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July 11, 1945

This document contains 26 pages

ISOTOPIC CONSTITUTION OF PLUTONIUM: II

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ABSTRACT

The abundance ratio Pu^{240}/Pu^{239} has been measured for four samples of plutonium which were made at different levels of neutron irradiation.

Re-irradiated at Clinton (C16 or CX2A)	$(1.18 \pm 0.08) \times 10^{-3}$
Re-irradiated at Hanford (CW1B)	$(6.51 \pm 0.20) \times 10^{-3}$
4W	$(2.96 \pm 0.06) \times 10^{-3}$
41H	$(1.11 \pm 0.02) \times 10^{-2}$

A high background appeared at every mass position between 235 and 290 in the sample re-irradiated at Clinton but this background became negligible after a period of distillation of the sample. The source of this extraneous material has been shown to be in the sample rather than in the spectrometer. A mass 241, the main portion of which is not isotopic with plutonium, has been observed (in CW1B); and a peak corresponding to (?)$^{241}O^{16}$ has been observed. The mass number of the main isotope of plutonium has been identified as 239 by superimposing the second-order plutonium spectrum over the first-order tin spectrum. The chemical atomic weight of plutonium containing 1 percent Pu^{240} has been calculated to be 239.05 using an experimentally determined packing fraction of $+(4.2 \pm 2.0) \times 10^{-4}$.

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ISOTOPIC CONSTITUTION OF PLUTONIUM: II

Changes in the Spectrometer Since the Last Report

Since the first report of this series was written (LA-168) several changes have been made in the plutonium mass spectrometer. A coaxial system of nichrome shields (shown in Fig. 1) has been devised to prevent the distillation of plutonium metal onto the pyrex insulators of the source. This change has extended the operation time between cleanings of the insulators from about 1 hour to approximately 15 hours.

Two plates of the source, the case between them, the electron collector and the filament slit, formerly made of copper to resist corrosion by UF_6 in the uranium hexafluoride analysis for which the instrument was designed, were replaced by nichrome parts. This was done to permit outgassing of all the metal parts of the source by heating them inductively to $\sim 900^\circ$ C in a separate vacuum system. In one of the copper plates which was replaced, the plutonium atoms entered the ionizing region through a circular hole in the center of the plate. The new nichrome plate has a rectangular hole (1/2" x 3/16") whose shape is approximately the same as that of the ionizing electron beam, thus presenting a larger area of the electron beam to the stream of plutonium atoms from the furnace (Fig. 1). The tungsten filament in the microfurnace was replaced by a tantalum filament, thus making the furnaces easier to fabricate.

Molten plutonium wets tantalum, so that during a run, the plutonium will tend to creep up over the mouth of the tantalum crucible and down the outside and it will then evaporate in all directions from all the outside surface of the crucible. Since this evaporation from the outside of the crucible does not contribute to the beam of atoms which are ionized, a large share of the sample is

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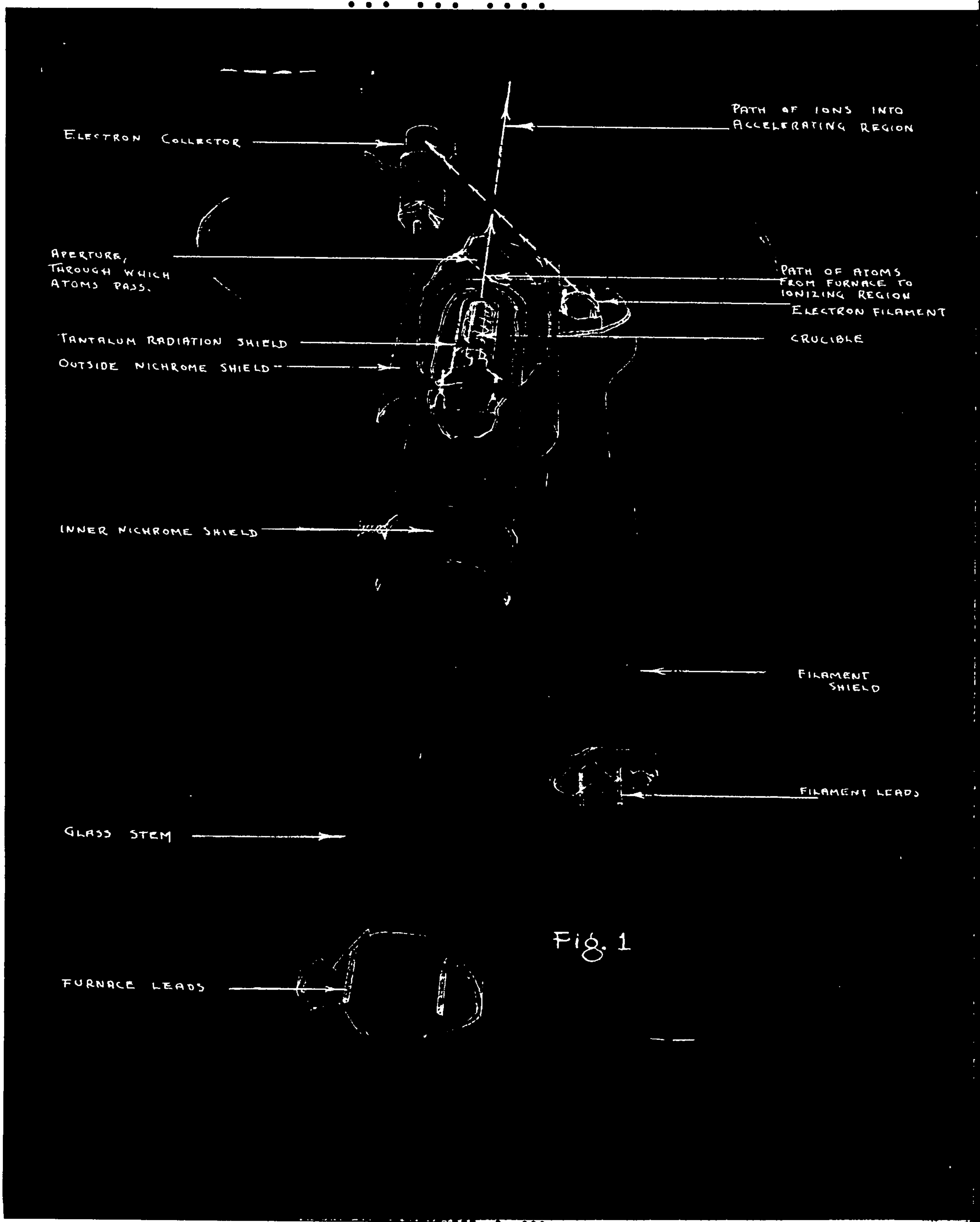
ELECTRON COLLECTOR
PATH OF IONS INTO ACCELERATING REGION
APERTURE, THROUGH WHICH ATOMS PASS.
PATH OF ATOMS FROM FURNACE TO IONIZING REGION
ELECTRON FILAMENT
TANTALUM RADIATION SHIELD
CRUCIBLE
OUTSIDE NICHROME SHIELD
INNER NICHROME SHIELD
FILAMENT SHIELD
FILAMENT LEADS
GLASS STEM
FURNACE LEADS

Fig. 1

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wasted. In spite of the system of shields, this added evaporation cuts down the life of the insulators between cleanings, so it was considered desirable to prepare crucibles that were not wet by molten plutonium.

Lipkin, Perlman, Spindel, and Weissman have shown that a tantalum crucible can be lined with zirconium nitride, and that this lining is not wet by molten plutonium. Accordingly, using their technique, tantalum crucibles were prepared with linings of ZrN. The steps in the preparation of these linings are:

1. Zirconium metal is melted in the crucible in a vacuum of about 10^{-6} mm.
2. The crucible is then heated to 1700 to 1725° C in an atmosphere of about 5 to 10 cm of purified nitrogen. This nitrogen is circulated over the heated crucible until the rate of change of nitrogen pressure becomes very slow, indicating that the reaction has been nearly completed. (The final reaction with tantalum is very slow.)
3. The crucible is then outgassed at 1700 to 1725° C until the pressure in the system is pumped down to $\sim 5 \times 10^{-6}$ mm. Under these conditions the tantalum nitride is decomposed whereas the zirconium nitride is not.

