

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

**THE VOLUMETRIC DETERMINATION OF URANIUM.  
POTENTIOMETRIC TITRATION OF REDUCED URANIUM  
SOLUTIONS WITH CERIC SULFATE, OR WITH POTASSIUM  
PERMANGANATE. APPLICATION OF THE DIFFERENTIAL  
METHOD**

BY N. HOWELL FURMAN AND IRL C. SCHOONOVER<sup>1</sup>

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**Introduction**

This investigation deals with the reduction of hexavalent uranium by amalgamated zinc, and with the potentiometric titration of the reduced solutions with standard permanganate or ceric sulfate solution. This study was found to be a necessary preliminary to the development of volumetric methods which are based upon the reactions of quadri- or hexavalent uranium with other substances as, for example, sodium, fluoride or phosphate ion.

The literature regarding the reduction of hexavalent uranium with zinc, or zinc amalgam, contains many contradictory statements. The chief point upon which disagreement has existed has been the extent to which reduction proceeds. A number of investigators have concluded that reduction proceeds quantitatively to the quadrivalent state.

Belohoubek<sup>2</sup> studied the reduction of uranyl sulfate, chloride, acetate, and nitrate with zinc. An attempt was made to exclude air while the solution cooled after the reduction. The solution was diluted "until the color disappeared," acid was added, and then the titration was made. Good results were reported for the sulfate and chloride solutions, poor ones in the case of the acetate and extremely poor ones for the nitrate solutions. No formation of trivalent uranium was observed.

Follenius<sup>3</sup> reduced uranyl acetate solutions with zinc and sulfuric acid; air was excluded. He found no reduction beyond the quadrivalent state; his results demonstrated clearly that the addition of hydrochloric acid before the titration caused too much permanganate to be consumed.

Zimmermann<sup>4</sup> treated 5 or 10 cc. portions of a uranium nitrate solution with 10 or 20 cc. of sulfuric acid of sp. gr. 1.23. After the mixture had been heated until sulfur trioxide was evolved, the solution was diluted and reduced with zinc in the absence of air. He found no evidence of the formation of trivalent uranium. In hydrochloric acid solutions, on the

<sup>1</sup> Merck Fellow in Chemistry.

<sup>2</sup> Belohoubek, *J. prakt. Chem.*, **99**, 231 (1866); *Z. anal. Chem.*, **6**, 120 (1867); application of the reaction to determination of phosphate, *ibid.*, **16**, 104 (1877).

<sup>3</sup> Follenius, *ibid.*, **11**, 179 (1872).

<sup>4</sup> Zimmermann, *Ann.*, **213**, 300 (1882).

contrary, trivalent uranium was formed. Zimmermann proved that the addition of manganous sulfate prevented the interaction between permanganate and hydrochloric acid, just as is the case with iron solutions.

Kern<sup>5</sup> reported that aluminum, magnesium, zinc, or zinc amalgam, reduce uranium quantitatively to the quadrivalent condition in sulfuric acid solution, whereas stannous chloride in hydrochloric acid solution forms some  $\text{UCl}_3$  as well as  $\text{UCl}_4$ .

Of the more recent investigations in which no over-reduction (*i. e.*, formation of  $\text{U}^{\text{III}}$ ) was found, especial mention should be made of those of Gustavson and Knudson<sup>6</sup> and of Müller and Flath.<sup>7</sup> Although these investigators excluded air very carefully during the reduction, and performed the titrations potentiometrically, they found no evidence of reduction beyond the quadrivalent state in sulfuric acid solutions.

Failure to find over-reduction may have been due to incomplete exclusion of air in the earlier investigations, or to high acid concentration. The difficulty of reduction of  $\text{U}^{\text{VI}}$  solutions increases with the square of the hydrogen-ion concentration (or rather activity), as is shown by the e. m. f. relation, at 25°

$$E = E_0 + \frac{0.0591}{2} \log \frac{(\text{UO}_2^{++})(\text{H}^+)^4}{(\text{U}^{++++})} = E_0 + \frac{0.0591}{2} \log \frac{(\text{UO}_2^{++})}{(\text{U}^{++++})} + 0.0591 \log (\text{H}^+)^2$$

Luther and Mitchie<sup>8</sup> found that this expression, in terms of concentration, applied accurately over the range 0.1 *N* to 1 *N* sulfuric acid concentration.

