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REPORT 84-11E

LEAD-210 IN CERTIFIED URANIUM REFERENCE ORES DL-1a, BL-4a, DH-1a AND BL-5

C.W. SMITH AND H.F. STEGER

MINERALS RESEARCH PROGRAM
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LEAD-210 IN CERTIFIED URANIUM REFERENCE ORES DL-1a, BL-4a, DH-1a AND BL-5

by

C.W. Smith* and H.F. Steger*

SYNOPSIS

Lead-210 radioactivity in uranium reference ores BL-4a and BL-5 and uranium-thorium reference ores DL-1a and DH-1a was determined by an interlaboratory program. Ten of eleven participating laboratories employed Amersham Corporation certified ^{210}Pb solutions for calibration for measurements by gamma-ray spectrometry, beta-counting of ^{210}Bi or alpha spectrometry of ^{210}Po following radiochemical separations. No significant methodological bias was detected. Recommended values for ^{210}Pb activities and associated parameters were determined by statistical treatment of the results.

The recommended values for the activity of ^{210}Pb are 1.40, 15.5, 30.8, and 866 Bq g^{-1} for DL-1a, BL-4a, DH-1a and BL-5, respectively. These values are consistent with secular equilibrium in the ^{238}U decay series in each material.

*Research Scientists, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, Ottawa, K1A 0G1

PLOMB-210 DANS LES MINERAIS D'URANIUM DE RÉFÉRENCE CERTIFIÉS
DL-1a, BL-4a, DH-1a ET BL-5

par

C.W. Smith* and Henry F. Steger*

RÉSUMÉ

La radioactivité du ^{210}Pb des minerais de référence d'uranium BL-4a et BL-5 et des minerais de référence d'uranium et de thorium DL-1a et DH-1a a été déterminée par une campagne interlaboratoires. Dix des onze laboratoires participants ont utilisé, pour fin de calibration, des solutions du ^{210}Pb certifiées par la Amersham Corporation pour l'étalonnage par la spectrométrie de rayon gamma, la mesure de particules beta du ^{210}Bi ou la spectrométrie à rayon alpha du ^{210}Po après la séparation radiochimique. Aucune préférence marquée pour certaines méthodes n'a été décelée. Les valeurs recomman- dées de la radioactivité du ^{210}Pb et les paramètres associés ont été calculés par une analyse statistique des résultats.

Les valeurs recommandées de la radioactivité du ^{210}Pb sont 1,40; 15,5; 30,8; et 866 Bq g^{-1}, pour le DL-1a, BL-4a, DH-1a et BL-5, respectivement. Ces valeurs sont conformes à l'équilibre radioactif séculaire dans la succession de désintégration de l'^{238}U pour chaque matériau.

*Chercheurs scientifiques, Laboratoires des sciences minérales, CANMET, Énergie, Mines et Ressources Canada, Ottawa, K1A 0G1.

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INTRODUCTION

Lead-210, a decay product of ^{238}U, reports to the tailings from uranium-ore processing where it poses a potential environmental hazard. Its accurate measurement is, therefore, important and the availability of similar compositional reference materials is desirable.

CCRMP uranium reference materials BL-4a and BL-5 and uranium-thorium reference materials DL-1a and DH-1a have previously been certified by interlaboratory consensus programs for uranium content (1-4) and ^{226}Ra activity (5). Within estimated uncertainties of the measurements, secular equilibrium between ^{238}U and ^{226}Ra is indicated in the four materials. Because of the relatively short half-life of ^{210}Pb and intervening isotopes in the decay series from ^{226}Ra, $^{226}Ra/^{210}Pb$ secular equilibrium should occur unless there has been recent leaching of lead from the ore in situ, lead losses during grinding, or significant emanation of the intermediate gaseous decay product ^{222}Rn from the pre-milled ore body. Consequently, it was deemed justifiable to establish the lead-210 activity unequivocally by measurement rather than use values based on a secular equilibrium assumption.

In accord with previous practice, the lead-210 activities were established by an interlaboratory measurement program. In addition to providing a result that minimizes possible laboratory-methodology bias, this procedure provides important information on the extent of consensus between participating laboratories, and by inference, between current methodological practice for lead-210 in general.

INTERLABORATORY PROGRAM

Eleven independent laboratories contributed results for ^{210}Pb activities for each of DL-1a, BL-4a, DH-1a and BL-5. Three laboratories obtained results by two independent methods; these were treated as statistically independent sets. Six laboratories determined lead-210 by beta-counting of bismuth-210 after radiochemical isolation from its lead-210 parent, with appropriate correction for the decay. Two laboratories determined lead-210 by measurement of its polonium-210 descendant by alpha spectrometry following radiochemical isolation. Six laboratories measured lead-210 by direct measurement of the emitted intensity of the 46.5 keV photons by high-resolution gamma-ray spectrometry employing various techniques to compensate sample self-absorption effects. [For convenience, the three general methodologies are designated as β, α, and γ respectively, in the Tables.]

