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 Series A

THE POLAROGRAPHIC DETERMINATION
OF URANIUM IN THE PRESENCE OF PLUTONIUM

by

Maynard E. Smith

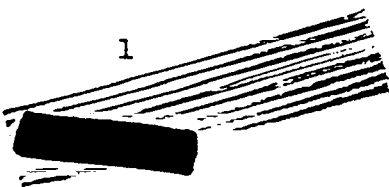
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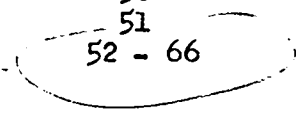
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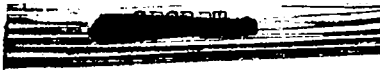
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CHEMISTRY AND METALLURGY DIVISION

ANALYTICAL GROUP

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ABSTRACT

Strubl's polarographic method for the determination of uranium in the presence of iron can be used for the determination of uranium in plutonium solutions. A hydroxylamine hydrochloride solution (2M) is used as the supporting electrolyte. This reduces the plutonium to the plus three oxidation state without reducing the uranium. The uranium may then be determined polarographically by measuring the height of the uranyl reduction wave (U^{VI} to U^V) at -0.35 volts (vs. S.C.E.) applied potential. Solutions with a U/Pu weight ratio as low as 3.5×10^{-3} were analyzed with an error of less than 2%. This error increased to 6% for solutions of 1×10^{-3} U/Pu ratio and is considerably larger for smaller U/Pu ratios.





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INTRODUCTION

The polarographic determination of uranium in the presence of iron using hydroxylamine to reduce the iron to the (II) oxidation state was first reported by Strubl⁽¹⁾. This method has been used subsequently by other investigators⁽²⁻⁹⁾ who also found that the uranyl ion was not reduced by the hydroxylamine and that a well defined reduction wave (U^{VI} to U^V) was produced at about -0.1 to -0.2 volts vs. S.C.E. The plutonium reduction wave for the plus four to the plus three oxidation state is similar to the ferric-ferrous wave in that it appears very close to the zero potential^(10,11,12). The polarographic wave for the reduction of the plus three state of plutonium to the metal evidently takes place at some potential greater than that required for the evolution of hydrogen. Since plutonium is reduced to its lower valence state (III) by hydroxylamine it seemed probable that Strubl's method could be applied to plutonium solutions containing small amounts of uranium (0.1 to 2%). This was found to be the case and a reproduction of a typical polarogram taken with the Leeds and Northrup Electrochemograph Type E is shown in Figure 1.

This method has the advantage of not requiring a separation of the plutonium from the uranium. The precision of the method is better than 2% in the uranium concentration range for which it was primarily designed.

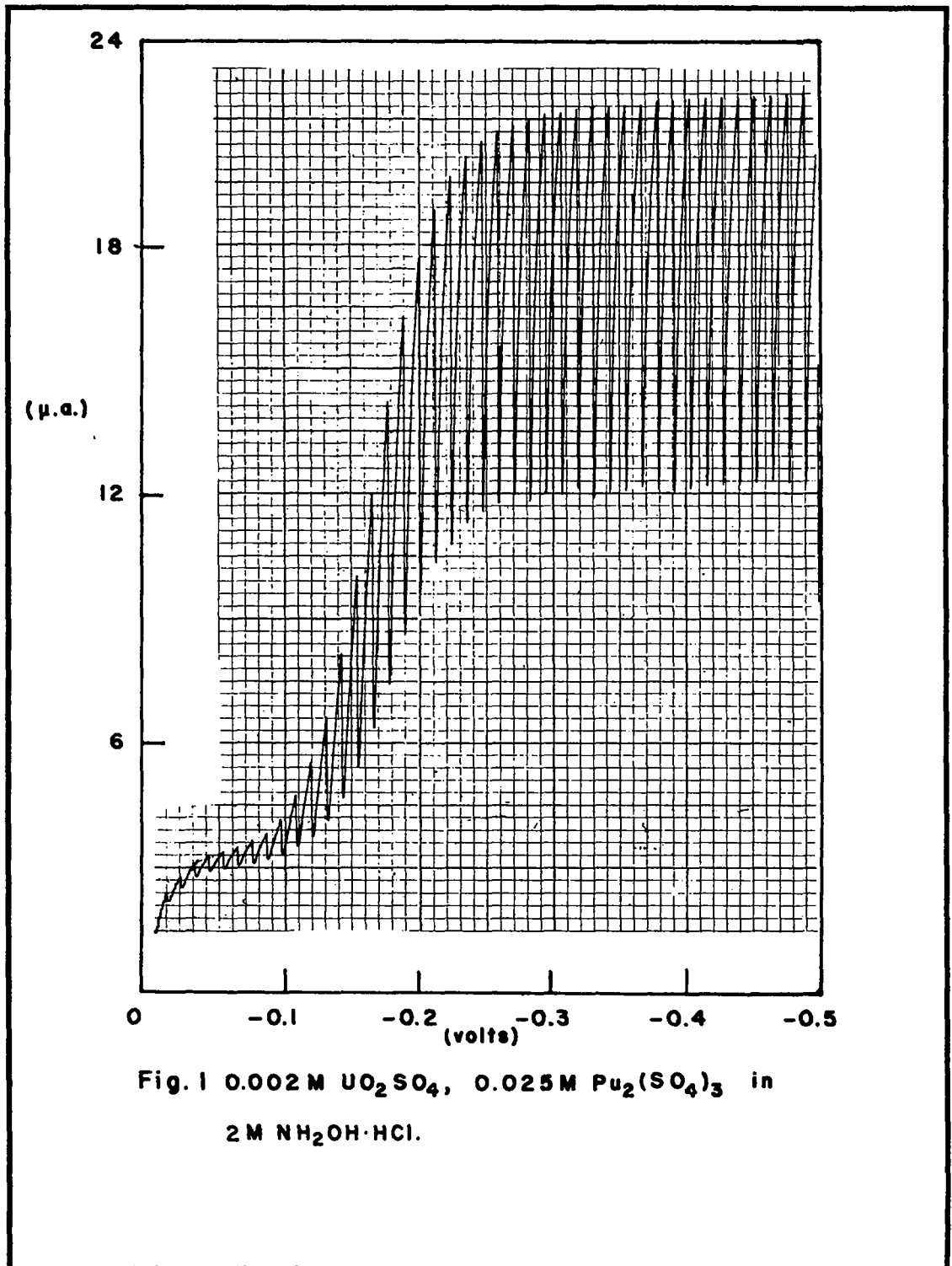


Figure 1



APPARATUS AND TECHNIQUE

Caution

Any work involving the handling of plutonium-containing materials should be done under approved conditions and in laboratories designed for the adequate protection of the worker. Rules recommended by the Health Group for the safe handling of such materials should be rigidly followed.

