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ISOLATION AND PROPERTIES OF CURIUM

Louis B. Werner

July 28, 1948

Berkeley, California

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ISOLATION AND PROPERTIES OF CURIUM

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Radiation Laboratory, University of California

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July 28, 1948

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Abstract

The isolation of curium, element number 96, in relatively pure form has been accomplished.

A method, involving a solvent extraction process, is given for the purification of americium from lanthanum and other ions. The discovery of a higher oxidation state of americium led to a method of separating americium from curium. Separation of the two elements was also accomplished by use of ion exchange resins. The details of the isolation of curium are given; the results of the spectrographic analysis, specific activity measurement, and calorimetric determination of half life showed the curium to be relatively pure.

The absorption of light of various wave-lengths by an aqueous solution of Cm(III) is described, and some physical effects of the radiation from the curium are noted.

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ISOLATION AND PROPERTIES OF CURIUM

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Louis B. Werner

Radiation Laboratory, University of California

Berkeley, California

July 28, 1948

I. Introduction.

The discovery of element number 96, curium, was realized by the preparation and identification of the isotope Cm^{242} by G. T. Seaborg, R. A. James and A. Ghiorso[1] by cyclotron bombardment of Pu^{239} with helium ions. Cm^{242} is an alpha-emitter having a 5-month half-life. It may also be prepared by neutron irradiation of Am^{241} according to the following reactions[2]:

$$Am^{241}(n, \ )Am^{242}$$

$$Am^{242} \xrightarrow[18\ \text{hrs.}]{\beta^-} Cm^{242} \qquad (1)$$

The 500-year isotope of americium, Am^{241}, was first isolated in microgram amounts by B. B. Cunningham[3] employing techniques similar to those described by Cunningham and L. B. Werner[4] for isolating plutonium and using chemical procedures described by Cunningham[3] and Werner and D. R. Miller[5]. Since the principal source of americium was one which contained large amounts of La(III), an efficient means of first separating americium from lanthanum was needed. One such method described by S. G. Thompson[6] depends upon precipitation reactions. The method to be described here (also reported by Werner and I. Perlman[7]) depends upon the chelation properties of the ions with certain diketones. Using these methods and others described by Cunningham[3] amounts of americium suitable for irradiation were isolated[3].

With the large neutron fluxes available from the chain reacting piles it seemed feasible to prepare microgram quantities of Cm^{242} by prolonged neutron irradiation of Am^{241} in one of the Hanford piles.

By having available essentially pure americium as a target material, the problem of isolating curium was largely that of separating curium from larger amounts of americium. Nevertheless it was recognized that a small amount of impurity relative to the amount of americium present could easily be comparable to or greater than the weight of curium formed during the irradiation.

The chemistry of curium as determined on the tracer scale has indicated that only the trivalent oxidation state exists in aqueous solution[8]. It shows very much the same precipitation properties as the trivalent rare earths, and attempts to oxidize or reduce it to other oxidation states proved unsuccessful.

This is to be expected if one assumes the elements in this region belong to a new "rare earth" series of "actinide" elements in which electrons are to be found in the 5f shell. Curium should thus occupy a position analogous to gadolinium and Cm^{+3} would have the stable configuration $5f^7$[9]. There seemed to be little possibility, therefore, of obtaining curium in other oxidation states which might prove useful as a basis of a chemical separation from americium and other similar tripositive ions. The most stable oxidation state of americium is the plus three state as shown by the x-ray identification of the trihalides[10], by the elution behavior of aqueous solutions of americium from cation exchange resins[11], and by the extraction behavior of

certain chelate compounds in organic solvents[7] compared with the behavior exhibited by tetrapositive and other tripositive ions.

Americium might be expected to possess at least one other relatively stable oxidation state analogous to the dipositive state of europium. A search for evidence of both a state higher as well as one lower than plus three was carried out by Cunningham[3]. Briefly, the conclusions reached were that the standard potential in ca. 1 M H^+ for the reaction

$$Am(III) + nH_2O = Am(III + x)O_n^{III + x - 2n} + 2nH^+ + e^-$$

is more negative than ca. -2.0 v, that is, is more negative than the potential for the reaction $Ag^+ = Ag^{++} + e^-$, since no evidence for the oxidation of Am(III) in the presence of Ag^{++} was obtained; a higher state of americium appeared to be reached by oxidation with BrO_3^- in concentrated HNO_3 solution, although the evidence was not considered to be conclusive; finally, since polarographic studies showed no well defined wave corresponding to the reversible reduction of Am(III), the potential for the reaction Am(III-y) = Am(III) + ye^- is more positive than ca. +1 v. The possibility of basing a separation of americium from curium on a higher oxidation state of americium seemed worth investigating.

The use of ion exchange methods for separating rare earth elements as the tripositive ions has been reviewed by W. C. Johnson, L. L. Quill and F. Daniels[12]. A particularly efficient ion exchange resin called Dowex-50[13] developed by the Dow Chemical Company has been used by D. H. Harris and E. R. Thompkins[14] for rare earth separations at Clinton Laboratories in Oak Ridge.

Preliminary experiments by Cunningham, L. B. Asprey, and Thompkins[11] at Berkeley showed that good separation of Am(III) from Cm(III) could be obtained, at least when relatively small amounts of the two elements were present. Such methods appeared to offer much in the way of simplicity of operations and in the specificity of the separations.

The transitions which are responsible for the characteristic absorption spectra of the tripositive rare earth ions in aqueous solution have not been assigned[15]. An interesting relationship has been observed, however. Gd^{+3}, having a configuration $4f^7$, shows absorption only in the ultra violet in aqueous solution. The rare earths preceding and following gadolinium show more or less absorption in the visible region of the spectrum. The tripositive ions of the heavy elements preceding curium show absorption in the visible region (see Fig. 11). It was then of interest to determine the nature of the absorption spectrum of curium which, according to the actinide theory[9], should bear an analogous position to gadolinium in the rare earth series.

II. Separation of Am(III) from La(III) and Other Ions by TTA* Extraction.

1. Methods and Equipment Used.

The use of diketones of the type, $RCOCH_2COCF_3$, to form metal chelate complexes that can be extracted into benzene has been de-

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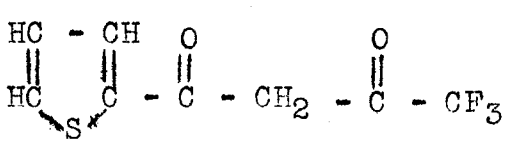
*This abbreviation for thenoyltrifluoroacetone will be used throughout this report:



veloped by M. Calvin and co-workers[16]. The extent of complex formation for a given ion depends upon the solution pH and upon the concentration of the diketone. The relative case with which different metal ions form complexes depends upon their respective charges and electron structures. Similar ions are separated by extracting at the pH at which the maximum difference in chelate stability is found.

The complete complexing or chelation of a trivalent cation by a compound such as TTA may be represented by the following equation:

$$Me^{+3} + 3\ Ke \longrightarrow MeKe_3 + 3H^+ \qquad (2)$$

In the case of TTA, the metal chelate is very much more soluble in benzene than in aqueous solution and may be readily extracted. As can be seen from equation (2), the extent of complexing is dependent upon the third power of both the hydrogen ion and diketone concentrations.

Special thanks are due Professor Calvin for his very helpful advice in carrying out these experiments, and to J. C. Reid for the preparation of the TTA, the diketone which was used.

It was found convenient to carry out most of the studies in an apparatus similar to that shown in Fig. 1. Measurement of the pH was made by drawing the aqueous phase up into the electrode chamber (a). Movement of the liquid was controlled by a syringe (b) Adjustment of pH was made by addition of base from the burette (c) or acid through opening (d). Measurement of the pH was made with the use of a 2 1/2" glass electrode mounted firmly in an outside ground glass joint and a calomel electrode inserted through a rubber stopper. Samples of both phases for analysis were withdrawn

Figure 1

Extraction Apparatus

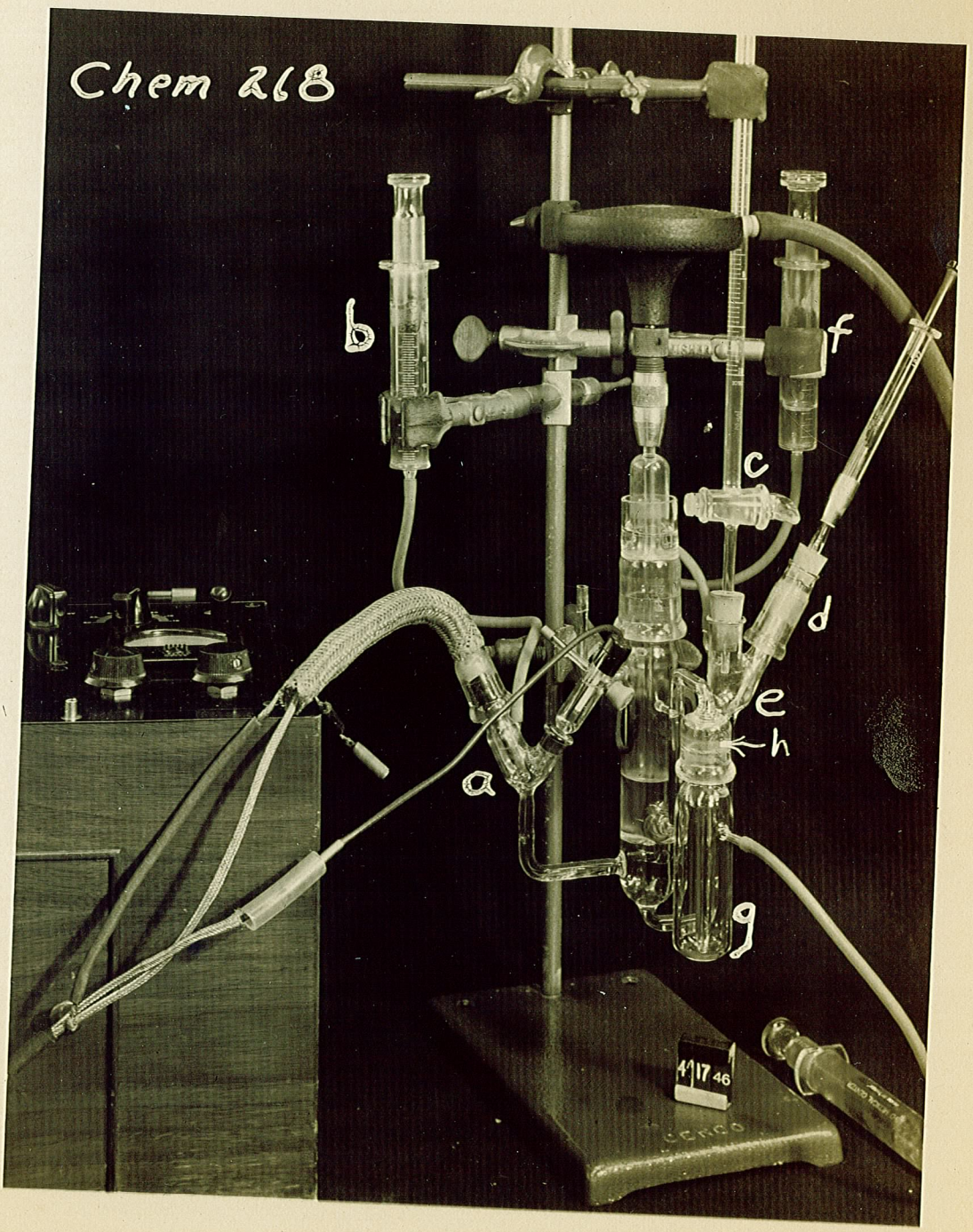


FIG. 1

by means of a syringe controlled pipette mounted and inserted at (d). The movement of the liquid into and out of chamber (e) was controlled by a syringe (f). The benzene layer was sampled by drawing the emulsion up into the sampling chamber (e) and allowing the phases to separate there. Mixing of the phases was accomplished by means of an air driven propellor stirrer operating through a water seal. The side arm (g) was added to allow the benzene phase to be removed as described below (Part 8).

Because of the low solubility of TTA in the aqueous phase, chelation and extraction are accomplished in a reasonable period of time only if the agitation is vigorous. In each case, after the final adjustment of pH had been made, i.e., last addition of acid or base, ten minutes of thorough stirring was allowed before the pH was read and samples removed for analysis. This was sufficient to allow equilibrium to be attained.

The concentration of TTA in benzene that was employed in most experiments was somewhat arbitrarily selected at 0.2M. This concentration was sufficient to permit extraction at relatively low pH. Also, the amount of metal ion undergoing chelation was sufficiently low so that the change in concentration of TTA was small.

The percent of a metal ion extracted into the TTA-benzene phase was determined in several ways.

1. For radioactive elements, or elements for which a radioactive tracer was available, a measure of the radioactivity of aliquots of the benzene and aqueous phases was made.

2. For elements having prominent absorption bands in solution, the extraction could be calculated from spectrophotometric analysis of either or both the phases.

3. Since hydrogen ions are liberated in the chelation reaction, it is possible, under certain conditions, to observe the pH range of the chelation from the buffering in that region. The necessary conditions are met if the amount of hydrogen ion released is comparable to the acid equivalent of the solution.

The third method is generally not applicable to metal ion concentrations below 10^{-3} - 10^{-4}M and cannot be used if chelation takes place in solutions as acid as 0.1M.

2. Extraction of Neodymium by TTA-Benzene.

The extraction of neodymium can be followed by measuring its characteristic absorption spectrum. The interest in neodymium lies in the possibility that small amounts of this element may be present with lanthanum.

The absorption spectrum of ca. .001M Nd in 0.1M HNO_3 solution was first determined over the range 3500 to 10850 A. Principal absorption peaks were found at 5400, 6050, 7925, 8575 and 9350 A*. The amount of extraction in this experiment was calculated from the decrease in optical density† at 7925, 8575 and 9350 A.

To 50 ml of ca. .001M Nd solution was added 50 ml of a 0.1M solution of TTA in benzene. The pH was adjusted by addition of 0.1N NaOH, and the final pH reading after each addition of base was taken after ten minutes of shaking.

The results are shown in Table I.

---

* These may vary somewhat from the true position of the peaks, since the calibration of the instrument was not checked.

† Log I_o/I. See also page 25.

Table I

Extraction of Neodymium by 0.1M TTA-Benzene

pH	Approx. % Nd Extracted at 0.1M TTA
1.13	0
2.83	0
3.20	10
3.58	25
4.20	86

Due to the difficulty in maintaining clear solutions, the accuracy of the values given above is not good. Turbidity in the solutions appeared to be caused by hydrolysis of an ion other than neodymium. The purity of the neodymium used in this study is unknown.

3. Determination of Lanthanum Extraction by Titration Procedure.

Examination of the chelation reaction suggests that a measure of the hydrogen ions released is an index of the extent to which the reaction occurs, provided other factors such as hydrolysis of lanthanum or the acidic nature of the TTA itself do not interfere. If lanthanum extracts at about pH 4, neither of these effects will interfere, since the hydrolysis of lanthanum and the neutralization of the TTA take place at considerably higher pH values.

The experiment was carried out by adding increments of standard NaOH (0.125N) to equal volumes of 0.0062M La^{+3} and 0.2M TTA in benzene and measuring the pH after each addition.

Two curves taken under presumably identical conditions are shown in Fig. 2. The TTA concentration represents only the initial value, since by the time all of the lanthanum was complexed,

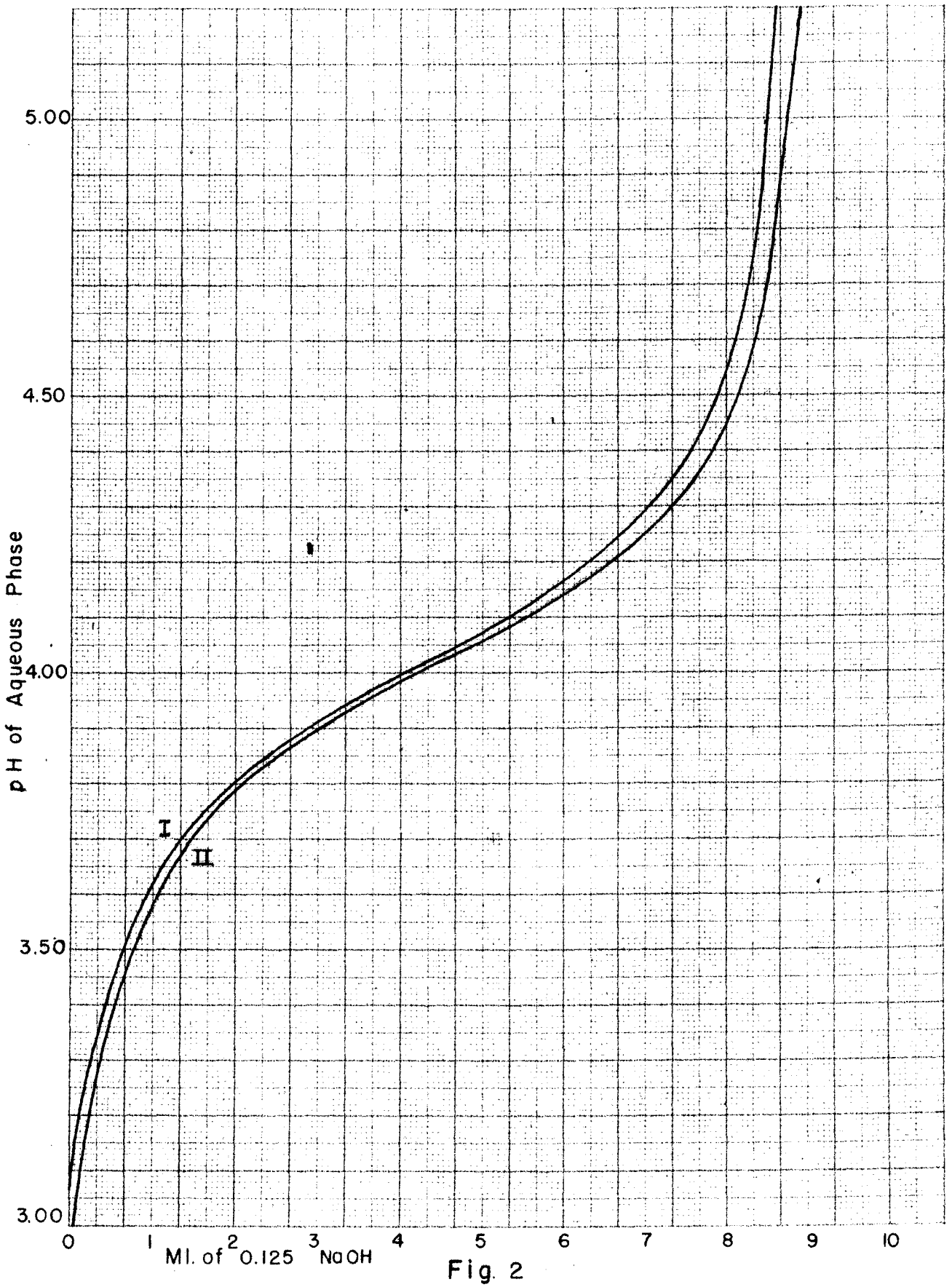


Fig. 2

Milliliters of NaOH vs pH during Extraction of 0.31 Millimoles of La by 0.2 M TTA-Benzene (I and II are Duplicate Experiments)

about 5% of the TTA was present as the chelate. Also at higher pH values some TTA reacts directly with NaOH.

From the titration curves the percent of lanthanum present as $LaKe_3$ may be calculated. This represents the percent extracted if it is assumed that the distribution of the $LaKe_3$ heavily favors the benzene layer. This is very nearly the case. The extraction curve calculated from those data is shown in Fig. 3. While this method gives a reliable determination of the pH range over which lanthanum extracts, the accuracy at low pH values is not as high as desirable.

4. Extraction Curve of Lanthanum Determined by Use of La^{140}.

The La^{140} was separated from the Ba^{140} parent by precipitations of $La(OH)_3$ in the presence of barium holdback carrier using carbonate-free NH_4OH. Each precipitate of $La(OH)_3$ was washed before dissolving. About 1 mg of La^{139} was used as carrier.

The lanthanum was dissolved and diluted to 10 ml and an equal volume of 0.2M TTA was added. The pH was adjusted by the addition of 0.5M NaOH, samples of both phases being taken after ten minute stirring periods and after the pH was found to be essentially constant. The lanthanum extraction was followed by determining the β activity of both phases. A typical extraction curve is shown as the solid line in Fig. 4.

The radioactive decay of the La^{140} samples was followed to check the purity of the preparation. A long-lived activity was present, and it was found to extract at a lower pH than did lanthanum. One decay curve indicated a half-life for the impurity of $\geq$52 days, but the impurity has not been further identified.

