RADIOACTIVE ORES DH-1, DL-1, BL-1, BL-2, BL-3 AND BL-4 — CERTIFIED REFERENCE MATERIALS

J.C. Ingles, R. Sutarno, W.S. Bowman and G.H. Faye

FOREWORD
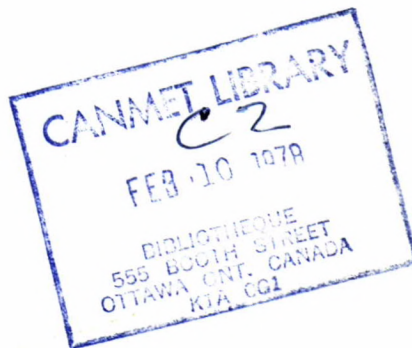
        The work described in this report contributes to the Canadian Certified Reference Materials Project (CCRMP). The CCRMP in turn contributes to the Mineral Technology Development Activity (Utilization Sub-Activity) of CANMET's Minerals Research Program by producing mineralogical and metallurgical reference materials (RM's) for use in industrial, commercial and government laboratories in Canada.

        The CCRMP was initiated in the early seventies in response to a demand from such laboratories for RM's that were not then available. Many of these laboratories now willingly contribute analytical information which is ultimately used in the CCRMP to certify RM's.

        Now that a relatively large number of reference ores and related materials have been made available, they are being used in a "feed-back" fashion to critically assess analytical methods that are essential for quality-control and research in Canadian enterprises.

R.L. Cunningham,
Chief,
Mineral Sciences Laboratories

AVANT-PROPOS

      Le travail qui est décrit dans le présent rapport apporte
une contribution au Programme canadien des matériaux de référence
certifiés (CCRMP). De son côté, le CCRMP collabore aux travaux de
l'Activité de la mise au point des techniques minérales (Sous-
activité de l'utilisation) du Programme de recherche sur les
minéraux de CANMET en normalisant des matériaux minéralogiques
et métallurgiques pour les différents laboratoires industriels,
commerciaux et gouvernementaux au Canada.

      Le CCRMP a été créé au début des années '70 pour répondre
à la demande formulée par les différents laboratoires qui voulaient
de tels matériaux de référence qui n'étaient pas disponibles
auparavant. Ainsi, plusieurs laboratoires effectuent maintenant
des travaux analytiques et par la suite léguent volontairement les
informations nécessaires au CCRMP pour certifier des matériaux de
référence.

      Maintenant qu'une quantité relativement abondante de
minerais de référence et apparentés sont disponibles, on les
utilise rétro-activement afin d'évaluer les méthodes analytiques
employées par les compagnies canadiennes pour contrôler la qualité
et faire de la recherche.

R.L. Cunningham,
Chef,
Laboratoires des sciences minérales

RADIOACTIVE ORES DH-1, DL-1, BL-1, BL-2, BL-3, AND BL-4

CERTIFIED REFERENCE MATERIALS

by

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SYNOPSIS

The preparation and characterization of a set of six ores of the naturally radioactive elements, for use as certified reference materials in chemical and radiometric analysis, is described.

The set consists of two series representing Canada's original uranium-producing areas—Elliot Lake in Ontario and Beaverlodge in Saskatchewan. The Elliot Lake series comprises two samples, one of ore and the other of waste-grade material, both of which contain uranium and thorium. The second series consists of essentially thorium-free material from Beaverlodge, covering the range of 0.02% to 1% U. The former is intended as a reference material for chemical determination of uranium and thorium, while the latter may also be employed in calibrating and verifying radiometric surveying and assaying equipment.

In addition to their uranium and thorium contents, supplementary information as to mineralogical composition, state of radioactive equilibrium, and composition with respect to most common and many trace elements of significance in ore processing is given.

The recommended values for uranium in DH-1, DL-1, BL-1, BL-2, BL-3, and BL-4 are respectively: 0.177%, 0.0041%, 0.022%, 0.453%, 1.02% and 0.173%; recommended values for thorium in DH-1, DL-1 and BL-1 are respectively: 0.104%, 83 ppm (83 μg/g) and 15 ppm (15 μg/g).

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RADIATION DOSE RATE

The radiation dose rate for the most radioactive of
the samples is 0.12 mR/h at the surface of the bottle, and 0.02
at a distance of 1 ft (0.3 m).   This is relatively insignificant,
but, on the principle that all unnecessary exposure to
ionizing radiation should be avoided, the bottles should be
kept tightly sealed and stored in an unfrequented place
when not in use.

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INTRODUCTION

In 1971, CANMET (formerly Mines Branch), in cooperation with the Canadian Uranium Producers Analytical Committee, undertook a program to chemically certify a set of six naturally radioactive ore samples for uranium and thorium. These reference ores were intended as a replacement for the first set of Canadian radioactive reference ores produced in 1948 and since exhausted. Subsequent to the interlaboratory certification program, coordinated by CANMET and described in this report, the storage and distribution of the six new reference materials came under the aegis of the Canadian Certified Reference Materials Project.

The suite of samples is made up of two series representing Canada's uranium producing areas – Elliot Lake in Ontario and Beaverlodge in Saskatchewan. The series from Elliot Lake consists of two samples, DH-1 of ore-grade material, and DL-1, of waste grade material. Both of these contain uranium and thorium. The second series covering the range of 0.02 to 1% uranium, is of essentially thorium-free material from Beaverlodge. The former series of reference samples is intended for use in the chemical determination of uranium and thorium, while the latter may be employed for both the chemical determination of uranium and the calibration and verification of radiometric surveying and analytical equipment.

The Canadian uranium industry played a major role, both in providing material and in contributing analyses for the interlaboratory certification program. However, because of the small number of laboratories involved, and especially the lack of experience of the Canadian industry in analyzing very low concentrations of thorium, the assistance of a number of particularly well-qualified laboratories in other countries was also enlisted. The need to confirm the state of equilibrium of the radiometric reference ores necessitated calling upon Canadian laboratories in the environmental and health fields. All the participants responded generously, providing not only the analyses requested, but also supplementary analyses for other elements, information as to difficulties encountered and suggestions on treating the data. Their names and contribution are acknowledged elsewhere in this report, but it is not amiss to express here sincere appreciation for their efforts.

NATURE AND PREPARATION OF SAMPLES

The samples from which these reference materials were prepared consisted of run-of-mine material from the Denison and the Eldorado Beaverlodge properties respectively. Since the mineralogy of both deposits has been extensively studied and documented, it was considered unnecessary to carry out individual mineralogical examinations on the samples received[1-4]. Brief summaries abstracted from the literature, as they apply to each sample, follow.

Mineralogy of reference ore DH-1

This sample is from a conglomerate zone, called the Denison Reef, in the Quirke ore zone, and is 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 2½ in. (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, and minute amounts of gold may also be present[1]. The radioactive minerals are principally uraninite and brannerite but some monazite and uranothorite are present. The zircon also contains radioactive elements and thucholite and coffinite may be present. The uraninite occurs as subhedral grains about 0.1 mm in diameter. It contains thorium and rare earths in addition to uranium, a typical analysis being U, 55%; Th, 6%; Pb, 14% and rare earth oxides, 5.7%. The rare earth component consists typically of Y_2O_3, 40.7%; Nd_2O_3, 12.1%; CeO_2, 10.6%; Dy_2O_3, 12.4%; Sm_2O_3, 6.4%; Er_2O_3, 6.1%; Pr_2O_3, 3.1%; La_2O_3, 1.2%; Gd_2O_3, 7.8%[2].

Elliot Lake brannerite differs from others having the composition $(U,Th)_{0.23-0.57} Ti_{2.77-2.43} O_6$. It calcium content is also anomalous at about 0.5% rather than 2.5-3%[5]. It occurs as fine grains in ovoid aggregates 0.25 to 1.5 mm in diameter and is intimately intergrown with anatase, rutile, quartz, and sericite. A recent electron microprobe analysis on a grain with a minimum of intergrowth gave the following values:

UO_2, 38.9%; ThO_2, 2.3%; FeO, 1.3%; CaO, 1.2%; Ce_2O_3, 0.3%; TiO_2, 48.4%, as well as some lanthanum, and traces of neodymium, samarium and gadolinium[6].

Monazite occurs as rounded grains, about 0.3 mm in diameter, often containing inclusions of uraninite[7]. A typical analysis is U_3O_8, 0.20%; ThO_2, 3.66%; P_2O_5, 24.8% and $(R.E.)_2O_3$, 58.8%. The rare earth component consisted of: La_2O_3, 15.7%; CeO_2, 26.4%; Pr_6O_{11}, 2.2%; Nd_2O_3, 6.8%; Sm_2O_3, 0.9%; Gd_2O_3, 0.2%; Yb_2O_3, 1.7%; and Y_2O_3, 0.57%[8].

Mineralogy of reference ore DL-1

This sample consists of waste-grade material from the Denison deposit. It is a pale yellow arkose sandstone having essentially the same radioactive minerals as DH-1.

Estimation of age of DH-1 and DL-1

Roscoe places the age of Elliot Lake ores at 2.5×10^9 years[2]. He notes that if all the lead in the ores were radiogenic and derived from radioactive minerals of this age, the thorium in the ores would have produced 0.26 times as much lead as the equivalent amount of uranium, and the ratio $Pb/(U + 0.26\,Th)$ would be 0.47. In the case of the Denison uraninite, whose analysis is given above, this ratio has the value 0.28, and, as will be seen later, the analyses reported in this study give this same value for both samples, even though the thorium:uranium ratios are nearly reversed. Roscoe, however, attributed the apparent lead loss to leakage into the surrounding matrix, and reported ratios ranging from 0.33 to 0.57 (both median and mean 0.47, with 90% of the lead being radiogenic) for ore-grade material from various mines in the area; this suggests, a common age for all these ores. As a result of this migration, however, $^{238}U/^{208}Pb$, $^{235}U/^{207}Pb$, and $^{232}Th/^{206}Pb$ ages present a complicated picture, and in the absence of an estimate of the time over which the events leading to loss of lead occurred, there is no method for deducing from published data the probable state of equilibrium of the U and Th series.

Mineralogy of reference ores BL-1 to BL-4

The ores from which these samples were selected are from the Fay-09 zone (Fay mine), with minor amounts from the Verna mine, both at the Beaverlodge Operation of Eldorado Nuclear Ltd. at Eldorado, Saskatchewan. The ores from the Fay mine are considered to be in radioactive equilibrium and because of this, have been analyzed routinely for many years by beta-counting only, with excellent agreement between radiometric and chemical results[9] (Appendix B). The bulk samples from which the reference samples were prepared were assembled over a period of several months by hand-sorting radiometrically-checked muck to give materials of the desired uranium content and maximum homogeneity[10].

The orebodies consist of complexes of disseminations and stringers, lenses and veinlets of pitchblende in reddish-brown mylonitized oligoclase saturated with dusty hematite, to which the colour is due. Pitchblende is the only radioactive mineral present[11]. About 10-20 ppm (10-20 μg/g) thorium is present, which is not correlatable to the uranium content, evidence that it is a constituent of the host rock rather than present in the pitchblende. This view is reinforced by the data of Whitfield et al. which give the average abundance of thorium in granitic rocks as 12 ppm (12 μg/g), and in those of the Canadian Shield as 11 ppm (11 μg/g)[12]. As further evidence, a small amount of pitchblende, isolated from BL-3 by heavy-liquid separation, was found to contain 18.1% U, but only 61 ppm (61 μg/g) Th. Comparing this with the analysis of the original sample and solving simultaneous equations to establish thorium contents of the uranium mineral and the gangue, a uranium: thorium ratio for the former of 3546 and a thorium content for the uranium-free gangue of 12.1 ppm (12.1 μg/g), are obtained.

As noted, the main gangue mineral is oligoclase saturated with hematite. Accessory gangue minerals include calcite, chlorite, and quartz, along with some pyrite, chalcopyrite and other sulphides. Traces of nolanite (an iron vanadate), and clausthalite (lead selenide) are also present[1,3,4].

Estimated age of reference ores BL-1 to BL-4

As with the Elliot Lake ores, assessing age of the uranium minerals is rendered uncertain by evidence of loss of radiogenic lead[4].

In general, evidence is that most of the pitchblende was deposited 1,780 ± 20 million years ago, with a possibility that some subsequent deposition occurred 1,110 ± 50 million years ago.

The lead losses occurred 1,100 ± 50 million years ago; 270 ± 20 million years ago, and 0-100 million years ago. Thus, once again the lead-uranium ages do not provide any evidence as to the possible state of equilibrium of these ores. (Recovery of equilibrium in the uranium series takes about 6×10^5 years). Direct evidence of the equilibrium status was therefore investigated on the actual standards and this work is described in a later section.

Preparation of reference ores

The ore samples (150 lb (68 kg) of DH-1, 110 lb (50 kg) of DL-1, 150 lb (68 kg) of BL-1, 120 lb (54 kg) of BL-2, 125 lb (57 kg) of BL-3 and 390 lb (177 kg) of BL-4) were crushed and dry ground to -200 mesh (74 μm) in conventional milling equipment, then blended in a baffled 45-gallon (200-ℓ) mixing drum. They were then bottled in 100- or 200-g units.

Size distribution, and uranium and thorium content of size fractions

A study of particle size distribution and composition of the size fractions is probably more important for ores of the radioactive minerals than for those of more common metallic ores. First there is the great disparity in specific gravity between the heavy uranium and thorium minerals and the much lighter gangue minerals. The radioactive minerals also tend to be softer and more brittle, so that they tend to be more finely ground than the gangue minerals. In a free-flowing product, having, for example, a relatively coarse grind (>44 μm) with a narrow size distribution, the difference in specific gravity can result in a sample which segregates readily and is not easily rehomogenized by mixing. The tendency of the radioactive minerals to concentrate in the finer sizes i.e., to "slime" , can result in such effects as the coating of lower-grade coarse particles by higher-grade fine material, with the consequent possibility of anomalous results for radiometric and X-ray emission measurements. For these measurements, size distribution is important because it can affect both smoothness of the surface presented for measurement and density of packing, and these in turn can affect measurements on which the analytical results are based [13,14].