The following investigators have all found evidence that the reduction proceeds partially to the trivalent stage in sulfuric acid solution with zinc or zinc amalgam as the reducing agent. Guyard<sup>9</sup> reported the formation of a mixture of salts of lower oxides upon reduction of acidified uranium solutions with zinc. He was unable to obtain accurate results with permanganate.

Pulman,<sup>10</sup> using a Jones reductor, found partial reduction of quadri- to trivalent uranium, and called attention to the rapidity with which the latter was reoxidized by air.

McCoy and Bunzel<sup>11</sup> found over-reduction with zinc, and proved that with a uranium solution which was 4 *N* in sulfuric acid, the trivalent form was rapidly converted to the quadrivalent, and the latter was only slowly oxidized by air at room temperature. The speed of oxidation of  $\text{U}^{\text{IV}}$  to  $\text{U}^{\text{VI}}$  was found to be approximately inversely proportional to the square root of the hydrogen-ion concentration.

<sup>5</sup> Kern, *THIS JOURNAL*, 23, 685 (1901).

<sup>6</sup> Gustavson and Knudson, *ibid.*, 44, 2756 (1922).

<sup>7</sup> Müller and Flath, *Z. Elektrochem.*, 29, 500 (1923).

<sup>8</sup> Luther and Mitchie, *ibid.*, 14, 826 (1908).

<sup>9</sup> Guyard, *Bull. soc. chim.*, [2] 1, 89 (1864), *cf.* especially pp. 94-95.

<sup>10</sup> Pulman, *Am. J. Sci.*, 16, 229 (1903); *Z. anorg. allgem. Chem.*, 37, 113 (1903).

<sup>11</sup> McCoy and Bunzel, *THIS JOURNAL*, 31, 367 (1909).

Pierle<sup>12</sup> found over-reduction in the Jones reductor with sulfuric acid concentrations approximating one volume of acid in six volumes of solution.

Treadwell<sup>13</sup> and Ewing and Eldridge<sup>14</sup> found over-reduction with zinc or cadmium, or with zinc amalgam, respectively. Air was carefully excluded by a current of carbon dioxide. The potentiometric titrations with potassium permanganate gave a sharp inflection in the e. m. f.-cc. graph at the completion of the oxidation,  $U^{III} \rightarrow U^{IV}$ , and a second sharp inflection at the end of the process  $U^{IV} \rightarrow U^{VI}$ .

Lundell and Knowles<sup>15</sup> pointed out the advantages of reducing *cold* solutions of iron, uranium and other elements, in the Jones reductor. Over-reduction of uranium occurs in the cold solution to about the same extent as in hot solutions. These investigators<sup>16</sup> demonstrated by quantitative tests that in solutions containing 5% of concentrated sulfuric acid by volume, the trivalent uranium which is formed is oxidized rapidly by the action of a stream of air in one to five minutes; the quadrivalent uranium is relatively stable in air at room temperature (as long as four hours), but is oxidized very rapidly by air at 60–80°.

The results of this investigation confirm the findings of Lundell and Knowles, Treadwell, Ewing and Eldridge, Pierle, McCoy and Bunzel and Pulman regarding the fact of over-reduction of uranium in solutions containing 2–5% of sulfuric acid of sp. gr. 1.84 by volume. Upon reduction of either hot or cold solutions in the Jones reductor the characteristic brownish color of a mixture of tri- and quadrivalent uranium salts was evident, and the potential (Pt *vs.* reference electrode) gave evidence of the presence of a more powerful reducing agent than  $U^{IV}$ . The amount of standard oxidizing agent which was consumed by the trivalent salt was extremely variable in duplicate determinations made under like conditions. In extreme cases more than 40% of the uranium was reduced to the trivalent state; generally from 25–40% of the uranium was in the trivalent condition.

