EQUILIBRIUM EXTRACTION CHARACTERISTICS
OF
ALKYL AMINES AND NUCLEAR FUELS METALS
IN
NITRATE SYSTEMS

PROGRESS REPORT X

JULY I, — DECEMBER 31, 1961

BY

EDWARD A. MASON

RICHARD E. SKAVDAHL

DEPARTMENT OF NUCLEAR ENGINEERING

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

CAMBRIDGE 39, MASSACHUSETTS

Equilibrium Extraction Characteristics

of

Alkyl Amines and Nuclear Fuels Metals

in

Nitrate Systems

Progress Report for the Period

July 1 - December 31, 1961

Progress Report X

by

Edward A. Mason

Richard E. Skavdahl

February 15, 1962

Massachusetts Institute of Technology

Cambridge 39, Massachusetts

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

Figures

TABLE OF CONTENTS (Cont'd.)

TABLE OF CONTENTS (Cont'd.)

1.0 Summary

During this report period, the effects of solution age, salting concentration, and amine (trilauryl amine in toluene) concentration on the solvent extraction characteristics of ruthenium nitrosyl nitrato complexes in nitrate systems were investigated. The effects of solution age and nitrate salting on absorption spectra of the RuNO-nitrato complexes aqueous solutions were also studied.

The effects of solution age, nitric acid concentration, aqueous ruthenium concentration, amine concentration, and nitrate salting concentration on the solvent extraction characteristics of the RuNO- nitro complexes were investigated. The effects of solution age and aqueous ruthenium concentration on the absorption spectra of the RuNO-nitro complexes were also studied.

The effects of temperature, fluoride ion, and sulfate ion on the solvent extraction characteristics of uranium were studied.

Results of the work on the RuNO-complexes indicate that an important variable in the solvent extraction process may possibly be the concentration of the unbound nitric acid in the organic phase.

The results of the work on the RuNO-nitrato complexes indicate that the more extractable forms of those complexes may be the tetra- and penta-nitrato complexes and that these complexes may be extracted in the acid forms rather than the anionic forms.

For the freshly prepared solutions, the RuNO-nitro complexes are much more extractable than the RuNo-nitrato complexes at low nitric acid concentrations.

The effect of temperature or uranium extraction results in an activation energy of $\Delta H = - 3.10 \frac{Kcal}{mole}$ in the range of 25-50°C. The addition of sulfate ion and fluoride ion to nitrate solutions of uranium result in a relatively small effect on uranium extraction with the distribution ratio varying by a factor of two or three.

2.0 Ruthenium Nitrosyl Nitrato Complexes

A discussion of the formulas and species of the ruthenium nitrosyl nitro (RuNO-nitro) and ruthenium nitrosyl nitrato (RuNO-nitrato) complexes to be found in aqueous nitric acid solutions is given in Reference (1).

A second batch (batch B) of RuNO-nitrato complexes solutions in nitric acid was prepared using ruthenium nitroso hydroxide as the starting material. The compound was purchased from A. D. Mackay, Inc. The first batch (batch A) of ruthenium in the form of nitrosyl nitrato complexes was prepared from ruthenium trichloride (2); absorption spectra and distribution ratios for the batch A have been reported previously (3).

For the batch B, 45 grams of the hydroxide was added to 500 ml of 9.2N. nitric acid and boiled for approximately two hours. The liquid level being kept constant by intermittent additions of distilled deionized water (DDW). After cooling, the solution was filtered through a sintered glass funnel and placed in an evaporating dish inside a vacuum oven and evaporated almost to dryness, yielding $RuNO(NO_3)_3$ $2H_2O$. The solution had the characteristic deep red color, as did the resultant sticky mass after evaporation.

The red mass was dissolved in DDW and the solution diluted to 250 ml in a volumetric flask. A quantitative analysis showed the stock solution to have a ruthenium concentration of 84.6 gm/liter. This quantitative analysis, as well as all of the following analyses, was done by the $KOH\text{-}KNO_3$ fusion method (2).

A set of solutions was then prepared by adding the appropriate amount and concentration of nitric acid and/ or sodium nitrate to aliquot portions of the stock solution. A summary of the solutions is listed in Table 1.

2.1 Extraction of Freshly Prepared Solutions

Extractions of most of the fresh solutions of batch B (age after dissolution of the $RuNO(NO_3)_3$ $2H_2O$ in DDW approximately 1-2 hours) were made for a two minute contacting time). The data are plotted in Figure 1. The curve for the nitric acid system with no salting is fairly flat with a maximum at about 3N nitric acid. The values of E_A^o range from 0.0060 at 3N HNO_3 to 0.0028 at 8.8N HNO_3; the acid concentration was varied from 0.5N to 8.8N

TABLE 1

Ruthenium Nitrosyl Nitrato Complexes Solutions

Nitric Acid Conc., N	Total Nitrate Conc., M	Ru Conc.,gm/l
0.52	0.52	6.45
0.89	0.89	"
1.32	1.32	"
3.10	3.10	"
4.91	4.91	"
6.85	6.85	"
8.74	8.74	"
10.08	10.08	"
0.50	1.22	"
0.48	3.28	"
0.46	5.37	"
0.47	6.20	6.00
1.27	3.16	6.45
1.29	5.18	"
1.27	6.19	6.00
3.09	5.00	6.45
3.10	6.17	6.00
5.05	6.35	"

FIGURE 1
Extraction of Freshly Prepared RuNO-Nitrato Complexes
Batch B
2-Minute Contacting at 25°C with 0.26 M TLA in Toluene

O = Nitric Acid System (No Salting)
Δ = Nitric Acid-Sodium Nitrate System(Total Nitrate = 2M

Final Aqueous HNO_3 Normality
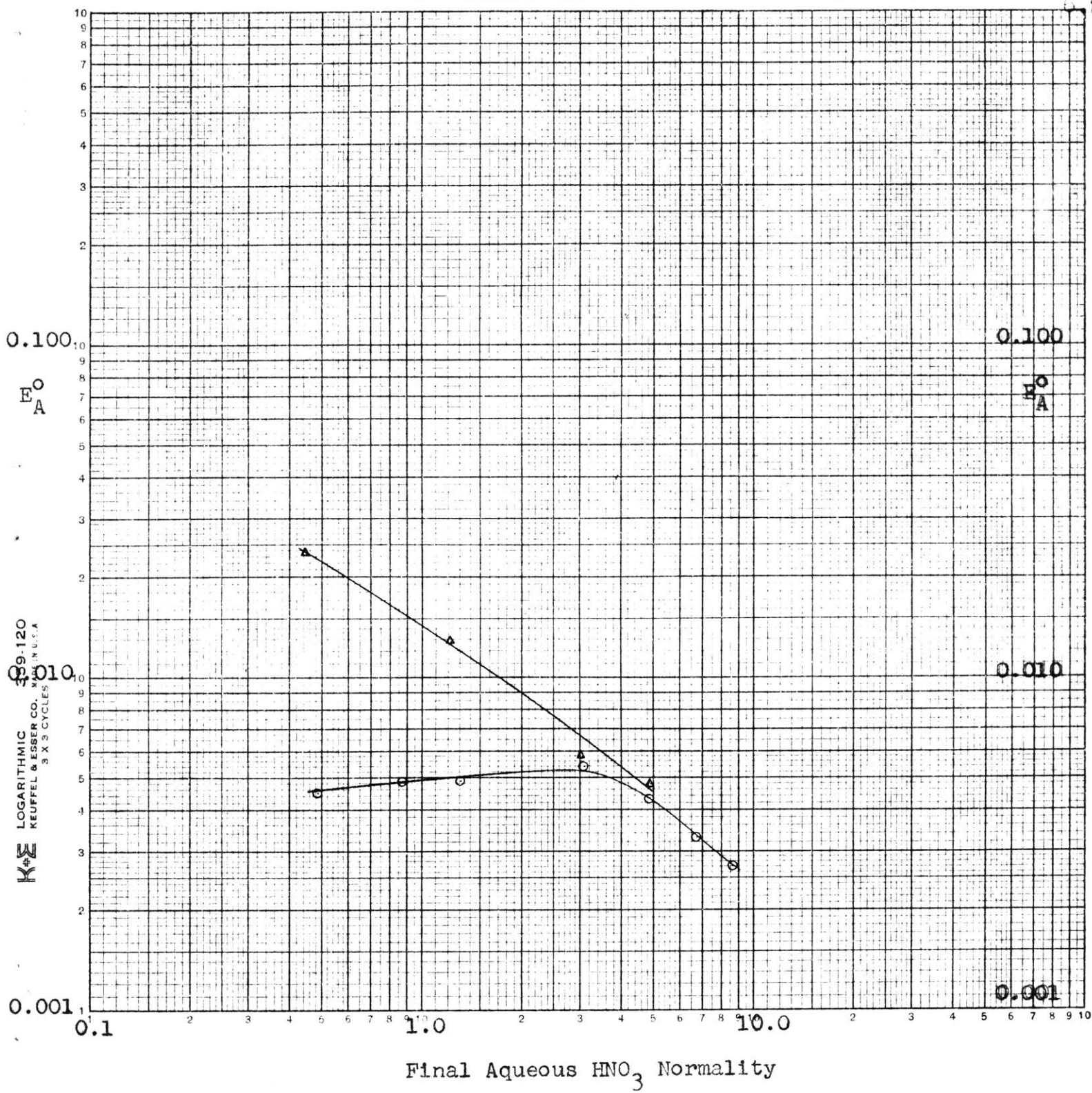
HNO_3. The data for a constant total nitrate concentration of approximately 6.2M show a decrease in E_A^O from 0.0249 at 0.45N HNO_3 to 0.0050 at 5.0N HNO_3, the data falling on a straight line on a log-log plot with a slope of about -0.7. The increase in the extraction of ruthenium with nitrate salting can be explained by an increase in the nitrate complexing, especially at the lower acid concentrations. At 0.5N HNO_3, the addition of nitrate salting to form a total nitrato concentration of 6.2 M raises the values of E_A^O by a factor of five.

2.2 Extraction of Aged Solutions

2.2.1 Comparison of the Two Batches of Solutions

The second batch of solutions was aged at room temperature for one month and then sample extractions were made to determine if this batch resembled batch A with respect to its extraction characteristics. Variations in the preparation methods of the two batches, in particular the two different starting materials ($RuCl_3$ for batch A and RuNO-hydroxide for batch B) could possibly result in products with dissimilar values of NO_3: Ru ratios and concentrations of nitro complexes, if any exist. A second important variable is the method and speed of evaporation of the solution to yield $RuNO(NO_3)_3$ $2H_2O$. In the two cases, the method of evaporation was very similar, in that the same equipment was employed and the temperature of evaporation was the same (30°C.)

Extractions were made for a 2 minute contacting time and a 24 hour contacting time and varying nitric acid concentration with no salting. The results are shown in Figure 2. It can be seen that, in general, the values of E_A^O are slightly lower for batch B than for Batch A. The maximum variation occurs at 1.3N HNO_3 for the 24 hour contact time and shows the value of E_A^O to be approximately 20% lower for batch B. For the two minute contact time, the maximum variation occurs at 4N HNO_3, when the batch B value is 35% below that of batch A. It appears that an even greater variation may occur at very low acid concentration and that the batch B values may be appreciably greater than the batch A values. However, analytic limitations prevent a closer investigation of this point, in that the ruthenium concentration in the resultant organic phase would be too small for accurate analysis by the $KOH-KNO_3$ fusion method. In addition, the differences between the batches seems to disappear, or at least reduce in magnitude, at the longer contact time.

FIGURE 2
Comparison of the Extraction Characteristics of Two Batches of RuNO-Nitrato Complexes Solutions Solutions Aged For One Month at Room Temperature Contacted at 25°C With 0.26 M TLA in Toluene

A = Batch A
B = Batch B

Comparison of the Over-all Characteristics of

Final Aqueous HNO_3 Normality
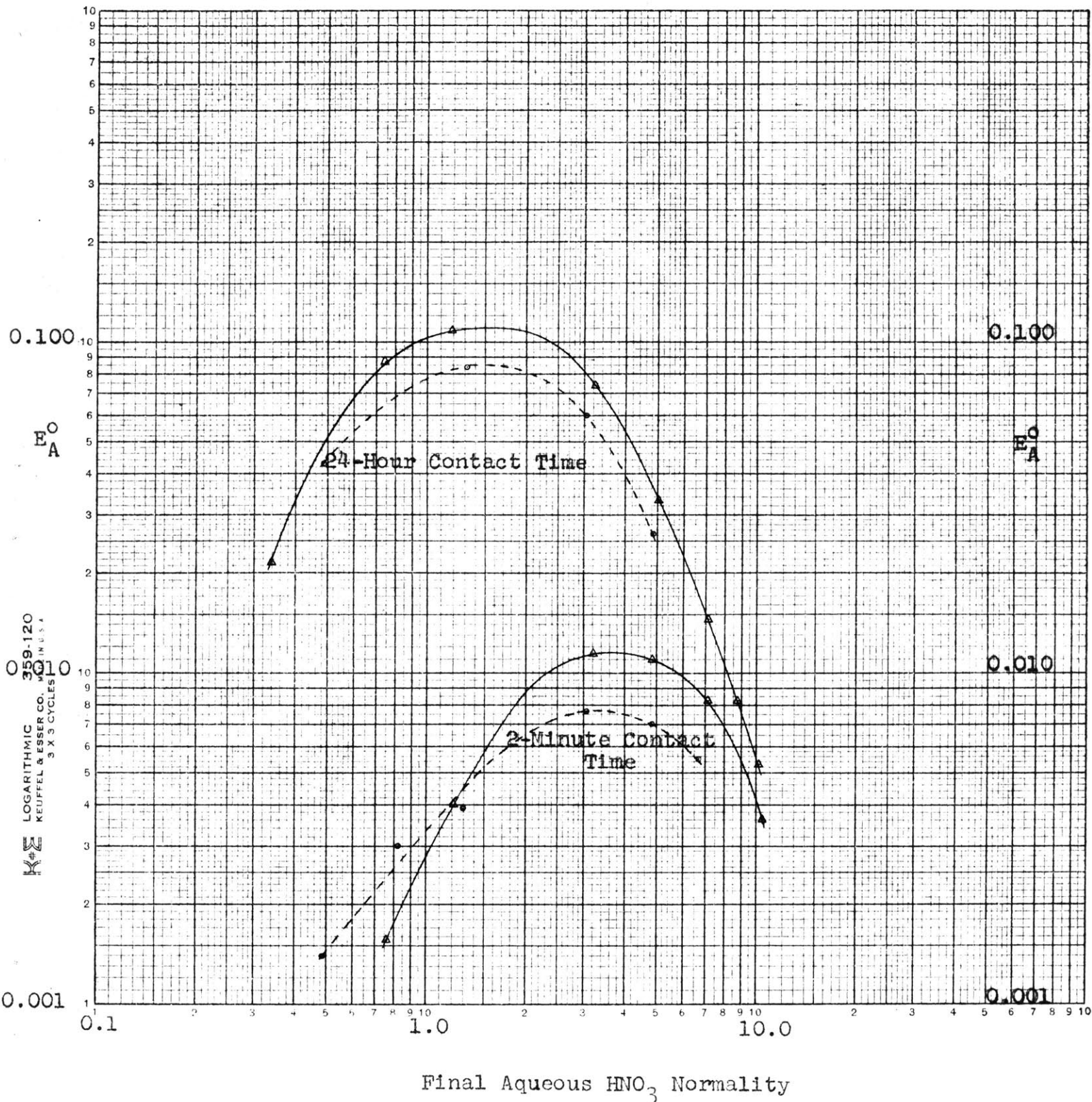
2.2.2 Effect of Age of Solution

In order to determine the effect of solution age on the extraction characteristics of the RuNO-nitrato complexes, extractions repeating the conditions of Figure 1 were carried out after the solutions had aged for one month. Figure 3 shows the two sets of d&ta. Of interest are several points. For the nitric acid system with no salting, distribution ratios of the aged solutions varied in a manner consistent with the observation of Fletcher et al (4) that nitrate complexing decreases with aging at the low acid concentrations and increases with aging at the higher acid concentrations. Aging had little effect on the salted solutions at a total nitrate concentration of 6.2M., indicating that the freshly prepared salted solutions were more nearly at equilibrium conditions with regard to the distribution of the RuNO-nitrato complexes than were the non-salted solutions. Above about 2.5N HNO_3 the data show the salted solutions to be less extractable than the non-salted solutions, a condition which is inconsistent with the usual findings that salting increases nitrate complexing and therefore increases the degree of extractability. However, the increase in nitrate complexing due to the salting is more than offset by an increase in the unbound nitric acid concentration in the organic phase which is caused by the nitrate common ion effect (see Section 2.2.3 for discussion). Thus, the net result is a decrease in the extraction of the complexes.

2.2.3 Effect of Salting Concentration

Using 24 hour contacting times, extractions were made to determine the effect of sodium nitrate salting on the extractability of RuNO-nitrato complexes. The data are plotted in Figure 4 so as to show the effect of varying aqueous nitric acid concentration at various levels of constant total nitrate concentration. As a result of cross plotting, Figure 5 shows the effect of varying total nitrate concentration with constant nitric acid concentration.

In Figure 4, above a nitric acid concentration of about 2.5N., salting appears to cause a slight decrease in the value of E_A^o. This apparent inconsistency can possibly be explained by considering the effect of changes in the concentration of nitric acid in the organic phase on the distribution ratios. The addition of $NaNO_3$ to an aqueous nitric acid solution results in an increase in the concentration of nitric acid in the contacting organic phase; see the data of Figure 6 which were obtained by titration of various organic phase samples. Nitrato salting can

FIGURE 3
The Effect of Age of Solution on the Extraction of RuNO-Nitrato Complexes

Solutions Aged at Room Temperature (Batch B)
2-Minute Contacting at 25°C with 0.26 M TLA in Toluene

O = Nitric Acid System, No Salting, Solution Age 1-2 Hours
Δ = Nitric Acid System, No Salting, Solution Age= One Month
● = Total Nitrate Concentration Constant at 6.2M, Solution Age = 1-2 Hours

▲ = Total Nitrate Concentration Constant at 6.2 M, Solution Age = One Month

Salting Agent = $NaNO_3$

Final Aqueous HNO_3 Normality

FIGURE 4
The Effect of Nitrate Salting on Extraction
of RuNO-Nitrato Complexes

Solutions Aged for One Month at Room Temperature (Batch B)
24-Hour Contacting at 25°C with 0.26 M TLA in Toluene
Salting Agent = $NaNO_3$

Final Aqueous HNO_3 Normality

FIGURE 5
The Effect of Nitrate Salting on Extraction of RuNO-Nitrato Complexes

Solutions Aged For One Month at
Room Temperature (Batch B)
24-Hour Contacting at 25°C With 0.26M TLA in Toluene
Salting Agent = NaNO$_3$

Final Aqueous Total Nitrate Concentration, M.

Final Organic Unbound HNO_3 Normality

0.04   0.08   0.12   0.16   0.20   0.24   0.28

Extraction of Nitric Acid

▽ — 6.1M Nitrate
□ — Total 3M Nitrate
● — Total 2M Nitrate
■ — Total 1M Nitrate
○ — HNO_3, No Salting

be seen to cause a substantial increase in the amount of unbound nitric acid in the organic phase.

A more meaningful correlation of the ruthenium extraction data can be obtained by plotting E_A^O as a function of the final concentration of the organic phase unbound nitric acid at various levels of total aqueous nitrate concentration (see Figure 7). Of significant interest and importance is the fact that this method of correlation yields the more logically expected trend, i.e. as total nitrate increases at constant unbound HNO_3, E_A^O increases. The inference is that the values of the partition coefficient of the individual complexes are dependent on the concentration of the unbound HNO_3 in the organic phase rather than on the concentration of HNO_3 in the aqueous phase. Therefore, in order to more fully investigate the effect of nitrate salting at constant HNO_3 concentration, the organic phase unbound nitric acid should be held constant rather than the aqueous phase nitric acid, as was done in Figure 5. Figure 8 illustrates this point by presenting the ruthenium extraction data for both constant aqueous phase nitric acid concentrations and constant organic phase unbound nitric acid concentrations. The values plotted were obtained from Figures 5 and 7. When compared on the basis of constant concentration of unbound nitric acid in the organic phase, ruthenium extraction is seen to increase with increasing nitrate salting of the aqueous phase the slope of the E_A^O vs. total aqueous nitrate curve on log-log paper is approximately 1.3 to 1.7 for the condition of constant concentration of unbound nitric acid in the organic phase.

2.2.4 Organic Phase Titration of Extractable Ruthenium

A very interesting result of the organic phase titrations discussed in the previous section was the apparent titration of extractable ruthenium in the organic phase. This was observed for samples having a relatively large concentration of ruthenium (approximately 2.5 gm/liter).

