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A PRELIMINARY SURVEY OF RADIOACTIVE
CONSTITUENTS IN RAINWATER AT ORNL

W. A. BROOKSBANK JR., A. H. EMMONS,
J. W. GOST AND S. A. REYNOLDS

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A Preliminary Survey of Radioactive Constituents in

Rainwater at ORNL

W. A. Brooksbank, Jr., A. H. Emmons,

J. W. Gost and S. A. Reynolds

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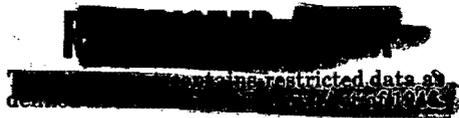
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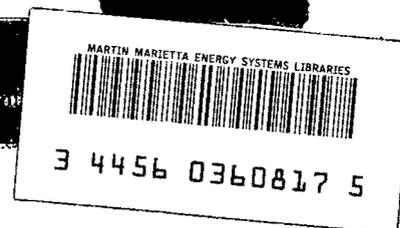
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Abstract

Large volumes of rainwater have been analyzed radiochemically for plutonium and uranium, and for fission products. Six determinations have been made from October, 1949 to April, 1950. The major fission products identified are: Ce^{144} - Pr^{144} , Sr^{89} , Sr^{90} - Y^{90} , Ru^{106} - Rh^{106} and Zr^{95} . The gross beta activity per hundred gallons varied from 9.6×10^3 to 1.64×10^5 c/m at 10% calculated counting geometry. Pu^{239} was identified by α -range analysis. The mean ratio of 5.2 grams Pu/ton of U was found. Overall carrying efficiencies for $Al(OH)_3$ scavenging of rainwater were determined for these elements, as well as for Pu and U.

Introduction

The objective of this survey was to analyze large volumes of rainwater for plutonium, uranium, and fission products. The work was undertaken as a joint problem by members of Analytical Chemistry and Health-Physics Divisions.

A method developed by members of the staff of the Naval Research Laboratory, Washington, D. C. was used, with modifications, until the present ORNL procedure was developed (Appendix B).

No attempt is made in this report to give detailed descriptions of all analyses conducted on a series of six collections between October, 1949 and April, 1950. Flowsheets showing the methods used have been substituted.

Experimental

A. Collection Area and Equipment.

A cylindrical, open-top, flat-bottom steel tank, 54 inches in diameter and 33 inches deep, with a 3/4 inch bottom drain, was used to store

the rainwater for these experiments. The tank was mounted on a platform of 4" x 4" timbers, 24" from the ground. The interior of the tank was cleaned by sand-blasting and painted with Amercoat #31 plastic paint. The top of the tank was covered at all times with a two-section wood lid until the chemical treatment was begun.

The roof of Building 104-B, a quadruple Quonset-type unit, was selected as a collection area because of the ease of collecting the rainwater run-off. An area of 2300 square feet in the valley between two of the peaks was marked off and scrubbed with a hose and stiff brushes. Rain from this area was by-passed over the normal gutter and into the tank. A two-way "flapper-type" valve was used to divert flow from the by-pass to normal channels when a large enough sample had been collected in the storage tank. (Photograph 1.)

B. Sample Preparation.

One ml of flocculating agent (815 grams $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ per gallon of stock solution) was added for each gallon of rainwater collected in the tank. The solution was stirred thoroughly with a "Lightning-mixer" and the pH of the solution adjusted to 6.9 - 7.1 by the addition of a saturated solution of Na_2CO_3 . The $\text{Al}(\text{OH})_3$ floc was kept suspended for at least an hour by mixing, and allowed to settle overnight.

All but a few gallons of supernate were siphoned off and discarded. The rest was drained from the bottom into a five-gallon carboy. The tank was scrubbed with sponges and a few gallons of water. This wash was drained into the same carboy. This sample was then transferred to the laboratory, allowed to settle for several hours, and again decanted. The $\text{Al}(\text{OH})_3$ concentrate was dissolved in acid and filtered, to prepare it for analysis.

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FIG. I
COLLECTION EQUIPMENT

C. Chemical Analysis.

I. Analyses Conducted.

- (a) Rainwater #1 - 311 gallons collected 10/1/49.

The analysis of this sample was attempted by the Naval Research Laboratory method (Flowsheet 1, Appendix A). Although this method is adequate for the natural activities, and for cerium and yttrium, it does not allow for determination of other fission products or plutonium. For this reason, it was modified in the manner indicated in Flowsheet #2 (Appendix A).

- (b) Rainwater #2 - 321 gallons collected 11/15/49.

Flowsheet #3 (Appendix A) gives the method employed for the analysis of this sample. This scheme resulted in the identification of 75% of the gross beta activity. The elements identified were Ce^{144} , Pr^{144} , Ru^{106} , Rh^{106} , Sr^{89} , Sr^{90} , Y^{90} , Zr^{95} , trivalent rare earths and Pu^{239} . The level of natural activities was so low (300 c/m for 300 gallons) that it was ignored. Ruthenium tended to carry on a number of precipitates making absorption studies difficult.

Losses incurred by carrying out the plutonium determination on a rare earth fraction were eliminated by determining Pu^{239} and Zr^{95} present from an aliquot of the original acid concentrate.

It is recommended that this method (Flowsheet #3, Appendix A) be used for preliminary survey studies. However, for routine work, a shorter method was devised to reduce the time required for the determinations (Flowsheet #5, Appendix A).

- (c) Rainwater #3 - 74 gallons collected 1/4/50.

Since the level of the activity in runs #1 and #2 was rather high, a smaller sample of rainwater was collected. For this reason, after preliminary separations, a scheme of aliquot samples with regular ORNL radiochemical isotope analysis was used (Flowsheet #4, Appendix A). The elements chosen were cerium, ruthenium, strontium, zirconium, trivalent rare earths, and plutonium. The Ru^{106} present still failed to follow any specific fraction, showing up in three fractions in appreciable amounts.

- (d) Rainwater #4, 5, 6, - 96 gallons, 163 gallons, 225 gallons collected 3/13/-3/20-3/27/50.

The final scheme of analysis is shown in Flowsheet #5 (Appendix A). The detailed procedure is given in Appendix B. This aliquot method was finally developed because it eliminated the ruthenium contamination problem and required a minimum of time. The air activity levels encountered at ORNL are high enough so that aliquot

methods are accurate. The analysis for the six major fission products present can be finished in twelve hours.

II. Identification of Radioelements.

The separated fractions of carrier elements were counted by normal counting techniques using end-window G-M tubes (Appendix C).

$Ce^{144}-Pr^{144}$ was identified by the chemistry followed by the carrier, by the beta absorption curve, and by a growth study of the Pr^{144} daughter. The beta energies as determined by the absorption study were about 0.35 MEV and 3.0 MEV. Since the half-life of Ce^{144} is 285 days, it was not practical to run a decay study. Instead, the cerium was purified of its praseodymium daughter, and a growth study started as soon as possible after separation. The daughter, Pr^{144} , had a half-life of 17 minutes and an energy of 3.0 MEV⁽¹⁾. This proved the presence of $Ce^{144}-Pr^{144}$ in the sample (Appendix A).

The presence of Sr^{89} and $Sr^{90}-Y^{90}$ were proved by similar methods. Beta absorption studies on separated SrC_2O_4 showed two beta components of 1.5 MEV and 0.6 MEV. The daughter grew in with a half-life of approximately 55 hours and an energy of 2.4 MEV. The reported values of the daughter Y^{90} are $T_{1/2} \approx 65$ hours and $E_{max} = 2.4$ MEV⁽¹⁾.

The $Ru^{106}-Rh^{106}$ activity was identified by the fact that it followed Ru chemistry in the distillation of RuO_4 from H_3PO_4 and $KMnO_4$ solution. Absorption studies showed a beta energy of about 4 MEV. There was no appreciable decay in the time it was studied.

Zr^{95} was identified by the chemistry it had undergone and the beta absorption study. TTA (thenoyltrifluoroacetone) extracts zirconium quantitatively from a 1 M HNO_3 solution⁽²⁾. Under the same conditions, neither ruthenium strontium, cerium^(III) nor the other rare earths will

extract⁽³⁾⁽⁴⁾. Because of the low counting rate an absorption study was run on only one of these samples. It was assumed that the beta activity in the other samples which were extracted under the same conditions was Zr⁹⁵.

Plutonium was extracted with 0.5 M TTA from a solution 1 M in HNO₃⁽³⁾. An α -range analysis, performed by Mr. E. Fairstein of the Chemistry Division, showed the peak of the tracer Pu²³⁹ standard to be directly below the maximum peak of the unknown curve (Appendix A). This proved that the energies were the same. This fact, plus the selectivity of the TTA chelation, proved the identity of Pu²³⁹.

Uranium was determined by the standard fluorimetric uranium analysis⁽⁵⁾⁽⁶⁾.
III. Determination of Carrying Efficiencies.

The determination of carrying efficiencies of Al(OH)₃ floc for the specific fission products and uranium was made by a series of three tracer run studies. Known amounts of the isotopes of interest were added to one hundred gallons of tap water, then the Al(OH)₃ floc was formed, concentrated, and analyzed, following the scheme given in Appendix B and Flowsheet #5 (Appendix A). The mean carrying efficiencies for the beta emitting fission products are given in Table III; those for plutonium and uranium are appended as a footnote to Table I. These mean experimental values were used as correction factors to calculate the specific activity levels given in Tables I and II.

D. Results.

Ce¹⁴⁴-Pr¹⁴⁴, Sr⁸⁹, Sr⁹⁰-Y⁹⁰, Zr⁹⁵, Ru¹⁰⁶-Rh¹⁰⁶, Pu²³⁹ and uranium have been isolated in quantities readily identifiable from rainwater collected at ORNL. The Ce¹⁴⁴-Pr¹⁴⁴ activity varies from 46 to 56% of the gross beta activity, the

Ru¹⁰⁶-Rh¹⁰⁶ from 5 to 9%, and the Sr⁸⁹⁻⁹⁰ from 3 to 9%. This does not necessarily mean that these are the most prevalent beta emitters present in rainfall, for there may be others which are not carried on the aluminum floc (e.g. Cs¹³⁷), but which might be present in quantity.

The gross beta activity carried on Al(OH)₃ per one hundred gallons of rainwater varied from 9.6×10^3 c/m to 1.64×10^5 c/m with a mean value of 5.35×10^4 c/m (0.24 microcuries per one hundred gallons) at 10% calculated geometry. These values represent at best the minimum beta activity present in the one hundred gallon collection since it is impossible to determine a correction for mean carrying efficiency because the beta emitters present, and their ratio one to another, varies from run to run.

The determination of plutonium to uranium ratio (Table I) was begun in March, 1950, with the thought that it might offer a clue as to the source of the plutonium. The plutonium count per one hundred gallons of rainwater was found to vary from 81 dis./min. (5.8×10^{-4} μ g) to 3872 dis./min. (2.7×10^{-2} μ g) with a mean, over the six months period, of 1199 dis./min. (8.6×10^{-3} μ g).

The method, in its present state of development, offers a reliable and rapid means of determining the extent of air contamination by five specific fission products as well as plutonium and uranium.

Table I

Plutonium per 100 Gallons Rainwater
and
Plutonium to Uranium Ratio*.

Date	Plutonium Dis./Minute	Uranium Micrograms	Grams Plutonium per Ton Uranium
10-1-49	291	--	--
11-15-49	2408	--	--
1-4-50	3872	--	--
3-13-50	461	1093	3.2
3-20-50	186	284	4.3
3-27-50	81	60	8.7

*Corrected for carrying efficiencies on Al(OH)₃ of 80% for uranium and 75% for plutonium.

Table II

Beta Activities per 100 Gallons* in Counts per Minute
at 10% (Calculated) Geometry.

Run Number	1	2	3	4	5	6
Collection Date	10-1-49	11-15-49	1-4-50	3-13-50	3-20-50	3-27-50
Gallons Collected	311	321	74	96	163	225
Gross β per 100 Gal.	-----	1.64×10^5	5.27×10^4	9.6×10^3	1.26×10^4	2.84×10^4
Cerium	8.86×10^3	1.85×10^4	4.33×10^4	1.07×10^4	9.6×10^3	2.36×10^4
Strontium	-----	4.05×10^4	2.32×10^4	8.33×10^3	1.4×10^4	1.06×10^4
Zirconium	-----	303	-----	166	116	222
Ruthenium	4.5×10^3	-----	1.7×10^3	1.5×10^3	2.3×10^3	2.86×10^3
Insolubles $\frac{\text{grams}}{100 \text{ gal.}}$	-----	4.49	-----	1.79	3.5 g.	124g

*Elements corrected for carrying efficiencies on Al(OH)₃.

Table III

Carrying Efficiency of $Al(OH)_3$

Trace Element	Mean Percent Carried (Approximate)
Cerium	60%
Strontium	8%
Zirconium	50%
Ruthenium	50%

Conclusions and Recommendations

Under conditions at the ORNL pile, it is possible to detect the release of fission products, plutonium and uranium to the air in rainfall collections. A method has been developed which provides a rapid means of determining gross changes in air contamination levels of cerium, strontium, ruthenium, zirconium, plutonium and uranium. The collection and analysis of rainwater can be performed by a competent, trained technician in less than three days.

It is suggested that further work be done along the following lines:

1. More detailed information should be obtained on the carrying efficiency of $Al(OH)_3$ floc, as used in the recommended procedure, for elements not isolated during this survey, i.e., Ba^{140} , La^{140} , Nb^{95} , "Saddle Elements", etc.
2. The carrying efficiencies of other coagulating agents should be investigated.
3. A more efficient collection arrangement, with a surface unaffected by air and rain corrosion, should be designed. The collecting area should be covered until the rainfall begins.
4. Surveys should be made at greater distances from ORNL, using the same scheme as was employed for Rainwater #3.
5. Routine rainwater analysis should be run at this installation for at least one year, with one or two runs per month, in an effort to establish a base line, or norm, for air activity at ORNL.

Acknowledgements

The authors wish to thank Mr. F. L. Moore for his helpful suggestions on the TTA extraction of Pu²³⁹, Mr. E. Fairstein for his pulse analysis of the plutonium, Mr. T. W. Brockett and Mr. J. H. Oliver for routine analysis and Mrs. E. Viles and Miss W. Bruce for the counting.

