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COULOMETRIC TITRATION OF URANIUM IN NITRIC ACID SOLUTIONS

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Analytical Chemistry Division

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ABSTRACT

A coulometric titration was developed for the determination of uranium in nitric acid solutions. Uranium was reduced to the (IV) state and was titrated with electrolytically generated cerium(IV). The colorimetric end point was detected automatically by a photometric technique. Interference from nitrate was eliminated by the addition of urea to the titration medium.

The coefficient of variation for the analysis of uranium was 3.2% for 1-mg samples and 0.3% for 100-mg samples. With the addition of urea as much as 4.5 milliequivalents of nitric acid in a 1 to 3-ml sample was tolerated.

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COULOMETRIC TITRATION OF URANIUM IN NITRIC ACID SOLUTIONS

INTRODUCTION

A general volumetric method for the analysis of uranium in nitric acid solutions is described by Rodden[1]. According to this procedure, the sample is heated with hydrochloric or sulfuric acid to remove nitrates and the uranium(VI) is then reduced to U(IV) in a lead reductor. Finally, the solution of U(IV) is titrated to a visual end point with standard ceric sulfate. Although this method provides excellent precision and accuracy, the analytical time is quite long due primarily to the time required for the removal of nitrates.

A refinement of the volumetric method involves the coulometric generation of the oxidant and automatic detection of the end point. Furman, Bricker, and Dilts[2] reported a coulometric method whereby U(IV) was titrated with generated cerium(IV) after the reduction of the uranium by cadmium amalgam. Wise, Gilles, and Reynolds[3] described an automatic coulometer in which the end point was detected by a photometric technique and showed that this technique eliminated some of the problems that are encountered in the use of electrometric end points. Significant savings in analytical time were offered by the automatic coulometer, and the precision and accuracy of titrations with this instrument were at least equal to those of conventional volumetric methods.

The objective of this work was to develop an analytical method for uranium that would avoid the need to remove nitrates from the sample. Most samples of uranium are in nitric acid solution, which causes high results in the Redox reactions.

In addition, it was desirable to minimize the amount of uranium required in the titration to permit the convenient analysis of samples that contain moderate levels of radioactivity.

SUMMARY

A method was developed for the coulometric titration of uranium in nitric acid solution. Uranium was reduced by cadmium amalgam and was added to an electrolyte that contained urea, iron(III), and cerium(III). The urea in the electrolyte destroyed nitrites formed in the reductor column. The Fe(II) formed by the oxidation of U(IV) was titrated with generated Ce(IV) to a colorimetric end point. A photometric technique then provided an automatic titration of uranium.

The coefficient of variation for the titration of uranium was 3.2% for 1-mg samples and 0.3% for 100-mg samples. There was no interference from as much as 4.5 milliequivalents of nitric acid. Although the precision and accuracy are below those of some existing methods, the

advantage gained by the elimination of interference from nitrates makes the method useful in situations where the better precision of slower methods is not required.

DISCUSSION

In this procedure U(VI) is reduced to U(IV) by cadmium amalgam and the solution is then added to the electrolyte that contains an excess of iron(III), cerium(III), and urea. The U(IV) is oxidized to the (VI) state by the Fe(III) and an equivalent quantity of Fe(II) is formed. Cerium(IV) is generated in the electrolyte and oxidizes Fe(II); at the end point of this reaction the color change of the indicator is detected photometrically and the generation of Ce(IV) is terminated automatically. The urea was added to remove the interference that was caused by the presence of nitrite ion.

Different methods were examined for the detection of the end point. After a suitable method was found, the procedure was used to study the elimination of interference from nitrates in the titration of uranium.

REAGENTS

ELECTROLYTE

In order to generate Ce(IV) with 100% current efficiency it is necessary to maintain a high concentration of Ce(III) in the electrolyte. Also, since Ce(IV) reacts slowly with U(IV), Fe(III) had to be present in the electrolyte. Iron(III) is reduced stoichiometrically by the U(IV) to Fe(II) which reacts rapidly with Ce(IV). Furman, Bricker, and Dilts[2] found that these requirements were met by a solution of 0.13M ferric sulfate - 0.17M cerous sulfate in 1.5M sulfuric acid.

