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PRELIMINARY REPORT ON METHODS OF ANALYSIS FOR VERY SMALL PERCENTAGES OF URANIUM

Revised July, 1945

Trace Elements Project Report No. 2

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PRELIMINARY REPORT
ON METHODS OF ANALYSIS
FOR VERY SMALL PERCENTAGES OF URANIUM

By M. D. Foster, F. S. Grimaldi and R. E. Stevens

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Abstract

Procedures are presented in detail of two methods for the determination of very small percentages of uranium (down to 0.002%). The methods are applicable to a wide variety of materials. Notes on the methods and confirmatory experiments are also given.

Introduction

The Chemical Laboratory of the Geological Survey was requested to develop methods by which accurate determinations of very small percentages of uranium could be made on rocks and ores of widely varying types. This report presents the procedures developed and now in use, and is preliminary; further work is in progress.

Samples for analysis are selected by geologists in the field on the basis of field counts of total radioactivity by means of a portable Geiger-Müller counter (see Trace Elements Project Report No. 1, by A. L. Slaughter and S. E. Clabaugh), and similar more accurate laboratory counts of total radioactivity.

The diversity of the samples to be analyzed, which include shales, phosphate rock, pegmatites, rhyolites, ores of various metals, fluorites, and other types, has made necessary a rather long process for the decomposition of the sample. It is considered unsafe to assume that no uranium is present in undecomposed material; the procedure therefore provides for the complete decomposition of the sample.

The elapsed time from the beginning to the completion of an analysis by either of the methods described in this report is about four days, and each analyst can complete approximately three analyses per day, provided the samples do not require special treatment. For the accuracy obtainable, see paragraphs 9 and 18 below.

Outline of procedure

The essential features of the methods are:

a) Complete decomposition of the sample.

b) Removal of nearly all Fe by extraction with ethyl acetate from a 1-1 HCl solution.

c) Collection of the uranium by:

Method A (carbonate) consisting of:

Removal of Ca, Th, Zr, Cr, Ti, rare earths, and part of the Al by precipitation with sodium carbonate.

Separation from V and coprecipitation of U and Al as phosphates.

Method B (cupferron) consisting of:

Precipitation by cupferron after reduction of U, Ti, V, Zr, etc. (separation from Al, Ca, P, etc.).

Ignition, fusion, and solution of the cupferron precipitate.

Separation of uranyl ion by extracting the cupferron compounds of other elements with ethyl acetate.

d) Colorimetric determination of uranium by peroxide in alkaline solution.

Decomposition of sample

by M. D. Foster and R. E. Stevens

1. Weigh out 5.00 g. of sample, ground to pass 60-80 mesh, for samples with total radioactivity counts equivalent to 0.015% U or less; for samples with higher counts, weigh out proportionally less.

2. Ignite at top heat of a Meker or Fischer burner if the sample contains organic matter or sulfides.

3. Digest in a covered platinum dish on the steam bath for 30 minutes with 40 ml. 1-1 HNO_3. Remove the cover, add 10-15 ml. of HF, and take to dryness on a slow steam bath. Repeat if there is much unattacked material. Evaporate to dryness twice with HNO_3. Transfer the dry residue in the platinum dish to porcelain or glass, rinse with 1-1 HCl, add 10 ml. of HCl and evaporate to dryness. Follow by two more evaporations to dryness with HCl. Digest the residue, covered, with 20 ml. of 1-1 HCl and filter. Wash with hot 1-1 HCl and finally with a little hot water. Ignite the residue in platinum, add a little HF and one drop of H_2SO_4 and take to dryness. Sinter the remaining residue with as little Na_2CO_3 as possible and dissolve in 1-1 HCl. If there is an unattacked residue, filter, adding the filtrate to the main sample and again sinter the residue with Na_2CO_3 and dissolve in 1-1 HCl.

If much SiO_2 separates when the fusion is treated with 1-1 HCl, evaporate to dryness in platinum, treat with HF and a few drops of H_2SO_4 and fume. Take up in 1-1 HCl and add to main sample. If little or no SiO_2 separates when the fusion is treated with 1-1 HCl, add the solution to the previous filtrates. Evaporate the combined filtrates to about 25 ml. If there is any residue, filter. Dissolve the residue in hot water and add this solution back to the main portion after Step 4 (next paragraph).

(See Notes, paragraphs 19 and 20, and Confirmatory Experiments, paragraph 32.)