The phenomenon was first noticed when the organic phase of sample number 128 was titrated and gave a value of 0.103 $\underline{M}$ for the difference between total acid and amine nitrate concentration. This difference is normally taken to represent the unbound nitric acid concentration. Sample 128 had a final aqueous nitric acid concentration of 0.37N and a final aqueous nitrate concentration of 6.1M. From Figure 6, the expected unbound HNO_3 concentration would be about 0.055M, a factor of about two less than the 0.103 M value. Closer inspection of the titration curve (Figure 9) revealed that a total of four inflection points rather than the customary two points of inflection were possibly present.
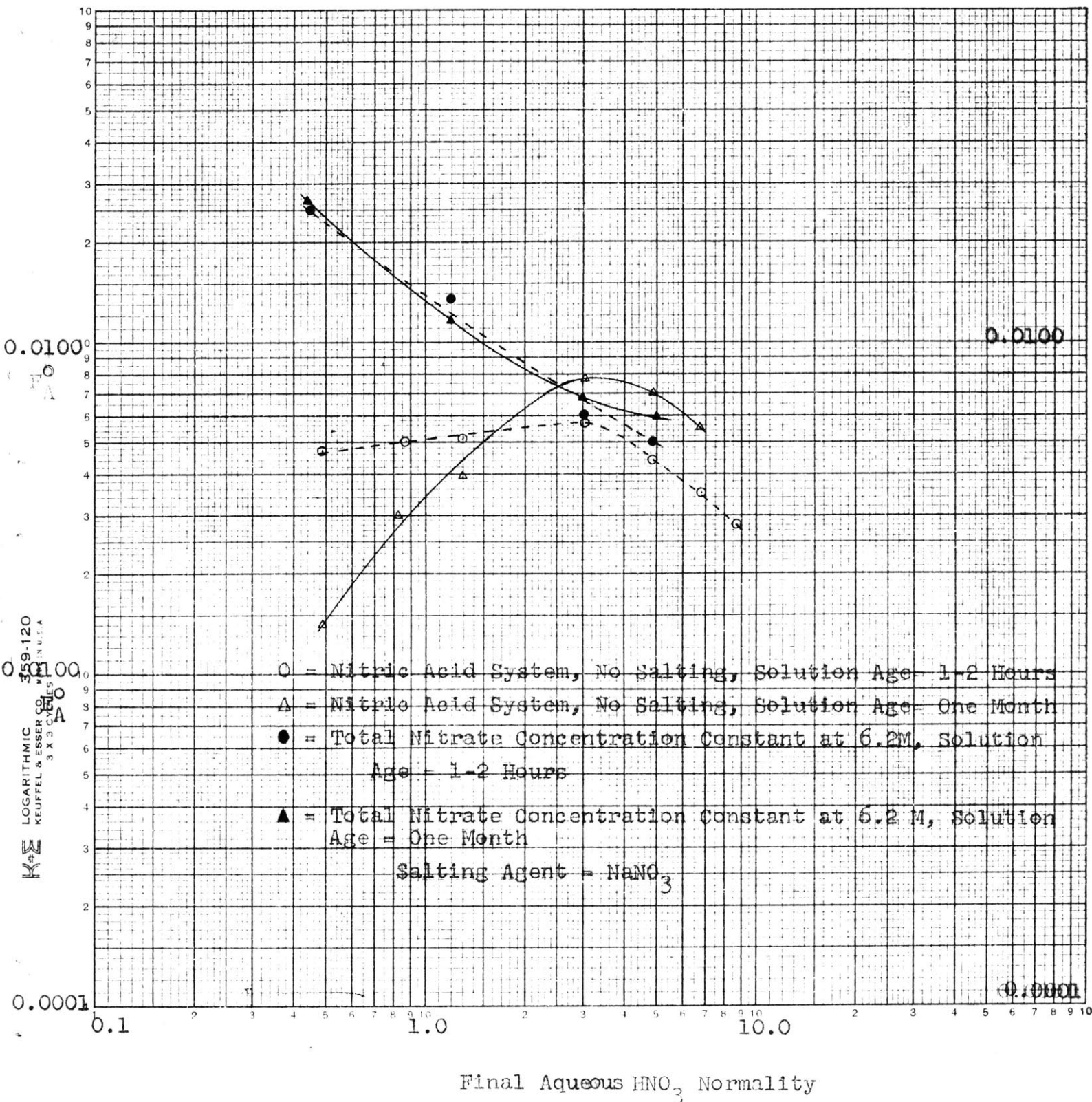
FIGURE 7
The Effect of Nitrate Salting on Extraction
of RuNo - Complexes

Solutions Aged for One Month at Room Temperature (Batch B)
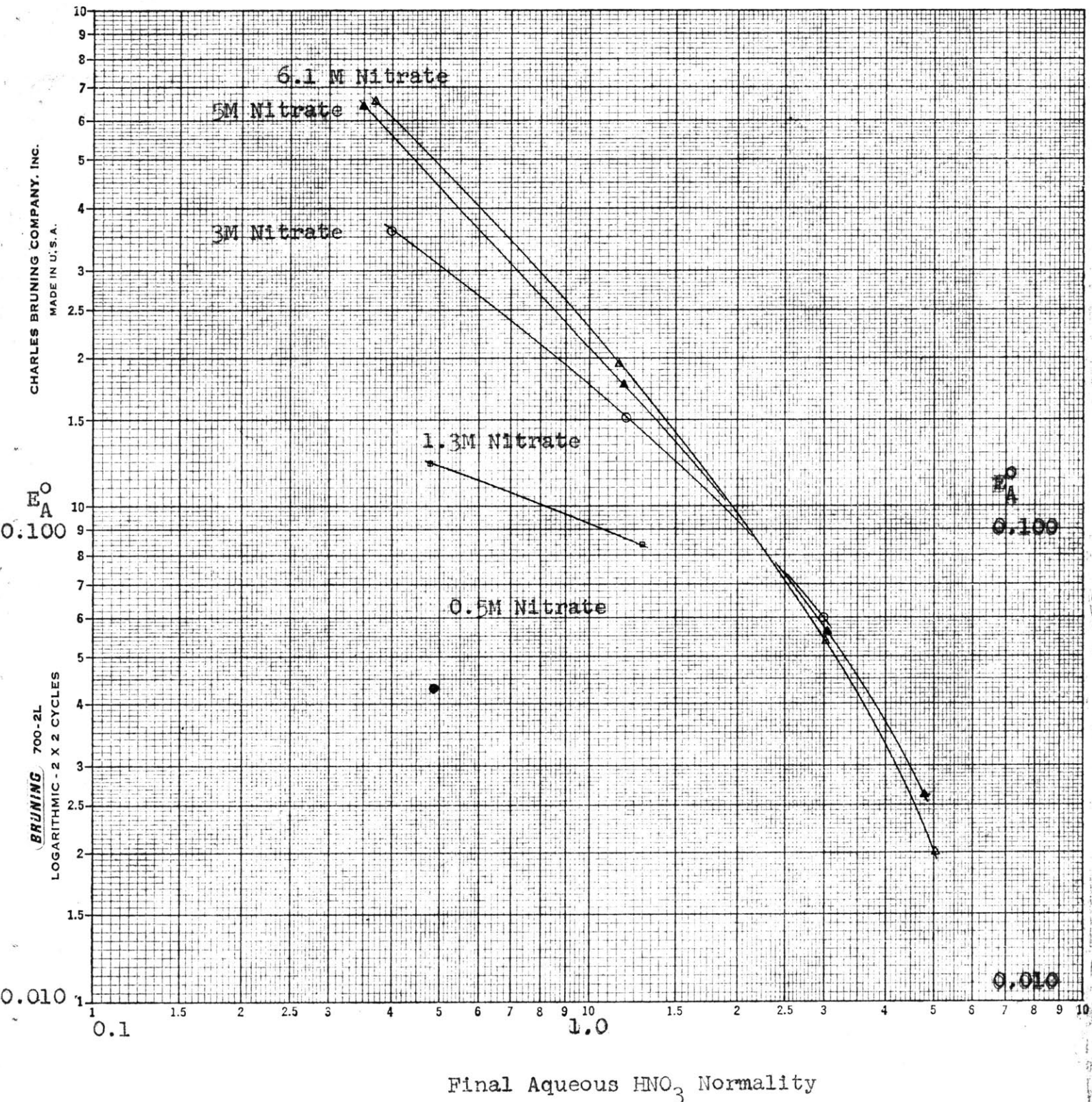24-Hour Contacting at 25°C with 0.26 M TLA in Toluene
Salting Agent = $NaNO_3$
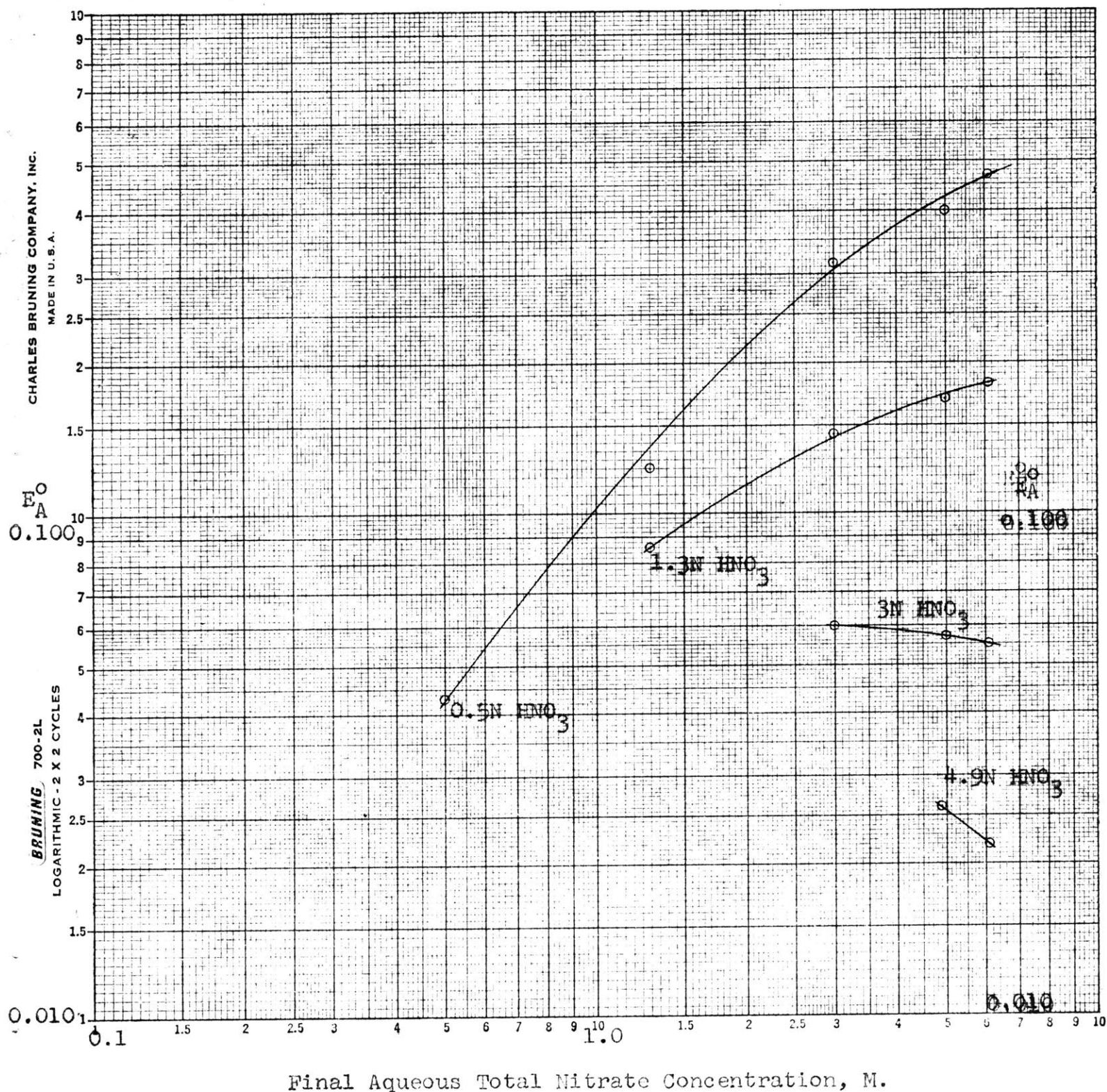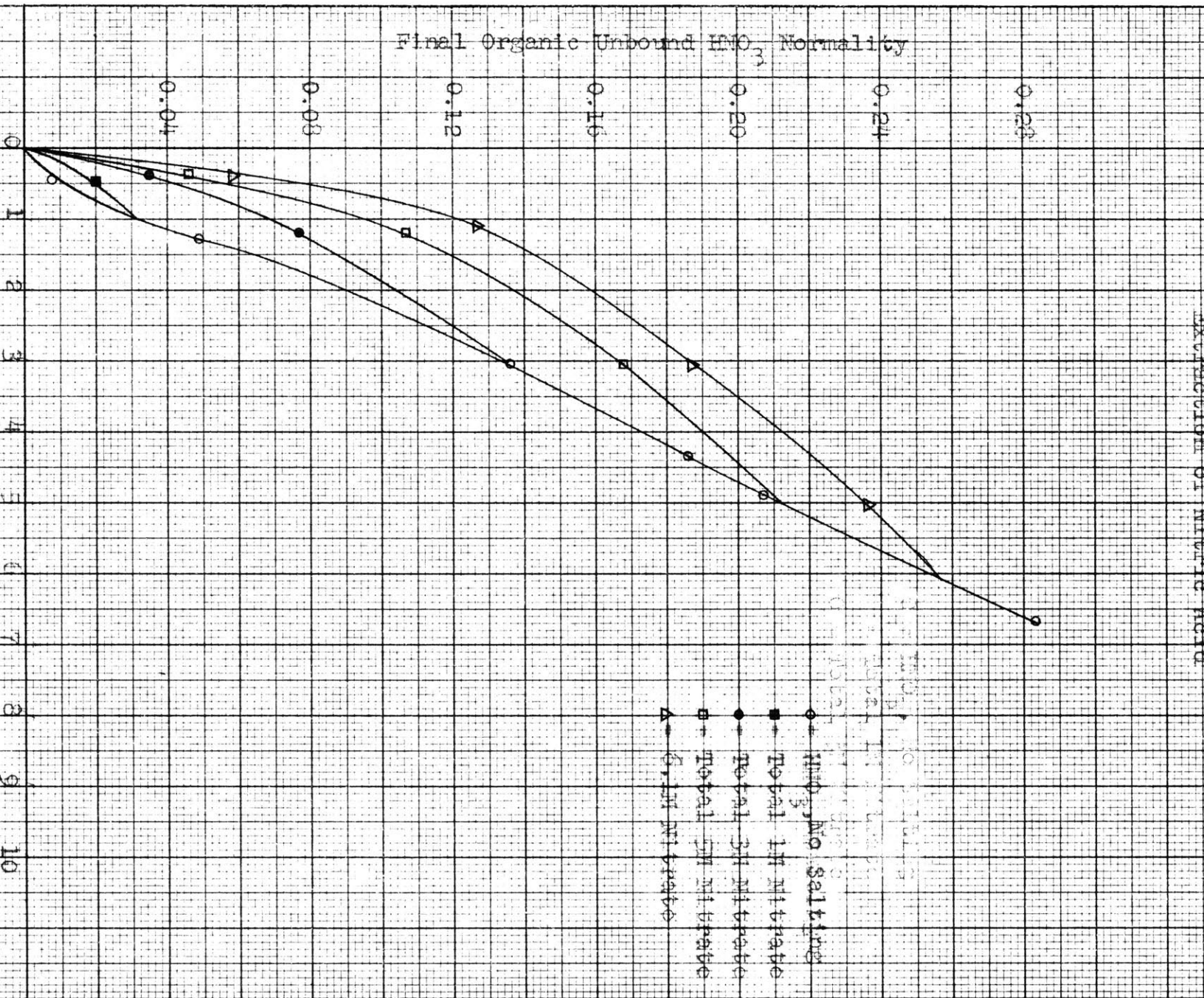
Final Organic Unbound HNO_3 Normality
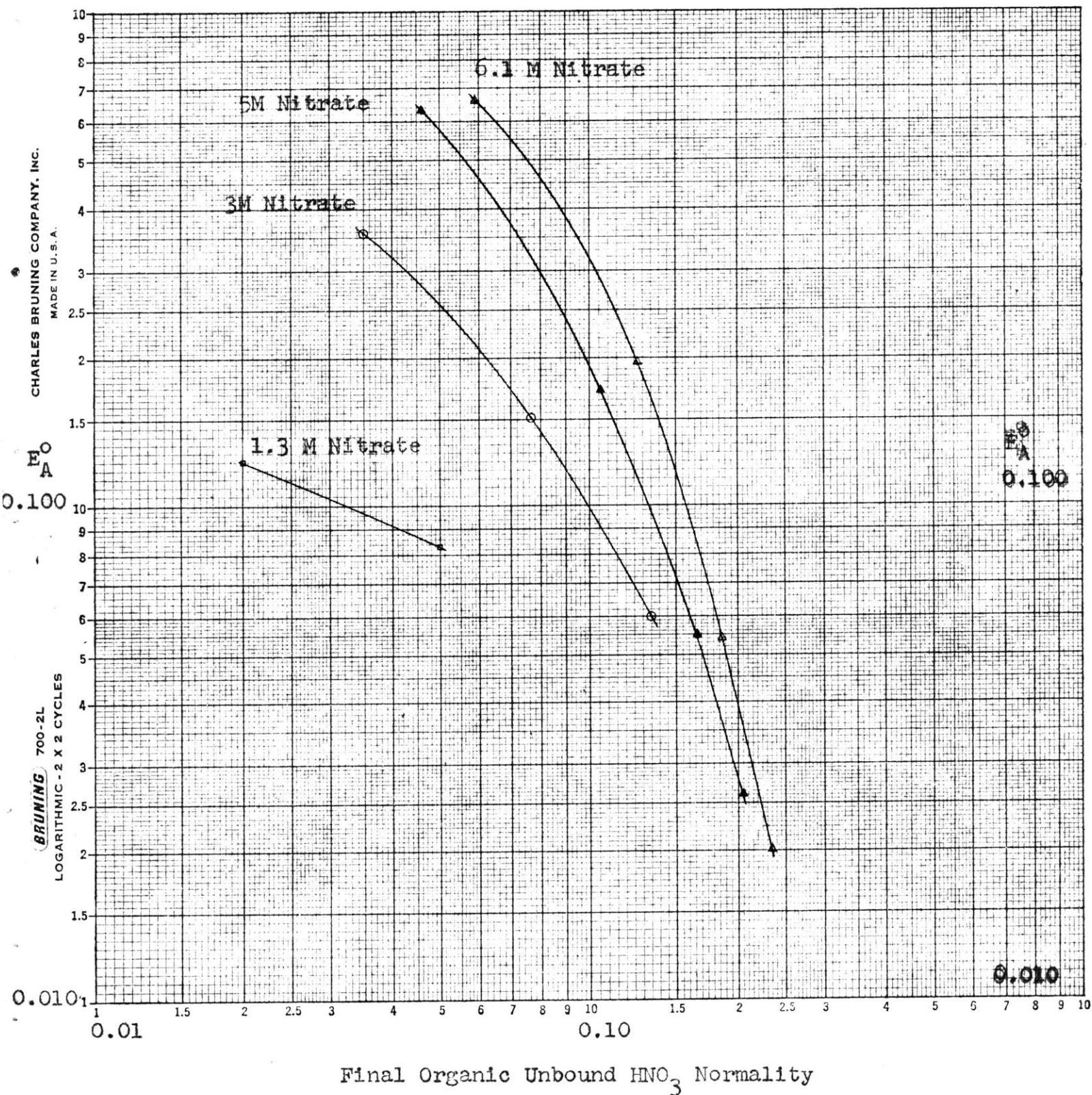
Figure 8

The Effect of Nitrate Salting on Extraction of
RuNO-Nitrato Complexes Aged for one Month
24-Hour Contacting at 25°C With 0.26 M TLA in Toluene

0.049N HNO$_3$ (Organic)

1.25N HNO$_3$ (Aqueous)

0.135N HNO$_3$ (Organic)

3.0N HNO$_3$ (Aqueous)

0.207N HNO$_3$ (Organic)

4.9 HNO$_3$ (Aqueous)

Final Aqueous Total Nitrate Molarity
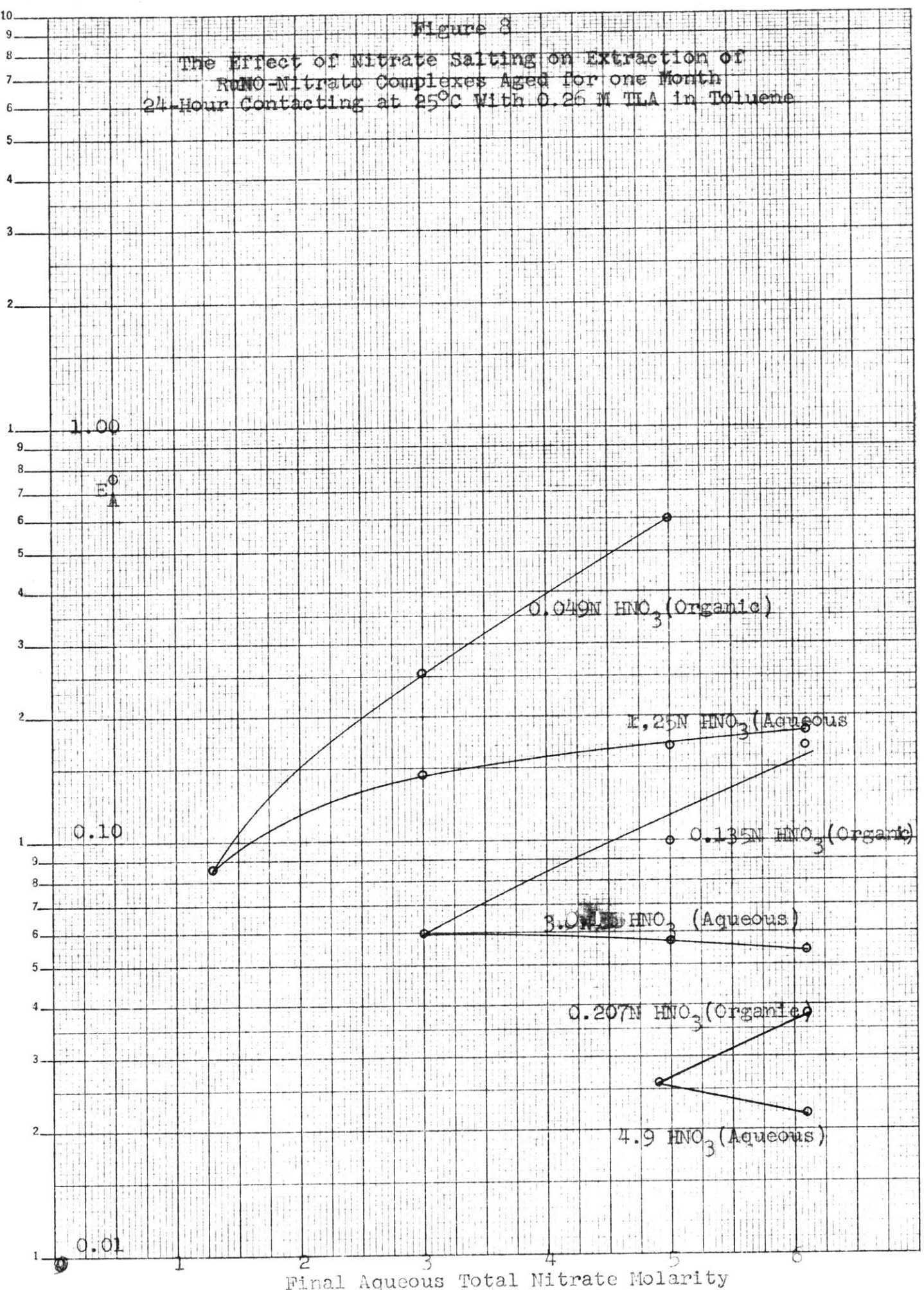
SEMI-LOGARITHMIC   359-73
KEUFFEL & ESSER CO.   MADE IN U.S.A.
3 CYCLES X 140 DIVISIONS

Figure 9

15

Organic Phase Titration of Sample 123
1ML of Sample vs 0.0975N NaOH

Millivolts

ML NaOH
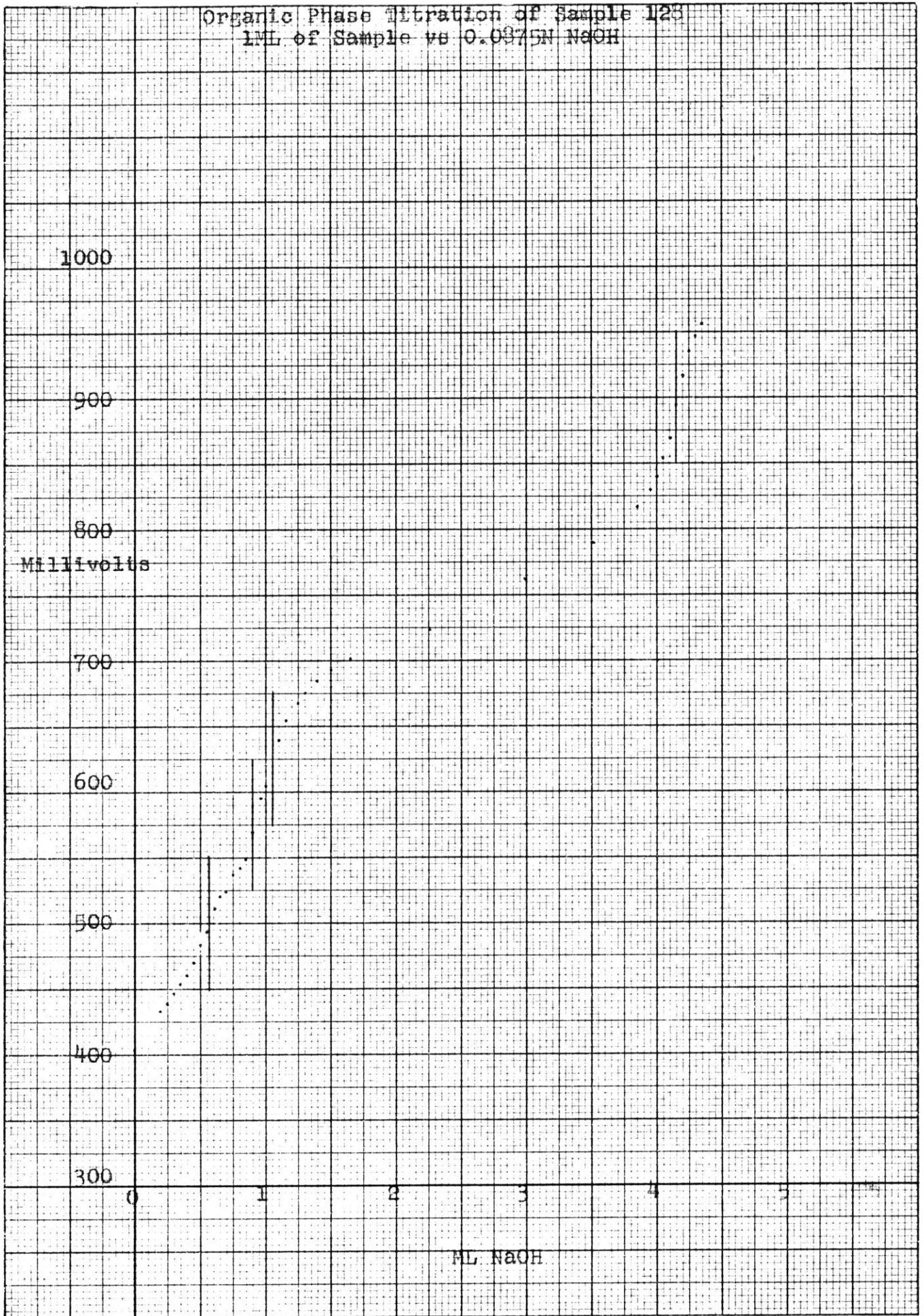
In order to investigate this phenomenon, the sodium
hydroxide was diluted by a factor of five (from 0.0875N
to 0.0175N) and the sample titrated again. Figure 10,
which shows the result of the re-titration, covers the
range corresponding to 0-1.3 ml on Figure 9. As can be
seen from Figure 10, the first portion of the curve yields
at least two inflection points and possibly more. The
first corresponds to a concentration of 0.059M, as would
be expected if this were the unbound nitric acid inflection
point. The difference between the first and second inflec-
tion points corresponds to a concentration of 0.038M.
By previous quantitative analysis, the ruthenium
concentration was found to be 2.38 gm/liter, 0.024M. If
it is assumed that the ruthenium in the organic phase is
mostly in the form of the acids of the tetra-and penta-
nitrato complexes of nitrosyl ruthenium (i.e., $HRuNO(NO_3)$
(H_2O) and $H_2RuNO(NO_3)_5$) which are neutralized between the
two end points marked on Figure 10 and if the mole
fraction of the penta-complex is represented by X, then

$$2 \times (0.024) + (1-x)0.024 = 0.038$$

and X then is equal to 0.58. The resultant concentration
of the complexes are 0.010M and 0.014 M for the tetra-
and penta-, respectively. Even closer inspection of
Figure 10 shows an irregularity in the titration curve at
about 5.25 ml. If it is assumed that the entire penta-
complex would be titrated before the tetra-complex, then
for a concentration of 0.014M, its neutralization would be
calculated to occur at 5.40 ml (which is very close to the
inflection found at 5.25 ml).

