MITNE-31

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

PROGRESS REPORT XI

April 1, — December 31, 1962

BY
EDWARD A. MASON
TAKASHI WATANABE

DEPARTMENT OF NUCLEAR ENGINEERING
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS

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of
Alkyl Amines and Nuclear Fuels Metals
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Nitrate Systems

Progress Report for the Period
April 1 - December 31, 1962

Progress Report XI

by
Edward A. Mason
Takashi Watanabe

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1.0 Summary

1.1 Niobium

During this period, April 1 through December, 1962, the following variables were studied in connection with the investigation of the extraction of niobium from nitric acid solution by alkyl amines:

(1) The distribution ratio of niobium as a function of nitric acid concentration for Primene JMT in toluene.

(2) The distribution ratio of niobium as function of amine concentration for Primene JMT in toluene.

(3) The distribution ratio as function of contact time for Primene JMT in toluene.

(4) The effect of diluent on niobium extraction by Primene JMT.

It was found that:

(1) The distribution ratio of niobium is greater than 10 for high acid and amine concentrations.

(2) There is a very strong dependence of distribution ratio on nitric acid concentration in the range of 8-12<u>N</u>.

(3) There is a marked dependence of distribution ratio on contact time.

(4) There is no significant effect of aqueous aging.

(5) The effect of different diluents is small.

1.2 Ruthenium

The previous work on the extraction of nitrato complexes of nitrosylruthenium by the tertiary amine, TLA, (1) was extended to include studies with the primary amine, Primene JMT, and the quaternary amine, Aliquat Q-336, (2). At low concentrations of HNO_3 (2N) the order of decreasing ruthenium extraction was found to be Q-336, TLA, and JMT. At high HNO_3 concentration (9N) Primene JMT had the highest ruthenium extractability.

Rapid dilution experiments were carried out with TLA and Q-336. The results plus those of the earlier TLA studies (1) were analyzed using an IBM 7090 to determine the number and aqueous phase concentrations of extractable species of ruthenium and the amine partition coefficients for thsse species. In accord with the earlier work (1), two extractable species were found. The mole fractions found in the TLA and (Q-336) experiments agreed (as predicted by the assumed model) and were found to increase with increasing HNO_3 concentration. The partition coefficients of Q-336 were found to be about an order of magnitude greater than those of the tertiary amine.

1.3 Effect of High U Loading on Zr and Ru Extraction by TLA

Limited studies in the effect of partial uranium saturation of TLA on the extraction of zirconium and nitrosylruthenium nitrato complexes were carried out at 25°C in 7N and 9N HNO_3 using 0.3M TLA in toluene (3). There was considerable scatter in the limited results obtained which can be represented by

$$E_A^o(\text{metal}) = Ae^{-0.020U} \pm 40\%$$

Where U = organic phase uranium concentration (gm/l) and the constant A varies with the metal specie and nitric acid concentration.

2.0 Niobium Studies

2.1 Objective

The objective of the work with niobium for this period was to establish a procedure which would yield reproducible results for the extraction of niobium into Primene JMT, primary amine with a highly branched chain mixture of 18-22 carbon atoms each. During the investigation of the extraction behavior, the distribution ratio was found to be time dependent, and this was investigated further.

2.2 Procedure

The experimental procedure adopted is presented in detail in Appendix 5.1. Here, only the main features of the procedure will be discussed.

Niobium-95 was obtained in form of oxalate complex in 5% oxalic acid solution for use as a tracer. A stock solution of natural niobium in oxalate complex form was obtained from potassium hexaniobate $(K_8Nb_6O_{19} \cdot 16H_2O)$ by dissolution of the hexaniobate in water, followed by the precipitation of niobic acid and subsequent dissolution of the precipitate by oxalic acid. Before dilution to the desired concentration, the natural niobium stock solution was analyzed by a gravimetric method (see Appendix). The stock natural niobium solution of 10^{-7}M was used to adjust the total concentration of niobium in each run, while the tracer niobium concentration was kept at less than 1% of the natural niobium concentration. The mixture of natural and tracer niobium oxalates was converted into nitrate complexes by evaporation with hydrogen peroxide and nitric acid to a few milliliters under an infrared lamp. Then the solution was diluted to the required acid concentration and heated for 1.5 hr at 100°C. The organic phase, prior to contact with the aqueous phase, was contacted with nitric acid of a concentration slightly higher than the aqueous phase to be used in actual run, to minimize the change in acid conditions during the run. The two phases (i.e. the aqueous phase containing niobium and the precontacted organic phase) were shaken together in a constant temperature bath at 25°C for a desired contact time. Then the mixture was centrifuged to separate the phases. Samples of each phase were counted directly for the γ activity using a sodium iodide scintillation counter. (Radiation Instrument Development Laboratory Model 10-2) Each phase was titrated for acid concentration. A typical titration curve for organic phase is presented in Appendix Section 5.14.

2.3 Results

2.3.1 Distribution Ratio

Data showing the effect of HNO_3 concentration on the niobium distribution ratios using Primene JMT in toluene and Amsco are presented in Figures 2.1 - 2.6. The distribution ratios for 24 hr. contact at 25°C are plotted versus final aqueous acid concentration on logarithmic coordinates. The use of the 24 hour values for the distribution ratios will be discussed later.

The main features of Fig. 1-6 are:

(a) The high value of the distribution ratio, which is about 10 for high acid concentration (12N) and high amine concentration (0.3M.)

(b) The very strong dependence of distribution ratio on acid concentration.

(c) The nearly linear relationship between log of distribution ratio and the log of acid concentration at acid strength of 8-12N.

(d) The relatively weak dependence of distribution ratio on the acid concentration at acid concentrations of 2-4N.

(e) Slightly lower distribution ratios were obtained with toluene as diluent than with Amsco, at low acid concentrations, and higher distribution ratios were obtained with toluene at the high acid concentration.

(f) Fig. 2.7 and 2.8 are plots of logarithm of distribution ratio versus logarithm of Primene JMT concentration for various aqueous phase acid concentrations. The experimental uncertainty due to the very sharp dependence on acid concentration accounts for the large uncertainties for 8-12N. The uncertainty at 2N was probably due to the presence of large percentage of inextractable polymeric species. The presence of polymeric species will be discussed in the following section.

2.3.2 Equilibrium Distribution Ratio

Early in the investigation extensive runs were made to determine the time required for the contact of organic and aqueous phase to reach an equilibrium value of the distribution ratio. Results of these runs are presented in Fig. 2.9. As can be seen, the distribution ratio has not reached constant value after 460 hours for 0.06 M Primene JMT contacted with 8N nitric acid.

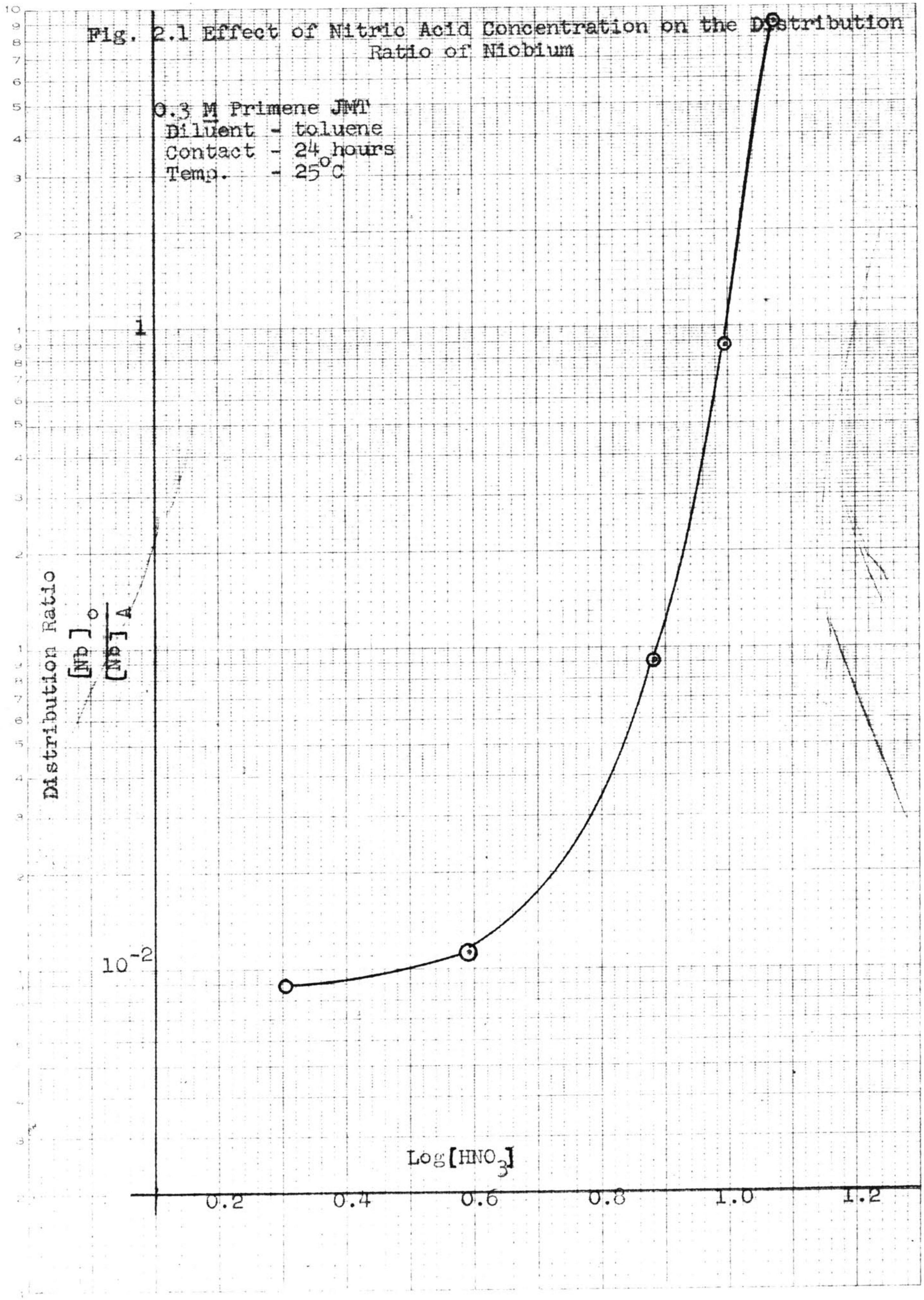


Fig. 2.1 Effect of Nitric Acid Concentration on the Distribution Ratio of Niobium