Size analysis of the samples was accomplished by means of screens down to a size of 400 mesh (37 μm) and by means of a cyclosizer, a subsieve sizer which fractionates the sample down to 10 μm using cyclones in water medium. The latter becomes necessary due to the difficulty and decreasing reliability of screening as particle size decreases. The selection of 400 mesh (37 μm) as the changeover point was made because it permitted an overlap between the two methods. This is desirable because the cyclosizer actually separates particles by weight rather than by size and shape. In the present case, therefore, where the radioactive minerals are much heavier than the gangue minerals, they will tend to report with a coarser-size fraction than the one to which they belong. The overlap was purposely employed to demonstrate this, and to give an indication of the size range in which the radioactive minerals are contained. The results of these tests are shown in Table 1. Cyclosizing was performed on the −400 mesh (−37 μm) material from the screen analysis. The +37 μm cyclosizer fraction thus represents material that is actually −400 mesh, but with a density such that the particle weight seems to be equivalent to that of a gangue particle −37 μm in size. One might expect that the uranium or uranium-thorium, content of this fraction would be the same for all the samples, but would vary in quantity. In fact, the quantity of the fraction is about the same for all the samples, and the concentration of the two radioelements in the fraction is more or less in fixed ratio to that of the original sample, i.e., about 7 times for uranium in the BL-1 and DL-1 samples, about 4.5 for uranium

and thorium in DH-1, and 11 for thorium in DL-1. This latter observation may have some bearing on the comment by one of the participating laboratories that the variation in the individual thorium results on reference ore DL-1 was greater than the normal analytical variation, an effect that was detectable because of the high precision normally obtained in that laboratory.

Tests for homogeneity

After separately blending each of the six reference ores, between-bottle homogeneity was tested by randomly selecting five bottles of each material from the total stock. Subsamples taken from each bottle were analyzed for uranium (Lα) by X-ray fluorescence. An analysis of variance of the results did not indicate evidence of bottle-to-bottle inhomogeneity. Using the thorium Lα line, reference ore DH-1 was tested in the same way with respect to thorium and, again, inhomogeneity was not detected. The thorium content of the other samples was too low to permit use of X-ray fluorescence to verify thorium homogeneity.

Subsamples (2 g) of the five bottles of both DH-1 and BL-4 were analyzed for uranium by the fluorimetric method, multiple spiking and internal standard X-ray emission methods, and by volumetric and absorptiometric wet chemical methods. In all cases the results confirmed the homogeneity of these two ores with respect to uranium.

As shown in Table 2 and Figure 1 the results reported in the interlaboratory certification program also confirm the homogeneity of all six reference ores.

INTERLABORATORY PROGRAM FOR CERTIFICATION OF THE SIX REFERENCE ORES

Sample distribution to participating laboratories

Two bottles of each reference material were sent to the 11 participating laboratories with the request that each be analyzed for uranium, thorium and other elements of interest in uranium ore processing, such as iron and sulphur. They were asked to carry out five separate determinations for each of the elements on each of the two bottles. Since the purpose of these materials is primarily to provide reference materials for the natural radioactive elements, no effort was made to obtain a complete analysis. However, laboratories 2, 4 and 10 were particularly helpful in their contributions of analyses for a number of additional elements (Appendix A), so that although recommended values are not given, the indicated values for aluminum, iron and sulphur on many of the samples agree sufficiently well that they also might be used for reference purposes, and useful information on the major constituents and many trace constituents is provided. A summary of the non-radioactive analyses is given in Tables 7 and 8.

TABLE 1

Size distribution, and uranium and
thorium contents of size fractions

Sizing method	Size of fractions μm (mesh)	% of total wt	Th wt %	U wt %	% of total wt	U wt %	% of total wt	U wt %
		DH-1			BL-1		BL-3	
Screen	+74 (+200)	0.9	0.124	0.143	1.3	0.0122	2.2	0.627
	+53 (+270)	8.2	0.102	0.156	2.7	0.0155	5.0	0.771
	+37 (+400)	13.2	0.107	0.160	8.4	0.0221	12.4	1.10
Cyclosizer*	+37*	3.5*	0.512*	0.598*	1.3*	0.129 *	2.3*	7.20 *
	+29	10.4	0.127	0.170	12.2	0.019	12.7	0.94
	+20	15.9	0.074	0.108	13.7	0.019	11.9	0.96
	+14	14.4	0.069	0.100	13.7	0.018	11.5	0.95
	+10	6.4	0.065	0.098	6.7	0.018	6.1	0.83
	-10	27.1	0.096*	0.118*	40.0	0.018*	35.9	0.67*
Weighted average, (calculated head)		100.0	0.113	0.147	100.0	0.0199	100.0	0.988
Value at time of sizing			0.106	0.182		0.0219		1.022
		DL-1			BL-2		BL-4	
Screen	+74 (+200)	0.5	0.0139	0.0053	3.6	0.268	1.3	0.204
	+53 (+270)	8.2	0.0080	0.0027	5.2	0.323	2.7	0.169
	+37 (+400)	12.4	0.0087	0.0025	11.1	0.507	6.0	0.219
Cyclosizer*	+37*	1.2*	0.091 *	0.0234*	1.7*	3.02*	0.8*	1.20 *
	+29	8.8	0.0098	0.0032	11.7	0.42	10.2	0.19
	+20	14.0	0.0069	0.0024	11.4	0.41	13.3	0.18
	+14	14.1	0.0073	0.0025	11.2	0.41	14.4	0.16
	+10	7.4	0.0058	0.0025	6.0	0.42	7.4	0.15
	-10	33.4	0.0062*	0.0037*	38.1	0.33*	43.9	0.13*
Weighted average, (calculated head)		100.0	0.0083	0.0032	100.0	0.426	100.0	0.165
Value at time of sizing			0.0087	0.0039		0.453		0.174

*Cyclosizing was done on the -400 mesh (-37 μm) screen fraction, i.e., the +37 μm fraction had already been removed. The +37 μm Cyclosizer fraction, therefore, actually consists of finer, but heavier, material. This "shift" of heavier minerals also accounts for the low uranium and thorium values in the -10 μm Cyclosizer fractions.

A summary of the analytical methods employed by the participants is given in Appendix A and the analytical results are given in Table 3 and Figure 1. For uranium and thorium analyses, the sample size varied from 2 g to 0.1 g. The small sample size tends to be favoured because of the necessity, particularly in the case of thorium, to ensure complete dissolution of the sample. Except for the observation of Laboratory 8 respecting micro inhomogeneity of sample DL-1, the weight taken for the individual determinations does not appear to have had a significant effect on the within-laboratory standard deviation.

Confirmation of homogeneity using results from certification program

The results reported by the participating laboratories on the two bottles of the six reference ores were examined statistically, using the t-test at 5% significance level. The results of this examination are summarized in Table 2 and are illustrated in Figure 1.

The analyses from most of the laboratories confirm that the samples are satisfactorily homogeneous in their uranium content. Undoubtedly, given a sufficiently high degree of precision in the analytical method, combined with a sufficiently small sample, evidence of inhomogeneity would appear. As noted above, this proved to be the case for the thorium results for sample DL-1 by Laboratory 8, which have better than average precision. Such behaviour with this sample is to be anticipated because the thorium is contained in a small amount of high-thorium minerals. It is to be expected also that the uranium analyses would exhibit a similar effect. It is considered however, that by the use of sufficiently large subsamples, the material is suitable as a reference material for most purposes.

Estimation of consensus values and 95% confidence limits

To avoid the possible introduction of bias to the estimates of mean and variance, certain sets of results were not included in the computations. These sets were those whose means differed by more than twice the overall standard deviation from the mean value, and also certain borderline cases with large coefficients of variation. These results are identified in Table 3.

The remaining results were subjected to a one-way ANOVA to estimate the mean and its variance. The data are assumed to fit the following model[15]:

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

where:

x_{ij} = the jth 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:

$$\bar{x}.. = \frac{\sum\limits_{i}^{k} \sum\limits_{j}^{n_i} x_{ij}}{\sum\limits_{i}^{k} n_i}$$

with the variance of the overall mean being given by:

$$V\left[\bar{x}..\right] = \frac{\sum\limits_{i}^{k} n_i^2}{\left(\sum\limits_{i}^{k} n_i\right)^2} \omega^2 + \frac{1}{\sum\limits_{i}^{k} n_i} \sigma^2$$

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

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

where:

n_i = the number of results reported in set i;

k = the number of sets.

The above values and other statistics computed from the one-way ANOVA are presented in Table 4.

TABLE 2

Summary of the t-test results between bottles within each method

Lab. No.	DH-1		DL-1		BL-1		BL-2		BL-3		BL-4	
	U	Th	U	Th	U	Th	U	Th	U	Th	U	Th
1	A	A	A/R	A	A	R	A	A	A	A	R/A	A
2	A	A	A	A	A	A	A	A	A	A	A	A
3	A	–	A	–	A	–	A	–	A	–	R	–
4	A	–	A	–	A	–	A	–	A	–	A	–
5	A	–	A	–	A/R	–	A	–	A	–	A	–
6	A	A	A	A	A	A	A	A	A	A	A	A
7	R	A	A	A	A	A	R	A	A	A	A	A
8	–	A	–	A	–	–	–	–	–	A	–	–
9	–	A	–	A	–	–	–	–	–	–	–	–
10	A	A	A	A	A	A	A	A	A	A	A	A
11	–	A	–	–	–	–	–	–	–	–	–	–

A = Null hypothesis accepted, i.e., there is no evidence of
   inhomogeneity.

R = Null hypothesis rejected, i.e., there is evidence of inhomogeneity.

– = Insufficient or no results available for a meaningful statistical
   analysis.

Note: In cases where more than two bottles were analyzed by a laboratory
   using the same method, by the same analyst, one-way analysis of
   variance technique was used instead of t-test.

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	$\sum_{i}^{k} \sum_{j}^{n_i} (x_{ij} - \bar{x}_{..})^2$	$\sum_{1}^{k} n_i - 1$		

Certification factor

The certification factor is a measure for evaluating the quality of reference materials issued by the CCRMP[16]. 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 to be of unacceptable quality for that constituent. For uranium, the CF values are less than 4 for all 6 of the materials. Their consensus values are therefore accepted as recommended values. The same is true for thorium in DH-1, DL-1, and BL-1. For thorium in BL-2, BL-3, and BL-4, however, the CF values are much larger than 4 and, the mean values from Table 4 are given for information only. The recommended values for for these materials are presented in Tables 5 and 6. The values listed have been used for several years and appear on the bottle labels. Because of an inadvertent error there is a trivial, last-place, difference between four of these and the values given in Table 4.

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TABLE 3

Uranium results for DH-1

URANIUM   (WEIGHT PERCENT)

LAB- 1 (Fluor.)	.1780	.1750	.1750	.1640	.1890	.1760	.1760	.1760	.1850	.1800
LAB- 1 (Color.)	.1700	.1730	.1730	.1730	.1700	.1740	.1730	.1710	.1740	.1710
LAB- 1 (XRE)	.1730	.1740	.1720	.1720	.1770	.1720	.1730	.1710	.1820	.1820
LAB- 1 (Vol.)	.1810	.1810	.1820	.1820	.1820	.1820	.1810	.1810	.1800	.1800
LAB- 2 (Fluor.)	.1800	.1810	.1800	.1800	.1800	.1810	.1800	.1780	.1820	.1820
LAB- 3 (Fluor.)	.1780	.1780	.1800	.1700	.1800	.1750	.1800	.1770	.1800	.1800
LAB- 4 (Fluor.)	.1710	.1700	.1700	.1660	.1710	.1660	.1750	.1700	.1790	.1760
LAB- 5 (Fluor. 1)	.1794	.1783	.1822	.1803	.1812	.1824	.1786	.1762	.1690	.1650
LAB- 5 (Fluor. 2)	.1777	.1793	.1803	.1858	.1828	.1804	.1815	.1826	.1786	.1843
LAB- 6 (Color.)	.1822	.1811	.1823	.1797	.1802	.1810	.1814	.1757	.1833	.1831
LAB- 6 (XRE)	.1679	.1721	.1687	.1696	.1747	.1721	.1730	.1687	.1787	.180A
LAB- 7 (Color.)	.1789	.1832	.1764	.2137	.1772	.1764	.2230	.1798	.1679	.1840
LAB-10 (Vol.)	.1750	.1749	.1750	.1757	.1748	.1715	.1748	.1720	.1815	.1713
	.1750	.1780	.1720	.1750	.1780	.1750	.1760	.1800	.1720	.1700

Thorium results for DH-1

THORIUM   (WEIGHT PERCENT)

LAB- 1 (Color.)	.1090	.1110	.1080	.1100	.1090	.1100	.1100	.1080	.1120	.1090
LAB- 2 (XRE)	.1090	.1060	.1110	.1090	.1070					
LAB- 6 (XRE)	.1050	.1050	.1050	.1035	.1055	.1085	.1020	.1085	.1040	.1065
LAB- 7 (Color.)	.0974	.0962	.0979	.0961	.0958	.0997	.0969	.0965	.0960	.0965
LAB- 8 (Fluor.)	.1025	.1036	.1041	.1044	.1067	.1023	.1039	.1039	.1051	.1056
LAB- 9 (Color.)	.1100	.1090	.1090	.1080	.1100	.1100	.1090	.1090	.1100	.1070
LAB-11 (XRE)	.1056	.1054	.1056	.1049	.1054	.1039	.1058	.1049	.1042	.1054
* LAB-10 (Color.)	.0880	.1100	.1000	.0950	.0990	.1100	.1000	.1000	.1140	.1070
	.1250	.1200	.1150	.1180	.1390	.1300	.1340	.1180	.1140	.1190

* possible outlier

Note: Fluor. = fluorimetric; Color. = spectrophotometric (colorimetric);

XRE = X-ray emission; Vol. = volumetric.