Participants were provided with one or more bottles of each material selected at random from stock and were asked to perform determinations on four independent samples, each with minimum 1 g masses. Calibrations were to be performed with RBZ.44, a certified solution reference material for ^{210}Pb and ^{210}Bi, available from Amersham International Ltd., in order to minimize possible calibration bias effects and ensure that results were traceable to a recognized ^{210}Pb certified reference material (CRM). CCRMP distributed aliquots of a volumetrically diluted solution of RBZ.44 to participants on request (Appendix A). Participants were asked to minimize controllable uncertainty components to a practical extent commensurate with the use of the results in the certification project, and to provide a propagated 1σ precision for each value obtained, as estimated from counting statistics and calibration and recovery measurement precisions, (exclusive of the CRM uncertainty). Currently accepted half-life values of 22.3 ± 0.2 y, 5.01 ± 0.01 d, and 138.38 ± 0.01 d were to be employed for decay corrections for ^{210}Pb, ^{210}Bi and ^{210}Po respectively (6,7).

DETERMINATION OF RECOMMENDED VALUES AND ESTIMATION OF UNCERTAINTIES

The recommended (consensus) value for ^{210}Pb activity is defined as the mean of the set mean values, with physical or statistical outlier set means excluded. Physical outliers were defined as set means exhibiting unusually large deviations from the consensus mean, judged to arise from physically defineable origins. Statistical outliers were determined by Dixon tests on the set mean extrema (8). Dixon's r statistic at the 5% significance level (two-sided) was used to identify set mean values having a sufficiently low probability of belonging to the assumed consensus universe to warrant exclusion from the consensus value determination.

A one-way analysis of variance (Model II) was performed using all individual values in the determination of the consensus mean to estimate the precision of this value and the significance of the between set component (9). The computed 95% confidence interval estimates the reproducibility of the consensus value if the same program were repeated 100 times.

Recommended values for ^{210}Pb activities and related statistical parameters are presented in Table 1. σ_A is the average within-set standard deviation.

The analytical data from the ^{210}Pb consensus program are presented in Tables 2-5. Participants and information on methodologies are compiled in Appendix A.

Table 1 - Recommended values and statistical parameters for ^{210}Pb, Bq g^{-1}

				95% CL		
Material	No. sets	No. values	Mean	Low	High	σ_A
DL-1a	13	54	1.40	1.38	1.41	0.045
BL-4a	14	58	15.55	15.12	15.97	0.36
DH-1a	14	58	30.75	29.84	31.66	0.87
BL-5	12	50	866.	847	889	20.

Table 2 - Results, set means, and standard deviations for ^{210}Pb in DL-1a

		^{210}Pb, Bq/g					Set mean	S.D.	1σ (lab est.)
Lab-1a	(β)	1.317	1.278	1.301	1.412	1.408	1.343	0.063	
Lab-2a	(β)	1.38	1.38	1.47	1.44		1.418	0.045	0.061
Lab-3	(β)	1.35	1.34	1.44	1.36		1.372	0.046	0.03
Lab-7	(β)	1.452	1.366	1.418	1.414		1.412	0.035	0.035
Lab-9	(β)	1.43	1.40	1.41	1.42		1.415	0.013	
Lab-11	(β)	1.46	1.39	1.33	1.35		1.385	0.057	0.012
Lab-5	(α)	1.37	1.40	1.42	1.50		1.423	0.053	0.063
Lab-6	(α)	1.470	1.382	1.369	1.453	1.323	1.392	0.048	
		1.369	1.400	1.371					
Lab-1b	(γ)	1.344	1.358	1.402	1.396		1.375	0.028	0.032
Lab-2b	(γ)	1.39	1.36	1.35	1.34		1.357	0.011	0.18
Lab-4	(Geγ)**	1.543	1.665	1.650	1.458	1.177***	1.579**	0.097	
	(NaIγ)*	1.771	1.750	1.789	1.760		1.768*	0.017	
Lab-8	(γ)	1.389	1.322	1.342	1.310		1.341	0.035	0.033
Lab-9b	(γ)	1.44	1.46	1.32	1.42		1.410	0.062	
Lab-10	(γ)						1.512†		0.032

*Physical outlier set; also statistical outlier set mean, $r_{22} = 0.62 > r(0.025, 15)$; ref. (8).

**Statistical outlier set mean, $r_{22} = 0.70 > r(0.025, 14)$; ref. (8).

***Outlier result within set.

†Four-sample weighted least-squares standard addition result.

