DEVELOPMENT OF BC CSR ANALYTICAL METHOD FOR SOLUBLE BARIUM

PHASE 3: INTERLABORATORY TESTING OF THE ANALYTICAL METHODS FOR SOLUBLE BARIUM AND BC SALM BARIUM

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1.0 INTRODUCTION

The BC CSR soluble barium method development project was conducted in three stages:

- Phase 1: Evaluation of Viable Soluble Barium Analytical Methods
- Phase 2: Development, Optimization and Ruggedness Testing of a BC Regulatory Analytical Method for Soluble Barium
- Phase 3: Interlaboratory Testing of the BC Regulatory Analytical Method for Soluble Barium

Based on the Phase 1 and 2 investigations, the Barite-Barium Issues Committee and the BCLQAAC Barite Task Group agreed that the proposed BC Soluble Barium analytical method was an environmentally relevant method for soluble barium, capable of quantifying soluble barium in coarse and fine soils over a wide range of concentrations, while providing limited recovery of barite barium. It was therefore recommended that interlaboratory testing proceed in Phase 3 to evaluate the ruggedness of the method.

Total barium methods were also evaluated in Phase 1 and 2 work. Phase 1 and 2 investigations determined that the total acid digest methods of EPA 3050B and BC SALM proved to be unreliable measures of total barium concentrations, particularly in fine soil types. Poor recoveries were demonstrated at barium contaminant concentrations that are likely typical of many barite field sites. The EPA 3050B method proved considerably more aggressive than the BC SALM method, but neither method demonstrated a clear concentration ceiling below which quantitatively accurate total barium results could be achieved. Additionally, Phase 2 work demonstrated that even small differences in laboratory methods can have significant impacts on strong acid leachable barium results. Recovery of barium in the BC SALM method is dependant on laboratory method variations in acid digest volumes, acid strength and sample size. The dependency of barium on these variables may not be identified during performance based validations of methods unless barite soils are specifically addressed.

However, although it does not generate quantitative total barium results, the BC SALM method is consistently much more aggressive than the calcium chloride method, and is considered an appropriate method to conservatively estimate levels of environmentally available metals. BC SALM produces more conservative (higher) barium measures than the calcium chloride method, but less conservative (lower) barium measures than 3050B or fusion techniques. Since the BC SALM barium will likely remain as the laboratory method of choice for quantifying "total" soil barium for BC CSR Schedule 5, the Barite-Barium Issues Committee and the BCLQAAC Barite Task Group recommended that these critical variables in laboratory methodology be identified and the BC SALM method be revised to reduce differences in laboratory methodology. The Phase 3 interlaboratory study included analysis of strong acid leachable barium in field and spiked soils by a proposed new draft of the BC SALM method that better defines several key variables important to barium analysis [For a copy of the draft method, refer to the 2nd report from this round robin pertaining to non-barium metals, "Report on Results of 2007 Interlaboratory Study to Re-establish Data Quality Objectives for BCMOE Strong Acid Leachable Metals (SALM) in Soil Method"].

2.0 PHASE 3 OUTLINE AND OBJECTIVES

Phase 3 of the project included 2 primary objectives:

3a. Interlaboratory Testing of the candidate BC Soluble Barium Method.
3b. Interlaboratory Testing of a proposed revision to the BC SALM Method.

Although the primary need for phase 3 was the evaluation of the SALM and $CaCl_2$ methods for barium, Phase 3 also provided a good opportunity to update the SALM DQOs for soil CRMs. The SALM method (Version 1.0) specifies that NIST 2711 and CANMET TILL-1 must be used for validation of the method. However, stocks of NIST 2711 are virtually depleted, and will cease to be available in less than a year. In addition, some of the values in the current DQOs (e.g. for Sb) were derived from the manufacturers' certified values alone. In some instances these manufacturers' certified values are not representative of the actual method performance. Furthermore, because the BCLQAAC Barite Task Group has recommended that certain key variables within the SALM reference method be better defined, this round robin presented an opportunity to establish DQOs for the proposed refined version of the method. The new DQOs generated by this round robin will be indicative of the anticipated refined version of the method for all commonly analyzed metals, including barium. Therefore, three certified reference materials were also included for analysis of metals of interest for the CSR using the proposed revised BC SALM method.

The Phase 3 study design is summarized as follows:

- 2 analytical methods:
    - Soluble barium extraction using 1.0 M $CaCl_2$
    - Total barium method BC SALM using the revised reference method exactly as written.
- 7 soils:
    - 2 field soils
        - one background site
        - one barite site
    - 2 spiked field soils
        - Sand spiked with soluble barium chloride
        - Sand spiked with barite
    - 3 certified reference materials (CRMs)
- 8 participating laboratories

The soils selected and prepared for the round robin were designed to provide a range of soil types and concentrations of soluble and insoluble barium at relevant concentrations. Barite levels assessed included background levels, as well as levels representative of highly contaminated barite and non-barite barium sites.

This report documents Phase 3 of the project for the stated objectives 3a and 3b specific for barium only. The interlaboratory study for developing new DQOs for the full suite of metals using the proposed revision of the BC SALM method is reported under separate cover.

The laboratories that participated in the study are listed in Appendix 2.

3.0 EXPERIMENTAL METHODOLOGY

3.1 PREPARATION OF TEST SOILS

Three field soils were used for the barium round robin study. Two soils, including a fine textured clay and a coarse sand, were collected from northeastern BC sites as background samples and have likely not been exposed to industrial contaminants. The clay and sand were collected and supplied by Newalta Inc. and were received at Bodycote Testing Group (BTG, formerly Norwest Labs), Edmonton AB on Feb 7, 2007. Note that the sand and clay described here are not the same soils used in the Phase 1 and 2 investigations, due to limited availability. The barite soil (CNRL #3) was a sandy loam

subsoil collected by Northern Envirosearch Inc. from a northeastern BC site known to have been historically associated with drilling waste disposal. The CNRL#3 subsoil was received at BTG Edmonton on October 30, 2006.

The three native soils were prepared by drying at 30℃, then disaggregating to <2 mm (but were not pulverized or sieved). These soils were characterized extensively for physical and chemical parameters (presented in Appendix 1). Key characteristics of the three soils that are most pertinent to barium methods are provided in Table 1.

