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SPECIFIC ALPHA ACTIVITY OF PLUTONIUM

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ABSTRACT

The specific alpha activity of plutonium was found to vary in proportion to the amount of isotope 240 present, which is proportional to the amount of plutonium in the uranium slug or to the amount of irradiation received by the slug. From determinations of the specific activity on four samples of different isotopic composition the half life of Pu^{239} was found to be 24,600 years; and, assuming that Pu^{238} contributes 13% of the increase in alpha activity, the half life of Pu^{240} is 6,260 years.

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SPECIFIC ALPHA ACTIVITY OF PLUTONIUM

Introduction

The specific activity of plutonium must be known in order to estimate its concentration in various solutions by the radioassay method. Inasmuch as the specific alpha activity had never been determined under the conditions imposed by the radioassay group's method, four determinations were made in this manner on plutonium samples of different isotopic composition. The results of the determinations give the specific alpha activity in recorded counts per minute per microgram of plutonium necessary for the radioassay method. These results are shown in the accompanying graphs. They do not take into account the geometry of the chamber of the counter. Assuming the geometry of the chamber to be 51%, the half-lives of Pu^{239} and Pu^{240} are determined to be 24,600 years and 6,260 years respectively.

Procedure

Reagents:
- Concentrated HNO_3
- 5N HNO_3
- Distilled water
- Acetone
- Quartz-distilled hydrochloric acid
- Quartz-distilled nitric acid
- Quartz-distilled water

Apparatus:
- Two 50 λ Misco pipets and syringe
- Uncalibrated weight pipet suitable for weight aliquoting a volume of approximately one ml and syringe to fit
- Pipet washer (This is made by attaching about two inches of rubber tubing by means of a piece of glass tubing to a rubber stopper, which is inserted into a suction flask connected to a vacuum line. There should be two of the rubber tubing-rubber stopper attachments.)
- Four dropping bottles to contain the first four reagents listed above.
- Magnifying glass
- Kleenex
- Three 1000-ml Normax volumetric flasks
- Three small (~ 10-ml) beakers
- Three 5-ml volumetric flasks

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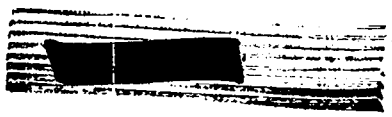

25-ml volumetric flask
Microscope cover glasses in small boxes
Two hot plates
Forceps
Nitrogen-chamber linear amplifier
Stop watch
Gold-soldered platinum boats made by folding and soldering 10-mil platinum cut out according to the accompanying diagram
Ainsworth VM (assay) balance
Ainsworth TC balance
Electric micro muffle furnace
Variac
Small desiccator with brass plate to hold boats
Platinum-tipped forceps
360° thermometer in aluminum block
Two small crystallizing dishes
One flat glass plate

Preparation of the samples and the determination of their plutonium concentration from the weight of the metal used: Two of the plutonium samples (lot numbers 224-7X and 4W) were supplied in the form of purified nitrate solutions of about 80 to 100 g/l concentration, and two (lot numbers 79H and 117H-120H) were in the form of essentially pure pieces of metal. All of the plutonium samples had been purified by at least one cycle of the "A" Process[1] (plutonium^{III} oxalate precipitation, sodium plutonyl acetate precipitation, and diethyl ether extraction of plutonyl nitrate). Before the alpha counting, the various assays, and the various analyses were performed, the metal pieces were converted to nitrate solutions. Inasmuch as it was desired to use the weight of the metal as a means of determining the concentration of the resulting plutonium solution, the following procedure for the preparation of the solution was used. A 25-ml volumetric flask was cleaned, rinsed out with quartz-distilled water, dried, and weighed on an Ainsworth TC balance. An approximately half-gram piece of plutonium was dropped into the flask which was reweighed. A little more than the calculated amount of quartz-distilled hydrochloric

