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C. D. Susano
J. S. Decker

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APPLICATION OF THE BECKMAN MODEL K AUTOMATIC TITRATOR TO THE POTENTIOMETRIC DETERMINATION OF URANIUM

C. D. Susano and J. S. Decker

ANALYTICAL CHEMISTRY DIVISION

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ABSTRACT

The applicability of the Beckman Model K Automatic Titrator for the determination of uranium was investigated to establish the utility of the instrument and to ascertain the optimum conditions for the titration. The automatic titrator was found to be satisfactory for the determination of uranium in the range of 20 to 100 mg. The precision established for uranium in this range was 0.2 per cent. For smaller quantities of uranium the precision was about 0.5 per cent.

The optimum conditions that were established for titration are: potential "settings" of -80 mv and 640 mv at temperatures of 90 to 95°C; the use of a gauze electrode instead of a smooth electrode; and titration with 0.01 N potassium dichromate in solutions which are about 1 N in H_2SO_4.

APPLICATION OF THE BECKMAN MODEL K AUTOMATIC TITRATOR TO THE POTENTIOMETRIC DETERMINATION OF URANIUM

C. D. Susano and J. S. Decker*

INTRODUCTION

Since a number of oxidizable and reducible constituents have been determined by means of the Beckman Model K automatic titrator[16], an investigation was undertaken to determine the applicability of this instrument for the potentiometric titration of uranium in quantities of 20 to 100 mg. In these studies, potassium dichromate, a readily available primary standard, was chosen as the oxidant for uranium while chromous sulfate was selected as the reductant.

A similar potentiometric method, as reported by Voss and Greene[15], involves the reduction of uranium in a sulfate solution with zinc-amalgam after which the reduced uranium is titrated with potassium dichromate at a constant potential. Although this method is the most precise volumetric method for the determination of uranium that has been reported, it has one disadvantage at least for this specific application, in that a prior knowledge of the uranium content is necessary.

Korack, Nessle and Casto[6] used potassium dichromate for the oxidation of uranium in certain types of solutions both on a macro as well as on a semi-macro scale. Casto[2], Noyce[10], Richmond and Rodden[12], Gantz, et al.[5], Pepkowitz[11], Martens, and others[9] and Simon, Asbury and Flaunders[14] outlined volumetric and potentiometric methods for the determination of uranium in which oxidizing agents other than potassium dichromate are recommended.

The most widely used reagents that have been reported for the reduction of uranium prior to oxidation with a standard oxidant are the zinc reductor, lead[5], stannous chloride[8], and chromous sulfate[7].

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DISCUSSION OF EXPERIMENTAL RESULTS

Since the purpose of this investigation was to determine the applicability of the Beckman Model K Automatic Titrator for the potentiometric titration of uranium, only those studies that were necessary to establish the utility of the instrument were made. Specifically, studies were made:

(1) To establish the potential "settings" of the instrument at room temperature and at 90° to 95°C;

(2) To determine the effectiveness of the gauze and smooth types of platinum electrodes;