Table 1. Primary Characteristics of Phase 3 Soils

Parameter Name	Units	Sand	Clay	CNRL#3
Texture	%	Sandy Clay Loam	Clay Loam	Sandy Loam
Sand	%	53	32	68
Silt	%	19	32	20
Clay	%	28	36	13
CEC	meq/100g	15.6	14.6	10.3
Barium by Fusion	mg/kg	515	634	7700
Barium (EPA 3050B)	mg/kg	161	300	5760
Barium (BC SALM)	mg/kg	144	139	647
BC Soluble Barium	mg/kg	63	14.1	52
Sulfate-S	mg/kg	11.5	566	199

Two spiked field soils were prepared by addition of barium sulfate or barium chloride to the sand. Sand was spiked with a supply of barite (Canamara United Supply, provided by Newalta) commonly used in drilling muds. An aliquot of sand was also spiked with laboratory grade barium chloride dihydrate. Both spiked soils were prepared by addition of chemical directly to the dried and disaggregated sand at the required target concentration (10,000 mg/kg as barium). The barium background levels in these soils are given in Table 1. The spiked dry soils were mixed using end-over-end rotation overnight. The soils were then hydrated with deionized water to achieve a saturated paste, in order to allow for soil chemical and physical interactions to occur. The hydrated soils were allowed to equilibrate for 24 hours, then dried at 30℃. The dried soils were disaggregated to < 2mm, then after analytical confirmation of target concentrations by the soluble barium and BC SALM methods, were separated into ten subsamples contained in EPA certified glass jars. Treated soils were stored at room temperature until shipment to participating labs.

The spiked barium samples were assigned the following sample names:

BTG-1 Background Field Clay
BTG-2 Barite Site CNRL#3
BTG-3 Barium Sulfate Spiked Sand (low solubility barium)
BTG-4 Barium Chloride Spiked Sand (high solubility barium)

Three certified reference materials were purchased for the interlaboratory study from the National Research Council of Canada (NRC): PACS-2, TILL 1 and TILL 3.

On Friday the 30th of March, 2007 each participating laboratory was sent the four spiked barium soils, one 250 gram bottle of NRC PACS-2 and one 100 gram bottle each of CCRMP TILL-1 & TILL-3. Each participant was instructed to analyze the materials as outlined in the INSTRUCTION sheets attached

using the proposed soluble barium method on the barium samples, and using the proposed revised BC SALM method on all seven samples (Refer to Appendices 3 and 4). Labs were asked to provide completed data sets back to JRD Consulting Company on or before Friday the 20th of April 2007.

All normal safety precautions applicable to the handling of potentially hazardous material were observed during the handling of these samples.

3.2 Chemical Analysis

Laboratories were instructed to conduct the soluble barium and SALM analysis following the draft reference methods exactly as written. This applied to prescribed elements as well as elements that may be open to performance based modification. Data generated by methods other than the reference method were not used when developing targets and confidence intervals for the reference materials.

3.2a BC Soluble Barium

Each participant was asked to analyze the barium soils as follows:

1. Prepare a 1.0 M $CaCl_2$ extraction solution as described in the Reagents section of the draft Soluble Barium method (see Appendix 5);
2. Weigh out triplicate 5.0 g $\pm$ 0.5 g subsamples from each of the sample bottles provided (BTG-1 through BTG-4);
3. Continue processing according to Sample Extraction Procedure steps 1 through 5, and Sample Analysis for Barium, steps 1 and 2 of the draft Soluble Barium method.

The detailed instructions provided to participants are provided in Appendix 6.

3.2b Revised BC SALM

Each participant was asked to analyze the barium soils and the three reference materials as follows:

1. Weigh out triplicate 1.00 - 1.25 gram sub-samples from each of the sample bottles provided;
2. Add 5.0 $\pm$ 0.1 mL of HCl and 5 $\pm$ 0.1 mL of HNO_3 to each of the sub-samples;
3. Continue processing according to Section d) Sample Digestion Procedure steps 1 through 8 of the proposed revised BC SALM method (Version 2.0 draft A).

The BC SALM method is a performance-based method. Reference conditions are specified, and known critical elements are prescribed, but labs may otherwise make changes to the method where equivalence is demonstrated. However, the effects of changes to digestion variables on recoveries of barium are more pronounced than for most other metals. Phase 1 and 2 work recognized that the sample size, acid volume and acid strength used in the BC SALM method had a direct influence on the recovery of barium from soils. It was also recognized that these variables were not clearly defined in the Version 1.0 reference method, and that variations in performance-based methods between labs could result in a high degree of variability in analytical results for barium by BC SALM. Therefore, the BC SALM method (Version 2) that the participating laboratories were instructed to follow was revised for several key variables as follows:

1. The weight of sample was specified to be 1.00 – 1.25, instead of the original specification of a minimum of 1.00 g to be digested.
2. The acid volume was changed from a minimum of 2.5 mL of HCl and 2.5 mL of HNO_3, to 5.0 mL of HCl and 5.0 mL of HNO_3

3. The concentrated acid to dry soil ratio to be used was specified to be between 8:1 and 10:1, where the original version indicated a minimum acid to sample ratio must be 5:1.
4. The method clarified that the addition of water to the soil:acid mixture is not a component of the reference method.
5. The revised method specifies that the digestion vessel must be covered with a reflux cap to prevent evaporation and to facilitate effective reflux of the acid during digestion.

Details of the influence of each of these key elements and the reasons for revising the BC SALM are described in the BCLQAAC Barite Task Group Phase 2 report (Draft Version: 05 June, 2007).

Participating laboratories were asked to analyze the resulting extracts by the most sensitive instrumental means available to them.

Each lab was asked to submit a total of 3 data sets (triplicate analyses for each of the three reference materials). Participants were also asked to indicate whether or not selected key elements of the BC Soluble Barium and BC SALM reference methods were followed.

3.4 Data Management

Eight data sets were received by JRD Consulting Company for compilation as a "blind" data set so that laboratory anonymity would be maintained. Data tables were then forwarded to Bodycote for statistical analysis and reporting.

Data sets were reviewed to ensure that participants followed the reference method as written. The data sets were subjected to a Grubb's test for outliers (Barnet, 1994) carried out at 95% confidence. This test was performed on pooled results and on pooled averages of each set of replicates within a given lab's data set. Summary statistics were done between and within lab results for each sample.

4.0 RESULTS AND DISCUSSION

A complete set of all data sets received is included in Appendix 3 and 4.

4.1 BC Soluble Barium

There were no indications from any of the labs that the BC Soluble Barium method was not followed precisely as instructed. Labs used centrifugation or filtration by paper or membrane filter for clarification. Either ICP-OES or ICP-MS were used by each of the eight labs. All labs performed a final dilution of the extract by 10 to 40 times to accommodate the upper linear range of instrument requirements for barium, and to reduce matrix effects due to the high salt content of the extracts.

Tables 1 to 5 present summaries of BC Soluble Barium results and statistics for BTG-1 to 4. Grubb's test resulted in exclusion of Lab 07 for samples BTG-2 and BTG-3 using pooled averages of each set of replicates within a lab data set. Results from Lab 07 were approximately 5 times lower than the mean results from all other labs for samples BTG-1, BTG-2, and BTG-3. The Grubb's test did not highlight the Lab 07 result for BTG-1 as an outlier because of higher interlab variability near the detection limit of the method. However, because of the consistent 5 fold difference from the interlab means, we feel there is a high probability that the same error or inconsistency occurred with the Lab 07 results for each of the BTG-1, BTG-2, and BTG-3 samples (Note: The Grubb's test is less able to

differentiate low outliers than high outliers. Even a result of zero for BTG-1 would not have been flagged as a statistical outlier by the Grubbs test). Therefore, we also removed the Lab 07 result for BTG-1 as an outlier. After the Lab 07 result for BTG-1 was removed, the Lab 04 result for BTG-1 was highlighted as a statistical outlier, and so was also removed.