1) LA-403, LA-405, LA-416

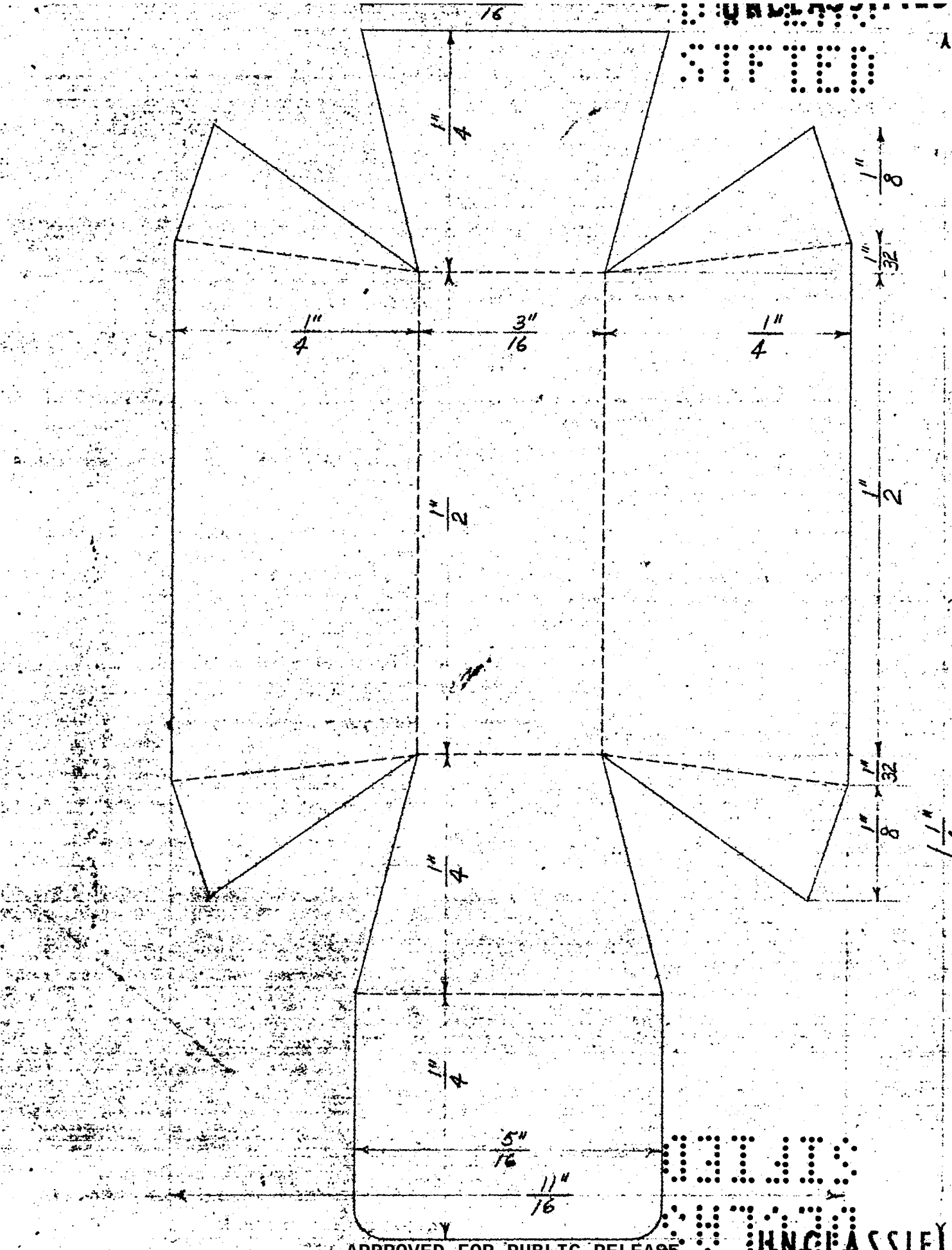

Fig. 1. Pattern for gold-soldered platinum boat.

acid was slowly added to dissolve the metal. Since it was not known whether a plutonium chloride solution could be converted to plutonium dioxide in a manner similar to the dioxide conversion of a plutonium nitrate or a plutonium sulfate solution by evaporation and ignition, five to ten ml of quartz-distilled HNO_3 were added, and the resulting solution was evaporated down to somewhat less than the volume of the initial HCl solution. Five to ten ml more quartz-distilled nitric acid were added, and, after a second evaporation, the resulting solution was diluted with quartz-distilled water and quartz-distilled nitric acid until the plutonium concentration was of the order of 50 to 75 g/l. The volumetric was then reweighed to determine the concentration of the plutonium per unit weight of solution.

Description of the aliquoting methods used: In the case of all four samples, aliquots of the nitric acid solutions were taken for the various determinations to be made upon them. The determinations made upon 224-7X and 4W were an oxide assay and an alpha count, whereas an oxide assay, a chemical titration assay, a chemical analysis, and an alpha count were run on 79H and 11 7H-120H.

