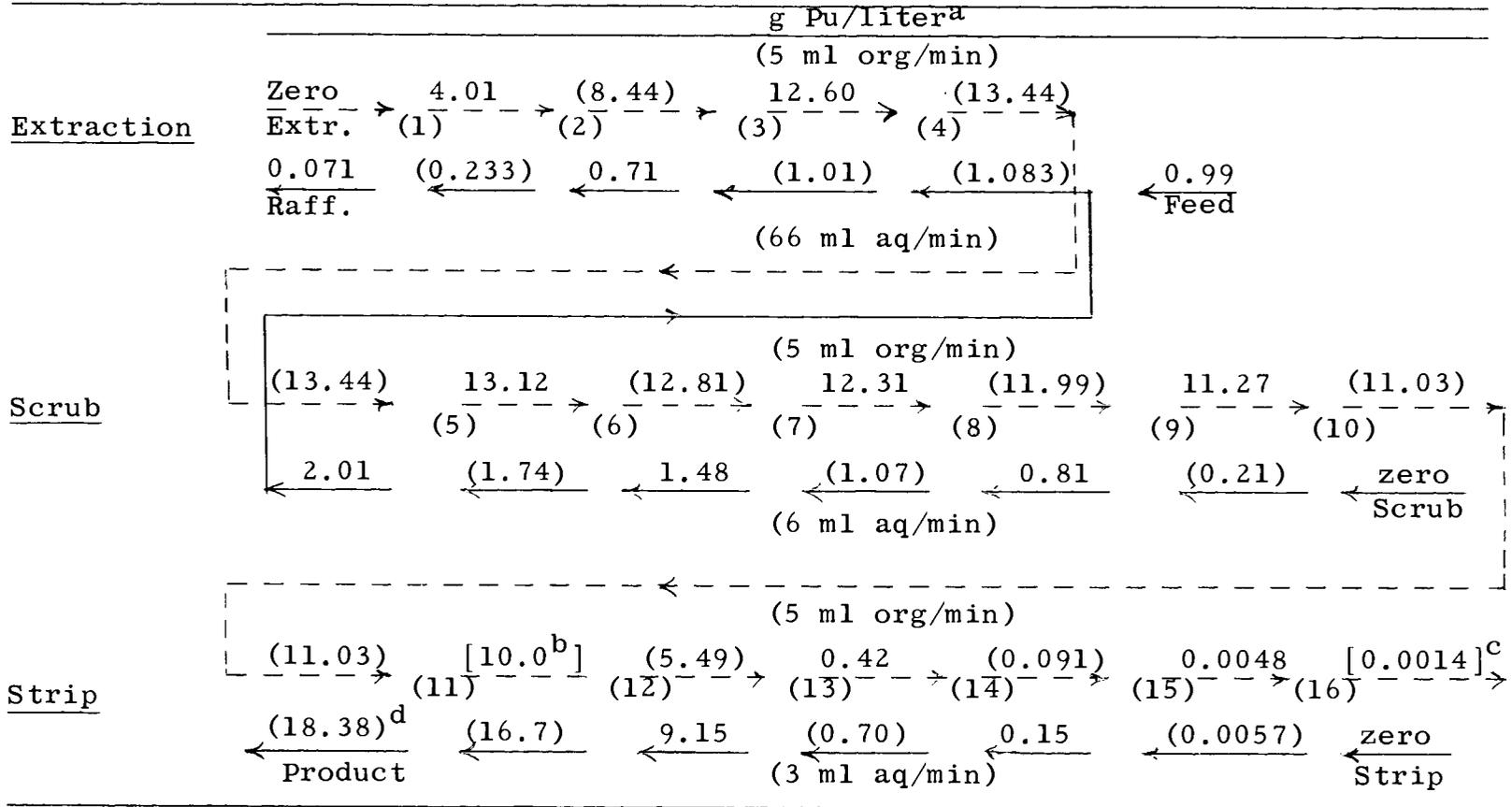


Fig. 2. McCabe-Thiele Diagram, Plutonium Purification Cycle.

Table 4. Profile of Plutonium Purification Cycle

Batch countercurrent test, single diamond contact pattern.
 0.3 M TLA in diethylbenzene; simulated lBP feed (Table 1);
 0.25 M HNO₃ scrub; 3 M HOAc strip



^aCalculated from $\Sigma \alpha$. Numbers in parentheses obtained by material balance.

^b[10.0] by interpolation on smoothed profile curve.

^c[0.0014] in stripped organic of preceding cycle.

^d(18.38) in average product by material balance; 20.7 in product sample of final cycle.

extraction coefficients for excess nitric acid and for plutonium.* As noted above, the completed run analyses showed that the reflux burden of plutonium built up under the earlier run conditions had not been completely discharged. Thus it appears likely that after a few more cycles the loading at stage 4 and particularly the aqueous concentrations through the scrub section would have been a little higher, resulting in a steeper alignment of the scrub equilibrium points.

Stripping. The stripping isotherm indicates that the final run conditions provided more than the necessary stripping power for six stages. The stripping equilibrium points fall along a reasonable-appearing smooth curve. However, it is not yet possible to draw a predicted equilibrium curve for comparison. Thus, at present, these stripping data can be applied only to rather similar stripping conditions. Analysis of the amine-acetic acid-nitric acid equilibrium is in progress,¹ and may be expected to produce theoretical or empirical relations which will then permit extrapolation of such stripping data to a wider range of conditions.

1.1.4 Zr-Nb Extraction. Zr⁹⁵-Nb⁹⁵ tracer was added to the feed solution at the highest level believed to be completely safe in the unshielded glove boxes, i.e., ~10⁶ γ counts/min ml. It was realized before starting that this level would not permit

*The aqueous nitric acid concentration leaving each scrub stage can be estimated by McCabe-Thiele calculations based on the end conditions of 1.25 M HNO₃ leaving stage 4 and 0.25 M HNO₃ entering stage 10, together with the reported extraction of excess nitric acid by trilaurylamine,² $E_a^{org}(xs\ HNO_3) = 0.17(M_{amine})$. The operating line is then $(M_{HNO_3})_{org} = 1.2(M_{HNO_3})_{aq} - 0.287$ for A/O = 6/5, giving the successive aqueous concentrations shown in the fourth column:

| Stage No. | (Pu) _{org} Obs. g/liter | E(Pu) Obs. | (HNO ₃) _{aq} Est. M | E ₁ (Pu) Predicted | E(Pu) Predicted |
|-----------|----------------------------------|------------|--|-------------------------------|-----------------|
| 5 | 13.12 | 6.5 | 0.292 | 225 | 3.8 |
| 6 | (12.81) | 7.4 | .252 | 166 | 3.2 |
| 7 | 12.31 | 8.3 | .2501 | 165 | 3.4 |
| 8 | (11.99) | 11 | .2500 | 165 | 3.6 |
| 9 | 11.27 | 14 | .2500 | 165 | 4.0 |
| 10 | (11.03) | 50 | .2500 | 165 | 4.1 |

Estimates based on other plutonium extractions at low nitric acid concentrations² (plus a small allowance for salting by the aqueous plutonium nitrate) leads to prediction of E(Pu) near 4 at each of observed organic phase plutonium concentrations (6th column), instead of the higher E's actually found (3rd column). At the same time, it should be remembered that the calculation of these predicted E's involved several assumptions whose uncertainty cannot be well assessed.

measurement of decontamination factors by gross gamma count if those decontamination factors were as good as hoped. However, the tracer test was included on the basis that it might give significant data by special analysis, might show up some otherwise-unexpected serious impairment of decontamination, and was not likely to interfere with the plutonium data. The results were that Zr-Nb activity could not be measured in the product by either gross γ or γ scan. A single radiochemical determination of zirconium in the product showed 116 γ counts/min ml, corresponding to a decontamination factor from zirconium of 5×10^4 . A corresponding radiochemical determination of niobium is in progress.

1.2 Extraction Performance of Degraded Process Extractants:
Effect of TBP on Degradation of Amsco 125-82 with Nitric Acid (C. A. Blake, J. M. Schmitt, W. E. Oxendine)

Previous reports³⁻⁶ have described experiments which showed that many of the anomalous extraction properties of degraded process extractants (e.g., 1 M TBP-Amsco 125-82), belong to products from nitration of the diluent. Specifically, it was found⁵ that nitroparaffins (e.g., RCH_2NO_2) gave the same infrared spectrum and performed in Zr-Nb⁹⁵ extraction tests similarly to nitric acid-degraded Amsco 125-82. The degradation was accomplished either by irradiating or by heating an intimately mixed 2-phase system of solvent and nitric acid. The solvent phase was Amsco 125-82 alone or in combination with TBP. Irradiation was by Co-60 gamma.

This testing of solvent degradation by both heating and irradiation has been continued. In recent experiments degradation of the Amsco 125-82 was shown to be more severe when TBP was present than when it was not. This is presumed to be a consequence of nitrate and nitrite extraction by TBP increasing the opportunity for nitration, and perhaps also of stabilization of the nitro groups by (previously observed) complexing with TBP. The degradations by irradiation and by heating were essentially equivalent with respect to effects detected by Zr-Nb⁹⁵ extraction, by total organic nitrogen analysis, and by spectrophotometric nitro-paraffin analysis.

The irradiation tests also provided estimates of the radiation induced decomposition of HNO_3 and formation of DBP and HNO_2 .

The assistance of W. Davis, Jr., in operating the Co-60 source is gratefully acknowledged.

1.2.1 Degradation by Irradiation. An apparatus described elsewhere⁷ was used to mix each solvent with an equal volume of 2 M HNO_3 during irradiation in a 10,000 curie Co-60 source.⁸ The effects of different irradiation conditions and subsequent treatments on Zr-Nb extraction by the solvents are compared in Fig. 3.

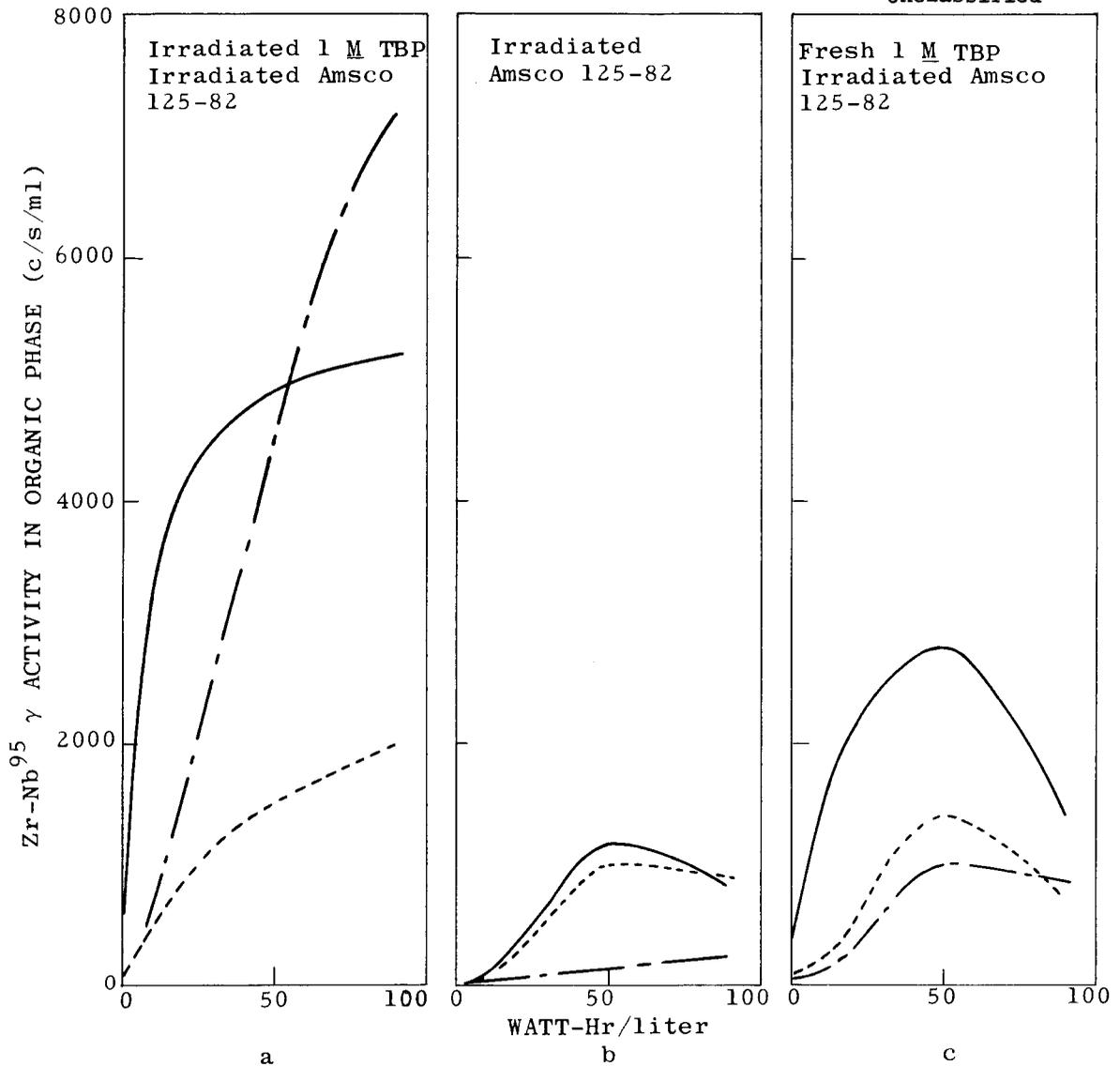


Fig. 3. Zr-Nb⁹⁵ Extraction Tests with Irradiated TBP-Amsco 125-82-
2 M HNO₃ Extraction from 2 M HNO₃, 10⁴ c/s/ml Zr-Nb⁹⁵ with

- As irradiated organic phase
- - - Organic phase after Na₂CO₃ scrubbing
- · - Organic phase after Na₂CO₃-Ca(OH)₂ scrubbing

Extractions at phase ratio organic-aqueous = 1, Room temperature,
10 min contact time.

The three graphs show separately irradiation of 1 M TBP in Amsco 125-82, irradiation of Amsco 125-82 alone, and irradiation of Amsco 125-82 alone followed by addition of fresh TBP at 1 M. In each graph, the solid curve shows extraction by the solvent without any clean-up treatment, the dotted curve, after scrubbing with sodium carbonate solution, and the dashed curve, after scrubbing with sodium carbonate solution and then solid calcium hydroxide.

When TBP was present during the irradiation (Fig. 3a), zirconium extraction was high with the unscrubbed solvent, dropped considerably after carbonate scrubbing to remove the low-weight acids DBP and MBP, and rose again sharply after calcium hydroxide treatment. As explained below, this is attributed to activation of nitroalkanes by reaction with the calcium hydroxide.

When Amsco 125-82 was irradiated and tested alone (Fig. 3b), the degradation-induced zirconium extraction was much lower although still significant. Sodium carbonate scrubbing had little effect (no DBP nor MBP formed in the absence of TBP), while the extraction was almost eliminated by the calcium hydroxide treatment. The latter effect can be reconciled with the marked enhancement of extraction in Fig. 3a by noting that the solid calcium hydroxide is known to sorb a portion of the impurities, but with limited capacity. When the impurity concentration is high the amount sorbed is relatively unimportant, but when it is low nearly all may be sorbed.

When fresh TBP was added to the irradiated Amsco 125-82 (Fig. 3c), all three extraction curves were higher than those with the degraded diluent alone, higher than could be accounted for by the additional extraction by TBP itself. This resulted from first, the presence in the untreated solution (solid line) of impurities in the fresh TBP reagent, and second, from the previously observed⁵ interaction between TBP and diluent degradation products to give synergistically enhanced extraction.

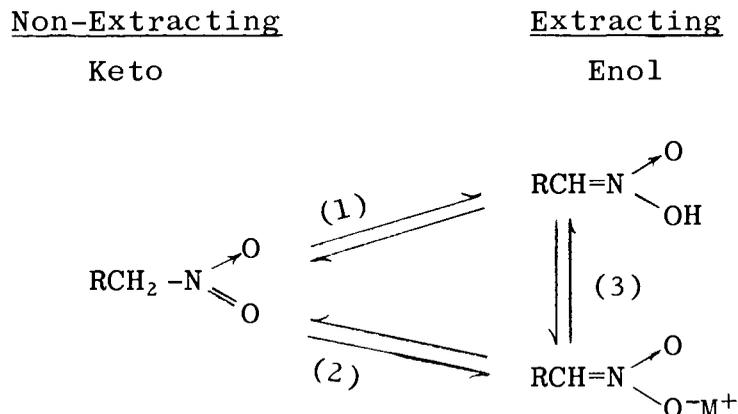
The opposite corresponding mixture of irradiated TBP and fresh diluent was not included in this test series. A previous test with such a mixture (under different conditions)⁶ showed no increase in zirconium extraction by the sodium carbonate-scrubbed solvent on TBP irradiation up to 60 watt-hr/liter.

Thus, it seems clear that degradation occurred in the diluent and was much more severe when TBP was present. It is very likely that the complexing of TBP with HNO_3 and nitroparaffins increased the total yield. Extraction of HNO_2 by TBP may also be important (see Par. 1.2.6).

The extraction maxima between 50 and 90 watt-hr/liter (seen in Figs. 3b and 3c but not in 3a) are not understood and require

further study, including irradiation tests of TBP alone above the 60 watt-hr/liter previously tested.

The increased zirconium extraction after calcium hydroxide treatment is explained in terms of the following tautomeric equilibria of primary and secondary nitroparaffins. Since tertiary nitroparaffins have no enolizable hydrogen atom they do not undergo these reactions and do not contribute to the extraction power of the solvent.



