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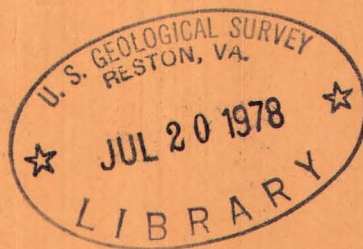
The determination of uranium (IV) in apatite

By Roy S. Clarke, Jr. and Zalman S. Altschuler

Trace Elements Investigations Report 637

**UNITED STATES DEPARTMENT OF THE INTERIOR
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THE DETERMINATION OF URANIUM (IV) IN APATITE

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ABSTRACT

Geologic and mineralogic evidence indicate that the uranium present in apatite may proxy for calcium in the mineral structure as U(IV). An experimental investigation was conducted and chemical evidence was obtained that establishes the presence of U(IV) in apatite.

The following analytical procedure was developed for the determination of U(IV). Carbonate-fluorapatite is dissolved in cold 1.5$\underline{M}$ orthophosphoric acid and fluorapatite is dissolved in cold 1.2$\underline{M}$ hydrochloric acid containing 1.5 g of hydroxylamine hydrochloride per 100 ml. Uranium (IV) is precipitated by cupferron using titanium as a carrier. The uranium in the precipitate is separated by use of the ethyl acetate extraction procedure and determined fluorimetrically. The validity and the limitations of the method have been established by spike experiments.

INTRODUCTION

An important occurrence of uranium is as a trace constituent of the phosphate mineral apatite. Geologic and mineralogic evidence and a consideration of ionic radii indicate that uranium may be present in the apatite structure as U(IV). Information on this oxidation state is pertinent to the study of the geology of phosphate deposits, the mineralogy of apatite, and the general geochemistry of uranium. As a result of these considerations an experimental investigation was undertaken to develop a

chemical method that would indicate if U(IV) is present in natural apatite and, if possible, to determine in what quantity it occurs.

There are two general classes of apatite that have been considered in this work. The first is carbonate-fluorapatite (Altschuler and others, 1952) which may be represented by the formula $Ca_{10}(PO_4,CO_3)_6F_{2-3}$. Apatite from the sedimentary phosphorites, such as those from Florida, the north-western United States, and Morocco, are examples of this type. The second class of apatite is fluorapatite which has the general formula $Ca_{10}(PO_4)_6F_2$. This is normally an accessory mineral in igneous rock. Carbonate-fluorapatite generally contains from 0.01 to 0.02 percent uranium and is readily soluble in cold 1.5$\underline{M}$ phosphoric acid.

In table 1 a general description of the various materials used in this work is summarized. The major constituents in all samples are Ca, P, and F.

Table 1.--Materials used in this investigation.

Sample designation	Description
AP-2	Synthetic fluorapatite
AP-3	Do.
B.L.-3	Carbonate-fluorapatite, Florida
Va.-7	Do.
Wa.-10	Do.
P.V.-5	Do.
Ho.-20	Do.
Mor.-11	Carbonate-fluorapatite, Morocco
Durango	A relatively pure fluorapatite of igneous origin, Mexico
G-25	A complex rare-earth apatite of igneous origin, Mountain Pass, California
F.K.-3	Fluorapatite from an apatite-magnetite body, Mineville, N. Y.
G.P.-19	Fluorapatite from a quartz monzonite, Boulder Creek batholith, Colorado
W-3841	Fossil bone, Montana

The solution of apatite for analysis is a critical step in the deter-
mination of U(IV). Naturally occurring apatite contains small quantities
of elements that may interfere by either oxidizing or reducing the uranium
initially present in the solid material. Specimens of both fluorapatite
and carbonate-fluorapatite may be handpicked to a fair degree of mineralogical
purity. However, even with the greatest possible care, minor elements may
be present in rather large concentrations relative to the uranium. The
nature of these minor constituents is evident from the semiquantitative
spectrographic analyses (Waring and Annell, 1953) of selected materials
(table 2). The chemical value for uranium is inserted in the table in its
proper position to show its abundance relative to the other elements present.