Table 3 - Results, set means, and standard deviations for ^{210}Pb in BL-4a

		^{210}Pb, Bq/g					Set mean	S.D.	1σ (lab est.)
Lab-1a	(β)	15.83	14.18	15.06	15.94	14.58	15.119	0.77	
Lab-2a	(β)	15.0	14.8	14.8	15.4		15.0	0.28	0.41
Lab-3	(β)	16.1	17.0	16.6	16.2		16.48	0.41	0.4
Lab-7	(β)	15.05	15.06	14.07	15.18		14.84	0.52	0.36
Lab-9a	(β)	15.1	15.4	15.1	15.3		15.2	0.15	
Lab-11	(β)	15.17	14.22	14.64	14.37		14.60	0.42	0.12
Lab-5	(α)	16.1	16.5	16.6	16.7		16.48	0.24	0.71
Lab-6	(α)	15.5	16.2	16.9	15.7	16.6	16.14	0.457	
		15.9	16.2	16.1					
Lab-1b	(γ)	15.85	15.56	15.62	15.86		15.72	0.16	0.20
Lab-2b	(γ)	15.0	15.0	15.7	15.2		15.23	0.33	2.2
Lab-4	(γ)	17.13	16.67	16.45	16.50		16.69	0.31	
	(NaIγ)*	17.25	16.77	16.61	16.13		16.69*	0.46	
Lab-8	(γ)	16.70	15.50	16.00	16.12		16.08	0.49	0.42
Lab-9b	(γ)	15.4	15.4	15.5	15.0		15.32	0.22	
Lab-10	(γ)						14.85†		0.25

*Declared 'physical' outlier set.

†Four-sample weighted least-squares standard additions result.

Table 4 - Results, set means, and standard deviations for ^{210}Pb in DH-1a

							Set mean	S.D.	1σ (lab est.)
		^{210}Pb, Bq/g							
Lab-1a	(β)	29.47	33.79	33.17	32.57	31.37	32.073	1.705	
Lab-2a	(β)	33.3	33.3	33.9	33.6		33.53	0.29	0.97
Lab-3	(β)	28.1	28.2	29.6	29.0		28.7	0.71	0.7
Lab-7	(β)	29.94	29.83	27.90	26.59		28.56	1.61	0.7
Lab-9a	(β)	30.0	31.7	30.8	32.0		31.13	0.91	
Lab-11	(β)	30.4	29.8	29.5	29.0		29.68	0.59	0.19
Lab-5	(α)	30.2	31.4	31.7	31.9		31.28	0.72	1.35
Lab-6	(α)	32.4	30.5	28.9	31.7	32.2	31.31	1.347	
		30.0	32.3	32.5					
Lab-1b	(γ)	31.64	31.70	31.98	31.39		31.68	0.24	0.37
Lab-2b	(γ)	30.1	28.8	28.1	31.0		29.50	1.30	3.2
Lab-4	(Geγ)	29.17	29.22	27.90	28.38		28.66	0.64	
	(NaIγ)*	34.94	35.75	36.22	35.62		35.63*	0.53	
Lab-8	(γ)	30.24	31.20	31.78	31.25		31.12	0.64	0.95
Lab-9b	(γ)	31.3	32.3	32.4	30.7		31.68	0.82	
Lab-10	(γ)						31.55†		0.60

*Declared 'physical' outlier set.

†Four-sample weighted least-squares standard additions result.

Table 5 - Results, set means, and standard deviations for ^{210}Pb in BL-5

	^{210}Pb, Bq/g					Set mean	S.D.	1σ (lab est.)
Lab-1a (β)	905	864	851	815	838	854.9	33.2	
Lab-2a (β)	875	902	869	912		889.5	20.8	25
Lab-3 (β)	860	870	860	870		865	5.8	20
Lab-7 (β)	839	838	816	838		833	11.2	20
Lab-9a (β)	861	875	861	874		867.5	7.8	
Lab-11 (β)	848	894	812	860		853.5	33.8	3
Lab-6 (α)	939	847	937	923	877	906.1	40.5	
	853	930	943					
Lab-1b (γ)	851	858	861	871		860.2	8.3	8
Lab-2b (γ)	923	915	948	929		929	14	130
Lab-4 (Geγ)*	1065	1027	1041	1055		1047**	16.5	
(NaIγ)*	1121	1100	1100	1137		1115*	17.8	
Lab-8 (γ)	846	820	812	852		832.5	19.7	13.7
Lab-9b (γ)	868	873	886	869		874	8.3	
Lab-10 (γ)						826.5†		35.3

*Physical outlier set; also statistical outlier set, r_{22} = > r(0.025, 14); ref. (8).

**Statistical outlier set-mean; r_{21} = 0.66 > r(0.025, 13); ref. (8).

†Four-sample weighted least-squares standard additions result.

DISCUSSION OF RESULTS

STATE OF SECULAR EQUILIBRIUM

Activities of ^{238}U-series radionuclides derived from three independent consensus programs are compared in Table 6. Within the indicated 95% confidence level uncertainty estimates, the radionuclide activity ratios are unity, i.e., secular equilibrium exists between ^{238}U and its lower decay series products in each of the four CCRMP reference materials. The $^{226}Ra/^{210}Pb$ activity ratios indicate that ^{222}Rn emanations from the source-rock used for these materials was not significant. Emanation rate measurements carried out on the powder reference materials indicate that ^{210}Pb activities should be gradually depleted relative to ^{226}Ra activities over a period of years characterized by the ^{210}Pb half-life to levels 2-8% below those of ^{226}Ra (Appendix B).

