ABOUT URANIUM DETERMINATIONS

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ABSTRACT. — The most important methods in connection with uranium analyses published up to date will be briefly outlined in this article. Here each method is not taken separately. Instead, methods applied by various authors in the separation of uranium from its associated elements — Such as extraction, precipitation, electrolysis, column chromatography, separation by means of ion exchangers — and the determination proper — such as gravimetric, volumetric, coloriroetric and spectro — photometric, fluorometric, electrometric and radiometric — are discussed as a whole.

Of these methods those which were actually put to test and their degree of precision checked up, using standard specimens, are discussed in detail.

INTRODUCTION

In the last few years, due to the rapid development observed in the means for putting to good use the atomic energy, analysis of radioactive minerals— especially the determination of elements Uranium and Thorium—won a wide interest. The physical and chemical analyses of these elements have, in pace with the marked development in this field in general, displayed considerable progress. Extensive work is being eagerly carried on and the results regularly published. This article is written with the purpose of briefly reviewing the current literature on the methods of uranium analysis, considered particularly important, and to describe those among them which are actually applied in our Institute.

PART I

URANIUM DETERMINATION METHODS

Various methods have been devised for the determination of uranium. In general, first step in any method is to free the uranium from its associated elements, interfering with the precision of the determinations, and then this is followed by the determination proper. For the uranium separation, either an extraction method or one using precipitation, electrolysis, column chromatography or ion exchangers is applied. As for the determination, any one of the methods that can be specified as gravimetric, volumetric, colorimetric and spectro - photometric, fluorometric, electronic or radioactive may be chosen.

In all methods, in order to decompose the ore containing uranium, the sample is treated with HNO_3 or some mixtures of acids such as (HNO_3+HC1O_4), $(HNO_8 + HF)$, $(HN0_3 + HG10_4 + H_2SO_4+ HF)$ in given proportions. Those which are not dissolved in acids are rendered soluble by means of special mixtures like $(NaOH+Na_2O_2)$, $(NaOH+NaNO_3)$, $(Na_2O_2+Na_2CO_3)$.

Separation of Uranium

1. Extraction methods.

This is based on the fact that some uranium salts are more readily decomposed in certain organic solvents than in an aqueous solution of a given composition. The organic solution which comes in contact with the one containing the uranium, either continuously or gradually, after a while absorbs all of the uranium. This is followed by ,evaporation, of by destruction, of the organic matter leaving uranium salt.

One of the methods used to recover uranium from low-grade ores is the ether extraction method. In this method the solution containing uranium is first acidified by adding nitric acid and, after being saturated with ammonium nitrate, is subjected to ether extraction in an extractor (1, 2, 3). An other method consists of ethyl acetate extraction from nitric acid solutions having a high concentration of or being saturated with aluminum nitrate (4, 5, 6, 7, 8). This method of separation for uranium is widely used and often applied prior to calorimetric, spectro - photometric and fluorometric determinations. Some authors prefer to apply ether acetate extraction method after adding hot aluminum nitrate to the solution containing nitric acid or heating the solution to the boiling point (9, 10, 11). In order to free the uranium— obtained with either of these two methods — from its organic solvent, this latter is evaporated.

Again, prior to colorimetric and fluorometric determinations, the tri-butyl phoshate extraction method may be applied to solutions containing uranium nitrate. In this method, in order to obtain two better-defined phases than in one using only tri-butyl phosphate, tri-butyl, phosphate + methyl isobutyl ketone or tri-butyl phosphate + diethyl ether or a 22 % solution of tri-butyl phosphate in n-hexane must be used (12). Lately, to extract uranium especially from ores or solutions where it exists in very small quantities, first a mixture of tri-butyl phosphase and n-hexane, then an ethyl acetate extraction have been , jointly used. In case the amount of U_3 $_8$ exceeds 0.05 gr. in a solution of the original sample, the tri-butyl phosphate separation is dispensed with (12).

According to a different method, the extraction of uranium is done by first adding sulfo-cyanide and then tin (II) chloride in a medium of hydrochloric acid, followed by further addition, within a given range of acidity (pH), of dibutoxytetraethylene glycol plus tin (II) chloride. As the latest publications have shown a penta-ether to give a purer product and do this more quickly than tri-butyl phosphate, this latter may preferably be substituted (13, 14).

