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A DIRECT QUANTITATIVE FLUORIMETRIC METHOD FOR THE DETERMINATION  
OF SMALL AMOUNTS OF URANIUM IN THE FIELD AND LABORATORY

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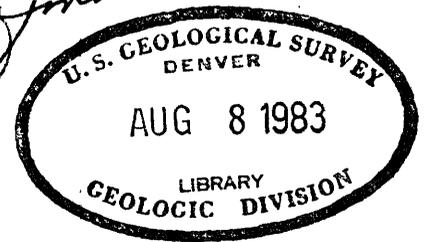
by

Frank Grimaldi, F. N. Ward, and Ruth Kreher

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Abstract

This paper describes a quantitative fluorimetric method for the determination of small amounts of uranium (0.001% to 0.01%), useful for field and laboratory. A small sample is fused directly with a fluoride flux, and the fluorescence of the uranium melt is measured photometrically or visually. Columbium and other elements tested do not give any fluorescence of their own in this procedure. Enhancement of the uranium fluorescence is observed in some samples.

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Introduction

The methods most commonly used for the field estimation of small amounts (about 0.001% to 0.01%) of uranium are purely physical. The most important technique generally involves

radiometric methods with an instrument such as a portable Geiger counter. Radioactivity measurements do not readily discriminate between the radioactivity associated with uranium and that due to other elements such as thorium and potassium. Therefore, it is highly desirable to supplement this method with an independent technique, preferably one which is specific for uranium.

The fluorescence of uranium-sodium fluoride phosphors has been used extensively as a laboratory method for the quantitative estimation of small amounts of uranium. However, this method has not been adapted as a field test for the quantitative determination of very small amounts of uranium in rocks.

The simplest procedure is to fuse a sample of the rock directly with one of the standard fluxes and measure the fluorescence of the melt. Contrary to expectations no serious difficulty was encountered with quenching of the fluorescence when this method was applied to shales, high-silica rocks, and phosphate rocks from different places. The results by this method proved to be so reliable and rapid that prior to its actual use in the field, it is being used as a routine laboratory procedure for screening samples containing 0.005% uranium or less.

In the laboratory the fluorescence is being measured with a Modified Oak Ridge Model R fluorimeter described by Fletcher and May. <sup>1/</sup> This instrument may also be used in the field

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<sup>1/</sup> Fletcher, Mary H., and May, Irving, An improved fluorimeter for the determination of uranium in fluoride melts (in manuscript).

provided an outlet of 110 volts A.C. is available. Work is in progress to develop a small portable battery powered unit so that the instrument will be completely self-contained and independent of an external power source.

#### Discussion of the Method

The procedure involves a direct fusion of 3.75 mg of sample with 3 g of flux in a platinum container. This size sample was selected for the following reasons:

1. It may be conveniently weighed in the field with a Roller-Smith (5 mg capacity) balance.
2. The fluorescence of the phosphors obtained with materials containing as little as 0.001% uranium is conveniently measured with the Modified Model R fluorimeter or by visual means.
3. This ratio of rock sample to flux was found to give negligible quenching of the fluorescence of uranium.

With shales and phosphate rocks ground to -100 mesh, a 3.75-mg sample was found to be representative. This conclusion is based on the fact that the results of all the samples run by the new method agreed (within experimental error) with those obtained by independent chemical methods employing large sample weights. This was confirmed by making repeated direct determinations on the same sample without obtaining any widely spurious results (table 5). A further check was made by grinding

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Table 5.--Direct fluorimetric uranium determinations  
on two Colorado Plateau samples

<u>Sample No.</u>	<u>Direct fluorimetric % U</u>
CT-277-A	0.017
B	0.018
C	0.019
D	0.020
E	0.019
F	0.020
G	0.019
H	0.019
I	0.019
J	0.023
CT-278-A	0.015
B	0.014
C	0.012
D	0.014
E	0.016
F	0.013
G	0.014
H	0.013
I	0.015
J	0.013

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several large samples very finely and comparing the results on these samples with those obtained on the original 100-mesh material (table 6). These results are consistent with the fact that no discrete uranium mineral has been found in phosphate rocks or shales. For those samples known to contain segregated uranium minerals a satisfactory procedure is to grind a representative 1-gram sample to a powder in a mortar prior to withdrawing the 3.75 mg sample for analysis.

