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THE DETERMINATION OF MERCURY, COPPER, AND ZINC BY DERIVATIVE POLAROGRAPHY - APPLICATION TO SOLUTIONS OF URANYL SULFATE CONTAINING CORROSION PRODUCTS

R. G. Ball
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ABSTRACT

Methods are presented for the determination of mercury, copper, and zinc in solutions of uranyl sulfate by derivative polarography. Mercury and copper are determined without prior separation by recording their polarograms, utilizing ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), or sodium citrate-ammonium carbonate as the supporting electrolyte. In making a choice of medium, the governing factors are the iron concentration and the concentration ratios of the components to be determined. In general, in the absence of iron, an EDTA medium is satisfactory. For small amounts of iron, NTA can be used to advantage, but, for large amounts of iron, the citrate-carbonate medium is necessary. From 2 to 20 micrograms per ml of copper and mercury can be measured with a coefficient of variation of about 4 per cent. Zinc is separated prior to the polarographic measurement by complexing it with diethyldithiocarbamate, extracting the complex with chloroform and then back-extracting the zinc with dilute HCl. The polarogram is then recorded. The method is applicable to the determination of 2 to 20 micrograms of zinc per ml with a precision of 2 per cent.

The effect of foreign substances has been evaluated and their tolerance levels have also been established. The major interference in the determination of mercury and copper is that of iron(III); however, this interference can be eliminated through the proper selection of a supporting electrolyte. The polarographic measurement of zinc is relatively free of interferences due to the efficiency of the separation step.

THE DETERMINATION OF MERCURY, COPPER, AND ZINC BY DERIVATIVE POLAROGRAPHY

Application to Solutions of Uranyl Sulfate Containing Corrosion Products

R. G. Ball, D. L. Manning, and Oscar Menis

In making analyses of solutions of uranyl sulfate for minor constituents such as copper, mercury, and zinc in the presence of corrosion products derived from stainless steel such as iron, nickel, and chromium, a method was desired which would preclude, if possible, lengthy chemical separations so that it would be possible to adapt the method to the analysis of radioactive solutions by remotely controlled mechanical devices. Derivative polarography was applied to these analyses as this approach appeared to offer the needed simplicity and directness. The advantages of the derivative polarographic instrument have been pointed out by Kelley and Fisher.(4) Among these advantages are better resolution of polarograms for systems involving more than one reduction reaction with closely spaced half-wave potentials, applicability to irreversible systems, and to dilute solutions (10^{-5} M) wherein maxima are seldom encountered.

Various supporting electrolytes containing complexing agents were tested for the determination of copper and mercury in solutions of uranyl sulfate. Complexation of one or both of the constituents is necessary to separate the copper and mercury reduction waves; otherwise, they coalesce. During the course of this work it was established that good resolution could be obtained in ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), or a mixture of sodium citrate and ammonium carbonate. Others have reported on the polarographic determination of copper in an EDTA complexing

medium,[9,11] and Horton, Thomason, and Kelley[3] applied the EDTA medium to the determination of copper in reactor fuels by remote control. Lingane[8] has utilized citrate as a complexing medium for the determination of iron, and the use of carbonate to prevent the hydrolysis of uranium is well known.[13] A supporting electrolyte which contains carbonate has been utilized for the polarographic determination of uranium.[13] Supporting electrolytes of this type which aid in the separation of the diffusion current waves of copper, mercury, iron, and uranium should be useful for the determination of these ions in the presence of each other.

In applying the polarographic method to the determination of zinc in solutions of uranyl sulfate, however, a separation of zinc from uranium is necessary. Various extraction methods have been applied to the separation of zinc, the most important of which are extractions with dithiozone[2,10,12] and diethyldithiocarbamate.[1,10] The diethyldithiocarbamate extraction method is used, after which the zinc is back-extracted into 0.1 M HCl. The zinc is then measured polarographically by a method which is based on the reduction of zinc(II) to metallic zinc at a potential of approximately -1.0 volt vs the SCE.

The width at the half-peak height of the derivative curves for the reduction of ions reported herein was also applied to the indication of the reversibility of the electrode reactions. Zittel[14] has shown that the value of the half-wave width agrees experimentally with that predicted by theory and from this measurement the number of electrons involved in the reduction and the degree of reversibility of the reaction can be deduced.

REAGENTS

Ammonium Carbonate Solution, 20 per cent (w/v). Dissolve 50 g of reagent-grade ammonium carbonate, $(NH_4)_2CO_3$, in water and dilute to 250 ml.

Chloroform, reagent grade.

Copper Sulfate Solution, 5 mg of copper per ml. Dissolve 20 g of reagent-grade copper sulfate, $CuSO_4 \cdot 5H_2O$, in water and dilute to 1 liter. Standardize by the electrogravimetric procedure.(7)

Disodium Ethylenediaminetetraacetic Acid (EDTA) Solution, 0.5 M. Dissolve 20 g of reagent-grade EDTA according to the directions set forth by Horton, et al.(3)

Hydrochloric Acid Solution, 0.1 N. Add 8 ml of concentrated HCl (12 N) to water and dilute to 1 liter.

Mercuric Nitrate Solution, 2 mg of mercury per ml. Dissolve 2.000 g of triple distilled mercury in 50 ml of 50-per cent HNO_3 and dilute to 1 liter with water.

Nitrilotriacetic Acid (NTA) Solution, 0.5 M. Weigh 10 g of NTA into a 150-ml beaker. Cover with water and add solid Na_2CO_3 until the pH is 7. Adjust to pH 9 by the addition of pellets of NaOH. Stir until all NTA is dissolved and then dilute to 100 ml with water.

Sodium Carbonate Solution, saturated. Add reagent-grade Na_2CO_3 to water until a saturated solution is obtained.

Sodium Chloride Solution, 3 M. Dissolve 18 g of reagent-grade NaCl in water and dilute to 100 ml.

Sodium Citrate Solution, 1 M. Dissolve 90 g of reagent-grade sodium citrate, $Na_3C_6O_7 \cdot 5\ H_2O$, in water and dilute to 250 ml.

Sodium Diethyldithiocarbamate Solution (DDTC), 2 per cent (w/v). Dissolve 2 g of technical-grade DDTC in water and dilute to 100 ml. Allow the solution to stand overnight; then filter off the elemental sulfur that forms.

Zinc Nitrate Solution, 0.65 mg/ml of zinc. Dissolve 3 g of reagent-grade zinc nitrate, $Zn(NO_3)_2 \cdot 6\ H_2O$, in water and dilute to 1 liter. Standardize volumetrically by titration with potassium ferrocyanide, using ferric chloride as the indicator.(6)

In the preparation of all reagents, distilled and deionized water and reagent-grade chemicals were used unless otherwise stated.

