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URANIUM ORE BL-5 — A CERTIFIED REFERENCE MATERIAL

G.H. FAYE, W.S. BOWMAN AND R. SUTARNO

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URANIUM ORE BL-5 — A CERTIFIED REFERENCE MATERIAL

by

G.H. Faye*, W.S. Bowman** and R. Sutarno***

SYNOPSIS

As a facet of the Canadian Certified Reference Materials Project, a uranium ore, BL-5, has been prepared as a compositional reference material. Approximately 370 kg of raw ore was dry-ground to minus 74 µm, blended, tested for homogeneity by X-ray fluorescence and chemical methods, and bottled in 200-g units.

In a "free-choice" program for certification of BL-5, 27 laboratories provided analytical results for uranium on each of two bottles of the ore. A statistical treatment of the data yielded a consensus value of 7.09 ± 0.03%.

Information was also obtained on the state of radioactive equilibrium of BL-5 and its Ra-226, Pb-210 and Th-230 content.

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Note: Major contributions were also made by other staff members of the Mineral Sciences Laboratories as well as of laboratories in other organizations.

MINERAI D'URANIUM BL-5 - UN MATERIAU DE REFERENCE CERTIFIE

par

G.H. Faye*, W.S. Bowman** et R. Sutarno***

SOMMAIRE

Un minerai d'uranium, le BL-5, a été préparé comme matériau de référence certifié en raison du Programme canadien de matériaux de référence certifiés. Environ 370 kg de minerai brut a été broyé à sec à une dimension de -70 µm, mélangé, analysé avec la fluorescence X et des méthodes chimiques pour en déterminer l'homogénéité et embouteillé en contenants de 200 g.

Vingt-sept laboratoires ont fourni des résultats pour l'uranium dans chacune des deux bouteilles de minerai selon le programme de "libre choix" de certification du BL-5. L'analyse statistique des données a donné lieu à une valeur acceptable de 7.09 ± 0.03%.

On a aussi obtenu l'information sur l'état d'équilibre radioactif du BL-5 et de sa teneur en Ra-226, Pb-210 et Th-230.

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Note: Avec la collaboration de d'autres membres du personnel des Laboratoires des sciences minérales ainsi que le personnel de laboratoire d'autres organismes.

INTRODUCTION

This report describes the characterization and preparation of a sample of a uranium ore, BL-5, for use as a certified compositional reference material. The work is a facet of the Canadian Certified Reference Materials Project (CCRMP) to certify mainly materials that are representative of Canadian ore deposits and have potential value in conventional analytical or earth sciences laboratories. Certified reference ores and related materials issued previously by CCRMP are described in a catalogue available from CANMET, Energy, Mines and Resources Canada, Ottawa (1).

BL-5 was chosen to extend to a higher concentration the popular suite of six uranium-thorium reference samples identified as DH-1, DL-1, and BL-1 to BL-4, previously issued by CCRMP (2).

A program was conducted to obtain uranium results from 27 laboratories using analytical methods of their choice, which are a good representation of those available for determining uranium in commercial and industrial establishments. Information was also obtained on the state of radioactive equilibrium of BL-5 and its Ra-226, Pb-210 and Th-230 content.

NATURE AND PREPARATION OF BL-5

The raw material for BL-5 was donated to CCRMP in September 1976 by the Resource Geophysics and Geochemistry Division, Geological Survey of Canada, Ottawa. This material is essentially a low-grade concentrate of ore from Beaverlodge, Saskatchewan. The mineralogical composition, approximate chemical composition, and a particle size analysis of the material as processed below are given in Tables 1 to 3 respectively.

In late 1976, BL-5 was dried at approximately 100°C and dry-ground to pass a minus 74-µm screen. The powdered material, weighing 370 kg, was tumbled in a 570-L conical blender for nine hours. Upon opening the blender, the bulk material was samples systematically and analyzed for uranium by X-ray fluorescence and chemical methods. It was found sufficiently homogeneous to qualify for the interlaboratory program and was bottled in 100-g units.

TABLE 1

Mineralogical composition of BL-5

(decreasing order of abundance)

plagioclase feldspar
quartz
uraninite
calcite + dolomite
hematite
chlorite + muscovite
galena
carbon
pyrite
magnetite
anatase + rutile
chalcopyrite
bornite
pyrrhotite
apatite

Note: Combined weight of above minerals from pyrite to apatite is approximately 2%.

