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POLAROGRAPHIC DETERMINATION OF URANIUM IN THE PRESENCE OF MOLYBDENUM

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ABSTRACT

A polarographic method was developed for the determination of small concentrations of uranium in nitric acid solutions that contain high concentrations of aluminum. There is no interference from molybdenum(VI), mercury(II), or iron(III) and the precision of the analysis is 2.5 per cent.

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POLAROGRAPHIC DETERMINATION OF URANIUM IN THE PRESENCE OF MOLYBDENUM

INTRODUCTION

A method was needed for the determination of uranium in highly radioactive solutions of uranium, molybdenum, aluminum, mercury, and fission products in nitric acid. The uranium concentration in the solutions was about 0.01M and was to be determined within five per cent.

The high radioactivity together with the low uranium concentration eliminated conventional colorimetric and volumetric procedures. Fluorophotometric analysis offered extreme sensitivity; however, the precision of this method is only about 20 per cent. Polarographic methods would be well suited for the analysis if sufficient sensitivity could be provided and if the interference of the molybdenum in the sample could be overcome.

It appeared that the required sensitivity might be achieved with the high-sensitivity polarograph designed by M. T. Kelley et al. at ORNL(1,2,3). This instrument has been used at this Laboratory to determine uranium at a concentration of 5×10^{-5}M with a precision of five per cent. The lowest detectable limit without the curve-follower circuit suggested by Kelley was 2×10^{-6}M. Thus a sample dilution of 1:200 would be acceptable for polarographic analysis with this instrument.

Interference by molybdenum was known to prevent the polarographic determination of U(VI) in nitric acid solution, but the work of Kolthoff(4) and Susic(5) gave promise of success with neutral or alkaline electrolytes. With nitric acid as the supporting electrolyte, molybdenum(VI) is reduced at a potential 0.04 volt more positive than that of uranium and the limiting current indicates that the molybdenum serves as a catalyst for the decomposition of the nitric acid electrolyte. Kolthoff reported that molybdenum is not reduced at the dropping mercury electrode in neutral or alkaline solutions, and Susic described a polarographic method for uranium in the presence of molybdenum in which ascorbic acid was the supporting electrolyte. Thus a polarographic method for uranium appeared feasible if a suitable electrolyte could be found.

SUMMARY

A polarographic method was developed for the determination of uranium in nitric acid solution. The method is applicable to the analysis of radioactive solutions that contain a high concentration of aluminum, and there is no interference from molybdenum(VI), mercury(II), or iron(III). The precision of the analysis is 2.5 per cent and the time required for duplicate analyses is one hour.

The sample size is chosen so that the concentration of uranium in the polarographic cell is about 5×10^{-5}M. Interference by molybdenum is eliminated by the use of a potassium phthalate solution (pH 6.0) as the supporting electrolyte, and the addition of ascorbic acid to the electrolyte avoids interference from iron(III) and mercury(II) at the concentrations expected in the sample.

DISCUSSION

Since the approach to this problem was to investigate the polarographic reduction of uranium and molybdenum as a function of pH, it was necessary to consider the effect of pH on other components in the sample.

The estimated composition of the samples to be analyzed for uranium was as follows:

$UO_2(NO_3)_2$	0.01M
$Hg(NO_3)_2$	0.015M
$Al(NO_3)_3$	1.8M
HNO_3	0.5M
Mo(VI)	0.005M

Mercury is reduced at a more positive potential than uranium, but no interference was anticipated as ascorbic acid will reduce mercury in nitric acid solution.

The high dilution factor (1:200) and the maximum dilution volume of 10 ml demanded by the activity of the sample presented no complications. Past experience indicated that the polarograph possessed the necessary sensitivity, and the large dilution factor would minimize changes in sample acidity.

In our tests the ascorbic acid method of Susic(5) gave a positive bias of 10 per cent at molybdenum-to-uranium ratios of 0.5. The pH specified for the method was 3.5. This pH approximates the buffer point of the neutralization of this acid with strong base. Attempts to increase the pH of this electrolyte resulted in precipitation of the uranium. A 0.5M solution of potassium phthalate of pH 6 containing 0.02M potassium ascorbate was found to be a suitable supporting electrolyte for this determination.

REAGENTS

A stock solution of 0.5M potassium phthalate of pH 6.0 was prepared by dissolving 102 grams of potassium acid phthalate and 10 grams of potassium hydroxide pellets in distilled water and diluting to one liter. The solution was then adjusted to pH 6.0 by the addition of potassium hydroxide pellets or concentrated nitric acid as required.

A stock solution of 1.0M potassium ascorbate was prepared by dissolving the required weight of ascorbic acid in distilled water and neutralizing to a pH of 7.0 with potassium hydroxide pellets. The solution was then diluted to volume. Neutral potassium ascorbate could be stored in glass for one week, whereas solutions of the acid deteriorate rapidly as evidenced by the marked discoloration produced on standing for a few hours.

The electrolyte was prepared just prior to use by diluting the ascorbate stock solution 1:50 with the phthalate buffer. Dilution of the synthetic samples 1:200 with the electrolyte lowered the pH of the final solution to 5.9. This change in pH had no effect on the analytical results.

Solutions of uranyl nitrate, mercuric nitrate, ammonium molybdate, and aluminum nitrate were prepared by dissolving the required weight of salt in distilled water and diluting to volume.

Nitrogen, which had been passed through two chromous sulfate bubblers followed by a dilute caustic bubbler, was used to remove atmospheric oxygen from the solutions. Atmospheric oxygen was completely removed from the solutions in ten minutes.