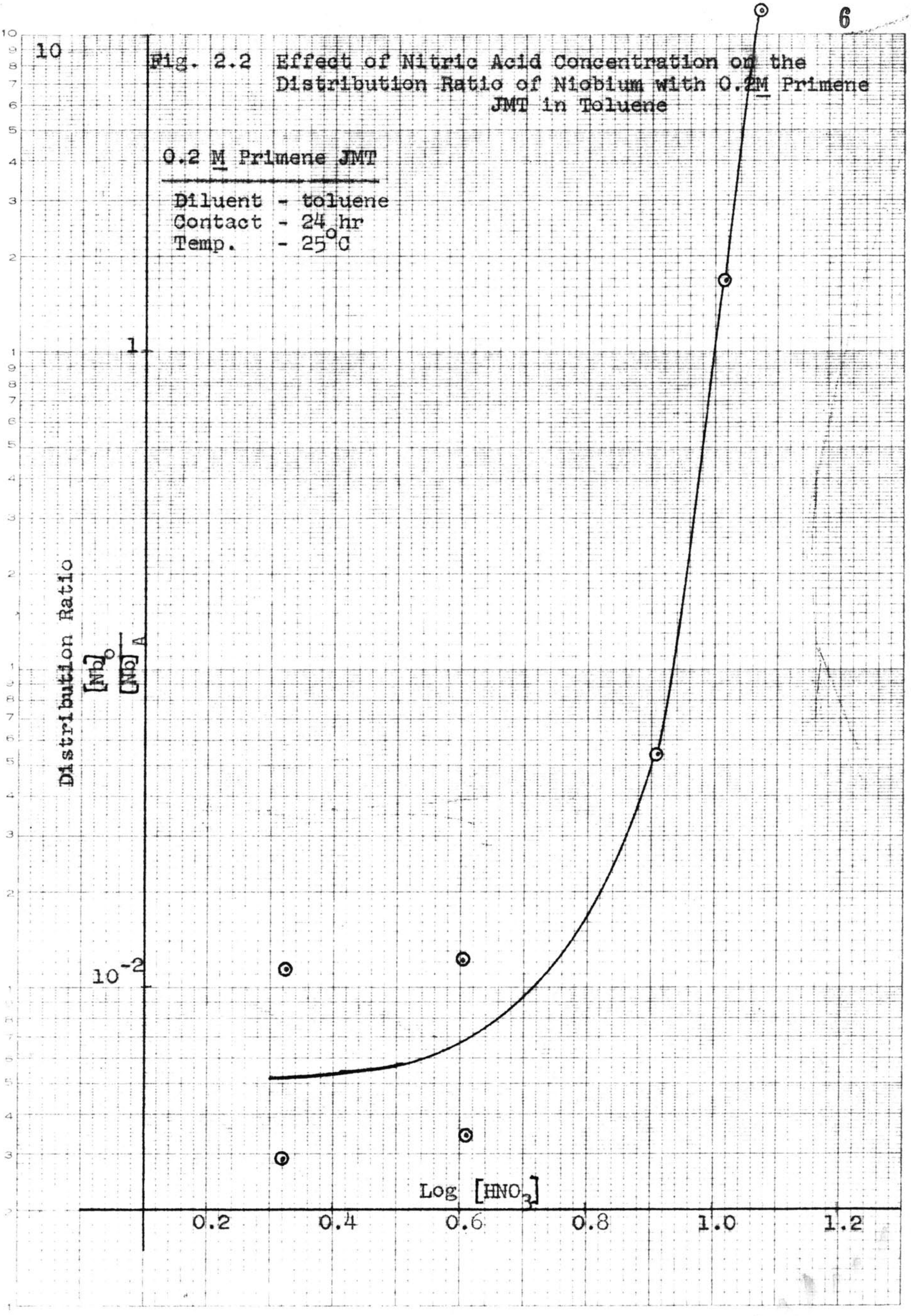


Fig. 2.2 Effect of Nitric Acid Concentration on the Distribution Ratio of Niobium with 0.2$\underline{M}$ Primene JMT in Toluene

0.2 $\underline{M}$ Primene JMT

Diluent - toluene
Contact - 24 hr
Temp. - 25°C

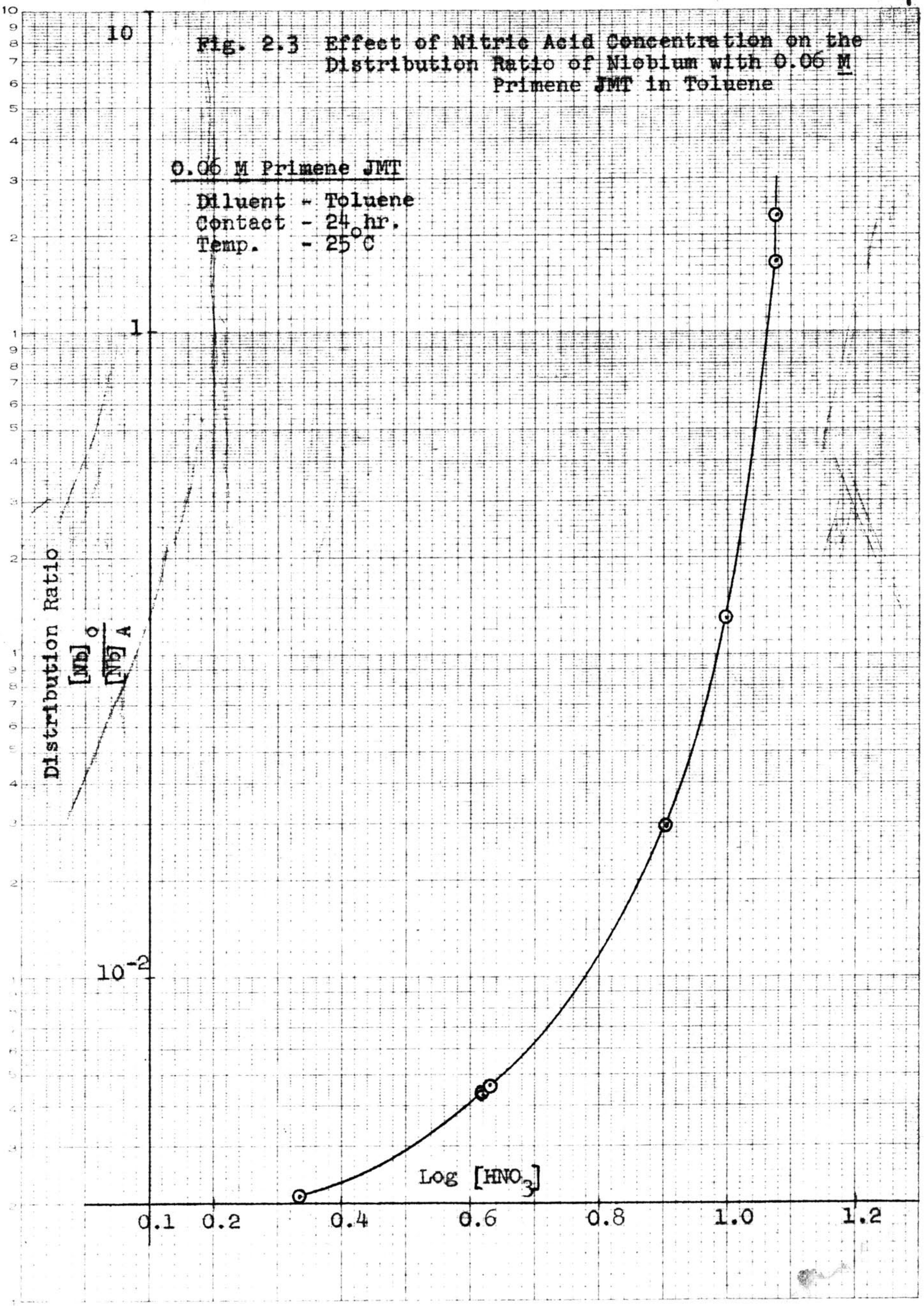


Fig. 2.3 Effect of Nitric Acid Concentration on the Distribution Ratio of Niobium with 0.06 M Primene JMT in Toluene