In acidic media the equilibrium of reaction (1) is far to the left (the keto form), and/or the rate of equilibration is slow. Reaction (2) occurs in basic media. Its equilibrium is farther to the right (salt of the enol form), and its rate of equilibration is relatively fast. Moreover, both the rate and the position of equilibrium vary with different bases. Contact with calcium hydroxide produces more of the enol salt, and more rapidly, than does contact with sodium carbonate or sodium hydroxide (Table 5; cf. Sect. 1.2.3). Thus, on treatment with calcium hydroxide a large proportion of the nitro groups enolize, and on acidification remain as enols long enough to be effective in extracting the zirconium. A test procedure was previously described, using this effect to detect nitro groups that are not detected by a simple direct extraction test.⁹

1.2.2 Degradation by Exposure to Boiling HNO₃. Boiling with an equal volume of 2 M HNO₃ under total reflux for relatively long times degraded Amsco 125-82 severely enough for its degradation products to extract Zr-Nb⁹⁵ strongly even without the presence of TBP. In Fig. 4 data are shown to compare the Zr-Nb extraction behavior of 1 M TBP in Amsco 125-82 and Amsco 125-82 alone as a function of reflux time. Prior to use both solvents were first scrubbed with Na₂CO₃, to remove DBP and MBP from the TBP solvent, and then with Ca(OH)₂ to "develop" the nitrohydrocarbons as extractants. As shown in Fig. 4, Zr-Nb extraction by the 1 M TBP-Amsco degraded for 4 hours was matched by that of Amsco alone degraded for about 22 hours. These results demonstrate again the accelerated diluent nitration that is brought about by the presence of TBP.

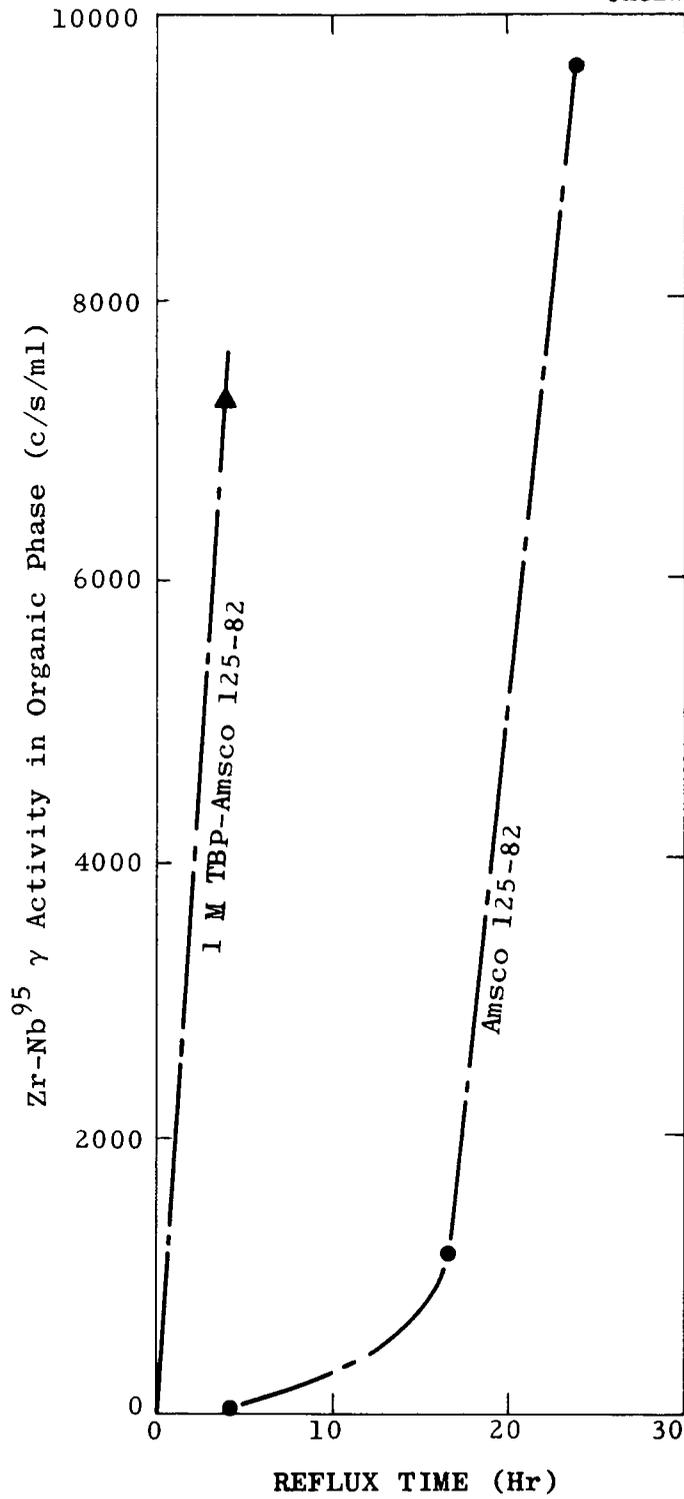


Fig. 4. Zr-Nb⁹⁵ Extraction Tests with TBP-Amsco 125-82 after Exposure to Boiling 2 M HNO₃.

Table 5. Rate of Extraction of Sodium from Alkaline Solution

Organic phase: 1 M TBP-Amsco irradiated 90 watt hr/liter, then scrubbed with 0.2 M Na₂CO₃ (2X), 2 M HNO₃ (2X), 2.6 M NaCl (2X), all at phase ratio = 1 and for 10 min
 Aqueous phase: 1 M NaOH, phase ratio = 1
 Room temperature

| <u>Time of Contact (Hr)</u> | <u>Sodium Extracted^a (N)</u> |
|-----------------------------|---|
| 0.17 (10 min) | 0.0046 |
| 0.5 | 0.0051 ^b |
| 1.0 | 0.006 |
| 4.0 | 0.009 |
| 16.0 | 0.013 ^c |

^a Calculated from analysis of 2 M HNO₃ used to strip Na from the organic extract.

^b For purposes of comparison, after contact of the organic phase with 200 g/liter solid Ca(OH)₂ for 30 min., the calcium analysis was 0.024 N.

^c For purposes of comparison, after contact of the organic phase with 5 g/liter solid Ca(OH)₂ for 16 hrs, the calcium analysis was 0.08 N.

1.2.3 Radiation vs Boiling HNO₃: Estimates of Nitration Product Concentrations

Ultraviolet Absorption Spectra: Previous reports⁵ have shown that nitroparaffins give the same infrared spectrum (and perform in Zr-Nb^{9,5} extraction tests in the same way) as Amsco 125-82 degraded with nitric acid. Recently studies have been made of nitroparaffin spectra in the ultraviolet to find whether such measurements would also be useful in examining the type and extent of solvent degradation. The ultraviolet absorption spectra of simple nitroparaffins are characterized by a low intensity band at 280 mμ and a band of greater intensity at around 200 mμ.¹⁰ The spectra at these wavelengths obtained with 1-nitro-n-decane in cyclohexane (colorless in this region) using a Cary Recording Spectrophotometer are shown in Fig. 5. Preliminary testing with degraded TBP-Amsco solutions showed much interference at the 280 mμ band, but at the higher intensity band (~205 mμ in our system) reproducible results were obtained. Amsco itself and HNO₃ also absorb in this region, but were apparently easily corrected for by using these solutions in the comparison cell. Conformity of the nitrodecane ~205 mμ band to Beer's law was shown over the range 0-0.0005 M nitrodecane (Fig. 6). In actual measurements with degraded solvents, the samples were diluted with cyclohexane until their absorbance was in the range shown in Fig. 6. In all cases reported here the dilution was 500X.

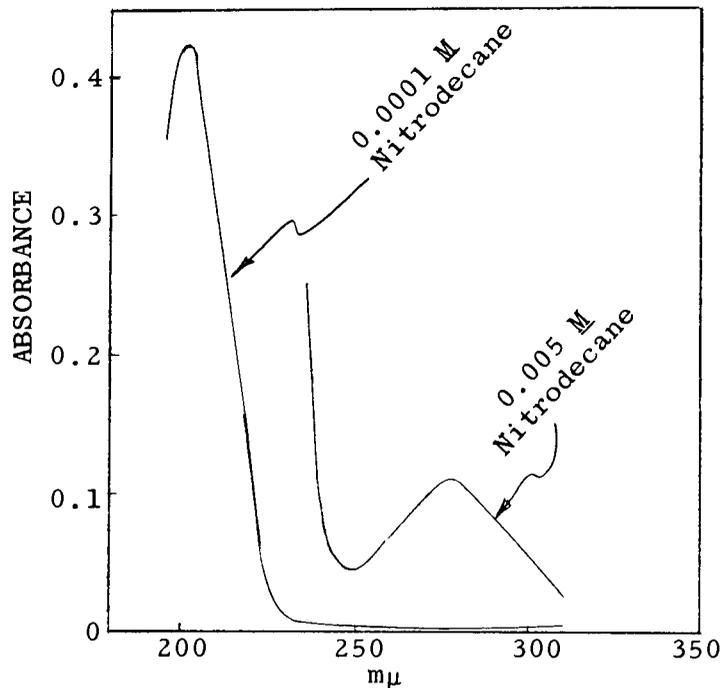


Fig. 5. Ultraviolet Spectra with n(1-nitro)decane.

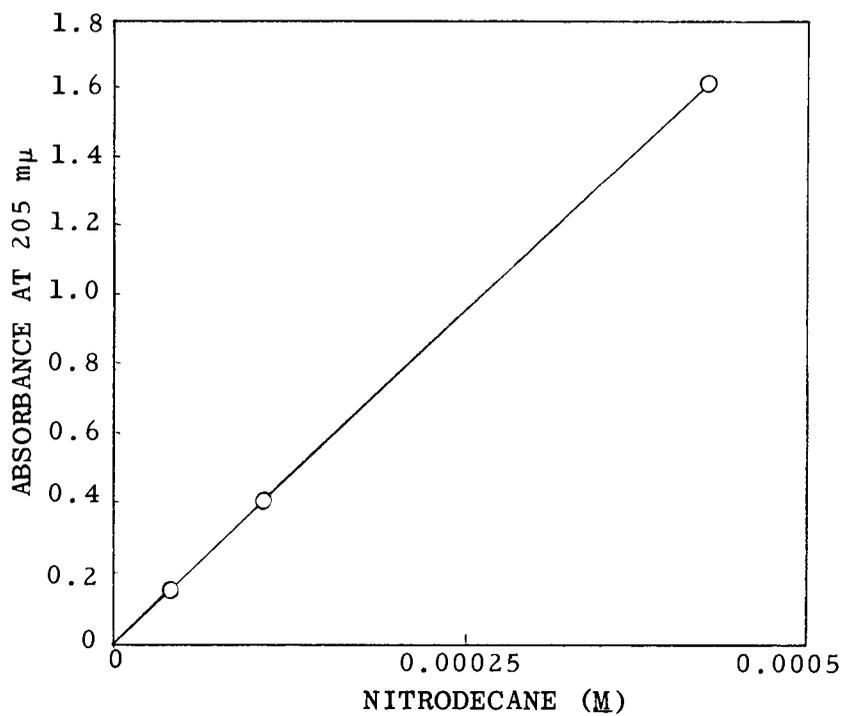


Fig. 6. Beer's Law Plot for n(1-nitro)decane.

These absorbances at 205 $m\mu$ have been measured for a number of samples of Amsco or Amsco-TBP which had been exposed to irradiation or boiling nitric acid for varying lengths of time. As shown in Fig. 7 the absorbance, and therefore the concentration of nitroparaffin, was found to increase linearly with amount of exposure for both the Amsco and TBP-Amsco. This was true whether the exposure was to irradiation or boiling nitric acid. In Fig. 7 the squares show chemical treatment and the circles radiation dosage and, for both, the closed points represent treatment of diluent alone and the open points treatment in the presence of TBP. The irradiation dose scale at the top was arbitrarily adjusted to make the slope of the closed circles match that of the closed squares, and this resulted in rather good agreement of the single open square with the open circles. In agreement with data reported elsewhere in this section the presence of TBP accelerated formation of nitroparaffins: the slopes of the two lines in Fig. 7 indicate that nitration was at least twice as fast in the presence of TBP.

Nitrogen Analysis: Chemical analysis for organic phase nitrogen was obtained for a few Amsco and Amsco-TBP samples which had been degraded by either irradiation or boiling nitric acid. As shown in Fig. 8, these limited data indicate a fairly constant proportionality of nitro groups (determined from UV measurements) to total nitrogen regardless of the type of degradation. The 1 M TBP-Amsco solution irradiated for 90 watt hr/liter contained 0.2 N nitrogen. Other samples which should have been even higher, e.g., Amsco boiled for 24 hrs with HNO_3 , were not analyzed. It should be noted that the concentration of total nitrogen in the solvent does not necessarily indicate the concentration of active or potentially active extractant. For example the analyses make no distinction between primary, secondary or tertiary nitroparaffins, or between other nitrogen containing compounds which may have been formed. As pointed out previously most extraction of Zr-Nb probably occurs with those products which are, or can become, acids, e.g., the primary and secondary nitroparaffins.

Titration: Simple 2-phase titration* with aqueous sodium hydroxide, which might have been expected to differentiate between the tertiary compounds and the acids, or potential acids, was unsuccessful, the difficulty being ascribed to the low rate of conversion from the neutral to the salt forms. Exemplary of the low rate, Table 5 shows that sodium ion uptake from 1 M NaOH by an irradiated 1 M TBP-Amsco 125-82 solution increased with contact time and was higher by 150% at 16 hr than it was at 4 hr. The highest sodium level reached (0.013 N) probably represented only partial neutralization of the acids since much higher calcium extraction (up to 0.08 N) was obtained under conditions listed in Table 5.

*Organic sample stirred rapidly in 70% ethanol while titrating with aqueous NaOH.¹³

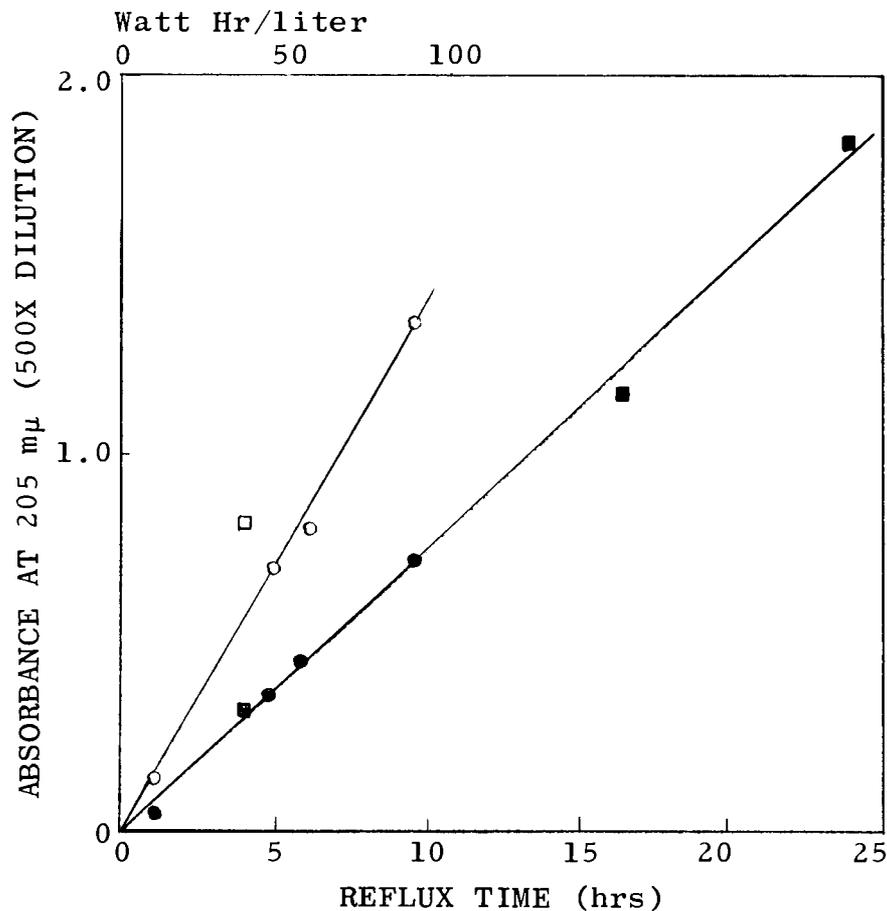


Fig. 7. Correlation of Type of Degradation with Absorbance.

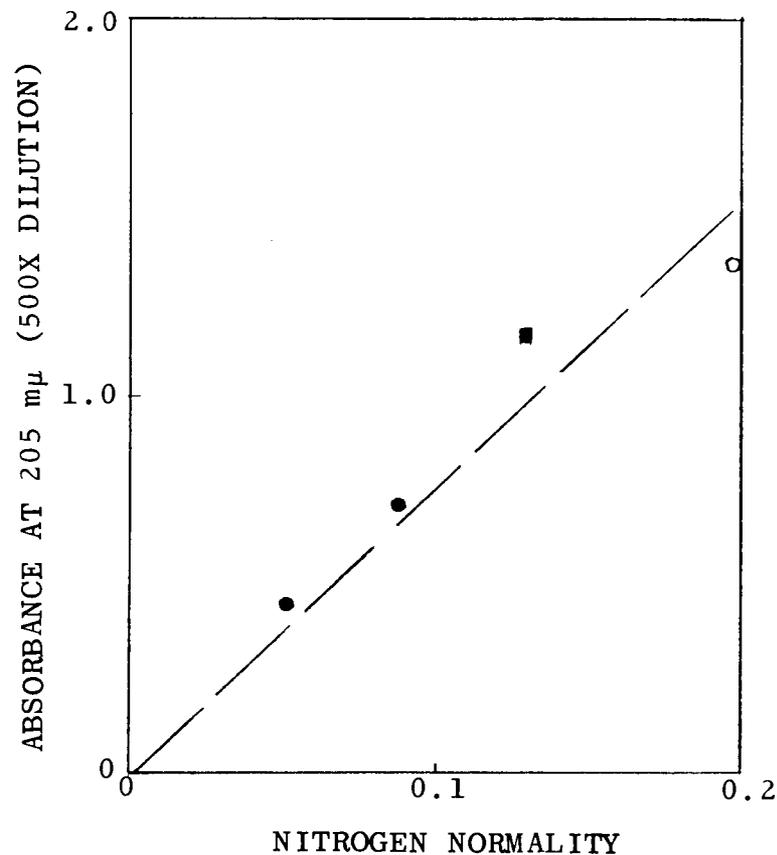


Fig. 8. Correlation of Organic Phase Nitrogen with Absorbance.