The spectrographic analyses, of course, indicate nothing of the
oxidation state of the elements that are present. However, it does show
in sample B.L.-3 that elements capable of acting as oxidizing or reducing
agents toward uranium are present in quantities comparable to or greater
than uranium. Manganese and chromium are present in the same general con-
centration as uranium. Iron, which as Fe(III) is used in analytical work
to oxidize U(IV), is also present in much larger amounts than the uranium.
In the Durango and G-25 samples the situation becomes more complex. It is
clear that precautions must be taken if U(IV) analyses are to be performed
on material of this complexity.

Fortunately in most apatite the total amounts of uranium and of the
elements that may act to change its oxidation state on solution are small.
This results in a concentration factor that could be expected to lead to
relatively slow attainment of equilibrium. There is also a kinetic factor
that could be expected to lead to slow attainment of equilibrium if the

Table 2.--Semiquantitative spectrographic analyses of minor constituents in apatite.

Range percent	B.L.-3 1/	Durango 2/	G-25 1/	Synthetic apatites AP-2 1/	AP-3 1/
1-5	Al		Ce Sr La		
0.5-1		Ce La Na Y	Nd Na Si		
0.1-0.5	Mg Fe Na	Si	Mg Al Y Fe Pr	Mg	Mg
0.05-0.1	Sr Ti	Mg Sr Al Fe	Ba Pb	Al	Al
0.01-0.05	Pb Mn Cr [U]	Nd Mn	Gd Zr Ti Mn	Si Rb	Si Sr
0.005-0.01	Ba	V Ni Ba Ti Se Yb	Dy B Er Yb [U]	Fe Sr	Fe Na
0.001-0.005	Cu V Y	[U]	Eu Cu Se V	Cr	Ba
0.0005-0.001	Zr	Cr Cu	Cr	Ba	Cr Ti Cu
0.0001-0.0005	Yb			Ti Cu	Ag

1/ Analyst, Katherine V. Hazel, U. S. Geological Survey.

2/ Analyst, Helen W. Worthing, U. S. Geological Survey.

temperature of the system is held as low as possible. If an appreciable delay in reaching equilibrium could be attained in practice, the U(IV) separated from solution could be inherent to the solid apatite and not merely a result of the establishment of equilibrium. To demonstrate the conditions under which interferences of this type could be considered negligible synthetic apatite relatively free of interfering elements was prepared (table 2, AP-2 and AP-3).

The organic precipitant cupferron may be used in acid solutions to separate quantitatively insoluble U(IV) cupferrate from the soluble U(VI) cupferrate. When only very small quantities of uranium are present, a carrier such as Ti may be required to give the precipitate sufficient bulk to be handled conveniently. Using this carrier technique it was possible to recover U(IV) additions quantitatively from a phosphoric acid solution of synthetic apatite. This leads to a straightforward procedure for the determination of U(IV) in apatite readily soluble in phosphoric acid if elements normally present in apatite can be prevented from interfering. Toohey and Kaufman (1954) have shown that this type of interference can lead to completely erroneous conclusions.

The first experimental problem was to determine conditions under which materials could be dissolved and the U(IV) precipitated without appreciable oxidation or reduction of the uranium. The second problem was to establish, in a general way, the quantitativeness of the results obtained. This was carried out by means of a series of spike experiments. In these experiments known additions, or spikes, were added to solutions of pure synthetic materials and to solutions of natural materials. It was found from these experiments that the results obtained from natural materials were similar

to those obtained from synthetic mixtures, thus indicating that the method developed is a valid determination of U(IV) when properly applied to selected materials.

GENERAL PROCEDURE

Carbonate-fluorapatite is readily soluble in cold 1.5$\underline{M}$ orthophosphoric acid. Baes (1953) has shown that at this concentration of phosphoric acid the tendency of Fe(II) to reduce U(VI) is at a minimum. Experiments that are discussed in detail later in this paper (table 4) show that the oxidation of U(IV) by Fe(III) at this acid concentration may also be held at a minimum by properly controlling conditions. As Fe(III) is the most common interference and the one generally present in the largest quantity, a solution of this concentration is a favorable medium for the solution of apatite without change of oxidation state of the uranium present.

Schreyer (1954) has shown that U(IV) orthophosphate is sufficiently soluble so that no phosphate precipitate of the small quantities of U(IV) found in carbonate-fluorapatite forms during the dissolution of the sample. Schreyer also points out that U(IV) in phosphoric acid solution is more stable to air oxidation than in hydrochloric or sulfuric acid solutions.