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 10. ORNL-Drawing Q-762
 11. Simpson, J. A., Jr., Rev. Sci. Inst., 18 884, ORNL-Drawing Q-844.
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Appendix A

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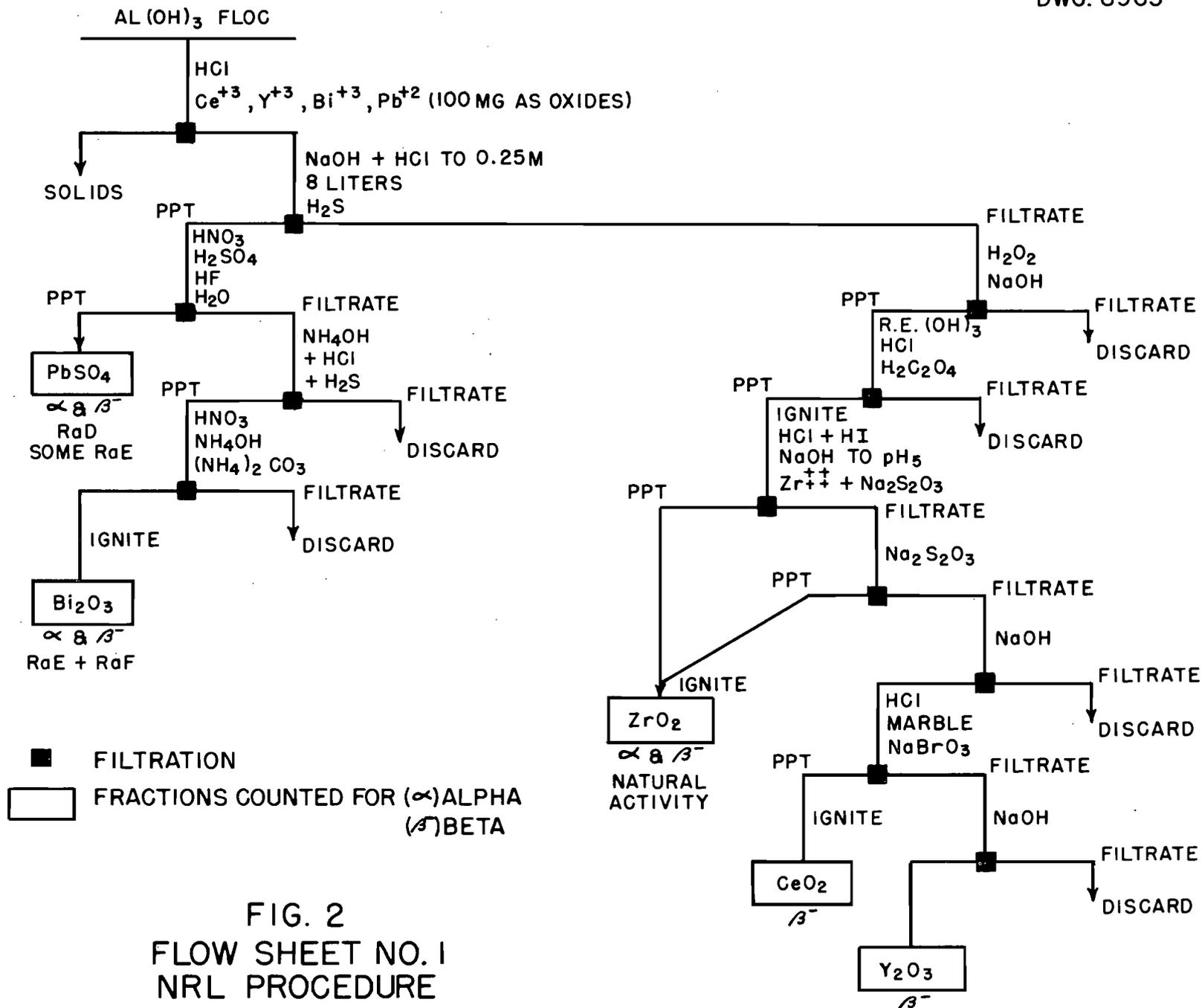


FIG. 2
FLOW SHEET NO. 1
NRL PROCEDURE

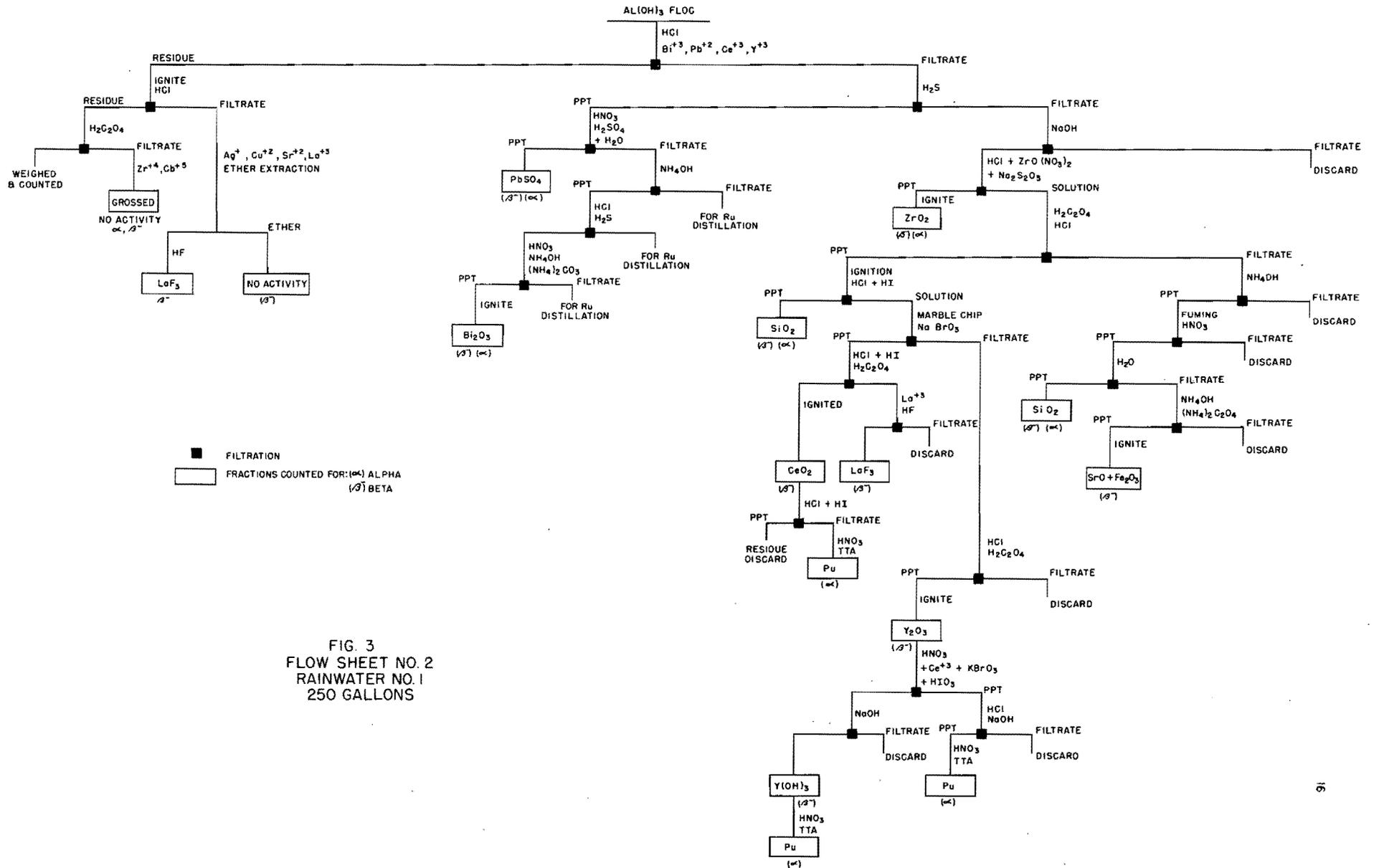


FIG. 3
FLOW SHEET NO. 2
RAINWATER NO. 1
250 GALLONS

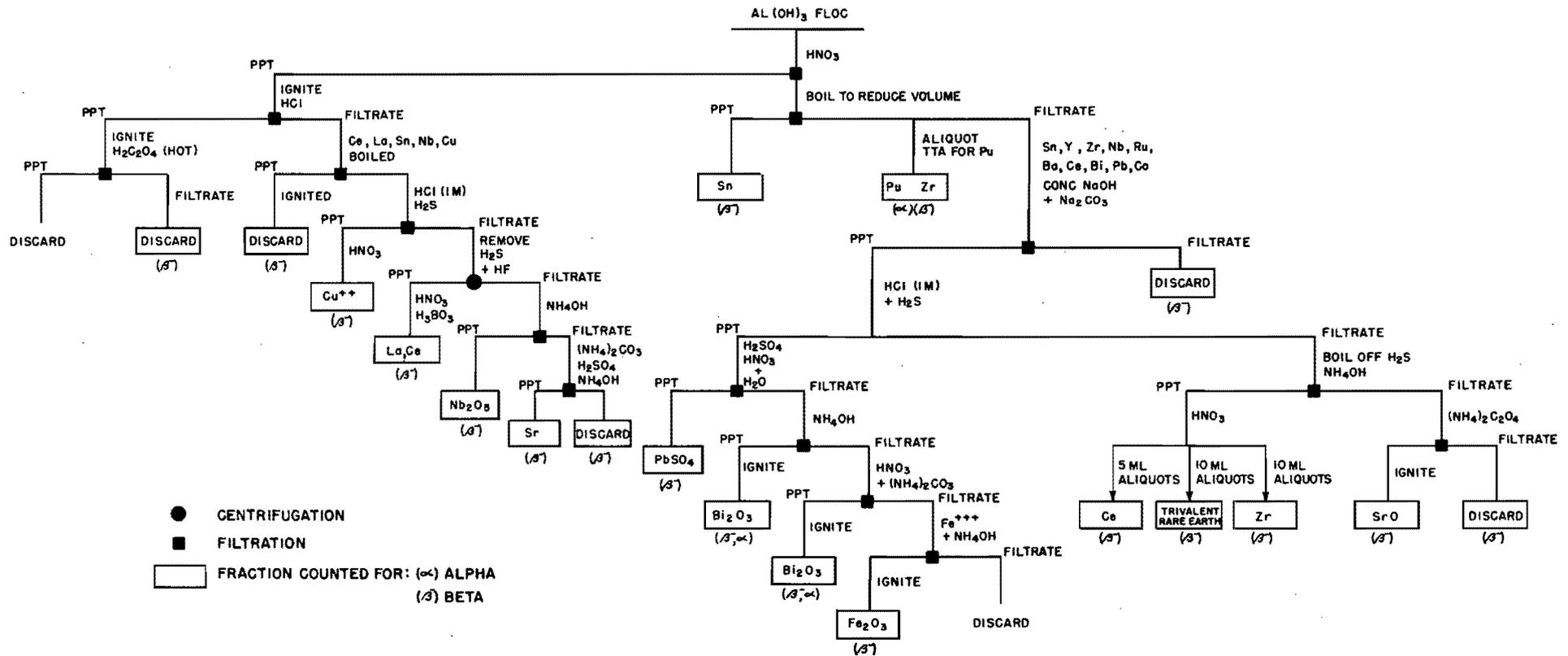
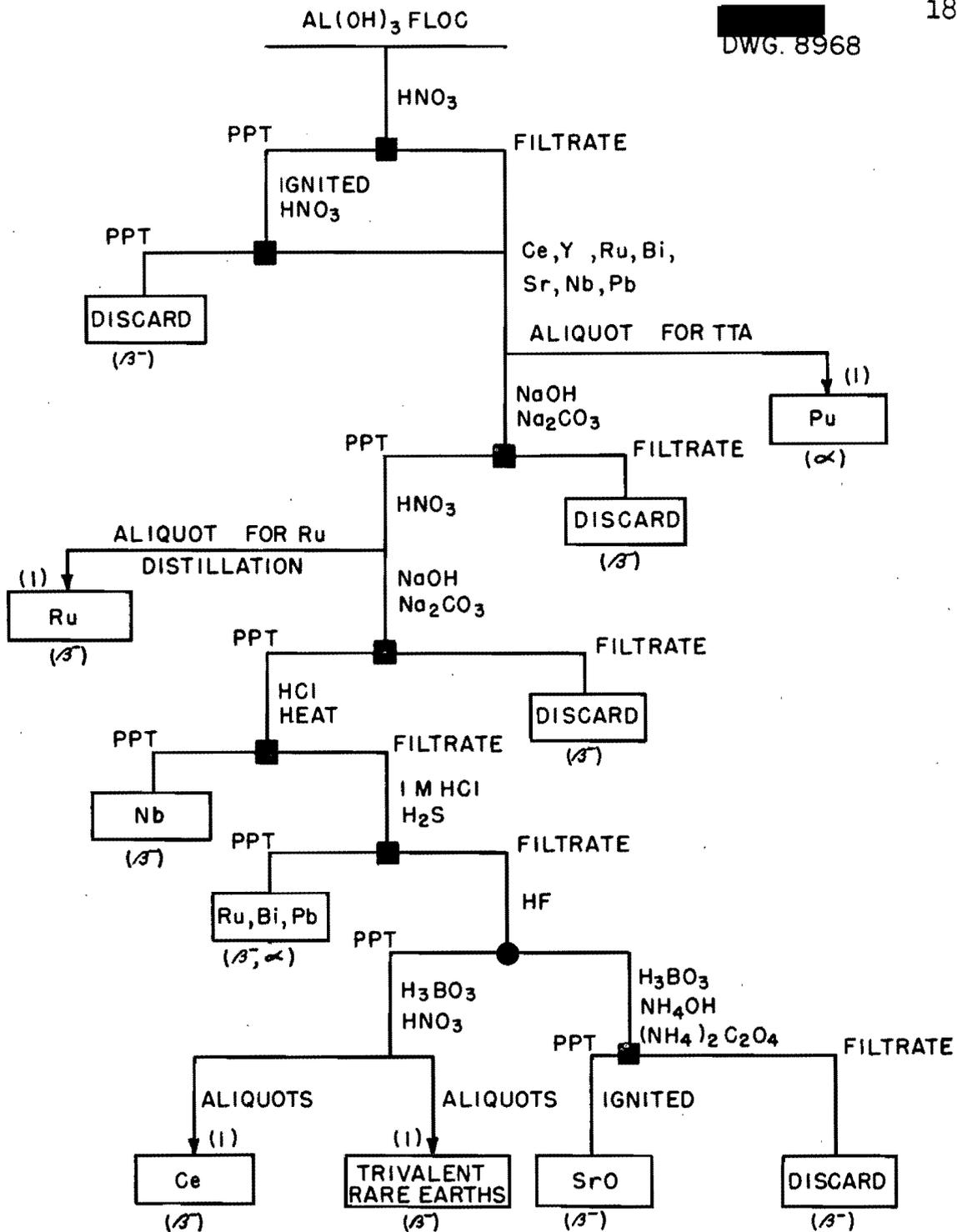