TABLE 3 (cont'd)

Uranium results for DL-1

URANIUM   (WEIGHT PERCENT)

Lab										
LAB-1 (Fluor.)	.004380	.004560	.004640	.004590	.004520	.004370	.004520	.004640	.004800	.004630
LAB-1 (Color.)	.004200	.004100	.004200	.003800	.004100	.004100	.004100	.003930	.003970	.003970
LAB-2 (Fluor.)	.003990	.004050	.004130	.004090	.004160	.004060	.004080			
LAB-3 (Fluor.)	.004280	.004360	.004020	.004360	.004450	.004110	.004240	.004070	.004360	.004360
LAB-4 (Fluor.)	.003730	.003730	.003560	.003560	.003560	.003560	.003730	.003730	.003810	.003650
LAB-5 (Fluor.)	.004100	.003920	.004170	.004160	.004080	.004160	.004060	.003930	.003900	.004120
LAB-6 (Color.)	.004150	.004240	.004240	.004150	.004070	.004150	.004150	.004240	.004070	.004150
LAB-6 (XRE)	.004070	.004240	.004240	.003990	.003990	.004240	.004240	.004070	.003990	.003990
LAB-7 (Color.)	.003900	.003730	.003560	.004240	.004320	.003990	.003820	.003650	.003990	.004150
* LAB-10 (Fluor.)	.003480	.003480	.003560	.003820	.003560	.003900	.003900	.003480	.003650	.003730
	.004269	.004287	.004079	.004293	.004314	.004281	.004297	.004278	.004279	.004289
	.002771	.002997	.002512	.003102	.002828	.002752	.002639	.002865	.002778	.003091

Thorium results for DL-1

THORIUM   (WEIGHT PERCENT)

Lab										
LAB-1 (Color.)	.00798	.00831	.00831	.00826	.00798	.00844	.00854	.00831	.00845	.00837
LAB-2 (XRE)	.00840	.00870	.00870	.00820	.00830					
LAB-6 (XRE)	.00850	.00900	.01000	.00950	.00900	.00950	.00800	.00900	.00850	.00900
* LAB-7 (Color.)	.00840	.00790	.00860	.00910	.00870	.00920	.00860	.00900	.00850	.00900
LAB-8 (Fluor.)	.00610	.00610	.00620	.00626	.00637	.00558	.00582	.00920	.00820	.00820
	.00850	.00800	.00810	.00810	.00890	.00800	.00860	.00610	.00626	.00643
* LAB-9 (Color.)	.00870	.00850	.00840	.00850	.00850	.00850	.00860	.00860	.00860	.00840
LAB-10 (Color.)	.00660	.00640	.00660	.00650	.00660	.00650	.00650	.00810	.00730	.00870
LAB-11 (XRE)	.00787	.00812	.00800	.00800	.00920	.00760	.00730	.00620	.00680	.00650
	.00830	.00680	.00740	.00700	.00710	.00760	.00730	.00850	.00870	.01000

* possible outlier

TABLE 3 (cont'd)

Uranium results for BL-1

URANIUM   (WEIGHT PERCENT)

Lab										
LAB- 1 (Fluor.)	.02320	.02240	.02390	.02380	.02270	.02320	.02290	.02150	.02260	.02430
LAB- 1 (Color.)	.02140	.02160	.02210	.02170	.02100	.02070	.02180	.02120	.02150	.02190
LAB- 2 (Fluor.)	.01950	.02120	.02040	.02120	.02120	.02040	.02080	.02080	.02080	.01990
* LAB- 3 (Fluor.)	.01700	.01700	.01700	.01870	.01950	.01870	.01780	.01950	.01950	.01950
LAB- 4 (Fluor.)	.02204	.02151	.02101	.02217	.02165	.02186	.02145	.02193	.02198	.02220
LAB- 5 (Fluor.)	.02205	.02196	.02213	.02357	.02348	.02357	.02137	.02205	.02230	.02247
LAB- 6 (Color.)	.02230	.02220	.02349	.02340	.02357	.02188	.02205	.02281	.02162	.02213
LAB- 6 (XRE)	.02090	.02040	.02060	.02040	.02200	.02090	.02130	.02120	.02150	.02150
LAB- 7 (Color.)	.02210	.02040	.02350	.02210	.02220	.02290	.02180	.02230	.02250	.02390
	.02230	.02172	.02225	.02281	.02234	.02244	.02231	.02238	.02240	.02239
* LAB-10 (Vol.)	.02600	.02500	.02550	.02400	.02350	.02750	.02500	.02550	.02450	.02600

Thorium results for BL-1

THORIUM   (WEIGHT PERCENT)

Lab										
LAB- 1 (Color.)	.00150	.00170	.00170	.00160	.00140	.00140	.00180	.00160	.00150	.00144
	.00142	.00141	.00149	.00144	.00152	.00161	.00161	.00151	.00154	.00136
	.00142	.00142	.00142	.00136						
LAB- 2 (XRE)	.00200	.00200	.00200	.00100	.00150	.00050	.00100	.00150	.00150	.00150
LAB- 6 (XRE)	.00140	.00140	.00190	.00170	.00170	.00170	.00170	.00140	.00160	.00160
LAB- 7 (Color.)	.00150	.00151	.00164	.00171	.00183	.00160	.00164	.00166	.00175	.00183
LAB- 8 (Fluor.)	.00141	.00141	.00141	.00141	.00139					
* LAB-10 (Color.)	.00240	.00270	.00220	.00230	.00180	.00310	.00220	.00340	.00270	.00220

*   possible outlier

TABLE 3 (cont'd)

Uranium results for BL-2

URANIUM   (WEIGHT PERCENT)

LAB-1 (Fluor.)	.4630	.4400	.4470	.4450	.4500	.4410	.4600	.4440	.4590	.4640
LAB-1 (Color.)	.4480	.4480	.4580	.4490	.4320	.4460	.4480	.4510	.4420	.4480
LAB-1 (Vol.)	.4470	.4490	.4500	.4470	.4500	.4520	.4500	.4490	.4480	.4480
*LAB-2 (Fluor.)	.4516	.4516	.4524	.4410	.4473	.4456	.4499	.4414	.4439	.4282
*LAB-3 (Fluor.)	.4189	.4266	.4282	.4232	.4300	.4392	.4460	.4282	.4248	.4308
LAB-4 (Fluor.)	.4536	.4579	.4442	.4507	.4500	.4445	.4515	.4404	.4477	.4543
LAB-5 (Fluor.)	.4571	.4550	.4765	.4627	.4660	.4649	.4539	.4711	.4608	.4627
LAB-6 (Color.)	.4645	.4700	.4625	.4550	.4649	.4601	.4644	.4655	.4631	.4591
LAB-6 (XRE)	.4480	.4530	.4660	.4470	.4630	.4420	.4320	.4610	.4340	.4530
LAB-7 (Color.)	.4630	.4600	.4690	.4610	.4720	.4620	.4680	.4650	.4660	.4710
	.4498	.4503	.4502	.4499	.4502	.4572	.4521	.4539	.4538	.4539
LAB-10 (Vol.)	.4570	.4510	.4530	.4590	.4500	.4500	.4510	.4500	.4550	.4570

Thorium results for BL-2

THORIUM   (WEIGHT PERCENT)

LAB-1 (Color.)	.00127	.00124	.00127	.00127	.00136	.00126	.00124	.00127	.00123	.00135
LAB-1 (Color.)	.00149	.00149	.00162	.00149	.00145	.00141	.00149	.00149	.00144	.00132
*LAB-2 (XRE)	.00050	.00050	.00050	.00150	.00100	.00050	.00100	.00100	.00100	.00050
*LAB-6 (XRE)	.00280	.00280	.00290	.00260	.00280	.00290	.00300	.00260	.00300	.00300
LAB-7 (Color.)	.00165	.00173	.00173	.00183	.00196	.00166	.00172	.00172	.00181	.00187
LAB-8 (Fluor.)	.00136	.00134	.00131	.00131	.00133					
LAB-10 (Color.)	.00230	.00180	.00205	.00190	.00215	.00200	.00180	.00185	.00215	.00170

* possible outlier

TABLE 3 (cont'd)

Uranium results for BL-3

URANIUM (WEIGHT PERCENT)

LAB- 1	(Fluor.)	1.0020	1.0090	1.0080	1.0160	1.0170	1.0300	.9930	1.0140	1.0160	1.0200
LAB- 1	(Color.)	1.0100	1.0220	1.0280	1.0070	1.0240	1.0200	1.0210	1.0140	1.0100	1.0240
LAB- 1	(Vol.)	1.0160	1.0190	1.0180	1.0230	1.0170	1.0160	1.0190	1.0190	1.0180	1.0180
LAB- 2	(Fluor.)	1.0380	1.0210	1.0290	1.0150	1.0130	1.0210	1.0260	1.0120	1.0190	1.0170
LAB- 3	(Fluor.)	1.0030	.9740	.9880	1.0080	1.0020	1.0080	1.0120	.9770	.9770	.9940
*LAB- 6	(Color.)	.9362	.9642	.9268	.9854	.9820	.9404	.9522	.9268	.9904	1.0070
LAB- 4	(Fluor.)	1.0150	1.0180	1.0280	1.0370	1.0190	.9990	1.0260	1.0310	1.0410	.9930
LAB- 5	(Fluor.)	1.0200	1.0230	1.0290	1.0260	1.0490	1.0460	1.0240	1.0520	1.0440	1.0290
		1.0220	1.0510	1.0300	1.0230	1.0220	1.0610	1.0240	1.0080	1.0240	1.0240
LAB- 6	(XRE)	1.0470	1.0300	1.0630	1.0010	1.0530	1.0350	1.0510	1.0840	1.0040	1.0720
LAB- 7	(Color.)	1.0220	1.0260	1.0190	1.0430	1.0350	1.0290	1.0300	1.0000	1.0180	1.0090
LAB-10	(Vol.)	1.0230	1.0230	1.0220	1.0200	1.0190	1.0280	1.0200	1.0190	1.0180	1.0250

Thorium results for BL-3

THORIUM (WEIGHT PERCENT)

LAB- 1	(Color.)	.00136	.00137	.00137	.00132	.00151	.00136	.00131	.00137	.00131	.00136
		.00140	.00130	.00140	.00140						
*LAB- 2	(XRE)	.00050	.00050	.00050	.00050	.00100	.00050	.00050	.00050	.00050	.00050
*LAB- 6	(XRE)	.00390	.00380	.00420	.00400	.00370	.00370	.00440	.00370	.00440	.00390
LAB- 7	(Color.)	.00158	.00171	.00185	.00194	.00197	.00159	.00165	.00181	.00175	.00193
LAB- 8	(Fluor.)	.00145	.00141	.00147	.00145	.00142	.00141	.00140	.00143	.00137	
*LAB-10	(Color.)	.00300	.00285	.00305	.00260	.00300	.00340	.00300	.00260	.00305	.00300

* possible outlier

TABLE 3 (cont'd)

Uranium results for BL-4

URANIUM   (WEIGHT PERCENT)

Lab	Values
LAB- 1 (Fluor.)	.1830 .1940 .1910 .1850 .1840 .1850 .1790 .1800 .1780 .1740
LAB- 1 (Color.)	.1710 .1740 .1780 .1680 .1760 .1670 .1740 .1720 .1770 .1670
	.1670 .1690 .1680 .1710 .1700 .1700 .1700 .1700 .1700 .1690
LAB- 1 (XRE)	.1695 .1690 .1705 .1690 .1730 .1715 .1715 .1700 .1700 .1705
LAB- 1 (Vol.)	.1750 .1740 .1760 .1760 .1730
LAB- 2 (Fluor.)	.1660 .1700 .1670 .1690 .1690
LAB- 3 (Fluor.)	.1740 .1680 .1680 .1660 .1660 .1710 .1670 .1660 .1680 .1680
LAB- 4 (Fluor.)	.1704 .1662 .1645 .1688 .1704 .1645 .1645 .1569 .1577 .1602
LAB- 5 (Fluor.)	.1731 .1738 .1771 .1802 .1707 .1799 .1799 .1829 .1751 .1718
LAB- 6 (Color.)	.1785 .1721 .1691 .1765 .1796 .1801 .1736 .1756 .1702 .1780
LAB- 6 (XRE)	.1703 .1723 .1763 .1725 .1722 .1766 .1722 .1729 .1766 .1705
LAB- 7 (Color.)	.1900 .1810 .1890 .1760 .1750 .1820 .1790 .1810 .1720 .1760
LAB-10 (Vol.)	.1740 .1750 .1780 .1750 .1810 .1750 .1730 .1820 .1810 .1780
	.1714 .1682 .1669 .1706 .1671 .1694 .1685 .1672 .1687 .1687
	.1860 .1880 .1790 .1800 .1790 .1780 .1750 .1800 .1820 .1790

Thorium results for BL-4

THORIUM   (WEIGHT PERCENT)

Lab	Values
LAB- 1 (Color.)	.00123 .00123 .00123 .00125 .00125 .00122 .00126 .00117 .00123 .00112
*LAB- 2 (XRE)	.00126 .00124 .00125 .00126 .00131 .00127
LAB- 6 (XRE)	.00150 .00050 .00100 .00150 .00050 .00050 .00050 .00100 .00150
LAB- 7 (Color.)	.00180 .00160 .00170 .00110 .00150 .00160 .00190 .00150 .00100 .00150
LAB- 8 (Fluor.)	.00122 .00138 .00143 .00152 .00155 .00122 .00122 .00145 .00145 .00152
*LAB-10 (Color.)	.00200 .00215 .00180 .00200 .00225 .00185 .00200 .00200 .00205 .00215

*   possible outlier

TH CONCENTRATION (PER CENT)

0.06   0.08   0.10   0.12   0.14   0.16

LAB- 1   (Color.)

LAB- 2   (XRE)

LAB- 6   (XRE)

LAB- 7   (Color.)

LAB- 8   (Fluor.)

LAB- 3   (Color.)

LAB-11   (XRE)

LAB-10   (Color.)

REFERENCE MATERIAL DH-1, THORIUM

Figure 1. Graphical presentation of analytical results

NOTE: For each set, different symbols were used for analyses on sub samples from different bottles.

U CONCENTRATION (PER CENT)

0.16   0.18   0.20   0.22   0.24   0.26

LAB- 1   (Fluor.)

LAB- 1   (Color.)

LAB- 1   (XRE)

LAB- 1   (Vol.)

LAB- 2   (Fluor.)

LAB- 3   (Fluor.)

LAB- 4   (Fluor.)

LAB- 5   (Fluor. 1)

LAB- 5   (Fluor. 2)

LAB- 6   (Color.)

LAB- 6   (XRE)

LAB- 7   (Color.)