The instrument used for recording the polarograms was a Leeds and Northrup Electrochemograph Type E⁽¹³⁾ (Figure 2). This is an automatic recording machine using a Speedomax Recorder. Although three degrees of damping are available with this machine, undamped polarograms were used and the curve envelope (maximum current) measured rather than the average current. The advantage of this technique has been pointed out by Schulman, Battey and Jelatis⁽¹⁴⁾. The instrument was found to be quite stable and very satisfactory.

Four cells were used, each surrounded by a tall-form beaker. These were immersed in a cylindrical thermostat bath (Figure 3). The beakers served to prevent contamination of the water bath in the event of breakage of the cells. The cells were kept at a temperature of $34 \pm 0.1^\circ \text{C}$. This temperature was chosen rather than 25°C so that cooling would be unnecessary. The apparatus was protected from vibration by mounting the entire water bath on sponge rubber. Stirring

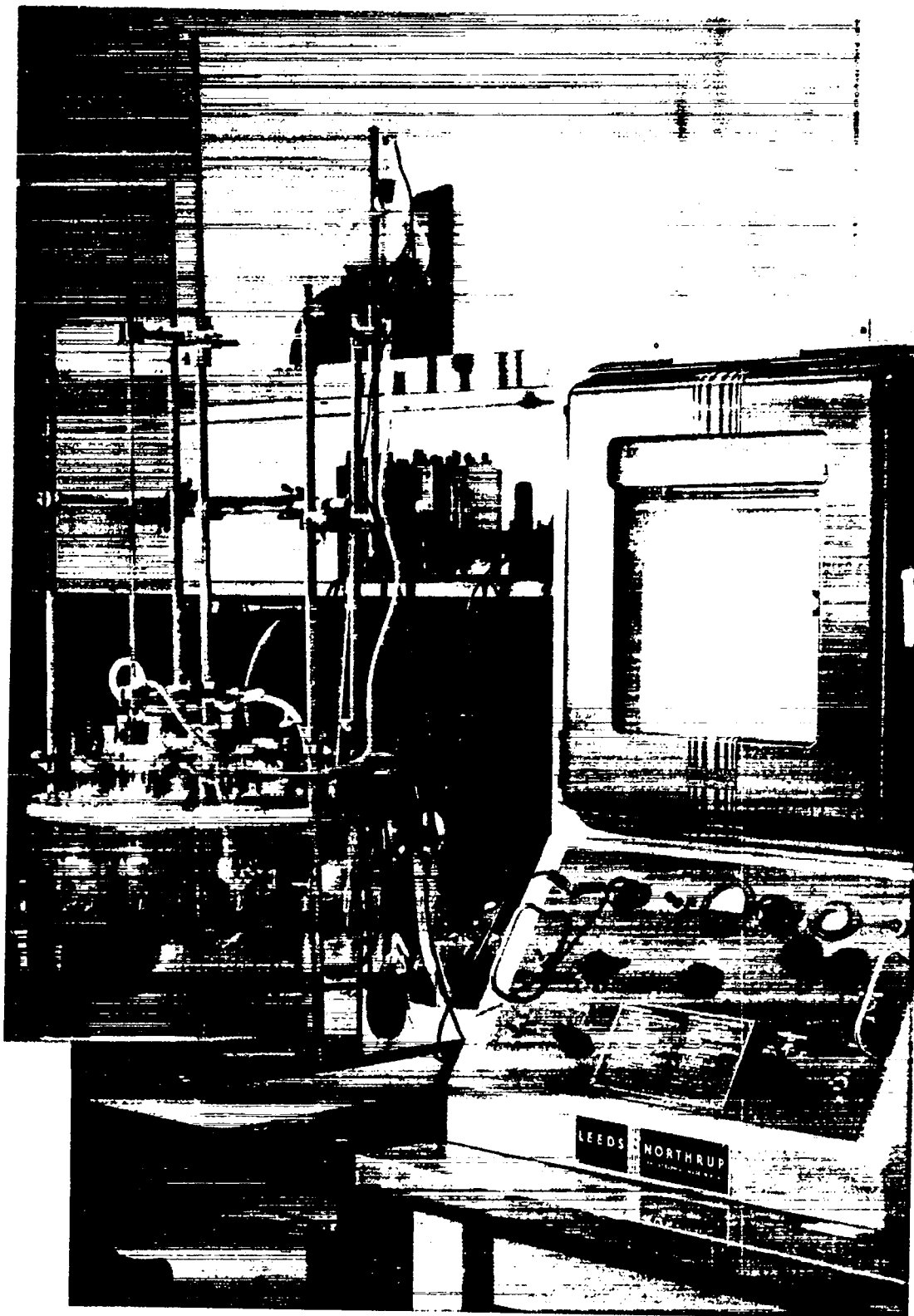


Figure 2

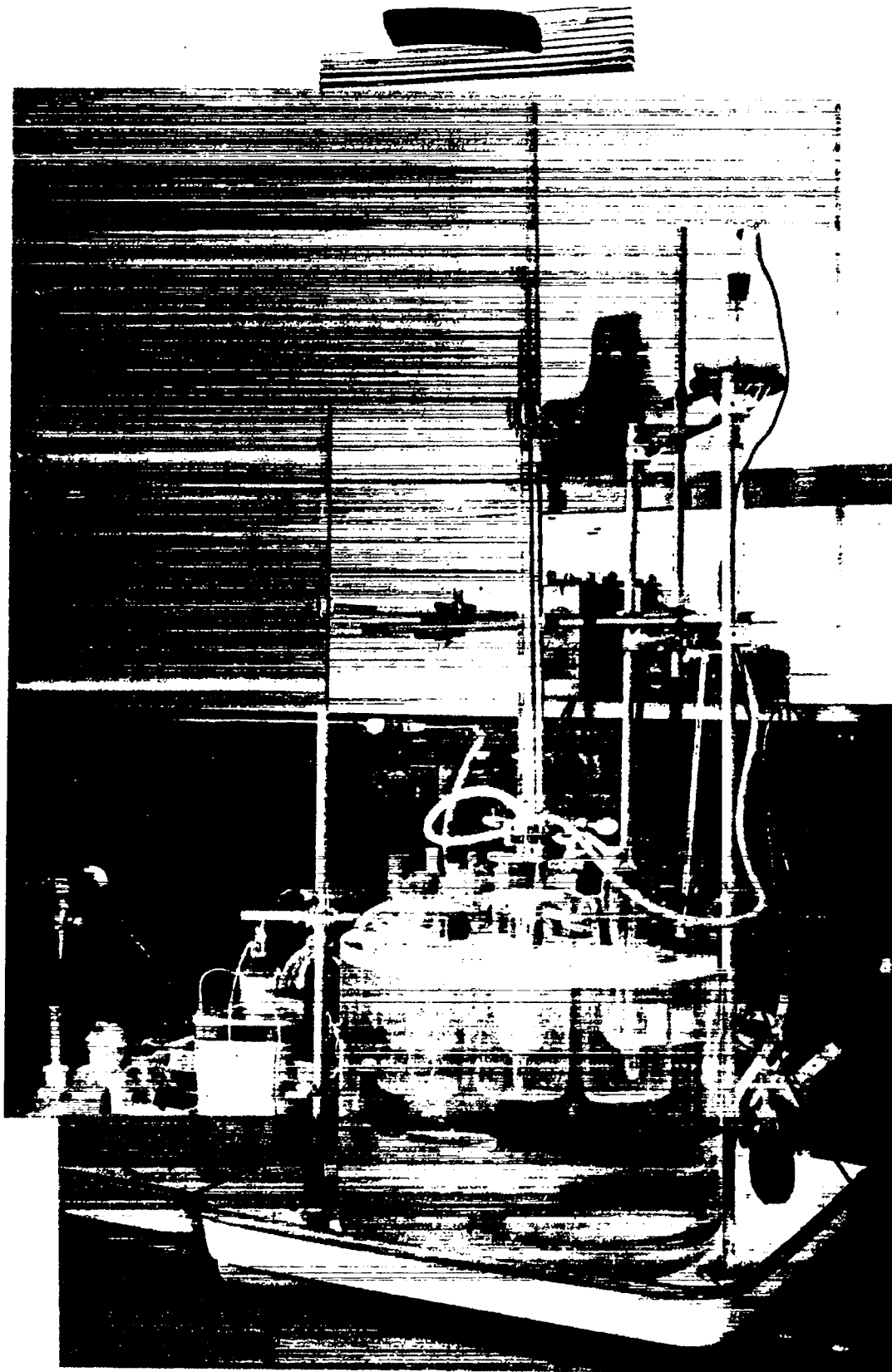


Figure 3



vibration was minimized by stirring the bath with a small circulating pump connected to the bath by six foot lengths of Tygon tubing. The same capillary and salt bridge were used for each cell. The solutions in the cells were degassed for twenty minutes with nitrogen gas which was first bubbled through 2M hydroxylamine hydrochloride solution contained in a washing bottle immersed in the bath.

The polarographic cells used were designed to hold a volume of one to ten milliliters. A diagram of the cell construction is shown in Figure 4. The inside diameter of the cell (A) is large enough to allow the insertion of the capillary and the KCl-agar filled "probe" bridge. The bridge and the capillary are held by a rubber stopper (B) which fits in the widened mouth of the cell. The bulb (C) is filled with mercury to such a level as to allow the mercury to just enter the cell space (A). The mercury in the bulb acts as a leveling device and in this way an appreciable amount of mercury can flow from the capillary before enough collects in the bottom of the cell to cover the tip of the capillary. This is a modification of a micro cell used by Majer⁽¹⁵⁾. Nitrogen gas is bubbled through the solution in the cell by opening the three-way stopcock (D). The other stopcock channel allows the cell to be opened to the atmospheric pressure after degassing. The gas outlet (E) is connected to a gas washing bottle of dilute sulfuric acid in order to prevent spray from contaminating the atmosphere. Mercury may be added to the reservoir bulb through the ground glass tapered joint (F). The cells were