Apart from these, based on the fact that the complex substance obtained by uranium (VI) with 8-hydroxykinoline is soluble in organise solutions, uranium is extracted, within a given pH range, using 8 - kinolinol (oxine) and its derivatives (such as di-chloro-oxine and di-bromo-oxine) and chloroform. The determination of uranium follows using spectro-photometry (21, 15, 16).

An other method, similar to the one above, is the cupferron or chloroform extraction in a medium of sulfuric acid or perchloric acid. In this method, in contrast to the previous ones, uranium (VI) is left in the aqueous solution, while cupferrates of the associated elements pass into the organic solution. This method of extraction is applied either before (20, 87) or after (3, 17, 18, 19) hydrogen sulfide group elements are separated; the advantage of the method being the possibility it offers for the double cupferron extraction, as the uranium may be of (IV) or (VI) valence (21,22). And this is based on the fact that in an acid medium cupferron and uranium (VI) do not give any precipitate, while uranium (IV) precipitates in the form of a cupferrate and decomposes in an organic solvent. Usually, after such a separation, the determination of uranium is made volumetrically.

2. Precipitation methods.

These methods make possible only group separations, due to the fact that uranium does precipitate with certain anions and cathions. Of course, they often are to be subjected to subsequent separation using any one of the extraction methods.

Frequently, uranium is precipitated from uranyl solutions, under the action of ammonium diuranate. This method makes possible the separation of uranium from certain anions and some cathions, such as Cu (II), Ni (II), which give complex substances with alkali, alkali earth (metals) and ammonia, and is only applied to solutions containing no fluor, carbonate, citrate or tartarate. Thus the uranium precipitate, partly separated from heavy metals, is decomposed in a special acid, subsequently to undergo further separation either by electrolysis or ether extraction. In this method pyridine or hexa-methylene tetramine are also used in place of ammonia (23,24,1).

In still another widely used method, hydrogen sulfide is passed through an acid solution containing uranium. Thus, after the heavy metallic sulfides are disposed of, cupferron - chloroform extraction is applied to the filtrate. Instead of passing hydrogen sulfide gas, the solution is treated, in an acid medium, by sodium sulfide or, as practiced lately, by thioacetamide (17, 18). A variation of this consists of precipitating uranium (VI) with certain other metals in the form of phosphates, followed by the cupferron - chloroform extraction (25).

Apart from these, as a special case, the sample solutipn is reduced with zinc amalgam and then treated with ammonium carbonate. During this process uranium (IV) carbonate is separated as a precipitate while iron (II) remains in the solution. This method is suggested mostly for the purpose of a rapid volumetric or gravimetric determination of uranium in the presence of excessive iron (26). Similarly, the ore is rendered soluble with the aid of potassium bifluoride and hydrofluoric acid and then treated with an excess of tin (II) chloride. In this manner, fluorides of uranium (IV), thorium, rare earth metals and earth alkali precipitate and are separated. This method is applied mainly to complex minerals, such as, samarskite, columbite-tantalite and titano-niobite (27).

3. Separation by electrolysis.

Electrolysis is used as an other approach to freeing uranium from the elements which might have misleading effects during a determination. The sample, put in a solution form for this purpose, is subsequently electrolyzed, often in a medium of sulfuric acid, using a mercury cathod. Under these conditions, iron, cobalt, nickel, copper, zinc, gallium, germanium, rhodium, palladium, silver, cadmium, indium, tin, iridium, platinum, gold, mercury, thallium, chromium, molybdenum, rhenium, bismuth, arsenic, selenium, tellurium, lead and osmium accumulate on the mercury cathod. Along with these, manganese, ruthenium and antimony are also partially separated. Following this, uranium, columbium (VI), tantalum, tungsten, titanium, vanadium and zirconium, which are left ,in the solution, are subjected to extraction for separation (28, 29, 30, 31).