Other samples with large ruthenium concentrations in
the organic phase were also titrated. At concentrations
of less than approximately 1 gm/liter, the results of the
titrations are inconclusive. However, sample number 127,
with an organic phase Ru concentration of 2.51 gm/liter
(0.025M), gave very similar results to those of sample 128.
The aqueous phase of sample 127 was 0.35N HNO_3 and a total
nitrate of 5.26 M. From Figure 6, the unbound nitric acid
concentration in the organic phase would be about 0.044M.
Titration of the organic phase (Figure 11) yielded end
points at 2.55 ml and 4.60 ml. The first end point gives
a concentration of 0.045M and the difference between the
end points corresponds to a concentration of 0.036M.
Again, assuming the Ru to be mostly in the form of the
acids of the tetra- and penta-complexes, the mole fraction
of the penta complex is calculated to be 0.44 and the
concentrations of the complexes are calculated to be 0.014M
and 0.011M for the tetra-and penta-complexes, respectively.

K+E 10 X 10 TO THE ½ INCH   359-11
KEUFFEL & ESSER CO.   MADE IN U.S.A.

Figure 10

Organic Phase Titration of Sample 128
1 ML of Sample vs 0.0175N NaOH

5.97 ML

3.80 ML

Start at 0.53 ML

Millivolts

700

600

500

400

300

0   1   2   3   4   5   6   7   8

ML NaOH
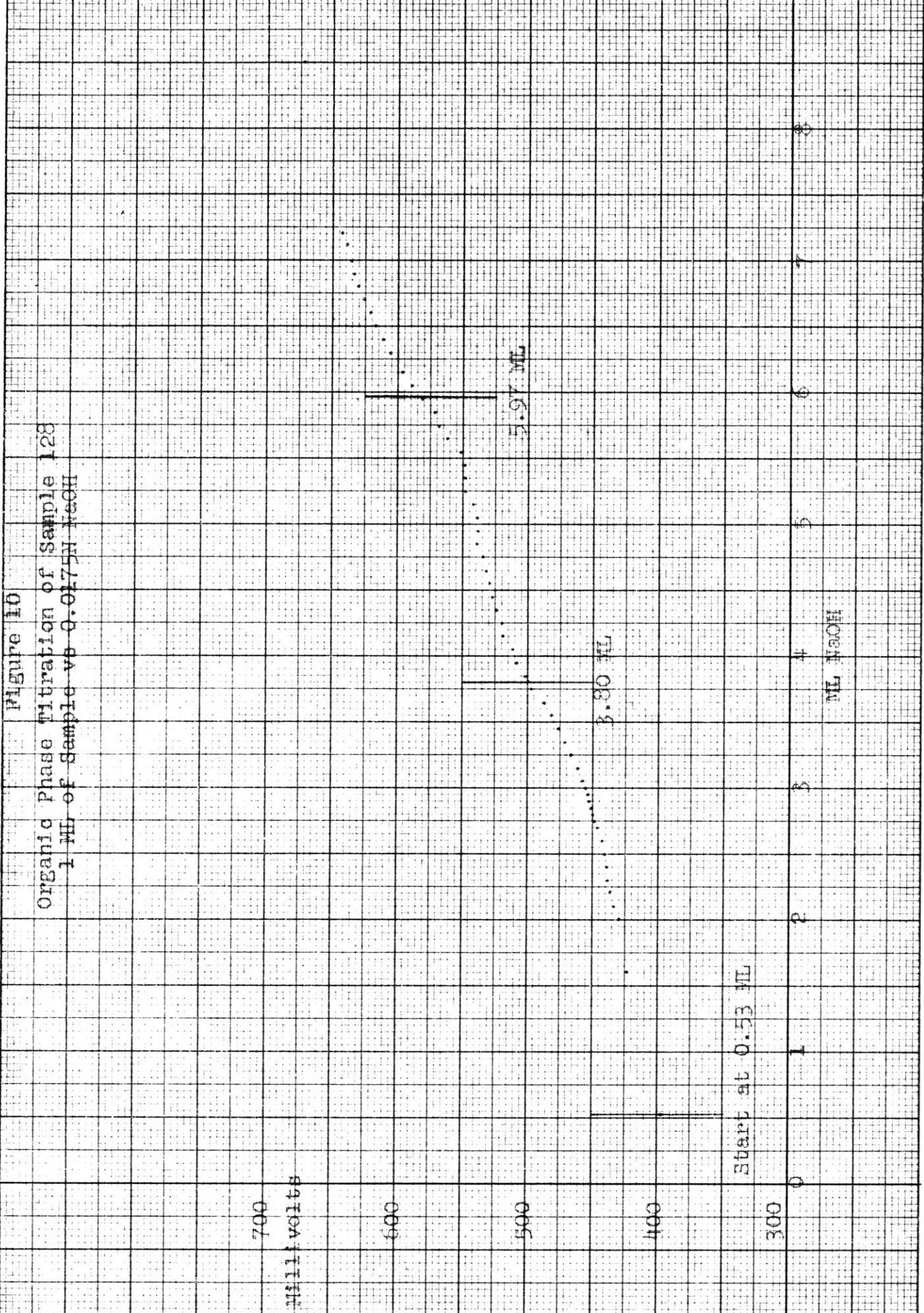
Figure 11
Organic Phase Titration of Sample 127
1ML of Sample vs. 0.0175 N NaOH

Although the titrations of samples 127 and 128 and their resultant interpretations do not present conclusive evidence for the more extractable forms of the RuNO-nitrato complexes, the indications are that the tetra-and penta-nitrato complexes of the nitrosyl ruthenium nitrato system are more highly extractable than the lower complexes.

2.2.5 Effect of Amine Concentration

A variation of TLA concentration was made to determine the effect of amine concentration on ruthenium extraction. The amine concentration was varied from 0.053M to 0.26 M. The extractions were made for 24-hour contacting time at 25°C. The aqueous phase contained aged (one month) RuNO-nitrato complexes in 1.3N HNO_3 solution with no salting. The data is presented in Figure 12. The value of E_A^o is seen to be initially dependent upon the 1.5 power of the amine concentration. Above an amine concentration of approximately 0.13M., the values of E_A^o fall below the line of slope 1.5. The reason for the falling-off of the values of E_A^o can be seen from Figure 13. Figure 13 shows the concentration of unbound HNO_3 in the organic phase as a function of TLA concentration.[3] It can be seen that above an amine concentration of about 0.13M, the values of the unbound HNO_3 concentration deviate from linearity and are larger than would be predicted. This could result in a decrease of the partition coefficients of the extractable species (See Figure 8) and therefore a lower value of E_A^o than would be predicted.

2.3 Spectra of Solutions

As a means of obtaining information about the aqueous solutions of the RuNO-nitrato complexes, in particular the effect of aging and the effect of salting, spectrophotometric studies were conducted. The equipment employed was a Beckman Model DU Spectrophotometer and 1 cm absorption cells. The wavelengths investigated ranged from 400 mμ, to 540 mμ. Below 400 mμ, the absorbance increases greatly and above 540 mμ, it becomes very small. Previous spectra (3) of RuNO- nitrato solutions have shown that an absorbance maximum exists at about 475 mμ and that the value of the absorbance at this wavelength increases with increasing nitric acid concentration.

2.3.1 Effect of Solution Age

In order to obtain some idea of the amount of time required for the aqueous solutions to reach equilibrium with regard to the distribution of the complexes in solution, spectrophotometric studies were made of the solutions at various solution ages.

FIGURE 12

The Effect of Amine Concentration on Extraction of RuNO-Nitrato Complexes

Solution Aged for One Month at Room Temperature (Batch B)
24-Hour Contacting at 25°C with 1.3N HNO_3 Aqueous Solution
of RuNO-Nitrato Complexes; Initial Aqueous Ru=6.45Gm/liter

Molarity of TLA in Toluene

Figure 13

21
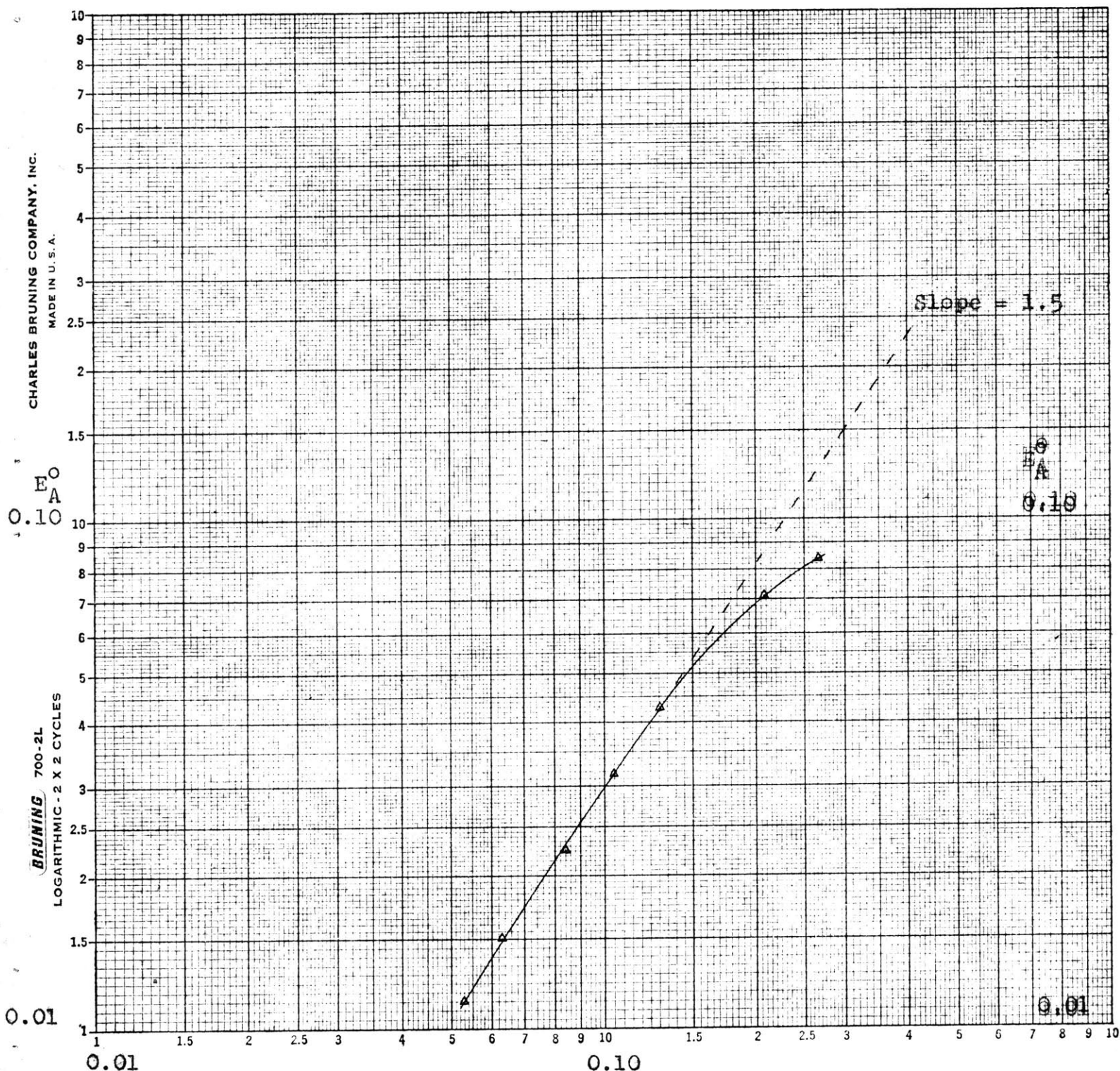
The Effect of Amine Concentration on Extraction of Nitric Acid
Equal Volume Contacting with 1.3N HNO_3

Final Organic Unbound HNO_3 Normality

Molarity of TLA in Toluene
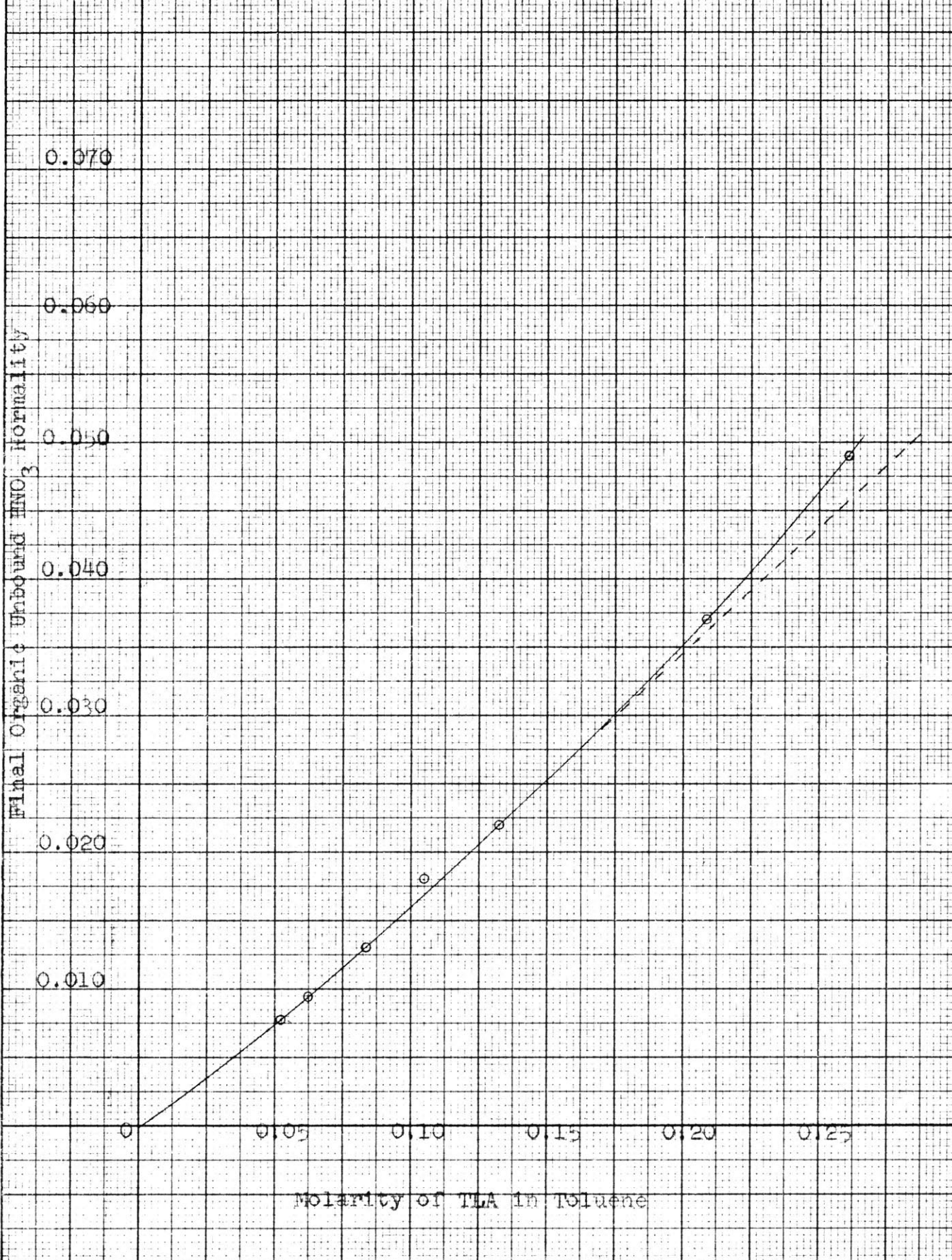
Figures 14 and 15 show the spectra of a solution of RuNO-nitrato complexes in 4.75N HNO_3 (no salting) with a ruthenium concentration of 1.78 gm/liter as a function of solution age. At any wavelength up to about 500mμ, the absorbance exhibits a maximum with increasing age. However, the maximum absorbance occurs at about 475 mμ, regardless of solution age. In Figure 14, the solution age is shown from 1-2 hours to 22 days. Little change is seen between 16 days and 22 days. Figure 15 shows solution ages of 22 days and 31 days. Essentially no change is discernible between the two.

Figure 16 shows spectra of a solution of RuNO-nitrato complexes in 1.2N HNO_3 (no salting) with a ruthenium concentration of 1.73 gm/liter at two solution ages, one month and six months. Once again, no appreciable change is noticeable. The conclusion to be reached from the previous spectra is that equilibrium has been attained in less than 31 days and probably in the range of 16 to 22 days.

2.3.2 Effect of Nitrate Salting

In an attempt to determine if the distribution of the RuNO-nitrato complexes in aqueous solutions is dependent only on the total nitrate concentration or only on the nitric acid concentration or on a combination of both, spectra were taken of three solutions at aged conditions.

Figure 17 shows that the $NaNO_3$ salted solution spectrum is intermediate between the solution having a nitric acid concentration equal to the nitric acid concentration of the salted solution and the solution having a nitric acid concentration equal to approximately the total nitrate concentration of the salted solution. Spectra at other solution conditions are yet to be made before an analysis of the data can be attempted.

Figure 14

The Effect of Solution Age on Absorption
Spectra of RuNO-Nitrato Complexed Solutions

RuNO-Nitrato Complexes in 4.75N HNO_3
Ru = 1.78 gm/liter

1 = Solution Age 23 Hours
2 = Solution Age 75 Hours
3 = Solution Age 16 Days
4 = Solution Age 22 Days
5 = Solution Age 1-2 Hours
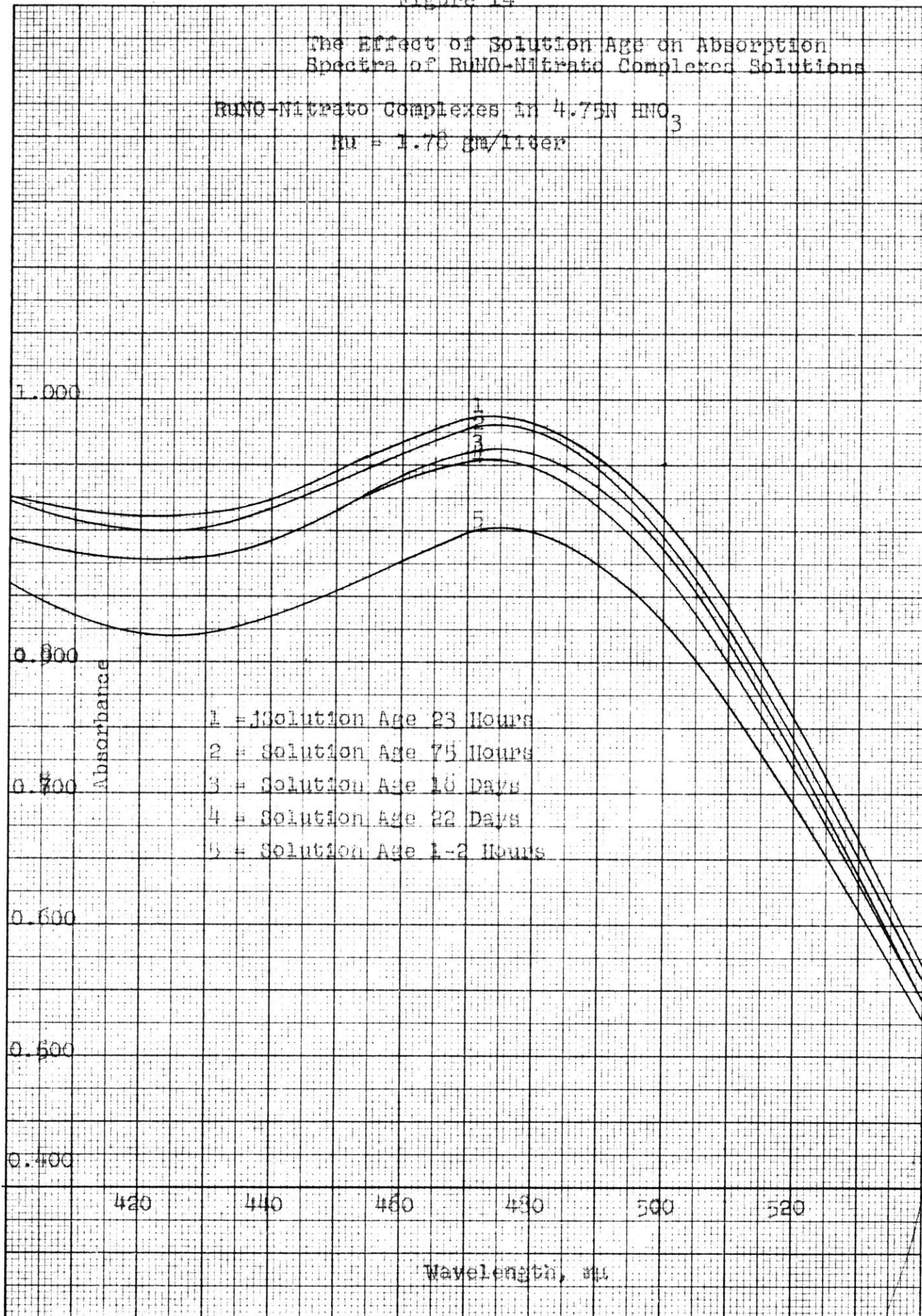
Figure 15

The Effect of Solution Age on
Absorption Spectra of RuNO-Nitrato Complexes
Solutions