Phosphoric acid dissolves the well crystallized fluorapatite from crystalline rocks so slowly that oxidation of U(IV) took place when using this solvent. For this reason, samples of igneous or similar apatite were dissolved in 1.2$\underline{M}$ hydrochloric acid containing 1.5 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) per 100 ml. Experimental data indicate that hydroxylamine hydrochloride functions to suppress the oxidation of U(IV) without reducing U(VI).

An outline of the procedure that was used to test the method for the determination of U(IV) follows. The sample is dissolved in cold 1.5M phosphoric acid if it is readily soluble or in 1.2M hydrochloric acid containing 1.5 g of hydroxylamine hydrochloride per 100 ml. The cold solution is filtered to remove any insoluble residue. A titanium solution is added and the cupferrates precipitated by the addition of 6 percent aqueous cupferron. The precipitate is filtered, washed, and ignited. The ignited residue is dissolved with a HF-HNO₃ mixture, taken to dryness with HNO₃, and finally made to volume in 7 percent HNO₃. Uranium is determined by the ethyl acetate extraction-fluorimetric procedure (Grimaldi and others, 1952).

When U(IV) spikes were used they were added either as the samples were being dissolved or after they had been dissolved. Spike solutions were prepared so that only a small volume, generally 1 ml or less, would have to be added to 50 or 100 ml of sample solution. The concentration of the U(IV) spike solutions was checked with each group of experiments performed. The same precipitation technique that was used on samples was used on an aliquot of U(IV) spike solution in a corresponding volume of 1.5M H₃PO₄ or 1.2M HCl to give the actual concentration of the U(IV) solution at the time of use.

PREPARATION OF SYNTHETIC FLUORAPATITE

The synthetic fluorapatites, AP-2 and AP-3, were prepared by thoroughly mixing stoichiometric quantities of $Ca_3(PO_4)_2$ (18.6 g) and CaF_2 (1.56 g). The mixture was placed in a platinum dish and covered with a platinum sheet. This was placed in a cold furnace and rapidly taken to 1250° C, at which temperature it was held for 2 hours. The temperature was slowly reduced

to 950° C over a period of 6 hours before the furnace was turned off. The material was left in the furnace until it reached room temperature.

The indices of refraction of the resulting apatite were $n_E = 1.630$ and $n_0 = 1.632$. The structure was checked by X-ray diffraction, and the pattern was that of fluorapatite without recognizable impurities present. The semiquantitative spectrographic analysis of this material is given in table 2.

EXPERIMENTS

To test the method for the determination of U(IV) in natural apatite one must know precisely how much U(IV) is present in such apatite or rely on synthetic mixtures of known composition. As apatite of known U(IV) content was not available the experimental procedure was applied to spiked samples of dissolved synthetic and natural apatite.

The fact that U(IV) spikes added to synthetic and natural apatite could be recovered quantitatively is established by the following experiment. Spikes were added to cold solutions of AP-3 and B.L.-3 and after standing an hour in the cold, U(IV) was determined. The results of this experiment together with the U(IV) value obtained when sample B.L.-3 is analyzed without a U(IV) spike are given in table 3. Experience at other levels of U(IV) concentration also support the conclusion that complete recovery is obtained.

As the most common impurities associated with apatite are Fe(III) oxides and hydrous oxides in the form of hematite, limonite, and goethite, it is important to establish the range of tolerance of Fe(III). Its oxidizing effect on U(IV) in the presence of dissolved apatite at approximately 25° C and 5° C over different periods of time was investigated. The results of this experiment are given in table 4.

Table 3.--Recoverability of U(IV) in presence of dissolved apatite.
50-ml quantities of 1.5$\underline{M}$ H_3PO_4 containing 100 mg of sample were used.

Sample	U(IV) present (micrograms)	U(IV) added (micrograms)	U(IV) determined (micrograms)	Percent recovery
AP-3	--	50	50	100
B.L.-3	13	50	61	97

Table 4.--The effect of Fe(III) concentration and temperature on the recoverability of U(IV) in the presence of dissolved apatite. 50-ml quantities of 1.5$\underline{M}$ H_3PO_4 containing 100 mg of synthetic apatite, AP-3, were used.