To test a crucible prepared in this way, 3.9 mg of plutonium were placed in a crucible and were evaporated into the spectrometer at a rate which gave the same beam intensity as is normally used. In tantalum crucibles, a rate of evaporation of 4 mg/hr had been observed. This sample gave the same beam intensity for 10 hours. It is interesting to note that the ratio between the outside area of the crucible and the area of the open end is 12.7.

The use of these lined crucibles has two advantages. First, an analysis can be made on as little as 2 mg of sample, and second, the time of operation of the tube between cleanings of the insulators has been further increased to about 100 hours. In the case of several consecutive runs, between which the insulators

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and source are not cleaned, there is evidence to indicate a small "memory effect". Metal from one sample which did not reach the ionizing electron beam but which was deposited on some of the nichrome parts, may later re-evaporate because of heat radiated from the microfurnace, and thus contribute to a later sample. Even though the magnitude of this effect is thought to be quite small the source was cleaned previously to running the following samples.

<u>Clinton Re-irradiated Sample</u> (designated by Segre's group as C-16; by Dodson as CX2A)

A sample of plutonium, re-irradiated at Clinton with a flux, nvt, of 2.8×10^{18} (LA-256, Deutsch) was examined. It had been purified and reduced at Los Alamos.

Curve A, Figs. 2 and 3, is a record of an early run on this sample and it is remarkable in several respects. Peaks may be counted at every mass position from 239 to above 290 with the high-mass peaks being less pronounced, and with the exception of the peaks explained below, all are of nearly the same height. On several runs a few peaks appeared below mass position 239. The peak at mass 255 corresponding to $Pu^{239}\,O^{16+}$ persisted throughout the entire run; the 255 peak remained even after the main 239 peak had disappeared because of the sample's running out. This peak has been further confirmed as the oxide, by the observation, in the correct ratio, of a peak at 257 corresponding to $Pu^{239}\,O^{18+}$. This was done after the low-background peaks had disappeared with continued distillation (see below). The peak heights at the 274- and 276-mass positions bear a 3-to-1 ratio to each other and are respectively 35 and 37 units above the 239 position, identifying them as due to $Pu^{239}\,Cl^{35+}$ and $Pu^{239}\,Cl^{37+}$.

The remaining peaks, which are unaccounted for, have the following properties. They are all of nearly the same height, and the ratio of this height

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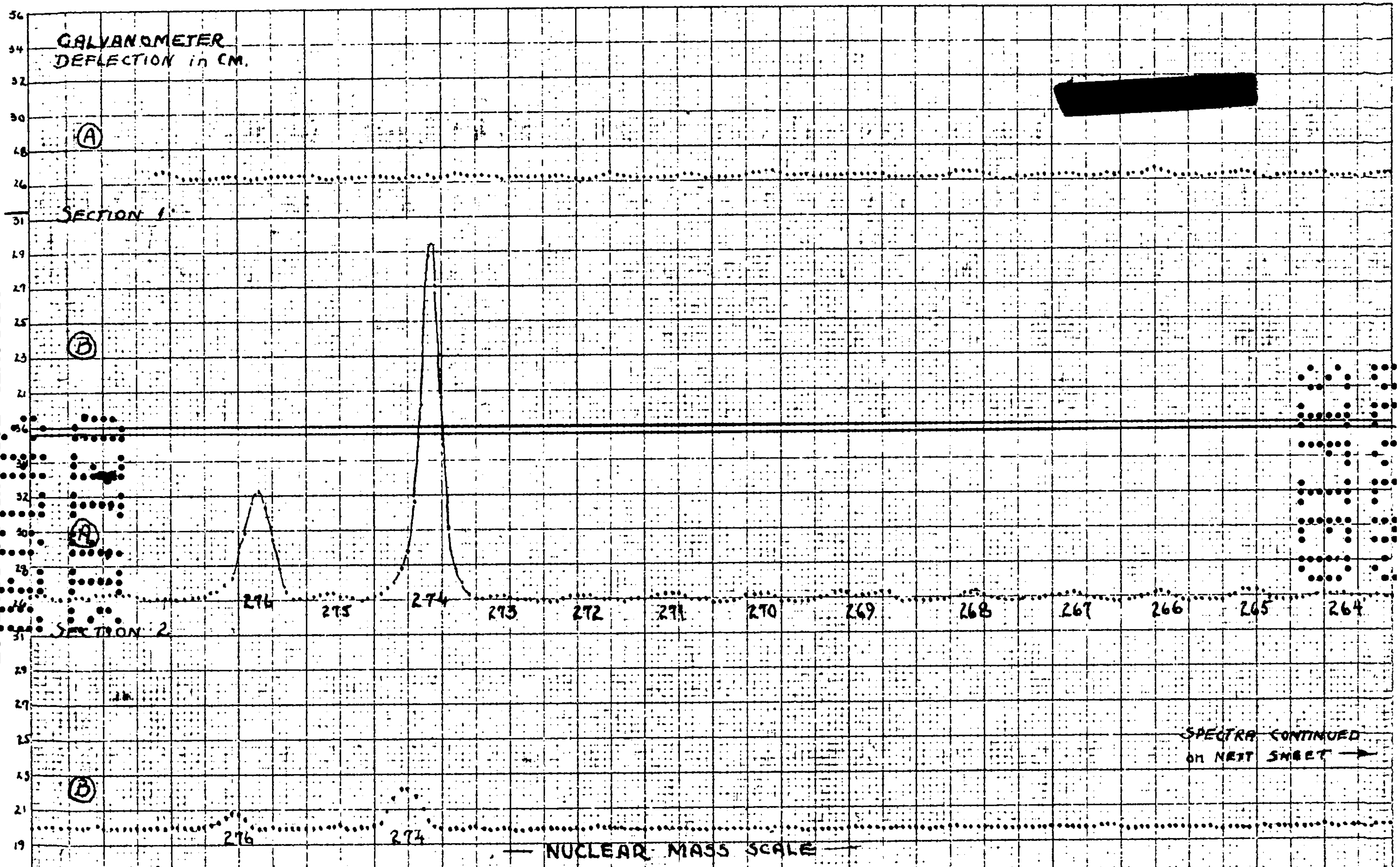

SHOWING – FOR COMPARISON – TWO SPECTRA of SAMPLE CONTAINING EXTRANEOUS MATERIAL.
(A) MATERIAL PRESENT (B) MATERIAL EVAPORATED AWAY

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Fig. 2.