Our results with regard to the ease of oxidation of  $U^{III}$  by air, and the relative stability of  $U^{IV}$  in air at room temperature confirm the findings of Lundell and Knowles.

A new method of determination, namely, titration of reduced uranium solutions with standard ceric sulfate, has been compared with the permanganate method; the potentiometric method was employed. The work of Treadwell and of Ewing and Eldridge has been confirmed with reference to the permanganate titration.

<sup>12</sup> Pierle, *Ind. Eng. Chem.*, **12**, 60 (1920).

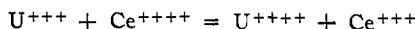
<sup>13</sup> W. D. Treadwell, *Helv. Chim. Acta*, **5**, 732 (1922).

<sup>14</sup> Ewing and Eldridge, *THIS JOURNAL*, **44**, 1484 (1922).

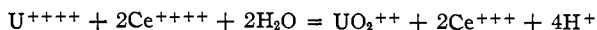
<sup>15</sup> Lundell and Knowles, *Ind. Eng. Chem.*, **16**, 723 (1924).

<sup>16</sup> Lundell and Knowles, *THIS JOURNAL*, **47**, 2637 (1925).

A small quantity of iron (1 mg. per 25 cc.) is present in the 0.1 *N* ceric sulfate solutions which are prepared directly from commercial rare earth oxides.<sup>17</sup> The graph of the potentiometric titration data, therefore, shows three inflections (see Fig. 2), the first at the end of the oxidation of the trivalent uranium



the second at the end of the reaction



and the third at the end of the reoxidation of the ferrous iron that is produced as the titration progresses. The amount of iron which is introduced up to the end of the oxidation of trivalent uranium is practically negligible. The experimental results show that the amount of ceric sulfate which is added between the first and the third inflections corresponds accurately to two equivalents of ceric ion per mole of  $U^{IV}$ . In other words, the ferrous iron is produced at the expense of an equivalent amount of quadrivalent uranium. It is more correct in principle to oxidize the trivalent uranium with air before starting the titration with ceric sulfate. It is at once evident that a crude ceric solution containing ferric iron should not be used in the simultaneous determination of uranium and iron.

It was found difficult or impossible to obtain concordant results when the side-arm of a saturated calomel half-cell dipped directly into the reduced solution. The use of a sulfate half-cell and bridge of saturated potassium sulfate eliminated the error. It was found that the differential titration method of MacInnes and Jones,<sup>18</sup> when used in the modified form which Clarke and Wooten<sup>19</sup> developed for work in an indifferent atmosphere, gave excellent results for all of the three inflections. This is apparently the first time that the possibility of the determination of a succession of oxidation-reduction end-points by the differential method has been demonstrated.

### Experimental

**Apparatus and Materials.**—The titration vessel (a 250-cc. extraction flask) and its accessories are represented in Fig. 1. The simple expedient of inserting electrodes, buret, reductor and thermometer through tightly-fitting rubber tubes (F), mounted on the tops of glass tubes which were permanently mounted in the rubber stopper (G), made it very easy to replace or modify parts of the apparatus.

A Leeds and Northrup students' type potentiometer and portable galvanometer (Type 2320d) and a Weston saturated standard cell were used. Various electrode assemblies were used: (1) Pt *vs.* saturated calomel; (2) Pt *vs.* saturated  $K_2SO_4/Hg_2SO_4/-Hg$ ; (3) Pt *vs.* W; (4) Pt *vs.* sheltered Pt (differential method; see H, Fig. 1).

The calibration of the volumetric glassware used was checked carefully, and the necessary corrections were applied. The tip of the buret was drawn down so that one drop of liquid amounted to 0.025 cc.

<sup>17</sup> Furman and Evans, *THIS JOURNAL*, 51, 1128 (1929).

<sup>18</sup> MacInnes and Jones, *ibid.*, 48, 2831 (1926).

<sup>19</sup> Clarke and Wooten, *J. Phys. Chem.*, 33, 1468 (1929).

Carbon dioxide from a cylinder was used.