FIG. 4
FLOW SHEET NO. 3
RAINWATER NO. 2
321 GALLONS



(1) SEE APPENDIX B

- CENTRIFUGATION
- FILTRATION
- FRACTION COUNTED FOR (α) ALPHA
(β) BETA

FIG. 5
 FLOW SHEET NO. 4
 RAIN WATER NO. 3
 74 GALLONS

ORNL ROUTINE PROCEDURE

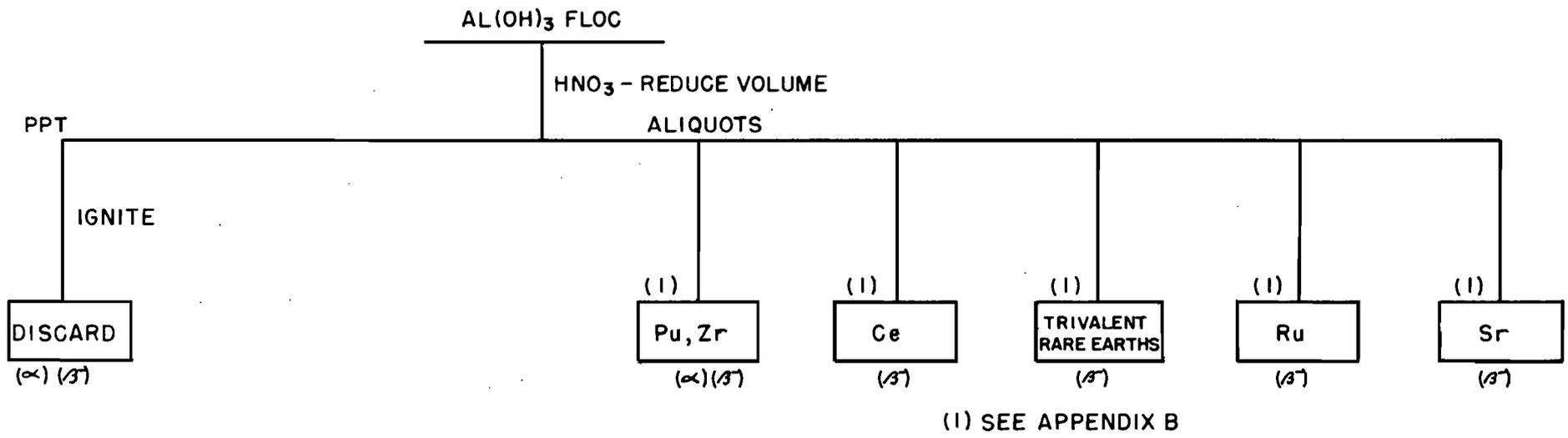


FIG. 6
FLOW SHEET NO. 5
RAIN WATER NO. 4, 5, 6, 7
96, 163, 225, 265, GALLONS

FIG. 7
BETA ABSORPTION CURVE #1

Ru¹⁰⁶ - Rh¹⁰⁶

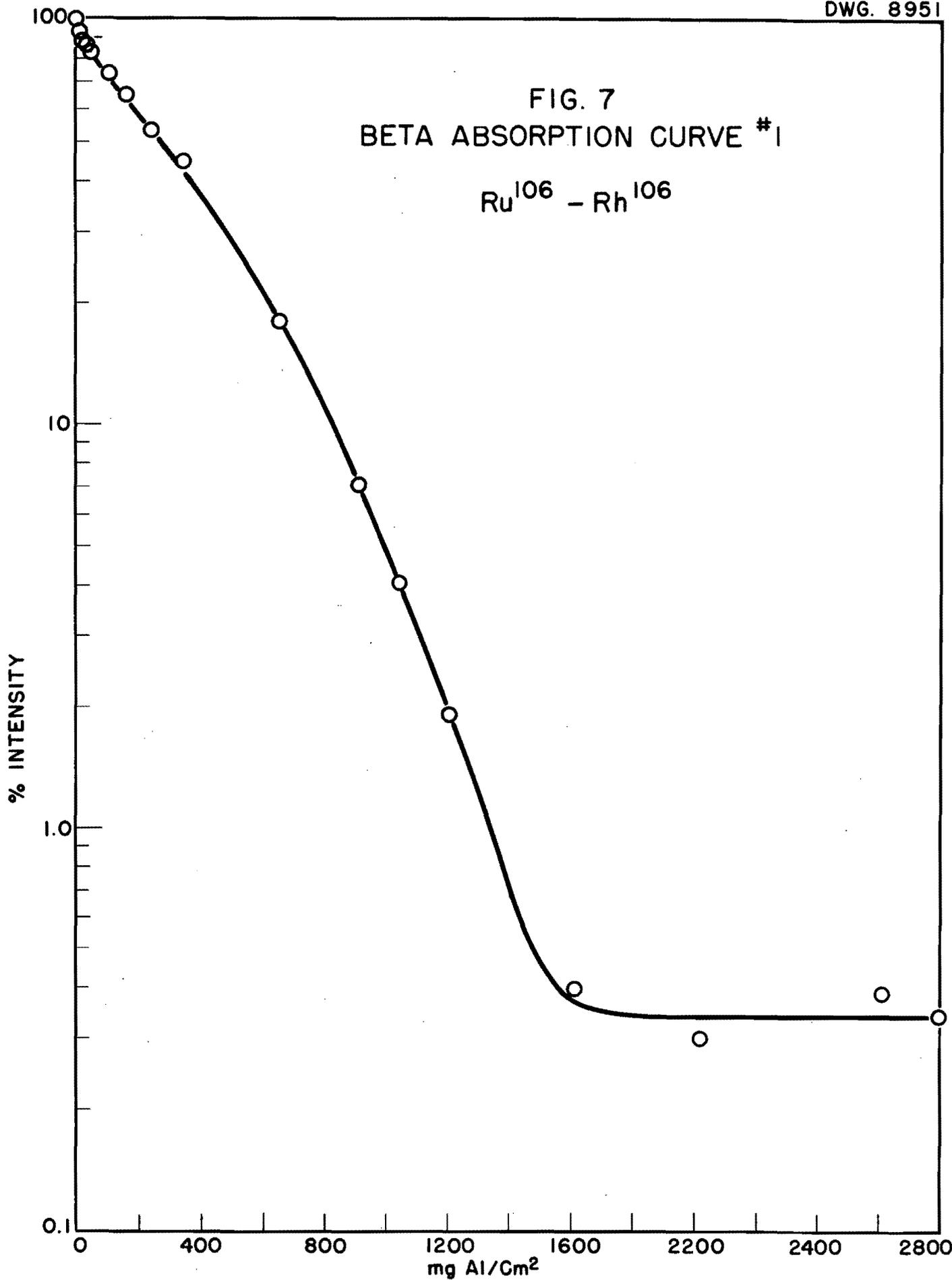
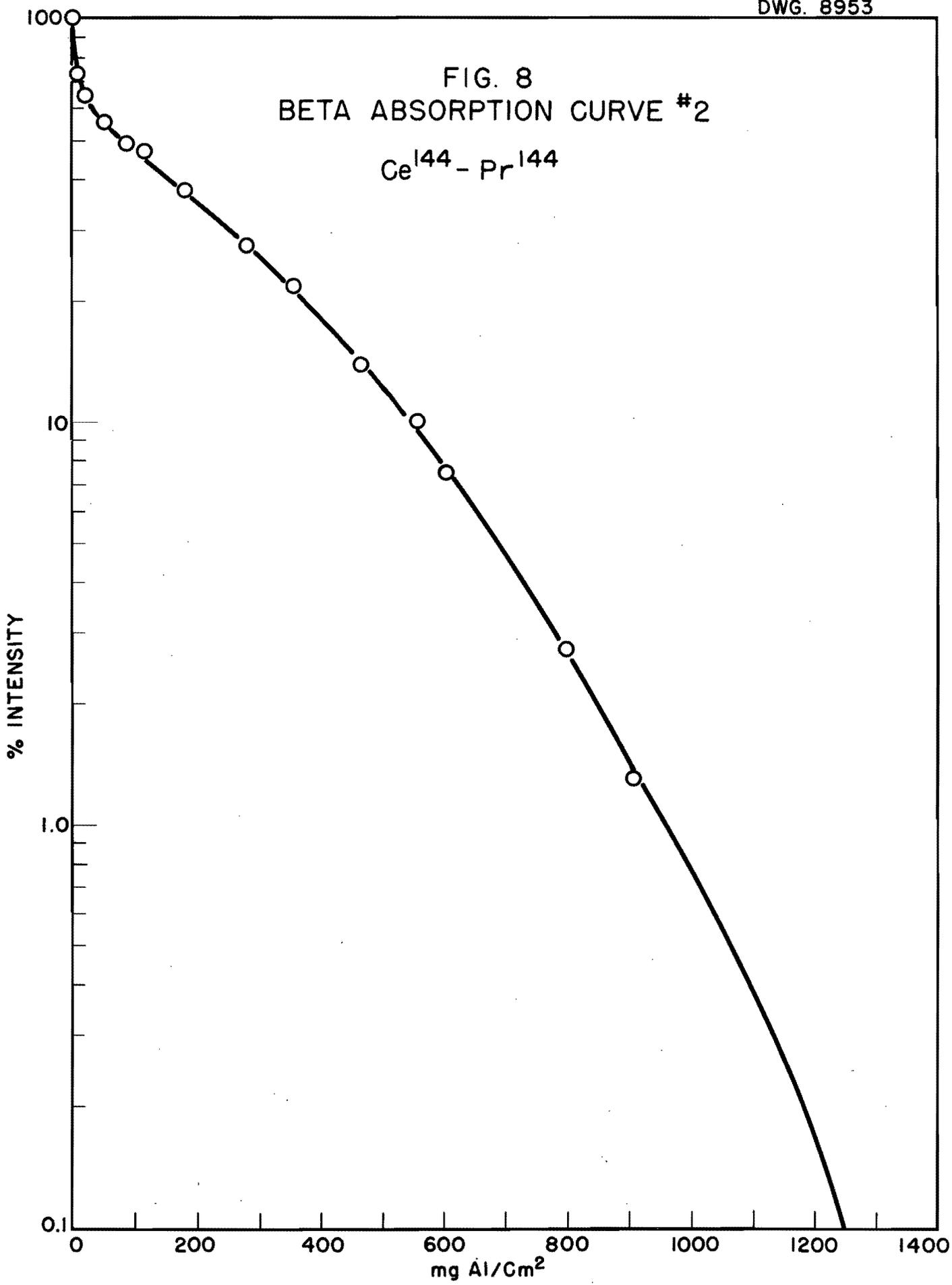