Samples 224-7X and 4W were aliquoted on a volumetric basis. Four platinum boats and three 1000-ml volumetric flasks were given a 50 λ cut each of the nitrate solution by means of a Misco pipet. In order to insure the quantitative discharge of the aliquot into the vessel in question, the pipet was rinsed in the following manner. Two drops (~ 75λ) of 5N HNO_3 were placed on a microscope cover glass and were drawn in and out of the pipet, being retained in the pipet on the third intake, which also was as complete as possible in order to prevent leaving excessive amounts of plutonium on the cover glass. The rinse was then discharged into the vessel that received the aliquot. The pipet was rinsed on the same

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cover glass and redischarged in the same way. A third rinse of the pipet, discharged onto the same cover glass, was sometimes counted to demonstrate that the pipet was quantitatively discharged. The pipet is washed and dried between aliquots by drawing through it in the washer concentrated nitric acid, distilled water, acetone, and air in that order. In order to remove any foreign matter from the outside of the pipet, it is wiped off with a piece of Kleenex moistened with acetone after it is removed from the washer. After the pipet is properly filled with the plutonium solution, it is again wiped off with Kleenex (if necessary, with Kleenex moistened with 5N HNO_3) in order to remove any plutonium on the outside of the pipet.

Samples 79H and 117H-120H were aliquoted on a weight basis. Approximately 100 mg of solution (containing 5 to 10 mg of Pu) were discharged into each of three flasks and at least four boats from an uncalibrated pipet. The pipet was weighed between aliquots on an Ainsworth TC balance. The aliquoting for the chemical titration was done at the same time in the same manner. The remainder of the solution was submitted to CM-9 for chemical analysis.

Determination of the plutonium concentration by the chemical titration: This work was done by Harold Boaz of CM-9. It will be described in detail in a forthcoming report. Briefly, the method consists of preparing sulfate solutions of Pu^{III} by fuming down the aliquots with sulfuric acid and then reducing the plutonium with liquid zinc amalgam. The Pu^{III} is then titrated to Pu^{IV} with ceric sulfate.

Determination of the plutonium concentration by the gravimetric PuO_2 method: At least four platinum boats were brought to a weight constant to five micrograms or less on the assay balance by first cleaning the boats in nitric acid and water and

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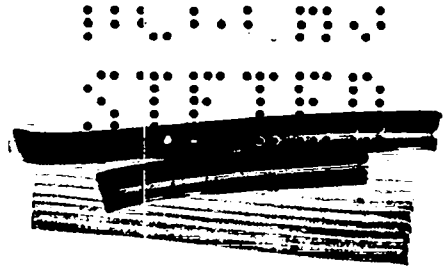
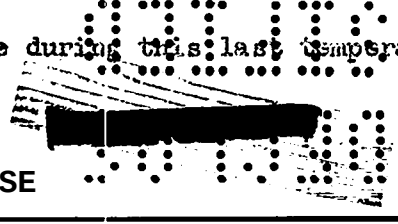
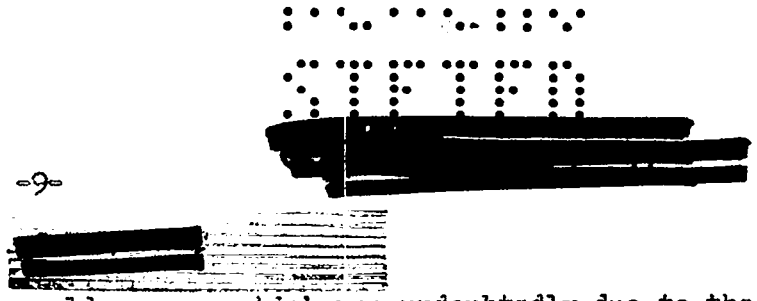


then repeatedly heating them to 1000° C in the muffle furnace. The boats were kept in the desiccator equipped with brass plates when not in use, except when they contained a nitric acid solution, the fumes of which corrode the brass. When the boats contained acid they were kept on the glass plate with a crystallizing dish inverted over them or on a hot plate with a crystallizing dish for a cover. Three 1000-ml volumetrics were washed with nitric acid until an aliquot of the wash solution showed no alpha contamination when evaporated onto a microscope cover glass and counted.

The hot plate was prepared by putting on it the thermometer in the aluminum block and two or three microscope cover glasses with a crystallizing dish inverted over the cover glasses. The cover glasses were used to prevent the boats from coming into contact with the hot plate, which corroded considerably during the evaporations which took place on it. The temperature was adjusted so that the thermometer read about 50° C. If the first part of the evaporation is done at a temperature higher than this, the solutions seem to creep excessively. The boats and the flasks were then loaded by one of the methods described above, after which each boat was transferred to the hot plate. The boats were warmed on the hot plate at about 50° C until the solutions had concentrated as far as they would at this temperature. The crystallizing dish was removed and drained now and then to prevent excessive amounts of the nitric acid which condensed on it from dropping onto the hot plate. Then the temperature is slowly raised. At about 80° to 90° the solutions began to boil, blowing rather large bubbles, hence it is necessary to raise the temperature slowly. The bubbles usually ceased forming around 120° to 130°, and then temperature was raised somewhat more rapidly until it was as high as the hot plate would produce (~ 230° C). Somewhere during this last temperature in-





terval a visible cloud of brown gas would appear, which was undoubtedly due to the decomposition of most of the plutonium nitrate. The boats were then transferred to the micro muffle furnace, which was turned all the way on but was controlled by means of a variac. The furnace was turned on with the variac set so that it would reach 1000° C, or approximately so by itself. The boats were usually left in the furnace for about two hours; during the last fifteen minutes to half an hour the temperature was about 1000° C. The boats were then cooled and weighed. The boats were reheated in the muffle furnace and reweighed until the weight became constant to five micrograms or less.