Zinc of high purity was amalgamated with about 1% of mercury by a solution of mercuric nitrate prepared from the calculated amount of pure redistilled mercury. Frequent blank tests were made by passage of measured amounts of the sulfuric acid wash solution through the reductor. Potentiometric tests of the solutions showed that no blank correction was necessary with 0.1 *N* permanganate or ceric sulfate when the best available materials were selected.

Potassium permanganate and ceric sulfate solutions<sup>20</sup> were standardized potentiometrically against Bureau of Standards sodium oxalate.

Crystallized uranyl acetate,  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ , of reagent grade was used. Careful qualitative tests proved the absence of vanadium, iron and the copper-tin group metals. A stock solution was prepared with 20.000 g. of the salt per liter of dilute sulfuric acid (2% of  $\text{H}_2\text{SO}_4$  of sp. gr. 1.84 by volume). The uranium content of measured portions of the solution was determined either volumetrically with permanganate by the potentiometric method of Treadwell<sup>13</sup> and Ewing and Eldridge<sup>14</sup> with the  $\text{Pt-K}_2\text{SO}_4/\text{Hg}_2\text{SO}_4/\text{Hg}$  electrode system, or gravimetrically as  $\text{U}_3\text{O}_8$  after ammonia precipitation.<sup>21</sup>

This extended series of titrations fully confirmed the observations of Treadwell, Ewing and Eldridge and others on the character of this potentiometric titration. The reductions were made in cold solution as described later (under determinations with ceric sulfate). The graphs of the titration data were analogous to that of Fig. 2, except that there was no inflection due to iron. Titrations were made in a carbon dioxide atmos-

<sup>20</sup> The ceric sulfate was prepared from rare earth oxides as described by Furman and Evans, *THIS JOURNAL*, 51, 1128 (1929). For standardization, *cf.* Willard and Young, *ibid.*, 50, 1322 (1928).

<sup>21</sup> Following the procedure given by Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1930, p. 368.

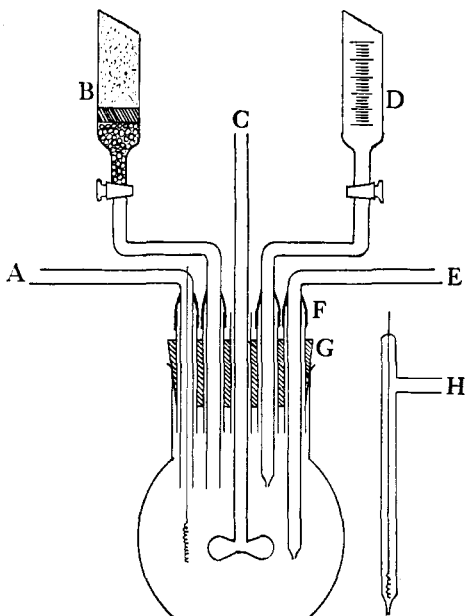


Fig. 1.—Titration vessel. A, Carbon dioxide inlet and electrode holder. A T-tube with adjustable platinum electrode was also used. B, Jones reductor. The top of the reductor was closed by a two-holed rubber stopper carrying a dropping funnel and a connection to the carbon dioxide line. C, Glass stirrer joined to a Cenco electric motor by a flexible shaft. D, Buret. E, Salt bridge to reference electrode. F, Rubber tubing. G, Rubber stopper. H, Sheltered platinum electrode which was substituted for E when the differential method was used. A T-tube, with a rubber bulb attached, was joined to the side tube of H; the T-tube was connected to the carbon dioxide supply by a tube carrying a stopcock. The stopper, G, was provided with an opening for a thermometer, not shown in the figure.

## GRAVIMETRIC STANDARDIZATION

U <sup>VI</sup> soln., cc.	20	30	25	25	10	10
U <sub>3</sub> O <sub>8</sub> found, g.	0.2653	0.3977	0.3308	0.3310	0.1318	0.1320
U found, g.	.2250	.3373	.2805	.2807	.1118	.1119

Average 0.1123 g. U per 10 cc.

