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Canada Centre for Mineral and Energy Technology

Centre canadien de la technologie des minéraux et de l'énergie

REPORT 82-6E

BL-2a AND BL-4a: CERTIFIED URANIUM REFERENCE ORES

H.F. STEGER, W.S. BOWMAN, G. ZECHANOWITSCH AND R. SUTARNO

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The captions for Fig. 1 and Fig. 2 on page 3 should read "Bottle mean and 2s limits for BL-2a" and "Bottle mean and 2s limits for BL-4a", respectively. Please note this change applies to the Contents page also.

BL-2a AND BL-4a: CERTIFIED URANIUM REFERENCE ORES

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H.F. Steger*, W.S. Bowman**, G. Zechanowitsch** and R. Sutarno*

SYNOPSIS

Samples of two uranium ores BL-2a and BL-4a from Beaverlodge, Saskatchewan, were prepared as compositional reference materials to replace the similar certified ores, BL-2 and BL-4, of which the stock had been exhausted. Each ore was ground to minus 74 μm, blended in one lot and bottled in 200-g units. The homogeneity of the ores with respect to uranium was confirmed by both a neutron activation and a fluorimetric analytical procedure performed by two commercial laboratories.

The recommended value for uranium is based on the results of one determination on each of 25 bottles by the volumetric-umpire method performed at CANMET. A statistical analysis of the data gave a recommended value for uranium of 0.426% for BL-2a and 0.1248% for BL-4a.

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*Research Scientists and **Technologists, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, Ottawa.

Note: Major contributions were also made by other staff members of the Mineral Sciences Laboratories.

BL-2a ET BL-4a - MINERAIS DE RÉFÉRENCE D'URANIUM

par

H.F. Steger*, W.S. Bowman**, G. Zechanowitsch** et R. Sutarno*

SYNOPSIS

Des échantillons de deux minerais d'uranium, BL-2a et BL-4a, provenant de Beaverlodge en Saskatchewan, ont été préparés comme matériaux de référence de composition pour remplacer les minerais certifiés analogues, BL-2 et BL-4, dont l'inventaire avait été épuisé. Chaque minerai a été broyé à une granulométrie de moins 74 µm, mélangé en un seul lot et embouteillé en unités de 200 g. Quant à l'uranium, l'homogénéité des minerais a été confirmée par deux laboratoires analytiques en utilisant des méthodes d'activation neutronique et fluorimétrique.

La valeur recommandée pour l'uranium est fondée sur les données d'une détérmination pour chacune des 25 bouteilles par la méthode "arbitre-volumétrique" utilisée à CANMET. L'analyse statistique des données a donné une valeur recommandée pour l'uranium de 0.426% pour le BL-2a et 0.1248% pour le BL-4a.

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*Chercheurs scientifiques et **Technologues, Laboratoires des sciences minérales, CANMET, Énergie, Mines et Ressources Canada, Ottawa.

Note: Avec le collaboration d'autres membres du personnel des Laboratoires des sciences minérales.

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INTRODUCTION

The preparation, characterization and certification of BL-2a and BL-4a is another example of the continuing endeavour of the Canadian Certified Reference Materials Project (CCRMP) to provide compositional reference ores, concentrates and related products typical of Canadian deposits and generally unavailable from other sources for use in analytical laboratories associated with mining, metallurgy and the earth sciences. Other certified reference materials are described in a catalogue available from CANMET, Energy, Mines and Resources Canada, Ottawa (1).

Bl-2a and BL-4a are intended to replace BL-2 and BL-4, the supplies of which are exhausted (2). The latter were part of a popular suite of seven uranium-thorium reference samples identified as DL-1, DH-1, BL-1 to BL-4 (2) and BL-5 (3). The first two have now been replaced by DL-1a (4) and DH-1a (5).

The between-bottle homogeneity of BL-2a and BL-4a was confirmed by two commercial analytical laboratories using different methods. The uranium content of these reference ores is certified on the basis of results obtained at CANMET with the widely accepted volumetric-umpire method (6).

