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SPECTROCHEMICAL ANALYSIS OF PLUTONIUM AND ITS COMPOUNDS

(I) THE COPPER SPARK METHOD

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Abstract

A method of extraordinary sensitivity is described for the determination of thirty elements. A solution to be analyzed is evaporated on the ends of copper electrodes, which are excited by a condensed spark discharge to produce the impurity spectrum. The method may be applied to the direct determination of impurities in solution, but finds particular application in cases wherein a chemical separation of the impurities precedes their determination.

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INTRODUCTION

Numerous references may be found in the spectrochemical literature to the use of graphite electrodes for the analysis of solutions.1,2,3) Although they are ideally suited to many methods they possess certain disadvantages:

1. Lowered sensitivity results from the penetration of solutions into the porous graphite. The use of kerosene, paraffin, or collodion to minimize penetration is not entirely satisfactory.
2. A valuable portion of the spectrum (i.e. that containing many of the rare earth lines) is obscured by the ultra-violet cyanogen band system.

Largely for the purpose of making the region 3600 - 4200 Å accessible, a kind of electrode material was sought which would open this region to view. Few non-metallic solids possess sufficient electrical conductivity to permit their use as electrodes, so that attention was directed to the list of pure metallic elements. The following considerations dictated the choice of the electrode material:

1. High purity with respect to the elements sought.
2. Simplicity of spectrum.
3. Expendability.
4. Availability in adequate quantity.
5. Reluctance to pit badly, melt, or oxidize during arcing or sparking.
6. Ease of machining on a lathe.

Copper and silver 4) fill these requirements to a higher degree than any other metals -- copper being preferred for its lower cost and higher commercial purity.

Choice of Excitation:

The view is widely held among spectroscopists that arc excitation gives

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higher sensitivities of detection for most metallic elements than spark excitation. Generally speaking this is probably true, since in the arc the number of states to which an atom may be excited is more limited than in the condensed spark. The population of a given excited state is apt to be greater in arc sources than in spark sources, and this relates directly to the intensity of the light emitted in an electron transition arising from this energy level.

Arcs between copper electrodes are notably subject to wandering and sputtering -- probably because of the ease with which the metal melts locally to form globules. The globules may run down the electrode or be spattered out of the arc by convection currents. In any case, the ease with which a residue which has been placed upon the electrode may be incorporated into a molten bead makes for lowered sensitivity and poor reproducibility. Condensed spark discharges enjoy a reputation for higher reproducibility than arc sources for the reason that neither electrode retains its polarity for more than a fraction of a milli-second, and the tendency of a discharge to seek out local spots of high emissivity is minimized.

Although it is probably true that condensed spark discharges between metal electrodes give somewhat poorer sensitivities than arc discharges between the same electrodes, this is due in large part to the greater consumption of material in the latter case. The thermal energy conveyed to electrodes in a typical spark discharge is low compared to that for conventional arcs, with the consequence that a smaller quantity of deep-seated impurities is distilled from the electrodes in the former case. Impurities in a superficial residue, on the other hand, are readily volatilized in a condensed spark discharge. In any event, sensitivities far beyond expectation were obtained when solutions containing traces of metallic impurities were

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dried on copper electrodes and the residues excited in a condensed spark discharge.5)

Experimental Procedure:

Standard stock solutions were prepared by dissolving weighed quantities of non-hygroscopic salts of the elements of interest in known volumes of quartz-distilled water. Series of standard solutions were prepared by dilution of the stock solutions so that the following concentrations were available: 100, 10, 5, 2, 1, 0.5 ...... 0.01, 0.005, 0.002, 0.001, 0.0005, and blank micrograms per milli-liter. Two mls. of quartz-distilled hydrochloric acid were added to 50 mls. of each standard to prevent the hydrolysis of certain cations.

An internal standard solution was also prepared by dissolving sufficient ammonium molybdate in quartz-distilled water to give a concentration of 40 micrograms of molybdenum per milliliter.

A number of pairs of ¼" dia. copper electrodes were prepared* and placed, by pairs, in a nichrome coil electrode evaporator (Figure 1). Fifty micro-liters of the internal standard solution were transferred, by means of a micro syringe pipet, to the top of each electrode and carefully evaporated thereon. Following this, 50 micro-liters of the most dilute standard were evaporated on each electrode of the first pair. One hundred micro-liters of the succeeding, stronger standards were evaporated on electrode pairs in the same manner. In this way a series of copper electrode pairs was obtained, bearing the following weights of elements on their top surfaces: blank, 0.00005, 0.0001, 0.0002 .... 0.01, 0.02 .... 0.5, 1.0, and 10.0 micrograms. Care was observed in keeping the droplets

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* ¼" dia. commercial electrolytic copper rod is very pure, and is adequate for the present use. The rods were cut to 1¼" lengths, one end being faced smooth and flat on a lathe. The sides were machined lightly from the finished end back for a distance of ½". The sharp edge was removed by very slight champfering in the lathe. This treatment is adequate to reveal a clean, bright copper surface, and is superior to "cleaning" methods involving scale removal by nitric acid followed by distilled water rinsing.

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of solution from becoming too large and running down the sides of the electrodes. The heat supplied by the coil was not high enough to cause spattering of the droplets.

Two spectrographs were employed: an Eagle-mounted* 3-meter grating (15,000 lines per inch, 6 inch aperture, f 20) and a Wadsworth-mounted** 21-foot grating (15,000 lines per inch, 6 inch aperture, f 21). The rulings of the latter grating were of such contour as to direct a large percentage of the diffracted light into the first-order ultraviolet. The first grating gave much higher sensitivities in the direction of the first-order red without serious loss in the first-order ultraviolet intensity.

The following photographic plates were found to be satisfactory:

1. Eastman 103-O plates for the region 2200 - 4600 Å.
2. Eastman I-F or 103-F plates for the region 5600 - 6800 Å.
3. Ammonia-sensitized Eastman I-N plates for the region 6800 - 8000 Å.

Alignment was achieved by projecting the electrode shadow-images on a graduated screen placed perpendicular to the optical axis. The overall reproducibility of the method was improved by resort to high magnification of the 2-mm. electrode separation. The electrode pairs were sparked, beginning with the blank and proceeding through the more concentrated standards. They were sparked in this sequence to avoid contamination of the weakest standards by dust from the stronger ones. Excitation was by means of a high-voltage condensed spark discharge unit*** operated at 2 kva nominal power input and 25,000 volts output. The circuit constants were: capacity = 0.021 μF, inductance = 0.32 mH.

Stepped spectra for plate calibration were photographed in the conventional manner, using a rotating logarithmic stepped sector. A direct current arc between iron electrodes was employed to avoid sector-synchro-

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* Manufactured by Baird Associates, Cambridge, Mass.

** Manufactured by the Jarrell-Ash Co.

*** Manufactured by A. R. L. - Dietert Co., Glendale, Calif.

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nization errors which would have attended the use of an alternating current source.

All plates were developed for three minutes in Eastman D-19 at 18.0° C., fixed in acid hypo for ten minutes, and washed for fifteen minutes in a stream of water.

Following plate processing the most sensitive impurity lines were located, and their transmissions determined by photometry. The transmission of the continuous background adjacent to each line was also determined. Line and background transmissions were then determined for molybdenum lines of suitable density and proximity to the analysis lines. The line transmissions were converted into relative intensities by means of the H & D curves obtained from the calibration spectra. Background corrections were made by subtracting the relative background intensity from the combined line and background intensity for impurity and internal standard lines.6) Log ratios of the net impurity and internal standard line intensities were then computed. Working curves were constructed by plotting log intensity ratios against log impurity concentrations.

Table I lists the sensitivities obtained for a number of elements with the spectrographs mentioned before. Figures 2 - 7 show a number of typical working curves prepared in the manner described using the Eagle spectrograph; the Wadsworth instrument was used in obtaining data for the working curves shown in Figures 8 - 13. For some kinds of work the accuracy of photometric evaluation was not required, and semi-quantitative results were obtained by visual comparison of the impurity lines with those of standard spectra photographed on the same plate. Visual sensitivities of detection were usually found to be better than photometric limits.

Effect of Large Quantities of Impurities on Line Intensities:

The probable effect of large quantities of various elements on the intensity ratios for trace constituents has not been thoroughly investigated

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because of the magnitude of the problem. Fifty micrograms of plutonium were found to be without effect on the impurity line intensities within the limits of experimental error, however, Table II shows the deviation of working curves for several impurities with 50 micrograms of plutonium and with no plutonium present. The existence of an enhancement or depressant effect on the trace constituent line intensities should be investigated for each case in which an appreciable quantity of foreign elements is present.

Application to the Analysis of Plutonium:

The occasion for the development of the copper spark method was the need for analyses of plutonium nitrate process solutions. The highest accuracy and precision were not demanded, a semi-quantitative analysis sufficing to reveal the nature and approximate quantities of impurities present which might necessitate special treatment in the ensuing purification steps. The complexity of the plutonium spark spectrum is such that if more than fifty micrograms were sparked the number of coincidences of plutonium lines with impurity lines and the general spectrum background would become prohibitive. The analysis of plutonium solutions was carried out in manner identical to that already described for the running of standards, except that consideration had to be given to the radioactive nature of the material. For health's sake it was necessary that the operation of electrode coating be carried out in a well-ventilated hood by an operator dressed for the occasion (i.e., wearing a tightly-fitting, full-length laboratory garment, rubber gloves, and a plastic face shield). The sparking of electrodes bearing plutonium residues was carried out in a special discharge chamber (Figure 14) to minimize the spread of radioactive dust.