Results appreciably higher than the best value were repeatedly obtained by the direct method on two samples of Florida phosphates (nos. 25 and 28, lot no. 645, table 1). The uranium content of these samples was established by many chemical analyses using standard methods, the results of which were in agreement with radiometric measurements. Chemists of the Battelle Memorial Institute have also encountered in some phosphate rocks enhancement of the uranium fluorescence which they ascribed to cerium. 2/

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2/ Private communication.

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Several elements have been reported as interferences in the fluorimetric procedure by virtue of their own fluorescence. These, as well as several other elements, were tested to determine the possibility of their interfering in the direct procedure. Under excitation of 2530 A, only columbium fluoresced, and under excitation of 3600 A, none of the elements tested showed any fluorescence. These results are presented in experiment number 3, and in table 7.

Table 6.--Effect of sample weight in the direct method

<u>Sample</u>	<u>Weight of sample in mg</u>	<u>Direct fluorimetric % U</u>
Shale	1.88	.005
	3.75	.006
	7.50	.004
	14.00	.004
Florida phosphate	1.88	.011
	3.75	.009
	7.50	.008
	14.00	.007
Idaho phosphate	1.88	.008
	3.75	.008
	7.50	.007
	14.00	.006

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Table 1.--Comparison of results of the standard fluorimetric and the new direct method on samples of Florida phosphates

Lot No.	Sample No.	% U, fluorimetric		Lot No.	Sample No.	% U, fluorimetric	
		Standard extraction	New direct			Standard extraction	New direct
612	27K	0.002	0.001	645	30	0.000	0.000
	28	0.001	0.001		32	0.006	0.008
	29	0.004	0.004		33	0.003	0.004
624	44	0.013	0.015	34	0.001	0.003	
638	14	0.006	0.007	35	0.003	0.001	
	15	0.006	0.005	37	0.002	0.002	
640	12G	0.003	0.003	39	0.003	0.003	
	13A	0.002	0.001	40	0.004	0.005	
	13B	0.010	0.006	41	0.005	0.004	
	13C	0.004	0.003	42	0.002	0.005	
	13D	0.005	0.005	45	0.002	0.003	
	13E	0.003	0.002	46	0.002	0.001	
	13F	0.006	0.006	47	0.008	0.008	
	13G	0.002	0.003	48	0.005	0.004	
	14Aa	0.001	0.001	50	0.003	0.004	
	14Ab	0.001	0.001	647	39	0.006	0.001
	14B	0.008	0.009	648	3C	0.011	0.011
	14C	0.003	0.002	3D	0.008	0.010	
	14D	0.005	0.006	3E	0.006	0.007	
	642	11-1	0.002	0.001	3F	0.001	0.002
11-2		0.005	0.004	3G	0.005	0.005	
644	53	0.004	0.003	3H	0.009	0.011	
	54	0.005	0.005	3I	0.009	0.010	
	55	0.001	0.002	3K	0.001	0.001	
	56	0.003	0.003	4A	0.007	0.008	
	57	0.001	0.001	821	38	0.016	0.015
645	23	0.003	0.004	61	0.018	0.017	
	25	0.008	0.013	122	0.015	0.015	
	26	0.001	0.002	822	55	0.014	0.015
	28	0.006	0.010	118	0.012	0.012	
	29	0.002	0.003	134	0.015	0.016	

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Table 7.--Effect of interfering elements on the direct method

<u>Material</u>	<u>Equivalent wt. of oxide in mg</u>	<u>Equivalent of % U</u>
La <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	6.7	0.000
Ta <sub>2</sub> O <sub>5</sub>	15.0	0.000
Cb <sub>2</sub> O <sub>5</sub>	15.0	0.000
Cerium ammonium nitrate	5.4	0.000
Neodymium nitrate	12.0	0.000
Yttrium nitrate	8.8	0.000
Blank	None	0.000

