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DH-1a: A CERTIFIED URANIUM-THORIUM REFERENCE ORE

H.F. STEGER, W.S. BOWMAN and G. ZECHANOWITSCH

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DH-1a: A CERTIFIED URANIUM-THORIUM REFERENCE ORE

by

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

SYNOPSIS

A 122-kg sample of a uranium-thorium ore, DH-1a, from Elliot Lake, Ontario, was prepared as a compositional reference material to replace the similar certified ore, DH-1, of which the stock had been exhausted. DH-1a was ground to minus 74 μm, blended in one lot and bottled in 200-g units. The homogeneity of DH-1a with respect to uranium was confirmed in CANMET using the volumetric-umpire method.

The recommended value for uranium is based on the data from the confirmation of homogeneity. For thorium, twelve laboratories provided results in a "free-choice" analytical program. A statistical analysis of the data gave a recommended value of 0.263% for uranium and 0.091% for thorium.

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

DH-1a: MINERAI DE REFERENCE CERTIFIE D'URANIUM-THORIUM

par

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

SYNOPSIS

Un échantillon de 122 kg d'un minerai d'uranium-thorium, DH-1a, provenant d'Elliot Lake en Ontario, a été préparé comme matériau de référence de composition pour remplacer le minerai certifié analogue, DH-1, dont l'inventaire avait été épuisé. Le DH-1a a été broyé à une granulométrie de moins 74 µm, mélangé en lot de minerai et embouteillé en unités de 200 g. La homogénéité du DH-1a a été confirmée quant à l'uranium au CANMET par la méthode de "arbitre-volumétrique".

La valeur recommandée pour l'uranium est fondée sur les données de la confirmation de la homogénéité. Pour le thorium, douze laboratoires ont soumis des résultats en vertu d'un programme analytique de "libre choix". L'analyse statistique des données a donné une valeur recommandée de 0.263% pour l'uranium et de 0.091% pour le thorium.

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

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INTRODUCTION

The preparation, characterization and certification of the uranium ore DH-1a 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, Canada (1).

DH-1a was intended to replace DH-1, the supply of which was exhausted (2). The latter was part of a popular suite of seven uranium-thorium reference samples identified as DH-1, DL-1, BL-1 to BL-4 (2) and BL-5 (3).

An interlaboratory program was conducted to obtain results for thorium from twelve commercial, industrial and government laboratories using analytical methods of their own choice. The results should therefore be indicative of the current "state-of-the-art" of thorium analysis.

The certification program for uranium represents a departure from the interlaboratary or consensus procedure previously followed by CCRMP. Instead, the uranium content of DH-1a is certified on the basis of results obtained with the widely-accepted volumetric-umpire method (4). However, for this initial attempt to certify uranium by this procedure, CCRMP requested six laboratories to provide results for uranium in addition to those for thorium. Three of these six each provided two sets of results by different techniques. Moreover, two other laboratories voluntarily submitted results for uranium. The 13 sets of results for uranium by 7 different techniques were treated as comprising an interlaboratory program, the results of which substantiate the certified value of uranium based on the CANMET volumetric-umpire method.

NATURE AND PREPARATION

The raw material for DH-1a was donated in April 1980 by Denison Mines Ltd. It had been handpicked and analyzed on-site to ensure a suitable uranium content. The mineralogy of DH-1a is essentially the same as that of DH-1. Both are samples from the Denison Reef, in the Quirke ore zone, and are typical of ore-grade material from Denison Mines Ltd. The ore is a pebble conglomerate, with a pebble-to-matrix ratio of 2 to 1. The pebbles, which have a median size of 64 mm are mainly quartz with some chert. The matrix is a sericitic, feldspathic quartzite containing about 10% pyrite on a whole-ore basis. The ore also contains minor to trace amounts of garnet, spinel, chromite, cassiterite, tourmaline, anatase, rutile, magnetite, hematite, ilmenite, sphene, apatite, fluorite, barite, muscovite, phlogopite, biotite, hornblende, clinopyroxene, orthopyroxene, greenalite, chamosite, grunerite, epidote, zoisite and zircon. Minute amounts of gold may also be present. The radioactive minerals are principally uraninite and brannerite but some monazite and uranothorite are present (2).

DH-1a was dry-ground in May 1980 to pass through a 74-µm screen. The powdered ore weighing approximately 122 kg was tumbled in a 570-L conical blender for 9 h and bottled in 200-g units. DH-1a was found to be sufficiently homogeneous for uranium by the volumetric-umpire method (4) to qualify as a reference material. The results of the confirmation of homogeneity of DH-1a are summarized in Appendix A.