FIG. 8
BETA ABSORPTION CURVE #2

Ce¹⁴⁴ - Pr¹⁴⁴



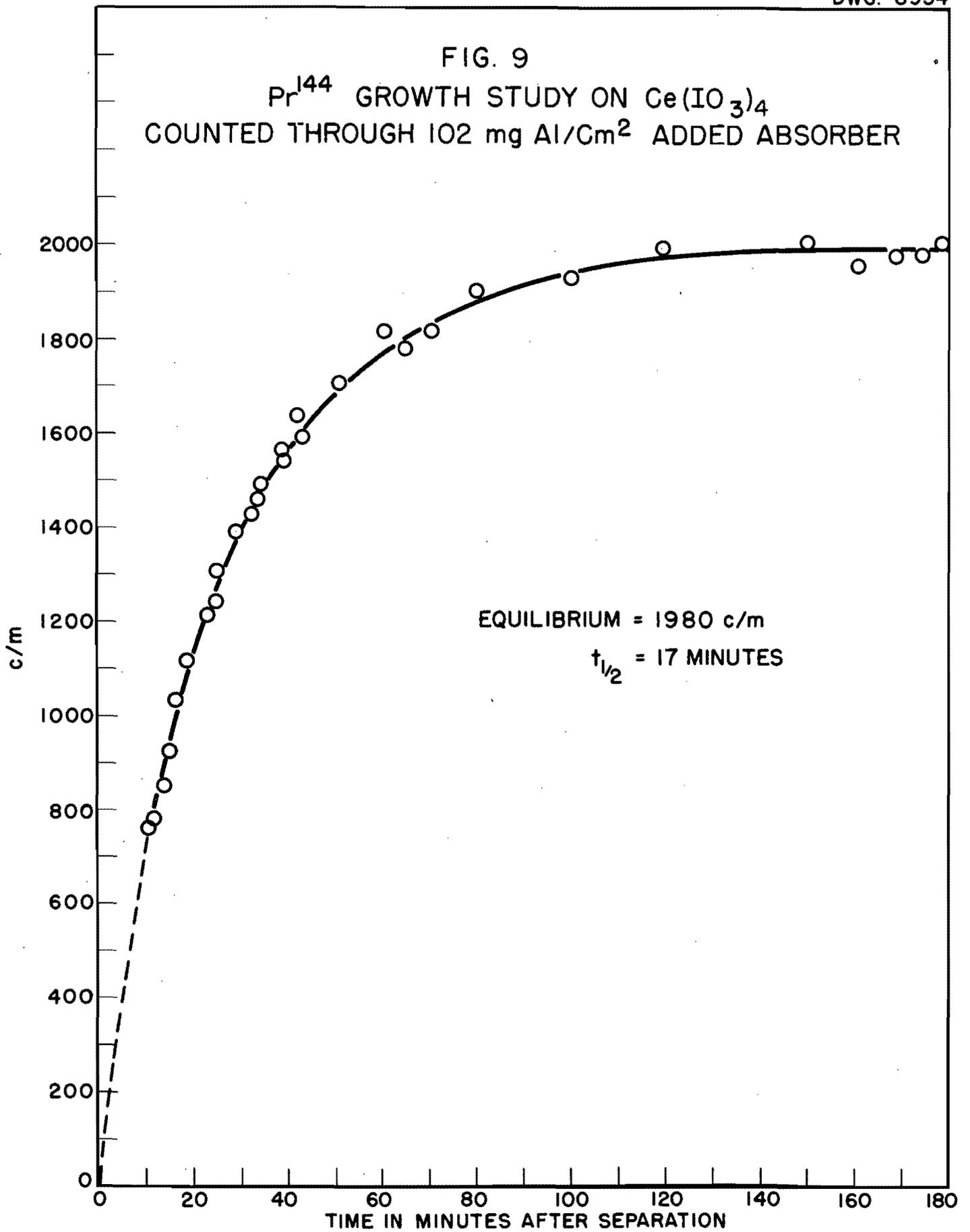


FIG. 10
BETA ABSORPTION CURVE #3

Zr⁹⁵

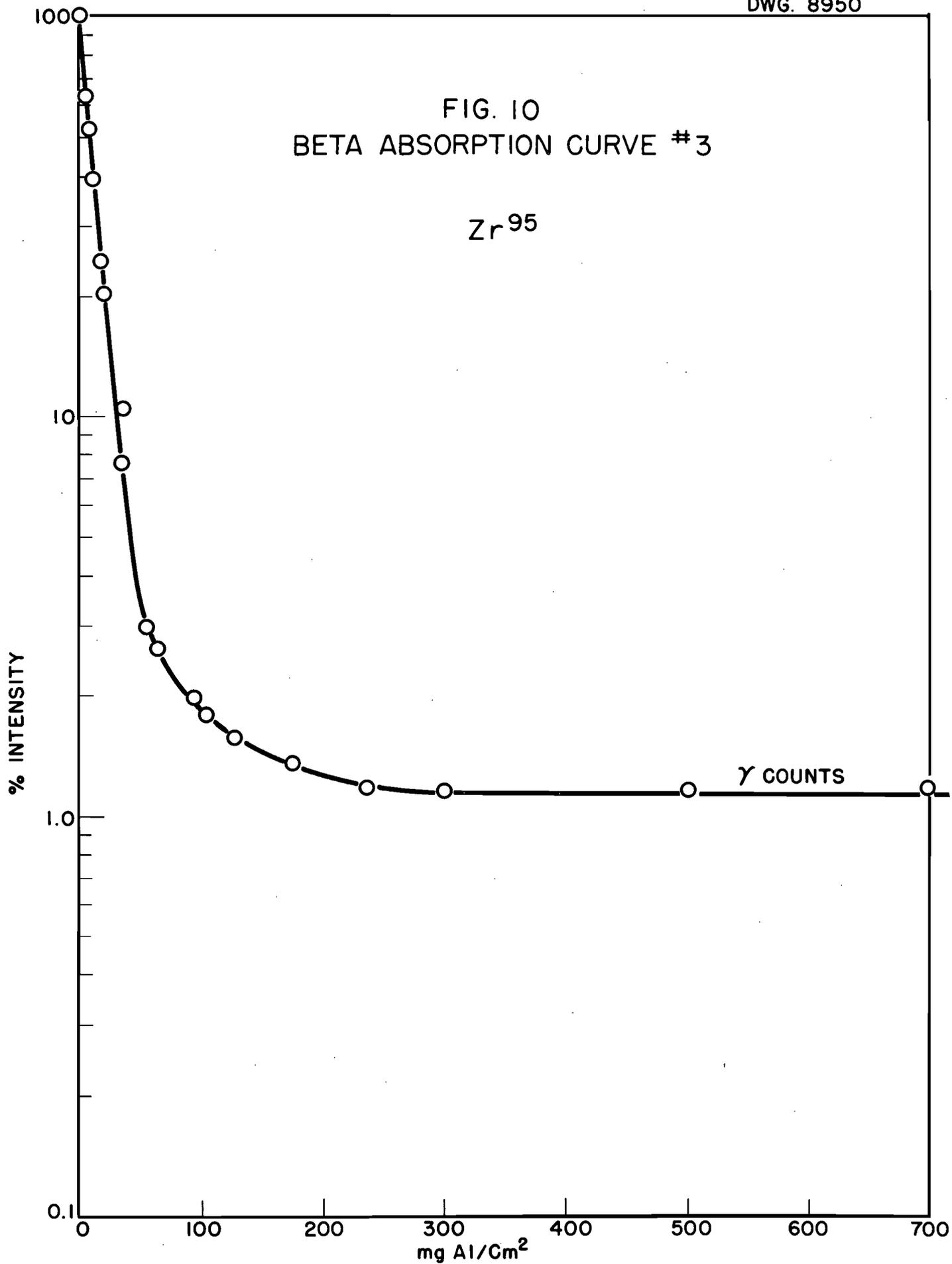
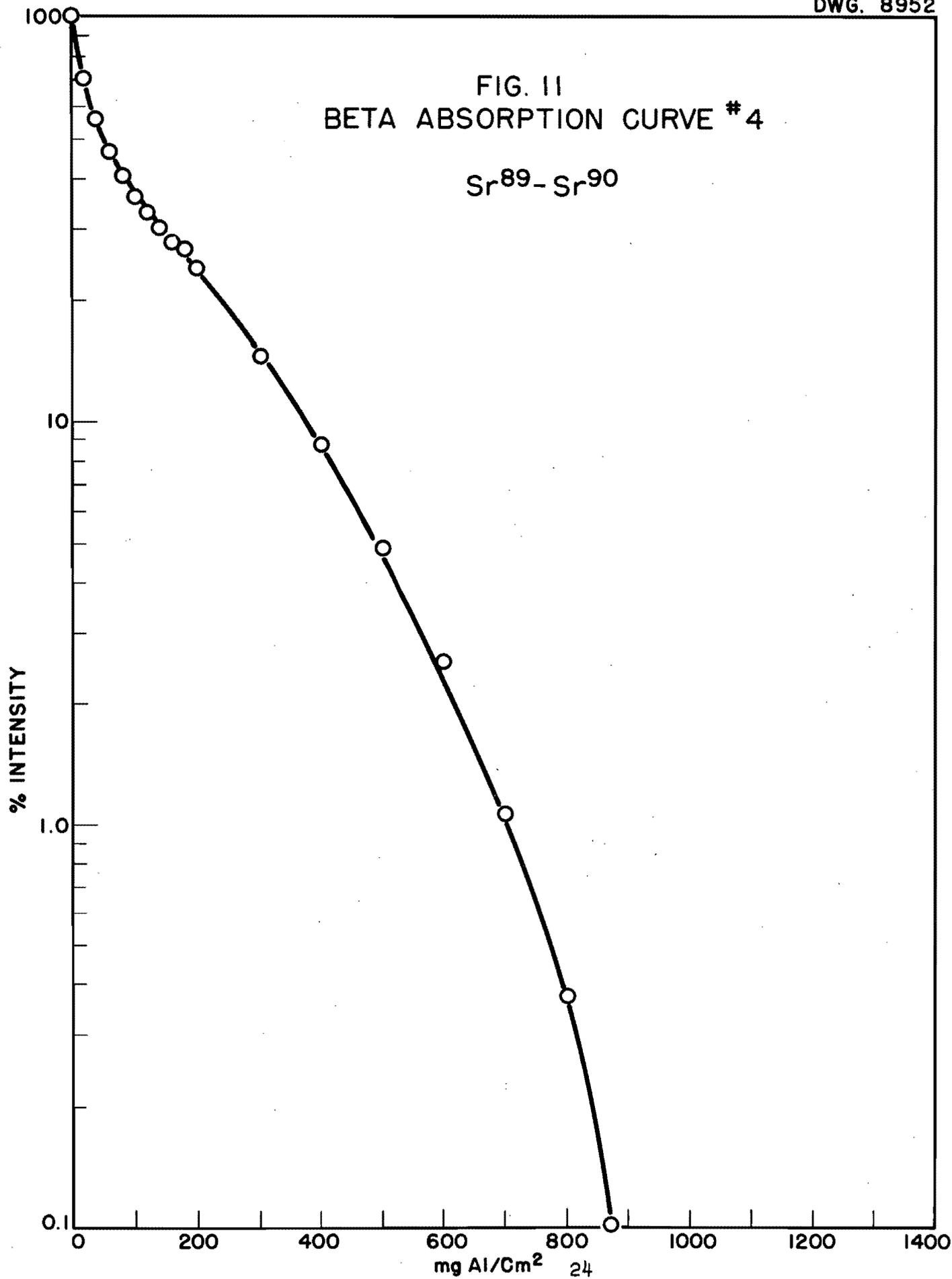
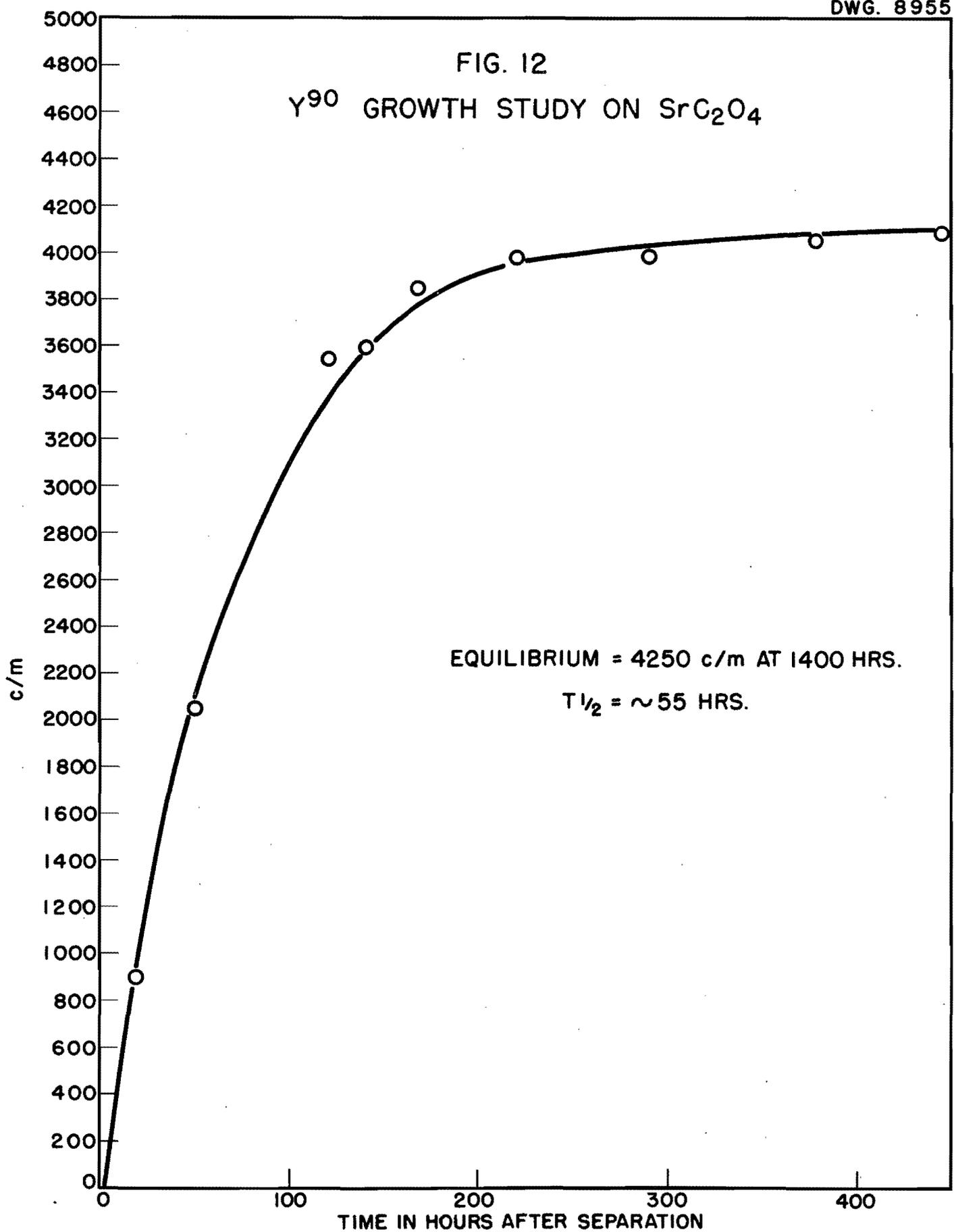