NATURE AND PREPARATION

The raw materials for BL-2a and BL-4a were donated in October 1979 by Eldorado Nuclear Limited. These ores are from the Fay mine, with minor amounts from the Verna mine, both at the Beaverlodge operations at Eldorado, Saskatchewan. They were hand-sorted and analyzed on-site to ensure suitable uranium contents.

The mineralogy of BL-2a and BL-4a is essentially the same as that of BL-2 and BL-4. The orebodies consist of complexes of disseminations and stringers, lenses and veinlets of pitchblende in reddish-brown mylonitized oligoclase saturated with dusty hematite. Pitchblende is the sole radioactive mineral present (7).

BL-2a and BL-4a were dry-ground in February 1981 to pass through a 74-µm screen to give 168 and 248 kg, respectively, of powdered ore. Each was tumbled for 16 h in a 570-L conical blender and bottled in 200-g units. The ores were found to be sufficiently homogeneous for uranium by both a neutron activation and a fluorimetric procedure performed by two commercial analytical laboratories to qualify as reference materials. The results of the confirmation of homogeneity of BL-2a and BL-4a are reported in Appendix A.

The approximate chemical composition and particle size analysis are shown in Tables 1 and 2.

Table 1 - Approximate chemical composition

	Wt %*	
Element	BL-2a	BL-4a
Si	27.59	28.57
Al	6.62	6.75
Fe	4.75	5.26
Ca	4.06	3.27
Na	3.42	3.24
Mg	1.50	1.38
K	0.33	0.36
S	0.36	0.28
Pb	0.090	0.031
L.O.I.	5.16	4.44
H_2O (110°C)	0.19	1.16

*Mean of duplicate determinations

Table 2 - Particle size analysis (wet screen)

	Wt %*	
Size of fraction (µm)	BL-2a	BL-4a
-104 + 74	< 0.1	< 0.1
-74 + 55	0.1	0.1
-55 + 46	18.8	20.0
-46 + 37	10.8	10.5
-37	70.3	69.4

*Mean of duplicate determinations

CERTIFICATION PROGRAM

The uranium content of BL-2a and BL-4a was certified on the basis of determinations performed at CANMET on 25 bottles of each reference ore using the well-established uranium-umpire method (6). This method is described in Appendix B. The 25 bottles were chosen as follows. The stock of 804 bottles of BL-2a and 1211 bottles of BL-4a was divided into 19 lots of 41 and 60 bottles and a lot 20 of 25 and 71 bottles, respectively. The code number of the first bottle was selected at random out of the first lot. The code numbers of the other 19 bottles were given by the code number of the preceding bottle plus 41 and 60 for BL-2a and BL-4a, respectively. In addition, bottles 1, 4, 7, 10 and 13 of the 15 used for the confirmation of the homogeneity of these ores were selected for the certification program. The results of the analysis are summarized in Tables 3 and 4.

Table 3 - Uranium values for BL-2a

Bottle	U wt %	Bottle	U wt %
28	0.4258	438	0.4265
47	0.4261	479	0.4276
69	0.4224	520	0.4275
110	0.4249	529	0.4279
151	0.4282	561	0.4267
192	0.4264	602	0.4243
208	0.4245	643	0.4237
233	0.4276	684	0.4255
274	0.4266	690	0.4260
316	0.4244	725	0.4249
356	0.4240	766	0.4268
369	0.4256	804	0.4270
397	0.4277		

Table 4 - Uranium values for BL-4a

Bottle	U wt %	Bottle	U wt %
46	0.1255	646	0.1238
67	0.1250	706	0.1254
106	0.1252	766	0.1254
166	0.1258	794	0.1248
226	0.1251	826	0.1238
286	0.1247	886	0.1249
309	0.1239	946	0.1254
346	0.1251	1006	0.1250
406	0.1253	1036	0.1251
466	0.1253	1066	0.1248
526	0.1234	1126	0.1250
551	0.1242	1186	0.1249
586	0.1236		

ESTIMATION OF RECOMMENDED VALUE AND STANDARD DEVIATION

The recommended value is estimated by the mean, $\bar{x}$, of the results of the certification program by

$$\bar{x} = \sum_{i}^{k} x_i \Big/ k$$

where x_i = the result for bottle i, and
k = the number of bottles

The standard deviation of the results is given by s as below:

$$s = \sqrt{\sum_{i}^{k} (x_i - \bar{x})^2 \Big/ k-1}$$

The recommended value and corresponding standard deviation for BL-2a and BL-4a are reported in Table 5. The results of this certification program, the recommended value and 2s limits are depicted in Fig. 1 and 2.