VOLUMETRIC STANDARDIZATION WITH 0.1147 *N* KMnO<sub>4</sub>

U <sup>VI</sup> soln., cc.	10	10	25	25	25	25 <sup>a</sup>	50	50
KMnO <sub>4</sub> , cc.	8.22	8.22	20.56	20.58	20.53	20.57	41.13	41.12
U found, g.	0.1125	0.1126	0.2808	0.2811	0.2804	0.2809	0.5617	0.5616

Average 0.1123 g. U per 10 cc.

<sup>a</sup> The acetate was expelled by repeated evaporations with excess of sulfuric acid before the solution was reduced.

phere, and the temperature was 80–90° at the second end-point (U<sup>IV</sup> to U<sup>VI</sup>). The initial volume ranged from 135–230 cc.

**Preliminary Experiments.**—Measured portions of uranyl solution at room temperature were passed through the reductor. In every case the characteristic color and low potential of a mixed solution of U<sup>III</sup> and U<sup>IV</sup> was obtained. It was proved that three to five minutes of stirring of the reduced solution with air reoxidized U<sup>III</sup> to U<sup>IV</sup>. The process was followed by potentiometer readings, and a sharp potential break (Pt *vs.* reference electrode) of over 0.1 volt was found at the end of the oxidation, thus confirming the conclusions of Lundell and Knowles.<sup>16</sup>

Several titrations of the U<sup>IV</sup> solutions were made in air at 80–90°. Too little ceric sulfate was required. For example, portions of solution which required 9.04 cc. of 0.1043 *N* ceric sulfate under carbon dioxide, required 8.32, 8.77 and 8.90 cc. in the presence of air.

Many preliminary titrations were made potentiometrically with permanganate or ceric sulfate using a Pt-saturated calomel electrode system. Fairly concordant results could be obtained at any given initial volume with a carefully standardized procedure and with a constant amount of uranium. If double the amount of uranium was used, or if the working conditions were varied slightly, the consumption of oxidizing agent was not constant per unit volume of uranium solution, as is illustrated by the following results

Initial volume: 150–170 cc.						
U <sup>VI</sup> solution used, cc.	10	10	20	20	25	25
Ceric solution used, cc.	10.08	10.07	19.75	19.67	24.57	24.48
Ceric solution calcd., cc.	9.58	9.58	19.16	19.16	23.95	23.95

Different uranium and ceric solutions were used from those described under "standardization."

A careful study of the various possible variables: nature of electrodes, presence or absence of acetate, total acidity, etc., established the fact that the variability vanished when the saturated potassium chloride was not

used. Too much oxidizing agent is consumed when chloride is present in appreciable amount. This observation confirms Follenius'<sup>8</sup> findings with regard to the error caused by the presence of hydrochloric acid. Others who have used the potentiometric method do not mention the error due to chloride; it is probable that the use of normal or 0.1 *N* potassium chloride would decrease the error.

The Pt-W electrode system failed to indicate the end of the oxidation of  $U^{III}$  to  $U^{IV}$ , but gave an excellent indication of the other end-points ( $U^{IV}$  to  $U^{VI}$  and  $Fe^{II}$  to  $Fe^{III}$ ).

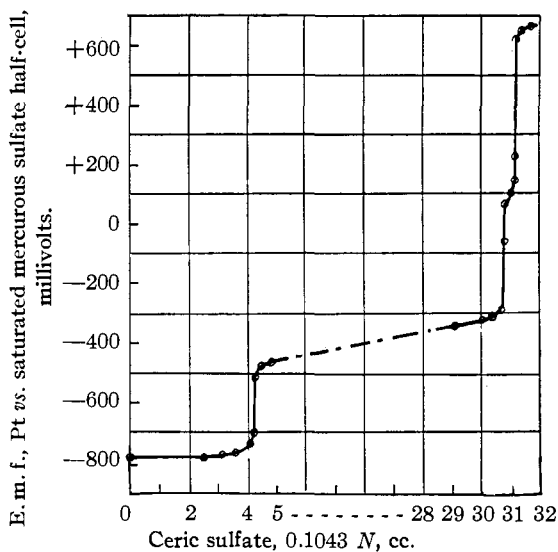


Fig. 2.—Graph representing potentiometric titration of 30 cc. of reduced uranyl solution with ceric sulfate (0.1043 *N*). The inflection at the left corresponds to the end of the oxidation of  $U^{III}$  to  $U^{IV}$ ; the next to oxidation of  $U^{IV}$  to  $U^{VI}$  and the last to  $Fe^{II}$  to  $Fe^{III}$ .