The within lab variability of the three replicate tests for each sample was exceptionally low for the BC Soluble Barium method, as indicated by the percent relative standard deviation (%RSD). The RSDs ranged from 0% to 7.1% for BTG-1, 0.6% to 6.7% for BTG-2, 0.7% to 9.7% for BTG-3 and 0.9% to 14.8% for BTG-4. There was no one lab that was consistently higher in variability.

With the exception of outlier data, between lab variability was reasonable for all samples. The percent relative standard deviation, calculated by computing the standard deviation of the mean barium concentration across labs, ranged from 9.8% to 54.2% before outlier removal. Removal of the outlying data in BTG-1, BTG-2 and BTG-3 lowered the %RSD considerably, such that the interlab precision ranged from to 9.8% to 21.1%, which we find acceptable. Lab 07 was consistently lowest for Samples BTG-1 to -3, and Lab 04 was consistently the highest for the same samples, suggesting that there may have been some sample processing difference from the method or remaining labs, or a possible instrument bias.

Table 2. Statistical Summary of Soluble Barium by Mean Data per Lab

Between Lab Summary	BTG-1		BTG-2		BTG-3		BTG-4
	All Data	Without Labs 4&7	All Data	Without Lab 7	All Data	Without Lab 7	All Data
n	8	6	8	7	8	7	8
Min	2.0	9.2	13.3	56.4	34.3	116.7	7493
Max	27.0	16.0	82.3	82.3	177.0	177.0	10333
Grand Mean	13.1	12.7	59.3	65.9	131.1	144.9	8776
Stdev (Between Lab)	7.11	2.67	20.15	8.44	43.13	19.7	858
% RSD (Between Lab)	54.2	21.1	34.0	12.8	32.9	13.6	9.8
Median	12.8	12.8	63.2	64.1	143.1	147.2	8885
Grand Mean Absolute Deviation	4.84	2.28	12.21	5.92	28.67	14.7	561.9
Relative Mean Deviation (Between Lab)	0.37	0.18	0.21	0.09	0.22	0.10	0.064

Table 3. BC Soluble Barium BTG-1

		BTG-1 Soluble Barium (mg/kg)							
		Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8
Within Lab	Result 1	15.9	11.7	9.8	27.0	9.2	13.2	2.0	15.7
	Result 2	14.1	11.9	10.7	27.0	9.4	13.2	2.0	15.6
	Result 3	16.0	11.2	10.2	27.0	9.2	15.2	2.0	15.6
	Mean (Within Lab)	15.3	11.6	10.2	27.0	9.3	13.9	2.0	15.6
	Std Dev (Within Lab)	1.08	0.32	0.45	0.00	0.12	1.15	0.00	0.03
	% RSD (Within Lab)	7.1	2.8	4.4	0.0	1.2	8.3	0.0	0.2
	Mean Absolute Deviation (Within Lab)	0.83	0.24	0.31	0.00	0.09	0.89	0.00	0.02
	Relative Mean Deviation (Within Lab)	0.054	0.021	0.030	0.000	0.010	0.064	0.000	0.001
Between Lab		**All Data**	**Without Labs 4&7**						
	Min	2.0	9.2						
	Max	27.0	16.0						
	Grand Mean	13.1	12.7						
	Stdev (Between Lab)	7.11	2.67						
	% RSD (Between Lab)	54.2	21.1						
	Median	12.8	12.8						
	Grand Mean Absolute Deviation	4.84	2.28						
	Relative Mean Deviation (Between Lab)	0.37	0.18						

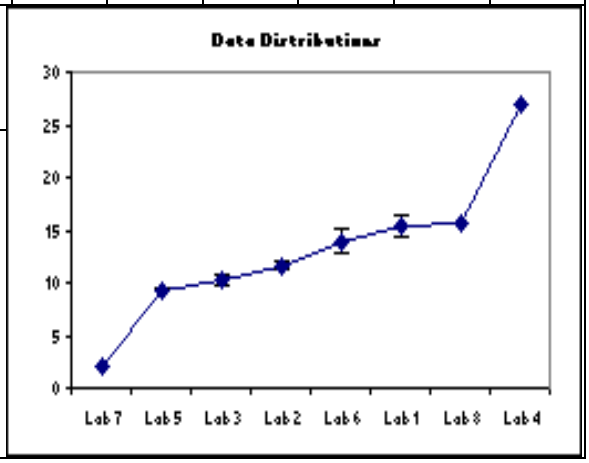


Table 4. BC Soluble Barium BTG-2

	BTG-2 Soluble Barium (mg/kg)							
Within Lab	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8
Result 1	70.4	61.9	58.2	83.0	66.2	63.2	14.0	69.7
Result 2	61.6	63.0	55.6	83.0	61.7	60.8	13.0	70.1
Result 3	65.3	61.8	55.5	81.0	64.4	56.4	13.0	70.5
Mean (Within Lab)	65.8	62.2	56.4	82.3	64.1	60.1	13.3	70.1
Std Dev (Within Lab)	4.42	0.65	1.53	1.15	2.26	3.45	0.58	0.40
% RSD (Within Lab)	6.7	1.1	2.7	1.4	3.5	5.7	4.3	0.6
Mean Absolute Deviation (Within Lab)	3.09	0.50	1.18	0.89	1.60	2.49	0.44	0.27
Relative Mean Deviation (Within Lab)	0.047	0.008	0.021	0.011	0.025	0.041	0.033	0.004

Between Labs	**All Data**	**Without Lab 7**
Min	13.3	56.4
Max	82.3	82.3
Grand Mean	59.3	65.9
Stdev (Between Lab)	20.15	8.44
% RSD (Between Lab)	34.0	12.8
Median	63.2	64.1
Grand Mean Absolute Deviation	12.21	5.92
Relative Mean Deviation (Between Lab)	0.21	0.09

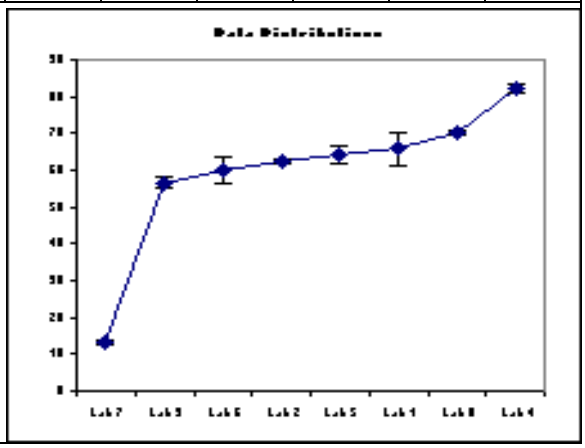


Table 5. BC Soluble Barium BTG-3

	BTG-3 Soluble Barium (mg/kg)							
Within Lab	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8
Result 1	145.0	150.5	120.0	176.0	163.0	114.0	36.0	140.1
Result 2	159.0	151.1	116.0	179.0	147.0	131.0	34.0	138.3
Result 3	151.0	139.9	114.0	176.0	156.0	138.0	33.0	138.9
Mean (Within Lab)	151.7	147.2	116.7	177.0	155.3	127.7	34.3	139.1
Std Dev (Within Lab)	7.02	6.30	3.06	1.73	8.02	12.34	1.53	0.94
% RSD (Within Lab)	4.6	4.3	2.6	1.0	5.2	9.7	4.5	0.7
Mean Absolute Deviation (Within Lab)	4.89	4.84	2.22	1.33	5.56	9.11	1.11	0.68
Relative Mean Deviation (Within Lab)	0.032	0.033	0.019	0.008	0.036	0.071	0.032	0.005