The measured activities of ^{234}U and ^{230}Th (Appendix B) strongly support that these CCRMP materials may be regarded as unaltered secular-equilibrium materials with respect to ^{238}U decay radionuclides.

PRECISION OF MEASUREMENTS

A one-way analysis of variance treatment of results according to a 'Model II' one-way classification (9) indicates that the between-sets component of variance is significant; the ratio of between- to within- mean square variances exceed critical values of the F statistic at the 5% significance level for all materials except DL-1a. The between-sets variance consequently dominates the uncertainty in the recommended value, which gives equal weighting to non-outlying set means.

The distributions of set means about the recommended values are shown in Fig. 1. There are no discernable patterns of either consistent set (laboratory) bias or of relative methodological bias. Mean results by method are compared in Table 7; the agreement between methods is substantial. Precisions for the lead-210 program (Table 1) are comparable to those obtained in the ^{226}Ra program (5). Average within-laboratory standard deviations (σ_A, %) show no significant activity-dependence over the range from DL-1a to BL-5. There is possibly a small matrix effect in that σ_A, % is slightly higher for the uranium/thorium materials.

Table 6 - Activities of ^{238}U-series isotopes certified by interlaboratory consensus, Bq g^{-1}

Material	U,%	^{238}U [1]	^{226}Ra [2]	^{210}Pb [3]
DL-1a	0.0116 ± 0.0003	1.432 ± 0.037	1.40 ± 0.04	1.40 ± 0.03
BL-4a	0.1248 ± 0.0007	15.41 ± 0.09	15.5 ± 0.5	15.55 ± 0.41
DH-1a	0.2629 ± 0.0003	32.46 ± 0.04	31.5 ± 1.1	30.8 ± 0.9
BL-5	7.09 ± 0.03	875. ± 4.	857. ± 38.	866. ± 20.

[1] From uranium values, 0.99274 abundance ^{238}U, and specific activity 12.437 ± 0.007 kBq g^{-1} ^{238}U.

[2] From interlaboratory consensus employing NBS ^{226}Ra calibration CRMs having total uncertainty <2% (5).

[3] From this program employing Amersham RBZ.44 calibration CRMs having total uncertainties less than 2.5% (6).

Table 7 - Comparison of method-mean activities for ^{210}Pb*

Material	$\bar{\bar{x}}_\beta \pm$ 95% CI		$\bar{\bar{x}}_\gamma \pm$ 95% CI		$\bar{\bar{x}}_\alpha$	No. sets			Bet. sets S.D.	
						N_β	N_γ	N_α	$s_{b\beta}$	$s_{b\gamma}$
DL-1a	1.391 ±	.031	1.399 ±	.095	1.407	6	5	2	.0298	.0682
BL-4a	15.21 ±	.692	15.65 ±	.696	16.31	6	6	2	.659	.663
DH-1a	30.61 ±	2.08	30.70 ±	1.36	31.30	6	6	2	1.982	1.298
BL-5	860.6 ±	19.6	864.4 ±	51.0	906.	6	5	1	18.7	41.0

*95% CI = $t_{.05,n-1}s_b/\sqrt{n}$, where t is student's t and s_b is the standard deviation of set means from the mean of set means, $\bar{\bar{x}}$.

TRACEABILITY

The 95% confidence intervals for the recommended values of ^{210}Pb activity indicate the current state of consensus achievable for compositional ore materials by experienced analysts in using accepted techniques. Because 12 of 14 set results were calibrated directly or indirectly using aliquots of Amersham Corp. RBZ.44 certified ^{210}Pb reference solutions, the recommended activities are traceable to this source. The overall uncertainty of the calibration solutions (approx. ±2.4%) (see Appendix A) is not incorporated in the precision estimates of Table 1.