U(IV) added (micrograms)	Fe(III) added (micrograms)	Time of standing before precipitation (hr)	U recovered (micrograms)	
			$\sim 25^\circ$ C	$\sim 5^\circ$ C
48	100	1	41	50
48	100	2	37	50
48	100	17	8	47
48	100	4		48
48	100	4		48
48	200	4		44
48	500	4		42
48	1000	4		34

Most iron incrustations also contain some Fe(II). The total Fe content and Fe(II) content of several samples of Florida apatite are given in table 5. Total Fe was determined by the o-phenanthroline method (Sandell, 1950). An estimation of the Fe(II) content was made by the same general procedure. The sample was dissolved in acid without heating and the o-phenanthroline-ferrous complex was developed without the addition of a reducing agent.

Table 5.--Percent total Fe and Fe(II) in some Florida apatite.

Sample	Total Fe (percent)	Fe(II) (percent)
B.L.-3	0.26	0.14
Va.-7	0.33	0.06
Wa.-10	0.60	0.04
P.V.-5	1.0	0.06

In an experiment similar to that reported in table 4 the reducing effect of Fe(II) on U(VI) spikes was studied. This experiment, the results of which are given in table 6, was conducted at room temperature.

Table 6.--The effect of Fe(II) concentration on U(VI) in the presence of dissolved apatite. 50-ml quantities of $1.5\underline{M}$ H_3PO_4 containing 100 mg of the synthetic apatite, AP-3, were used.

U(VI) added (micrograms)	Time of standing before precipitation (hr)	Fe(II) added (micrograms)	U in precipitate (micrograms)
30	1	--	1.1
30	4	100	2.5
60	4	500	5.0

The small quantity of uranium recovered (table 6) in the experiment with Fe(II) and U(VI) is undoubtedly only partly due to reduction. The last few percent of the uranium present are often not separated due probably to incomplete washing and other mechanical problems. Had this experiment been carried out at 5° C, any reduction effect would undoubtedly have been less.

Having established the independent effect of both Fe(II) on U(VI)- and Fe(III) on U(IV)-spiked synthetic apatite, the effect of addition of both of these forms of iron to a U(IV)-spiked natural apatite B.L.-3 was examined (table 7). Sample B.L.-3 contains significant and approximately equal amounts of Fe(II) and Fe(III) (table 5). In this experiment cold sample solutions that stood for approximately 1 hour before precipitation were used.

Table 7.--The effect of Fe(II) and Fe(III) additions on U(IV) in the presence of dissolved natural apatite. 50-ml quantities of $1.5\underline{M}$ H_3PO_4 containing 100 mg of the natural apatite, B.L.-3, were used.

U(IV) added (micrograms)	Fe(III) added (micrograms)	Fe(II) added (micrograms)	U(IV) determined (micrograms)	Percent recovery of U(IV)
Unspiked B.L.-3	--	--	13, 13, 15	--
42	--	--	56, 55	100
48	100	--	60	97
48	--	100	56	91

The conclusions that can be drawn from the experiments reported in tables 4 through 7 should be emphasized. These experiments show that interference of ferric iron can be the cause of serious error unless the conditions of the experiment are carefully controlled. In table 4, 100 micrograms of Fe(III) is equivalent to 0.1 percent Fe in a 100-mg sample of apatite. At this level of Fe(III) concentration very little oxidation has resulted even after 4 hours. If samples are dissolved in cold acid and the precipitation carried out after a reasonably short period of time (1 hour or less) it would be expected that several tenths of a percent Fe(III) could be tolerated without seriously influencing the results.

The results for sample B.L.-3 are in agreement with the results for the synthetic material. The recovery figure on the addition of 100 micrograms of Fe(II) is low (table 7), but the expected effect would be to increase the U(IV) figure. Sample B.L.-3 contains 16 to 17 micrograms of total uranium per 100 mg, therefore, presumably 3 to 4 micrograms of U(VI) that could be reduced.

The problem of solution of materials that are not readily soluble in cold 1.5$\underline{M}$ H_3PO_4 was overcome by using cold 1.2$\underline{M}$ HCl. Treatment with this acid readily dissolves all apatite in a short time. Table 8 shows the percent U(IV) obtained when five natural apatite samples are dissolved in cold 1.2$\underline{M}$ HCl. This table also includes data on percentages obtained when these materials are dissolved in 1.2$\underline{M}$ HCl containing 1.5 percent hydroxylamine hydrochloride. The use of $NH_2OH \cdot HCl$ gave either comparable or higher results than those obtained with HCl alone. The presence of the hydroxylamine hydrochloride seems to add stability to the U(IV) in solution and reproducibility to the analytical results.