Between Labs	**All Data**	**Without Lab 7**
Min	34.3	116.7
Max	177.0	177.0
Grand Mean	131.12	144.9
Stdev (Between Lab)	43.13	19.7
% RSD (Between Lab)	32.9	13.6
Median	143.1	147.2
Grand Mean Absolute Deviation	28.67	14.7
Relative Mean Deviation (Between Lab)	0.22	0.10

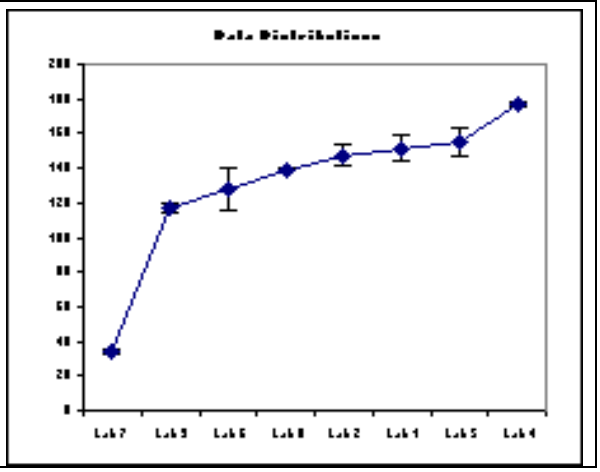
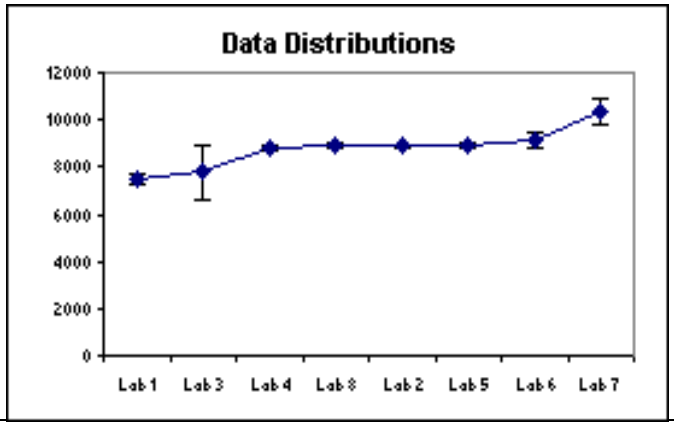


Table 6. BC Soluble Barium BTG-4

	BTG-4 Soluble Barium (mg/kg)							
Within Lab	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8
Result 1	7300	8965	6600	8760	8830	8700	10000	8987
Result 2	7460	8898	8900	8870	9080	9290	10000	8858
Result 3	7720	8805	7940	8690	8830	9340	11000	8797
Mean (Within Lab)	7493	8889	7813	8773	8913	9110	10333	8881
Std Dev (Within Lab)	212	80	1155	91	144	356	577	97
% RSD (Within Lab)	2.83	0.90	14.79	1.03	1.62	3.91	5.59	1.09
Mean Absolute Deviation (Within Lab)	151	56	809	64	111	273	444	71
Relative Mean Deviation (Within Lab)	0.020	0.006	0.104	0.007	0.012	0.030	0.043	0.008

Between Labs	All Data
Min	7493
Max	10333
Grand Mean	8776
Stdev (Between Lab)	858
% RSD (Between Lab)	9.8
Median	8885
Grand Mean Absolute Deviation	561.9
Relative Mean Deviation (Between Lab)	0.064



4.1 BC SALM Barium

There were no indications from any of the labs that the BC SALM revised method was not followed precisely as instructed, with one exception. Lab 04 included this description in their BC SALM data set:

> "Samples being analyzed by ICPMS require a chloride reduction step. 1 mL of filtered digest is pipetted into a digestion tube which has been pre-rinsed with 10% HNO3. 2 mL concentrated HNO3 is added and the digest tube is placed in a 90 ± 5º C hotblock for approximately 45 minutes with open lid until the sample is almost dry. Samples are removed from the hotblock, diluted to 30 mL with deionized water and submitted for analysis. A study is on file which shows this procedure does not affect the ability to achieve the DQO as outlined in Method 8."

Labs used centrifugation or filtration by paper or membrane filter for clarification. Either ICP-OES or ICP-MS were used by each of the eight labs. All labs performed a final dilution of the extract by 10 to 200 times to accommodate the upper linear range of instrument requirements for barium, and to reduce matrix effects due to the high acid content of the digests.

Tables 7 to 11 present summaries of BC SALM Barium results and statistics for BTG 1 to 4. Grubb's test for outliers resulted in exclusion of Lab 04 for samples BTG-2 and BTG-3 using pooled averages of each set of replicates within a lab data set. There were no statistically determined outliers for BTG-1 or BTG-4.

Like the BC Soluble Barium method, the within lab variability of the three replicate test results for each sample with individual labs was exceptionally low for the BC SALM method. The RSD ranged from 0.9% to 5.4% for BTG-1, 0.9% to 25.6% for BTG-2, 1.9% to 9.9% for BTG-3 and 0.5% to 11.1% for BTG-4. There was no one lab that was consistently higher in intra-lab variability.

With the exception of outlier data on BTG-2 and -3, between lab variability was reasonable for all samples (Table 7). The percent relative standard deviation, calculated by computing the standard deviation of the mean barium concentration across labs, ranged from 8.3 to 25.7%. Removal of the outlying data in BTG-2 and BTG-3 lowered the RSD considerably, so that the RSD ranged from 8.3% to 15.0%, which we find acceptable. Interlab variability from this round robin represents a vast improvement over what was achieved in the original BC SALM round robin for barium, which achieved RSDs that ranged from 7.7% to 53%, with an average of 31% RSD over 6 samples.