TABLE 2

Approximate chemical composition of BL-5

Constituent	X-ray Fluorescence[a]	Chemical[b]
Si	22.2 (wt %)	21.8 (wt %)
Al	6.0	6.0
Fe	5.8	5.9
Ca	3.9	4.1
Mg	1.4	1.5
Na	3.5	3.6
K	0.4	0.4
Ti	0.4	0.4
V	-	0.1
Mn	0.05	-
Pb	1.5	1.4
Cr	0.01	-
Sr	0.03	-
Zr	0.04	-
P	0.07	-
S	0.3	-
Th	-	0.004
U	7.06	7.09[c]
C	-	1.9
Moisture (105°C)	-	0.3

[a] Mean of 10 replicate determinations by Lab-26.
[b] Mean of 2 replicate determinations by Lab-1.
[c] Consensus value from Table 6.

TABLE 3

Particle size analysis (wet screen)

Size of fraction (μm)	wt %[a]
-74 +55	8.3
-55 +46	10.3
-46 +37	2.7
-37	78.7

[a] Mean of duplicate determinations

INTERLABORATORY PROGRAM FOR CERTIFICATION OF BL-5

Laboratories participating in the BL-5 program are listed alphabetically below. Each of these was arbitrarily assigned a code number so that analytical results could be recorded while preserving the anonymity of the laboratory. The code numbers bear no relation to the alphabetical order of the laboratory name.

Each laboratory was requested to contribute five replicate results for uranium on each of two bottles of BL-5 by a method of their choice, and to report their results on a "dry basis", i.e., after correcting for loss in weight after two hours at 105°C. All results in Tables 4 to 6 have been corrected for moisture; however seven laboratories deviated from the request for 10 replicate determinations. In cases where a participant provided results by more than one method, each set of results was considered statistically independent.

Participating laboratories

Analabs (W.A.) Pty. Ltd., W.A., Australia.

Atomic Weapons Research Establishment, Aldermaston, Berkshire, England.

Australian Atomic Energy Commission, Nuclear Science and Technology Branch, Lucas Heights, N.S.W., Australia.

British Ceramic Research Association, Stoke-on-Trent, Staffordshire, England.

British Columbia Department of Mines and Petroleum Resources, Victoria, British Columbia.

Canada Centre for Mineral and Energy Technology, Mineral Sciences Laboratories (four independent analysts).

Chemex Labs. Ltd., North Vancouver, British Columbia.

Correlation Laboratories Ltd., Cobden, Ontario.

Denison Mines Ltd., Elliot Lake, Ontario.

Eldorado Nuclear Ltd., Metallurgical Laboratories, Ottawa, Ontario.

Eldorado Nuclear Ltd., Mining Division, Eldorado, Saskatchewan.

Ledoux and Co., Teaneck, N.J., U.S.A.

Loring Laboratories Ltd., Calgary, Alberta.

Ontario Ministry of Natural Resources, Mineral Research Branch, Toronto, Ontario

Rio Algom Ltd., Process Development Dept., Elliot Lake, Ontario.

Saskatchewan Research Council, Saskatoon, Saskatchewan.

Sherritt Gordon Mines Ltd., Sherritt Research Centre, Fort Saskatchewan, Alberta.

Turkish Atomic Energy Commission, Ankara Nuclear Research and Training Center, Ankara, Turkey.

United States Department of Energy, New Brunswick Laboratory, D-350, Argonne, Ill., U.S.A.

University of California, Los Alamos Scientific Laboratory, Los Alamos, N.M., U.S.A.

University of Vienna, Analytical Institute, Division of Analysis of Nuclear Raw Materials, Vienna, Austria.

Washington State University, Nuclear Radiation Center, Pullman, Wash., U.S.A.

X-ray Assay Laboratories Ltd., Don Mills, Ontario.

STATISTICAL TREATMENT OF ANALYTICAL RESULTS

Detection of outliers

Three sets of results whose means differed by more than twice the overall standard deviation from the initial mean value were not used for subsequent computations to avoid the possibility of biasing the statistics. One other set (Lab-18), whose mean was slightly above the lower limit was also excluded for methodological reasons. These sets of results are identified in Table 4 which gives the analytical results classified by method. A single value, identified by Dixon's test was deleted from Lab-20 (3).