APPARATUS

Polarograph, Derivative with Diode Filter, ORNL Model Q-1673, with dropping mercury and saturated calomel (SCE) electrodes.

RECOMMENDED PROCEDURE

Mercury: Iron Absent. Transfer an aliquot of sample that contains from 25 to 250 μg of mercury into a 10-ml volumetric flask. Add 5 ml of 0.5 M EDTA reagent and 3 ml of 3 M NaCl solution. Dilute to volume with water. Transfer the sample to a polarographic cell and deaerate with nitrogen. Immerse the electrodes in the sample and set the polarograph selector switch to the derivative position. Discharge the diode filter by depressing the discharge button for approximately 30 seconds. Record the polarogram of the sample by scanning from -0.1 to -0.3 v vs the SCE at a scan rate of 0.05 v

per full scale. Record the polarogram of a reagent blank in order to measure the residual current. Measure the diffusion current of the mercury reduction wave at the half-wave potential, -0.2 v vs the SCE, and subtract the residual current of the medium. Determine mercury in the sample by the standard-addition or standard-curve technique.

Mercury: Iron Present. Transfer an aliquot of sample that contains from 20 to 200 μg of mercury and not more than 3 mg of iron into a 10-ml volumetric flask. Add 3 ml of 20-per cent ammonium carbonate solution and 3 ml of 1 M sodium citrate solution. Dilute to volume with water. Transfer the sample to a polarographic cell and deaerate the solution. Immerse the electrodes in the solution and record the polarogram according to the procedure outlined above for mercury in an EDTA medium. Scan from 0 to -0.2 v vs the SCE at a scan rate of 0.05 volts per inch of chart travel. Record the polarogram of a reagent blank consisting of ammonium carbonate and sodium citrate in order to determine the residual current. Determine mercury by either a standard-curve or a standard-addition technique.

Copper. Transfer an aliquot of sample that contains from 0.02 to 1 mg of copper to a 10-ml volumetric flask. Add 5 ml of 0.5 M EDTA and dilute to volume with water. Transfer the solution to a polarographic cell and deaerate the solution. Then immerse the electrodes in the sample solution and record a derivative polarogram, scanning from -0.3 to -0.17 v vs the SCE at a scan rate of 0.1 v per inch of chart travel with an instrument sensitivity of 1 to 10 μa per full scale. Measure the diffusion current of the copper reduction wave at the half-wave potential of -0.5 v vs the SCE. Determine copper in the sample by the standard-addition or standard-curve technique.

Zinc. Transfer an aliquot of sample that contains 25 to 200 μg of zinc to a 125-ml separatory funnel. Add saturated Na_2CO_3 solution until the sample is basic to litmus. Add 2 ml of 2-per cent diethyldithiocarbamate (DDTC) solution and extract the zinc-DDTC complex into 10 ml of chloroform by shaking for 3 to 4 minutes. Remove the zinc from the chloroform phase by extracting twice with two, 5-ml portions of 0.1 N HCl. Transfer the two HCl solutions directly to a polarographic cell. Deaerate with nitrogen and immerse the electrodes in the solution. Record the polarogram by scanning from -0.7 to -1.1 v vs the SCE at a scan rate of 0.1 v per inch of chart travel and an instrument sensitivity of 2 to 10 μa per full scale. Measure the diffusion current of the zinc reduction wave which occurs at a half-wave potential of -1.0 v vs the SCE. Determine the zinc in the sample by the standard-addition or standard-curve technique.

EXPERIMENTAL

Mercury and copper in uranyl sulfate solution were measured polarographically in three different supporting electrolytes, namely, ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and a medium composed of sodium citrate and ammonium carbonate. Each medium exhibits some advantages over the other two, depending on the composition of the sample and will be discussed separately.

EDTA Medium. The determination of mercury in 0.25 M EDTA, 0.9 M NaCl medium is based on the reduction wave of the divalent ion to the metallic state at a half-wave potential of -0.2 v vs the SCE. A typical polarogram of the reduction wave for mercury is presented in Figure 1. This wave

coincides with the oxidation wave of mercury from the dropping electrode and, consequently, the residual current of the oxidation reaction must be subtracted from the total current in order to arrive at the diffusion current which is due to the reduction process.

The diffusion current of mercury was recorded for standard solutions in order to establish the sensitivity and precision of the method. These data are shown in Table I. A factor of 196 μg of mercury per μa was obtained over a concentration range of 25 to 250 μg of mercury in a volume of 10 ml. The coefficient of variation is of the order of 3 per cent. A standard curve for the measurement of mercury in this medium is shown in Figure 2.

Table I

Calibration Data for the Determination of Mercury by Derivative Polarography

Conditions:

Volume, ml	10
Medium: EDTA, molarity	0.25
NaCl, molarity	0.9
$E_{1/2}$, volts vs the SCE	- 0.2

Mercury μg	i_D, μa	Factor μg/μa
24.8	0.130	191
24.8	.130	191
74.4	.397	187
74.4	.380	196
99.2	.500	198
99.2	.480	206
124	.632	196
124	.630	197
248	1.23	202

X = 196 μg/μa

Standard deviation, S = 6.

Coefficient of variation, V = 3%

For the measurement of copper, the Cu(II)$\longrightarrow$ Cu^0 reduction wave was used which exhibits a half-wave potential of -0.5 volts vs the SCE. Polarograms of copper are presented in Figure 1 and the data which illustrates the reliability of the polarographic method are shown in Table II. It is indicated from the data that from 20 to 200 micrograms can be ascertained with a coefficient of variation of 3 per cent. This is in agreement with the findings of Horton, et al.[3] The sensitivity of the method is of the order of 60 μg of copper per μa.

Table II

Calibration Data for the Determination of Copper by Derivative Polarography

Conditions:

Volume, ml	10
Medium, EDTA in Na_2CO_3 and NaOH, molarity	0.25
$E_{1/2}$, volts vs the SCE	- 0.5

Copper, μg	i_D, μa	Factor, μg/μa
19.7*	0.333	59.2
24.7	.400	61.8
39.4*	.665	59.2
49.3	.820	60.1
59.2*	.920	64.3
98.6	1.65	59.8
98.6*	1.60	61.6
147.9	2.50	59.2
172.6	2.90	59.5
	Average =	60.5
		S = 2.
		V = 3%

* UO_2SO_4 present.