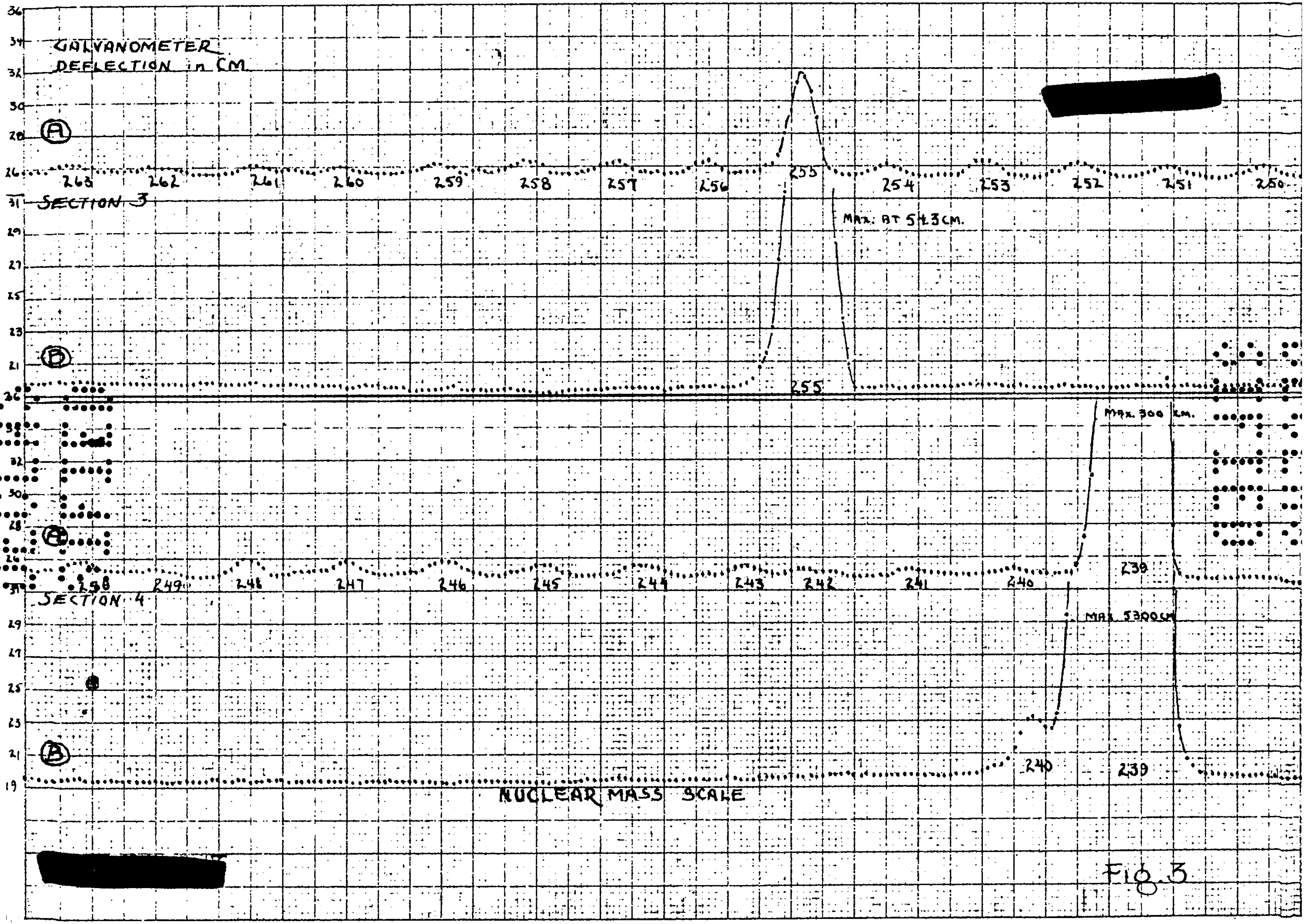

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Fig. 3

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to the height of the 239 peak decreases rapidly with time of distillation. Curve B, Figs. 2 and 3 shows a run after most of these peaks had disappeared. During this distillation, the Pu^{240}/Pu^{239} abundance ratio decreased from $30,000 \times 10^{-6}$ to a constant value of 1180×10^{-6}. The average deviation from the mean of a series of 20 measurements of this ratio after the background peaks had disappeared, was only $\pm 15 \times 10^{-6}$. The indicated error of $\pm 80 \times 10^{-6}$ represents the uncertain background due to the tail of the 239 peak contributing at the 240 position and the possible residual background related to the extraneous peaks.

The resolution of the two peaks that was attained is shown in Figs. 4 and 5, these being runs which were made after the extraneous peaks had disappeared with continued distillation. The collector slit was opened about 1/3 the width of the beam in Fig. 4 and it was open about 1/10 the width in Fig. 5. In order to improve the precision of the measurements of the Pu^{240}/Pu^{239} abundance ratio, it is necessary to eliminate the background due to this extraneous material. An extensive investigation, described below, has been carried out to ascertain the source of these peaks.

It seems clear, from the fact that over a wide range every mass position shows a peak, that this extraneous material must be hydrogeneous. The masses of these ions suggest hydrocarbons or other organic material, but it seems unlikely that any such substance could persist for any length of time in contact with molten plutonium in a crucible at 1200°C. To explain this persistence, one must assume that, if the material comes from the sample, it is distilled out during the first few seconds that the furnace is heated and that it then condenses on adjacent plates of the source. Radiation of heat from the furnace heats these plates to some extent so that the material that was initially condensed may then distill into the

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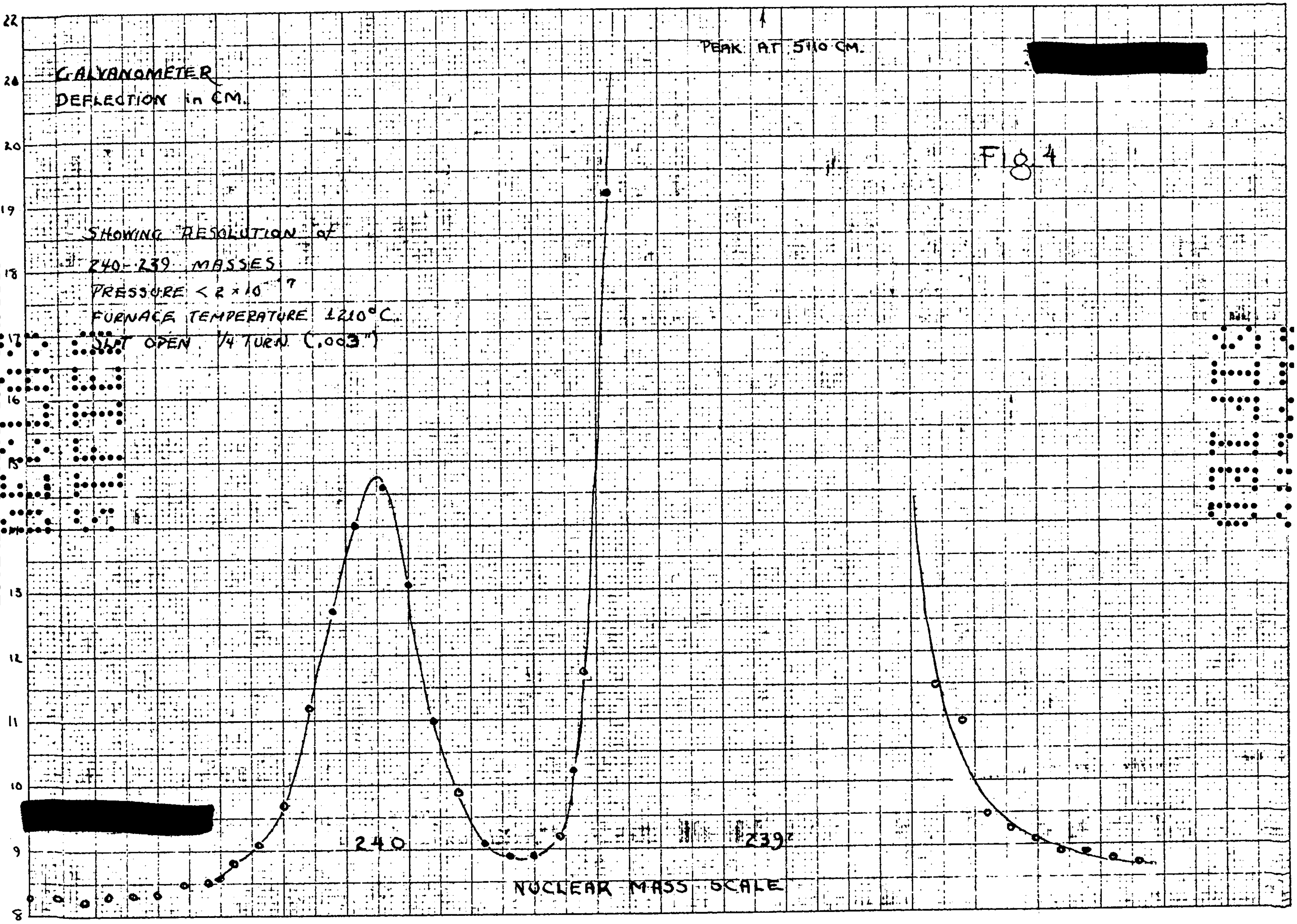

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Fig 4

SHOWING RESOLUTION of
240-239 MASSES
PRESSURE < 2 × 10⁻⁷
FURNACE TEMPERATURE 1210°C.
SLIT OPEN 1/4 TURN (.003")