EQUIPMENT

A high-sensitivity polarograph, ORNL Q-1338, was employed for this study. Both normal and derivative polarograms were recorded. This instrument was developed at ORNL by Kelley et al.; a complete description of the instrument together with the circuit has not been published to date. The current-measuring resistors of the instrument have a tolerance of one per cent. Calibration of the recorder indicated that the current readings were low by 4.0 per cent; however, the calibration was linear over the entire range. Since only the relative changes in current were important in this work, no attempts were made to correct the chart readings to absolute current values. The span potential was adjusted by means of a 0 - 1.5 voltmeter. The meter had a precision of 2.0 per cent of full scale. Since a span of one volt was employed throughout this study, the half-wave potentials are probably correct to 0.02V.

A conventional polarographic cell and dropping mercury electrode were employed in this study. All potentials were measured versus the saturated calomel electrode (SCE). The dropping mercury electrode had a capillary characteristic of 2.14 $\mathrm{mg}^{2/3}\,\mathrm{sec}^{-1/2}$ at -0.45V in 0.5M phthalate buffer of pH 5.4. The polarographic cell was held at 25 ±0.1°C by means of a constant-temperature bath.

PROCEDURE

All samples were diluted 1:200 in the phthalate electrolyte. Radioactive samples were handled by standard remote techniques.

A 50-µl sample aliquot was pipeted into a 10-ml volumetric flask containing 9 ml of pH 6 electrolyte and 200 µl of 1M potassium ascorbate. The contents of the flask were diluted to 10.0 ml with electrolyte. A micro stirring bar was added to the flask, and the flask was placed on a magnetic stirrer for one minute.

The solution was then transferred to the polarographic cell, and nitrogen was bubbled through the solution for ten minutes. Normal and derivative polarograms were recorded at 0.1V per minute from -0.2 to -0.8V. A current sensitivity of 0.5 μa full scale was employed for 5×10^{-5}M uranium in the electrolyte.

The diffusion currents and derivative peak heights were obtained from the polarograms as illustrated in Figure 4. The uranium concentration was then read from a standard curve prepared by the analysis of known samples.

Half-wave potentials obtained from the derivative polarograms were displaced by -0.06V due to the time delay in the derivative circuit. All half-wave potentials reported from derivative polarograms were corrected on this basis.

CHOICE OF ELECTROLYTE

Electrolytes were selected and evaluated on the following bases: (1) the precipitation of hydrolyzable ions must be prevented, (2) the buffer range of the electrolyte must approximate the pH required to prevent molybdenum interference, and (3) the electrolyte must be suitable for the polarographic determination of uranium.

Experiments with 0.5M potassium oxalate and 0.5M potassium phthalate, both containing 0.02M potassium ascorbate as the supporting electrolytes, indicated that a pH of 6 would be required to eliminate the molybdenum wave. The sensitivities and half-wave potentials for the uranium reduction were comparable for both media and the observed half-wave potential for the U(VI)-U(V) reduction was -0.45V.

Phthalic acid was selected for further evaluation because the secondary ionization constant for the acid indicated a buffer range near pH 5.4 as compared to pH 4.2 for oxalic acid and pH 4.5 for tartaric acid. Synthetic samples could be diluted 1:200 in the phthalate buffer without precipitation. Aluminum precipitated after standing for several hours but adequate time was available for analysis before precipitation occurred.

EFFECT OF pH ON THE POLAROGRAMS OF MIXTURES OF URANIUM AND MOLYBDENUM IN PHTHALATE BUFFER

A study was made of the effect of pH on the resolution of the uranium(VI) and molybdenum(VI) waves in 0.5M potassium phthalate containing 0.02M potassium ascorbate. Solutions containing 5×10^{-5}M uranyl nitrate and 10^{-4}M molybdate were prepared, and normal and derivative polarograms were recorded. The polarograms are shown in Figure 1, and the half-wave potentials as a function of pH are recorded in Table I.

The half-wave potential of the molybdenum(VI) reduction wave was shifted to more negative values with increasing pH. At a pH of 6.0, the molybdenum reduction wave was completely eliminated within the working range of the electrolyte, which was -0.2 to -1.4V.

The half-wave potential, $E_{1/2}$, for the uranium(VI) reduction was changed from -0.39 to -0.47V over the pH range of 3.9 to 6.0.

URANIUM REDUCTION IN PHTHALATE BUFFER

The reduction of uranium(VI) in phthalate buffer at the dropping mercury electrode was studied at pH 5.4 and 6.0. The uranium(VI)-(V) wave was best defined at pH 6.0 and was well suited for polarographic analysis. Typical polarograms are shown in Figure 2.

At a pH of 5.4 the uranium(VI) ion was reduced in two steps, giving waves at -0.44 and -0.95V. The first wave was well defined and the diffusion current constant was 1.39. A plot of E_{de} (potential of dropping mercury electrode) versus log $i/(i_d-i)$, as shown in Figure 3, gave a straight line whose slope was 0.0563. At a pH of 6.0, the uranium(VI) reduction gave a single wave with an $E_{1/2}$ of -0.47V. The diffusion current constant was 1.23. The equation of the wave was tested by plotting the E_{de} versus log $i/(i_d-i)$, and the value found for the slope was 0.0596 which corresponds to a one-electron reduction from U(VI) to U(V).

In view of the hydrolysis of the uranyl ion and the disproportionation of the U(V) ion into U(IV) and U(VI), the number of electrons involved in the reduction was calculated by means of the Ilkovic equation. In this calculation, the diffusion coefficient for the uranyl ion was taken as 0.6 x 10^{-5} cm^2/sec(6). The calculated values for n were 0.94 at pH 5.4 and 0.84 at pH 6.0 where n was the number of electrons involved in the reduction. These results indicated that the effects of hydrolysis and disproportionation at pH 6.0 were small, and the sensitivity of the method corresponded to the expected value for a one-electron reduction.