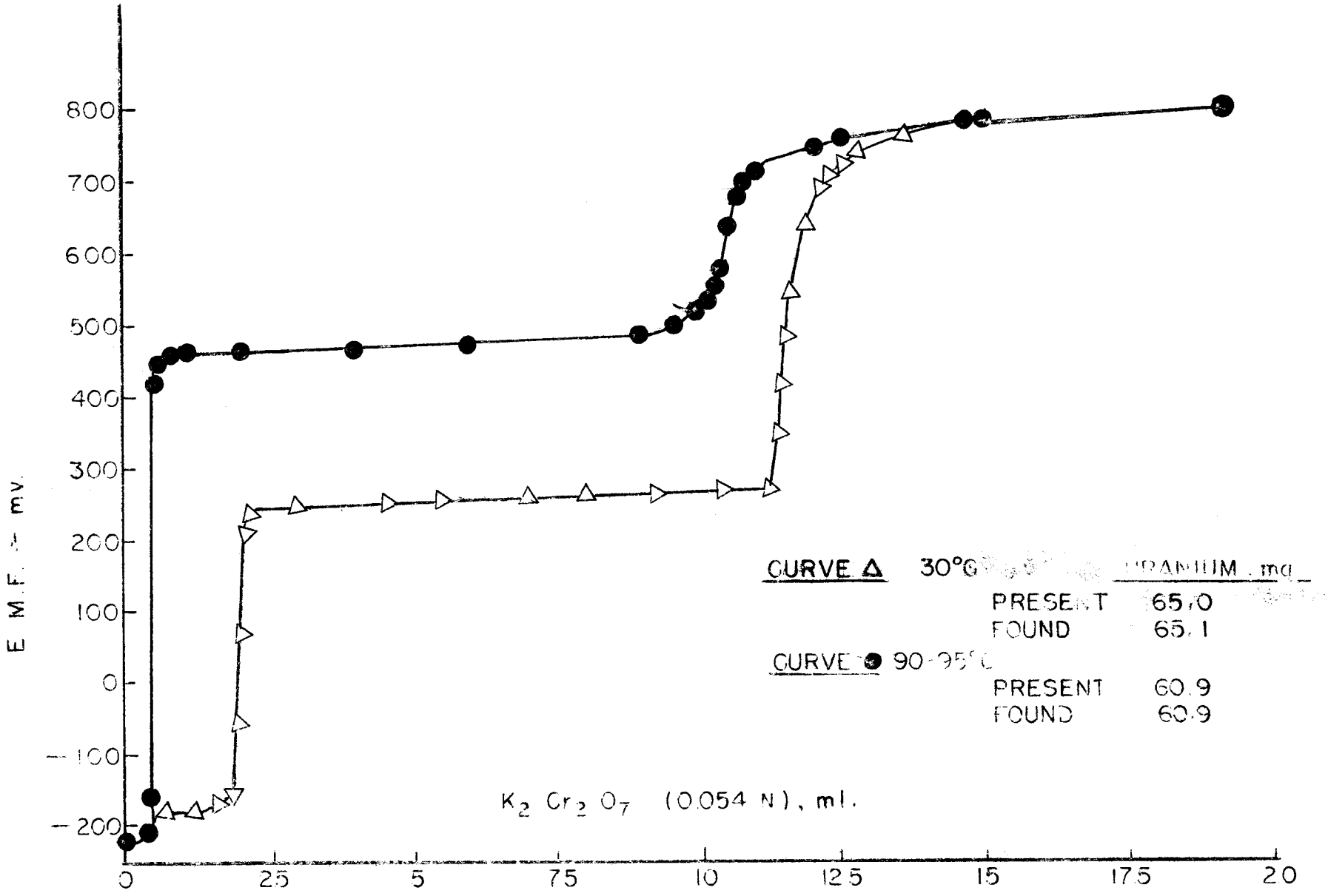
(3) To ascertain the effect of various concentrations of $K_2Cr_2O_7$ and of the hydrogen-ion; and

(4) To compare the automatic titrator with manual methods of titration.

After the optimum conditions for the automatic titrator had been established, several materials that contained other constituents such as zirconium, iron, nickel and chromium were analyzed for uranium in order to establish the reproducibility of the method in the presence of these substances.

Details of the procedure that was used in these tests as well as directions for the preparation of the necessary reagents are given in the section of this report entitled "Recommended Method" which starts on page 9

Potential Setting. To establish the potential "settings" for the automatic titrator, portions of a standard solution of uranyl sulfate were titrated with $K_2Cr_2O_7$. The potentials at the Cr^{+2} to Cr^{+3} and U^{+4} to U^{+6} end-points were measured with a Leeds and Northrup Potentiometer. In order to establish the best operating conditions, titrations were made at room temperature and at 90 to 95°C. It is apparent from the titration curves (See Fig. 1) that the break at the higher potential is much sharper and the steep portion of the curve is longer at the higher temperatures than at room temperature. At temperatures of 90 to 95°C, the first break in potential is noted in the range of -150 to 250 mv while the second break is observed in the range of 275 to 700 mv. Consequently, potential "settings" for the automatic titrator were arbitrarily selected at -80 mv and 640 mv as the end points for the titration at temperatures of 90 to 95°C. These potentials and temperatures were used in all subsequent tests.



POTENTIOMETRIC TITRATION OF URANIUM WITH A LEEDS--NORTHRUP POTENTIOMETER

FIGURE 1

Comparison of Platinum Electrodes. After the potential "settings" were established, a series of tests were made to determine the effectiveness of a platinum gauze electrode as compared to a smooth platinum electrode (Beckman No. 1281). The gauze electrode was of the type which is ordinarily used as the cathode in electro-analytical work. The surface area of the gauze electrode was about 20 times greater than that of the smooth electrode or about 196 sq mm as compared to 9 sq mm. As a result of these tests, which are summarized in Table I, the gauze electrode was found to be slightly better than the smooth electrode.