In many cases the sensitivities of detection of impurities obtained by the direct sparking of plutonium residues were inddequate. It was

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necessary to effect a chemical separation of the plutonium from the impurities before determining the latter. One method of carrying out such a separation, making use of cupferron, is described elsewhere.7)

Application to the Analysis of Water and Mineral Acids

The copper spark method has been applied to the determination of metallic impurities in stream waters, commercial acids, and water and acids which had been triply-distilled from quartz vessels. Five ml. of the water or acid were reduced to 0.1 to 0.2 ml. by evaporation on a special balance. The balance was connected to an infra-red lamp which would automatically turn off when the desired weight was reached (Figure 15). The remaining concentrate was then evaporated on a pair of copper electrodes and sparked in the manner described. Quartz vessels were used throughout. The copper spark method is not adapted to the analysis of sulfuric, nitric, and phosphoric acids, since these attack copper badly during evaporation and leave a crust of copper salts.

Precision and Accuracy:

The average deviation from the mean of 119 intensity ratios run in quadruplicate was 7.6%. This was the average error obtained for a number of elements, and was computed from the data used to construct the working curves. Since no chemical separations are involved in this procedure the determination of impurities in known solutions is identical with the running of standards. For this reason no additional information would be gained by running "recovery" experiments.

[redacted]

Bibliography

1. Duffendack, O. S. & Wolfe, R. A., Ind. Eng. Chem., Anal. Ed. 10, 161 (1938)
2. Wilhelm, H. A., Ind. Eng, Chem., Anal. Ed. 10, 211 (1938)
3. Owens, J. S., Ind. Eng. Chem, Anal. Ed. 11, 59 (1939)
4. Classified Report CK 670, Rollefson, G. K. & Dodgen, H. W., May 19, 1943
5. Classified Report CK 877, August 7, 1943
6. Pierce, W. C. & Nachtrieb, N. H., Ind. Eng. Chem., Anal. Ed. 13, 774 (1941)
7. Classified Report LA 387, "The Spectrochemical Analysis of Plutonium and its Compounds: (II) The Cupferron Method."

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TABLE I

SENSITIVITIES OF DETECTION OF ELEMENTS IN CONDENSED SPARK DISCHARGE BETWEEN COPPER ELECTRODES.

Element	Minimum detectable amount (micrograms) Wadsworth	 Eagle	Wave length Å
Li	0.0005	0.00005	6707.84
Be	0.0001	0.0002	3131.07
Mg	<0.01	-	2790.78
	-	0.0001	2798.06
Al	0.01	0.002	3944.03
K	0.1	0.01	7664.91
Ca	<0.001	-	3933.67
Sc	0.5	0.005	3996.61
Ti	0.5	-	4186.12
V	0.05	0.02	3185.40
Cr	0.02	0.002	2677.16
Mn	0.001	0.0002	2605.69
Fe	0.1	0.02	4045.82
Ni	0.01	-	3492.96
Co	0.01	-	3453.51
Zn	0.1	-	2800.87
Ga	0.02	-	4172.06
As	0.1	0.1	2780.20
Rb	-	0.01	7800.23
Sr	0.005	0.0002	4215.52
Zr	0.01	-	3958.22
Cb	0.5	-	4229.15
Sn	0.05	0.02	2839.99
Sb	0.5	0.2	3040.67
Pt	0.5	0.1	2830.30
Ce	0.1	0.1	4151.97
Pb	0.1	0.1	2833.07
Th	0.1	0.05	4019.14
Bi	0.05	0.005	3167.72
W	0.05	0.05	4008.75
La	0.005	0.003	4333.73

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TABLE II

EFFECT OF 50 MICROGRAMS OF PLUTONIUM ON WORKING CURVES

Element	Δ*
Cr	20%
Zr	45
V	15
Ca	0
La	0
Al	11

* Δ is the error obtained in the determination of an element in the presence of 50 micrograms of plutonium when working curves are used which were prepared from standards not containing this amount of plutonium.

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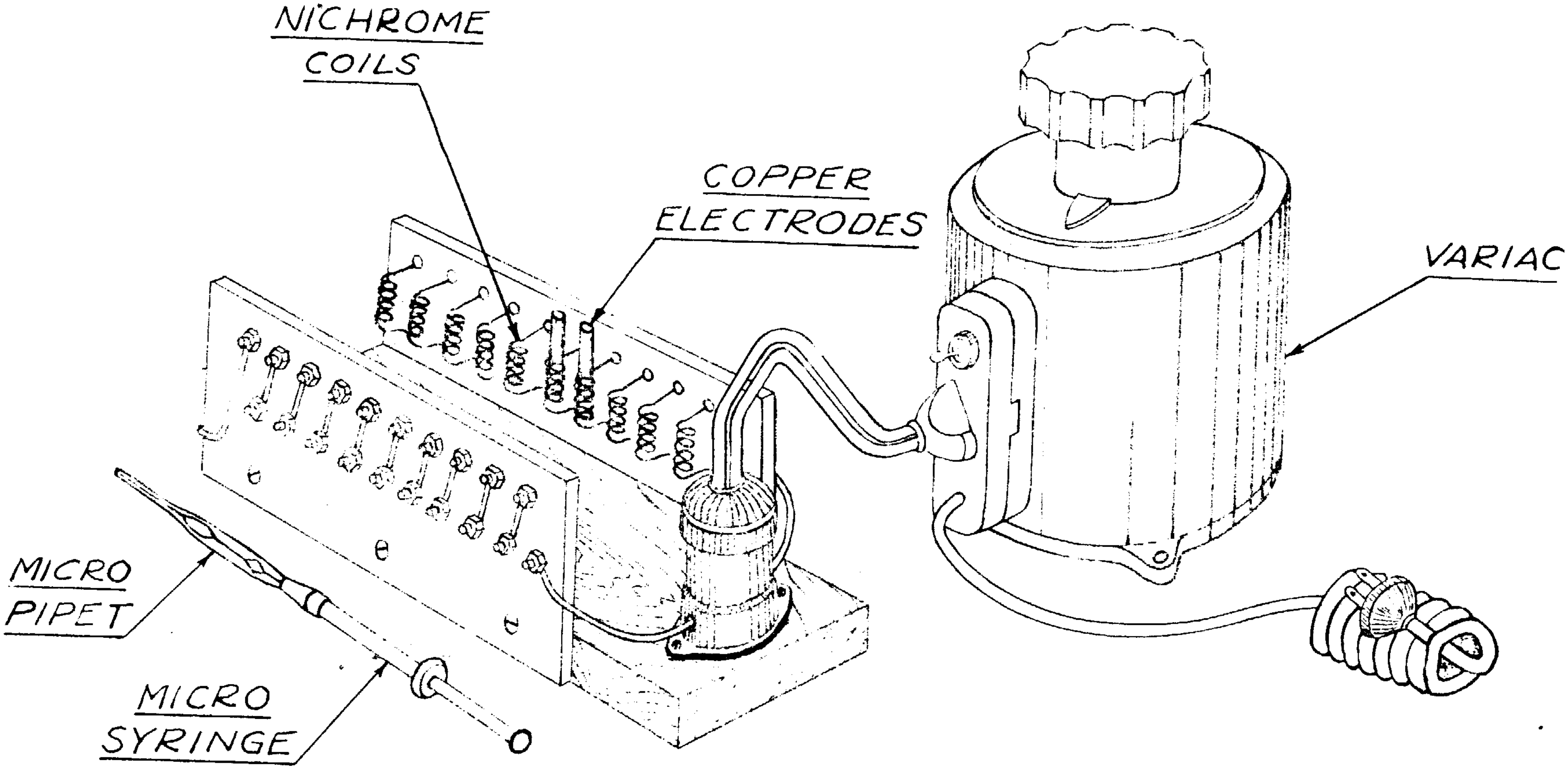
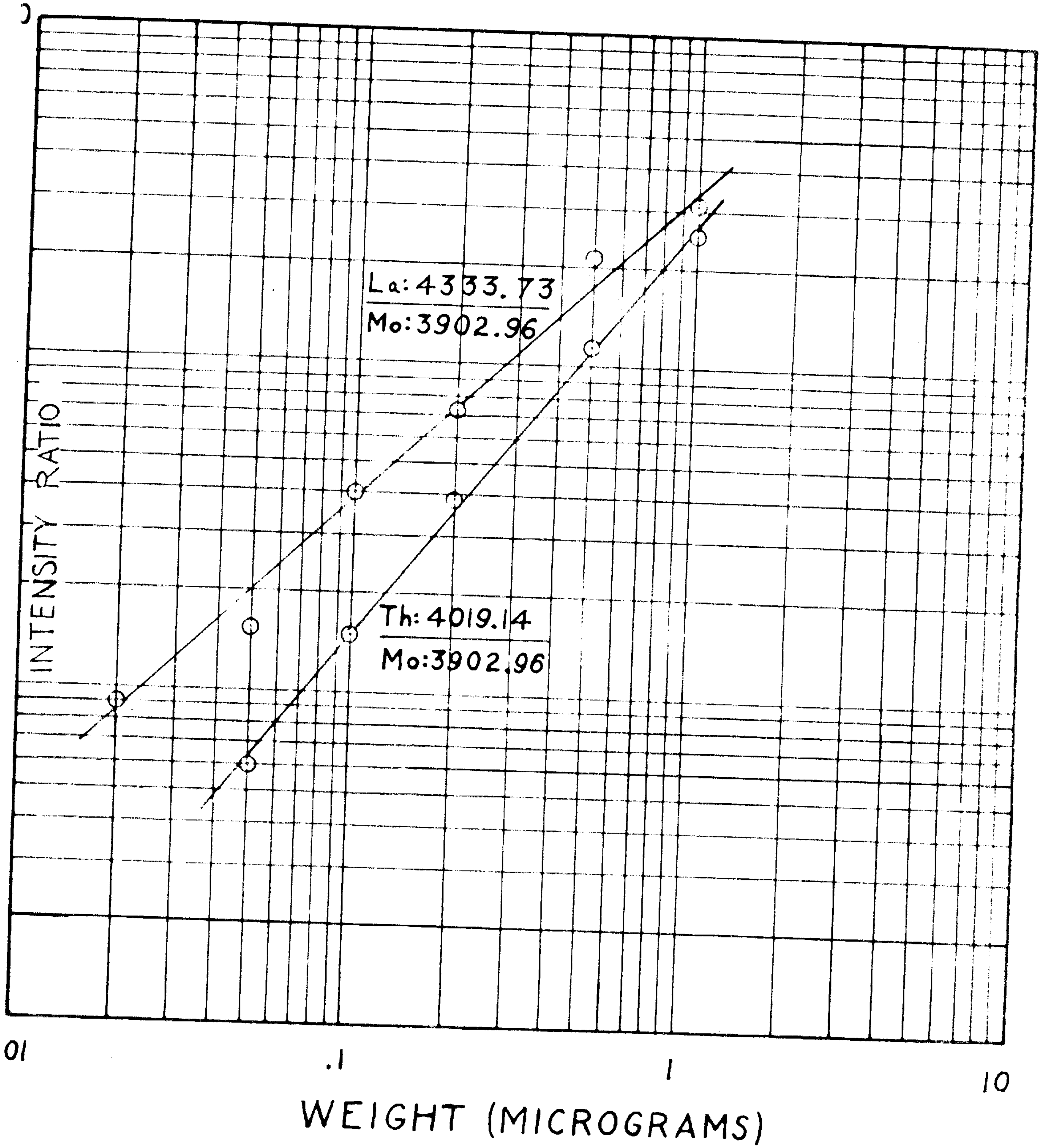