EFFECT OF MOLYBDENUM ON URANIUM REDUCTION AT pH 6.0

Synthetic samples containing various ratios of uranium to molybdenum were run to determine the effect of molybdenum on the uranium diffusion current. The results are given in Table II. Figure 4 is a typical polarogram which demonstrates the elimination of the molybdenum reduction wave.

A comparison of the precision of the method at various concentrations of uranium is given in Table II. The results obtained by the derivative procedure are similar to those obtained by normal polarography.

EFFECT OF SAMPLE VARIABLES ON URANIUM DETERMINATION AT pH 6.0

The effect of varying the concentrations of nitric acid, mercuric nitrate, and aluminum nitrate was studied in a factorial experiment. Results are given in Table III. The uranium concentration was held constant at 5 x 10^{-5}M. The data show that the method was not affected by the sample variables within the limits that were studied.

DERIVATIVE PEAK HEIGHT AND DIFFUSION CURRENT AS A FUNCTION OF CONCENTRATION

The effect of the uranium concentration in the electrolyte at pH 6.0 on the uranium reduction current was studied in the range 10^{-6} to 2 x 10^{-4}M uranium. The data are given in Table IV and a plot of peak height and diffusion current versus concentration is shown in Figure 5.

The data for the range 2 x 10^{-5} to 2 x 10^{-4}M uranium were taken from Table II. The results covering the range 10^{-6} to 10^{-5}M uranium are the averages of duplicate determinations. No attempt was made to measure the diffusion current below 2 x 10^{-5}M because the unfavorable ratio of diffusion to residual current results in distortion of the uranium waves. The derivative peak heights were determinable to 10^{-6}M. In each case the derivative peak height was measured as illustrated in Figure 4.

The results show the method to be applicable in the range from 2 x 10^{-6} to 2 x 10^{-4}M, and that the derivative peak height and diffusion current are a linear function of concentration in the concentration ranges that were studied.

SIMULTANEOUS DETERMINATION OF URANIUM AND MOLYBDENUM AT pH 5.4

A procedure was developed for the simultaneous determination of uranium and molybdenum in phthalate electrolyte of pH 5.4. The molybdenum reduction current was a critical function of the aluminum and ascorbic acid concentrations, and it was necessary to control these variables for precise results.

A series of sixteen synthetic samples containing uranium and molybdenum in the concentration range of 2 x 10^{-5} to 2 x 10^{-4}M was prepared and the derivative polarograms recorded. The peak heights of the uranium and molybdenum waves were measured as illustrated in Figure 6. The peak heights were plotted against each other as a function of concentration because of the simplicity of this treatment. The results are shown in Figure 7.

The results show that both the uranium and molybdenum concentrations in a sample can be obtained from a derivative polarogram in conjunction with a standard curve.

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TABLE I

HALF-WAVE POTENTIALS AS A FUNCTION OF pH

pH	$E_{1/2}$ Uranium	$E_{1/2}$ Molybdenum
3.9	-0.39V	-0.49V
4.1	-0.42V	-0.52V
4.4	-0.45V	-0.58V
4.8	-0.45V	-0.67V
5.2	-0.45V	-0.92V
5.6	-0.46V	no wave
6.0	-0.47V	no wave

TABLE II

EFFECT OF MOLYBDENUM ON URANIUM RESULTS AT pH 6.0

Concentration in Electrolyte		Uranium Wave	
Uranium Molarity x 10^5	Molybdenum Molarity x 10^5	Normal Polarograms i_d, µa	Derivative Polarograms Peak Height, µa
2	0	0.051	0.046
2	2	0.052	0.045
2	5	0.048	0.045
2	10	0.051	0.048
2	20	0.050	0.044
		σ = 3.4%	σ = 3.3%
5	0	0.135	0.116
5	2	0.132	0.118
5	5	0.134	0.117
5	10	0.133	0.117
5	20	0.133	0.120
		σ = 0.92%	σ = 1.2%
10	0	0.265	0.233
10	2	0.263	0.233
10	5	0.265	0.234
10	10	0.265	0.233
10	20	0.263	0.235
		σ = 0.41%	σ = 0.43%
20	0	0.542	0.467
20	2	0.536	0.472
20	5	0.542	0.471
20	10	0.538	0.469
20	20	0.538	0.475
		σ = 0.50%	σ = 0.63%

TABLE III

EFFECT OF VARIABLES ON URANIUM REDUCTION

5 x 10^{-5}M Uranium in Phthalate Electrolyte of pH 6.0

Concentration in Electrolyte				Results	
$Al(NO_3)_3$ Molarity x 10^2	HNO_3 Molarity x 10^3	$Hg(NO_3)_2$ Molarity x 10^4	$MoO_4^=$ Molarity x 10^4	Normal Polarograms i_d, μa	Derivative Polarograms Peak Height, μa
1.6	4	0	0	0.136	0.122
1.6	4	1.5	0	0.137	0.121
1.6	4	0	2	0.136	0.121
1.6	4	1.5	2	0.133	0.121
1.6	8	0	0	0.138	0.122
1.6	8	1.5	0	0.137	0.120
1.6	8	0	2	0.133	0.120
1.6	8	1.5	2	0.136	0.121
2.4	4	0	0	0.133	0.116
2.4	4	1.5	0	0.136	0.118
2.4	4	0	2	0.136	0.118
2.4	4	1.5	2	0.135	0.118
2.4	8	0	0	0.135	0.118
2.4	8	1.5	0	0.135	0.120
2.4	8	0	2	0.133	0.120
2.4	8	1.5	2	0.133	0.118
			Average	0.135	0.120
			2σ	±2.5%	±3.4%