FIG. II
BETA ABSORPTION CURVE #4

Sr⁸⁹-Sr⁹⁰





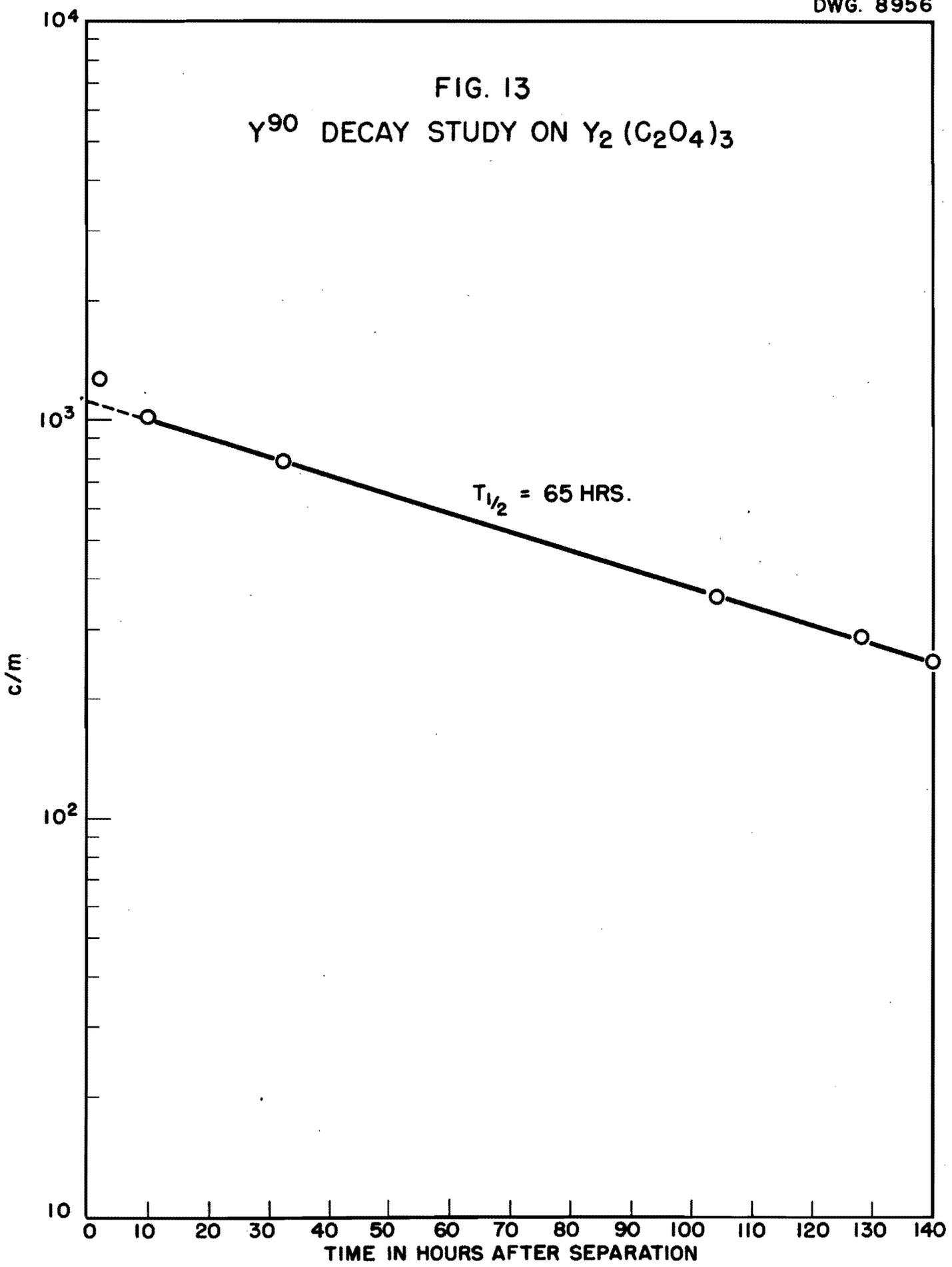
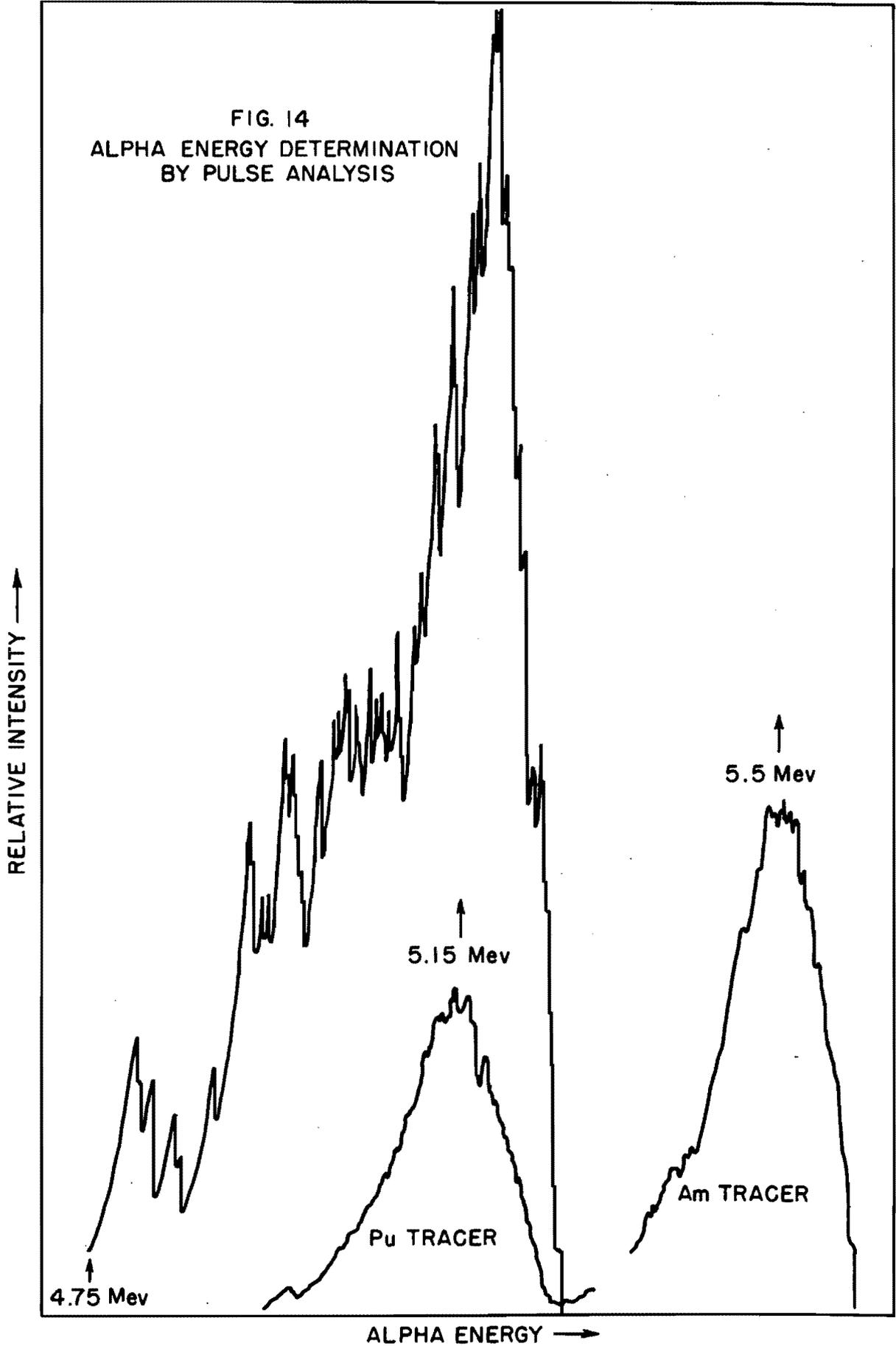
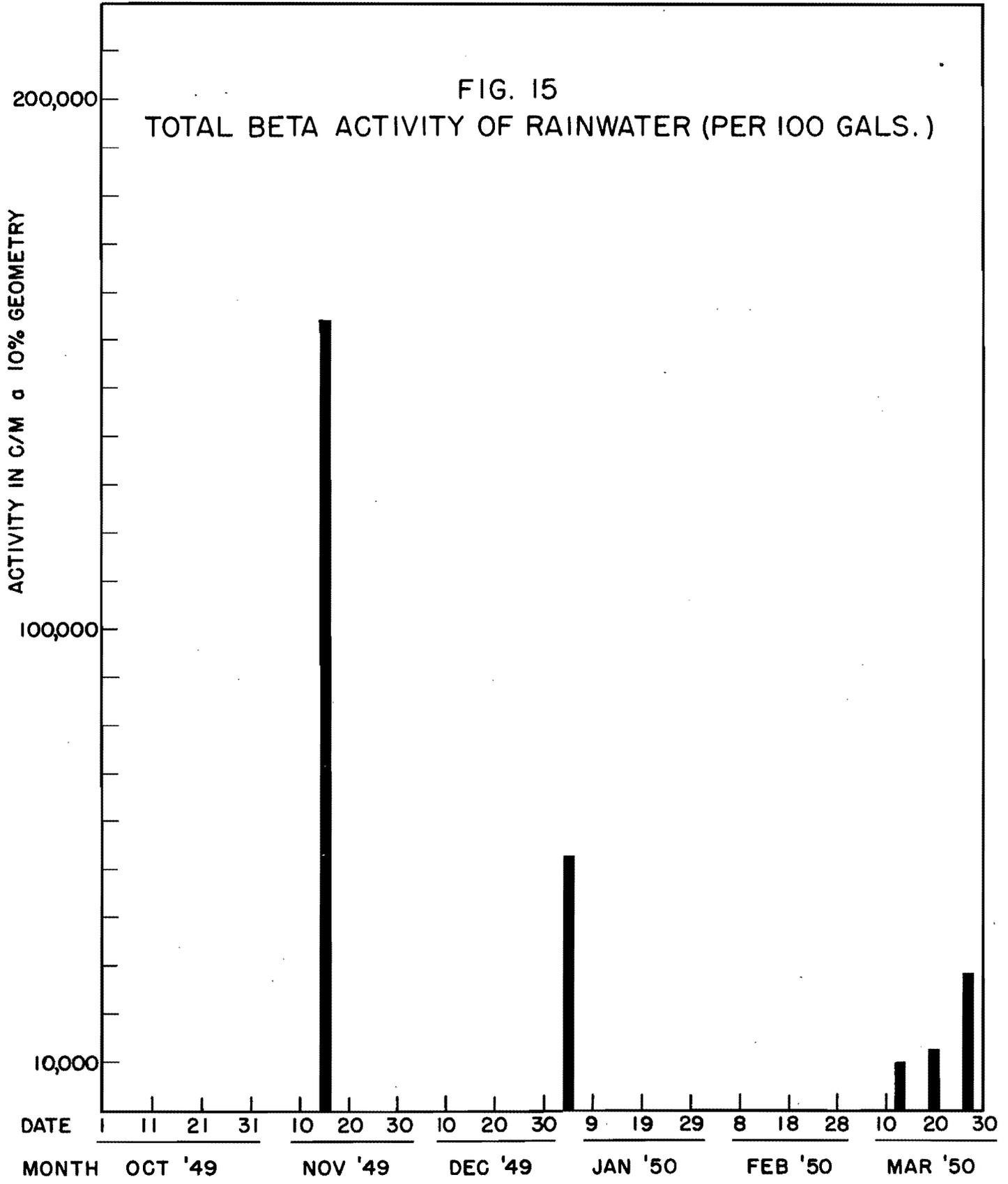
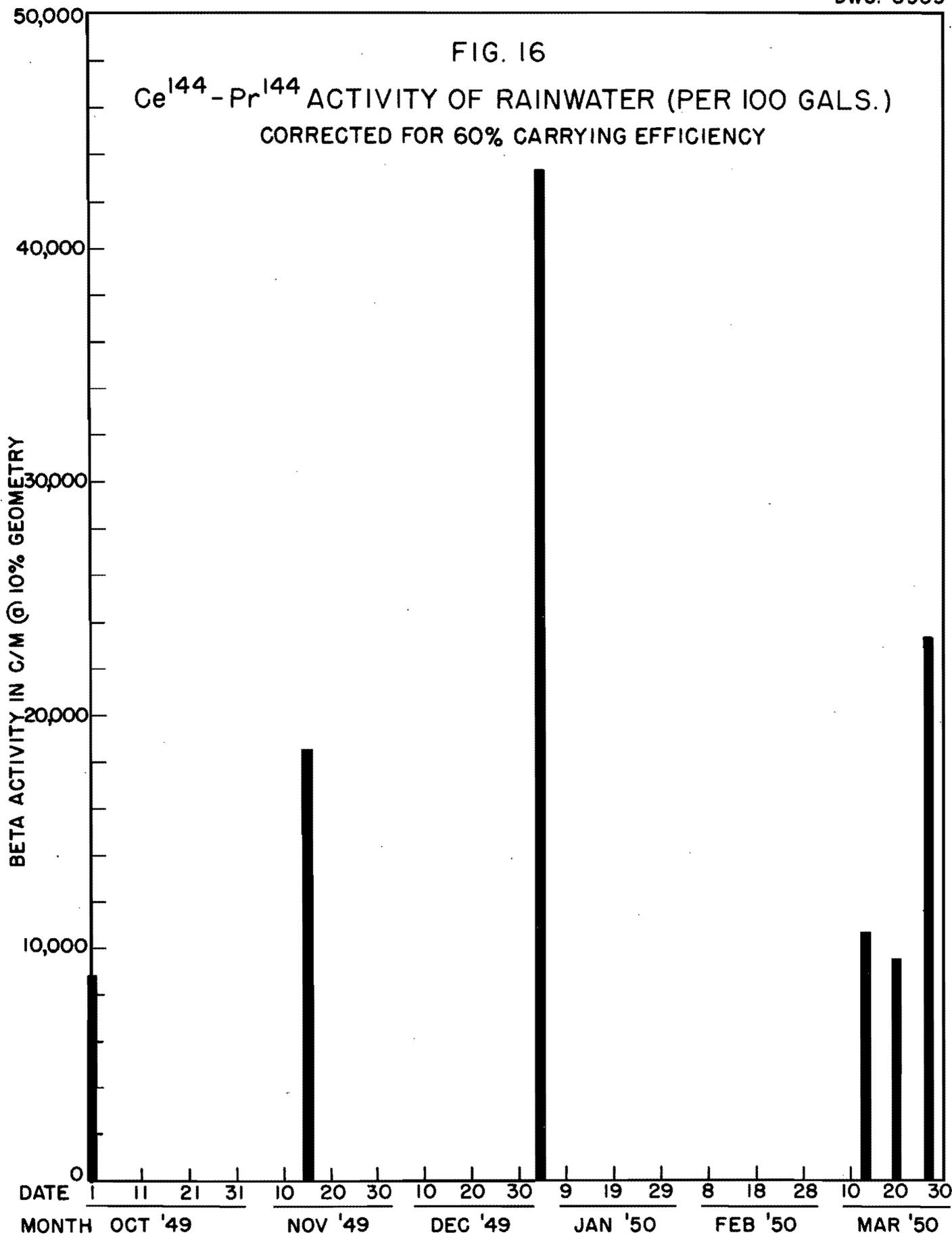