To prevent the precipitation of ferric salts during the preparation of this solution, 50 grams of ferric sulfate was heated with 42 ml of concentrated sulfuric acid until a thick, pasty mass was formed. This mixture was then dissolved in water, 120 grams of cerous sulfate octohydrate was added, and the solution was diluted to 1 liter with water.

FERROIN INDICATOR

The commercially available 0.025M solution of o-phenanthroline ferrous sulfate was used as an indicator.

STANDARD URANYL NITRATE SOLUTION

Uranyl nitrate hexahydrate was dissolved in 1.5M nitric acid. To standardize this solution, aliquots were evaporated to dryness and ignited to U_3O_8 at 950°C.

STANDARD URANYL SULFATE SOLUTION

One volume of sulfuric acid was added to six measured volumes of the standard solution of uranyl nitrate. This solution was evaporated to fumes of sulfuric acid, tested for traces of nitrate, and diluted to the original volume. This procedure gave a solution approximately 3M in sulfuric acid.

CADMIUM AMALGAM

The cadmium amalgam was prepared as suggested by Furman, Bricker and Dilts[2]. Mercury was covered with 6N sulfuric acid and heated until the acid began to boil. Cadmium metal was added to the hot mixture until no more would dissolve in the mercury, and the solution was then cooled slowly with constant stirring to prevent the formation of lumps. When the mixture had cooled, a granular amalgam of 26% cadmium was obtained.

APPARATUS

The apparatus consisted of a cadmium amalgam reductor column, a Beckman Model B spectrophotometer, a titration cell, a constant current generator, and a control unit from a Beckman Model K automatic titrator. A schematic diagram of the apparatus is shown in Figure 1.

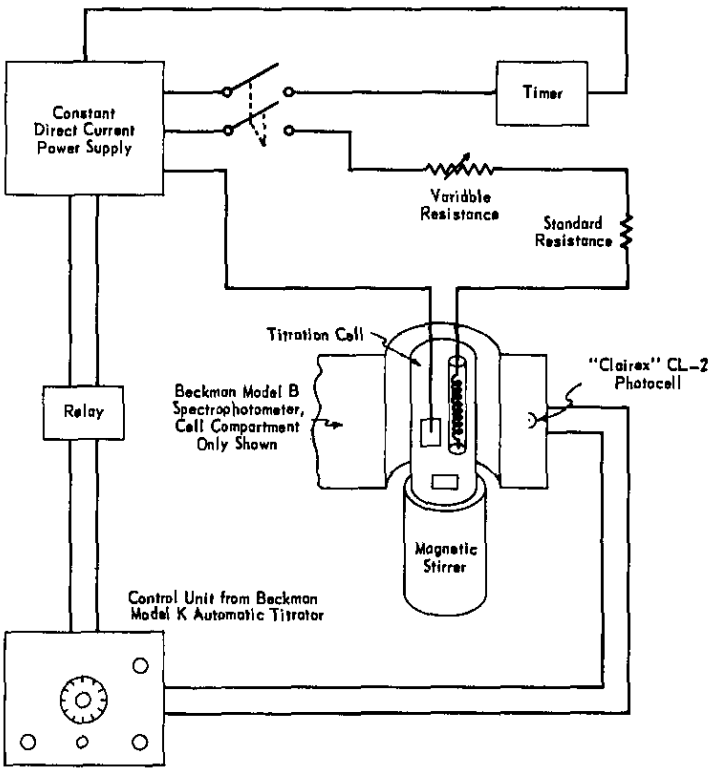


FIG. 1 SCHEMATIC DIAGRAM OF APPARATUS

In order to ensure complete reduction of the uranium in a minimum volume of solution, the cadmium amalgam was packed into columns that were varied in size with the quantity of uranium in the sample. Column dimensions for two quantities of uranium are given in the following table.