4. Column chromatography.

In this method separation is done in a column. The sample acidified with nitric acid is passed through a column of specific dimensions which contains a certain amount of active cellulose. Of the elements, totally or partiaily absorbed in the cellulose, in direct relationship with their speed in the column, uranium is quantitatively extracted, using ether which contains nitric acid. ' In order to reduce the speed of some element atom ions in the column, certain substances such as Fe $(NO_3)_3$ and Na_2 HPO_4 are added to the sample solution. Thus foreign elements are kept off being held in the column. As extraction solution, ether containing 1-3 % nitric acid is used. After the evaporation of the organic matter, the determination of uranium is done in any one of the followig methods; namely, volumetric calorimetric, polarographic or fluorometric (32, 33,34, 35, 36, 37, 38, 39). Recently, it was proposed to use a mixture consisting of 20 ml of petroleum ether + 190 ml of ether + 10 ml of HNO_3 (d. 142) as an extraction solution (40).

5. *Separation by means of ion exchangers.*

In order to eliminate the ions having a misleading effect on the determination of uranium, this method is found to be of service. Often synthetic resins are used as ion exchangers. In general, organic cathion exchangers contain an acid group (sulfonic acid, carboxyl group) and ion exchangers a basic group (such as amino group). These resins, placed in a column will absorb cathions or anions that are present in the solution with which they come in contact, in accordance with their own character. To be able to extract the desired cathions and anions from among those absorbed in the column, certain solution must be run through this latter (41). The name of some of the resins used in these procedures are: (a) Amberlite 1R-4B, Amberlite IRA-400, Amberlite IRA-410, Dowex-1, Dowex 2 (as ion exchanger resins) and (b) Amberlite IR-100, Amberite IR- 120 and Dowex-50 (as cathion exchanger resins).

Making use of the ion exchangers for the separation of uranium and its associated elements, present in minute quantities (trace), a solution containing UO_2 $(NO_3)_2$ is run through a column which in turn contains Amberlite IR-120. After this the extraction of U, Fe and Cu is done with 0.5 N oxalic acid, that of Ca, Ni, Go and Mn with normal HG1 and finally a 5 % ammonium citrate is used for rare earths (42).

In an other method serving to separate uranium from thorium, these two elements are absorbed by Amberlite IRA-400 in ethylene diamine tetra-acetate. Afterwards, uranium is extracted with 0.02 N HC1 (43).

In order to determine small quantities of uranium in the presence of an excess of Fe, Al, Mg and SO_4, this former is absorbed by a strongly basic anion exchanger of a certain pH value (such as Dowex-2) and thus separated from the rest (44).

Anion exchanger resins are also used to separate the other elements from uranium prior to its colorimetric determination. The uranium absorbed is extracted by $HG1O_4$ (44,45). Here Amberlite IRA-400 which contains ammonium group $(NH_4)_4$ is utilized.

Lately, by a new method, uranium acetate is absorbed in a cathionic resin formed by p - phenol - sulfonic acid and poly-condensation of phenol and formaldehyde. Its extraction is later brought about, using first ammonium sulfocyanide followed by hydrochloric acid (46).

II. Determination of Uranium

The uranium which is totally or partially separated from the other elements— using one of the methods briefly outlined in the previous paragraphs— is now determined with the aid of various methods described below.

1. *Gravimetric determination methods-*

Having first precipitated the uranium with ammonium hydroxide and then weighing it as oxide is an old method now rarely used. Because, to be able to precipitate the uranium using ammonia, the solution must contain none of the other elements. Consequently, uranium is sometime precipitated from uranyl nitrate solution which is extracted using ether and then burnt under perfect oxidizing conditions, prior to its weighing. However, the fact that the precipitation of uranium (IV) with ammonia is quick and advantageous still holds its place in current literature (1, 26).

Besides these, according to methods devised recently, the precipitation of uranium as phosphate, in the presence of complexon, prior to its determination, is possible (47); likewise, its determination as oxinate, using complexon as a shielding means (48), and finally application of gravimetry for the same purpose, using salisilhydroxamic acid, are methods actually in practice (49).