Table 7. Statistical Summary of BC SALM Barium by Mean Data per Lab

	BTG-1	BTG-2		BTG-3		BTG-4
Between Lab	**All Data**	**All Data**	**Without Lab 4**	**All Data**	**Without Lab 4**	**All Data**
Min	199	1640	1640	1983	1983	7957
Max	297	3030	2247	4126	2977	10533
Grand Mean	232	1978	1827	2647	2435	9452
Stdev (Between Lab)	34.73	468	211	680.8	351.8	786
% RSD (Between Lab)	15.0	23.7	11.5	25.7	14.4	8.3
Median	226	1781	1773	2426	2294	9570
Grand Mean Absolute Deviation	26.48	330	156	486	288	559
Relative Mean Deviation (Between Lab)	0.11	0.17	0.09	0.18	0.12	0.059

Lab 04 was consistently highest for all four samples, although their high bias was marginal for BTG-1 and BTG-4. It is possible that nitric acid treatment conducted by Lab 04 subsequent to the BC SALM reference method (v2) may have had an unforeseen and unpredictable affect on barium recoveries.

Table 8. BC SALM Barium BTG-1

	BTG-1 BC SALM Barium (mg/kg)							
	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8
Within Lab	236	204	198	293	279	218	198	249
Result 2	228	196	194	294	255	222	199	236
Result 3	232	203	206	305	254	219	206	236
Mean (Within Lab)	232	201	199	297	263	220	201	240
Std Dev (Within Lab)	3.79	4.09	6.24	6.66	14.15	2.08	4.36	7.51
% RSD (Within Lab)	1.6	2.0	3.1	2.2	5.4	0.9	2.2	3.1
Mean Absolute Deviation (Within Lab)	2.60	3.13	4.58	5.11	10.89	1.56	3.33	5.78
Relative Mean Deviation (Within Lab)	0.011	0.016	0.023	0.017	0.041	0.007	0.017	0.024

Between Lab	
Min	199
Max	297
Grand Mean	232
Stdev (Between Lab)	34.73
% RSD (Between Lab)	15
Median	226
Grand Mean Absolute Deviation	26.48
Relative Mean Deviation (Between Lab)	0.11

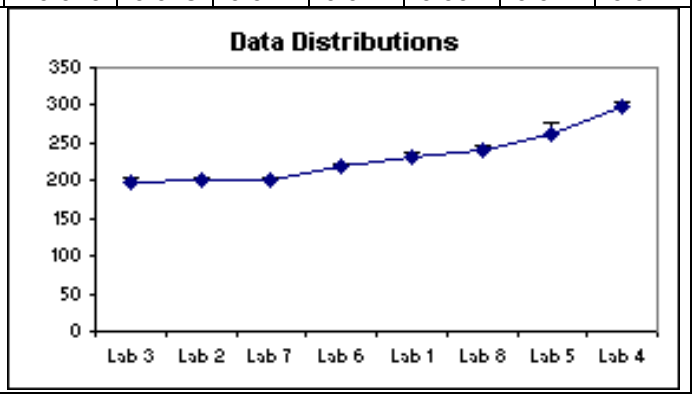


Table 9. BC SALM Barium BTG-2

	BTG-2 BC SALM Barium (mg/kg)							
Within Lab	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8
Result 1	1650	1835	1800	3065	2190	1690	2210	2015
Result 2	1570	1887	1700	3075	2340	1670	1370	1939
Result 3	1700	1596	1870	2950	2210	1660	1570	1904
Mean (Within Lab)	1640	1773	1790	3030	2247	1673	1717	1953
Std Dev (Within Lab)	65.6	155.2	85.4	69.5	81.4	15.3	438.8	56.7
% RSD (Within Lab)	4.0	8.8	4.8	2.3	3.6	0.9	25.6	2.9
Mean Absolute Deviation (Within Lab)	46.7	117.8	60.0	53.3	62.2	11.1	328.9	41.6
Relative Mean Deviation (Within Lab)	0.028	0.066	0.034	0.018	0.028	0.007	0.192	0.021

Between Labs	**All Data**	**Without Lab 4**
Min	1640	1640
Max	3030	2247
Grand Mean	1978	1827
Stdev (Between Lab)	468	211
% RSD (Between Lab)	23.7	11.5
Median	1781	1773
Grand Mean Absolute Deviation	330	156
Relative Mean Deviation (Between Lab)	0.17	0.09

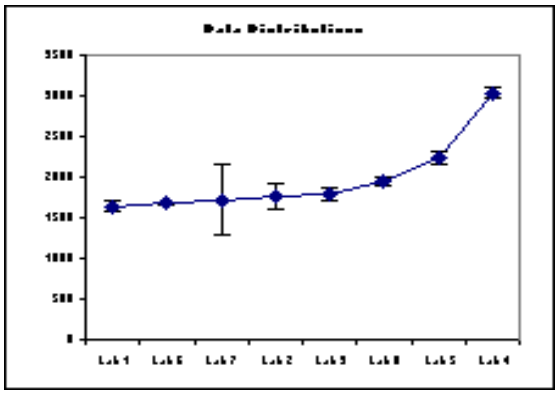


Table 10. BC SALM Barium BTG-3

	BTG-3 BC SALM Barium (mg/kg)							
Within Lab	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8
Result 1	2420	2307	2800	4303	3070	1920	2480	2484
Result 2	2030	2167	2820	3888	3060	1910	2270	2582
Result 3	2070	2408	2720	4188	2800	2120	2100	2606
Mean (Within Lab)	2173	2294	2780	4126	2977	1983	2283	2557
Std Dev (Within Lab)	214.6	121.0	52.9	214.3	153.1	118.5	190.4	64.6
% RSD (Within Lab)	9.9	5.3	1.9	5.2	5.1	6.0	8.3	2.5
Mean Absolute Deviation (Within Lab)	164.4	84.7	40.0	158.9	117.8	91.1	131.1	48.9
Relative Mean Deviation (Within Lab)	0.076	0.037	0.014	0.039	0.040	0.046	0.057	0.019

Between Labs	**All Data**	**Without Lab 4**
Min	1983	1983
Max	4126	2977
Grand Mean	2647	2435
Stdev (Between Lab)	680.8	351.8
% RSD (Between Lab)	25.7	14.4
Median	2426	2294
Grand Mean Absolute Deviation	486	288
Relative Mean Deviation (Between Lab)	0.18	0.12

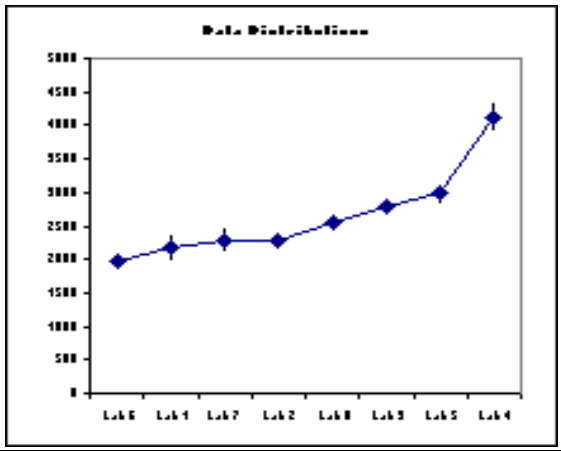
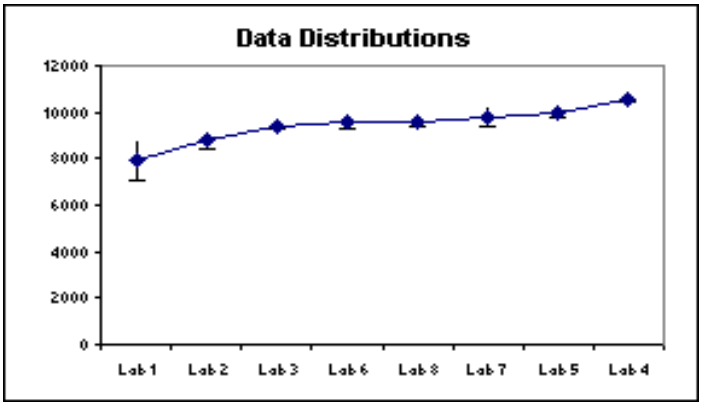