- , ■ Exposure to boiling 2 M HNO₃ (Equal vol aqueous and organic phases under total reflux)
- , ● Exposure to Co-60 γ while in contact with 2 M HNO₃ (Equal vol aqueous and organic phases, mixed during irradiation)
- , ○ 1 M TBP-Amsco 125-82
- , ● Amsco 125-82

The effect of the slow salt formation on titration is seen in the curves of Fig. 9. Here the same 1 M TBP-Amsco 125-82 solution irradiated for 90 watt/hr liter in the presence of HNO_3 was titrated in the as-irradiated condition (curve A). The titre of 0.25-0.35 meq/ml represented the combined concentrations of extracted HNO_3 , acid decomposition products of TBP (primarily DBP) and whatever nitroparaffins were neutralized during titration. Severe drifting of the pH level was noted above pH 9, a direct consequence of the slow titration of nitroparaffins (carbon dioxide was excluded). After the organic phase was scrubbed with 2.6 M NaCl the neutralization equivalent (curve B) was lowered (by the removal of HNO_3), but the drifting of the pH levels was again noted. Curve C shows a titration with the same organic extractant after a treatment designed to remove HNO_3 and DBP and to convert the primary and secondary nitroparaffins to their acid forms. First, it was treated as in the $\text{Ca}(\text{OH})_2$ test for solvent quality.⁹ The calcium extracted in this process was then removed by scrubbing with HNO_3 , and the HNO_3 thus introduced was removed by scrubbing with NaCl solution. Finally, the solvent was titrated with aqueous NaOH. Neutralization proceeded rapidly with a fairly sharp inflection and no apparent drifting, and with a neutralization equivalent of ~0.06 meq/ml. In a duplicate test the equivalent was ~0.07 meq/ml. These data coupled with the 0.08 N calcium measured directly in the organic extract (Table 5) give some promise that this method may, with more development, become a useful quantitative tool.

1.2.4 Zr-Nb Extraction Stoichiometry. Approximate Zr extraction coefficients with degraded Amsco 125-82 have been plotted as a function of the concentration of nitro groups determined by UV absorption spectra. In the log-log plot (Fig. 10) the points are fitted reasonably well by a line of slope 4, signifying a combining ratio of 4 for extractant to extracted zirconium. Such a conclusion may be considered somewhat tenuous however since (1) the concentration of the extracting agent need not, as implied, be a linear function with total nitration products, (2) the zirconium extraction coefficients shown in Fig. 10 were not determined with great accuracy, and (3) the proper slope for high combining ratios is always difficult to establish from limited data. Supporting the conclusion, however, is the reasonableness of a combining ratio of 4 between tetravalent zirconium and monobasic nitroparaffin acids.

The data of Fig. 10 represent degradation of Amsco 125-82 alone. There are not sufficient additional data to permit consideration of complications introduced when TBP also is present.

1.2.5 Decomposition of HNO_3 during Irradiation. Degradation of HNO_3 by irradiation has been the subject of previous investigation.¹¹ The G values reported (molecules destroyed per 100 ev dose) have varied from G=5 to G=10. In the present studies the

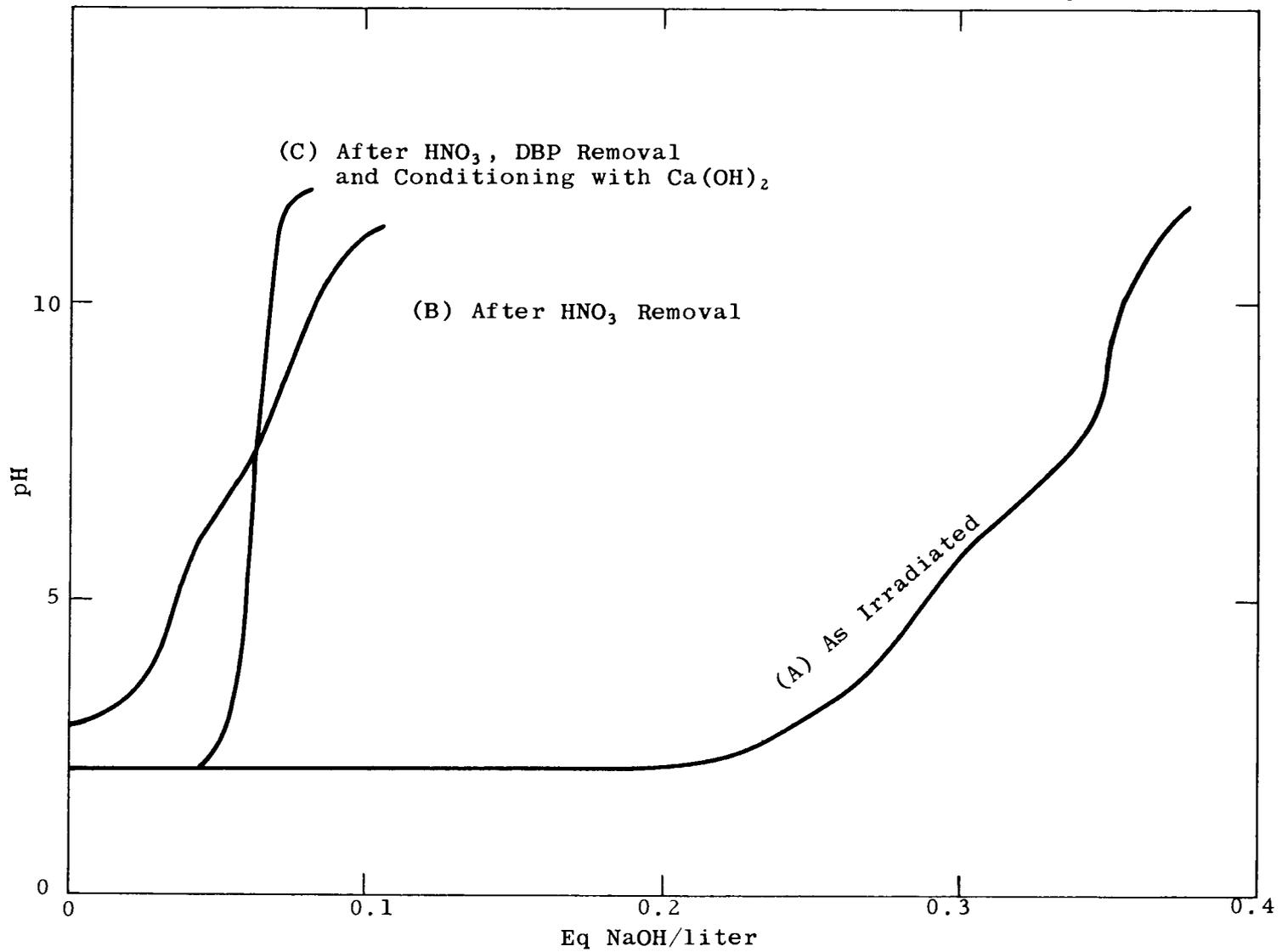


Fig. 9. 2-Phase Titration of 1 M TBP-Amsco 125-82 Irradiated 90 Watt hr/liter (Co-60 γ) in Presence of 2 M HNO₃.

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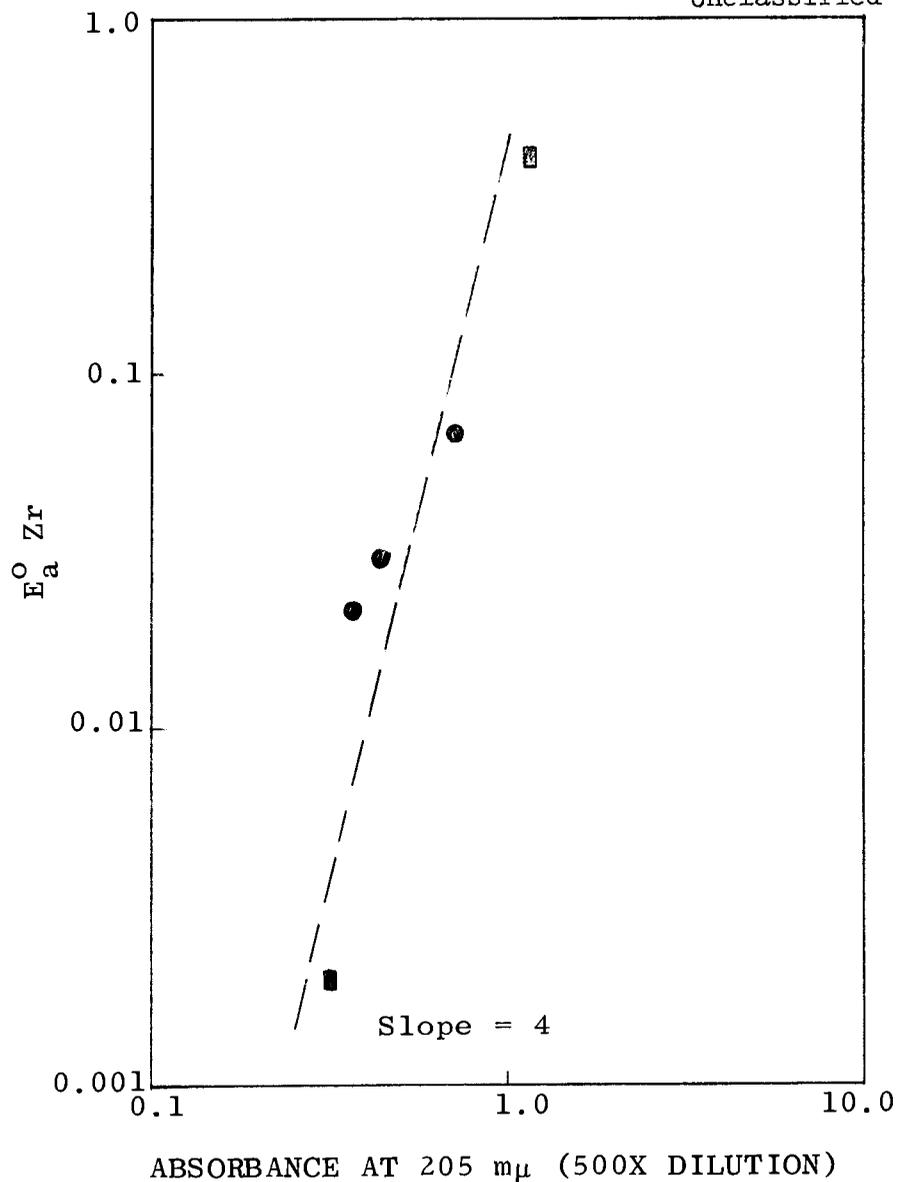


Fig. 10. Correlation of Zr⁹⁵ Extraction Coefficient of Degraded Amsco 125-82 with Absorbance.

- Exposure to HNO₃ and Co-60
- Exposure to Boiling HNO₃

organic and aqueous phases of the test irradiations described in Par. 1.2.1 were analyzed for HNO_3 and the molecules found missing in each system have been plotted against the radiation dose (Fig. 11). The open circles represent data for Amsco 125-82 irradiated alone and the closed circles represent data for Amsco containing 1 M TBP. A line with slope 10 fits these data reasonably well. However, since a part of the HNO_3 was consumed in chemical reaction this value cannot be correct. Consequently, where analyses were available, adjustments for the chemically combined nitrogen were made and the corrected values are replotted on Fig. 11 as triangles. The new values and indeed, one of the old ones at low radiation dose (little chemical reaction), are represented with fair approximation by a line with slope $G=5$. Failure to make the correction for chemically combined nitrogen may account for the wide variation in G_{HNO_3} determined elsewhere.¹¹

1.2.6 Formation of HNO_2 during Irradiation. The aqueous HNO_2 concentration increased during irradiation reaching 0.03-0.04 M at 90 watt hr/liter (Fig. 12). No analyses were made for HNO_2 in the organic phase so the total amount formed during the treatment could not be calculated. HNO_2 is known to extract readily into TBP,¹² but it is not known whether HNO_2 will extract into Amsco 125-82 alone.

In addition to the nitrohydrocarbons formed by HNO_3 -diluent reaction, it is possible that additional amounts could be contributed by nitrosation with HNO_2 . One mechanism could involve formation of a nitroso compound ($-\text{CH}-\text{N}=\text{O}$), with accompanying enolization to the oxime ($-\text{C}=\text{NOH}$), and oxidation of both to the nitrocompound ($-\text{CNO}_2$).

1.2.7 Formation of DBP. The curves of Fig. 9 demonstrate that DBP determination in degraded solvents by simple 2-phase titration is difficult, primarily because of interference from nitroparaffins. However, a rough estimate has been made of DBP formed during irradiation of 1 M TBP solution, contacted with 2 M HNO_3 , to a dose of 90 watt hr/liter. The irradiated organic phase, scrubbed free of HNO_3 , was shaken for 16 hr with an excess of 1 M NaOH. Another portion of the HNO_3 -free organic was further scrubbed with Na_2CO_3 to remove DBP and it, too, was shaken with excess NaOH. The base consumed in each test was determined by back titration with HCl. The difference, giving an approximation of the DBP, was 0.06 eq/liter. At the 90 watt hr/liter dose this concentration of DBP formed represents a G value of approximately 2, in agreement with previous determinations.¹¹

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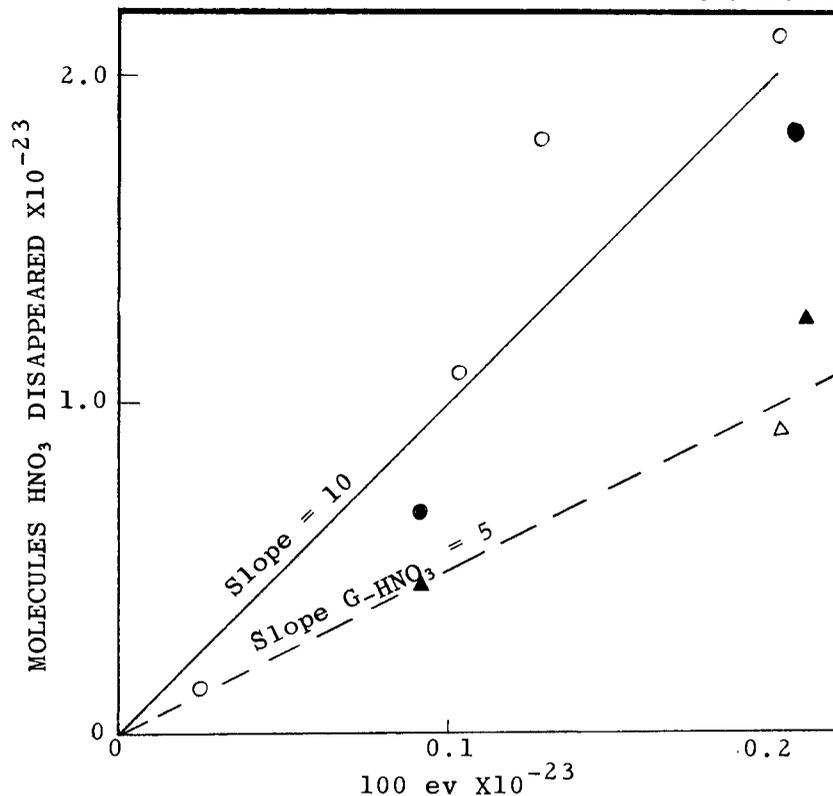


Fig. 11. Decomposition of HNO₃ during Irradiation Based on Total Loss of HNO₃ after Contact with: ○.1 M TBP-Amsco 125-82, ● Amsco 125-82. Corrected for Chemically Combined HNO₃: △▲.

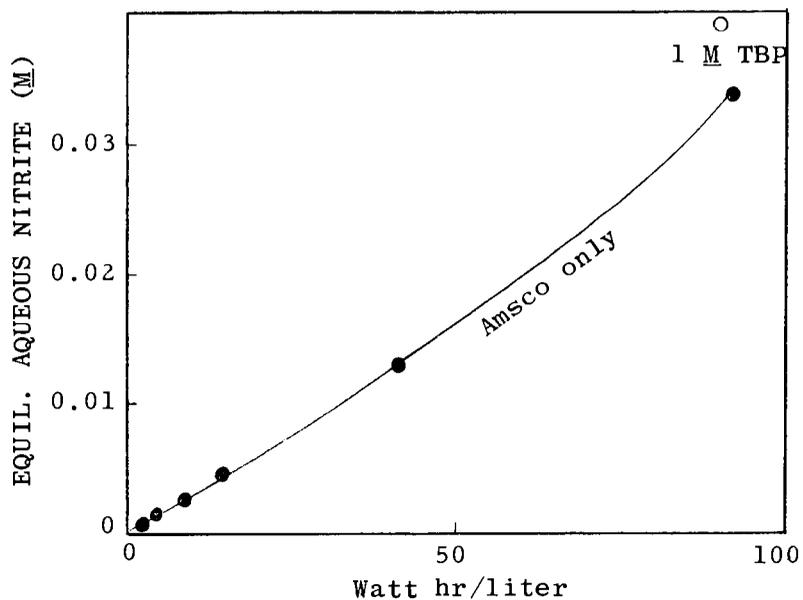


Fig. 12. Buildup of HNO₂ in Aqueous Phase During Irradiation (Initially 2 M HNO₃).