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

INTERLABORATORY PROGRAM FOR CERTIFICATION OF THORIUM

The laboratories that participated in the certification program are listed in Appendix B. Each was assigned a code number which bore no relation to its alphabetical order.

Each laboratory was requested to contribute five replicate results for thorium on one bottle of DH-1a by methods of their own choice, and to report the results on an "as is" basis. Some laboratories however deviated from the request for 5 results for thorium. For Laboratory 7 which submitted results by two techniques, each set was considered to be statistically independent.

The recommended value for thorium is presented in Table 3. Methodological and statistical information is presented in Tables 4 and 5.

Table 1 - Approximate chemical composition of DH-1a

Element	weight %*
Si	37.28
Fe	5.17
S	4.82
Al	3.44
K	1.43
Mg	0.07
Ca	0.04
Na	0.04
C (total)	0.05
H_2O (105°C)	0.07

*Mean of duplicate determinations

Table 2 - Particle size analysis (wet screen)

Size of fraction (μm)	weight %*
-104 + 74	0.3
- 74 + 55	16.2
- 55 + 46	4.5
- 46 + 37	10.4
- 37	68.6

*Mean of duplicate determinations

Detection of Outliers

The individual outlying result in the set from Laboratory 1 was detected according to Dixon's test (5).

Estimation of consensus values and 95% confidence limits

A one-way analysis of variance technique was used to estimate the consensus value and its variance. This approach considers the results of the described certification program to be only one sampling out of a universal set of results. The analytical data were assumed to fit the model (5)

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

where x_{ij} = the j^{th} result in set i,
μ = the true consensus value,
y_i = the discrepancy between the mean of the results in set 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 variances of ω^2 and σ^2, respectively. The significance of ω^2 is detected by comparing the ratio of between-set mean squares to within-set mean squares with the F statistic at the 95% confidence level and with the appropriate degrees of freedom.

Table 3 - Recommended values and statistical parameters (outliers excluded)

Element	No. of laboratories	No. of results	Overall mean	95% CL		σ_A*
				Low	High	
				wt %		
U	CANMET	45	0.2629	0.2626	0.2632	0.009
Th	12	66	0.091	0.088	0.094	0.002

*Average within-set standard deviation

Table 4 - Summary of analytical methods for thorium

Laboratory	Decomposition, separation, measurement techniques, etc.
1	HNO_3, HCl, H_2SO_4 and HF; residues fused with $K_2S_2O_7$; Th extracted with TTA in xylene and stripped with dilute HNO_3; colorimetry with thoron.
2	Measurement of gamma emission after irradiation with thermal neutrons.
3	X-ray fluorescence.
4	X-ray fluorescence.
5	X-ray fluorescence; polyvinyl alcohol binder.
6	X-ray fluorescence; fused $Na_2B_4O_7$ discs.
7(a)	Measurement of gamma emission after irradiation with thermal neutrons.
(b)	Measurement of ^{233}Th 86.9-KeV γ-ray after irradiation with epithermal neutrons.
8	HNO_3 HF and $HClO_4$ in Teflon bomb; Th separated by ion-exchange in dilute HNO_3; colorimetry with Arsenazo III.
9	Measurement of ^{233}Pa 311.8 KeV X-ray after irradiation with thermal neutrons.
11	Measurement of 262 MeV γ-ray from ^{208}Tl after sample was sealed in metal can for 30 days.
12	Measurement of 312 KeV γ-ray after irradiation with thermal neutrons.
CANMET	Na_2O_2 fusion; taken up on dilute HCl; Th separated by ion-exchange on Zerolit 225; colorimetry with thoron.

Table 5 - Analytical results, laboratory means and standard deviations for thorium

						Mean	S.D.
	weight %						
Lab- 1 (Color)	.0910	.1190*	.0910	.0880	.0840	.0946	.0139
Lab- 2 (NAA)	.0928	.0868	.0916	.0960	.0959	.0925	.0038
Lab- 3 (XRF)	.0860	.0860	.0880	.0870	.0880	.0870	.0010
Lab- 4 (XRF)	.0949	.0971	.0960	.0978	.0963	.0964	.0011
Lab- 5 (XRF)	.0830	.0800	.0810	.0820	.0800	.0812	.0013
Lab- 6 (XRF)	.0956	.0967	.0955	.0966	.0987	.0968	.0011
Lab- 7 (NAA)	.0894	.0876	.0877	.0879	.0888	.0883	.0008
Lab- 7 (NAA)	.0890	.0883	.0895	.0901	.0886	.0891	.0007
Lab- 8 (Color)	.0859	.0878	.0886	.0889	.0897		
	.0901	.0905	.0926			.0893	.0020
Lab- 9 (NAA)	.0952	.0932	.0926	.0961	.0939	.0942	.0014
Lab-11 (Radio)	.0840	.0900	.0865	.0855		.0865	.0025
Lab-12 (NAA)	.0919	.0926	.0915	.0924	.0921	.0921	.0004
Lab-13 (Color)	.0996	.1026	.1024	.1012	.0978	.1007	.0020

