[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF PURDUE UNIVERSITY]

The Volumetric Determination of Uranium in Highly Ferriferous Ores[1]

BY WALLIS R. BENNETT

In the course of work upon Swedish kolm in coöperation with the Committee of the National Research Council on the Measurement of Geologic Time by Atomic Disintegration it became evident that various methods for the determination of uranium in such material gave highly discrepant results.

In this kolm Wells[2] reported from gravimetric methods: U = 0.440, 0.412, 0.442 and 0.425%. By emanation method[3] Traxler and Rosenbloom under S. C. Lind found U = 0.11%; H. Schlundt by two different methods found 0.247 and 0.313%; Moore and Bennett found 0.287%.

About 20 lb. of the kolm had been received from the Committee. About one-half was ground to 60-mesh size, lumps being picked at random from the whole sample. This ground material was mixed thoroughly. A portion sent to R. C. Wells constituted the material used in the work reported by him.

The ground kolm was ashed in an electric muffle at bright red heat. The ashing was done in covered porcelain crucibles each containing 2 g. of kolm. In this manner about a kilogram of carbon-free ash was obtained which was thoroughly mixed and stored in glass-stoppered bottles. Accurate determinations of the ash/kolm ratio, 12 in all, were made at regular intervals: average 30.88%; maximum 31.10%, minimum 30.63%.

The ash of this kolm consists chiefly of silica, alumina and iron oxide. It contains small amounts of various other elements of which only molybdenum, vanadium, titanium and traces of rare earths and tellurium are capable of interfering with the volumetric determination of uranium. The purpose of this work was to find or devise a reliable method for the accurate determination of uranium in such material.

Experimental

In absence of interfering elements uranium can be determined volumetrically with permanganate in sulfuric acid solution after reduction to the quadrivalent state by a Jones reductor. Any over-reduced uranium is oxidized to the quadrivalent state by passing a current of air through the solution for five minutes before titrating.[4]

In the kolm the uranium had first to be separated from large amounts of iron and aluminum and from small amounts of titanium, molybdenum and vanadium. Preliminary experiments were carried out with solutions containing known amounts of uranium, iron, aluminum and titanium in approximately the amounts present in 3.5 g. of kolm ash.

The first method tried was the sodium carbonate and hydrogen peroxide separation of iron and aluminum from uranium, recommended by the Bureau of Mines.[5] Five determinations of uranium in a solution containing in each portion taken 0.03802 g. of U, 0.3 g. of Al, 0.4 g. of Fe and 6 mg. of Ti gave discrepant values varying from 0.0357 g. to 0.048 g. of uranium. Iron was found in the titrated solutions and the large Fe–Al precipitate contained uranium even after three re-precipitations.

The relatively enormous bulk of the precipitate made a separation of iron from uranium by cupferron unsatisfactory.

The second method tried was the extraction of iron by the use of ether saturated with hydrogen chloride from solutions containing known amounts of iron, uranium, aluminum, and titanium as chlorides. Qualitative tests showed that a trace of iron remained in the aqueous layer, even after three extractions had been made. This method might have been used as a means of removing the greater part of the iron except for the fact that the stopcock of the separatory funnel was clogged by aluminum chloride hexahydrate precipitate which formed in the ether layer. Due to this difficulty the method was abandoned.

The third approach to the problem of separating uranium from large amounts of iron was suggested by the work of E. F. Smith,[6] who has shown that by electrolysis with a mercury cathode in

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[1] From a thesis submitted to the Graduate School of Purdue University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Wells. *J. Wash. Acad. Sci.*, **21**, 409 (1931).

[3] Annual Mimeographed Report of "The Committee on Measurement of Geologic Time by Atomic Disintegration," edited by A. C. Lane. Appendix H, p. 18, 1931.

[4] Lundell and Knowles, THIS JOURNAL. **47**, 2637 (1925).

[5] Moore and Kithil, U. S. Bureau of Mines, *Bull.* **70** (1916).

[6] Smith. "Electro-analysis," P. Blakiston's Son & Co., Philadelphia, Pa., 5th ed., p. 267.

dilute sulfuric acid solution elements such as U, Al, V and Ti can be separated quantitatively from elements such as Fe, Mo, Cr, Zn, Ni and Cu, which are deposited in the mercury cathode.