Extraction of iron

4. Extract Fe by shaking the 1-1 HCl solution with ethyl acetate in a separatory funnel. Two extractions are sufficient as it is not necessary to remove the Fe completely. Use 40 ml. of ethyl acetate for the first extraction, and 20 ml. for the second. Combine the ethyl acetate layers and wash twice with 1-1 HCl (5 ml. each), and add the washings to the acid water layer. Finally discard the ethyl acetate layer containing the iron. Proceed to the determination of uranium by method A (carbonate) or method B (cupferron).

Method A (carbonate)

by M. D. Foster and R. E. Stevens

Procedure

5. Evaporate the combined acid water layers to 25 ml. (This step is important as it limits the acid concentration and subsequent salt concentration of the solution.)

6. Dilute--in a 400 ml. beaker--to 275 to 300 ml. with distilled water and heat to boiling. Add 50% NaOH solution until a slight permanent cloud forms (about 15 ml. of 50% NaOH solution is required) and then dry Na_2CO_3--very carefully--until efferescence no longer takes place--then 2 g. of Na_2CO_3 in excess. Place the beaker in a cold water bath and filter after 3/4 to 1 hour through #40 Whatman 12.5 cm. paper. Reserve the filtrate.. Transfer the precipitate from the paper to the beaker with a stream of distilled water, add 10 ml. HCl. After the precipitate has dissolved dilute the solution to 275 to 300 ml., heat to boiling and precipitate with 50% NaOH and dry Na_2CO_3. Cool and filter as before and wash the precipitate 5 times with a solution containing 10 g. of Na_2CO_3 per liter. Add the filtrate and washings to the filtrate from the first precipitation. Make the filtrate acid with HCl, then add 2 ml. in excess, noting the approximate amount of Al precipitated as the neutral point is passed (see notes, paragraphs 22 and 23).

7. Heat to boiling and reduce the volume of the combined filtrates to about 150 ml. (Some time may be saved here if the filtrate from the 1st carbonate precipitation is made acid and evaporated down during the 2nd carbonate precipitation and filtration). Add $AlCl_3$ solution (1 ml. = 5 mg. Al_2O_3), 7-10 ml. if the solution contains no Al, 4-5 ml. if in the process of neutralization the solution was found to contain some Al. If a precipitate forms, add sufficient 1-1 HCl to dissolve it. Add 1 g. of dry $(NH_4)_2HPO_4$ and, with the solution at the boiling point, add NH_4OH until the solution is just alkaline to methyl red, then add sufficient ammonium acetate-acetic acid buffer solution (containing 308 g. of ammonium acetate and 460 ml. of acetic acid per liter) to make the solution distinctly acid. Again heat the solution (with ppt.) to boiling, and digest on the steam bath for 1/2 hour. Filter through

#42 Whatman 9 cm. paper and wash the precipitate 5 times with a solution containing 20 ml. of the ammonium acetate-acetic acid buffer solution above in 100 ml. of water. (See Notes, paragraph 22).

8. After the precipitate has drained, transfer it from the paper to a 100 ml. beaker with a fine jet of distilled water, keeping the volume below 50 ml. Add HCl dropwise until the precipitate just dissolves, then 2 ml. of HCl in excess. Add 3 drops of superoxol. Subsequent steps depend on the amount of V in the solution as indicated by the development of a reddish-brown color on addition of superoxol. If the color indicates that less than 1 mg. of V is present in solution,make the solution just alkaline with 50% NaOH and add 5 ml. in excess. Adjust tho volume to 50 ml. and filter to remove paper fibers and possible traces of Fe and Ce. The filter paper should have been/treated previously with a NaOH-superoxol solution solution of the same strength. (See Confirmatory Experiments, paragraph 34.) Compare visually or with a spectrophotometer (at 370 mμ) with U standards containing the same amount of NaOH and superoxol in the same volume.

If the color of the acid solution of the phosphates after the addition of superoxol indicates that the solution contains from 1-3 mg. of V, add NaOH as before but heat the solution to boiling and boil for 1-2 minutes* and cool before proceeding with the filtration and comparison.

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* As suggested by N.B.S., Report A-1074, March, 1945.

If the color of the acid solution on addition of superoxol indicates that the solution contains more than 3 mg. of V, transfer the solution to a 250 ml. beaker, make the volume up to about 150 ml., add 2 g. of NaCl and proceed with the precipitation, digestion, filtration and washing of the phosphates as before. Transfer the phosphate precipitate to a beaker, add NaOH and superoxol and filter and compare as indicated above.