Making the alpha counts: The flasks were diluted to the mark with 5N HNO_3 and small portions were poured into 5-ml volumetrics, using small beakers to aid the transfer, merely for the purpose of making the subsequent aliquoting easier. Three samples for counting were prepared from each flask. Two microscope cover glasses were used for each sample and were dusted with a soft brush to remove all dust and lint prior to their use. A different Misco pipet and a different pipet fitting for the pipet washer were used to avoid contamination from the original solution, which was 20,000 times more concentrated than the one to be counted. The washing of the pipet and the taking of the aliquots were done in the same manner as in the case of the initial solutions of samples 224-7X and 4W described above. However, the aliquot was discharged onto a cover glass, and the rinsing, with 3 drops of 5N HNO_3, was done on another. In this case the rinse was left on the second cover glass after being drawn into the pipet several times, and the two cover glasses were counted together after being dried on a hot plate different from the one on which the boats were heated[2]. The pipet was washed and dried as described before between

2) One rinsing was found to be sufficient as may be checked by counting a third

each sample. The samples were counted in a so-called 50%-geometry-nitrogen-chamber linear amplifier for two eight-minute intervals. Samples 79H and 117H-120H were counted for two eight-minute intervals on three occasions, each sample being counted a total of 48 minutes.

Results

The specific activities and the half lives of Pu^{239} and Pu^{240}: The various assays yielded the amount of plutonium corresponding to the counting results, and thus the specific activity was determined. The results of the four experiments in observed counts per minute per microgram of plutonium together with their calculated probable errors are[3]:

224-7X:	69,574 ± 115 c/m/γ Pu
4W:	70,057 ± 136 c/m/γ Pu
79H:	72,616 ± 84 c/m/γ Pu
117H-120H:	73,069 ± 115 c/m/γ Pu

Data from other sources in regard to the amount of irradiation received by the plutonium samples and in regard to the amount of isotope 240 in them, when combined with the specific activity data, show that the variation of the specific activity is proportional to the amount of plutonium present in the uranium slug, to the amount of irradiation the uranium slug received, and to the amount of isotope 240 present in the plutonium. The accompanying figures illustrate these relations. There are two figures of specific activity versus Pu^{240} content, the one on the coarser scale extrapolating the specific activity to higher values of Pu^{240}

3) The values have been revised somewhat since they appeared in LAMS-293, but they are the results of the same experiments. The new values are about 0.15% higher than the old.

Fig. 2 Specific Activity versus Pu^{240} content. The crosses indicate the probable errors.