2.0 FISSION PRODUCT RECOVERY

2.1 Solvent Extraction of Cesium (B. Weaver, D. E. Horner, W. B. Howerton, Janet Bartlett)

The previously reported studies¹⁴ of organic compounds having ability to extract cesium have been extended and new compounds have been tested for possible process application. These compounds include dinonylnaphthalenesulfonic acid (DNNSA) or its sodium sulfonate salt (Na-DNNS), sodium tetraphenyl boron ($\text{Na}\phi_4\text{B}$) monoheptadecylphosphoric acid (HDP), and p-dodecylphenol (DDP).

Sodium dinonylnaphthalenesulfonate (0.5 M in hexone) selectively extracts cesium ($E_a^O \sim 0.5$) from a simulated low nitric acid (formaldehyde treated) Purex LWW waste which has been complexed with tartrate and neutralized to pH ~ 12 . Dilute nitric acid readily strips the cesium and sodium from the solvent. In spite of the low extraction coefficient, this compound or like compounds may be useful for separating cesium from the bulk ions in waste liquors. Subsequent processing would be required for final cesium-sodium separation. In this regard monoheptadecylphosphoric acid has been found to extract cesium preferentially to sodium from acidic cesium-sodium nitrate solution with a single-stage separation factor up to ~ 40 . Direct application of this reagent to cesium extraction from Purex LWW, however, has not been promising owing to low extraction coefficients and/or the formation of stable emulsions.

Cursory tests show that p-dodecylphenol extracts cesium (E_a^O 1-3) from sodium tartrate solution and tartrate-complexed, formaldehyde treated LWW at high pH with an indicated Cs-Na separation factor of about 5.

Insignificant cesium extraction from 0.5 M NaNO_3 solutions (pH 1 to 11) was obtained with various phosphonic acids, half-esters of phosphonic acids, oil-soluble polycarboxylic acids, and a group of structurally different water-soluble sulfonic acids.

2.1.1 Cesium Extraction by Sodium Dinonylnaphthalene-sulfonate. It was reported earlier¹⁴ that sodium dinonylnaphthalenesulfonate extractions of cesium were quite low from the usual Purex LWW waste which had been complexed with tartrate and adjusted to pH ~ 6 with caustic. Recent tests, however, have shown better extractions when starting with a low nitric acid (formaldehyde-treated) waste. Table 6 describes the composition of the simulated low acid Purex LWW used in the tests. Aqueous feeds were prepared by adjusting to 1 M tartrate and neutralizing with concentrated NaOH solution to the desired pH (total dilution factor ~ 3). The higher cesium extraction from the low acid Purex LWW are undoubtedly due to the lower NaNO_3 concentration in the adjusted feed (See p. 43-44, ORNL-CF-60-5-114).¹⁴

Table 6. Composition of Synthetic Formaldehyde-Reduced
Purex lWW Waste

| Ion | Concentration | |
|------------------------------|---------------|---------|
| | Molarity | g/liter |
| Na | 0.6 | |
| Fe ³⁺ | 0.5 | |
| Al ³⁺ | 0.1 | |
| Sr ²⁺ | | 0.17 |
| Ce ³⁺ | | 0.47 |
| Zr ⁴⁺ | | 0.60* |
| Ru | | 0.29 |
| Cs | | 0.37 |
| Sm ³⁺ | | 0.87 |
| H ⁺ | 0.2 | |
| SO ₄ ⁻ | 1.0 | |
| NO ₃ ⁻ | 0.6 | |

*As precipitate

As shown in Table 7 and 7A, moderate extraction of cesium was obtained with 0.5 M sulfonate reagent in hexone over a wide pH range from the adjusted, low-acid lWW. Between pH of 1 and 10, the cesium extraction coefficients were all between 0.6 and 0.8. As shown in Figures 13 and 14, however, the selectivity of cesium extraction was best at the high pH level. Also, in general, separation factors increased with increasing cationic charge. Thus, single-stage separation factors >100 were obtained for Cs over Zr-Nb, Ru, and rare-earths; >20 for Cs over Al, Fe and Sr; but only ~1.5-2 for Cs over Na. Separation factors decreased markedly with pH with the exception of Cs to Na. Sodium extraction (Table 8), like cesium, was approximately constant at pH ~1 to >10. Strontium, aluminum, and rare-earth extraction coefficients increased rapidly with decreasing pH and exceeded the cesium extraction coefficient in the lower pH range ~1-3. Iron, zirconium-niobium and ruthenium extractions also increased with decreasing pH, but never exceeded that of cesium.

Between 0.1-0.5 M NaDNNS in hexone cesium extraction coefficients from the adjusted waste at pH 10 varied in almost direct proportion to variation in the extractant concentration (Fig. 15). The cesium was readily stripped from the solvent by 3 M HNO₃ (Table 9).

Phase separation times of ~2-3 minutes were required with DNNSA in hexone and longer times in xylene and Amsco 125-82. Other sulfonic acids with more hydrophobic character and less surface activity may require less separation time and compounds of this type have been ordered. It is hoped that some of these compounds may give higher cesium extraction coefficients.

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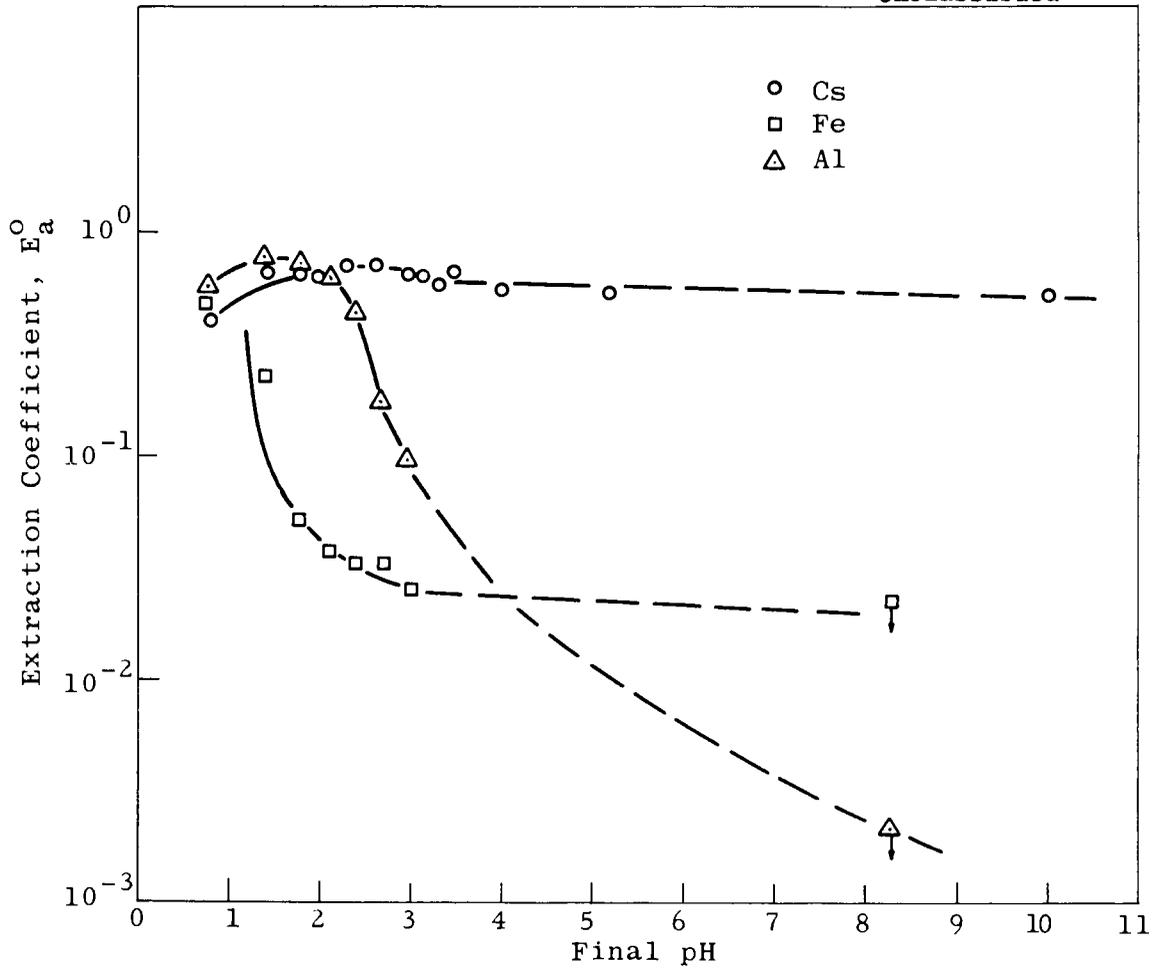


Fig. 13. Cs, Fe, and Al Extraction Coefficients as a Function of Equilibrium pH from Adjusted Purex Waste.

Organic: 0.5 M DNNSA (or Na salt) in hexone

Aqueous: synthetic formaldehyde-reduced Purex 1WW, initially 1 M tartrate; neutralized with NaOH; Cs¹³⁴-traced. Dilution factor 3.0

Equilibrations: batch, 10 min; phase ratio 1.0

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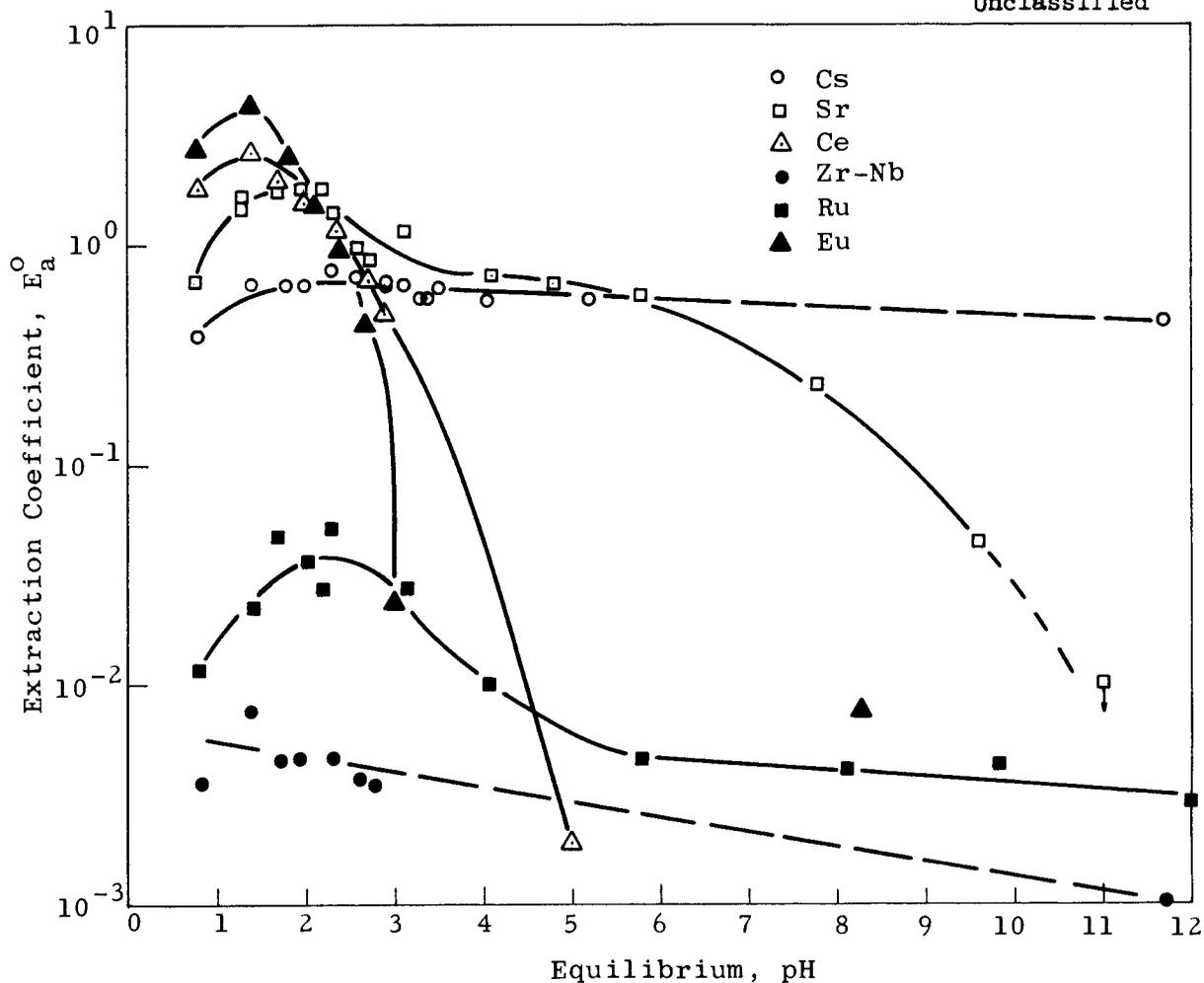


Fig. 14. Cs and other Cation Extraction Coefficients as a Function of Equilibrium pH from Adjusted Purex Waste.

Organic: 0.5 M DNNSA (or Na salt) in hexone

Aqueous: synthetic formaldehyde-reduced Purex 1WW plus various tracers, initially 1 M tartrate; neutralized with NaOH.
Dilution factor 3.0

Equilibrations: batch, 10 min; phase ratio 1.0

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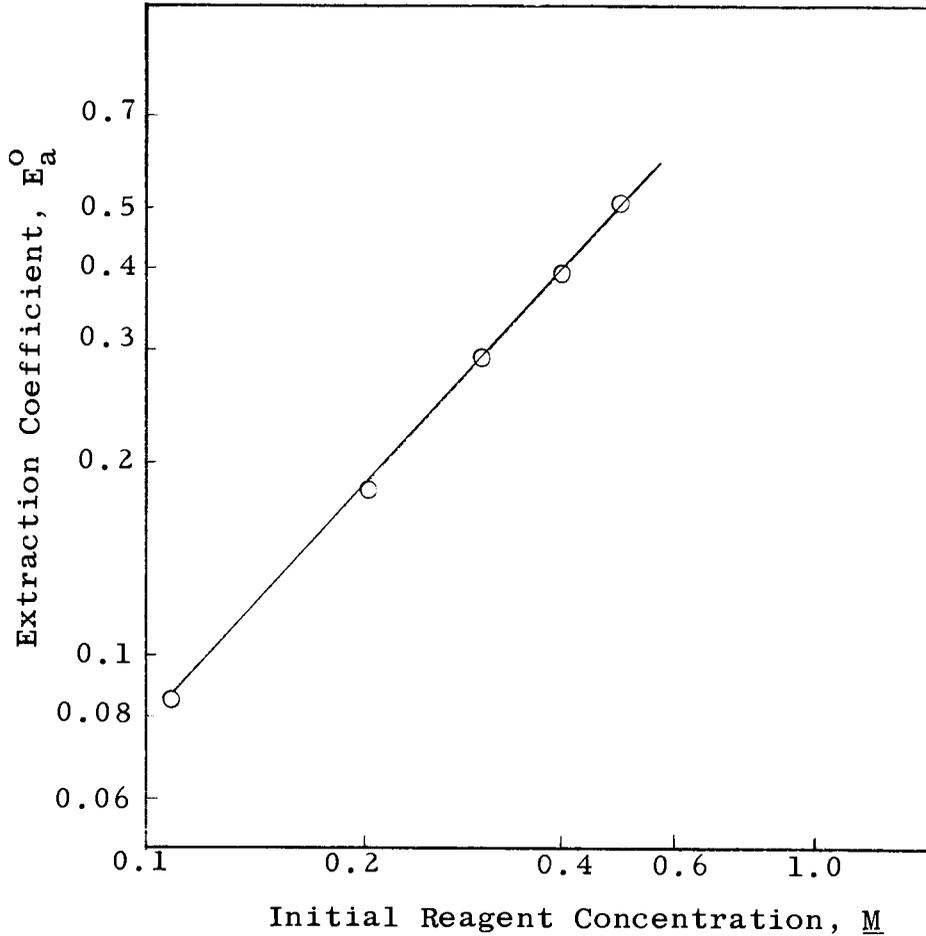


Fig. 15. Cs Extraction Coefficient as a Function of Na-DNNS Concentration from Adjusted Purex Waste.

Organic: Na-DNNS in hexone at concentration shown

Aqueous: synthetic formaldehyde-reduced Purex lww, initially 1 M tartrate; neutralized with NaOH. Cs¹³⁴-traced. Dilution factor 3.0.