Table 8.--U(IV) values for natural apatite dissolved in 1.2$\underline{M}$ HCl and in 1.2$\underline{M}$ HCl containing 1.5 percent $NH_2OH \cdot HCl$.

Sample	Percent U(IV)	
	HCl as solvent	HCl containing $NH_2OH \cdot HCl$ as solvent
B.L.-3	0.012	0.012
Durango	0.0002	0.0002
G.P.-19	0.0008	0.0009
F.K.-3	0.0015	0.020
G-25	0.0014	0.0019

A series of experiments was performed to establish the recovery and reproducibility of the recovery of U(IV) spikes added to solutions of apatite in 1.2M hydrochloric acid containing 1.5 percent hydroxylamine hydrochloride. Two different levels of U(IV) were first precipitated from acid solution containing hydroxylamine hydrochloride without apatite being present. In these blank determinations essentially complete recovery was obtained. Synthetic apatite AP-2 which contains no uranium and three natural carbonate-fluorapatite samples were analyzed for U(IV). These materials were reanalyzed for U(IV) after known additions of U(IV) were made to the sample solution. In the presence of apatite less than complete recovery of U(IV) spikes was obtained. The results of this experiment are given in table 9. In summarizing, it can be stated that the average percent recovery for these 12 analyses on 4 different samples is 79, with a range of values from 67 to 87. It is worth noting that despite the fact that the spikes varied from 20 to 500 micrograms of uranium the standard deviation from the average percent recovery is only 5.4.

Katz and Rabinowitch (1951) point out that there is evidence for U(IV)-fluoride ion complex formation, and Ahrland and Larsson (1954) have made a detailed study of U(IV) complexes with chloride, bromide, and thiocyanate ions. It is possible that the formation of a U(IV)-fluoride ion complex causes the consistent 20 percent low recovery in the above experiments (table 9). The apatite used contained from 3 to 4 percent fluorine, the carbonate-fluorapatite being at the high end and the fluorapatite being at the low end of this range.

Table 9.--Recovery of U(IV) spikes from solutions of apatite in

1.2M HCl containing 1.5 percent NH$_2$OH·HCl.

Sample 0.100 g	U(IV) in spike (micrograms)	U(IV) determined (micrograms)	Total U(IV) recovered (percent)
Blank	20	20	100
Do.	100	97	97
AP-2 (synthetic no U)	0	0	--
Do.	20	15	75
Do.	40	35	87
Do.	100	84	84
Do.	500	400	80
B.L.-3	0	12	--
Do.	20	25	78
Do.	40	41	79
Do.	100	88	79
Do.	500	370	72
Va.-7	0	4.0	--
Do.	20	20	83
Do.	40	36	82
Wa.-10	0	1.6	--
Do.	20	17	77
Do.	40	28	67

An indication of possible complexing action was obtained by an experiment using the carbonate-fluorapatite sample B.L.-3. The U(IV) was precipitated and filtered in the normal way and the filtrate from this operation was then checked for additional U(IV). A value of 0.010 percent U(IV) was obtained from the first precipitation (a low value for this sample). An additional 0.0028 percent U(IV) which was obtained from the second precipitation accounts for 47 percent of the uranium remaining in solution.

That a 20 percent deficiency in recovery could be attributed to a
U(IV)-fluoride complex was established by comparing the recoveries of
known spikes of U(IV) from solutions of tricalcium phosphate and calcium
fluoride. The concentrations of calcium phosphate and calcium fluoride
used were equivalent to those obtained upon dissolving apatite as in
the normal experimental procedure. In calcium phosphate alone the spike
was completely recovered, whereas with calcium fluoride alone only 80
percent of the spike was recovered. These experiments would seem to
establish that a U(IV)-fluoride ion complex is operating to cause the
low recoveries.