Homogeneity tests using interlaboratory results

The degree of homogeneity of BL-5 is illustrated in Fig. 1, in which, for each set, the difference between the means of the results for the two bottles is plotted against the corresponding mean of the results of both bottles. The vertical bar represents the 95% confidence interval of the former. If a bar does not intersect the abscissa, the null hypothesis is rejected.

Table 5 gives the means and coefficients of variation of each set of results and also the results of the *t*-tests of differences between bottles at the 5% significance level. For 7 out of 29 sets of results the null hypothesis of no difference between bottle means was rejected. Four of these 7 sets were by the X-ray fluorescence method; 2 of these 4 were judged to be outliers. That there could be some problem in using this method for BL-5 is supported by labs 9 and 13 whose repeat analysis on the same bottles, by a different method in the latter case, did not show a significant between-bottle difference. Furthermore, a two-way analysis of variance of the accepted results did not indicate significant between-bottle inhomogeneity. Estimates of the components of variance are given in Table 5.

Estimation of consensus values and 95% confidence limits

A one-way analysis of variance technique was used to calculate the consensus value (mean) and its variance. The analytical data were assumed to fit the following model (4):

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

where:

x_{ij} = the j^{th} result reported in set i;

μ = the true value that is estimated by the overall mean $\bar{x}..$;

y_i = the discrepancy between the mean of the results from set i ($\bar{x}_i.$) and μ; and

e_{ij} = the discrepancy between x_{ij} and $\bar{x}_i.$.

It is assumed in this analysis 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 can be 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. The magnitude of ω^2 and σ^2 can be estimated from the ANOVA table.

The consensus value, in the above model, can be estimated by the overall mean $\bar{x}..$, thus:

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

with the variance of the overall mean being given by:

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

The 95% confidence limits for the overall mean are then given by:

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

where:

n_i = the number of results reported in set i;

k = the number of sets.

Analysis of variance and expected mean squares for the one-way classification

Source of variance	Sums of squares	Degrees of freedom	Mean squares	E [Mean squares]
Between-sets	$\sum_i^k n_i (\bar{x}_i. - \bar{x}..)^2$	k-1	S_2^2	$\sigma^2 + \frac{1}{k-1}\left(\sum_i^k n_i - \frac{\sum_i^k n_i^2}{\sum_i^k n_i}\right)\omega^2$
Within-sets	$\sum_i^k \sum_j^{n_i} (x_{ij} - \bar{x}_i.)^2$	$\sum_i^k n_i - k$	S_1^2	σ^2
Total	$\sum_i^k \sum_j^{n_i} (x_{ij} - \bar{x}..)^2$	$\sum_i^k n_i - 1$		

The above values and other statistics computed from the one-way ANOVA are presented in Table 6.

Certification factor

The certification factor is a measure for evaluating the quality of reference materials issued by CCRMP (5). It is computed from the following expression:

$$CF = 200 \left[t_{0.975,(k-1)} \cdot \sqrt{V[\bar{x}..]} \right] / \bar{x}.. / \overline{cv}$$

where $\overline{cv}$ is the average of the within-set coefficients of variation and is given by:

$$\overline{cv} = \sum_{i}^{k} cv_i / k$$

The critical value of CF is 4. If a selected constituent has a CF greater than 4, the reference material is considered of unacceptable quality with respect to that constituent.

The certification factor for uranium in BL-5 is 1.2 (Table 6).

Discussion of methodology and consensus value for uranium

It is CCRMP policy to recommend or "certify" the consensus value for a constituent if its certification factor is 4 or less. This factor is the ratio of the confidence interval of the consensus value, expressed as a percentage, to the mean of the within-laboratory coefficients of variation (5). It is thus a measure of quality of the reference material as it takes into account the degree of precision required in the usual applications in commercial and industrial laboratories. Table 6 shows that the overall mean for uranium in BL-5 is 7.09% and its certification factor is 1.2; thus BL-5 clearly qualifies as a suitable reference material for use with most methods in Table 7. There is methodological evidence, however, suggesting that the consensus value may have a small negative bias.