Equilibrations: batch, 10 min; phase ratio 1

Table 7. Cs Extraction with DNNSA from Tartrate-Complexed Synthetic Purex 1WW

Organic: 0.5 M DNNSA - hexone
 Aqueous: synthetic formaldehyde-reduced Purex 1WW
 initially 1 M tartrate; neutralized with NaOH
 Cs¹³⁴-traced. Dilution factor 3.0
 Equilibrations: batch, 10 min; phase ratio 1.0

| pH | | Cs Ext. Coef. (E_a^O) |
|---------|-------|---------------------------|
| Initial | Final | |
| 1.0 | 0.8 | 0.38 |
| 1.9 | 1.4 | 0.67 |
| 3.0 | 1.8 | 0.65 |
| 4.1 | 2.0 | 0.66 |
| 6.0 | 2.3 | 0.75 |
| 8.0 | 2.6 | 0.71 |
| 10.0 | 2.9 | 0.6 |
| 10.0 | 2.9 | 0.63 |
| 10.8 | 3.1 | 0.63 |
| 11.0 | 3.3 | 0.56 |
| 11.2 | 3.4 | 0.55 |
| 11.5 | 3.5 | 0.62 |
| 11.7 | 4.05 | 0.57 |
| 11.8 | 5.2 | 0.54 |
| >11.5 | 11.7 | 0.43 |

Table 7A. Cs Extraction with Na-DNNS from Tartrate-Complexed Synthetic Purex 1WW

Organic: 0.5 M DNNSA and Na-DNNS in hexone
 Aqueous: synthetic formaldehyde-reduced Purex 1WW,
 initially 1 M tartrate; neutralized with NaOH;
 Cs¹³⁴-traced. Dilution factor 3.0
 Equilibrations: batch, 10 min; phase ratio A/O = 1/3

| pH | | Organic | | Cs Ext. Coef. (E_a^O) |
|---------|-------|---------|-----------|---------------------------|
| Initial | Final | % Acid | % Na Salt | |
| 1.9 | 1.0 | 75 | 25 | 0.69 |
| 1.9 | 1.3 | 50 | 50 | 0.75 |
| 1.9 | 1.6 | 25 | 75 | 0.76 |
| 4.25 | 4.35 | 0 | 100 | 0.63 |

Table 8. Na Extraction with DNNSA from Tartrate-Complexed

Synthetic Purex 1WW

Organic: 0.5 M DNNSA in hexone

Aqueous: synthetic formaldehyde-reduced Purex 1WW, initially 1 M tartrate neutralized with NaOH. Dilution factor 3.0

Equilibrations: batch, 10 min; phase ratio 1.0

| pH Final | Na Conc., g/liter | | Na Ext. Coef. (E_a^O) |
|-------------|-------------------|---------|---------------------------|
| | Organic | Aqueous | |
| 0.75 | 3.8 | 19.1 | 0.20 |
| 1.3 | 7.1 | 19.1 | 0.37 |
| 1.7 | 8.9 | 21 | 0.42 |
| 2.0 | 9.5 | 23 | 0.41 |
| 2.3 | 12.0 | 27 | 0.44 |
| 2.6 | 12.7 | 29 | 0.44 |
| 2.7 | 12.8 | 29 | 0.44 |
| 2.9 | 12.6; 13.3 | 28; 23 | 0.45; 0.58 |
| 3.1 | 12.4 | 28 | 0.44 |
| 3.3 | 13.8 | 31 | 0.45 |
| 3.4 | 14.3 | 31 | 0.46 |
| 3.5 | 10.8 | 29 | 0.37 |
| 4.1 | 11.1 | 30 | 0.37 |
| 5.2 | 13.6 | 34 | 0.40 |
| 11.1 | 13.7 | 40 | 0.34 |

Table 9. Cs Stripping from Na-DNNS with HNO₃

Organic: 0.5 M Na-DNNS in hexone; Cs \approx 0.04 g/liter; Cs¹³⁴-traced

Aqueous: 1 and 3 M HNO₃

Equilibrations: batch; 10 min; phase ratios (A/O): 1/3, 1/5

| Conc. HNO ₃ , M | P.R. (A/O) | Strip Coef. (S _q) |
|----------------------------|------------|-------------------------------|
| 1 | 1/3 | 2.4 |
| 1 | 1/5 | 2.0 |
| 3 | 1/3 | 10 |
| 3 | 1/5 | 9.7 |

2.1.2 Cesium Extraction with Monoheptadecylphosphoric Acid. Previous preliminary tests¹⁵ have indicated that monoalkyl-phosphoric acids have ability to extract cesium in preference to sodium from dilute sodium nitrate solutions. This observation has been confirmed in recent tests with monoheptadecylphosphoric acid (HDPa) which promises to be a particularly acceptable reagent for this application. Cesium extraction, and Cs-Na separation ability of the HDPa, is shown by data in Tables 10 and 11. It is estimated that a cesium coefficient of ~4 and a Cs-Na separation factor of 20-40 could be obtained by extracting from 0.5 M NaNO₃, pH ~1, with 1 M HDPa in Amsco 125-82.

Table 10. Cs Extraction from NaNO₃ Solution
as a Function of HDPa Concentration

Organic: monoheptadecylphosphoric acid in Amsco 125-82
Aqueous: 1 M NaNO₃; int. pH = 5; Cs¹³⁴-traced
Equilibrations: batch, 10 min; phase ratio (A/O) 3.0

| Reagent Conc., M | pH | | Cs Ext. Coef., E _a ^o |
|---------------------|---------|-------|--|
| | Initial | Final | |
| 0.1 | 5.0 | 2.0 | 0.18 |
| 0.2 | 5.0 | 1.7 | 0.37 |
| 0.5 | 5.0 | 1.4 | 0.96 |
| 1.0 | 5.0 | 1.2 | 1.9 |
| 1.5 | 5.0 | 1.1 | 2.3* |
| 2.0 | 5.0 | 1.0 | 3.4* |

*Emulsion (precipitation)

Table 11. Cs-Na Extraction-Separation with HDPa
as a Function of pH

Organic: 0.5 M HDPa in Amsco 125-82
Aqueous: 0.5 M NaNO₃-NaOH; initial pH as shown;
0.1 g Cs/liter; Cs¹³⁴-traced
Equilibrations: batch, 10 min; phase ratio (A/O) 3.0

| pH | | Ext. Coef., E _a ^o | | S.F. Cs/Na |
|---------|-------|---|-------|---------------|
| Initial | Final | Cs | Na | |
| 1.0 | 1.0 | 1.9 | 0.048 | 40 |
| 2.7 | 1.6 | 2.4 | 0.10 | 24 |
| 4.1 | 1.7 | 2.4 | 0.11 | 22 |
| 5.8 | 1.65 | 2.4 | 0.11 | 22 |
| 10.9 | 1.75 | 2.4 | 0.12 | 20 |
| 11.7 | 4.7 | 0.66 | 0.44 | 1.5 |

The cesium extraction coefficient is proportional to the first power of the HDP A concentration as shown in Figure 16. The Cs-Na separation factor decreases with increasing pH as shown in Fig. 17 but was still >5 at pH ~ 3 . In all tests phase separation was rapid when the HDP A concentration in Amsco 125-82 was 1 M or less. Emulsions were formed when extracting from 1 M NaNO_3 solution at higher HDP A concentration.

Direct application of HDP A to cesium extraction from 1WW solution does not appear promising. For example, cesium coefficients <0.05 were obtained with 0.4 M HDP A in Amsco 125-82 from acidic 1WW at pH ~ 0.5 and unmanageable, stable emulsions formed in equilibrations with tartrate-complexed 1WW ranging in pH 2-8. The cesium extraction coefficient at pH ≈ 4 was <0.3 .

2.1.3 Cesium Extraction with Alkyl Phenols. Long chain alkyl-substituted phenols, e.g., dinonylphenol¹⁴ and p-dodecylphenol, also show ability to extract cesium from sodium tartrate solutions or tartrate-complexed formaldehyde-treated 1WW solution at high pH (~ 12). One molar p-dodecylphenol in xylene extracted cesium with a coefficient up to 2.8 from various concentrations of sodium tartrate solutions (Table 12). As shown in Table 13, the same organic extracts cesium with a coefficient of 1.3 from simulated tartrate-complexed, formaldehyde-treated 1WW solution, pH ~ 12 . Corresponding aluminum and iron extraction coefficients were <0.003 ; the Cs-Na separation factors in these tests were ~ 5 . Data given in Table 13 also show that the cesium extraction coefficient is proportional to approximately the second power of the DDP concentration.

Emulsions and precipitates (presumably the sodium phenate salt) were formed when the aqueous sodium concentration exceeded 2 M or the organic phenol concentration exceeded 1 M. Other diluents will be tested for increased solubility of the phenate salt.

Several short-chain dialkyl phenols and a short-chain monoalkyl phenol showed insignificant cesium extraction from 0.25 M sodium tartrate solutions at pH 1 to 12. These compounds included di-t-amyl-, t-butyl m-cresol, and di-t-butylphenol.

2.1.4 Screening of Other Reagents. A group of water soluble sulfonic acids were tested to determine if they would form a cesium complex which would favor the organic phase. All results were negative using 0.3 M extractant in xylene and Cs-134 traced 0.5 M NaNO_3 solution at pH ≈ 4 . Compounds tested were sodium 1-naphthol-2-sulfonate, 1,8-dihydroxynaphthalene-3,6-disulfonic acid, 1-amino-8-naphthol-4-sulfonic acid, 1-amino-2-naphthol-4-sulfonic acid, 1-naphthylamine-4,8-disulfonic acid, 4,4'-biphenyldisulfonic acid, naphthalene- β -sulfonic acid, sodium 2-bromoethanesulfonate, 7-iodo-8-hydroxyquinoline-5-sulfonic acid, 8-hydroxyquinoline-5-sulfonic acid, 2-aminotoluene-4-sulfonic acid, 4-nitrochlorobenzene-2-sulfonic acid, 2,4 dinitro-1-naphthol-7-sulfonic acid, 2-nitrobromobenzene-4-sulfonic acid, 2,4 dinitro-

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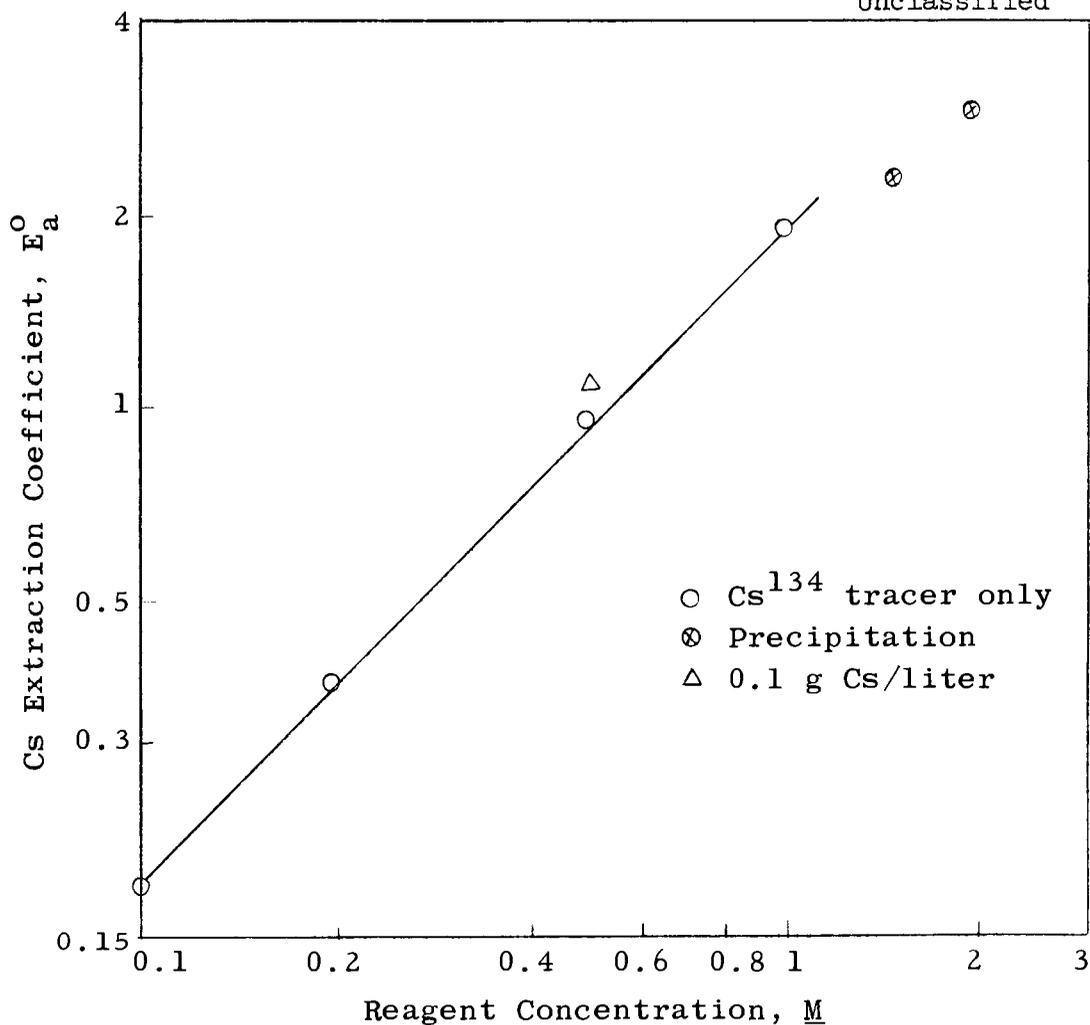


Fig. 16. Cs Extraction Coefficient as a Function of HDPA Concentration.

Organic: HDPA in Amsco 125-82

Aqueous: 1 M $NaNO_3$ (final pH 1-2)

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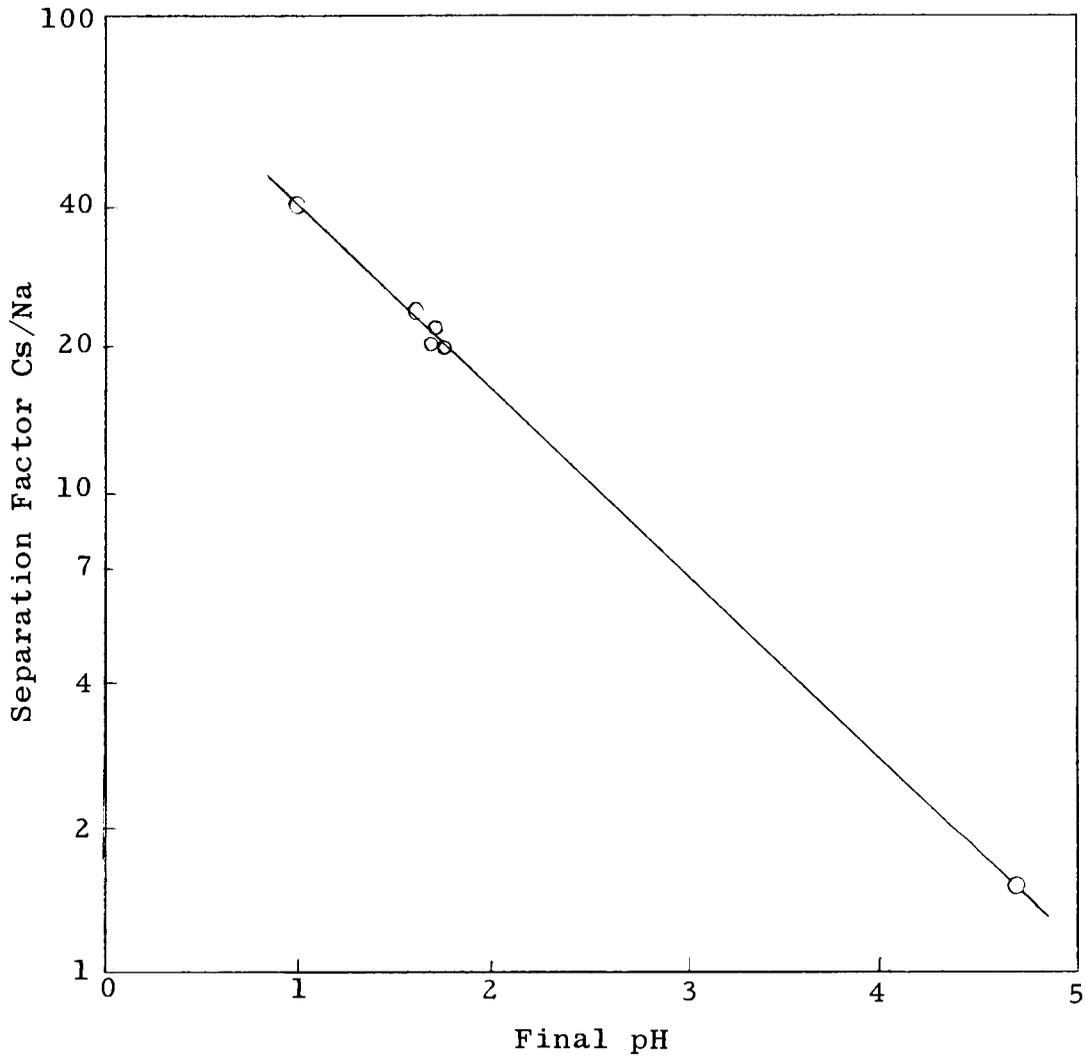


Fig. 17. Cs/Na Separation Factor as a Function of pH.

Organic: 0.5 M HDP A in Amsco 125-82

Aqueous: NaNO_3 -NaOH Solutions ($\Sigma\text{Na}=0.5 \text{ M}$)

Table 12. Cs Extraction with p-Dodecylphenol
from Sodium Tartrate Solution

Organic: p-dodecylphenol in xylene
Aqueous: various concentration sodium tartrate-sodium hydroxide solutions (pH ~12); Cs¹³⁴-traced
Equilibrations: batch, 10 min; phase ratio 1.0

| Sodium Tartrate Concentration, M | Na Conc., M | Cs Ext. Coef. E_a^O |
|----------------------------------|-------------|-----------------------|
| 0.1 | 0.2 | 1.8 |
| 0.2 | 0.4 | 2.8 |
| 0.5 | 1 | 2.4 |
| 1 | 2 | 1.5* |
| 2 | 4 | 0.92* |

*Heavy emulsion and precipitate.

Table 13. Cs and Na Extraction as a Function
of p-Dodecylphenol Concentration

Organic: p-dodecylphenol in xylene at concentrations shown
Aqueous: synthetic formaldehyde-reduced Purex 1WW. Initially 1 M tartrate; neutralized to pH ~12 with NaOH; Cs¹³⁴-traced. Dilution factor 3.0
Equilibrations: batch, 2 min; phase ratio 1.0

| Reagent Conc., M | Final pH | Na Conc. (g/liter) | | Ext. Coef., E_a^O | | S.F. Cs/Na |
|------------------|----------|--------------------|----------|---------------------|-------|------------|
| | | Organic | Aqueous* | Cs | Na | |
| 0.3 | 12 | 0.49 | ~23 | 0.17 | 0.022 | 7.7 |
| 0.5 | | 1.6 | ~21 | 0.48 | 0.076 | 6.3 |
| 0.8 | | 3.7 | ~19 | 1.0 | 0.20 | 5 |
| 1 | | 4.5 | ~18 | 1.3 | 0.25 | 5 |
| 2 | 11.8 | 7.0 | ~16 | 2.6** | 0.44 | 6 |

*Calculated value

**Heavy emulsion and precipitate

benzenesulfonic acid, p-nitrobenzenesulfonic acid, m-nitrobenzenesulfonic acid, dl-camphorsulfonic acid.