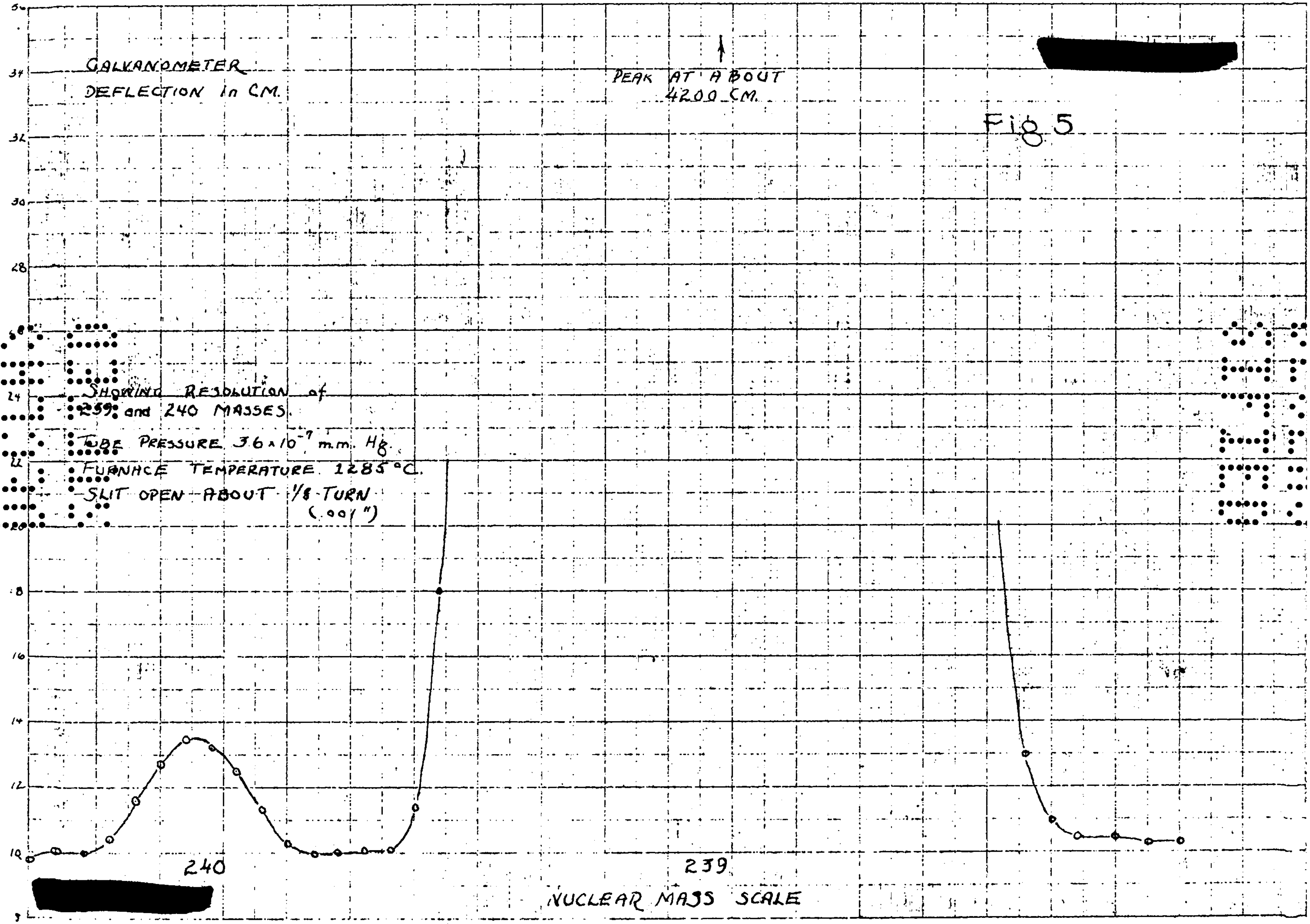

Fig 5

PEAK AT ABOUT 4200 CM.

SHOWING RESOLUTION of 239 and 240 MASSES

TUBE PRESSURE 3.6 x 10^{-7} mm. Hg.

FURNACE TEMPERATURE 1285 °C.

SLIT OPEN ABOUT 1/8 TURN (.001")

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ionizing region, giving rise to the observed peaks.

The results of a series of investigations of these peaks are summarized here. The following facts have been demonstrated experimentally:

1. The furnace and source plates have been completely outgassed.
2. Material producing the extraneous peaks has not been distilled from the spectrometer tube onto the source plates during the outgassing of the system.
3. No oil or other material which might produce the peaks has been introduced with the helium which was used to break the vacuum. Helium was used to prevent oxidation of the thin film of plutonium which had been evaporated onto the source plates.
4. Oil from the mechanical fore pump has not diffused back into the spectrometer tube.
5. No oil has been swept into the tube from the glass-wool-spindle oil trap which was used as a safety precaution during glass blowing.

The following experiments have indicated that the source of the extraneous material is in the handling of the samples before they are placed in the tube:

1. One of the final treatments in the preparation of the metal from which this sample (CX2A) was taken, was a pressing under mineral oil at 225°C. This oil has the proper molecular weight range (225 to 300) and some of it may have been occluded in the sample. Arrangements were made whereby a sample of normal Clinton metal was split, one half to be pressed in oil and electrolytically cleaned (the usual procedure), and the other half was not to have this treatment. The samples were delivered in vials, and the sample that had not had the oil treatment was run first. The extraneous peaks appeared.

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2. Sample CW1B which was not reduced at Los Alamos, but rather by Seaborg at Chicago, showed none of these extraneous peaks.
3. Sample 4W was reduced here, but was delivered in the crucible in which the vacuum remelt was carried out. It was transferred from the remelt crucible to the spectrometer crucible without being touched with tweezers or any other tools. It showed none of these peaks.
4. Likewise sample 41H was reduced and remelted at Los Alamos. It was transferred into the source crucible using tweezers that had been washed in carbon tetrachloride. This sample did not show these extraneous peaks either.
5. A small nondescript piece of plutonium that had not been remelted, which was delivered in a glass vial, and which was handled with unwashed tweezers, showed some (but not all) of these extraneous peaks.

Conclusions drawn from these experiments are:

1. The material producing the peaks did not originate from faulty instrumental techniques.
2. The material was present in the samples.
3. The specific identity of the material is not clear.
4. The material may be eliminated by proper sample-handling technique.

Sample CW1B

This sample of plutonium was produced at Clinton and then re-irradiated in the Hanford pile with a flux, nvt, of 2.1×10^{19} (LA-256, Deutsch). This sample was purified here, then sent to Seaborg at Chicago for reduction, and then returned here to be examined mass spectrometrically.

The first run on this sample is shown in Fig. 6. The peak at 255 is due to $Pu^{239}O^{16+}$ and the peak at 258 is due to $Pu^{239}F^{19+}$. Except for the peaks at 239 and 240, the rest of the peaks were produced by $PbCl_2$ in the sample, the

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peaks at 241, 242, 243, 244, and 245 being produced by ions of the form $PbCl^+$, and the peaks at 276, 277, 278, 279, and 280 being formed by ions of the form $PbCl_2^+$. The relative heights of these peaks qualitatively and quantitatively fit the distribution of masses that one may calculate from the known distribution of the lead and chlorine isotopes. Fortunately, no ion of the form $PbCl^+$ has a mass of 240. Calculations show some $PbCl_2$ ions should have masses of 274, 281, and 282, but the expected abundance of each of these masses is so small that these peaks would not show up at this intensity. Mass 277 is higher than the calculated $PbCl_2$ values would lead one to expect. This is presumed to be due to superposition of a $Pu^{239}F_2^{19+}$ ion. From these observations, it was predicted that the normal lead spectrum should appear in the mass region above mercury, and an examination of this region showed the normal lead spectrum (Fig. 7). The first run of this region showed small unexplained peaks at 203, 205, and 209, which rapidly disappeared.

A series of 15 measurements of the Pu^{240}/Pu^{239} abundance ratio were made at different furnace temperatures, giving a value of 6.51×10^{-3}. The average deviation of the mean was 0.08×10^{-3} or 1.2 percent, but considering the small and unknown correction for the fact that some of the tail of the 239 peak may contribute to the measured height of the 240 peak, this value is reported as $(6.51 \pm 0.20) \times 10^{-3}$.