Laboratory-1 (CANMET) used the thoroughly proven ferrous ion-phosphoric acid reduction titrimetric method with a potentiometrically indicated end-point (6). This method has been used extensively for umpire purposes at CANMET and, as indicated in Tables 4 and 5, it yielded 60 results on six bottles of BL-5 with a mean of 7.14% and a cv of 0.14%. A second independent analyst (Lab-38) at CANMET also obtained a mean of 7.13% for 20 determinations on four bottles by a dichromate titrimetric finish after a cupferron separation of interfering substances and reduction of uranium with titanous sulphate (7). These cases are cited because all procedural details are known, including standardization, tests for for completeness of decomposition, and possible effects of interfering substances. The overall mean of the 161 accepted titrimetric results is 7.11% (Table 7), somewhat higher than the consensus value but significantly lower than the CANMET results. BL-5 does not contain any interfering substance in sufficient concentration to cause a positive error in the method used by CANMET; it is considered therefore, that the CANMET mean of 7.13% may be closer to the "true value" than the consensus value. Although there is no direct evidence given by contributors for negative errors associated with the lower titrimetric means, i.e., by Labs 10, 11, 21 and 24, low results could possibly be generated, for example, by incomplete dissolution of uranium, losses during separation steps or by incomplete reduction of U(VI) prior to titration.

Additional support for the CANMET results comes from Lab-34 which also obtained a mean of 7.13% by the well documented isotope dilution-mass spectrometric method (8).

Because of the small number of results by each of the non-titrimetric methods (Table 7) generalizations on methodology are of limited value. However, it is worth noting that results by the purely physical methods of radiometry and neutron activation (Table 7) are also higher than the consensus value.

As mentioned in the section on homogeneity above, the majority of laboratories employing the X-ray fluorescence method experienced difficulties with between-bottle homogeneity or with accuracy or both. It is recommended that analysts intending to use this method on BL-5 exercise all possible care to avoid such problems.

Despite the above caveat, it is to be emphasized that the consensus value reflects the "state of the art" as practised collectively by participants in the BL-5 program and it should be useful in most applications as a reference material.

Evidence for radioactive equilibrium of BL-5

Laboratory-32 used gamma-ray spectrometry of the 63 keV peak of Th-234 to obtain a mean value of 7.10% uranium. This agreement with the consensus value of 7.09% is a good indicator that BL-5 is in radioactive equilibrium. Additional radiometric measurements were made by Lab-32 which determined the U-235/U-238 ratio by comparing the photopeak ratios of Pb-210 at 46.5 keV with that from Th-234 at 63 keV and the Pb-214 at 295 keV for samples aged for 30 days with Th-234 at 63 keV. These ratios for BL-5 and a standard pitchblende sample (9) were found to be the same within statistical error thus indicating that U-238/Ra-226/Pb-210 are in equilibrium in BL-5.

Ra-226, Pb-210 and Th-230 content of BL-5

The Saskatchewan Research Council (SRC) at Saskatoon, provided duplicate determinations for Ra-226, Pb-210 and Th-230 by radiochemical methods as outlined below. Results are given in Table 8. Also given in Table 8 is a value for Ra-226 determined by gamma spectrometry in Lab-35 which assumed secular equilibrium for BL-5.

Methods used by SRC

Ra-226 - Radium was coprecipitated with $BaSO_4$, and Ra-226 was determined by gross alpha counting with a solid-state detector.

Pb-210 - Pb-210 was determined indirectly through its immediate daughter Bi-210 with which it is known to be in equilibrium. Bismuth was extracted with ammonium diethyldithiocarbamate, precipitated as BiOCl, and the activity of Bi-210 measured with a low-background beta counter.

Th-230 - Thorium was coprecipitated with LaF, extracted with thenoyltrifluoroacetone and electrodeposited onto a stainless steel disc. The Th-230 activity was determined by alpha-spectroscopy.