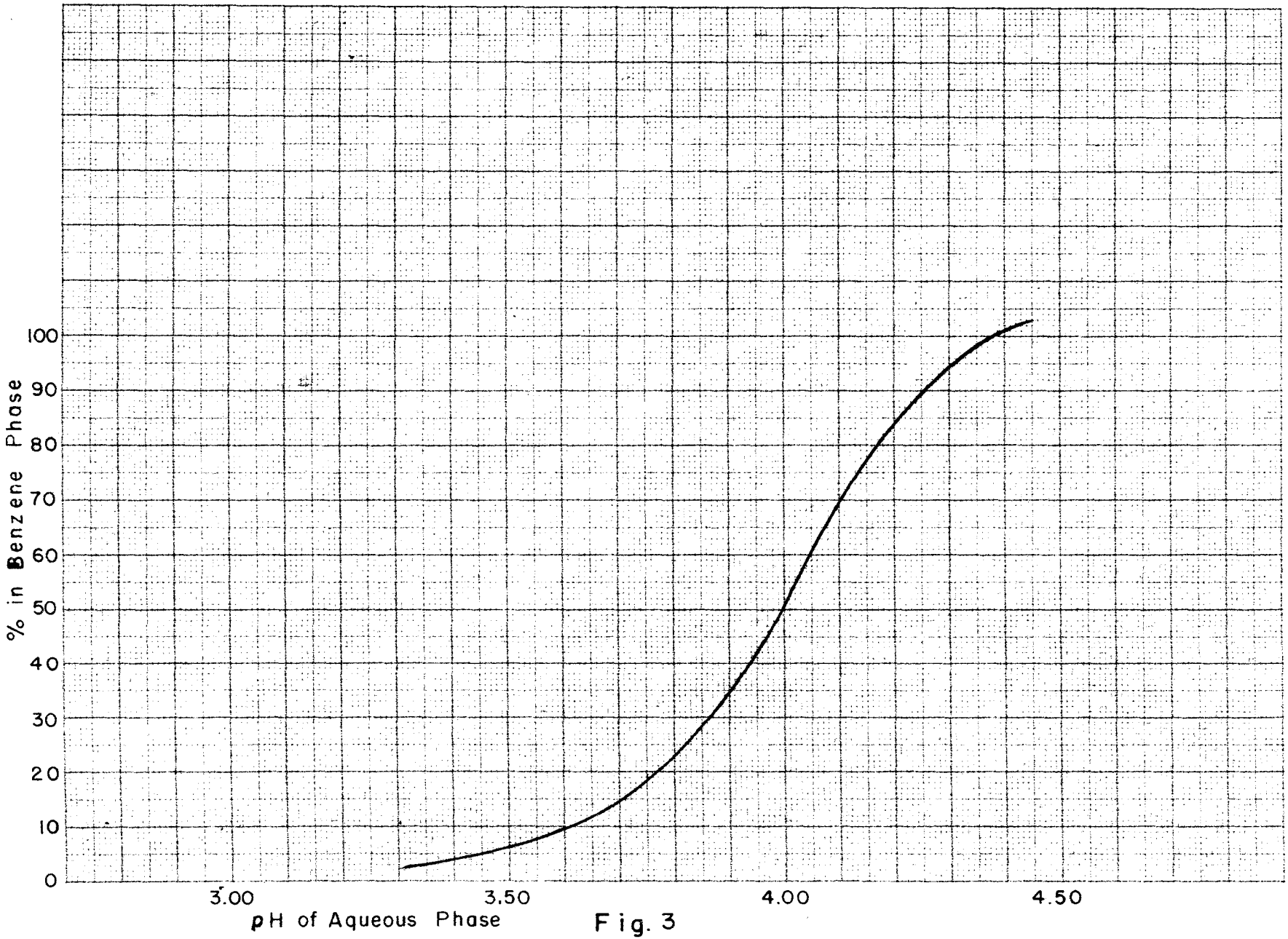


Fig. 3

Extraction of La by 0.2 M TTA-Benzene as Calculated from Titration Data (Fig. 2)

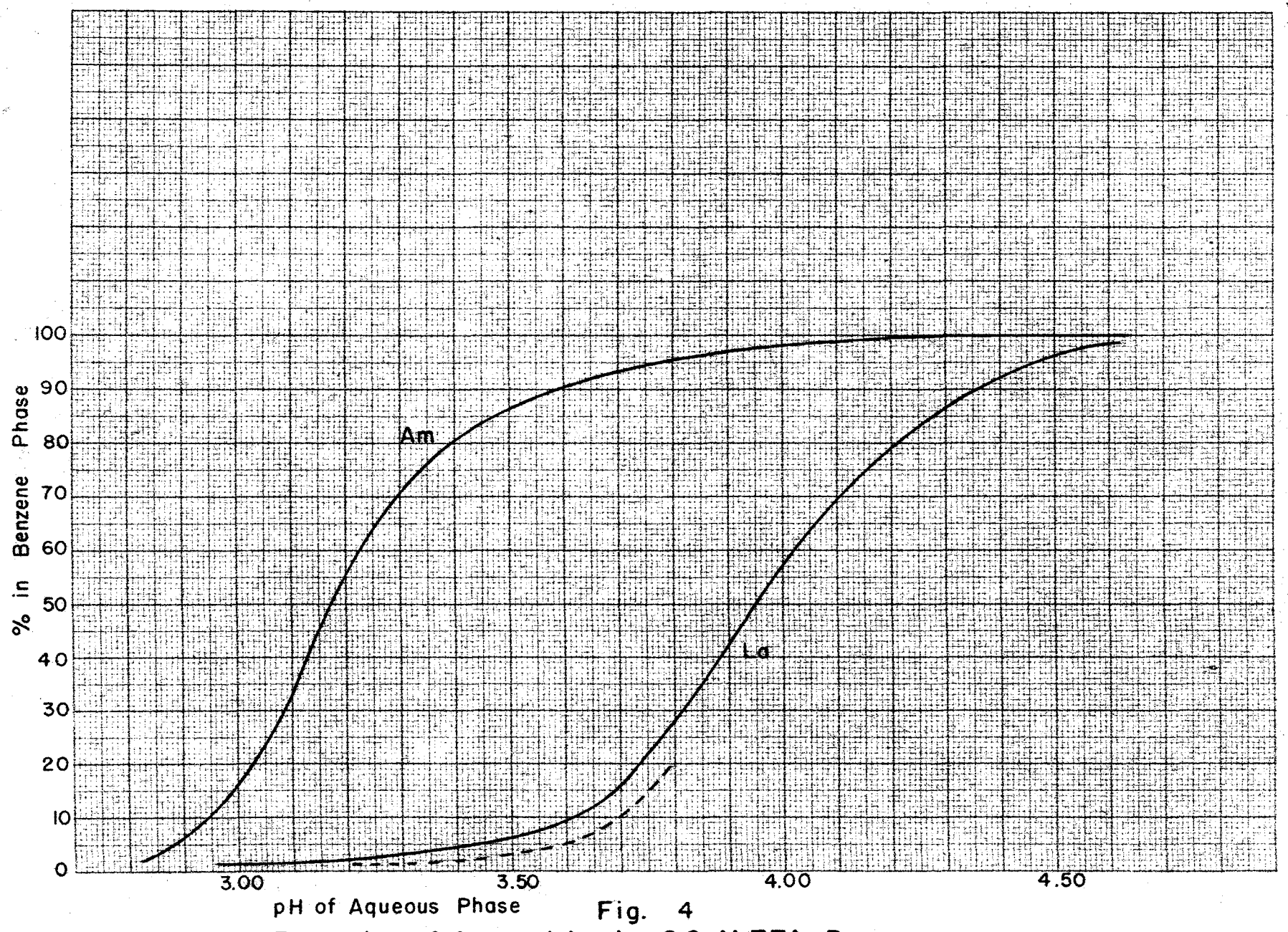


Fig. 4

Extraction of Am and La by 0.2 M TTA–Benzene as Determined by Radio Active Measurement

The corrected extraction curve for lanthanum in the low pH region is shown as the dotted line in Fig. 4.

5. Extraction of Americium with TTA and Benzene.

A procedure similar to that described above in section 4 for lanthanum was used for americium. The samples taken in this case were counted in an α-chamber. The extraction curve is shown in Fig. 4. It is seen that americium undergoes chelation and extraction in a more acid solution than does lanthanum.

6. Effect of Ammonium Ions on Extraction.

During the course of the experiments with lanthanum and americium, a decrease in extraction with time of contact was noted and traced to the presence of ammonium ions. At a given pH there was found to be as much as a 50% decrease in extraction after four hours contact with the aqueous phase which had been made 0.3M in ammonium ion.

This is presumably due to a coupling reaction between TTA and ammonium ions, tending to lower the effective concentration of TTA. For this reason care must be taken to avoid the presence of ammonium ions in solutions being extracted with TTA.

7. Removal of Lanthanum from Americium.

The results of parts 4 and 5 made it seem likely that a satisfactory separation of americium from lanthanum could be achieved and the method was tested on an americium-lanthanum solution which contained appreciable amounts of iron.

For the americium-lanthanum separation the extraction vessel shown in Fig. 1 was used. The side arm (h) extended somewhat below the benzene-aqueous interface with an aqueous volume of 10 ml, and joined a removable receiver (g) for the benzene phase.

By drawing part of the aqueous phase up into the sampling chamber, the level of the interface could be adjusted to allow the benzene phase to be removed fairly completely. Usually three or four one-ml rinses with 0.2M TTA in benzene were used after removing the benzene layer.

Due to the β-activity associated with the americium, it was not possible to follow the actual percent extraction of lanthanum by measuring La^{140} activity with the limited amount of La^{140} available. Instead, only the distribution of the americium activity was checked and it was assumed that the percent of lanthanum extracted at the pH measured was that previously found experimentally (Fig. 4).

Since contact of the aqueous phase with several portions of TTA benzene can be made rather readily, the pH at which highest efficiency is attainable is along the flat part of the lanthanum extraction curve where a small percent of the lanthanum is extracted. The point selected was pH = 3.27. Here the extraction for each contact is 70% for americium and 1 - 2.5% for the lanthanum. After three contacts, the amount of americium left in the aqueous phase is 2.7% and the amount of lanthanum extracted with the americium is 3 - 7.5% of the total. The americium and lanthanum are then removed from the combined benzene layers by shaking with about 1 ml of 0.5M HNO_3 and prepared for a second extraction. If four such extractions (of three contacts each) are made, and if the original ratio of La/Am is as high as 2500, the lanthanum is 0.2 - 8% of the americium in the final preparation, depending on the exact position of the lanthanum extraction curve. A value considerably lower than 8% is indicated by the

actual spectrographic analysis of the final product.

Before the solution was put through the process described in Table II, it was subjected to eight extractions at pH 1 in order to remove the remaining iron. The last three fractions were analyzed and it was found that only 0.1 - 0.3% of the α-activity was removed.

A summary of the final separation of americium from lanthanum is shown in Table II. The time of contact of the benzene and aqueous phases during extraction was in all cases ten minutes or longer after the final adjustment of the pH. Complete re-extraction from the benzene phase into dilute HNO_3 required from 1/2 to 1 hour contact time with stirring.

The acid solution of americium was evaporated to dryness, redissolved and the hydroxide precipitated by addition of NH_4OH. The precipitate was slightly brown in color suggesting the presence of ferric hydroxide, so it was dissolved in 0.1N HNO_3 and extracted with an equal volume (100 μl) of 0.2M TTA in benzene. After this treatment the hydroxide was again precipitated and was only slightly tan in color. The extraction was repeated and this time the hydroxide was pink in color. This color for the hydroxide has been described by Cunningham[3].

One-half of the sample (ca. 10 μg) was submitted for spectrographic analysis*. The results are shown in Table III. The impurities of greatest concern, lanthanum and neodymium, apparently were separated adequately.

In view of the similarity of the chemical properties of Am(III)

---

*Performed by the Metallurgical Laboratory Spectrographic Laboratory.

Table II

Separation of Americium from Lanthanum

Cycle No.	Contact No.	Vol. 0.2M TTA ml	Vol. Aq. ml	pH of Aq.	α Activity in Benzene (%)	α Activity in Aq. (%)	% Am Extracted in Cycle	% Am in Aq. Phase in Cycle	Accumulated % Am in Aq. Phase
1	1	10	13	3.23	74*	26*			
	2	10	13	3.28	72	28			
	3	10	13	3.31	74	26	98	2	
	re-extraction	40	1	0.5M HNO_3	2.5	97.5			95.5
2	1	5	8.3	3.27	75	25			
	2	5	8.3	3.27	69	31			
	3	5	8.3	3.32	--**	--	97.5	2.5	
	re-extraction	27	0.5	1M HNO_3	1	99			92.2
Fe removal	1	5	8.5	2.52	0.7	99.3			
	2	5	8.5	2.52	--	--			
	3	5	8.5	2.52	--	--	2	98	90.4
3	1	2.5	8.75	3.31	89	11			
	2	2.5	8.75	3.27	76	24			
	3	2.5	8.75	3.27	--	--	99	1	
	re-extraction	16.5	0.5	1M HNO_3	0.5	99.5			89.0
4	1	2.5	7.5	3.27					
	2	2.5	7.5	3.25					
	3	2.5	7.5	3.39			99.5	0.5	
	re-extraction	16.5	0.25	1M HNO_3	0.6	99.4			88

*These figures in each case represent the percent distributed between aqueous and benzene phases based upon the amount present during the particular extraction.

**No analysis made.

Table III

Spectrographic Analysis

of 10 μg of Final Americium Product

Element	Milli-μg in Sample	% of 10 μg Am	Element	Milli-μg in Sample	% of 10 μg Am
Al	100	1	Ni	100	1
As	<500		Pb	500	5
Au	< 20		Pd	<50	
Ba	<100		Pr	<50	
Bi	200	2	Pt	<20	
Ca	200	2	Rh	<200	
Cb	<20		Sb	<500	
K	<100		Sc	< 5	
Ce	<100		Si	2000	20
Cr	< 5		Sr	<50	
Eu	<5		Ta	<100	
Fe	500	5	Th	<50	
Ga	<100		Ti	<10	
Gd	<50		U	<500	
In	<100		V	< 5	
Ir	<500		W	< 50	
La	50	0.5	Y	20	0.2
Lu	<200		Yb	<10	
Mg	50	0.5	Zn	<200	
Mn	5	0.05	Zr	< 50	
Mo	<5				
Nd	<50	<0.5			

and Cm(III) it is very likely this method may equally well be used to separate Cm(III) from La(III), a conclusion verified by later work.

III. Higher Oxidation State of Americium

1. Dark Hydroxide of Americium.

It has been observed that precipitation of Am(III) by an alkaline peroxide solution gives a flocculent compound similar in physical characteristics to the pink hydroxide of Am(III) but having, instead, a dark brown color. It has been suggested that the dark color of the precipitate is due either to a higher oxidation state of americium or to a colored peroxide compound of Am(III)[3].

The observation of the dark hydroxide was verified. Addition of KOH to a solution of Am(III) containing H_2O_2 invariably resulted in the formation of the brown hydroxide. If the brown hydroxide is actually a higher oxidation state, such as Am(IV), it is possible that it may be sufficiently stable to be detected shortly after dissolution in a complexing acid such as HNO_3. Ce(IV) forms a nitrate complex in relatively concentrated HNO_3 solutions. The light absorption spectrum of Am(III + x) might be expected to be different from Am(III) and in that case provide a convenient means of observing either the higher state or absence of the lower state. The absorption spectrum of Am(III) in concentrated HNO_3 (15.4 M) (using 16M HNO_3 as a blank) was determined using 1 cm light path micro quartz cells in the Beckman spectrophotometer. A plot of the molar extinction coefficient

ϵ^*, versus wavelength in Angstrom units for two regions of the spectrum is shown in Fig. 5.

A portion of brown hydroxide was washed and 50 µl of a slurry added to 0.3 ml of a concentrated HNO_3 solution at 0°C. The optical density was measured at 5030-5040 A within 60 seconds after dissolving. Log I_o/I was found to be 0.092. Subsequently the readings shown in Table IV were taken.

Table IV

Absorption Spectrum after Dissolution of the Dark Hydroxide of Americium

A	**log I_o/I	†log I_o/I	A	†log I_o/I
5000	.053	---	7750	0.010
5010	.057	---	7900	0.030
5020	.065	---	8000	0.038
5030	.077	---	8100	0.038
5040	.100	.111		
5050	.122	---		
5060	.128	.121		
5070	.128	.121		
5080	.126	.118		

$$^*\epsilon = \frac{\log I_o/I \times \text{molecular weight}}{\text{concentration in g/l} \times \text{cell length}}$$

where I_o is the intensity of the incident light and I is the intensity of the transmitted light.

** Taken within five minutes after dissolving.

† Taken within ca. twenty minutes after dissolving.

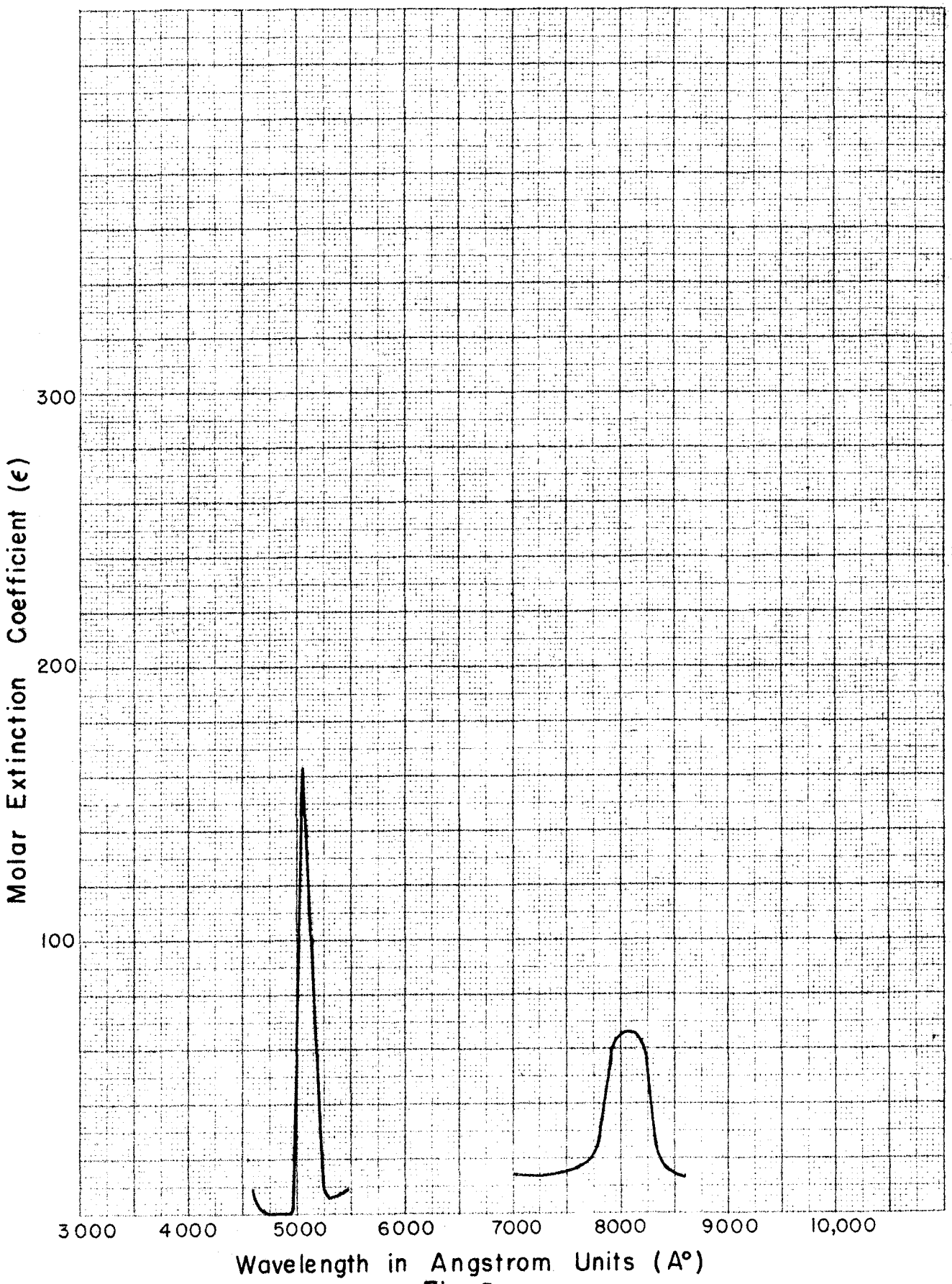


Fig. 5

Absorption Spectrum of Am(III) in 15.4 M HNO_3

The concentration of americium as determined by alpha assay of an aliquot* was 0.18 mg/ml giving

$$\epsilon_{5060\ A} = 162$$

$$\epsilon_{8100\ A} = 51$$

From Fig. 5 $\epsilon_{5060} = 162$ and $\epsilon_{8100} = 66$. Comparison of values of ϵ_{5060} suggests that all the americium was present as Am(III); comparison of the values of ϵ_{8100} suggests that some of the americium may have been present in some other state. Due to the low absorption at 8100 A, ϵ_{8100} may be somewhat less accurate than ϵ_{5060}.