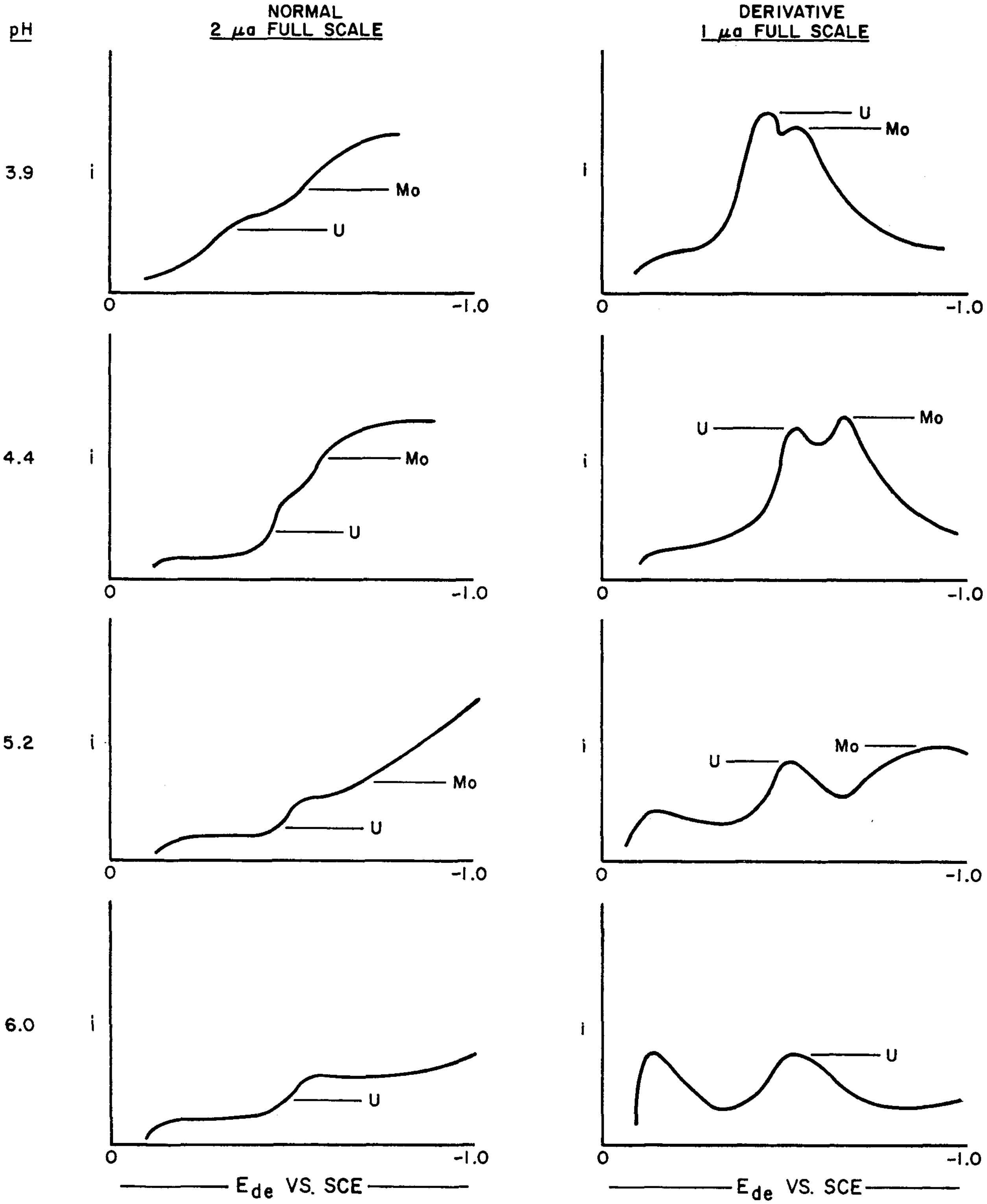
TABLE IV

DERIVATIVE PEAK HEIGHTS AND DIFFUSION CURRENTS AS A FUNCTION OF THE URANIUM CONCENTRATION

Phthalate Buffer of pH 6.0

Uranium Molarity x 10^6	Derivative Polarograms Peak Height, µa	Normal Polarograms Diffusion Current, µa
1	0.0023	------
2	0.0043	------
5	0.0114	------
10	0.0227	------
20	0.0458	0.0504
50	0.118	0.133
100	0.234	0.264
200	0.471	0.539