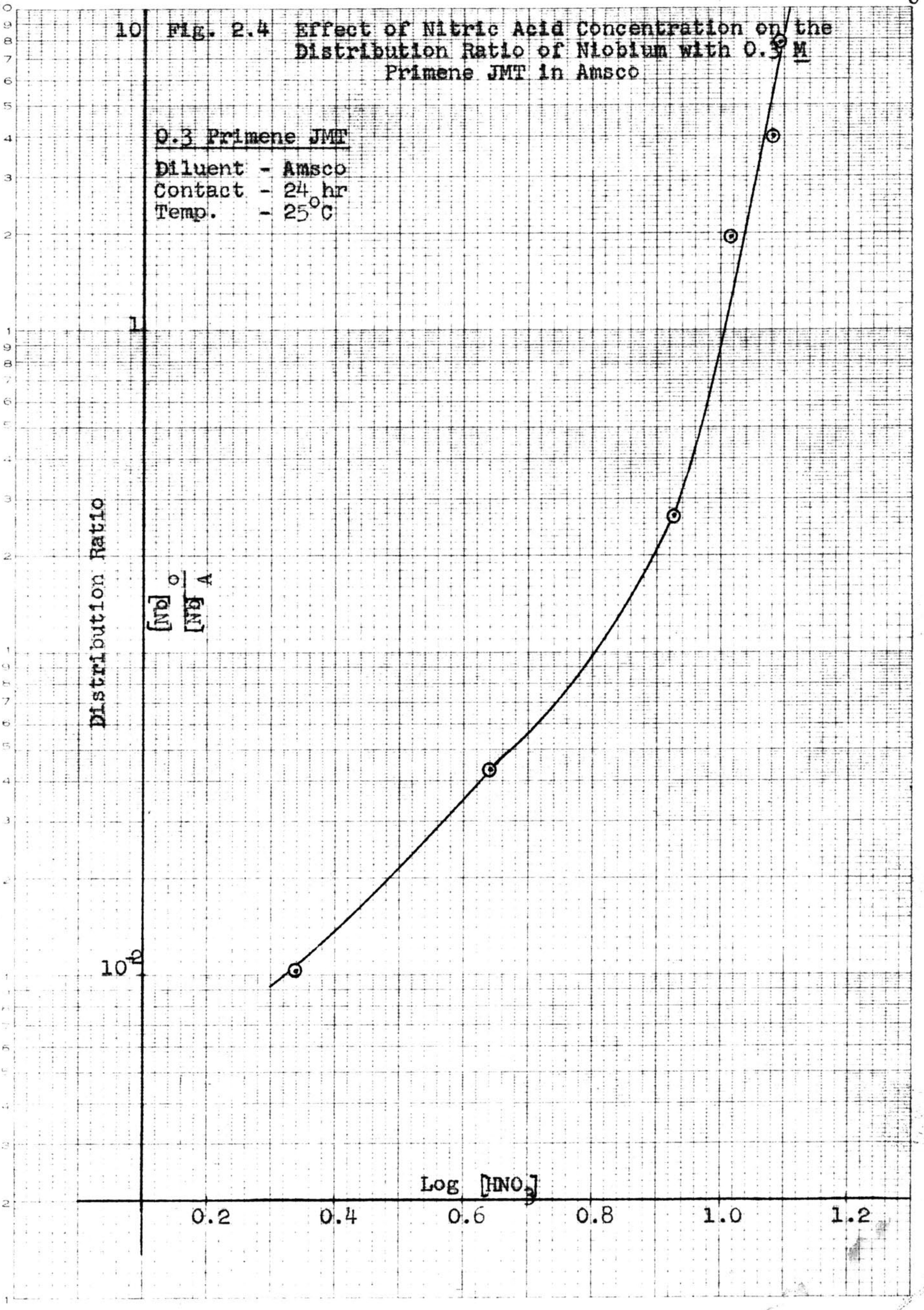


Fig. 2.4 Effect of Nitric Acid Concentration on the Distribution Ratio of Niobium with 0.3 M Primene JMT in Amsco

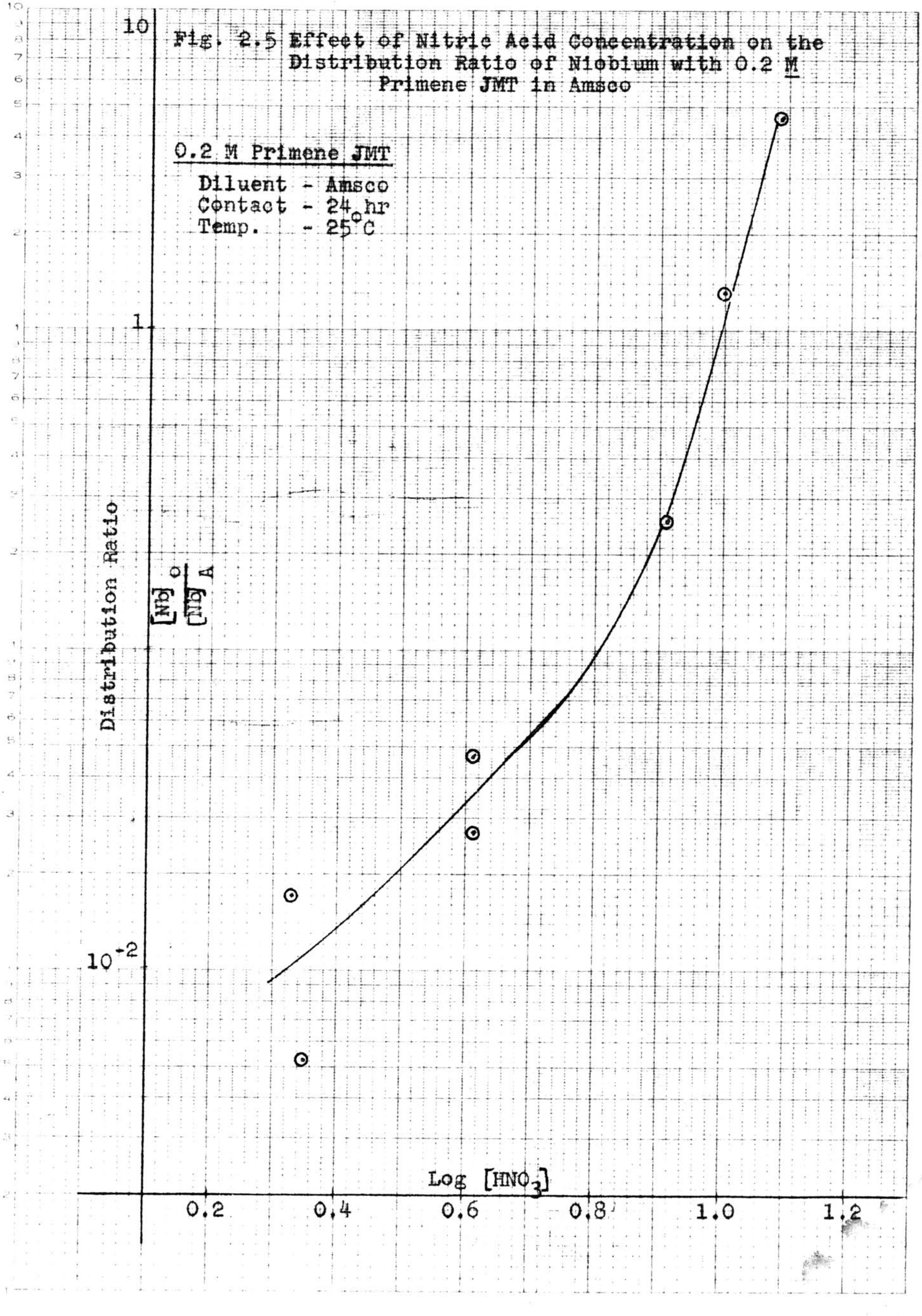


Fig. 2.5 Effect of Nitric Acid Concentration on the Distribution Ratio of Niobium with 0.2 M Primene JMT in Amsco

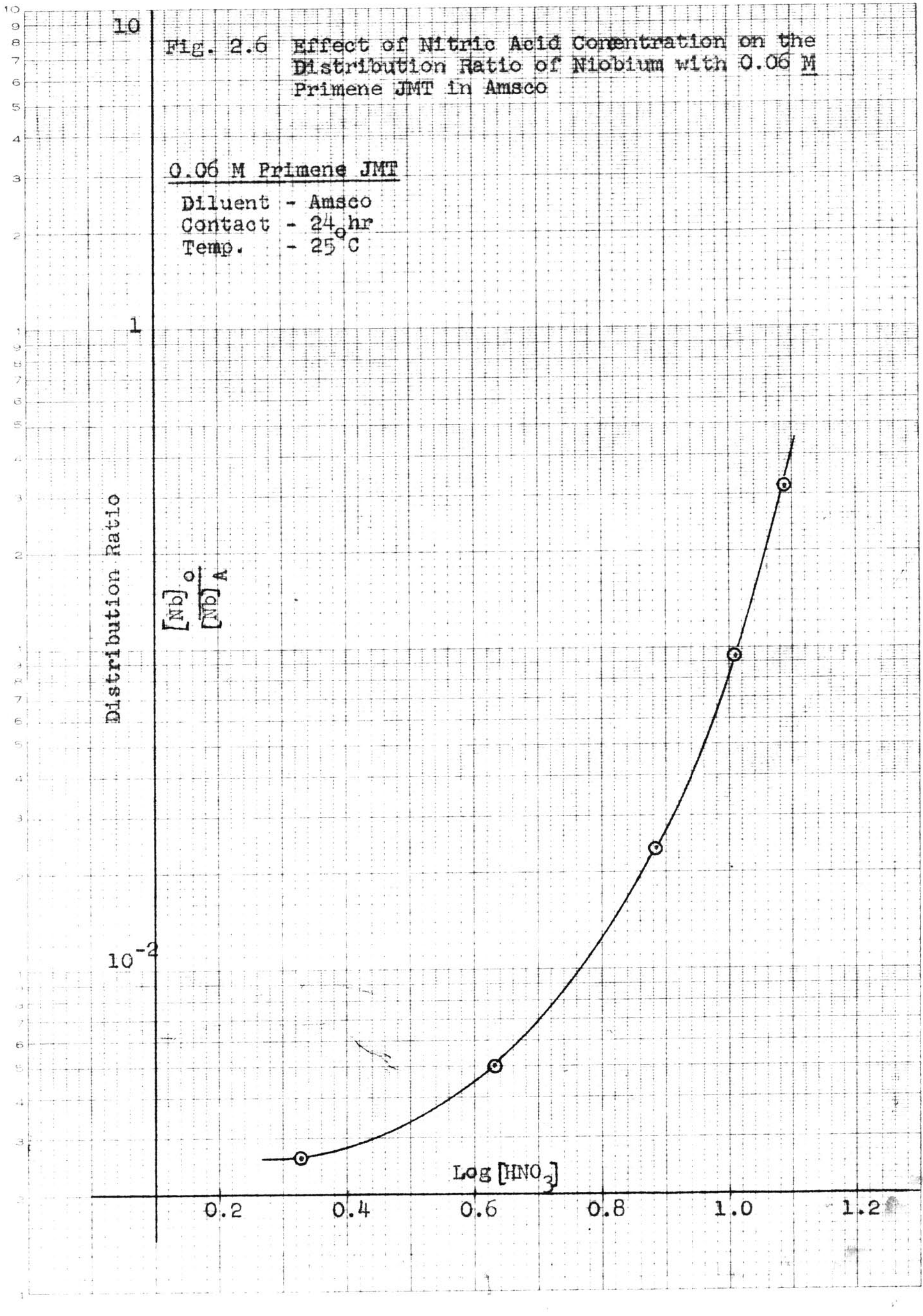


Fig. 2.6 Effect of Nitric Acid Concentration on the Distribution Ratio of Niobium with 0.06 M Primene JMT in Amsco