Table 11. BC SALM Barium BTG-4

	BTG-4 BC SALM Barium (mg/kg)							
Within Lab	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8
Result 1	8430	8517	9260	10600	10000	9770	10100	9406
Result 2	8500	8637	9420	10500	10300	9540	9330	9752
Result 3	6940	9203	9450	10500	9740	9340	10000	9612
Mean (Within Lab)	7957	8786	9377	10533	10013	9550	9810	9590
Std Dev (Within Lab)	881	366	102	58	280	215	419	174
% RSD (Within Lab)	11.1	4.2	1.1	0.5	2.8	2.3	4.3	1.8
Mean Absolute Deviation (Within Lab)	678	278	78	44	191	147	320	123
Relative Mean Deviation (Within Lab)	0.085	0.032	0.008	0.004	0.019	0.015	0.033	0.013

Between Labs	
Min	7957
Max	10533
Grand Mean	9452
Stdev (Between Lab)	786
% RSD (Between Lab)	8.3
Median	9570
Grand Mean Absolute Deviation	559
Relative Mean Deviation (Between Lab)	0.059



5.0 CONCLUSIONS

The results of this interlaboratory study indicate that the proposed BC Soluble Barium method is an acceptably rugged method, demonstrating relatively low intra- and inter-laboratory variability. These results were expected, due to the method's simple extraction process combined with the reliability and precision of most ICPOES and ICPMS instrumentation. Therefore, the BCLQAAC Barite Task Group recommends that the province adopt the proposed BC Soluble Barium method as the required methodology for assessment of soluble barium in soils at verifiable barite sites.

This study also demonstrated that the BC SALM method for barium is robust, providing that the revised method instructions (Draft v2) are followed precisely and without modification. Although it is recognized that the BC SALM method does not provide a measure of true total barium, it is capable of demonstrating reproducible quantification of barium with much higher absolute recoveries than would be achieved by the BC soluble barium method, and with results that are likely a conservative estimate of environmentally available barium. Therefore, the BCLQAAC Barite Task Group recommends that the province formally release the BC SALM barium method, Revision 2, as used in this study (or after additional updates as required and endorsed by the BCLQAAC Technical Subcommittee).

For the revised BC SALM method, we recommend to extend the performance based nature of the method, but suggest that testing for equivalence of soils spiked with barite be included as a new requirement for the demonstration of equivalence. We recommend that equivalent results for soluble barium by modified methods be defined as where intra-lab mean results for a given barite soil sample lie within 25% of results generated by the reference method, using inter-lab mean results where

available (25% is two times the average inter-lab standard deviation observed in this study, and thus represents approximately the 95% confidence interval for inter-lab variability).

6.0 REFERENCES

Barnett, 1994, Outliers in Statistical Data (3rd edition), V. Barnett and T. Lewis, Wiley, 1994.

BCMOE, 2001, Strong Acid Leachable Metals (SALM) in Soil, British Columbia Ministry of Environment, Contaminated Sites Regulation (Method 8), June 26, 2001.

Taylor, 1987, Quality Assurance of Chemical Measurements, John Keenan Taylor, Lewis Publishers, 1987.

Appendix 1. Detailed Characterization of Background Soils

Method		Parameter Name	Unit	Detection Limit	Newalta Soils (523805) Phase 3 Sand	Newalta Soils (523805) Phase 3 Clay	CNRL #3 (503905) Phase 3 and Kd Studies #3
Physical and Aggregate Properties	Moisture	Moisture	%	0.1			
	Particle Size Analysis - GS	Texture			**Sandy Clay Loam**	**Clay Loam**	**Sandy Loam**
		Sand	%		53	31.6	67.6
		Silt	%		19	32.4	19.8
		Clay	**%**		**28**	**36**	**12.6**
Salinity	Saturated Paste in General Soil	pH	pH		6.3	7.2	7.4
		EC	dS/m	0.01	0.5	3.59	2.22
		SAR			0.2	0.8	0.2
		% Saturation	%		37	60	42
		Calcium	meq/L	0.01	3.87	31.4	25.2
		Calcium	mg/kg		28.9	375	213
		Magnesium	meq/L	0.02	2.15	28.5	4.13
		Magnesium	mg/kg		9.7	205	21.1
		Sodium	meq/L	0.04	0.29	4.2	0.79
		Sodium	mg/kg		2	57	8
		Potassium	meq/L	0.03	0.09	0.56	0.58
		Potassium	mg/kg		1	13	10
		Chloride	meq/L	0.03	0.25	0.21	5.1
		Chloride	mg/kg		3	4	76
		Sulfate-S	meq/L	0.06	1.92	59.4	29.5
		Sulfate-S	**mg/kg**		**11.5**	**566**	**199**
		TGR	T/ac		<0.1	<0.1	<0.1
Barium	Total Barium Methods	**Fusion-XRF or ICP**	**mg/kg**	**0.1**	**515**	**634**	**7700**
		EPA3050B	**mg/kg**	**0.1**	**161**	**300**	**5760**
		BCSALM*	**mg/kg**	**0.1**	**144**	**139**	**647**
	0.1 M $CaCl_2$ Extractable Barium	**AENV**	**mg/kg**	**0.05**	**27**	**2.6**	**18.4**
	1.0 M $CaCl_2$ Soluble Barium	**BC**	**mg/kg**	**0.05**	**63**	**14.1**	**52**

Appendix 1. Detailed Characterization of Background Soils (cont'd).