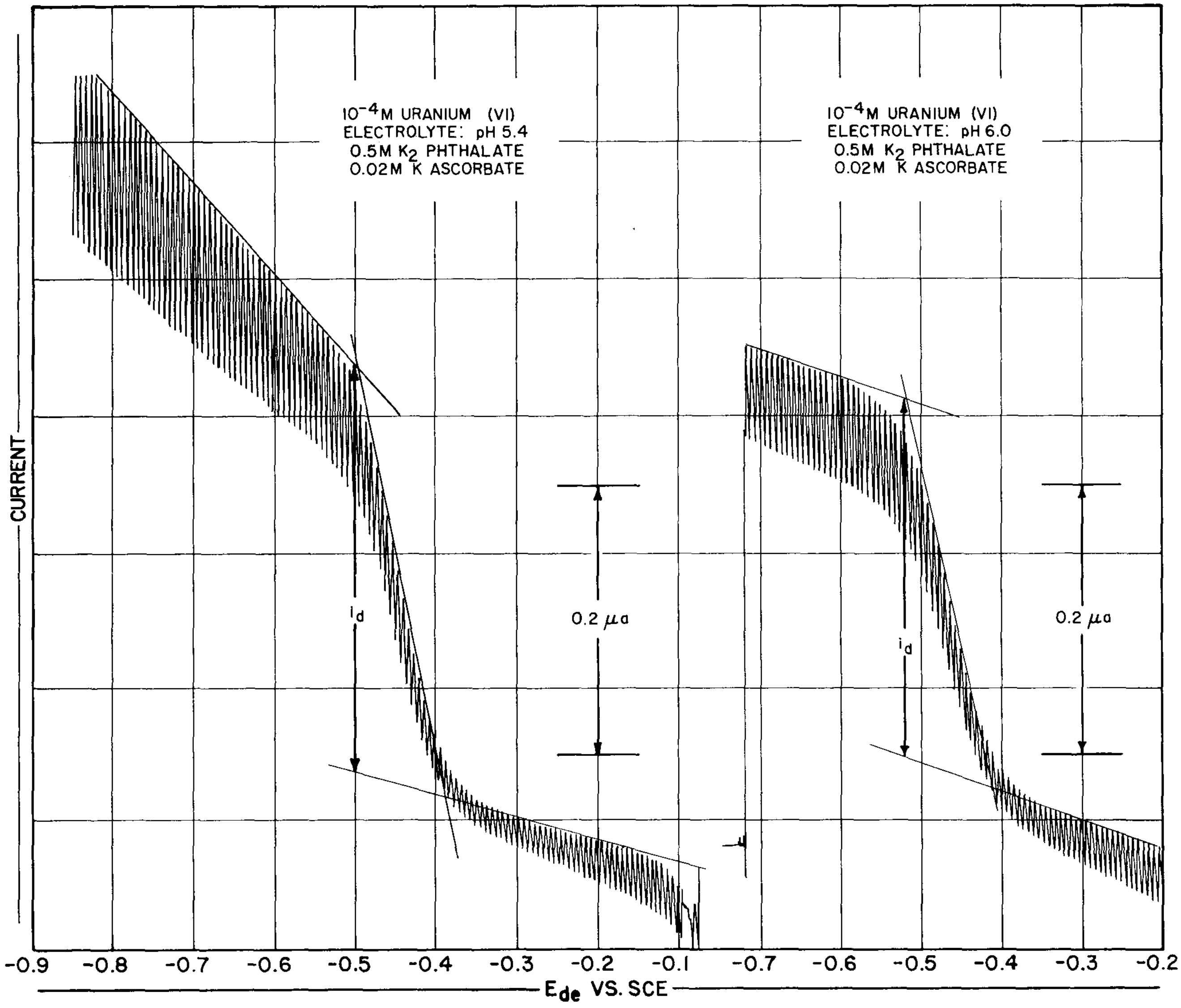
FIGURE 1



EFFECT OF pH ON POLAROGRAMS OF MIXTURES
OF URANIUM AND MOLYBDENUM IN PHTHALATE ELECTROLYTE

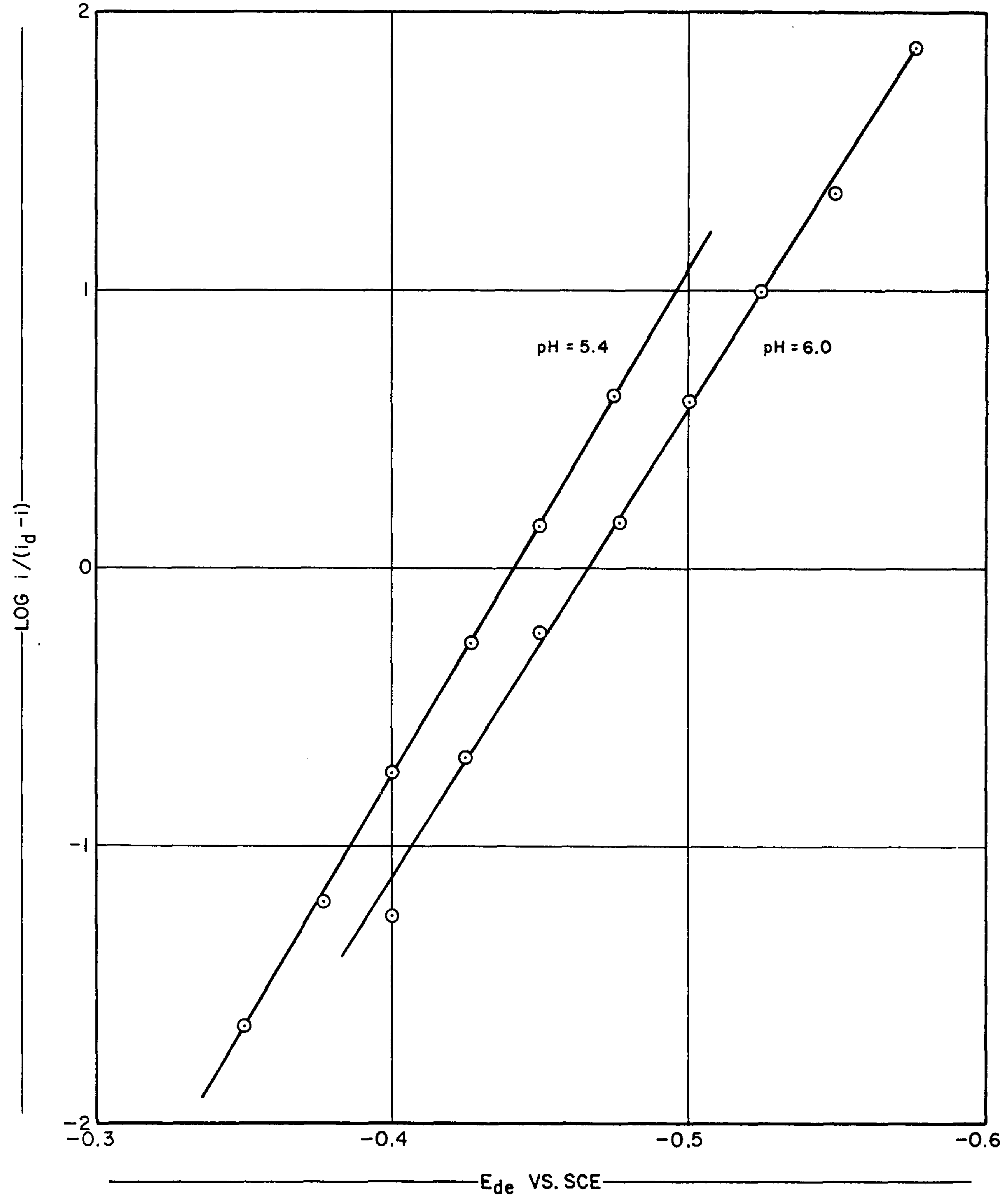
10^{-4} M Uranium (VI) – 5×10^{-5} M Molybdenum (VI)