Experiments to study the effect on U(IV) values of changing the
hydroxylamine hydrochloride concentration in 1.2M hydrochloric acid were
performed. The data from these experiments are given in table 10. Several
different materials were used and 100-mg portions were allowed to stand
in the cold acid solutions with occasional stirring for 1 hour. To the
solutions containing the synthetic fluorapatite, AP-3, 1.0 ml of a spike
solution that contained approximately 20 micrograms of U(IV) per milliliter
was added. Sample B.L.-3, a carbonate-fluorapatite, was used because a
fluorapatite of simple chemical composition at this relatively high level
of U(IV) content was not available. The Durango fluorapatite is of
relatively simple chemical composition whereas the fluorapatite F.K.-3
is of more complex composition. The compositions of AP-3, B.L.-3, and
Durango are given in table 2 and that of F.K.-3 is given by McKeown and
Klemic (1956).

Table 10.--U(IV) values obtained on solution of samples in 1.2M HCl
containing various concentrations of NH₂OH·HCl.

Percent NH₂OH·HCl in 1.2M HCl	Percent U(IV)			
	AP-3 1/ spiked to contain ~0.02 percent U(IV)	B.L.-3 (Total U 0.016 percent)	Durango (Total U 0.00087 percent)	F.K.-3 (Total U 0.074 percent)
0	0.015	0.012	0.0002	0.0015
0.15	0.019	0.012	0.00025	0.0010
0.75	0.019	0.012	0.00030	0.015
1.5	0.020	0.013	0.0002	0.020
3.0	0.018	0.012	0.00032	0.022
15	0.019	0.013	0.00034	0.030

1/ Uranium free.

The U(IV) values obtained for the spiked synthetic AP-3 and sample
B.L.-3 are essentially constant over the range of hydroxylamine hydrochloride
concentrations studied. This constancy demonstrates that the 1.5 percent
hydroxylamine hydrochloride concentration, selected for use as a solvent
for fluorapatite, is well within a range of concentrations that can be
varied without causing variation in U(IV) values for a number of materials.
The results on the Durango material probably fall, in a general way, into
the pattern of AP-3 and B.L.-3. However, the data on Durango are not
conclusive because of the low level of U in this material.

The U(IV) values obtained for the complex material F.K.-3 increase
markedly with increasing hydroxylamine hydrochloride concentration. This
kind of response is a general indication of unsuitability of a particular
apatite specimen or group to this type of U(IV) analysis.

The lack of constancy of U(IV) values in sample F.K.-3 is not surprising when its chemical composition is considered. The material contains over 10 percent rare earths (more than 1 percent Ce) and several elements such as Fe, Mn, and As in the 0.0X to 0.X percent range which could act to change the oxidation state of uranium. This material also contains Co in the 0.0X percent range and Cu in the 0.00X percent range. Pannell (1950) has shown that both Co and Cu, along with Mo and silicate, catalyze the air oxidation of uranium.

A possible explanation of the behavior observed with sample F.K.-3 is that hydroxylamine hydrochloride in the presence of an unknown catalytic agent reduces some U(VI) to U(IV), resulting in an increase in apparent U(IV) with increased hydroxylamine hydrochloride concentration. That this type of behavior does not usually occur is shown by the results with AP-3 and B.L.-3. It should be noted that for sample B.L.-3 an essentially constant U(IV) value was obtained with all the various solvents used in this work (1.2$\underline{M}$ HCl, 1.2$\underline{M}$ HCl containing various concentrations of $NH_2OH \cdot HCl$, table 10, and 1.5$\underline{M}$ H_3PO_4, table 7). It should also be noted that there is appreciable uranium, 25 percent of the total, in sample B.L.-3 that is not accounted for as U(IV). This uranium is presumably present as U(VI).

An experiment was conducted to see if Fe(II) spikes could reduce U(VI) when the samples are dissolved in 100 ml of hydrochloric acid-hydroxylamine hydrochloride solution. The synthetic apatite, which is essentially iron free, and a natural apatite, B.L.-3, containing 0.26 percent total Fe and 0.14 percent Fe(II) were used. The iron and U(VI) spikes were added with stirring to the cold sample solution. The cupferron precipitation was made after approximately 1 hour. The results are given in table 11. This experiment demonstrates that relatively large quantities of Fe(II) as compared to uranium can be tolerated under these conditions.

Table 11.--The effect of Fe(II) additions on U(IV) values for samples

dissolved in 100 ml of 1.2$\underline{M}$ HCl containing 1.5 percent NH$_2$OH·HCl.

