Mines Branch Information Circular IC 266

THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM IN ORES, RESIDUES AND OTHER MATERIALS

by

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ABSTRACT

A spectrophotometric method, reported by Johnson and Florence , has been used for the determination of uranium in ores, residues, and other materials. The method makes use of the very sensitive chromogenic reagent 2-(5-bromo-2-pyridylazo)-5diethylaminophenol (Br-PADAP) which gives a red complex with uranium at pH 7.6 for which $\lambda_{max} = 578$ nm. In the presence of a complexing solution containing (1,2-cyclohexylenedinitrilo)tetraacetic acid (CyDTA), sulphosalicylic acid, and sodium fluoride, the only serious interference is caused by chromium (III), vanadium (V), and phosphate. By extraction of uranium into tri-n-octylphosphine oxide (TOPO)-cyclohexane solution the method becomes highly specific for uranium.

A number of diverse uranium-containing materials have been analysed for uranium by this method, and the results are reported here. Comparison is made with results obtained by fluorimetric, X-ray fluorescence, and volumetric methods.

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Direction des mines

Circulaire d'information IC 266

LA DETERMINATION SPECTROPHOTOMETRIQUE DE L'URANIUM DANS

LES MINERAIS, LES RESIDUS ET AUTRES MATERIAUX

par

A. W. Ashbrook*

RESUME

Une méthode spectrophotométrique décrite par Johnson et Florence a été utilisée pour la détermination de l'uranium dans les minerais, les résidus et autres matériaux. La méthode fait usage d'un réactif chromogène très sensible 2-(5-bromo-2-pyridylazo)-5-diéthylaminophénol (Br-PADAP) qui donne un complexe rouge avec de l'uranium à pH de 7.6 dont 578 nm. En présence d'une solution de complexation contenant de l'acide (1,2-cyclohexylénédinitrilo) tétraacétique (CyDTA), de l'acide sulfosalicylique et du fluorure de sodium, la seule interférence sérieuse est causée par le chrome (III), le vanadium (V) et le phosphate. La méthode devient très spécifique pour l'uranium lorsqu'il y a extraction de ce métal par une solution d'oxyde tri-n-octylphosphine (TOPO)-cyclohexane.

On a analysé en se servant de cette méthode un certain nombre de matériaux uranifères et les résultats sont donnés dans le présent rapport. Les résultats sont comparés avec ceux obtenus en employant les méthodes fluorimétriques, à fluorescence (rayons-X) et volumétriques.

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INTRODUCTION

Methods in general used in this laboratory for the determination of uranium in ores and allied materials are fluorimetric, x-ray fluorescence, and volumetric. The fluorimetric method is used for the determination of small amounts of uranium, usually from 0.005 to 1%, with a relative precision at this level of from 3 to 5%. X-Ray fluorescence is useful over the range 0.01 to >70% uranium. A precision of $\pm 5\%$ is to be expected, although this can be improved by special techniques². The volumetric determination, using a modification of the Davies and Gray method³, has shown that uranium in the range 0.02 to 80% can be determined with excellent precision⁴.

Reagents for the colorimetric determination of uranium are many,⁵ but generally suffer from lack of sensitivity or from non-specificity. The most recent of these, Br-PADAP, has been reported by Johnson and Florence¹. A method for the determination of uranium, complementary to the fluorimetric method, was required in this laboratory and the method of Johnson and Florence was investigated.

The use of this method in the determination of uranium in ores and similar materials is reported here. The procedure is at least as precise as the fluorimetric method and has been used over the range 0.0001 to 5% uranium.

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EXPERIMENTAL

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Apparatus and Reagents

Absorbance readings were determined using either a Beckman Model B or a Hitachi-Perkin Elmer 139 spectrophotometer. Absorption cells used were 1.0, 2.0 or 4.0-cm depending on the amount of uranium being determined.

The reagents used and the method of preparation of Br-PADAP were as reported by Johnson and Florence¹ except for the diazotisation procedure⁶, which is given below because it has not, as yet, been reported in the literature.