FIGURE 1. ELECTRODE EVAPORATOR


La:4333.73
Mo:3902.96
Th:4019.14
Mo:3902.96
INTENSITY RATIO
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.1
1
10
WEIGHT (MICROGRAMS)

FIG. 2

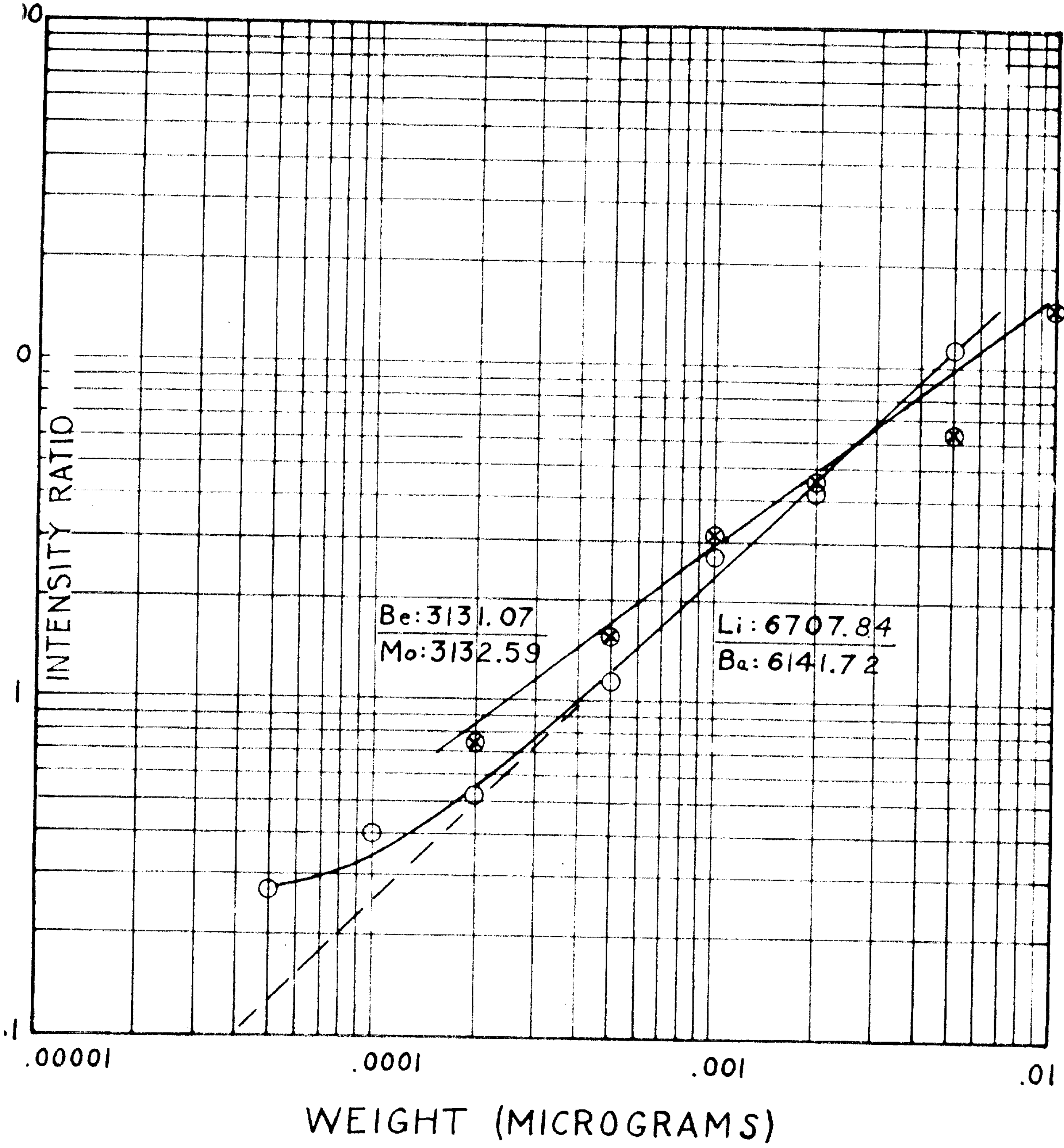

INTENSITY RATIO
00
0
1
.1
.00001
.0001
.001
.01
Be:3131.07
Mo:3132.59
Li:6707.84
Ba:6141.72
WEIGHT (MICROGRAMS)