Table 5 - Recommended value and standard deviation

Reference material	No. of results	Recommended value	Standard deviation
		wt %	
BL-2a	25	0.426	±0.0015
BL-4a	25	0.1248	±0.0007

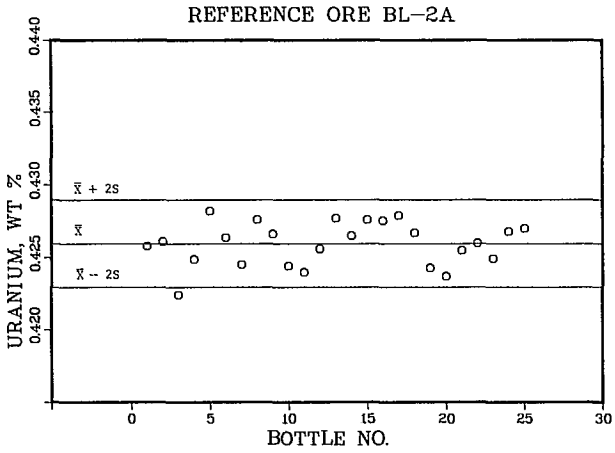

Fig. 1 - Histogram for BL-2a

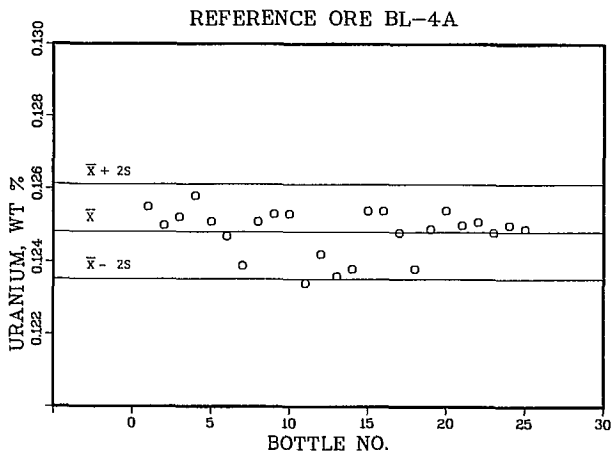

Fig. 2 - Histogram for BL-4a

DISCUSSION

The derivation of the recommended values for uranium in BL-2a and BL-4a from the results of analyses performed at CANMET differs from that of their predecessors BL-2 and BL-4 which were certified on the basis of an interlaboratory program. The uncertainty of the recommended values for BL-2a and BL-4a, expressed as a standard deviation in Table 5, are smaller than the corresponding uncertainty for the recommended values for BL-2 and BL-4 because the former do not include the uncertainty due to the between-laboratory and between-method variations. Since the between-bottle variation was proven to be statistically insignificant by the homogeneity test data, the uncertainty in the recommended values for BL-2a and BL-4a can be attributed mainly to the within-method variation, i.e., precision of the method. In this regard however, it should be noted that the standard deviation of the results used for certification is lower than that obtained by both sets of results used in the assessment of the homogeneity of these reference ores.

It is reasonable to assume that the majority of future users of BL-2a and BL-4a will be unable to attain the high level of precision of the results used for certification. Consequently, the standard deviation of the certified uranium value is not a realistic measure for assessing either analytical results or methods when these reference materials serve for purposes of quality control. Instead, each laboratory must be aware of its attainable precision.

REFERENCES

1. Steger, H.F. "Certified reference materials"; CANMET Report 80-6E; CANMET, Energy, Mines and Resources Canada; 1980.

2. Ingles, J.C., Sutarno, R., Bowman, W.S. and Faye, G.H. "Radioactive ores DH-1, DL-1, BL-1, BL-2, BL-3 and BL-4 - certified reference materials"; CANMET Report 77-64; CANMET, Energy, Mines and Resources Canada; 1979.