RuNO-Nitrato Complexes in 4.75N HNO_3

Ru = 1.78 gm/liter

1 = Solution Age 31 Days
2 = Solution Age 22 Days
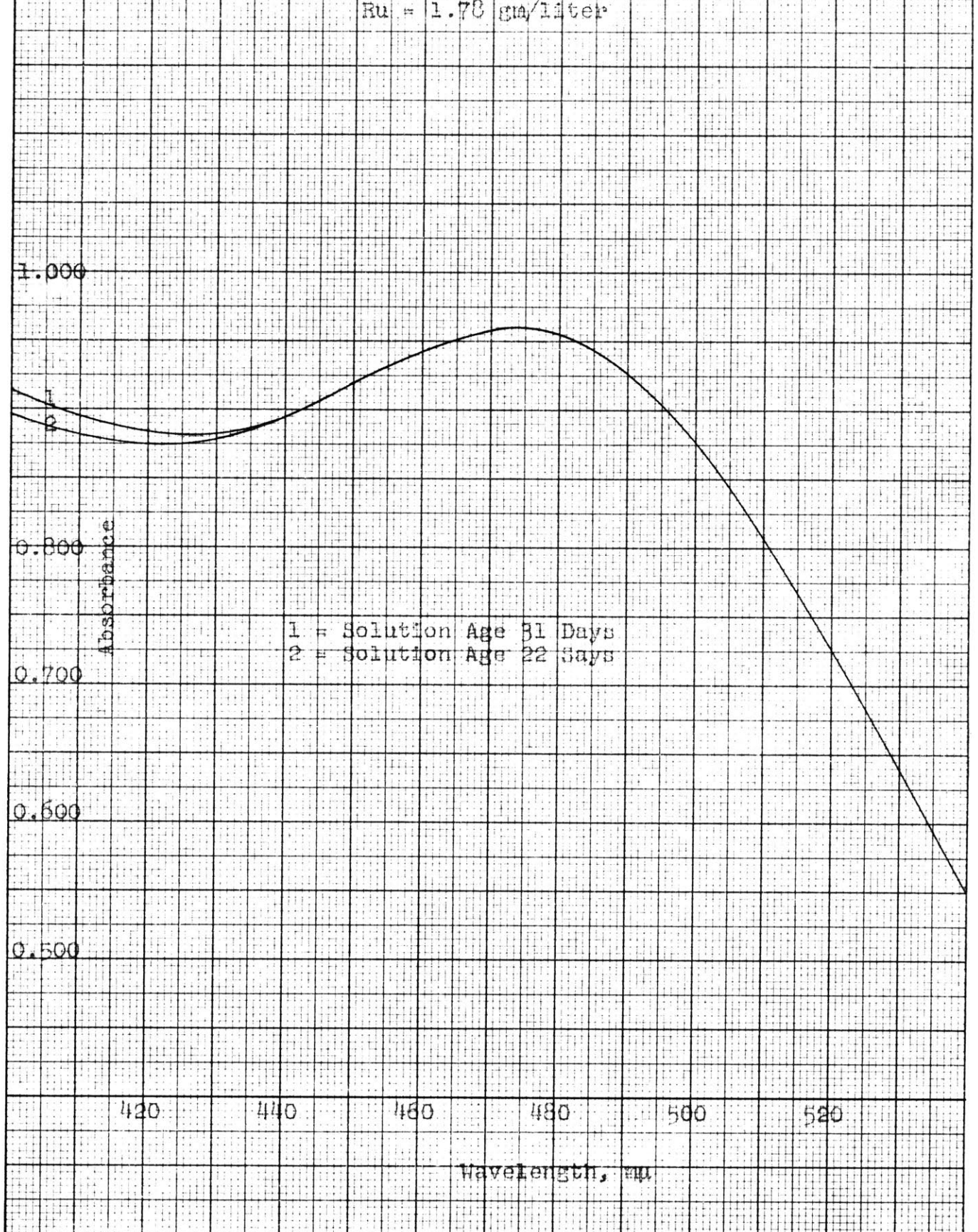
Figure 16

The Effect of Solution Age on
Absorption Spectra of RuNO-Nitrato Complexes
Solutions

RuNO-Nitrato Complexes in 1.2N HNO_3
Ru = 4.73 gm/liter

1 = Solution Age Six Months
2 = Solution Age One Month
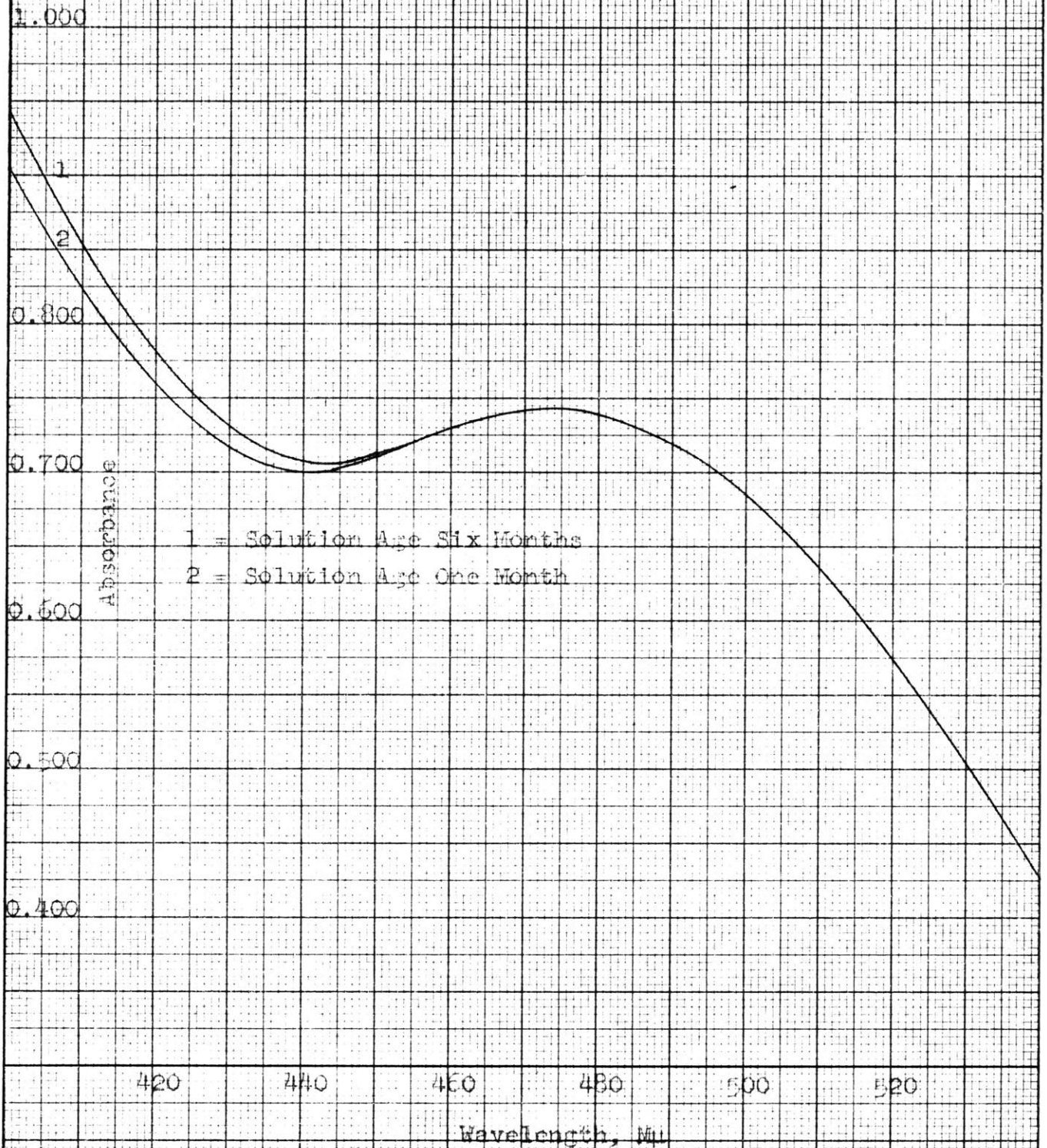
Figure 17

The Effect of Nitrate Salting on the
Absorption Spectra of RuNO-Nitrato Complex
Solutions

1 = 4.9N HNO₃, No Salting
2 = 1.3N HNO₃ - Total 5.1M Nitrate
3 = 1.3N HNO₃, No Salting

Ruthenium Concentrations = 1.29 gm/liter
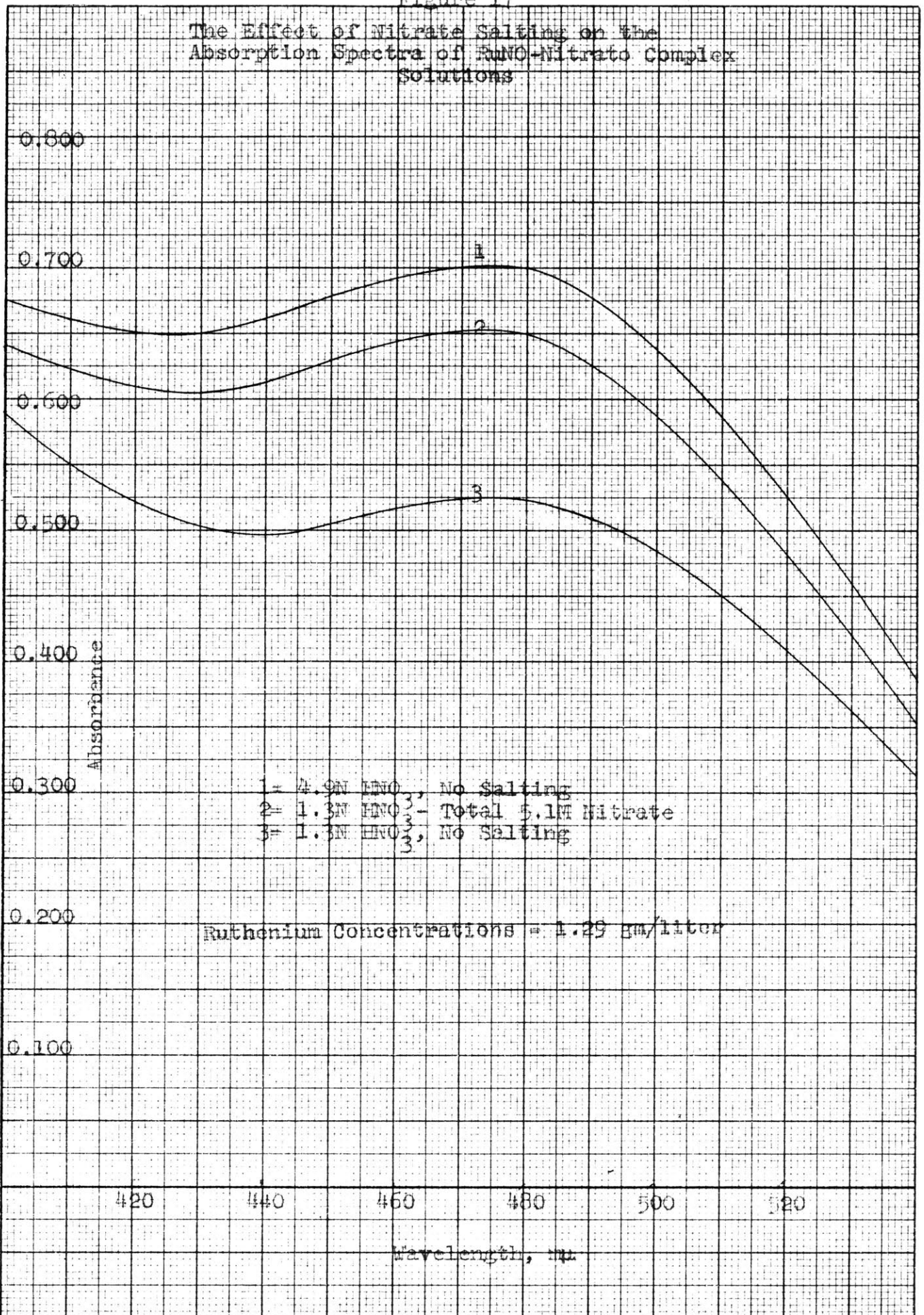
3.0 <u>Ruthenium Nitrosyl Nitro Complexes</u>

Concluding the description of preparation III as started in the previous report (3) the solution was evaporated nearly to dryness and yielded a deliquescent brown-orange solid $RuNO(NO_2)_2OH(H_2O)_2$. The solid was dissolved in DDW and diluted to 256 ml in a volumetric flask. Analysis showed the ruthenium content to be 55.3 gm/liter.

A set of solution was then prepared by adding the appropriate amount and concentration of nitric acid and/or sodium nitrate to aliquot portions of the stock solution. A summary of the solutions is listed in Table 2.

3.1 <u>Extraction of Freshly Prepared Solutions</u>

Extractions of most of the fresh solutions (age after dilution of compound in DDW approximately 1-2 hours) were made for a two-minute contacting time. The data are shown plotted in Figure 18. Of interest are three observations:

(1) The curve shows no maximum but decreases steadily with increasing nitric acid concentration. In fact, plotting the data for the nitric acid system with no nitrate salting on semi-log paper (Figure 19) yields a straight line that can be described empirically by $E_A^o = 0.26e^{-0.64N}$, where N is the nitric acid normality.

(2) From Figure 18, it appears that sodium nitrate salting decreases the extractability of the freshly prepared nitro complexes. However, by plotting the values of E_A^o against the final organic phase nitric acid concentration rather than the final aqueous phase nitric acid concentration, it can be seen (Figure 20) that actually the salting has no observable effect. The organic phase nitric acid concentration was not determined by organic phase titration of the samples but was obtained from Figure 6.

(3) The freshly prepared RuNO-nitro complexes are more highly extractable than the freshly prepared RuNO-nitrato complexes, particularly at low acid concentrations. Figure 21 shows the two systems plotted so as to enable comparison. At 0.5N HNO_3, the value of E_A^o for the nitro complexes is a factor of approximately 40 times that for nitrato complexes.

The effect of sodium nitrate salting of the RuNO-nitro complexes, as shown in Figure 20, is negligible. This would indicate that neither replacement of the nitro ligands by nitrato ligands for higher nitrato complexes formation has occurred in the 1-2 hours of solution aging.

TABLE 2

Ruthenium Nitrosyl Nitro Complexes Solutions

HNO$_3$ Conc., N	Total Nitrate Conc., M	RuConc., gm/liter
0.42	0.42	5.43
0.77	0.77	"
1.22	1.22	"
2.94	2.94	"
4.51	4.51	"
6.29	6.29	"
8.22	8.22	"
9.60	9.60	"
0.42	1.00	"
0.41	2.99	"
0.38	4.96	"
0.36	6.34	4.94
1.16	2.94	5.43
1.07	4.85	"
1.01	6.26	4.94
2.97	3.07	5.43
2.76	4.86	"
2.60	6.33	4.94
4.60	5.10	5.43
4.31	6.58	4.94

FIGURE 18
Extraction of Freshly Prepared RuNO-Nitro Complexes
2-Minute Contacting at 25°C with 0.26 M TLA in Toluene

O = Nitric Acid System (No Salting)

Δ = Nitric Acid-Sodium Nitrate System
(Total Nitrate = 6.3M)

Final Aqueous HNO_3 Normality
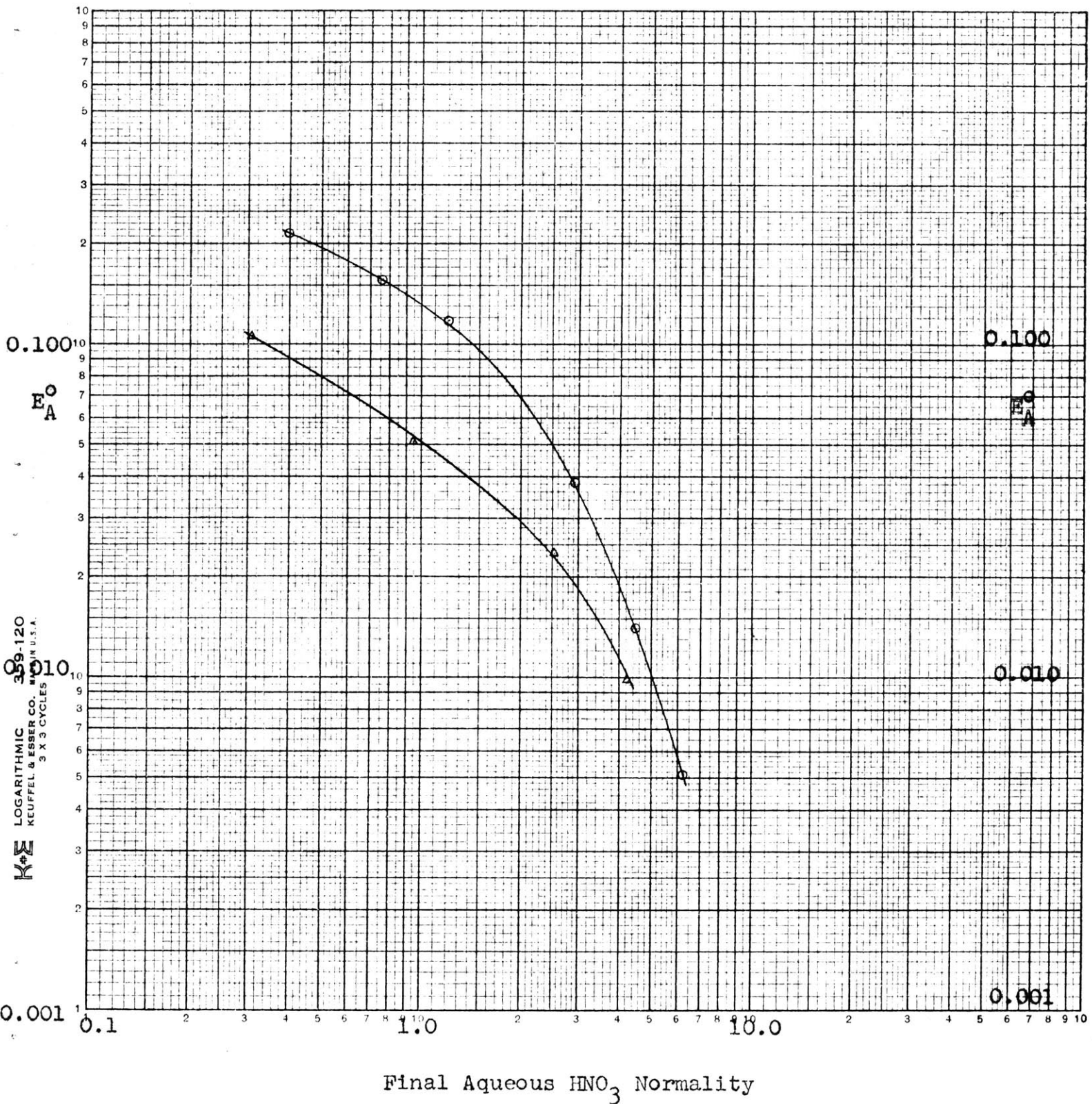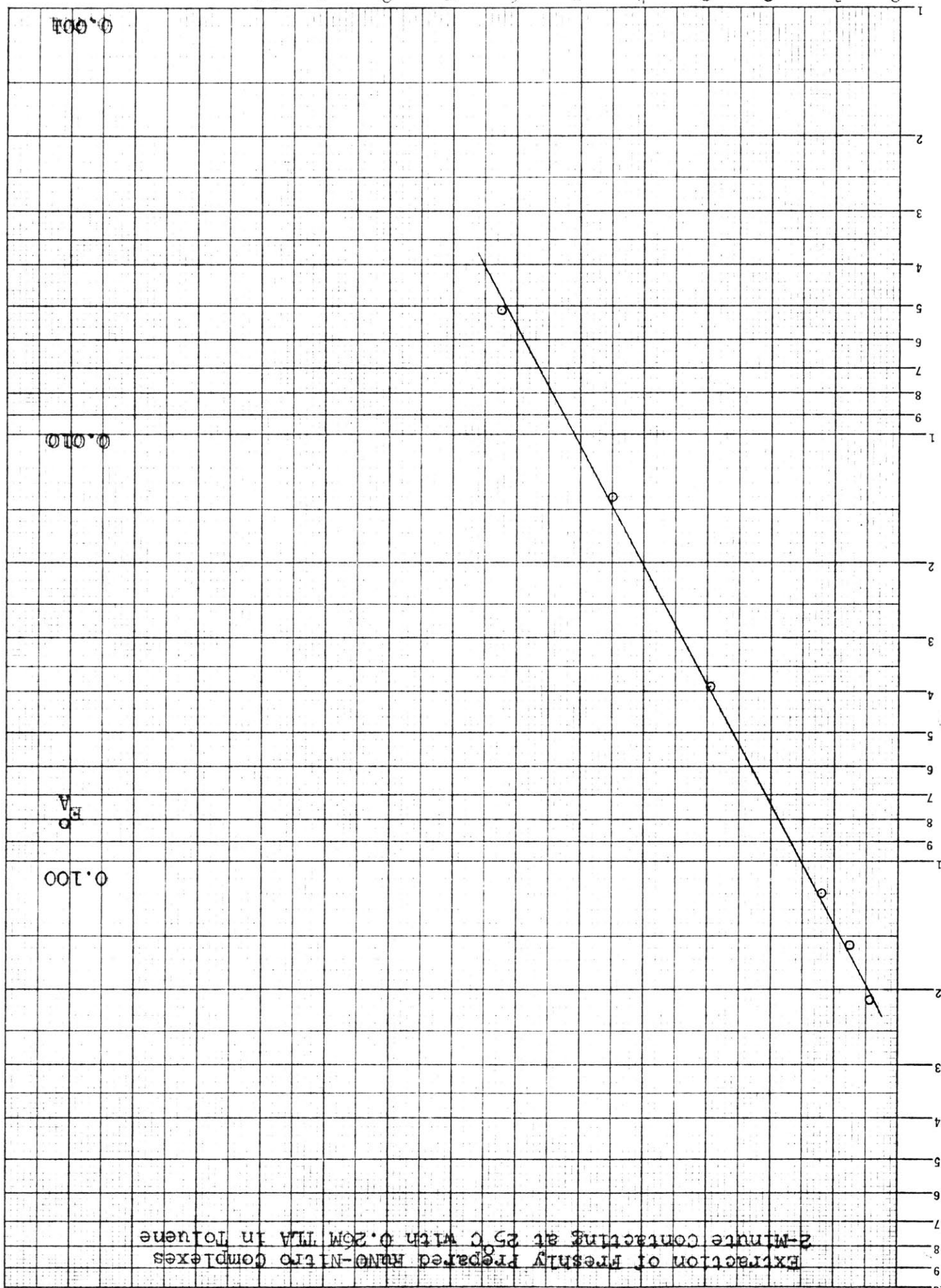
FIGURE 19

Extraction of freshly prepared HNO-nitro complexes
2-minute contacting at 25 C with 0.25M TLA in Toluene

Final Aqueous HNO, Normality

FIGURE 20
Extraction of Freshly Prepared RuNO-Nitro Complexes
2-Minute Contacting at 25°C With 0.26M TLA in Toluene

O = Nitric Acid System (No Salting)

△ = Nitric Acid-Sodium Nitrate System
(Total Nitrate = 6.3M)