FIGURE 2



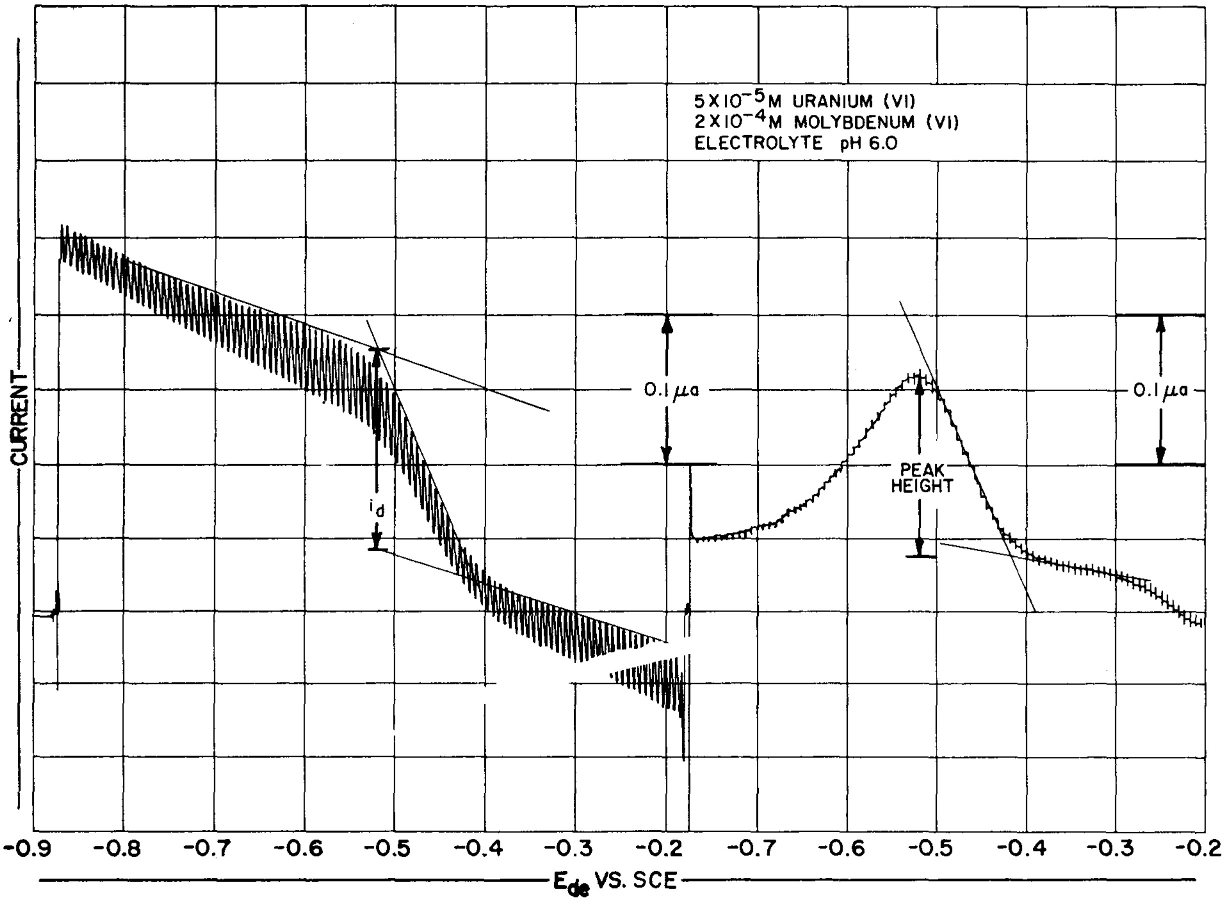
URANIUM REDUCTION WAVES

FIGURE 3



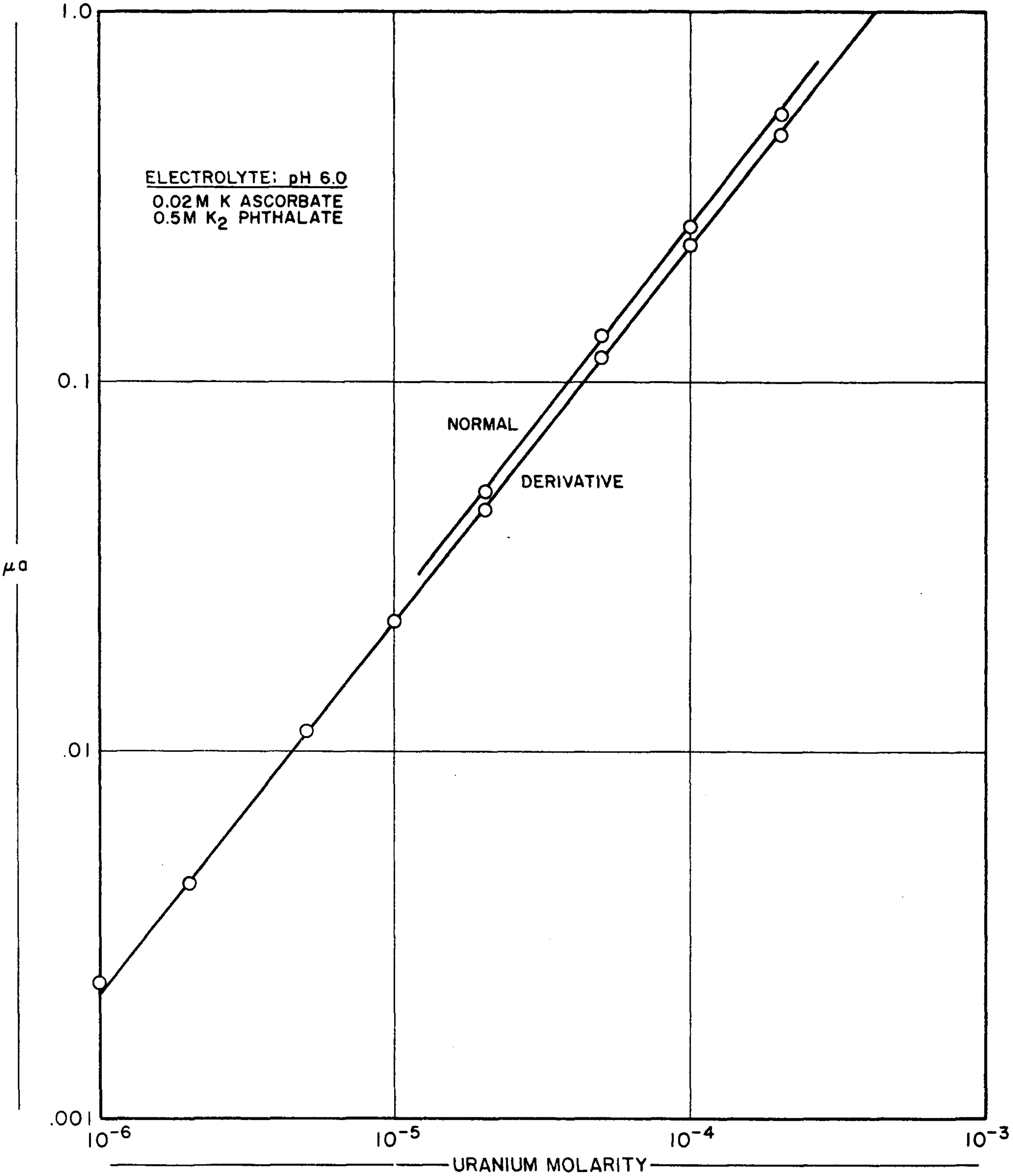
PLOT OF E_{de} VERSUS LOG $i/(i_d - i)$ FOR URANIUM REDUCTION