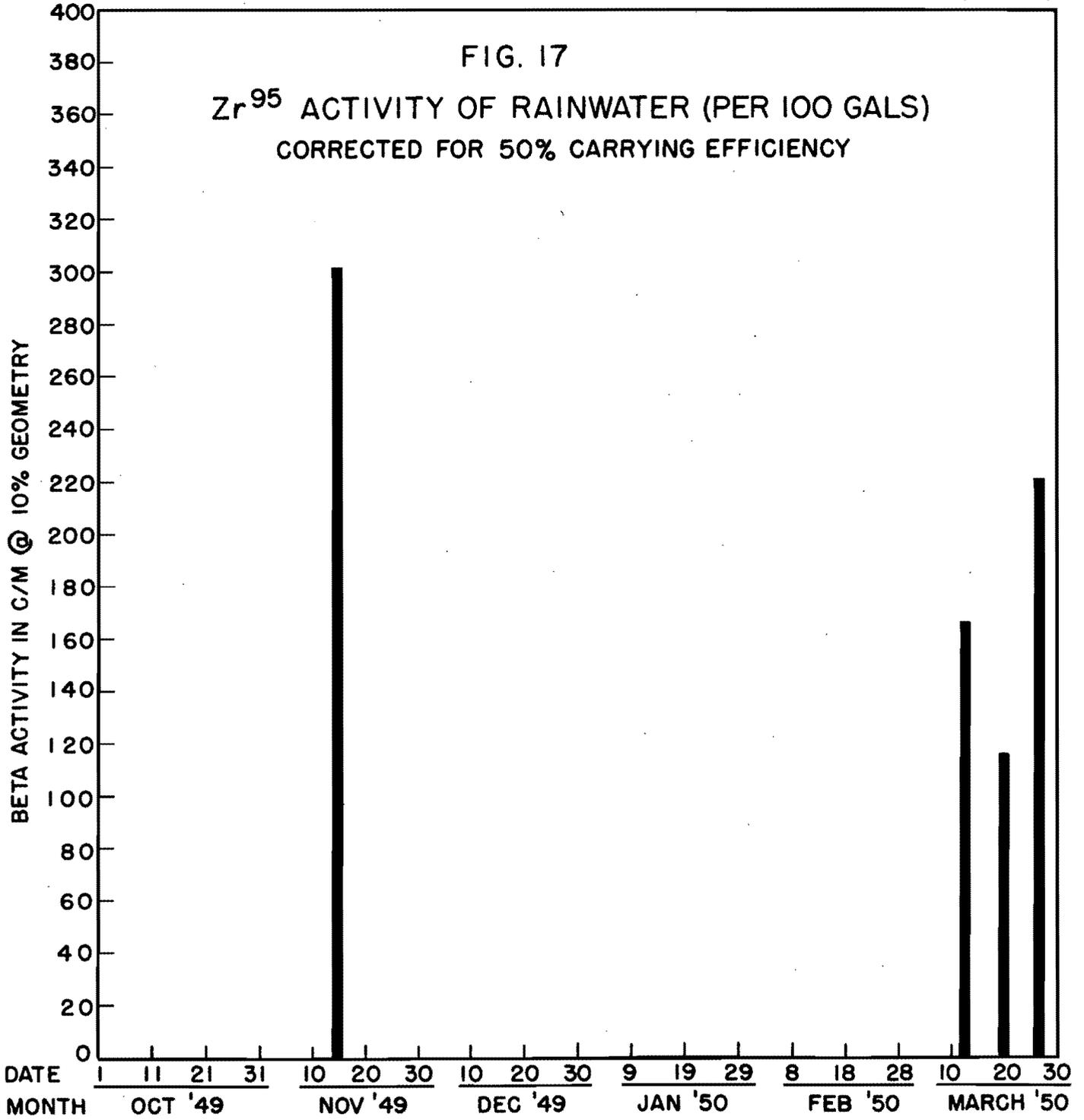
FIG. 14
ALPHA ENERGY DETERMINATION
BY PULSE ANALYSIS







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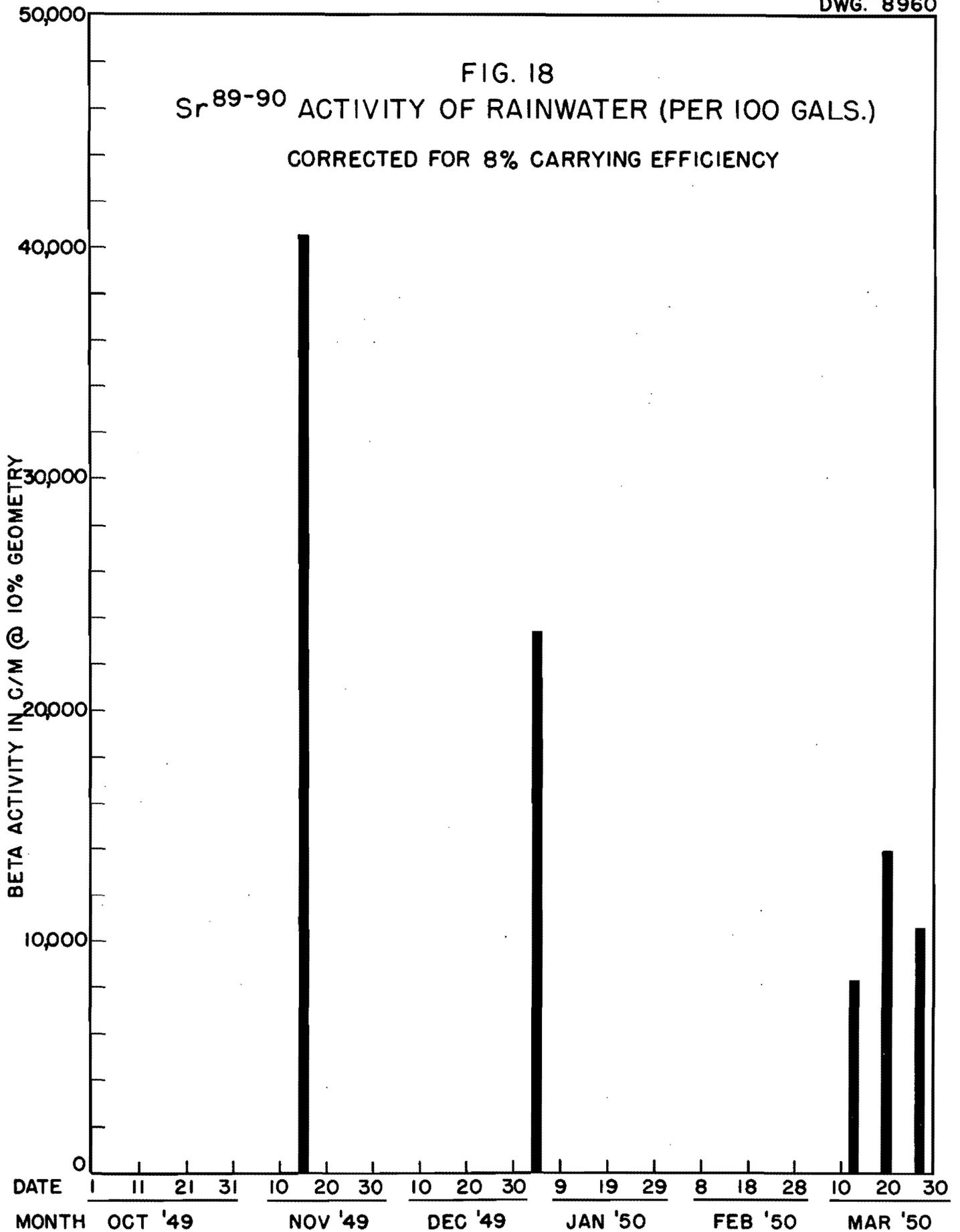


FIG. 19

$Ru^{106} - Rh^{106}$ ACTIVITY OF RAINWATER (PER 100 GALS.)

CORRECTED FOR 50% CARRYING EFFICIENCY

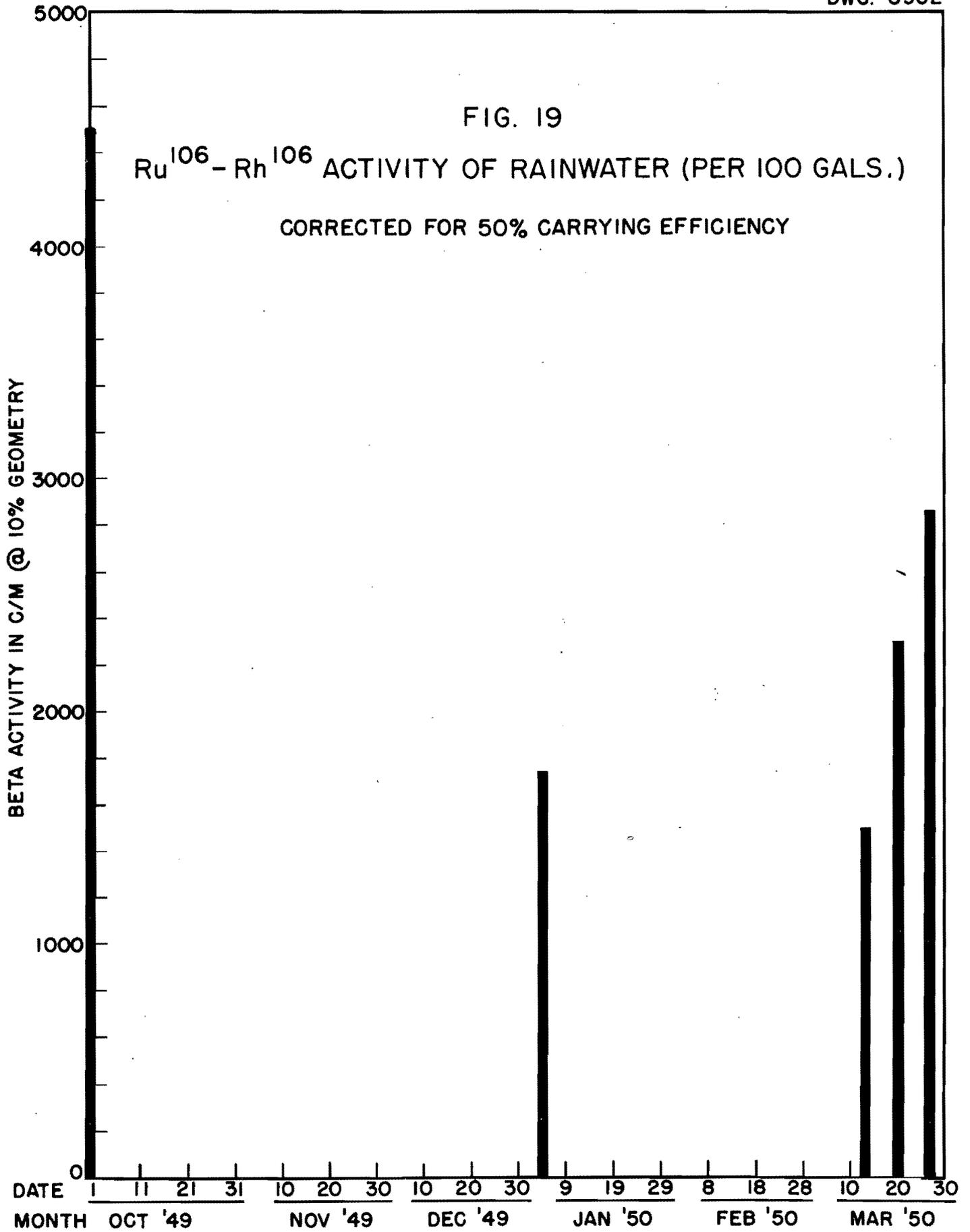
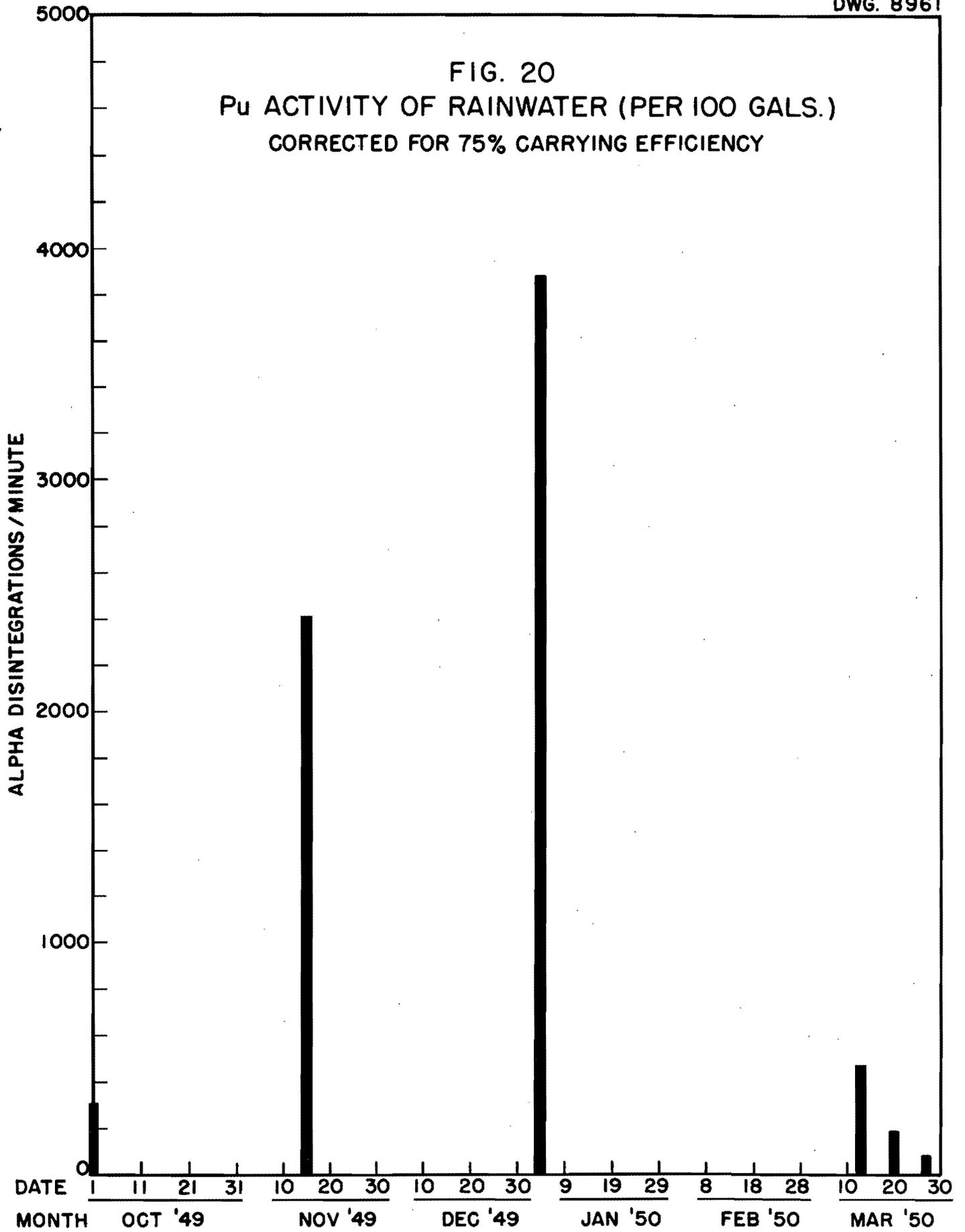


FIG. 20
Pu ACTIVITY OF RAINWATER (PER 100 GALS.)
CORRECTED FOR 75% CARRYING EFFICIENCY





Appendix B



Appendix B. Procedures

1. Naval Research Laboratory Procedure as Received August 26, 1949.

(a) Treatment of Water with Aluminum Hydroxide Flocc

The water sample to be treated is placed in a suitable tank (100-500 gallons capacity) equipped with some provision for stirring and 1 ml of aluminum sulfate stock solution (815 grams of $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ per gallon) is added for each gallon of water present. If considerable organic matter is present this quantity of floccing agent may be increased. The pH of the solution is adjusted to 6.9 - 7.1 by the addition of sodium carbonate; stirring is continued for an hour and then the solution allowed to stand until the floc is well settled. Settling is generally satisfactory after twelve hours. At this time the supernatant liquid is siphoned or pumped off, then the aluminum hydroxide floc transferred to a smaller container (5 gallon glass carboy) and further concentrated. If a larger sample of water is required, more water may be pumped into the tank with the previously settled floc, and the floc again stirred up and the above treatment with aluminum sulfate solution repeated. After a sufficiently large sample of water has been treated, the floc is transferred to a glass carboy for further concentration by settling and decantation.