In the determination of copper, the EDTA medium has one advantage over the other two studied, namely, it is the only one in which moderate amounts of iron, up to 50 μg per ml, do not interfere. In the determination of mercury, the disadvantage of the EDTA medium is that iron must be absent since, in this medium, the reduction waves of iron and mercury coincide. For solutions which do not contain iron, both mercury and copper can be measured simultaneously without a prior separation.

NTA Medium. In an effort to overcome the serious interference of iron(III) on the polarographic determination of mercury as was encountered in the EDTA supporting electrolyte, the applicability of a medium composed of the closely related nitrilotriacetic acid was investigated. A typical polarogram of mercury, copper, iron, and uranyl sulfate in a medium which was 0.25 M NTA and 0.9 M NaCl is shown in Figure 5. The mercury reduction wave occurs at a half-wave potential of -0.1 v vs the SCE. The iron reduction wave is shifted to -0.22 v and the $Cu(II) \rightarrow Cu^{o}$ reduction wave occurs at -0.4 v. The separation of the iron wave from the mercury wave, even by only 0.1 v, is enough so that more iron can be tolerated than in the EDTA medium in which the two waves coalesce. Correspondingly, it was found that as much as 50 μg of iron per ml could be present without affecting the precision of the determination of mercury. This demonstrated a definite advantage of NTA over the EDTA medium for the estimation of mercury in the presence of traces of iron.

With regard to the polarographic determination of copper, however, it was established that the use of NTA is less desirable than EDTA as a supporting electrolyte because the interference of iron on the diffusion current

of copper is more pronounced in the NTA medium. The maximum amount of iron that can tolerated in measuring 100 micrograms of copper in EDTA and NTA is 500 and 100 micrograms, respectively. Calibration curves for copper are shown in Figure 6.

Citrate-Carbonate Medium. The citrate-carbonate system was investigated in order to eliminate iron interference in the determination of mercury and copper. The polarography of iron(III) in a citrate medium has been studied systematically by Lingane.[8] The reduction of the ferric complex to the ferrous state produces a well defined wave at approximately -0.5 volts vs the SCE. This suggested the possibility of eliminating the interference of iron in the polarography of mercury and copper since these metals are reduced at potentials which are less negative than -0.5 volts. In order to shift the uranium wave and prevent hydrolysis, a supporting electrolyte which consisted of a mixture of sodium citrate and ammonium carbonate was used.

A polarogram of a solution containing uranium, mercury, copper, and iron in a supporting electrolyte of 0.3 M sodium citrate and 0.6 M ammonium carbonate is shown in Figure 3. The mercury wave occurs at a half-wave potential of -0.06 v vs the SCE and the iron wave is shifted to -0.55 v. For this reason even large quantities of iron (up to 3 mg) do not interfere in the measurement of the mercury. Copper exhibits two reduction waves, Cu(II)-Cu(I) at -0.21 v vs SCE and Cu(I)-Cu(0) at -0.41 v. Uranyl ion, UO_2(II), being complexed by carbonate, is reduced at a half-wave potential of approximately -0.9 v vs the SCE. The advantage of the citrate-carbonate medium is that mercury can be determined in the presence of large quantities of iron. It is somewhat less desirable for the determination of copper since the

reduction waves for copper are crowded between those of mercury and iron. The polarograms can, however, be used for the determination of copper if necessary; otherwise, it is recommended that the EDTA supporting electrolyte be substituted for the determination of this element.

To establish the sensitivity and the precision for the determination of mercury in the citrate-carbonate medium, standard solutions of mercury were reduced at the DME. These data are shown in Table III and are graphically presented in Figure 4. Within a concentration range of 25 to 150 μg of mercury in a volume of 10 ml, a coefficient of variation of 3 per cent was achieved with a sensitivity of 152 μg per μa.

Table III

Calibration Data for the Determination of Mercury in a Citrate-Carbonate Medium

Conditions:

Volume, ml		10
Medium:	Sodium citrate, molarity	0.3
	Ammonium carbonate, molarity	0.6
$E_{1/2}$, volts vs the SCE		- 0.06

Mercury, μg	i_D, μa	Factor, μg/μa
24.8	0.165	150
49.6	.345	144
74.4	.480	155
99.2	.652	152
124	.815	152
149	.950	157
	Average =	152

S = 5
V = 3%

Determination of Zinc. The polarographic measurements of zinc in the presence of uranium is largely dependent upon the suppression of the diffusion current of uranium, which is obtained first, and then the measurement of the diffusion current of the zinc which occurs at a more negative potential. Due to the high concentrations of uranium encountered in this work, it was not possible to resolve the large diffusion current with this instrument. Consequently, it became necessary to remove the zinc prior to carrying out the polarographic measurement. This was accomplished by an extraction with diethyldithiocarbamate (DDTC) into chloroform, following which the zinc was then extracted from the DDTC into 0.1 N HCl. The polarogram was recorded directly in the HCl. Calibration data for this measurement are shown in Table IV.

Table IV

Calibration Data for the Determination of Zinc by Derivative Polarography Following Extraction with Diethyldithiocarbamate

Conditions:

Medium, HCl, N	0.1
Sample volume, ml	10
$E_{1/2}$, volts vs the SCE	- 1.05

Zinc, µg	i_D, µa	Factor, µg/µa
20.6*	0.330	62.4
32.5	.510	63.7
32.5	.510	63.7
32.5	.520	62.5
65.0	1.03	63.1
103	1.66	62.0
130	2.00	65.0
195	3.04	64.1

Average = 63.3

S = 1
V = 2%

* UO_2SO_4 present.

Interferences. A study was made of the effect of some of the typical interfering substances in the determination of Hg, Cu, and Zn in uranyl sulfate solution. These substances are introduced inadvertently by the corrosion of stainless steel. The ions studied included Fe(III), Ni(II), Cr(VI), Mo(VI), Ti(IV), Sn(IV), and U(VI). The results of these studies are shown in Table V.

