Fluorometric Microdetermination of Uranium. II.
Extraction of Uranium

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Various properties of the fluorescent material of sodium fluoride containing a small quantity of uranium were investigated in the previous paper with the same title. To prepare the fluorescent material for the determination, it is required to extract uranium from the sample for analysis in an adequate form of compound.

Precautions must be taken lest any loss of uranium should be made throughout the procedures, and since the fluorescent materials are generally liable to be affected by impurities, they should always be guarded against such effects. But as was mentioned in the previous paper, the fluorescence of sodium fluoride activated by uranium is fortunately less affected by impurities, so far as the analytical application is concerned. For example, heavy metals and insoluble matters are made ineffective in the determination, if their amounts are decreased at least to the amount comparable with that of the uranium present with them. According to the writer's experiences, this is satisfactorily accomplished by the careful operations in the chemical separation procedures.

It is attempted in the present paper to survey each individual process for extracting a minute quantity of uranium from any sample, and to establish a method as satisfactory as possible.

1. Outline of the Extraction from the Sample

In dealing with the solid sample, it must be first brought into a solution of uranyl salt. For example, a rock sample is ground and fused in a platinum crucible with sodium carbonate, then extracted with hot water.

This treatment must be repeated at least three times, for only one process does not suffice to perfect the extraction. The extraction with hot water instead of any acid makes the following scheme simpler, because many other metals are separated from uranium and the latter is in general completely brought into the solution.

The following represents the outline of extraction method of uranium in usual natural substances, in which are included solutions derived from rock samples, sea-water, hot-spring water, etc. In case when the sample contains unfamiliar constituents, a special scheme of the analysis must be chosen, but this consideration is omitted here for simplicity.

The application of the fluorometric method of analysis is practically limited to the solution, in which the uranium content is so small that the element is not quantitatively precipitated by any direct way. To precipitate uranium from such a dilute solution, iron hydroxide is effectively employed as carrier or co-precipitator, as is often the case with the precipitation of a small amount of substance.

The extract from sodium carbonate fusion is carefully treated with dilute hydrochloric acid and boiled to expel a large amount of carbon dioxide. The resulting solution free from carbonates is evaporated on a water-bath to dryness, and silica is, if necessary, removed as usual from this residue. Since organic matters and carbonates seriously interfere with

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the coprecipitation of uranium with iron, it is better in the case of an aqueous sample, *e. g.*, natural water, to begin with the evaporation to remove silica and then to destroy the organic substances with nitric acid or a mixture of nitric acid and sulfuric acid.

The residue is dissolved into a clear solution. Add ammonium chloride and an adequate amount of ferric chloride solution (corresponding to about 20 mg. of Fe_2O_3), boil for a few minutes, then add ammonia containing no trace of carbonate. Almost all uranium is coprecipitated with iron hydroxide. The precipitate is heated for a while with its mother liquor, which is followed by filtration and washing with a hot ammoniacal ammonium chloride solution containing no trace of carbonate. To complete the precipitation of uranium, this procedure is repeated three times.

Some considerations will be made in the following in connection with these treatments and the coprecipitation phenomenon.

In the next stage of analysis, uranium coprecipitated must be separated from iron and other possible impurities, but this will be detailed in the following papers.

2. Required Amount of Iron for Coprecipitation

The following experiment provides some knowledges how much ferric salt will be needed to precipitate the minute quantity of uranium together with iron hydroxide.

Different quantities of ferric chloride solution were added to 50 ml. of uranyl nitrate solutions, each containing 1.00×10^{-5} g. of uranium. In these mixtures, precipitation with ammonia was performed, and the uranium content of each precipitate was determined by the fluorometric method described later.

Table 1

$FeCl_3$ added, mg. as Fe_2O_3	Amount of uranium in each bead, 10^{-7} g.		$\frac{\text{Observed}}{\text{Expected}}$, %
	Expected	Observed	
1	8.78	8.27	94
		9.18	104
3	9.78	9.85	101
		8.75	89
10	8.66	8.85	102
		8.27	95
		9.18	106

Table 1 represents the experimental results, which prove that 1 mg. as well as 10 mg. of iron is equally sufficient to precipitate about 10^{-5} g. of uranium. The experiment with the smaller amount of iron than 1 mg. was omitted, for it is considered unavailable in practical cases.