Column Dimensions Required for Complete Reduction of Uranium

Uranium, mg	Minimum Column Dimension, mm
10	6 x 100
100	25 x 450

A Beckman Model B spectrophotometer was modified to hold a titration cell and to permit a stirring apparatus to be placed under the titration cell. To increase the sensitivity of the end point, the photocell of the spectrophotometer was replaced by the more sensitive CL-2 photocell of Clairex Corporation.

The titration cell housed the generating electrodes in such a way that they did not interrupt the light path from the monochromator to the photocell. The electrodes used for the generation of Ce(IV) were a platinum sheet cathode and an isolated platinum wire anode. When the cathode surface was 1 x 2 cm or larger, current efficiencies of 100% were obtained with generating currents of 1 to 180 ma. To ensure this high current efficiency the cathode dimensions were made 2 x 4 cm. The anode was a helix of platinum wire immersed in 3M sulfuric acid. The anode compartment was a 1 x 10-cm glass tube that was separated from the electrolyte by an anion exchange membrane.

The constant current power supply had a range of 0.116 to 182 ma and a precision of 0.01% over this range.

A convenient response of the control unit Beckman titrator throughout a titration was 0 to 1 volt. To adjust the unit to operate in this range a titration of the indicator was carried 0.5 minute beyond the visual end point, and the voltage divider for the output of the photocell was adjusted so that the titrator balanced at 1 volt.

ANALYTICAL PROCEDURE

To avoid an indicator or electrolyte blank, it was necessary to pretitrate the indicator and impurities in the electrolyte. The apparatus was assembled with 35 ml of electrolyte in the cell, and two drops of ferroin indicator and 2 g of urea were added. The wavelength was set at 512 mμ and the titrator was turned on to start the generation of Ce(IV). An anticipator setting was used such that the titrator anticipated the end point at least four times. After the end point, the titrator was turned off, and the timer was reset to zero.

A sample of 1 to 3 ml was reduced in the reductor column and the column was washed with 10 ml of 1.5M sulfuric acid. To ensure complete reduction of the uranium the flow from the reductor column to the titration cell was adjusted to a maximum rate of 100 drops per minute. The titration was carried out according to the procedure described above. During the titration the potential across the standard resistance was measured, and the total time for the titration was recorded. From these measurements the uranium concentration of the sample was calculated.

DETECTION OF THE END POINT

MANUAL DETECTION OF THE END POINT

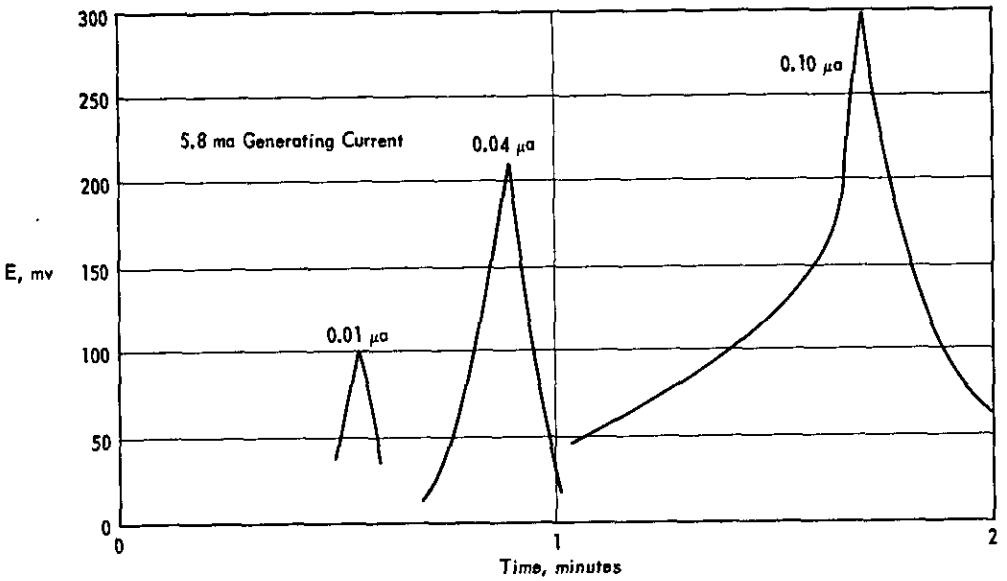
Various end point techniques were tried manually in order to find a system that might be used automatically. Of these the derivative polarographic and photometric end points proved most satisfactory.