FIG. 3

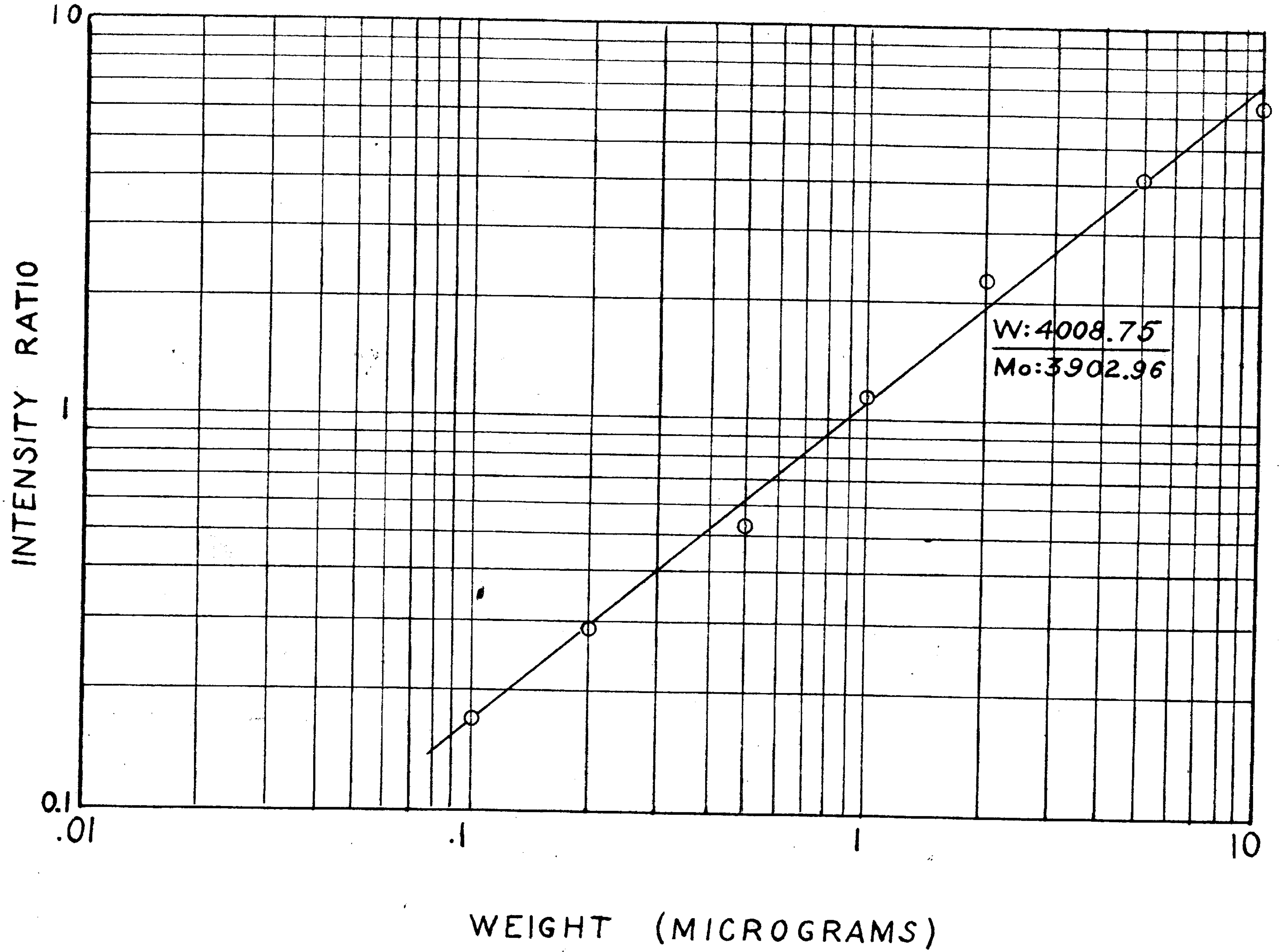

10
1
0.1
.01
.1
1
10
INTENSITY RATIO
WEIGHT (MICROGRAMS)
W:4008.75
Mo:3902.96

FIG. 4

LA-386

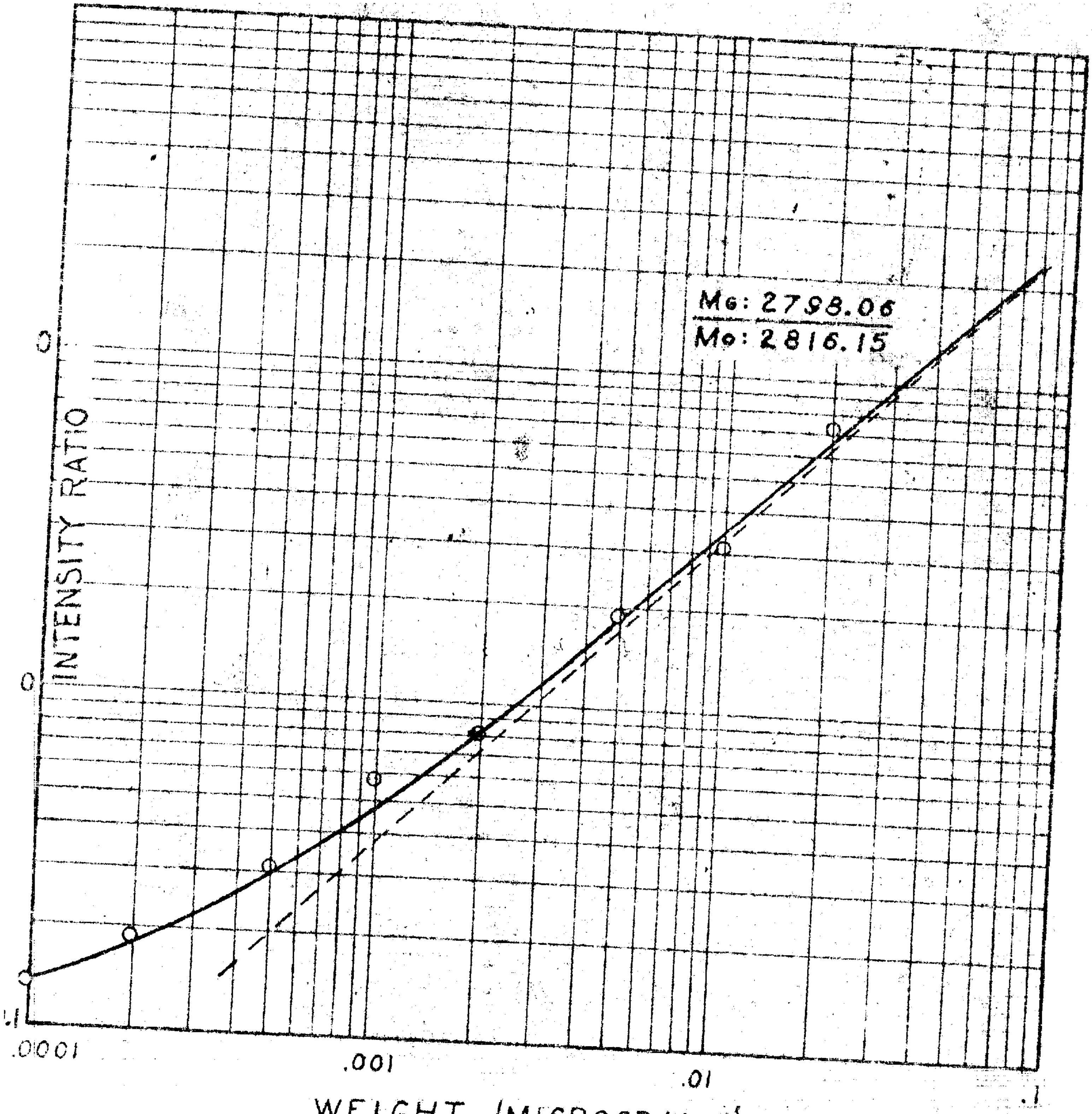

Mg: 2798.06
Mo: 2816.15
INTENSITY RATIO
.0001
.001
.01
.1
WEIGHT (MICROGRAMS)