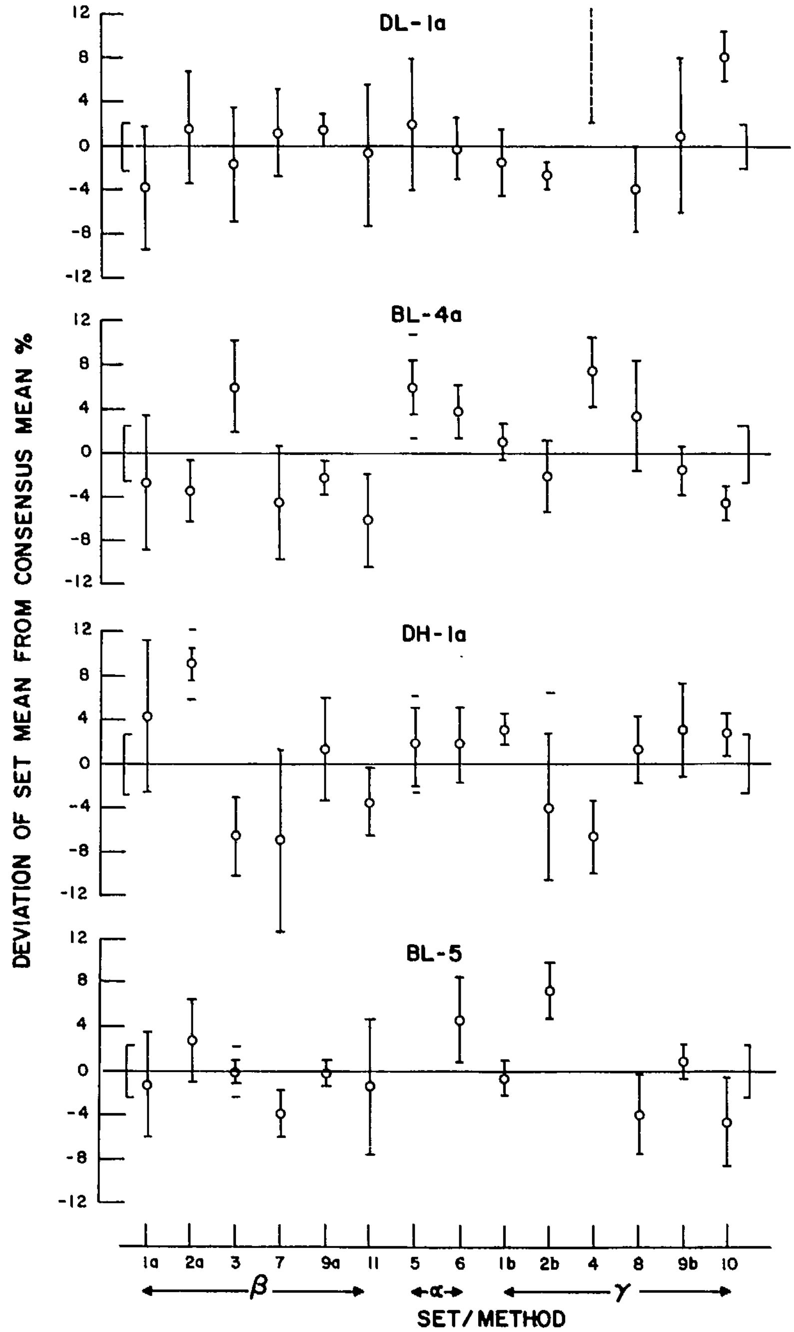

Fig. 1 - Distribution of set-mean values for activity of ^{210}Pb about the mean of set means (recommended value). Vertical bars are the 95% confidence-interval precision estimates for the set means from replicate values. Brackets indicate the estimated 95% confidence intervals of the recommended values.

ACKNOWLEDGEMENTS

CCRMP acknowledges the participation of the laboratories identified in Appendix A of this report and particularly of those who contributed without remuneration.

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APPENDIX A

PARTICIPATING LABORATORIES

Lab-1 Canada Centre for Mineral and Energy Technology,
Mineral Sciences Laboratories,
Chemical Laboratory,
Ottawa, Canada.

a. J.L. Dalton and R.H. McCorkell
b. C.W. Smith and Junhao Yang

Lab-2 Chemex Labs, Ltd.,
North Vancouver,
British Columbia.

a. M. LeGeyt and E. Savoy
b. M. LeGeyt and H. Blok

Lab-3 Eldorado Resources Limited,
Ottawa, Ontario.

- M.C. Miedema and G.B. Moodie

Lab-4 Flett Research Ltd.,
Winnipeg, Manitoba.

- R. Flett and D. Campbell

Lab-5 Freshwater Institute,
Fisheries and Oceans Canada,
Winnipeg, Manitoba.

- P. Wilkinson

Lab-6 Geological Survey of Canada,
Geochemistry Exploration Research Section,
Ottawa, Canada.

- W. Dyck, J.C. Pelchat and H. Schneeberger

Lab-7 Monenco Consultants Ltd.,
Monenco Analytical Laboratories,
Calgary, Alberta.

- N. Chiu and J. Dean

Lab-8 Oak Ridge National Laboratory, Environmental Sciences Division,
Oak Ridge, Tennessee.

- I.L. Larsen

Lab-9 Saskatchewan Research Council,
Analytical Services Sector,
Saskatoon, Saskatchewan.

- G. Smithson, L. Macdonald and D. Chorney

Lab-10 University of Calgary,
Physics Department,
Calgary, Alberta.

- C.J. Bland, P. Overend and J.G. Dufour

Lab-11 University of Waterloo Research Institute,
Waterloo, Ontario.