Verification

9. The accuracy of the method is shown by the results of Table 1.

Table 1. Verification of method A

No.	Sample	Mg. U added	Mg. U recovered 1st filtrate	Mg. U recovered 2nd filtrate	Total U recovered
1	a/35 ml. synthetic mixture	.25	.23	... b/	.23
2	..........Do..............	.50	.45	... b/	.45
3	..........Do..............	1.00	.80	.20	1.00
4	..........Do..............	1.50	1.15	.32	1.47
5	..........Do..............	2.00	1.42	.50	1.92
6	..15......Do..............	2.00	2.01	... b/	2.01
7	..........Do..............	5.00	4.65	.34	4.99
8	..........Do..............	10.00	8.30	1.62	9.92
9	..........Do..............	20.00	18.00	1.76	19.76

a/ Synthetic mixture--10 g. $CaCl_2$, 20 g. $Na_3PO_4.12H_2O$, 30 g. $AlCl_3.6H_2O$, 5 g. $MgCl_2.6H_2O$, 1 g. $MnCl_2.4H_2O$ in 1 liter of 10% (by vol.) HCl.

b/ U not determined in 2nd filtrate.

Method B (cupferron)
by F. S. Grimaldi

Procedure

10. Evaporate the combined water layers to dryness. Add 10 ml. of 1-1 HCl. Digest on the steam bath for 15 minutes. Add 20 ml. of water and digest until the soluble salts dissolve. Filter. Wash with water. Reject the residue. (See Notes, paragraph 24.)

11. Pass the solution, 50 ml. in volume, through a small Jones reductor (see Notes, paragraph 25). Collect the solution directly into 15 ml. of 6% cupferron solution contained in a 125 ml. Erlenmeyer flask immersed in an ice bath, shaking the flask during the passage. Wash the reductor column with 10 ml. of 5% HCl and then with enough water to make the contents of the flask 100 ml. Let stand in the ice bath for about 5 minutes, stirring occasionally. Mix in a little paper pulp and filter. Wash with cold 6% HCl containing 1.5 g. per liter of cupferron. (See Notes, paragraphs 26 and 27.)

12. Burn the cupferron precipitate in porcelain, starting the ignition at low heat until the paper is carbonized, and then increasing the heat until the carbon is burned off. The final temperature should be about 750°C. (See Notes, paragraph 28.)

13. If the solution before passage through the reductor (Step 10) showed no visible green chromium color, omit steps 13 and 14 and proceed directly to Step 15.

Fuse with a little potassium pyrosulfate. Keep the melt in quiet fusion until the residue is dissolved and any carbon that might be present due to faulty ignition of the cupferron precipitate is also gone. Allow the melt to cool. Dissolve the melt in 50 ml. of water containing 4.5 ml. of HCl.

14. Pass the solution through the reductor as in Step 11. This second reduction is not necessary if the solution before the first passage through the reductor (Step 10) showed no visible green chromium color.

15. Fuse the second ignited cupferron precipitate with potassium pyrosulfate. Keep the melt in quiet fusion until the residue is dissolved and any carbon that might be present due to faulty ignition of the cupferron precipitate is also gone. Cool. Add a little niter (about 10-25 mg.) and fuse again until the nitrate is gone. Cool and dissolve the melt in 30 ml. of water containing 3.5 ml. of HCl. (See Notes, paragraph 29.) Cool the solution in an ice bath.

16. Transfer the solution to a separatory funnel. Add 15 ml. of cold 6% cupferron solution. Shake several times. Add 20 ml. of cold ethyl acetate, shake, allow to settle, and separate the layers. Make 2 more extractions of the water layer with ethyl acetate. Wash the combined ethyl acetate layers once with 15-20 ml. of cold 8% HCl. Wash this HCl layer once with cold ethyl acetate. Combine all aqueous acid layers. Reject the ethyl acetate layers. (See Notes, paragraph 30.)

17. Evaporate the water layer to a small volume. Add 15 ml. of HNO_3 and take to dryness. Add 1 ml. H_2SO_4, cover with watch glass, fume gently on the hot plate. Destroy the last trace of organic matter by cautious dropwise addition of 1 ml. of nitric or fuming nitric acid. Allow to fume for 5 minutes after the nitric acid is gone. Repeat with a 1 ml. portion of fuming nitric acid. Allow to fume 5 minutes after the nitric acid is gone. While still fuming add cautiously 2 ml. of water dropwise from a pipette to remove any traces of nitrous fumes and then bring to fumes of sulfuric acid again. Cool.

18. Add 35 ml. of water and boil gently until a solution is obtained. Cool to about 50°C. Add 6 drops of superoxol, then 50% NaOH solution drop by drop until neutral, then 1 ml. in excess. Cool. Stir in some paper pulp and make to 50 ml. in a graduated cylinder. Filter through a 7 cm. Whatman #40 paper but do not wash. The solution is now ready for color comparison. (See Notes, paragraph 31.)