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TABLE 4

Uranium results for BL-5 (wt %)

	LAB- 1 (TITR)	7.135	7.151	7.142	7.149	7.156	7.145	7.136	7.144	7.151	7.151
		7.147	7.142	7.147	7.143	7.149	7.119	7.114	7.141	7.139	7.141
		7.135	7.128	7.142	7.142	7.147	7.139	7.143	7.138	7.155	7.143
	LAB- 1 (TITR)	7.112	7.141	7.147	7.140	7.132	7.140	7.121	7.147	7.133	7.123
		7.145	7.125	7.133	7.128	7.118	7.131	7.140	7.138	7.128	7.131
		7.138	7.127	7.127	7.144	7.123	7.129	7.137	7.129	7.128	7.139
	LAB- 4 (TITR)	7.083	7.084	7.086	7.082	7.105	7.121	7.127	7.116	7.119	7.095
	LAB- 5 (TITR)	7.310	7.360	7.310	7.310	7.310	7.310	7.310	7.310	7.310	7.310
	LAB-10 (TITR)	7.040	7.020	7.040	7.020	6.960	7.020	6.980	7.080	7.050	7.070
	LAB-11 (TITR)	7.007	7.027	7.025	7.053	7.044	6.991	7.013	7.066	7.028	7.088
	LAB-14 (TITR)	7.116	7.071	7.101	7.101	7.101	7.129	7.122	7.077	7.167	7.062
*	LAB-18 (TITR)	6.829	6.835	6.867	6.892	6.904	6.814	6.832	6.869	6.889	6.901
	LAB-20 (TITR)	7.136	6.936*	7.081	7.084	7.081	7.132	7.130	7.084	7.111	7.105
	LAB-21 (TITR)	6.983	6.986	6.988	6.992	6.993	7.011	7.018	7.018	7.028	7.028
	LAB-24 (TITR)	7.010	7.040	7.020	7.030	7.030	7.030	7.050	7.010		
	LAB-24 (TITR)	7.050	7.050	7.050	7.050						
	LAB-38 (TITR)	7.130	7.150	7.130	7.140	7.140	7.140	7.150	7.120	7.160	7.140
		7.090	7.070	7.080	7.140	7.140	7.110	7.120	7.130	7.130	7.130
	LAB-11 (COLOR)	7.065	7.061	7.057	7.067	7.054	7.062	7.063	7.067	7.057	7.065
	LAB-22 (COLOR)	7.138	7.131	7.142	7.131	7.123	7.131	7.139	7.131	7.131	7.125
	LAB-36 (COLOR)	7.170	7.040	7.170	7.040	6.980	7.200	6.990	7.030	6.930	7.200
	LAB-37 (COLOR)	7.140	7.000	7.070	7.120	7.110	7.040	7.040	7.080	7.040	7.040
	LAB-13 (FLUOR)	7.149	6.988	6.818	6.918	6.979	7.149	6.959	6.848	6.878	7.159
	LAB-14 (FLUOR)	7.293	7.240	7.209	7.086	7.164	7.230	7.574	6.906	7.048	6.943
*	LAB-16 (FLUOR)	6.551	6.636	6.618	6.841	6.903	6.592	6.650	6.909	6.771	6.756
	LAB-17 (FLUOR)	7.050	7.020	7.010	7.050	7.030	6.990	6.980	6.980	6.950	7.040
	LAB- 9 (XRF)	7.210	7.390	7.020	7.240	7.220	7.150	7.290	6.960	7.170	7.140
*	LAB- 9 (XRF)	6.790	6.720	6.680	6.810	6.820	6.680	6.650	6.600	6.730	6.680
	LAB-13 (XRF)	7.146	7.231	7.176	7.110	7.138	7.076	7.017	7.070	7.029	7.177
	LAB-15 (XRF)	6.840	6.860	6.890	6.840	6.850	6.890	6.840	6.880	6.850	6.890
	LAB-26 (XRF)	7.069	7.034	7.051	7.057	7.026	7.080	7.045	7.062	7.068	7.037
		7.056	7.065	7.062	7.079	7.068	7.071	7.080	7.077	7.094	7.083
*	LAB-30 (XRF)	6.684	6.683	6.691	6.693	6.677	6.638	6.647	6.664	6.659	6.668
	LAB-35 (XRF)	7.000	6.690	6.840	7.120	6.600	6.980	7.140	7.040		
	LAB-27 (NAA)	7.120	7.230	7.035	7.090	7.124	7.243	7.294	7.099	7.022	7.014
	LAB-31 (NAA)	7.170	6.790	7.190	7.030	6.960	6.930	7.130	7.330	7.310	7.380
	LAB-23 (GRAV)	7.061	7.071	7.071	7.071	7.081	7.071	7.051	7.081	7.091	7.091
	LAB-32 (RADIO)	6.941	7.035	7.209	7.185	7.012	7.147	7.185	6.934	7.268	
	LAB-34 (ID)	7.146	7.140	7.142	7.156	7.107	7.151	7.123	7.101	7.156	