*Individual result judged to be outliers

The consensus value of the assumed model is estimated by the overall mean $\bar{x}..$:

$$\bar{x}.. = \sum_i^k \sum_j^{n_i} x_{ij} \Big/ \sum_i^k n_i$$

where n_i = the number of results in set i, and k = the number of sets.

The value of σ^2 is estimated by s_1^2 which is given by

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

The value of ω^2 is estimated by

$$\omega^2 = (s_2^2 - s_1^2) \Big/ \frac{1}{k-1} \left(\sum_i^k n_i - \sum_i^k n_i^2 / \sum_i^k n_i \right)$$

where

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

The variance of the overall mean is given by

$$V[\bar{x}..] = \left(\sum_i^k n_i^2 / (\Sigma n_i)2 \right) \omega^2 + \left(1/\sum_i^k n_i \right) \sigma^2$$

and the 95% confidence limits for $\bar{x}..$ are

$$\bar{x}.. \pm t_{0.975,\ (k-1)} \sqrt{V[\bar{x}..]}$$

It should be noted that the 95% confidence limits denote that if the certification program were performed 100 times, the overall mean in 95 would fall within the prescribed limits.

The average within-set standard deviation, σ_A, where

$$\sigma_A^2 = \frac{1}{k} \sum_i^k \sum_j^{n_i} (x_{ij} - x_i.)^2 / n_i,$$

is a measure of the average within-bottle precision as determined by the analytical methods used. The implication exists therefore that a laboratory using a method of average or better repeatability should obtain individual results for a given certified element with a precision that is at least comparable to the reported value of σ_A.

CERTIFICATION PROGRAM FOR URANIUM

The uranium content of DH-1a was certified on the basis of the CANMET results obtained in the establishment of its homogeneity. Table 6 illustrates the accuracy of the volumetric-umpire method when applied to the previously certified uranium reference materials of CCRMP (4). The recommended value and 95% confidence intervals for uranium are given in Table 3.

Tables 7 and 8 summarize the results and methodology for uranium. The 13 sets of uranium results were considered to comprise an interlaboratory program and were treated statistically as described for thorium. The set of results by Xrf from Laboratory 1 was deleted because its mean differed by more than twice the overall

Table 6 - Accuracy of volumetric-umpire method

Reference material	No. of detns.	U (wt %) Certified[a]	U (wt %) CANMET
DH-1	5	0.177	0.177
DL-1	5	0.0041	0.00400
DL-1a	20	0.0116	0.0114
BL-1	10	0.022	0.0208
BL-2	5	0.453	0.453
BL-3	5	1.02	1.021
BL-4	10	0.173	0.171
BL-5	5	7.09[b]	7.15
DH-1a	45	0.260[c]	0.263

[a] All certified by consensus method

[b] Isotope-dilution - Mass spectrometric method by National Bureau of Standards indicates the "true-value" to be closer to 7.13 - 7.14% U (3).

[c] Mean value of all uranium results (Table 8). See below.

Table 7 - Summary of analytical methods for uranium

Laboratory	Decomposition, separation, measurement techniques, etc.
1(a)	HNO_3, HCl, H_2SO_4 and HF; fluorimetric finish.
(b)	Energy dispersive X-ray fluorescence.
2	Measurement of delayed neutron emission after irradiation with thermal neutrons.
4(a)	HNO_3, $HClO_4$ and HF; taken to dryness and dissolved in 1 N HCl; laser fluorescence.
(b)	X-ray fluorescence.
5	HNO_3 and HF; aliqots evaporated and fused with carbonate-fluoride flux; fluorimetric finish.
6	X-ray fluorescence; fused $Na_2B_4O_7$ discs.
7(a)	Measurement of delayed neutron emission after irradiation with thermal neutrons.
(b)	Measurement of ^{239}U 74.66 keV γ-ray after irradiation with epithermal neutrons.
11	Measurement of ^{124}Bi 1.764 MeV γ-ray after sample sealed in metal can for 30 days.
12(a)	Measurement of 228 KeV γ-ray after irradiation with thermal neutrons.
(b)	Measurement of delayed neutron emission after irradiation with thermal neutrons.
CANMET	Volumetric-umpire method - Reference 4.

standard deviation from the initially calculated overall mean. To avoid giving an unduly heavy weighting to the contribution from CANMET, only 5 results selected at random out of the 45 available were included. The calculated statistical parameters are given in Table 9.