				Newalta Soils (523805) Phase 3		CNRL #3 (503905) Phase 3 and Kd Studies
Method	**Parameter Name**	**Unit**	**Detection Limit**	**Sand**	**Clay**	**#3**
Cation Exchange Capacity (CEC) for General Soil	Calcium	mg/kg	4	2460	11300	4280
	Magnesium	mg/kg	2	506	969	150
	Potassium	mg/kg	20	100	200	100
	Sodium	mg/kg	12	10	94	20
	Base Saturation	%	1	108	445	224
	Calcium	meq/100g	0.0003	12.3	56.4	21.3
	Magnesium	meq/100g	0.0008	4.16	7.96	1.3
	Sodium	meq/100g	0.003	0.06	0.41	0.088
	Potassium	meq/100g	0.003	0.4	0.4	0.2
	ESP	%	0.2	0.4	2.8	0.85
	TEC	meq/100g	2	17	65	23
	CEC	**meq/100g**		**15.6**	**14.6**	**10.3**
Carbon and Nitrogen in Soil	Organic matter	%	1	1.3	2.7	3
	Carbon	%	0.05	0.67	1.35	1.74
Hot Water Soluble Boron	Boron	ug/g	0.1	0.4	0.8	0.6
Metals Strong Acid Digest (EPA 3050)	Mercury	ug/g	0.01	0.02	0.04	0.02
	Antimony	ug/g	0.2	<0.2	<0.2	<0.2
	Arsenic	ug/g	0.2	11.3	10.9	8.9
	Barium	ug/g	1	161	300	5760
	Beryllium	ug/g	0.1	0.9	0.8	0.5
	Cadmium	ug/g	0.01	0.16	0.52	0.13
	Chromium	ug/g	0.5	25.8	25.8	12
	Cobalt	ug/g	0.1	8.9	11	6.2
	Copper	ug/g	1	20	26	7
	Lead	ug/g	0.1	10.6	12.4	9.9
	Molybdenum	ug/g	1	2	2	<1
	Nickel	ug/g	0.5	28.1	33.2	29.9
	Selenium	ug/g	0.3	1.2	1	0.4
	Silver	ug/g	0.1	0.1	0.2	<0.1
	Thallium	ug/g	0.05	0.25	0.31	0.08
	Tin	ug/g	1	1	1	<1
	Vanadium	ug/g	0.1	51.5	48.6	24.5
	Zinc	ug/g	1	91	99	61

Appendix 2. Participant Laboratories

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Appendix 3. BC Soluble Barium Results Table

LAB_ID	Sample_ID	Rep.	Soluble Barium mg/kg)	Date_Extracted	Date_Analysed	Weight Extracted	Method Instrument
Lab01	BTG-1	A	15.9	4/16/2007	4/16/2007	5.01	ICP-MS
Lab01	BTG-1	B	14.1	4/16/2007	4/16/2007	5.01	ICP-MS
Lab01	BTG-1	C	16.0	4/16/2007	4/16/2007	5.00	ICP-MS
Lab02	BTG-1	A	11.7	4/11/2007	4/13/2007	5.09	ICP-OES
Lab02	BTG-1	B	11.9	4/11/2007	4/13/2007	5.01	ICP-OES
Lab02	BTG-1	C	11.2	4/11/2007	4/13/2007	5.01	ICP-OES
Lab03	BTG-1	A	9.8	4/18/2007	4/18/2007	5.00	ICP-OES
Lab03	BTG-1	B	10.7	4/18/2007	4/18/2007	5.00	ICP-OES
Lab03	BTG-1	C	10.2	4/18/2007	4/18/2007	5.00	ICP-OES
Lab04	BTG-1	A	27.0	4/12/2007	4/12/2007	5.03	ICP-OES
Lab04	BTG-1	B	27.0	4/12/2007	4/12/2007	5.02	ICP-OES
Lab04	BTG-1	C	27.0	4/12/2007	4/12/2007	5.01	ICP-OES
Lab05	BTG-1	A	9.2	4/16/2007	4/18/2007	5.00	ICPOES
Lab05	BTG-1	B	9.4	4/16/2007	4/18/2007	5.00	ICPOES
Lab05	BTG-1	C	9.2	4/16/2007	4/18/2007	5.00	ICPOES
Lab06	BTG-1	A	13.2	4/3/2007	4/3/2007	5.00	ICP-MS
Lab06	BTG-1	B	13.2	4/3/2007	4/3/2007	5.00	ICP-MS
Lab06	BTG-1	C	15.2	4/3/2007	4/3/2007	5.00	ICP-MS
Lab07	BTG-1	A	2.0	4/17/2007	4/17/2007	5.00	ICP-MS
Lab07	BTG-1	B	2.0	4/17/2007	4/17/2007	5.00	ICP-MS
Lab07	BTG-1	C	2.0	4/17/2007	4/17/2007	5.00	ICP-MS
Lab08	BTG-1	A	15.7	4/19/2007	4/19/2007	5.00	ICP-MS
Lab08	BTG-1	B	15.6	4/19/2007	4/19/2007	5.00	ICP-MS
Lab08	BTG-1	C	15.6	4/19/2007	4/19/2007	5.00	ICP-MS
Lab01	BTG-2	A	70.4	4/16/2007	4/16/2007	5.01	ICP-MS
Lab01	BTG-2	B	61.6	4/16/2007	4/16/2007	5.00	ICP-MS
Lab01	BTG-2	C	65.3	4/16/2007	4/16/2007	5.00	ICP-MS
Lab02	BTG-2	A	61.9	4/11/2007	4/13/2007	5.05	ICP-OES
Lab02	BTG-2	B	63.0	4/11/2007	4/13/2007	5.01	ICP-OES
Lab02	BTG-2	C	61.8	4/11/2007	4/13/2007	5.06	ICP-OES
Lab03	BTG-2	A	58.2	4/18/2007	4/18/2007	5.00	ICP-OES
Lab03	BTG-2	B	55.6	4/18/2007	4/18/2007	5.00	ICP-OES
Lab03	BTG-2	C	55.5	4/18/2007	4/18/2007	5.00	ICP-OES
Lab04	BTG-2	A	83.0	4/12/2007	4/12/2007	5.03	ICP-OES
Lab04	BTG-2	B	83.0	4/12/2007	4/12/2007	5.02	ICP-OES
Lab04	BTG-2	C	81.0	4/12/2007	4/12/2007	5.02	ICP-OES
Lab05	BTG-2	A	66.2	4/16/2007	4/18/2007	5.00	ICPOES
Lab05	BTG-2	B	61.7	4/16/2007	4/18/2007	5.00	ICPOES
Lab05	BTG-2	C	64.4	4/16/2007	4/18/2007	5.00	ICPOES
Lab06	BTG-2	A	63.2	4/3/2007	4/3/2007	5.00	ICP-MS
Lab06	BTG-2	B	60.8	4/3/2007	4/3/2007	5.00	ICP-MS
Lab06	BTG-2	C	56.4	4/3/2007	4/3/2007	5.00	ICP-MS
Lab07	BTG-2	A	14.0	4/17/2007	4/17/2007	5.00	ICP-MS
Lab07	BTG-2	B	13.0	4/17/2007	4/17/2007	5.00	ICP-MS
Lab07	BTG-2	C	13.0	4/17/2007	4/17/2007	5.00	ICP-MS

Appendix 3. BC Soluble Barium Results Table (cont'd).