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## Procedure

1. Grind sample to -100 mesh and mix.
2. Weigh out 3.75 mg of sample and transfer to a 25-ml platinum crucible.
3. Burn off organic matter if present.
4. Add 3 g of fluoride flux (made by grinding together 9 g NaF, 45.5 g Na<sub>2</sub>CO<sub>3</sub>, 45.5 g K<sub>2</sub>CO<sub>3</sub>)
5. Heat over an open flame at a temperature  $\leq 750^{\circ}\text{C}$ , swirling the contents of the crucible frequently until the sample is completely decomposed.

Important: Use the lowest possible temperature at which the flux remains fluid. Heat for 30 seconds more to allow the melt to collect in the bottom of the crucible. Cool.

6. Measure the fluorescence of the disc in a fluorimeter or visually against a set of standards.

## Results of Analyses

Samples of phosphate from Florida and the northwest, of black shales, and of Colorado Plateau carnotites were analyzed by the direct procedure and also by the standard extraction fluorimetric procedure involving a preliminary extraction of uranium nitrate with an organic solvent. The results shown in tables 1, 2, 3, and 4 show satisfactory agreement between the two methods.

Table 2.--Comparison of results of the standard fluorimetric and the new direct method on samples of northwest phosphates

Lot No.	Sample No.	% U, fluorimetric		Lot No.	Sample No.	% U, fluorimetric		
		Standard extraction	New direct			Standard extraction	New direct	
1200	LES-			1230	WOM-			
	184-47	0.001	0.001		1278	0.003	0.001	
	187-47	0.000	0.000		1279	0.001	0.000	
	189-47	0.001	0.001		1290	0.001	0.000	
	200-47	0.021	0.018		1291	0.001	0.000	
1202	DML-				1292	0.005	0.002	
	10-47	0.005	0.006		1296	0.011	0.009	
	11-47	0.004	0.004		1233	RPL-		
	12-47	0.001	0.000			1330	0.008	0.009
	13-47	0.001	0.000			1331	0.011	0.011
	14-47	0.001	0.000			1332	0.007	0.004
	16-47	0.004	0.004			1333	0.009	0.007
	17-47	0.005	0.003			1334	0.007	0.006
	19-47	0.005	0.006					
1203	VEM-			RPS-				
	120-47	0.001	0.000	1340	0.001	0.001		
	121-47	0.001	0.000	1341	0.002	0.001		
	122-47	0.001	0.000	RAH-				
	123-47	0.001	0.000		1368	0.003	0.003	
	124-47	0.001	0.000		1369	0.002	0.001	
	125-47	0.008	0.008	1234	OAP-			
	132-47	0.004	0.006		10	0.001	0.001	
	134-47	0.000	0.000		11	0.002	0.004	
	135-47	0.000	0.000		12	0.001	0.002	
	143-47	0.001	0.000		13	0.005	0.005	
	144-47	0.000	0.000					
	146-47	0.001	0.000	FSH-				
	152-47	0.002	0.002	15	0.002	0.004		
	1205	LES-			16	0.004	0.005	
18-47		0.003	0.003	17	0.003	0.002		
19-47		0.002	0.001	18	0.004	0.005		
20-47		0.000	0.000	19	0.002	0.003		
21-47		0.001	0.000	1235	JWH-			
23-47		0.002	0.001		2109	0.001	0.000	
FCA-					2112	0.002	0.001	
46-47		0.001	0.002		2114	0.002	0.002	
47-47	0.001	0.001	2115		0.001	0.000		
1230	WOM-			1244	4964	0.013	0.012	
	1277	0.001	0.001	5310		0.015	0.015	

Table 3.--Comparison of results of the standard fluorimetric and the new direct method on samples of black shales