Negative results were also obtained in somewhat similar tests with a variety of other compounds including cyclohexanecarboxylic acid, isodecanoic acid, 2-ethylhexyl 2-ethylhexylphosphonic acid, capryl phenylphosphonic acid, dimer acid [Empol 1014]*, dimer acid [Empol 1024]*, trimer acid [3162D].*

*Emery Industries, Inc., Cincinnati, Ohio.

3.0 FUNDAMENTAL CHEMISTRY

3.1 Interface Mechanism for Uranium Extraction by Amine Sulfate (W. J. McDowell, G. N. Case)

There has been considerable speculation concerning the mechanism by which the extraction of uranium by amines might proceed at the organic aqueous interface. Where sulfate systems are involved the question most discussed has been whether the transfer of uranium from aqueous to organic phase involved the dipositive uranyl ion, the neutral uranyl sulfate molecule, or an anionic complex such as $\text{UO}_2(\text{SO}_4)_2^-$. The latter process has been strongly considered since considerable quantities of the anionic species are known to exist in acidic sodium sulfate solutions containing uranium¹⁶ and because of the analogy between the behavior of amine extractants and that of anion exchange resins which are sometimes presumed (possibly more because of their name than any real evidence) to sorb uranyl sulfate by exchange of anionic species. The experiments described in the following are designed to give some insight into which of these transfer processes is most important.

These experiments are based on the following ideas: (1) that S^{35} (as H_2SO_4 attached to alkyl amine) should transfer from organic to aqueous phase at some rate proportional to the driving force involved until isotopic equilibria is attained, that is, until $\text{S}_{\text{org}}^{35}/\text{S}_{\text{aq}}^{35} = \Sigma\text{SO}_4_{\text{org}}/\Sigma\text{SO}_4_{\text{aq}}$. (2) That this transfer of S^{35} should proceed in the same manner (if not exactly the same rate) if extraction of uranium is taking place in the system by the transfer of neutral or cationic species at the interface. (3) That if anionic species from the aqueous phase were transferred intact across the interface, sulfate from the organic phase would be transferred back to the aqueous phase to maintain electrical neutrality thus forcing more S^{35} into the aqueous phase at some time during the course of the equilibration than would be expected from the total sulfate ratio.

In these experiments the organic phase was di-n-decylamine sulfate in benzene. The S^{35} activity in the organic phase was approximately 0.1 mc/ml. The equilibrations were done by quiescent interface techniques in an apparatus previously described in connection with kinetic studies.¹⁷ Each phase was stirred by a small paddle rotating at 24 rpm near the interface. All equilibrations were run under identical conditions so that direct comparison between runs is possible. Samples of the appropriate phases were removed at intervals as the equilibration proceeded. Analyses for S^{35} were by liquid scintillation counting and uranium analyses were by fluorimetric methods.¹⁸

The acidity of the extraction system was adjusted in each case so that the amine was as near 100% in the normal sulfate form as possible. This was necessary since the extraction of

uranium into an amine solution partly in the bisulfate form returns sulfuric acid to the aqueous phase.¹⁹ This, of course, would force large quantities of S^{35} from organic to aqueous phase in a way which would be impossible to duplicate with a uranium free system. The effects of such a transfer of S^{35} would therefore be very difficult to account for.

Let us examine first a system in which the aqueous phase contains only sulfuric acid in addition to uranyl sulfate. The acidity was adjusted to that corresponding to normal amine sulfate in the organic phase, $\sim 0.0001 \text{ M H}_2\text{SO}_4$. Since the uranyl sulfate was 0.012 M initially this constituted the major fraction of the aqueous sulfate. Thus as extraction proceeded the total sulfate ratio changed markedly. This effect may be seen in Fig. 18 where the total sulfate ratio, $\Sigma\text{SO}_4\text{org}/\Sigma\text{SO}_4\text{aq}$ and the isotopic ratio, $S_{\text{org}}^{35}/S_{\text{aq}}^{35}$ are plotted as a function of time. It is important to note that although there are initial rapid changes in the S^{35} distribution (see Fig. 19 for % of approach to final equilibrium) the ratio $S_{\text{org}}^{35}/S_{\text{aq}}^{35}$ does not approach or cross the $\Sigma\text{SO}_4\text{org}/\Sigma\text{SO}_4\text{aq}$ ratio until uranium equilibrium is attained. No conclusions can be drawn from such data, of course, at points where isotopic equilibrium is attained.

The rapid change in total sulfate ratio due to uranium extraction (Fig. 18) makes interpretation of the isotope distribution difficult. One question which arises is how would the S^{35} distribute under the influence of a driving force which varies with time if no uranium were being extracted. An experimental answer to this question was attempted as follows: At each time interval for which a sample (Fig. 18) was taken the org/aq sulfate ratio was calculated. Such a ratio was constructed by adjusting the sodium sulfate content of an aqueous phase. The transfer of S^{35} from organic phase to this uranium free aqueous phase was then followed as a function of time. The amount of S^{35} which had been transferred at the required time was then determined from the resulting plot (Fig. 20) of amount transferred vs time. The synthesized plot of S^{35} transfer following a changing total sulfate ratio vs time may be seen compared with the transfer during uranium extraction in Fig. 21. The fact that much greater quantities of S^{35} were transferred in the absence of uranium extraction offers no support to a mechanism of uranium transfer across the interface in which aqueous anionic sulfate complexes cross as unbroken entities. In addition such large difference in amounts of S^{35} transferred suggests that the extraction of uranium may in some way hinder the transfer of S^{35} from organic to aqueous phase. Some possible ways in which this might occur are (1) a blocking of the interface by the uranium-amine sulfate complex or (2) continual transport of organic sulfate away from

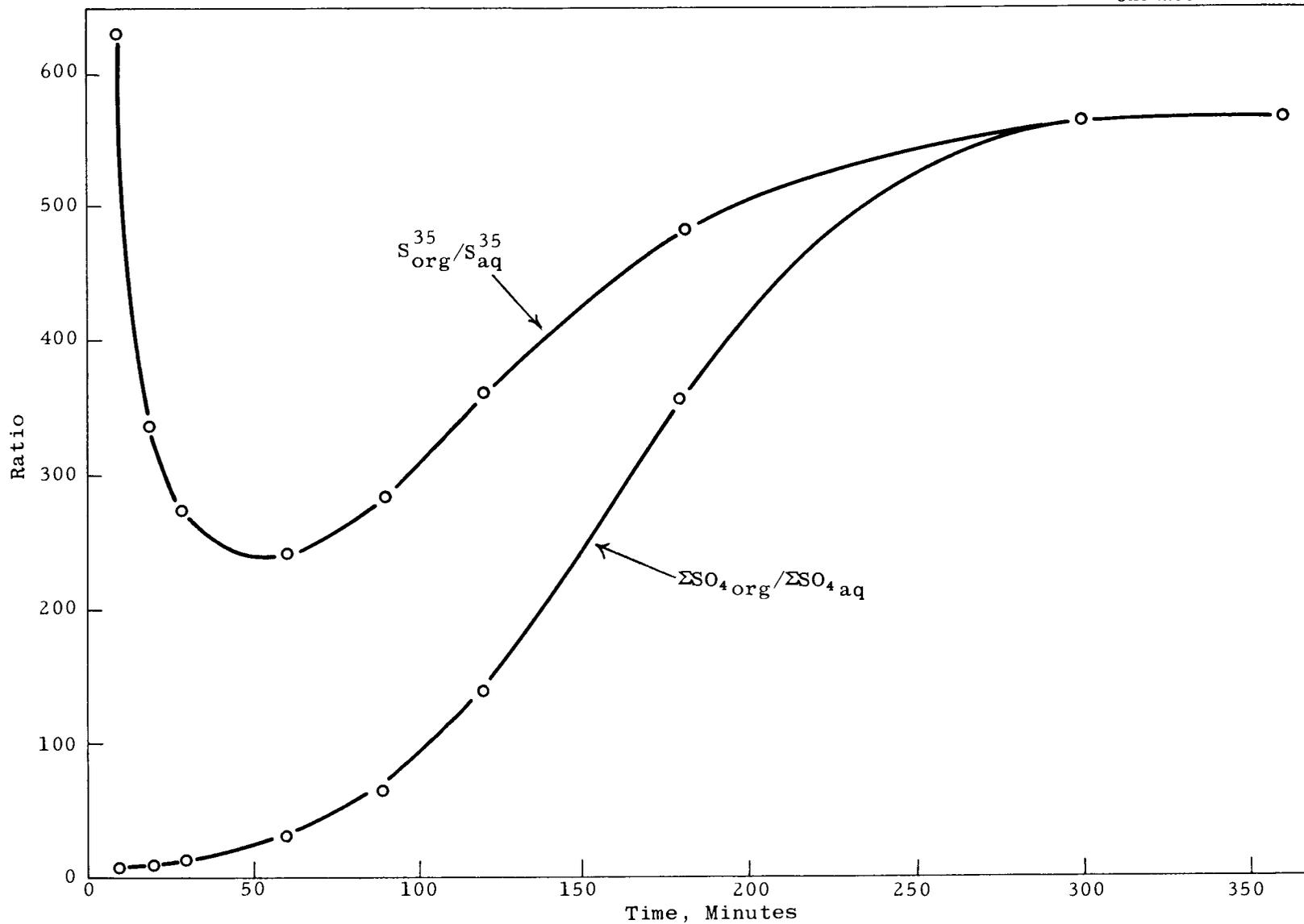


Fig. 18. Total Sulfate and S^{35} Distribution Between Phases as a Function of Time during Extraction of Uranium. Aqueous phase here was $\sim 0.0001 \text{ M H}_2\text{SO}_4 + 0.012 \text{ M UO}_2\text{SO}_4$, initially.

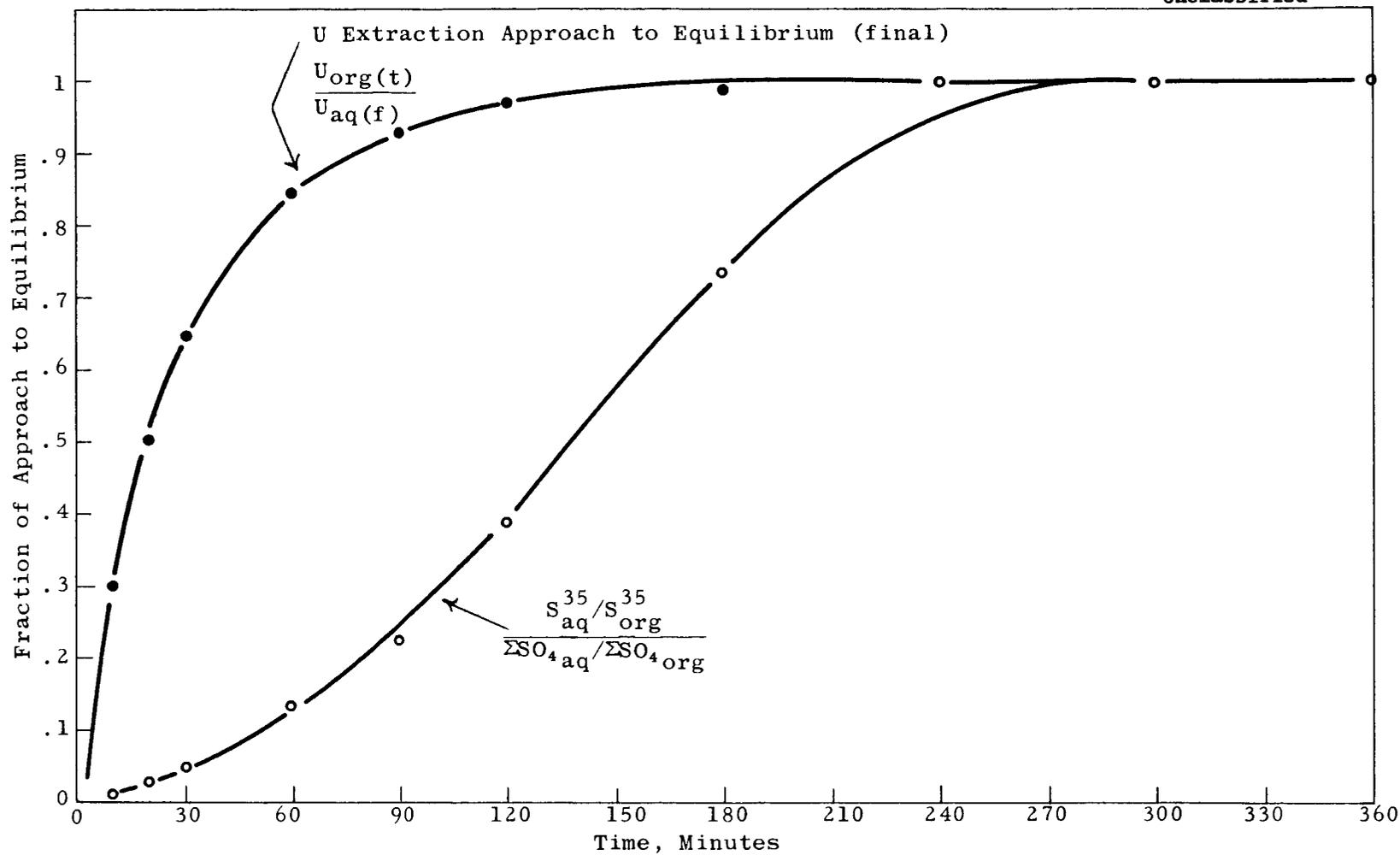


Fig. 19. S³⁵ Approach to Equilibrium Specified by the ΣSO_4 Ratio at any Time, t.

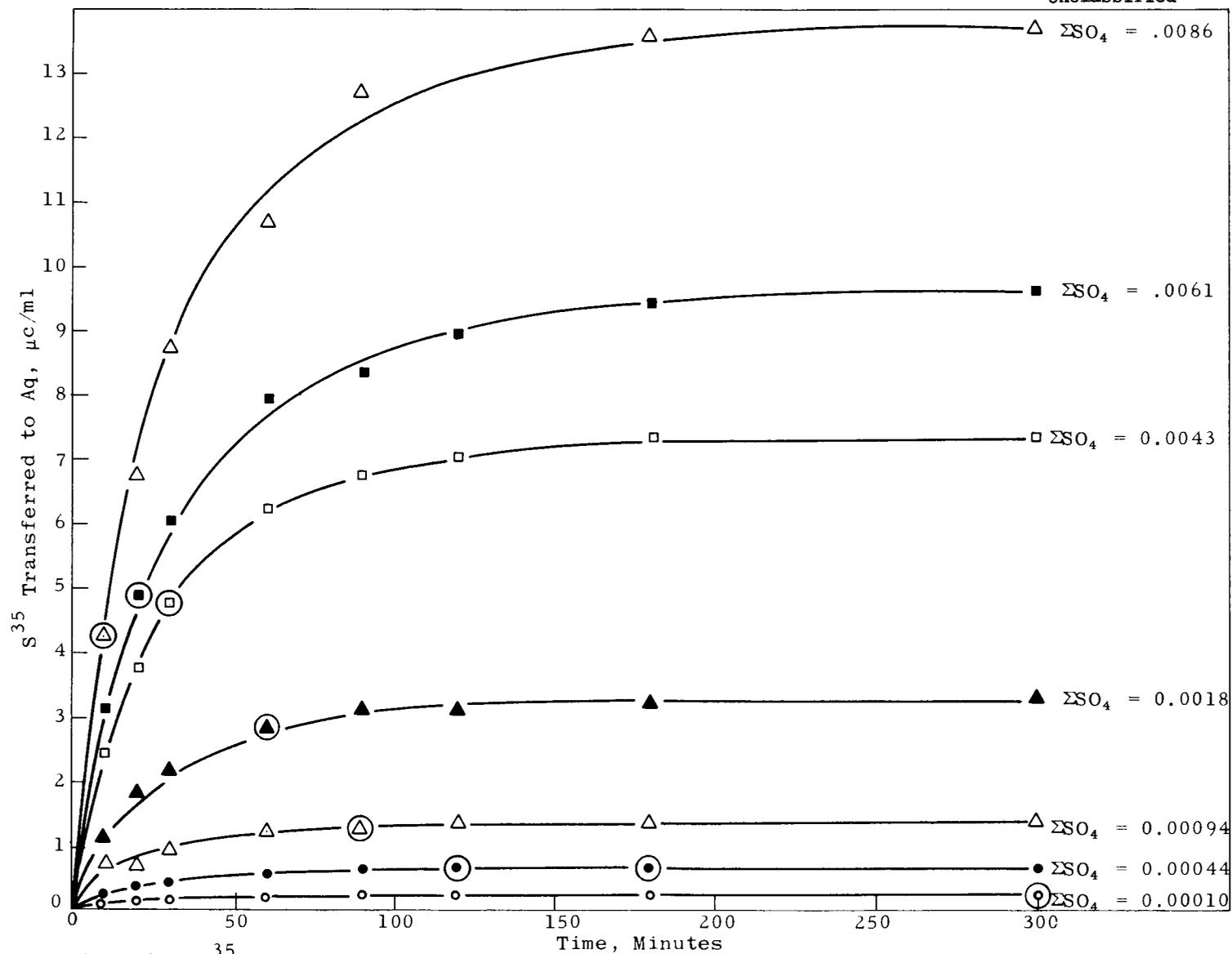


Fig. 20. S^{35} Transfer as a Function of Time at Various Aqueous SO_4 Levels. Circled values used in Fig. 21.