-H.D. Sharma and B. Hauck

REPORTS FROM CONTRACTING LABORATORIES

Table A1 - Reports from contracting laboratories[1]

Laboratory	Title	Contract[2] Requisition No.	Contract[2] Serial No.
Eldorado Resources Ltd.	Radiochemical determinations of CCRMP reference materials for certification purposes: lead-210 activity measurements	26SQ.23440-3-9148-1	OSQ83-00163
Waterloo Research Institute, University of Waterloo	Radiochemical determinations of CCRMP reference materials for certification purposes: lead-210 activity measurements	26SQ.23440-3-9148-2	OSQ83-00164
Chemex Labs Ltd.	Radiochemical determinations of CCRMP reference materials for certification purposes: lead-210 activity measurements	26SQ.23440-3-9148-3	OSQ83-00165
Monenco Consultants Ltd. (Monenco Analytical Labs.)	Determination of Lead-210 in uranium-bearing reference materials for certification purposes	26SQ.23440-3-9148-4	OSQ83-00166
Flett Research Ltd.	Radiochemical determinations of CCRMP reference materials for certification purposes: lead-210 activity measurements	26SQ.23440-3-9148-5	OSQ83-00167
Saskatchewan Research Council	Radiochemical determinations of CCRMP reference materials for certification purposes: lead-210 activity measurements	26SQ.23440-3-9148-6	OSQ83-00168
University of Calgary, Physics Department	Radiochemical determinations of CCRMP reference materials for certification purposes: lead-210 activity measurements	26SQ.23440-3-9148-7	OSQ83-00169

[1]Reports filed with Research Program Office, CANMET, 555 Booth St., Ottawa, Ont., Canada, K1A 0G1.
[2]Funded from CANMET Minerals Research Program, Reference Materials Project, 380101.

SUMMARY OF RADIOCHEMICAL METHODOLOGIES

Table A2 - Summary of radiochemical methodologies

Set	Isot. Meas. (method)	Sample (g)	Decomposition[1]	Separation[2]	Recovery tracer[3] method	Calibration[4] SRM	References cited
1a	^{210}Bi (β)	1-2	acid digestion (a)	solvent extrn./pptn. (b)	Bi (XRF)	RBZ.44	M1, M2
2a	^{210}Bi (β)	1-2	acid digestion (a)	solvent extrn./pptn. (a)	Bi (AAS)	RBZ.44	M1
3	^{210}Bi (β)	1-2	acid digestion (c)	solvent extrn./pptn. (a)	Bi (AAS)	RBZ.44 (a)*	M1, M3
7	^{210}Bi (β)	0.5-2	acid digestion (a)	solvent extrn./pptn. (a)	(a)	RBZ.44 (c)	
9a	^{210}Bi (β)	1	acid digestion (c)	solvent extrn./pptn. (a)	Bi (AAS)	RBZ.44 (a)	M1
11	$^{210}Bi/^{210}Pb$ (β)	1	acid digestion (b)	solvent extrn. (c)	(b)	RBZ.44 (a)	M4
5	^{210}Po (α)	0.5-3	acid digestion/fusion (d)	ion-exchange (Pb) spont. depos. on Ag (Po)(d)	Pb (AAS); ^{209}Po (int. std.)	NBS-4953c (b)	M5
6	^{210}Po (α)	1	acid digestion (a)	spont. depos. on Ni from 0.5 M HCl		RBZ.44	M6, M7

1 a. Repeated digestions with nitric, hydrofluoric and perchloric acids in polyfluorethylene beakers followed by evaporation to near dryness.

b. Acid digestion (a) carried out in polyfluorethylene-lined bomb at 150°C.

c. Following digestion with nitric and perchloric acids, the insol. is separated and treated with hydrofluoric and sulphuric acids in polyfluorethlene beakers, evaporated to near-dryness, and redissolved in hydrochloric acid. The soluble fraction is evaporated, redissolved in hydrochloric acid and recombined with the treated insol.

d. Acid digestion (a) followed by treatment with sulphuric acid and low-temperature fusion with potassium pyrosulphate. Residue is redissolved in ion hydrochloric acid for ion-exchange separations.

2 a. Bismuth, including added carrier, is selectively extracted from the matrix in 2M hydrochloric acid containing ascorbic acid into 0.1% (W/V) diethylammonium diethlydithiocarbonate (DDTC) in chloroform. The extract is evaporated, treated with nitric acid, diluted volumetrically and an aliquot is sampled to measure bismuth recovery. Bismuth is further purified by successive precipitations as hydroxides and then as the oxychloride in the presence of additional bismuth carrier (M1).

b. Analagous to a, but all carrier bismuth is added following decomposition, extraction is carried out from 4M hydrochloric acid into 1% DDTC, and the oxychloride is redissolved following beta-counting for the recovery measurement.

c. Bismuth and lead are extracted with DDTC into xylene from 1M hydrochloric acid containing ascorbic acid and a small amount of diethylenetraminepentaacetic acid. The extract (~6 mL) is evaporated in a planchet for β-counting.

d. Polonium is removed by passing the 10M HCl solution through an anion exchange column (1x2, Cl^-). AAS of an eluate aliquot is used to measure lead recovery. Following a measured ^{210}Po ingrowth period (>4 months), a ^{209}Po tracer/internal standard is added and polonium is spontaneously deposited on a silver disc (1.5M HCl) for alpha spectrometry measurements.