Table V

Interferences in the Determination of Mercury, Copper, and Zinc by Derivative Polarography

Conditions:
Sample taken: 1 ml of uranyl sulfate containing 100 μg Hg; 100 μg Cu; 100 μg Zn; and 44 mg U(VI)
Volume: 10 ml
Media: Hg; 0.25 M EDTA, 0.9 M NaCl
Cu; 0.25 M EDTA
Zn; 0.1 N HCl

Interference	Tolerance Limit,* Weight Ratio		
	Metal/Mercury	Metal/Copper	Metal/Zinc**
Fe(III)	0.1	5	10
	5(a)	1(a)	-
	30(b)	-	-
Ni(II)	20	20	10
Cr(VI)	1	1	10
Mo(VI)	20	5	10
Ti(IV)	1	1	5
Sn(IV)	5	10	10
U(VI)	100,000	100,000	44,000

* The maximum quantity of interfering substance that can be present without causing deviations greater than the precision of the method.
** The zinc was separated prior to the polarographic measurement by a diethyldithiocarbamate extraction.
(a) 0.25 M NTA, 0.9 M NaCl medium.
(b) 0.3 M sodium citrate, 0.6 M ammonium carbonate medium.

The major interference in the determination of mercury is that of Fe(III). This interference is virtually eliminated by use of a citrate-carbonate medium. As much as 115 moles of Fe per mole of Hg can be tolerated without causing deviations greater than the precision of the method. The only other serious interferences found were Cr(VI) and Ti(IV). As much as 4 moles of both Ti and Cr(VI) per mole of Hg can be tolerated without interference.

In the determination of copper, the major interferences are again Cr(VI) and Ti(IV). The maximum tolerance levels are 1.2 moles of Cr and 1.4 moles of Ti per mole of copper in both the NTA and EDTA supporting electrolytes. Iron(III) interferes to a greater extent in the NTA medium, but when the EDTA supporting electrolyte is substituted, the tolerance level is of the order of 6 moles of iron per mole of copper. Since the zinc is separated by a diethyldithiocarbamate extraction, none of the elements studied interfere seriously in the determination of this constituent. Iron extracts to some extent if more than one mg is present in the test portion, whereas the tolerance limit for titanium is 0.5 mg. Uranium(VI) accompanies the zinc to some extent when more than 44 mg is present in the aqueous phase from which the zinc is removed. However, in the determination of zinc in impure solutions of uranyl sulfate, the contaminants are generally below the maximum tolerance limits, and do not interfere seriously with the polarographic measurement.

APPLICATION

To ascertain the applicability of the method to actual sample types, mercury, copper and zinc were determined in a solution of uranyl sulfate which contained a known amount of these constituents and, in addition, approximately 100 μg/ml of iron, nickel and chromium. These data are tabulated in Table VI.

Table VI

Determination of Zinc, Copper, and Mercury in Solutions of Uranyl Sulfate

Composition:

Constituent	Conc., mg/ml
U(VI)	44.0
Cu(II)	0.10
Hg(II)	0.10
Zn(II)	0.10

Element	Uranyl Sulfate Solution Taken, ml	Supporting Electrolyte	Element, μg Present	Found	Per Cent Error
Cu(II)*	0.2	EDTA	20	19.7	- 1
	0.4		40	40	0
	0.6		60	56	- 5
	1.0		100	95.0	- 5
Hg(II)*	0.2	Citrate-Carbonate	20	19.6	- 1
	0.4		40	40.8	+ 3
	0.6		60	60.5	+ 2
	1.0		100	102	+ 3
Hg(II)**	0.2	EDTA	20	22.2	+ 11
	0.4		40	41.5	+ 4
	0.6		60	60.8	+ 1
	1.0		100	102	+ 2
Zn(II)***	0.2	HCl	20	21	+ 2
	0.4		40	40	0
	0.6		60	64	+ 6
	1.0		100	106	+ 6

* Iron present. ** Iron absent. *** After separation of diethyldithiocarbamate complex.

Reversibility of the Electrode Reactions

For reversible reactions in derivative polarography, the number of electrons involved can be calculated from the following relationship:[14]

$$n = \frac{90.7}{\Delta E}$$

where ΔE at one-half of the peak height is expressed in millivolts and n is the number of electrons transferred. It is possible, therefore, to calculate n from the derivative polarogram or, knowing n, to ascertain the degree of reversibility by comparing the theoretical ΔE with the ΔE which is established experimentally.

The half-peak widths of the derivative polarograms were measured and compared with theoretical values to establish the degree of reversibility or irreversibility of the substances reported herein. These data are presented in Table VII. Since the derivative curves which were recorded during the course of this work tend to show slight asymmetry to the right of the center line of the curve, a measurement was made from the left side of the curve to a vertical line dropped through the center of the peak. This value multiplied by two gives better agreement with theoretical values since the latter are based on symmetrical polarograms. The experimental values for copper in EDTA and NTA media showed good agreement with theoretical values and indicated a reversible two-electron reduction which is in agreement with previous observations.[11] Similarly, zinc and ferric ions were found to be reversibly reduced as expected.[6,8] The two copper waves occurring in a citrate-carbonate medium were indicative of reversible one-electron reductions. Because the Hg(II) wave merges with the anodic dissolution wave of mercury from the dropping electrode, it was not possible to establish the

reversibility of this reaction from the derivative polarogram with any degree of certainty.

Table VII

Reversible Electrode Reactions

Electrode Reaction	Medium	$E_{1/2}$, v vs SCE	Half-Wave Width, mv Found	Half-Wave Width, mv Theoretical
$Cu(II) \rightarrow Cu^{o}$	EDTA, 0.25 M	- 0.48	50	45.4
$Cu(II) \rightarrow Cu^{o}$	NTA, 0.25 M	- .40	56	45.4
$Cu(I) \rightarrow Cu^{o}$	Citrate-Carbonate	- .41	90	90.7
$Cu(II) \rightarrow Cu(I)$	Citrate-Carbonate	- .21	86	90.7
$Zn(II) \rightarrow Zn^{o}$	HCl, 0.1 N	- 1.05	60	45.4
$Fe(III) \rightarrow Fe(II)$	Citrate-Carbonate	- .55	104	90.7

