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THE SORPTION OF CURIUM, BERKELIUM, CALIFORNIUM, AND
EINSTEINIUM ON CATION EXCHANGE RESIN FROM NITRIC
ACID SOLUTIONS*

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THE SORPTION OF CURIUM, BERKELIUM, CALIFORNIUM, AND EINSTEINIUM ON
CATION EXCHANGE RESIN FROM NITRIC ACID SOLUTIONS

J. M. Chilton

This work, on the sorption of the transplutonium ions, particularly curium through einsteinium, on cation resin was an outgrowth of studies of a different problem in the Transuranium Processing Facility at the Oak Ridge National Laboratory.

In the course of another investigation, it was desirable to remove all that was practical of the radioactive material from some Dowex 50 resin that had been used in one step of the chemical processing of curium that had been irradiated in the High Flux Isotope Reactor. The prime objective of this irradiation was the production of Californium-252. Analysis of this spent resin was made by ignition of a sample to ash, dissolving in nitric acid, and making alpha and neutron counts. It was found that each milliliter of the resin contained about 1 microgram of Curium-244, about 0.4 microgram of Californium-252, and about 0.2 nanogram of Einsteinium-253. One of the reagents that was tried to leach the resin was concentrated nitric acid, which seemed logical at the time. An analysis of the results showed that this was a rather poor decontaminant, in fact, was apparently not as good as a less concentrated nitric acid solution. Noting this fact, I made a search of the literature to find what had been reported about the sorption of the transuranic elements on cation resins from nitric acid solutions of varying concentrations. I was somewhat surprised to find information about other systems, especially perchloric, hydrochloric, and hydrobromic acids, but almost nothing in the nitric acid system. Since I was in the very fortunate position of having

access to relatively pure solutions of the transplutonic elements, as well as facilities for working with them, I undertook a study of the sorption of several of these elements from nitric acid of varying concentrations.

Before I begin to present the results of these investigations, I will briefly outline the various techniques which were followed.

All sorption coefficients were determined by batch equilibrium. A stock solution of each element was prepared by boiling a nitric acid solution to dryness and then dissolving the residue in 6.0 molar nitric acid. Small spikes of the stock solution were added to nitric acid solutions of the desired molarity and the resulting molarity calculated. The dilute solutions were then analyzed by either alpha, beta, or neutron counting, as required. A weighed sample of Dowex 50-X8 resin, air dried at room temperature, was added to a measured volume of each acid solution and the mixture agitated gently for one hour. A sample of the supernate solution was then withdrawn and counted again. The amount of the element adsorbed was calculated from the difference in the two analyses. The dry weight of the resin was determined by drying a sample at 110° for 3 hours. In this series of experiments, the chief emphasis was put on the difference between the sorption from different acid concentrations, rather than obtaining an ultra-precise number for any one set of conditions. Several years ago, when we were doing similar work with various valence states of plutonium, we learned that different batches of the same type of resin would give various sorption coefficients, depending on such factors as batch number, age, exposure to air, etc.

Since curium comprised the largest fraction of the actinides present on the resins we were studying, the techniques were developed and the first data

were obtained with this ion. A stock solution, in 6.0 M nitric acid, was prepared as described above, containing curium-244 and californium-252 in a ratio of about 2:1. Dilutions of this stock solution in nitric acid concentrations from 1.9 molar to 15.5 molar were made and equilibrated with Dowex 50W-X8 ion exchange resin, 100-200 mesh. The results are shown in Slide 1, on which is plotted the distribution coefficient, defined as the amount of ion adsorbed on 1 gram of dry resin, divided by the amount present per milliliter of solution, versus the concentration of nitric acid in solution. Despite the fact that there is obviously some experimental error involved in the calculation of these few points, nevertheless the general shape of the curve describing the relationship is unmistakable. The most notable fact is the minimum in the curve which occurs at about 6.5 molar acid. This is similar to the reported results with perchloric acid, which we will discuss later.

These curium values were obtained by gross alpha counts in a gas proportional counter and an alpha pulse height analysis using a 400-channel discriminator. Since these solutions also contained californium-252, which emits both alpha particles and neutrons, the same solutions were also counted for total neutron emission. From these neutron data, values for the distribution coefficients for californium were calculated, and these are shown in Slide 2. It is obvious that the distribution is very similar to that of curium, and that a minimum occurs at an acid concentration of about 7.0 molar.