100 mg sample	Treatment	Percent U(IV)
AP-2	15 micrograms U(VI) + 0.12 mg Fe(II)	0.00030 [1]
AP-2	15 micrograms U(VI) + 0.12 mg Fe(II) + 0.06 mg Fe(III)	0.00035 [1]
B.L.-3	0.31 mg Fe(II)	0.013 [2]
B.L.-3	3.1 mg Fe(II)	0.014 [2]

[1] Less than 2.5 percent of total uranium present.

[2] Unspiked values run from 0.011 to 0.013 percent U.

A comparison of results obtained on natural materials that are soluble in both the phosphoric acid and the hydrochloric acid-hydroxylamine hydrochloride solutions is given in table 12. With the exception of sample Mor.-11, the results of phosphoric acid solution of the sample are higher than those of hydrochloric acid-hydroxylamine hydrochloride. This fits in with the data on fluoride-complex formation in the hydrochloric acid-hydroxylamine hydrochloride medium. On the average these determinations are lower by 12 percent than those using phosphoric acid. This is not far out of line with the 80 percent recovery figure on U(IV) spike experiments. Perhaps the values obtained using phosphoric acid are also a little low.

Table 12.--Comparison of U(IV) values of natural materials using

two different methods of sample solution.

Sample	Dissolved in HCl-NH$_2$OH·HCl		Dissolved in H$_3$PO$_4$	
	Percent U(IV)	Percent of total U in reduced state	Percent U(IV)	Percent of total U in reduced state
B.L.-3	0.012	71	0.013	82
Va.-7	0.0040	45	0.0055	57
Wa.-10	0.0016	21	0.0028	37
P.V.-5	0.0024	34	0.0029	39
Ho.-20	0.011	48	0.015	65
Mor.-11	0.0009	9	0.0005	5
W-3841	0.40	48	0.50	60

Sample Mor.-11 is an oxidized material containing an appreciable amount of goethite and therefore would be expected to contain little U(IV). When 50 micrograms of U(IV) spike was added to a phosphoric acid solution of Mor.-11 and the U(IV) precipitated, only 46 micrograms of uranium was recovered rather than the 51 micrograms that would be expected--a 90 percent recovery.

REAGENTS

All chemicals used were reagent grade.

1.5M orthophosphoric acid.

1.2M hydrochloric acid containing 1.5 g of hydroxylamine hydrochloride (NH$_2$OH·HCl) per 100 ml.

6 percent aqueous cupferron.

Wash solution: Add 25 ml of 6 percent cupferron solution and 60 ml of hydrochloric acid to water and dilute to 1 liter.

Titanium solution: 0.437 g of titanium oxide, TiO_2, was fused with 5 g of potassium pyrosulfate. The product of the fusion was dissolved in 200 ml of water containing 25 ml of concentrated sulfuric acid. This solution is diluted to 250 ml, yielding a solution containing 1.0 mg of Ti per milliliter.

Uranium (IV) spike solution: A solution of 200 micrograms of uranium per milliter in 5 percent H_2SO_4 prepared from 99.9 percent U_3O_8 was reduced on a Jones reductor and was stored in a refrigerator when not in use. Solutions of various strengths were prepared from it by dilution with cold 5 percent H_2SO_4. Fresh solutions were prepared every few days because of appreciable oxidation.

DETAILED ANALYTICAL PROCEDURE

The choice of solvent depends on the nature of the sample. Cold phosphoric acid should be used for carbonate-fluorapatite and any other material that will dissolve in this medium. The use of hydrochloric acid-hydroxylamine hydrochloride solution is required for apatite of igneous origin or other highly crystalline fluorapatite.

Solution of sample in phosphoric acid

The sample is ground to a fine powder, 0.100 g is weighed, put into a 100-ml beaker, and 50 ml of 1.5M phosphoric acid that has been chilled to at least 5° C is added. The acid is stirred to suspend the sample, the beaker is covered and placed in a cold water bath regulated at 4° to 5° C for one hour. The suspension is stirred several times during this period. More frequent stirring is required for less readily soluble samples.

Solution of sample in hydrochloric acid-hydroxylamine hydrochloride solution

The sample is ground to a fine powder, 0.100 g is weighed, put into a 250-ml beaker, and 100 ml of a solution of 1.2$\underline{M}$ hydrochloric acid containing 1.5 percent hydroxylamine hydrochloride that has been chilled to 5° C or below is added. The solvent is stirred to suspend the sample, the beaker is covered and placed in the cold water bath regulated at 4° to 5° C. The sample is stirred at frequent intervals until it is in solution. This can take from 20 minutes to 1 hour.