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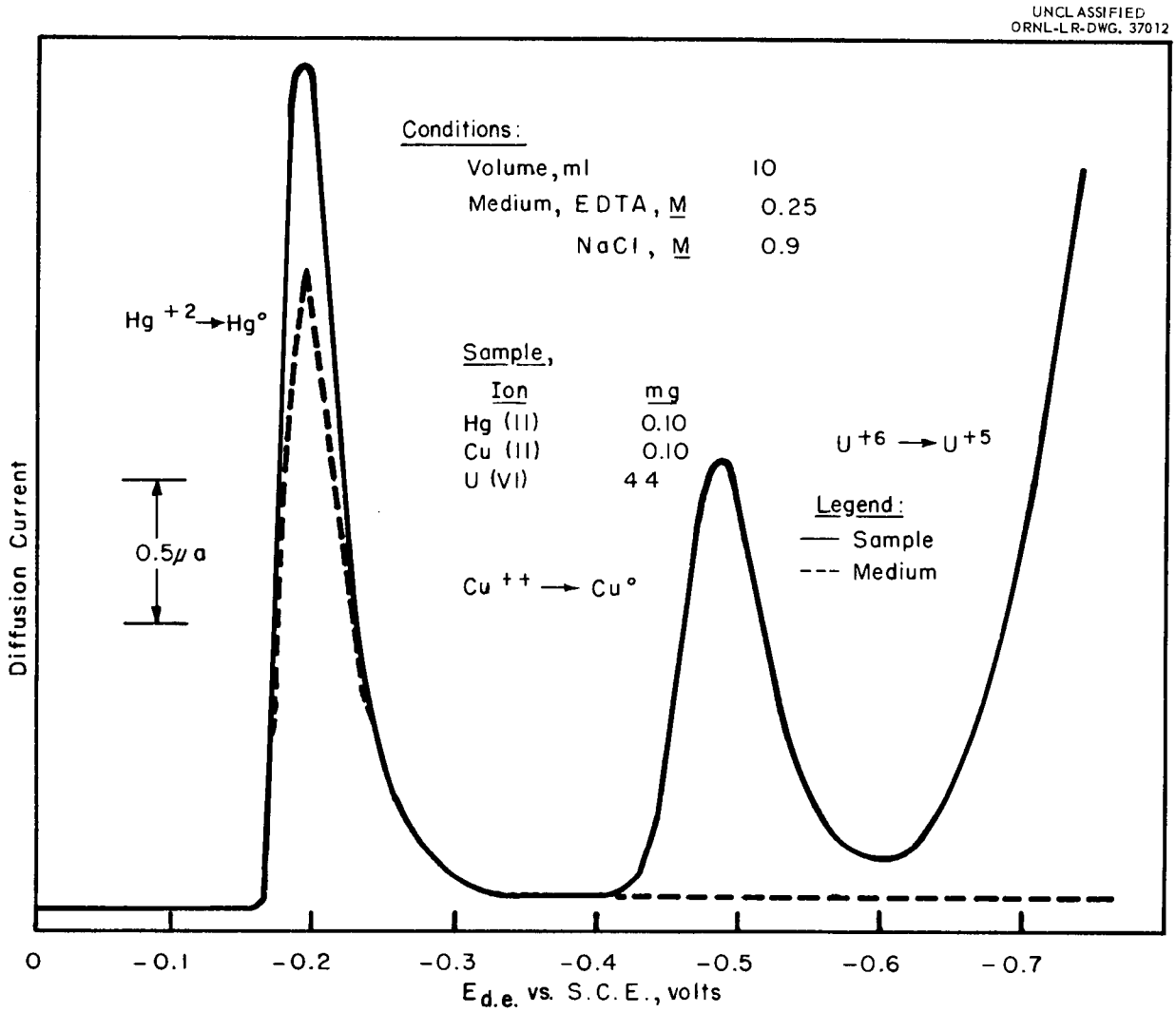