LAB-10   (Vol.)
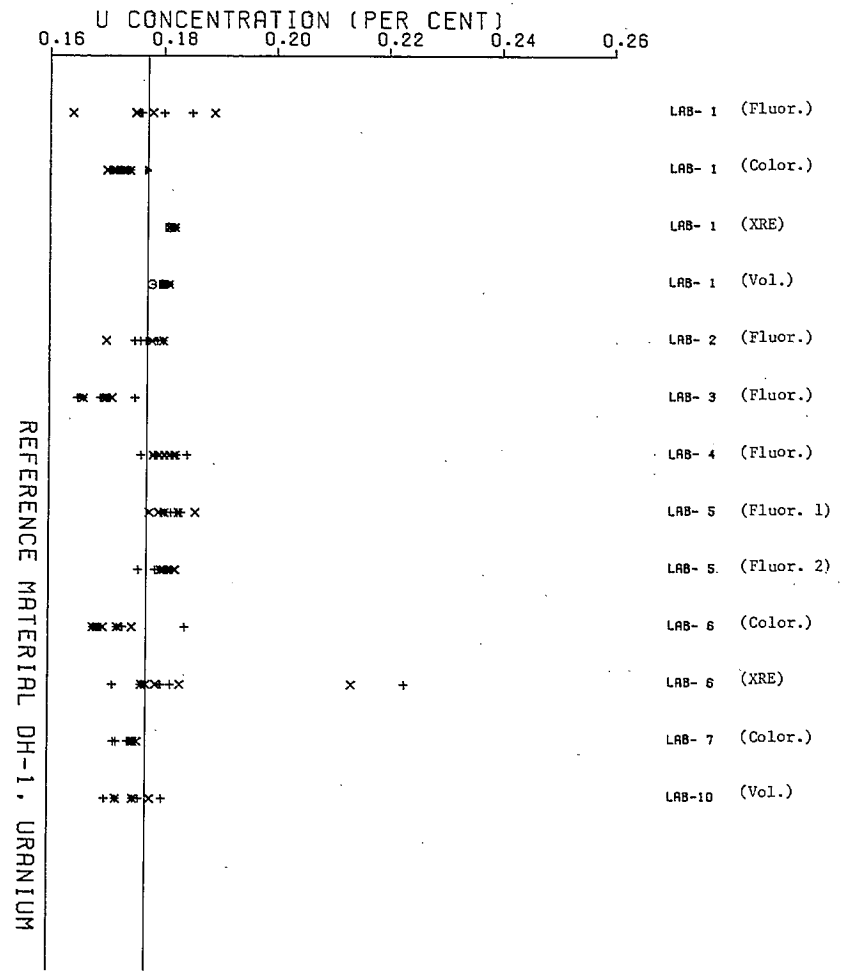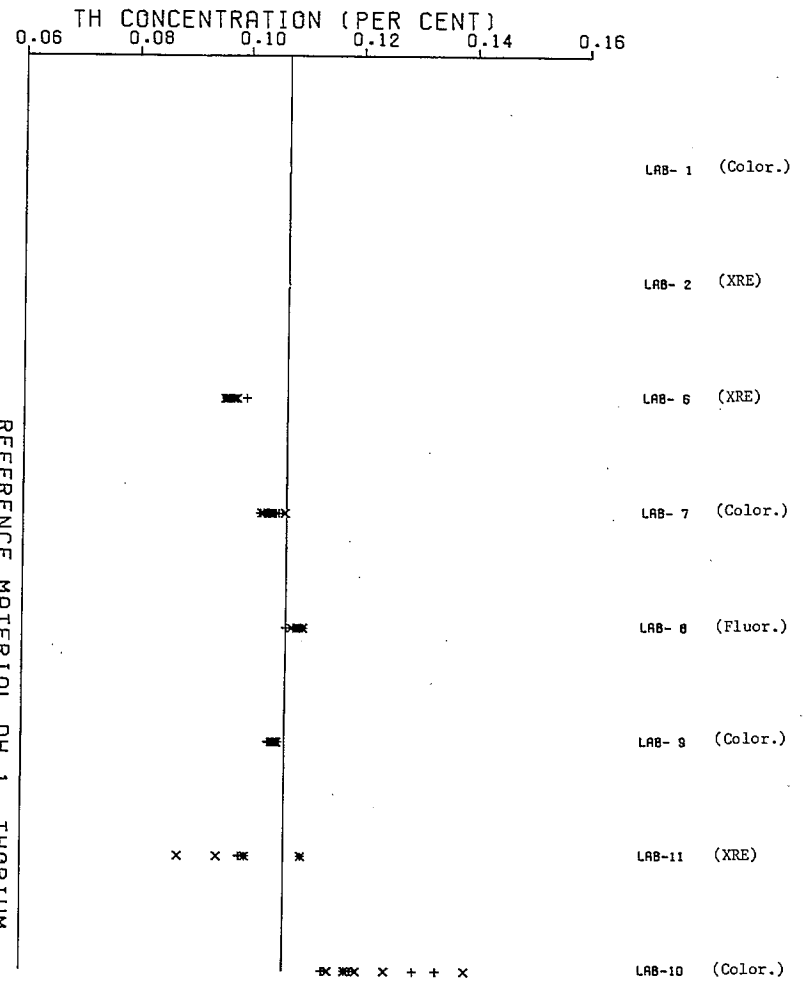
REFERENCE MATERIAL DH-1, URANIUM

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Figure 1. (cont'd)   REFERENCE MATERIAL DL-1, THORIUM

REFERENCE MATERIAL DL-1, URANIUM

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Figure 1. (cont'd)
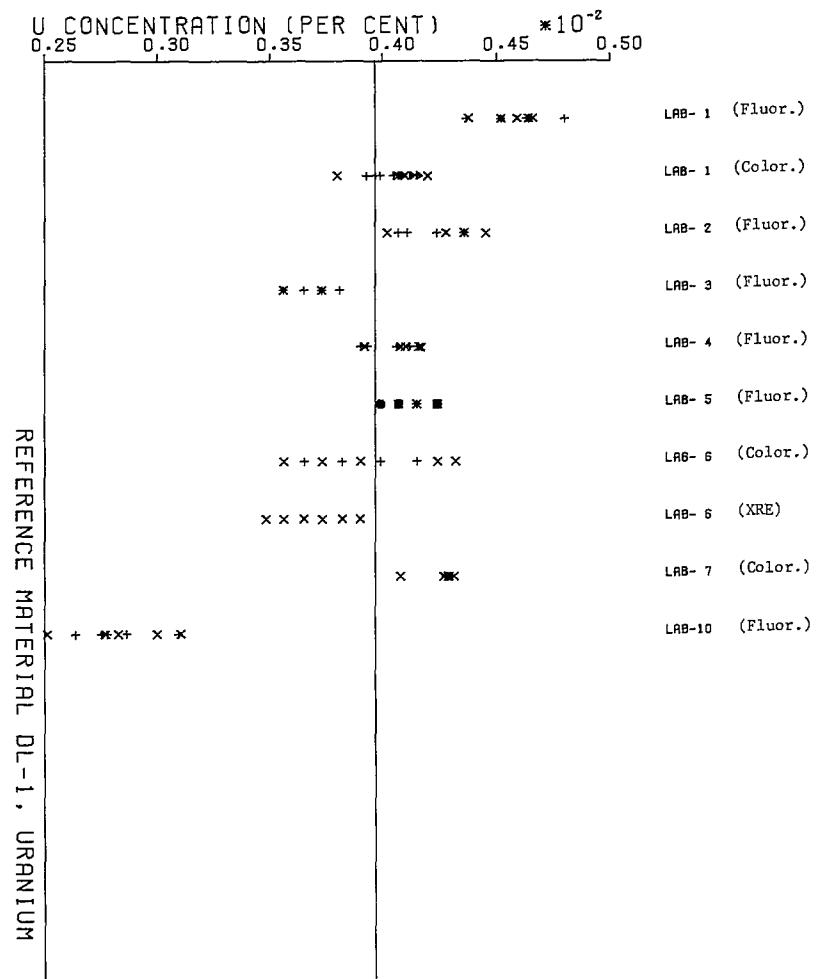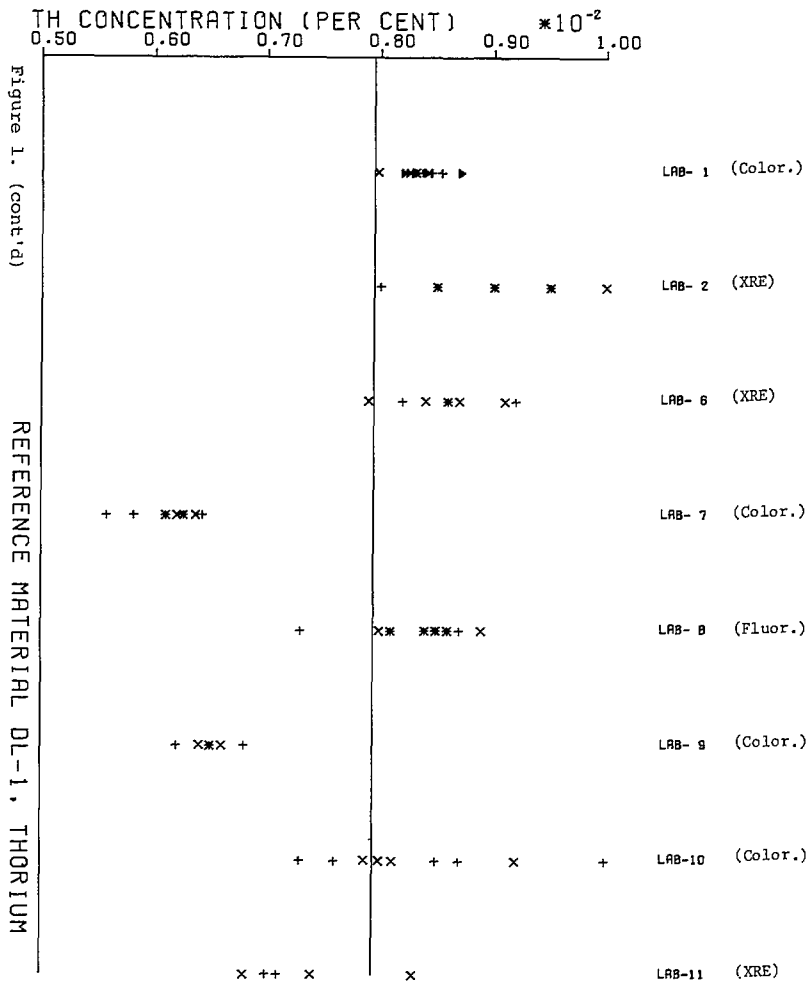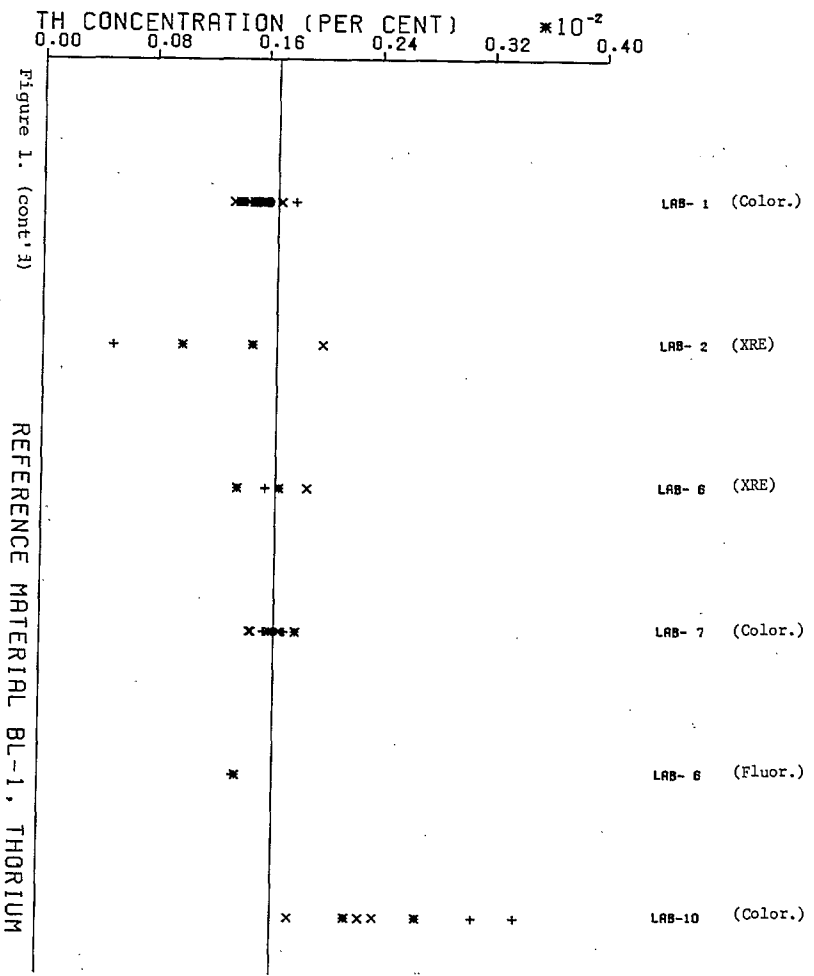
TH CONCENTRATION (PER CENT)   *10⁻²
REFERENCE MATERIAL BL-1, THORIUM

U CONCENTRATION (PER CENT)   *10⁻¹
REFERENCE MATERIAL BL-1, URANIUM

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Figure 1. (cont'd)

TH CONCENTRATION (PER CENT)   *10⁻²

REFERENCE MATERIAL BL-2, THORIUM

U CONCENTRATION (PER CENT)

REFERENCE MATERIAL BL-2, URANIUM

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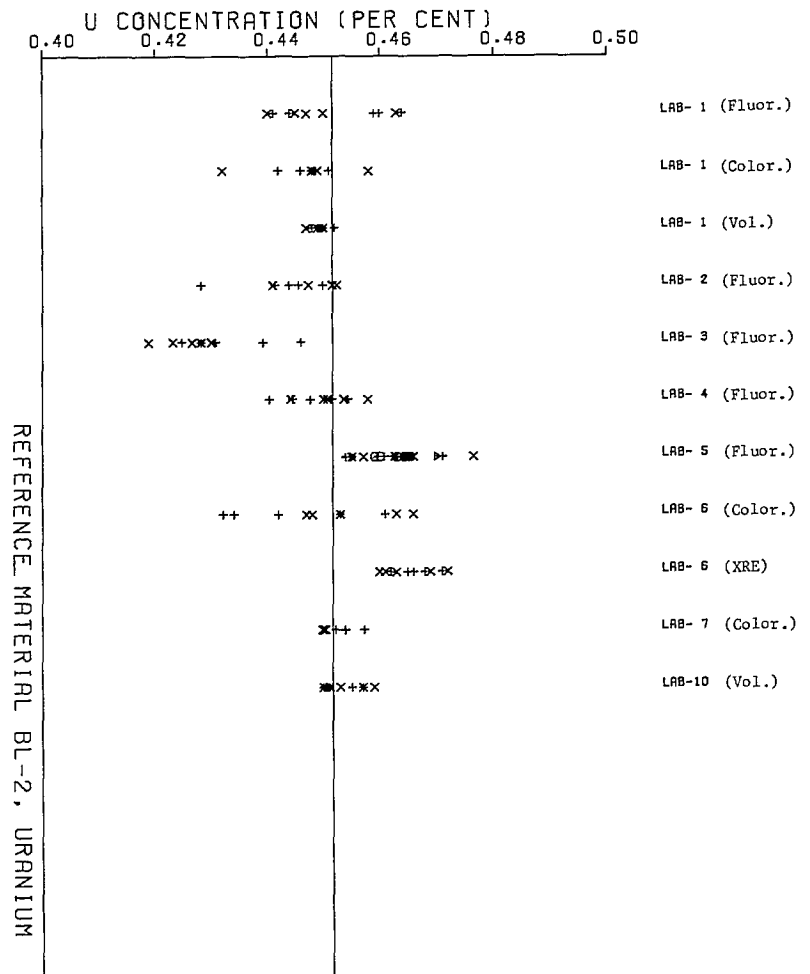
Figure 1. (cont'd)