FIGURE 4

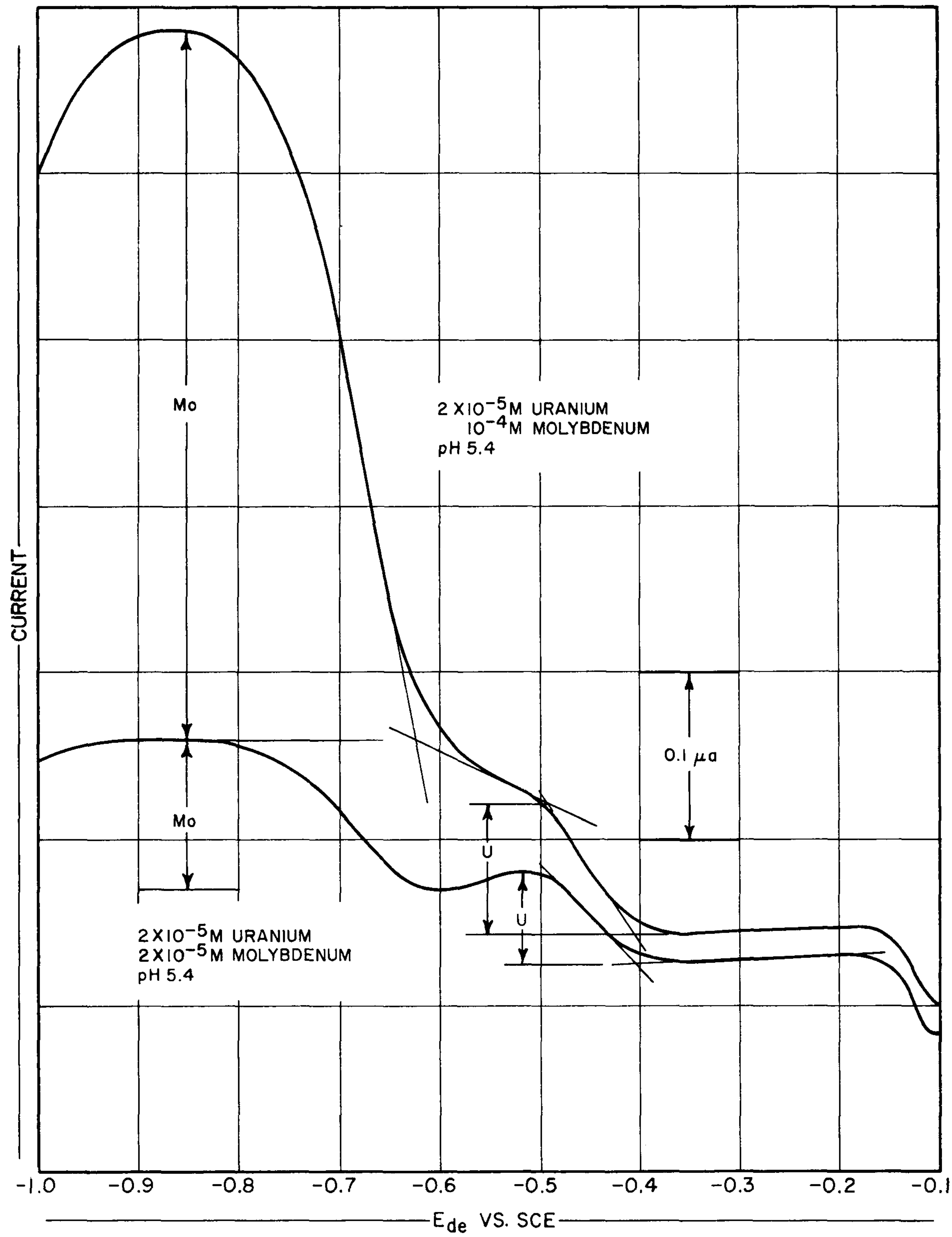


POLAROGRAMS OF URANIUM IN PRESENCE OF MOLYBDENUM

FIGURE 5

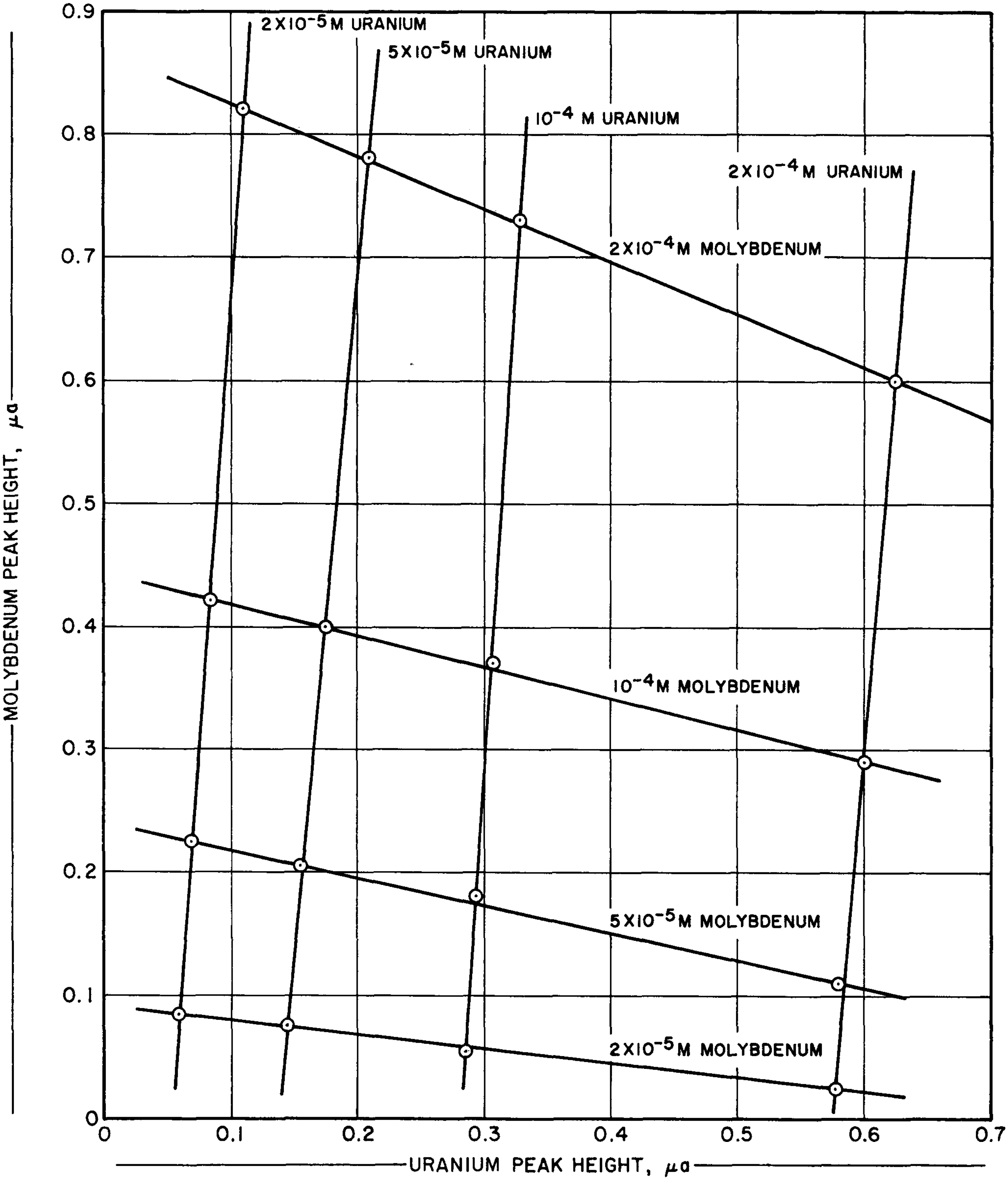


DERIVATIVE PEAK HEIGHT AND DIFFUSION CURRENT VS. CONCENTRATION



DERIVATIVE POLAROGRAMS OF MIXTURES OF URANIUM AND MOLYBDENUM AT pH 5.4

FIGURE 7



CURVE FOR SIMULTANEOUS DETERMINATION OF URANIUM AND MOLYBDENUM