FIG. 5

LA-306

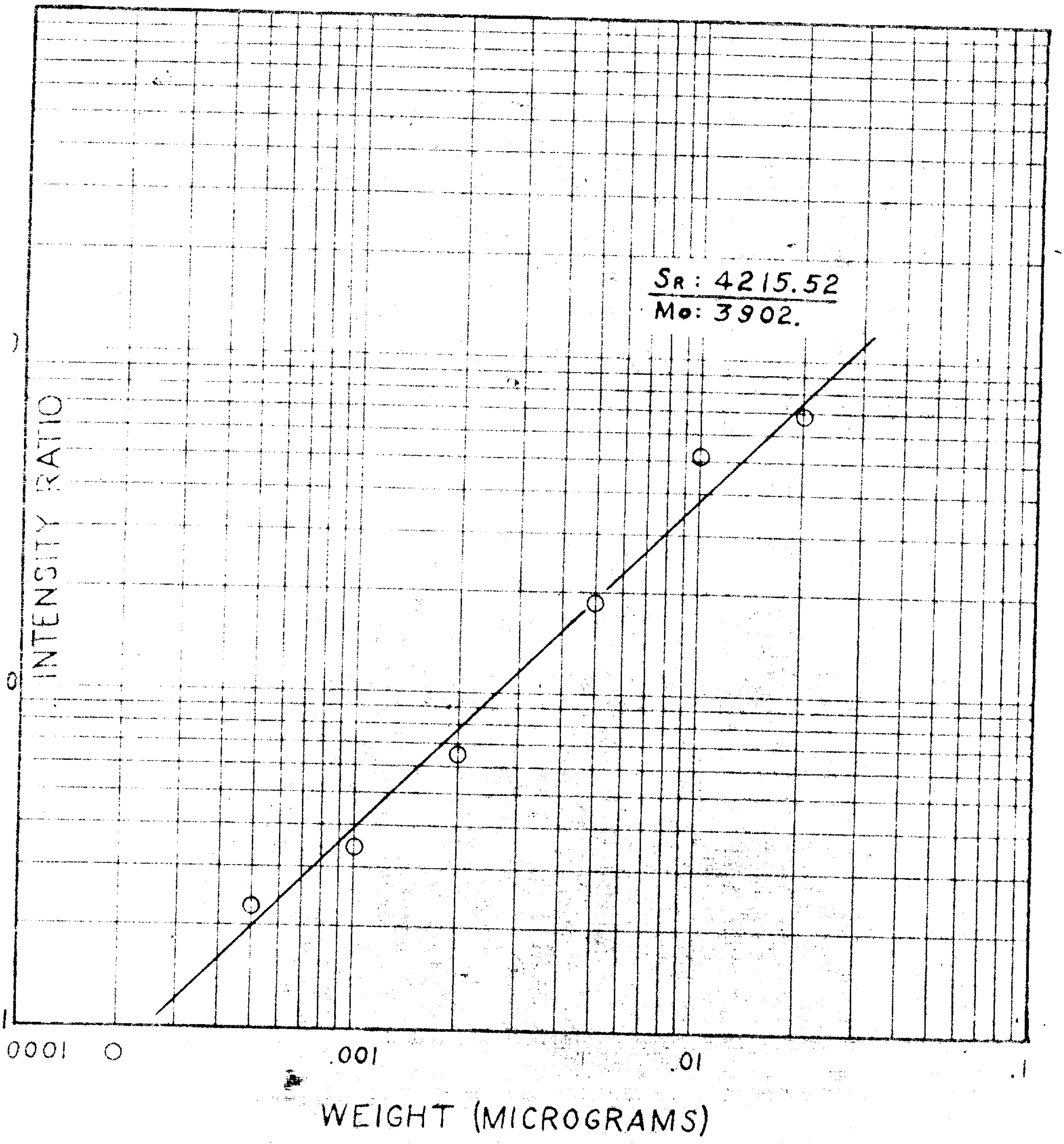
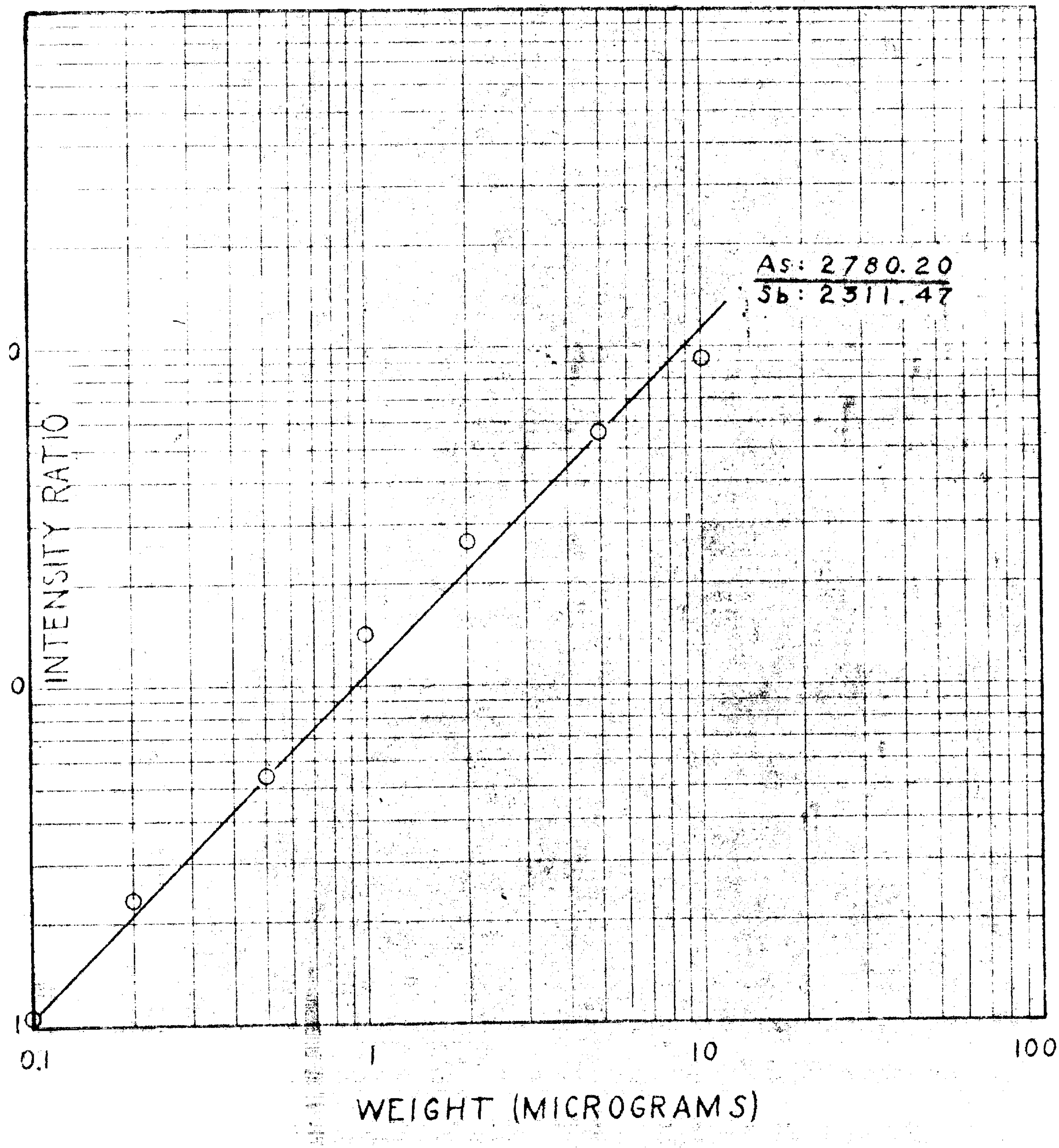

SR: 4215.52
Mo: 3902.
INTENSITY RATIO
1
0001
0
.001
.01
.1
WEIGHT (MICROGRAMS)

FIG. 6

LA-386


As: 2780.20
Sb: 2311.47
INTENSITY RATIO
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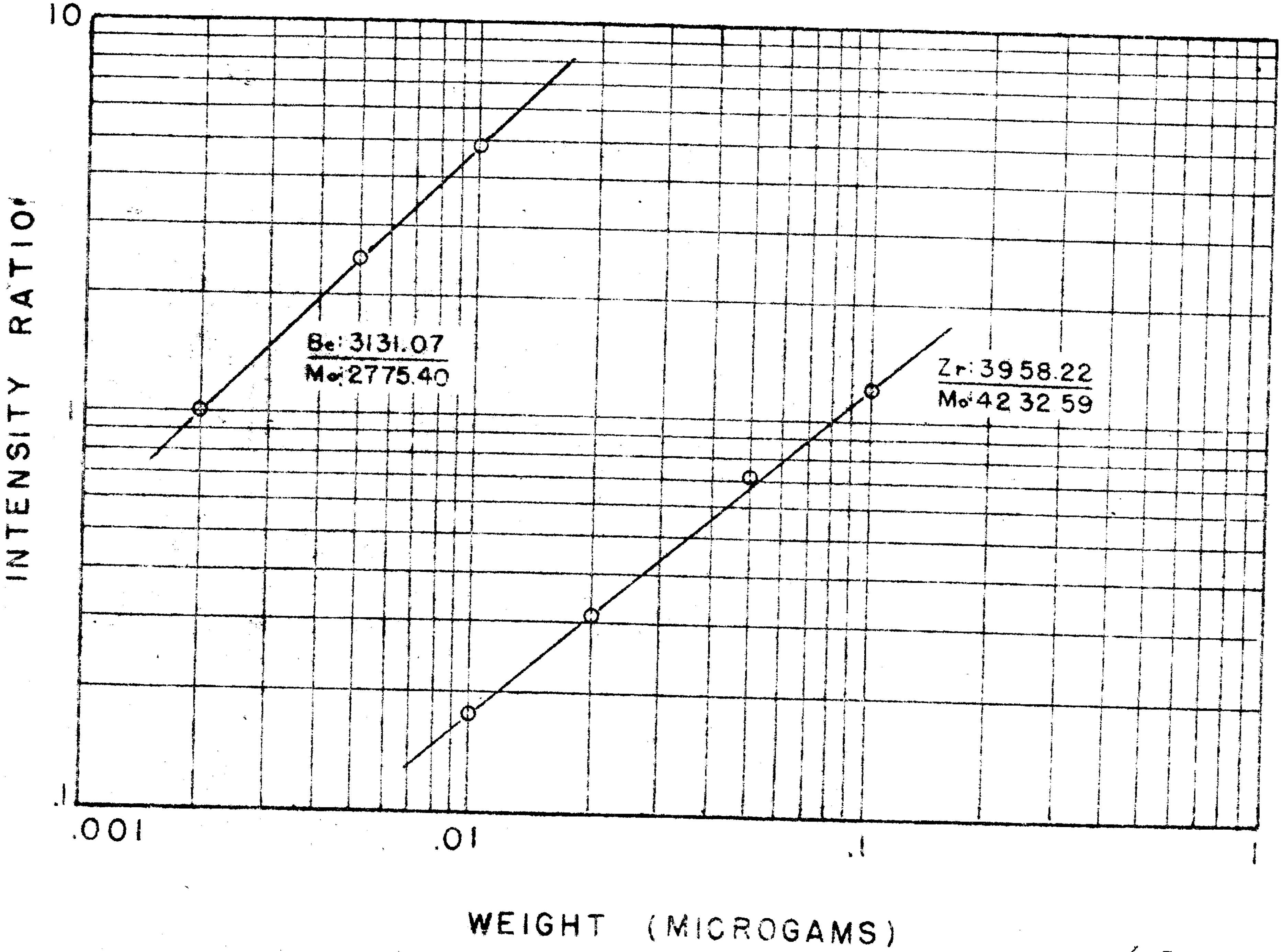
0
1
0.1
1
10
100
WEIGHT (MICROGRAMS)

FIG. 7

LA-326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.01
.1
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INTENSITY RATIO
WEIGHT (MICROGAMS)
Be: 3131.07
Mo: 2775.40
Zr: 3958.22
Mo: 4232.59