19. Compare the solution visually or with a spectrophotometer with solutions containing known quantities of uranium made up to 50 ml. volume and containing 1 ml. of 50% NaOH solution and 5 drops of superoxol.

Verification

18. Table 2. Verification of method B

Sample	Mg. U in sample	Mg. U added	Total mg. U found
Synthetic mixture a/	None	0.3	0.3
........Do..........	None	.6	.6
........Do..........	None	1.30	1.25
........Do..........	None	2.5	2.5
65-7 (sandstone)	.15	None	.15
........Do......	.15	.6	.75
108-54 (shale)	.5	None	.5
........Do....	.5	.3	.8

a/ Synthetic mixture: 50 g. quartz, 50 g. albite, 50 g. $Na_3PO_4 \cdot 12H_2O$, 50 g. $CaCO_3$, 50 g. Fe_2O_3, 10 g. $MgCO_3$, 10 g. MnO_2, 1 g. chrome alum, 1 g. V_2O_5, 0.2 g. TiO_2. The analyses were made on five grams of the synthetic mixture after known quantities of uranium had been added.

Notes on the methods

19. The procedure for decomposition of the sample (paragraphs 2-3) is suitable for most materials, but has to be modified for some unusual samples. A few examples will illustrate. Samples containing much iron oxide may be digested with 1-1 HCl, evaporated to dryness, taken up in HCl and filtered. The residue is then treated with HNO_3 + HF as usual and the HCl filtrate added back. Samples containing much fluorite are best attacked by fuming to dryness with $HClO_4$. If $HClO_4$ is used, diethyl ether should be used in the subsequent extraction of Fe instead of ethyl acetate, which tends to form emulsions in the presence of $HClO_4$. Some samples contain appreciable amounts of minerals such as cassiterite, rutile or columbite not readily attacked by the procedure of paragraph 3. Fusion with $KHSO_4$ in porcelain or with KOH in a nickel crucible should be substituted for fusion with Na_2CO_3 for such material.

20. The residue insoluble in 1-1 HCl and filtered off (at end of paragraph 3) is usually NaCl and occasionally $PbCl_2$. This is dissolved in hot water and added back to the main portion after iron has been removed (paragraph 4). The procedure may leave residues containing Ta, Cb, Sn, Ti, Zr, W, Th, and P_2O_5. These may be ignored as they do not occlude uranium if decomposition was complete. (See Confirmatory experiments, paragraph 32.)

21. Copper, if present, is largely precipitated as the carbonate (paragraph 6). If precipitation of copper is not complete as the carbonate, as indicated by a blue hue in the filtrate from the carbonate precipitation, acidify and reduce the volume of the filtrate as in paragraph 7, adjust the acidity to 5% and pass in H_2S to precipitate the remainder of the Cu. After filtering off this precipitate, boil off H_2S from the filtrate before proceeding to the phosphate precipitation.

22. The amount of U retained in the 1st carbonate precipitation depends on the amount of U present and on the bulk of the carbonate precipitate. With the amount of precipitate to be expected from solutions resulting from the decomposition of a 5 gram sample, less than 4% of the U is retained after 2 precipitations if the U

content is less than 2 mg. (see Table 1, paragraph 9). With the amount of precipitate to be expected from solutions resulting from the decomposition of a 2 gram sample less than 2% of the U is retained after 2 precipitations if the U content is less than 20 mg.

23. The elements Cr and Ti which might interfere in the colorimetric determination of U with H_2O_2 in alkaline solution are removed by the carbonate precipitation but V is not. The phosphate precipitation is essentially for the purpose of separating U from V and is not necessary if the V content of the solution is less than 1 mg. The U can then be determined directly on the filtrate from the carbonate precipitation after the volume has been reduced. However the salt content of the filtrate is usually so great that the volume cannot be reduced sufficiently when the U content is very low and precipitation of the U as phosphate, using $AlPO_4$ as a collector, with subsequent solution in NaOH, makes it possible to obtain the U in a smaller volume for comparison.

24. A clear solution is generally obtained at this point (paragraph 10). Sometimes, however, some additional TiO_2 may separate out. This should be filtered off and rejected. (See Confirmatory experiments, paragraph 32.)