Since these two elements behaved very similarly to each other, we assumed that all of the trivalent actinide ions would behave in this manner. To check this out, a few samples of einsteinium-253 solution were run over the range from 2 to 12 molar nitric. As predicted, the results were quite similar to those for curium and californium; these are shown in the next slide

(Slide 3). The only notable difference is apparently a somewhat lower distribution at acidities above about 3 molar.

The remaining actinide in this part of the periodic table is berkelium, which can exist in two valence states, plus-3 and plus-4. In order to complete the picture, distribution coefficients were determined for this element in the same way as was used for the others. The values for the plus-3 ion were easily obtained and fell along a curve as anticipated. These values are shown in Slide 4. More points were determined for this curve than the previous ones in order to get a fairly accurate picture of the position of the curve. Values taken from this curve were used in the subsequent calculations of the distribution of berkelium-4 plus ions.

There is no reason to expect that the berkelium plus 4 ion should behave like the plus 3 actinides, but its behavior was investigated to see whether this minimum distribution at 6 to 7 molar acid is repeated in this system. Berkelium is the only transplutonium element with a plus 4 valence state that is stable in aqueous solution. The potential of the berkelium four-three pair was reported to be 1.56 volts in 6 molar nitric acid by Musikas and Berger in 1967. This is almost exactly the same potential as the cerium four-three couple. This high potential requires a strong oxidizing reagent to prepare the four state, and chromic oxide, dichromate, persulfate, bromate, bismuthate, and lead dioxide have been used under a variety of conditions for this purpose.

Since, in this work, the introduction of large amounts of extraneous cations was to be avoided, no experiments were done with dichromate, bismuthate, or lead dioxide. Numerous procedures, using persulfate and/or bromate, were evaluated to prepare berkelium 4 solutions that remained stable in the presence

of the ion exchange resin for the duration of the measurements. Without mentioning the details of the other methods, the technique that proved most effective involved mixing the berkelium 3 stock solution in 6 molar nitric acid with an equal volume of freshly prepared 1 molar sodium bromate in 6 molar nitric acid and using this "berkelium-4 stock" for dilutions for the adsorption measurements. The berkelium-3 content of the solutions, after contact with the resin, was determined in every case by extraction of an aliquot with di-2-ethylhexyl phosphoric acid and counting the berkelium remaining.

Since the berkelium stock solution was essentially free of any other activity, all concentrations were determined by beta counting on a proportional counter. The results of these measurements, after correcting for the berkelium-3 sorption, calculated from the previous experiments, are graphed on the next slide (Slide 5). Also shown on this slide is the distribution reported for plutonium-4 by Hardy in the "Progress in Nuclear Energy" series. We see that the values are quite similar. We see that the distribution coefficient at 1 molar acid is about 300, which is somewhat lower than might be expected for a plus-4 ion. As expected, the sorption decreases as the acidity increases until at 6 molar acid, the D.C. is slightly less than 1. Attempts were made to measure the sorption on up to 11.5 molar acid, but the values were too low to be determined reliably by this procedure.

Various hypotheses can be advanced to explain this difference in behavior of the plus-4 ion compared with the plus-3 ion, at the higher acidities. One might propose that, in the high nitrate concentrations, the plus-4 ion forms an anionic nitrate complex, similar to the action of cerium plus-4. This question was studied by Moore, at Oak Ridge, in 1967, and he found that although the cerium plus-4 ion would load on anion resin from strong nitric acid, berkelium plus-4 would not load, and he proposed this as a basis for

a method of separation of the two elements. Using Dowex 1-X8 resin, we tried to check the distribution of the berkelium-4 on anion resin, using the same procedure as was used for the cation resin. We calculated distribution coefficients of 1.0 in 4 molar nitric acid and 0.9 in 7 molar acid, but were unable to obtain any meaningful results at higher acids. Since the experimental error is large in the determination of low coefficients by this technique (that is, by batch equilibration) we would hesitate to say that the results for the 4 molar and the 7 molar acids are significant. The most likely explanation is the formation of a neutral complex between the nitrate and the berkelium plus-4. It was shown by Rao, Mason, and Peppard, at Oak Ridge, in 1968, that berkelium-4 can be quantitatively extracted by a 1/2 molar solution of di-(2ethylhexyl)phosphoric acid in dodecane at any nitric acid concentration from 0.1 to 10 molar. Since this reagent typically extracts neutral nitrate complexes, we can assume that an equilibrium amount of a neutral nitrate complex is formed, even at very low nitrate concentrations.