FIG. 8

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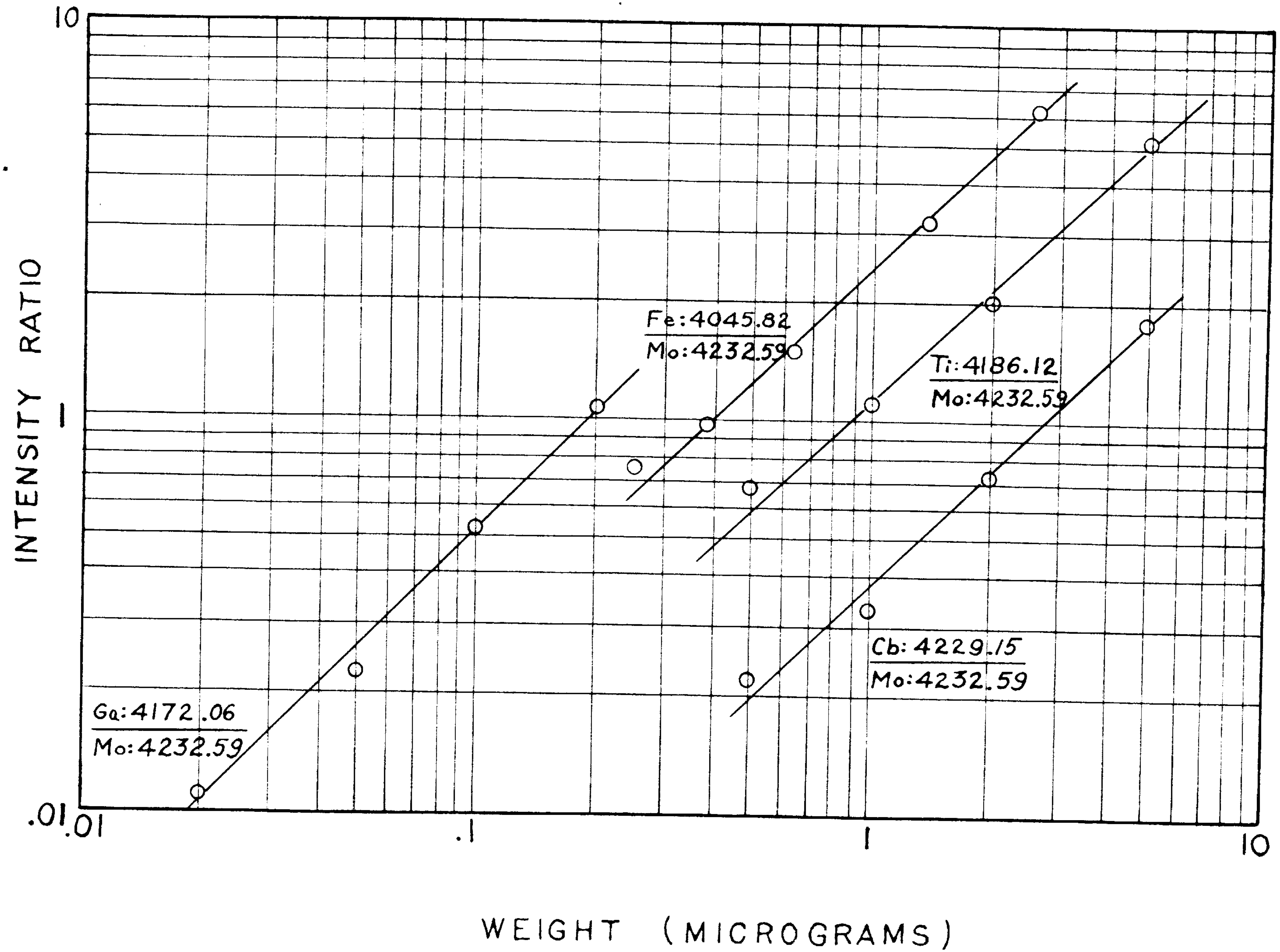
10
1
.01
.01
.1
1
10
INTENSITY RATIO
WEIGHT (MICROGRAMS)
Fe:4045.82 / Mo:4232.59
Ti:4186.12 / Mo:4232.59
Cb:4229.15 / Mo:4232.59
Ga:4172.06 / Mo:4232.59

FIG. 9

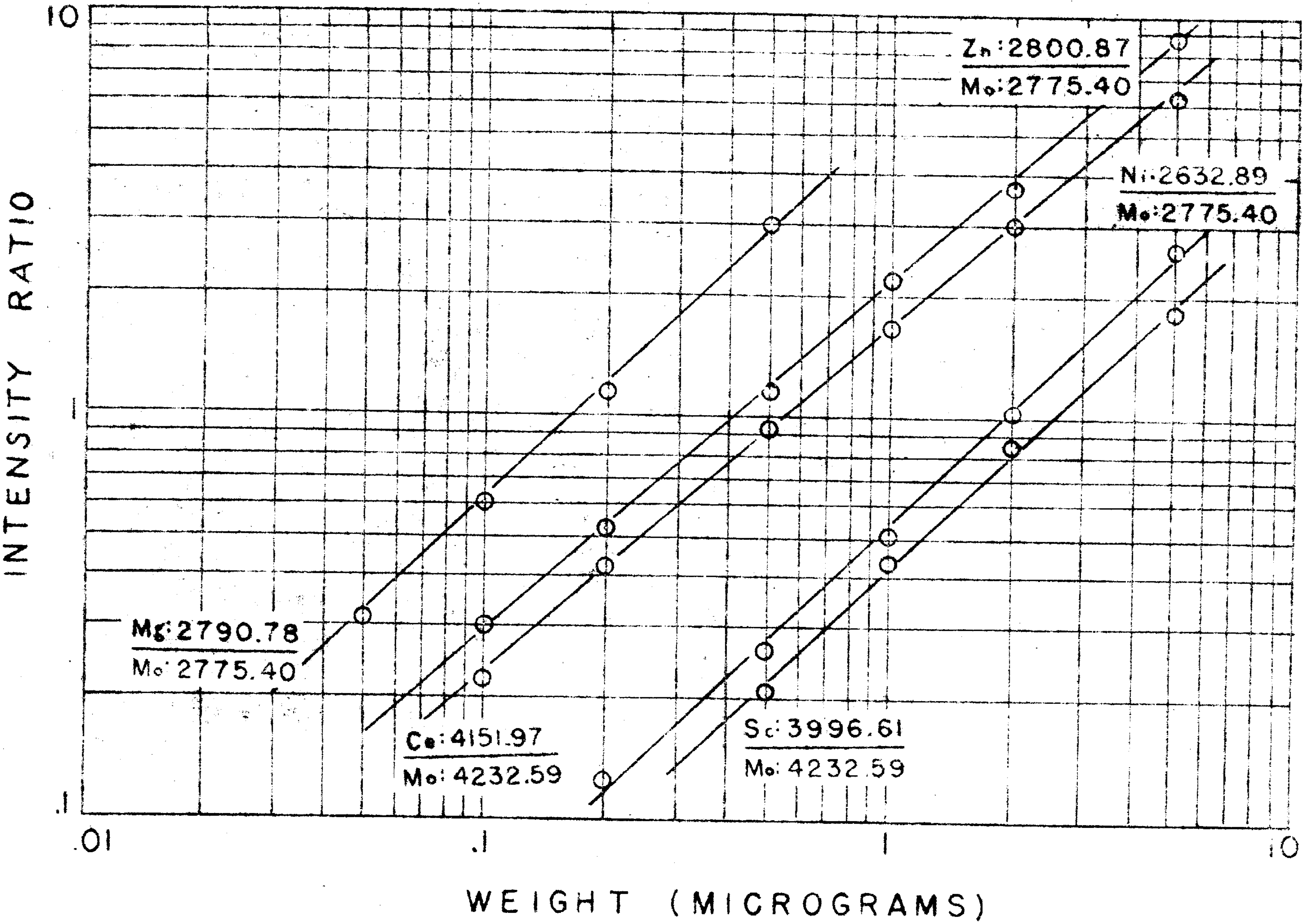
10
1
.1
.01
.1
1
10
INTENSITY RATIO
WEIGHT (MICROGRAMS)
Zn: 2800.87 / Mo: 2775.40
Ni: 2632.89 / Mo: 2775.40
Mg: 2790.78 / Mo: 2775.40
Ce: 4151.97 / Mo: 4232.59
Sc: 3996.61 / Mo: 4232.59