On increasing the furnace temperature, a peak was observed at mass position 241. Curves in Figs. 8 to 9 show how the relative heights of 240 and 241 varied with furnace temperature. This variation with temperature indicated that the main portion of the mass giving this peak is not isotopic with plutonium. The 241 peak persisted throughout the entire run, and remained a short while after

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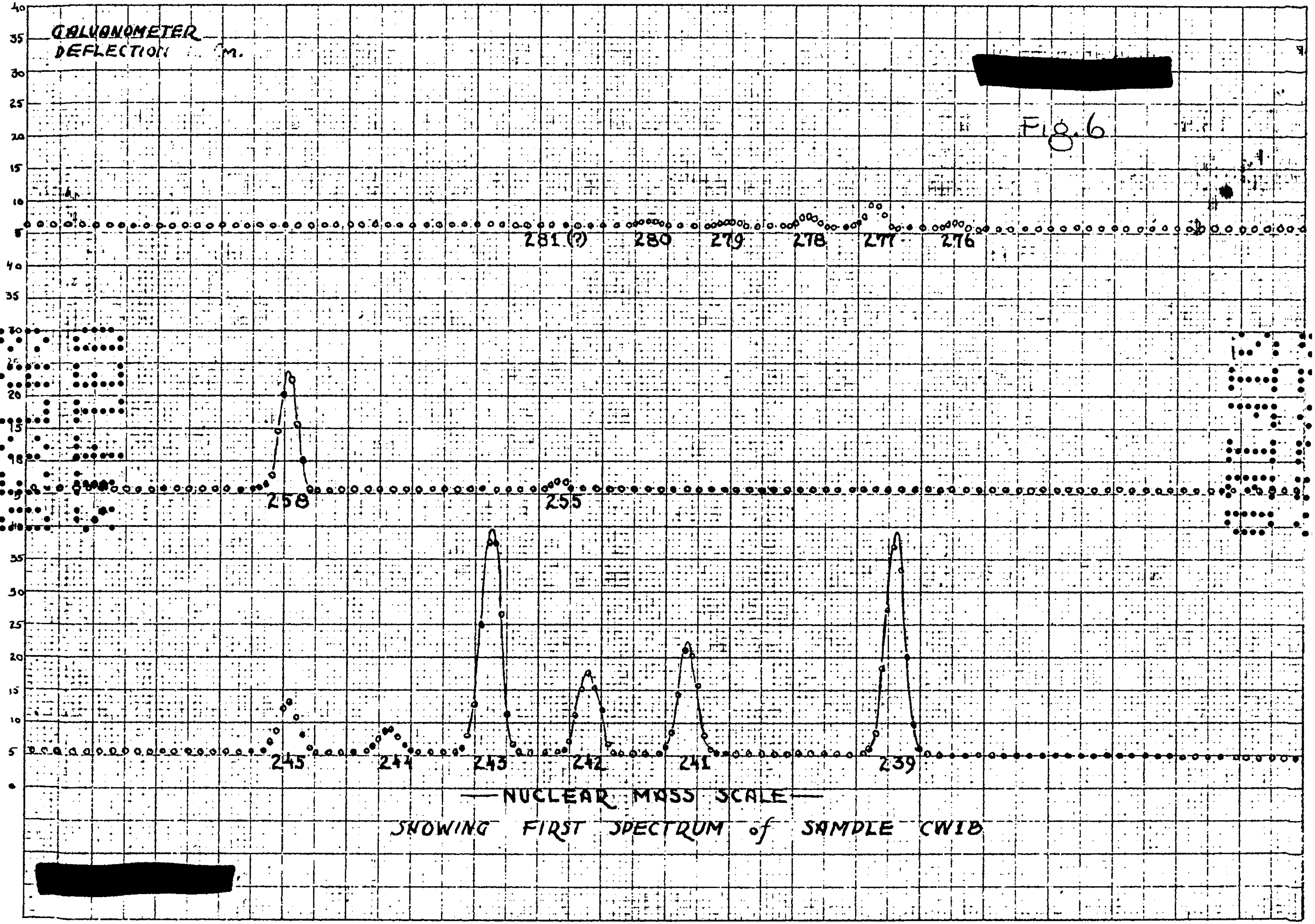
Fig. 6



SHOWING FIRST SPECTRUM of SAMPLE CWIB

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all of the plutonium had been evaporated away. By changing the furnace temperature, 241 could be made so small as to be below the limit of observation, or it could be built up to a height greater than that of the Pu 240 peak. Examination of the surrounding mass positions showed nothing, and examination of the oxide region (Fig. 10) showed the following. Peak 255 is due to $Pu^{239}O^{16+}$ and peak 256 is due to $Pu^{240}O^{16+}$ in the correct abundance. $Pu^{239}O^{18+}$ gives a mass 257, but the observed height of this peak is more than one would expect from the O^{16}/O^{18} abundance ratio. It is assumed that $(?)^{241}O^{16+}$ contributes the remainder of this peak. Unknown vapor pressures and unknown ionization cross sections make it impossible to say how much of this new material is present.

No organic material would be expected to produce a single peak such as this, and a study of the literature was made to find known isotopes of the elements, which in combination, would produce ions of mass 241 as well as small amounts of mass 239 and 240. Hydrides, halides, oxides, sulfides, selenides, tellurides, and nitrides were all considered. The following is a list of possible compound ions which might explain the 241 peak as well as the absence of peaks above 241 and below 239:

$Pu^{239}\ D^{2+}$

$Pu^{239}\ H_2^{\ 1+}$

$Bi^{209}\ O_2^{\ 16+}$

$Ir^{193}\ O_3^{\ 16+}$

It should be pointed out that, in selecting the above list, many compound ions of mass 241 were not considered as being the source of this single peak, because one or both of the elements involved occurred in nature with several isotopes, so that ions of masses adjacent to the region 239 to 241 should occur with the

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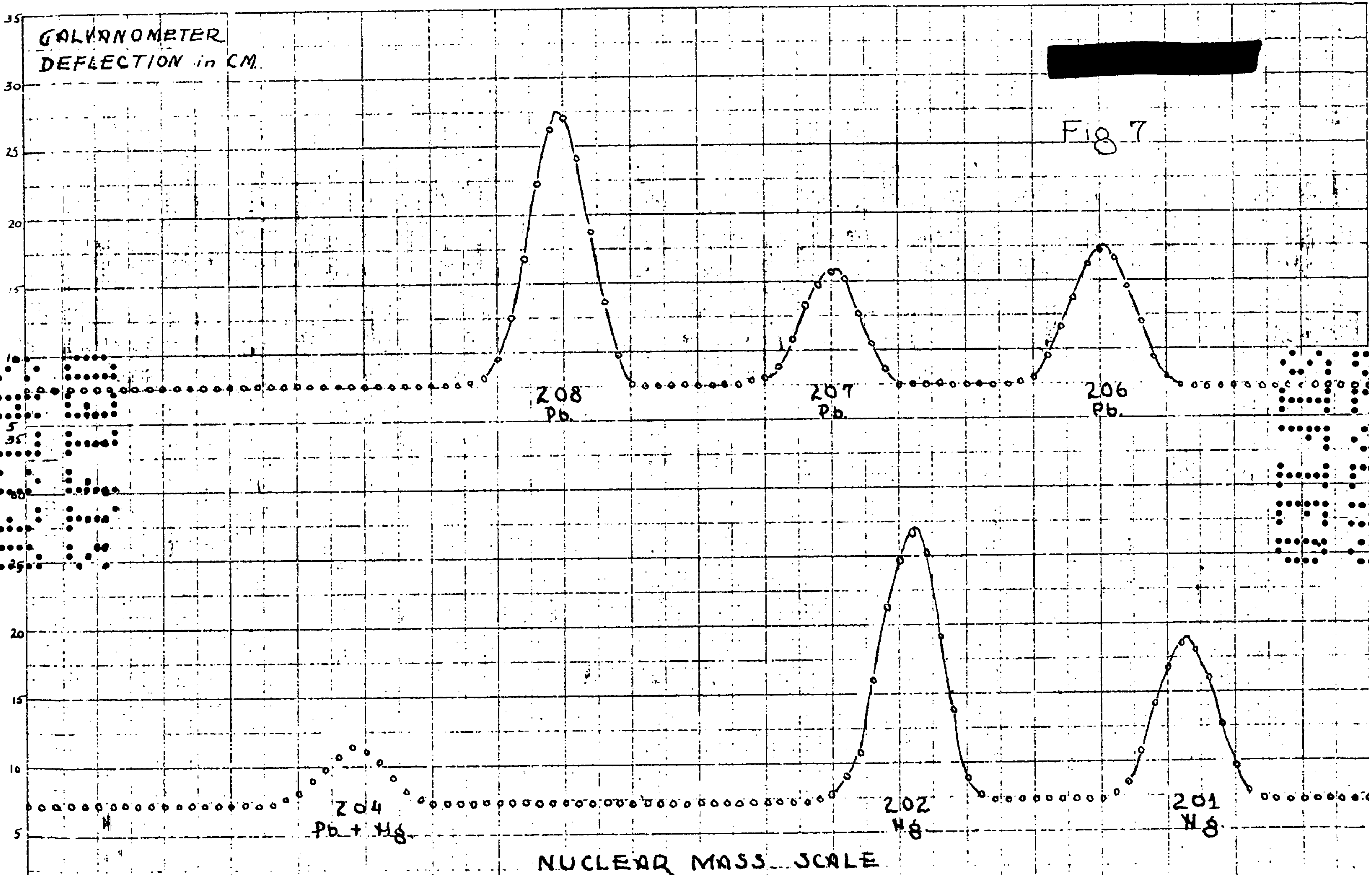