Let us now look at the compilation of all of these results on a single graph (Slide 6). These curves are simply transferred from the previous graphs, without the location of the data points. The most obvious fact in looking at this is that all four of the plus-3 ions behave in a very similar manner, that is, all exhibit a minimum sorption at a nitric acid concentration around 6 or 7 molar. The differences in distribution coefficients are not large, with the possible exception of the difference between berkelium and einsteinium at 6.5 molar acid. Since more efficient methods of separating these two elements exist, such as isobutyrate complexation, this phenomenon has little practical interest. However, it is interesting to speculate about the mechanism responsible for the

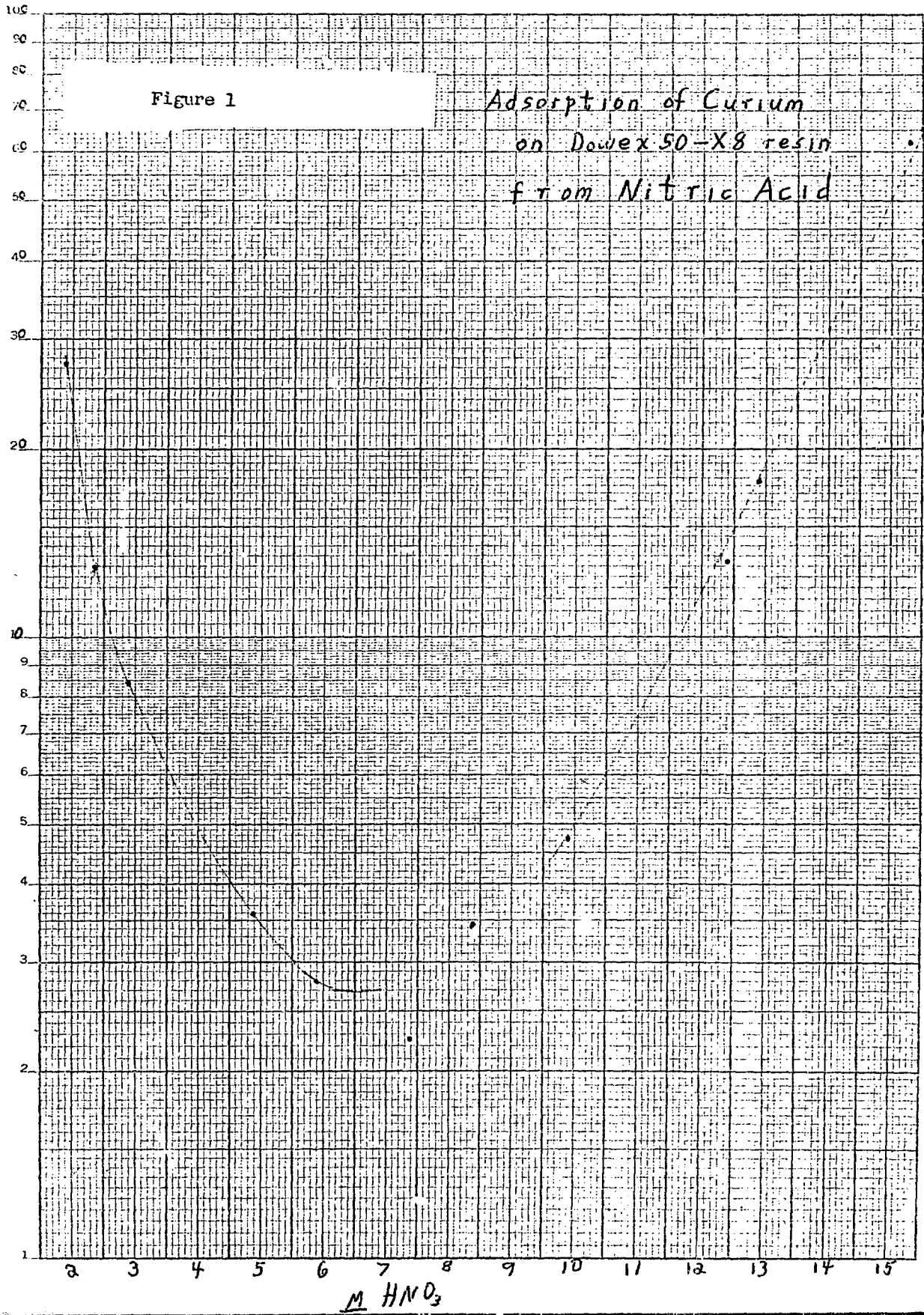
increase in adsorption of these plus-3 ions in the higher nitric acid concentrations. Starik and Ginzburg, in 1961, using Americium-3, found that positive nitrate complexes existed in nitric acid concentrations up to 4 molar, while a neutral complex was formed in the range 4 to 16 molar acid. Marcus, Choppin, and others, have studied the behavior of americium-3 in lithium nitrate solutions and have found adsorption on anion resins in the range from 3 to 10 molar lithium nitrate. As noted above, this is in contrast with what we found for the nitric acid system. Choppin, Harvey, and Thompson also published some work on the sorption of americium-3 from various acids on cation resin. They found that adsorption from perchloric acid went through a minimum at about 4.5 molar and then increased very rapidly at higher acids. They attributed this result to the formation of ion pairs with the perchlorate ion in the ion exchange phase. Other authors have noted the same effect, and Guseva and Tikhomirova attribute this to the dehydration effect of the concentrated acid. As I stated earlier, there does not appear to be any reference in the literature about this similar behavior in nitric acid, but the results shown here are quite unambiguous. We do not intend to pursue this investigation further, in order to find an explanation for this phenomenon, but it seems that any theoretical explanation that is given must take account of the fact that it applies only to the trivalent actinides, and possibly the trivalent lanthanides, and not to other positive ions.