3. Amount of Uranium not Precipitated

It is generally recommended to repeat the procedure two or three times in precipitating a small amount of substance with carrier. The next experiment reveals the efficiency, with which uranium precipitates with a relatively large amount of iron.

To the hot 100 ml. solution containing 2×10^{-6} g. U and 20 mg. Fe_2O_3 in the forms of uranyl nitrate and ferric chloride respectively, ammonia was added, and the precipitated iron hydroxide was filtered. Then the amount of uranium not precipitated was determined in the filtrate by means of the fluorometric method.

As a result of this experiment it was observed that only a trace of uranium was found in the filtrate and almost all of it was dragged down with the hydroxide precipitate. Approximately from 0.3 to 0.4% of the uranium in the original solution gets rid of the coprecipitation and remains in the filtrate. The values determined were not precise in this experiment, for the uranium content of each bead is in the order of 10^{-9} g., corresponding approximately to the lower limit to produce faint fluorescence.

Since the error in the determination of this fluorometric method amounts to about 10%, a single coprecipitation procedure of uranium with iron will serve in practical cases. But the coprecipitation procedure is preferably repeated three times as a rule, for it is suspected that the efficiency will be lowered if the solution contains various other substances.

4. On Adsorption

The iron hydroxide precipitate adsorbs other impurities, as is well known, on account of its colloidal property. In the experiment mentioned, therefore, special precautions will be needed in the operations, if uranium is precipitated by mere adsorption with iron hydroxide. But it is valid from the following experiments that the adsorption, if any, is neglected, and the suitable condition will be shown thereby.

a. At the room temperature.—The hydrochloric acid solution of uranyl nitrate containing 1.05×10^{-5} g. U was boiled to expel carbon dioxide, left standing to coolness, and ammonia was added, where no noticeable precipitate was produced. On the other hand, the hydrochloric acid solution of ferric chloride containing 2 mg. Fe_2O_3 was kept boiling for a while, and after cooled to the room temperature iron hydroxide was precipitated with ammonia. The two solutions were mixed together immediately after adding ammonia (volume of the resultant solution being about 100 ml. and the concentration of ammonia 1 *N*), shaked for 5 minutes and filtered through a hard filter paper under suction. The precipitate was dissolved in hot dilute hydrochloric acid and after iron being separated uranium was determined by the fluorometric method. The numerical data are given in Table 2 (a). The amount of uranium apparently included in the precipitate reaches as much as 8.10% of that taken. This fact gives an impression that a part of uranium in the solution is adsorbed on the surface of iron hydroxide precipitate. But in the above treatment, iron precipitate had been completed before mixing with uranium solution, and the filtration followed soon after mixing. Therefore the so-called occlusion or the compound formation may not be the case. Considering that uranium belongs to those elements which are precipitated in an ammoniacal medium, it is suspected that from such a dilute solution uranium may form an unnoticeable precipitate remaining on the filter paper. To make this clear, a similar experiment was made with the solution which contains uranium only, and is not added with iron precipitate. After the filtration, the filter paper was ignited to ash, and. the uranium content in the ash was estimated as before. 12.2% of the total amount of uranium taken was found as given in Table 2 (b).

Table 2

	Uranium taken, 10^{-7} g.	$FeCl_3$ added, mg. as Fe_2O_3	Temperature, °C.	Uranium found in the precipitate, 10^{-7} g., and % to the total	
(a)	105.4	2	20	8.53	8.10%
(b)	〃	none	〃	12.9	12.2 〃
(c)	10.54	20	at boiling	1.39	13.2 〃
(d)	〃	〃	〃	1.33	12.6 〃
(e)	〃	〃	〃	1.90	18.0 〃
(f)	〃	none	〃	1.69	16.0 〃

It seems contradictory that in the experimental results the amount of uranium remaining with the iron precipitate ((a) in Table 2) is smaller than that remaining on the filter paper only ((b) in Table 2) where no iron precipitate was present. But the state of uranium precipitate from such a dilute solution might delicately depend upon the conditions in the procedure, and it has therefore almost no meaning to discuss the difference.

In conclusion, the adsorption of uranium to iron precipitate is practically negligible at the room temperature, and its contribution, if any, is not so large as to explain the fact that nearly all of uranium in the solution is precipitated with iron hydroxide as described in the above section (3).

b. At the higher temperature.—Since in practical cases the procedure to precipitate a small amount of uranium with iron is performed at the hot condition, the examination on the adsorption at a higher temperature is more significant than that at a lower temperature. In fact, it is known that the iron hydroxide precipitate changes its structure by aging at a higher temperature,(2) and from this fact further examinations are required to see whether uranium is adsorbed to iron hydroxide precipitate at the hot condition or not.