3 a. Twelve CRM aliquots interspersed with samples had an RSD of 2.4% for the calibration factor.

b. Recovery of extracted CRM aliquots was ~99.9% relative to evaporated aliquots.

c. Reproducible recovery assumed (~90%; CRM aliquots plus silica were carried through extraction for calibration.

4 RBZ.44 is an activity-certified solution CRM of $^{210}Pb/^{210}Bi/^{210}Po$ produced by Amersham Corp.

a. Refers to a volumetrically-diluted solution of RBZ.44 (50/8/54) distributed by CCRMP.

b. The ^{209}Po solution used as an internal standard was standardized against the ^{226}Ra CRM by alpha spectrometry measurements of evaporated aliquots.

SUMMARY OF GAMMA-RAY METHODOLOGIES

Table A3 - Summary of gamma-ray methodologies

Set	Sample aliquots (g)	Source geometry (diam x thickness, cm x cm)	Detector[1]	Calibration SRM[2]	Calibration methodology	Absorption correction[3]	References cited
1b	1.2-8	5.7 mL Al cap, mylar face (3 x 0.8)	HPGe, planar (1000 mm^2 x 5 mm)	RBZ.44 (a)	CRM aliquots absorbed on SiO_2 and mineral matrices	a	M8, M11
2b	31-65	50 mL, 25 mL thin plastic vials (5.1 x 2.5; 5.1 x 1.3)	Ge (Li) coaxial (17% efficient)	RBZ.44	CRM solution aliquots	b	M9
4	5	pressed Al foil enclosed discs (5 x 0.15)	HPGe; 3 x 3" NaI	RBZ.44 (a) to standardize ^{210}Pb solution used	RM additions to source	n.a.	
8	5-112	90 mL Al cans	HPGe, planar (2000 mm^2 x 16 mm)	RBZ.44	CRM aliquots absorbed on mineral, and chemical matrices	a	M8
9b	10	10 cm diam plastic petric dish	HPGe, planar (1000 mm^2 x 10 mm)	secular equil. uranium-bearing materials	measurement of uranium-bearing secular equil. materials	c	
10	1-30	PVC cylinder, 2 mm thick face (8 x 1)	HPGe (PGT IGC-13)	RBZ.44	standard additions to source: CRM aliquots absorbed on IX resin, blended into sample	n.a.	M10

1. HPGe: 'intrinsic' high-purity germanium crystal; Ge(Li): lithium-doped germanium crystal.
2. RBZ.44 is a certified solution CRM of $^{210}Pb/^{210}Bi/^{210}Po$.
 a. Refers to a volumetrically diluted solution of RBZ.44 solution #50/8/54 distributed by CCRMP.
3. Correction for different sample-source and calibration source self-absorption of 46.5 keV photons:
 a. Photopeak intensities multiplied by $-\ln(T/T_o)/(1-T/T_o)$, where T and T_o are the transmitted 46.5 keV photopeak intensities (less sample contribution) from a ^{210}Pb 'point' source through the sample and empty container respectively.
 b. Photopeak intensities multiplied by $\mu'm/[1-\exp(\mu'm)]$, where $\mu' = \mu t/V$ and μ, t and V are respectively the mass attenuation coefficient (cm^2/g), thickness, and volume of the sample. The value of μ for the sample is estimated from tabulated elemental photon cross-sections, and published composition data.
 c. Relative sample self-attenuation factors derived from transmitted intensities from ^{133}Ba and ^{241}Am sources (81 and 59.5 keV).

METHODOLOGY REFERENCES

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CALIBRATION CERTIFIED REFERENCE MATERIAL DISTRIBUTED BY CCRMP

Source material

Amersham International Corporation product code RBZ.44 solution number 50/8/54, sealed in ampoule. Certified at 1200 GMT, 1 May 1980 (certificate P18537), as 189 kBq ^{210}Pb. The overall uncertainty is stated as ±2.4%, with a 3σ random component of 0.6% and a 1.8% systematic uncertainty. The ^{210}Bi/^{210}Pb activity ratio was stated as 1.0006. The ^{210}Po/^{210}Pb activity ratio was stated as 0.9559 at the certification time, rising to a theoretical maximum of 1.0179. There is no guarantee of all ^{210}Po remaining in solution. The solution was 5.3303 g containing 2 M nitric acid and 100 μg/mL of each Pb and Bi.

Dilution description

A diluent solution containing 0.18 M nitric acid, and 100 μg per mL of lead, and 99 μg per mL of bismuth was prepared from an atomic absorption standard solution of lead in 1% nitric acid, high-purity bismuth metal (6-9 s) dissolved in nitric acid, and reagent-grade nitric acid. The source material was transferred quantitatively to a 100 mL volumetric flask by twelve successive rinsings of the vial with the diluent. This solution was diluted to the mark with the diluent and mixed thoroughly. After three days, 14.98 ± 0.02 mL of this stock was transferred to a 1 L volumetric flask, and the solution was diluted to the mark with the diluent and mixed thoroughly. Aliquots of 49.85 ± 0.03 mL of this solution were transferred to 125 mL Nalgene bottles, which were capped and sealed for shipping (83-11-20).