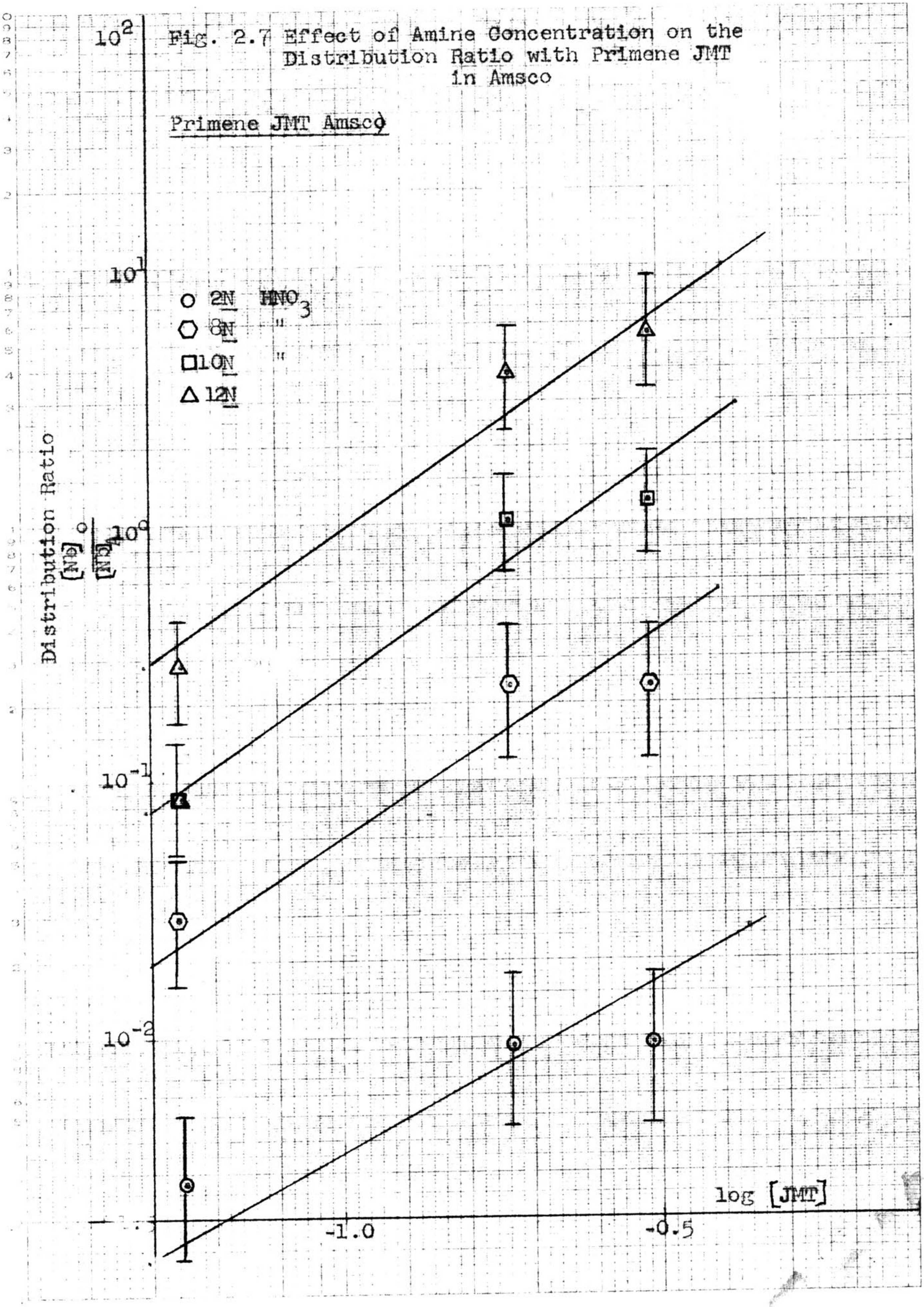


Fig. 2.7 Effect of Amine Concentration on the Distribution Ratio with Primene JMT in Amsco

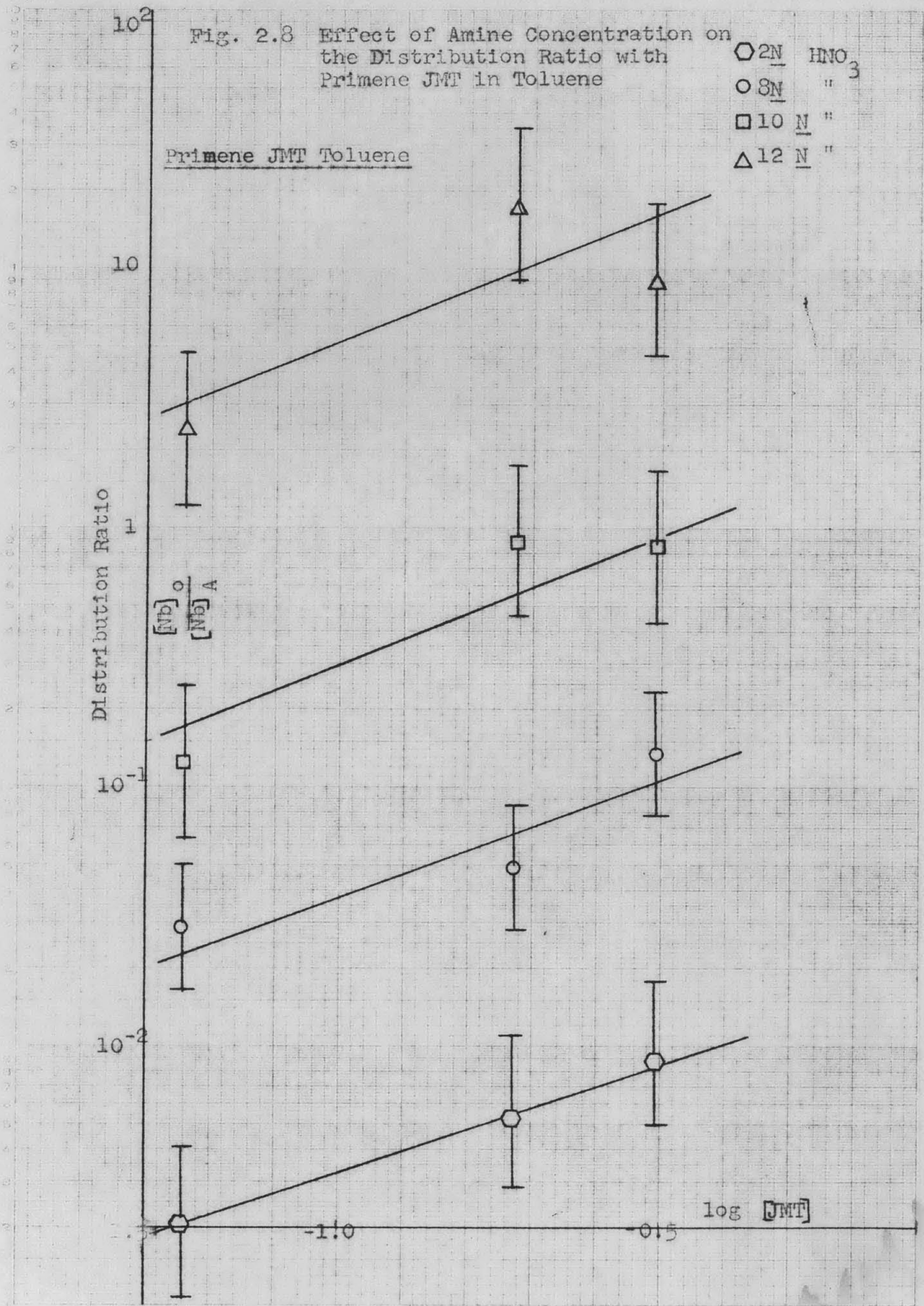


Fig. 2.8 Effect of Amine Concentration on the Distribution Ratio with Primene JMT in Toluene

