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LOS ALAMOS, NEW MEXICO

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Report written:
July, 1953

MAY 11 1955

PUBLICLY RELEASABLE
Per E.M. Sandoval, FSS-16 Date: 9-21-88
By [illegible], CIC-14 Date: 3-11-96

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LA-1843 This document consists of 26 pages

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THE POLAROGRAPHIC BEHAVIOR OF VARIOUS METAL IONS IN PLUTONIUM SOLUTIONS

by

C. G. Warren

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E. M. Sandoval SEP 21 1988
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ABSTRACT

The reported procedures for the polarographic determination of uranium, vanadium, and titanium in plutonium were investigated to ascertain if they could be used to determine other common metals in plutonium. It was found that the procedure using hydroxylamine hydrochloride to reduce plutonium to the (III) oxidation state could be used to determine bismuth, platinum, rhodium, copper, tin, lead, thallium, indium, and cadmium. The procedure using zinc and zinc amalgam in hydrochloric acid to reduce the plutonium to the (III) oxidation state is quite limited, but it might be used to determine molybdenum.

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INTRODUCTION

The previously-reported polarographic determination of uranium(1), vanadium(2) and titantium(3) in plutonium-containing solutions is, in each case, based on the observation that plutonium(III) in a chloride solution does not produce a polarographic wave within the range 0.0 to -0.9 volt (vs. S.C.E.). In one case hydroxylamine hydrochloride and in the other case zinc and zinc amalgam were used as reducing and holding agents for the plutonium, obviously with no interference from the reducing agent in the determination of the element in question. It is clear that the technique used in the above procedures should apply to the determination of other metallic ions which exhibit polarographic waves within this voltage range.

For this reason, this work was undertaken in order to explore possible extensions of the above technique to the determination of other elements in plutonium-containing solutions. The value of such information lies in the fact that polarographic techniques often afford a short and convenient method of analysis, usually having satisfactory precision and being applicable to fairly low concentration ranges.

Because the work was exploratory in nature, complete procedures for determining various elements such as bismuth, platinum, rhodium, copper, tin, lead, thallium, indium and cadmium are not described. It is quite possible that changes in the chemical composition of the solution, such as the introduction of a complexing agent, would permit the satisfactory

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determination of additional metallic ions in the presence of plutonium.

It was obvious that the reducing potential of zinc and zinc amalgam is sufficiently large that its use would be quite limited. This was found to be the case. Hydroxylamine hydrochloride was found to be more suitable and appears to have use in the determination of several metallic elements in the presence of plutonium.

EXPERIMENTAL

Apparatus

A Leeds and Northrup Electrochemograph, Type E, was used to record all polarograms. The polarographic cell was identical to that used in previous work(1,2,3) and was kept at 34 ± 0.1° C. in a suitable water bath.

Three different capillaries, with the following constants, were employed:

$m^{2/3}\ t^{1/6} = 2.09$ for measurements made on rhodium in hydroxylamine hydrochloride-plutonium solutions.

$m^{2/3}\ t^{1/6} = 1.61$ for measurements made on other metals in hydroxylamine hydrochloride-plutonium solutions.

$m^{2/3}\ t^{1/6} = 2.18$ for measurements made on molybdenum in zinc chloride solutions.

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The reference electrode was saturated calomel with probe-type salt bridge filled with 20 percent potassium chloride and 2 percent agar.

Reagents and Stock Solutions

Hydroxylamine hydrochloride stock solution, 3.33 M, prepared by dissolving the salt in distilled water. Upon standing several months, the solution was found to produce the objectionable wave shown in Figure 1. Therefore, the solution should be freshly prepared and on dilution to 2 M should produce a polarogram similar to Figure 2. It is advisable to check the solution before use.

Stock solutions of the metal ions to be investigated were prepared as given below. In each case the concentration of the metal ion was 5 millimoles per liter.

Antimony, prepared by dissolving antimony oxychloride from Fisher Scientific Company, in concentrated hydrochloric acid.

Bismuth, prepared by dissolving bismuth oxychloride from J. T. Baker Chemical Company in concentrated hydrochloric acid.

Cadmium, prepared by dissolving cadmium metal from J. T. Baker Chemical Company in small excess of hydrochloric acid and diluting with distilled water.

Cobalt, prepared by dissolving cobalt nitrate from J. T. Baker Chemical Company in distilled water.

Copper, prepared by dissolving copper metal from Mallinckrodt Chemical Works in a small excess of nitric acid and diluting with distilled water.

Europium, prepared by dissolving the oxide from Johnson Matthey and Company in a small excess of hydrochloric acid and diluting with distilled water.

Gallium, prepared by dissolving gallium sulfate from A. D. Mackay Company in distilled water.

Indium, prepared by dissolving indium sulfate from the Indium Corporation of America in distilled water.

Iridium, prepared by dissolving iridium tetrachloride from A. D. Mackay Company in distilled water.

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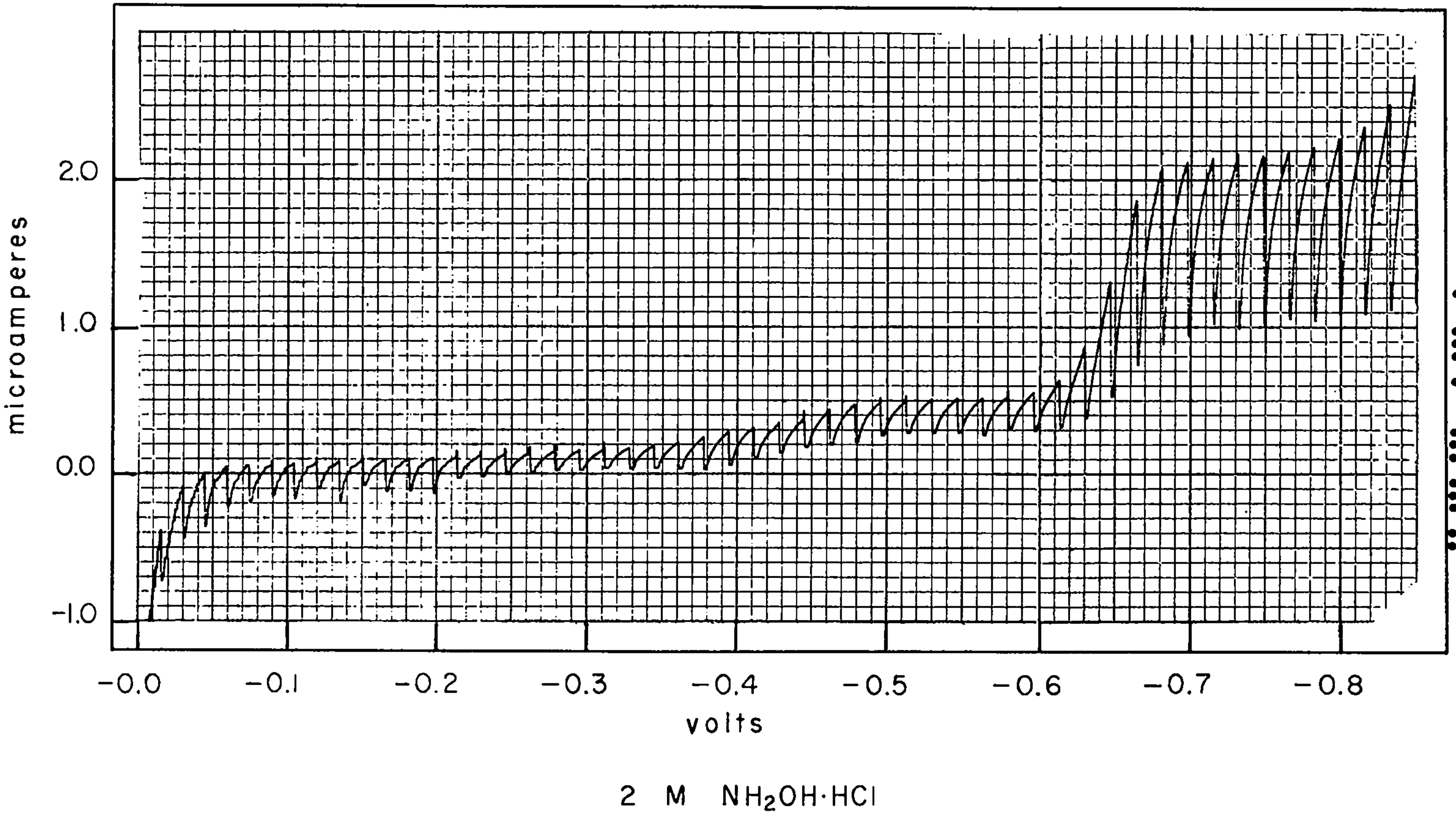

Figure 1. The polarogram of a 2 M hydroxylamine hydrochloride solution several months after being prepared.