Lot No.	Sample No.	% U, fluorimetric		Lot No.	Sample No.	% U, fluorimetric	
		Standard extraction	New direct			Standard extraction	New direct
1001	LC-201-104M	0.005	0.005	1026	20U-8-1 2	0.002 0.001	0.001 0.001
1005	LC-105A-1	0.001	0.001		21V-10-1 2	0.002 0.001	0.002 0.001
	12	0.006	0.004		22-L-1 2	0.004 0.002	0.002 0.001
	13	0.007	0.006		22-M-3	0.003	0.000
	14	0.007	0.005		23-L-4-1 2	0.001 0.004	0.002 0.003
	15	0.004	0.003		25-X-11 12	0.002 0.002	0.001 0.002
	21	0.003	0.001		S-9-1 2	0.002 0.002	0.001 0.002
	43	0.001	0.000		1027 19M-6-4 6 8 10	0.005 0.003 0.001 0.003	0.006 0.003 0.001 0.003
	44	0.001	0.000		20M-13-8	0.003	0.003
	45	0.001	0.000		20U-16-1 2 3 4 5 6	0.005 0.004 0.003 0.001 0.001 0.001	0.004 0.004 0.002 0.001 0.001 0.001
	51	0.002	0.001		7 8 9 10	0.001 0.002 0.002 0.001	0.001 0.001 0.001 0.000
	52	0.003	0.002				
	53	0.002	0.002				
	LC-113A-12	0.005	0.004				
	13	0.004	0.004				
	14	0.002	0.003				
	15	0.003	0.003				
	16	0.004	0.003				
	17	0.005	0.004				
	18	0.002	0.003				
1014	RC-2-21	0.001	0.002				
	32	0.003	0.003				
	52	0.002	0.002				
	53	0.003	0.002				
	54	0.002	0.001				
1026	19-M-6	0.002	0.002				
	7	0.001	0.000				
	20-M-5	0.001	0.002				

Table 4.--Comparison of results of the standard fluorimetric and the new direct method on samples of Colorado Plateau carnotites

<u>Lot No.</u>	<u>Sample No.</u>	<u>% U, fluorimetric</u>	
		<u>Standard extraction</u>	<u>New direct</u>
2000	CT- 84	0.001	0.000
	85	0.001	0.000
	86	0.001	0.001
	87	0.001	0.000
	88	0.001	0.000
	209	0.005	0.005
	210	0.006	0.003
	211	0.006	0.004
	212	0.002	0.001
	214	0.004	0.003
	215	0.002	0.001
	216	0.005	0.004
	225	0.013	0.012
	232	0.010	0.008
	233	0.006	0.004
	234	0.001	0.001
	235	0.001	0.000
	236	0.001	0.000
	237	0.001	0.001
	238	0.001	0.001
	243	0.005	0.004
	244	0.003	0.004
	245	0.004	0.004
	246	0.004	0.003
	247	0.006	0.004
	248	0.004	0.002
	270	0.002	0.002
	271	0.014	0.015
	272	0.002	0.002
	273	0.001	0.000
	274	0.002	0.003
	277	0.014	0.019
278	0.009	0.012	
279	0.002	0.002	
280	0.000	0.000	
282	0.001	0.001	
283	0.000	0.000	
284	0.001	0.000	
285	0.001	0.001	
286	0.001	0.000	
294	0.001	0.000	
297	0.008	0.009	
298	0.002	0.001	

## Experiments

No. 1.--Materials containing segregated uranium minerals  
such as carnotite. A 1-g portion of each of two samples (CT-277 and CT-278) was ground in a mullite mortar and ten different 3.75-mg portions of each sample were taken for direct analysis to determine whether this size sample is representative. Table 5 gives the results obtained. These results indicate that such a size sample is representative.

No. 2.--Effect of sample weight. The amounts of uranium in three shales were determined by the direct method using four sample weights, 1.88, 3.75, 7.5, and 14.0 mg. The results shown in table 6 indicate that 3.75 mg as a sample weight is satisfactory when compared with the other weights.

No. 3.--Fluorescence of other elements in the  
NaF-Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> flux. Salts or oxides of six elements were weighed, ignited, and fused with 3 g of flux. These discs were read on the fluorimeter, employing excitation of 3600 A. As shown in table 7 no interference by any of these elements was observed.