Diazotisation

Suspend 20.6 g (0.12 mole) of 2-amino-5-bromopyridine (Aldrich) in 160 ml of ether in a dry, 250-ml three-necked R.B. flask fitted with a reflux condenser and a nitrogen inlet tube. Pass nitrogen, slowly, into the solution, and reflux gently for 5 minutes. Add to the flask 6.4 g (0.12 mole) of sodium methoxide (Fisher) followed by 10 ml of ethanol. Reflux gently for 30 minutes. Allow the flask to cool while maintaining the nitrogen flow, add 14.0 g (0.12 mole) of isopentylnitrite (Eastman) and reflux for a further 90 minutes. After cooling, pour the mixture into 200 ml of ether contained in an 800-ml beaker and filter under suction through a Whatman #3 filter paper (Buchner funnel). The coupling procedure with m-diethylaminophenol is as previously reported¹.

DETERMINATION OF URANIUM

Procedures used for the dissolution of ores and similar materials were as described by Johnson and Florence¹.

A few techniques, found to increase the precision of the procedure, are given here:

(i) the time allowed for pipette drainage, especially when
 measuring TOPO and Br-PADAP solutions, must be controlled. A
 15-second drainage time, with the pipette in a vertical position,
 has been found to be satisfactory;

(ii) spectrophotometric cells must be stoppered during absorbance measurements because ethanol evaporates quite rapidly and can cause eddy currents in the solution which may give rise to erroneous readings;

(iii) because a volume change occurs when ethanol and water are mixed, the addition of ethanol (16.0 ml) to the 25-ml flask should be carried out so that maximum mixing occurs during this addition. If the stream of ethanol from the pipette is directed directly down the center of the flask neck rather than down the side, sufficient turbulence is created in the flask to provide adequate mixing of the contents;

(iv) in a 1.0-cm cell, the blank has an absorbance of 0.07

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and four times this in a 4.0-cm cell, it is imperative, therefore, to ensure that the reagent is accurately measured;

(v) a uranium standard should be carried through with each set of determinations.

RESULTS

The determination of uranium in a wide range of materials has been carried out using the colorimetric procedure. Results are given below and are compared, where possible, with results obtained by other methods. In some cases, sufficient determinations have been made to assess statistically the precision of the method.

Uranium Ores

Thirteen different uranium ores and tailings, ranging from 0.004 to 0.63% uranium, have been analysed. Most of the samples were fused with sodium fluoroborate, the remainder were acid treated.

Five separate samples of an ore from the Beaverlodge Mine of Eldorado Nuclear Ltd., prepared for use as a uranium ore standard, were analysed for uranium. Two weighed portions of each samples were taken for analysis and two aliquots from each solution, after dissolution, were taken for uranium determination.

Results are given in Table 1 and are compared with

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average results obtained by X-ray fluorescence, fluorimetric, and volumetric methods. The average uranium content of the five samples was 0.171% uranium, with relative standard deviation and 95 percent confidence limits (10 duplicate determinations) of $\pm 0.78\%$ and $\pm 0.55\%$ respectively. The major components of the ore are given in Table 6.

In Table 2 are given analyses obtained on IAEA standard samples⁷ of torbernite, carnotite, and uraninite together with comparative uranium analyses. For the sample of carnotite (EM 231), the average value found was 0.354% uranium, with a relative standard deviation of $\pm 0.46\%$ and 95 percent confidence limits of $\pm 0.58\%$ for five duplicate determinations.

Table 3 lists uranium analyses obtained on a waste ore, samples of Denison Mines Ltd. (Elliot Lake, Ontario) feed and tailings, and on a CUPAS Standard Sample #15 (Algom Nordic Mines Ltd., Elliot Lake, Ontario). Approximate analyses of these materials is given in Table 6.

Standard ores from the Australian Atomic Energy Commission were also analysed for uranium. Results are given in Table 4, and are compared with results obtained by other methods. Spectrographic analyses of these samples are shown in Table 6.

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Sample		$%$ U a		
No.	Color	X-ray ^{b,c}	Fluorimeter ^{b,c}	Volumetric ^{b, c}
EMQ 3007	(1) 0.169, 0.170 (11) 0.168, 0.170	0.175	0.171	0.166
EMQ 3008	(i) 0.171, 0.170 (ii) 0.169, 0.169	0.174	0.178	0.170
EMQ 3009	(1) 0.175, 0.171 (11) 0.172, 0.171	0.176	0.176	0.167
EMQ 3010	(1) 0.172, 0.171 (11) 0.169, 0.171	0.176	0.174	0.169
EMQ 3011	(i) 0.173, 0.172 (ii) 0.171, 0.170	0.173	0.177	0.169
Average Values	0.171	0.175	0.175	0.168

URANIUM IN A BEAVERLODGE ORE

TABLE 1

- (a) On an 'as-received' basis
 - (b) Average values of several determinations
 - (c) Acid dissolution
 - (i) and (ii) refer to different sample portions on which duplicate determinations were carried out.