46 5130
4600 IN. U.S.A.
2 CYCLES X 140 DIVISIONS
KEUFFEL & ESSER CO

$\frac{g. Curium}{ml. solution}$
Distribution Coefficient

Figure 1

Adsorption of Curium
on Dowex 50-X8 resin
from Nitric Acid



M HNO₃

Distribution Coefficient $\frac{g. \text{ resin}}{ml. \text{ solution}}$

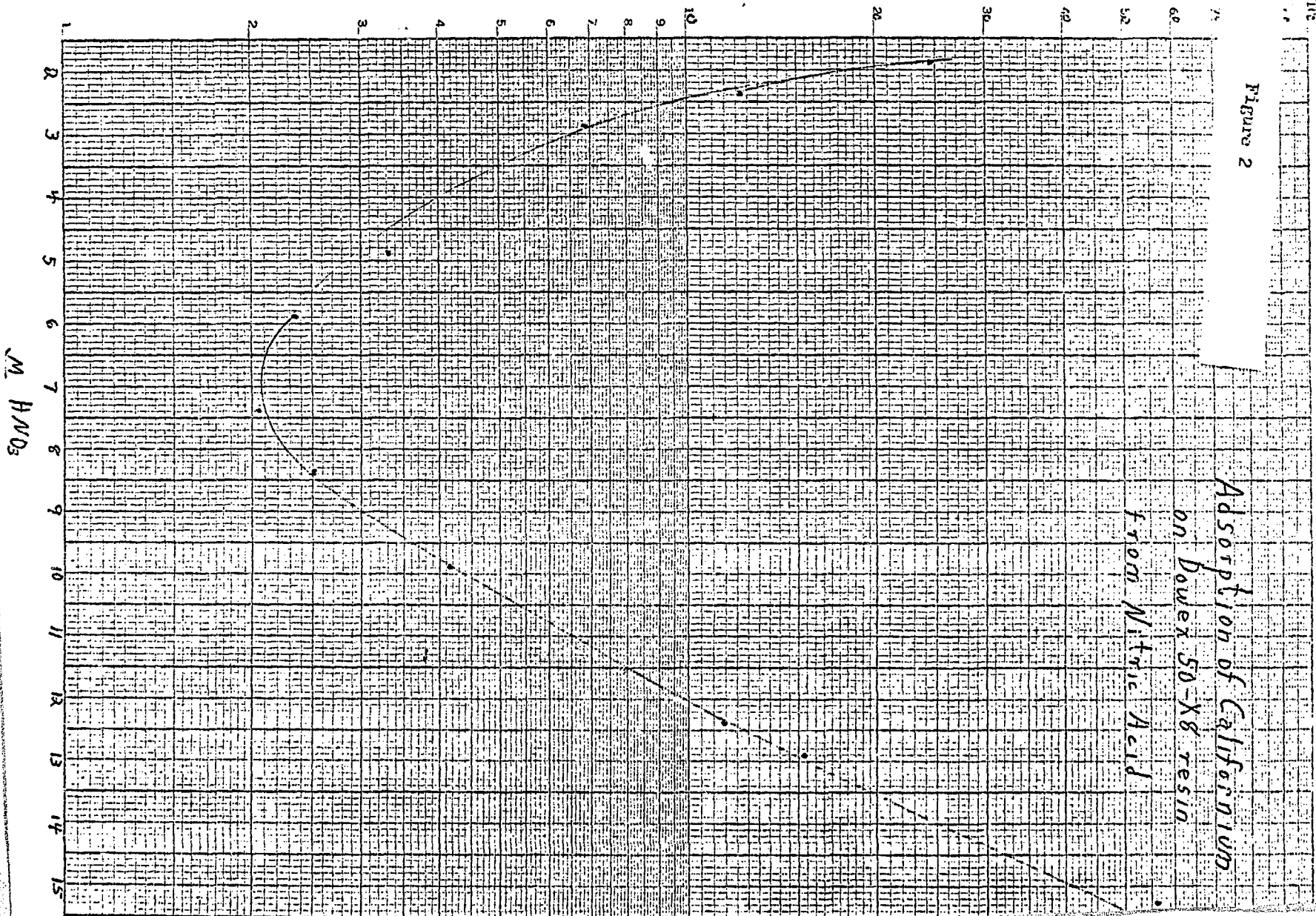


Figure 2

Adsorption of Californium
on Dowex 50-X8 resin
from Nitric Acid

M HNO₃

Figure 3

Adsorption of Einstein
on Dowex 50-X8 resin
from Nitric Acid