3. Faye, G.H., Bowman, W.S. and Sutarno, R. "Uranium ore BL-5 - A certified reference material"; CANMET Report 79-4; CANMET, Energy, Mines and Resources Canada; 1979.

4. Steger, H.F. and Bowman, W.S. "DL-1a - A certified uranium-thorium reference ore"; CANMET Report 80-10E; CANMET, Energy, Mines and Resources Canada; 1980.

5. Steger, H.F., Bowman, W.S. and Zechanowitsch, G. "DH-1a - A certified uranium-thorium reference ore"; CANMET Report 81-11E; CANMET, Energy, Mines and Resources Canada; 1981.

6. Hitchen, A. and Zechanowitsch, G. "Titrimetric determination of uranium in low-grade ores by the ferrous ion-phosphoric acid reduction method"; Talanta 27:383-389; 1980.

7. Management and Staff Eldorado Mining and Refining Ltd. "Featuring the Beaverlodge operation: geology"; Can Min J 81:6:84-90; June 1960.

8. Brownlee, K.A. "Statistical theory and methodology in science and engineering"; John Wiley and Sons, Inc., New York; 1960.

APPENDIX A

CONFIRMATION OF HOMOGENEITY

HOMOGENEITY OF BL-2a AND BL-4a

The homogeneity of BL-2a and BL-4a was confirmed by the analysis of 15 bottles for uranium in triplicate. The bottles were chosen by a stratified random selection procedure. The stock was divided into 8 lots of 54 bottles interspersed with 6 lots of 53 bottles for BL-2a, and into 10 lots of 81 bottles interspersed with four lots of 80 bottles for BL-4a. The code number of the first bottle was selected at random out of the first lot. The code numbers of the other 14 bottles were given by the code number of the preceding bottle plus the number of bottles in that lot. The contents of each bottle were split and analyzed by Chemex Laboratories Limited, North Vancouver, British Columbia, using a neutron activation analysis procedure and by Bondar-Clegg and Company Limited, North Vancouver, using a fluorimetric procedure. The results are reported in Tables 6 and 7.

A one-way analysis of variance technique was used to assess the homogeneity (8). Herein, the ratio of the between-bottle to within-bottle mean square is compared with the F-statistic at the 95% level of probability. In this treatment, the analytical data are assumed to fit the model (8).

$$x_{ij} = \mu + y_i + e_{ij}$$

where x_{ij} = the j^{th} result in bottle i,
μ = the true consensus value,
y_i = the discrepancy between the mean of the results in bottle i ($\bar{x}_i$.) and μ, and
e_{ij} = the discrepancy between x_{ij} and $\bar{x}_i$

It is assumed that both y_i and e_{ij} are normally distributed with means of zero and variance of ω^2 and σ^2, respectively.

Table 6 - Confirmation of homogeneity of BL-2a

	U (wt %)							
	Neutron activation				Fluorimetric			
Bottle	Individual			Mean	Individual			Mean
47	0.4226	0.4263	0.4215	0.4237	0.44	0.43	0.44	0.437
101	0.4204	0.4267	0.4213	0.4227	0.43	0.44	0.43	0.433
154	0.4170	0.4231	0.4188	0.4197	0.44	0.45	0.43	0.440
208	0.4203	0.4292	0.4258	0.4250	0.43	0.44	0.43	0.433
261	0.4236	0.4202	0.4197	0.4213	0.44	0.44	0.44	0.440
315	0.4225	0.4192	0.4183	0.4200	0.44	0.43	0.43	0.443
369	0.4166	0.4246	0.4261	0.4227	0.43	0.44	0.43	0.443
422	0.4239	0.4223	0.4164	0.4207	0.43	0.43	0.44	0.443
476	0.4235	0.4223	0.4242	0.4233	0.44	0.43	0.43	0.443
529	0.4193	0.4219	0.4201	0.4203	0.43	0.44	0.44	0.437
583	0.4206	0.4286	0.4227	0.4243	0.43	0.44	0.44	0.437
637	0.4229	0.4288	0.4243	0.4253	0.43	0.44	0.44	0.437
690	0.4261	0.4234	0.4203	0.4230	0.43	0.43	0.43	0.430
744	0.4290	0.4192	0.4232	0.4237	0.43	0.44	0.43	0.433
797	0.4181	0.4264	0.4219	0.4220	0.44	0.43	0.44	0.437
Overall mean				0.4225				0.435
Standard deviation				0.0033				0.006