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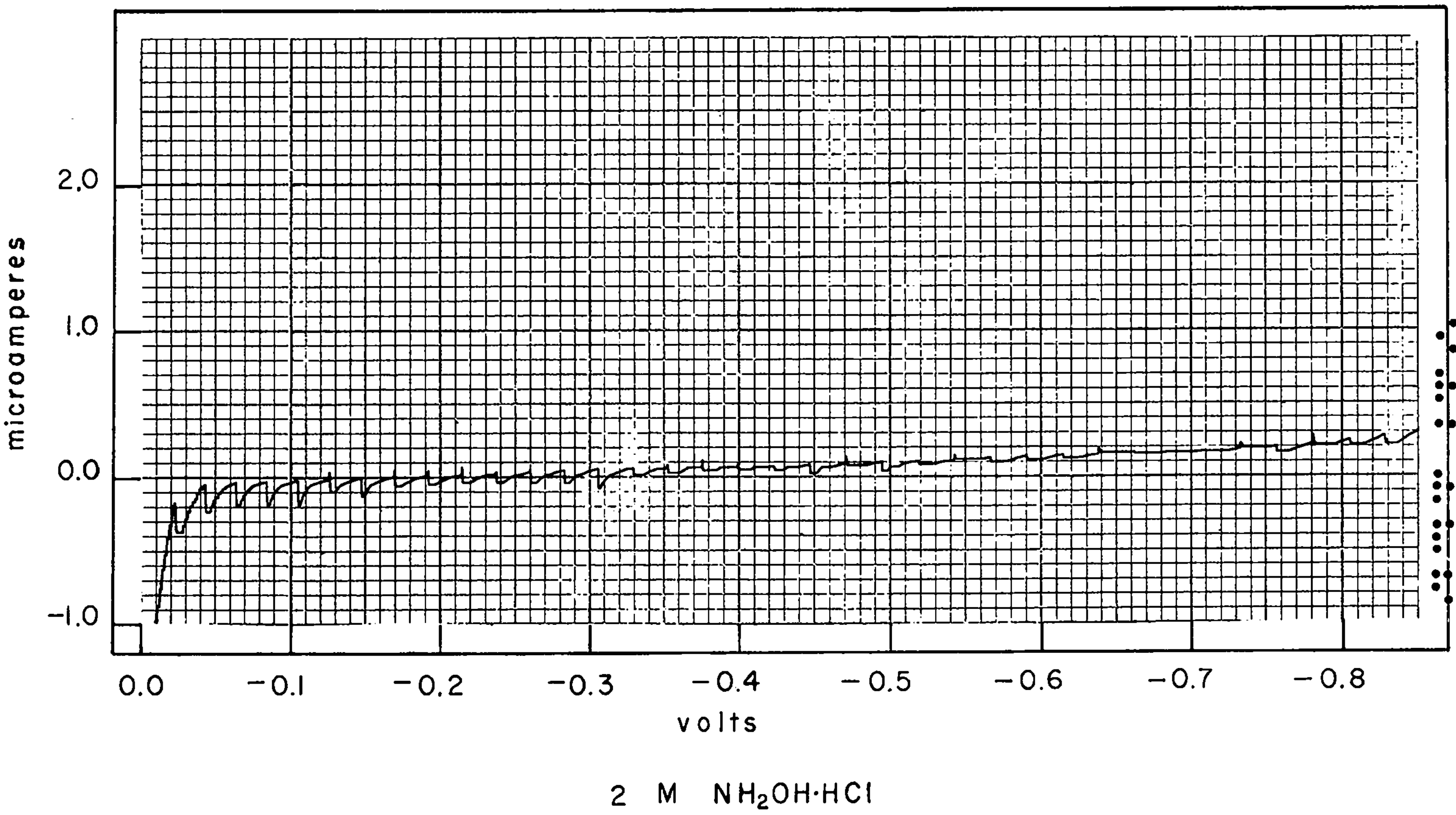

Figure 2. The polarogram of freshly prepared 2 M hydroxylamine hydrochloride.

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Lead, prepared by dissolving lead chloride from J. T. Baker Chemical Company in distilled water.

Molybdenum, prepared by dissolving ammonium molybdate from J. T. Baker Chemical Company in distilled water.

Nickel, prepared by dissolving nickel ammonium sulfate from Mallinckrodt Chemical Works in distilled water.

Palladium, prepared by dissolving palladium chloride from A. D. Mackay Company in about 6 N hydrochloric acid.

Platinum, prepared by dissolving ammonium chloroplatinate in a small excess of nitric acid and diluting with distilled water.

Rhodium, prepared by dissolving rhodium chloride from Baker and Company, Inc., in distilled water.

Ruthenium, prepared by dissolving ruthenium chloride from J. Bishop and Company in distilled water.

Silver, prepared by dissolving silver nitrate from Mallinckrodt Chemical Works in distilled water.

Tungsten, prepared by dissolving sodium tungstate from J. T. Baker Chemical Company in distilled water.

Thallium, prepared by dissolving thallous chloride obtained from A. D. Mackay Company in distilled water.

Tin, prepared by dissolving tin metal from Mallinckrodt Chemical Works in concentrated hydrochloric acid with a small amount of nitric acid.

A stock solution of plutonium chloride was prepared by dissolving plutonium metal in hydrochloric acid with a small amount of nitric acid and diluting with distilled water. It contained 100 grams of plutonium per liter.

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Technique

The investigations of the polarographic behavior of the various metal ions in the presence of plutonium were made under the following conditions:

A. Use of Hydroxylamine Hydrochloride as a Reducing Agent

To a 5-milliliter volumetric flask was added 1 milliliter of the metal-ion stock solution, 1 milliliter of the plutonium stock solution, 0.5 milliliter each of 3 M hydrochloric acid, 3 M sulfuric acid, and 8 M nitric acid. The solution was then evaporated to apparent dryness under an infra-red lamp. To the contents of the flask was added 3 milliliters of 3.33 M hydroxylamine hydrochloride solution. The solution was then diluted to the mark with distilled water. The final solution was 10^{-3} M in the metal ion to be investigated, 2 M hydroxylamine hydrochloride, 0.3 M sulfate, 0.4 M hydrogen ion, and 0.0837 M plutonium(III). This solution was placed in the thermostated polarographic cell, nitrogen bubbled through for 20 minutes, and the polarogram recorded.

B. Use of Zinc and Zinc Amalgam as a Plutonium-Reducing Agent

The use of zinc and zinc amalgam is quite limited, as would be expected because of its high reducing power. In the few cases where they apply, the solutions were prepared and polarograms recorded in a manner similar to that described in (A).

RESULTS AND DISCUSSION

Using the conditions stated in (A), the metal ions listed in Table I exhibited well-defined polarographic waves.