The derivative polarographic end point was described by Reilly, Cooke, and Furman[4] and was used by Furman, Bricker, and Dilts[2] in the coulometric titration of uranium. Two platinum wire electrodes about 1 cm in length are polarized by a small constant current, 1 μa or less. The potential difference across these electrodes reaches a maximum at the end point of a titration. A comparison is given in Figure 2 of curves for end points observed for different values of the indicating current across the electrodes. Also shown in Figure 2 are the curves obtained when various generating currents are used.

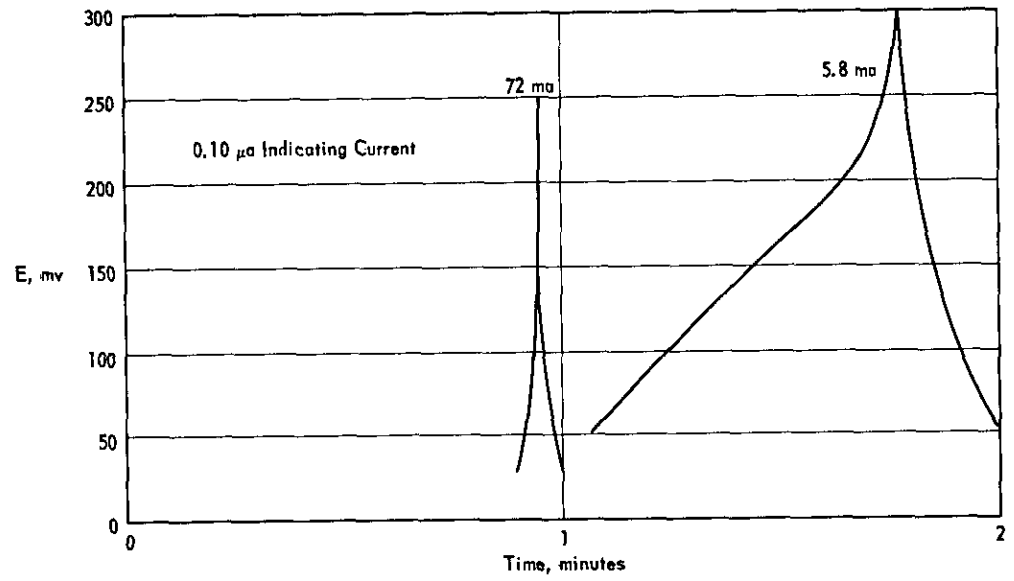
As seen in the figure, the sharpness of the end point increased when a higher generating current or a lower indicating current was used. However, the increase in sharpness was accompanied by a lower peak height. As the peak height is lowered it becomes increasingly difficult to detect the end point automatically. In addition, the electrode reactions reached equilibrium slowly so that it was necessary to generate the titrant in small increments near the end point. For these reasons the derivative polarographic technique was not adapted to automatic detection of the end point. The derivative technique gave accurate and precise results for the manual titration of uranium as shown by the data in the following table.

Results With Manual End Points

Uranium Concentration, mg/ml	Titration Time, min	Generating Current, ma	Indicating Current, μa	Recovery, %	Coefficient of Variation, %	Samples Run, No.
Derivative Polarographic End Point						
0.9	7	1.7	0.02	100.1	0.90	8
8.8	20	5.8	0.04	99.9	0.20	8
88	16	76.0	0.10	99.9	0.10	8
Photometric End Point						
8.8	8.4	11		100.7	0.20	7
88	14	84		100.4	0.20	8



Effect of Indicating Current Value on Sharpness of End Points



Effect of Generating Current Value on Sharpness of End Points

FIG. 2 DIFFERENTIAL POLAROGRAPHIC END POINT

Curves are shown in Figure 3 for photometric end points obtained with various generating currents. These end points were obtained by absorbance measurements at 512 mμ, which is the wavelength of maximum absorbance of ferroin indicator in the reduced state. For all generating currents the end points were sharp and the magnitude of the change in absorbance was sufficient for detection by an automatic technique. The response of the photometric end point was much faster than the differential polarographic end point, and for this reason the photometric technique was evaluated for automatic detection at the end point. Results for the manual titration of uranium in nitric acid solutions with the photometric end point are given in preceding table.