2. *Volumetric determination methods'*

Often a volumetric determination is applied to uranium solutions which are freed by extraction from their foreign elements. For this purpose, uranium is first treated with, a reducing agent to uranium (IV) and subsequently titrated using an oxidizing solution. As a reducing solution generally a solid zinc amalgam (Jones Reducer) is utilized (17,20, 50,63, 70). Also liquid zinc amalgam (31),. cadmium reducer, cadmium amalgam (51), silver reducer (Walden-silver reducer) (52, 56), metallic copper, metallic aluminum spiral (53), titan (III) chloride or titan (III) sulfide solution, tin (II) chloride solution (54) and lead reducer (18,20,55), are among the rather frequently used ones. In the course of treatment with some of these reducing agents, the valence of uranium does not remain at 4, but reduces to 3, as in the cases with Jones Reducer and cadmium reducer. In such instances, the oxidation of uranium (III) into uranium (IV) is done by sending a draught of air through the solution.

The titration of the reduced uranium is done using such titrated oxidizing solutions as potassium permanganate, potassium bichromate, cerium sufate, potassium ferricyanide and sodium vanadate. For this purpose, one of the following may be selected: Potassium Bichromate Titration (29,54, 56, 57, 63), using as indicator sodium or barium salts of diphenylamine sulfonic acid or diphenylamine or n-phenylanthranilic acid (57), as calalyst $FeCl_3$ solution; Potassium Permanganate Titration (17,50,56) using as indicator ferroin (1,10) phenanthroline iron (II) sulfate; Cerium Sulfate Titration (17,52, 55, 58,59,61,62) performed in room temperature, using as indicator ferroin or diphenylbenzidine and n-phenylanthranilic acid (59), as catalyst ortho-phosphoric acid H_3PO_4; Sodium Vanadate (Na_3VO_4) Titration (68,69), performed in room temperature, using as indicator n-phenylanthranilic acid or diphenylbenzidine (in this case H_3PO_4 and $H_2C_2O_4$ are added as catalysts). Only the reduction of U (VI) into U (IV) is handled in a different manner than the rest, involving photo-chemistry. For this purpose, Uranium (VI) solution is exposed, in a medium of ethylalcohol and sulfuric acid, to sunshine or to Philip's Repro lamps. The uranium thus reduced to valence (IV) is then titrated with sodium vanadate (69).

In addition to those mentioned above, potassium ferricyanide and cerium sulfate titration is used indirectly. In this method, uranium (IV) is oxidized into uranium (VI) by treating it with a certain amount of potassium ferricyanide and then, the ferrocyanide formed during this reaction, in an equivalent amount, is titrated back using cerium sulfate (53).

In the iodometric determination of uranium, the solution of uranyl sulfate or uranyl chloride which is cleaned from foreign elements is acted upon with potassium iodate (KIO_3) of a certain pH value, potassium iodide (KI) and chloroform. The iodine, which goes into a free state and dissolves in chloroform, is titrated using sodium thiosulfate or arsenite solution (64).

There can also be mentioned a reduction titration method, though seldom used, consisting of uranyl solution being titrated with chromium (II) chloride and a precipitation titration method, used for micro-determination, consisting of uranium (VI) solution being titrated with sodium phosphate or potassium ferricyanide. The reading of the turning points in these titrations is done potentiometrically (65, 66, 67). According to the method, in which the last point may be read spectro-photometrically (80), the simultaneous determination of iron and uranium may be possible. In this procedure a 90 % cadmium amalgam serves as a reducing agent and the subsequent titration is done with cerium sulfate.

3. Colorimetric and spectro-photometric determination methods.

The determination of uranium using colorimetric and spectro - photometric .methods is widely practiced. It is based on the absorption of light by the uranium (IV) and (VI) ions themselves, or inorganic compounds or complexes of uranium, in an aqueous or organic solution. This absorption is measured either in a colorimeter or, as it is often done, in a spectro - photometer of the reflection type.

A separation prior to a colorimetric determination is usually required. Alkali-peroxide method is applied to low-grade concentrates following an ether extraction (2, 3,24), or a cupferron ethyl acetate (or ether) extraction (71) or, for high-grade concentrates, following the separation by ethyl acetate and taken into aqueous solution (72). A method with wide-spread application is that of thiocyanate. Uranium, after its separation by ethyl acetate, is'treated with reagents either directly in ethyl acetate or following its transfer from ethyl acetate into water. Subsequently, spectro-photometric measurement of the absorption for a given range of wave-lengths takes place (73, 74, 75).