Table I

Comparison of the Smooth and Gauze Type, Platinum Electrodes

Potassium Dichromate Normality	Electrode Type	No. Detns. N	Uranium Average $\bar{X}$ mg	Uranium Standard Deviation S mg	Uranium Coefficient of Variation V Per Cent
0.0994	Smooth	6	27.1	0.3	1.1
	Gauze	4	27.7	0.1	0.2
0.0101	Smooth	9	27.2	0.3	1.0
	Gauze	6	27.6	0.1	0.5

Apparently, polarization of the platinum electrode is reduced with the gauze electrode because as the titration proceeds and the solution increases in volume, a clean surface of platinum is continually coming in contact with the solution. For this reason and because it was noted that with the smooth electrode the uranium values were lower and less precise, the gauze electrode is recommended for use in this method.

Potassium Dichromate Concentration. The operating conditions for the titrator having been established, a third series of tests were made to determine the optimum concentration of $K_2Cr_2O_7$ to use as an oxidant for uranium. Uranium, in quantities of 5 to 65 mg, was determined by titration with varying concentrations of $K_2Cr_2O_7$. The concentration of $K_2Cr_2O_7$ in these tests ranged from 0.0016 N to 0.539 N. The results, which are shown in Table II, indicate that the precision is, as was expected, essentially the same for $K_2Cr_2O_7$ in the range of 0.003 N to 0.55 N. In all but one series of tests, the coefficient of variation was 0.5 per cent or less. On the basis of these results it can be stated that no loss in precision occurs as a consequence of using dilute solutions of $K_2Cr_2O_7$ as the titrant.

Table II

Effect of Potassium Dichromate in the

Concentration Range of 0.001 to 0.539 N

$K_2Cr_2O_7$ Normality	No. Detns. N	Uranium Average $\bar{X}$ mg	Uranium Standard Deviation S mg	Uranium Coefficient of Variation V Per Cent
0.002	9	4.83	0.8	1.6
0.003	8	6.11	0.02	0.3
0.008	4	24.36	0.02	0.1
0.009	6	13.67	0.07	0.5
0.009	7	27.22	0.05	0.2
0.031	6	64.5	0.02	0.2
0.033	9	60.4	0.07	0.3
0.539	5	64.9	0.04	0.5

Hydrogen-Ion Concentration. Only two experiments were made to ascertain the effect of hydrogen-ion concentration on the determination of uranium by the automatic titrator because the concentrations of H_2SO_4 selected, 2 N and 0.1 N, were considerably greater and less, respectively, than the 5 v/v per cent (~ 1 N) H_2SO_4 that was used in the previous tests. It was found, from the results given in Table III, that the precision at the higher hydrogen-ion concentration was essentially the same as that obtained for solutions in which the acidity was about 1 N. At the lower hydrogen-ion concentration, however, a decrease in precision was noted and the potentials at the end-points were more negative; the results were also significantly lower. Inasmuch as the precision attained at the higher hydrogen-ion concentrations of 1.98 N and 1 N was essentially the same, a hydrogen-ion concentration of 1 N or 5 v/v per cent in H_2SO_4, which was used in earlier tests, is recommended.

Table III

Effect of Hydrogen-Ion Concentration

H_2SO_4 Normality	$K_2Cr_2O_7$ Normality	Potential Range mv Low	Potential Range mv High	No. Detns. N	Uranium Average $\bar{X}$ mg	Uranium Standard Deviation S mg	Uranium Coefficient of Variation V Per Cent
2	0.01	200	400	6	27.67	0.06	0.2
1	0.01	-	-	7	27.22	0.05	0.2
0.1	0.01	-80	640	4	26.20	0.10	0.5

Comparison of Methods. In order to compare the automatic titrator and the manual methods, such as are ordinarily used for the determination of uranium, samples that contained approximately 39 per cent zirconium, 12 per cent sodium, and 9 per cent uranium were analyzed by both methods. Two samples, each 2.5 mg in weight, were dissolved in H_2SO_4. Various aliquots of this solution were selected, such that different amounts of uranium were present; namely, 11 to 13 mg, 20 to 25 mg, and 80 to 100 mg. The recommended procedure (See p. 9) for the automatic titration was followed. In Table IV, a summary of these results and of those obtained by the manual method of titration with ceric sulfate(13) is given. The results obtained by means of the automatic titrator were somewhat more precise, but not significantly so, than the results secured by the manual method when the quantity of uranium present was greater than 20 mg. For smaller amounts of uranium the precision of the two methods is essentially the same.