(b) Treatment of Water from Roof Scrub with Aluminum Hydroxide Flocc

Tar paper or tarred roofs that have been exposed to the atmosphere for any length of time have been found to collect and hold appreciable quantities of natural activity and, in some cases, of fission activity. A large quantity of this may be recovered by scrubbing the roof area (2000 - 3000 sq. ft.) with water using stiff brushes (no soap or detergent!), flushing the roof with a hose and collecting and treating the water as in A.

Because of the large amount of dirt, organic matter, etc., present in the water from the scrub, it has been found desirable to add about one pound of ammonium chloride/100 gallons of water to aid in floccing. After addition of the ammonium chloride, 3 ml aluminum sulfate stock solution/gallon is added, the pH adjusted to 6.9 - 7.1, the floc allowed to settle and then collected as in A.

(c) Analysis of Aluminum Hydroxide Floc

The aluminum hydroxide floc from the treatment of rain water or other sample is dissolved in HCl, and cerium, yttrium, lead and bismuth carriers (about 100 mg of each as the oxide) are added. After boiling, cooling and filtering to remove undissolved solid matter, the pH is adjusted with NaOH and HCl so that the hydroxides are just kept in solution. The solution is diluted to eight liters, heated to boiling, gassed with H₂S for an hour while cooling and allowed to settle. Paper pulp may be added to aid in settling. The precipitated sulfides (PbS, Bi₂S₃, Ru₂S₃) are removed by filtration with suction (filtrate saved), transferred to a 400 ml Vycor beaker, 30 ml concentrated HNO₃, then 20 ml concentrated H₂SO₄ added, and the solution heated to fumes of SO₃. If the solution is not clear, more HNO₃ is added and the solution again fumed. If silicic acid is present, it is removed with a few drops of HF, and the solution again taken to fumes of SO₃. The solution is cooled, diluted to 200 ml, heated to 90° C, cooled to room temperature and the precipitated PbSO₄ separated by filtration with #42 Whatman paper. The precipitate is washed ten times with small portions of 10% (by volume) H₂SO₄. The precipitate is ignited to PbSO₄ at 550 - 600° C, weighed and counted for alpha and beta activity. This fraction contains RaD (Pb²¹⁰)

and some RaE (Bi^{210}).

The filtrate from above is made slightly basic with NH_4OH and then just sufficient HCl added to dissolve the BiOCl precipitate. Bi_2S_3 is precipitated by addition of an aqueous solution containing 0.2 g of thioacetamide (or H_2S) to the above solution and boiling for thirty minutes, and the precipitate filtered onto #40 Whatman paper, and washed with hot water. The Bi_2S_3 , together with the filter paper, is transferred to the original beaker, 20 ml 1:1 HNO_3 added and digested until the Bi_2S_3 is in solution. The solution is filtered and the undissolved paper pulp washed with hot 2% HNO_3 . The filtrate is diluted to 300 ml, NH_4OH added until a faint turbidity persists barely redissolved in HNO_3 , then just sufficient $(\text{NH}_4)_2\text{CO}_3$ added to make the solution alkaline. The solution is heated to boiling; the precipitated bismuth subcarbonate allowed to settle, filtered, ignited at 550°C , weighed as Bi_2O_3 and counted for alpha and beta activity. This fraction contains RaE (Bi^{210}) and Po^{210} .

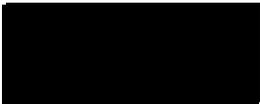
The filtrates from the bismuth precipitations may be examined for Ru activity by the usual distillation procedure after chloride ions are removed by fuming with sulfuric acid.

The filtrate from the original sulfide precipitation is boiled to expel H_2S , oxidized with H_2O_2 , and then made sufficiently alkaline with NaOH to keep the aluminum in solution as aluminate. The precipitated rare earth (and iron) hydroxides are separated by filtration, dissolved in HCl , NH_4OH added until a permanent precipitate appears, (if much Fe is present an isopropyl ether extraction may be necessary here) sufficient HCl added to just redissolve the precipitate, and then 1 ml excess concentrated $\text{HCl}/100$ ml solution added. The solution is filtered at this stage, if necessary (to remove silica), heated nearly to boiling and the

rare earth oxalates precipitated by the slow addition of a saturated solution of oxalic acid. After cooling and standing 2 - 3 hours, the oxalates are separated by filtration, washed and ignited to the oxides. The rare earth oxides are dissolved in boiling dilute HCl containing some HI. The solution is decolorized with a trace of NaHSO₃, filtered if necessary to remove silica or alumina, 150 mg of ZrO₂ added (in solution) and then the pH adjusted with NH₄OH and HCl until only slightly more acid is present than is required to keep the hydroxides from separating. The solution is diluted to 600 ml, heated to boiling, 100 ml of 30% Na₂S₂O₃ added and the solution boiled for 45 minutes. The precipitated material is separated by suction filtration and washed with hot water. The filtrate is boiled for another thirty minutes with 20 ml Na₂S₂O₃ solution, filtered and washed. The precipitated material is ignited and counted. This fraction contains such natural activity as Th, RaE, Po, UX, and possibly other elements. The filtrate from above is made alkaline with NaOH solution to precipitate the rare earth hydroxides. These hydroxides are filtered, washed, redissolved in dilute HNO₃ and NaOH until the solution is just sufficiently acid to keep the rare earth hydroxides in solution. A pea-sized piece of clean marble and 10 grams of sodium bromate are added to the solution (200 ml) and the solution boiled gently for two hours. At the end of this time the cerium should be completely precipitated as a basic ceric compound. The solution is filtered and the filtrate tested for cerium by the addition of ammonium hydroxide and hydrogen peroxide (cerium will give an orange-red color to the precipitated hydroxides; in the absence of cerium the hydroxides are white). The filtrate containing the yttrium

fraction is treated with NH_4OH to precipitate the hydroxide, filtered, the hydroxide redissolved in dilute dilute HCl , precipitated as the oxalate, filtered, ignited, weighed and counted. The cerium precipitate is dissolved in HCl containing some NaHSO_3 , precipitated as the hydroxide by NH_4OH , and finally converted to the oxide by the procedure employed with the yttrium fraction.

Absorption and decay measurements of the activities of these separated fractions (Pb, Bi, Ce, Y) are made to identify the isotope involved.



Appendix B. Procedures

2. Tentative Oak Ridge National Laboratory Procedure (5)(6)(7).

Chemical Analysis of $\text{Al}(\text{OH})_3$ Floc for Plutonium, Zirconium, Ruthenium, Strontium, Cerium and Trivalent Rare Earths by an Aliquot Method.

(a) Pretreatment

1. Dissolve floc in 8 M HNO_3 , filter with suction, wash insolubles with 8 M HNO_3 and discard insolubles.
2. Evaporate the filtrate to a convenient volume (100 to 250 ml) just large enough to retain the salts in solution.
3. Measure the volume and make a series of gross beta counts.

(b) Plutonium and Zirconium

1. Take duplicate aliquots of 10 ml each and adjust to 1 M in HNO_3 .
2. Add 5 ml 1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ to each sample, heat nearly to boiling, and transfer the samples to 125 ml separatory funnels.
3. Slowly add 8 ml 1 M NaNO_2 to each sample and wait for the reaction to subside.
4. When the sample has cooled, add 10 ml 0.5 M TTA (111 grams thenoyl-trifluoroacetone per liter in xylene).
5. Shake for ten minutes, allow the organic phase to separate, drain, and discard aqueous phase. Transfer organic phase to a 10 ml graduate.*
6. Transfer the entire organic phase, 1 ml at a time, onto a stainless steel plate and dry. Do not allow any water, which may settle out in the graduate, to be transferred. (A drop of water will leave a salt deposit which will decrease the alpha count.)
7. From the residual volume of organic and the known initial addition of organic, calculate the effective yield assuming quantitative extraction in one pass.
8. Count the prepared plates for alpha, correct for yield and aliquot taken, and report as plutonium.
9. Count the same plates for beta, correct for yield and aliquot taken, and report as zirconium.

*There is a small volume loss of organic into the aqueous phase - 1 to 3%.

(c) Cerium

1. Pipette duplicate 5 ml aliquots of the sample into two 50 ml lusteroid centrifuge tubes. To each, add 20 mg Ce carrier, 20 mg each of La holdback carrier and Zr holdback carrier. Swirl, make 2 M in HNO_3 . Add about 2 ml conc. HF and swirl. Centrifuge and discard supernate. Add about 10 ml water; slurry precipitate by stirring; transfer contents to a 50 ml glass centrifuge tube using a minimum of additional water. Equalize the liquid level in tubes; centrifuge. Discard supernate.
2. Add about 1 ml saturated H_3BO_3 to the supernate. Stir well. With stirrer still in, add about 8 ml conc. HNO_3 . Stir to dissolve; a drop or two more of H_3BO_3 may be necessary. With tubes in hood, add about 3.5 grams NaBrO_3 with stirring. Wait about one minute. If reaction has started, let it go to completion; if reaction has not started, very gently warm to start the reaction and then set tube aside. The solution, after reaction, should be clear and have no gas evolving. The color should be deep red-orange. If not, add another scoop of NaBrO_3 and repeat as above. Place tubes in ice-bath and add about 20 ml of a 0.35 M solution of HIO_3 . Stir. Digest one to two minutes or longer. Centrifuge. Discard supernate. Wash precipitate by stirring well in about 20 ml water. Centrifuge and discard supernate wash.
3. To yellow ceric iodate precipitate, add two drops conc. HCl and two drops 30% H_2O_2 . Stir well. With stirrer still in, add 8 ml conc. HNO_3 . Stir to dissolve. Treat with NaBrO_3 as above. Add about 20 ml 0.35 M HIO_3 . Stir. Digest. Centrifuge and discard supernate. Wash precipitate by stirring up well in about 20 ml H_2O . Centrifuge and discard supernate wash.
4. Repeat Step 3. Record time of precipitation.
5. To yellow Ce iodate precipitate, add 1 drop conc. HCl and three drops 30% H_2O_2 . Add 8 ml conc. HNO_3 . Stir to dissolve. Add 20 mg Zr holdback carrier. Should slight precipitate appear, add 2 more drops conc. H_2O_2 and HCl to dissolve same. Stir well. Digest five minutes. Centrifuge and transfer solution to new tubes, discarding white solid.
6. Set tubes in ice bath. Precipitate the Ce as $\text{Ce}(\text{OH})_3$ by stirring and cautiously adding excess (about 8 ml) 19 M NaOH; add minimum amount more if a reddish color persists. Centrifuge and discard supernate. Add 2 ml 6N HCl to the precipitate, swirl to dissolve; dilute to 10 ml volume. Add about 1 ml of 6% H_2SO_3 and swirl. (Red color should appear and disappear.)
7. Precipitate the Ce by adding conc. NH_4OH dropwise with stirring. Add two drops in excess. Centrifuge and discard supernate.
8. Wash the precipitate twice with 10 ml portions of water.

9. Dissolve the $Ce(OH)_3$ in 2 ml 6 N HCl (gentle heat may be necessary). Add about 15 ml H_2O . Heat to boiling and add, with stirring, 15 ml saturated $H_2C_2O_4$. Continue to stir until precipitate appears, and a short while afterward. Cool tubes and digest in ice bath for ten minutes.
10. Centrifuge and discard supernate. Swirl in 5 - 10 ml water and filter with suction on a moistened tared paper (Fisher "Filtrator"). Wash three times with hot water, three times with alcohol, and three times with ether. Dry one minute.
11. Weigh as cerium oxalate. Mount, count no sooner than two hours after Step 4.

(d) Trivalent Rare Earths (Y^{90} , Y^{91} , La^{140} , Pr^{143} , Nd^{147} , Pm^{147}).