Table I

THE POLAROGRAPHIC BEHAVIOR OF VARIOUS METALLIC IONS
IN THE PRESENCE OF PLUTONIUM(III) IONS AND
HYDROXYLAMINE HYDROCHLORIDE

Metal Ion	Range of Observation (volts vs. S.C.E.)		Diffusion Current (microamperes)	Half-wave Potential (volts vs. S.C.E.)
Bi(III)	-0.05	-0.35	10.40	-0.12
Pt(II)	-0.05	-0.35	5.88	-0.12
U (VI)	-0.05	-0.35	7.64	-0.17
Rh(III)	-0.10	-0.40	11.8	-0.19
Cu(I)	-0.09	-0.50	4.67	-0.22
Sn(IV)	-0.05	-	12.30(II + IV)	-0.24
Sn(II)	-	-0.60	-	-0.48
Pb(II)	-0.30	-0.60	7.36	-0.46
Tl(I)	-0.38	-0.61	2.91	-0.51
In(III)	-0.50	-0.75	15.80	-0.61
Cd(II)	-0.50	-0.80	8.71	-0.65

The well-defined shape and magnitude of the diffusion current in the above cases strongly suggested that these ions might be quantitatively determined under the conditions of the experiment. Although further work in this direction was not done, the information in Table I was sufficient for calculating an approximate sensitivity in each case. These are shown in Table II.

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Table II

ESTIMATED LOWER LIMITS OF DETERMINATION OF METALS IN PLUTONIUM

Metal	Sensitivity*	Estimated Lower Limit** (Percent of Metal in Pu)
Bi	6.46	0.07
Pt	3.65	0.10
U	3.94	0.10
Rh	5.65	0.04
Cu	2.90	0.04
Sn	7.64	0.03
Pb	4.54	0.10
Tl	2.73	0.20
In	9.81	0.03
Cd	5.41	0.04

* The sensitivity (S) was calculated in the usual manner, microamperes per millimole of metal per unit capillary constant

$$S = \frac{i_d}{C \times m^{2/3}\ t^{1/6}}$$

** The estimated lower limit of the determination is derived from the grams per liter of metal producing 1 microampere at a capillary with a constant of 2.3, divided by 20 grams of plutonium per liter.

Under similar experimental conditions no waves were obtained for cobalt, indium, nickel, and ytterbium. Tungsten and palladium were not soluble under these conditions. Gold ions were, of course, reduced to the metal by the hydroxylamine hydrochloride. Poorly defined and non-reproducible waves were obtained for silver, antimony, molybdenum, europium and ruthenium.

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Figures 3-11 show typical polarograms obtained for bismuth, platinum, rhodium, copper, tin, lead, thallium, indium, and cadmium ions in the presence of hydroxylamine hydrochloride and plutonium ions. The polarogram for uranium(1) has been previously reported.

The following elements were not tried because their reduction potentials, as indicated in the literature(4,5,6,7), are not within the voltage range of the method: lithium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium, barium, radium, zinc, scandium, yttrium, lanthanum, most rare earths, aluminum, gallium, germanium, zirconium, hafnium, thorium, niobium, tantalum, manganese, and iron.

Attempts to use zinc and zinc amalgam as a plutonium-reducing agent met with only limited success for the reasons stated in (B). Molybdenum (see Figure 12) produced an anodic wave with a half-wave potential of approximately -0.06 volt in a solution 1 M in zinc chloride and 1 M in tartaric acid. However, the anodic oxidation of mercury interfered so that accurate measurements of the diffusion current could not be made. Chromium produced a small poorly-defined anodic wave unsuitable for any measurements. Vanadium(2) and titanium(3) are covered in previous reports.

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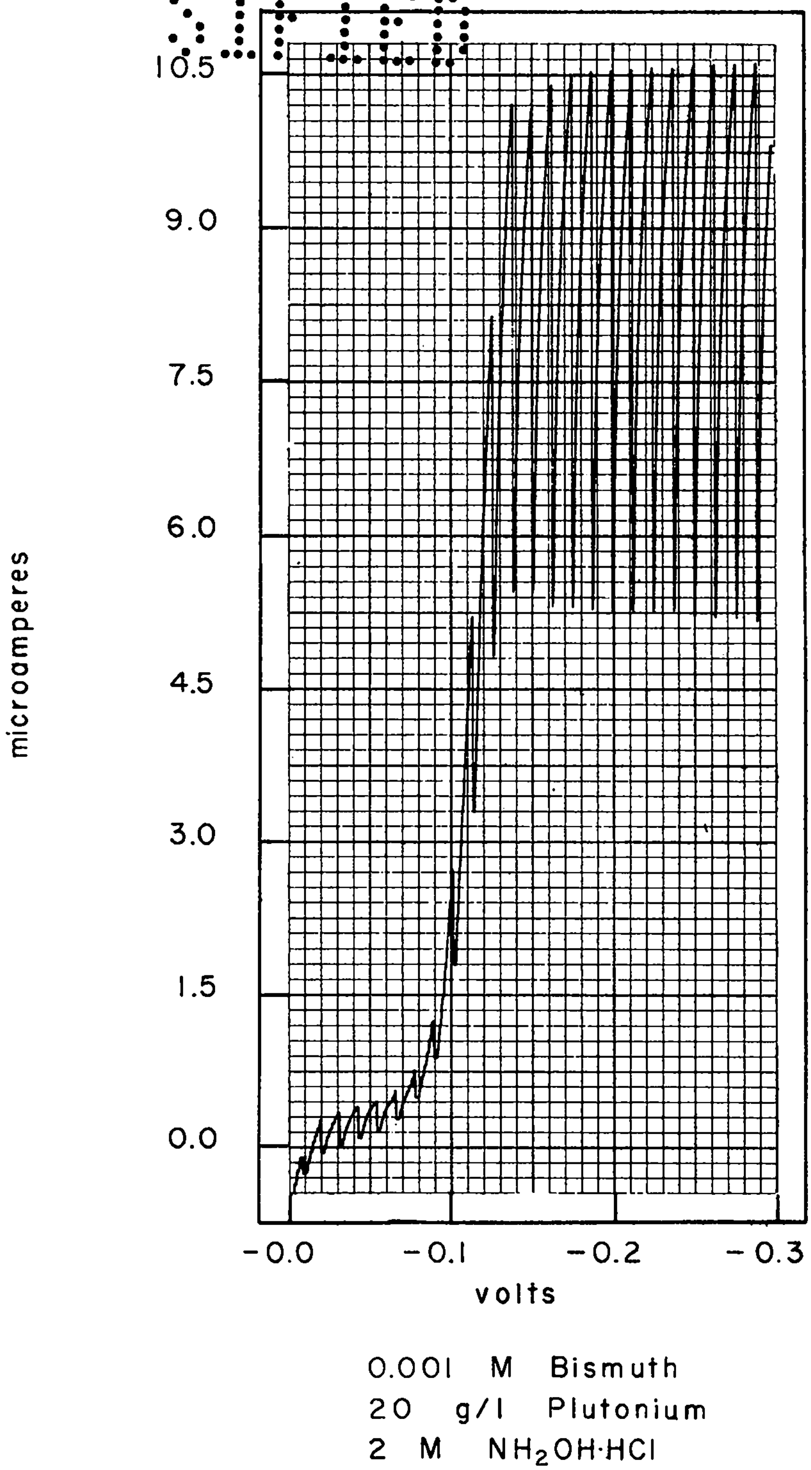

Figure 3. The polarogram of 0.001 M bismuth in a solution of 0.084 M plutonium and 2 M hydroxylamine.