If the brown hydroxide is a higher state, then it is likely either that the americium is oxidized incompletely (surface oxidation) or that it is reduced rapidly to Am(III) on dissolving in acid or perhaps by peroxide not removed by washing. The initial reading at 5030-5040 A is probably consistent with the readings more carefully made later.

2. Oxidation of Am(III) by BrO_3^- Solutions.

An attempt was made to reproduce the experiment performed by Cunningham and Asprey(3) in which evidence was obtained consistent with the oxidation of Am(III) in concentrated HNO_3 - BrO_3^- solutions. Briefly, their experiment was carried out as follows:

The absorption at 5060 A in a solution of Am(III) in 15.3M HNO_3 - 0.02M BrO_3^- was measured using as a blank a solution of 15.3M HNO_3 - 0.02M BrO_3^-, the latter being used in an attempt to compensate for the light absorption of bromine liberated by decomposition of the bromate in concentrated nitric acid. There

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*Specific activity of Am^{241} is 6.46 d/m/μg. See (3).

was an apparent decrease in optical density of the americium solution at 5060 A by a factor of nearly 4. The decrease was linear with time for twenty minutes followed by a slow increase to the original value. A similar but less pronounced decrease in optical density was observed at 8000 A.

Experiments similarly performed were found to give erratic results. This behavior seemed explainable after it was observed that the inception of the Br_2 evolution in the sample and in the blank were not concurrent. A procedure was adopted in which the optical density was measured at three wave lengths in each of the two regions, 4950, 5060, 5250, 7600, 8100 and 8400 A. It was assumed that the absorption curve of all chemical species other than Am(III) would fall on a straight line connecting 4950 and 5250 A, and connecting 7600 and 8400 A where the absorption due to Am(III) is negligible as seen in Fig. 5. The straight line relationship is not precise, but, as may be seen in Fig. 6, it provides a reasonable approximation. An experiment was then performed under the following conditions:

Sample solution

0.02M BrO_3^-

15.3M HNO_3

0.15 mg Am(III)/ml

Blank solution

0.02M BrO_3^-

15.9M HNO_3

or 16M HNO_3

The results are shown in Table V.

Table V

Oxidation of Americium in
BrO_3 - HNO_3 Solutions

Time (min)	Optical Density at 5060 A	Optical Density at 8100 A
0	.098*	.029*
40	.094*	.030*
89	.094	.030
121	.092	.029
151	.084	.032
161	.085	.028

* Using 0.02M BrO_3^- - 15.9M HNO_3 as a blank solution.

It is apparent that oxidation, if any, was incomplete. A subsequent experiment performed at higher BrO_3^- concentrations gave similar results. The results of a study of the absorption spectrum of a freshly prepared BrO_3^- - HNO_3 solution are shown in Fig. 6. It can be seen that a minimum in the absorption at 5060 A occurred within ten minutes after the addition of $KBrO_3$; the absorption subsequently increased, presumably as Br_2 began to be evolved. The explanation of this behavior is not known. It must, however, be considered when evaluating the results of experiments on Am(III) oxidation as described above, since it could be interpreted as a decrease in the concentration of Am(III). Since oxidation, if it occurred at all, appeared to be neither rapid nor complete under the conditions used, its possible use as a basis of Am-Cm separations seemed remote.

3. Oxidation of Am(III) in Alkaline Solution.

It had been shown in the case of plutonium[17] that all the

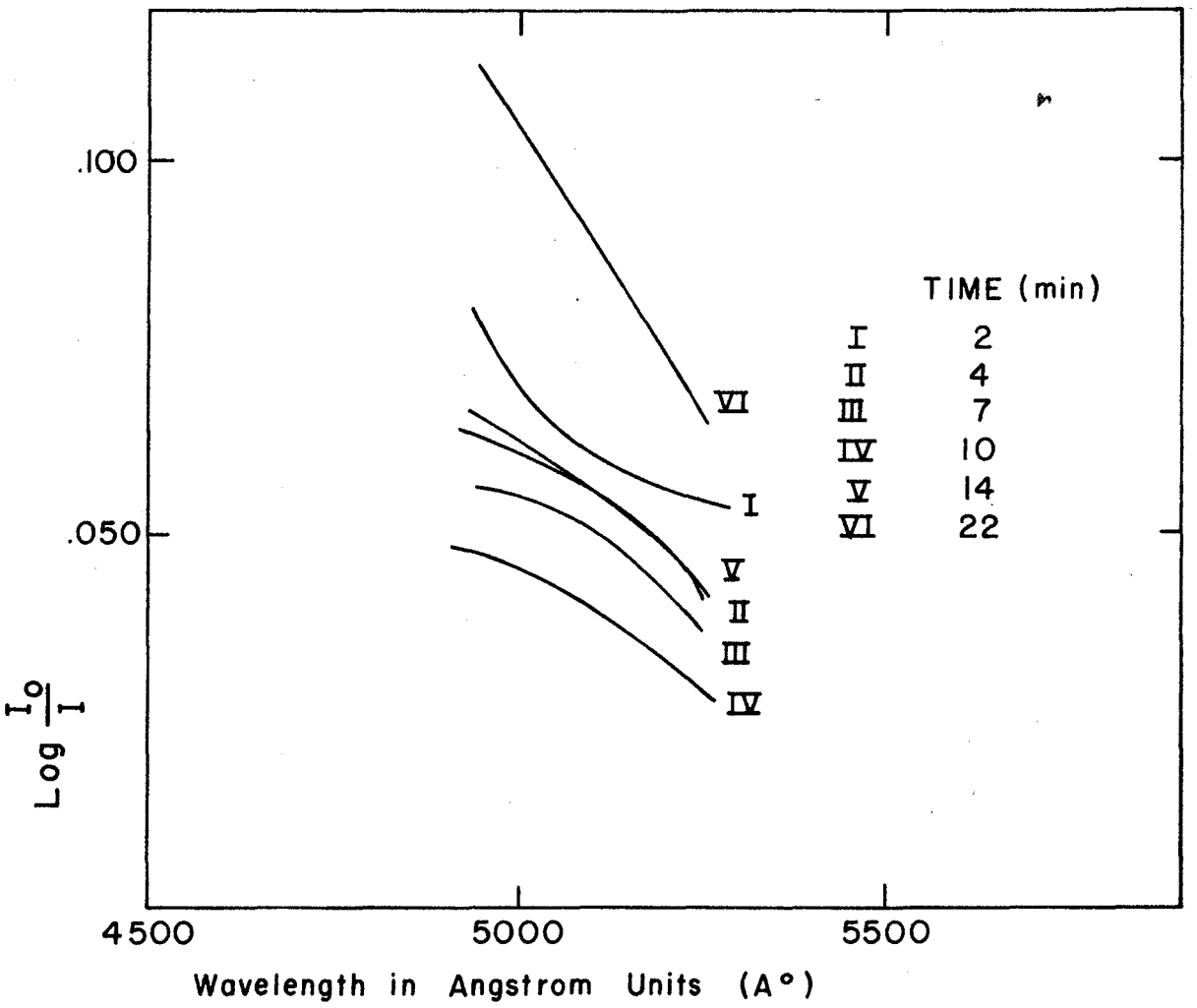

Fig. 6

Absorption Spectrum of ca 0.1M BrO_3^- – 16 M HNO_3

known oxidation states III, IV, V and VI could be obtained in concentrated potassium carbonate solutions. All states were quite soluble, with the exception of Pu(V) which precipitated out of 40% K_2CO_3 solution on standing and attained an apparent solubility of the order of 0.1 mg Pu/ml. The solubility of the other states was sufficiently high (ca. 0.005M Pu) so that use could be made of the characteristic absorption spectra of the various states of plutonium in order to follow the course of oxidation-reduction reactions and to determine the concentrations of the various species.

3.1 Effect of Peroxide on Am(III) in Carbonate Solution. The absorption spectrum of a 40% K_2CO_3 solution containing 0.428 mg Am(III)/ml was measured in the Beckman spectrophotometer using quartz micro absorption cells having a light path of 1 cm.

The absorption spectrum is shown in Fig. 7. Prominent absorption bands occur at 5080 and 8180 A. The values for molar extinction coefficients are 270 and 44 respectively. The solution was then made ca. 0.35M in H_2O_2 and the absorption at 4950, 5080 and 5300 A followed with time. The position of the peak at 5080 A was not altered. Immediately after addition of H_2O_2 ϵ_{5080} was calculated to be 262 (cf. 270). This value remained essentially unchanged (within 3%) for two hours or longer, and at the end of 18 hours was found to be 265. It was concluded that no appreciable oxidation had occurred.

3.2 Oxidation of Am(III) by Hypochlorite in Carbonate Solution. The experiment was repeated except that 15 µl of a 5% NaOCl solution, instead of H_2O_2, was added to 170 µl of K_2CO_3-Am(III) solution (ca. 0.05M OCl^- and 0.415 mg Am(III)/ml). No change was observed in the relative height of the 5080 A peak on standing 50

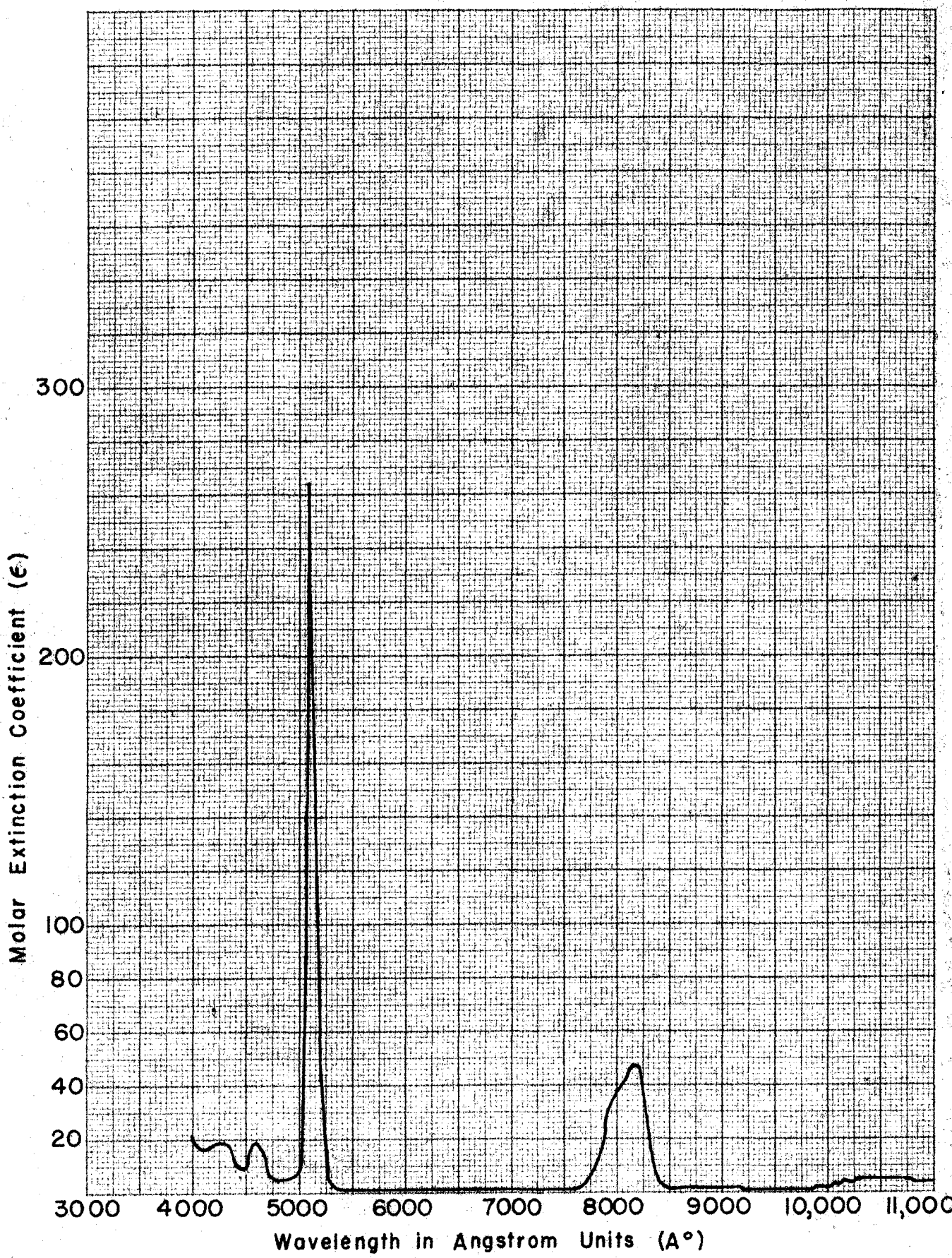

Fig. 7

Absorption Spectrum of Am(III) in 40% K_2CO_3 Solution

minutes at room temperature. However, after 24 hours the peak had dropped to ca. 35% of the initial height and a nearly white precipitate had settled out. The data are shown in Table VI.

Table VI

Log I_o/I of a K_2CO_3 Solution Containing

0.38 mg Am/ml after Hypochlorite Addition

A	Time					
	0	5 min.	15 min.	20 min.	50 min.	24 hours
4950	.034	---	---	0.033	.035	.052
5080	.443	---	---	0.449	.458	.187
5300	.028	---	---	0.023	.026	.044
7700	---	.017	.016	---	.016	.022
8180	---	.085	.085	---	.084	.039
8450	---	.013	.013	---	.013	.012

In a subsequent experiment the 5080 A peak was observed to drop to 17% of its initial value after a five minute period of heating at 95°C after addition of NaOCl solution. Within five minutes after heating, precipitation occurred. The Am(III) concentration remained essentially constant which was shown by the constant peak height above the background absorption (due principally to presence of the precipitate) as measured at 4950 and 5300 A. These data are shown in Table VII.

Table VII

Log I_o/I of a K_2CO_3 Solution Containing 0.39 mg Am/ml after Hypochlorite Addition and Heating

A	Time					
	0*	2 min.	5 min.	10 min.	20 min.	30 min.
4950	.033	.018	.022	.051	---	.201
5080	0.440	.093	.095	.128	---	.277
5300	.027	.019	.022	.054	---	.202
7700	---	.024	---	---	.132	.203
8180	.090	.032	---	---	.153	.207
8450	---	.015	---	---	.137	.188

*Calculated from data in Fig. 7.

Further addition of NaOCl solution and heating at 95°C for five minutes left no detectable peak at 5080 A.

Another experiment was performed using identical Am(III) and K_2CO_3 concentrations, in which the effect of heating in the absence of NaOCl was shown neither to affect the height of the peak at 5080 A nor cause precipitation. After addition of NaOCl and oxidation the 5080 A peak could be caused to reappear by addition of sodium hydrosulfite ($Na_2S_2O_4$), a strong reducing agent. The results are shown in Table VIII.

Table VIII

Effect of Addition of Hypochlorite and Hydrosulfite to a K_2CO_3 Solution Containing 0.24 Mg Am/ml

A	*log I_0/I	Remarks
5080	0.264	Before addition of NaOCl
8180	0.045	Before addition of NaOCl
5080	0.171	After NaOCl addition and heating.
8180	0.029**	After NaOCl addition and heating.
5080	0.258	After addition of sodium hydrosulfite.
8180	0.042	After addition of sodium hydrosulfite.

*"Background" absorption measured at 4950, 5300, 770 and 8450 A has been subtracted as previously described.

** A value calculated from the 5080 A peak and data of Fig. 7 was also found to be 0.029, showing excellent agreement with the observed value.

In a subsequent experiment a solution which contained finally 0.24 mg Am/ml was made ca. 0.1M in OCl^- and heated at 95°C for five minutes. Oxidation was found to be complete. After twenty hours the americium had precipitated to the extent of .035 mg/ml being left in solution. Addition of $Na_2S_2O_4$ at 25°C caused a gradual reappearance of the 5080 and 8180 A peaks in the same ratio.

This seemed to be good evidence that the Am(III) was being oxidized to a higher state, which is slowly precipitated as an unidentified insoluble salt, presumably either a carbonate or a hydroxide (hydrous oxide).

An experiment was performed in which the oxidation of Am(III) and precipitation of Am(III + x) was studied at various K_2CO_3 concentrations. The initial concentrations were ca. 0.05M NaOCl and ca. 1 mg Am/ml. The samples were heated at 95°C for five

minutes. Additional NaOCl was subsequently added to insure complete oxidation. The results are summarized in Table IX.

Table IX

Solubility of Am(III + x) in K_2CO_3 Solutions in mg Am/l

K_2CO_3 concentration	0.1*	0.4	0.8	1.5	2.3	3.0
4.5 hours	--	62	41	28	24	23
24 hours	--	51	26	4	7	6
6 days	5	2	2	2	2	3

*0.1M K_2CO_3 was not sufficiently concentrated to hold this amount of Am(III) in solution. An initial pink precipitate which formed was undoubtedly $Am(OH)_3$. On standing for six days it was converted to a white precipitate.

The remarkably low solubility which is eventually attained is not dependent on the carbonate concentration. For shorter periods of time higher carbonate concentrations appear to favor low solubilities.

4. Absorption Spectrum of Am(III + x).

If the rate of reduction of the higher state in acid solution is sufficiently slow, the possibility exists that one might be able to measure the absorption spectrum of Am(III + x) in acid solution. The higher state was prepared and precipitated in the usual way from a K_2CO_3-NaOCl solution. The precipitate was washed three times with water and dissolved in 0.1M H_2SO_4.

From time to time as the absorption curve was being measured, the absorption of Am(III) at 5040 A was checked as a measure of the rate of reduction of the higher state. It was found that this rate was sufficiently slow to allow the spectrum to be observed. For each interval of time during the measurement, the concentration

of Am(III) was calculated from the height of the 5040 A peak and data from Fig. 8*. The absorption due to the higher state was then obtained by subtracting the Am(III) absorption from the total. The curve shown in Fig. 9 was calculated knowing the concentration of the higher state during each interval. The correction for reduction of Am(III + x) was hardly appreciable, since only about 3% was reduced over a period of 2 1/2 hours during which the spectrum was being measured.

5. Oxidation Number of the Higher State of Americium.

A portion of a precipitate of Am(III + x) prepared as previously described was dissolved in 0.1M H_2SO_4. The absorption spectrum at 4950, 5040 and 5300 A was observed. The spectrum was again observed after the addition of 0.214 μ equivalents of Fe(II). The amount of Am(III) which had been produced by the reduction was calculated from the molar extinction coefficient of Am(III) in the same solution (calculated two days later after complete reduction had occurred). Total americium present was determined by alpha count of an aliquot of the solution. The amount of americium found to be reduced was 0.122 micromoles. Calculation using the Am(III) peak at 8180 A showed the amount of americium reduced to be 0.123 μ moles. This gives a ratio of

$$\frac{\text{equivalents Fe(II)}}{\text{moles Am reduced}} = 1.75.$$

This ratio corresponds most closely

*The values for the molar extinction coefficients in 1M HCl shown in Fig. 8 are nearly identical with those obtained by D. C. Stewart for Am(III) dissolved in a "non-complexing" acid (1M $HClO_4$). (In $HClO_4$ solution $\epsilon_{5040} = 320$, $\epsilon_{8170} = 60$; in 1M HCl $\epsilon_{5040} = 332$, $\epsilon_{8170} = 60$). The correction used for Am(III) absorption is accurate, either if the Am(III) is not appreciably complexed in 0.1M H_2SO_4 or if such complexing does not alter the absorption spectrum of the americium.