25. A miniature Jones reductor is used (paragraph 11), 10 inches in length and of about 1/2 inch bore, containing zinc amalgamated with 3% of mercury. With ores containing copper or lead, it may be necessary to pretreat the solution with zinc to avoid precipitation of copper or lead in the reductor. The solution to be passed through the reductor should have as small a volume as is consistent with solution of the salts. The solution should contain approximately 10% by volume of HCl. Passage of the solution through the reductor reduces uranium to the trivalent and quadrivalent states, both of which are quantitatively precipitated by the cupferron in the receiver flask. The cupferron precipitation is conducted at acidities of HCl of 4 to 8% by volume. Perchlorate and sulfate do not interfere.

26. The cupferron will precipitate U (paragraph 11), along with all Fe, Ti, Zr, Hf, V, Cb, Ta, Mo, Sn and part of the W that escaped previous separation. The process separates these elements from the bulk of the elements, such as Al, P, Mn, Co, Ni, Ca and Cr present in the solution.

27. Hillebrand-Lundell points out that bivalent Cr will be partially precipitated by cupferron. Tests were made to determine to what extent this takes place under the conditions used in the analysis. Duplicate solutions containing 25 mg. Cr_2O_3 in 50 ml. of 10% by volume of HCl were passed through the Jones reductor and caught in 15 ml. of 6% cupferron solution according to the procedure of paragraph 11. The cupferron precipitates were ignited and found to be free of chromium. However experience with actual rock samples has shown that some chromium is occluded with the cupferron precipitate either when the amount of chromium is high or when the cupferron precipitate is large. There is evidence that this occlusion is not due to actual precipitation of bivalent chromium but to mechanical occlusion. A sample containing 62 mg. V_2O_3 and 32 mg. Cr_2O_3 showed an occlusion of chromium of 0.24 mg. Cr_2O_3 with 1 reduction. It has been our experience that for most samples containing chromium, the occlusion of chromium in the first cupferron precipitate will very rarely exceed 0.3 mg. Cr_2O_3. This conclusion is a result of tests on over 80 samples containing relatively large amounts of chromium. Since chromium gives an alkaline peroxide color identical with and five times as intense as that given by the same weight of uranium, it is imperative to make certain of its complete removal. In general, samples containing more than 3 mg. Cr_2O_3 may give some chromium interference. Chromium may be removed in several ways:

1, By reprecipitation with cupferron after a second reduction. This procedure has been extensively tested and has been adopted for general work. (See Confirmatory experiments, paragraph 33.)

2. By volatilization of the chromium as chromyl chloride. This procedure has not been thoroughly tested but six tests indicated that it is practicable. This procedure could handle much larger quantities of chromium and may be useful in the analyses of material of very high chromium content. (See Confirmatory experiments, paragraph 34.)

29. The niter is necessary (paragraph $\overset{10}{15}$) to insure that uranium is in the sexivalent state to prevent its precipitation in the next step of the procedure.

30. This step (paragraph $\overset{11}{16}$) effects the quantitative separation of uranium from Fe, Ti, Zr, V, Mo, and other elements that form insoluble precipitates with cupferron; U^{+6} is not precipitated. These cupferron precipitates are soluble in ether or ethyl acetate and are completely extracted, leaving the uranium quantitatively in the aqueous layer. The acidity of the solution at the start of the extraction of the cupferrates is 8% by volume of HCl. In the extraction, practically all of the excess cupferron dissolves in the ethyl acetate. (See Confirmatory experiments, paragraph 35.)

31. The solution is filtered (paragraph 18) to remove hydrated oxides of rare earths which may have escaped previous separation. The color produced by cerium in NaOH-H_2O_2 solution is about twice as strong as that produced by an equal weight of uranium. The cupferrate of cerium is not extracted by ethyl acetate (see Confirmatory experiments, paragraph 35); any cerium precipitated with U^{+3} and U^{+4} will accompany uranium and interfere in the final color comparison unless it is removed at this point. If 25 mg. Ce^{+3} is originally present, about 0.6 mg. Ce is found in the first cupferron precipitate. If 2 mg. Ce^{+3} is originally present, enough Ce escapes separation to give a very faint but definite yellow in the final NaOH-H_2O_2 test. It is furthermore likely that even more cerium is carried down in the cupferron precipitate when elements such as U^{+4}, Fe, V, Ti, etc. are present. Filtration of the final NaOH-H_2O_2 solution separates uranium quantitatively from

cerium. (See Confirmatory experiments, paragraph 35.) If the NaOH-H_2O_2 precipitate is large it should be dissolved and reprecipitated to recover any small amount of uranium it may occlude.