Table IV

Comparison of Automatic and Manual Methods of Titration

Number of Determinations	Uranium mg	$K_2Cr_2O_7$ Normality	Coefficient of Variation, V Automatic Per Cent	Coefficient of Variation, V Manual Per Cent
16	11 to 13	0.004	0.5	0.4
24	20 to 25	.008	0.2	0.5
12	80 to 100	.03	0.2	0.4

The coefficient of variation was calculated by using the following method:

$$\text{Coefficient of variation, } V = \frac{D^2}{2P}$$

Where D = difference between duplicates, per cent

P = number of pairs of duplicates

Analysis of Sulfate Solutions Further tests were made with 11 different sulfate solutions that contained known amounts of uranium, zirconium, iron, nickel and chromium to ascertain the effect of these constituents on the determination of uranium by the automatic titrator method. Zirconium, nickel and chromium were not expected to interfere but it was known that any iron present would be reduced and oxidized in the same manner as uranium. The results given in Table V have been corrected for the amount of iron present because it can be reasonably assumed to be completely oxidized under the conditions of the test. The results of these tests confirm the fact that zirconium, nickel and chromium do not interfere in the potentiometric titration of uranium.

Although the uranium results given in Table V are about 1 per cent lower than the known value, this was not unexpected because the automatic titrator method tends to yield results that are consistently lower than the established value. The precision, however, was better than 0.5 per cent.

Table V

Effect of Large Amounts of Zirconium and Lesser Amounts of Iron, Nickel and Chromium on the Determination of Uranium

Iron mg	Chromium mg	Nickel mg	Zirconium mg	Uranium(1) Taken A	Uranium(1) Found B	Uranium(1) Difference B - A
0.25	3.50	1.00	110	42.64	41.13	- 1.51
0.35	1.50	0.25	120		41.26	- 1.38
0.50	0.25	0.50	110		41.23	- 1.41
2.00	0.10	1.00	90		42.48	- 0.16
0.35	1.50	0.15	100	36.95	36.56	- 0.39
0.75	0.10	0.25	120		36.57	- 0.38
0.75	2.50	0.15	100		36.24	- 0.71
1.00	0.25	0.50	90		36.07	- 0.32
0.50	1.00	2.50	100	28.43	28.62	+ 0.19
1.00	1.00	0.50	120		27.69	- 0.74
1.00	0.50	2.50	110		28.04	- 0.39

(1) Corrected for iron present, on the assumption that complete oxidation of the ferrous iron takes place.

SUMMARY

The Beckman Model K Automatic Titrator was found to be satisfactory for the potentiometric titration of uranium with potassium dichromate. The precision for uranium in the range of 20 to 100 mg is 0.2 per cent whereas for smaller quantities of uranium the precision is of the order of 0.5 per cent. When the amount of uranium being titrated was less than 20 mg, the coefficient of variation of the automatic and manual methods of titration is essentially the same; otherwise, the precision of the automatic method is better.

On the basis of the tests that were made these conditions were selected for the use of the automatic titrator,

(1) Potential "settings" at - 80 mv and 640 mv as the end-points for the titration at temperatures of 90 to 95°C;

(2) Gauze type of platinum electrode;

(3) Approximately 0.01 N potassium dichromate; and

(4) Hydrogen-ion concentration of about 1 N in H_2SO_4.

After optimum conditions for the automatic titrator were established, samples that contained other constituents were tested for uranium. The precision obtained for the analysis of these samples was comparable to that achieved when standard solutions of uranium were tested by this method. The negative bias, which was found to be characteristic of the automatic titrator method, was also noted for the analysis of these samples.

ACKNOWLEDGMENTS

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RECOMMENDED METHOD

Potentiometric Titration of Uranium With the Beckman Model K Automatic Titrator

The method that was used to determine the applicability of the Beckman Model K Automatic Titrator[17] for the potentiometric titration of uranium is described in detail in this section. Directions for the preparation of the reagents are also included.