FIGURE 1. POLAROGRAMS FROM EDTA MEDIUM

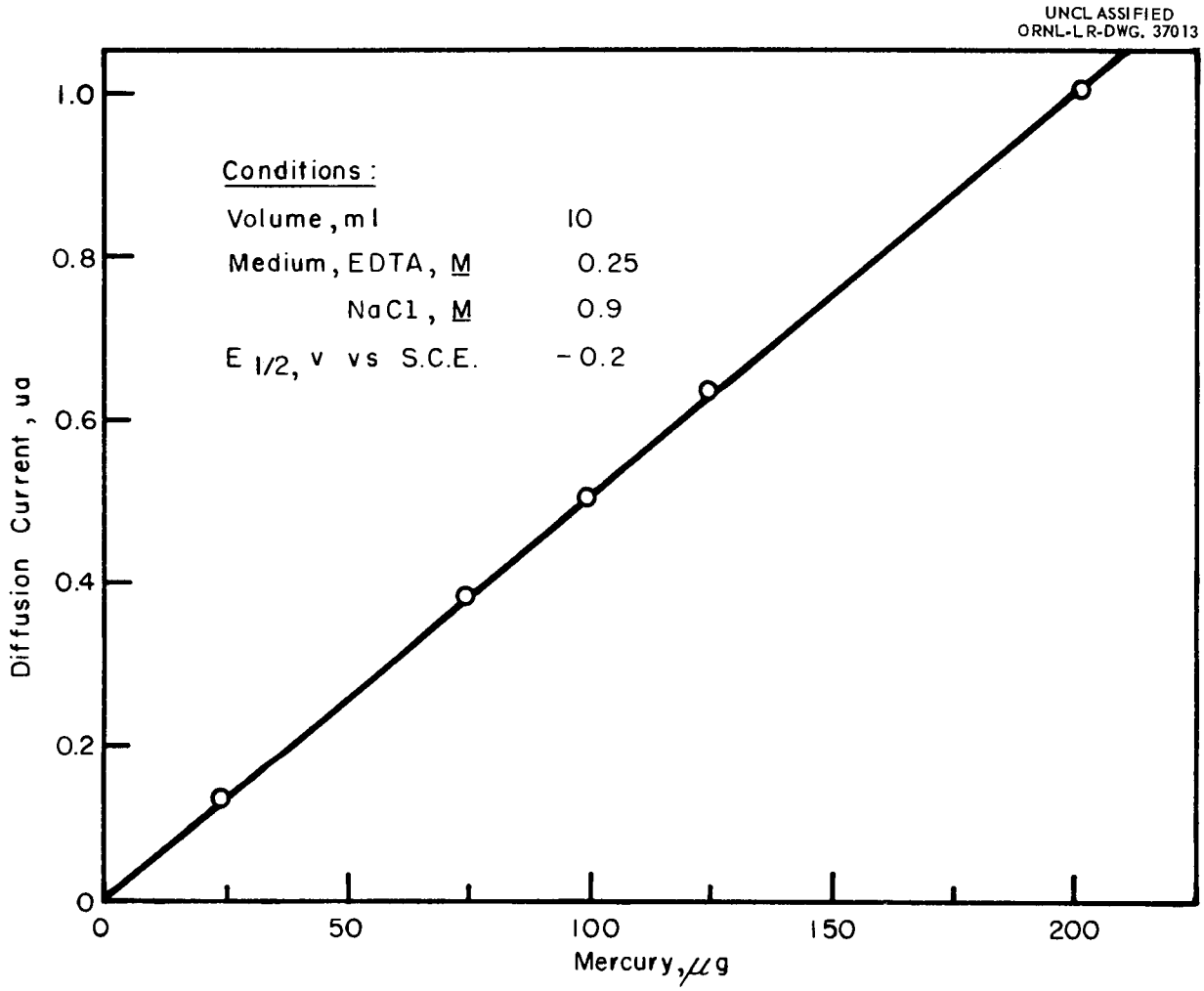

FIGURE 2. CALIBRATION CURVE FOR THE DIFFUSION CURRENT OF MERCURY IN EDTA

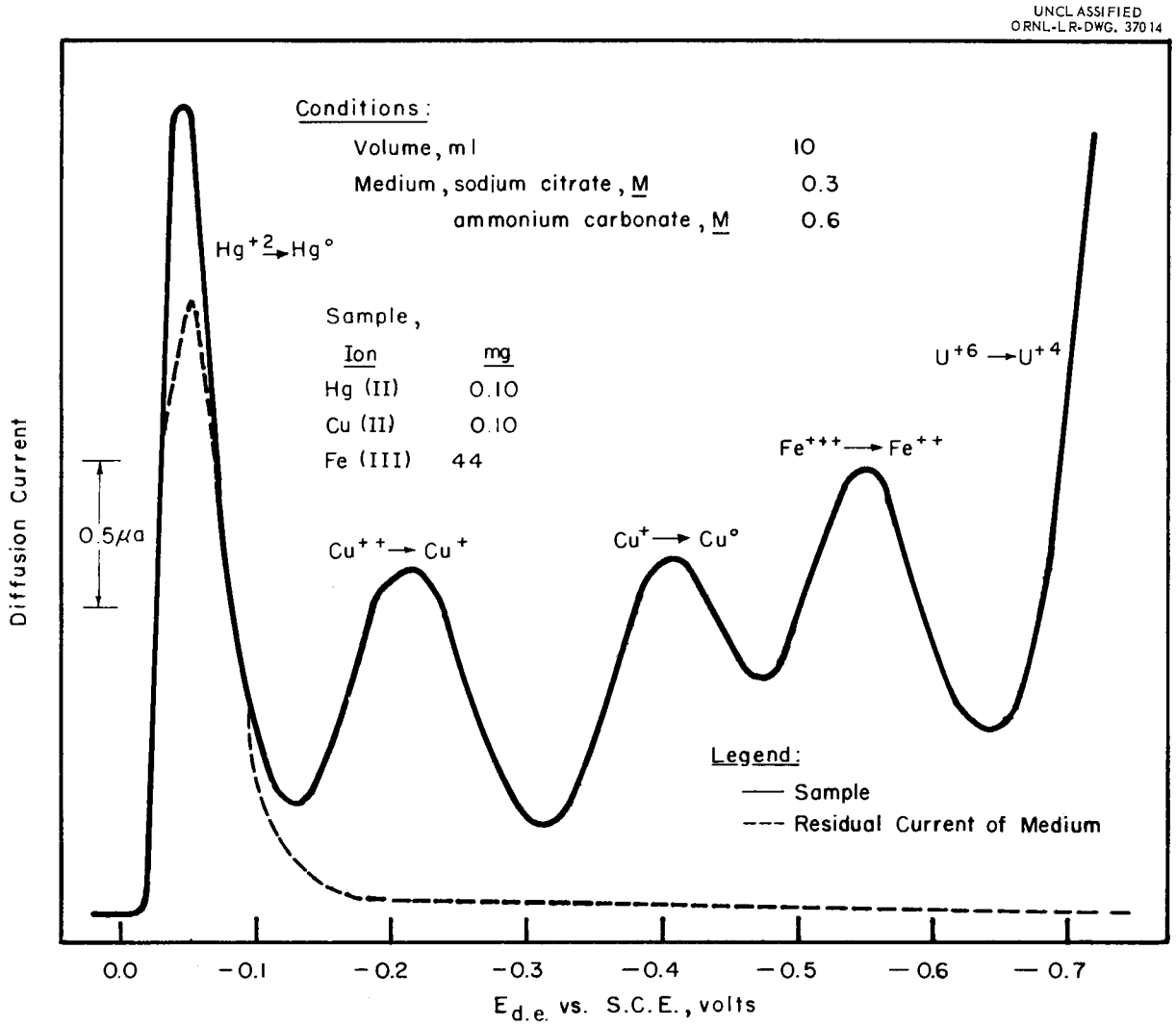

FIGURE 3. POLAROGRAMS: FROM CITRATE - CARBONATE MEDIUM