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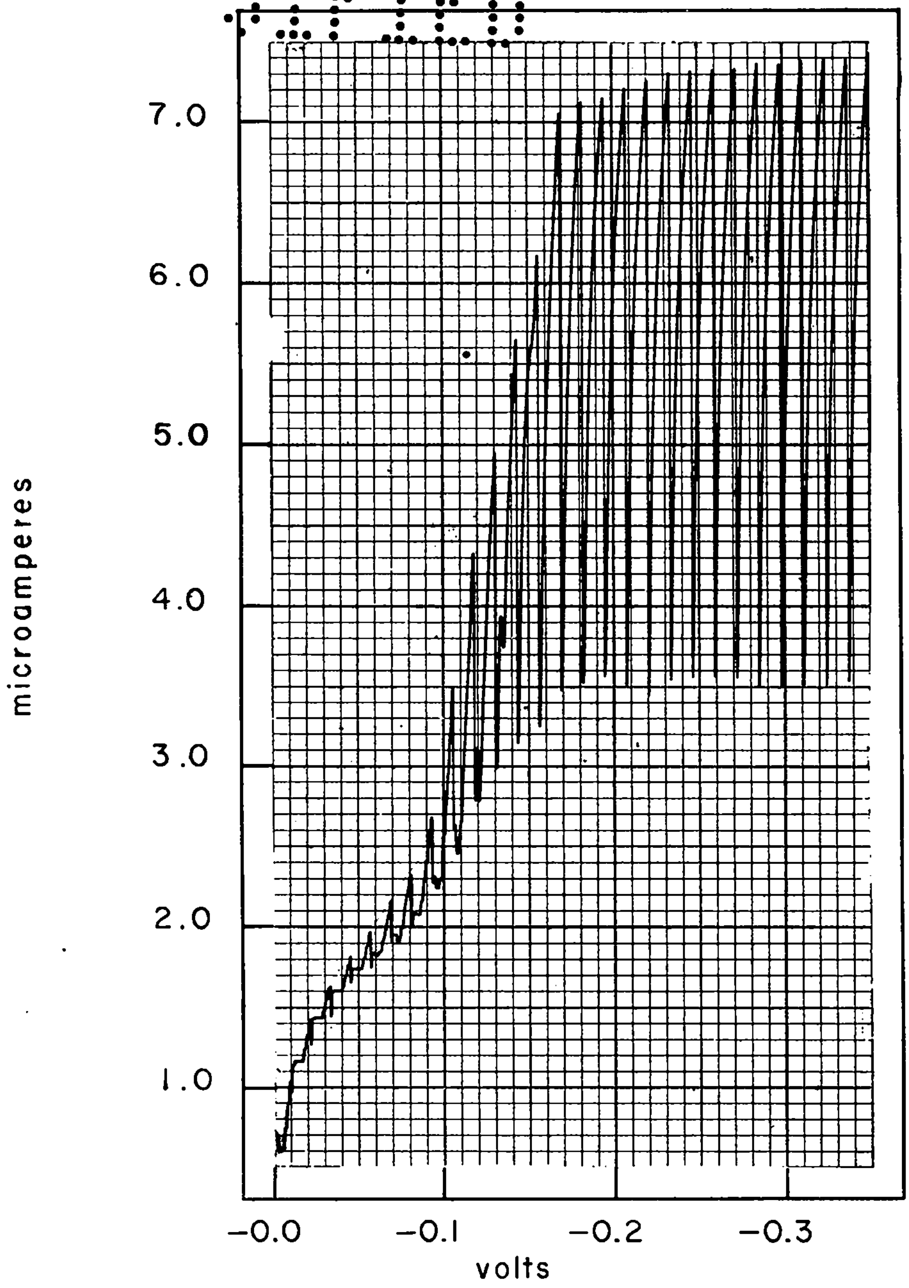

0.001 M Platinum
20 g/l Plutonium
2 M $NH_2OH \cdot HCl$

Figure 4. The polarogram of 0.001 M platinum in a solution of 0.084 M plutonium and 2 M hydroxylamine hydrochloride.

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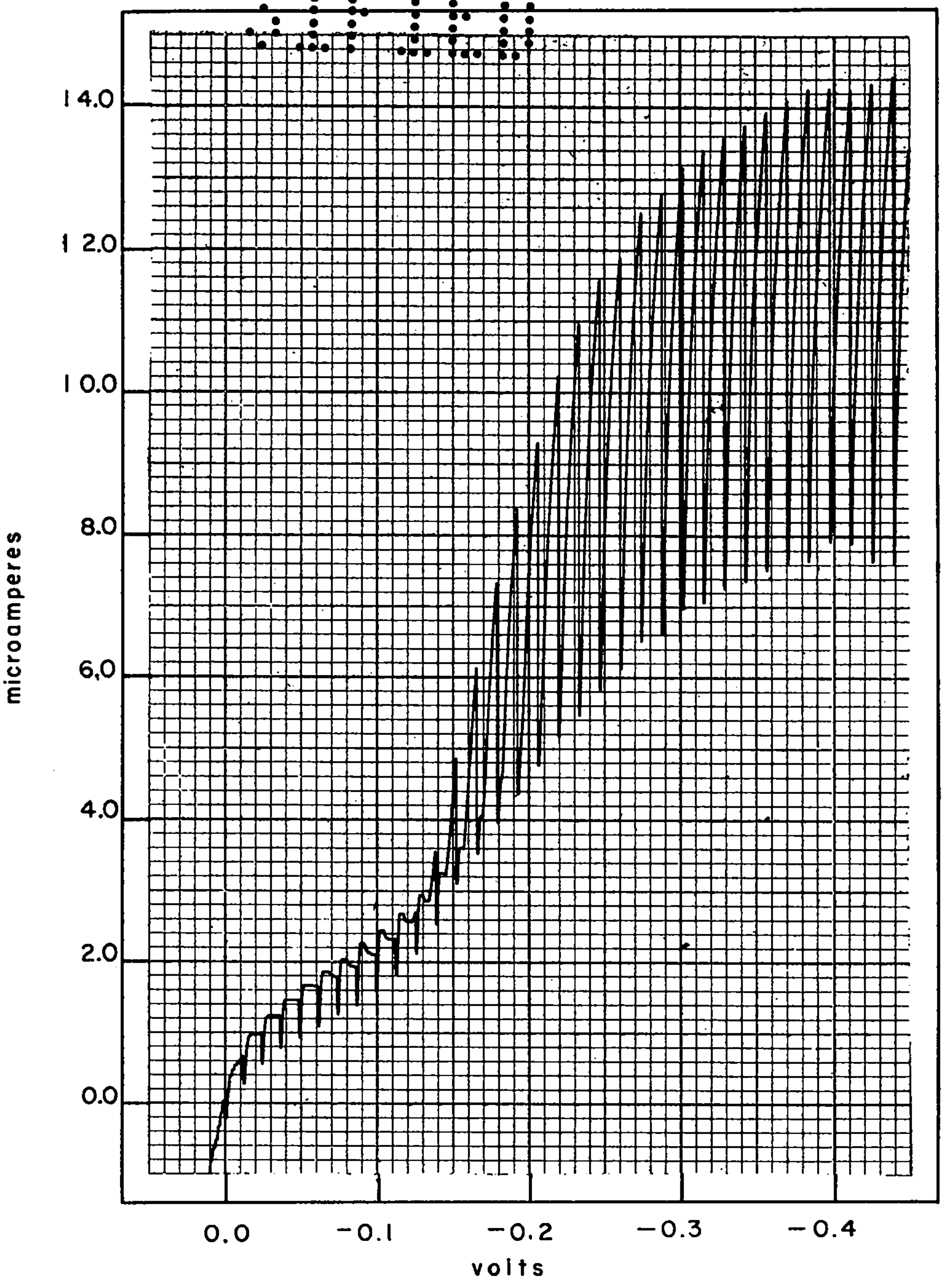

0.001 M Rhodium
20 g/l Plutonium
2 M $NH_2OH \cdot HCl$

Figure 5. A polarogram of 0.001 M rhodium in a solution of 0.084 M plutonium and 2 M hydroxylamine hydrochloride.