REFERENCE MATERIAL BL-3, THORIUM
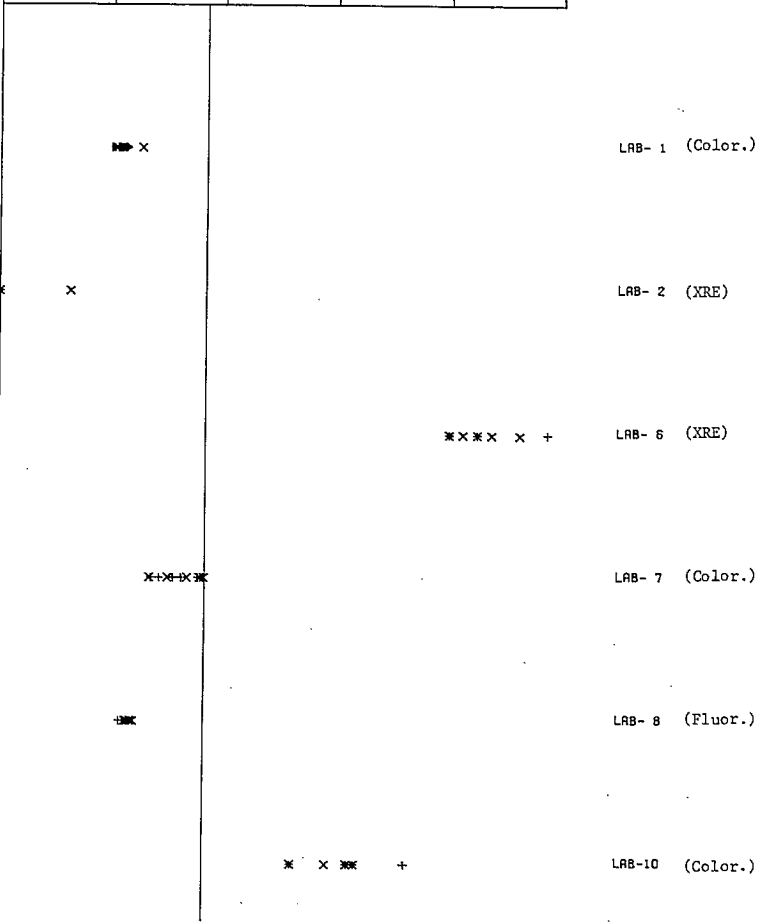
REFERENCE MATERIAL BL-3, URANIUM

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Figure 1. (cont'd)
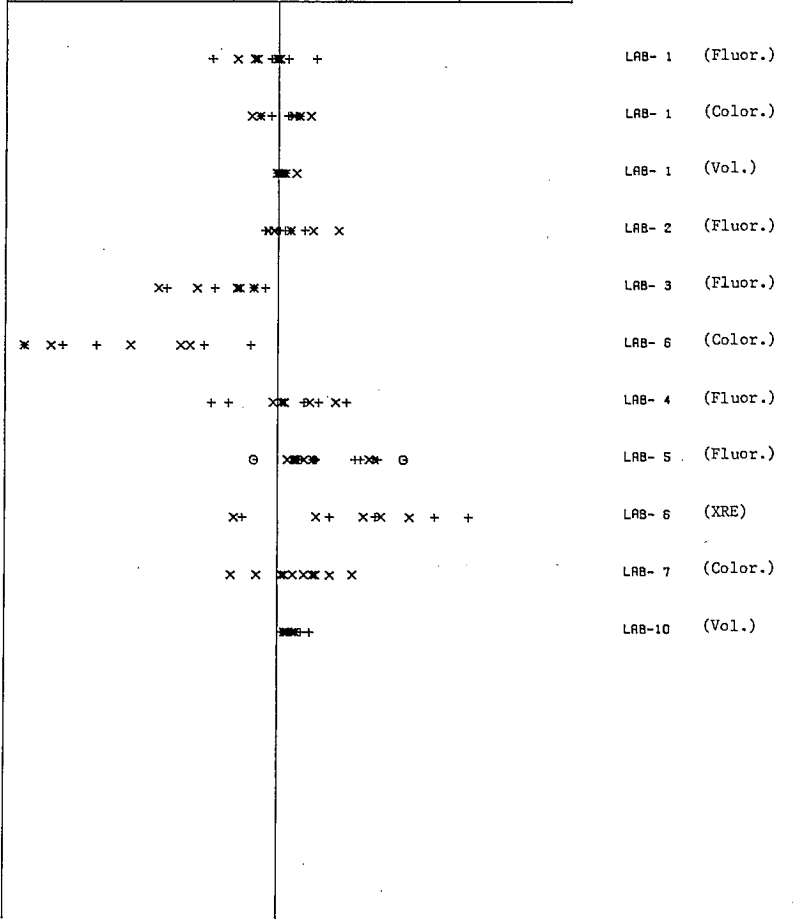
TH CONCENTRATION (PER CENT)   *10⁻²

REFERENCE MATERIAL BL-4, THORIUM
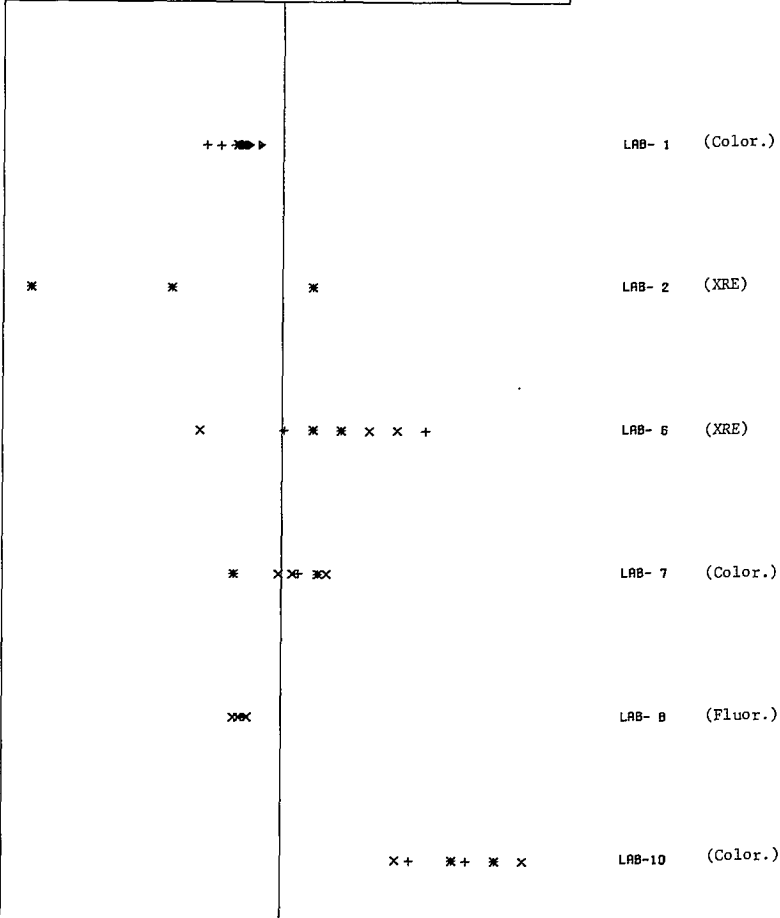
U CONCENTRATION (PER CENT)   *10⁻¹
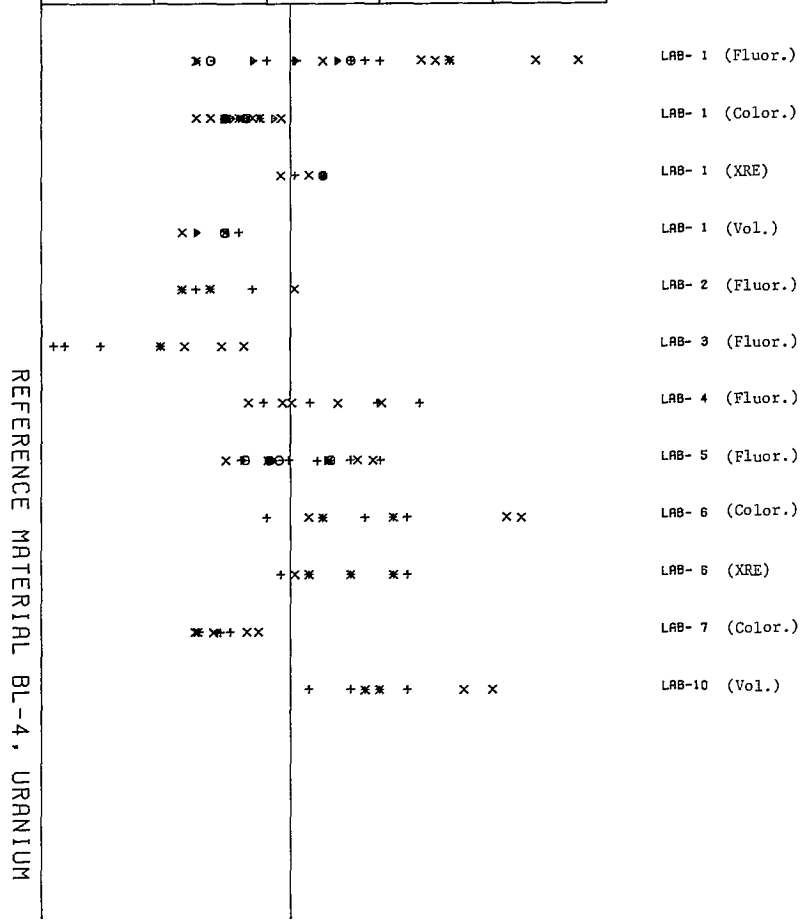
REFERENCE MATERIAL BL-4, URANIUM

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TABLE 4

Estimation of statistical parameters for radioactive ores (after rejection of outliers)

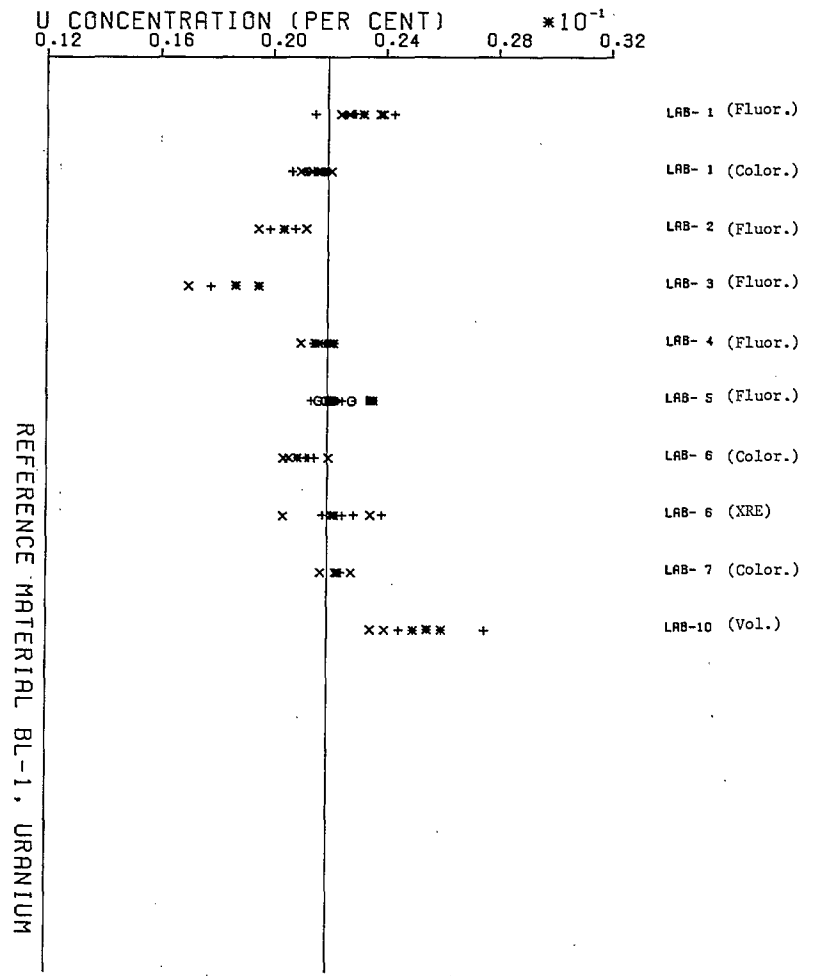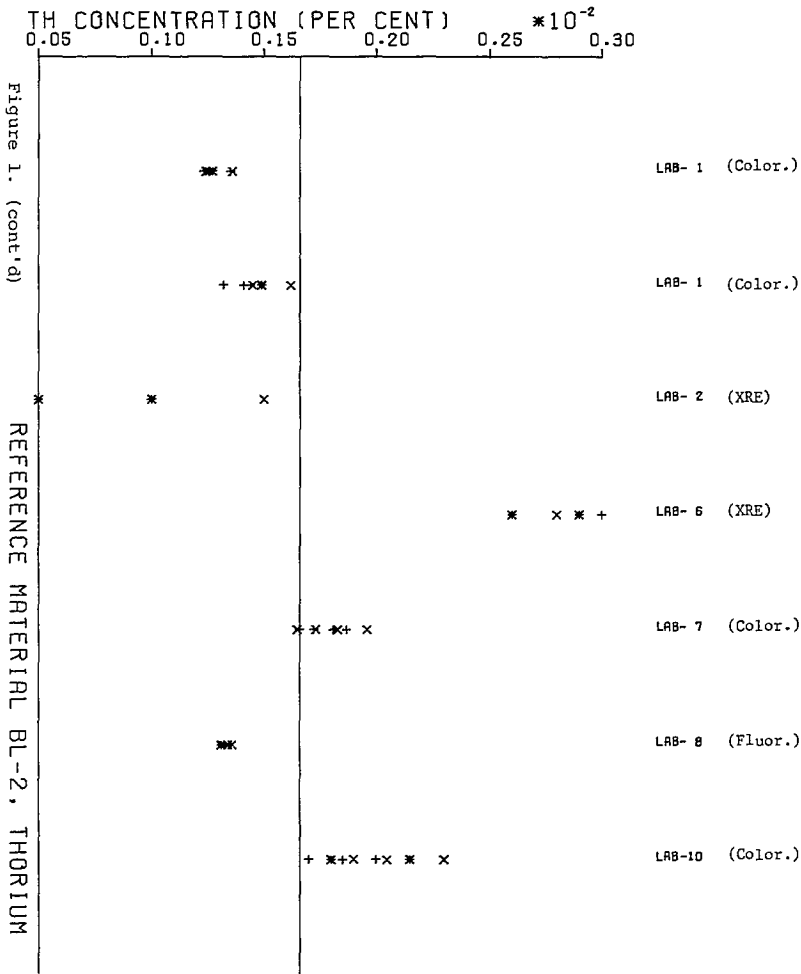| Material	Element	No. of labs	No. of sets	Total no. of results	Median, wt %	Mean, wt %	95% confidence limits for the mean		Av. within-set cv, %	Certification factor
							Low	High		
DH-1	uranium	8	13	138	0.177	0.177	0.174	0.180	2.1	1.6
	thorium	7	7	73	0.105	0.105	0.100	0.109	2.1	3.9
DL-1	uranium	7	9	107	0.0041	0.0041	0.0039	0.0043	3.2	3.3
	thorium	6	6	70	0.0084	0.0084	0.0079	0.0089	6.0	1.9
BL-1	uranium	6	8	90	0.022	0.022	0.021	0.023	2.7	2.4
	thorium	5	5	59	0.0015	0.0015	0.0014	0.0017	12.0	1.4
BL-2	uranium	7	10	110	0.452	0.454	0.448	0.459	1.3	1.8
	thorium	4	5	45	0.0015	0.0016	0.0012	0.0020	5.1	9.5
BL-3	uranium	8	10	110	1.02	1.02	1.01	1.03	1.1	1.6
	thorium	3	3	33	0.0014	0.0015	0.0009	0.0021	4.7	15.8
BL-4	uranium	8	12	140	0.173	0.174	0.170	0.177	2.0	2.1
	thorium	4	4	41	0.0013	0.0014	0.0011	0.0016	7.2	5.5