E_A^O

Final Organic Unbound HNO_3 Normality

FIGURE 21
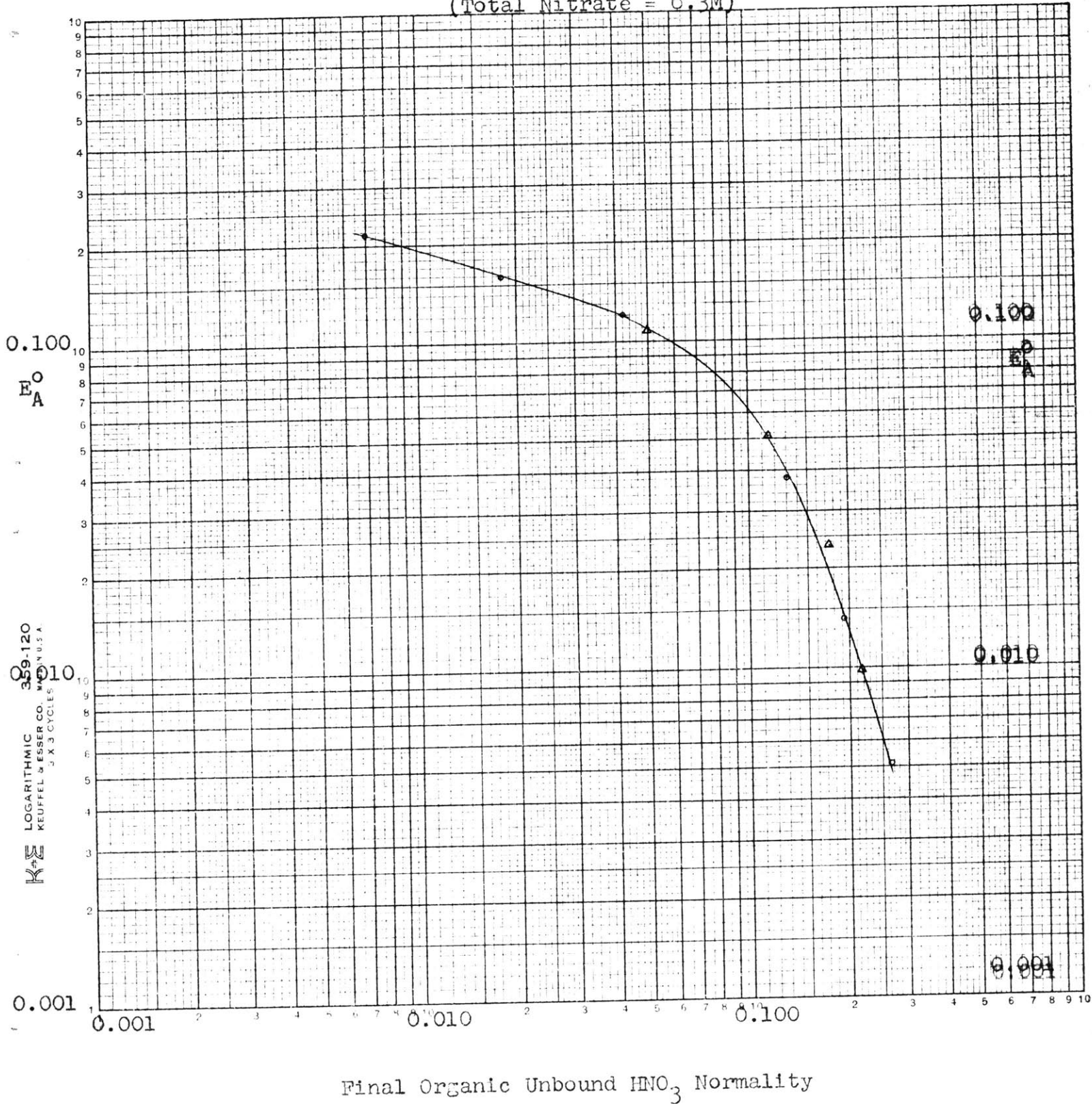
Extraction of Freshly Prepared RuNO-Nitrato and RuNO-Nitro Complexes

2-Minute Contacting at 25°C with 0.26 M TLA in Toluene
O = RuNO-Nitro Complexes
Δ = RuNO-Nitrato Complexes
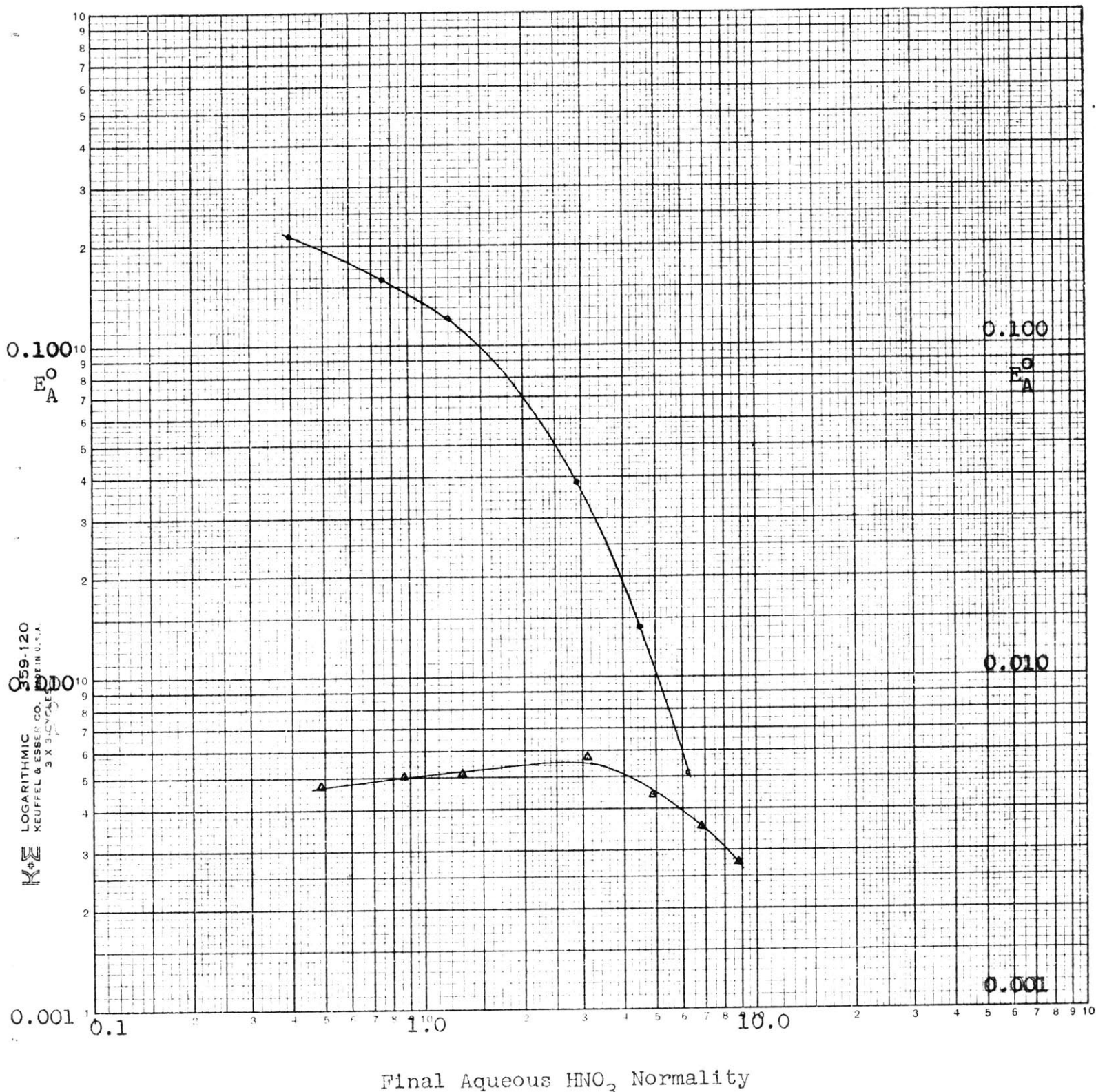
Final Aqueous HNO_3 Normality

This is consistent with the work of Brown (6) on the RuNO-nitro complexes reaction rates.

3.2 Extraction of Aged Solutions

After aging at room temperature for one month, a series of extraction studies were conducted on the solutions.

3.2.1 Effect of Nitric Acid Concentration

A set of extractions was made for two-minute conctacting of the aged solutions with the acid and nitrate concentrations in the samples the same as those for the freshly prepared two-minute contacting. The data is shown plotted as a function of final aqueous nitric acid concentration in Figure 22 and as a function of final organic excess nitric acid concentration in Figure 23.

From Figure 23, it is seen that after aging for one month, the sodium nitrate salting has had the effect of increasing the extractabiltiy of the complexes. It is believed that this is due to either replacement of nitro ligands by nitrato ligands, the formation of higher nitrato complexes, or, more likely, a combination of both.

Of interest is the point (in Figure 23) at which the line of the salted sample merges with the line of the non-salted samples. The intersection is not at the organic phase excess acid concentration corresponding to 6.3N HNO_3 in the aqueous phase, but at a lower point. This is consistent with the previous discussion of the spectra of salted RuNO-nitrato complexes solutions in Section 2.3.2 and indicates again that nitrate in the form of nitric acid is more effective with regard to nitrato com lexing than is nitrate in the form of sodium nitrate. This may possibly indicate that the tetra- and penta-nitrato complexes exist in solution in the form of the acids of the species $(HRuNO(NO_3)_4(H_2O)$ and $H_2RuNO(NO_3)_5)$ rather than as anions $(RuNO(NO_3)_4(H_2O)^-$ and $RuNO(NO_3)_5^=)$.

Comparison of the aged RuNO-nitro complexes with the freshly prepared RuNO-nitro complexes (Figure 24) shows that aging has resulted in decreasing the extractability of the complexes, although it appears that at an acid concentration of approximately $7NHNO_3$ and higher that the extractability may have been increased.

FIGURE 22
Extraction of Aged RuNO-Nitro Complexes

Solutions Aged For One Month at Room Temperature
2-Minute Contacting at 25°C with 0.26 M TLA in Toluene
O = Nitric Acid System (No Salting)
Δ = Nitric Acid-Sodium Nitrate System (Total Nitrate=6.3M)

Final Aqueous HNO_3 Normality

FIGURE 23
Extraction of Aged RuNO-Nitro Complexes
Extraction of Aged RuNO-Nitro Complexes
Solutions Aged For One Month at Room Temperature
2-Minute Contacting at 25°C with 0.26 M TLA in Toluene
O = Nitric Acid System (No Salting)
Δ = Nitric Acid Sodium Nitrate System (Total Nitrate= 6.3M)
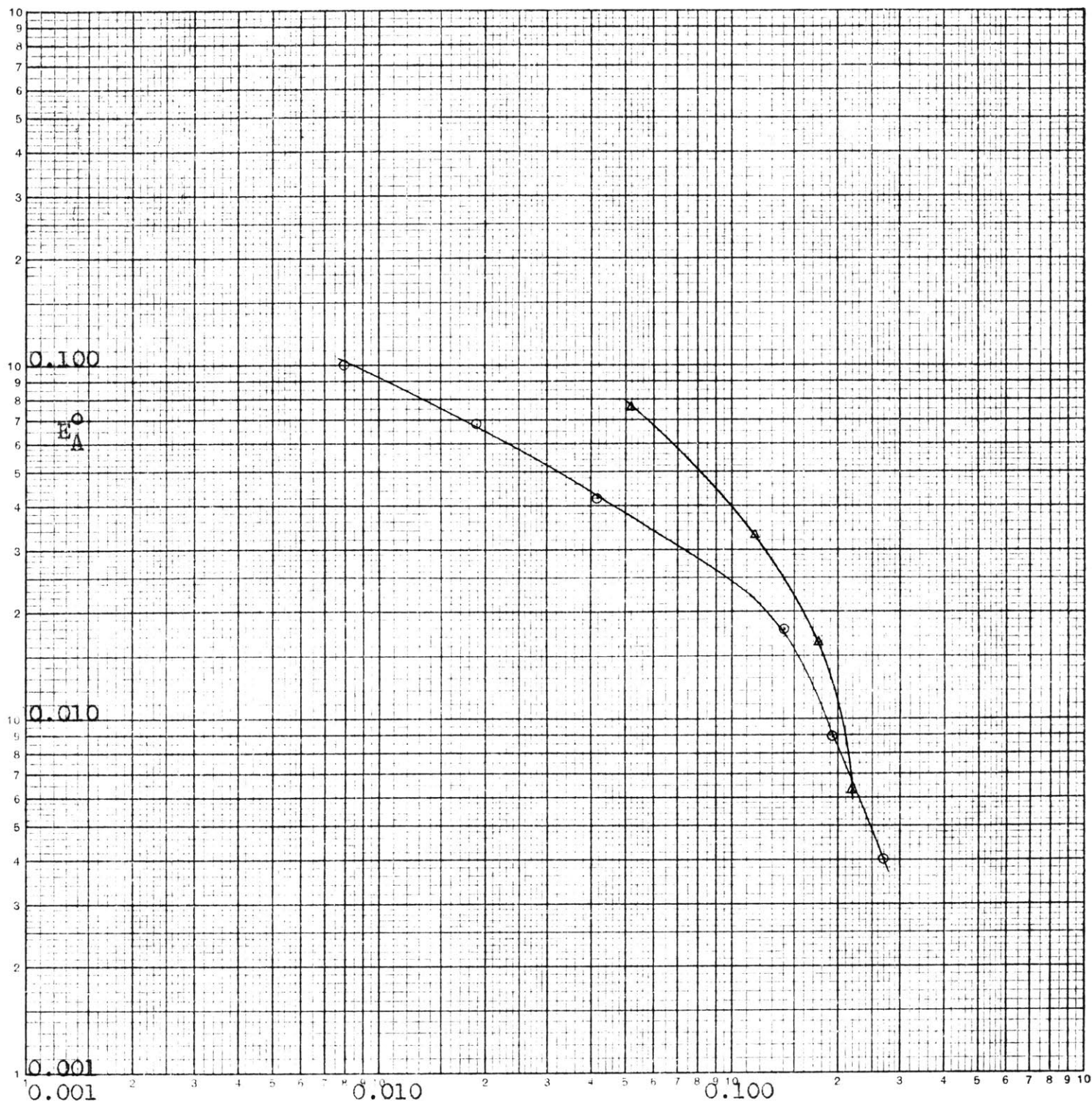
Final Organic Unbound HNO_3 Normality

FIGURE 24
The Effect of Solution Age on Extraction of
RuNO-Nitro Complexes

2-Minute Contacting at $25^\circ C$ with 0.26 M TLA in Toluene
O = Freshly Prepared Solutions
Δ = Solutions Aged for One Month at Room Temperature
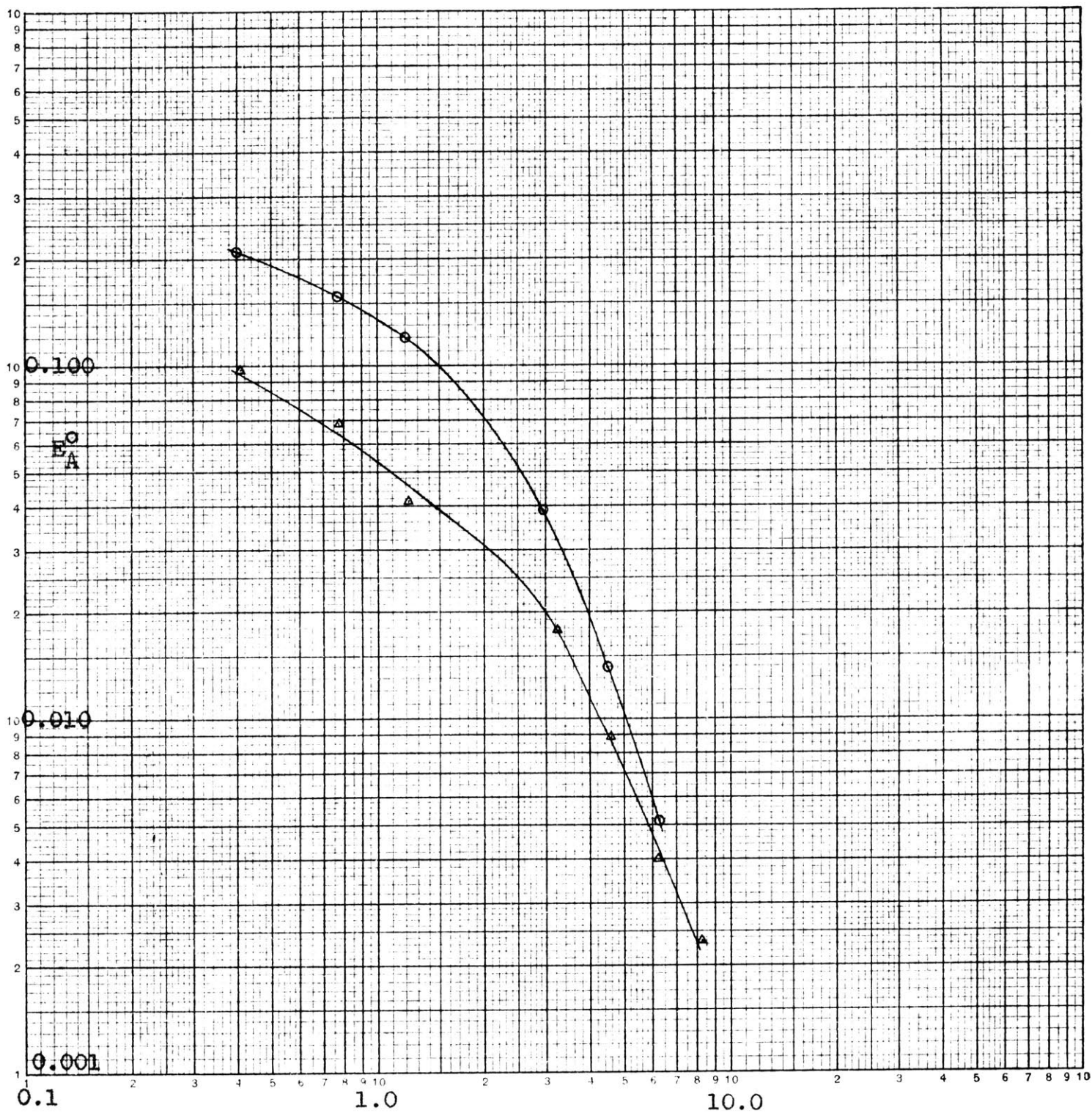
Final Aqueous HNO_3 Normality

The decrease in extractability is thought to be due to the formation of nitro-nitrato complexes and/or lower less than tetra-) nitrato complexes which are believed to be less extractable than either the higher nitrato complexes or the nitro species initially in solution.

In Figure 24 are plotted the values of E_A^o as a function of final organic nitric acid concentration for aged (one month) RuNO-nitro complexes for a 24-hour contacting time. By comparison with Figure 23, it can be seen that for the salted solutions the rate of increase of E_A^o with contacting time is greater than that of the non-salted solutions. For instance, at a final organic HNO_3 concentration of 0.060 M, the values of E_A^o for the non-salted solutions are 0.035 and 0.095 for the two-minute contacting and 24-hour contacting respectively; a ratio of 2.71. The corresponding values for the salted solutions are 0.066 and 0.340, or a ratio of 5.15. This again is consistent with the previously mentioned difference of rates of reaction and redistribution between the RuNO-nitrato complexes and RuNO-nitro complexes. This difference is shown more clearly in Figures 26 and 27. Figure 26 shows the values of E_A^o for the non-salted aged RuNO-nitro complexes for the two-minute and 24-hour contacting times plotted so as to enable comparison. Figure 27 shows the value of the ratio (R) of the E_A^o values at 24 hour contacting to the E_A^o values at 2 minute contacting as a function of final organic HNO_3 concentration for the aged (one month) RuNO-nitrato complexes and the aged (one month) RuNO-nitro complexes. The organic phase nitric acid concentration corresponding to an aqueous phase concentration of 3M HNO_3 is marked for reference purposes. It should be noted that since the RuNO-nitro complexes are very slow (compared to the RuNO-nitrato complexes) in approaching equilibrium in the aqueous phase, the aged RuNO-nitro solutions will be labeled as to the length of the aging time. Whereas for the RuNO-nitrato complexes there exists no appreciable difference in solution composition at ages of one month or six months, the RuNO-nitro complexes solutions appear to be changing even at an age of four months. This topic will be discussed in more detail in Section 3.3.1.

3.2.2 Effect of Aqueous Ruthenium Concentration

In Figure 28 are plotted the values of the final organic ruthenium concentration as a function of final aqueous ruthenium concentration for the RuNO-nitro complexes aged for two months. The aqueous ruthenium concentrations were varied at two different levels of acid concentrations. Both studies show the final organic