Confirmatory experiments

32. Even though the sample is completely decomposed, it may not be completely dissolved by 1-1 HCl. The insoluble may contain Cb, Ta, W, Ti, Zr, Sn, Th, with or without phosphorous. Hydrolyzed oxides of these elements do not occlude uranium when precipitated in the procedure, either when present alone or in combination, as shown in the experiments in Table 3.

To a mixture of the elements under investigation, as soluble ions, was added 10 ml. of HCl and 5 ml. of HNO_3. The solution was evaporated to dryness three times with intermediate addition of 10 ml. portions of HCl. The dry salts were then digested with 8 ml. of 1-1 HCl, diluted to 35 ml., again digested. The insoluble was filtered off, ignited and weighed, and uranium was determined in the filtrate. Although it is apparently safe to reject any hydrolysis precipitate, it is perhaps preferable not to do so when the precipitate is large (greater than about 0.2 g.). Thus for ilmenite concentrate where the hydrolysis products may amount to several grams, the hydrolysis precipitate is filtered off and reworked in this way: Ignite the precipitate and fuse it with potassium pyrosulfate. Dissolve the cooled melt in 400 ml. of water containing 5 ml. of sulfuric acid and 35 ml. of HCl. Cool in an iced bath. Transfer to a one-liter separatory funnel and add sufficient cold cupferron solution to completely precipitate the titanium (sometimes as much as 150 ml. of 6% cupferron is needed). Extract three times with ethyl acetate. The water layer will be essentially free from titanium and will contain any uranium that may have been occluded in the hydrolysis precipitate.

Since the filtrate from the hydrolysis precipitate of the ilmenite concentrates also contains large amounts of soluble titanium, a similar preliminary cupferron extraction is made after adjusting the volume of the solution to 400 ml. of 10% by volume of HCl. The water layers from the extractions are combined and treated further in this way. Evaporate to fumes of sulfuric acid. Add nitric acid to remove organic matter and bring the solution to fumes of sulfuric acid. Add water, evaporate the solution, and then take to fumes again. Cool. Add 30 ml. of water and warm. Filter off and reject any insoluble material. The filtrate is made to 50 ml. with water and is ready for passage through the reductor. (Paragraphs 11 through 19 of the procedure.) 6-14

Table 3. Non-occlusion of uranium in insoluble residues

Amount taken, g.			Wt. insoluble residue, g.	U found in filtrate, g.
1.	U	.0006		.0006
	TiO_2	.300	0.23	
2.	U	.0006		.0006
	TiO_2	.300	0.315	
	H_3PO_4,85%	2 drops		
3.	U	.0003		.0003
	Cb_2O_5 a/	.100	.098	
4.	U	.0003		.0003
	Cb_2O_5 a/	.100	.112	
	H_3PO_4, 85%	2 drops		
5.	U	.0003		.0003
	Ta_2O_5 a/	.100	.098	
6.	U	.0003		.0003
	Ta_2O_5 a/	.100	.103	
	H_3PO_4,85%	2 drops		
7.	U	.0003	$<$ .001	.0003
	ZrO_2	.070		
8.	U	.0003		.0003
	ZrO_2	.070		
	H_3PO_4,85%	2 drops	.144	
9.	U	.0003		.0003
	SnO_2	.100	None	
10.	U	.0003		.0003
	SnO_2	.100	.002	
	H_3PO_4,85%	2 drops		
11.	U	.0003		.0003
	WO_3	.105	.105	
12.	U	.0003		.0003
	WO_3	.105	None	
	H_3PO_4,85%	2 drops		
13.	U	.0003		.0003
	Ce_2O_3	.100	None	
14.	U	.0003		.0003
	Ce_2O_3	.100	None	
	H_3PO_4,85%	2 drops		

Table 3. Non-occlusion of uranium in insoluble residues--Continued.

Amount taken, g.			Wt. insoluble residue, g.	U found in filtrate, g.
15.	U	.0003		.0003
	Sb_2O_3	.100	.005	
16.	U	.0003		.0003
	Sb_2O_3	.100	None	
	H_3PO_4, 85%	2 drops		
17.	U	.0003		.0003
	Bi	.060	None	
18.	U	.0003		.0003
	Bi	.060	None	
	H_3PO_4, 85%	2 drops		
19.	U	.0003		.0003
	Cb_2O_5, a/	.100		
	Ta_2O_5, a/	.100	.37	
	TiO_2	.300		
	ZrO_2	.070		
	SnO_2	.100		
	WO_3	.105		
20.	U	.0003		.0003
	Cb_2O_5, a/	.100		
	Ta_2O_5, a/	.100	.67	
	TiO_2	.300		
	ZrO_2	.070		
	SnO_2	.100		
	WO_3	.105		
	H_3PO_4, 85%	4 drops		
21.	U	.0025		.0027
	Cb_2O_5, a/	.100		
	Ta_2O_5, a/	.100	.67	
	TiO_2	.300		
	ZrO_2	.070		
	SnO_2	.100		
	WO_3	.105		
	H_3PO_4, 85%	4 drops		

a/ Added after Na_2CO_3 fusion.