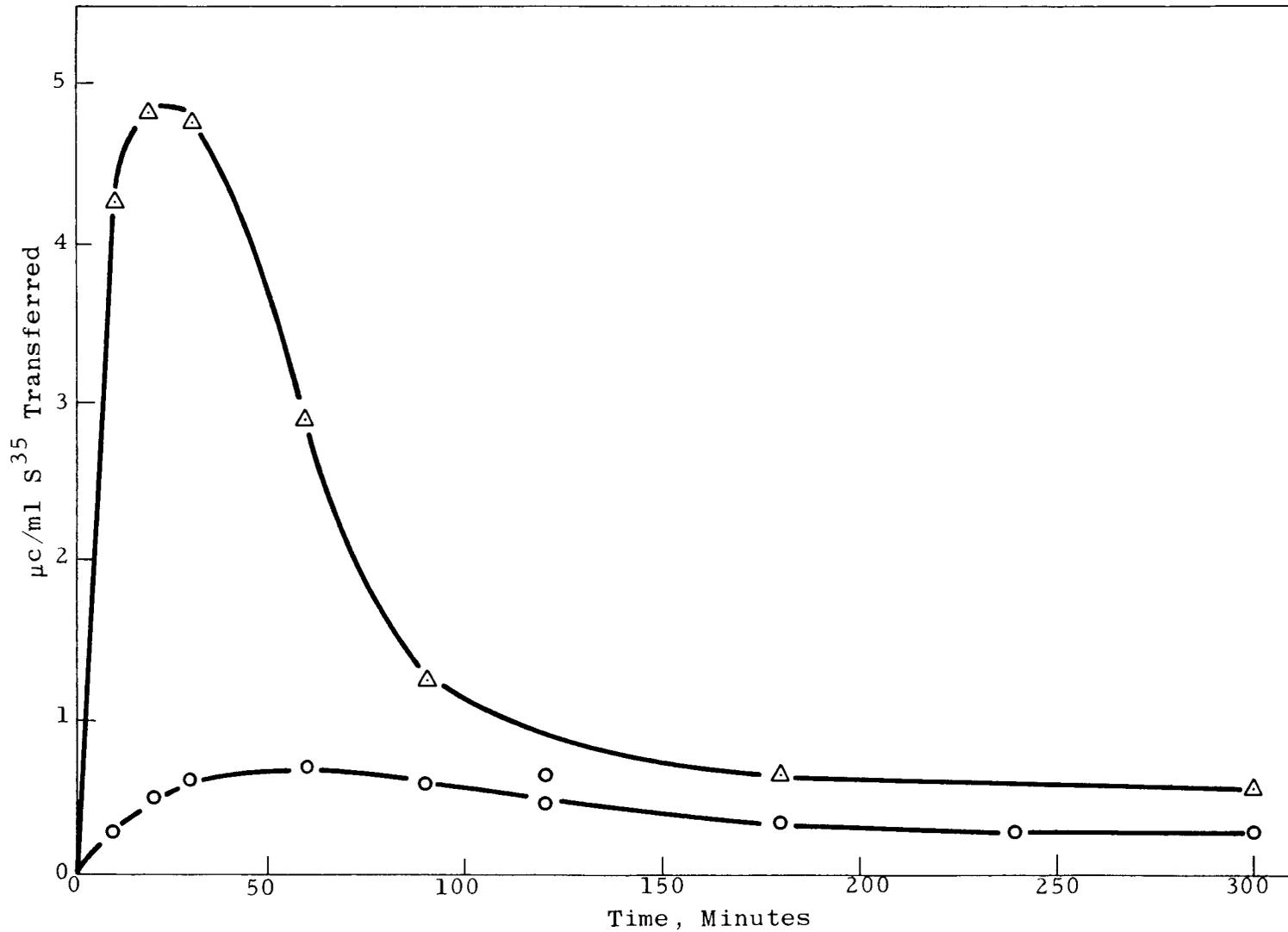


Fig. 21. Comparison of S^{35} Transfer during Extraction of Uranium from 0.0001 N H_2SO_4 , \circ , with S^{35} Transfer to Na_2SO_4 Solutions Synthesized to Match Aq ΣSO_4 Content at a given Time in the Uranium Extraction, \triangle .

the interface by extraction of UO_2SO_4 by amine sulfate.*

In the system just discussed the aqueous uranium species was predominately UO_2^{++} . In order to obtain more convincing evidence against anion transfer at the interface similar results involving extraction from an aqueous system containing a preponderance of the species $\text{UO}_2(\text{SO}_4)_2^{--}$ would be desirable. In 0.5 M Na_2SO_4 75% of the uranium is in this form. Fig. 22 shows the ΣSO_4 and S^{35} ratios obtained by extraction from such an aqueous system by an amine in the normal sulfate form as before. Here again to have evidence for anion transfer from aqueous to organic phase requires that $\text{S}_{\text{org}}^{35}/\text{S}_{\text{aq}}^{35}$ fall below $\Sigma\text{SO}_{4\text{org}}/\Sigma\text{SO}_{4\text{aq}}$. This does not occur.

The 0.5 M SO_4 system has the additional advantage that the total sulfate ratio does not change much during the extraction. Thus interpreting the meaning of the S^{35} ratio variation with time is more simple. In addition the comparison of the approach to equilibrium between U extraction and S^{35} transfer is more straightforward (Fig. 23) and shows clearly that the uranium extraction approaches equilibrium more rapidly than does the S^{35} transfer.

One can conclude from the foregoing that there is no indication of any anion form of uranium transferring through the aqueous-organic interface. One cannot say however, that there is definite proof that such does not occur as part of an over all reaction. Certain other data do, however, have a bearing on the question. First, the data in Fig. 20, and previous kinetic studies¹⁷ indicating UO_2^{--} ion to be the most effective of the aqueous species present (mole for mole) in transporting uranium to the interface, both suggest neutral species transfer rather than anion transfer. In addition, interfacial tension data showing the sulfate form of the amines to be more interface active than many other common anion forms indicates that the sulfate part of the amine sulfate remains strongly associated with the organic amine at the interface and does not predominately ionize.⁶ These facts, taken together, strongly suggest that uranium is transferred across the interface of the systems described here as neutral uranyl sulfate.

*A third possibility has been suggested in which UO_2^{++} is extracted by amine bisulfate as follows: $\text{UO}_2 + 2\text{R}_3\text{NH}_2\text{SO}_4 \rightarrow (\text{R}_3\text{NH})_2\text{UO}_2\text{SO}_4 + 2\text{H}^+$. For such a reaction to be effective in extracting uranium into a solution containing infinitesimal quantities of bisulfate (as did the one used here) would require that the bisulfate form of the amine be enormously more interface active than the normal sulfate. Interfacial tension measurements do not at present indicate this to be the case.

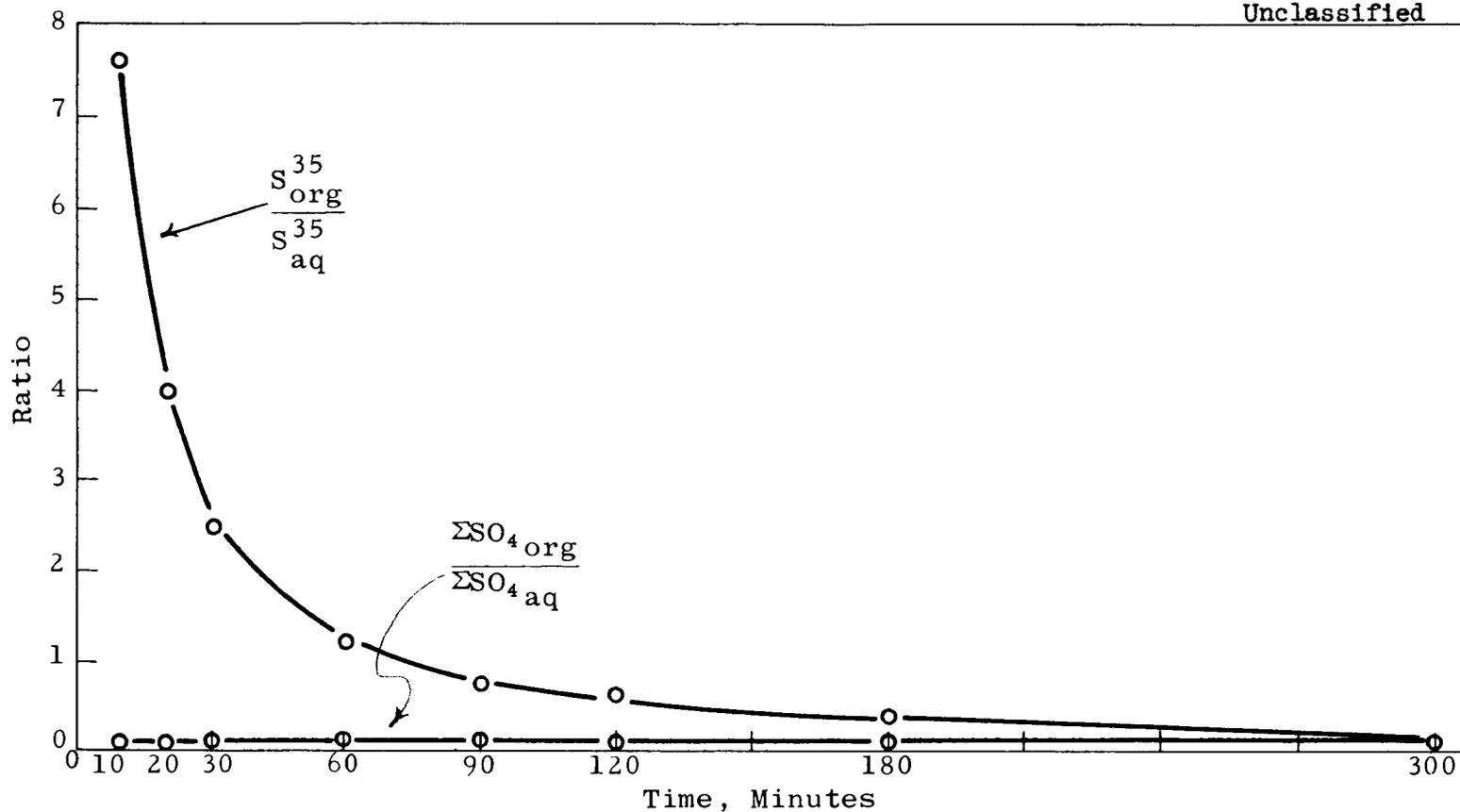


Fig. 22. Total Sulfate and S^{35} Distribution between Phases as a Function of Time during the Extraction of Uranium. Organic phase 0.10 N di-n-decylamine sulfate in benzene. Aqueous phase 0.5 M Na_2SO_4 + ~ 0.0001 N H_2SO_4 + 0.012 M UO_2SO_4 initially.

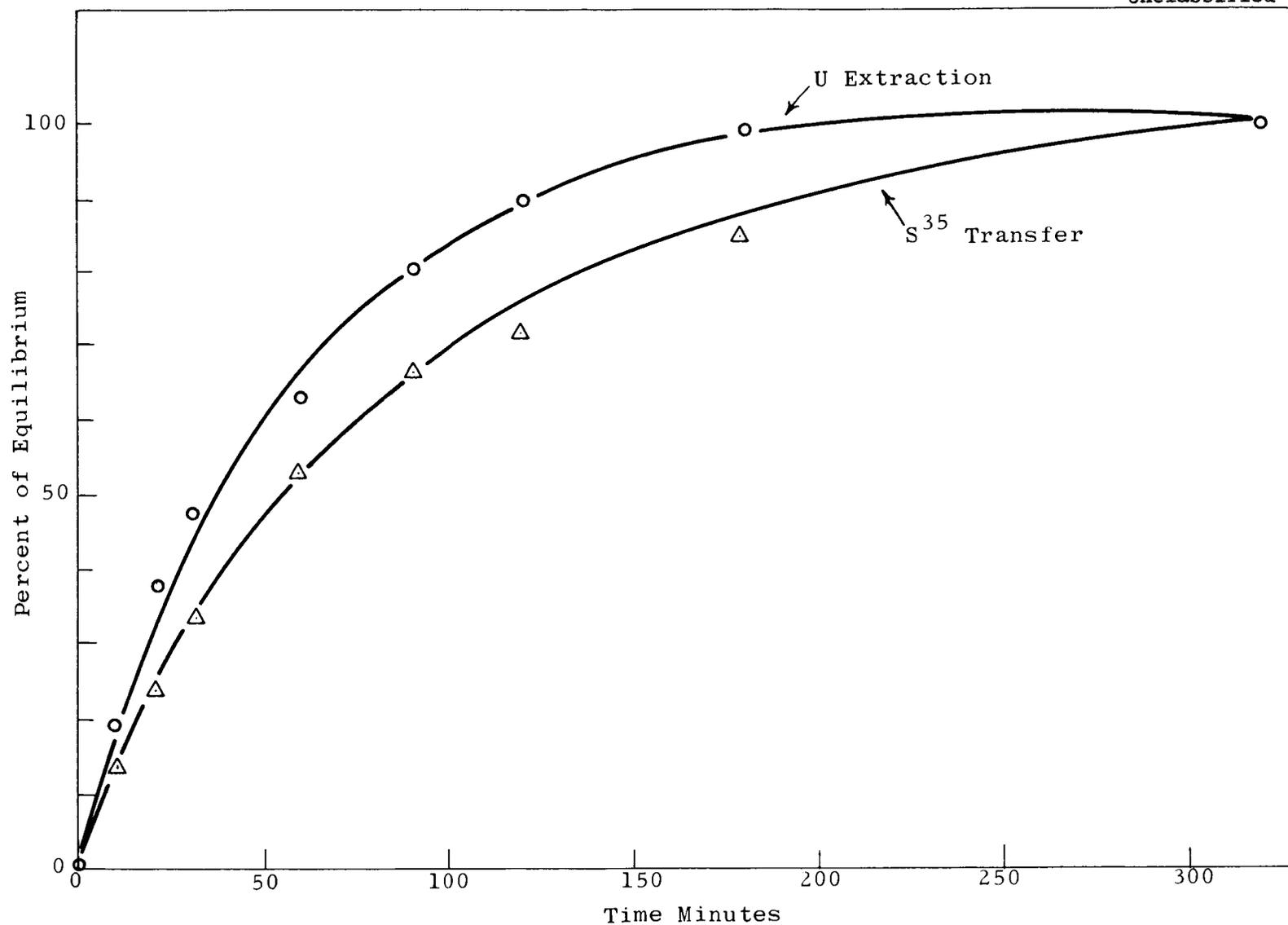


Fig. 23. Approach to Equilibrium of Uranium and S³⁵ during Extraction of U from 0.5 M Na₂SO₄; 0.0001 M H₂SO₄. Organic phase 0.10 N DDAS in benzene.

3.2 Alkaline Earth Extraction by Di(2-ethylhexyl)phosphoric Acid (D2EHPA) and Sodium Di(2-ethylhexyl) Phosphate (NaD2EHP) (W. J. McDowell, G. N. Case)

In a continuation of work previously reported on strontium extraction by D2EHPA²⁰ two developments have aided and simplified the investigation. The first was confirmation that the extraction of tracer quantities (10^{-8} M) of Sr⁸⁵ by D2EHPA-NaD2EHP did not change the apparent hydrogen ion concentration of the aqueous phase. Previous indications of $[H^+]$ change were traced to D2EHPA losses in the procedure used for sampling the organic phase to determine extraction coefficients. Thus it became possible to obtain a complete titration curve and a complete $E = f(\text{pH})$ curve at the same time by the same two-phase titration if a method of removing, counting and replacing samples in the system without loss could be developed. This was done and is the second of the two developments referred to above.

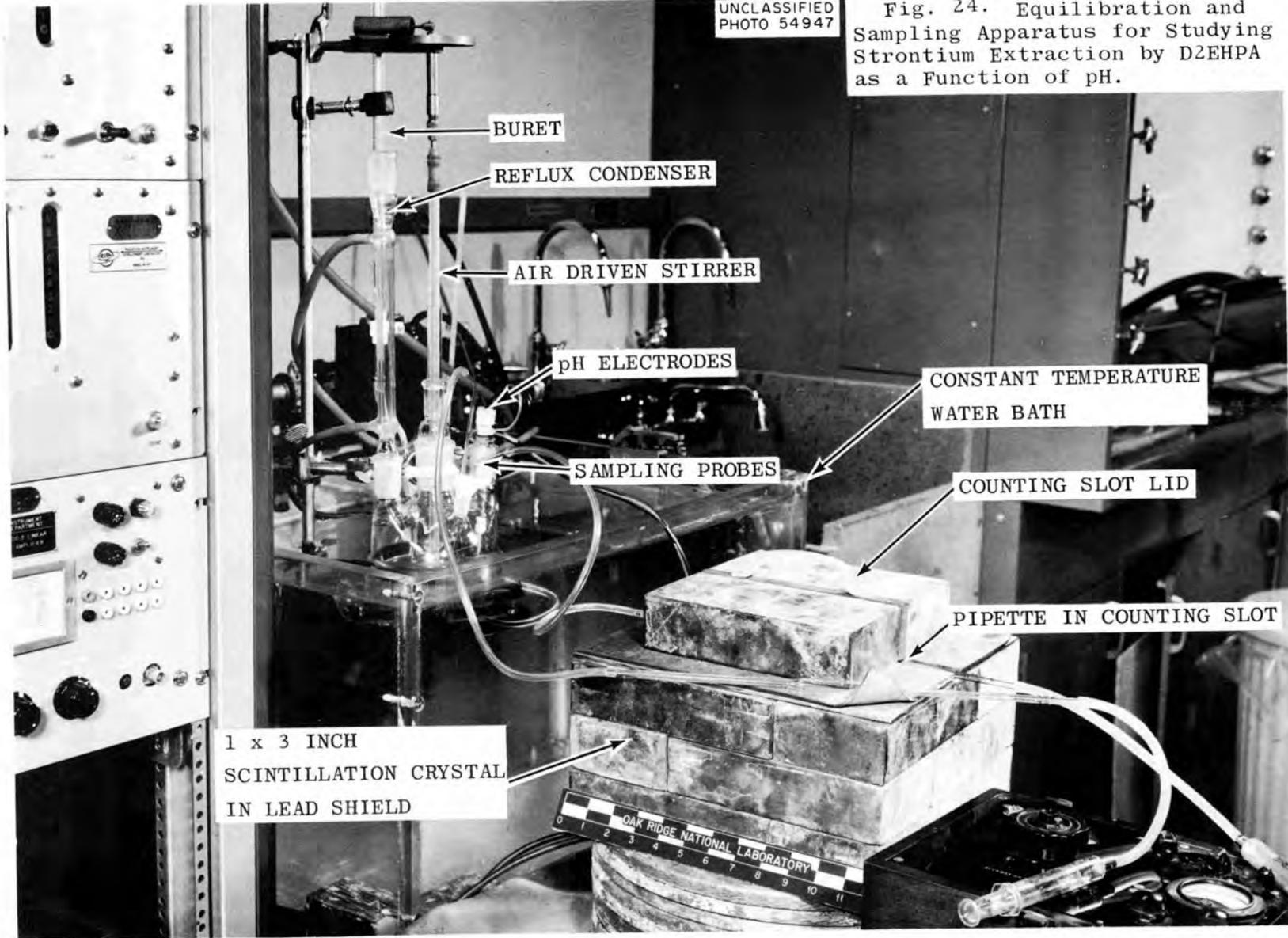
The experimental set up used to obtain extraction and titration curves simultaneously is shown in Fig. 24. After the addition of each increment of standard base in 4 M NaNO₃ the two phases were mixed for a few minutes. The stirrer was then stopped and the aqueous and organic phase allowed to separate. A sample of first one phase and then the other was drawn into a pipette, the pipette placed on top of the crystal and counted. The pH of the aqueous phase was also recorded. Thus it was possible to obtain the extraction coefficient and the composition of both phases at each point.