TABLE 5

Recommended values for radioactive ores

Reference ore		Recommended value	95% Confidence limits	
			low	high
DH-1	uranium	0.177%	0.174%	0.180%
	thorium	0.104%	0.100%	0.109%
DL-1	uranium	0.0041%	0.0039%	0.0043%
	thorium	83 ppm (83 μg/g)	79 ppm (79 μg/g)	89 ppm (89 μg/g)
BL-1	uranium	0.022%	0.021%	0.023%
	thorium	15 ppm (15 μg/g)	14 ppm (14 μg/g)	17 ppm (17 μg/g)
BL-2	uranium	0.453%	0.448%	0.459%
BL-3	uranium	1.02%	1.01%	1.03%
BL-4	uranium	0.173%	0.170%	0.177%

TABLE 6

Thorium values (for information only)

Reference ore	Mean ppm (μg/g)
BL-2	16
BL-3	15
BL-4	14

TABLE 7

Major constituents of radioactive ores

(elements other than uranium and thorium)

Element	DH-1	DL-1	BL-1	BL-2	BL-3	BL-4
	wt %					
Si	38.5	37.1	30.4	28.1	27.8	28.7
Al	2.3	5.1	7.4	7.3	7.3	7.1
Fe	6.1	0.83	4.8	5.4	5.3	5.0
Mg	0.03	0.05	1.2	1.4	1.4	1.3
Ca	0.03	0.06	1.9	2.8	2.9	2.5
Na	0.04	0.07	3.9	4.2	4.2	4.2
K	1.1	2.5	1.0	0.66	0.66	0.65
S	6.3	0.3	0.27	0.33	0.36	0.17
CO_2 (ev.)	<0.05	<0.04	2.1	3.5	3.8	2.9
Loss at 110°C − 24 hrs −	0.19	0.12	0.23	0.24	0.25	0.29

TABLE 8

Minor constituents of radioactive ores

Element	DH-1	DL-1	BL-1	BL-2	BL-3	BL-4
	ppm (µg/g)					
Ba	130	160	420	350	370	410
Bi	40	10	20	20	20	20
Cd	0.27	0.2	0.36	0.25	0.31	1.2
Co	89	11	26	25	23	18
Cu	73	74	63	78	91	67
Mo	5	4	34	36	41	35
Pb	523	18	71	922	1710	346
$(R.E.)_2O_3$+ Y_2O_3	6000	280	--	--	--	--
Sr	5	4	50	70	70	60
Ti	2000	800	--	--	--	--
V	14	24	210	841	834	720

APPENDIX A

LIST OF PARTICIPATING LABORATORIES,
SUMMARY OF ANALYTICAL METHODS, AND
RESULTS FOR NON-RADIOACTIVE ELEMENTS

PARTICIPATING LABORATORIES

Laboratories that participated in the certification program are listed alphabetically below. The Chemical Laboratory of CANMET (formerly Mines Branch), acted as the distributor of the samples and coordinator of the certification program. The Radiation Protection Laboratory of the Ontario Ministry of Health, generously provided the radiometric background on the samples (see Appendix B). The other laboratories are not identified, except where they have published their results the publications are listed among the references.

Australian Atomic Energy Commission,
Lucas Heights, N.S.W., Australia.

T.M. Florence, Head,
Inorganic Chemistry Section.

Analysts: P. Pakalns, B. McAllister

Denison Mines Ltd., Elliot Lake, Ontario.

F. De Luca, Mill Superintendent

D.H. Kim, Analytical Laboratory Supervisor

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

H.H. Wirch, Laboratory Supervisor

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

K.W. Brooke, Chief Chemist.

Chemical Laboratory, CANMET, Department of Energy, Mines and Resources, Ottawa.

J.C. Ingles, formerly Head,
Chemical Analysis Section
(now Assistant Chief, Mineral Sciences Laboratories).

National Institute for Metallurgy,
Johannesburg, South Africa.

T.W. Steele, Head, Analytical Chemistry Division

National Research Council of Canada,
Division of Chemistry, Ottawa, Ontario.

D.S. Russell, Head, Analytical Chemistry Section

Analysts: G.A. Ducharme and S. Berman

Rio Algom Mines Ltd., Research and Development Dept., Elliot Lake, Ontario.

John W. Fisher, Research Supt.

Analyst: L.M. Halama

U.S. Atomic Energy Commission, Health Services Laboratory, Idaho Operations Office, Idaho Falls, Idaho, U.S.A.

Claude W. Sill, Chief, Analytical
Chemistry Branch.

Analysts: T.D. Filer and F.D. Hindman

U.S. Geological Survey, U.S. Department of the Interior, Branch of Analytical Laboratories, Washington, D.C.

F.J. Flanagan, Liaison Officer

Analyst: Lillie Jenkins

University of Vienna, Analytical Institute, Vienna, Austria

J. Korkisch, Chief, Analysis of Nuclear Raw Materials Division.

Laboratory Services Branch, Ontario Ministry of Health.

J. Tai Pow, Chief, Radiation Protection Laboratory.
(This laboratory is now part of the Ontario Ministry of Labor).

SUMMARY OF ANALYTICAL METHODS

URANIUM

Laboratory 1

Fluorimetric (all six samples): Fluorescence measured in fused 98:2 NaF:LiF beads without prior separations [A-1].

X-ray Emission Spectrometry (DL-1, DH-1, and BL-4): (a) Multiple spiking method [A-2]. (b) Internal standard methods [A-2] using both Tl and Sr internal standard.

Note: This laboratory also used direct counting of pressed whole-ore powder for homogeneity tests on all six samples.

Volumetric (DH-1, BL-2, BL-3, BL-4):
Ferrous reduction in phosphoric acid [A-3].

Colorimetric (all six samples): Using as
reagent 2-(5 bromo-2 pyridylazo) - 5-
diethylaminophenol (bromo-PADAP), after
isolation of uranium by tri-octyl phosphine
oxide extraction [A-4,5].

Laboratories 2,3,4,5

Fluorimetric (all six samples): In general,
the same method as used by Laboratory 1 [A-1].
Laboratory 5 ran 2 sets, one using reference
ores and one using pure uranium solutions
for calibration.

Laboratory 6

Colorimetric (all six samples): Using as
reagent 2-(2 pyridylazo) - 5-diethylamino-
phenol (PADAP), after isolation of uranium
by tri-octyl phosphine oxide extraction [A-6].

X-ray Emission Spectrometry (all six
samples):

Instrumentation
Philips model 1540 X-ray spectrometer;
Mo tube, 2.5 kW power; LiF 220 cut
analyzing crystal.

Methods

DL-1 - A single reading on each of five
whole-rock pressed-powder pellets.

Analytical values established by
comparison with reference ores treat-
ed in the same way. Molybdenum K_α
Compton scatter used as a reference
for matrix correction.

Others - Each result is the average of
duplicate readings on one of five
glass discs prepared by pressing
the melt resulting from fusion of
the sample with a mixed $Li_2B_4O_7/CaF$
flux. Molybdenum K_α Compton scatter
used for matrix correction.

Laboratory 7

Colorimetric (all six samples): Same as
Lab-1.

Laboratory 10

Anion Exchange-Colorimetric and Fluorimetric:
Initially DL-1 only; but see supplementary
results.

Anion Exchange Separation: After treatment
of the sample with hydrochloric acid,
uranium was separated from matrix elements
by adsorption on a column of the strongly
basic anion-exchange resin Dowex 1X8 from
an organic solvent system consisting of IBMK,
tetrahydrofuran and 12M hydrochloric acid in the
proportion of 1:8:1 by volume. Following re-
moval of iron, molybdenum and co-adsorbed elements
by washing, first with the organic solvent system
and then with 6M hydrocloric aicd, the uranium
was eluted with 1M hydrochloric acid. In the
eluate, uranium was determined by means of the
spectrophotometric arsenazo III method or
fluorimetrically [A-7].

Colorimetric: Ten ml of the 9M hydrochloric
acid solution of the uranium were transferred
to a 100-ml wide-neck Erlenmeyer flask, 0.3 g
of oxalic acid and 1.10 g of zinc added and
the flask covered loosely with a stopper.
During the reduction, the flask was shaken
carefully until all the zinc had dissolved.
Immediately afterwards, 1.0 ml of the arsenazo
III solution was added and the absorbence
measured at 665 nm against a reagent blank
prepared in the same way.

Fluorimetric: A suitable volume such as 0.1
ml of the uranium eluate or 25 ml
of the 9M hydrochloric acid solution con-
taining the uranium was evaporated in a
small platinum dish and after addition of a
"Fluorbase" pellet, a melt was prepared under
strictly controlled conditions. The fluor-
escence intensity of the cold flux was
measured and compared with the intensity of
fluxes of known uranium concentrations.

Volumetric (all samples except DL-1):
Method of Davies and Gray [A-8].

THORIUM

Laboratory 1

Cation-Exchange Colorimetric (all six samples):
Thorium isolated by cation exchange from 4M
HCl, followed by elution with 4M sulphuric
acid, and determined colorimetrically with
Thorin [A-9].

Laboratory 2

X-ray Emission Spectrometry (all six samples):
Details not given.

Laboratory 6

X-ray Emission Spectrometry (all six samples).

Instrumentation: same as for uranium above.

Method for DL-1 and BL series
One reading on each of five whole-rock, pressed-powder pellets. Angles for background correction were selected by scanning one pellet for each of the materials. The thorium L_α peak was measured and the molybdenum K_α Compton-scatter peak was used as a reference for matrix correction.

The calibration curve was prepared using reference ore G-2 (Th = 25 ppm (25 μg/g)) and GSP-1 (Th = 110 ppm (110 μg/g)).

With samples BL-2, BL-3 and BL-4, it was reported that the lead content made background correction difficult; consequently the high results for these reference ores were due to possible errors arising from inadequate correction for the contribution from the lead $L_{\beta 3}$ and $L_{\beta 5}$ lines at the thorium L_α line.

Reference ore DH-1
Five fusion pellets were prepared by fusing sample portions with $Li_2B_4O_7$ and pressing a pellet from the crushed fusion bead.

The calibration curve was prepared using fusion pellets containing pure ThO_2.

Laboratory 7

Solvent Extraction – Colorimetric (all six samples): Solvent extraction with Alamine, followed by colorimetric finish using Arsenazo III [A-10,11].

With the BL series, the analyst had difficulty keeping sample constituents in solution in the 25 ml of 6M HCl specified in the method and was therefore obliged to dilute to 50 ml. It is felt that this change may have been responsible for what is considered to be poorer than usual precision.

Laboratory 8

Carrier Precipitation – Fluorimetric Method (all six samples): Thorium was isolated by coprecipitation on barium sulphate, and the determination completed fluorimetrically using morin [A-12]. Lab-8 performed 20 determinations on DL-1, 10 on DH-1, 9 on Bl-3, and 5 each on BL-1, BL-2, and BL-4.

Laboratory 8 considered sample DL-1 to be inhomogeneous with respect to thorium because the spread of values observed is greater than that normally obtained.

DL-1 was also analyzed by gamma spectrometry; the value obtained was 80 ppm ± 3 ppm.

Laboratory 9

Colorimetric (DH-1 and DL-1): This method employed fluoride, hydroxide and iodate separations, and was completed colorimetrically using arsenazo III [A-13].

Laboratory 10

Anion Exchange – Colorimetric method (all six samples): Thorium was isolated by anion exchange from strong nitric acid [A-14]. The determination was completed colorimetrically using arsenazo III.

Laboratory 11

X-ray Emission Spectrometry (DH-1 and DL-1): After decomposition by fusion with potassium bifluoride and leaching of the fusion with hydrofluoric acid, the insoluble phase was filtered off and dissolved in nitric and perchloric acids. Lanthanum was added to the combined solutions as a carrier and a double precipitation was made using a homogeneous fluoride precipitation method. Thorium was extracted using thenoyl trifluoroacetone, precipitated as the hydroxide, filtered through a Millipore filter, and determined by X-ray spectrometry.

RADIUM-226

Laboratory 1

Alpha Spectrometry on Radium: Radium-226 was coprecipitated on barium-lead sulphate. Then, using a "ruggedized" silicon surface-barrier detector and a multichannel analyzer, the net area under the ^{226}Ra alpha peak at 4.78 MeV was measured on the filter cake and compared with standards prepared from massive Port Radium pitchblende (39.9% U)[A-15].