Experiment 1.—A 50 ml. solution containing 1.05×10^{-6} g. U as uranyl nitrate and 1 g. of ammonium chloride was heated to boiling and ammonia was added, where no visible precipitate took place. On the other hand another 50 ml. solution containing 20 mg. Fe_2O_3 in chloride form and 1.5 g. of ammonium chloride was heated to boiling and ammonia was added. The latter solution with iron precipitate in it was immediately transferred to the ammoniacal solution of uranium, the mixture being heated again with stirring for 1 minute, and then filtered under suction without washing. The precipitate remaining on the filter paper was dissolved in hot dilute hydrochloric acid and uranium was determined ((c) in Table 2).

Experiment 2.—After mixing two ammoniacal solutions of uranium and iron treated as before, the combined solution was kept on heating with the precipitate in it for 10 minutes. Other treatments were the same as the above. ((d) in Table 2).

Experiment 3.—Before mixing with an ammoniacal solution of uranium, iron hydroxide precipitate was aged with the mother liquor for 10 minutes at the boiling temperature. Other details were the same as in Experiment 1. ((e) in Table 2).

Experiment 4.—The same treatment as in Experiment 1 was carried out without iron precipitate, to determine the amount of uranium remaining on the filter paper. ((f) in Table 2).

As given in the table, the amounts of uranium

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(2) A. Krause, *Z. anorg. allgem. Chem.*, **176**, 398 (1928); **204** (1932); **206**, 328 (1932); **211** (1933); **219**, 213 (1934).

which remain with the precipitate are not constant, but they are in the same order of magnitude as that obtained when uranium solution is treated without iron. Besides, these values are dependent to a large extent upon the conditions of the precipitation procedure. When uranium is precipitated alone, the precipitate of small sizes will perhaps remain adsorbedly on the filter paper.

Conclusions from the experimental results above mentioned are as follows. The precipitation phenomenon of uranium with iron is not attributed to the mere adsorption. Even the adsorption should take place, it may be limited only to a smaller part, and may not play an important role. It is reasonably concluded that a larger part of uranium will be coprecipitated with iron in some structural binding. In consequence, this procedure of precipitation is effectively made at a convenient hot condition, and the washing will not cause any loss of the element.

5. On Aging.

If uranium should combine loosely with iron hydroxide precipitate, it may be possible that the former is let free from the latter and again gets into the solution during digestion at the high temperature. Now that uranium itself is slightly soluble in an ammoniacal medium, there will be almost nothing to apprehend, but an exact proof for it is required, because the amount of uranium taken is negligibly small for the ordinary chemical manipulations. The following experiments will meet the purpose.

A 100 ml. solution containing 1×10^{-6} g. U in nitrate form and 20 mg. Fe_2O_3 in chloride together with 2.5 g. of ammonium chloride was acidified with hydrochloric acid, boiled for 1 minute, and 10 ml. of 6 N ammonia was added. In one experiment the precipitate of iron hydroxide obtained was immediately filtered, while in the others the precipitate was digested at 95° for 3, 10 and 60 minutes respectively before filtration. After filtered in each case uranium remaining in the filtrate was determined by the fluorometric method. The values obtained were very small, which correspond to about 0.5% of the total amount taken in each case. According to our present method of procedures, an amount of uranium close to 10^{-9} g. gives too weak a luminescence to obtain the exact value.

This amount of uranium which gets rid of the coprecipitation with iron, however, agrees satisfactorily with that which remains in the solution after a single coprecipitation procedure as described before (section 3). Therefore it is concluded here that there is no loss even if we keep the precipitate heated with its mother liquor as long as an hour. Furthermore, this procedure of boiling gives a favorable result, for aging for a while at the boiling temperature makes the iron hydroxide precipitate more filterable.

Summary

A minute amount of uranium suitable for the fluorometric method of determination is effectively precipitated from the solution together with hydrous ferric oxide as co-precipitator. The efficiency of co-precipitation seems to be nearly perfect for the purpose, and the adsorption and the digestion effect were observed in particular from the analytical standpoint.

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