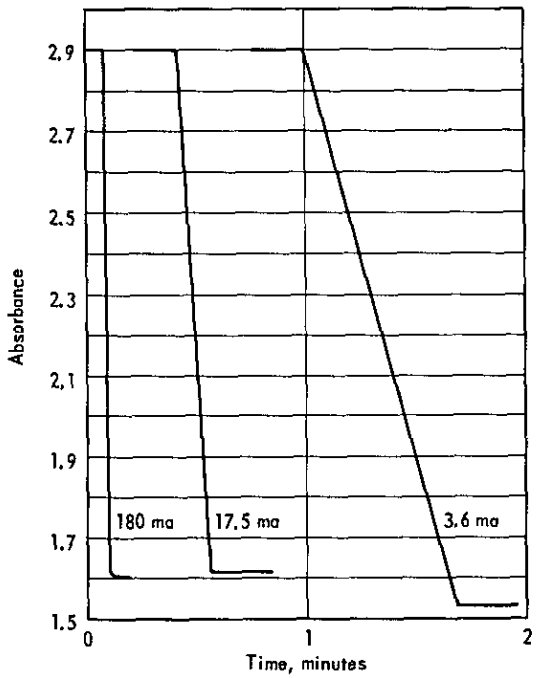


FIG. 3 MANUAL PHOTOMETRIC END POINT

AUTOMATIC DETECTION OF THE END POINT

In order to adapt the photometric end point to an automatic titration the signal from the photocell was divided with a voltage divider so that the maximum output was 1.00 v. This signal was fed into the control unit of the Beckman titrator. A relay system between the titrator and the constant current power supply was used to shut off the current automatically at a preselected potential.

To determine the proper end point potential some photometric titrations were followed manually with the relay system disconnected. As shown in Figure 4, the maximum rate of change in potential occurred at 400 mv, which therefore was used as the shut-off potential for all of the automatic end points.

To compare the photometric titration with a potentiometric titration a Pt | | Ag | AgCl electrode system was inserted in the electrolyte during some of the titrations. Potential readings were taken with a pH meter during the titrations and the potentiometric curves were plotted at the same time as the photometric curves. As shown in Figure 4, the photometric end point was much sharper than the potentiometric end point. Also, the color change of the indicator was more rapid than the response of the electrode system, and was more suitable for an automatic titration.