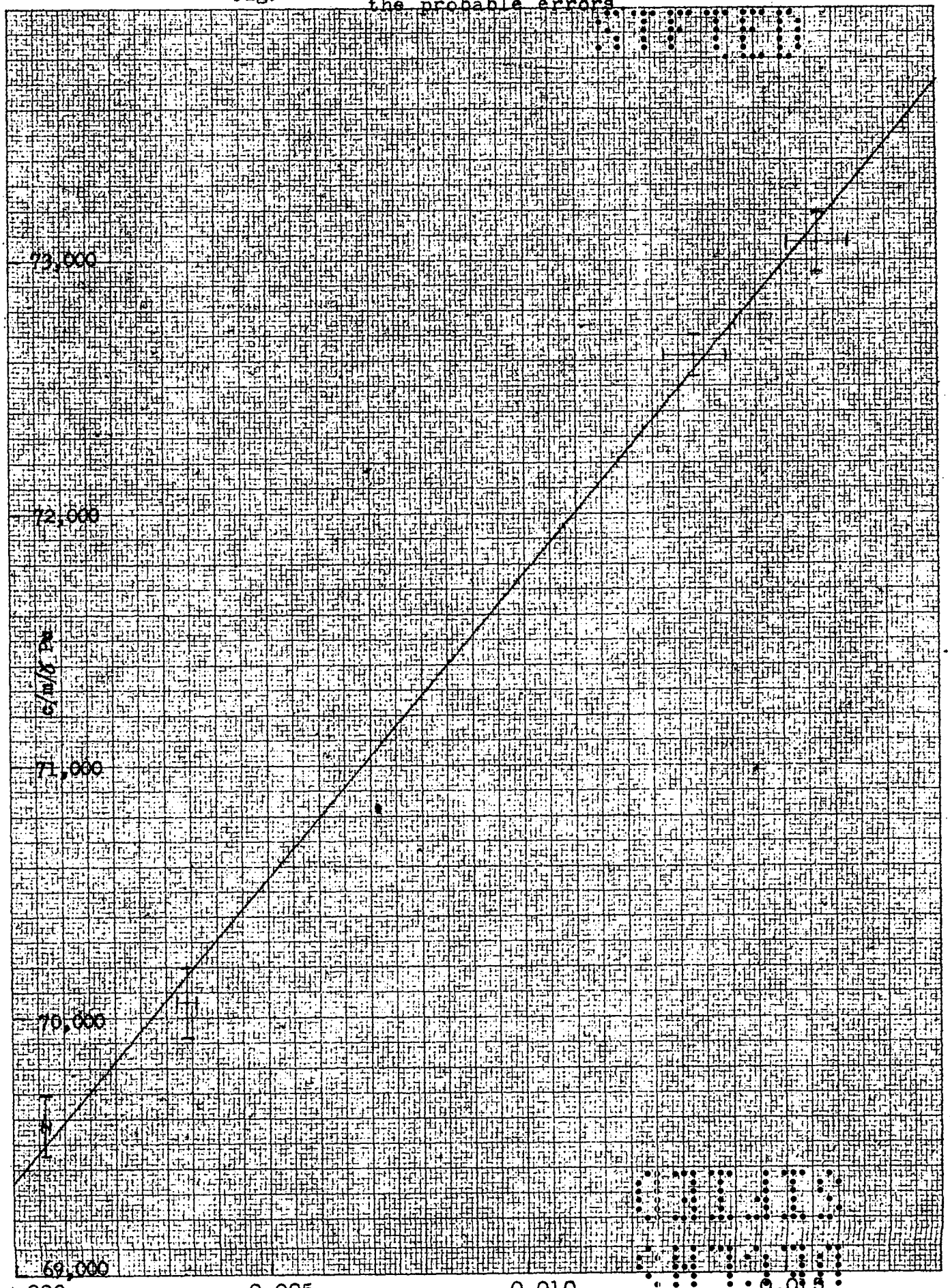