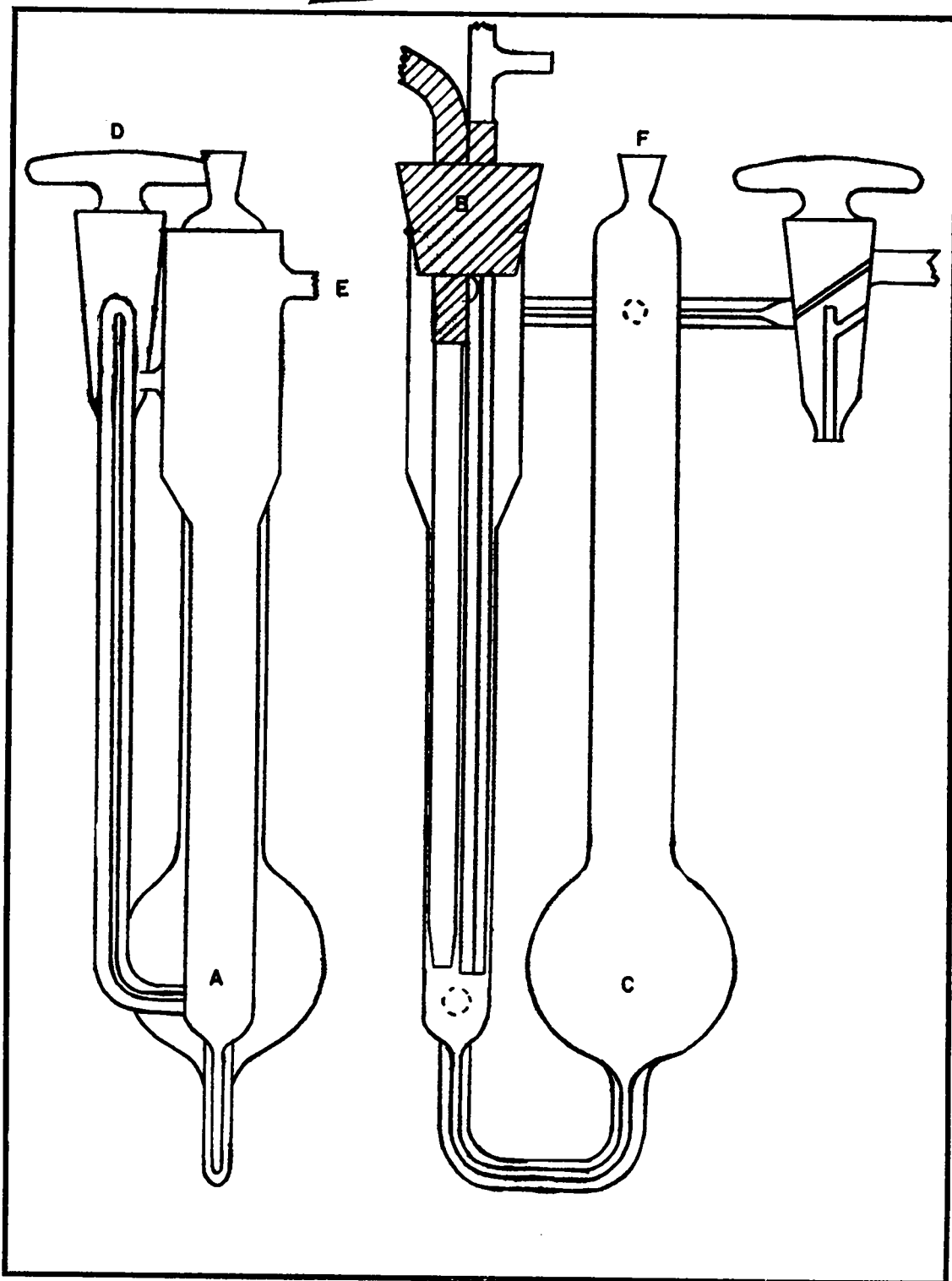
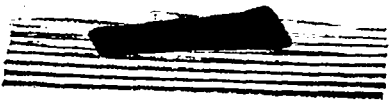


Figure 4



emptied by inserting in the cell a small Tygon tube connected to a suction bottle and were cleaned by rinsing three times with distilled water and twice with acetone.

The capillary used was a piece of 0.05 mm bore marine barometer tube 17 cm long. When not in operation it was kept immersed in mercury and frequently cleaned by immersion in concentrated nitric acid. The height of the mercury in the leveling tube was kept constant at 70 cm (measured from the tip of the capillary). The capillary constant was measured frequently and was determined as $m^{2/3} t^{1/6} = 2.29$ in 1M KCl with shorted electrodes. This value changed less than 1/2% over a period of five months.

The KCl-agar bridge connecting the saturated calomel electrode was of the type recommended by Hume and Harris⁽¹⁶⁾ except that the sintered glass plug was omitted. The probe of the bridge containing the KCl-agar was a 11.5 cm long 7 mm O.D. glass tube slightly tapered at the end. Readjustment of the agar plug was achieved by applying pressure with a hypodermic syringe connected to a stopcock inserted in the top of the calomel cell (see Figure 5). This bridge was easily replaceable and reproducible. The reproducibility was within ten ohms and the actual resistance was checked each time a new bridge was made. A 1000 cycle conductivity bridge (Model RC, Industrial Instruments Inc) was used to measure the resistances.