Fig 7

SHOWING ELEMENTARY LEAD FROM SAMPLE CW1B AND RESIDUAL MERCURY FROM PUMPS.

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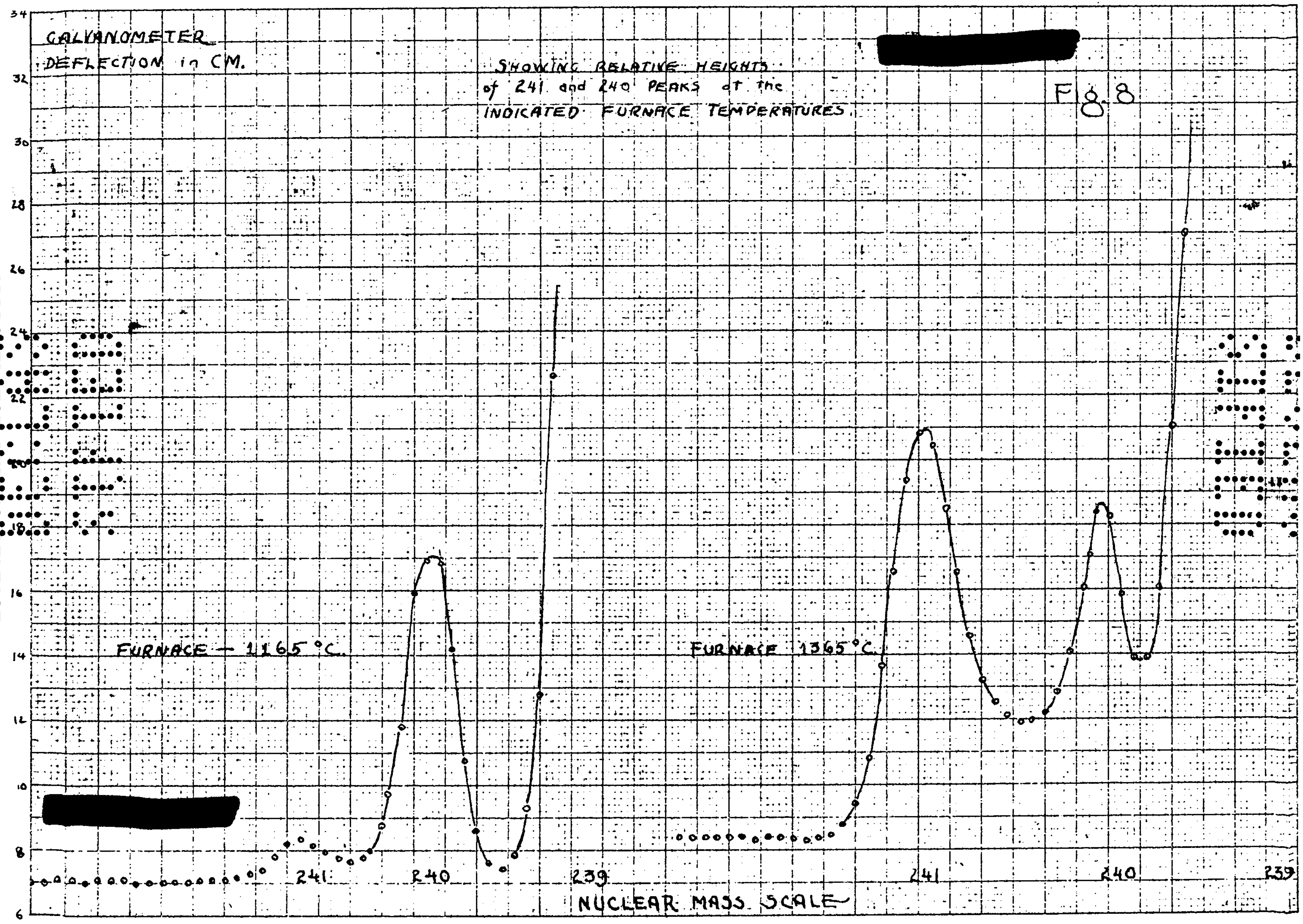
Fig 8



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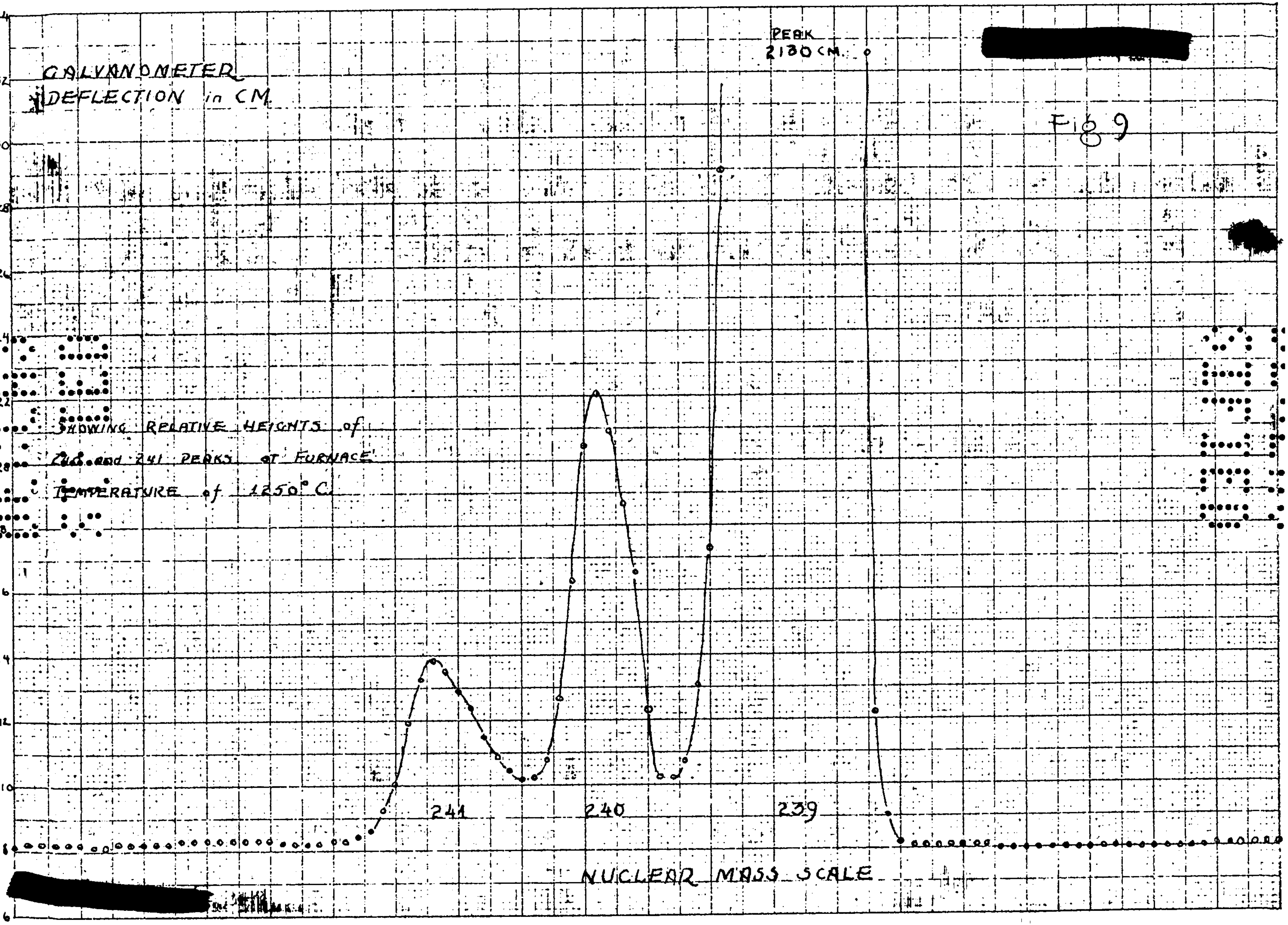