**Determinations with Ceric Sulfate Using the Pt vs.  $K_2SO_4$  (Satd.)  $Hg_2SO_4$ -Hg Electrode System.**—The reductions prior to all determinations to be described subsequently were made by a procedure analogous to that given by Lundell and Knowles.<sup>15,16</sup>

Air was displaced from the receiving flask because it was desired to obtain data upon the extent of over-reduction. Measured portions of uranyl solution containing 2% by volume of concd. sulfuric acid were forced through the reductor by carbon dioxide pressure at room temperature; the reductor was washed with 25–50 cc. portions of 2% (volume) sulfuric acid, and finally with water, until the total volume of the solution was 130–240 cc.

The heating of the reduced solution was commenced, and the titration was started; the first inflection (Fig. 2) was found while the solution was warm, and the final inflections were found in hot solution (80–90°). The graph of the data of a typical titration is shown in Fig. 2. We attribute the third inflection to iron (ferric) that is present in the ceric solution, since the same inflection is found whether acetate is present or absent (see "acetate"). An entirely analogous form of graph was produced in permanganate titrations by adding a little ferric sulfate to the uranium solution after the first inflection had been passed. Quadrivalent uranium reduces ferric iron, and in so far as all of the ferrous iron is produced by oxidation of  $U^{IV}$  to  $U^{VI}$ , it is obvious that the distance from the first to the third inflection (Fig. 2) should be equivalent to the total uranium (process  $U^{IV}$  to  $U^{VI}$ ). The amount of iron (ferric) that was introduced in the ceric solution up to the first inflection rarely exceeded 0.18 mg. and was generally less than half of this amount.<sup>22</sup> In principle it is preferable to oxidize the trivalent uranium with air before beginning the titration with ceric sulfate. The inflections were determined by the maxima of the  $\Delta e. m. f. / \Delta cc.$  values. The results are summarized in Table I. In this series of determinations the initial volume ranged from 160–240 cc.

TABLE I

POTENTIOMETRIC TITRATION OF REDUCED URANIUM SOLUTIONS WITH CERIC SULFATE  
(0.1053 *N*, Nos. 1–10; 0.1043 *N*, Nos. 11–14)

No.	$U^{VI}$ soln., cc.	$Ce(SO_4)_2$ required for $U^{IV}$ , cc.	U present, g.	U found, g.	Error, mg.	Over-reduction $Ce(SO_4)_2$ used for $U^{III}$ , cc.	% of $U^{IV}$ red. to $U^{III}$
1	10	9.00	0.1123	0.1128	+0.5	1.75	39.1
2	10	9.00	.1123	.1128	+ .5	1.55	34.6
3	10	8.96	.1123	.1123	≐ .0	1.46	32.6
4	10	8.97	.1123	.1124	+ .1	1.38	30.8
5	10	8.98	.1123	.1126	+ .3	1.47	32.8
6	20	17.97	.2246	.2253	+ .7	3.05	34.0
7	20	17.93	.2246	.2248	+ .2	3.14	35.0
8	20	17.96	.2246	.2252	+ .6	3.22	35.9
9	30	26.93	.3369	.3376	+ .7	4.22	31.4
10	30	26.92	.3369	.3375	+ .6	3.87	28.8
11	25	22.63	.2808	.2810	+ .2	3.15	27.9
12	50	45.16	.5615	.5608	- .7	4.05	17.9
13	50	45.22	.5615	.5616	+ .1	7.60	33.6
14	50	45.17	.5615	.5610	- .5	4.43	19.6

The last column of the table shows clearly the extreme variability in the extent of reduction beyond the quadrivalent stage.