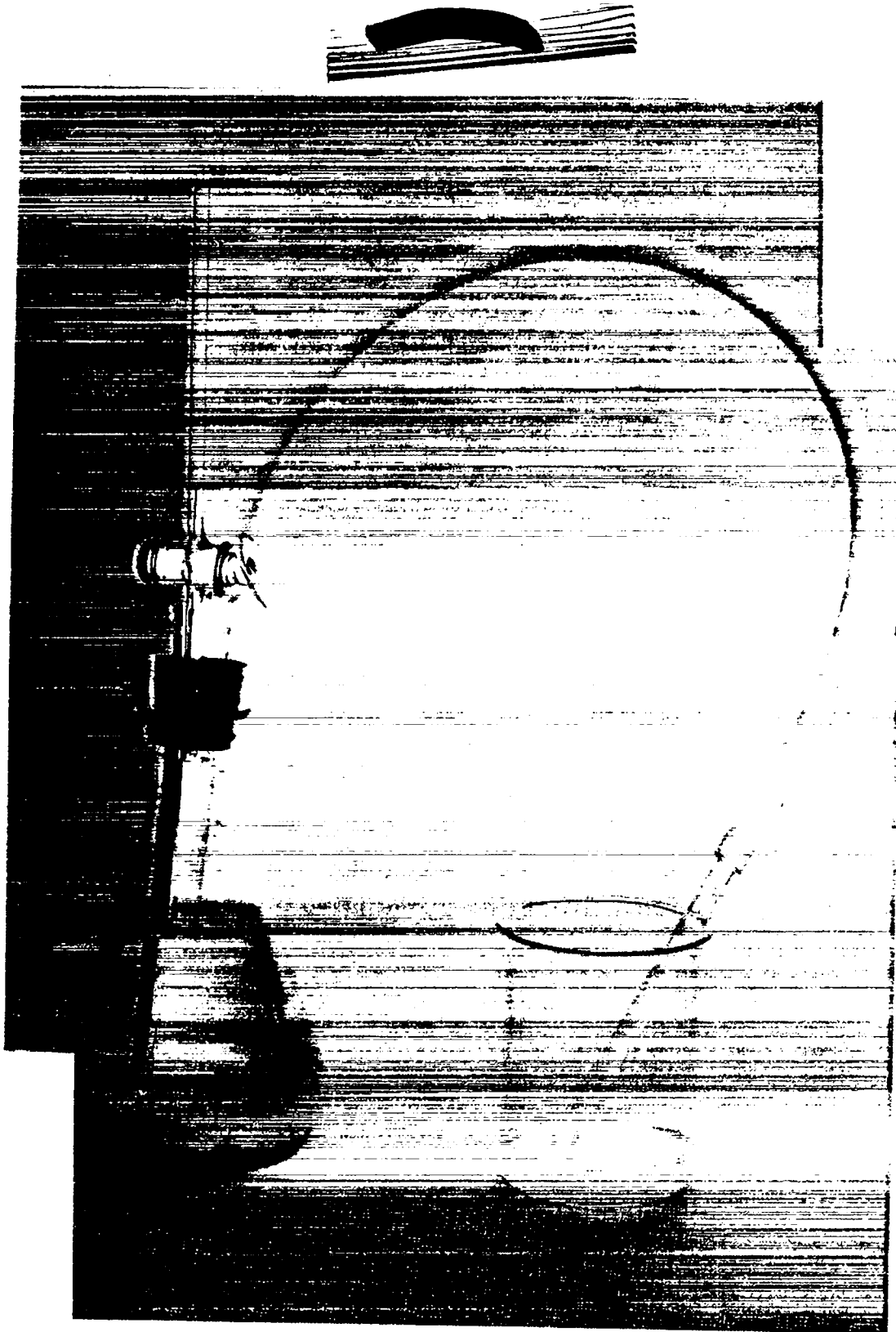


Figure 5



Apparatus for the preparation of the solutions to be analyzed is shown in Figure 6. Calibrated 5 ml volumetric flasks placed in test tubes and covered by funnels were used for the evaporation of the sample solutions to the sulfate crystals. In case of "bumping" this method offers some chance of recovery. Side holes were made in the test tubes to allow the water vapor to escape. The test tubes placed in a beaker were heated by means of an infra-red lamp. The sulfate crystals were treated in the flasks with hydroxylamine hydrochloride solution and after heating the solutions were cooled to room temperature by immersing the flasks in water using the apparatus shown at the right in Figure 6. The solutions adjusted to the proper volume were transferred to the polarographic cell by means of a 3 ml volumetric pipette equipped with a syringe. All these operations should be carried out in a dry-box designed for the handling of plutonium solutions.

REAGENTS

Agar - Braun Corporation, Los Angeles, California.

Acids - Baker's Analytical Reagents.

Hydroxylamine Hydrochloride - Eastman's "pure" grade.

Mercury - Distilled mercury.

Nitrogen - Tank nitrogen (further purification found unnecessary).

Plutonium - 99.8% pure metal.

Uranium - 99.9% pure metal

Fresh distilled water was used in preparing all solutions.





Figure 6

RECOMMENDED PROCEDURE

The following procedure is recommended for the polarographic determination of uranium in a plutonium-uranium sample. The method may be used for solid samples such as metal, oxide or fluoride or for acid solutions. In the case of solid fluoride samples, the sample is converted to the sulfate by heating with strong sulfuric acid and the excess acid removed by fuming. Oxide samples may be converted to the sulfate by treating the solid samples with hydriodic acid and removing the excess hydriodic acid by fuming with sulfuric acid. For samples consisting of sulfuric acid solutions of the metal, it is advisable to heat the solutions almost to dryness in order to get rid of the excess sulfuric acid. The samples are then analyzed according to the following procedure omitting Steps 1 and 2. The amount of the sample taken may be weighed or measured volumetrically depending on the type of sample and on the units in which the uranium content is to be expressed.

1. Electropolish⁽¹⁷⁾ approximately 128 mg of the metal alloy sample and weigh accurately in a calibrated 5 ml volumetric flask.
2. First dissolve the sample by adding 0.5 ml of 3M HCl, and then add 0.5 ml of 6N H₂SO₄ and 0.5 ml of 8M HNO₃. Micropipettes (500 λ) equipped with syringes are used for adding the acids.
3. Place the flask containing the sample in a test tube with two side holes near the top and cover the test tube with a small funnel in such a manner that the stem of the funnel is outside the



- flask.
4. Place the test tube containing the flask and solution in a beaker underneath an infra-red heating lamp, and evaporate to dryness (about 5 hours).
 5. Moisten the crystals with distilled water and again evaporate to dryness to remove traces of volatile acids.
 6. To the still hot crystals, add cautiously 3 ml of 3.33M hydroxylamine hydrochloride. Cover the flask with a small glass bulb and heat again for ten minutes.
 7. Turn off the heat, remove the bulb from the mouth of the flask and wash off the tip into the flask with approximately one ml of distilled water.
 8. Place the flask in a clamp and immerse in water for three minutes.
 9. At the end of this time remove the flask from the clamp and adjust the volume to the 5 ml mark by adding distilled water from a micropipette.
 10. Place the stopper in the flask and mix the solution thoroughly by inverting the flask several times.
 11. Use a 3 ml pipette fitted with a syringe to transfer approximately 3 ml of the solution in the flask to the polarographic cell.
 12. Cover the cell with a stopper and allow nitrogen gas to bubble through the solution for twenty minutes. In the meantime immerse the capillary and salt bridge in a small beaker of 2M hydroxylamine hydrochloride.



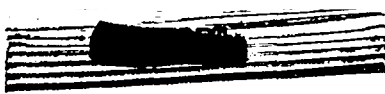


13. When the degassing is completed replace the rubber stopper of the cell with the electrode assembly, shut off the nitrogen and open the cell to the atmosphere by turning the three-way stopcock. Rinse capillary and the salt bridge with distilled water from a wash bottle and dry with "Kleenex" tissue before immersing in the cell solution.
14. Adjust the mercury level to the predetermined height and record the drop time with the circuit open. Determine the proper sensitivity range and record a polarogram between 0 and -0.4 volts. Record at least two polarograms for each solution.
15. Determine the maximum current in microamperes from the polarograph at -0.05 volts and at -0.35 volts.