DISCUSSION

Thorium

Table 4 illustrates that the majority of the sets of results were obtained by instrumental techniques such as neutron activation, X-ray

Table 8 - Analytical results, laboratory means and standard deviations for uranium

						Mean	S.D.
			weight %				
Lab- 1 (Fluor)	.2520	.2710	.2630	.2590	.2570	.2604	.0071
Lab- 1 (XRF)*	.2360	.2330	290	.2280	.2320	.2316	.0032
Lab- 2 (NAA)	.2540	.2530	.2520	.2500	.2530	.2524	.0015
Lab- 4 (Fluor)	.2670	.2600	.2560	.2760	.2560	.2630	.0085
Lab- 4 (XRF)	.2600	.2670	.2630	.2700	.2660	.2652	.0038
Lab- 5 (Fluor)	.2470	.2610	.2690	.2770	.2540	.2616	.0119
Lab- 6 (XRF)	.2638	.2638	.2650	.2647	.2658	.2646	.0008
Lab- 7 (NAA)	.2640	.2620	.2610	.2600	.2530	.2600	.0042
Lab- 7 (NAA)	.2510	.2650	.2620	.2600	.2510	.2578	.0065
Lab-11 (Radio)	.2510	.2513	.2505	.2519		.2512	.0006
Lab-12 (NAA)	.2570	.2580	.2600	.2610	.2580	.2588	.0016
Lab-12 (NAA)	.2540	.2550	.2530	.2550	.2550	.2544	.0009
Lab-13 (TITR)	.2635	.2630	.2635	.2622	.2630	.2630	.0005

*Outlying set

Table 9 - Consensus value and other statistics for uranium in DH-1a (outlier excluded)

No. of laboratories	9
No. of sets	12
No. of results	59
Mean, wt %	0.260
95% confidence limits for the mean, low, wt %	0.257
high, wt %	0.262
σ_A*, wt %	0.004

*Average within-laboratory standard deviation

fluorescence or radiometric analysis for which little or no sample treatment is required. The two sets of results using a colorimetric finish appear to fall in the upper range of the thorium values received. This cannot, of course, be confirmed by statistical analysis because of insufficient data.

Uranium

The certified value for uranium as determined by the volumetric-umpire method is slightly higher than the overall mean of the results from the interlaboratory program. It must be noted, however, that the majority of the results for uranium, just as was the case for thorium, were obtained by an instrumental technique requiring little or no sample treatment. Those sets of results where sample decomposition was necessary (e.g., the fluorimetric or titrimetric finish) have means that fall in the upper range of uranium values received. It is possible therefore that had a more even balance between chemically and instrumentally determined results been submitted, the agreement between the certified value and the mean of the interlaboratory program would have been better.

DH-1a is the first reference material of CCRMP where two values are reported for the statistical parameters associated with a certified element. The difference in the significance of these "seemingly - same" parameters must therefore be emphasized. The 95% confidence intervals of the certified value for uranium (Table 3) pertain to one method and one laboratory. They represent the uncertainty in the certified value due to the repeatability of this method and any between-bottle difference. The 95% confidence intervals

of the mean of the interlaboratory program represent the uncertainty in this mean due to the repeatability of several methods, any between-bottle difference, any between-method difference and any between-laboratory difference. The latter two factors are the largest contributions to the higher magnitude of the 95% confidence intervals of the mean of the interlaboratory program compared with that of the certified value.

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APPENDIX A

CONFIRMATION OF HOMOGENEITY

HOMOGENEITY OF DH-1a

The homogeneity of DH-1a was confirmed at CANMET by the analysis of 15 bottles for uranium in triplicate using the volumetric-umpire method (4). These bottles were selected as follows. The stock of 600 bottles was divided into 15 lots of 40 bottles. 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 40. The results of the analyses are shown in Table 10.

A one-way analysis of variance technique was used to assess the homogeneity (5). Herein, the ratio of the between-bottle to within-bottle mean square is compared with the F-statistic at the 95% level of probability. No evidence of bottle-to-bottle inhomogeneity was found for uranium.

The degree of homogeneity of DH-1a is also depicted graphically in Fig. 1 wherein the uranium content is plotted for each bottle.