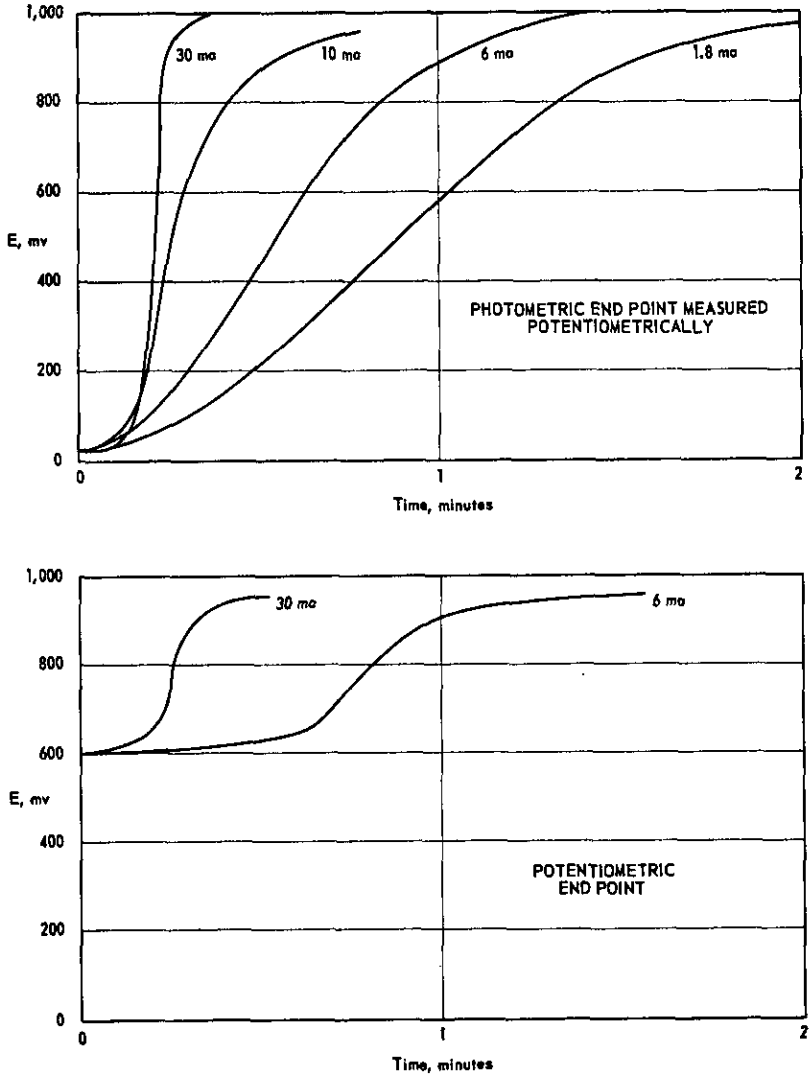


FIG. 4 COMPARISON OF PHOTOMETRIC AND POTENTIOMETRIC END POINTS

ELIMINATION OF INTERFERENCE BY NITRIC ACID

When samples of uranium in sulfuric acid were reduced and titrated according to the procedure described above, stoichiometric results were obtained; however, when nitric acid was present a fading end point occurred and the results for uranium were more than 25% high. This fading was similar to that which causes high results in the volumetric procedure when nitrates are present in the sample. When sodium nitrite was added to the titration cell at the end point or when nitric acid was added through the reductor column, the end point also faded. Since no fading occurred when nitric acid was added directly to the titration cell, the interference was attributed to formation of nitrous acid by reduction of nitrate in the reductor column.

Urea destroys the nitrite ion by the following reaction:

$$2H^{+} + 2NO_2^{-} + CO(NH_2)_2 \longrightarrow 2N_2 + CO_2 + 3H_2O$$

When urea was added to the titration cell, the end point did not fade in any of the treatments described in the previous paragraph and accurate results were obtained for the titration of uranium. A high concentration of urea in the titration medium was required for complete destruction of nitrites. As shown in the results the addition of 2 g of urea to the electrolyte, prior to addition of the samples from the reductor, was sufficient to eliminate the interference from as much as 4.5 meq of nitric acid in sample sizes of 1 to 3 ml.

RESULTS

As a demonstration of the method, replicate coulometric analyses were made on three standard solutions of uranium in 3M H_2SO_4. Then four standard solutions of uranium in 1.5M HNO_3 were similarly analyzed with 2 g of urea added to the electrolyte in each case. The recoveries are shown in the table below and the precisions were comparable to existing methods. This method required about 20 minutes in contrast to the 120 minutes that is required for the volumetric determination of uranium in nitric acid. Although the results become less precise as smaller amounts of uranium are taken in the aliquot, the precision is adequate for the analysis of moderately radioactive solutions. By appropriate shielding, larger samples may be analyzed with a corresponding gain in precision. The results are given in the following table.

Coulometric Titration of Uranium

U Std., mg/ml	No. Determinations		Coefficient of Variation		Recovery, %	
	3M H_2SO_4	1.5M HNO_3	3M H_2SO_4	1.5M HNO_3	3M H_2SO_4	1.5M HNO_3
1.4	-	10	-	3.2	-	98.6
7.1	7	46	0.39	1.5	101.1	100.2
35.7	7	32	0.44	0.53	99.0	100.7
107.1	7	14	0.82	0.27	96.9	98.9

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