CALIBRATION DATA

Four uranium stock solutions were prepared by dissolving weighed amounts (0.8000 ± 0.0002 grams) of the clean metal (pickled in HNO_3) in a mixture of hydrochloric and nitric acid, and adjusting the total volumes to 500 ml with distilled water. Ten dilutions were made on each of the four stock solutions to produce ten sets of solutions of different uranium concentration. Each set consisted of four separately prepared solutions of the same uranium content. These solutions were made up by pipetting the appropriate amounts into 50 ml volumetric flasks and diluting to the mark with distilled water. The smallest pipette used in this operation was a 2 ml pipette. A two ml sample





was taken from each of these diluted solutions and added to a 5 ml volumetric flask containing 2 ml of plutonium chloride solution (128 mg Pu). The solutions in the flasks were then analyzed according to the previously described "Recommended Procedure".

All the pipettes and the four 500 ml volumetric flasks were calibrated. One 50 ml volumetric flask and one 5 ml volumetric flask were calibrated and the volumes of the other flasks checked with the volumes of mercury measured by the corresponding calibrated flasks. From the calibration data for the flasks and pipettes it was concluded that the standard deviation contributed by the volumetric apparatus would be in the order of $\pm 1\%$.

It was found that the concentration (C) of uranium in mg/l was proportional to the measured diffusion current (i_d) in microamperes according to the following equation: $C = K (i_d - A)$ where K and A are constants. The diffusion current (i_d) was measured as the difference in current in microamperes at -0.35 and -0.05 volts. The value K was determined by selecting a value of A such that C was directly proportional to ($i_d - A$). It was found that in the range studied the value, $A = 0.19 \mu.a.$ gave the most constant ratio between the uranium concentration and the corrected diffusion current ($i_d - A$). This is shown in Table I.

Table I

Relationship of the Diffusion Current
to the Uranium Concentration

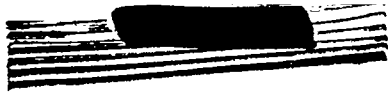
A = 0.19 μ .a. Pu conc. = 25.6 grams Pu/l σ = standard deviation

<u>U/Pu</u> ($\times 10^3$)	<u>C</u> (mg U/l)	<u>i_d</u> (μ .a.)	<u>σ</u>	<u>$K = C/i_d - A$</u>	<u>σ</u>
1.00	25.60	1.01 \pm	0.0141	31.49	\pm 0.5475
2.00	51.20	1.81 \pm	0.0177	31.57	\pm 0.3446
3.50	89.60	3.03 \pm	0.0217	31.58	\pm 0.2416
5.00	128.00	4.24 \pm	0.0146	31.60	\pm 0.1140
7.50	192.00	6.19 \pm	0.0374	32.02	\pm 0.1998
10.00	256.00	8.27 \pm	0.0404	31.69	\pm 0.1585
12.50	320.00	10.34 \pm	0.0616	31.54	\pm 0.1916
15.00	384.00	12.35 \pm	0.0740	31.59	\pm 0.1923
17.50	448.00	14.27 \pm	0.1100	31.83	\pm 0.2487
20.00	512.00	16.41 \pm	0.0746	31.58	\pm 0.1453

The first column in Table I shows the weight ratio of the uranium and plutonium present in the cell solution.

Each value for i_d is the average of eight measurements, two on each of the four separately prepared solutions of the same uranium concentration. The uranium concentration was determined from the dilution of the stock solution assuming no pipetting or measuring errors. The fact that the relationship of C to $i_d - A$ is linear was established statistically by making two groups of K values from Table I (each group consisting of alternate values) and comparing the mean K values of each group.

These two averages with their standard deviations were compared to determine whether one group was significantly different from the other. A "t" test was applied⁽¹⁸⁾ and the "t" value was determined as 0.39



which is less than the value 1.67 for the 95% confidence limit. Therefore, the populations of the two groups were concluded to be the same within this degree of assurance. This justifies the conclusion that K is actually a constant value. The average value of K was determined as $K = 31.65 \text{ mg/l } \mu\text{.a}^{-1}$.

Very dilute uranium-plutonium solutions in which the U/Pu ratio was less than 10^{-3} were prepared from the stock solutions and these solutions picked at random were analyzed. The results on these low uranium concentration solutions are shown in Table II.

Table II

Relationship of the Diffusion Current
to the Uranium Concentration

$A = 0.30 \mu\text{.a.}$ Pu conc. = 25.6 grams/l σ = standard deviation

$\frac{U}{Pu}$ ($\times 10^3$)	C (mg U/l)	i_d ($\mu\text{.a.}$)	σ	$K = C/(i_d - A)$	σ
0.500	12.8	0.67	± 0.0200	34.59	± 1.8700
0.250	6.4	0.50	± 0.0184	32.60	± 3.0560
0.125	3.2	0.40	± 0.0141	33.86	± 5.0525
0.068	1.6	0.35	± 0.0120	34.41	± 8.8797

The value for the diffusion current (i_d) is the average value for eight measurements two on each of the four separately prepared solutions. It was found that in this range a reasonably linear relationship between the concentration and the diffusion current was obtained if the value $A = 0.30$ was subtracted from the measured diffusion current.

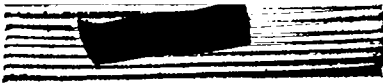




In order to measure the effect of varying plutonium concentration on the calibration constant (K), diffusion currents were measured for solutions of different plutonium concentration keeping the uranium concentration constant. Two different uranium concentrations were used, 512 mg U/l and 89.6 mg U/l. The concentrations of plutonium were 12.8 grams Pu/l and 6.4 grams Pu/l. The calibration constant K for the determination of uranium in solutions of plutonium concentration 25.6 grams/l was previously determined as $K = 31.65 \text{ mg U/l } \mu\text{.a}^{-1}$. The effect on this value of varying plutonium concentration was determined. In each case two measurements of the diffusion current for each of four separately prepared solutions were made. The uranium calibration constant (K) was determined for each value of the diffusion current and the percent difference between it and the value for K at 25.6 grams Pu/l calculated. In Figure 7 the percent decrease of the calibration constant is plotted against the plutonium concentration.