Reagents

Potassium Dichromate, $K_2Cr_2O_7$, 0.01 N, National Bureau of Standards No. 136. Prepare by dissolving 0.5 g of the salt, $K_2Cr_2O_7$, in 250 ml of an aqueous solution which contains 50 ml of concentrated sulfuric acid. Dilute to volume in a one-liter volumetric flask.

Chromic Sulfate, $Cr_2(SO_4)_3$, approximately 0.04 N. Prepare by dissolving 15 g of the reagent grade salt, $Cr_2(SO_4)_3 \cdot 18H_2O$, in one liter of 5 v/v per cent sulfuric acid.

Uranyl Sulfate, standard solution. Weigh an appropriate amount of U_3O_8 to the nearest 0.1 mg. Dissolve the U_3O_8 to the nearest 0.1 mg. Dissolve the U_3O_8 in 1:1 nitric acid, add a few ml of conc. sulfuric acid, then evaporate the solution to fumes of sulfur trioxide. Dilute with a few ml of water; repeat the addition and evaporation of sulfuric acid to fumes of sulfur trioxide. Dilute to an appropriate volume then adjust the acidity to 5 v/v per cent sulfuric acid.

Chromous Sulfate, $Cr_2(SO_4)_3$. This solution is prepared as required, by passing a 0.04 N solution of chromic sulfate through a column that contains 20 ml of zinc amalgam. The chromous sulfate solution is added directly from the reductor to the solution which is to be analyzed.

Sulfuric Acid, H_2SO_4, 5 v/v per cent or approximately 1 N. Prepare by diluting 50 ml of conc. H_2SO_4 to one liter.

Procedure

Sample Conditions. The uranium content of the sample portion should be 20 to 100 mg/100 ml of solution. The acidity of the solution should be about 5 v/v per cent in H_2SO_4 or approximately 1 N. If the acidity is other than 5 v/v per cent in H_2SO_4, some slight loss in precision and accuracy must be anticipated.

Reduction Process. In carrying out the reduction step, the solution to be analyzed is placed in the position indicated in Figure 2. The solution is heated by means of a tantalum coil heater to 90 - 95°C, while being stirred and deaerated simultaneously with nitrogen (See Note A) for about one minute. The "acid-set-base" switch is set at "acid", while the potential indicator (pH-MV dial) is turned to -80 mv. After these steps, a volume of chromous sulfate sufficient to reduce the uranium is added (See Note B).

Notes:

A. Flatt and Sommers[4] report that U^{+4} is slowly oxidized in air. For this reason, the titrations are carried out in an inert atmosphere of nitrogen. The gas is washed with 50 per cent KOH, passed through "Oxsorbant" and then bubbled into the titration medium through a porcelain frit.

B. After the sample solution has been stirred, deaerated, and heated for one minute the chromous sulfate is added from the Jones reductor in small amounts until the indicator light comes on and remains on. The pH-MV dial is then set at -140 mv while the "acid-set-base" switch is turned to "base." A slight excess of Cr^{+2} is permitted to flow until the anticipator begins clicking. While the chromous sulfate is being added the stopcock to the buret that contains the dichromate solution must be in the off position.

Oxidation Process. The oxidation process is carried out immediately after the reduction of uranium with chromous sulfate. In this step of the procedure, the controls for the automatic titrator are set while the potential indicator is adjusted to -80 mv; the dichromate solution is then allowed to flow into the solution of reduced uranium. The flow of the dichromate solution continues until the light on the indicator knob re-appears. This is the end-point of the first oxidation step (See Note C).

The potential indicator is then re-set at either 540 or 640 mv, (See Note D) after which the addition of the dichromate solution is continued until the light re-appears. At this point the oxidation of uranium is complete.

Notes:

C. The titration of the first sample of a series should be watched carefully. The first position of the pH-MV dial should be at 150 mv. When the indicator light starts flashing, advance the pH-MV dial 20 to 40 mv. When this is done, the indicator light stops flashing, thus permitting the free flow of the solution to continue. This process is repeated until the advance of 20 mv on the dial causes only a more rapid flashing of the indicator light. The flashing is permitted to continue until the indicator light flashes on and remains on. The anticipator must cause the light to flash at least 8 to 10 times before an accurate end-point can be expected.