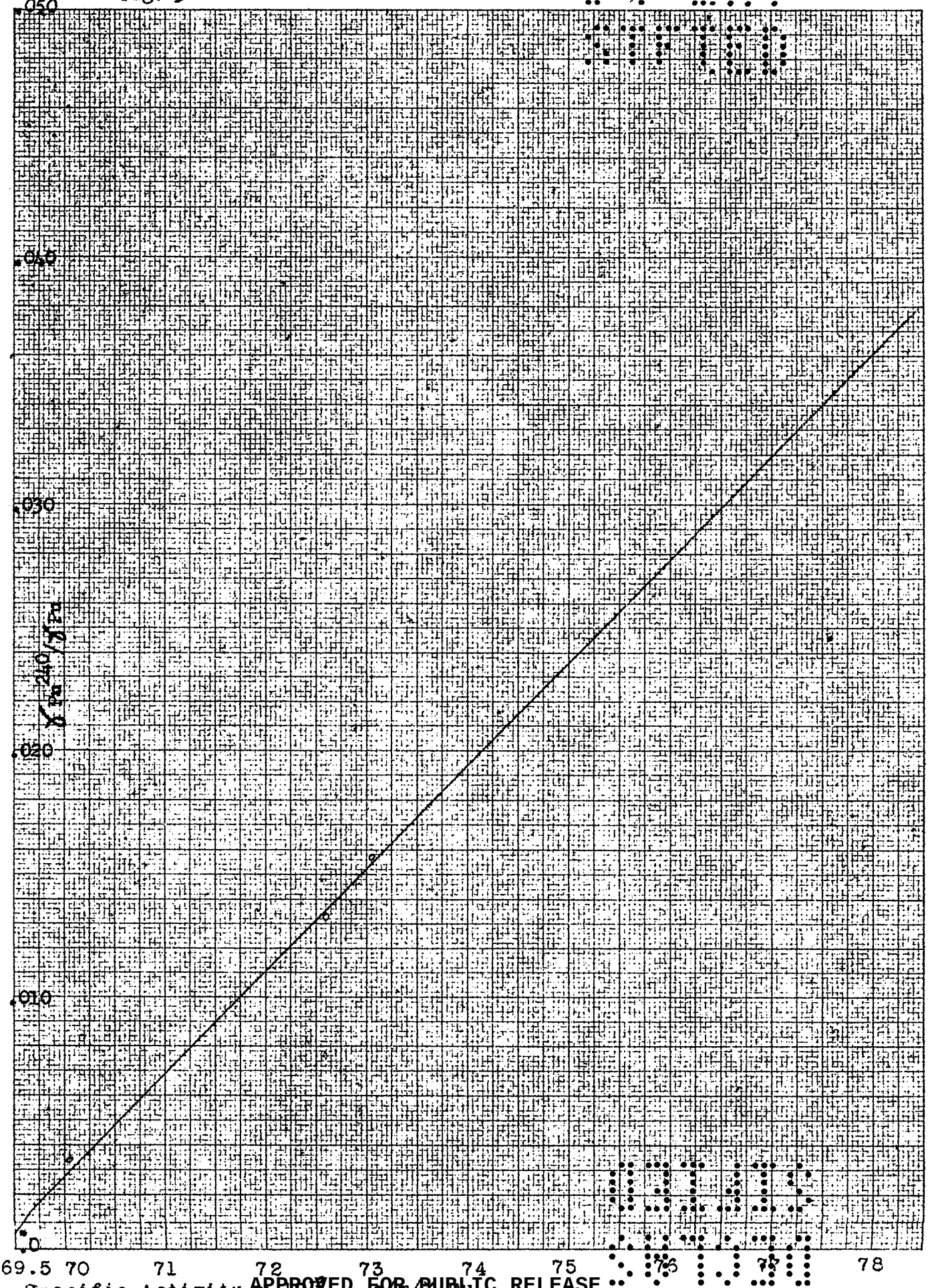
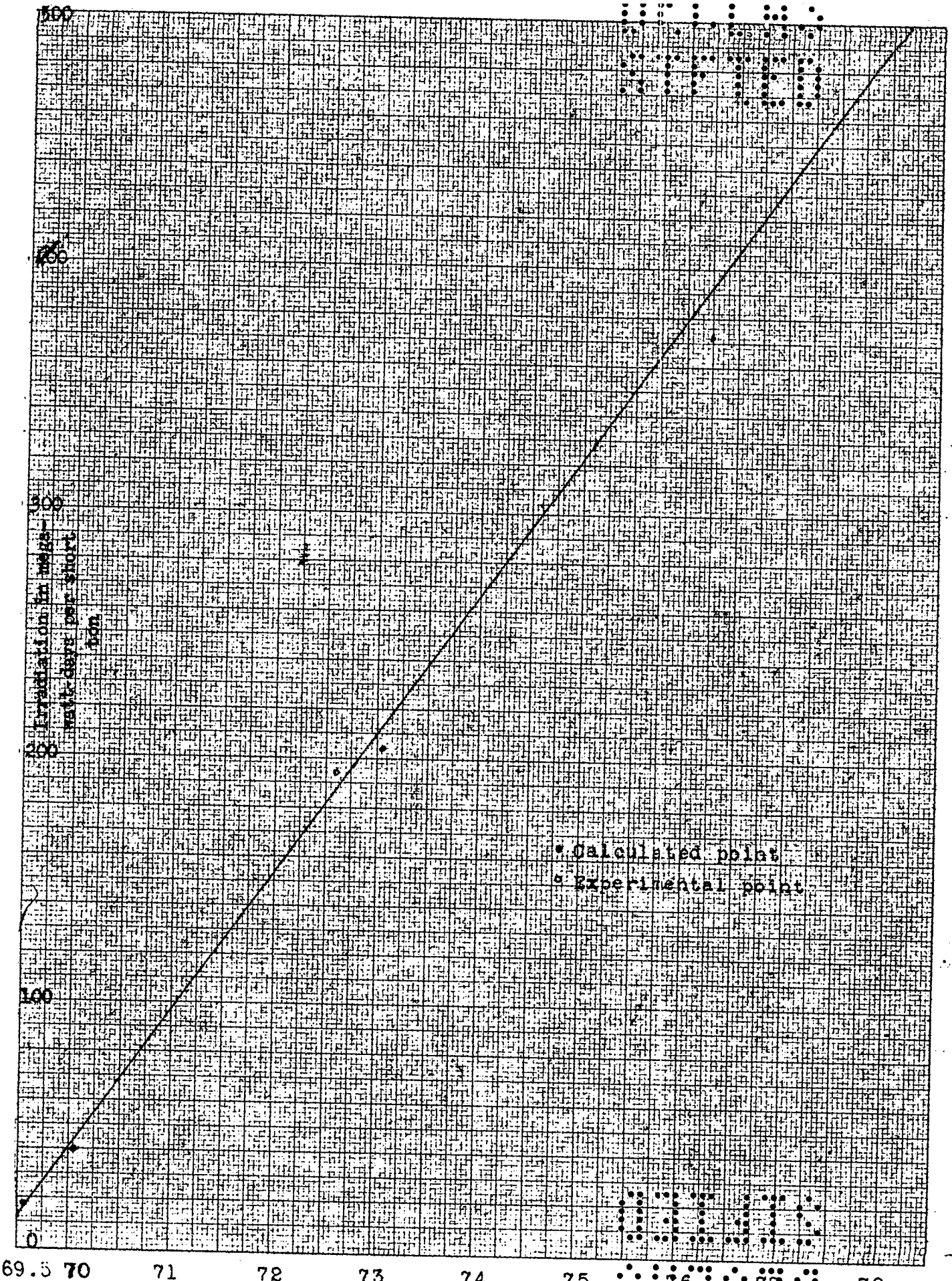