In order to test the reliability of the conditions prescribed by Smith, experiments were carried out with ferric alum solutions. The cell which was constructed for this work was considerably larger than Smith's cell, having a capacity of about 200 ml. The cell was 20.3 cm. high with a diameter of 3.8 cm. and was provided with a stopcock by means of which the solution was drawn off after the electrolysis had taken place. One hundred grams of mercury was used as the cathode. This mercury was removed after each experiment and replaced with fresh mercury. For each of the various experiments carried out to establish the best conditions for the removal of iron by electrolysis, 100-ml. portions of a ferric alum solution, containing 5 mg. of Fe per ml., were used. The results of these experiments showed that the best conditions for the complete removal of iron are as follows: the solution should be 2 to 3% acid by volume with sulfuric acid, the voltage must be at least 8 volts and a current of 2 to 3 amperes passed for two and one-half hours.

With the conditions established for the removal of iron from sulfate solution by electrolysis using a mercury cathode, the next step was to determine whether or not any uranium would be lost from solution during such an electrolysis. In order to determine this, experiments were carried out using solutions containing a mixture of ferric alum and uranyl sulfate. These solutions were placed in the electrolysis cell and current allowed to pass through the solution for three hours using the same conditions that had been established for iron. At the end of this time the solution was drained off and the cell washed out with about 50 ml. of water which was allowed to drain into the main solution. This solution was evaporated to about 50 ml.; sulfuric acid was added until the solution was 5% acid by volume. The solution was passed through a Jones reductor to reduce sexivalent uranium to quadrivalent. Air was bubbled into it for five minutes to oxidize any tervalent uranium and then the solution was titrated with standard potassium permanganate solution. It should be mentioned here that the potassium permanganate solutions used in the various experiments of this thesis were standardized against Bureau of Standards sodium oxalate. These solutions were standardized on the same day they were used, as potassium permanganate solutions at the concentration (0.03 normal) which was used in most of the experiments did not remain stable longer than three or four days. As an aid in establishing the end-point of these titrations, three to four drops of a 0.05 molar solution of the barium salt of diphenylamine sulfonic acid were added. The use of this oxidation–reduction indicator made the color change so distinct that the usual correction for the masking of the end-point caused by the green uranium solution was not necessary. Five determinations of uranium in a solution containing in each portion taken 0.08236 g. of U, and 0.5 g. of Fe gave for uranium 0.08238, 0.08183, 0.08220, 0.08228, 0.08249 g. The agreement of the results indicates that uranium can be separated quantitatively from iron by electrolysis using a mercury cathode.

The next problem was to find a method of determining uranium when present in solution with aluminum, vanadium, and titanium, as these elements, like uranium, will remain in solution during the separation of iron by electrolysis.

Hillebrand and Lundell[7] state that tervalent titanium is oxidized in the presence of air. With this statement in mind it seemed probable that tervalent titanium could be oxidized by air to quadrivalent titanium without oxidizing quadrivalent uranium. If such a procedure could be carried out then only the separation of vanadium from the other three elements, uranium, aluminum and titanium, would be necessary.

However, in experiments designed to test whether or not such a method for the volumetric determination of uranium in the presence of titanium could be worked out, it was found that with an acid concentration in which quadrivalent uranium is stable, tervalent titanium is not oxidized completely by air; if the acid concentration is decreased so that tervalent titanium is oxidized completely by air, then quadrivalent uranium also is oxidized. Thus the volumetric determination of uranium in the presence of titanium cannot be carried out accurately.

Hillebrand and Lundell[8] give a list of elements including titanium and vanadium which can be separated from sexivalent uranium by using cupferron as the precipitating agent. Experiments were carried out to test this method in which solutions containing known amounts of uranium, iron, titanium and aluminum were used.

First, the iron was separated electrolytically by the method already described. The solution was drawn off from the electrolytic cell and evaporated to 150 ml.; sulfuric acid was added until the solution contained 10% acid by volume. Potassium permanganate was added to the solution until it was barely pink to make certain that all of the uranium was in the sexivalent condition. The resulting solution was cooled down to 6°. The cupferron reagent was added drop by drop until no further precipitation took place; the precipitate containing the titanium was filtered off and washed with cold 10% sulfuric acid solution containing about 0.5% cupferron. The filtrate, which contained the uranium and aluminum, was evaporated to about 25 ml. At this point 10 ml. of concentrated nitric acid was added to the hot solution to destroy excess cupferron. The evaporation was continued until fumes of sulfuric acid appeared. Then the beaker containing the material was placed in an air-bath and sulfuric acid fumed off until about 5 ml. of acid remained. At this

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(7) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, N. Y., 1929, p. 459.