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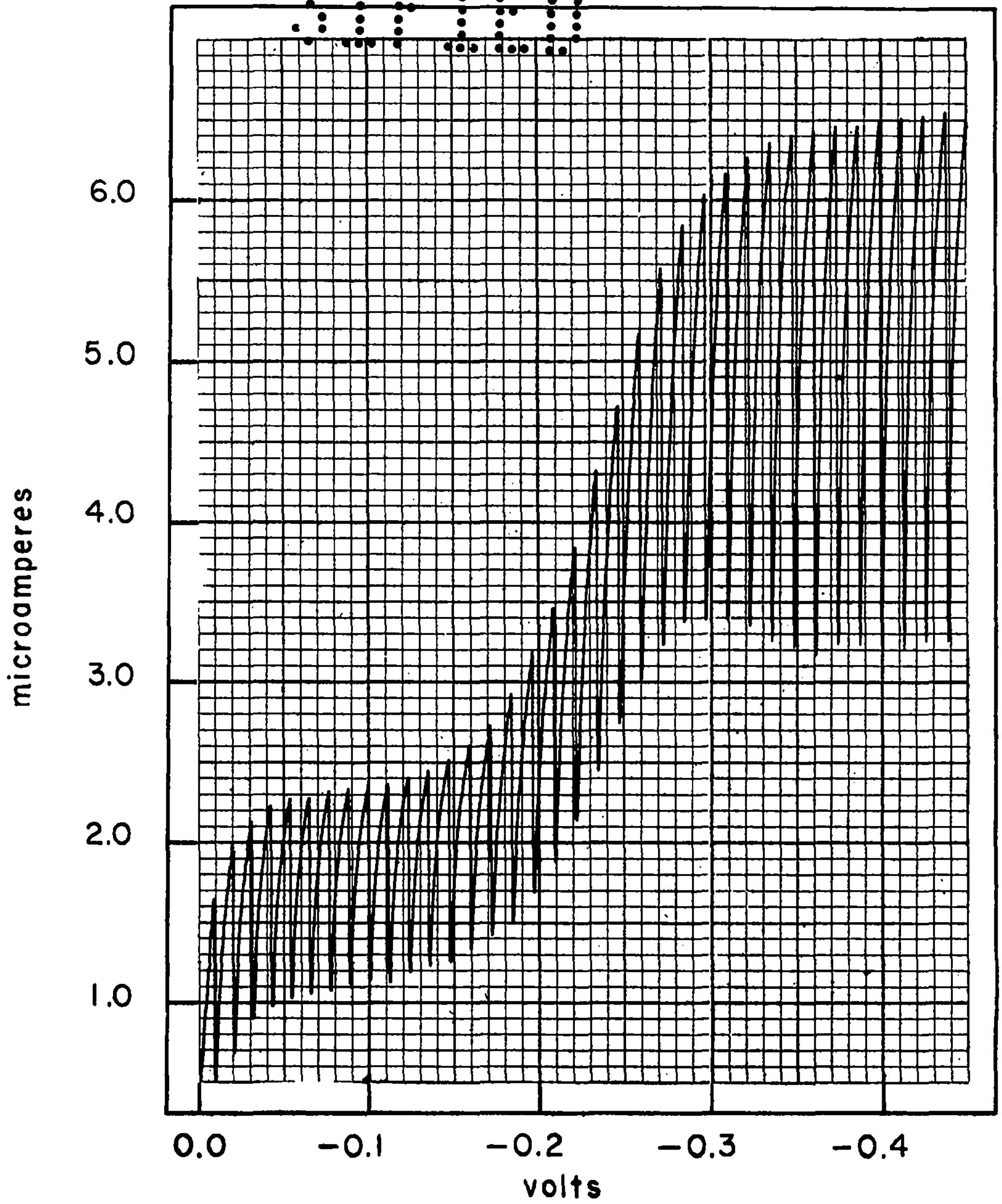

0.001 M Copper
0.01 % Gelatin
20 g/l Plutonium
2 M $NH_2OH \cdot HCl$

Figure 6. A polarogram of 0.001 M copper in a solution of 0.01% gelatine, 0.084 M plutonium, and 2 M hydroxylamine hydrochloride.

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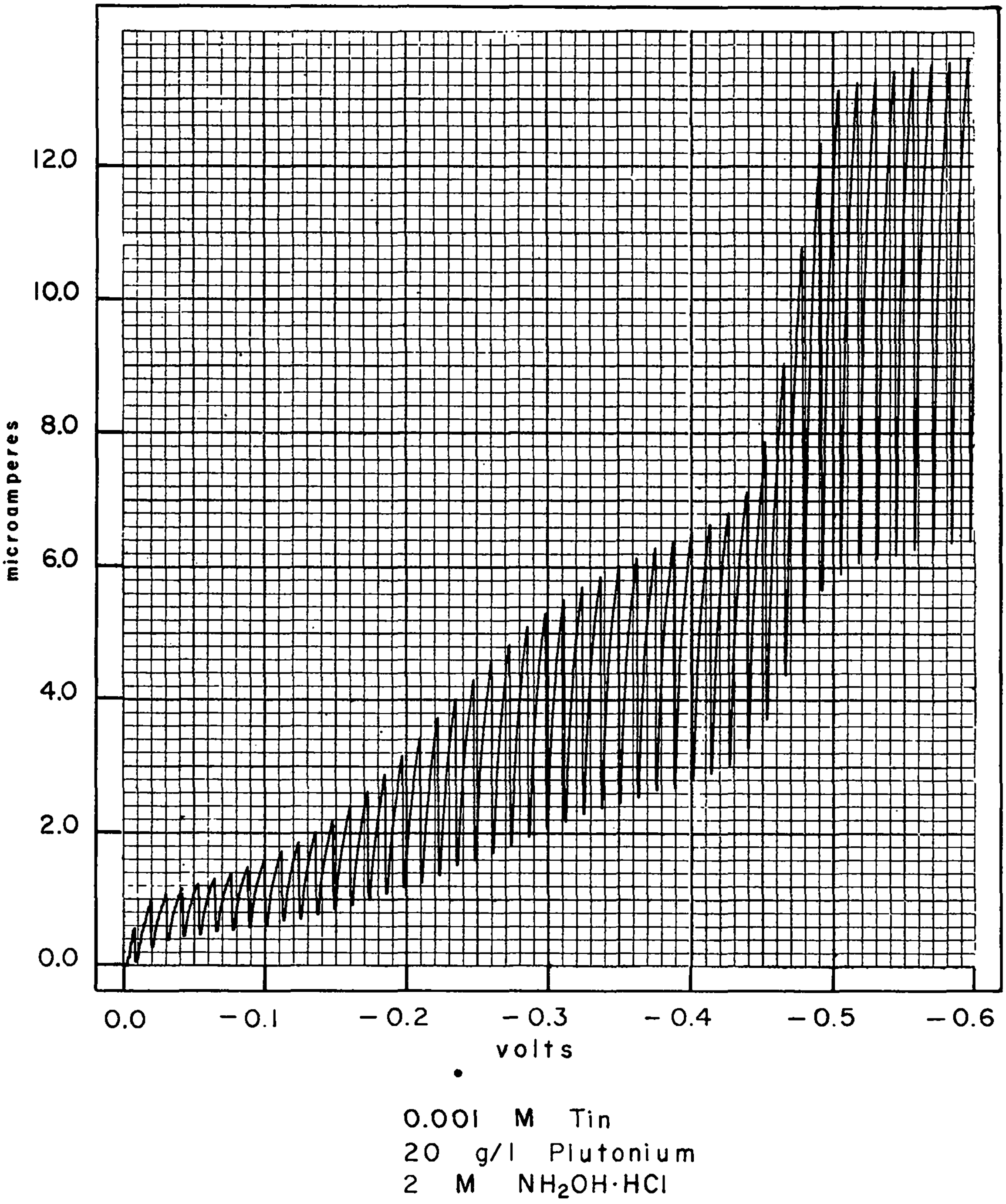

Figure 7. A polarogram of 0.001 M tin in a solution of 0.084 M plutonium and 2 M hydroxylamine hydrochloride.