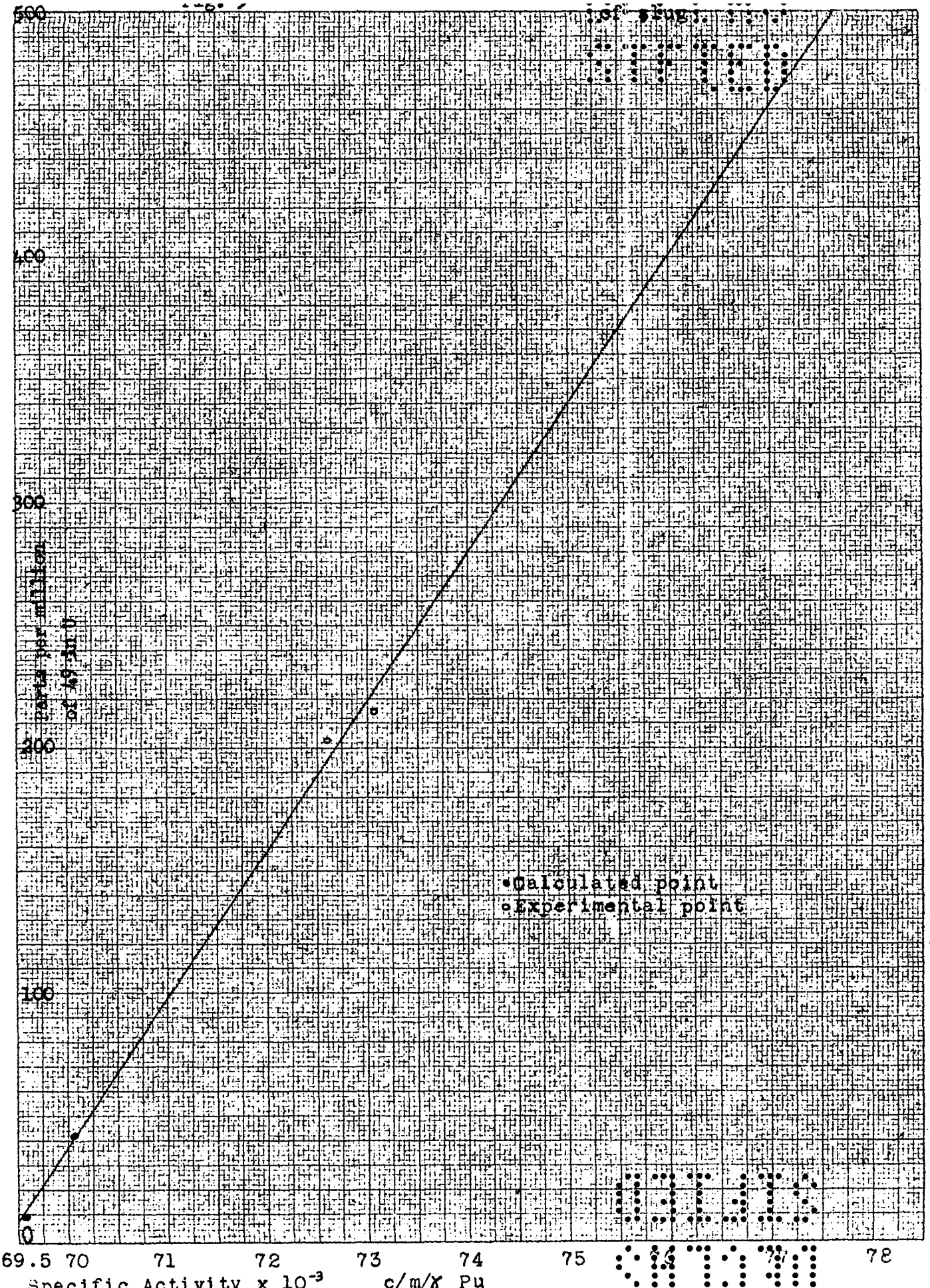


