Fluorometric Microdetermination of Uranium. III. Isolation of Uranium and Preparation of the Fluorescent Material

By Masaki NAKANISHI (1)

(Received March 9, 1950)

This series of reports aims to tell in detail the fluorometric method of determination of uranium, and the procedure fitted for the estimation of such a small amount of the element as we often encounter in the analysis of some geochemical samples. The most suitable amount to deal with is within the limit from

---

(1) Present address, Ochanomizu University, Tokyo.

10^{-5} g. to 10^{-7} g. of uranium.

The first step in treating the sample is just the same as in the ordinary chemical analysis, the details of which have been mentioned in the preceding paper. To extract uranium from the solution, ferric hydroxide *precipitate* is effectively used as carrier. A minute quantity of uranium is completely coprecipitated with this carrier, and this phenomenon has been reported in detail from the analytical point. In this report the separation of uranium from iron and other impurities will be taken into account.

1. Separation from Iron

The minute quantity of uranium in the solution from the sample is concentrated in the iron precipitate as was described in the foregoing paper. The coprecipitation procedure must be repeated at least three times for completeness.

If the original solution contains those elements which produce precipitates in the ammoniacal medium, they will naturally contaminate the precipitate of iron. Besides, the colloidal property of the precipitate will also cause adsorption or inclusion of some elements or compounds. As it is, of course, profitable for the following processes to avoid the latter sort of contaminations, the iron precipitate containing uranium is dissolved in hot dilute hydrochloric acid, and reprecipitated along with uranium. In case of the relatively concentrated solution of alkali or alkaline earth metals, e. g., solutions obtained from rocks, minerals, sea water, etc., the re-precipitation is necessary.

In the treatment of ordinary natural substances, except some special ones, impurities by coprecipitation are eliminated in the next stage of procedures, and a smaller part of them remaining with uranium affects, according to our experiences, not so much as to interfere in the fluorometric determination.

The total precipitate of iron hydroxide containing a small amount of uranium obtained from the original solution is dissolved out, as soon as possible after filtration and washing in hot dilute hydrochloric acid. No trace of uranium remains adsorbed to the filter paper. And from this solution the iron hydroxide is again precipitated together with uranium. A little ferric chloride solution corresponding to a few milligrams of Fe_2O_3 is added to the filtrate, and the recovery of uranium is repeated in the same way as in the preceding paper. These precipitates of iron containing uranium too are dissolved in hydrochloric acid.

From this acid solution of iron and uranium, the most part of the former is separated from the latter, with the aid of ammonia in the presence of ammonium carbonate.(2)

In this procedure of separating iron, ammonium chloride is added to the acid solution *which is almost neutralized with ammonia*. Keeping the solution at about 60°, ammonium carbonate and ammonia are added, and the solution is kept warm with the iron precipitate in it for several minutes. The decomposition of ammonium carbonate begins here if the temperature rises higher than about 80°. The iron precipitate is now filtered off, which contains almost no uranium if the directions are followed.

But it is not easy to wash the precipitate obtained here, for it has been formed at a rather lower temperature. On this account the washing is omitted in this stage, and the precipitate is re-dissolved in hot dilute hydrochloric acid, and the procedure is repeated as given to complete the dissolution of uranium.

Since the filtrate occasionally contains a trace of iron, it is treated with hydrogen sulphide, and the precipitate formed is filtered off.

2. Separation of Other Impurities

The filtrate separated from iron precipitate contains, besides all of uranium taken, some impurities which behave in the same way as uranium in the coprecipitation with and separation from iron. But these give almost no unfavorable effects on the determination so far as common samples are dealt with. In cases where the samples are rich in beryllium, rare earth metals, zirconium, thorium, etc., special procedures of chemical separation are necessary in addition to the simpler one described in the foregoing sections.

The filtrate is cautiously made acid with hydrochloric acid, and evaporated in a porcelain dish. If any heavy metals are still present, these may be precipitated with the help of organic reagents such as 8-hydroxyquinoline in the presence of ammonium carbonate. Here the repeated operations are necessary to prevent the precipitation of uranium compound.

The filtrate is gently evaporated in a porcelain vessel. The residue mostly consists of ammonium salts, and these must be eliminated. If these are heated directly, a little loss of uranium is likely to occur. So the ammonium

---

(2) The ammonium carbonate reagent is prepared as follows, 40 g. of the commercial reagent is dissolved in 1 l. of 1 N ammonia, warmed at about 60° for 10 minutes, and filtered if necessary.

salts are preferably removed as follows: Add concentrated nitric acid to the residue, and the vessel covered with a watch glass is warmed on a water-bath. After the violent reaction has ceased it is further evaporated to complete dryness.

That the latter method is superior to the former is evident from the next experiment. The solution containing 1.00×10^{-6} g. U as nitrate and 1 g. of ammonium chloride was evaporated to dryness. The residue obtained was heated into fume, and the fluorometric method was applied to determine the remaining uranium. In comparison with this, the ammonium chloride residue was decomposed with nitric acid, and the remaining uranium determined. Table 1 represents the results obtained.