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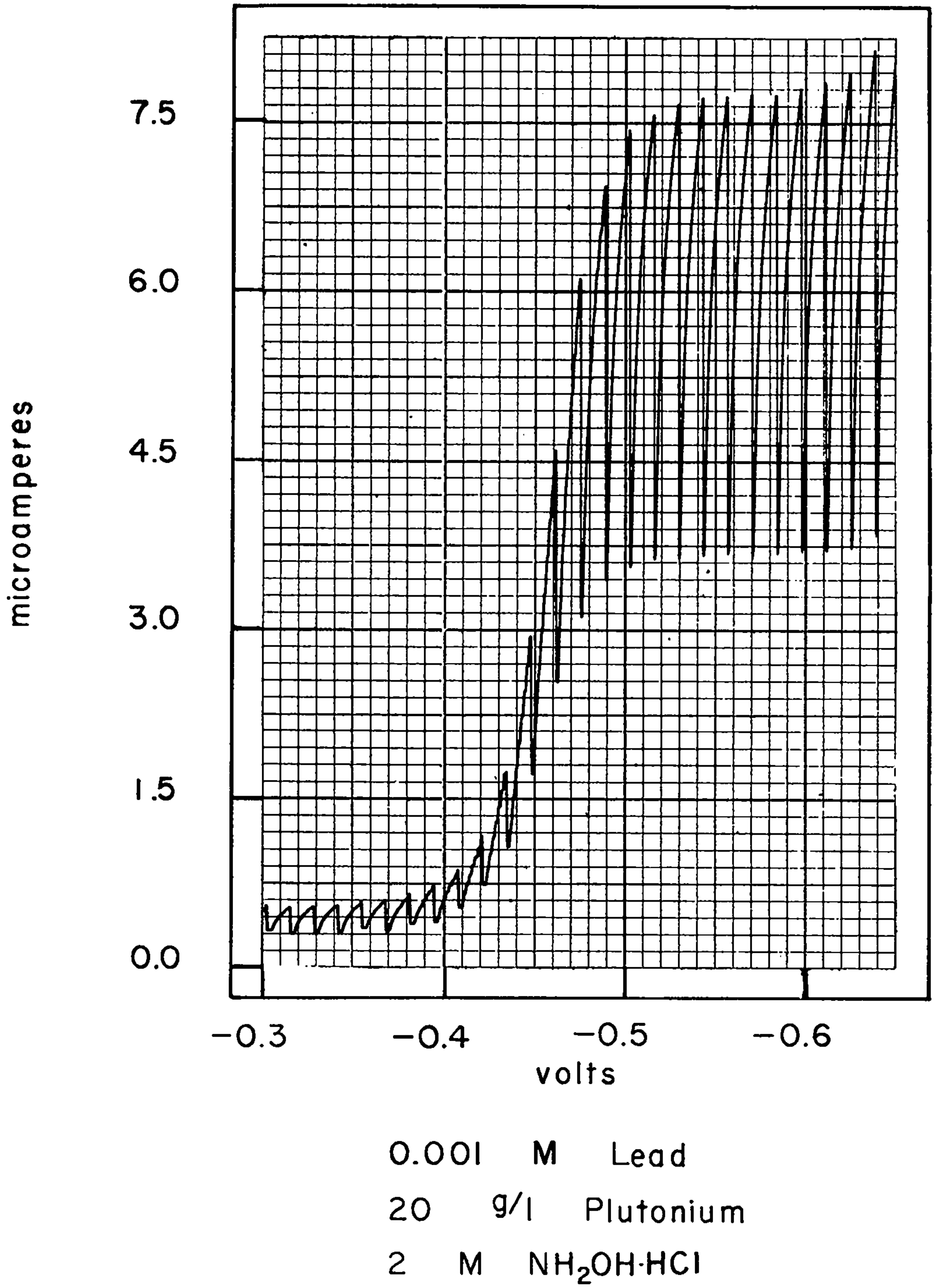

Figure 8. A polarogram of 0.001 M lead in a solution of 0.084 M plutonium and 2 M hydroxylamine hydrochloride.

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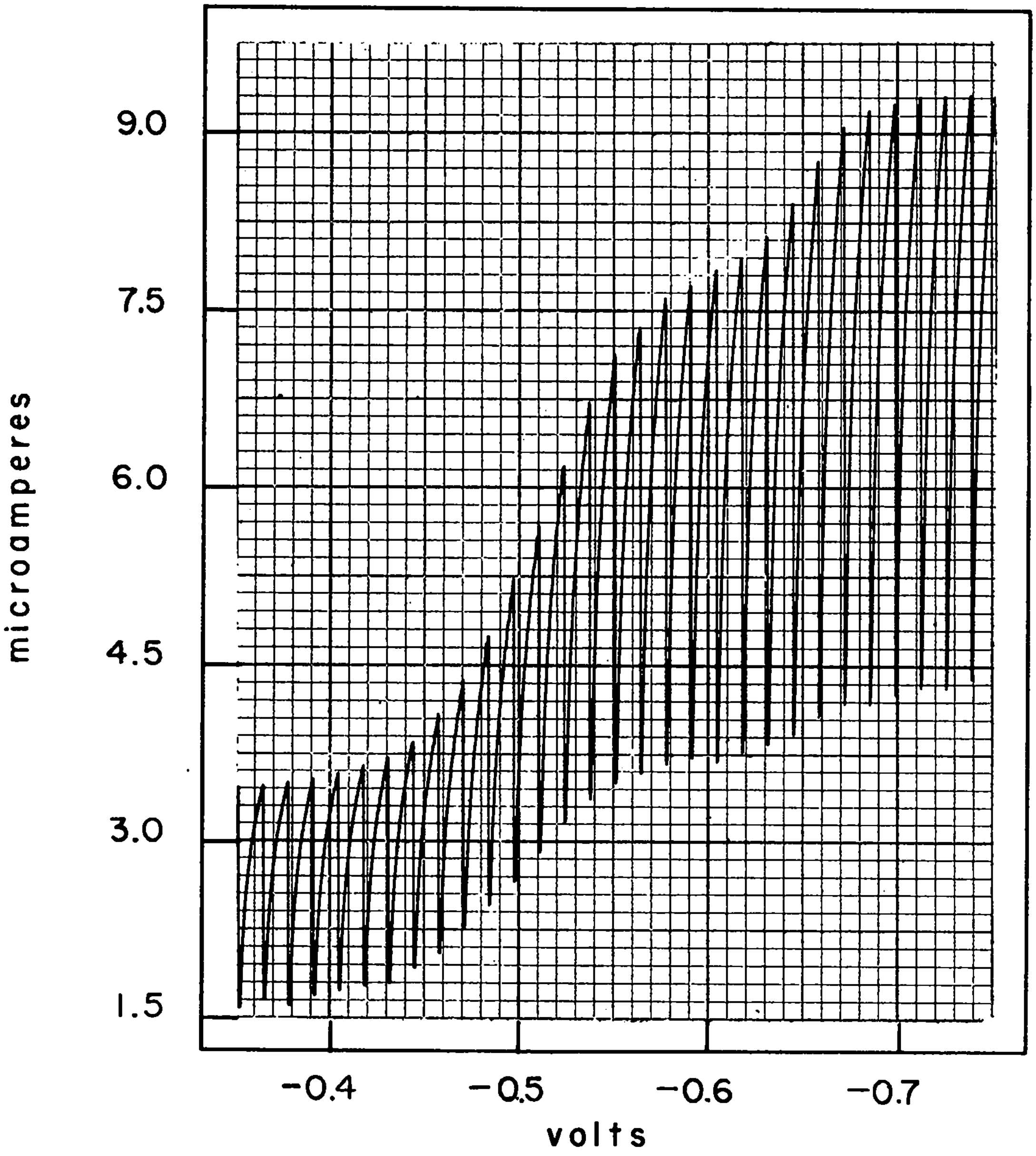

0.001 M Thallium
20 g/l Plutonium
2 M $NH_2OH \cdot HCl$

Figure 9. A polarogram of 0.001 M thallium in a solution of 0.084 M plutonium and 2 M hydroxylamine hydrochloride.