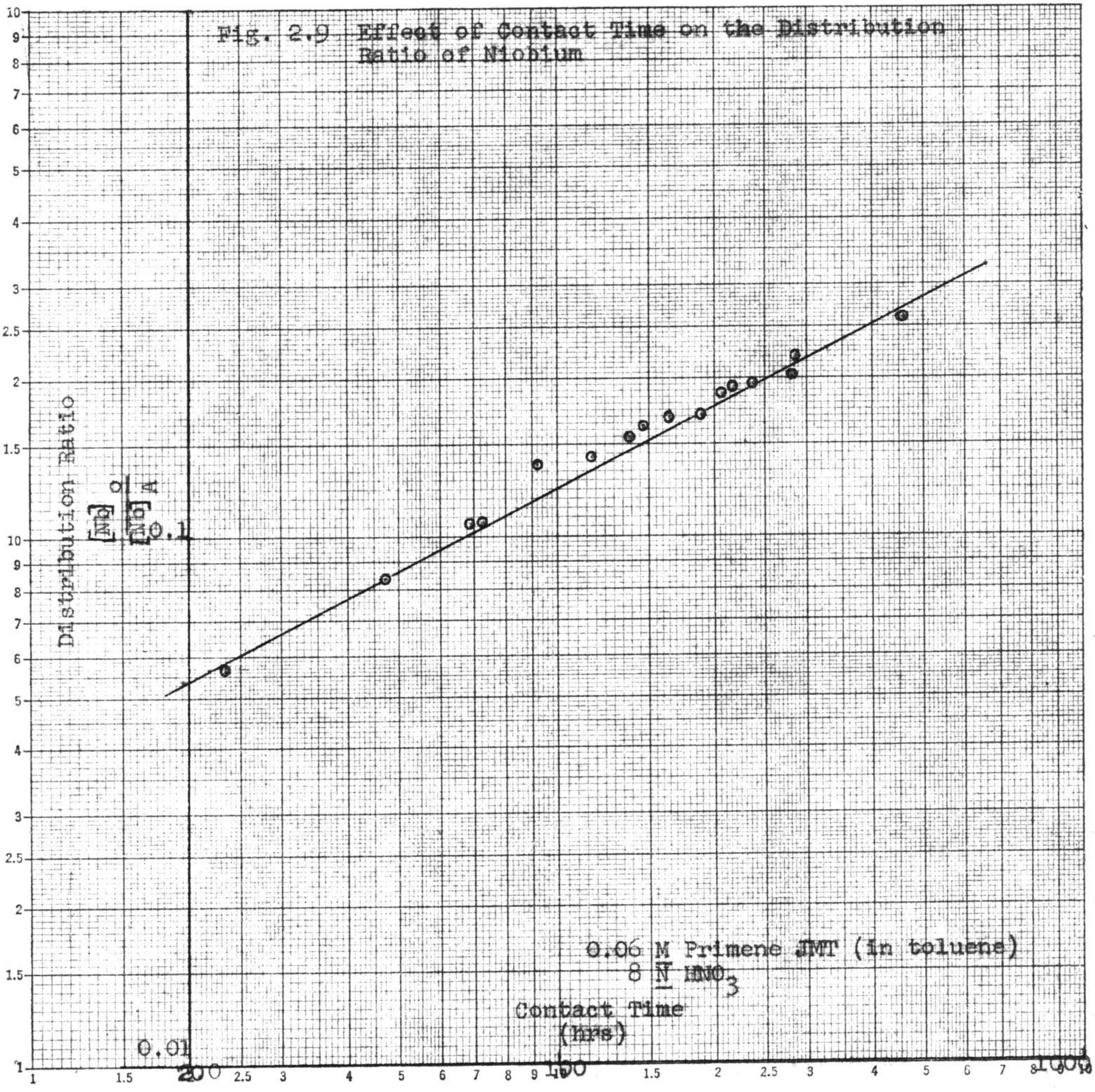


Fig. 2.9 Effect of Contact Time on the Distribution Ratio of Niobium

There are several possible explanations for the phenomena observed in Fig. 2.9. One possibility, the simplest one, is a lack of efficient contact between aqueous and the organic phases, but considering the long contact times used this appears an unlikely explanation. Another possibility is slow diffusion of the extractable complexes of niobium. This again was not considered a likely explanation in view of the long contact times and since cerium studied previously on this project has not shown such behaviors (4). Another possibility is the presence of an inextractable polymeric form of niobium which is convertible to the extractable form. There are two possibilities under this category. One is the possibility that the inextractable form is in unfavorable equilibrium with respect to extractable form of niobium and the rate at which equilibrium is achieved is slow. The other is that the equilibrium favors the inextractable species, but again with a slow rate of exchange between species. To separate these two possibilities, runs were carried out using aged aqueous solutions. The aqueous phase, after preparation by the standard method, was stored for various lengths of time before contact with the organic phase. The results are presented in Fig. 2.10. Up to 77 hours of aqueous phase aging, no significant increase in extraction was noticed between aged and unaged solutions. Thus the increasing distribution ratio observed with increasing contact time in Fig. 2.9 does not appear to be due to a slow conversion from inextractable to extractable species, with equilibrium highly favoring the extractable species. An explanation for Fig. 2.9 is an equilibrium in which the extractable specie is not favored coupled with a slow rate of conversion from specie to specie. If the inextractable species are in equilibrium with the extractable nitrate complexes of niobium, continuous extraction of extractable species into organic phase could gradually cause more and more niobium to be converted from inextractable to extractable species. To determine the presence of inextractable species, several attempts were made early in the investigation to analyze for the percentage of inextractable species present using the Martin technique (5). This technique consists of a plot of organic phase concentration versus aqueous phase concentration of niobium for various volume ratios of organic to aqueous. For extractable species in rapid equilibrium a straight line passing through the origin results. The presence of inextractable species in slow equilibrium shifts the intercept of the straight line on the aqueous phase concentration axis to a point proportional to the quantity of inextractable species present. The early experiments made using this method to determine the presence of the inextractable species were failures because, at the time, the very sharp dependence of the distribution ratio on the acid concentration was not taken into account. These experiments are to be repeated shortly.

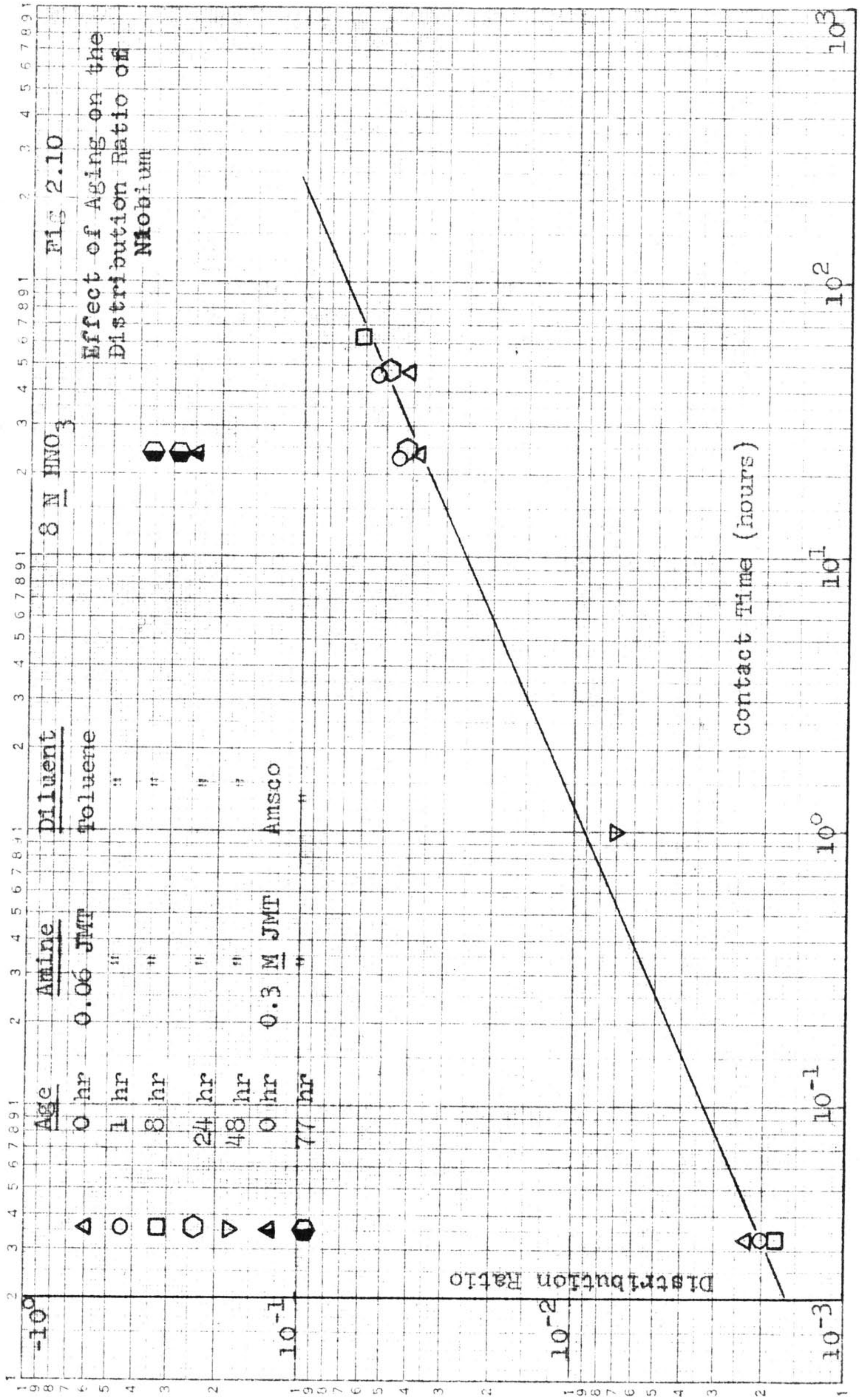


Fig 2.10 Effect of Aging on the Distribution Ratio of Niobium

In a study of Nb-HNO_3-TBP system, Hardy and Scargill (6) at Harwell made use of the Martin technique to determine the percentage of niobium present as inextractable species. Their results are reproduced on Figure 2.11. Their data were for inextractable species present after about 5 minutes of contact. Since the details of the procedure used at Harwell and the procedure used on this project is slightly different, no attempt was made to use the Harwell data quantitatively for the analysis of our results. The presence of a large quantity of inextractable, polymeric species at 2-4N indicated by the data from Harwell is probably responsible for large uncertainty in our data at 2-4N acid concentration. Conversely presence of only small quantities of niobium in inextractable polymeric form at 8-12N probably accounts for the better reproducibility of our data at these acid concentrations.