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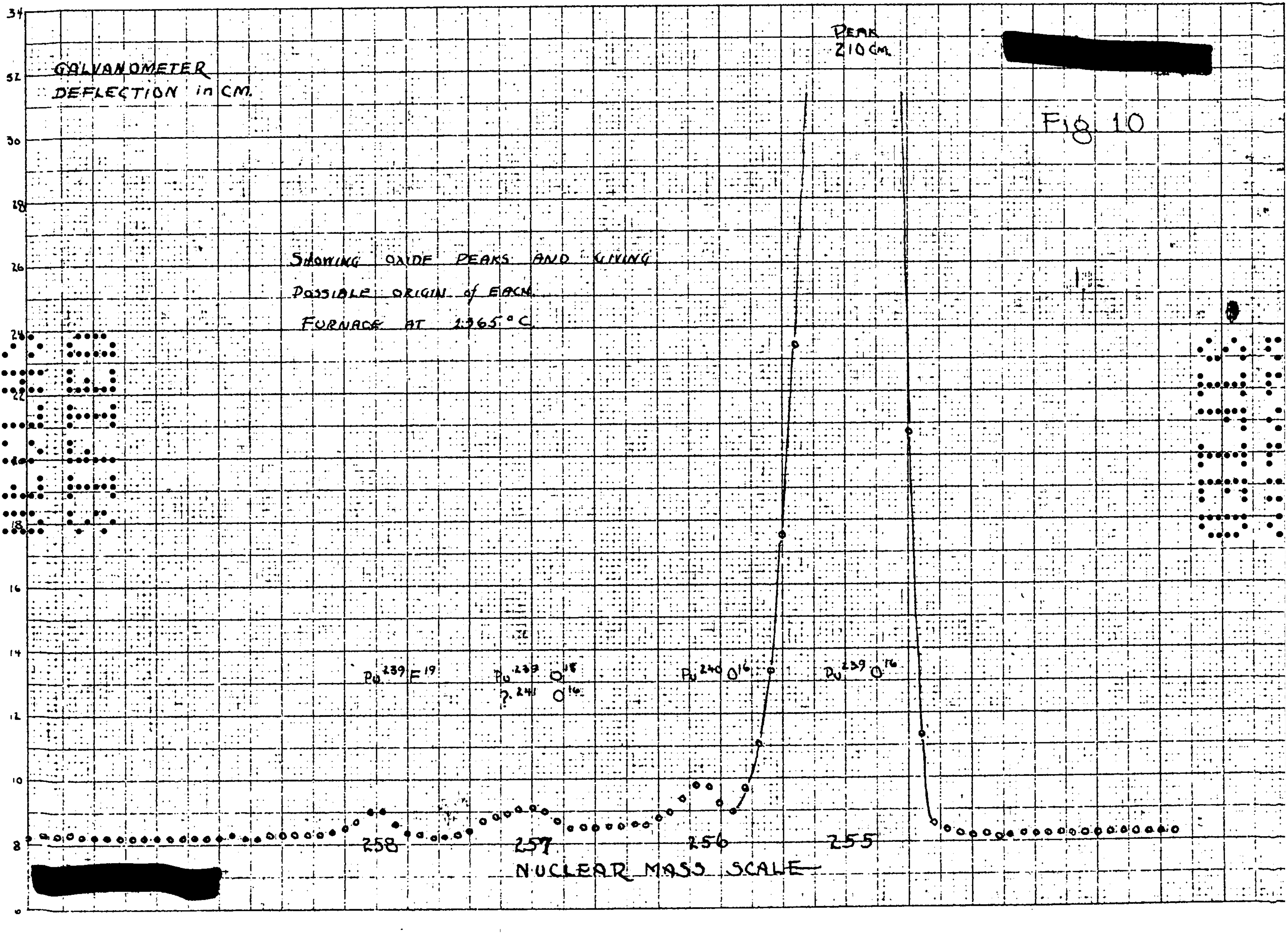
Fig. 10



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occurrence of an ion of mass 241. No ions were observed at these adjacent mass positions.

Elements formed in the pile by neutron irradiation or by other pile processes would not be expected to occur with the normal isotopic distributions and it is possible that traces of some of these elements might persist through the chemical purification. In this case, no molecules of mass 241 could be eliminated from consideration for the reason mentioned above, which is based on the isotopic distribution in nature.

The possibility that the hydride of plutonium has caused the 241 peak cannot be eliminated because the pressure in the spectrometer tube during the investigation of this peak was a factor of 5 to 10 higher than usual ($\sim 1 \times 10^{-6}$ mm) because of a very slow leak. A gas phase reaction with water vapor could have produced hydride. Deuteride from this source could not have produced a peak at 241 without also producing a large peak at 240. That this did not occur is shown by the constancy of the Pu^{240}/Pu^{239} abundance ratio with changes in furnace temperature. Bismuth oxide, if present, probably would be rapidly reduced by molten plutonium and, if so, it could not cause a persistent $Bi^{209}O_2^{16+}$ ion. Also, no ion corresponding to $Bi^{209}O^{16+}$ has been found at mass position 225. Iridium forms no oxide higher than IrO_2 so that there is small probability of the formation of IrO_3^+.

In connection with the purification of this sample, Seaborg observed a new alpha activity which he believes is best explained by assuming that plutonium^{240} undergoes the following reactions:

$$Pu^{240}(n,\gamma)Pu^{241} \xrightarrow{\beta^-} (95)^{241}$$

[redacted]

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It may be the isotope 95^{241} which has been observed here. The observation of a peak at mass 257 which could be $95^{241}\ O^{16+}$ is strongly in support of this. Seaborg has observed that the new alpha activity is due to an isotope which has properties like a trivalent rare earth and so is easily separable from plutonium.

Sample CW1B was purified approximately four to six weeks after it was pushed out of the pile. Sample 4W was purified approximately four months after it was pushed out of the pile. In order to explain the difference in apparent amounts of 241 in 4W and CW1B on the above theory, it is necessary to assume a half life of 94^{241} of the order of 10 days. Seaborg thinks that 94^{241} has a "long" half life (CF 2968), i.e., of the order of a year or longer. Except for this discrepancy, this theory seems to be the best one reported to date.

To summarize - the identity of the substance in sample CW1B which produced an ion of mass 241 is still unknown. A number of possible sources of this material have been pointed out, but none of these possibilities give an entirely satisfactory explanation. Work has been planned which, it is hoped, will give more information as to the source of this material.

Samples 4W and 41H

A sample of metal (4W) produced at Hanford was examined and was found to contain 0.295 ± .006 percent Pu^{240}. Examination of the 241 mass region showed a very small peak bearing a ratio to the 239 peak of about 1 part in 10^5. The smallness of this quantity made it impossible to study the height as a function of temperature.