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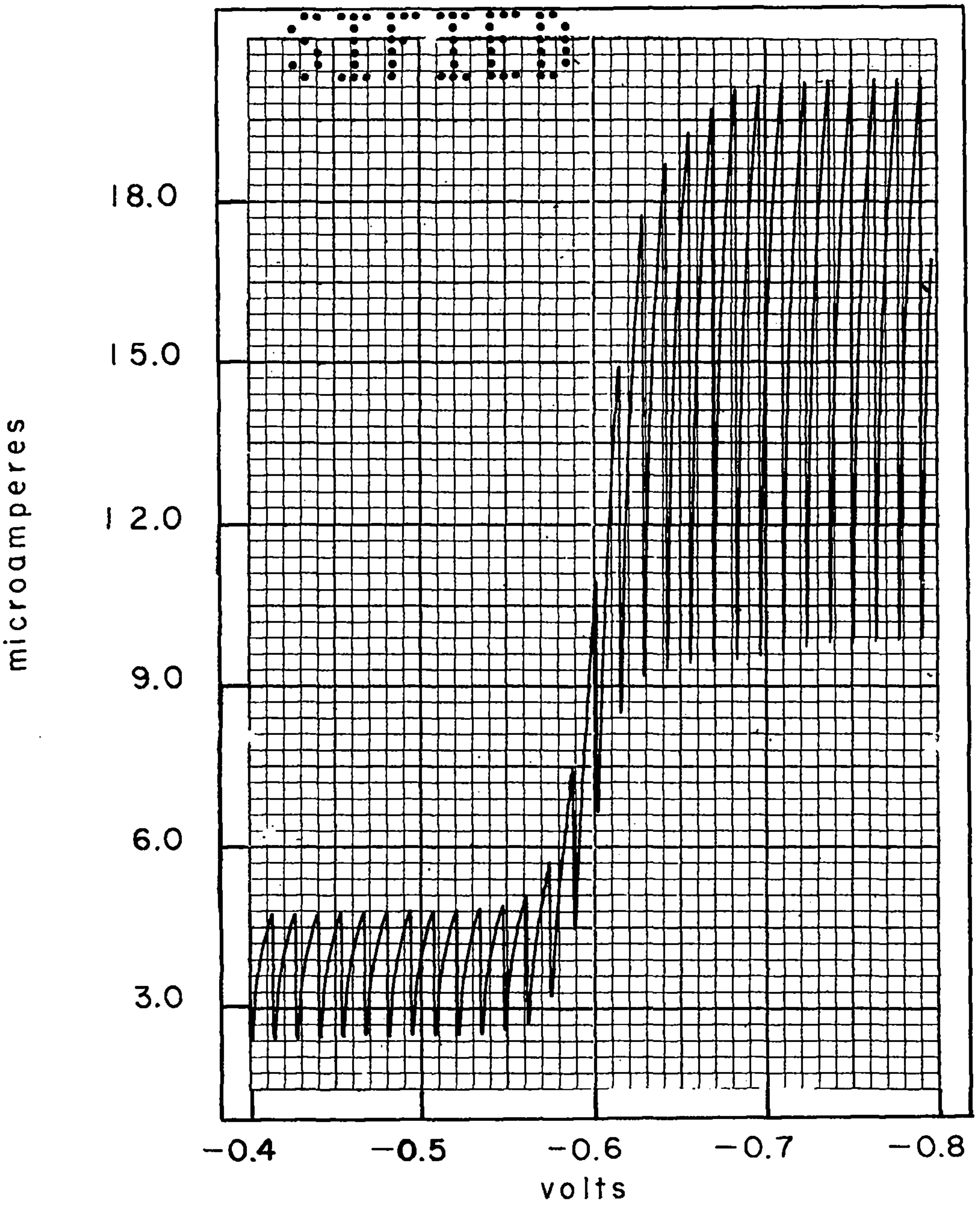

Figure 10. A polarogram of 0.001 M indium in a solution of 0.084 M plutonium and 2 M hydroxylamine hydrochloride.

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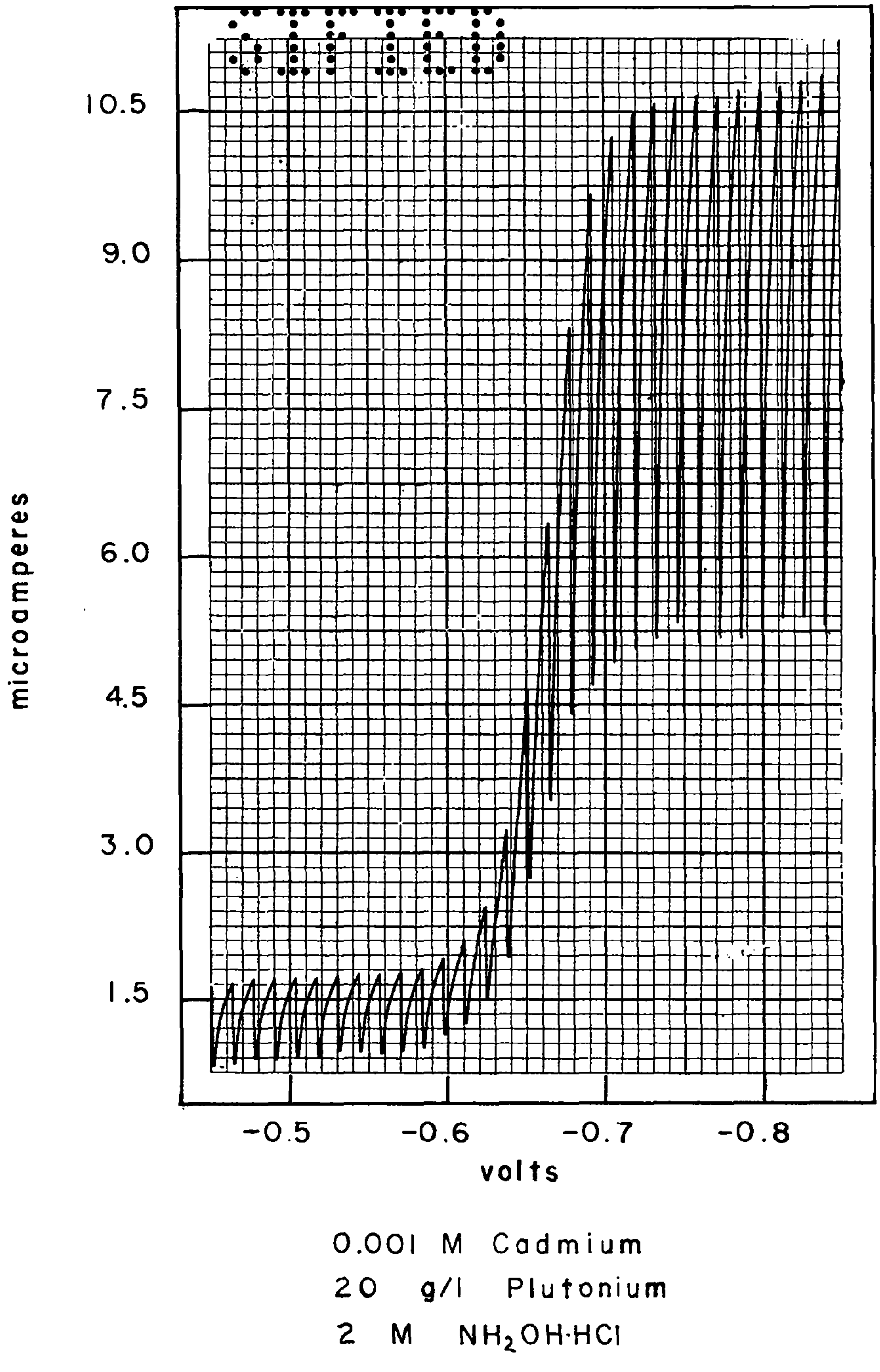

Figure 11. A polarogram of 0.001 M cadmium in a solution of 0.084 M plutonium and 2 M hydroxylamine hydrochloride.