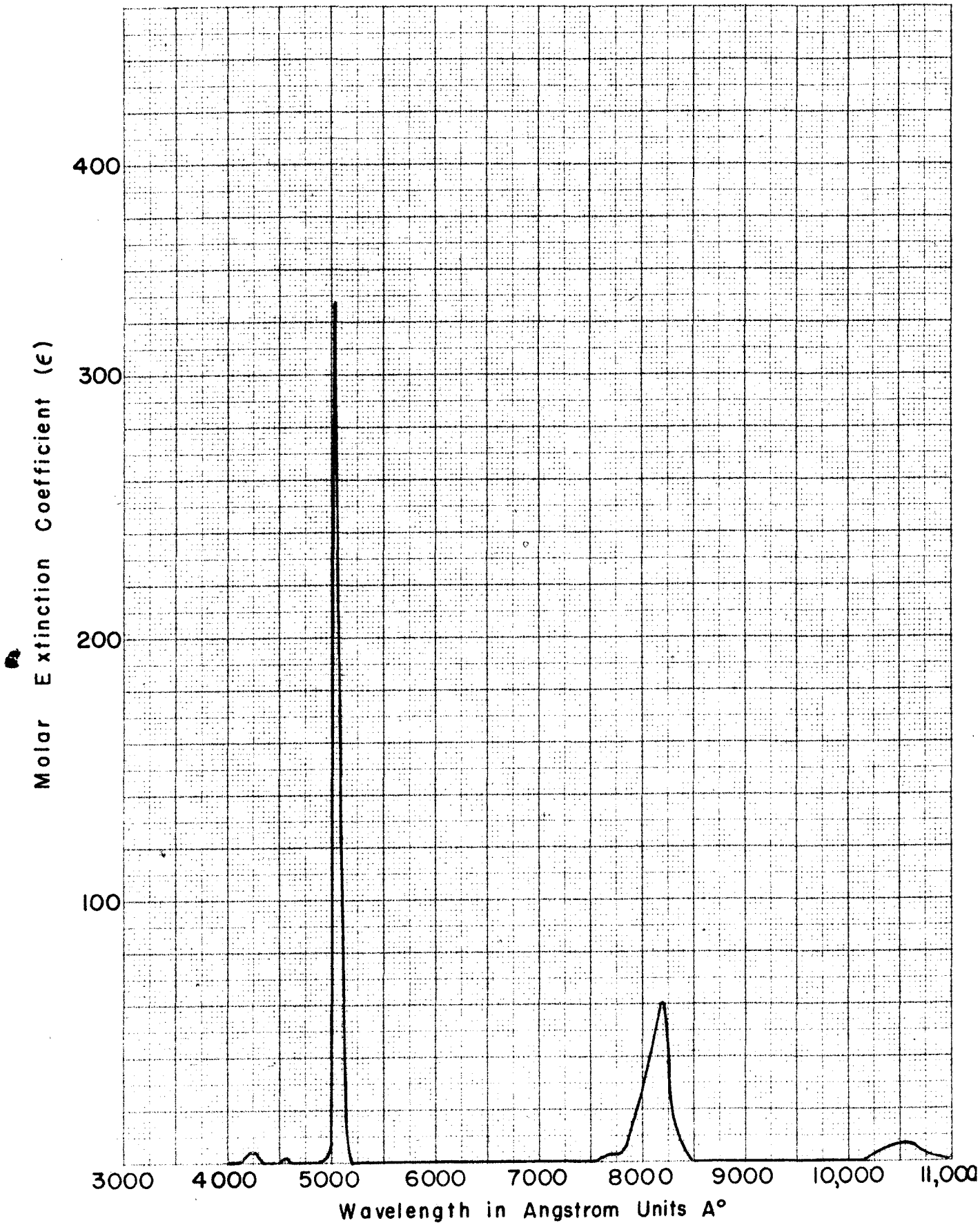

Fig. 8

Absorption Spectrum of Am(III) in 1MHCl

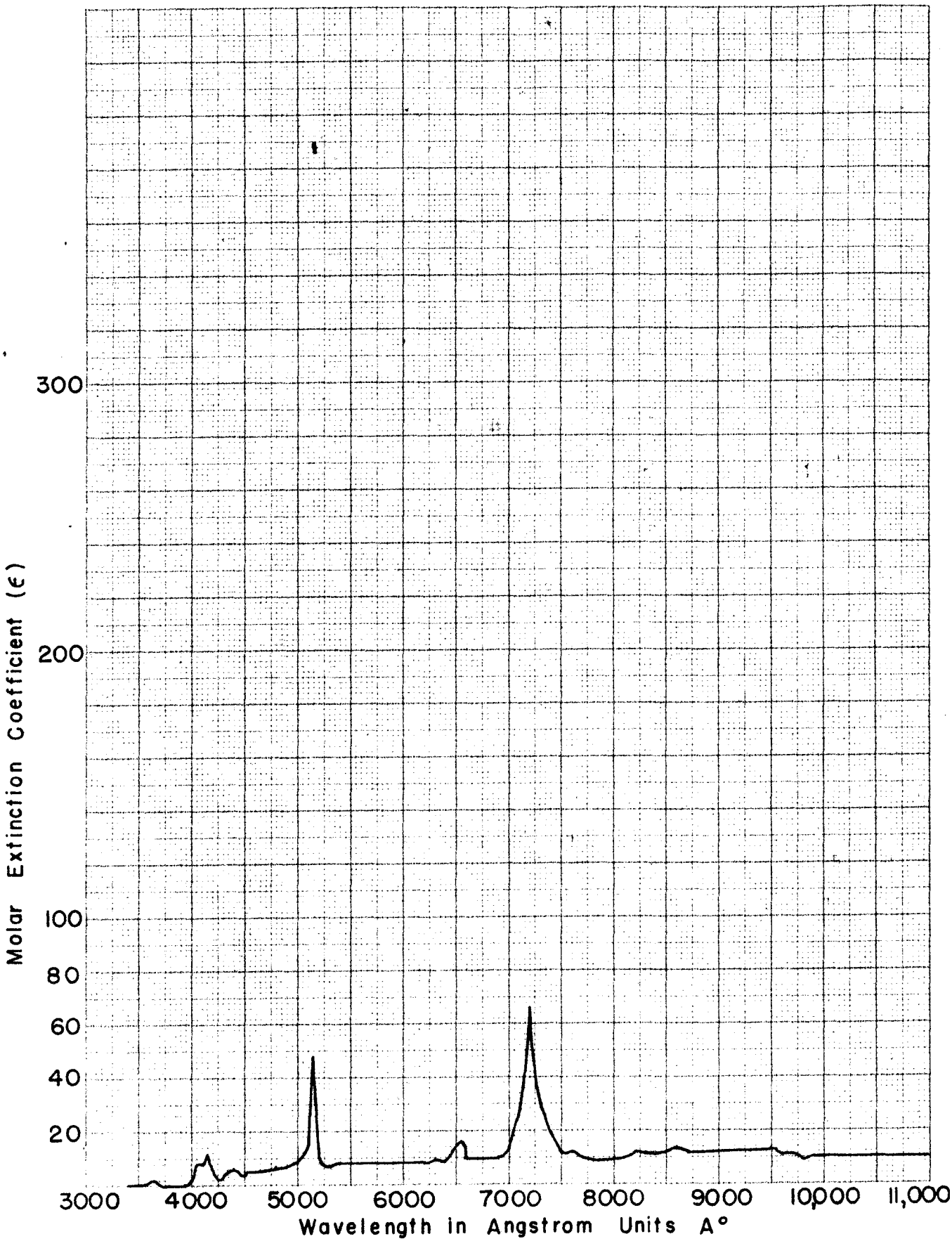

Fig. 9

Absorption Spectrum of Am (V) in 0.1 M H_2SO_4

to that expected if the higher state is Am(V), i.e., R = 2.0. The reason a non-integral value was found is not known. Though not conclusive, the data suggest that the higher state may be Am(V) rather than Am(IV) or Am(VI). This is supported by comparison with the behavior of the corresponding states of plutonium. Both Pu(IV) and Pu(VI) are relatively soluble in K_2CO_3 solutions, whereas Pu(V) exhibits a low solubility. Furthermore, K_2CO_3 solutions of Ce(IV) and Th(IV) when heated with NaOCl showed no tendency to precipitate either shortly after heating or on standing for as long as thirty days.† Both Pu(V) and Np(V) are thought to exist in aqueous solution as the oxygenated ions PuO_2^+ and NpO_2^+(18). The americium ion may similarly be AmO_2^+.

With the need of confirmatory experiments in mind, the higher state of americium will hereafter be referred to as Am(V).

IV. Separation of Curium from Americium.

1. Separation of Curium from Americium in Carbonate Solutions.

Since the chemistry expected of curium would not include the possibility of a higher state, the precipitation property of Am(V) appeared to be a method for separation of americium from curium.

1.1 Precipitation of Am(V) from Carbonate Solution Containing Cm(III). An aqueous 40% K_2CO_3 solution of americium and curium was prepared. The initial concentration of americium was

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† Evidence for a plus five oxidation state of praesodymium has been reported(19). An experiment was performed to determine whether NaOCl could oxidize Pr(III) in K_2CO_3 solution. The absorption spectra of a ca. 0.01M Pr(III)-40% K_2CO_3 solution was determined. NaOCl was then added and the solution heated. No decrease in the height of the absorption peaks could be detected. As a further check an excess of $Na_2S_2O_4$ was then added but no increase in the peak heights was found corresponding to reduction of previously undetected oxidized praseodymium.

ca. 1 mg/ml whereas the curium was present at essentially tracer concentrations (ca. 10^{-3} mg/ml). An aliquot was removed for alpha analysis. The solution was made ca. 0.2M in NaOCl and heated at 95° for five minutes. After standing specified times the solution was centrifuged and an aliquot of the supernatant removed for alpha analysis. The relative amounts of the two alpha emitters were conveniently determined by use of the alpha-particle pulse analyzer designed by Ghiorso, A. H. Jaffey, H. P. Robinson and B. Weissbourd[20].

By means of this apparatus one can determine the numbers of alpha particles having the range of each of the two isotopes. The pulses from selected limits of ranges are fed into 48 channels connected to 48 registers. A plot of counts per minute against the register number then shows a distribution illustrated in Fig.10. The position of the peaks, the separation of the peaks or resolution, as well as the peak width, is dependent upon the design, operation and performance of the counter and on the preparation of the sample to be counted. Thick, uneven samples tend to decrease appreciably in a non-uniform way the effective range of the alpha particles in air.

The initial ratio of the alpha activity of americium to that of curium was about 3 to 1 as seen from Fig. 10a. After oxidation and standing for about 7 1/2 hours the ratio was found to be 2 to 3 (Fig. 10b). Definite enrichment of curium relative to americium was accomplished in the solution. 95% of the curium was accounted for in the final oxidized supernatant, but only 22% of the americium remained in solution.

In a subsequent experiment the americium precipitate from an

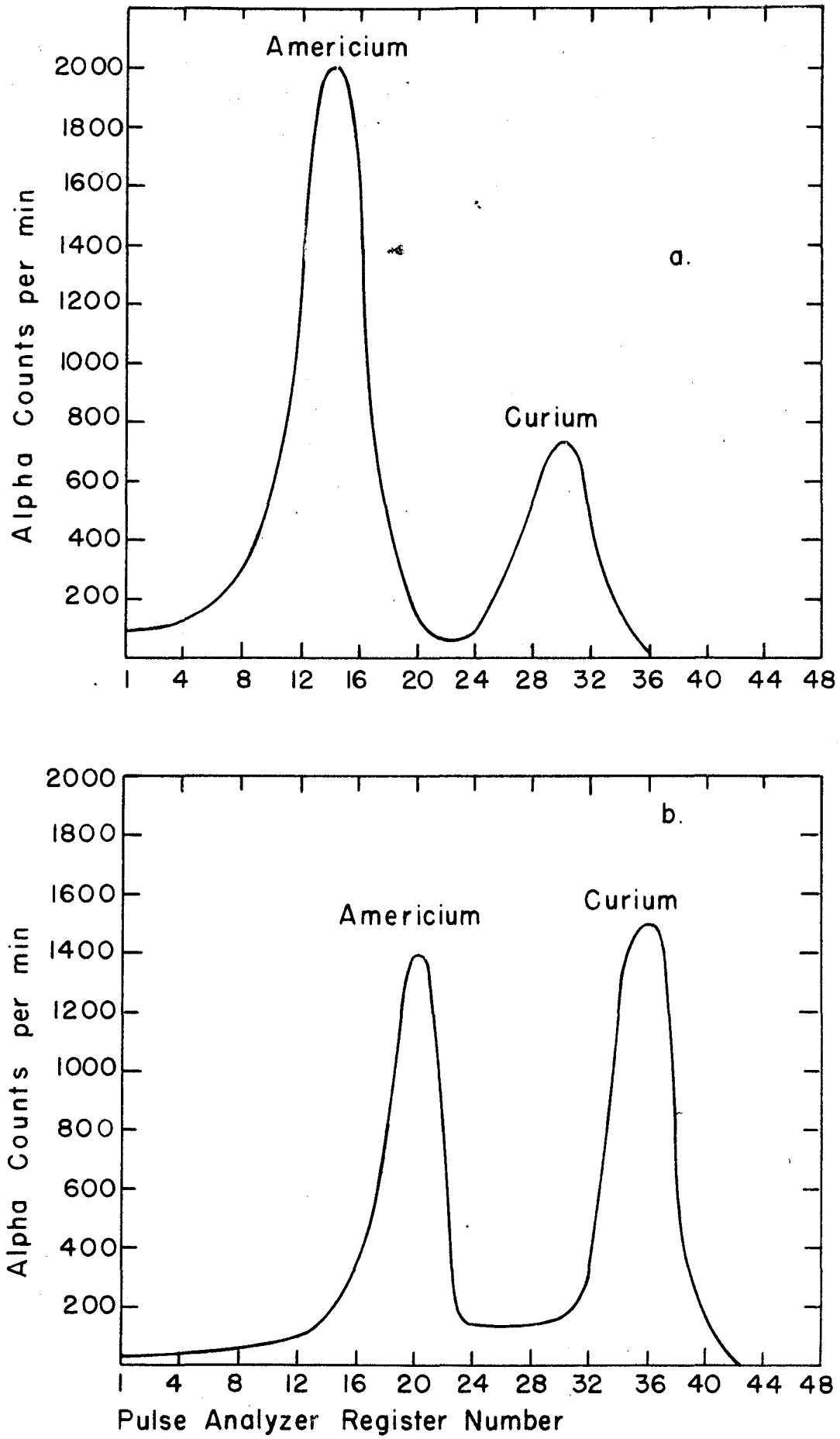

Fig. 10

Alpha Range Analysis of Americium–Curium Mixtures

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Am-Cm carbonate solution was washed three times with 40% K_2CO_3-NaOCl solution and dissolved in acid. Pulse analysis indicated a single alpha emitter was present which was Am^{241}. Limits of detection of the curium alpha activity would have allowed a maximum of about 8% of the total curium to have been present. These experiments and subsequent routine separations of americium from curium have shown the curium loss to be small.

1.2 Carrying of the Am(V) by Ta(V). Although precipitation of Am(V) from carbonate solutions of curium affords a convenient separation of the two elements, the degree of separation is limited by the solubility of the Am(V) compound, as well as the minimum volume in which it is convenient to work. Separation of small amounts of americium by precipitation with large amounts of some other element, which in turn could be more easily removed when present in trace concentrations, seemed worth investigating.

On the assumption that the oxidized form of americium is Am(V), Cb(V) and Ta(V) are suggested as possible carrier materials. Doubt exists, however, of the ability to remove readily traces of either element from curium. A simple experiment was nevertheless run to test the carrying by Ta(V). A portion of an unstable solution of Ta(V) in 2.7M K_2CO_3 solution (ca. 75 mg Ta/ml) was added to a 1M K_2CO_3 solution containing ca. 5 μg Am/ml which had been oxidized at 95°C with NaOCl. Further heating caused precipitation of the Ta(V). Alpha count of an aliquot showed that approximately 20% of the americium had precipitated. Precipitation of a second portion of Ta(V) raised this to 28%.

1.3 Carrying of Am(V) by Pu(V). Np(V) or Pu(V) should be very similar chemically to Am(V). Due to the non-availability of

neptunium the experiments were limited to use of plutonium.

The conditions under which Pu(V) is prepared in carbonate solutions are quite different from those producing Am(V)[17]. In carbonate solutions containing NaOCl, Pu(VI) is the stable oxidation state. Pu(V) may be prepared by treating Pu(VI) - carbonate solutions with Na_2SO_3. Having Pu(V) and Am(V) in the same solution would then depend upon the existence of a slow rate of reduction of Am(V) or a slow rate of oxidation of Pu(V) or possibly both.

100 µg of Pu(IV) was dissolved by adding 25 µl of dilute acid plutonium solution to 150 µl of 40% K_2CO_3. Oxidation of the plutonium to Pu(VI) with NaOCl was accompanied by a change in color from the light green of Pu(IV) to the bright intense green of Pu(VI). With the addition of an excess of solid Na_2SO_3 the color disappeared and the light tan colored precipitate of Pu(V) began to form within an hour. After forty hours the solution was centrifuged and the solid washed twice with carbonate solution. To the precipitate was added ca. 75 µl of a centrifuged Cm-Am-NaOCl carbonate solution which had stood for about a week and which had the following composition:

ca. 25 µg Am/ml
0.1 µg Cm/ml
28% of alpha activity was Am^{241}
72% of alpha activity was Cm^{242}

After stirring the mixture for ten minutes at room temperature, the Pu(V) compound was centrifuged out and an aliquot of supernatant removed for alpha analysis.

Pulse analysis showed 80% of the activity to be Cm^{242}. This

corresponded to a 2% decrease in the concentration of curium and a 35% decrease in the americium concentration. Stirring overnight reduced the americium activity to 5% of its original value leaving a concentration of ca. 3 μg Am/ml. Since previously this low concentration had been achieved without the aid of carrier (Table 9), "the carrying" of Am(V) by Pu(V) may not have been properly demonstrated. The presence of Pu(V) compound did appear to have a profound effect as also illustrated by the following experiment:

An Am-40% K_2CO_3 solution was found by alpha assay to contain 45 μg Am/ml. The americium was oxidized with NaOCl and a solution of approximately 1 mg of Pu(V) in 0.1N HNO_3 was added after cooling both solutions to 0°C. The Pu(V) precipitated immediately as a flocculent white compound. The solution was centrifuged after 15 minutes and an aliquot of the supernatant taken for alpha assay. Pulse analysis indicated that 8% of the total alpha activity was due to Am^{241}. This corresponds to 3 μg Am/ml. Taking into account dilution of the original Am-K_2CO_3 solution, it was calculated that 89% of the americium had precipitated.

One further experiment was performed using the Am-K_2CO_3 solutions listed in Table IX. To each of the solutions containing from 2 to 5 μg Am/ml was added ca. 40 μg of Pu(V) dissolved in 0.1N HNO_3. The solutions were kept in an ice bath for fifteen minutes. For the next fifteen minutes the tubes were removed one by one beginning with the 3.0M K_2CO_3 solution, centrifuged and aliquoted. During centrifugation the temperature of the tubes increased with a consequent increase in the rate of oxidation of Pu(V) to Pu(VI) by the excess of OCl^-. This was apparent from the appearance of

the bright green color characteristic of Pu(VI).

Alpha-pulse analyses were run on each sample to determine what percent of the alpha activity was plutonium. One could thus calculate the concentration of americium remaining in solution. The results are shown in Table X.

Table X

Carrying of Am(V) by Pu(V) Solutions

Initial K_2CO_3 Concentration	0.1M	0.4M	0.8M	1.5M	2.3M	3.0M	3.0M*
Percent of Am removed by Pu(V) precipitation	90	91	89	89	72	91	26

*No NaOCl added.

The results are seen to be uniform with exception of the 2.3M K_2CO_3 solution. Why carrying was low in this case is not known. The apparent carrying of 26% of americium in the solution to which no NaOCl had been added is somewhat surprising. Am(III) should behave like Cm(III), which does not appear to be carried by the Pu(V) precipitate (see above).

2. Use of Ion Exchange Resins as a Means of Curium Purification.

The action of the exchange resin may be represented by the following reaction:

$$3\ NH_4R + Me^{+3} \rightleftharpoons MeR_3 + 3\ NH_4^+$$

Due to difference in the ion exchange equilibria, americium and curium are separated into two bands as a solution is passed through a column of resin. Cm(III) is less strongly adsorbed by the resin and hence comes off the column first. Elution by a complexing agent, such as citrate solution, where a difference in the strength of the complexes of Cm(III) and Am(III) exists,

may enhance the separation. Separation of Am(III) from Cm(III) can be obtained by proper choice of column size, eluting agent and flow rate[11].

V. Isolation of Curium; Determination of the Specific Activity of the Oxide; Calorimetric Determination of the Half-Life.

1. Isolation of Curium.

Results of the previous section indicated that complete separation of americium from curium was feasible. Two samples of americium as the oxide were prepared by Cunningham, Stewart and Thompson for bombardment in one of the Hanford piles. The first sample was denoted as 51 NA and the second as 51 NB. The purity of both samples was as follows:

	%
Am^{241} (by diff.)	96.5
La	3.0
Y	0.3
Ca	0.2
Mg	0.02

1.1 Irradiation of the Americium in the Hanford Pile. Both samples were irradiated in the Hanford pile and were shipped to Berkeley immediately after being discharged. Sample 51 NB received a somewhat longer bombardment than 51 NA.

