Alkaline Iodine as an Oxidant for Uranium. IV.

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New volumetric methods of estimating uranium based on the reduction of U(VI) to U(IV) and re-oxidation of the latter by selenious acid or alkaline ferricyanide have been recently reported from our Laboratories[1,2]. In these procedures uranium was actually determined by performing iodometric titrations of the excess oxidising agents and also by estimating the products. Thus in the selenious acid method the metallic selenium was weighed and in the ferricyanide procedure the $K_4Fe(CN)_6$ formed was titrated directly with standard solution of $Ce(SO_4)_2$.

The oxidising action of iodine in alkaline medium is well known[3,4]. Its use as an oxidant for tetravalent uranium, however, finds little mention in the existing literature. Preliminary experiments showed that when an aqueous solution of iodine in KI was added to uranous sulphate solution followed by NaOH, rapid oxidation of U(IV) to U(VI) occurred. It was interesting therefore to study this redox process in some detail and utilize it for the quantitative determination of uranium.

Experimental

Uranyl sulphate solution was prepared by dissolving E. Merck's extra pure sodium uranate in sulphuric acid. Its uranium content was determined by the classical oxinate method. An aliquot volume of the uranyl sulphate solution was taken in a stoppered flask and reduced by means of pure zinc and H_2SO_4 in the cold. It was allowed to stand for about 15 minutes until the yellow colour of the uranyl sulphate changed to apple green characteristic one of the uranous sulphate. The contents of the flask were filtered through a Gooch crucible and the unreacted zinc was washed several times with dilute H_2SO_4 and then with distilled water. A stream of air was now bubbled through the cold uranous solution for five minutes to oxidise any U(III) formed to U(IV)[5].

An inert atmosphere was maintained by passing a slow stream of nitrogen gas, and a measured excess of standard iodine solution was added and then followed by 3N NaOH solution until a yellow precipitate was obtained. The contents of the flask were left over for 15~20 minutes, acidified and the unreacted iodine was determined in the usual way by titration with standard thiosulphate to the starch end point. In another set, the alkali was just neutralised with dilute H_2SO_4, followed by an excess of borax-boric acid buffer to maintain a pH 8~10 appropriate for iodine-arsenite reaction. The buffer solution was prepared by dissolving 8% and 4% by weight of crystallised borax and pure boric acid respectively in water as recommended by Chapin[6]. The unused iodine was then titrated with standard As_2O_3 solution to the starch end point.

The difference in the volume of thiosulphate and arsenious oxide before and after the reaction thus corresponds to the iodine consumed for the

TABLE I

Expt. No.	Normality of $Na_2S_2O_3$(N)	Vol. of Thio $= I_2$ reacted (ml.)	Normality of As_2O_3(N)	Vol. of $As_2O_3 = I_2$ reacted (ml.)	Weight of uranium (g.) Oxinate method (x)	$Na_2S_2O_3$ Method (a)	As_2O_3 Method (b)	Difference x—a	x—b
1.	0.09781	25.80	0.1000	25.25	0.3008	0.3006	0.3007	0.0002	0.0001
2.	0.1000	20.20	〃	20.20	0.2406	0.2406	0.2406	nil	nil
3.	0.08322	21.30	〃	17.75	0.2118	0.2113	0.2113	0.0005	0.0005
4.	0.1030	15.20	〃	15.65	0.1866	0.1866	0.1864	nil	0.0001
5.	0.1000	10.10	〃	10.10	0.1203	0.1203	0.1203	nil	nil
6.	0.08320	10.65	〃	8.85	0.1059	0.1056	0.1054	0.0003	0.0005
7.	0.1030	7.60	〃	7.825	0.09330	0.09330	0.09320	nil	0.0002
8.	0.1000	5.05	〃	5.05	0.06015	0.06015	0.06015	nil	nil
9.	0.1030	4.15	〃	4.55	0.05401	0.05403	0.05419	0.0002	0.00018
10.	0.05000	5.05	0.05000	5.05	0.03006	0.03007	0.03007	0.00001	0.00001
11.	0.06035	3.65	〃	4.40	0.02635	0.02624	0.02620	0.00011	0.00011

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oxidation of U(IV) to U(VI). The amount of uranium was calculated as follows,

$I_2+2NaOH \longrightarrow 2NaI+H_2O+O$ .....(i)

$UOSO_4+O \longrightarrow UO_2SO_4$. .....(ii)

Thus, $1U \equiv I_2 \equiv 2Na_2S_2O_3 \equiv 2/1As_2O_3$.

It follows that 1 ml. of 0.1 N $Na_2S_2O_3$ or As_2O_3 is equal to 0.01191 g. of uranium. Results of a series of experiments are returned in Table I. It will be seen that they are in fair agreement with those obtained by the classical oxinate procedure.

Iodine reacts with hydroxyl ions to form iodide and the extremely unstable hypoiodite; the latter is rapidly converted into iodate and iodide by self-oxidation-reduction[7].

$I_2+2OH^- \rightleftarrows I^-+IO^-+H_2O$ .....(iii)

$3IO^- \rightleftarrows 2I^-+IO_3^-$ .....(iv)

Since reaction (ii) is very fast and iodate rarely acts as an oxidising agent in alkaline medium, it is evident that tetravalent uranium is oxidised to the hexavalent state by hypoiodite, which in turn is reduced to iodide. After the oxidation process is completed and the system is acidified, an amount of iodine equivalent to the iodate formed is libereted according to the following equation,

$5NaI+NaIO_3+3H_2SO_4 \longrightarrow 3I_2+3Na_2SO_4+3H_2O$ (v)

This is titrated with standard $Na_2S_2O_3$ or As_2O_3 which corresponds to the unreacted iodine.

Titrations of U(IV) to U(VI) are generally carried out at elevated temperatures and involve the risk of aerial oxidation[8,9]. Since in the present method an excess of the oxidant is used in an inert atmosphere this possibility is eliminated. An additional advantage of this method, besides its simplicity and accuracy, is the use of As_2O_3, as a primary standard.

Summary

A new method for the determination of uranium based on the reduction of U(VI) to U(IV) and re-oxidation of the latter by alkaline iodine is described. The excess iodine is titrated with standard $Na_2S_2O_3$ or As_2O_3 and the results are found to be accurate and reproducible.

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