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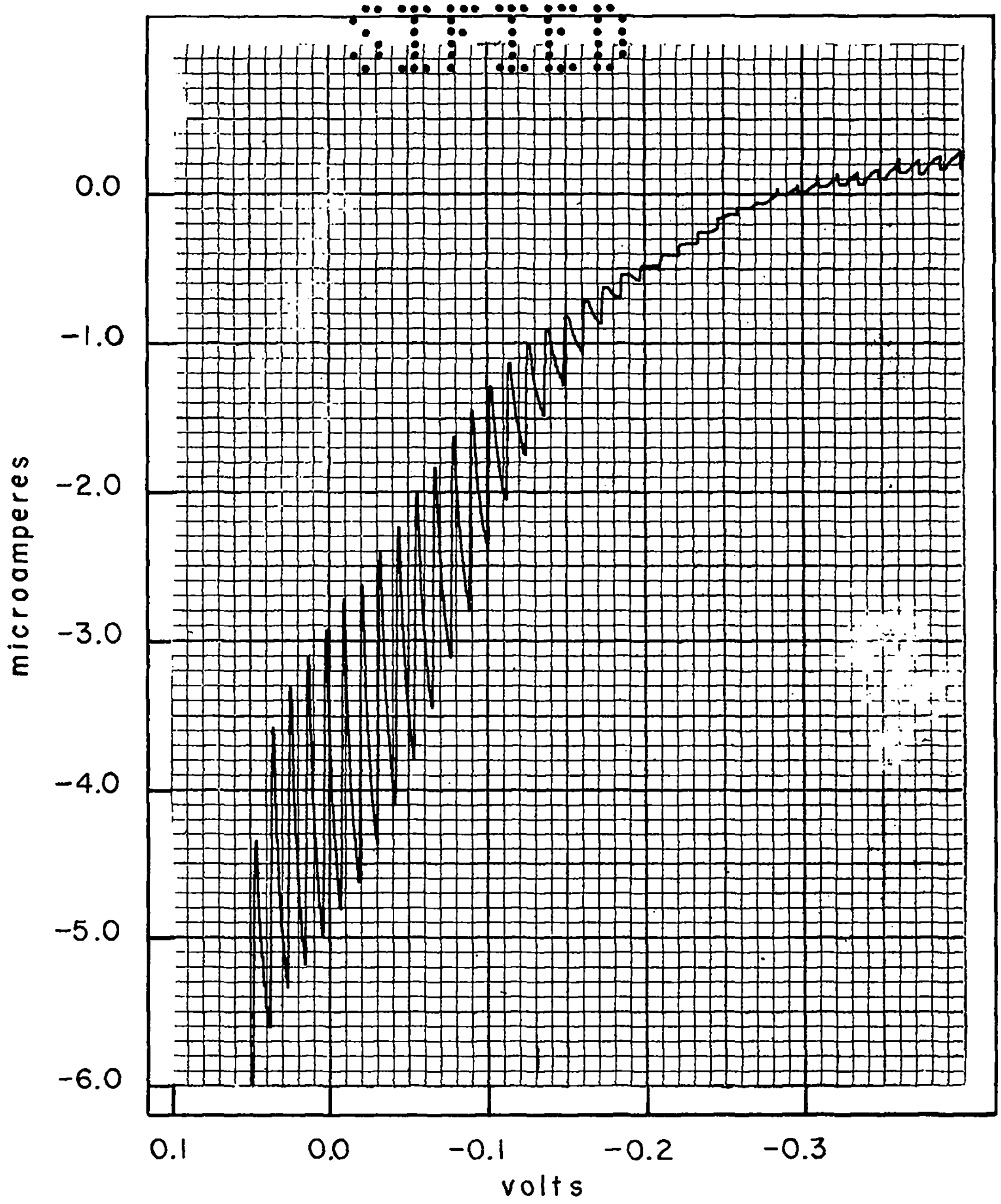

.001 M Molybdenum
1 M Zinc Chloride
1 M Tartaric acid

Figure 12. A polarogram of 0.001 M molybdenum in a solution of 1 M zinc chloride and 1 M tartaric acid.

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SUMMARY

The hydroxylamine hydrochloride procedure for the determination of uranium in plutonium may be used to determine bismuth, platinum, rhodium, copper, tin, lead, thallium, indium, and cadmium in plutonium. A chart of the half-wave potentials of these metals in hydroxylamine hydrochloride plutonium chloride solutions has been constructed (see Figure 13) and their lower limits of detection estimated.

Very few metal ions may be determined by the zinc and zinc amalgam procedure. Most metal ions are either removed from solution by the metallic zinc or the half-wave potential is beyond the range of the procedure. The zinc and zinc amalgam procedure permits the determination of vanadium, titanium, and perhaps molybdenum in plutonium without the interference of other metals.

By changing the conditions of the procedure, it may be possible to determine some of the metals for which negative results were obtained in this survey.

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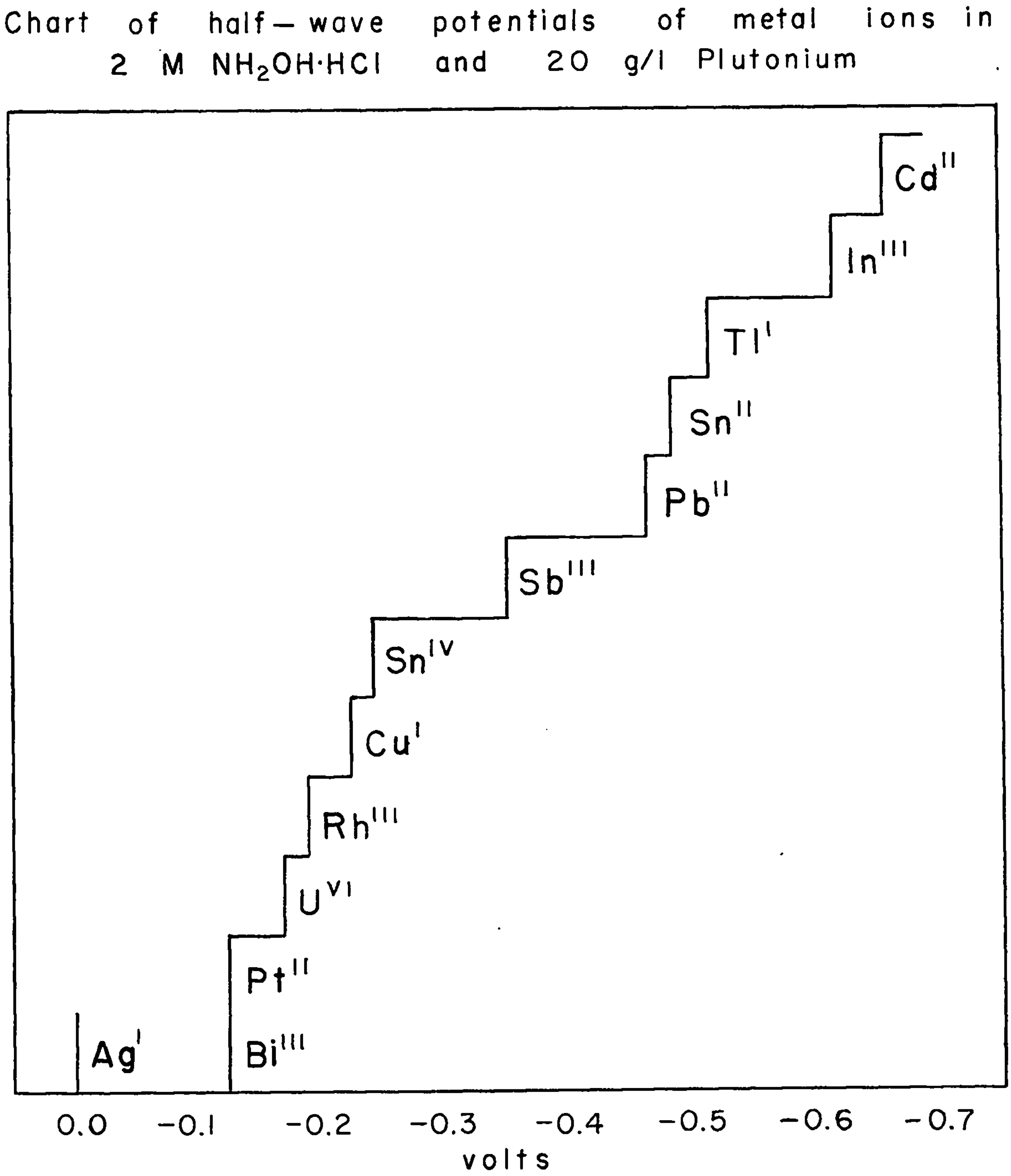

Figure 13. A chart of the half-wave potentials of the metal ions in a solution of 0.084 M plutonium and 2 M hydroxylamine hydrochloride.

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(1) Smith, M. E., LA-1249, June 1951.

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