Distribution Coefficient $\frac{g. \text{ resin}}{\text{ml. solution}}$

SEMI-LOGARITHMIC 46 5130
2 CYCLES X 140 DIVISIONS
KEUFFEL & ESSER CO

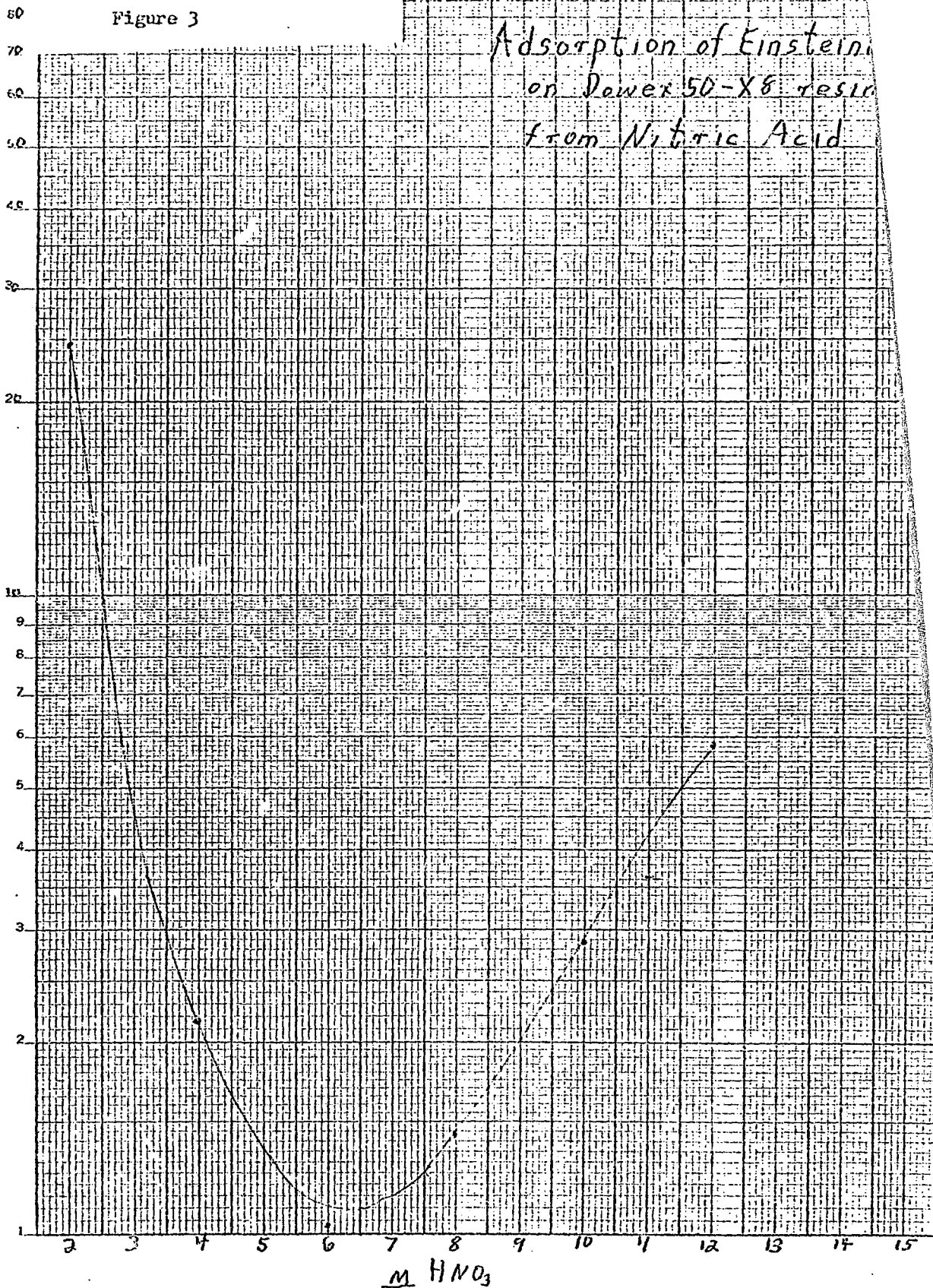
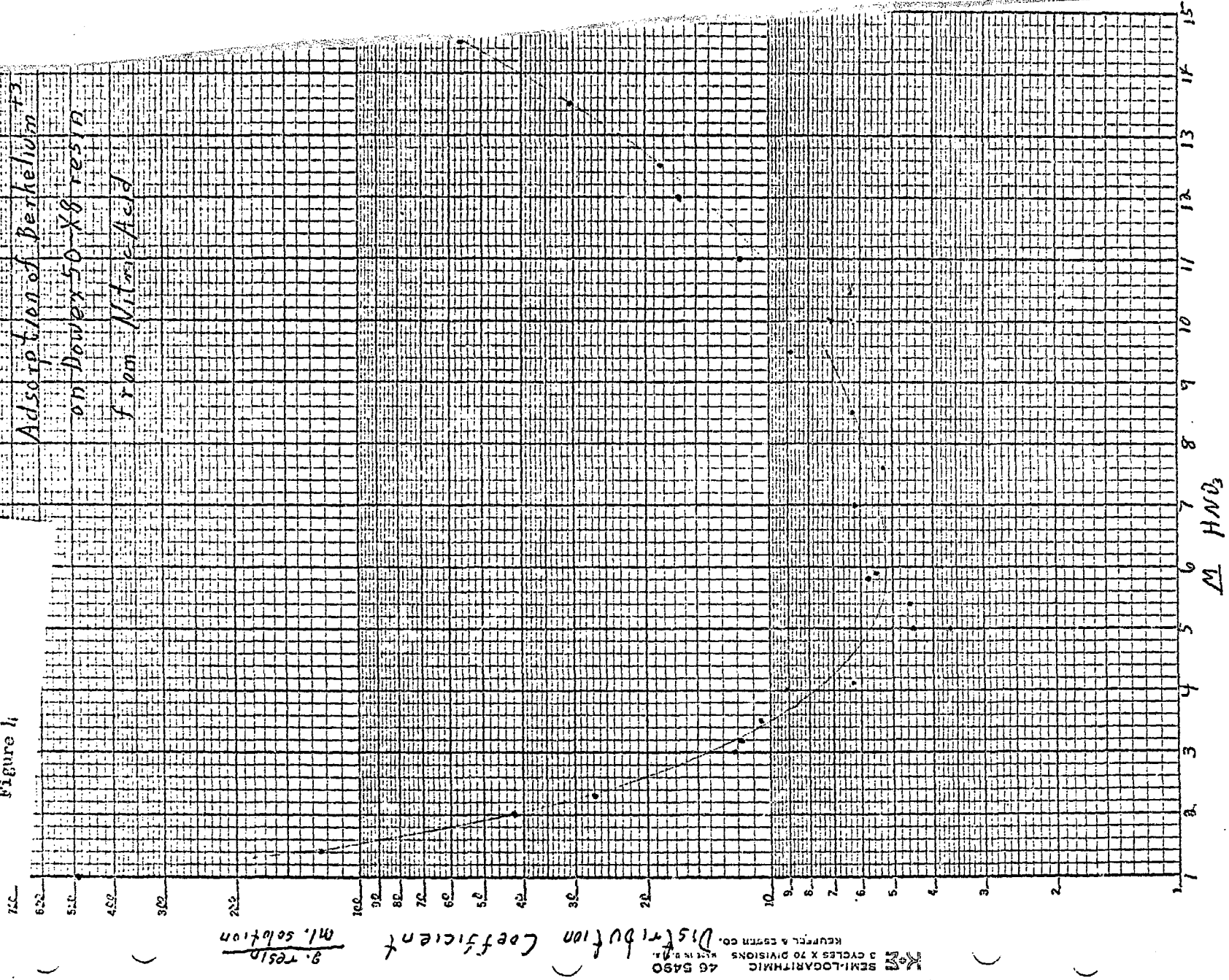