2.4 Program of Investigation for the Next Period

(a) Determination of the contact time required to have the extractable species reach equilibrium.

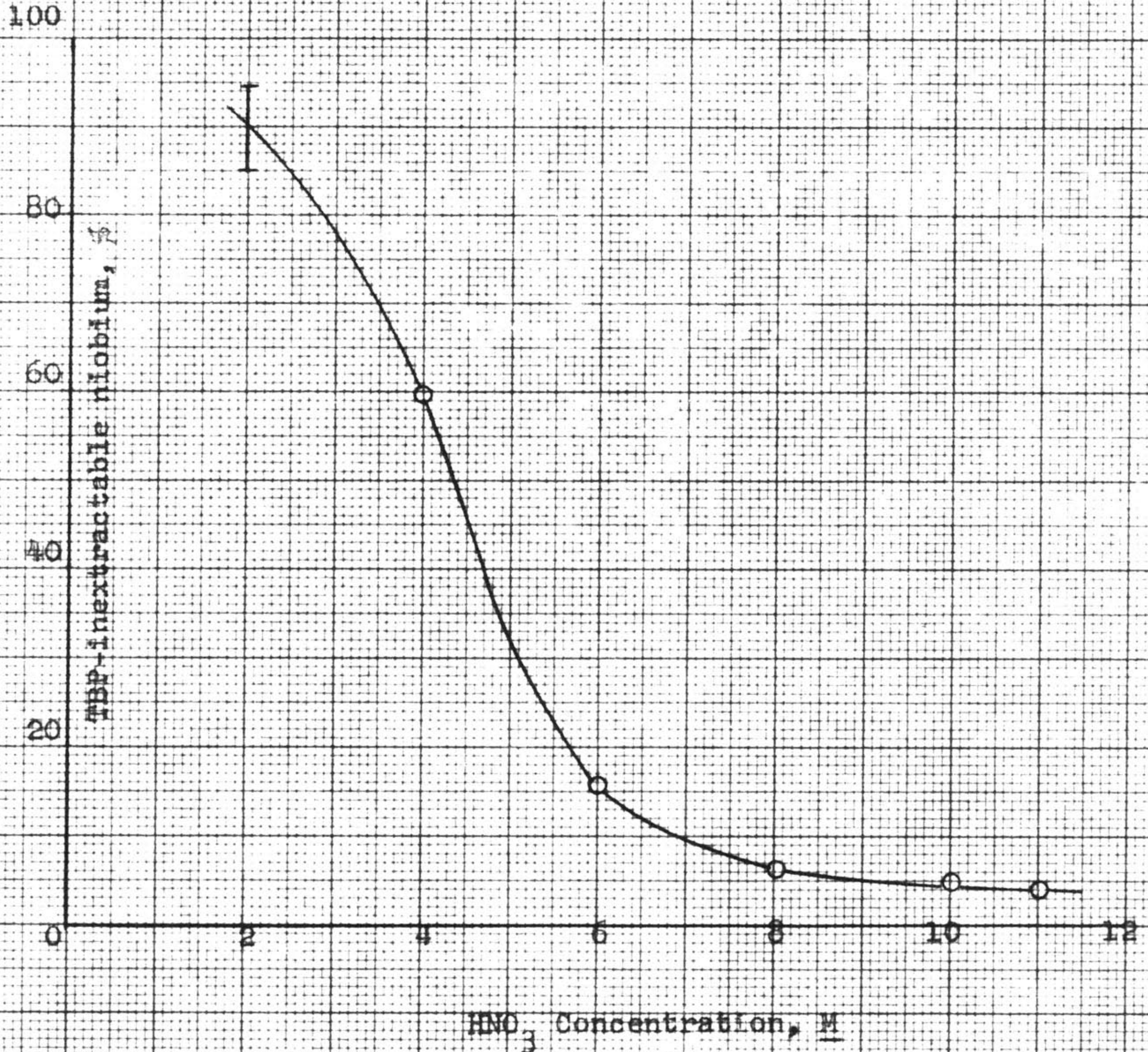
(b) Determination of the quantity of inextractable species present as a function of acid concentration.

(c) Studies of disttibution ratios with TLA, S-24 and Aliquat 336, as functions of acid concentrations, amine concentrations and types of diluent.

Fig. 2.11

Variation in the Amount of
TBP-Inextractable Niobium
with the Nitric Acid Concentration

Data of
C. J. Hardy and
D. Scargill (6)



3.0 Ruthenium Studies

The effect of amine type on the solvent extraction behavior of the mixed nitrosyl ruthenium nitrato complexes in nitrate systems was investigated. The amines used were a primary amine (Primene JMT) and a quarternary amine (Aliquat 336), and the results of this study were compared with the extraction behavior of the tertiary amine, TLA (1). The extraction characteristics of the amines were determined by varying the aqueous nitric acid concentration, $NaNO_3$ salting concentration, amine concentration, phase contact time, and phase volume ratio. The effect of these variables on the nitric acid extraction into the organic phase was also thoroughly investigated.

The order of increasing nitric acid extraction for the three amines was found to be Primene JMT, TLA, and Aliquat 336. As expected, salting with sodium nitrate increased the unbound nitric acid in the organic phase significantly in all three cases. The nitric acid extraction data for Primene JMT and Aliquat 336 and for both salted and unsalted aqueous phases correlated well on the basis of the undissociated nitric acid activity in the aqueous phase. A similar result was found for TLA (1). The unbound organic acid concentration was found to be linear with amine concentration in the region 0.26M to 0.50M for Aliquat 336.

The tertiary amine, TLA, and the quarternary amine, Aliquat 336, exhibited similar trends in ruthenium extraction over the range of nitric acid concentration studied. The peak extraction for both amines was found to occur about 1.5N aqueous HNO_3. The primary amine, Primene JMT, exhibited an increasing ruthenium extraction with increasing aqueous nitric acid concnetration and showed no maximum up to 9.8N HNO_3. The order of increasing ruthenium distribution ratio is Primene JMT, TLA, and Aliquat 336 up to about 5N aqueous HNO_3, but above about 8.5N HNO_3 this order becomes TLA, Aliquat 336, and Primene JMT. At constant aqueous HNO_3 concentration, salting with $NaNO_3$ was found to increase the ruthenium distribution ratio for all three amines at low acid concentrations but decreased the distribution ratio of TLA and Aliquat 336 at high acid concentrations. Between 0.26M and 0.50M amine concentration the ruthenium distribution ratio for Aliquat 336 was found to depend approximately on the 0.5 power of the amine concentration. Washing prior to precontacting had little effect on the extraction behavior of Primene JMT.

Forty-two rapid dilution extractions were alanyzed to determine the number of extractable species of nitrosylruthenium in nitric acid systems, the mole fractions of these species in the aqueous phase at various HNO_3 concentrations, and corresponding partition coefficients of the amines for these extractable species. This study included 29 TLA extractions by Skavdahl (1), 3 TLA extractions and 10 Q-336 extractions from this investigation. JMT was not suitable for rapid dilution extraction because of low distribution ratios. Computer analysis indicated that the extraction data could be represented only by assuming two extractable species. The mole fractions and partition coefficients of these two extractable species were determined as functions of the initial aqueous HNO_3 concentration and the final aqueous HNO_3 concentration, respectively, by a least-squared-error analysis.

The mole fractions of both species in the aqueous phase were found to increase with increasing aqueous HNO_3 concentration, reaching a combined mole fraction for the two species of 0.35 at the highest HNO_3 concentration investigated, 10.1N. The partition coefficients of TLA for the extractable species were found to decrease exponentially with increasing HNO_3 concentration. The more extractable specie had a partition coefficient 12-40 times greater than the less extractable specie in the 1.0N-4.9N HNO_3 concentration region. Q-336 was found to have partition coefficients at 5N HNO_3 concentration which were about an order of magnitude greater than corresponding TLA partition coefficients. Equations for the mole fractions and the TLA partition coefficients over the range of acid concentrations investigated have been developed. It was found that significant amounts of both extractable species are extracted into the organic phase under all conditions of HNO_3 concentration and phase volume ratios used in these rapid dilution extractions.

The details of this study are presented in a separate report (2).

4.0 Effect of Uranium Loading on Extraction of Zirconium and Ruthenium by TLA

Limited studies on the effect of partial uranium saturation of TLA on the extraction of zirconium and nitrosylruthenium complexes were performed by Price (3).

The objective was to determine the effect of large amounts of uranium in the organic phase on the extraction of zirconium and the aged nitrosyl ruthenium (RuNO) nitrato complex by trilaurylamine (TLA) in toluene. Since uranium is extracted to a much greater degree than zirconium or ruthenium, the effect of uranium competition is to lower the free amine concentration and thus to lower ruthenium and zirconium extraction.

Conditions of the extraction were 7N and 9N aqueous nitric acid, 0.3M TLA in toluene as the organic phase, and 24 hour contacting at 25°C and 1:1 phase volume ratio. This represents equilibrium contacting for uranium and zirconium, and an intermediate condition of very slowly varying ruthenium extraction.

Conventional chemical separation and spectrophotometric analysis was used. The uranium spectrophotometric analysis is based on the thiocyanate complex. Ruthenium was removed if present in more than (1:100 = Ru:U) by volatilization as the tetroxide, and carbonate by acidification and boiling. Ruthenium was separated by the tetroxide distillation, and collected and measured in basic solution by precipitation as barium fluozirconate, carried with barium fluosilicate; fluoride was removed, the acidity adjusted, and the Alizarine Red S color developed and read. Other methods were used when the separation was not required.

Uranium distribution ratios in the presence of ruthenium and zirconium are shown in Figure 4.1. There is little effect of either metal. Uranium extraction at high loadings continues to rise, causing failure of a correlation found valid by Vaughen and Mason at lower loadings, and indicating that there are significantly fewer than two TLA molecules associated with each uranium atom in the organic phase at high loadings. Further investigation of this, varying total amine concentration, and at the conditions of salting and acidity of previous work is recommended.