Analysis of variance table

Source of variations	Degrees of freedom	Mean square
(1) Neutron activation		
Between bottles	14	9.483×10^{-6}
Within bottles	30	1.189×10^{-5}
Total	44	
Calculated F statistic =	0.797	
(2) Fluorimetric		
Between bottles	14	2.317×10^{-5}
Within bottles	30	3.333×10^{-5}
Total	44	
Calculated F-statistic =	0.695	
F.95(14,30) =	2.031	

Null hypothesis of no difference between bottles is accepted for both analytical methods

where n_i = the number of results in bottle i, i.e., 3, and

k = the number of bottles

The between-bottle mean square is estimated by s_2^2, which is given by

$$s_2^2 = \sum_i^k n_i (\bar{x}_i. - \bar{x}..)^2 \Big/ k - 1$$

The within-bottle mean square is estimated by s_1^2, which is given by

$$s_1^2 = \sum_i \sum_j^{n_i} (x_{ij} - \bar{x}_i.)^2 \Big/ \sum_i^k n_i - k$$

The calculated F-statistic is therefore s_2^2/s_1^2.

Table 7 - Confirmation of homogeneity of BL-4a

	U (wt %)							
	Neutron activation				Fluorimetric			
Bottle	Individual			Mean	Individual			Mean
67	0.1299	0.1295	0.1286	0.1293	0.13	0.13	0.13	0.130
148	0.1270	0.1277	0.1280	0.1277	0.12	0.13	0.12	0.123
228	0.1290	0.1284	0.1282	0.1283	0.12	0.12	0.13	0.123
309	0.1289	0.1297	0.1291	0.1293	0.12	0.13	0.13	0.127
390	0.1284	0.1273	0.1299	0.1283	0.12	0.13	0.12	0.123
471	0.1300	0.1284	0.1276	0.1287	0.13	0.12	0.12	0.123
551	0.1276	0.1301	0.1298	0.1293	0.12	0.13	0.13	0.123
632	0.1284	0.1292	0.1278	0.1283	0.13	0.13	0.13	0.130
713	0.1299	0.1289	0.1267	0.1287	0.13	0.13	0.13	0.130
794	0.1287	0.1299	0.1291	0.1293	0.13	0.13	0.13	0.127
874	0.1301	0.1284	0.1280	0.1287	0.12	0.13	0.13	0.130
955	0.1287	0.1297	0.1292	0.1293	0.13	0.13	0.13	0.130
1036	0.1264	0.1283	0.1279	0.1273	0.13	0.13	0.14	0.133
1117	0.1287	0.1266	0.1298	0.1287	0.13	0.13	0.13	0.130
1197	0.1296	0.1285	0.1286	0.1293	0.13	0.13	0.13	0.130
Overall mean				0.1287				0.128
Standard deviation				0.0010				0.005

Analysis of variance table

Source of variations	Degrees of freedom	Mean square
(1) Neutron activation		
Between bottles	14	0.941×10^{-6}
Within bottles	30	1.011×10^{-6}
Total	44	
Calculated F statistic	= 0.930	
(2) Fluorimetric		
Between bottles	14	3.175×10^{-5}
Within bottles	30	1.778×10^{-5}
Total	44	
Calculated F-statistic	= 1.786	
F.95(14,30)	= 2.037	

Null hypothesis of no difference between bottles is accepted for both analytical methods

APPENDIX B

THE VOLUMETRIC-UMPIRE METHOD FOR URANIUM

THE VOLUMETRIC-UMPIRE METHOD FOR URANIUM

APPARATUS

An expanded-scale or digital pH-meter equipped with calomel and platinum electrodes is used for the potentiometric titrations. The platinum electrode is a coil of sturdy wire which is cleaned daily by immersion in hot 16M nitric acid for several min, rinsed with water, then heated to redness in a burner flame.