Figure 4

Adsorption of BenkeliumTM
on Dowex 50-X8 resin
from Nitric Acid



9. RESIN
ml. solution

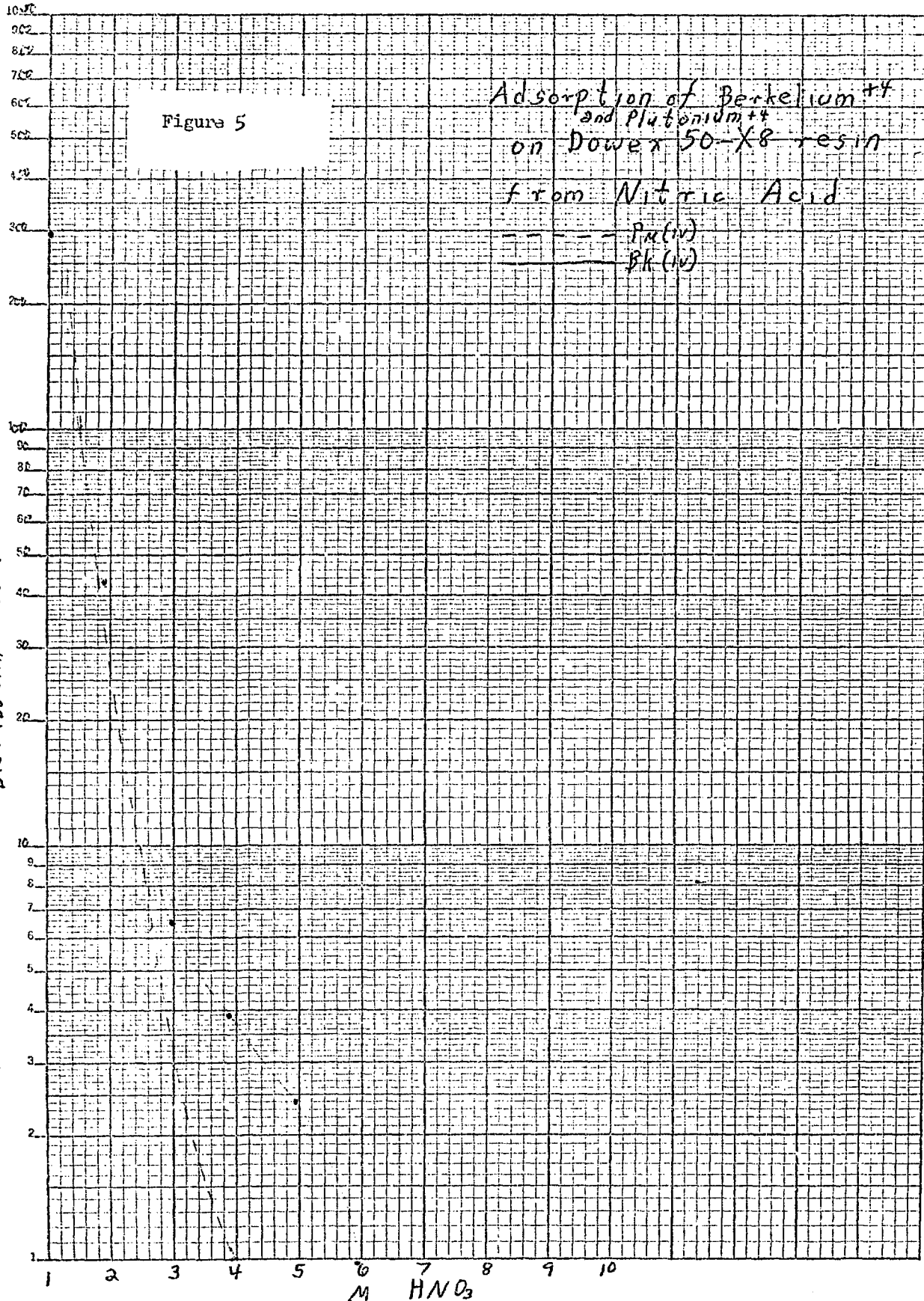
Coefficient

Distribution

KEUFFEL & ESSER CO.