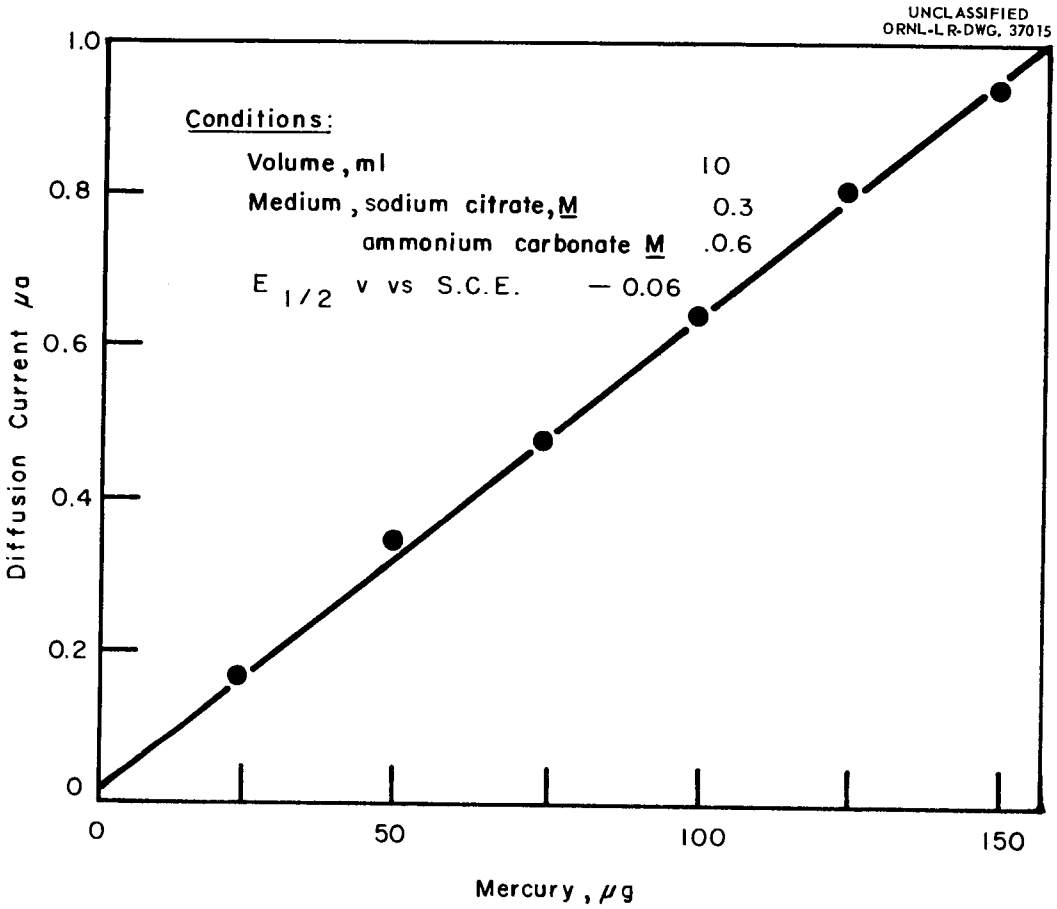

FIGURE 4 CALIBRATION CURVE FOR THE DIFFUSION CURRENT OF MERCURY IN CITRATE–CARBONATE MEDIUM

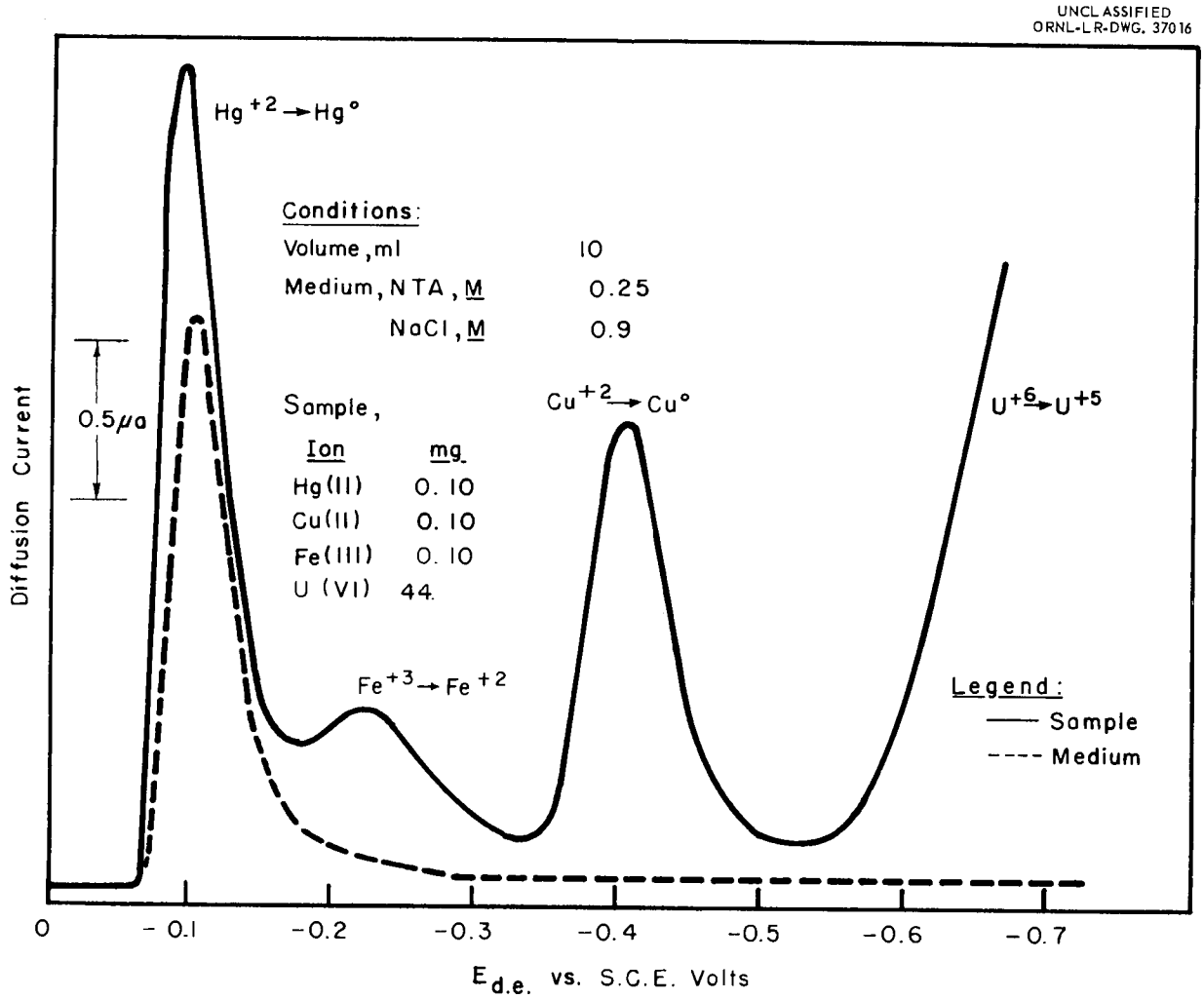

FIGURE 5. POLAROGRAMS: FROM NTA MEDIUM