Ruthenium and zirconium distribution ratios are shown in Figures 4.2 and 4.3 as functions of the organic phase uranium concentration. Considerable scatter of the points due to imprecise analyses is evident. This is due partly to the low concentrations of zirconium and ruthenium in the organic phase. Improvements in the precision could be made by using tracer amounts of radioisotopes for extraction and

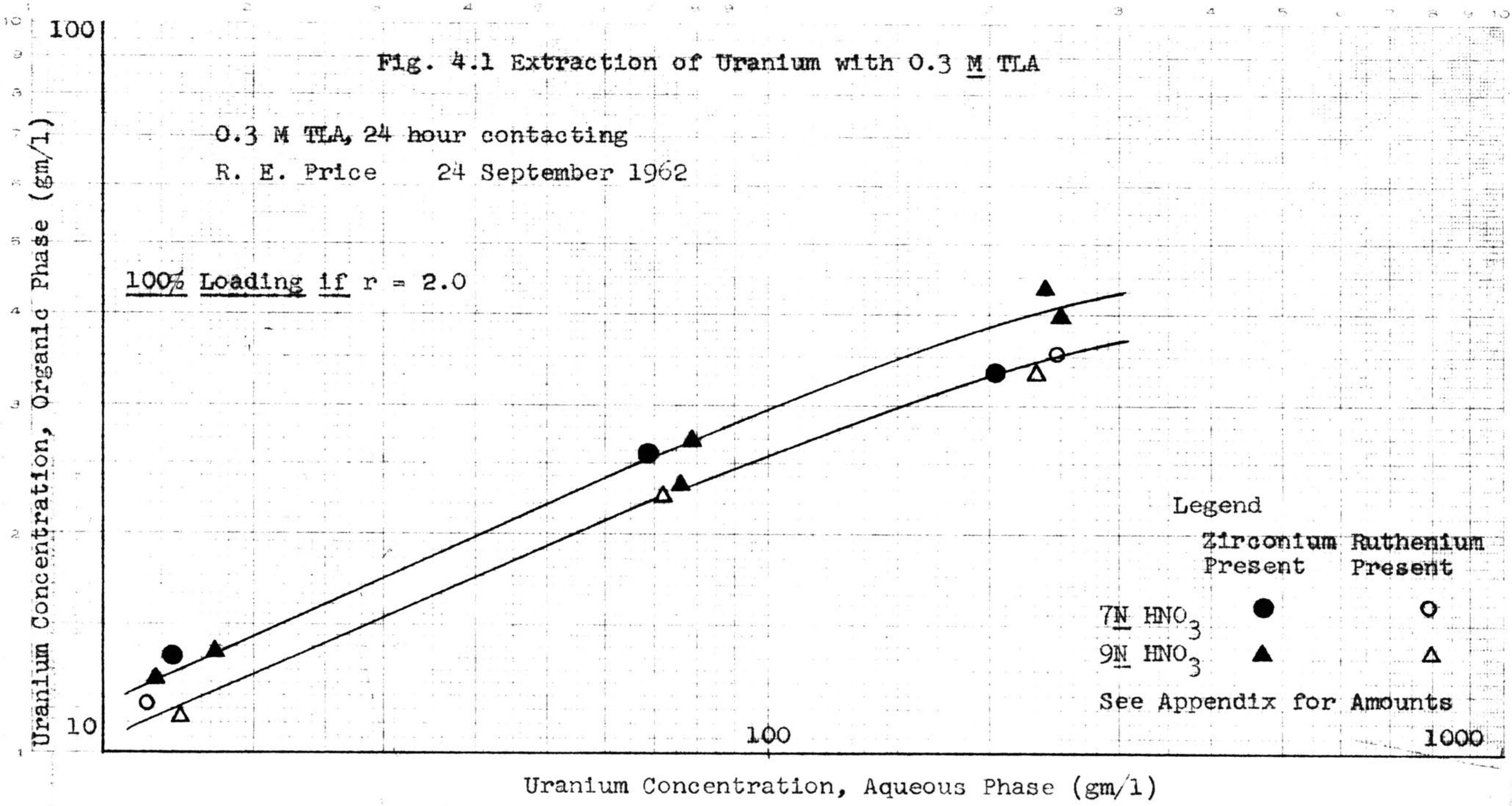


Fig. 4.1 Extraction of Uranium with 0.3 M TLA

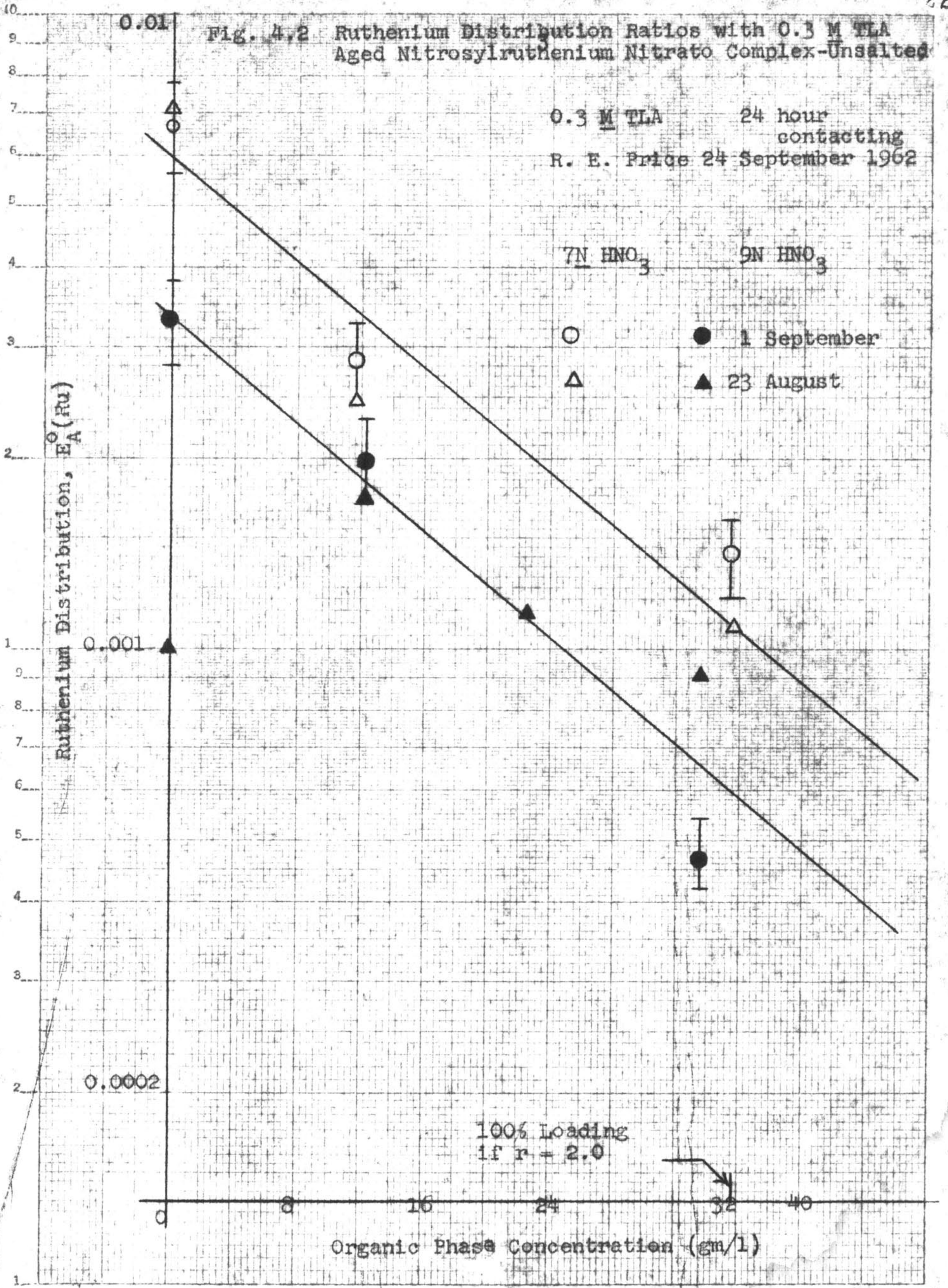


Fig. 4.2 Ruthenium Distribution Ratios with 0.3 M TLA Aged Nitrosylruthenium Nitrato Complex-Unsalted