* Outliers, not used in computation of mean

LEGEND: TITR - titrimetry; COLOR - colorimetry; FLUOR - fluorimetry; XRF - X-ray fluorescence; NAA - neutron activation analysis; GRAV - gravimetry; RADIO - gamma ray spectrometry; ID - isotope dilution-mass spectrometry.

TABLE 5

Laboratory means, coefficients of variation and summary of *t*-tests on between bottle uranium results for BL-5

		BOTTLE 1			BOTTLE 2			NULL HYPOTH.	OVERALL			
		N	MEAN	ST.DEV.	N	MEAN	ST.DEV.		N	MEAN	ST.DEV.	C.V.(%)
LAB- 1	(TITR)	THERE ARE MORE THAN 2 BOTTLES							30	7.1418	.0092	.13
LAB- 1	(TITR)	THERE ARE MORE THAN 2 BOTTLES							30	7.1325	.0088	.12
LAB- 4	(TITR)	5	7.0880	.0096	5	7.1156	.0122	REJECT	10	7.1018	.0179	.25
LAB- 5	(TITR)	5	7.3200	.0224	5	7.3100	.0000	A	10	7.3150	.0158	.22
LAB- 9	(XRF)	5	7.2160	.1316	5	7.1420	.1182	A	10	7.1790	.1242	1.73
LAB- 9	(XRF)	5	6.7640	.0611	5	6.6680	.0476	REJECT	10	6.7160	.0723	1.08
LAB-10	(TITR)	5	7.0160	.0329	5	7.0400	.0406	A	10	7.0280	.0371	.53
LAB-11	(COLOR)	5	7.0608	.0054	5	7.0628	.0038	A	10	7.0618	.0045	.06
LAB-11	(TITR)	5	7.0312	.0179	5	7.0372	.0394	A	10	7.0342	.0290	.41
LAB-13	(FLUOR)	5	6.9704	.1207	5	6.9986	.1476	A	10	6.9845	.1280	1.83
LAB-13	(XRF)	5	7.1602	.0460	5	7.0738	.0631	REJECT	10	7.1170	.0692	.97
LAB-14	(TITR)	5	7.0981	.0163	5	7.1114	.0423	A	10	7.1048	.0310	.44
LAB-14	(FLUOR)	5	7.1983	.0785	5	7.1402	.2731	A	10	7.1692	.1919	2.68
LAB-15	(XRF)	5	6.8560	.0207	5	6.8700	.0235	A	10	6.8630	.0221	.32
LAB-16	(FLUOR)	5	6.7098	.1530	5	6.7356	.1222	A	10	6.7227	.1312	1.95
LAB-17	(FLUOR)	5	7.0320	.0179	5	6.9880	.0327	REJECT	10	7.0100	.0340	.48
LAB-18	(TITR)	5	6.8654	.0334	5	6.8610	.0371	A	10	6.8632	.0333	.49
LAB-20	(TITR)	5	7.0638	.0753	5	7.1127	.0198	A	10	7.0883	.0580	.82
LAB-21	(TITR)	5	6.9884	.0042	5	7.0207	.0074	REJECT	10	7.0045	.0179	.26
LAB-22	(COLOR)	5	7.1330	.0073	5	7.1314	.0050	A	10	7.1322	.0060	.08
LAB-23	(GRAV)	5	7.0712	.0071	5	7.0772	.0168	A	10	7.0742	.0125	.18
LAB-24	(TITR)	5	7.0260	.0114	3	7.0300	.0200	A	8	7.0275	.0139	.20
LAB-24	(TITR)	2	7.0500	0.0000	2	7.0500	0.0000	***R**	4	7.0500	.0000	.00
LAB-26	(XRF)	10	7.0529	.0174	10	7.0735	.0113	REJECT	20	7.0632	.0177	.25
LAB-27	(NAA)	5	7.1198	.0711	5	7.1344	.1281	A	10	7.1271	.0980	1.37
LAB-30	(XRF)	5	6.6856	.0065	5	6.6552	.0124	REJECT	10	6.6704	.0185	.28
LAB-31	(NAA)	5	7.0280	.1641	5	7.2160	.1857	A	10	7.1220	.1926	2.70
LAB-32	(RADIO)	THERE ARE MORE THAN 2 BOTTLES							9	7.1018	.1233	1.74
LAB-34	(ID)	3	7.1428	.0027	6	7.1323	.0253	A	9	7.1358	.0207	.29
LAB-35	(XRF)	4	6.9125	.1875	4	6.9400	.2361	A	8	6.9263	.1979	2.86
LAB-36	(COLOR)	5	7.0800	.0857	5	7.0700	.1239	A	10	7.0750	.1006	1.42
LAB-37	(COLOR)	5	7.0880	.0554	5	7.0480	.0179	A	10	7.0680	.0442	.62
LAB-38	(TITR)	THERE ARE MORE THAN 2 BOTTLES							20	7.1270	.0234	.33