A 3-min timer is used to time the oxidation of the ferrous iron in the procedure.

A 5- or 10-mL burette, reading to 0.01 mL, is used to add the titrant and a magnetic stirrer with Teflon bar is used to stir the sample solution. A Thermolyne water-cooled cooling plate is used, when necessary, to prevent heat from the magnetic stirrer warming the sample solution.

REAGENTS

Standard 0.025N potassium dichromate solution. Prepare in the usual way and prepare 0.005N or 0.0125N solutions from it by dilution with water. Standardize against NBS 950a U_3O_8 or NBS 960 uranium metal by the potentiometric procedure, taking 4 or 5 aliquots of a standard uranium solutuon containing from 1 to 100 mg of uranium, with calibrated silicone-coated pipettes, and correcting for the temperature and blank.

DECOMPOSITION PROCEDURES

The samples may be brought into solution by a multi-acid treatment:

Transfer a 1-5 g sample of the ore or a 10-g sample of waste material to a covered 400-mL Teflon beaker. Add 25 mL of 48% hydrofluoric acid and digest at low heat for 20-30 min or until the sample is decomposed. Add 10 mL of concentrated hydrochloric acid and 10 mL of concentrated nitric acid and digest for another 30 min or until most of the black material is oxidized. Remove the cover, add 15 mL of 72% perchloric acid and evaporate the solution to fumes. Cool, rinse the walls of the beaker with a little water and fume again. Cover the beaker and boil the perchloric acid solution vigorously to remove the black coating on the walls of the beaker. Transfer the residual solution with a minimum of water to a 400-mL glass beaker. Rinse the walls of the Teflon beaker with a few mL of concentrated hydrochloric acid from a dropping bottle, cover the beaker, and warm it on the hot-plate for a few min to remove traces of sample from the walls of the beaker. Add the hydrochloric acid rinse to the perchloric acid solution and evaporate the combined solutions to near dryness. Most samples are decomposed by this procedure but some may leave a small amount of unattacked black material. This should be filtered off and fused with sodium fluoroborate and the cooled melt combined with the original filtrate before the evaporation to near dryness*. Add 70 mL of 85% phosphoric acid to the residue, cover the beaker, and boil the solution until it is clear.

Cool to room temperature and add 50 mL of 20% v/v sulphuric acid. Determine the uranium by the potentiometric procedure.

REDUCTION AND TITRATION OF URANIUM

Potentiometric procedure. This is applicable to the determination of from 1 to 300 mg of uranium but normally between 1 and 70 mg of uranium is determined in ore samples.

To the sample solution add 5 mL of 1.5M sulphamic acid. Warm the solution to about 48° and stir the solution continuously, but moderately, with a Teflon-coated magnetic stirring bar. Pipette 5 mL of 1M ferrous sulphate into the solution without touching the walls of the beaker. When the temperature of the solution reaches 41°, generally within 5 min, wash down the beaker sides with 15 mL of nitric acid-sulphamic acid-molybdate solution. Exactly 3 min (use a timer equipped with an alarm) after the disappearance of the brown-black colour, add 100 mL of water and 5 mL of 0.1M vanadyl sulphate or 100 mg of solid vanadyl sulphate. Immediately insert the platinum and calomel electrodes in the solution, stir briskly

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*Sodium fluoroborate fusion. Mix the residual black material with 4-5 times its weight of sodium fluoroborate and fuse the mixture in a platinum crucible over a Méker burner until dissolution is complete (~5 min).

without spattering, and titrate with 0.005N or 0.0125N potassium dichromate to a fixed potential near 630 mV. Complete the titration within 3 min of adding the water. Correct the volume of titrant used for the ambient temperature and, if necessary, for the blank. Correction for ambient temperature need not be made if the volume of titrant is less than 10 mL or if high accuracy is not required but a blank correction is necessary for a low titrant volume.