Laboratory 12

(a) Alpha Counting of ^{222}Rn: The ^{226}Ra content of samples BL-2 and BL-4 was determined by alpha counting of the ingrown ^{222}Rn (after preliminary de-emanation) [A-16].

(b) Gamma Counting of ^{226}Ra and ^{214}Bi: A 25-g portion of each sample was sealed with wax in a plastic jar and after a suitable ingrowth period, the 186 KeV gamma from ^{226}Ra and the 609 KeV gamma from ^{214}Bi were measured. All measurements were referred to the ^{226}Ra values obtained on BL-2 and BL-4 measured in (a).

LEAD-210

Laboratory 12

Solvent Extraction – Beta Counting: The
lead was isolated by first removing heavy
metals by solvent extraction, then separ-
ating the lead as the dithizone com-
plex [A-16]. ^{210}Pb was then measured
directly by counting its beta radiation,
or indirectly by counting radiations from
the ingrowth of ^{210}Bi or ^{210}Po.

RARE EARTHS

Laboratory 1

Chemical Concentration – X-Ray Emission
Spectrometry (DH-1 and DL-1) [A-17,18]
The samples weighing 25-60 g were first attacked
with nitric and hydrofluoric acids to
volatilize the bulk of the silica. The
fluorides were treated with potassium
hydroxide to eliminate fluoride and re-
dissolved in nitric and perchloric acids.
A separatory fluoride precipitation was
then performed, followed by an oxalate
separation. Thorium and other metallic
impurities (now at a low level) were re-
moved by solvent extraction with 8-quino-
linol at pH 4.2-4.3. The rare earths were
then precipitated with either ammonium
hydroxide or cinnamic acid at pH 3.5-3.8.
The precipitate was ignited, weighed, and
utilized for the determination of individual
rare earths by X-ray spectrometry.

Two weighed portions of the ignited prec-
ipitate, one twice the weight of the other,
were dissolved separately in nitric acid
and absorbed on 2-g portions of diatoma-
ceous earth. The powders were dried,
moistened with a solution of 0.5 g of
carnauba wax in trichloroethylene, allowed
to dry, and pressed into pellets in Spex-
caps.

The filled caps were then counted on a
Philips 1220 X-ray spectrophotometer at
each of the rare earth lines and at two
points for calculated back-ground corr-
ections. Correction for matrix effects was
based on the data-treatment equations of
the Tertian Double Dilution method. Corr-
ections were also made for mutual inter-
ferences of rare earths, involving several
iterations in some cases.

SILICA

Laboratory 1

Atomic Absorption [A-19]

ALUMINUM

Laboratory 1

Atomic Absorption [A-20]; Flame Emission [A-20];
Chelatometric [A-21]

Laboratory 2

Atomic Absorption: details not given.

IRON

Laboratory 1

Spectrophotometry with o-phenanthroline [A-22];
Atomic Absorption:

Laboratory 2

Volumetric dichromate-method, using
stannous chloride for reduction.

Laboratory 3

Volumetric: same as Lab-2, test lead
reduction.

Laboratory 4

Volumetric: same as Lab-2.

SULPHUR

Laboratories 1,3, and 11

Barium sulphate, gravimetric.

Laboratory 2

Induction furnace combustion with Leco
automatic titrator.

Laboratory 4

All samples by combustion except DH-1;
DH-1, barium sulphate gravimetric.

Laboratory 11

Precipitated as barium sulphate, collected
on Millipore filter and determined by X-ray
spectrometry of barium.

VANADIUM

Laboratory 1

Volumetric (Amperometric): Vanadium was
oxidized to V^{+5} by fuming with perchloric
acid and adding a slight excess of
potassium permanganate which was destroyed
by treatment with sodium nitrite followed
by urea. The solution, made 5-10% v/v with
perchloric acid, was titrated amperometrically
with a standard ferrous sulphate solution.

Laboratory 2

Atomic Absorption: details not given.

Laboratory 10

> Anion Exchange – Atomic Absorption: Vanadium
> and molybdenum were first separated from
> each other and from matrix elements by means
> of anion exchange on Dowex 1 x 8 from 6M
> aqueous hydrochloric acid medium. Vanadium
> was unabsorbed and collected separately,
> while the molybdenum was subsequently
> eluted with 6M methanolic hydrochloric acid.
> Both elements were then determined by
> atomic absorption spectrophotometry [A-24].

MOLYBDENUM

Laboratory 10 – as for vanadium: see above.

CADMIUM

Laboratory 10

> Anion Exchange – Spectrophotometric: After
> anion exchange (details unknown), cadmium
> was determined with dithizone.

COBALT

Laboratory 10

> Anion Exchange – Spectrophotometric: After
> an anion exchange separation (details
> unknown) cobalt was determined using
> nitroso-R salt.

LEAD

Laboratory 10

> Anion Exchange – Atomic Absorption: After
> separation by anion exchange from 2M HBr
> medium on Dowex 1 x 8, lead was determined
> by atomic absorption spectrophotometry [A-25].

COPPER

Laboratory 10

> Anion Exchange – Atomic Absorption and
> Spectrophotometry: Copper was separated
> from matrix elements by anion exchange from
> a solution 90 volume per cent methanol, 10
> volume per cent 1.5M hydrobromic acid on
> Dowex 1 x 8. All other elements pass in
> the effluent. The absorbed copper was
> eluted with 6M hydrochloric acid and
> determined both by atomic absorption, and
> by spectrophotometry as the diethyl
> dithiocarbonate [A-26,27].

SUMMARY OF RESULTS FOR NON-RADIOACTIVE
ELEMENTS

Abbreviations		Methods of analysis
comb	=	combustion (for sulphur)
evol	=	evolution by acid attack (for CO_2)
color	=	colorimetric
grav	=	gravimetric
vol	=	volumetric
AA	=	atomic absorption spectrophotometry
IX-AA	=	atomic absorption spectrophotometry following an anion exchange separation
IX-color	=	colorimetry following an anion exchange separation
flame	=	flame emission spectrometry

TABLE A-1 (a)

Summary of analytical results for non-radioactive elements—
radioactive ore DH-1

Major constituents

Element	Laboratory	Method	Number of determinations	Average wt %	σ ±
Si	1	AA	5	38.45	0.23
Al	1	vol	2	2.38	--
	1	AA	5	2.29	0.018
	1	flame	9	2.09	0.06
	2	AA	10	2.38	0.05
Fe	1	vol	10	6.13	0.060
	2	vol	10	6.00	0.036
	3	vol	10	6.06	0.032
	4	vol	4	6.13	0.032
Mg	1	AA	1	0.028	--
	2	AA	10	0.027	0.0006
Ca	1	AA	1	0.026	--
	2	AA	10	0.040	0.003
Na	1	AA	1	0.032	--
	2	AA	10	0.043	0.008
K	1	AA	1	1.02	--
	2	AA	10	1.15	0.032
Ti	1	color	2	0.13	--
	2	AA	10	0.29	0.038
S	1	grav	2	6.46	--
	1	grav	10	6.33	0.055
	2	comb	10	6.81	0.042
	3	grav	10	6.43	0.042
	4	grav	4	6.37	0.104
	11	grav	2	5.81	--
	11	X-ray	5	5.77	0.0877
CO_2	1	evol/grav	2	<0.05	--

TABLE A-1 (b)

Summary of analytical results for non-radioactive elements —
radioactive ore DH-1

Minor constituents

Element	Laboratory	Method	Number of determinations	Average ppm(μg/g)	σ $\pm$
Ba	1	AA	2	134	--
Bi	1	AA	2	40	--
Cd	10	IX-color	2	0.27	--
Co	10	IX-color	2	89	--
Cu	10	AA	1	67	--
	10	IX-AA	2	76	--
	10	IX-color	1	73	--
Mo	10	IX-AA		5	--
Pb	1	AA	4	665	--
	10	AA	1	562	--
	10	IX-AA	2	523	--
Sr	1	AA	2	5	--
V	10	IX-AA	2	14	--
(R.E.)$_2$O$_3$ + Y$_2$O$_3$	1	grav	2	6,000	--
Individual Rare Earths (as elements)					
La	1	X-ray on	2	1,150	--
Ce		gravi-		2,400	
Pr		metric		200	
Nd		concen-		750	
Sm		trate		150	
Eu				<10	
Gd				90	
Tb				20	
Dy				40	
Ho				<10	
Er				<10	
Tm				<10	
Yb				<30	
Lu				<10	
Y				180	

TABLE A-2 (a)

Summary of analytical results for non-radioactive elements—
radioactive ore DL-1

Major constituents

Element	Laboratory	Method	Number of determinations	Average wt %	σ ±
Si	1	AA	5	37.15	0.234
Al	1	vol	2	4.78	
	1	AA	5	4.99	0.014
	1	flame	10	5.20	0.061
	2	AA	10	5.64	0.105
Fe	1	color	2	0.83	
	1	color	10	0.84	0.02
	1	AA	10	0.815	0.007
	2	vol	10	0.75	0.016
	3	vol	10	0.84	0.0088
	4	vol	4	0.91	0.03
Mg	1	AA	2	0.058	
	2	AA	10	0.0401	0.003
Ca	1	AA	2	0.071	
	2	AA	10	0.0406	0.0045
Na	1	AA	2	0.053	
	2	AA	10	0.086	0.025
K	1	AA	2	2.41	
	2	AA	10	2.60	0.11
Ti	1	color	2	0.065	
	2	AA	10	0.099	0.0133
S	1	grav	10	0.293	0.0067
	2	comb	10	0.300	0.0067
	3	grav	10	0.326	0.017
	4	comb	4	0.271	0.014
	11	grav	2	0.225	
	11	X-ray	4	0.218	0.011
CO_2	1	evol/grav	2	<0.04	--

TABLE A-2 (b)

Summary of analytical results for non-radioactive elements —
radioactive ore DL-1

Minor constituents

Element	Laboratory	Method	Number of determinations	Average ppm (μg/g)	σ $\pm$
Ba	1	AA	4	157	--
Bi	1	AA	2	10	--
Cd	10	IX-color	2	0.2	--
Co	10	IX-color	2	10.6	--
Cu	10	AA	1	67	--
	10	IX-AA	2	79	--
	10	IX-color	1	69	--
Mo	10	IX-AA	2	4	--
Pb	1	AA	4	30	--
	10	AA	1	28	--
	10	IX-AA	2	18	--
Sr	1	AA	2	4	--
V	10	IX-AA	2	24	--
$(R.E.)_2O_3$ + Y_2O_3	1	grav	2	280	--
Individual rare earths (as elements)					
La	1	X-ray on gravimetric concentrate	1	52	--
Ce				98	
Pr				9.6	
Nd				38	
Sm				6.9	
Eu				<1	
Gd				3.3	
Tb				<1	
Dy				2.1	
Ho				<1	
Er				<1	
Tm				<1	
Yb				1.3	
Lu				<1	
Y				17	

TABLE A-3 (a)

Summary of analytical results for non-radioactive elements —
radioactive ore BL-1

Major constituents

Element	Laboratory	Method	Number of determinations	Average wt .%	σ ±
Si	1	AA	5	30.37	0.22
Al	1	AA	4	7.27	0.04
	1	AA	5	7.48	0.11
	2	AA	10	7.49	0.11
Fe	1	AA	4	4.91	0.080
	2	vol	10	4.57	0.035
	3	vol	10	4.73	0.031
	4	vol	4	4.96	0.014
Mg	1	AA	4	1.24	0.015
	2	AA	10	1.19	0.094
Ca	1	AA	4	1.93	0.006
	2	AA	10	1.94	0.176
Na	1	AA	4	3.85	0.048
	2	AA	10	3.88	0.111
K	1	AA	4	0.99	0.022
	2	AA	10	1.09	0.066
S	1	grav	4	0.27	0.002
	2	comb	10	0.28	0.016
	3	grav	10	0.28	0.007
	4	comb	4	0.249	0.0075
CO_2	1	evol/grav	4	2.11	0.057

TABLE A-3 (b)

Summary of analytical results for non-radioactive elements —
radioactive ore BL-1

Minor constituents

Element	Laboratory	Method	Number of determinations	Average ppm (μg/g)	σ ±
Ba	1	AA	2	420	--
Bi	1	AA	2	20	--
Cd	10	IX-color	2	0.25	--
Co	10	IX-color	2	24.7	--
Cu	10	AA	1	75	--
	10	IX-AA	2	80	--
	10	IX-color	1	78	--
Mo	10	IX-AA	2	34	--
Pb	1	AA	4	100	--
	10	AA	1	89	--
	10	IX-AA	2	71	--
Sr	1	AA	2	50	--
V	1	vol	4	380	66
	2	AA	10	210	68
	10	IX-AA	2	211	--

TABLE A-4 (a)

Summary of analytical results for non-radioactive elements—
radioactive ore BL-2

Major constituents

Element	Laboratory	Method	Number of determinations	Average wt %	σ ±
Si	1	AA	5	28.10	0.49
Al	1	AA	4	7.23	0.096
	1	AA	5	7.37	0.040
	1	flame	6	7.06	0.05
	2	AA	10	7.42	0.38
Fe	1	AA	4	5.33	0.051
	2	vol	10	5.15	0.032
	3	vol	10	5.55	0.044
	4	vol	4	5.49	0.063
Mg	1	AA	4	1.39	
	2	AA	10	1.38	0.072
Ca	1	AA	4	2.72	0.033
	2	AA	10	2.91	0.197
Na	1	AA	4	4.25	0.035
	2	AA	10	4.25	0.137
K	1	AA	4	0.606	0.013
	2	AA	10	0.713	0.022
S	1	grav	4	0.34	0.01
	2	comb	10	0.347	0.021
	3	grav	10	0.311	0.010
	4	comb	10	0.33	0.01
CO_2	1	evol/grav	4	3.52	0.13

TABLE A-4 (b)

Summary of analytical results for non-radioactive elements —
radioactive ore BL-2

Minor constituents

Element	Laboratory	Method	Number of determinations	Average ppm (µg/g)	σ ±
Ba	1	AA	2	350	--
Bi	1	AA	2	20	--
Cd	10	IX-color	2	0.25	--
Co	10	IX-color	2	24.7	--
Cu	10	AA	1	75	--
	10	IX-AA	2	80	--
	10	IX-color	1	78	--
Mo	10	IX-AA	2	36.2	--
Pb	1	AA	2	1200	--
	10	AA	1	890	--
	10	IX-AA	2	922	--
Sr	1	AA	2	70	--
V	1	vol	4	1000	40
	2	AA	10	830	53
	10	IX-AA	2	842	--