1.2 First Attempt at Curium Purification and Isolation. Initial operations on sample 51 NA begun September 26, 1946, were carried out jointly with other members of the laboratory including Cunningham, Thompson, P. R. O'Connor and James and with the helpful cooperation of Nelson Garden and his Health Chemistry Group. The sample, mounted in a platinum capsule, was first removed from the lead slug and the aluminum capsule in which it had been irradiated. The oxide was dissolved out of the platinum tube with nitric acid, then placed in K_2CO_3 solution and oxidized with hypochlorite. After precipitation of the americium, the curium and americium which remained in solution were precipitated as hydroxides, dissolved in nitric acid and again put into K_2CO_3 solution. The oxidation-precipitation cycles were repeated twice. The hydroxide was finally dissolved in 1M HNO_3. An alpha assay was carried out to determine the amount of Cm^{242} present. Later calculations from absorption spectra data on this solution (described in section 10) showed that appreciable quantities of americium remained in the solution.

In principle, it should be possible to separate americium from a concentrated solution of curium in aqueous K_2CO_3 solution by oxidation of the americium with NaOCl as described above. In a .01M Cm(III) solution the amount of americium which would remain unprecipitated if the solubility of Am(V) were ca. 2 μg/ml would be 0.1% of the weight of the curium present. This, however, requires that the total volume of the K_2CO_3 solution be of the order of a few microliters. In practice, the difficulties of maintaining an oxidizing medium in the presence of peroxide produced from water decomposition by curium alphas proved to be

insuperable. It was found necessary to dilute the sample appreciably and depend on carrying of Am(V) by Pu(V). By this means it proved to be possible to remove americium to the point where it could not be detected by measurement of the absorption spectrum of the sample solution.

Among the impurities detected by spectrographic analysis of the americium placed in the pile, lanthanum was the most abundant, being present to the extent of about 3% of the total weight of the sample. The concentration of La(III) was thus quite appreciable. Separation from La(III) appeared feasible by use of the method, described in section II, of TTA extractions at selected hydrogen ion concentrations. Use of the TTA extraction resulted in difficulty which was apparently due to the alpha activity of the sample. Phase separation was poor; relatively large amounts of an insoluble material often formed from which it proved to be difficult to recover curium. Decay of the curium and mechanical losses considerably reduced the total amount of the sample. Accidental recontamination with iron of the final sample, which was to have been used for a gravimetric specific activity determination, made further efforts at purification of this sample impractical.

1.3 Isolation of Curium as a Pure Compound. Operations on sample 51 NB were begun on July 17, 1947, immediately after it was received from Hanford. Due to the high level of beta and gamma radiation from the container and from the sample itself, the initial operations were carried out in a "hot laboratory". This room, designed by Nelson Garden's Health Chemistry Group, afforded a well shielded, ventilated area in which remote control opera-

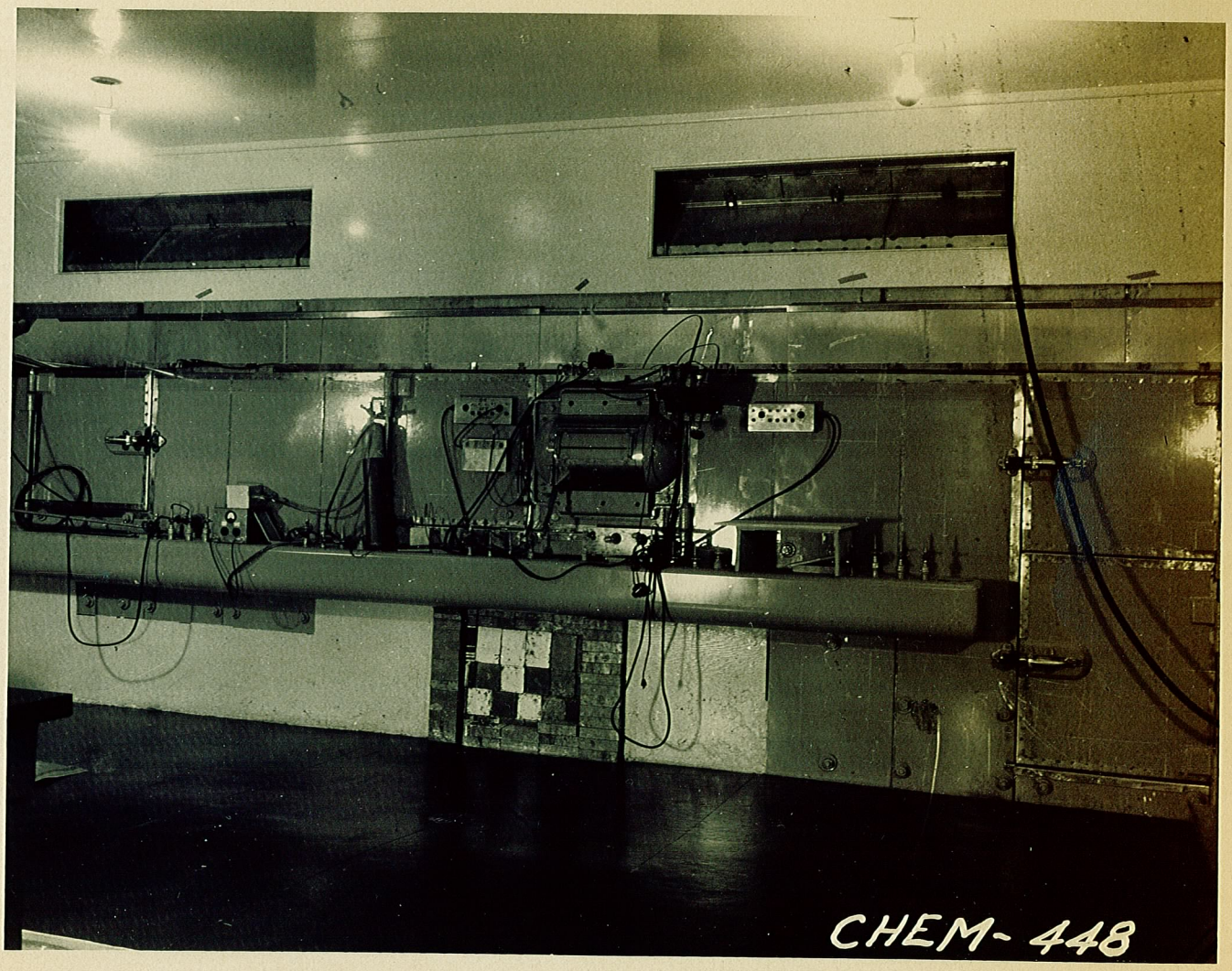
tions could be carried out and viewed with the aid of periscopes and mirrors. (see Fig. 11). Special equipment was designed and constructed, and valuable assistance in the actual operations was performed by John Gifford, Carroll Gordon and other members of Garden's Health Chemistry Group.

The americium oxide sample was dissolved from its platinum container, which had been removed from the slug, and put through a series of chemical reactions designed to remove other isotopes of interest. This phase of the work was directed by Thompson. The sample was received as a dilute HCl solution containing americium and curium. 25% of the entire sample had been retained.

a. Column Separation of Americium and Curium. Separation of americium from curium was achieved by the use of columns packed with the ammonia form of colloidal agglomerates of Dowex 50. The irregularly shaped agglomerates were sieved between approximately 200 and 325 mesh. It was anticipated that difficulty was gas formation and consequent blocking within the column might be encountered with the extremely high level of alpha activity present. Three measures were adopted to minimize this difficulty. 1) The diameter of the column, hence the total volume, was made as large as possible commensurate with the amount of resin available. By this means larger volumes of eluting solution would flow through the column tending to dissolve the gas formed. 2) Argon was bubbled through the eluting solution to remove oxygen and increase the capacity to dissolve oxygen formed by decomposition of the water by radiation. 3) Spongy palladium was mixed with the resin to afford a surface at which the re-combination of hydrogen and oxygen could be catalyzed.

Figure 11.

Shielded "Cave" for Working with High Levels of Gamma Radiation.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The separation consisted of three steps: 1) a 10 cm length, 8 mm diameter column designated to test the operation under conditions to be used with the longer columns, 2) A 50 cm-8 mm diameter column to separate the bulk of the Am^{241} from the curium, 3) A 50 cm-8mm diameter column to separate the last traces of americium from a cut containing impure curium. Samples were introduced on the columns by first adsorbing them from acid citrate solution (ca. pH = 1) using as small an amount of resin as possible. This was then transferred to the top of the resin in the column, giving an active layer several millimeters thick. In all cases 0.25M citrate solution at pH = 3.05 was used to elute curium and americium. In the case of the 50 cm columns, collection of samples was greatly facilitated by an automatic sample changer shown in Fig. 12 and designed by Robinson. The first two column runs were carried out in cooperation with Cunningham and James.

Further details follow:

Column 1 was run at a flow rate of 0.4 $ml/cm^2/min$. Thirty milliliters of effluate were discarded. The next 100 milliliters of effluate collected contained essentially all the americium and curium. Lanthanum present in the original sample remained on the resin, since at pH 3.05 it is very strongly adsorbed from citrate solution. The Am-Cm fraction was re-run on column 2.

Column 2 was run at a flow rate of 0.4 $ml/cm^2/min$. 142 samples having a volume of 2.5-3.0 ml each were collected. The distribution of the alpha activity was determined by counting aliquots of the solution and is shown in Fig. 13. Intermediate fractions which contained both Am^{241} and Cm^{242} were subjected to pulse analysis. From this data, relative amounts of the two

Figure 12.

Automatic Sample Changing Apparatus.

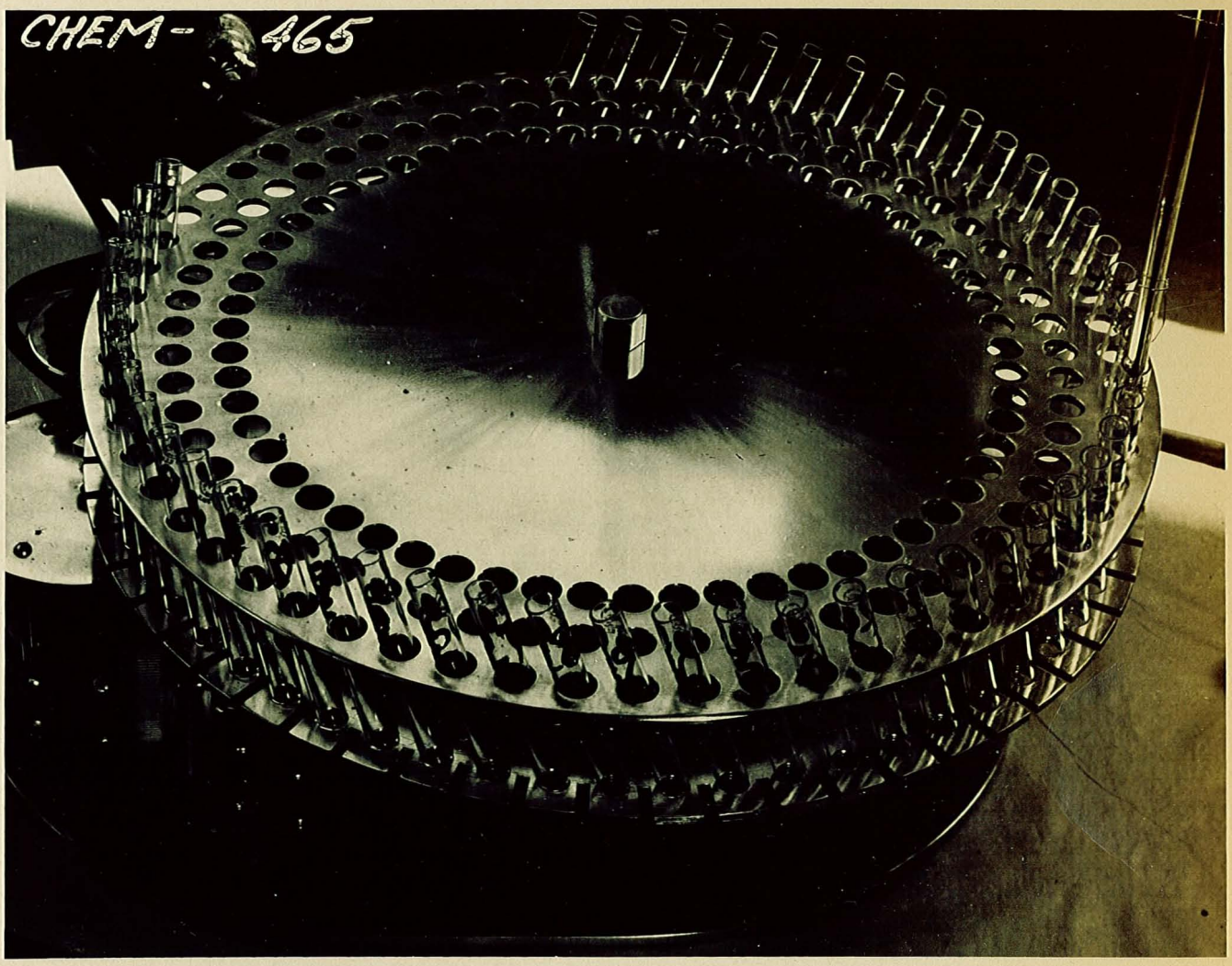

FIG. 12

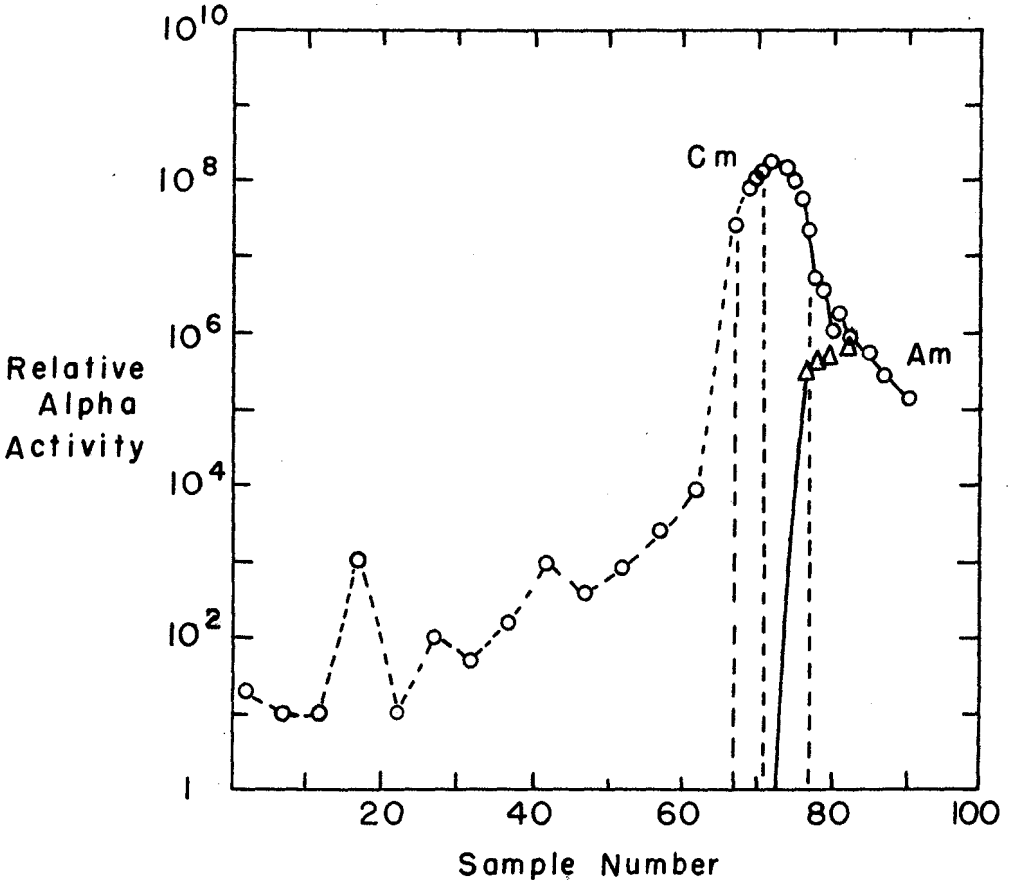

Fig. 13

Elution Curve of Americium and Curium (Second Column)

isotopes could be calculated. However, the first part of the elution curve for americium was inferred from the shape of the curium curve. The curium activity in these intermediate samples far overshadowed that due to Am^{241}. Samples 67 to 71 inclusive contained approximately 40% of the curium and an estimated amount of americium equal to 0.3% of the weight of curium in the sample. Samples 78 to 90 inclusive contained the bulk of the americium with approximately 1% of the total curium. Samples 72 to 77 inclusive contained about 59% of the total curium and a comparable weight of americium. These samples were combined, acidified and readsorbed on resin for further separation in column 3.

Column 3 was the same as column 2, the resin having been rinsed with citrate solution following the first run. The flow rate was again 0.4 $ml/cm^2/min$. 85 samples were collected, and the distribution of activities was found to be that shown in Fig. 14. Retention of samples 61 to 70 inclusive discarded approximately 1% of the total curium and included an estimated amount of americium equal to 0.2% of the weight of the curium run through column 3.

The curium fractions from columns 2 and 3 were combined and assayed. 78% of the original amount of curium was present. 5% of the loss was due to radioactive decay.

It was expected that this fraction would contain no lanthanum, no yttrium, (since experiments have shown Y(III) to be eluted ahead of Cm(III)), and a small percent of Am(III).

b. <u>Concentration of the Cm(III)</u>. The curium was put through a series of chemical reactions designed to concentrate the Cm(III) and to remove impurities.

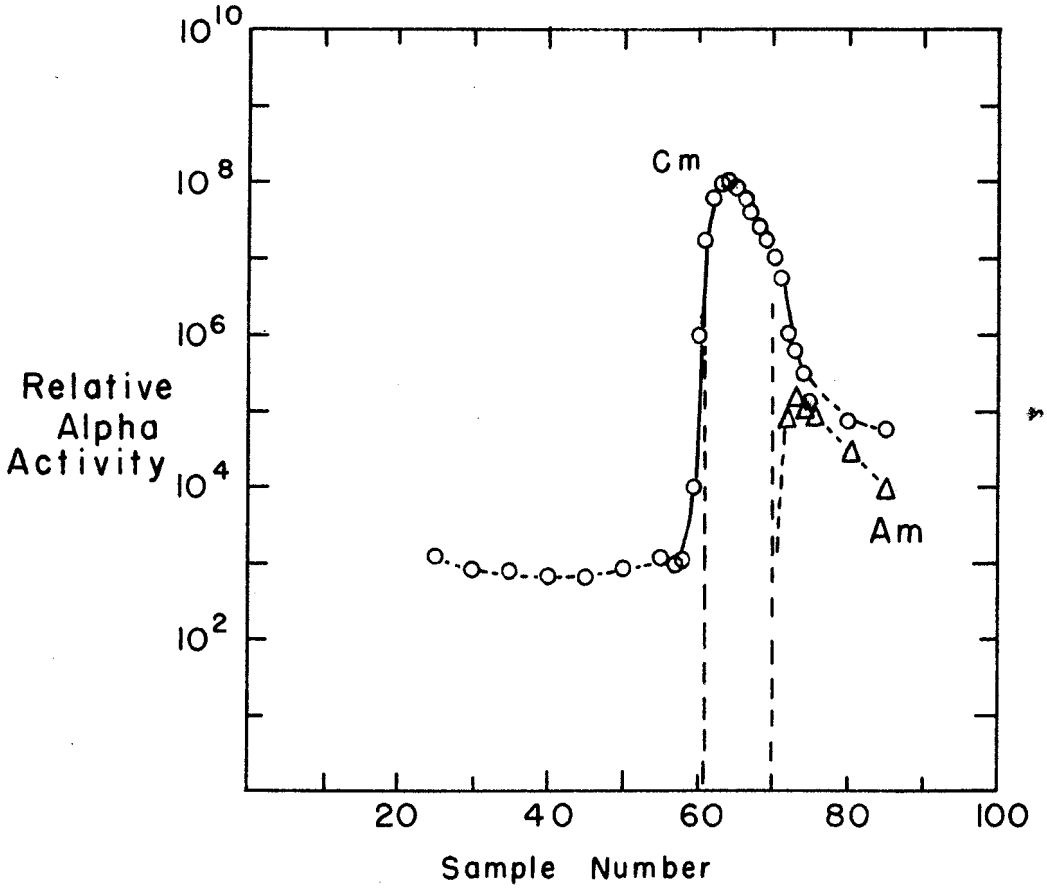

Fig. 14

Elution Curve of Americium and Curium
(Third Column)

To the combined curium fractions having a volume of ca. 50 ml was added 0.4 ml of 12N HCl. Three separate portions of 0.1 ml volumes of resin (ammonia form) were added, stirred and removed. Only 0.3% of the curium was not adsorbed by this treatment. Addition of three separate portions of 0.25M citrate solution at pH = 5.0 eluted 99.8% of the Cm(III). This solution having a volume of ca. 1.5 ml was evaporated to dryness, and the citrate decomposed by addition of concentrated HNO_3 and H_2SO_4 and heating. The residue, after heating to dryness, was dissolved in a minimum amount of water and NH_3 gas blown in. The gelatinous, yellowish precipitate which formed bubbled vigorously. The concentration of Cm(III) remaining in solution was ca. 37 μg/ml. The solution was centrifuged, the precipitate washed, dissolved in dilute acid and NH_3 gas again blown in. The hydroxide appeared slightly lighter in color than before. An enlarged photograph is shown in Fig. 15.

c. Purification of Cm(III) from Pu^{238} and Fluoride Soluble Impurities. The Cm(III) was placed in dilute HNO_3 solution which was made ca. 0.1M in Ag^+. Solid ammonium persulfate was then added until the brown color of Ag^{+2} was apparent. Under these conditions plutonium is known to be oxidized to fluoride soluble Pu(VI).