Cupferron precipitation

The cold sample solution (either method of preparation) is filtered with suction through a 2.1-cm glass fiber filter paper in a Gooch crucible. The beaker and crucible are washed twice with small quantities of water. The filtrate is received in a 150-ml beaker sitting in ice water.

Immediately 3.0 ml of a cold solution of 1.0 mg of Ti per milliliter in 10 percent sulfuric acid is added. This is followed by the addition with stirring of 3.0 ml of a cold aqueous 6 percent cupferron solution. The beaker containing the cupferrate is placed in the freezing compartment of a refrigerator for 10-15 min before filtration with suction through a 9-cm close-textured filter paper. The precipitate is washed a total of eight times with a cool solution of 6 percent hydrochloric acid and 0.15 percent cupferron. The paper containing the precipitate is placed in a 25-ml platinum crucible and charred under an infrared lamp and then ignited over a burner.

Determination of uranium

The ignited residue must be put into a 7 percent by volume nitric acid solution for extraction of the uranium. This may be done by two methods, either (a) potassium pyrosulfate fusion or (b) HF-nitric acid treatment.

a) Add 0.5 g of potassium pyrosulfate to the residue and heat over an open flame at as low a temperature as possible until solution is complete.

b) Add 5 ml of 1+1 nitric acid and 5 ml of HF to the residue. Evaporate to dryness on the steam bath. Add 1 ml of 1+1 nitric acid and again take to dryness.

Take up the residue from either method of treatment with enough 1+1 nitric acid to yield on dilution a convenient volume of 7 percent by volume nitric acid. Warm on the steam bath to dissolve the material and transfer the solution and any insoluble material to a volumetric flask and dilute to volume. A 5.0-ml aliquot of this solution is added to a glass-stoppered test tube containing 9.5 g aluminum nitrate of low uranium content. Uranium is then determined by a standard ethyl acetate extraction-fluorimetric procedure (Grimaldi and others, 1952).

It may be convenient when working with small amounts of material or with materials that are quite low in uranium to take up the whole sample in a volume of 5 ml of 7 percent by volume nitric acid. If this is to be done, 9.5 g aluminum nitrate of low uranium content is added directly to the crucible containing the residue from either treatment (a) or (b) given above. Five milliliters of 7 percent by volume nitric acid is added and the crucible and contents heated on the steam bath until the salt dissolves and as much as possible of the residue is in solution. The contents of

the crucible are then transferred (without washing) to a glass-stoppered
test tube for extraction.

SUMMARY

The data obtained by spike experiments demonstrate that the method
outlined in this paper can be used to estimate the U(IV) content of
selected apatite samples. The purity of the sample material determines
the applicability of the method. Spectrographic analyses or other suitable
tests are suggested to check on unusual content of elements that may act
either to oxidize or to reduce uranium.

Materials of the carbonate-fluorapatite type can be put into solution
with the phosphoric acid treatment. Analyses based on this method of
solution are on a more secure footing than those based on solution of
sample in hydrochloric acid-hydroxylamine hydrochloride. For this reason,
phosphoric acid solution is used whenever the sample is readily soluble
in it. Hydrochloric acid-hydroxylamine hydrochloride solution is used
only on the less soluble materials.

U(IV) results should be evaluated in terms of all the information
available on a particular material. Knowledge of the general chemical
composition of the material, particularly with reference to iron and other
elements that may act as oxidizing or reducing agents, is helpful.

The reliability of particular analysis may be checked by use of a
U(IV) spike. The spike should be recovered nearly completely if phosphoric
acid is used to dissolve the sample. If the more drastic hydrochloric
acid-hydroxylamine hydrochloride treatment is required, the spike should
be recovered at about the 80 percent level. It should also be noted that
values obtained when using this latter solvent are probably 20 percent low.

Experience indicates that little confidence can be placed on any U(IV) figure that is less than 10 percent of the total uranium present in the material analyzed. Only when spiking experiments indicate that it is a valid result should any significance be attributed to such a low value.

The analytical procedure developed has been advantageously applied to several types of apatite in the course of a study of the geochemistry of uranium in apatite and phosphorite samples; this study will be the subject of a later report.

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