(8) Hillebrand and Lundell, Ref. 7, p. 109.

point a large amount of salts had crystallized out of solution and almost continuous stirring was necessary to prevent bumping. After the material in the beaker had cooled, water was added, cautiously at first, until the volume reached 100 ml. This solution was warmed to about 60° to bring all of the salts into solution and potassium permanganate added drop by drop to a permanent pink color to ensure complete oxidation of organic matter. The solution was allowed to cool to room temperature, passed through a Jones reductor, then air bubbled through the solution for five minutes and the amount of uranium present determined by titrating the solution with standard permanganate. Using this procedure five determinations of uranium in a solution containing in each portion taken exactly 0.08600 g. of U, and approximately 0.5 g. of Fe, 0.3 g. of Al and 3.6 mg. of Ti, gave for U found, 0.08620, 0.08616, 0.08612, 0.08606, and 0.08613 g. The agreement of these results indicated that this was a satisfactory procedure for the quantitative determination of uranium. The determination of uranium in the kolm was then undertaken.

A 3.5-g. sample of thoroughly dried kolm ash was placed in a platinum dish and 10 ml. of concentrated sulfuric acid added, followed by 15 ml. of hydrofluoric acid which was added drop by drop. The resulting pasty mass was digested on a steam-bath for one-half hour, then moved to an air-bath and heated for two hours. The temperature during this heating period was maintained just high enough to cause a gentle evolution of sulfur trioxide. Then 100 ml. of water was added and the mixture heated to 60° for one-half hour to dissolve the sulfates present. It was then filtered. The small reddish residue which had not gone into solution was again treated with sulfuric and hydrofluoric acids, fumed until sulfur trioxide was given off, water added and filtered, allowing the filtrate to run into the previous filtrate. A little residue still remained even after this second treatment. This was fused with potassium acid sulfate, the melt dissolved in water, and added to the main solution. Since the hydrogen sulfide group, except for a little molybdenum and a trace of tellurium, was absent, the ammonium hydroxide group was precipitated directly from this solution. Ammonium molybdate would remain in solution. The volume of the solution was increased to 500 ml. by adding distilled water, brought nearly to boiling, and ammonium hydroxide added in excess. The solution was digested on a hot-plate for about ten minutes. The precipitate was allowed to settle, then filtered using suction. The filtrate was made just acid with sulfuric acid, evaporated to about 100 ml. and ammonium hydroxide again added in excess. Next the solution was boiled until only a faint odor of ammonia could be detected. The solution was filtered and any precipitate present was added to the first precipitate.

This precipitate, which contained all of the uranium as diuranate accompanied only by the other elements of the ammonium hydroxide group present in the kolm, was dissolved in 18 ml. of 6 normal sulfuric acid. The solution was diluted to 50 ml. with distilled water and filtered. The clear solution was then electrolyzed to remove iron and molybdenum, titanium and vanadium were removed by cupferron as described above and the solution freed of these interfering elements titrated with permanganate.

The results of five analyses of the kolm ash using this method are given in Table I.

TABLE I

DETERMINATION OF URANIUM IN KOLM

Expt.	Kolm ash, g.	Calcd. kolm, g.	Uranium found, g.	Uranium in kolm ash, %	Uranium in kolm, %
1	3.5184	11.3943	0.05265	1.496	0.462
2	3.4980	11.3277	.05249	1.500	.463
3	3.5378	11.4569	.05322	1.504	.464
4	3.4884	11.2965	.05204	1.492	.460
5	3.5124	11.3740	.05278	1.502	.464
			Average	1.499	.462

As a further check on the availability of the method, it was then applied to the determination of uranium in a Canadian uraninite which also had been analyzed by Wells.[9]

The method used was practically the same as that for the kolm. However, since this mineral contains elements of the hydrogen sulfide group and also rare earths, particularly cerium, whose tervalent form is oxidized by permanganate solution, two modifications were necessary: first, removal of hydrogen sulfide group; second, removal of rare earth group. The modified method was as follows:

A 0.5-g. sample of the mineral was placed in a beaker and 10 ml. of concentrated nitric acid and 10 ml. of concentrated sulfuric acid were added. This mixture was evaporated on a hot-plate until only 3 ml. remained, then 100 ml. of distilled water was added, the solution warmed to 60° and saturated with hydrogen sulfide.