For the fluoride precipitation an HF-resistant, specially prepared lusteroid tube* was used. The end of a 5 x 25 mm tube was dipped in nearly boiling glycerine and the end pushed out to a point by means of an appropriately shaped wooden mandrel. A relatively small amount of precipitate could then be centrifuged

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*Mfg. by Lusteroid Container Corp., 50 Parker Ave., S.Orange, N.J.

Figure 15.

Curium Hydroxide Precipitate.

the axis of a wheel calibrated either in degrees or in arbitrary divisions. Barely visible in Fig. 16 are the hangdown fibers which run from the ends of the beam down into the pan wells and which are provided with a hook for attachment of a pan hanger. Fig. 17 shows a pan well and hanger (best seen from its shadow on the rear wall) holding a platinum weighing capsule. The length of the capsule is approximately 8 mm. Addition of weight to one side of the balance is compensated for by rotation of the wheel, and the balance is thus restored to the horizontal position or null point. An optical system focuses on portions of a fine index fiber at both extremities of the beam and projects the images on a ground glass screen on two sides of a split field. The null point is easily found by bringing the two images into apposition. The scale is indicated by the one inch high date marker resting on the balance case. The inner balance case is covered by an additional cover shown in Fig. 18. Also shown in Fig. 18 are the ground glass screen (at the far left), in the center of which is mounted a telescope for reading the balance, as well as controls for arresting the beam, rotating the wheel and adjusting the optical system. The particular balance used has withstood total loads of ca. 20 mg on each side of the balance, and compensated for ca. 200 μg or more of untared weight, representing over 360° of revolution of the end of the torsion fiber.

Calibration of such a balance has previously been achieved in two ways. 1) A standard salt solution is prepared, and a small but accurately known volume is delivered quantitatively onto a weighed container, then dried and re-weighed. Knowing the weight of dry salt on the pan a relationship is established between this

Figure 17.

Pan Well of Quartz Microbalance.

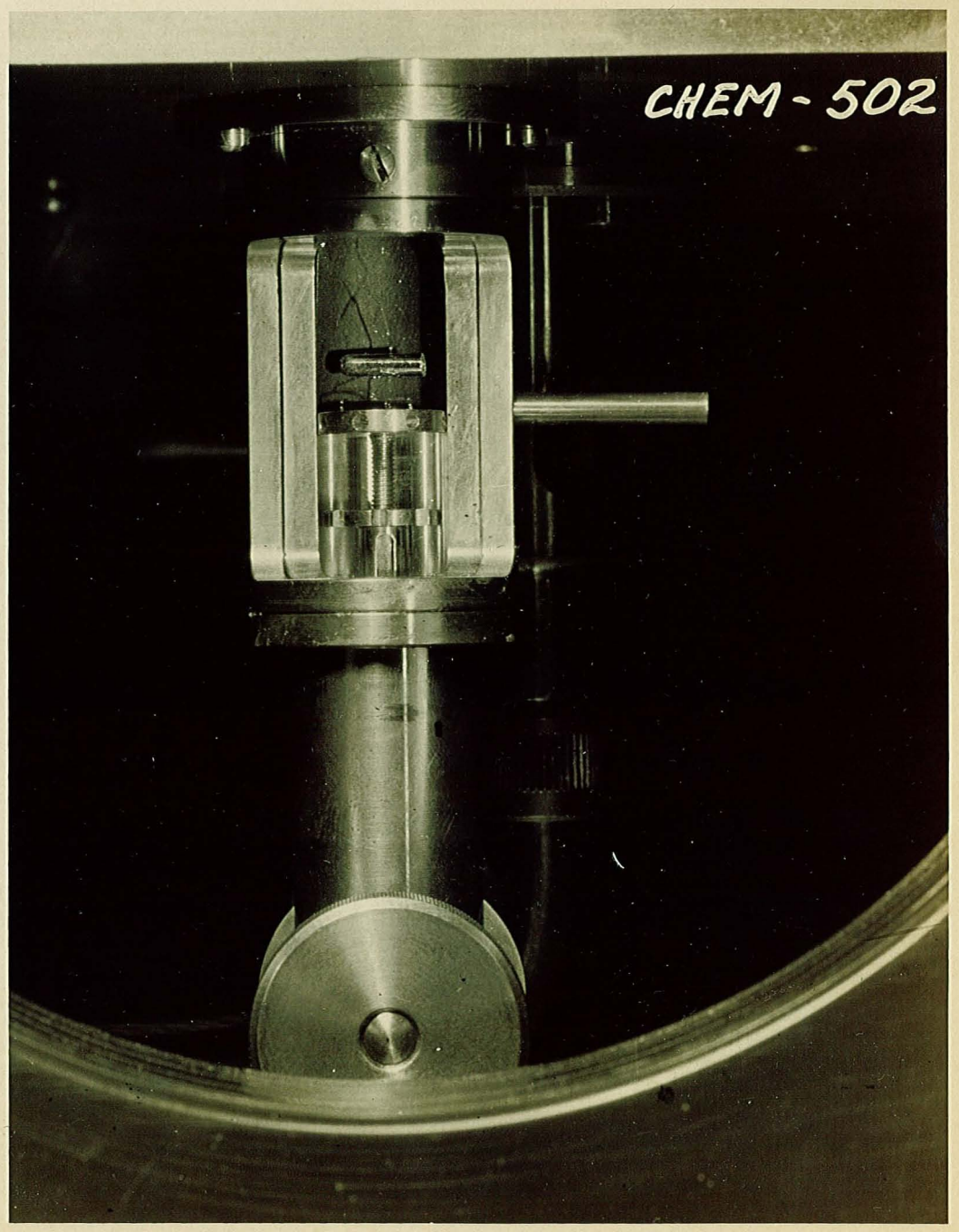
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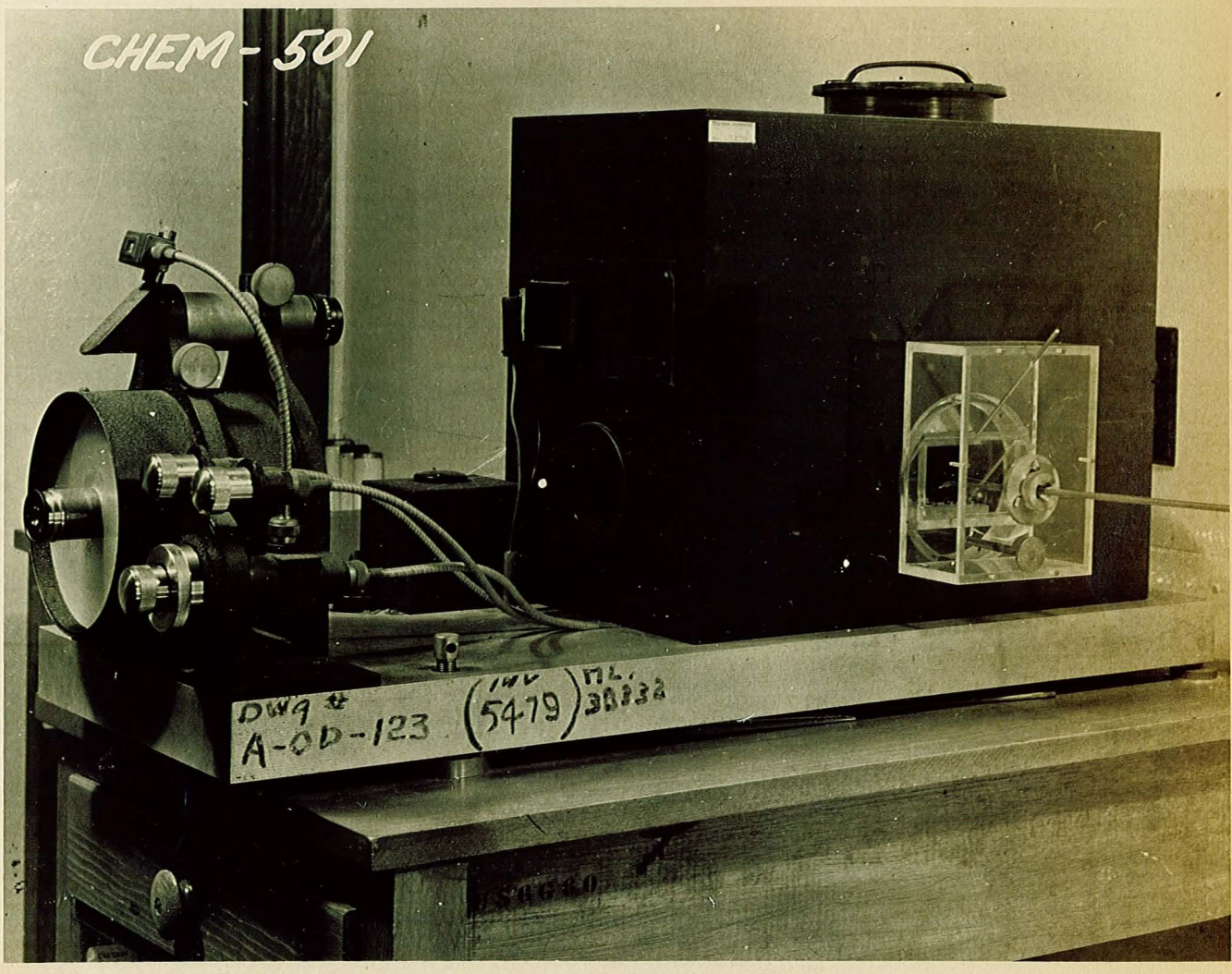
Figure 18.

Quartz Microbalance.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weight and the number of degrees (or divisions) by which the torsion fiber has to be rotated to restore the beam to the horizontal position[4]. 2) A series of weights is prepared each being well within the capacity of the balance. The "weight" (in degrees or divisions) of each one is accurately determined using the quartz balance. A sufficient number of these weights is then combined so that the total weight may be determined to the desired precision on a conventional micro-balance. From this data the relation between divisions and weight of sample is established. The balance used was provided with a wheel whose circumference was marked with 1000 equal divisions. A vernier scale allowed reading to the nearest 0.05 division.

The success of the first method is dependent largely upon proper choice of a salt to be weighed. It should be one which may be readily dried to a constant composition which is stable on exposure to air, within a reasonable range of humidity. Although sodium oxalate is reported to possess these characteristics, its use did not give reproducible results. One division was found to correspond to 0.176 ± 0.009 μg.

In using the second method, 19 aluminum strips approximately 0.5 x 5 mm in size were cut from 1 mil Al foil. A hook to facilitate handling on the balance was bent on the end of each strip. The "weight" in divisions of every strip was added and found to be 15,436.85 divisions. All 19 strips were weighed twice on the Ainsworth micro-balance; the weights were found to be 2.658 mg and 2.652 mg, giving an average of 2.655 mg. The calibration factor

is then $\frac{2655}{15436}$ = 0.1720 μg/div. An independent calibration using platinum weights was made by Stewart. His value was 0.173 ± .001 μg/div. An average of 0.1725 μg/div was taken as the best value.

The calibration was found to be the same when the balance was loaded with ca. 13 mg on each side, this being the weight of the containers used for the curium weighing.

The linear relation between displacement and weight was also checked over the range of 50 to 150 μg. Four aluminum strips were weighed separately and then in various combinations, 1 + 2, 1 + 2 + 3, 1 + 2 + 3 + 4. It was found that in all cases, the sum of the individual weights agreed with the weight of the combinations to within 99.9% or better.

2.2 Preparation of Containers for Weighing Cm_2O_3. Handling a dry compound of such high activity posed a very serious problem. Inhalation or ingestion of extremely small portions of the sample could become a significant health hazard. It was decided to weigh the oxide in two closed containers, one within the other. Due to the limited capacity of the quartz balance, the total load had to be restricted to less than 20 mg on each side of the balance. For the outer container an aluminum capsule 2.5 x 8 mm was machined to a wall thickness of about 1 mil. A tight fitting aluminum cap was made to fit over the end of the capsule. The weight of this capsule was about 9 milligrams.

For the inner container platinum appeared to be the most desirable material because of its chemical inertness as well as its ability to withstand without loss of weight the temperatures required to form Cm_2O_3.

In order to have the weight sufficiently low, the capsules

were made of 0.25 mil platimun foil. The foil was cut into pieces ca. 6 x 5 mm. These were carefully examined for the presence of pin holes. By placing a piece on the palm of the hand and stroking with a dissecting needle, the foil could be rolled into a cylinder. This was then slipped over a tungsten rod 2 mm in diameter, which allowed about 1 mm of the foil to overlap (Fig. 19). The oxy-gas flame of a micro torch was then played along the overlap, heating it to bright red heat, while the overlap was simultaneously rolled with a quartz rod. This treatment is sufficient to weld completely the surfaces together. One end of the platinum tube was then crimped at four places around the edge in such a way that the now closed end had the appearance of a plus sign. Excess platinum was trimmed off using a new razor blade. The end was now sealed by heating, rolling, and hammering lightly against the round end of the tungsten mandrel. These operations were more easily performed when viewed under a low power stereoscopic microscope. The tube was then cleaned with acid and tested for leaks by filling with a concentrated dye solution. The weight was ordinarily 9-10 mgs.

In order to carry the sample to the balance and load it safely, a lucite container with a sliding door was constructed by John Gifford of the Health Chemistry Group (Fig. 20, 18). On one end of a brass tube moving through a ball and socket joint was placed a fine platinum tube (ca. 0.6 mm i.d.). The other end could be connected to vacuum so that when the platinum tip was brought near the capsule, the latter could be picked up and deposited in a new position by pinching off the vacuum line.

A piece of quartz capillary was fused to a section of

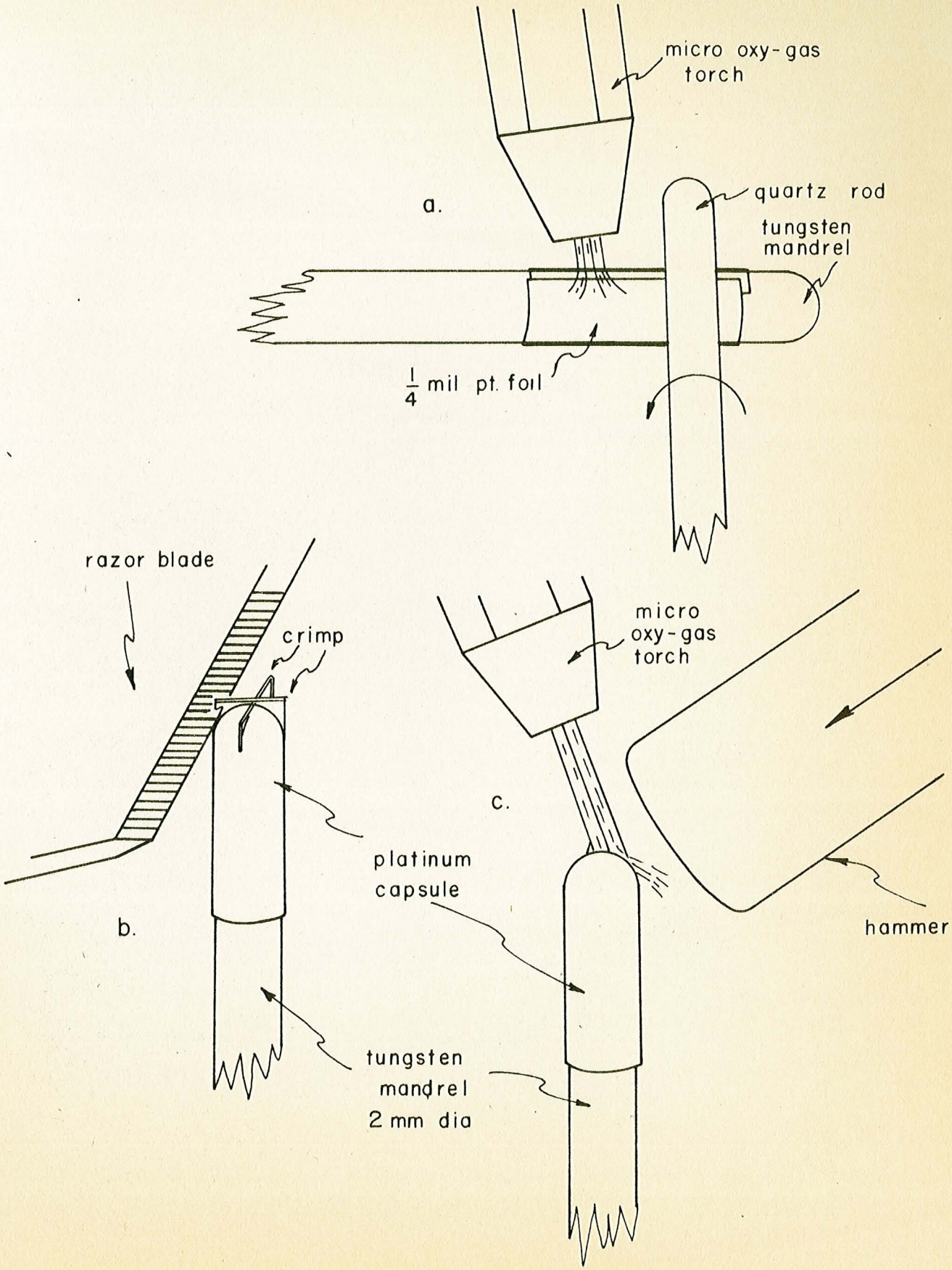
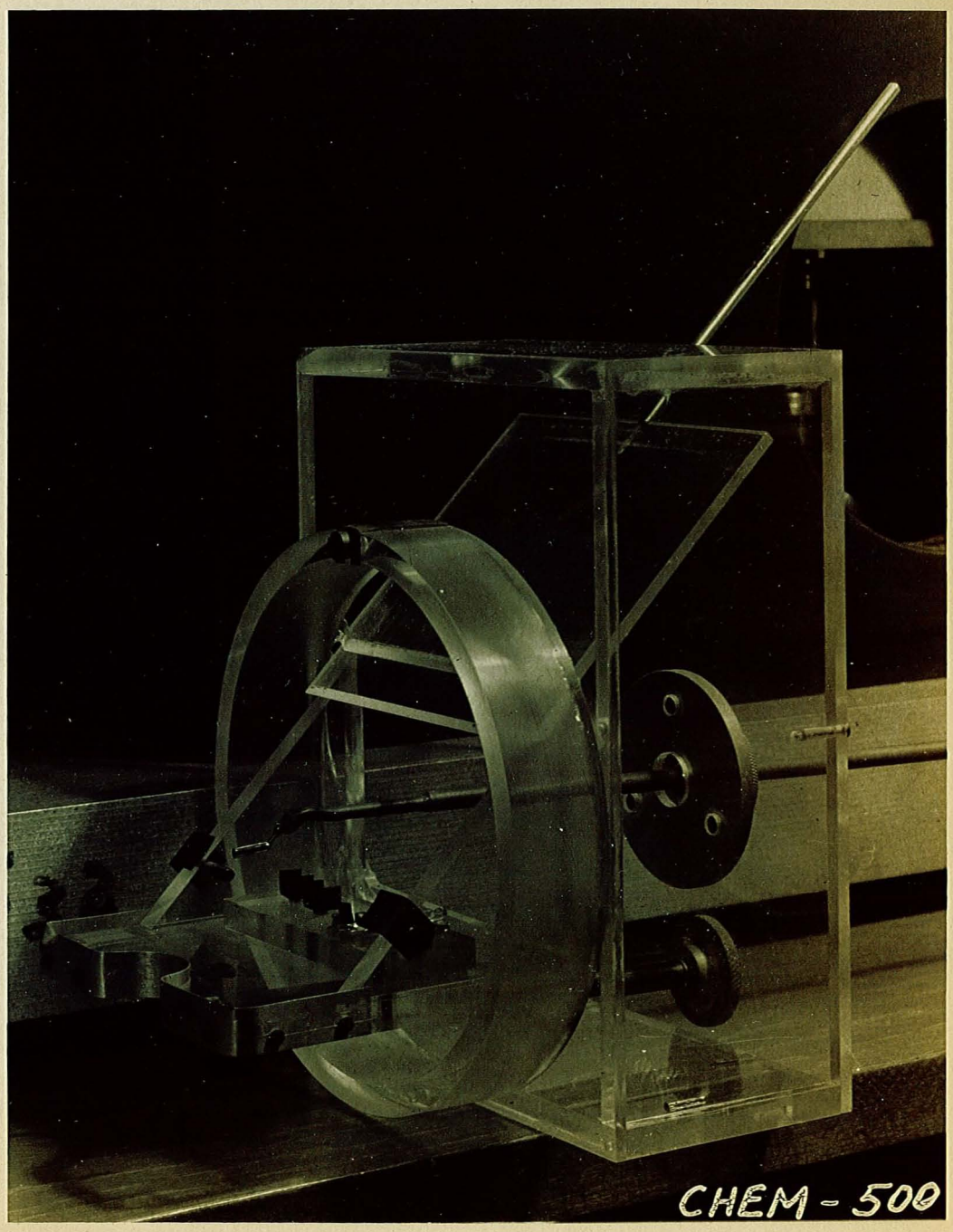


Fig. 19
Construction of Platinum Weighing Capsule

Figure 20.