Table 10 - Confirmation of homogeneity of DH-1a

Bottle No.	U (wt %)			
	Individual			Mean
9	0.2631	0.2625	0.2627	0.2628
49	0.2635	0.2624	0.2632	0.2630
89	0.2635	0.2628	0.2629	0.2631
129	0.2629	0.2629	0.2627	0.2628
169	0.2630	0.2635	0.2642	0.2636
209	0.2630	0.2627	0.2632	0.2630
249	0.2628	0.2616	0.2655	0.2633
289	0.2634	0.2616	0.2615	0.2622
329	0.2635	0.2615	0.2634	0.2628
369	0.2647	0.2632	0.2611	0.2630
409	0.2640	0.2622	0.2639	0.2634
449	0.2622	0.2644	0.2640	0.2635
489	0.2628	0.2635	0.2609	0.2624
529	0.2631	0.2612	0.2623	0.2622
568	0.2630	0.2623	0.2629	0.2626
			Overall mean =	0.2629

Analysis of variance table for uranium

Source of variations	Degrees of freedom	Mean square
Between bottles	14	5.795×10^{-7}
Within bottles	30	1.062×10^{-6}
Total	44	

Calculated F statistic = 0.5455

F.95 (14, 30) = 2.0374

Null hypothesis of no difference between bottles is accepted

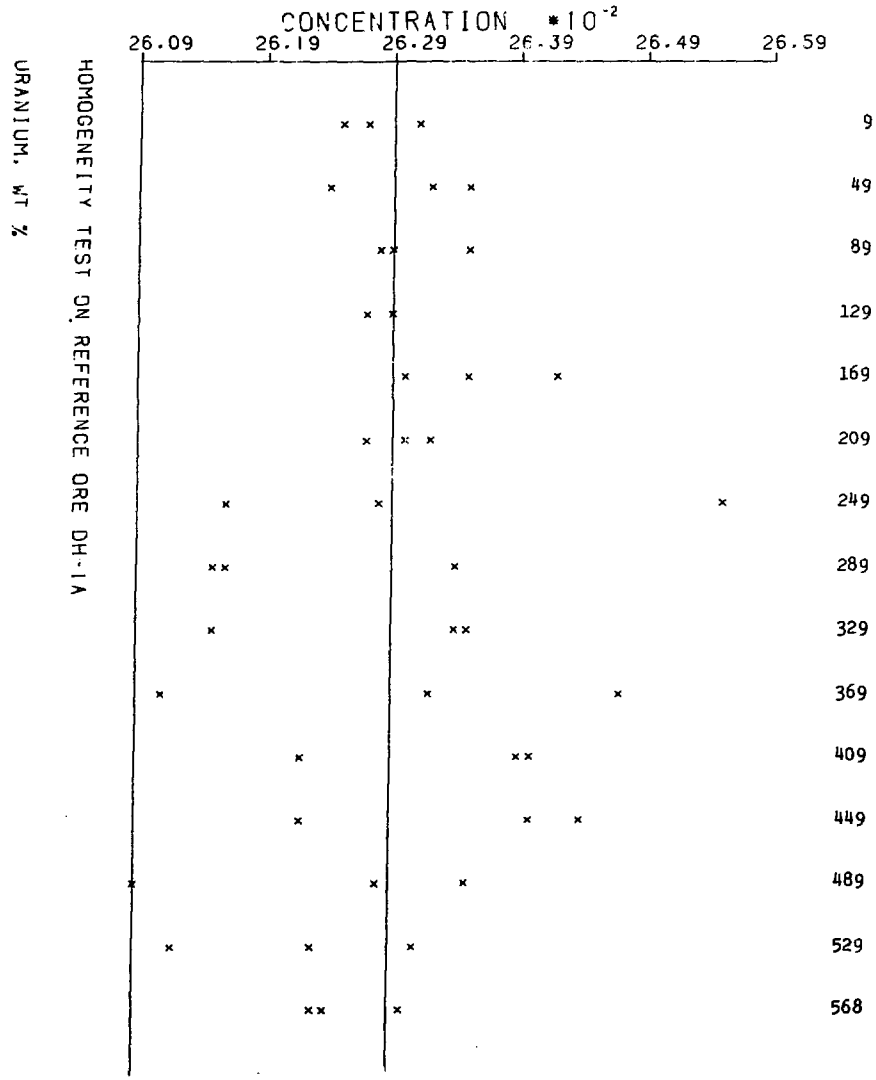

Fig. 1 - The uranium content of the subsamples from each bottle of DH-1a to confirm the homogeneity.

APPENDIX B

PARTICIPATING LABORATORIES

Atomic Energy of Canada Limited, Isotope Products Group, Ottawa, Ontario.
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