FIGURE 25
Extraction of Aged RuNO-Nitro Complexes
Solutions Aged For One Month at Room Temperature
24-Hour Contacting at 25°C With 0.26 M TLA in Toluene
O = Nitric Acid System (No Salting)
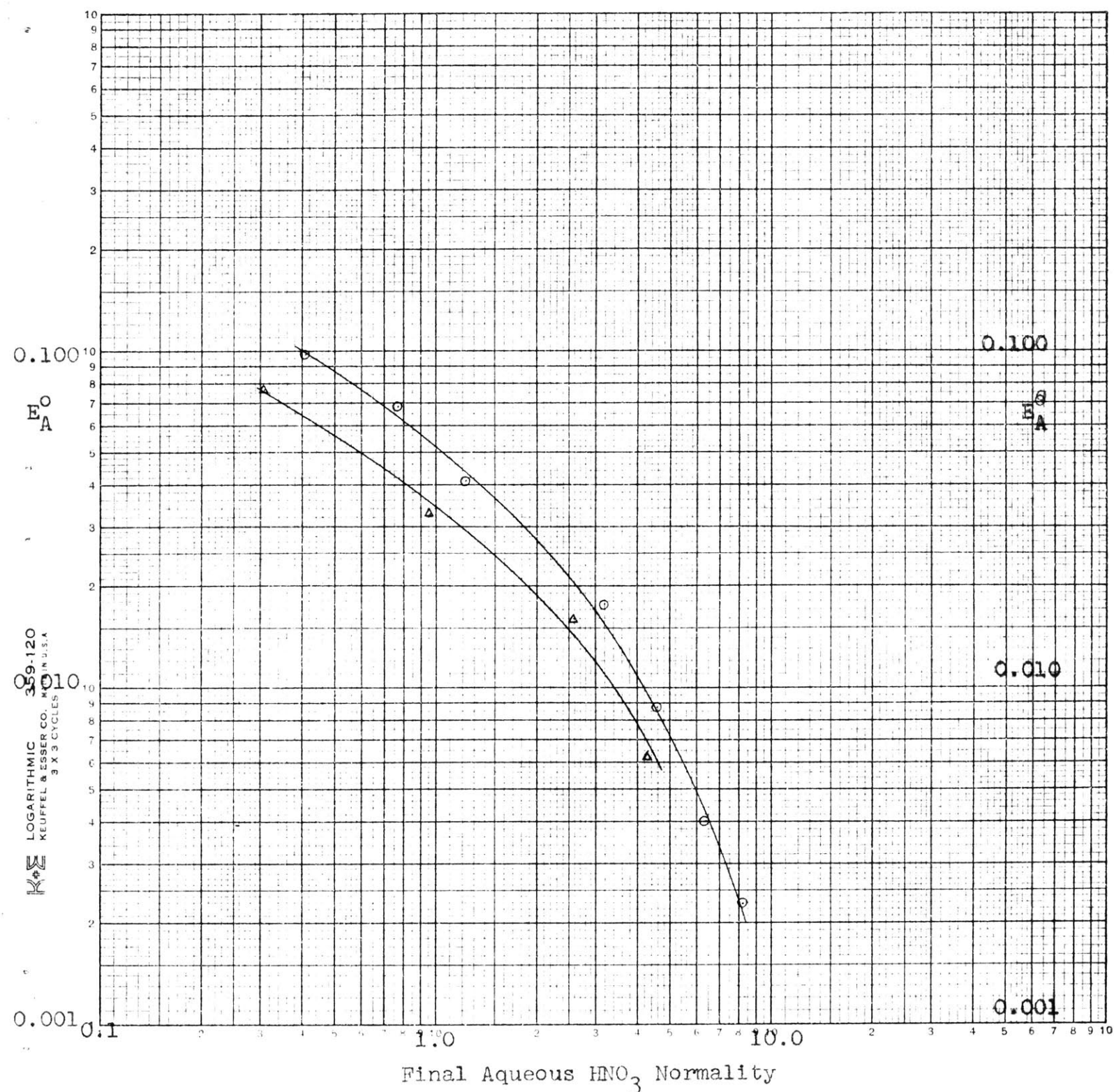△ = Nitric Acid-Sodium Nitrate System (Total Nitrate=6.3M)
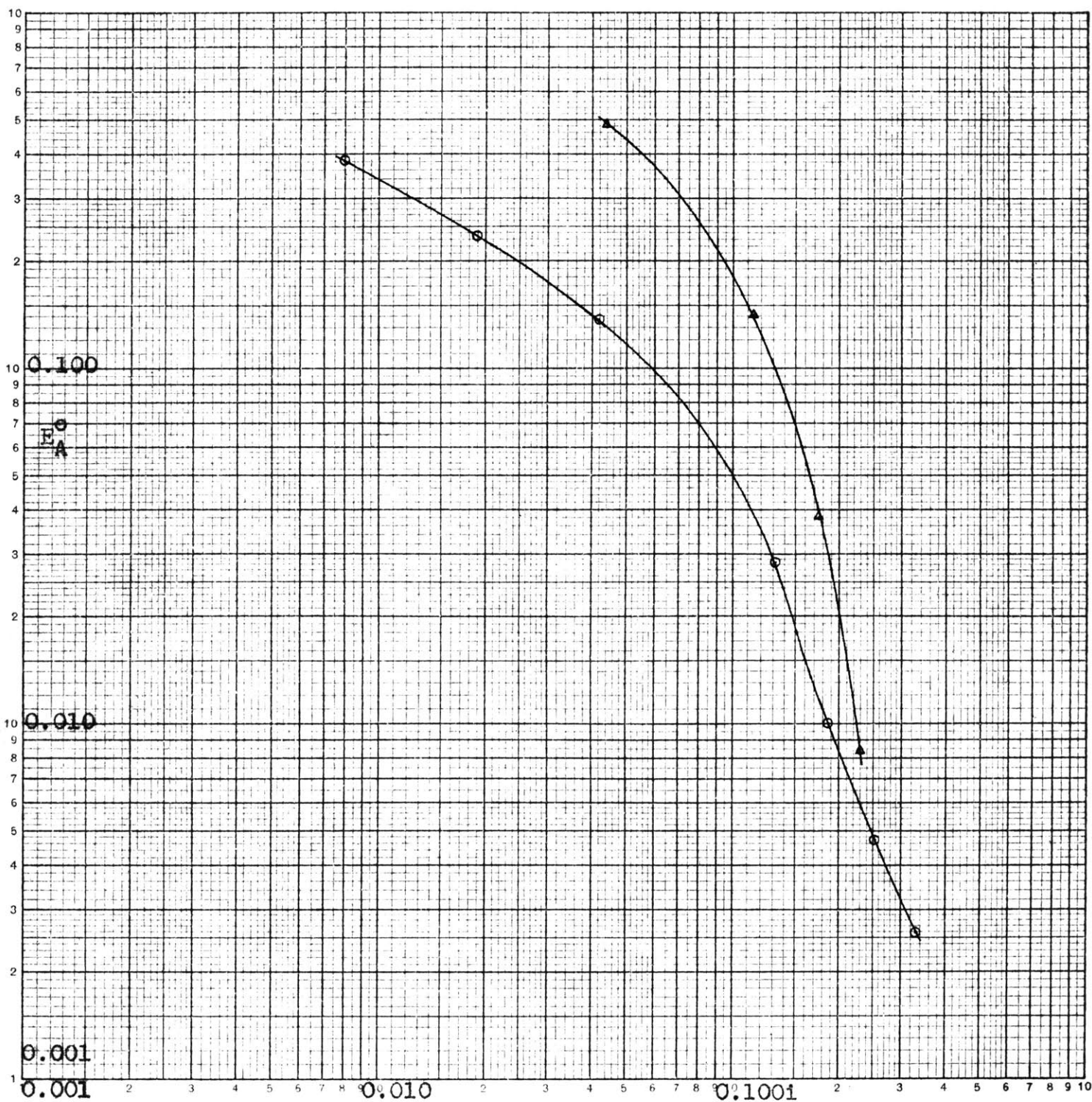
Final Organic Unbound HNO_3 Normality

FIGURE 26
The Effect of Contact Time on the Extraction
of RuNO-Nitro Complexes

Solutions Aged for One Month at Room Temperature
0.26M TLA in Toluene

Δ = 2 Minute Contacting at 25°C
O = 24 Hour Contacting at 25°C
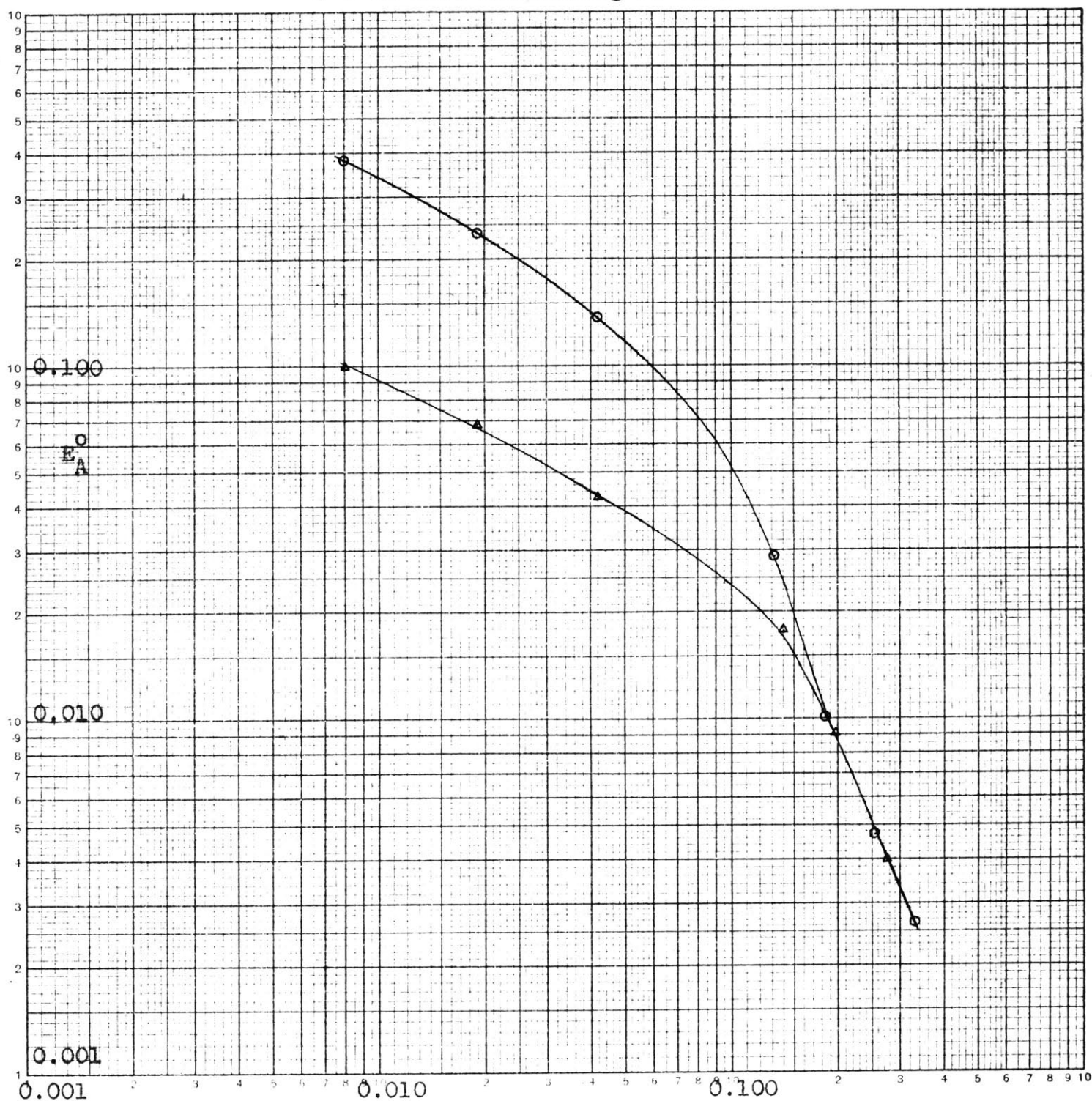
Final Organic Unbound HNO_3 Normality

FIGURE 27
The Effect of Contact Time on the Extraction of
RuNO-Nitro and RuNO Nitrato Complexes

Solutions Aged For One Month at Room Temperature
0.26 M TLA in Toluene

O = RuNO-Nitro Complexes
D = RuNO-Nitrato Complexes   No Salting

$$R = \frac{E_A^0 \text{ for 24-Hour Contacting at } 25^0C}{E_A^0 \text{ for 2-Minute Contacting at } 25^0C}$$

Final Organic Unbound HNO_3 Normality

FIGURE 28   41

The Effect of Aqueous Ruthenium Concentration on Extraction of RuNO-Nitro Complexes
Solutions Aged for Two Months at Room Temperature
24-Hour Contacting at 25°C with 0.26 M TLA in Toluene

Final Organic Ru Conc., gm/liter (y-axis)

Final Aqueous Ru Conc., gm/liter
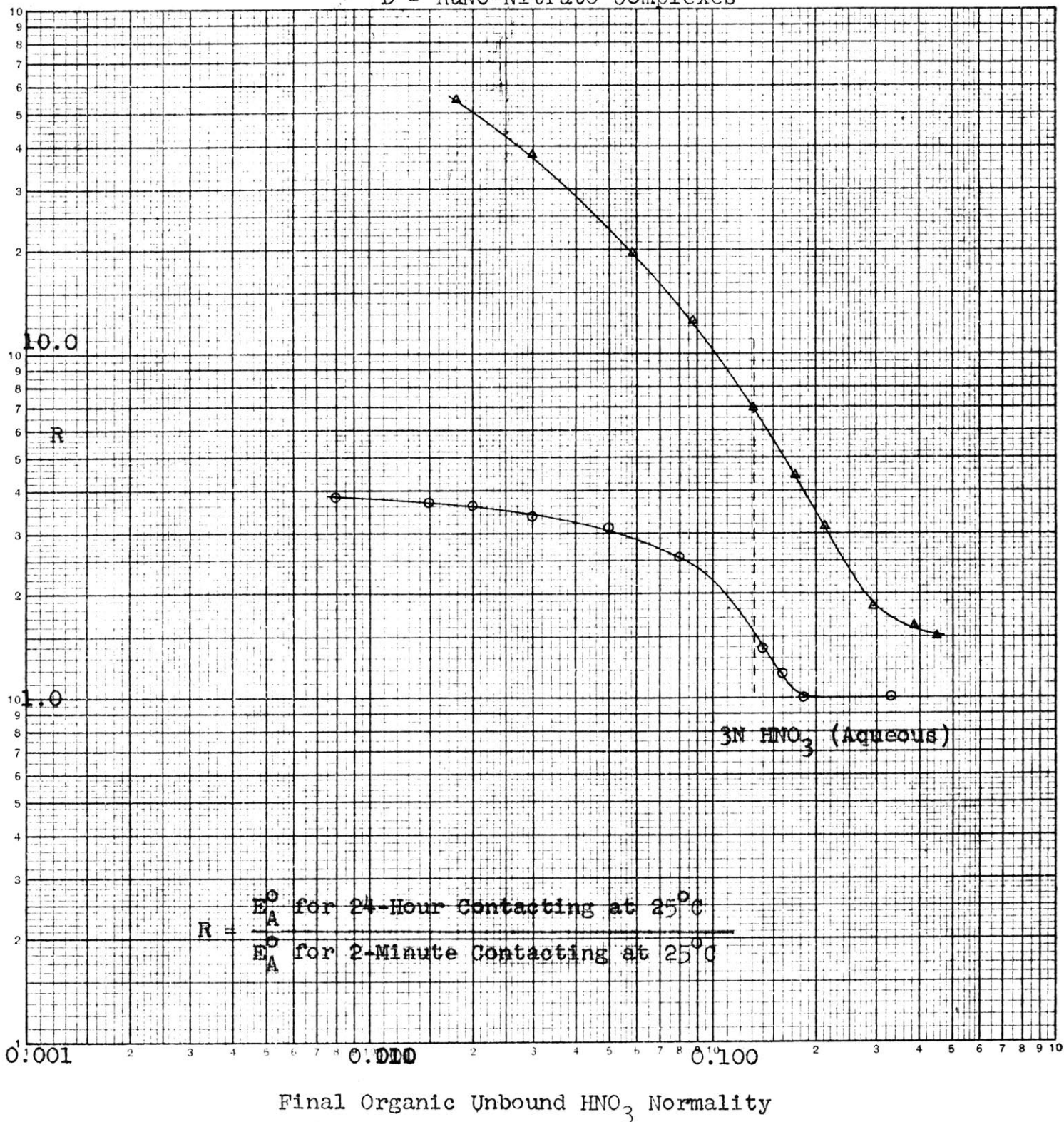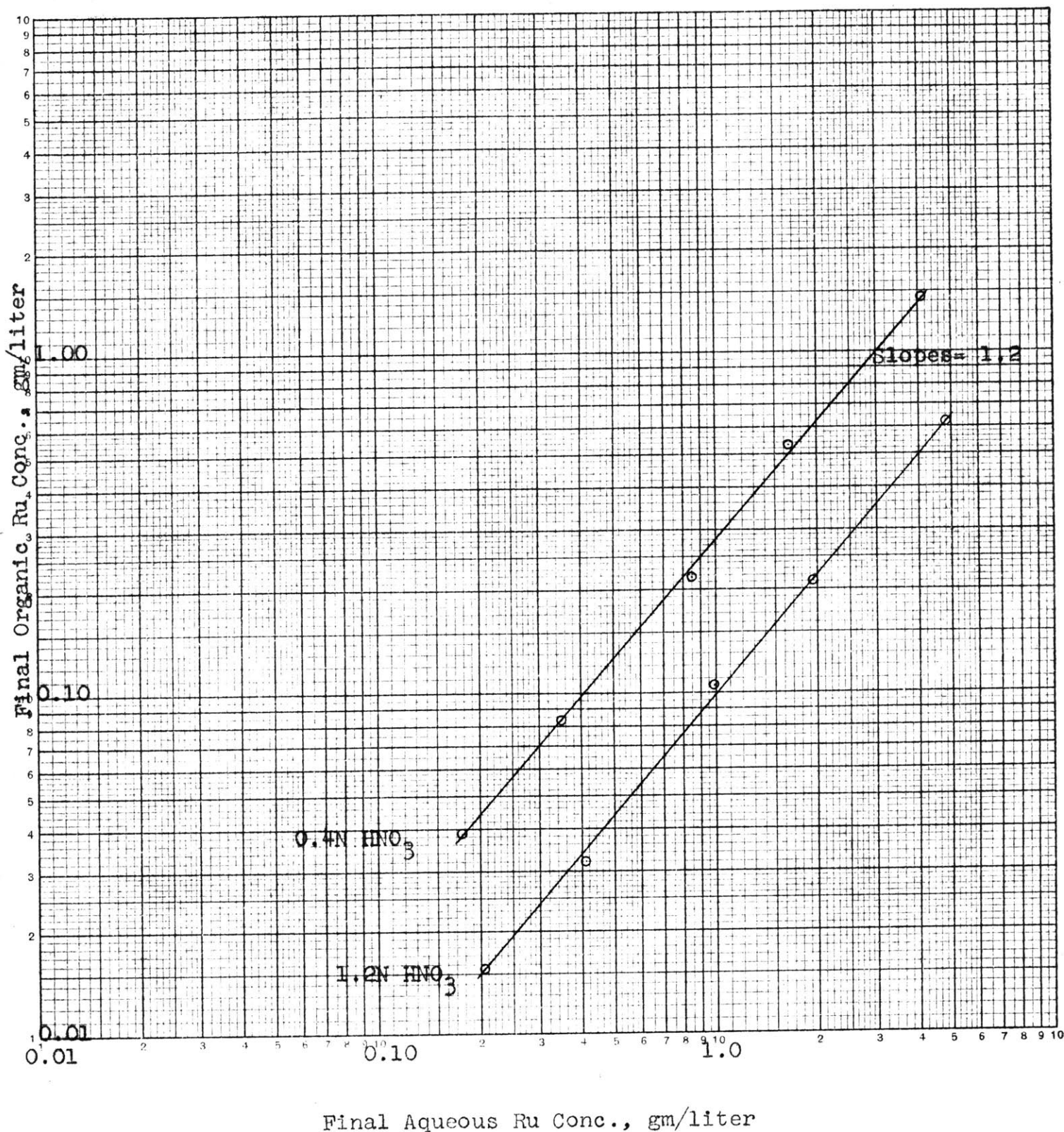
ruthenium concentration to be dependent upon the 1.2 power of the final aqueous ruthenium concentration in the range of final aqueous ruthenium concentrations of from about 0.2 gm/liter to 5 gm/liter. This dependence upon a power greater than unity may be due to self-salting of the RuNo-nitro complexes. A few extractions with added amounts of sodium nitrite to RuNO-nitro complexes will be·made in the near future to determine the effect of nitrite salting.

3.2.3 Effect of Amine Concentration

In a similar fashion to the aged RuNO-nitrato complexes, the distribution ratio of aged (two-months) RuNO-nitro complexes increases initially with the 1.2 power of the amine concentration and then tapers off to a lower power dependence above an amine concentration of approximately 0.13M. (see Figure 29) The tapering off can again be explained by the higher concnetration of unbound nitric acid in the organic phase than would be the case if the ratio of unbound acid concentration to amine concentration were constant.

3.2.4 Effect of Nitrate Salting

Following the method employed in Section 2.2.3, the values of E_A^o for 24 hour contacting of the aged (one month) RuNO-nitrate complexes are plotted in Figure 30 as a function of final organic unbound nitric acid concentration for constant total aqueous nitrate concentrations of 1.2M, 3M, 5M, and 6.3M. Cross plotting from Figure 30 gives Figure 31, where the values of E_A^o are plotted as a function of total aqueous nitrate concentration for constant organic unbound acid concentrations.

From Figure 31, it appears that the distribution ratio varies as the 0.8 to 4.7 power of the total aqueous nitrate concentration. A particularly strong function of total nitrate concentration seems to be apparent in the small range of 5M to 6.3M total nitrate. However, as was shown in Section 3.2.1, the rate of increase of E_A^o with contacting time is greater for the salted solutions (6.3M total nitrate) than for the non-salted solutions.

Therefore, in order to obtain a better idea of the dependence of E_A^o on total aqueous nitrate concentration, the dependence on contact time should be eliminated as much as possible. This can be accomplished by plotting the values of E_A^o for the two-minute contacting time. Cross plotting from Figure 23 yields Figure 32 which shows the values of E_A^o for two minute contacting of aged solution at the non-salted conditions and the salted

FIGURE 29

43

The Effect of Amine Concentration on Extraction of
RuNO-Nitro Complexes

Solution Aged for Two Months at Room Temperature
24-Hour Contacting at 25°C with 0.4N HNO_3 Aqueous

Solution of RuNO-Nitro Complexes
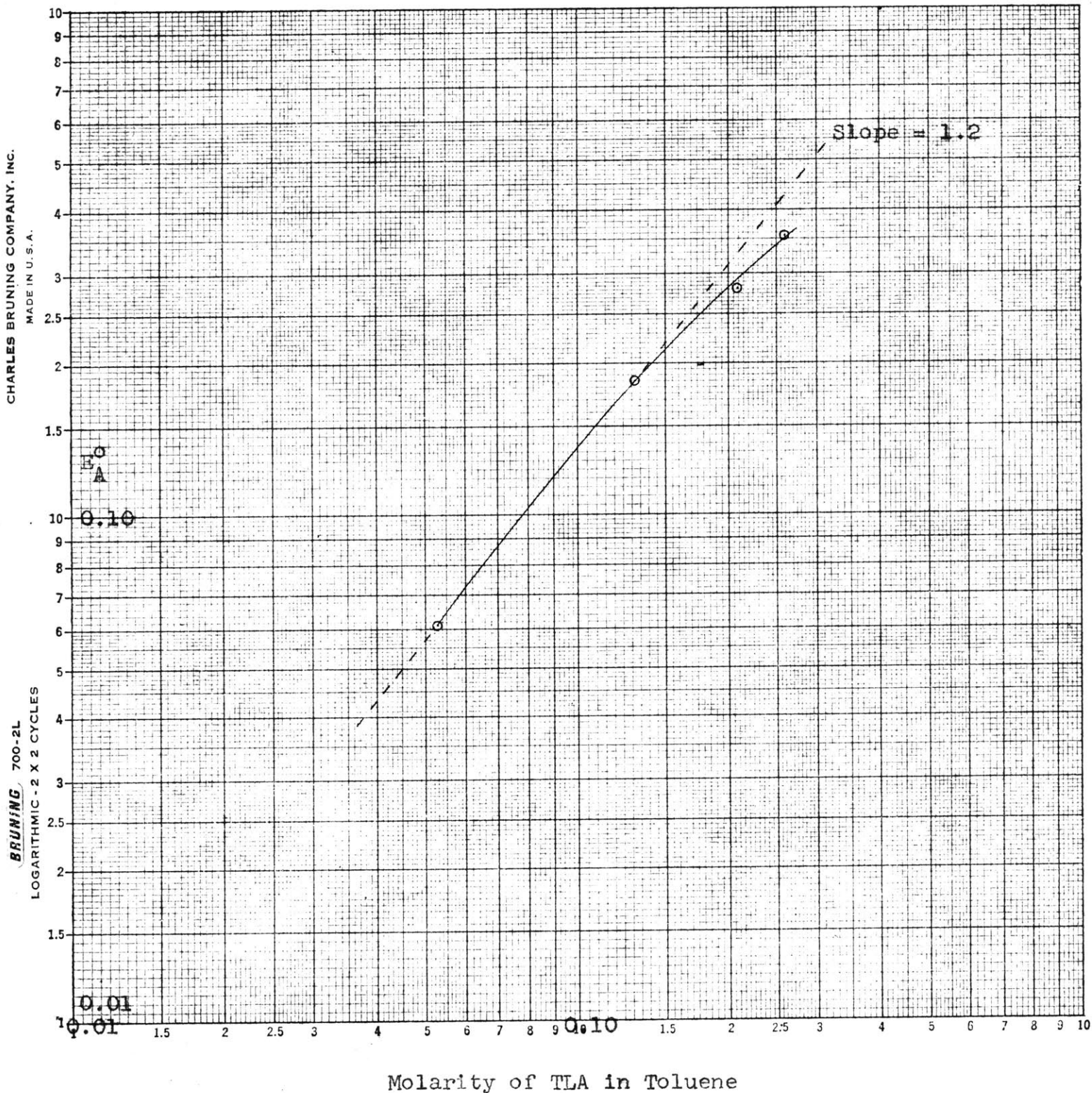
Molarity of TLA in Toluene

FIGURE 30

44

The Effect of Sodium Nitrate Salting on Extraction
of RuNO-Nitro Complexes

Solutions Aged for One Month at Room Temperature
24-Hour Contacting at 25°C with 0.26 M TLA in Toluene