Table 1

	Amount of uranium, 10^{-6} g.		
	Calculated	Observed	
By direct heating	1.00	0.72	mean: 0.83
		0.91	
		0.73	
		0.84	
		0.97	
		0.79	
Decomposition with nitric acid	1.00	0.73	mean: 0.96
		0.89	
		1.03	
		0.94	
		1.02	
		0.97	
		1.10	
		0.90	

It is obvious from the table that the operation to remove the ammonium salts by fuming gives rise to a loss of uranium, and the loss may be due either to the actual loss that a minute quantity of uranium is spattered with the fume of ammonium salts, or to the apparent loss that uranium is transformed by heating into an insoluble compound and is not mixed up into the fluorescent material.

The residue after decomposing the ammonium salts in which the total amount of uranium is contained is very small, if the directions are followed with care, and such a small amount of contamination, does not interfere in the fluorescence test.

Nitric acid is used again, if necessary, to decompose the chlorides completely. Then the content of the vessel is transferred into a small platinum dish, moistened with nitric acid and evaporated again on a water-bath. Mixed with sodium fluoride, the final residue is next brought into the fluorescent material as given in the section (3).

The impurities in the final residue, if they are much, may interfere with the formation of the normal fluorescent material as a result of contamination. Therefore it is required to pay attention to every stage of the operation, and to perform the separation of impurities if necessary. As for vessels, porcelain of good quality is preferable to glass, especially for the long-during evaporation, since the dissolution of constituents of glass is thus avoided. The platinum vessel is used after chlorides are decomposed with nitric acid.

3. Preparation of the Fluoresent Material

a. Mixing with sodium fluoride.—The total amount of uranium is now brought together in a platinum dish. About 150 mg. of solid sodium fluoride and a little water are added into it. Then the solution is evaporated to complete dryness on a water-bath. The dried mass of sodium fluoride in which uranium is contained is scraped off and preserved in a dessicator.. Pour several ml. of water into the dish to dissolve the possible remainder of uranium salt. Then add more 50 mg. of sodium fluoride and evaporate to dryness.

The sodium fluoride masses obtained by the successive operations are gathered together, and heated gently in a platinum dish to remove the moisture completely. The obtained powder mixture is preserved in the desiccator and the fluorescent beads are made from this mixture as will be mentioned in the following section.

Speaking from the writer's experiences, it is not profitable in the last operation of mixing to use hydrofluoric acid instead of water for the following reasons. (i) First, if hydrofluoric acid is used, a molecular compound **NaF·HF** is formed, from which hydrogen fluoride is liberated on heating and the mechanical loss of the fluorescent material takes place at times in the preparation of fluorescent beads. Besides, the beads prepared from such material become much smaller than expected, and do not develop into a disk-shaped bead. (ii) Secondly, there is a fear that impurities of the acid are mingled, while it is rather an undesirable work to purify the acid. (iii) Moreover, the writer experienced no objection in using water instead of hydrofluoric acid.

b. Preparation of fluorescent beads.—Weigh the total of the dried powder mixture of uranium and sodium fluoride, and make it homogeneous in a mortar. The fluorescent bead is prepared from a portion of this mixture on a platinum loop. But as it is difficult to treat such a powdered sample, this is conveniently pressed into a small tablet of about 20 mg. in weight. Each tablet is weighed exactly.

The preparation of the fluorescent bead runs as follows: A tablet of a known weight is put on the clean platinum loop, and gradually heated by the burner flame to clear fusion in the end. This state of fusion is kept for 5 minutes in the oxidizing flame. Both sides of the disk-shaped bead are to be equally heated, and this condition must be the same for every bead. After 5 minutes' fusion, the bead is quickly cooled down rotating the shaft attached to the loop, by which procedure the surface of the bead becomes flat and suitable for the determining the fluorescence intensity.

To obtain a disk-shaped bead, the proportion of the loop diameter to the amount of the powder mixture is important, and this is decided by trials. The writer uses regularly the loop of 2.5 mm. diameter for about 20 mg. of the mixture.

The time of ignition in the burner flame is fixed to 5 minutes. The intensity of fluorescence depends much upon the time of heating and, during the first few minutes, the longer the time is, the more intense the fluorescence becomes, since it takes some time for heating to form a proper fluorescent material. But the intensity increases very gradually with time when heated for more than several minutes, which means that there is a relative increase of uranium content in the bead due to the evaporation of sodium fluoride under heating. This is the reason why the duration of the heating treatment must be constant for every bead, and the heating for 5 minutes was chosen by trials.

The bead of the fluorescent material prepared is somewhat hygroscopic. It is not desirable to repeat the ignition since it might cause the change of the intensity. Therefore it is better to prepare the bead immediately before testing the intensity.

c. Preparation of the standard beads.— The intensity of fluorescence of the bead from an unknown sample is compared, as will be described in the following paper, with those of the standard beads, the uranium contents of which are already known. These stndard beads are prepared as follows: to the known amount of purified sodium fluoride in a platinum dish, add an adequate amount of the standard solution of uranyl nitrate, evaporate the mixture up to complete dryness and weigh the total. Make the mixture homogeneous in the mortar. From this prepare tablets of about 20 mg. each and reserve them. The uranium content of each tablet is known from its weight comparing with that of the total mixture. The following procedures of preparation of the standard beads go as in the case of the unknown samples.

Summary

The procedures to isolate uranium, which is coprecipitated with the iron hydroxide, are related. The minute quantity of uranium obtained is mixed with sodium fluoride and the fluorescent beads for the fluorometric determination are made from the mixture.

The writer is indebted to Professor Kenjiro Kimura for his generous advice and criticism in the course of this investigation.

Chemical Institute, Faculty of Science,
the University of Tokyo, Tokyo