33. Removal of chromium by double precipitation from reduced solution.*

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* Experimental work by W. G. Schlecht and F. S. Grimaldi.

Uranium was determined on 21 samples containing from 8 to 40 mg. of Cr_2O_3 by double precipitation with cupferron after reduction. After the uranium was determined by NaOH-H_2O_2, the solutions were tested for chromium by ether extraction of the chromium compound with peroxide, from ice cold barely acid solutions in this manner: The alkaline solution (50 ml. in volume) were made barely acid with HCl and then alkaline again with a few drops of excess NaOH. The solutions were then cooled in an ice bath and next transferred to a separatory funnel. 25 ml. of ice cold ether was added and HCl drop by drop until the solutions were slightly acid. The mixtures were immediately shaken and then allowed to settle. The water layers were drawn off and treated in the same manner 3 more times. This method of removal of chromium was suggested to us by Margaret D. Foster of this laboratory and additional tests made by ourselves confirmed that small amounts of chromium may be completely removed without loss of uranium.

After four extractions the solutions were made alkaline and the uranium determined again. Table 4 illustrates the typical results obtained with only 1 reduction. Table 5 illustrates the typical results obtained after 2 reductions. The constant decreases in intensity after extraction (Table 5) are too small to be considered significant as evidence for the presence of chromium; even the highest discrepancy, 0.004% occurred in a solution found free from chromium. Such decreases may be due to other causes such as presence of organic matter, presence of much nitrate in the final NaOH-H_2O_2 test, and other as yet unknown factors,

Table 4. Chromium occlusion with uranium in high chromium samples after 1 reduction and precipitation with cupferron

(Original chromium content from 8 to 42 mg. Cr_2O_3)

Sample No.	Apparent % U before extraction	% U after extraction	Difference	Mg. Cr_2O_3 occluded
CC-4	0.008	0.008	None	None
CC-19	.011	.007	0.004	0.10
JJ-20	.007	.004	.003	.06
JJ-24	.011	.004	.007	.12
JJ-29	.009	.006	.003	.05
278	.019	.008	.011	.20
658	.026	.014	.012	.24
659	.026	.013	.013	.25
1537	.008	.006	.002	.03
1540	.010	.008	.002	.03
1541	.014	.005	.009	.20
1544	.023	.007	.016	.30

Table 5. Removal of chromium by 2 reductions and precipitations with cupferron

(Chromium content 8 to 42 mg. Cr_2O_3)

Sample No.	Apparent % U before extraction	% U after extraction	Difference
174	0.008	0.007	0.001
175	.011	.011	None
186	.015	.011	.004
234	.009	.009	None
278	.008	.008	None
651	.006	.006	None
655	.004	.004	None
656	.007	.007	None
657	.007	.007	None
658	.014	.014	None
659	.013	.013	None
660	.004	.004	None
661	.007	.007	None
662	.005	.005	None
721	.010	.008	.002
722	.009	.008	.001
724	.008	.006	.002
743	.008	.008	None
744	.009	.007	.002
1285	.013	.012	.001
1544	.007	.007	None

34. Removal of chromium by volatilization as chromyl chloride.*

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* Experimental work by W. G. Schlecht and F. S. Grimaldi.

Chromium is oxidized to the sexivalent state by fuming perchloric acid and is then volatilized as chromyl chloride by addition of sodium chloride. This procedure has been described by Smith (Smith, F. W., Ind. Eng. Chem. Anal. Ed. 10, 360 (1939)). The perchloric acid remaining in the solution causes, in the later stages of the analysis, the precipitation of potassium perchlorate in samples containing sufficient potassium. To avoid the precipitation of much potassium perchlorate, the perchlorate is removed by essentially the method described by Noyes and Bray (Noyes, A. A. and Bray, W. C., A System of Qualitative Analysis for the Rare Elements. New York (1927), pp. 237 and 463).