Final Organic Unbound HNO_3 Normality

Figure 31

45
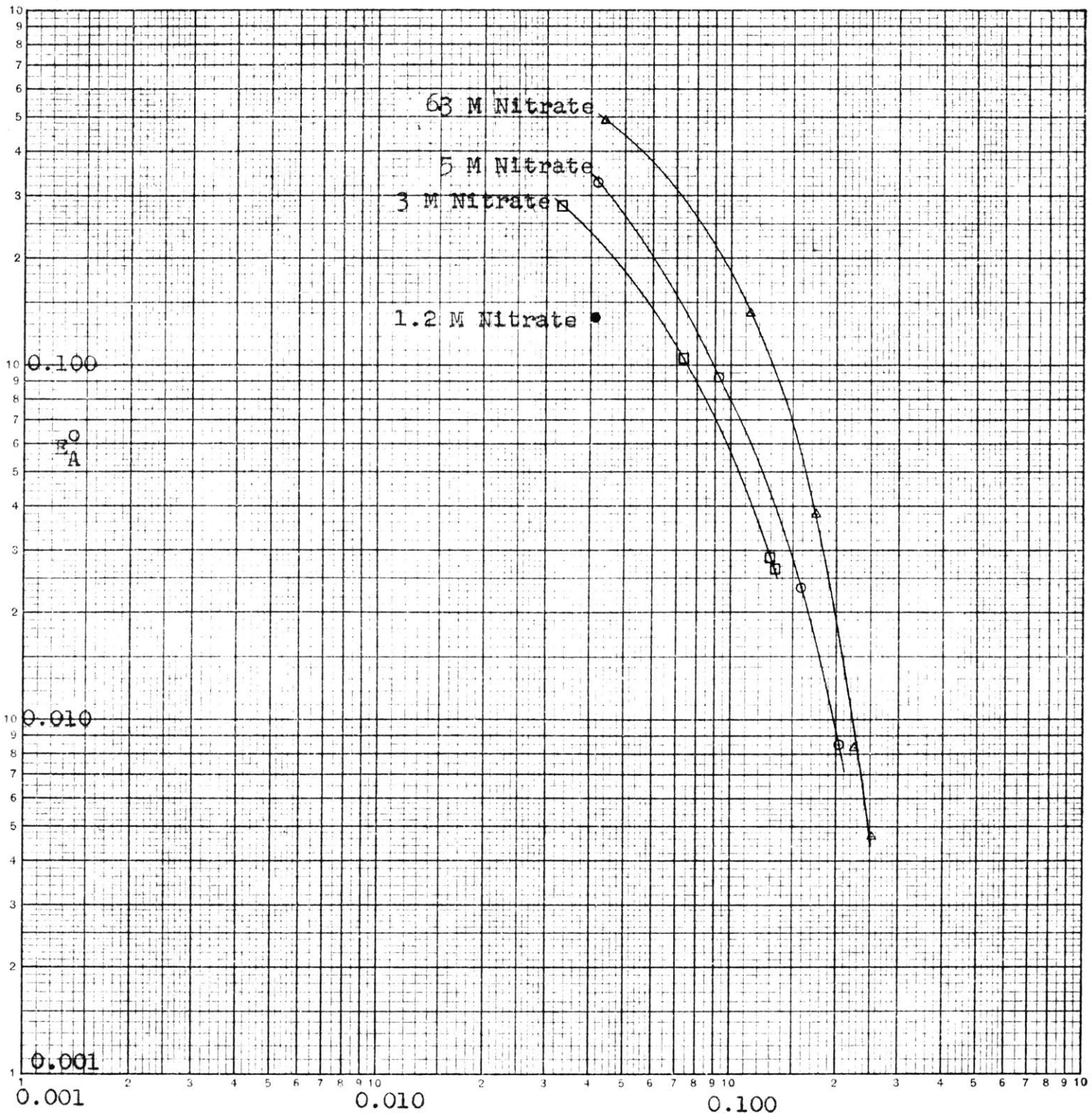
The Effect of Sodium Nitrate Salting on Extraction
of RuNO-Nitro Complexes Solutions Aged for One Month
24-Hour Contacting at 25°C with
0.26M TLA in Toluene

Final Aqueous Total Nitrate Molarity

Figure 32
The Effect of Sodium Nitrate Salting on
Extraction of RuNO-Nitro Complexes

2-Minute Contacting of One Month
Aged Solutions at 25°C with 0.26M TLA
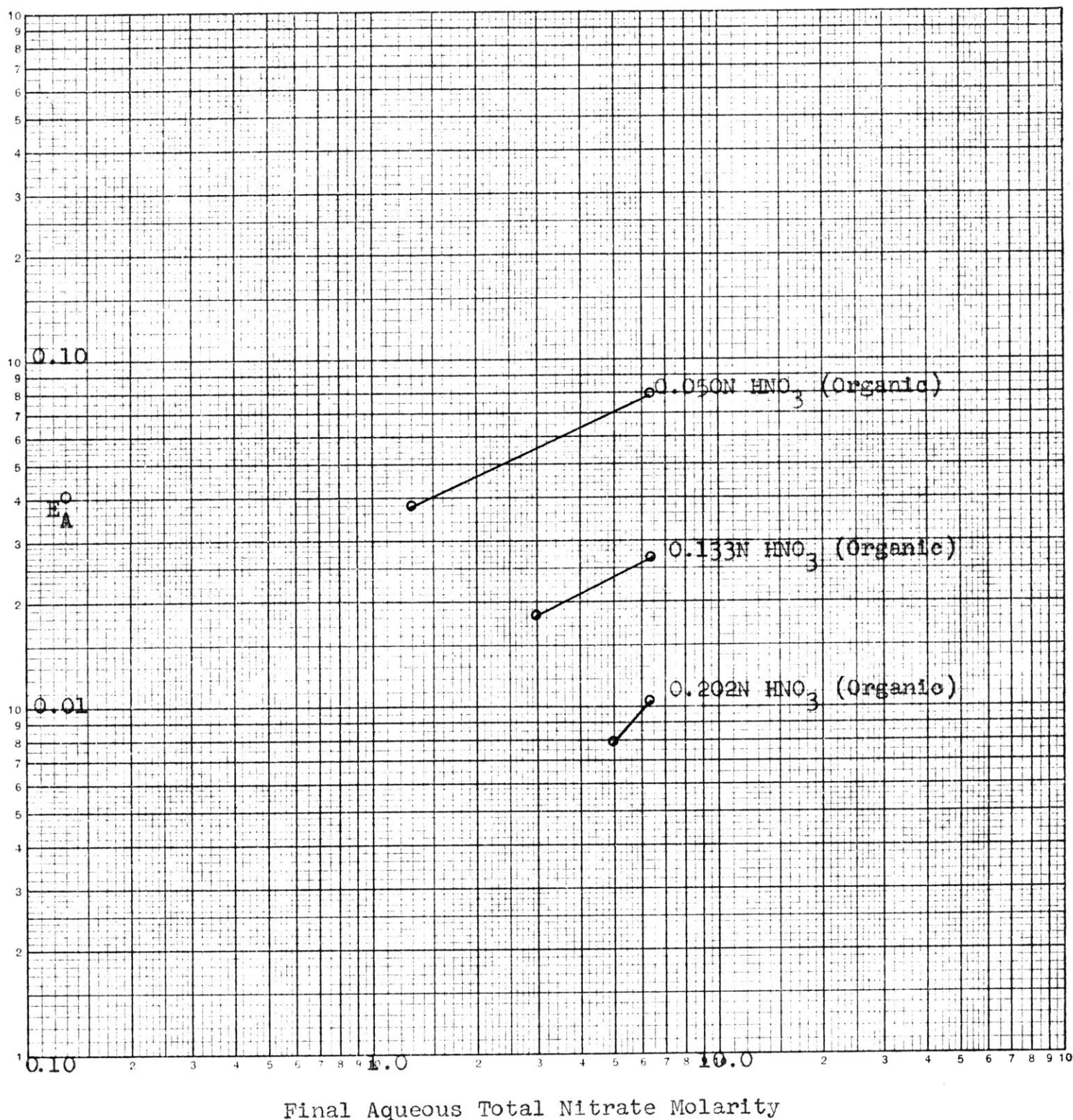
condition of 6.3M total aqueous nitrato concentration. The values of E_A^O for the intermediate salted solutions are not plotted because those data points were taken only for the 24 hour contacting time and not for the two minute contacting time.

From Figure 32, the value of E_A^O is seen to be dependent upon the 0.4 to 0.8 power of the total aqueous nitrate concentration. The actual exponent is probably closer to 0.4 than 0.8, since the slope of 0.8 is a result of two closely spaced points and a small error in their values could result in a large error in the slope of the line drawn through them.

3.3 Spectra of Solutions

Spectra of the RuNO-nitro complexes solutions were made on a Beckman Model Du Spectrophotometer in order to discover any similarities and/or differences between these solutions and the RuNO-nitrato complexes solutions.

3.3.1 Effect of Solution Age

As a means of determining the length of aging time required for the RuNO-nitro complexes to come to equilibrium in aqueous nitric acid solutions, spectra were made of three RuNO-nitro complexes solutions at aging times of seven weeks and four months. The spectra are shown plotted in Figure 33.

Several points are of interest:

(1) The spectra of the RuNO-nitro complexes at both solution ages are similar to the aged RuNO-nitrato complexes from the aspect of exhibiting a minimum in the value of the absorbance between 400 mμ and 450 mμ and a maximum between 450 mμ and 500 mμ. They are also similar in that the absorbance at the maximum increases with increasing nitric acid concentration.

(2) A significant difference is that the position of the maximum shifts with acid concentration. Whereas in the aged RuNO-nitrato complexes solutions the maximum remained at 475 mμ, in the seven weeks aged RuNO-nitro solutions the position of the maximum moves from 485 mμ at 1.2N HNO_3 to 500 mμ at 9.6 N HNO_3. Although the absorbance at the maximum increases with acid strength, it does not increase nearly so much as does the peak absorbance for the aged RuNO-nitrato solutions.

(3) At the seven weeks aging time, the absorbance minimum for the RuNO-nitro solutions is much more

Figure 33

The Effect of Solution Age on Absorption
Spectra of RuNO-Nitro Complexes

RuNO-Nitro Complexes in Nitric Acid
Ru = 1.11 gm/liter

1 = 9.6N HNO₃
2 = 4.5N HNO₃
3 = 1.2N HNO₃

-+-+- = Solution Age 7 Weeks
_____ = Solution Age 4 Months
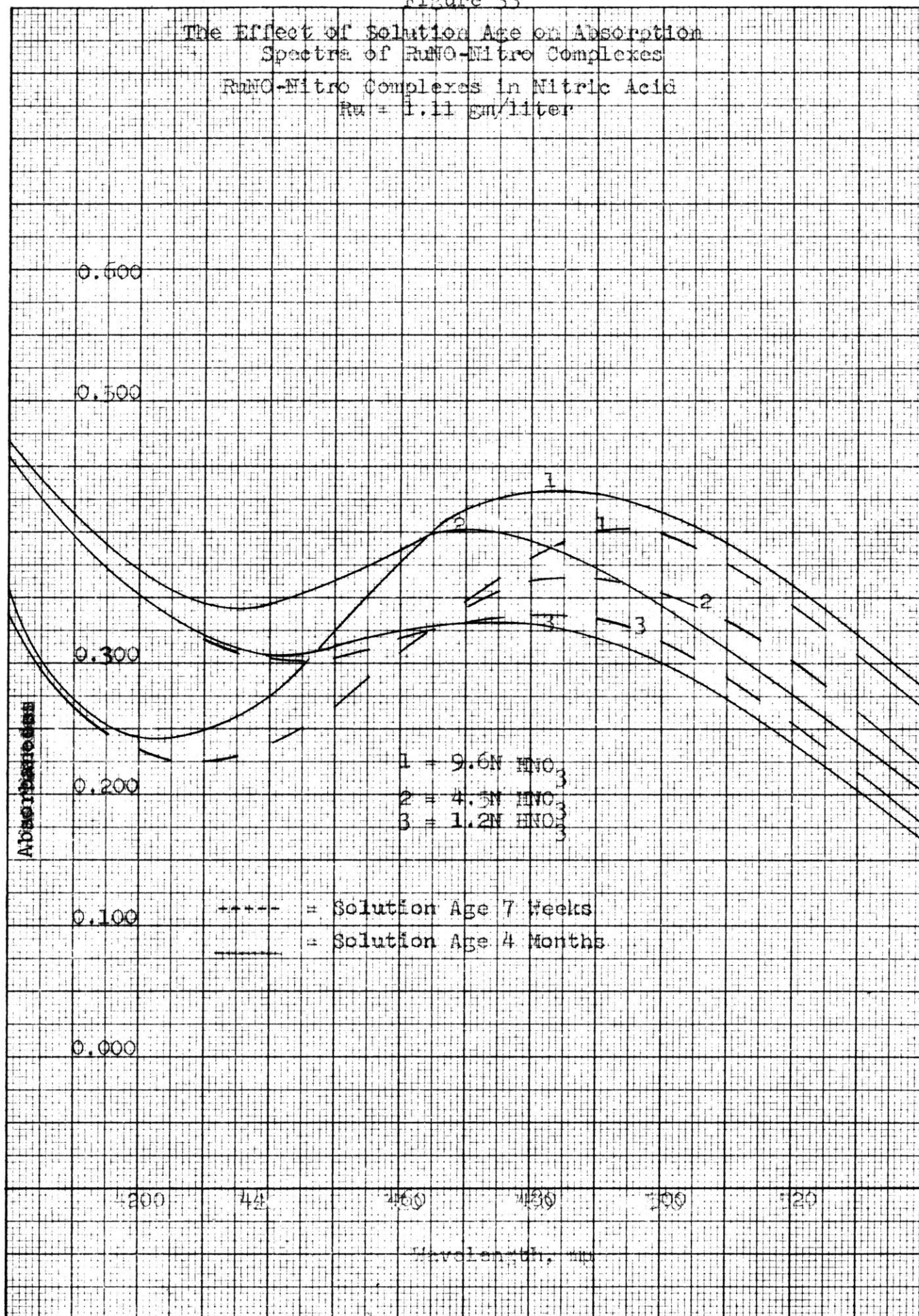
pronounced, especially at higher acid concentrations,
than for the RuNO-nitrato solutions. A large shift in
both position and absorbance of the minimum is seen
between 1.2N HNO_3 and 4.5N HNO_3 but practically no
difference in either position or absorbance is observed
between 4.5N HNO_3 and 9.6N HNO_3.

(4) The effect of aging is generally to increase
the absorbance over the entire range of 400 mμ to 540 mμ
(except for the 1.2N HNO_3 solution above 420 mμ) and to
shift the position of the maximum to lower values of wave-
length. Little effect of aging is observed for the 1.2N
HNO_3 solution, but a large effect of aging is seen in
the 4.5N HNO_3 and 9.6N HNO_3 solutions. In the latter
two cases, the spectra are seen to be changing so as to
more nearly approximate the spectra of the RuNO-nitrato
complexes solutions. The position of the maximum for the
4.5N HNO_3 solution has shifted to about 475 mμ, the
same as for the RuNO-nitrato complexes, and the position
of the maximum for the 9.6N HNO_3 solution has shifted
from about 500 mμ to about 485 mμ. The absorbance
maximum in the 1.2N HNO_3 solution appears to have shifted
from 485 mμ to about 475 mμ, but the value of the
absorbance at wavelengths greater than 470 mμ appears
to have decreased. However, the change in the spectrum
of the 1.2 N HNO_3 solution has been little, and its
interpretation must be somewhat limited.

The general conclusions to be reached are:
(1) that the RuNO-nitro complexes solutions are very slow
in attaining equilibrium (relative to the RuNO-nitrato
complexes solutions.) Equilibrium has not been reached
after seven weeks aging and possiblynnot after four
months aging; however, more spectra will have to be taken
as aging continues before the latter statement can be
shown to be true or not.

(2) From the appearance of the manner of the change in
the spectra with solution aging, it appears that the
RuNO-nitro complexes are slowly being transformed,
either wholly or in part, to the RuNO-nitrato complexes
and/or mixed RuNO-nitro-nitrato complexes. This conclusion
is consistent with the conclusion drawn from the extraction
studies on the RuNO-nitro and RuNO-nitrato complexes.

3.3.2 Effect of Ruthenium Concentration

In Section 3.2.2, the value of E_A^o for the aged (two
months) RuNO-nitro complexes was found to be dependent
upon the 1.2 power of the aqueous ruthenium concentration.
Although this effect is believed due to self-salting of

the RuNO-nitro complexes, a series of spectra
measurements was performed to determine if the spectra
changed as a function of aqueous ruthenium concentration.

The measurements were made on 1.2N HNO_3 solutions
of RuNO-nitro complexes. This solution was chosen
for two reasons:

(1) The spectra of the 1.2N HNO_3 solution changes
very little with solution age (see Figure 33).

(2) The value of 1.2N HNO_3 falls within the range
of acid concentrations that displayed the dependence of
the value of E_A^O on the 1.2 power of aqueous ruthenium
concentration (see Figure 28).

Figure 34 shows the spectra for 1.2N·HNO_3 solutions
with aqueous ruthenium concentrations of 0.22, 0.44,
1.09, and 2.17 gm/liter. The solution had been diluted
from the original stock solution concentration of 5.43
gm/liter with 1.2N HNO_3 after the stock solution had aged
for two months. The diluted solutions were aged for two
weeks before the extractions were made and the spectra
taken. The spectra appear to be very regular with
regard to one another and do not display any noticeable
variations other than the expected decrease of absorbance
with decreasing ruthenium concentration. In fact, the
value of the absorbance at the maximum (480mμ) varies
linearly with concentration as shown by Figure 34. Visual
inspection of Figure 34 shows that the linearity holds
true at the lowest wavelength measured (400 mμ), the
highest wavelength measured (540mμ), and at the position
of the minimum (440 mμ).

Although the regularity of the spectra cannot be
considered proof of a lack of effect of ruthenium
concentration on the amount and/or type of RuNO-nitro
complexes in solution, it would indicated that the
observed dependence of E_A^O on the 1.2 power of the
ruthenium concentration is probably due to the effect
of self-salting.
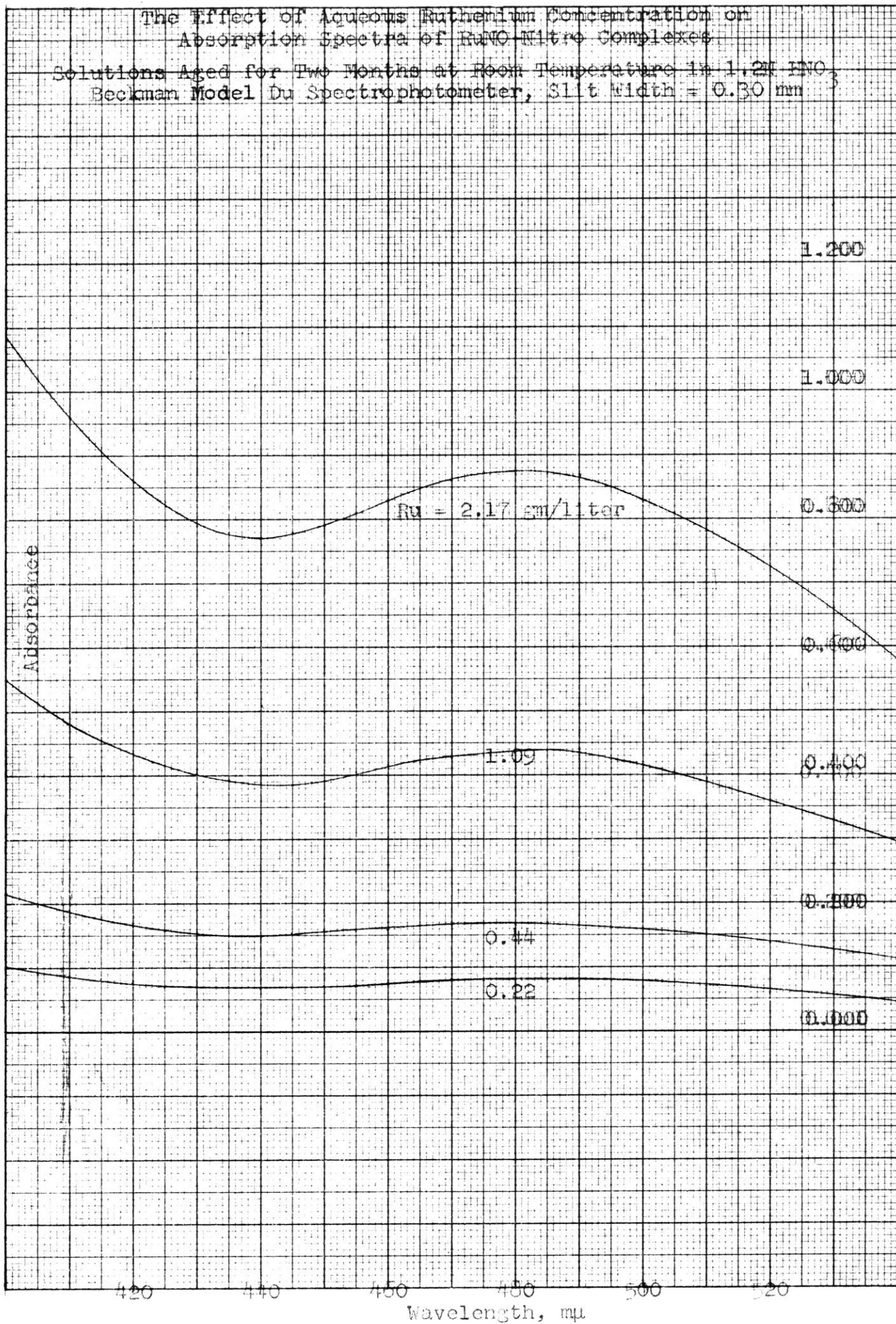
FIGURE 34

The Effect of Aqueous Ruthenium Concentration on Absorption Spectra of RuNO-Nitro Complexes

Solutions Aged for Two Months at Room Temperature in 1.2N HNO₃

Beckman Model Du Spectrophotometer, Slit Width = 0.30 mm

FIGURE 35

52

The Effect of Aqueous Ruthenium Concentration on Absorption Spectra of RuNO-Nitro Complexes

Solutions Aged for Two Months at Room Temperature in 1.2N HNO_3

Beckman Model Du Spectrophotometer, Slit Width = 0.30 mm
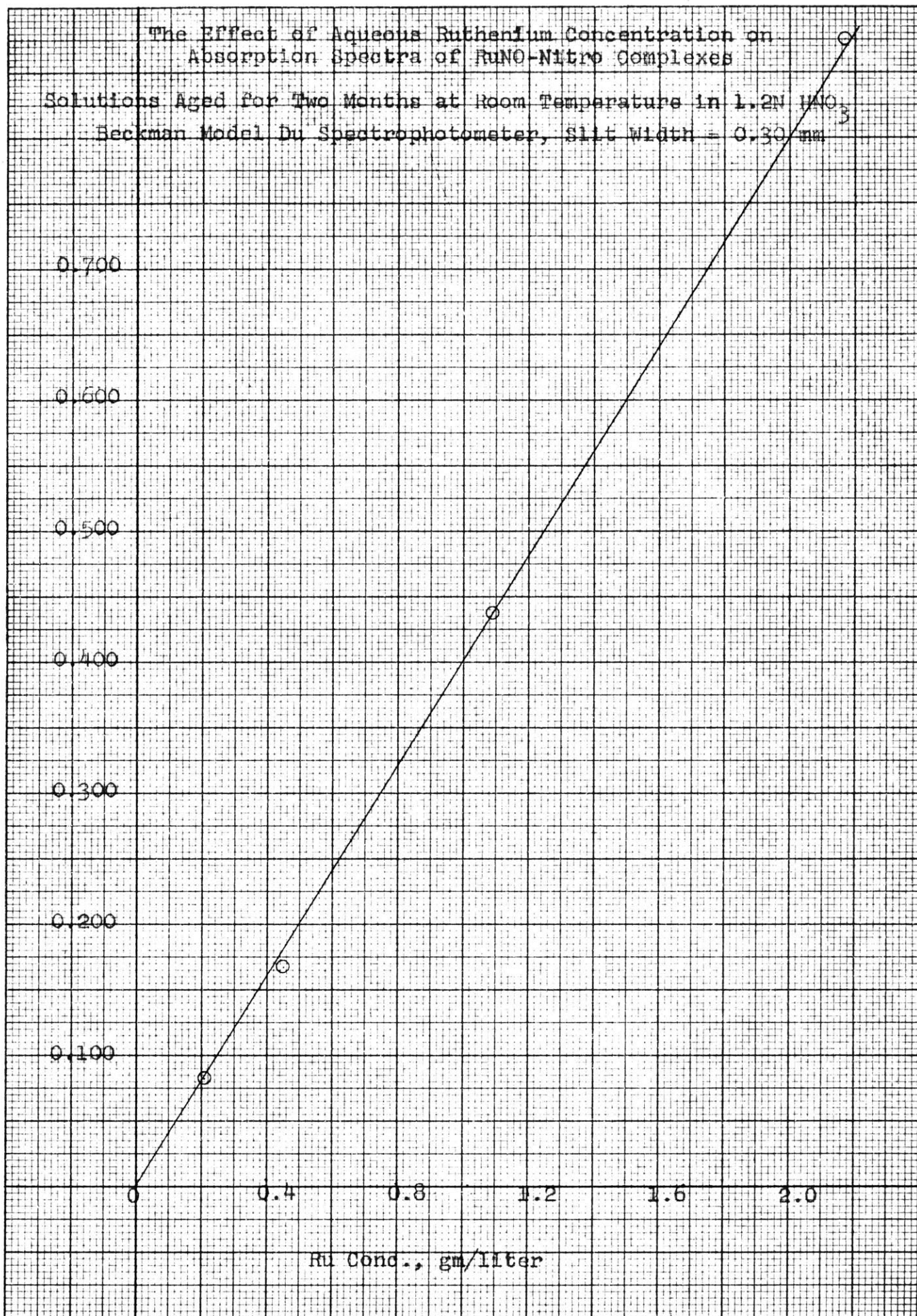
TABLE 3