The linearity of the relationship between the percent change in the calibration constant and the plutonium concentration was established statistically by calculating the correlation coefficient (r)⁽¹⁹⁾. This value was determined as $r = 0.72$ which according to the degrees of freedom represented by the data indicates that the probability of the relation being linear is 1000 to 1. The best straight line through the points was determined by the method of least squares⁽¹⁹⁾. This was drawn considering the concentration of plutonium in grams/l to be the independent variable. This line is shown in Figure 7 as the





solid line and its equation is $y = 6.10 - 0.23X$, where y equals the percent change in the value of K and X is the plutonium concentration in grams/l. The standard deviation of the points from the line was determined as $\sigma = 1.15\%$ and the 95% confidence limit of $\pm 2.3\%$ is shown by the dotted lines in Figure 7. Since the change in the calibration constant with plutonium concentration in this range is small but significant (about 6%), an equation to show the change in K with the plutonium concentration was derived. This relationship is expressed by the equation $K = 29.72 + 0.073X$, where X equals the plutonium concentration in grams/l. Accordingly, a variation of 17 mg in the sample size would introduce an error of less than 1% in the calibration constant K .

ACCURACY AND PRECISION

The confidence errors for the determination of uranium in solutions of U/Pu ratio ranging from 3.5×10^{-3} to 20×10^{-3} are $\pm 1.2\%$ for the 95% confidence level and $\pm 1.6\%$ for the 99% confidence level. These values were calculated from the data in Table I and were based on 63 degrees of freedom.

The confidence errors determined for the lower U/Pu ratios 2×10^{-3} and 1×10^{-3} are shown in Table III and are based on 7 degrees of freedom.

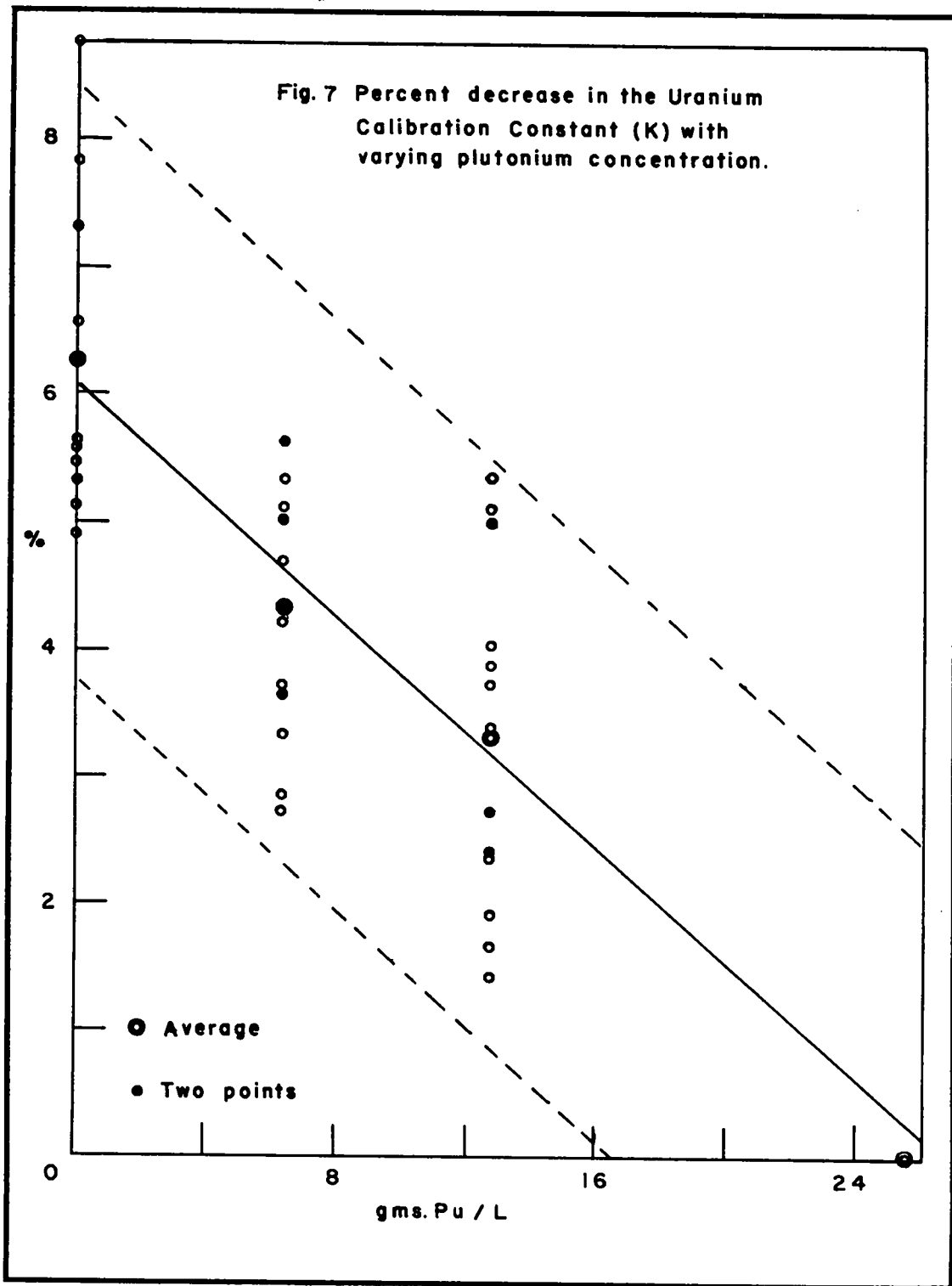
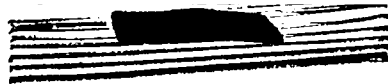


Figure 7



Table III

Confidence Errors for U/Pu Ratios 10^{-3} and 2×10^{-3}

<u>U/Pu x 10^3</u>	<u>% Error at Confidence Level</u>	
	<u>95</u>	<u>99</u>
2	± 2.6	± 3.8
1	± 4.1	± 6.1

The confidence errors determined for very low U/Pu ratios are given in Table IV. These are based on seven degrees of freedom.