A = null hypothesis accepted

REJECT = null hypothesis rejected

***R** = zero variance, test not considered valid

Variance between sets, between bottles and within bottles = 6.80×10^{-3}, 1.01×10^{-4} and 5.97×10^{-3}, respectively.

TABLE 6

Consensus value and other statistics for uranium in BL-5

(outliers excluded)

No. of laboratories	24
No. of sets	29
Total no. of results	337
Median, %	7.10
MEAN, %	7.09
95% confidence limits for the mean: low, %	7.06
high, %	7.12
Spread, %	0.94
Av within-set cv, %	0.79
Certification factor	1.2

TABLE 7

Methodological classification of uranium results (outliers excluded)

Method	Decomposition, separations, etc.	N	Lab nos.	n	$\bar{x}$ (wt %)
Titrimetric (Dichromate)	HNO_3 + HCl + HF + $HClO_4$ (or H_2SO_4); U(VI) reduced to U(IV) with Fe(II) (see reference 6)	6	1,4,10,11,14,21	110	7.10
	Acid decomp.; interferants sep'd from U by ion exchange or cupferron; U(VI) reduced with Zn amalgam	1	24	12	7.04
	Na_2CO_3 fusion; cake dissolved in HNO_3; U ext'd with TBP, U(VI) reduced with Fe(II)	1	20	9	7.11
	HNO_3 + HCl + HF + $HClO_4$ + H_2SO_4; interferants sep'd from U by extn with cupferron, U(VI) reduced with titanous sulphate	1	38	20	7.13
	HNO_3 + HCl + HF + H_2SO_4; amm. carb. sepn of Fe from U; U(VI) reduced with Zn amalgam	1	5	10	7.32
Colorimetric (spectrophotometric)					
Thiocyanate	HCl + HNO_3 + HF + $HClO_4$; interferants sep'd from U with cupferron	2	36, 37	20	7.07
Peroxide	HCl + HNO_3 + HF + H_2SO_4; U sep'd by extn with ethyl acetate; differential finish	2	11, 22	20	7.10
Fluorimetric	HCl + HNO_3 + HF + H_2SO_4; aliquot fused with 98:2 NaF-LiF pellet	2	13, 14	20	7.08
	HNO_3 + HF; aliquot fused with 5:5:5 Na_2CO_3-K_2CO_3-NaF	1	17	10	7.01
Gravimetric	HNO_3 + H_2SO_4; after removal of interferants U ppt'd with NH_3, ppt calcined to U_3O_8 and weighed	1	23	10	7.07
X-Ray Fluorescence		5	9,13,15,26,35	58	7.04
Neutron Activation	Measurement of delayed neutron emission following irradiation with thermal neutrons	2	27, 31	20	7.12
Radiometric	Gamma counting of 63 keV peak of Th-234; using three uranium standards including NBS SRM 950b	1	32	9	7.10
Isotope Dilution-Mass Spectrometric	(see reference 8)	1	34	9	7.14