1. To lusteroid tubes add 20 mg Pr carrier and 5 ml of sample. Swirl. Add 20 mg Zr carrier and make 2 M in HNO_3 . Add 2 ml conc. HF. Swirl. Centrifuge and discard supernate. Wash 10 ml H_2O , centrifuge and discard wash.
2. To the precipitate, add 1 ml saturated H_3BO_3 and stir to break up lumps. Add 8 ml conc. HNO_3 , and stir until dissolved. Add 20 mg Ce holdback carrier, add 10 drops of 1 M $NaBrO_3$, stir, and add 20 ml 0.35 M HIO_3 . Digest 2 - 3 minutes in an ice bath. Centrifuge and transfer the supernate to a glass tube.
3. Add to the supernate a second portion of bromate, 10 mg of Ce holdback carrier and 10 mg Zr carrier. Mix thoroughly and allow to stand five minutes in an ice bath. Centrifuge, and transfer the supernate (filtering if not clear) to another centrifuge tube. Change stirring rods.
4. Set tube in an ice bath and cautiously add an excess (about 9 ml) of 19 M NaOH. Stir well and centrifuge. Discard supernate and wash the precipitate with 10 ml of water. Centrifuge and discard wash. Dissolve in 1 ml conc. HCl, dilute to 8 ml, and swirl. Add 1 ml 6% H_2SO_3 (more may be necessary, a red color should appear and disappear).
5. Precipitate with a minimum amount of conc. NH_4OH . Centrifuge and discard the supernate. Wash the precipitate and tube walls thoroughly twice with 10 ml portions of water.
6. Dissolve the precipitate in 1 ml 6 N HCl. Dilute to 15 ml. Heat to boiling and add, with stirring, 15 ml of saturated $H_2C_2O_4$. Cool in an ice bath ten minutes. Centrifuge and discard supernate. Add a little water, filter on a tared paper, wash three times with hot water, three times with alcohol and three times with ether. Dry one minute, and weigh to determine yield. Mount and count as usual.

(e) Strontium

1. Add 5 ml sample to centrifuge tubes. Add 20 mg Ba holdback carrier

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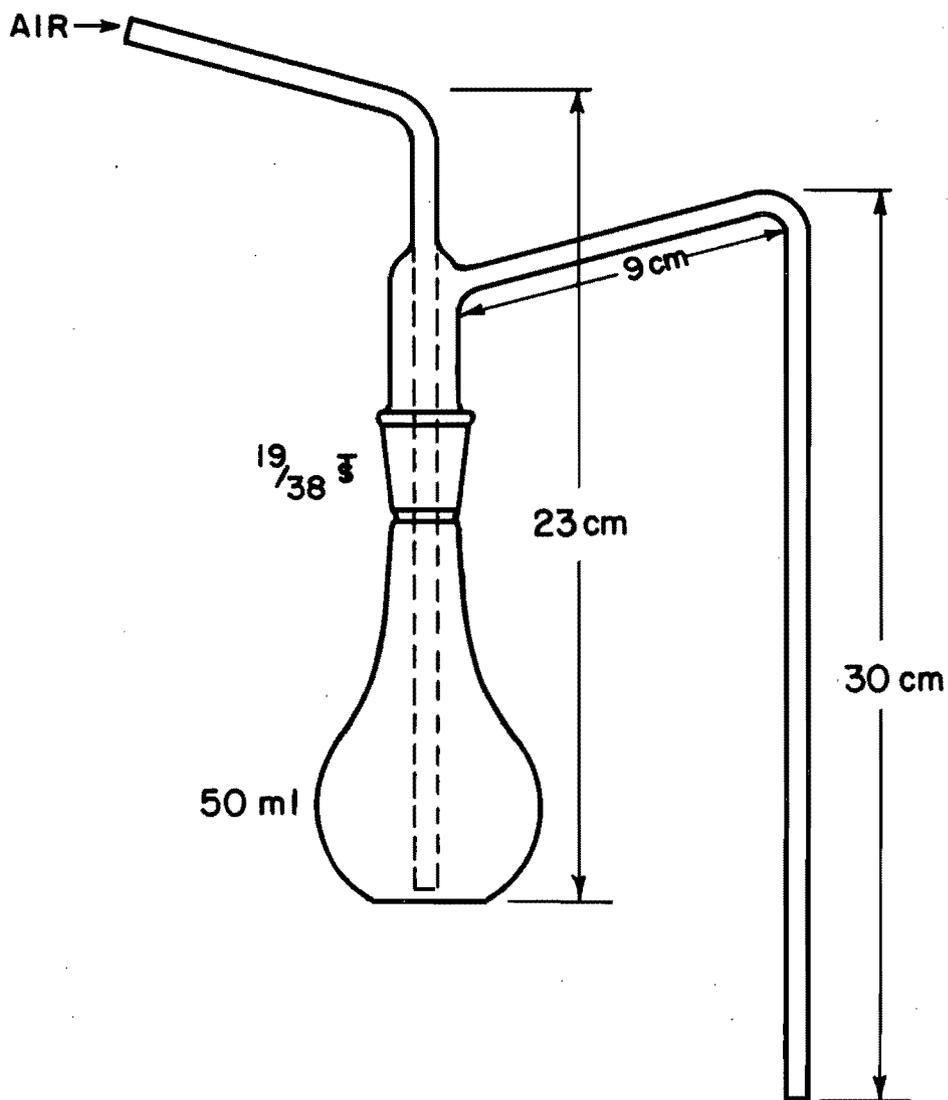


FIG. 21
RUTHENIUM STILL

and 20 mg of Sr carrier.

2. Add 30 ml fuming nitric acid to each tube. Place tubes in ice bath. Stir one minute. Digest five minutes. During digestion, tare papers. Centrifuge two minutes. Discard supernate.
3. Dissolve precipitate in about 2 ml H_2O . (Heat may be necessary.) Reprecipitate with 15 ml fuming nitric, digest one minute, centrifuge and discard supernate.
4. Dissolve precipitate in 5 - 10 ml H_2O . Add a few drops 0.1% Aerosol O.T. and one drop phenolphthalein indicator solution. Add 10 mg Fe carrier, and precipitate $Fe(OH)_3$ with about 2 ml 6 M NH_4OH . Centrifuge; decant supernate into new tubes; discard $Fe(OH)_3$.
5. Neutralize supernate with 6 M HNO_3 , add 2 ml 6 M NH_4 acetate and 1 ml 6 M HAC. Heat solution nearly to boiling and add 1 ml of 1.5 M Na_2CrO_4 dropwise, with stirring. Stir one minute, cool, and centrifuge.
6. Filter supernate into new tubes. Discard $BaCrO_4$ precipitate.
7. To clear supernate, add 2 ml conc. NH_4OH , heat nearly to boiling and add 5 ml saturated $(NH_4)_2C_2O_4$ slowly, with stirring. Stir one to two minutes, cool and centrifuge; discard supernate.
8. Transfer precipitate to filter paper with water, filter with suction on moistened tared paper. Wash three times with H_2O , three times with alcohol and three times with ether. Dry for one minute. Mount and count as usual.

(f) Ruthenium (Permanganate Method)

1. To each of two distillation flasks (see drawing), add 8 - 10 ml $KMnO_4$ (5 gms/100 ml), 5 ml H_3PO_4 , 10 ml of sample, 20 mg of Ru carrier and 2 or 3 glass beads. In each of two centrifuge tubes place 12 ml 6 M NaOH.
2. Set up a Ru still in a hood. The flask and tube above are incorporated into the system, the tube being set in an ice bath. Use asbestos-center wire gauze under flask. Adjust air into the system to give one to two bubbles per second. Heat the flask gently at first, then distill rapidly. During this last operation, set the burner directly under the flask and move back from the hood; notice that bumping does not occur. A yellow oil should distil over. Continue heating until the tube and flask have been rinsed properly.
3. Add 3 ml of 95% ethanol to the distillate, mix, dry tube bottom, and heat just to boiling by swirling over free flame until precipitate forms. Cool tube, centrifuge and note if supernate is colored. If the supernate is not colored, discard supernate and proceed to Step 5.
4. If the supernate is colored, pour into new centrifuge tube, neutralize

with conc. HCl, with methyl red indicator. Add 1 ml 6 M NaOH. Make an ethanol precipitation as in (3). Centrifuge and discard supernate. Wash the precipitate into the tube with the first precipitate. Use 10 ml of H₂O for this purpose.

5. In 10 ml H₂O, shake to suspend precipitate, add 1 ml 6 M NaOH, heat just to boiling to dissolve, and add 10 ml water. Add 0.2 gram powdered Mg metal in small portions, shaking after each addition. Add a few drops 0.1% Aerosol O.T. to minimize frothing and boil gently until Ru is well precipitated. Continue boiling for two minutes.
7. Cool tubes slightly; place in water bath, slowly wash down the tube walls with 5 ml conc. HCl to remove excess Mg, wipe tube and again boil until Ru coagulates well. Centrifuge and discard supernate. Swirl precipitate in water. Filter with suction on a moistened tared paper. Wash three times with hot water, three times with alcohol, and three times with ether. Dry one minute, mount and count.

Appendix C

Appendix C. Counting Methods

For beta counting, the detector consisted of a bell-shaped Geiger-Mueller tube⁽⁸⁾ held in a "Constant Geometry Tube Support"⁽⁹⁾ (Photograph 2). Shielding against cosmic and external gamma radiations was provided by a cylindrical lead shield. The tube was connected to a conventional "scale-of-64" circuit containing a high-voltage supply, an amplifier, and a scaling and recording circuit⁽¹⁰⁾.

The proportional alpha counter⁽¹¹⁾ was used for measurement of Pu. Samples were prepared by evaporation on 1-3/4" stainless steel discs. The solid content must be $< 1 \text{ mg/cm}^2$ to avoid excessive self-absorption.

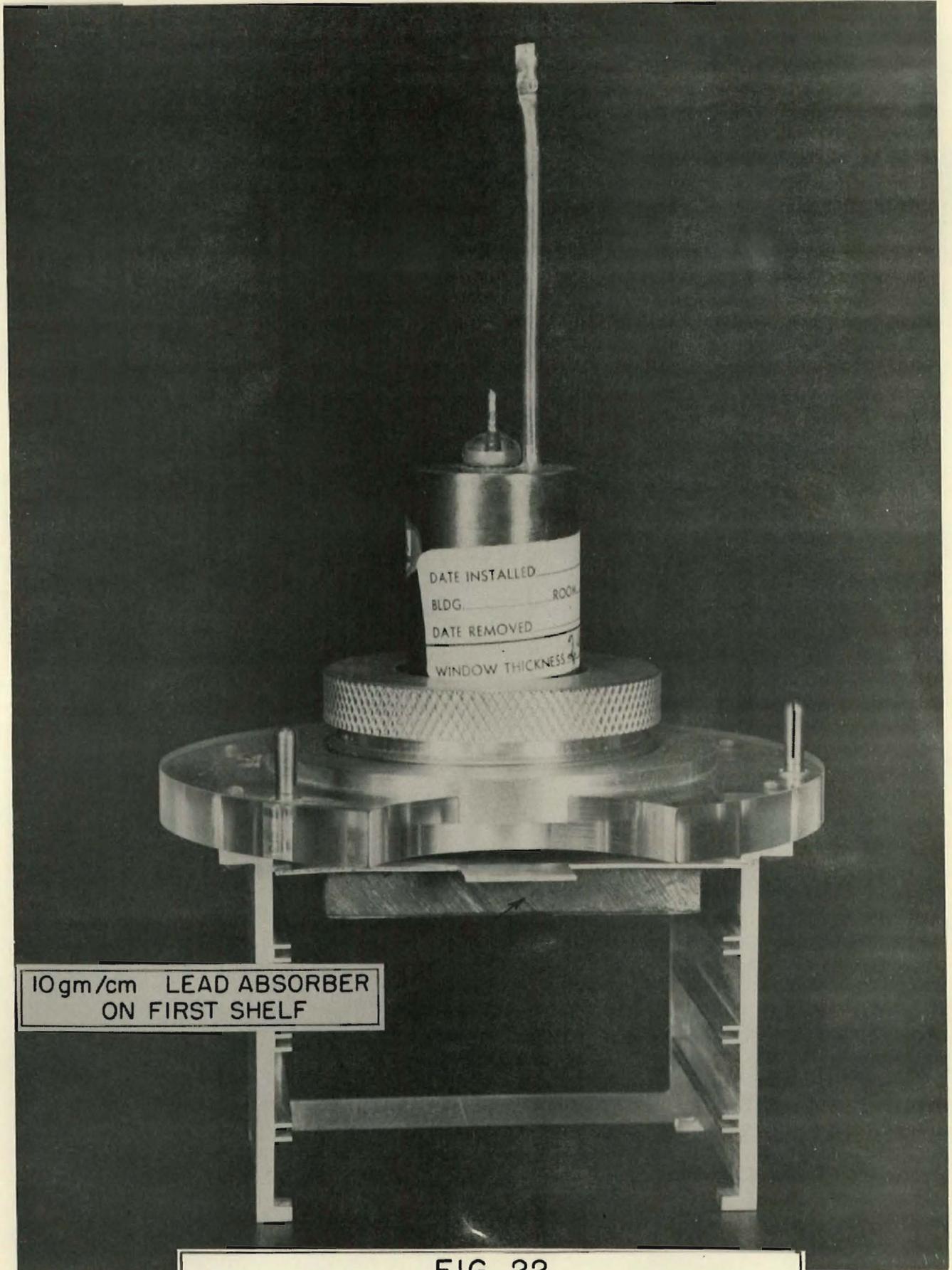
For measurement of gross beta activity, 1 ml or less of sample solution was evaporated on a one-inch watch glass by means of an infra-red lamp. The watch glass was mounted in the well formed by stretching a piece of scotch tape over a one-inch hole in the center of a 2-1/2" x 3-1/4" aluminum card. The watch glass was covered with cellophane ($\sim 3 \text{ mg/cm}^2$) and the sample was counted on the "second shelf" of the tube support (2 cm from the tube window). This arrangement gave about 7.5% geometry. Absorption curves were taken with the aluminum absorbers on the top shelf.

When the radiochemically separated activities were to be counted, the filter paper disc with precipitate was mounted in the center of a solid card (2-1/2" x 3-1/4"), covered with cellophane, and counted as above.

No corrections were made in this work for self-scattering and absorption in air and window. The answers are thus relative, and the disintegration rates given are usually low. For demonstration of the method, however, these results are adequate.

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PHOTO 6474



10gm/cm LEAD ABSORBER
ON FIRST SHELF

FIG. 22
CONSTANT GEOMETRY TUBE SUPPORT