Farwell has counted 4W for spontaneous fission and found a rate of 5930 fissions/gram hour. From this figure and from the above composition data, one calculates a spontaneous fission rate for Pu^{240} of 2.01×10^6 f/g hr. This

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is 20 percent higher than the rates previously calculated for this isotope from measurements on two samples, (CX2A and CW1B), one of which contained less, and one of which contained more Pu^{240} than did this sample. The reason for this disagreement is not clear. However, the samples (for fission counting and for mass spectrometry) were obtained from two different sources, several weeks apart, so there is some question as to the identity of the samples. This hypothesis is supported by the fact that data on samples from batch 41H (see below) check the previously determined value of this constant.

Measurements of the Pu^{240}/Pu^{239} abundance ratio were made on a sample of plutonium 41H (reduction no. 7078) to compare with fission counting by Farwell. Care was taken to see that both samples were taken from the same batch. Mass spectrometric measurements gave the value:

$$Pu^{240}/Pu^{239} = 0.0111 \pm 0.0002 \text{ or } 1.10 \text{ percent } \pm 0.02 \text{ percent } Pu^{240}$$

Farwell's count of this sample gave:

18,200 f/g hr. ± 6 percent

giving $(1.65 \pm 0.10) \times 10^6$ f/g hr. for $(94)^{240}$

Comparison with Tin

Doubly ionized plutonium atoms would produce a peak at mass position 119.5, which falls between two of the tin isotope peaks. Since tin and plutonium have comparable vapor pressures, it should be possible to mix them, and through this superposition of the second-order plutonium spectrum on the first-order tin spectrum, make a positive identification of the actual mass of the main plutonium peak. This large peak has always been assumed to be due to Pu^{239}.

A preliminary run with a 50-50 mixture by weight of plutonium and tin showed a peak extraneous to the tin spectrum between the Sn^{119+} and Sn^{120+} peaks.

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This is due to doubly charged Pu^{239} ions. However, with this mixture, the tin peaks were many times higher than the second-order plutonium peak. It was found that mixture of 30 mg of plutonium and 10 mg of tin gave peaks whose heights were of the same order of magnitude. A curve of this region is shown in Fig. 11. A series of measurements of the Sn^{119+} - Pu^{239++} peak separation gave a value of 0.61 ± 0.02 mass units. From this value the calculated packing fraction of Pu^{239} is $(4.2 \pm 2.0) \times 10^{-4}$. An extrapolation of Dempster's curve (Phys. Rev., 53, 869 (1938) gives 5.7×10^{-4}. This instrument was not designed for precise mass measurements so a very large error is attached to the calculated value of the packing fraction.

It is then possible to compute the atomic weight of plutonium, using the packing fraction of 4.2×10^{-4}. The result is 239.10 ± 0.04 + x/100, (where x is the percent of Pu^{240} present) on the physical-weight scale. On the chemical-weight scale this becomes 239.04 ± 0.04 + x/100. The correction for Pu^{240} is very small and since Hanford material contains about 1 percent Pu^{240}, 239.05 ± 0.04 is a good value for the chemical atomic weight of the present shipments.

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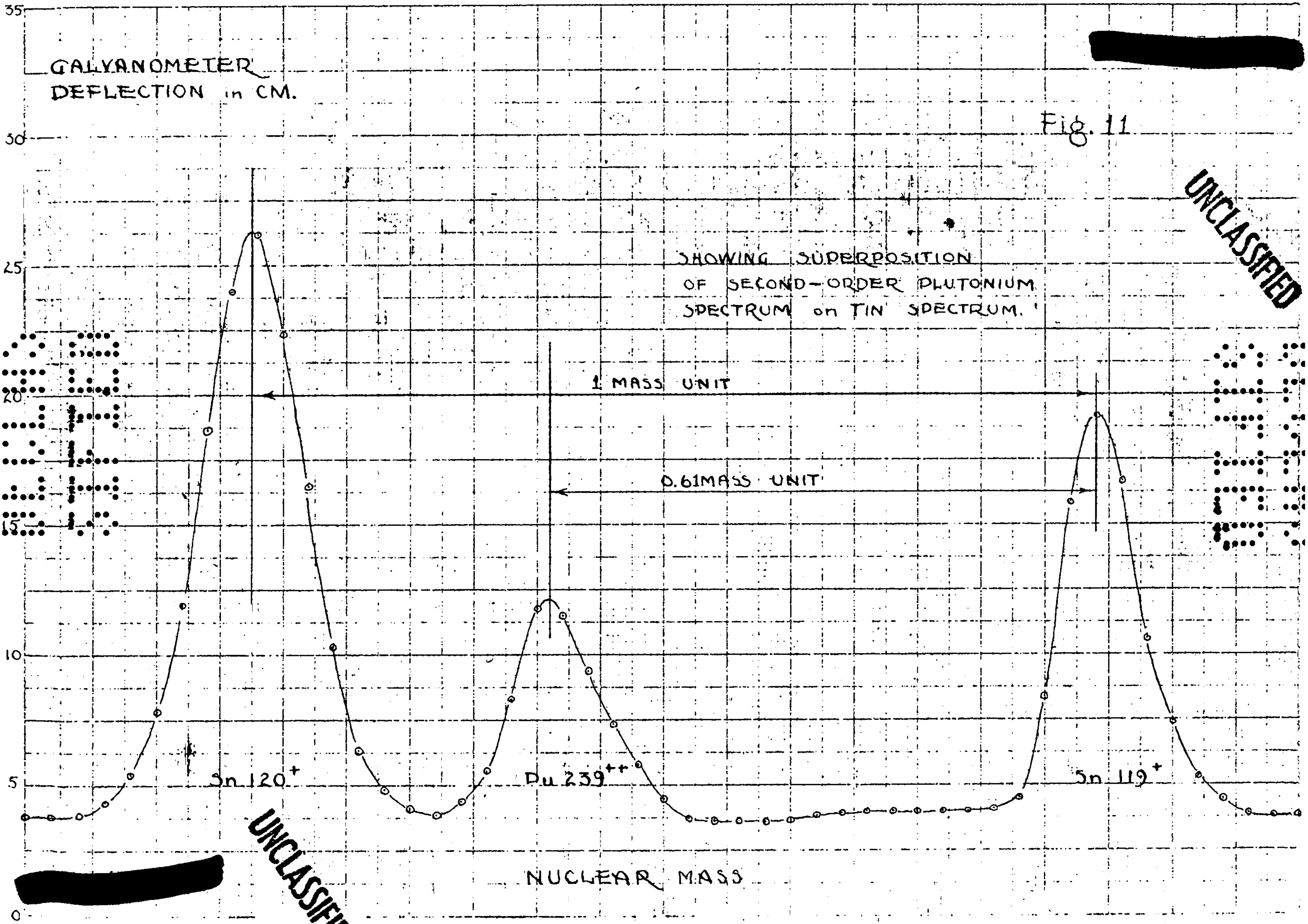
Fig. 11



SHOWING SUPERPOSITION OF SECOND-ORDER PLUTONIUM SPECTRUM on TIN SPECTRUM.

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Summary of Data

The following table gives a summary to date of mass spectrometric measurements of the abundance ratio Pu^{240}/Pu^{239} along with spontaneous fission counting by Segre's group and the corresponding fission rate $(94)^{240}$.

Material	Percent Pu^{240} Mass Spectrometer	Spontaneous Fission Rate Segre's Group f/g hr. of sample	f/g hr. of Pu^{240}
Normal Clinton Plutonium	0.033 ± 0.005	----	
Clinton Re-irradiated Plutonium (C16 or CX2A)	0.118 ± 0.008	1910 (± 10%)	$(1.62 \pm 0.15) \times 10^6$
Hanford Re-irradiated Plutonium (CW1B)	0.647 ± 0.020	10,900 (± 5%)	$(1.67 \pm 0.08) \times 10^6$
41H	1.10 ± 0.02	18,200 (± 6%)	$(1.65 \pm 0.10) \times 10^6$
		ave f/g.hr. of Pu^{240}	$(1.65 \pm 0.07) \times 10^6$

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