Using the yellow-colored complex which uranium gives with dibenzoylmethane, this element is spectro-photometrically determined. This complex displays a maximum of absorption for a certain value of pH, in a medium containing ethyl alcohol of a certain concentration, and along a certain range of wave-lengths. The separation of uranium is carried out either by ether or ethyl acetate extraction or by cellulose column-chromatography (76,77). This method is used to determine the minute quantities of uranium present in minerals and rocks. An other way of determining the amount of uranium spectro - photometrically is the one making use of the red-brown complex (78) this former gives, in a medium containing ammonia, by morine (3, 5, 7,2', 4' - pentahydroxy - flavanol) which is an other organic reagent; or the orange-color complex it gives with 8-quinolinal and its derivatives (79). The latter is particularly advantageous as it is found to display a greater stability in colors and is better suited for application to low-grade ores.

In the course of direct spectro-photometric determinations, the amount of absorption acquired by the uranium ions in an aqueous acid solution, without any prior separation whatever, plays a significant part. The absorption values, at 660 or 700 mm of reduced or unreduced uranium ions are measured in a medium of sulfuric acid containing certain ions in a given concentration (81). In a different method, after the decomposition of the sample, a direct determination is carried out on the uranium solution, using a Beckman spectro-photometer (82). Similarly, the colorimetric absorption value of a uranium solution is determined in a medium of perchloric acid, at 415-420 mm using a Beckman DU spectro-photometer (83). For small quantities of uranium', the absorption values corresponding to a wave-length of of 430 m[x are measured in a medium of dilute sulfuric acid, with the aid of a highly sensitive spectro-photometer (84). When using a differential spectro-photometric method (85, 86), either the absorption at 430 mm wave-length of the uranyl ion in a medium of sulfuric acid or its relative absorption at 418 mm. wave-length is measured as compared to a standard of high value. The different absorption values obtained offer a dependable clue for a very accurate determination of the uranium concentrations in the so1ution tested. These direct spectroscopic methods are preferred to the others as being quick and sensitive.

4. Fluorometric determination methods-

The fluorometric methods of analysis used for the determination of uranium are of high speed and accurate. They are based on the fact that even the least concentrations of uranium, so small as to be called traces, will display fluorescence in sodium fluoride. The presence of certain ions whose direct effect would decrease the intesity of fluorescence, is taken care of either by dilution or extraction. For this purpose ethyl acetate extraction is often used (30, 96, 97, 98). In fluorometric determination, a very small quantity of the uranium containing solution is first placed in a gold or platinum crucible and, after evaporation is completed, the residue is dissolved in a compound which contains sodium fluoride. At the end of this procedure a tiny bead is formed and, under the ultra violet light, the fluorescence it emits is measured by means of a fluorometer. As a solvent that will contain sodium fluoride, the following may be used: Sodium fluoride by itself, or a mixture of sodium and potassium carbonate and sodium fluoride (89, 91, 92, 93) or a mixture of 98 % sodium fluoride and 2 % lithium fluoride (98).

5. Electrometric and radiometric determinations.

Before the list is brought to a close, a brief mention of these methods is also deemed proper. As compared with chemical methods of determination, electrometric determinations are much faster and more accurate.

In a potentiometric determination, which is used to determine the true point of equivalence, usually the urajiium (IV) solution is titrated with such oxidizing solutions as potassium permanganate, potassium bichromate, cerium sulfate or iron (III) (99, 100, 101).

The coulometric determination of uranium is rarely applied (102, 103). In the polarographic determination method, — also rarely used — the uranium is first freed from the other elements by means of one of the extraction methods and then, with the aid of sensitive measuring devices, its polarogram is obtained in a suitable electrolytic medium (104, 105, 106, 107, 108). This method is successfully applied in micro - determinations, in particular.

The radiometric determinations make good use of the fact that all uranium minerals emit alpha, beta and gamma rays. The intensity of radiation (or emission) is quantitatively measured in an instrument such as a Geiger-counter or a scintillomcter, which are used for the purpose. This radioactive radiation intensity is dependent upon the element bringing about this radiation; the mass of the active element present in the mineral; the distance of the element to the measuring instrument and finally the direction and composition of the rays. As the analysis of uranium through chemical methods and procedures takes a long time, selecting one of the radiometric or fluorometric methods, especially when a large number of analyses must be taken up all at once, is duly suggested (110).

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