TABLE A-5 (a)

Summary of analytical results for non-radioactive elements—
radioactive ore BL-3

Major constituents

Element	Laboratory	Method	Number of determinations	Average wt %	σ ±
Si	1	AA	5	27.83	0.42
Al	1	AA	4	7.29	0.051
	1	AA	5	7.20	0.032
	2	AA	10	7.44	0.26
Fe	1	AA	4	5.32	0.072
	2	vol	10	5.03	0.063
	3	vol	10	5.63	0.0028
	4	vol	4	5.37	0.045
Mg	1	AA	4	1.36	0.006
	2	AA	10	1.41	0.034
Ca	1	AA	4	2.84	0.024
	2	AA	10	2.95	0.080
Na	1	AA	4	4.18	0.017
	2	AA	10	4.20	0.135
K	1	AA	4	0.62	0.011
	2	AA	10	0.69	0.015
S	1	grav	4	0.371	0.008
	2	comb	10	0.753	0.020
	3	grav	10	0.361	0.011
	4	comb	4	0.353	0.007
CO_2	1	evol/grav	4	3.76	0.12

TABLE A-5 (b)

Summary of analytical results for non-radioactive elements —
radioactive ore BL-3

Minor constituents

Element	Laboratory	Method	Number of determinations	Average ppm (µg/g)	σ ±
Ba	1	AA	2	370	--
Bi	1	AA	2	20	--
Cd	10	IX-color	2	0.25	--
Co	10	IX-color	2	24.7	--
Cu	10	AA	1	75	--
	10	IX-AA	2	80	--
	10	IX-color	1	78	--
Mo	10	IX-AA	2	36.2	--
Pb	1	AA	2	1200	--
	10	AA	1	890	--
	10	IX-AA	2	922	--
Sr	1	AA	2	70	--
V	1	vol	4	1150	70
	2	AA	10	860	23
	10	IX-AA	2	834	--

TABLE A-6 (a)

Summary of analytical results for non-radioactive elements —
radioactive ore BL-4

Major constituents

Element	Laboratory	Method	Number of determinations	Average wt %	σ ±
Si	1	AA	5	28.71	0.30
Al	1	vol	2	7.07	—
	1	flame	6	7.06	0.055
	1	AA	5	7.38	0.064
	2	AA	10	7.07	0.760
Fe	1	vol	4	5.08	0.026
	2	vol	10	4.80	0.03
	3	vol	10	4.98	0.03
	4	vol	4	5.06	0.03
Mg	1	AA	4	1.36	0.042
	2	AA	10	1.27	0.12
Ca	1	AA	4	2.63	0.022
	2	AA	10	2.30	0.16
Na	1	AA	10	4.05	0.042
	2	AA	10	4.41	0.128
K	1	AA	4	0.58	0.006
	2	AA	10	0.71	0.026
S	1	grav	4	0.16	0.005
	2	comb	10	0.182	0.0063
	3	grav	10	0.183	0.0065
	4	comb	4	0.16	0.003
CO_2	1	evol/grav	2	2.87	—

TABLE A-6 (b)

Summary of analytical results for non-radioactive elements —
radioactive ore BL-4

Minor constituents

Element	Laboratory	Method	Number of determinations	Average ppm (µg/g)	σ ±
Ba	1	AA	2	410	--
Bi	1	AA	2	20	---
Cd	10	IX-color	2	1.22	--
Co	10	IX-color	2	17.5	--
Cu	10	AA	1	54	--
	10	IX-AA	2	72	---
	10	IX-color	1	68	--
Mo	10	IX-AA	2	35	---
Pb	1	AA	2	450	---
	10	AA	1	383	---
	10	IX-AA	2	346	--
Sr	1	AA	2	60	--
V	1	vol	2	590	---
	2	AA	10	730	29
	10	IX-AA	2	700	---

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APPENDIX B

RADIOMETRIC ANALYTICAL APPLICATIONS

EXAMPLE OF THE USE OF BL-1, BL-2, BL-3 AND
BL-4 IN ROUTINE MINE-SITE RADIOMETRIC ANALYSES

One of the prime applications of the BL
series is for radiometric analysis. Counting
factors can be determined by the slope of the
regression line of the net counts per unit
time versus the recommended values as deter-
mined in the certification program (Table 5).

This point is ilustrated by results
from two laboratories that performed
radiometric measurements on the BL series
under typical mine-site conditions. These are
presented in Table B-1 and Figure B-1.

Laboratory A used about 17 times as much
sample as Laboratory B; this resulted in a larger
factor and hence permitted shorter counting
times. Although both laboratories normally
use only beta-counting for routine assaying, the
set-up of Laboratory A was of the "equilibrium
type", permitting simultaneous beta and gamma
counting. The equipment, and counting con-
ditions used by the laboratories were:

Laboratory A: scaler-timer, Nuclear Chicago
Model 8775; β/γ counting castle, Electronic
Associates Ltd., Type EA-C6; 1-min counting
time (preset); sensitivity setting –
β-250 mV, γ-10V; sample size – 70 g.

Laboratory B: scaler, Electronic Associates
Ltd., Type SC 3T; shielded sample chamber,
Tracerlab SC 9D; Geiger tube, Tracerlab
TG Cl, mica end window; 5-min counting time;
sample size ~4 g (contents of 25 mm dia. by
8 mm deep stainless steel planchet);
sample to window distance – 18 mm.

Table B-1 shows that in all cases excellent
correlations were observed between the counts
and the uranium contents with the regression
lines virtually passing through the origin.
Thus, the counting factors for laboratory A were
4237 for β radiation and 8814 for γ-radiation,
and, for the conditions used by laboratory B
the counting factor was 1759 for β-radiation.

^{226}Ra AND ^{210}Pb CONTENT OF THE REFERENCE ORES

Reference materials in which the daughter
elements of the natural radioactive series are
in equilibrium are essential in applications to
radiometric analysis. In uranium analysis the
most important isotopes are ^{234}U, ^{230}Th, ^{226}Ra
and ^{210}Pb, all in the ^{238}U series. The ^{235}U
series contributes less than 1% of the total
measured activity, and is, therefore, not
considered significant[12].

Although it was not possible to obtain
data for the ^{230}Th content of the six reference
ores, values for the ^{226}Ra and ^{210}Pb content
(Table B-3) were provided by two laboratories.

This information should make the samples useful
as reference materials   for   determination of
the two isotopes in mine waste, in
connection with environmental control studies.

^{226}Ra and ^{210}Pb by γ-spectroscopy and β-counting

Gamma and beta determinations on the ores
were performed at the Radiation Protection Lab-
oratory of the Ontario Ministry of Health, now
a unit of the Ontario Ministry of Labour.

The ^{226}Ra content was determined by gamma
spectrometry measurements on 25-g samples of the
ores sealed with wax in plastic jars. The
intensities of two gamma peaks, one from ^{226}Ra
at 186 keV and one from ^{214}Bi at 609 keV, were
measured, and the relative ratio at each of these
energies was recorded for each sample against an
arbitrary value of 1.0 for sample DL-1
These values are given in Table B-2.

The ^{226}Ra content of samples BL-2 and
BL-4 were then determined by ^{222}Rn de-emanation
(for which the laboratory has calibration) and
the values were used in conjunction with the above
ratios to determine the values given below in
Table B-3.

^{210}Pb was measured by putting the samples
in solution, removing interfering heavy metals
by solvent extraction, then isolating lead as
the dithizone complex. Direct counting of
the beta radiation of ^{210}Pb or the radiations
from the ingrowth of ^{210}Bi or ^{210}Po permits
calcuation of the ^{210}Pb content. Provisional
values based on this procedure are also given in
Table B-3.

^{226}Ra by α-spectrometry

The ^{226}Ra content of the ores given in Table
B-3, was determined at CANMET (Lab-1) by α-energy
spectrometry after fusion dissolution of the
samples and coprecipitation on barium sulphate
carrier. The energy spectra were obtained with
an Ortec 450 mm^2 "ruggedized" silicon surface
barrier detector; Ortec model 428 detector bias
supply; model 121 charge sensitive preamplifier;
model 485 linear amplifier; model 408A biased
amplifier; and a Northern Scientific NS 600 512-
channel analyzer. Samples were mounted for
counting in an Ortec model 805 vacuum chamber,
at a distance of 1 cm from the detector surface.
^{226}Ra concentrations were computed from the
net area under the ^{226}Ra peak at 4.78 MeV.
Radium recovery was better than 95%.

Table B-3 shows there is reasonable
agreement between the γ-and α-spectrometric
technique.

TABLE B-1

Results of radiometric measurements of BL-1, BL-2, BL-3 and BL-4 performed by
Laboratories A and B

	Recommended value wt % U	Laboratory A				Laboratory B	
		β net counts		γ net counts		β net counts	
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
BL-1	0.022	95	96	194	–	35	34
BL-2	0.453	1970	1934	3989	–	795	786
BL-3	1.02	4286	4355	9007	–	1795	1783
BL-4	0.173	736	725	1565	–	298	–
Regression lines:							
slope		4237		8814		1759	
intercept		8		13		– 5	
correlation coefficient		0.99989		0.99998		0.99999	

TABLE B-2

Ratio of intensity of gamma ray peaks of each sample to the
intensity of sample DL-1, for ^{226}Ra and ^{214}Bi

Reference ore	Ratio to DL-1 intensity	
	at 186 keV (^{226}Ra)	at 609 keV (^{214}Bi)
DL-1	1.0	1.0
DH-1	44.0	49.0
BL-1	5.7	5.7
BL-2	113.0	126.0
BL-3	253.0	276.0
BL-4	42.0	45.0

TABLE B-3

^{226}Ra and ^{210}Pb content of reference ores

Reference ore	^{226}Ra				^{210}Pb	
	γ-spectrometry		α-spectrometry		by β-counting of daughters	
	pCi/g[a]	% of equilibrium value	pCi/g[b]	% of equilibrium value	pCi/g[d]	% of equilibrium value
DL-1	13.2 ± 0.7	96.2	13.72[c]	100.0	13.6	99.1
DH-1	578 ± 12	93.6	604.15[c]	96.4	573	92.8
BL-1	75 ± 4	99.9	72.63[c]	96.2	56	74.2
BL-2	1490 ± 30	96.2	1581.61	102.4	1230	82.6
BL-3	3330 ± 70	97.1	3246.09	94.6	2730	79.6
BL-4	566 ± 12	97.0	571.75	98.0	516	88.5

a = uncertainty as ±2 σ

b = by comparison with Port Radium massive pitchblende (39.9% U)

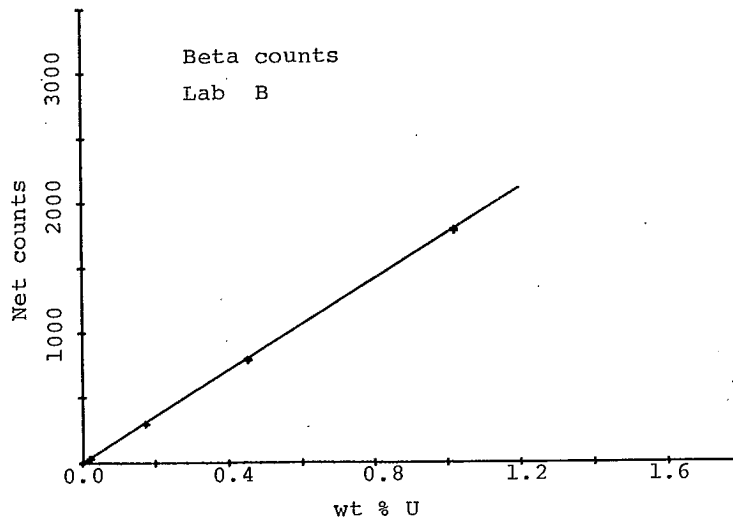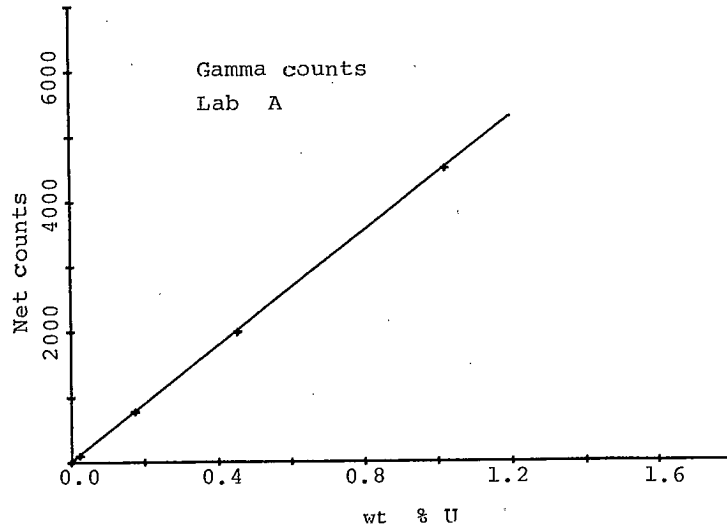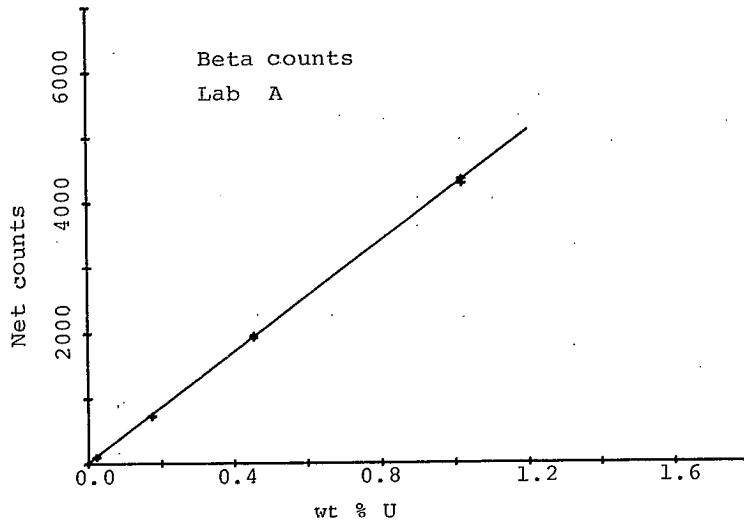c = corrected for carrier recovery, using ^{133}Ba tracer

d = provisional values

Figure B-1. Radiometric measurements on BL-1, BL-2, BL-3, and BL-4