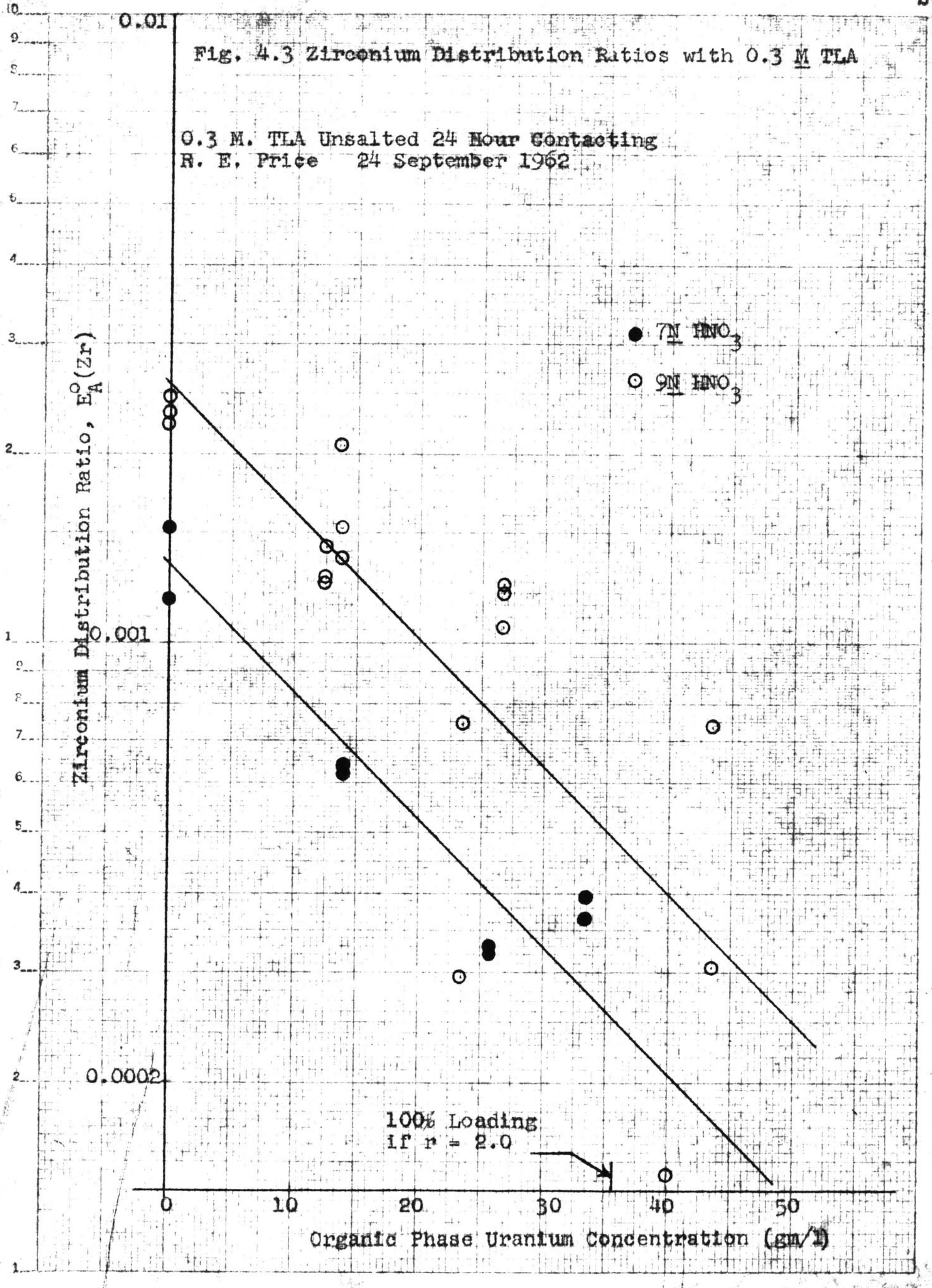


Fig. 4.3 Zirconium Distribution Ratios with 0.3 $\underline{M}$ TLA

0.3 M. TLA Unsalted 24 Hour Contacting
R. E. Price 24 September 1962

radioanalysis. An added advantage would be the lower aqueous ruthenium:uranium and zirconium:uranium ratios required and closer conformity with expected process conditions. The lines in Figures 4.2 and 4.3 are given by:

$$E_a^o = Ae^{-0.02U},$$

where U = organic uranium concentration, gm/l

and A = constant for each case as follows:

Metal	Aqueous HNO_3 Concentration	
	7N	9N
Ru	0.0034	0.0059
Zr	0.0013	0.0026

Within the units of the scatter of the experimental data, the results can be correlated by the same function.

5.0 Appendix

5.1 Detailed Procedures

5.1.1 Preparation of Niobium Stock Solution

1) Dissolve 2.6g $K_8Nb_6O_{19}O$ 16 H_2O in 20 ml of DDW (Distilled, Deionized Water).
2) Heat to nearly boiling.
3) Add 1.5 ml conc. HNO_3.
4) Continue heating and stirring for 2-3 min.
5) Centrifuge to collect the precipitate.
6) Decant.
7) Add 5.0 ml hot 2% NH_4NO_3 solution.
8) Centrifuge.
9) Repeat steps (6), (7) and (8) three times.
10) Add 20 ml of sat. oxalic acid.
11) Heat with stirring until niobic acid dissolves.
12) Cool and dilute with DDW to required concentration.

5.1.2 Gravimetric analysis of Niobium stock solution

1) Add 12 ml 6M HNO_3 and 0.4 g of $KClO_3$ to 2 ml of the stock solution to be analyzed.
2) Heat to boiling
3) Boil gently with occasional stirring for 5 min.
4) Cool the mixture, add conc. NH_4OH with stirring to pH of 8-10.
5) Filter on a Whatman No. 42 filter paper (Recycle filtrate if not clear)
6) Wash with hot DDW.
7) Ignite in a porcelain crucible at 800°C. for 15 min.
8) Weigh as Nb_2O_5

5.1.3 Preparation of the Aqueous Phase

1) Place 10 ml of 1.0 μc/ml solution of Nb-95 into a siliconed graduated test tube.

2) Add 2 ml of 5.6×10^{-7} M natural niobium stock solution (in 5% oxalic acid).

3) Add 0.75 of 30.4% H_2O_2.

4) Add 5 ml 15.4 N HNO_3.

5) Evaporate under infrared heater to 2 ml.

6) Add 3 ml 15.4 M HNO_3

7) Evaporate under infrared heater to 3 ml.

8) Add HNO_3 to make 7.5 ml of 9.65 N solution.

9) Place in capped, siliconed glass tube and heat in oven for 1 hr at 100°C.

10) Make up desired concentration of aqueous phase by dilution or by addition of HNO_3.

11) Heat in capped, siliconed glass tube for 1.5 hr at 100°C.

12) Cool to room temp.

5.1.4 Titration of Organic Phase for Nitric Acid Content

Figure 5.1 shows a typical titration curve obtained by titration of the organic phase with sodium hydroxide. The first inflection determines the unbound nitric acid and the second inflection determines the total acid. The bound acid is represented by the difference between the two inflections.

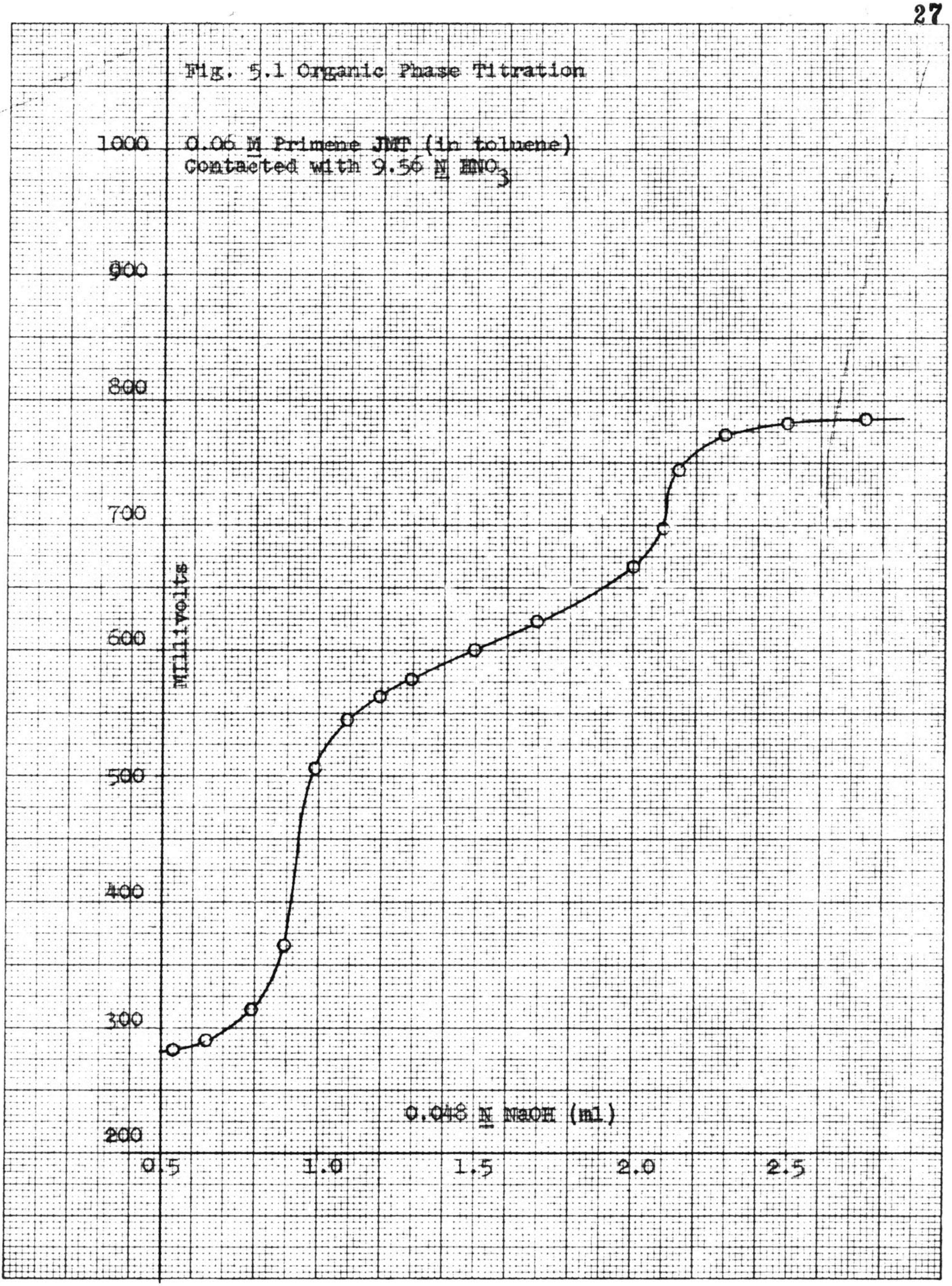


Fig. 5.1 Organic Phase Titration

0.06 $\underline{M}$ Primene JMT (in toluene)
Contacted with 9.56 $\underline{N}$ HNO_3

5.2 References

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