<sup>22</sup> The amount of iron was determined by passing measured volumes (50 cc.) of the ceric solution through a Jones reductor, followed by potentiometric titration with standard permanganate. Found 3.20 and 2.9 mg. Average 3.1 mg. per 50 cc. of ceric solution.



**Acetate.**—Belohoubek<sup>2</sup> stated that acetate caused erratic results if present during the reduction. The results present in Table I show that the error is non-existent, or within the experimental error of the ability of an operator to read an ordinary buret, when uranyl acetate is used. Titrations were also made in absence of acetate.

Portions of the uranyl solution were evaporated to dryness after adding an excess of sulfuric acid. Sulfuric acid was again added, and the acid heated to strong fuming. After cooling and diluting to about 2% sulfuric acid content, the solutions were reduced and titrated in the usual manner. The results are shown in Table II (Nos. 1-4). In other instances weighed portions of the U<sub>3</sub>O<sub>8</sub>, after the gravimetric determination, were dissolved in sulfuric acid, reduced and titrated (Table II, Nos. 5-6).

TABLE II

TITRATION OF REDUCED SOLUTIONS OF URANIUM IN ABSENCE OF ACETATE, WITH 0.1043 N CERIC SULFATE

No.	U <sup>VI</sup> soln., cc.	Ce(SO <sub>4</sub> ) <sub>2</sub> required for U <sup>IV</sup> , cc.	U present, g.	U found, g.	Error, mg.	Over-reduction % used for U <sup>III</sup> , cc.	of U <sup>IV</sup> red. to U <sup>III</sup>
1	10	9.05	0.1123	0.1124	+0.1	1.43	31.6
2	20	18.10	.2246	.2248	+ .2	3.23	35.7
3	10	9.07	.1123	.1126	+ .3	1.08	23.9
4	25	22.61	.2808	.2808	± .0	4.45	39.4
5	20	18.13	.2246 <sup>a</sup>	.2252	+ .6	2.74	30.3
6	30	27.10	.3369 <sup>b</sup>	.3366	- .3	5.85	43.1

<sup>a</sup> Found gravimetrically, 0.2250; <sup>b</sup> 0.3373 g. of uranium.

Practically the same range of error and percentage of over-reduction is found whether acetate is present or absent. In both series of determinations (Tables I and II) the results with ceric sulfate average slightly higher than those with permanganate, or by the gravimetric method. We believe that this slight discrepancy is in large part accounted for by the reduction of a small amount of iron by the trivalent uranium.

In other determinations 10 cc. of glacial acetic acid was added to the uranium solution before it was reduced. The other conditions were the same as in the previous determinations. The acetic acid (10 cc.) consumed a drop of ceric sulfate (0.05 cc.) in the absence of uranium, and this correction was applied to the volumes of ceric sulfate found. The results were as follows.

U <sup>VI</sup> soln., cc.	Ce(SO <sub>4</sub> ) <sub>2</sub> required, cc.	U present, g.	U found, g.	Error, mg.	Ce(SO <sub>4</sub> ) <sub>2</sub> used for U <sup>III</sup> , cc.	Over-reduction, %
10	9.10	0.1123	0.1130	+0.7	0.85	19.8
10	9.08	.1123	.1128	+ .5	.45	9.96
10	9.04	.1123	.1128	+ .5	.65	14.3
20	18.15	.2246	.2254	+ .8	.55	6.1

The results appear to be consistently high in the presence of a large quantity of free acetic acid but, due to the uncertainty introduced by the correction, we are not convinced that pure acetic acid occasions any error. Errors of the same order of magnitude were observed in the absence of acetate (Table II). The percentage of over-reduction is markedly less in the solutions which contain acetic acid.