46 5490
SEMILOGARITHMIC
3 CYCLES X 70 DIVISIONS
MIL. IN. H. I.

$\frac{g/resin}{ml\ solution}$
Distribution Coefficient



46 SEMI-LOGARITHMIC 46 5490
3 CYCLED X 70 DIVISIONS MADE IN U.S.A.
NEUFFEL & CASER

resid
ml. solution

Distribution Coefficient

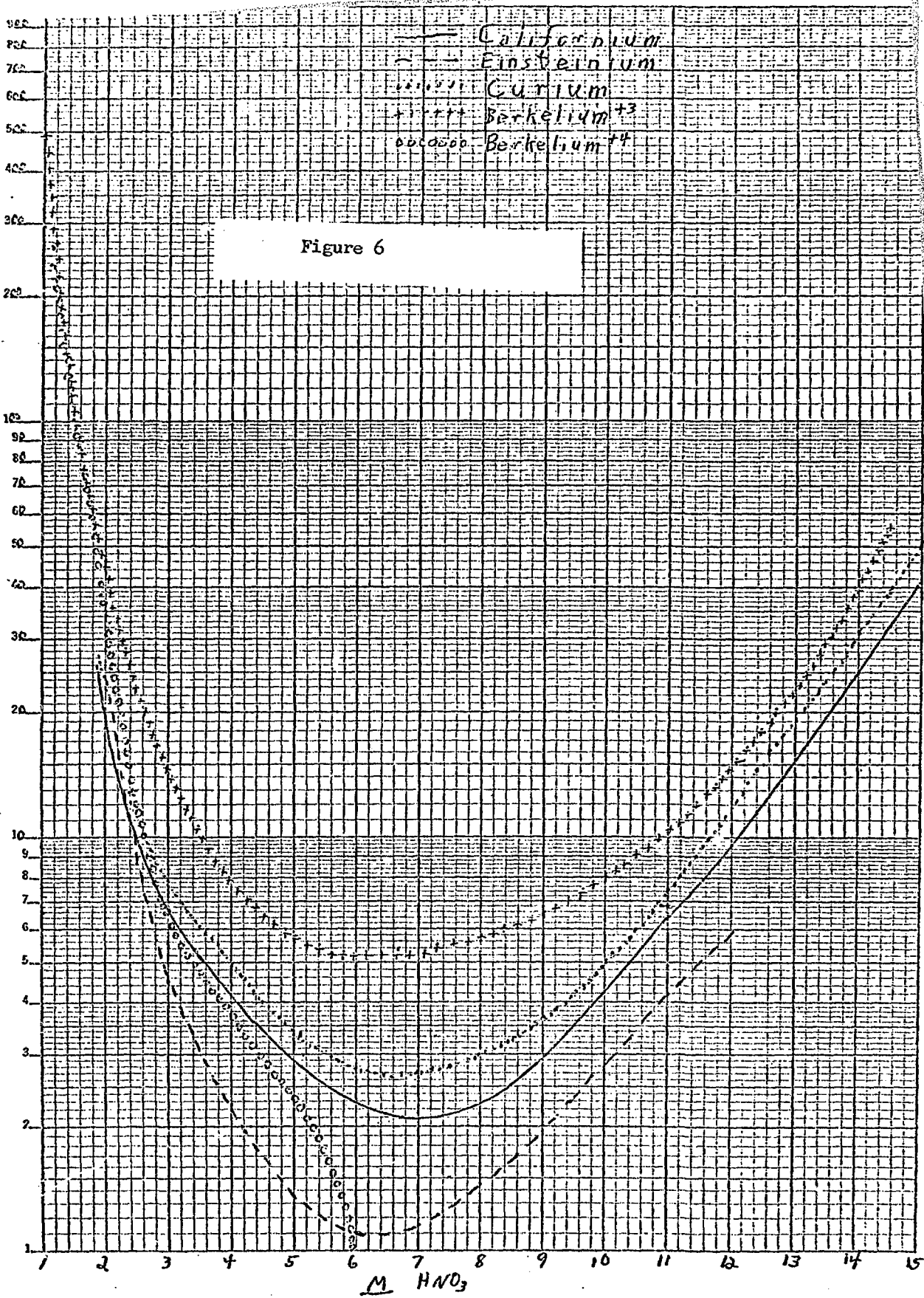


Figure 6

$M HNO_3$