Table IV

Errors for 95% Confidence Level

<u>U/Pu x 10^3</u>	<u>Error (%)</u>
0.500	± 11.0
0.250	± 19.2
0.125	± 30.2
0.068	± 52.6

These values indicate that the method is chiefly valuable as a means of estimation at these extremely low uranium concentrations.

Since the data for the calibration and precision were obtained by analyzing quadruplicate samples, it is of interest to know how the precision would be affected by analyzing duplicate samples. An indication of this effect is given by Table V which shows the results of the analysis of ten uranium-plutonium "unknowns".

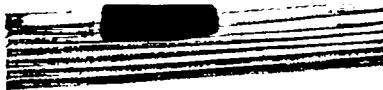


Table V

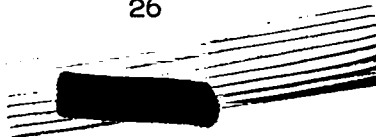
Analysis of Plutonium-Uranium "Unknowns"

<u>U/Pu (X 10³)</u>	<u>mg U/l (taken)</u>	<u>mg U/l (found)</u>	<u>Percent Difference</u>
1.25	32.00	31.82	- 0.6
1.50	38.40	39.09	+ 1.5
2.50	64.00	63.63	- 0.6
3.50	89.60	89.43	- 0.2
6.50	166.40	165.2	- 0.8
7.50	192.00	191.0	- 0.6
10.00	256.00	257.2	+ 0.5
11.50	294.40	297.4	+ 1.0
22.50	576.00	566.7	- 1.6
24.00	614.40	608.7	- 0.9

These data were obtained by analyzing in duplicate each solution of different uranium concentration. The precision obtained in these analyses falls within the limits predicted by statistical treatment of the data. It would therefore seem advisable in actual analysis to take a resample if duplicate samples disagree more than 2%.

CALCULATIONS

The concentration (C) of the uranium in the cell solution may be calculated in mg/liter by using the formula $C = K (i_d - A)$. This applies to solutions having a U/Pu ratio greater than 10^{-3} . The difference in the current in microamperes measured at -0.35 volts and -0.05 volts S.C.E. is the value (i_d) and A is a constant equal to 0.19. The proper value for K is determined by the equation $K = \frac{(29.72 + 0.073X)B}{2.29}$



where X equals the plutonium concentration in grams/l and B is the capillary constant $m^{2/3} t^{1/6}$ determined in 1M KCl at 34° C with shorted electrodes. It should be emphasized that this expression for K is only valid if the measurements of the diffusion currents are carried out at $34 \pm 0.1^\circ$ C. Knowing the uranium concentration in the polarographic cell and the amount of the original sample taken, the uranium content of the sample may be expressed in weight percent, or concentration, depending on whether the sample is a solid or a solution. For example, the percent by weight of uranium in a metal alloy sample is given by the formula,

$$\% \text{ U in alloy} = \frac{K (i_d - A) 0.5}{\text{wt. of sample in mg}}$$

From the following two formulae the uranium content of a solution may be calculated according to whether the amount of the sample was measured volumetrically or weighed.

$$\text{mg U/l in sample} = \frac{5 K (i_d - A)}{\text{Vol. of sample in ml}}$$

$$\text{mg U/gram of solution} = \frac{0.005 K (i_d - A)}{\text{grams of solution}}$$

INTERFERENCES

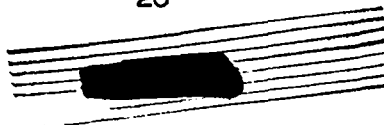
Previous investigators have listed interfering constituents in the polarographic determination of uranium in hydroxylamine acid solutions (2,5,20-22). Of the negative ions, halogen ions are removed from the solution by the preliminary fuming with sulfuric acid. Nitrate ion



which would interfere if present in moderate concentration is also removed by this process. Orthophosphoric acid which interferes⁽²⁰⁾ is converted to the pyro and meta acid by this fuming with sulfuric acid and in this form well defined diffusion currents can be obtained⁽²¹⁾. However, the presence of phosphate would probably affect the position of the wave and the wave height and therefore require recalibration of the method. Organic anions such as oxalate, tartrate and citrate would interfere if allowed to remain in the solution, however, if they are known to be present they can be easily destroyed by fuming with nitric and perchloric acid before conversion of the sample to the sulfate.

Interfering positive ions can in many cases be predicted by the values of their half-wave potentials. Some of the metals known to interfere are Sb, Ag, Be, Mo, Sn, Ti, Cu and V⁽²⁾. The interferences of Mo, Ti, and V can be eliminated according to Haight by using a supporting electrolyte consisting of 5% sodium tartrate and 1M $\text{NH}_2\text{OH}\cdot\text{HCl}$ ⁽⁵⁾. He also has reported a modification of this method to overcome the interference of Cu⁽⁵⁾. Of course, any change of the supporting electrolyte would mean determination of a new calibration constant.

Positive ions that do not interfere in a hydroxylamine hydrochloride supporting electrolyte when present in moderate amounts are Cr^{+3} , Pb^{+2} , Sn^{+4} , Zn^{+2} , Ni^{+2} and Fe^{+3} .⁽²²⁾





Small amounts of Fe^{+++} , Ga^{+++} , and La^{+++} added to a plutonium solution before analysis produced no noticeable effect on the polarographic wave. This would be expected from the general position of their half-wave potentials.

SUMMARY

1. Uranium may be determined polarographically in the presence of plutonium using hydroxylamine hydrochloride as a supporting electrolyte. The reproducibility of the method is better than $\pm 2\%$ for U/Pu weight ratios as low as 3.5×10^{-3} , and falls off rapidly at lower ratios.
2. Iron, gallium and lanthanum were found not to interfere with the analysis when present in small amounts.

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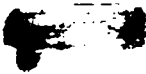
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