TABLE 2

URANIUM IN VARIOUS IAEA URANIUM ORE STANDARDS^g

			%u ^a	<u> </u>		
No.	Material	Color	Color ^e	b,d Fluor.	Vol ^{b,c}	Polarog ^e
EMM 228	Torbernite (Australia)	(i) 0.401, 0.402 (ii) 0.401, 0.400 (iii) 0.400	0.400	0.401	0.399	0.407
EMM 229	Torbernite (Spain)	Av: = 0.400 (i) 0.266, 0.267 (ii) 0.267, 0.267 (iii) 0.267, 0.264	0.268	0.258	0.260	0.257
EMM 231	Carnotite (USA)	Av: = 0.266 (i) $0.349^{b,f} 0.349^{b,f}$ (ii) $0.357, 0.356$ (iii) $0.355, 0.356$ (iv) $0.354, 0.352$ (v) $0.356, 0.356$ (vi) $0.353, 0.353$	0.360	0.350	0.353	0.349
EMM 230	Uraninite (Australia)	Av: = 0.354 (i) 0.311, 0.310 (ii) 0.309 ^b 0.310 ^b (iii) 0.311 Av: = 0.310		0.310	0.308	

(a) On an 'as-received' basis

(b) Acid dissolution

(c) Average of several determinations

(d) Ref. 7

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(e) Determined by Aust. AEC (ref. 8)

(f) Omitted from average value

(g) Certificate values are: Torbernite (Aust), 0.399; Torbernite (Spain), 0.265; Carnotite (USA), 0.354 Uraninite (Aust), 0.318% U.

TABLE 3

URANIUM IN VARIOUS ORES AND TAILINGS

Sample		%U ^a											
No.	Material	Color			X-ray ^{b,c}	Fluor ^{b, c,}	Vol ^{b,c}						
EMQ 2030	Denison Feed		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	170 ^b 174 173 171	0.183	0.177	0.180						
EMQ 2037	Denison Tails	(i) (ii) (iii) (iv)	Av. = 0.1 0.0042, 0.0 0.0041, 0.0 0.0038, 0.0 0.0042	73 0041 0041 0041	-	0.0044	-						
	Eldorado Waste Ore	(i) (ii)	Av. = 0.00 0.0195, 0.1 0.0195, 0.1 Av. = 0.02	041 0203 0204 199	· · · ·	-	0.0200						
	CUPAS Std #15 ^d	(i) (ii)	$\begin{array}{l} 0.103, 0.1\\ 0.105, 0.1\\ \text{Av.} = 0.1 \end{array}$	105 105 05		_	0.107						
	i												

(a) On an 'as-received' basis

(b) Acid dissolution

(c) Average value of several determinations

(d) Certified value: 0.107% U

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TABLE 4

URANIUM IN AUSTRALIAN AEC STANDARD ORES

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Sample	AAEC	%U ^a										
No.	No.	Color	X-ray ^{b,c,}	Fluor ^{b, c}	Vol							
EMQ 3875	S-316	<pre>(i) 0.0112, 0.0113 (ii) 0.0114, 0.0114 Av.= 0.0113</pre>	_	0.0111	-							
EMQ 3876	S-317	<pre>(i) 0.111, 0.112 (ii) 0.112, 0.112 Av. = 0.112</pre>	0.11	0.11	0.115 ^c							
EMQ 3877	S-3 18	<pre>(i) 0.634, 0.638 (ii) 0.638, 0.640 Av. = 0.638</pre>	0.64	0,64	0.644 ^C							
EMQ 3878	S-319	(i) 0.248, 0.251 (ii) 0.251, 0.250 Av. = 0.250	0.24	0.25	0.233 ^d							

- (a) On material dried at 110°C
- (b) Average value of several determinations
- (c) Acid dissolution
- (d) Av. of results obtained by acid and fusion dissolution

Other Materials

Other materials on which the colorimetric method was tried were a rare earth concentrate, monazite sand, pyrochlore, cobalt-nickel arsenide concentrate, euxenite, zirconium metal and lead-zirconate-titanate (PZT). Results of analyses are given in Table 5 together with results by other methods. In Table 6 are given the major constituents of the materials.