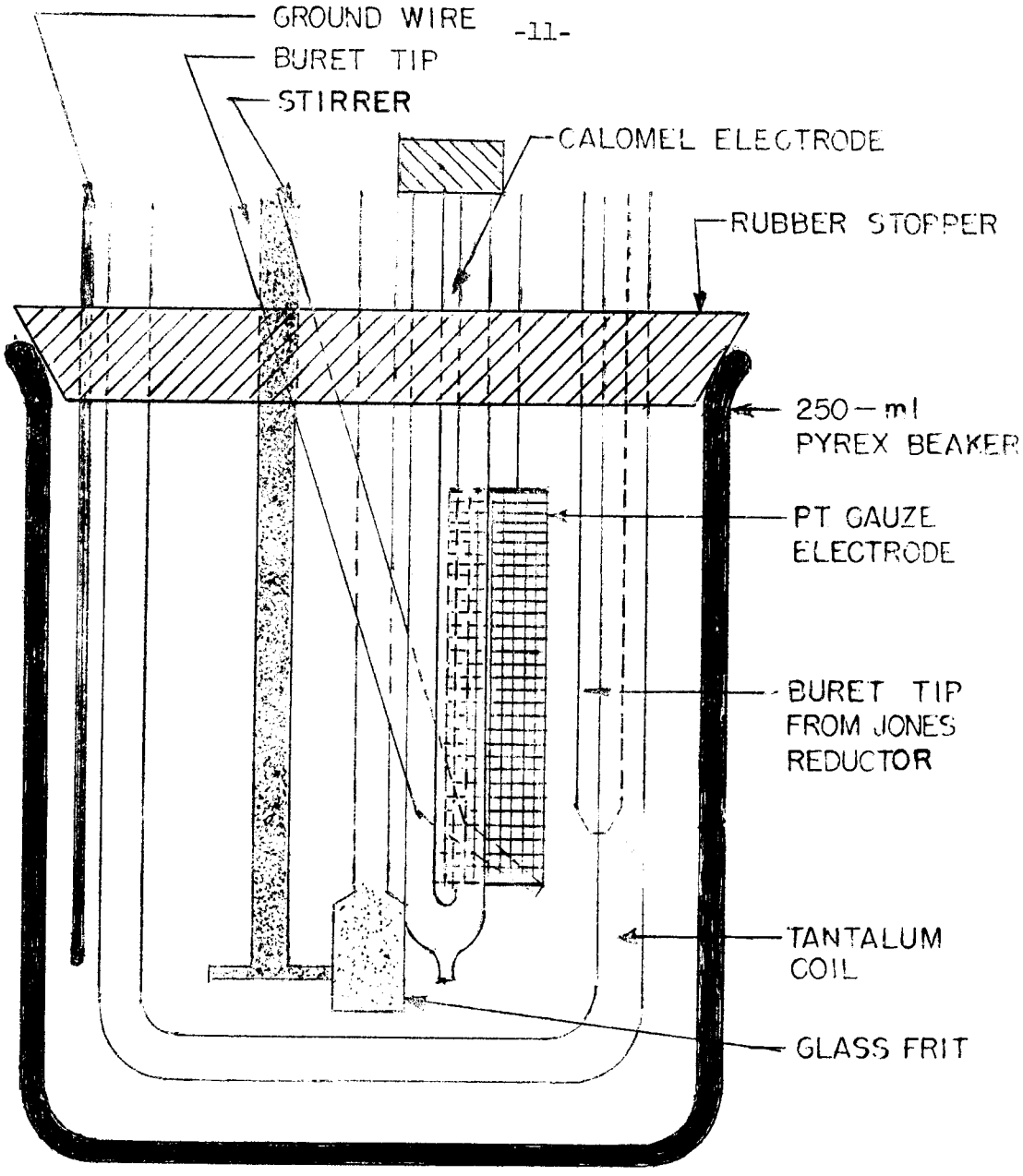

FIGURE 2. TITRATION ASSEMBLY

D. For solutions in which the quantity of uranium is more than 20 mg/100 ml the anticipator is set at 4, the pH-MV dial is first set at -140 mv, and then it is advanced to -80 mv. The titration is continued until the indicator light flashes on and remains on; then the potential is advanced gradually to 640 mv. For more dilute solutions the potential is advanced to 540 mv rather than 640 mv. This gradual increase in the voltage in all cases allows the solution to become thoroughly mixed as well as permitting the potential between the electrodes to become more stable.

Calculations. From the volume of dichromate solution that is required to oxidize the uranium, the concentration of uranium is calculated by multiplying the milliequivalents of potassium dichromate by 119, the milliequivalent weight of uranium.

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