The complete procedure follows:

After the extraction of iron from 1:1 HCl solution by ethyl acetate, bring the solution to near dryness in a casserole. Add 5 ml. of nitric acid and 15 ml. of perchloric acid and bring to fumes of perchloric acid. Cover the casserole with a watch glass and strongly fume for a few minutes until the chromium is oxidized to chromate. Add 1 g. of NaCl from a spatula and fume until the chloride is eliminated. Bring to fumes of perchloric acid again and repeat twice with 0.5 g. portions of NaCl. If the perchloric acid is greatly depleted it should be replenished before each addition of NaCl. Cool. Add 5 g. of solid NH_4Cl, cover, and digest on the steam bath for about 30 minutes. Remove the cover and heat on the hot plate until excess perchloric acid is driven off. Now cover and carefully heat strongly on the hot plate until a gentle deflagration takes place. Cool. Add 10 ml. of 1:1 HCl and digest on the bath. From here the procedure follows the text as to reduction of uranium and so on.

Five samples were tested in the above manner and the final $NaOH-H_2O_2$ solutions were tested for chromium by extraction of the perchromic acid. Table 6 illustrates the results obtained.

Table 6. Removal of chromium by volatilization as chromyl chloride

Sample No.	Apparent % U before extraction	% U after extraction	Difference
278	0.008	0.008	None
658	.015	.014	0.001
1543	.009	.008	.001
1544	.006	.006	None
1547	.004	.003	.001

35. The following tests were made to determine the effectiveness of ether and ethyl acetate in extracting the precipitates formed with cupferron (Procedure, paragraph 16), The elements taken were contained in 30 ml. of solution containing 4 ml. of HCl. This solution was cooled in an ice bath and 10 ml. of cool 6% cupferron solution was added. The mixture was extracted 3 times with 15 ml. portions of ether or ethyl acetate. The aqueous layer or organic solvent layer was them tested for the elements in question after destruction of the organic matter.

Table 7. Effectiveness of ether and of ethyl acetate in extracting cupferron precipitates

Elements taken, g.	Amount in g. left in aqueous layer after extraction with		Method of detection
	Ethyl Acetate	Ether	
0.018 Fe^{+3}	.000005 Fe	.000003	KCNS-acid
.015 Ti^{+4} + Fe^{+3}	No Ti	No Ti	H_2O_2-acid
.025 Ce	.025 Ce	....	NaOH-H_2O_2 b/
.014 V^{+5} + .004 Fe^{+3}	$<$ .000005	$<$ .000005	Phospho tungstic acid
.017 Mo^{+6} + .004 Fe^{+3}	.000005 Mo	....	$SnCl_2$-KCNS
.024 W^{+6} + .7 ml. 85% H_3PO_4	.020 W	....	Evaporation of ethyl acetate and ignition to WO_3
.024 W^{+6} + .7 ml. 85% H_3PO_4 + .004 Fe^{+3}	.020 W	....	Acid cinchonine b/
.017 Cr^{+3} + .004 Fe^{+3}	.017 Cr	....	Na_2O_2 Fusion b/
.018 Zr^{+4} + .004 Fe^{+3} a/	No Zr	....	NH_4OH
.022 Th^{+4} + .004 Fe^{+3}	.002 Th	....	NH_4OH
.020 Sn^{+4}	No Sn	....	Acid H_2S

a/ Zr cupferrate did not dissolve completely in ethyl acetate but floated in it and was just as effectively removed from the water layer.

b/ Ethyl acetate layer tested.

36. The removal of cerium by the $NaOH-H_2O_2$ precipitation is essentially complete, as shown in the experiments in Table 8.

Table 8. Separation of Ce from U by $NaOH-H_2O_2$

Ce taken, mg.	U taken, mg.	U found in filtrate, mg.
5.0	None	None
5.0 (Repeat)	None	None
5.0	0.3	0.3
2.0	None	None
2.0	0.3	0.3
1.0	None	None
1.0	0.3	0.3
0.2	None	None
0.2	0.3	0.3
0.1	None	None
0.1	0.3	0.3
0.03	None	None
0.03	0.3	0.3

Comparison of results by methods A and B

Table 9. Comparison of results by methods A and B

Sample No.	Type of material	% U Method A	% U Method B
65-7	Sandstone	.003	.003
BC 59-480	Shale	.005	.006
BC 76-612	Shale	.005	.007
BC 81-654	Shale	.005	.006
MB 1-4	Phosphate rock	.005	.008
BC 100-815	Shale	.006	.005
BC 101-825	Shale	.006	.006
BC 90-738	Shale	.006	.007
MGR 5-295	Phosphate rock	.007	.009
BC 67-542	Shale	.007	.007
21-3	Gold concentrate	.013	.012
150-9-64	Phosphate rock	.016	.014
21-2	Gold concentrate	.026	.028
BC X-22	Shale	.036	.038