N = number of laboratories; n = number of results; $\bar{x}$ = overall mean

TABLE 8

Ra-226, Pb-210 and Th-230 values for BL-5

Laboratory	Ra-226	Pb-210	Th-230	U equivalent
	(pCi/g X 10^3)			(wt %)
SRC	22.9	23.1	22.3	6.7
	23.6	23.4	22.9	
Lab-35	25.7	-	-	7.5

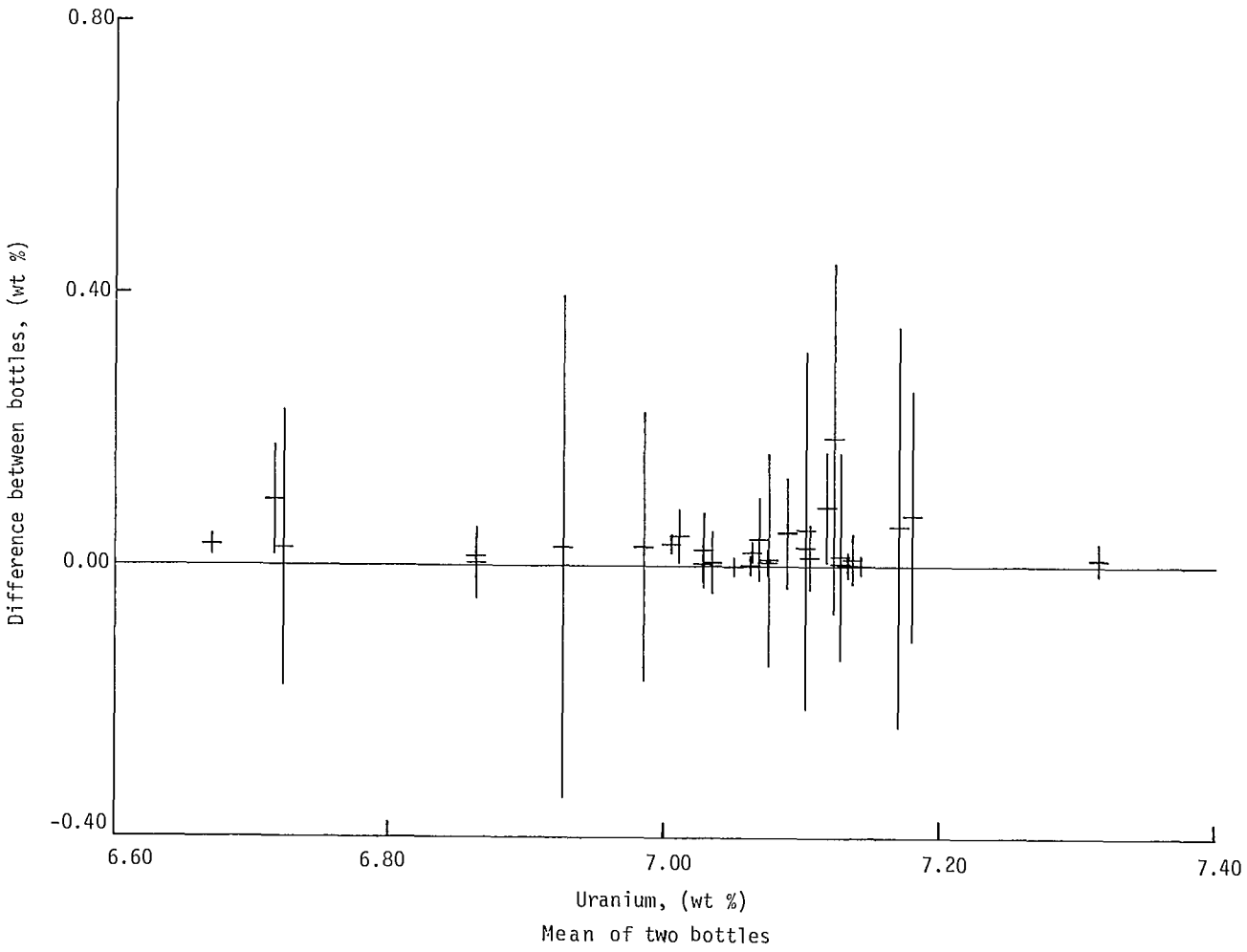

Fig. 1 Degree of homogeneity of uranium in BL-5.
Vertical bars represent 95% confidence interval for the difference between the means of two bottles for each laboratory.