The results of a series of such titrations at various total reagent concentrations may be seen in Fig. 25. These are of the same general character as have been reported elsewhere.^{20,21} Absolute value of the extraction coefficient may vary considerably, however, depending on the organic diluent used, the composition of the aqueous phase and whether or not a diluent modifier is used. In connection with the above it is possible to show from data on the pH of 4 M NaNO₃ solutions that glass electrode pH is a linear function of the $\log [H^+]$ in such a system within experimental error (see Fig. 26). The relationship is $\text{pH} + 0.6 = -\log [H^+]$. Thus the slope of the lines as drawn in Fig. 25 is meaningful in interpreting the $[H^+]$ dependance of the strontium extraction. If Sr replaces hydrogen on the reagent the slope expected would be -2 if $\log [H^+]$ is plotted or +2 if pH is plotted. The slopes of the lines in Fig. 25 are all a little less than 2 (average ca. 1.7) thus indicating that on the average approximately 2 hydrogens (or two sodiums with accompanying readjustment of the free reagent Na-H form ratio) are exchanged for each strontium extracted.

From data illustrated in Fig. 25, the extraction coefficient has been plotted as a function of total reagent concentration at a number of reagent (sodium form-acid form) compositions. As

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Fig. 24. Equilibration and Sampling Apparatus for Studying Strontium Extraction by D2EHPA as a Function of pH.



BURET

REFLUX CONDENSER

AIR DRIVEN STIRRER

pH ELECTRODES

SAMPLING PROBES

CONSTANT TEMPERATURE
WATER BATH

COUNTING SLOT LID

PIPETTE IN COUNTING SLOT

1 x 3 INCH
SCINTILLATION CRYSTAL
IN LEAD SHIELD

OAK RIDGE NATIONAL LABORATORY
0 1 2 3 4 5 6 7 8 9 10 11

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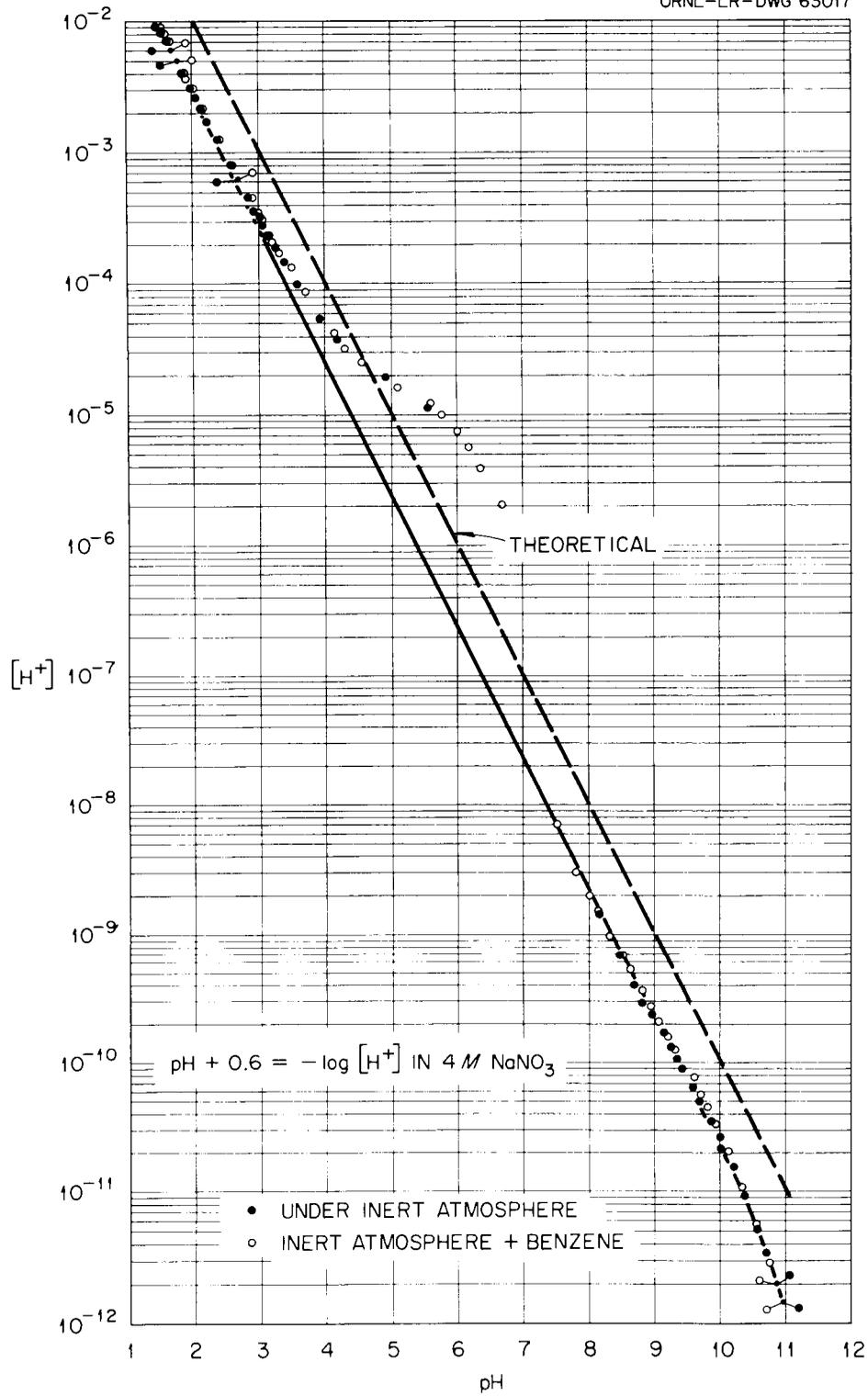


Fig. 26. $[H^+]$ vs pH for 4 M $NaNO_3$ Solutions.

shown in Fig. 27, although there is some variation, these slopes are all essentially 1. This is in agreement with previous results^{20,22} and may be interpreted to mean (1) that a single aqueous Sr unit is being extracted by a single organic extractant unit (monomer, dimer, tetramer etc.) or (2) that the reagent in the organic phase is a very large micelle which extracts Sr into itself without depolymerizing. Vapor pressure measurements are being made in an effort to determine the degree of polymerization of the reagent in the organic phase.

Another arrangement of the data from Fig. 25 is illustrated in Fig. 28. Here the extraction coefficient is plotted as a function of the fraction of extractant in the sodium form. Extrapolation of the straight portions of the curve places the maximum extraction coefficient at 25% Na form in each case (ΣR conc's of 0.5, 0.25, 0.125, 0.0625, 0.031 and 0.0156). At present, several explanations may be suggested: (1) an extracted complex containing both Sr and H thus requiring hydrogen transfer $org \rightarrow aq$ at low pH and $aq \rightarrow org$ at high pH, (2) a unique organic species of Ca 1Na to 3H form molecules having a high affinity for Sr, or (3) a minimum in intermolecular bonding at this particular composition thus making the organic extractant more available. Other interpretations are not excluded.

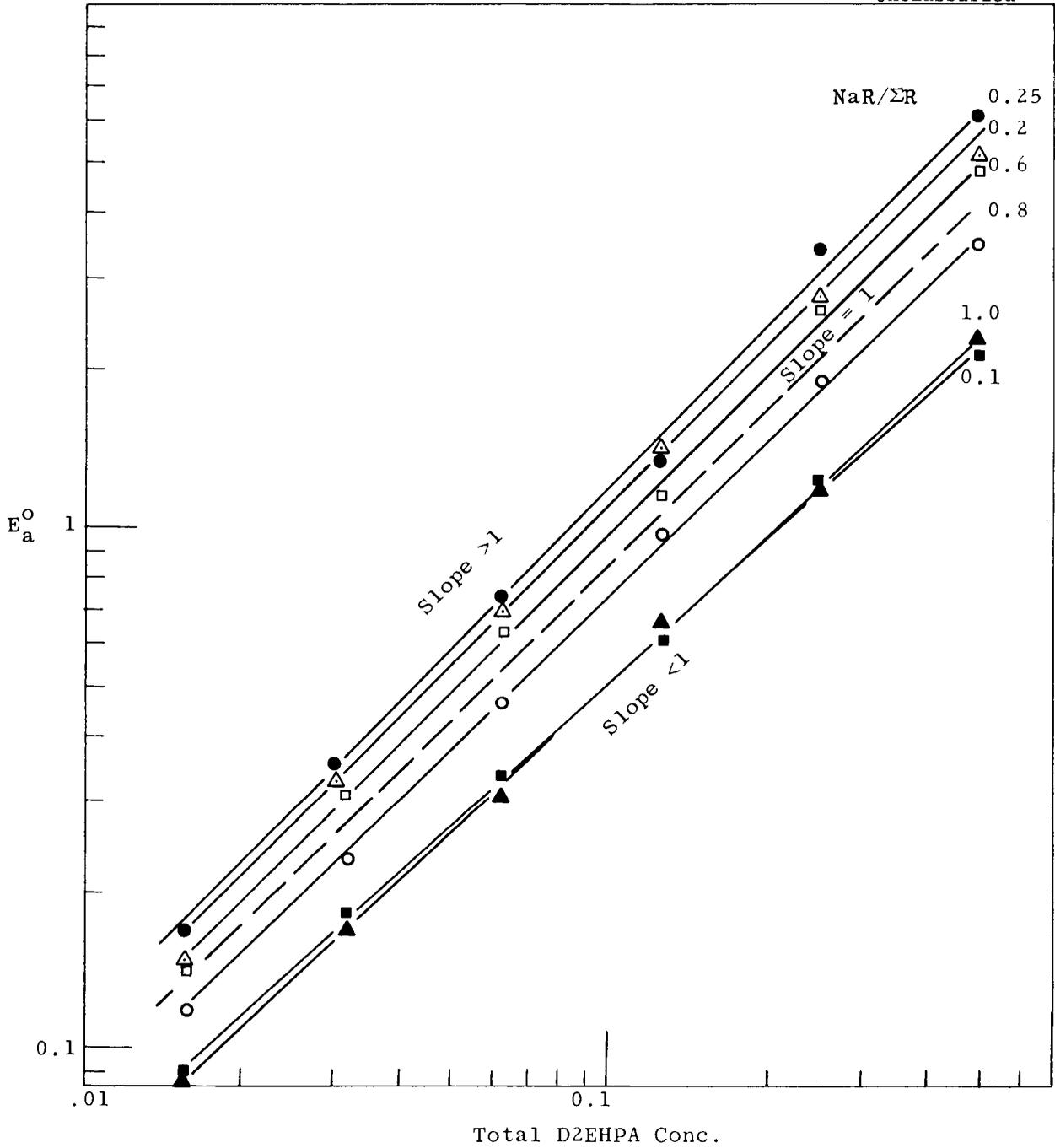


Fig. 27. Extraction of Sr as a Function of NaD2EHP-D2EHPA Conc. in Benzene at Various NaD2EHP/D2EHPA Ratios.

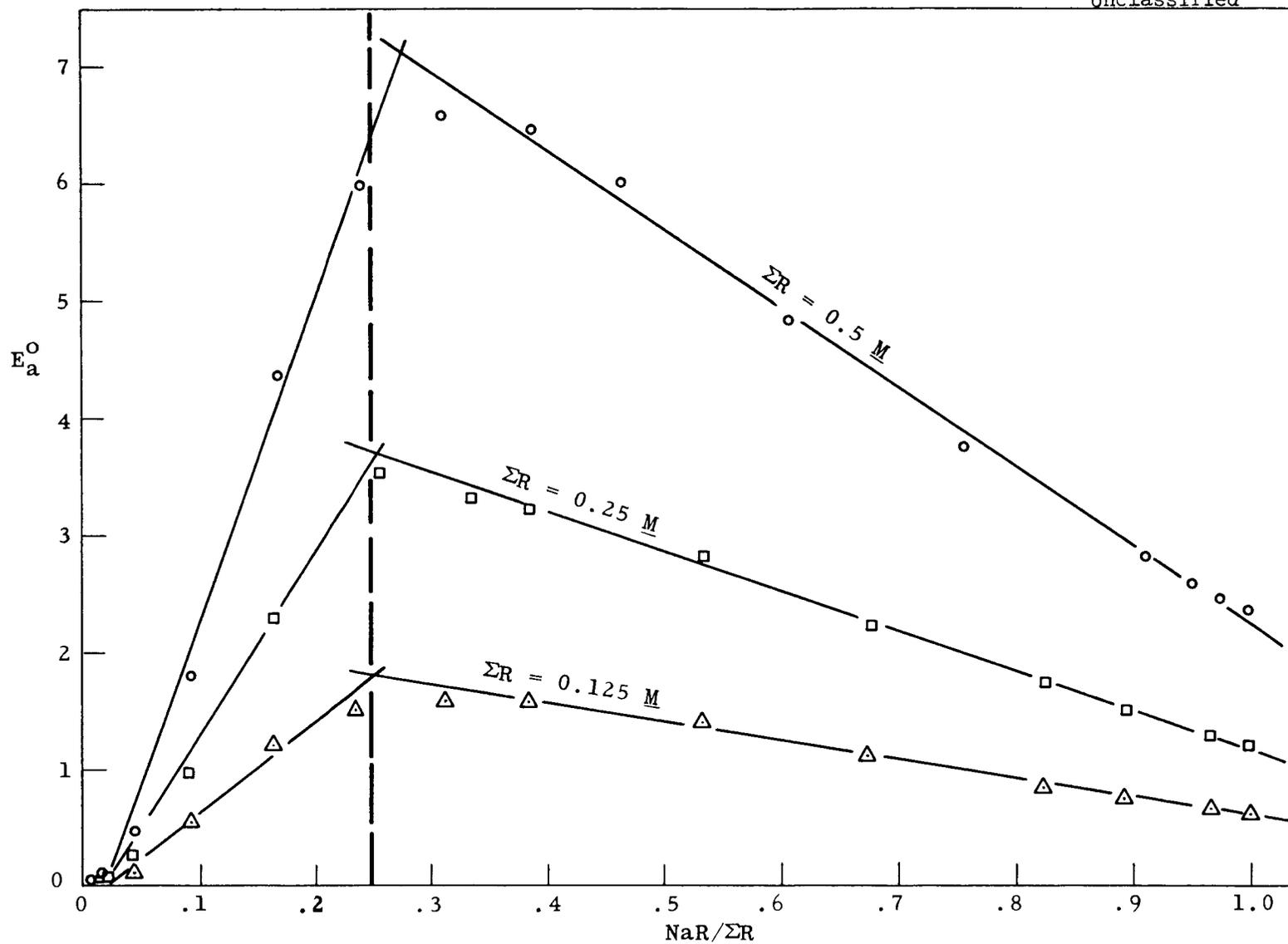


Fig. 28. E_a^0 vs Fraction of D2EHPA in Sodium Form. Concentrations of 0.0625, 0.031 and 0.0156 M Reagent gave the same Result.

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| 22. | A. R. Irvine | 75. | F. W. Melvanin, Eldorado Mining and Refining, Ltd., Ottawa |
| 23. | F. A. Kappelmann | 76. | J. B. Clemmer, B. of Mines Salt Lake City |
| 24. | Eugene Lamb | 77. | E. M. Kinderman, SRI |
| 25. | W. H. Lewis | 78. | Raymond E. Burns, Hanford |
| 26. | J. T. Long | 79. | J. I. Stevens, ICPP |
| 27. | W. J. McDowell | 80. | James A. Buckham, ICPP |
| 28. | R. H. Rainey | 81. | C. M. Slansky, ICPP |
| 29. | J. T. Roberts | 82. | Kenneth L. Rohde, ICPP |
| 30. | A. D. Ryon | 83. | R. A. McGuire, ICPP |
| 31. | J. M. Schmitt | 84-99. | Laboratory Records |
| 32. | F. G. Seeley | 100. | ORNL-RC |
| 33-35. | E. M. Shank | 101. | C. E. Stevenson, Idaho Falls |
| 36. | M. J. Skinner | 102-106. | DTIE |
| 37. | E. G. Struxness | | |
| 38. | J. A. Swartout | | |
| 39. | J. W. Ullmann | | |
| 40. | Boyd Weaver | | |
| 41. | R. G. Wymer | | |