Summary of Ruthenium Extraction Data

Sample No.	Type of Complex	Age of Soln.	Contact Time	Temp°C	Initial HNO_3	Final HNO_3	Final Total NO_3	Initial Ru,gm/l	TLA,M	Final Ru,gm/l	E_A^o
42	NO	F	2m	25	0.421	0.403	0.403	5.43	0.25	0.954	0.212
43	"	"	"	"	0.766	0.755	0.755	"	"	0.742	0.158
44	"	"	"	"	1.219	1.196	1.196	"	"	0.582	0.120
45	"	"	"	"	2.938	2.93	2.93	"	"	0.205	0.0382
46	"	"	"	"	4.51	4.48	4.48	"	"	0.075	0.0140
47	"	"	"	"	6.29	6.24	6.24	"	"	0.0276	0.0051
48	"	"	"	"	8.22	8.11	8.11	"	"	0.02	0.0037
49	"	"	"	"	9.60	9.56	9.56	"	"	0.02	0.0037
50	"	"	"	"	0.358	0.307	6.29	4.94	"	0.480	0.1076
51	"	"	"	"	1.006	0.947	6.20	"	"	0.240	0.0511
52	"	"	"	"	2.60	2.55	6.28	"	"	0.114	0.0236
53	"	"	"	"	4.31	4.26	6.53	"	"	0.048	0.0098
54	NA	F	2m	"	0.47	0.45	6.18	6.00	0.25	0.146	0.0249
55	"	"	"	"	1.27	1.21	6.13	"	"	0.0796	0.0134
56	"	"	"	"	3.10	3.05	6.12	"	"	0.0354	0.0060
57	"	"	"	"	5.05	4.98	6.28	"	"	0.0301	0.0050
58	"	"	"	"	0.52	0.49	0.49	6.45	"	0.0303	0.0047
59	"	"	"	"	0.89	0.87	0.87	"	"	0.0324	0.0050
60	"	"	"	"	1.32	1.31	1.31	"	"	0.0328	0.0051
61	"	"	"	"	3.10	3.07	3.07	"	"	0.0364	0.0057
62	"	"	"	"	4.91	4.92	4.92	"	"	0.0285	0.0044
63	"	"	"	"	6.85	6.86	6.86	"	"	0.0224	0.0035
64	"	"	"	"	8.74	8.84	8.84	"	"	0.0183	0.0028
65	"	"	"	"	10.08	10.19	10.19	"	"	0.018	0.0028
66	NO	A	"	"	0.42	0.41	0.41	5.43	"	0.487	0.0986
67	"	"	"	"	0.77	0.77	0.77	"	"	0.345	0.0679
68	"	"	"	"	1.22	1.21	1.21	"	"	0.217	0.0417
69	"	"	"	"	2.94	3.20	3.20	"	"	0.0944	0.0177
70	"	"	"	"	4.51	4.59	4.59	"	"	0.0472	0.0088

TABLE 3 (cont.)

Sample No.	Type of Complex	Age of Soln.	Contact Time	Temp°C	Aqueous Initial HNO_3	Final HNO_3	Final Total NO_3	Initial Ru,gm/l	TLA,M	Organic Final Ru,gm/l	E_A^o
71	NO	A	2m	25	6.29	6.42	6.42	"	"	0.0216	0.0040
72	"	"	"	"	8.22	8.16	8.16	5.43	0.25	0.0125	0.0023
73	"	"	"	"	9.60	9.81	9.81	"	"	0.0140	0.0026
74	"	"	"	"	0.36	0.31	6.29	4.94	"	0.345	0.0752
75	"	"	"	"	1.01	0.96	6.21	"	"	0.155	0.0324
76	"	"	"	"	2.60	2.59	6.32	"	"	0.0767	0.0160
77	"	"	"	"	4.31	4.38	6.65	"	"	0.0302	0.0061
78	"	24 hrs.	"	"	0.42	0.41	0.41	5.43	"	1.50	0.382
79	"	"	"	"	0.77	0.77	0.77	"	"	1.03	0.234
80	"	"	"	"	1.22	1.21	1.21	"	"	0.650	0.136
81	"	"	"	"	2.94	2.98	2.98	"	"	0.149	0.0282
82	"	"	"	"	4.51	4.34	4.34	"	"	0.0541	0.0101
83	"	"	"	"	6.29	5.98	5.98	"	"	0.0251	0.0041
84	"	"	"	"	8.22	8.21	8.21	"	"	0.0141	0.0026
85	"	"	"	"	9.60	9.74	9.74	"	"	0.0104	0.0019
86	"	"	"	"	0.42	0.41	0.99	"	"	1.23	0.293
87	"	"	"	"	0.41	0.36	2.94	"	"	1.19	0.281
88	"	"	"	"	0.38	0.33	4.91	"	"	1.33	0.324
89	"	"	"	"	0.36	0.26	6.24	4.94	"	1.62	0.488
90	"	"	"	"	1.16	1.13	2.91	5.43	"	0.515	0.105
91	"	"	"	"	1.07	0.95	4.73	"	"	0.449	0.0902
92	"	"	"	"	1.01	0.91	6.16	4.94	"	0.615	0.142
93	"	"	"	"	2.97	2.57	2.67	5.43	"	0.139	0.0263
94	"	"	"	"	2.76	2.77	4.87	"	"	0.123	0.0232
95	"	"	"	"	2.60	2.55	6.28	4.94	"	0.180	0.0378
96	"	"	"	"	4.60	4.65	5.15	5.43	"	0.045	0.0084
97	"	"	"	"	4.31	4.38	6.65	4.94	"	0.0406	0.0083
98	"	"	"	"	0.42	0.41	5.43	5.43	"	1.415	0.353
99	"	"	"	"	0.42	0.41	0.41	2.17	"	0.525	0.320
100	"	"	"	"	0.42	0.40	0.40	1.09	"	0.235	0.277
101	"	"	"	"	0.42	0.40	0.40	0.435	"	0.0831	0.236

TABLE 3 (cont.)

Sample No.	Type of Complex	Age of Soln.	Contact Time	Temp °C	Aqueous Initial HNO$_3$	Aqueous Final HNO$_3$	Aqueous Final Total NO$_3$	Initial Ru, gm/l	TLA, M	Organic Final Ru, gm/l	E$_A^o$
102	NO	A	24 Hrs.	26	0.42	0.41	0.41	0.217	0.25	0.0386	0.217
103	"	"	"	"	0.42	0.41	0.41	5.43	0.20	1.195	0.282
104	"	"	"	"	0.42	0.42	0.42	5.43	0.125	0.847	0.185
105	"	"	"	"	0.42	0.44	0.44	5.43	0.05	0.313	0.0612
106	"	"	"	"	1.22	1.21	1.21	5.43	0.25	0.631	0.127
107	"	"	"	"	1.22	1.21	1.21	2.17	"	0.212	0.108
108	"	"	"	"	1.22	1.20	1.20	1.09	"	0.105	0.107
109	"	"	"	"	1.22	1.19	1.19	0.435	"	0.0323	0.080
110	"	"	"	"	1.22	1.19	1.19	0.217	"	0.0154	0.076
111	NA	A	2m	"	0.47	0.44	6.17	6.00	"	0.154	0.0264
112	"	"	"	"	1.27	1.21	6.13	6.00	"	0.069	0.0116
113	"	"	"	"	3.10	3.02	6.09	6.00	"	0.040	0.0067
114	"	"	"	"	5.05	4.99	6.29	6.00	"	0.035	0.0059
115	"	"	24 Hrs.	"	3.10	3.04	3.04	6.45	"	0.364	0.0600
116	"	"	"	"	4.91	4.90	4.90	6.45	"	0.164	0.0261
117	"	"	"	"	3.09	3.03	4.94	6.45	"	0.337	0.0552
118	"	"	"	"	3.10	3.02	6.09	6.00	"	0.307	0.0540
119	"	"	"	"	5.05	5.01	6.31	6.00	"	0.117	0.0200
120	"	"	"	"	1.32	1.31	1.31	6.45	"	0.502	0.0844
121	"	"	"	"	1.27	1.21	3.10	6.45	"	0.848	0.151
122	"	"	"	"	1.29	1.18	5.07	6.45	"	0.969	0.177
123	"	"	"	"	1.27	1.16	6.08	6.00	"	0.987	0.197
124	"	"	"	"	0.52	0.49	0.49	6.45	"	0.266	0.043
125	"	"	"	"	0.50	0.48	1.20	6.45	"	0.709	0.124
126	"	"	"	"	0.48	0.40	3.20	6.45	"	1.70	0.358
127	"	"	"	"	0.46	0.35	5.26	6.45	"	2.51	0.637
128	"	"	"	"	0.47	0.37	6.10	6.00	"	2.38	0.657
129	"	"	"	"	1.32	1.31	1.31	6.45	0.20	0.430	0.0714
130	"	"	"	"	1.32	1.32	1.32	6.45	0.125	0.265	0.0428
131	"	"	"	"	1.32	1.32	1.32	6.45	0.05	0.074	0.0116
132	"	"	"	"	1.32	1.31	1.31	6.45	C.10	0.197	0.0315
133	"	"	"	"	1.32	1.33	1.33	"	0.08	0.143	0.0227
134	"	"	"	"	1.32	1.32	1.32	"	0.06	0.095	0.0150
135	"	"	2m	"	0.52	0.49	0.49	"	0.25	0.009	0.0014
136	"	"	"	"	0.89	0.82	0.82	"	"	0.019	0.0030
137	"	"	"	"	1.32	1.31	1.31	"	"	0.025	0.0039

TABLE 3 (Cont.)

| Sample No. | Type of Complex | Age of Soln. | Contact Time | Temp.$^{\circ}$C | Aqueous | | | Initial Ru,gm/l | Organic | | |
					Initial HNO_3	Final HNO_3	Final Total NO_3		TLA,M	Final Ru,gm/l	E°_A
138	NA	A	2m	26	3.10	3.02	3.02	6.45	0.25	0.049	0.0039
139	"	"	"	"	4.91	4.82	4.82	"	"	0.045	0.0070
140	"	"	"	"	6.85	6.71	6.71	"	"	0.035	0.0055

4.0 Uranium Extraction

Mr. David Sabo worked on the project as a Research Assistant for two months in the Summer, 1961, to investigate the effect of temperperature, sulfate ion, and fluoride ion on the extraction of uranium.

4.1 Effect of Temperature

A brief study of the effect of temperature upon uranium extraction consisted of five parallel samples, three at $25°C$ and two at $50°C$. The results are listed in Table 4 and plotted in Figure 36.

TABLE 4

Uranium Temperature Study

Aqueous Phase = 4.88 gm/liter of uranium as uranyl nitrate in 5.8N HNO_3 solution.
Organic Phase = 0.086M TAL in toluene
Contact time = 24 hours

Sample No.	Temperature, °C	Final Ag. HNO_3,N	U,gm/l	Final Org. U,gm/l	E_A^o
1	25	--	3.72	0.953	0.256
2	25	5.60	3.88	0.883	0.227
3	25	5.76	3.84	0.946	0.247
4	50	5.73	4.25	0.661	0.163
5	50	5.75	4.00	0.643	0.163

It was found that a 33% decrease in the value of the distribution ratio resulted when the temperature was increased from $25°C$ to $50°C$. This corresponds to an activation energy of $\Delta H = -3.10 \frac{Kcal}{mole}$.

4.2 Effect of Sulfate

In order to study the effect of sulfate on uranium extraction in nitrate systems, solutions of uranyl nitrate were made such that the nitric acid and total nitrate concentrations remained at 2M, while the sulfate concentration (as sodium sulfate) varied in steps of 0.5M, 1.0M, and 2.0M. The data are listed in Table 5 and shown plotted in Figure 37.
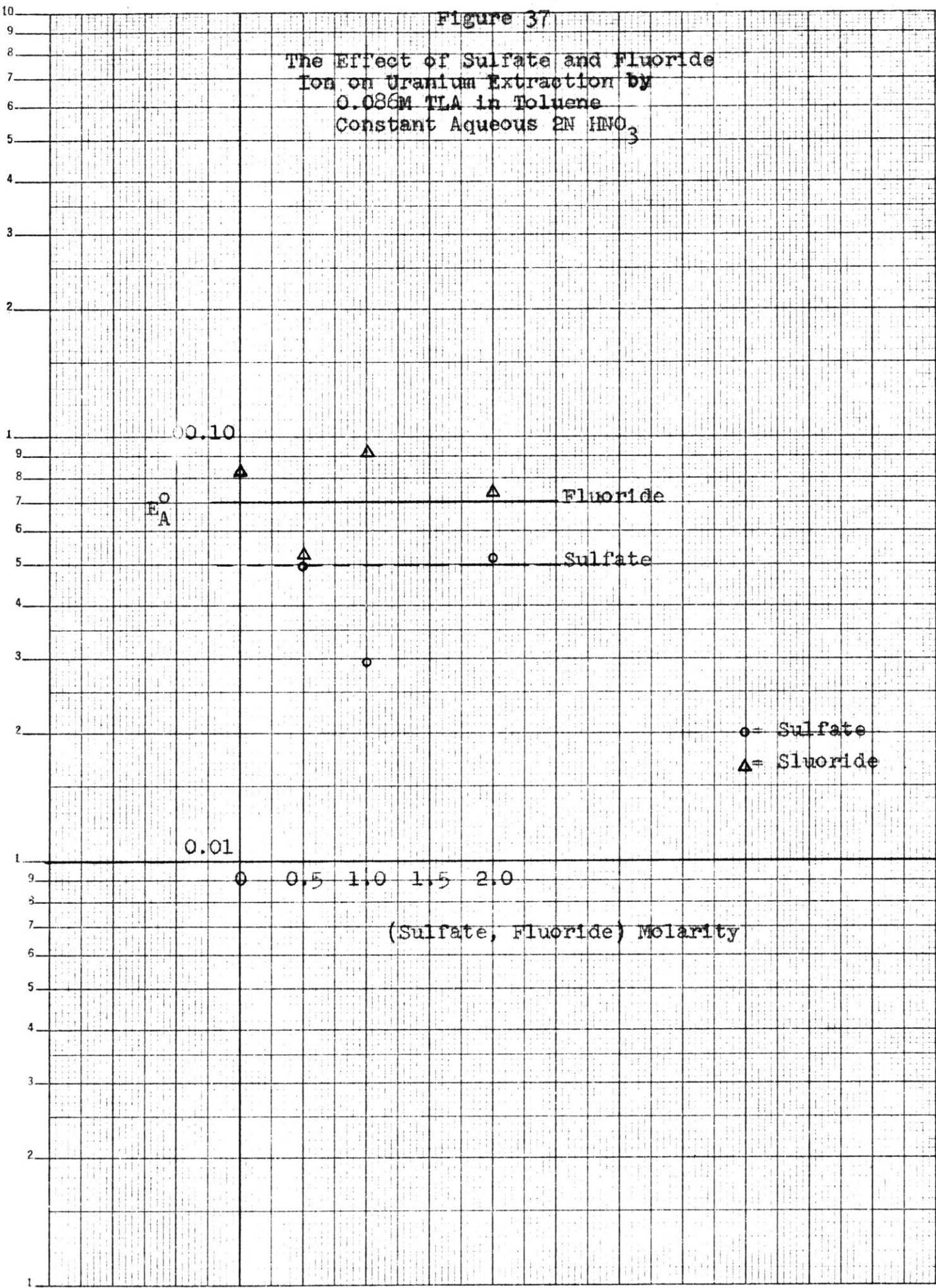
Figure 36

The Effect of Temperature on the Extraction
of Uranium by 0.086M TLA in Toluene
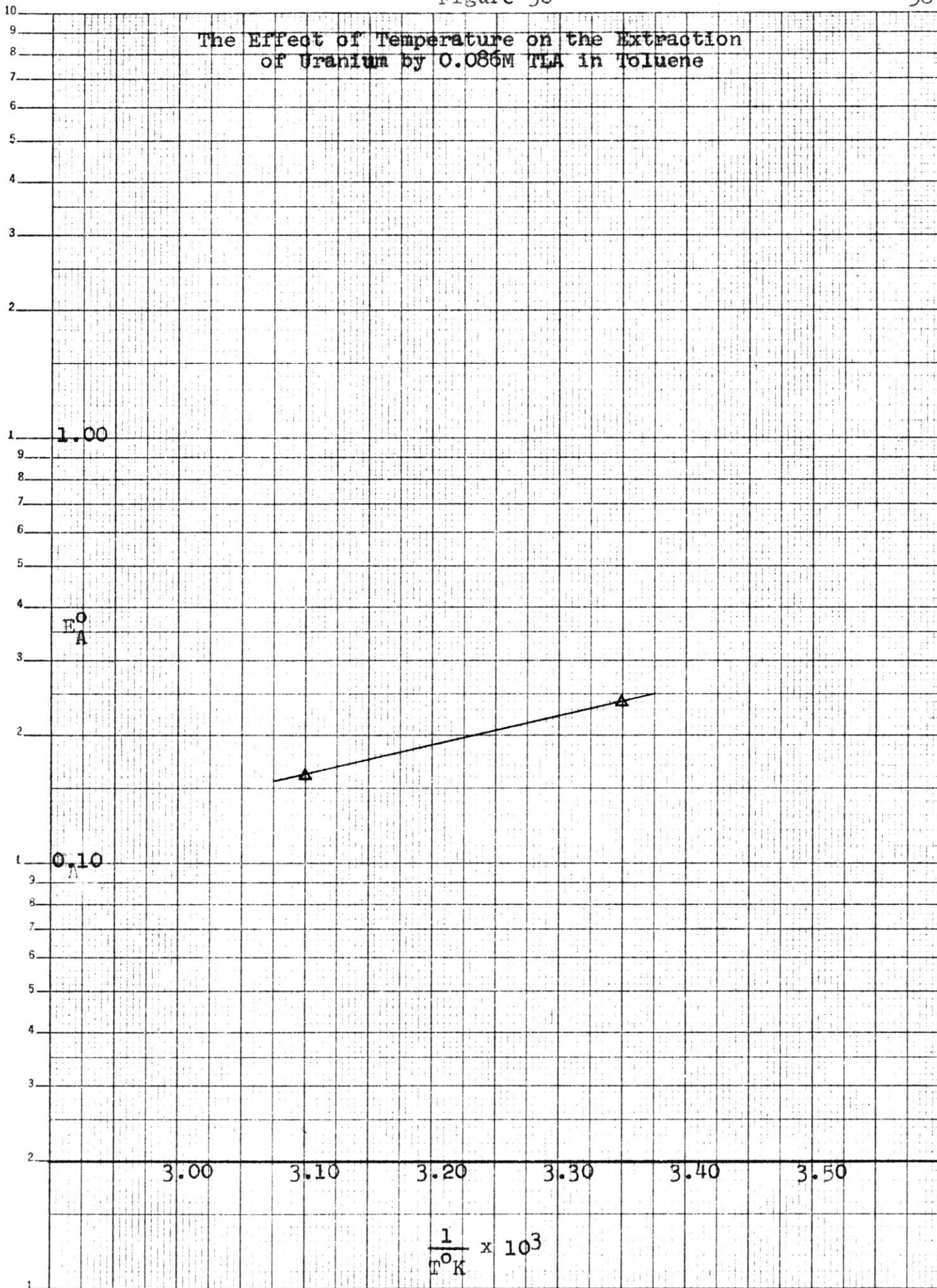
E_A^O

$\dfrac{1}{T\,^{o}K} \times 10^3$

Figure 37

The Effect of Sulfate and Fluoride Ion on Uranium Extraction by 0.086M TLA in Toluene Constant Aqueous 2N HNO₃

TABLE 5

Uranium - Sulfate Study

Aqueous Phase: HNO_3 = total nitrate = 2M

Contact time = 24 hours at $25^\circ C$

Organic Phase = 0.086 M TLA in toluene

Sulfate,M	U aq.,i	gm/liter U aq., f	U org, f	E_A^o
0.0	4.89	4.47	0.376	0.0841
0.5	4.92	4.63	0.232	0.0501
1.0	4.74	4.60	0.136	0.0296
2.0	4.67	4.44	0.232	0.0523

The addition of sulfate is seen not to affect uranium extraction by any order of magnitude, but may possibly affect it by a factor of two or three.

4.3 Effect of Fluoride

Parallel solutions of fluoride, similar to the sulfate solutions, were prepared, using ammonium fluoride as the source of fluoride ion. The data are listed in Table 6 and plotted in Figure 37.

TABLE 6

Uranium - Fluoride Study

Aqueous Phase: HNO_3 = total nitrate = 2M
Organic Phase: 0.086M TLA in toluene
Contact time : 24 hours at $25^\circ C$

Fluoride,M	Uaq.,i,gm/l	Uaq.,f	Uorg,f	E_A^o
0.0	4.89	4.47	0.376	0.0841
0.5	4.43	4.19	0.221	0.0530
1.0	4.63	4.24	0.385	0.0908
2.0	4.52	4.21	0.312	0.0741

Similar to the sulfate addition, the addition of fluoride does not affect uranium extraction by an order of magnitude, but may possibly affect it by a factor of two or three. In the sulfate and fluoride cases, a more careful and detailed study would be required to determine their exact effect on uranium extraction.

5.0 References

(1) Mason, E.A., and Skavdahl, R.E., "Equilibrium Extraction Characteristics of Alkyl Amines and Nuclear Fuels Metals in Nitrate Systems," Progress Report VII, M.I.T. Nuclear Engineering Department, November 1, 1960. Also released as TID-11196.

(2) Mason, E.A., and Skavdahl, R.E., "Equilibrium Extraction Characteristics of Alkyl Amines and Nuclear Fuels Metals in Nitrate Systems," Progress Report VIII, M.I.T. Nuclear Engineering Department, May 1, 1961. Also released as TID-12848.

(3) Mason, E.A., and Skavdahl, R.E., "Equilibrium Extraction Characteristics of Alkyl Amines and Nuclear Fuels Metals in Nitrate Systems," Progress Report IX, M.I.T. Nuclear Engineering Department, August 1, 1961.

(4) Fletcher, J.M., et al, "Nitrosylruthenium Nitrato Complexes In Aqueous Nitric Acid," Journal of Inorganic and Nuclear Chemistry, Vol. 12, pp. 154-73. (1959)

(5) Brown, P.G.M. Fletcher, J.M. Wain, A.G., AERE-C/R-2260 (1957)

(6) Brown, P.G.M., "Nitro Complexes of Nitrosylruthenium," Journal of Inorganic and Nuclear Chemistry, Vol. 13, pp. 73-83 (1960).

RFS/2/20/62