Fig. 3 Specific activity versus Pu-238 content







content than have yet been incurred, and the one on the finer scale being used to calculate the specific activities of isotopes 239 and 240. The Pu^{240} concentrations were obtained from LAMS-293.

Material	Grams Pu per metric ton U in slug	Irradiation received in megawatt days per short ton	$\gamma Pu^{240}/\gamma$ Pu and probable error
224-7X	*	*	0.00063 ± 0.00006
4W	42	*	0.0034 ± 0.0002
79H	203	194	0.0133 ± 0.0006
117H-120H	215	204	0.0157 ± 0.0006

*The values for these points on the graphs were calculated using the conversion factors given below.

Conversion factors:

from $\gamma Pu^{240}/\gamma$ Pu to grams Pu/metric ton U: 1.44×10^4

from $\gamma Pu^{240}/\gamma$ Pu to megawatt days/short ton: 1.36×10^4

These conversion factors were calculated from the irradiation data and the Pu^{240} analysis on lots 60H, 79H, 90H, 110H, 117H-120H, 130H, 150H, 170H.

From Fig. 2 it may be seen that the specific activity of Pu^{239} is 69,340 c/m/γ. Assuming a 51% geometry for the chamber, the specific alpha activity of Pu^{239} is 1.36×10^5 disintegrations per minute per microgram. The half life of Pu^{239} is then 24,600 years with an estimated probable error of 2%, arising mainly from the uncertainty of the geometry of the chamber.

At a Pu^{240} concentration of 1% the specific alpha activity of Pu is 71,770 c/m/γ. Therefore,

$$71,770 - (69,340)(0.99) = 3,120 \text{ c/m/}\gamma \text{ Pu}$$

arise from substances other than Pu^{239} at this isotopic composition. Perlman and Seaborg[4] say that 13% of this increase in the specific activity is due to

4) Perlman and Seaborg, MUC-GTS-1872, July 28, 1945.

amounts of Pu^{238}. Assuming that the remainder of the increase is due to Pu^{240}, if the geometry of the chamber is 51%, its specific alpha activity is 5.33×10^5 disintegrations per minute per microgram and its half life is 6,260 years with an estimated probable error of 10%.

Probable errors: The probable errors of the specific alpha activities in recorded counts per minute per microgram were calculated from the statistical error of the counting and the probable errors of the various other measurements. The probable error of the volume of an aliquot was obtained from the pipet calibration data. The probable errors of the concentrations of the initial nitrate solutions were obtained from the assay (gravimetric oxide, chemical titration, weight of metal) data. The probable error of the volume to which the aliquots were diluted was estimated on semi-quantitative basis. A generous estimate here still gave a negligible contribution to the total error.

The probable error on the size of an aliquot was 0.028% (result of three determinations). The probable error on the volume to which the aliquots were diluted arose from the expansion of the solution after dilution. It was estimated to be 0.025%.

The probable errors on the various assays (and the number of determinations in each case in parentheses) follows:

Material	Gravimetric Oxide	Chemical Titration	Metal
224-7X	0.061% (3)	. . . . .	. . . . .
4W	0.145% (3)	. . . . .	. . . . .
79H	0.187% (4)	0.027% (3)	0.03% (*)
117H-120H	0.033% (5)	0.017% (5)	0.02% (*)

*These probable errors were estimated from the various chemical analyses run on the nitrate solution of the plutonium. There were not four boats on 224-7X and 4W as one result in each case was incompatible with the rest of the data.

The largest contributor to the probable error of the specific activity in recorded counts per minute per microgram was the counting data. The following table gives the probable error of the counting for each sample together with the number of cover glasses counted and the approximate total number of counts recorded for each glass. There were not always nine cover glasses, since accidents occasionally befell them, and some were so far out of line that their inclusion in the counting data would be obviously fallacious.

Material	Probable counting error	Number of cover glasses	Total counts per cover glass
224-7X	0.147%	6	0.3×10^6
4W	0.119%	8	0.2×10^6
79H	0.104%	8	1.0×10^6
117H-120H	0.155%	9	1.5×10^6

Comparison of radioassays with chemical titration assays: As a check on the specific activity values, it was hoped to show that a number of radio assays on samples that had received known amounts or irradiation agreed with the chemical titrations of those samples. However, the data on 40 samples show that the radioassays average about 0.7% lower than the chemical titrations. This discrepancy could be explained by a consistent faulty calibration of the radioassay group's pipets. An investigation of five pipets indicated that they seemed to be rated 0.25% too high on the average. If this is approximately the average discrepancy of the calibration, a correction on the radioassays would make them average out about 0.1% below the chemical titrations.