TABLE 5

URANIUM IN VARIOUS MATERIALS

Sample		%1	_U a		
NO.	Material	Color	X-ray	Fluor.	Vol.
EMD 7321	Rare earth Conc. (Rio Algom)	(1) 0.0083 (11) 0.0082		0.0076 ^b	-
EMD 4152	Monazite (Eldorado)	<pre>(i) 0.145, 0.145 (ii) 0.145, 0.144 Av. = 0.145</pre>	-	0.110 ^b	party .
EMI 289	Pyrochlore (St. Lawrence Columbium)	(i) 0.066 (ii) 0.066 Av. = 0.066	-	0.058 ^b	
EMP 3052	Ni-Co-As Concentrate	(i) 1.09^{b} , 1.10^{b} (ii) 1.11^{b} , 1.11^{b} Av. = 1.10	-	-	1.14 ^b
EMD 415 3	Euxenite	(1) 4.92, 4.92 (11) 4.93, 4.92 Av. = 4.92	4.88 ^d		4.88
	Zr metal (Eldorado)	(i) $0.0115^{b}, 0.0118^{b}$ (i) $0.0051^{b}, 0.0053^{b}$ (i) $0.0013^{b}, 0.0014^{b}$		$\begin{array}{c} 0.0120^{\rm C} \\ 0.0050^{\rm C} \\ 0.0016^{\rm C} \end{array}$]
EMQ 4518 EMQ 4519	Lead zirconate titanate(PZT)	0.0023, 0.0023 <0.0001,<0.0001		0.023 ^e <0.0001 ^e	

(b) Acid dissolution

(e) NaBF₄ fusion

(c) Eldorado Nuclear Ltd. fluorimetric results

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Sample												E	lement	%									
No.	Material	Al	As	Ca	Co	Cu	Fe	Mg	Mn	Мо	Ni	Nb	Р	Pb	S	Si	Ta	Th	Ti	V	Zn	Zr	RE*
3007-3011	B.V. ore	6.95		3.2			4.8	1.1	0.05				0.1		0.35	25			0.1	0.1	0.5		
228, 229	Torbernite	3.4		<0.1		<0.1	2.5	0.2	<0.1		<0.1		<0.5			40				<0.1			
230	Uraninite	8.7		0.4	<0.1	<0.1	9.0	6.4	0.1		<0.1		0.2			27			0.5	<0.1			
231	Carnotite	3.2		0.4		<0.1	0.3	0.7	<0.1				<0.1			>37			0.2	0.3	<0.1		
2030-2033	Denison						4.6			0.01		0.01	0.05		3.7		0.1	0.07	0.5				
	CUPAS Std.		0.01				5.3			0.01	-	0.01	0,05		4.2		0.1	0.02	0.05	0.01			
3875	Aust. Std.	0.26				0.02	PC	0.2	0.01							PC			0.1	0.02			
3876	**	0.26		0.3		0.02	PC	0.3	0.02							PC			0.1	0.02			
3877	**	0.3		0.36		0.02	PC	0.3	0.02							PC			0.1	0.05			
3878	11	0.3		PC		0.05	PC	0.2	0.1							PC			0.1	0.01			
4152	Monazite																						60.2
289	Pyrochlore																						11.4
3052	Ni-Co-As		39.5		8.8	0.09	2.2				11.5				6.4								
4153	Euxenite																						18.1
4518,4519	PZT											0.5		60					6			12	

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* Total rare earths as RE₂O₃ PC = principle constituent

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DISCUSSION

The colorimetric method¹ for the determination of uranium in a variety of materials has been shown to be both accurate and precise. The range, from a few ppm to as high as 5% uranium, makes it quite versatile.

Dissolution of samples by fusion with sodium fluoroborate provided complete solution of all the materials tried. The fusion technique is, however, slower than multi-acid treatment when large numbers of samples are to be analysed.

Because of the high sensitivity of the reagent for uranium ($\epsilon = 6.6 \times 10^4 M^{-1} cm^{-1}$ at 578 nm) only small amounts of sample, usually 0.05 to 0.2 g, are required. This sample size results in a minimum time for sample dissolution, but requires that samples be homogeneous.

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