FIG. 10

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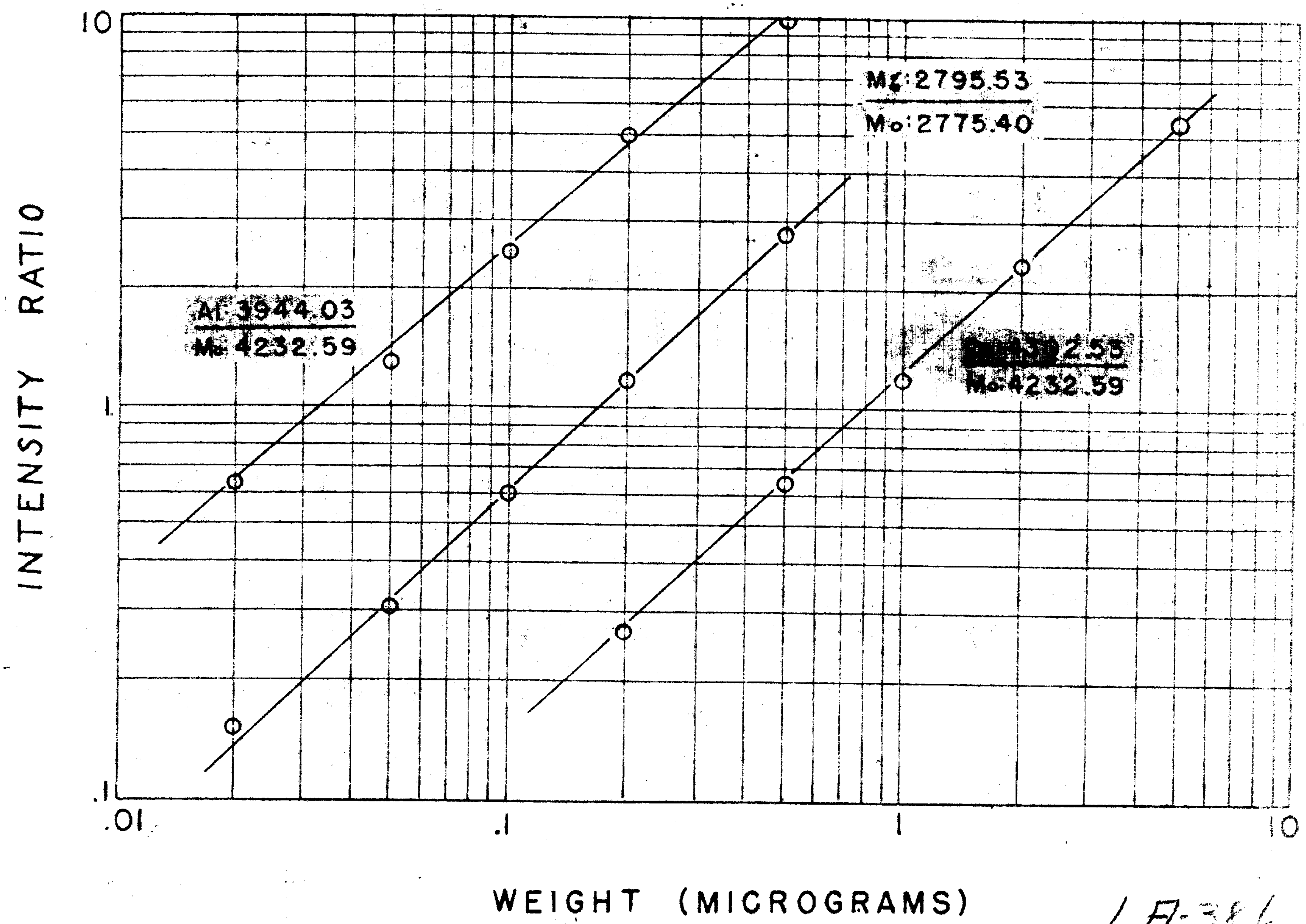
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1.
.1
.01
.1
1
10
INTENSITY RATIO
WEIGHT (MICROGRAMS)
Al 3944.03
Mo 4232.59
Mg 2795.53
Mo 2775.40
[illegible]2.53
Mo 4232.59

FIG. 11

LA-386

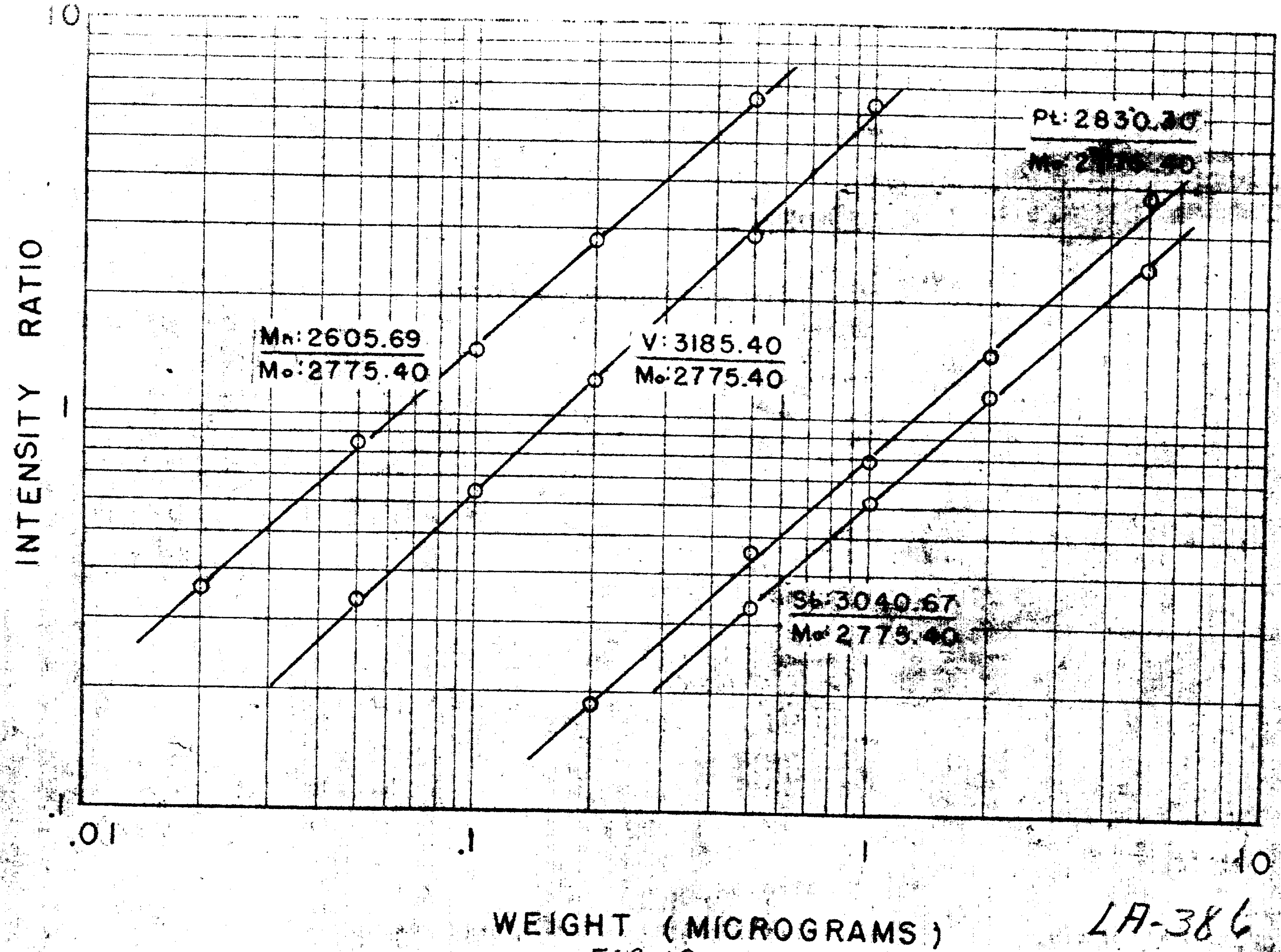
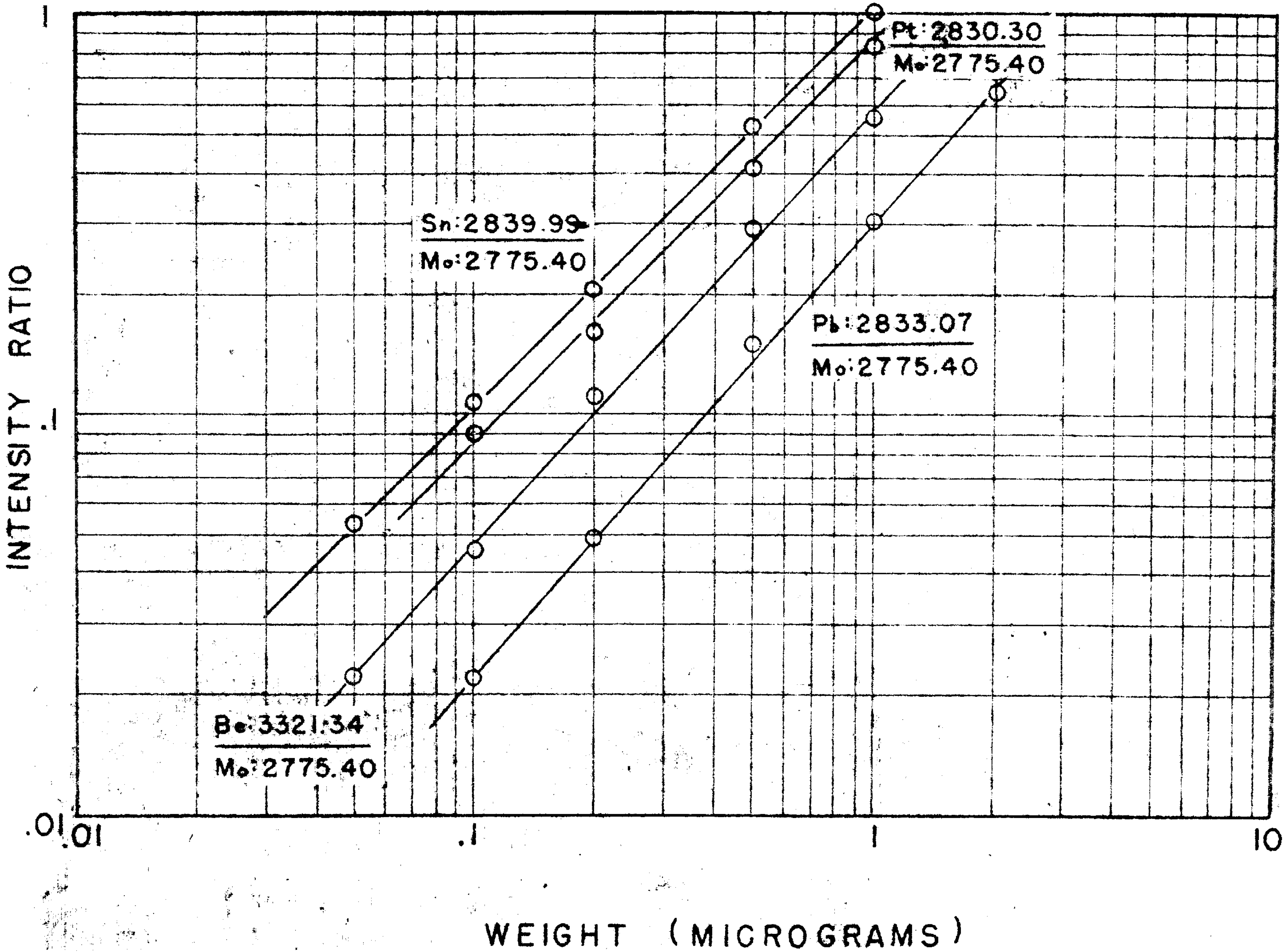