The sulfide precipitate was filtered off, washed, and the filtrate boiled to expel the hydrogen sulfide. From this hot solution the rare earths were precipitated by means of a hot saturated oxalic acid solution which was added drop by drop until no more precipitate was formed and then an additional 2 ml. of oxalic acid added. The oxalate precipitate was allowed to stand in a warm place overnight and then filtered off. The filtrate was electrolyzed by means of the mercury cathode cell. The electrolysis was allowed to proceed for two hours under a current of 3 amperes and a potential of 8 volts. The solution was drained off from the mercury and the cell carefully washed out, allowing the washings to drain into the main solution. At this point 10 ml. of concentrated nitric acid and 10 ml. of sulfuric acid were added to the solution in order to destroy the oxalate which had not been oxidized during the electrolysis. The solution was heated on a hot-plate to copious fumes of sulfuric acid. The volume of the solution was increased to 100 ml. by the addition of water and then cooled to 6°. Potassium permanganate was added to the solution until it was barely pink to make certain that all of the uranium was in the sexivalent condition. The procedure for the remainder of the analysis was the same as that for the kolm. The results of four determinations of uranium in Canadian uraninite by this

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(9) THIS JOURNAL, **52**, 4852 (1930).

method, gave for the per cent. of U: 53.60, 53.44, 53.52 and 53.32, average 53.47.

Discussion of Results

The results show that uranium can be separated from iron and titanium by electrolysis of a solution containing these elements followed by the precipitation of titanium with cupferron. The uranium then can be determined volumetrically.

The average value of the uranium content found for kolm is slightly higher than that of Wells,[2] 0.462% compared to his average, 0.432%. This value, 0.462, also increases the discrepancy between the chemical analysis and the radioactive analysis of the kolm.

It is of interest to note that the uranium content of the Canadian uraninite found by the above described volumetric method (53.47%) is in close agreement with the value (53.52%) found by Wells, who made a gravimetric analysis on material taken from the same twenty-pound sample.

Summary

1. Large amounts of iron can be separated completely from small amounts of elements such as titanium, vanadium and uranium by electrolysis using a mercury cathode.

2. Uranium cannot be determined accurately in presence of titanium by titration with permanganate after reduction by zinc.

3. The color change of permanganate in cold colored solutions is remarkably intensified by the presence of a little diphenylamine sulfonic acid.

4. Uranium in kolm ash and in a Canadian uraninite was determined volumetrically. Results on both substances agree well with the gravimetric results reported by R. C. Wells.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF KENTUCKY]

Kinetics of the Reaction of the Thiosulfate Ion with the Ions of Brominated Malonic and Succinic Acids

BY M. H. BEDFORD, R. BURGESS MASON AND C. E. MORRELL

The velocities of ionic reactions of the second order have been found to be greatly influenced by the magnitude and sign of the charges on the reacting ions. Also it is well known that there is a marked dependence of the rate of such reactions on the ionic strength of the reaction medium. These effects have been considered in connection with the theory of interionic attraction and have been given a satisfactory explanation by Brönsted,[1] who has proposed the following well-known equation for the specific reaction rate in terms of the ionic charges and the ionic strength of the medium

$$\log k_1 = \log k_0 + Z_A Z_B \sqrt{\mu}$$

This equation has been tested by several investigators[2] and in a number of cases has been found to agree quite closely with experiment for very small values of the ionic strength.

However, reactions that do not conform to the Brönsted equation have been studied and their kinetics reported in the literature.[3] The kinetics of these reactions are of special interest because the anomalies they exhibit are probably due to the superposition on the Brönsted primary salt effect of influences arising from the nature of the structure of one or both of the ions. The kinetic effects due to the relative position within the ion of the ionic charge and the reacting group have been studied by La Mer and Kamner in the case of the bromopropionate ions.

In order to make a further study of such structural effects we have investigated the kinetics of the reaction of the thiosulfate ion with the ions of monobromomalonic acid and monobromosuccinic acid

$$S_2O_3^{=} + {}^{-}OOCHBrCOO^{-} \longrightarrow Br^{-} + {}^{=}OOC(S_2O_3)CHCOO^{-}$$

$$S_2O_3^{=} + {}^{-}OOCHBrCH_2COO^{-} \longrightarrow Br^{-} + {}^{=}OOC(S_2O_3)CHCH_2COO^{-}$$

These reactions were chosen because they involve ions containing a seat of charge at each end and a more or less centrally located reacting group. In order to obtain some information about the reactivity of the bromine atom due to its structural position in the molecule and independent of any interaction of ionic charges, the following

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[1] J. N. Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

[2] (a) J. Brönsted and C. E. Teeter, Jr., *J. Phys. Chem.*, **28**, 579 (1924); (b) J. Brönsted and R. Livingston, THIS JOURNAL, **49**, 435 (1927); (c) Victor K. La Mer, *ibid.*, **51**, 3341 (1929).

[3] (a) Victor K. La Mer and Mildred E. Kamner, *ibid.*, **53**, 2832 (1931); (b) J. B. Conant and W. D. Peterson, *ibid.*, **52**, 1220 (1930).