**Application of the Differential Method.**—In searching for the cause of the erratic results which were obtained when chloride was present (*cf.* preliminary experiments), the differential method of MacInnes and Jones<sup>23</sup> was applied satisfactorily to the determination of the three inflections of

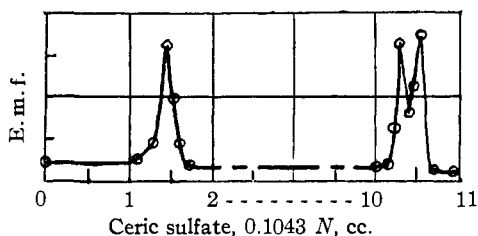


Fig. 3.—Differential titration of 10 cc. of reduced uranyl solution with ceric sulfate (0.1043 *N*). The maxima, left to right, correspond, respectively, to completion of oxidation of (1)  $U^{III}$ , (2)  $U^{IV}$ , (3)  $Fe^{III}$ .

each titration. It was found to be necessary to exclude air from the tube (H, Fig. 1) which contained the sheltered platinum electrode; otherwise very rapid oxidation of the hot solution occurred. It was found to be advisable to attach a small rubber bulb to a T-tube in the carbon dioxide line which was joined to H (Fig. 1), as was suggested by Clarke and Wooten.<sup>19</sup>

This bulb acts as a pressure regulator during slight changes in temperature, and serves as a means of expelling the liquid which surrounds the sheltered electrode. If the liquid is not changed after each addition of reagent near the end-point, the electrode, H, acts as a reference electrode, and the graph of the titration data resembles that of Fig. 2. If the liquid in the tube is changed after addition of each small increment of reagent, the succession of maxima is obtained

TABLE III  
DIFFERENTIAL TITRATION OF REDUCED URANIUM SOLUTIONS WITH CERIC SULFATE (0.1043 *N*)

No.	$U^{VI}$ soln., cc.	$Ce(SO_4)_2$ required for $U^{IV}$ , cc.	$U$ present, g.	$U$ found, g.	Error, mg.	Over-reduction $Ce(SO_4)_2$ used for $U^{III}$ , cc.	Over- reduction, %
1	10	9.08	0.1123	0.1128	0.5	1.38	30.5
2	10	9.03	.1123	.1121	— .2	1.34	29.6
3	10	9.05	.1123	.1124	.1	1.15	25.4
4	10	9.07	.1123	.1126	.3	1.35	29.9
5	20	18.10	.2246	.2248	.2	3.40	37.6
6	20	18.10	.2246	.2248	.2	3.00	33.2

The general conditions of reduction and titration were the same as those which were described for the first series of determinations (Table I).

<sup>23</sup> MacInnes and Jones, *THIS JOURNAL*, **48**, 283 (1926).

as shown in Fig. 3, which is typical of a number of titrations. A summary of the results obtained is shown in Table III.

The distance between the second and third inflections was, in general, closely proportional to the amount of ceric solution used, and was close to but slightly greater than the value calculated from the amount of iron known to be present in the ceric solution. For example, with 10 cc. of ceric sulfate used, the value should have been 0.10 cc.; found, 0.11, 0.20, 0.13, 0.20. It is probable that a reliable correction could be made for the iron if the trivalent uranium were oxidized by air before the start of the titration.<sup>24</sup>

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### Summary

This investigation has confirmed the fact that amalgamated zinc reduces hot or cold acidified uranyl solutions partially beyond the quadrivalent stage. Quantitative data are presented upon the extent of over-reduction. The ease of oxidation of trivalent uranium by air has been observed.

It has shown that a new method of oxidation of reduced uranium solutions, namely, by standard ceric sulfate, gives satisfactory results by the potentiometric method. Chloride interferes, causing erratic high results. The presence of small amounts of acetate causes no measurable interference.

The differential titration method has been applied to the determination of a succession of oxidation-reduction end-points in the titration of reduced uranium solutions with ceric sulfate.

PRINCETON, NEW JERSEY

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<sup>24</sup> During the correction of the proof of this work a communication along similar lines by D. T. Ewing and Mrs. M. Wilson appeared [THIS JOURNAL, 53, 2105 (1931)]. These investigators report interference of acetate, which we failed to find. We have subsequently applied the uranium titration with excellent results to the indirect determination of sodium in triple sodium magnesium uranyl acetate precipitates. We shall discuss the question of the interference or non-interference of acetate further in our report on the indirect determination of sodium by means of the uranium titration. Ewing and Wilson reduced boiling hot solutions, whereas the reductions reported in our work were made at room temperature; this difference in procedure may be significant.