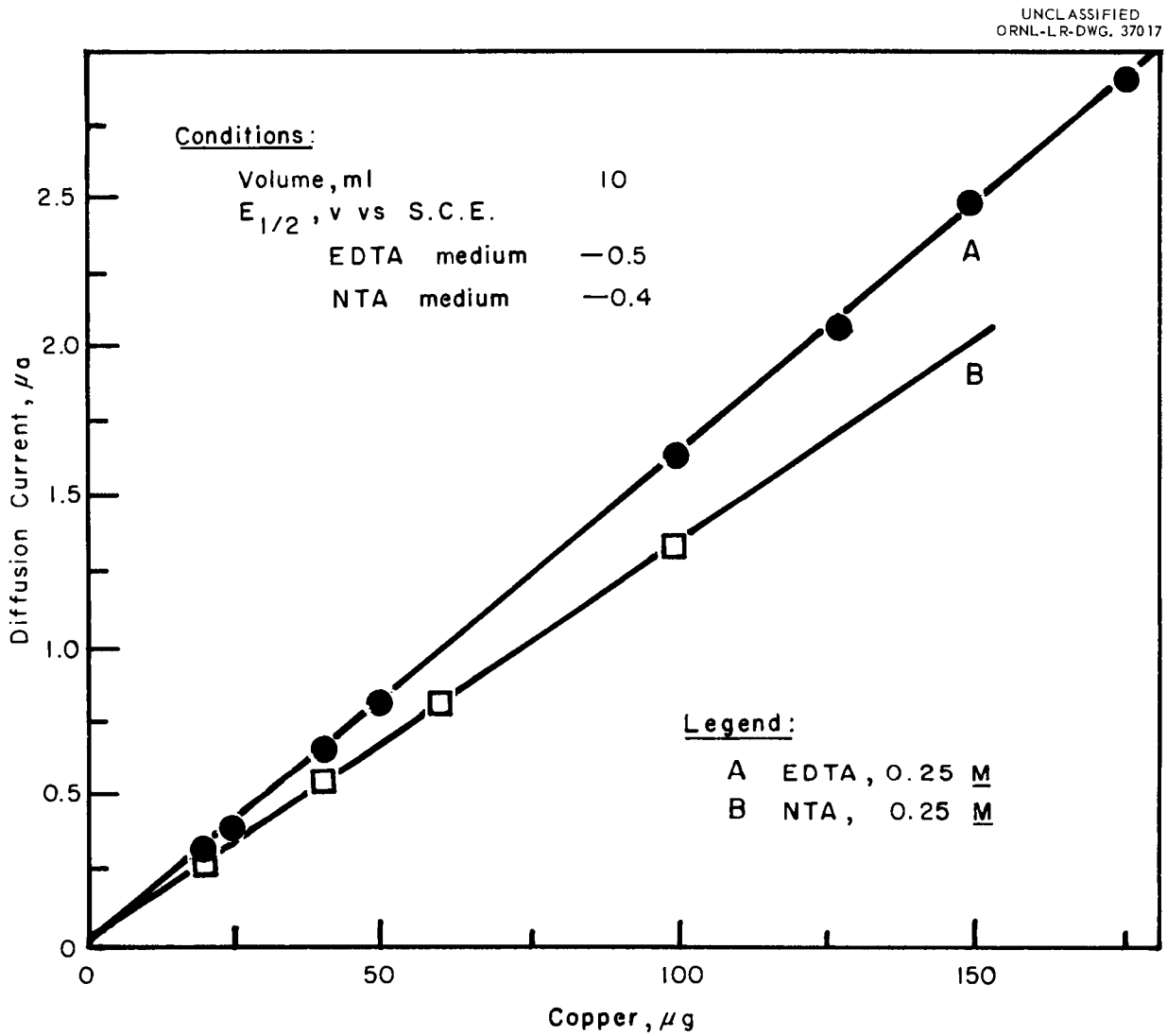

FIGURE 6. CALIBRATION CURVE FOR COPPER IN EDTA AND NTA MEDIA

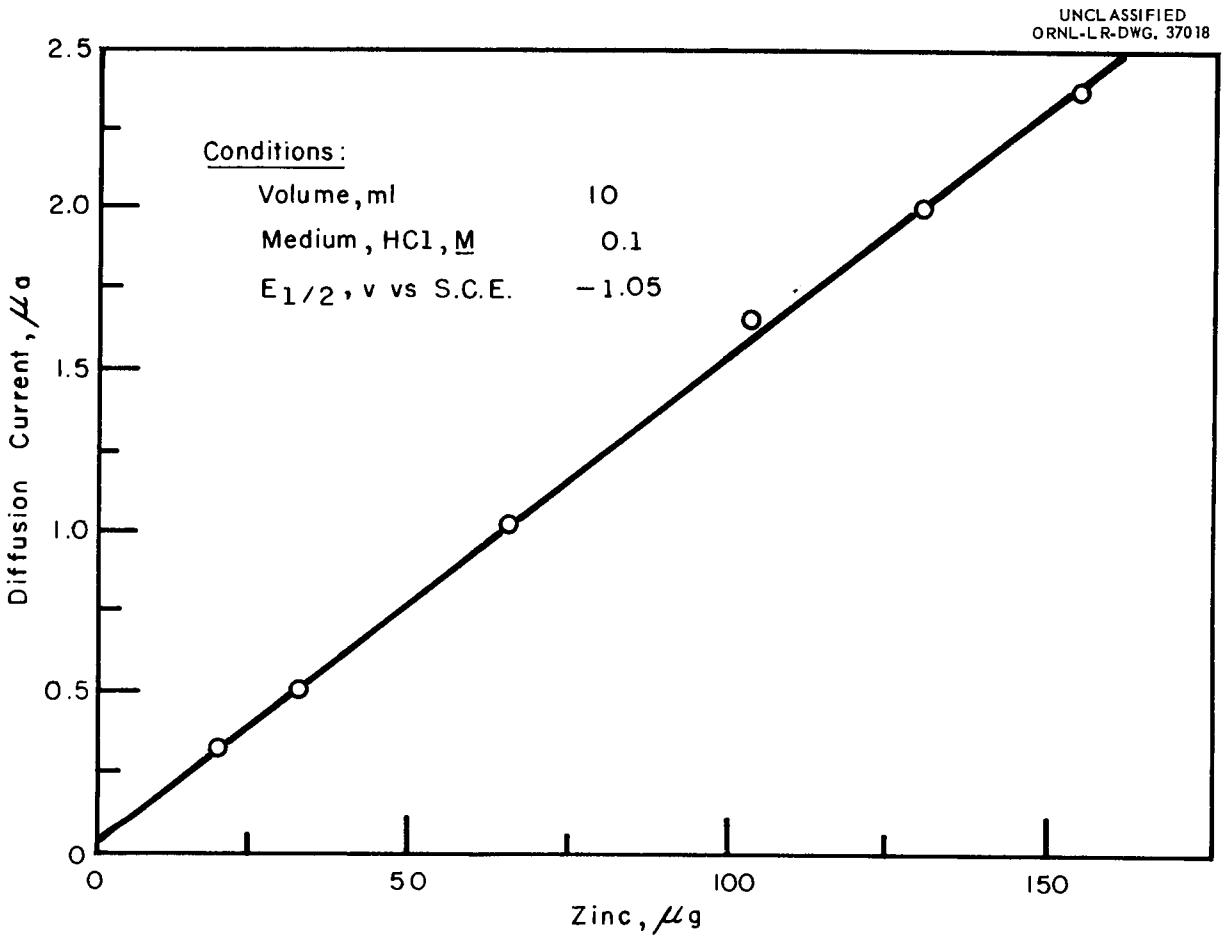

FIGURE 7. CALIBRATION CURVE FOR ZINC

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