Lucite Transfer Box.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quartz tubing sufficiently large to hold the platinum weighing capsule. By connecting the end of the capillary to a slight vacuum the platinum tube could be held firmly while loading or manipulating it (Fig. 21).

2.3 Preparation and Weighing of Cm_2O_3. The nitric acid solution of the purified Cm(III) was introduced in two portions into the platinum capsule by use of a fine tipped capillary pipette mounted on a micromanipulator. The platinum capsule had previously been heated to constant weight. The second portion of Cm(III) solution was added after the first had been evaporated to dryness by blowing a gentle stream of warm air from a capillary tube into the capsule. The second portion was nearly lost by formation in the bottom of the capsule of a gas bubble which began forcing the liquid out. Centrifugation succeeded in saving the solution, although contamination of the upper outside edge undoubtedly occurred. The dried curium nitrate was then ignited in air to the oxide using the arrangement shown in Fig. 21. The weighing capsule was kept in the shadow of the quartz holder to avoid evaporation of platinum from the coil onto the capsule. The temperature of the coil was gradually increased until it reached white heat. This was sufficient to heat the capsule to red heat, where it was held for ca. 1/2 hour. After cooling, the top of the capsule was folded down so that only a small slit remained. The capsule was then placed in the aluminum container and transferred to the balance. After the initial reading was made, an unaccountable behavior was observed. The apparent weight of the sample increased rapidly and over a period of ten days nearly tripled. The following observations were made during

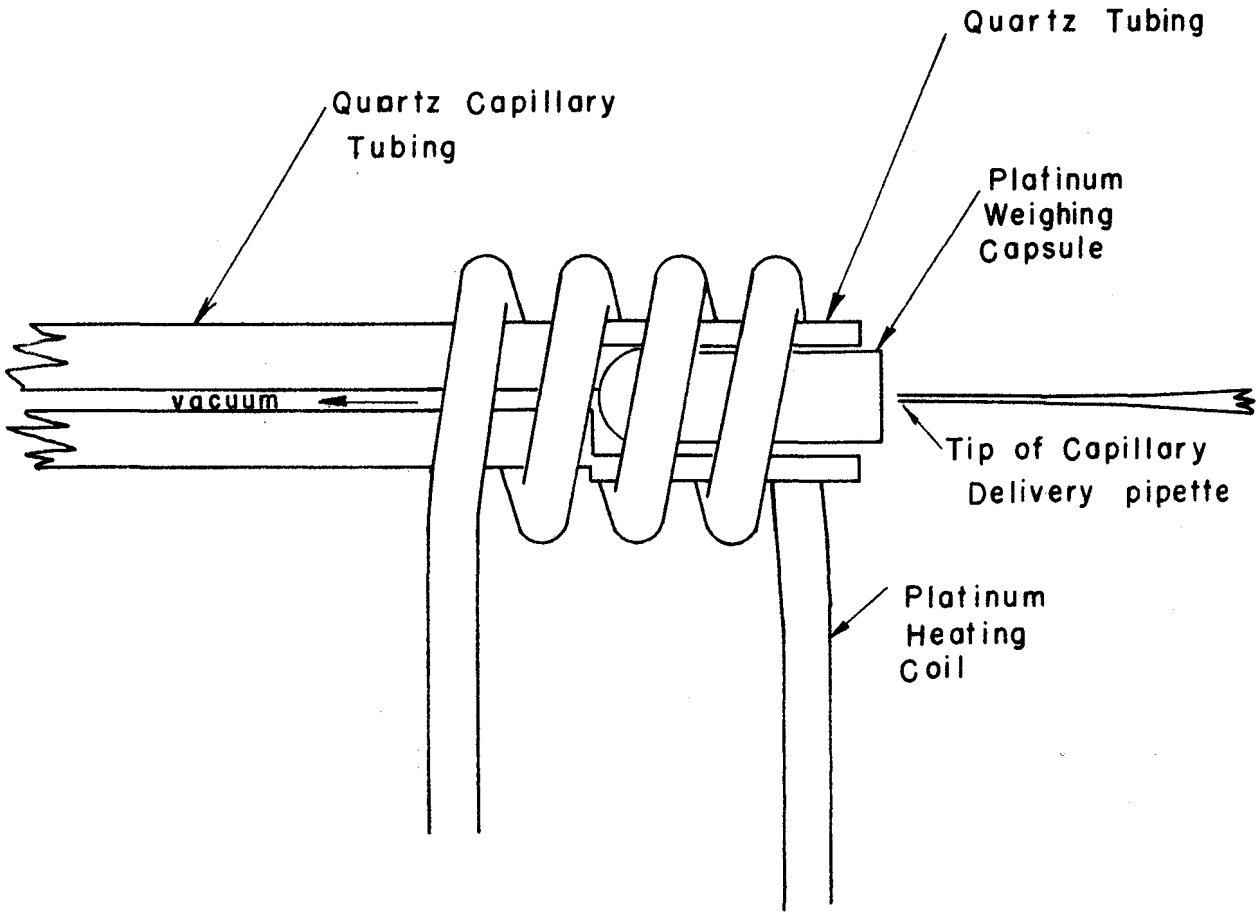

Fig. 21

Arrangement for Loading Weighing Capsule and Igniting $Cm(NO_3)_3$ to Cm_2O_3

this period.

1) The zero point of the balance (empty) did not change.
2) Substitution of an empty platinum tube for the one containing curium was made and the weight found to remain constant.
3) Use of a new aluminum container with the curium did not stop the weight increase.
4) Substitution of a platinum outer container for the aluminum one gave a much slower rate of weight increase. By heating both platinum containers it was found on two occasions that the weight reverted to a constant value, then subsequently increased gradually.

No explanation for this behavior is known. Absorption of water vapor by the sample was ruled out by a calculation showing that a volume of air many times the volume of the sample containers would be necessary to provide the amount of water which would account for the weight increase. It does not seem reasonable to suppose that the presence of radiation had any specific effect on the balance itself. Although the containers should be warm due to the radioactivity and perhaps give rise to convection currents within the balance, it is difficult to see how this could give the gradual apparent weight increase. Air currents have been observed to disturb the balance in a random manner.

The weight of the sample was finally determined by extrapolating the curve of balance readings versus time back to the time the sample was removed from the furnace.

2.4 Alpha Assay and Calculation of Specific Activity. A portion of concentrated HNO_3 solution was added to the Cm_2O_3. After warm-

ing for five minutes it appeared to have dissolved completely. The solution was diluted to exactly 1 ml in a micro volumetric tube and 1.075 µl aliquot removed and counted in a chamber having a calculated geometry factor of 7490 to convert to 50% geometry.

After dissolving the Cm_2O_3 the platinum capsule was rinsed, dried, and reweighed. By difference a second value for the weight of the oxide could be calculated. Assuming no impurities other than those detected and taking into account the decay of the curium, the composition of the final oxide preparation was calculated to be:

Cm_2O_3	83.7%
AmO_2	4.9%
PbO	1.0%
PuO_2	10.4%
	100.0%

The weight of curium in the sample was then compared with the amount of Cm^{242} determined by alpha-analysis. This indicated that ca. 3% of the sample may have been undetected impurities.

Using the first weight determined and the quantities of known impurities, the composition of the oxide was found to be:

Cm_2O_3	88.7%
AmO_2	4.9%
PbO	1.0%
PuO_2	5.3%
	99.9%

Correcting for decay from the time the sample was weighed until the alpha analysis was performed the amount of the Cm^{242} was

compared with the weight of curium. These data suggested that the undetected impurities may have been 12% of the sample.

It is difficult to evaluate these results without knowing the cause of the gradual apparent increase in weight of the sample. It is possible that much of the increase while using the aluminum capsule was due to a chemical reaction, such as oxidation, initiated by the radioactivity of the sample. Platinum containers should show no such effect. Although the heat liberated by the sample was measured accurately, neither the temperature attained by the capsules nor the effect on the balance of weighing a warm sample is known.

2.5 Appearance of Cm_2O_3. In the rare earth elements the colors of the sesquioxides are very similar to the colors of the aqueous ions. By analogy, Cm_2O_3 would be expected to be nearly white. Microscopic examination of the oxide after weighing showed it to be dark brown in color. The color could be caused by the presence of undetected impurities. However, an interesting appearance of color in the mixed oxides of trivalent and tetravalent rare earth elements has been observed and may be the phenomenon responsible for much of the color observed in the Cm_2O_3. Mixed oxides of Ce(III) and Ce(IV)[23], Tb(III) and Tb(IV)[24], and of La(III) and Ce(IV)[25] show a dark color not characteristic of either oxide separately. Since both Pu(IV) and Am(IV) are present in significant amounts in the Cm_2O_3, the presence of a dark color is not surprising.

3. Calorimetric Determination of the Half Life of Curium.

At the time that the Cm_2O_3 sample was contained in platinum capsules, a calorimetric determination of the half life was per-

formed by Edgar F. Westrum[26]. The energy liberated by the curium sample was determined in four ways: 1) observation of the steady state temperature differential between the calorimeter and thermostat, 2) observation of the approach rate to this temperature from both directions, combined with the thermal leakage modulus and the heat capacity of the calorimeter, 3) and 4) achieving conditions identical with either 1) or 2) above, by input of an equivalent input of electrical energy. All of these methods indicate that the minute sample liberated energy at the rate corresponding to a half life of 158 ± 6 days on the basis of the known range of the alpha particle and the range-energy relationship of Halloway and Livingston. This half life is in agreement with the value of 164 days observed by James from radioactive measurements extending over a period of several months. The larger uncertainty in the half life than in the energy measured calorimetrically arises from the difficulties in the weighing of the sample. Calculations were based on the initial extrapolated weight.

VI. Absorption Spectrum of Cm(III); Spark Spectrum of Curium.

1. Absorption Spectrum of Cm^{+3}.

The nitric acid solution of curium and americium described in Section V, paragraph 1.2, was placed in a micro quartz absorption cell* having a light path of 1 cm. The cell had been fitted with a ground glass stopper as shown in Fig. 22. A Beckman Spectrophotometer was fitted with a ventilated box (equipped with air filters) enclosing the chamber where the sample was placed (Fig.23). The design and construction of this box was carried out by Herman

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*Pyrocell Mfg. Co., 207-11 East 84th Street, New York 28, New York.

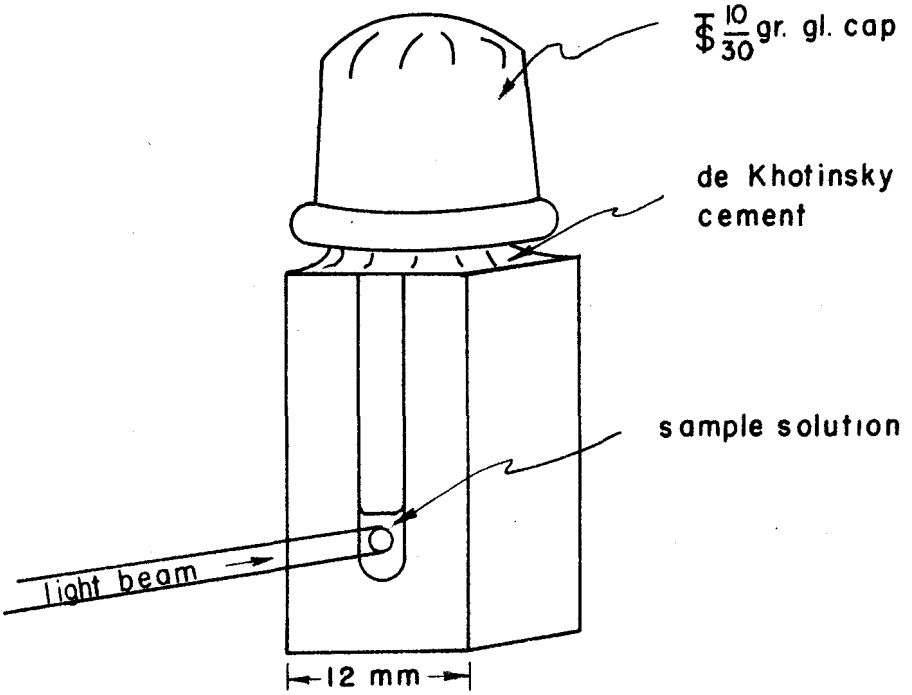
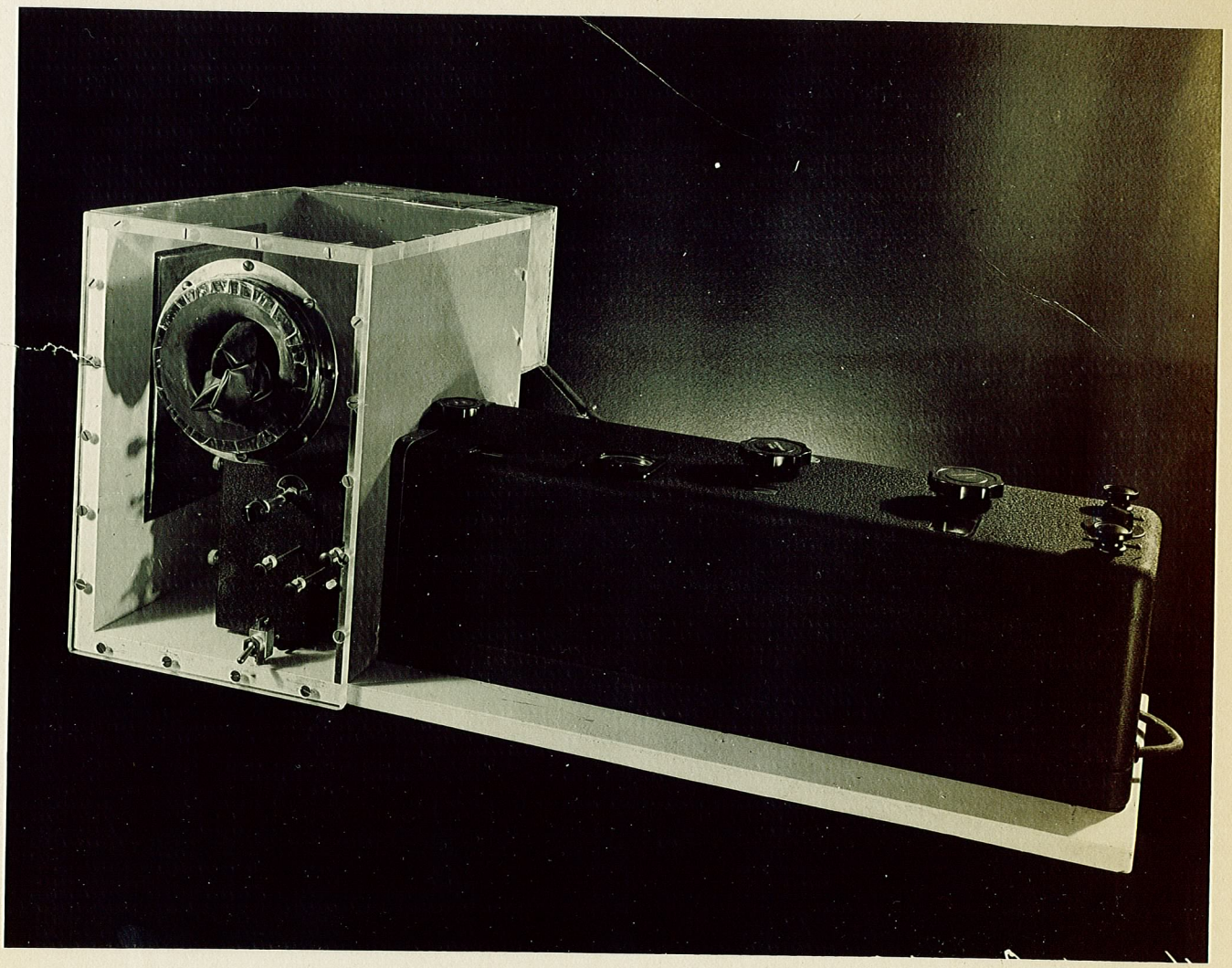


Fig. 22

Quartz Micro Absorption Cell

Figure 23.

Spectrophotometer Used with Highly Active Solutions



Bradley. The intense radioactivity present in the solution caused a considerable amount of bubble formation from decomposition of water. This interfered seriously with the measurement of the absorption spectrum. It was found necessary to either stir or tap the micro cell holder sharply at frequent intervals to dislodge the bubbles. The concentration of americium present was calculated from the height of the peaks at 5040 and 8180 A. The absorption due to Am(III) at every point measured was then calculated and subtracted from the observed absorption. The resulting curve, nearly identical to the one shown in Fig. 24, showed no appreciable absorption in the visible spectrum, but rather high absorption in the ultra violet.

A more accurate determination of the absorption spectrum was made using curium from the second irradiation of americium. The $Cm(OH)_3$ described in section V, paragraph 1.3b was redissolved in 0.5M HCl. An alpha analysis was made at this point to determine the amount of curium present. The curium solution again was placed in the quartz micro absorption cell fitted with a ground glass stopper shown in Fig. 22. Differences in the absorption characteristics of the two cells used for sample and blank solutions had previously been measured with distilled water in both. The Beckman Model DU Spectrophotometer used had been calibrated using three prominent lines of the mercury arc spectrum.