10
1
.1
.01
.1
1
10
INTENSITY RATIO
WEIGHT (MICROGRAMS)
Mn: 2605.69 / Mo: 2775.40
V: 3185.40 / Mo: 2775.40
Pt: 2830.30 / Mo: 2[illegible].40
Sb: 3040.67 / Mo: 2775.40

FIG. 12

LA-386


INTENSITY RATIO
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.1
.01
.01
.1
1
10
Pt:2830.30
Mo:2775.40
Sn:2839.99
Mo:2775.40
Pb:2833.07
Mo:2775.40
Be:3321.34
Mo:2775.40
WEIGHT (MICROGRAMS)

FIG. 13

LA-386

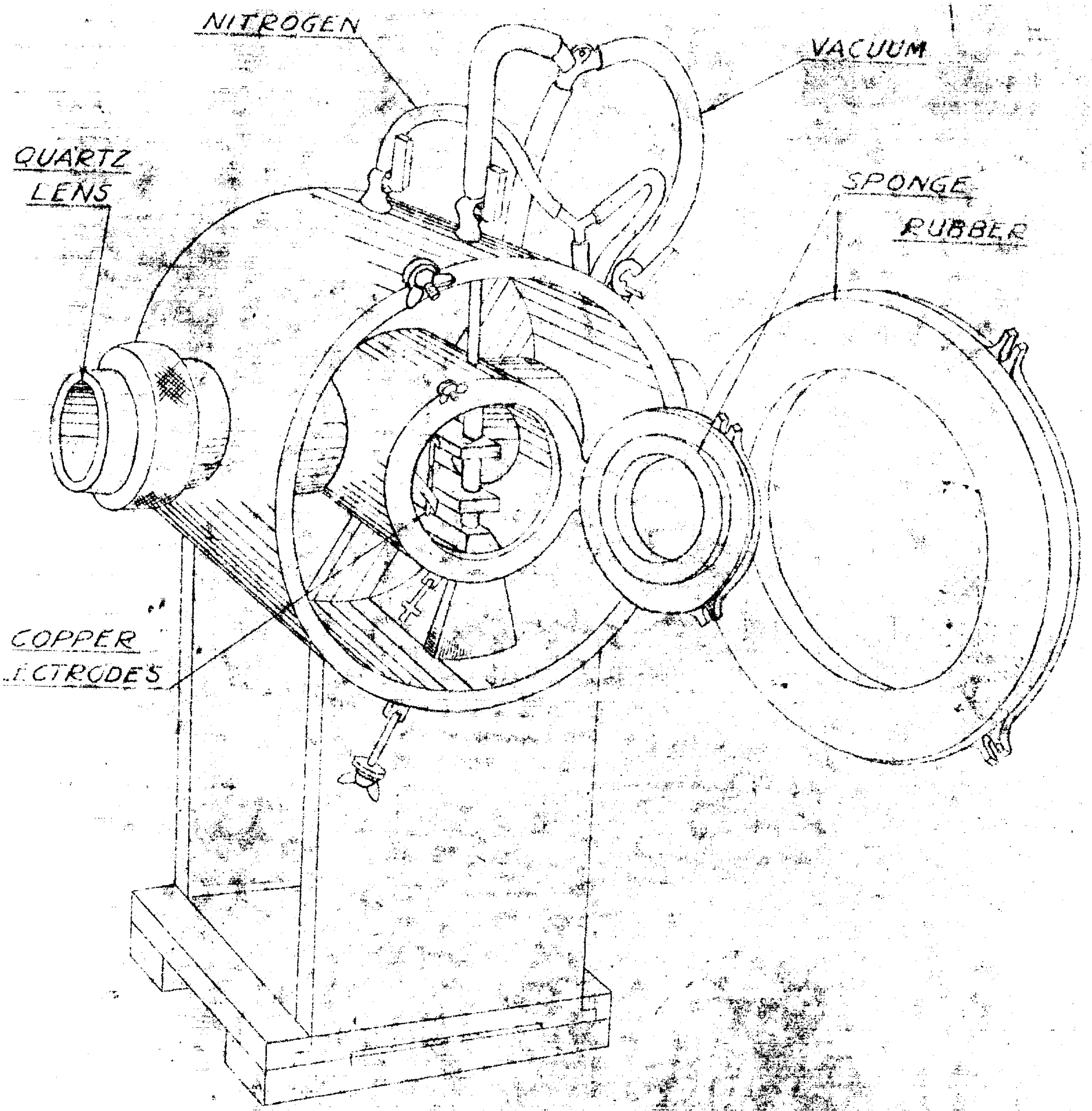
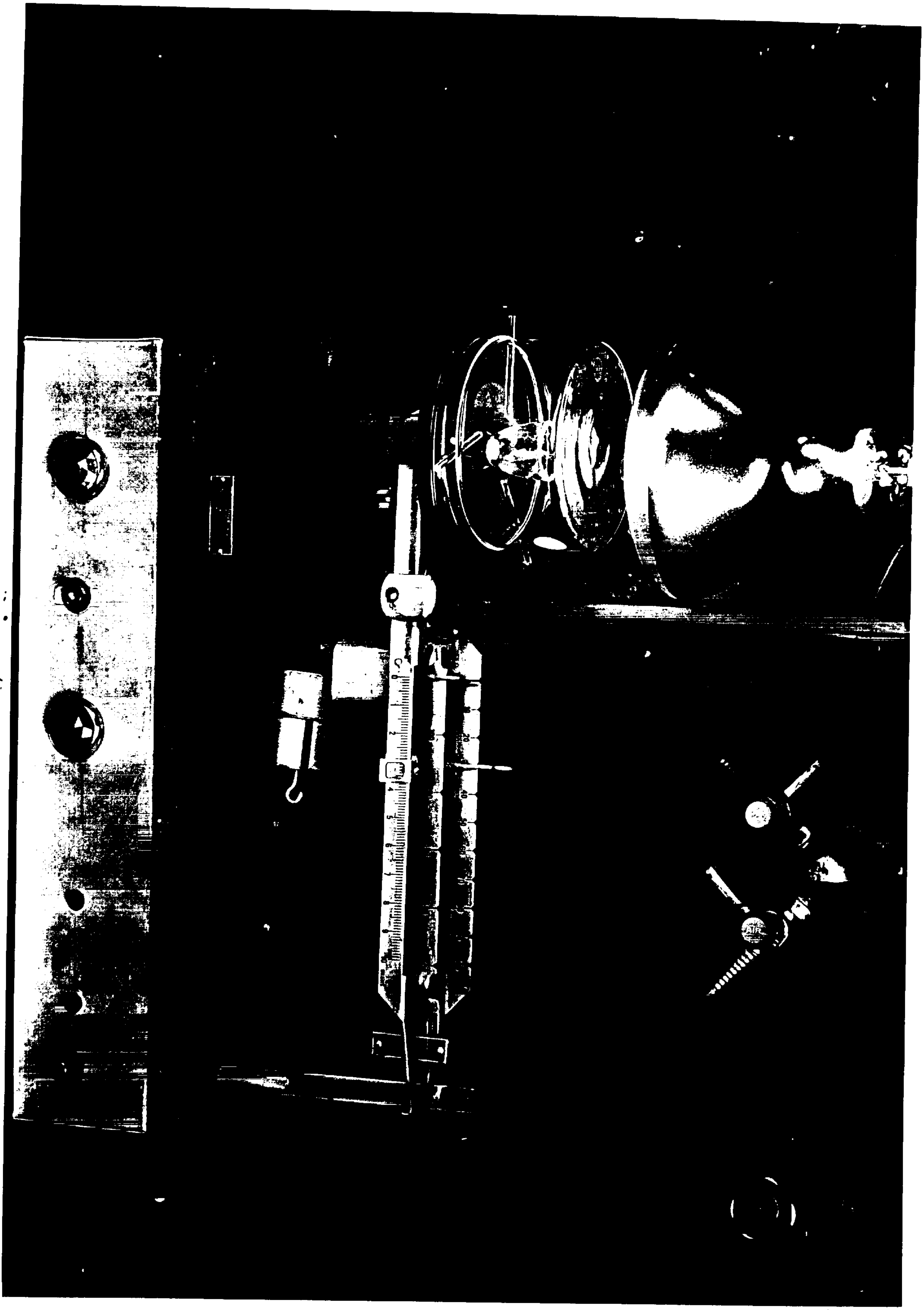


FIGURE 14 SPARK DISCHARGE CHAMBER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