Activity calculation

The calculated activity of ^{210}Pb on 83-12-01 was 25.3 Bq mL^{-1} (684 pCi mL^{-1}), based on the certified activity, a decay period of 3.584 y, a half-life of 22.3 y, and the dilution. The total activity uncertainty was estimated as ±2.8% (3σ = 0.6%, systematic error in activity = 1.8%, and estimated maximum error in dilution = 0.4%).

Matrix

The solution is 0.18 M in nitric acid and contains 100 μg/mL Pb and 99 μg/mL Bi.

APPENDIX B

RADON EMANATION EFFICIENCY OF POWDER CCRMP REFERENCE ORES

Table B1 - Radon emanation efficiency of powder CCRMP reference ores

	Dry powder into air[1]	Dry powder into air[2]	Slurried powder into water[2]
DL-1a	6.1 ± 2.5	3 ± 2	15.8 ± 0.5
BL-4a	7.1 ± 0.9	5 ± 3	18.8 ± 0.3
DH-1a	5.0 ± 0.9	6 ± 3	33.9 ± 0.4
BL-5	2.9 ± 0.6	2 ± 2	6.5 ± 0.2

[1] Measured ^{222}Rn emanation rates cf. production rates from published ^{226}Ra activities.

McCorkell, R.H. "Radon emanation rate studies: interlaboratory standard reference materials and the effects of powdering and pelletizing". CANMET Division Report MRP/MSL 83-34(J). CANMET, Energy, Mines and Resources Canada; 1984. (Submitted to CIM Bulletin).

[2] Dry powder rates from relative ^{214}Bi gamma-ray activity measurements one day and greater than thirty-five days following sealing of powder sample. Rates into water from comparisons of radon emanation rates of slurried ore material to total measured radon activity.

Grasty, R.L. and Dyck, W. "Radioactive equilibrium studies on four Canadian uranium reference ores". Current Research, Part A, Paper 84-1A: 53-56. Geological Survey of Canada, Energy, Mines and Resources Canada; 1984.

SINGLE LABORATORY ACTIVITY VALUES FOR UNCERTIFIED ^{238}U- AND ^{232}TH- DECAY SERIES ISOTOPES

Table B2 - Single laboratory activity values for uncertified ^{238}U- and ^{232}Th-decay series isotopes[1]

Material	Mass (g)	Activity + 95% CI, Bq/g[2,3]				
		^{238}U	^{234}U	^{230}Th	^{232}Th	^{212}Pb (=^{228}Th)
DL-1a	3	1.43 + 0.08	1.40 ± 0.08	1.45 ± 0.13	0.333 ± 0.030	0.337 ± 0.008
		(.035, .08, 4)	(.023, .08, 4)	(.13, .13, 4)	(.012, .030, 4)	(.005, .007, 4)
	0.5	1.43 ± .08	1.41 ± 0.08	1.43 ± 0.12	0.344 ± 0.030	0.359 ± 0.026
		(.035, .08, 4)	(.023, .08, 4)	(.094, .12, 4)	(.024, .030, 4)	(.016, .026, 4)
BL-4a	0.5	15.7 ± 0.3	15.2 ± 0.3	15.5 ± 0.7	0.083 ± 0.011	-
		(.46, .83, 8)	(.28, .83, 8)	(.65, .96, 8)	(.012, .006, 5)	
DH-1a	0.5	30.7 ± 1.3	29.5 ± 1.2	32.2 ± 2.1	4.02 ± 0.28	3.89 ± 0.22
		(.96, 1.70, 7)	(.84, 1.65, 7)	(1.37, 2.78, 7)	(0.26, 0.37, 7)	(0.12, 0.22, 4)

1 Results submitted by Laboratory 5 (see Appendix A). Uranium, thorium, and lead are separated by anion exchange and solvent extraction procedures. ^{232}U and ^{228}Th are used as yield tracers. Alpha particle spectrometry measurements on evaporated aliquots are used to determined ^{238}U, ^{234}Th, ^{230}Th. Gamma-ray spectrometry of unspiked samples is used to determine ^{228}Th from the ^{239}keV photopeak due to ^{212}Pb.

2 Activities are the mean of n determinations. Uncertainties are $2\sigma/\sqrt{n}$ where 2σ is the estimated precision of a single measurement provided by Laboratory 5. The provided values, σ, generally exceed the standard deviations of individuals from the mean, s. Values of s, σ and n respectively are shown in brackets below the mean activities.

3 Activities of ^{238}U and ^{232}Th computed from the certified concentrations of uranium and thorium and specific activities of 123.46 and 40.4 Bq g^{-1}/% respectively are 1.432 ± 0.037 and 0.307 ± 0.016 (DL-1a); 15.41 ± 0.09 and unknown (BL-4a); and 32.46 ± 0.04 and 3.68 ± 0.13 (DH-1a).