Again, difficulty due to vigorous bubbling of the solution was experienced. The cell carriage was removed and tapped sharply at frequent intervals to dislodge bubbles. Whenever necessary, readings were repeated to insure accuracy. The filter provided with the instrument was used with the tungsten filament lamp over

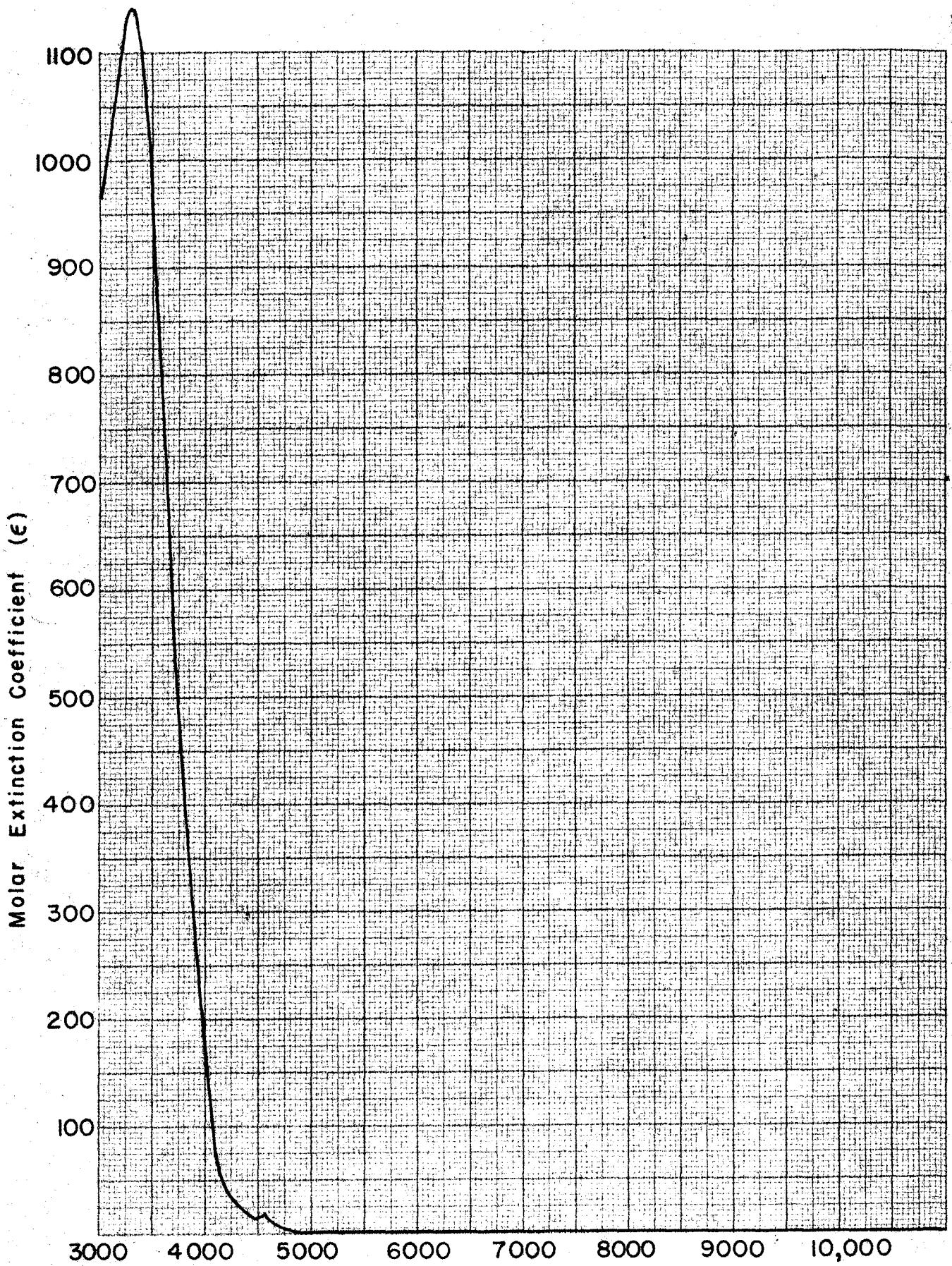


Fig. 24

Absorption Spectrum of Cm (III) in 0.5 M HCl

the range of 3200 to 4000 A. The absorption spectrum was observed at 25 A intervals from 3200 to 4000 A; at 20 A intervals from 4000 to 6000 A; at 25 A intervals from 6000 to 8000 A; at 50 A intervals from 8000 to 10,000 A; and at 250 A intervals from 10,000 to 11,000 A. From the height of a small peak at 5040 A a total americium content of 4.7% of the amount of curium was calculated. Corrections were made for the absorption due to Am(III) and blank absorption, and the curve of Fig. 24 was calculated and plotted. As in the case of the 51 NA sample no absorption maxima in the visible region were observed. A previously undetected apparent maximum in the absorption in the ultra violet was found. The absorption spectrum of curium may be compared with that of other actinide elements and rare earths by reference to the data in Fig. 25 which was compiled and drawn by E. H. Covey.

2. Spark Spectrum of Curium.

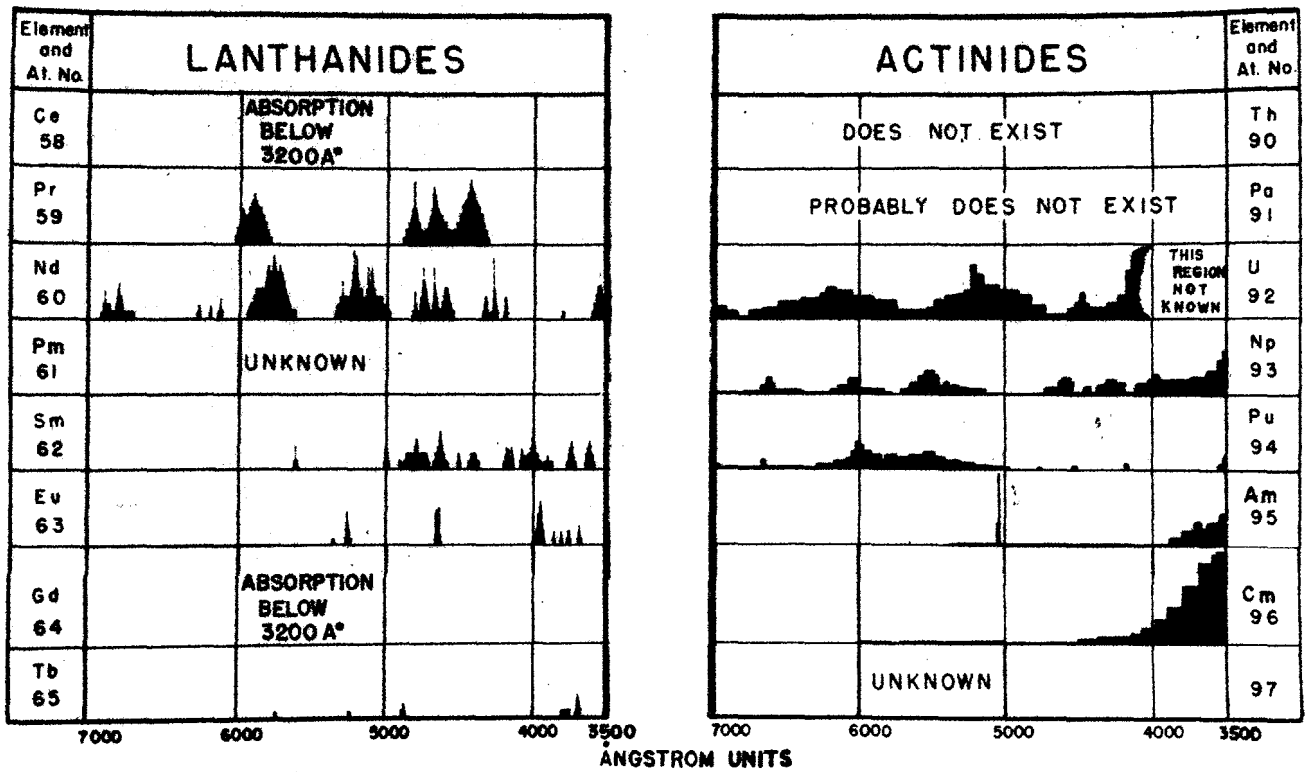
In the course of the spectrographic analysis, 45 lines of the curium spectrum were reported by Conway. The most prominent of these fell at 3220.5, 3426.5, 3472.8, 3546.3, 3905.2, 3909.4 and 4207.5 A.

VII. Special Effects of the High Level of Alpha Activity; Health Precautions.

1. The Decomposition of Water.

This effect was found particularly troublesome in attempts to separate precipitates of relatively pure curium compounds from supernatant solutions. Gas evolution from within the precipitate churned up centrifuged compounds within a few seconds. The difficulty was more pronounced in alkaline solutions. Hydrogen peroxide is a product of water decomposition by radiation and

Absorption Spectra of the Aqueous Tripositive Ions



NOTE: The molar extinction coefficients of the prominant absorption bands of the actinides are generally of the order of ten times greater than those of the rare earths. If plotted to the same scale the absorption spectra of the actinides would therefore appear relatively sharper. The absorption spectra of the rare earths are taken from Prandtl and Scheiner (Z. anorg. allgem. Chem. 220, 107 (1934)) and those of the actinide elements from various sources on the Plutonium Project.

FIG. 25

and is more rapidly decomposed in alkaline than in acid solution to give H_2O and O_2 gas.

2. Effect on Pyrex.

In one instance a concentrated Cm(III) solution was stored in a heavy walled pyrex tube for several weeks. This exposure to alpha particles was sufficient to both darken the glass and cause the formation of many fine cracks on the inner surface of the glass as shown in Fig. 26.

3. Production of Visible Light.

It was interesting to note that the curium preparation emitted light and could be seen rather plainly in complete darkness after a few minutes of eye adaptation. The hydroxide precipitate lying along the bottom side of the inclined tube shown in Fig. 15 was brighter than the solution itself. It appeared that the air just above the meniscus of the solution was brightest of all. After standing overnight the precipitate had redissolved presumably due to NH_3 having been swept out of solution by gas evolution, since later addition of NH_3 caused the hydroxide to re-precipitate. A photographic plate was exposed* to the light emitted by the curium solution in the complete absence of extraneous light. An enlarged print is shown in Fig. 27.

4. Use of Glove Boxes in Work Dealing with High Levels of Alpha Activity.

The work on the isolation of curium reported in this paper was considerably aided by the cooperation of Garden and his Health Chemistry Group in the design and construction of special equip-

* Super Panchro Press "Type B" film f/4.7 opening with Kodak Ektar 127 mm. lens and 8 hour exposure. We are indebted to W. D. Hail for taking this photograph and many others appearing in this paper.

Figure 26.

Effect of Exposure of Pyrex Cone

to High Level of Alpha Activity.

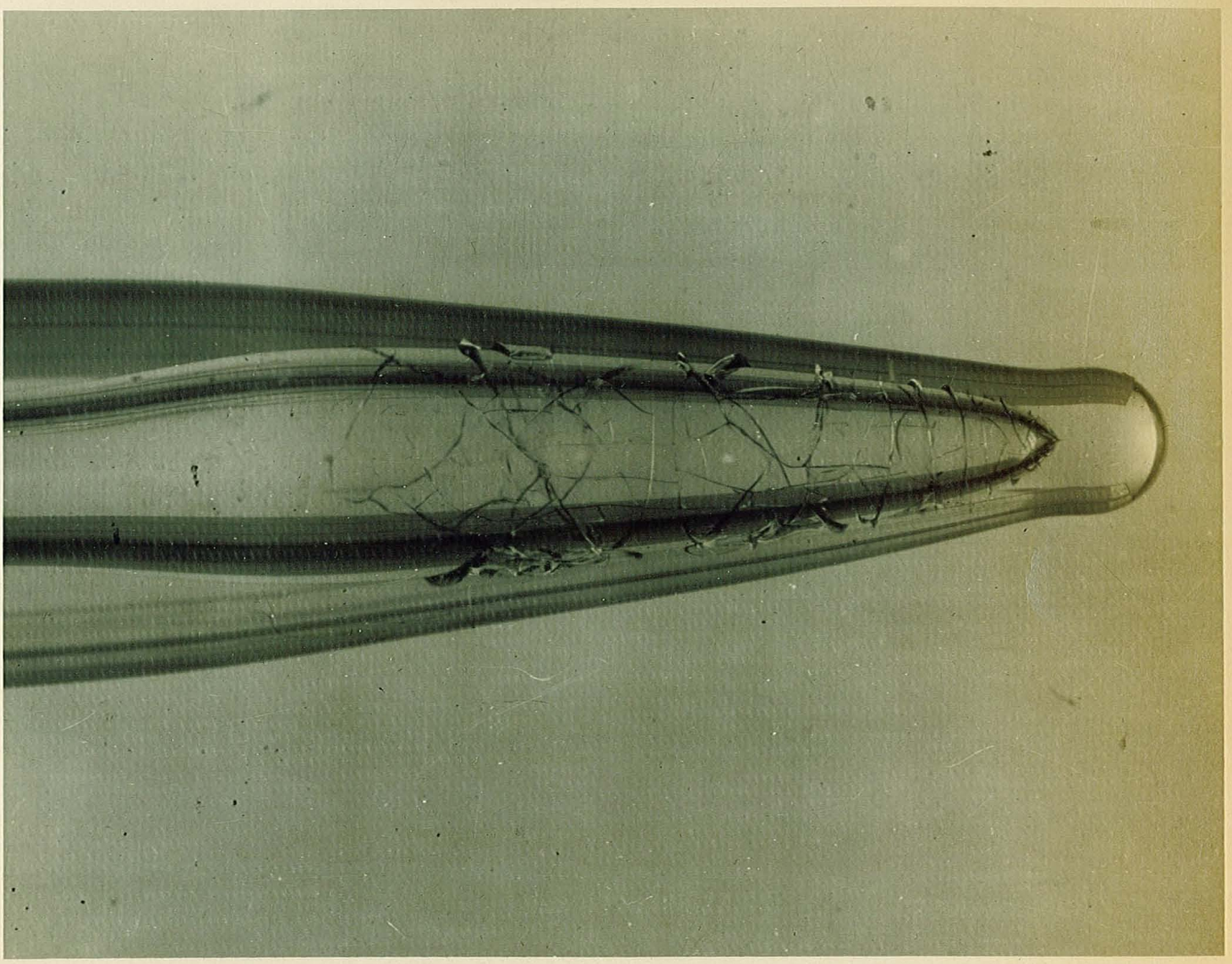
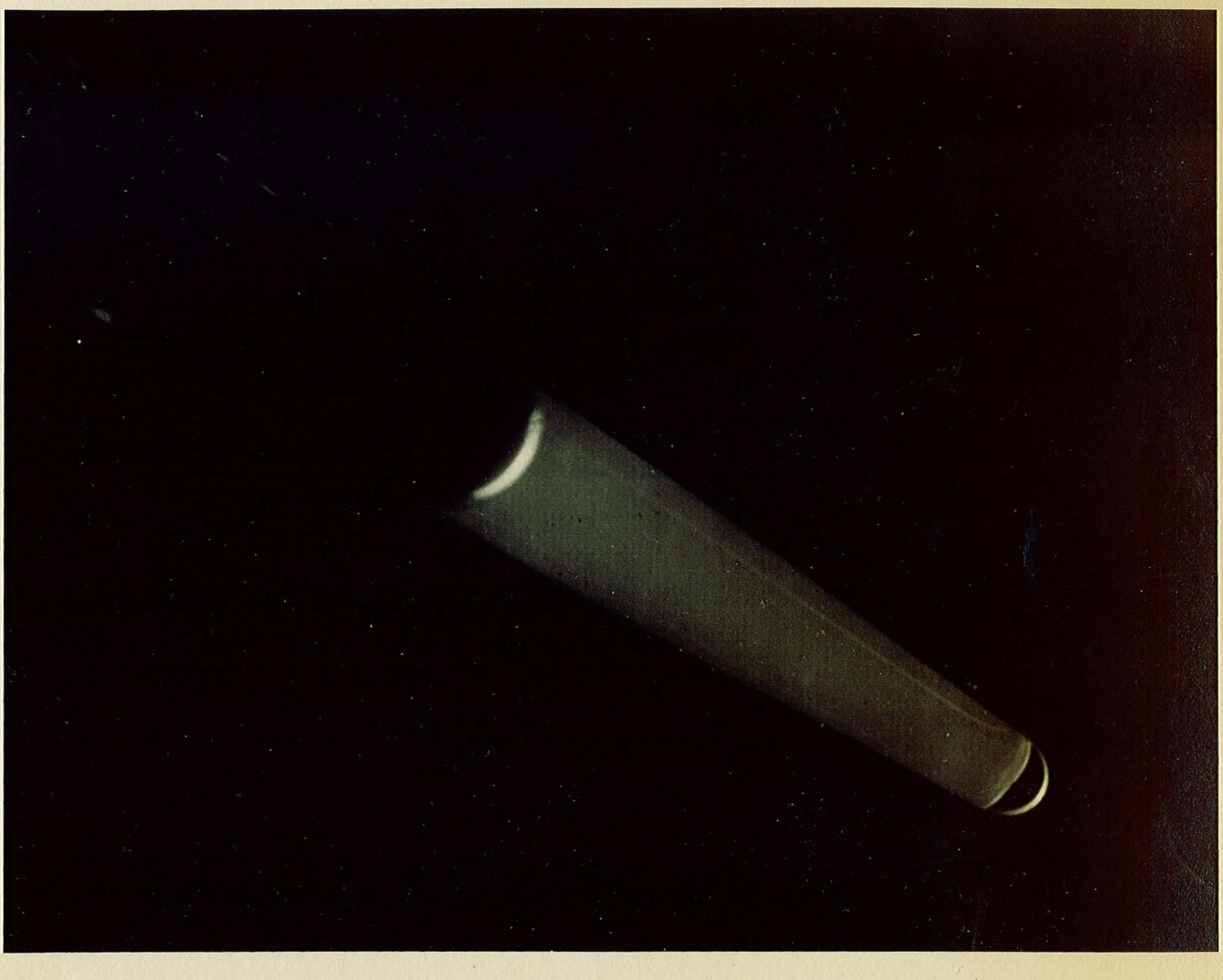


FIG. 26

Figure 27.

"Self-Portrait" of a Curium Solution.

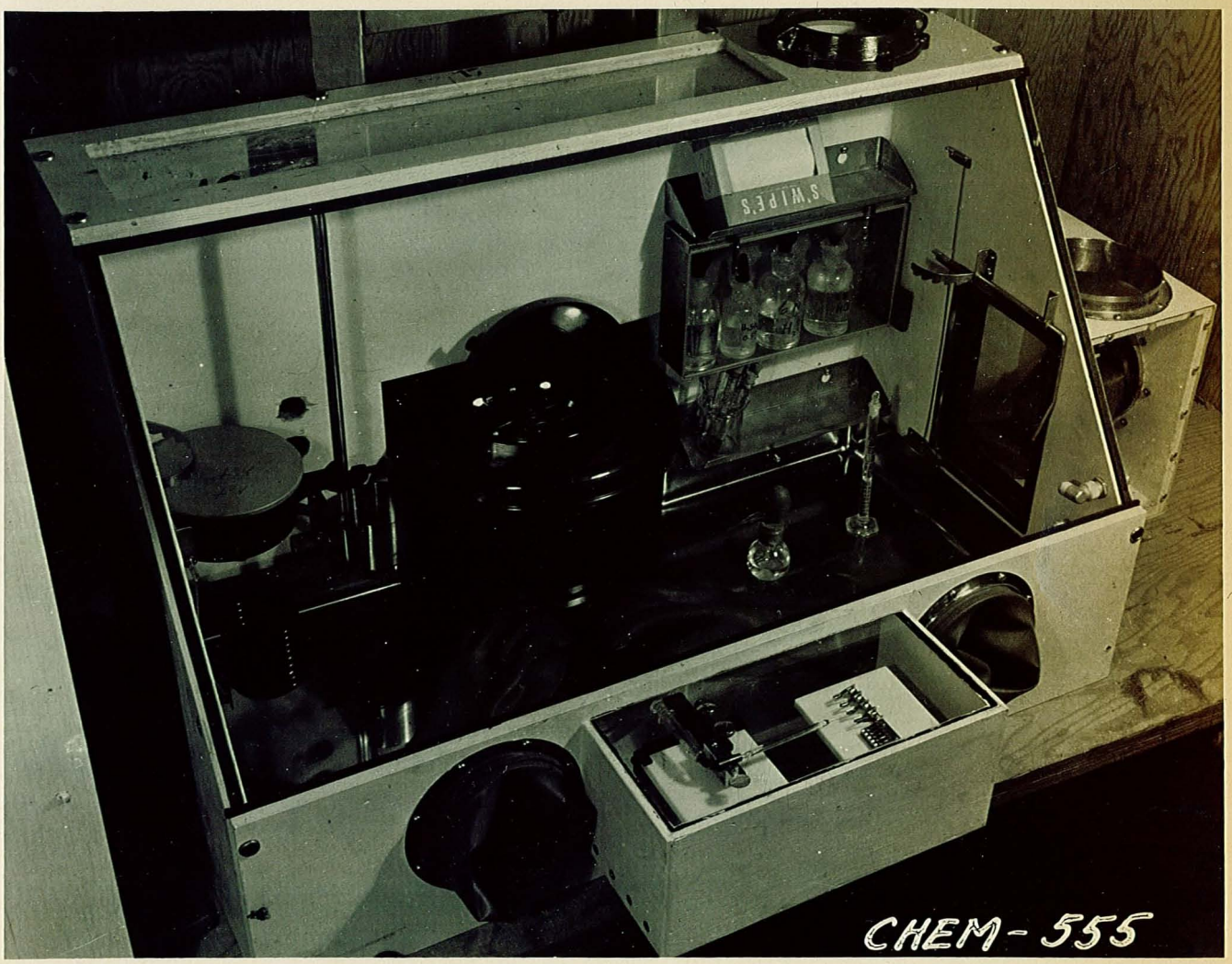


ment. Essentially all chemical operations were carried out in glove boxes of the type illusteated in Fig. 28. Special thanks are due Herman Bradley for installation and much of the design of these boxes. In addition to the centrifuge, hot plate, induction heating coil, and shelves shown in the figure, the box was also equipped with a hot drain, electrical outlets, gas outlets, fluorescent light, stirrer, glass dome for tall columns, sealed extension on the right for an alpha chamber, etc. The special extension on the front of the box was devised for micro manipulators on which microcones and pipettes were mounted and viewed through a stereoscopic low power microscope. The entire sloping front of the box was covered with safety glass, and a stream of air was drawn constantly through filters out of the box.

In short, the boxes were so constructed as to confine completely the active materials, and so equipped that every operation could be performed within the box, even the mounting and counting of samples for alpha analysis. It was found possible by this means to reduce contamination of surrounding areas to essentially zero.

Figure 28.

Glove Box Used in Working with Highly Active Alpha Emitters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MDDC	Manhattan District declassified report
BC	University of California Radiation Laboratory
ANL	Argonne National Laboratory
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