LAB_ID	Sample_ID	Rep.	Soluble Barium mg/kg)	Date_Extracted	Date_Analysed	Weight Extracted	Method Instrument
Lab08	BTG-2	A	69.7	4/19/2007	4/19/2007	5.00	ICP-MS
Lab08	BTG-2	B	70.1	4/19/2007	4/19/2007	5.00	ICP-MS
Lab08	BTG-2	C	70.5	4/19/2007	4/19/2007	5.00	ICP-MS
Lab01	BTG-3	A	145.0	4/16/2007	4/16/2007	5.01	ICP-MS
Lab01	BTG-3	B	159.0	4/16/2007	4/16/2007	5.01	ICP-MS
Lab01	BTG-3	C	151.0	4/16/2007	4/16/2007	5.00	ICP-MS
Lab02	BTG-3	A	150.5	4/11/2007	4/13/2007	5.10	ICP-OES
Lab02	BTG-3	B	151.1	4/11/2007	4/13/2007	5.05	ICP-OES
Lab02	BTG-3	C	139.9	4/11/2007	4/13/2007	5.05	ICP-OES
Lab03	BTG-3	A	120.0	4/18/2007	4/18/2007	5.00	ICP-OES
Lab03	BTG-3	B	116.0	4/18/2007	4/18/2007	5.00	ICP-OES
Lab03	BTG-3	C	114.0	4/18/2007	4/18/2007	5.00	ICP-OES
Lab04	BTG-3	A	176.0	4/12/2007	4/12/2007	5.02	ICP-OES
Lab04	BTG-3	B	179.0	4/12/2007	4/12/2007	5.00	ICP-OES
Lab04	BTG-3	C	176.0	4/12/2007	4/12/2007	5.02	ICP-OES
Lab05	BTG-3	A	163.0	4/16/2007	4/18/2007	5.00	ICPOES
Lab05	BTG-3	B	147.0	4/16/2007	4/18/2007	5.00	ICPOES
Lab05	BTG-3	C	156.0	4/16/2007	4/18/2007	5.00	ICPOES
Lab06	BTG-3	A	114.0	4/3/2007	4/3/2007	5.00	ICP-MS
Lab06	BTG-3	B	131.0	4/3/2007	4/3/2007	5.00	ICP-MS
Lab06	BTG-3	C	138.0	4/3/2007	4/3/2007	5.00	ICP-MS
Lab07	BTG-3	A	36.0	4/17/2007	4/17/2007	5.00	ICP-MS
Lab07	BTG-3	B	34.0	4/17/2007	4/17/2007	5.00	ICP-MS
Lab07	BTG-3	C	33.0	4/17/2007	4/17/2007	5.00	ICP-MS
Lab08	BTG-3	A	140.1	4/19/2007	4/19/2007	5.00	ICP-MS
Lab08	BTG-3	B	138.3	4/19/2007	4/19/2007	5.00	ICP-MS
Lab08	BTG-3	C	138.9	4/19/2007	4/19/2007	5.00	ICP-MS
Lab01	BTG-4	A	7300.0	4/16/2007	4/16/2007	5.01	ICP-MS
Lab01	BTG-4	B	7460.0	4/16/2007	4/16/2007	5.00	ICP-MS
Lab01	BTG-4	C	7720.0	4/16/2007	4/16/2007	5.00	ICP-MS
Lab02	BTG-4	A	8965.0	4/11/2007	4/13/2007	5.09	ICP-OES
Lab02	BTG-4	B	8898.0	4/11/2007	4/13/2007	5.04	ICP-OES
Lab02	BTG-4	C	8805.0	4/11/2007	4/13/2007	5.07	ICP-OES
Lab03	BTG-4	A	6600.0	4/18/2007	4/18/2007	5.00	ICP-OES
Lab03	BTG-4	B	8900.0	4/18/2007	4/18/2007	5.00	ICP-OES
Lab03	BTG-4	C	7940.0	4/18/2007	4/18/2007	5.00	ICP-OES
Lab04	BTG-4	A	8760.0	4/12/2007	4/12/2007	5.03	ICP-OES
Lab04	BTG-4	B	8870.0	4/12/2007	4/12/2007	5.02	ICP-OES
Lab04	BTG-4	C	8690.0	4/12/2007	4/12/2007	5.01	ICP-OES
Lab05	BTG-4	A	8830.0	4/16/2007	4/18/2007	5.00	ICPOES
Lab05	BTG-4	B	9080.0	4/16/2007	4/18/2007	5.00	ICPOES
Lab05	BTG-4	C	8830.0	4/16/2007	4/18/2007	5.00	ICPOES
Lab06	BTG-4	A	8700.0	4/3/2007	4/3/2007	5.00	ICP-MS
Lab06	BTG-4	B	9290.0	4/3/2007	4/3/2007	5.00	ICP-MS
Lab06	BTG-4	C	9340.0	4/3/2007	4/3/2007	5.00	ICP-MS

Appendix 3. BC Soluble Barium Results Table (cont'd).

LAB_ID	Sample_ID	Rep.	Soluble Barium mg/kg)	Date_Extracted	Date_Analysed	Weight Extracted	Method Instrument
Lab07	BTG-4	A	10000.0	4/17/2007	4/17/2007	5.00	ICP-MS
Lab07	BTG-4	B	10000.0	4/17/2007	4/17/2007	5.00	ICP-MS
Lab07	BTG-4	C	11000.0	4/17/2007	4/17/2007	5.00	ICP-MS
Lab08	BTG-4	A	8987.1	4/19/2007	4/19/2007	5.00	ICP-MS
Lab08	BTG-4	B	8858.5	4/19/2007	4/19/2007	5.00	ICP-MS
Lab08	BTG-4	C	8796.6	4/19/2007	4/19/2007	5.00	ICP-MS

Appendix 4. BC SALM on Barium Spiked Soils Results Table.

LAB ID	Sample ID	Rep.	Result	Date Digested	Date Analysed	Weight Digested	Method Instrument
Lab01	BTG-1	A	236	4/16/2007	4/16/2007	1.00 g	ICP-MS
Lab01	BTG-1	B	228	4/16/2007	4/16/2007	1.01 g	ICP-MS
Lab01	BTG-1	C	232	4/16/2007	4/16/2007	1.01 g	ICP-MS
Lab02	BTG-1	A	204	4/11/2007	4/11/2007	1.00 g	ICP-OES
Lab02	BTG-1	B	196	4/11/2007	4/11/2007	1.00 g	ICP-OES
Lab02	BTG-1	C	203	4/11/2007	4/11/2007	1.00 g	ICP-OES
Lab03	BTG-1	A	198	4/16/2007	4/18/2007	1.00 g	ICP-OES
Lab03	BTG-1	B	194	4/16/2007	4/18/2007	1.00 g	ICP-OES
Lab03	BTG-1	C	206	4/16/2007	4/18/2007	1.00 g	ICP-OES
Lab04	BTG-1	A	293	4/11/2007	4/12/2007	1.01 g	ICP/MS
Lab04	BTG-1	B	294	4/11/2007	4/12/2007	1.02 g	ICP/MS
Lab04	BTG-1	C	305	4/11/2007	4/12/2007	1.00 g	ICP/MS
Lab05	BTG-1	A	279	4/16/2007	4/17/2007	1.25 g	ICPOES
Lab05	BTG-1	B	255	4/16/2007	4/17/2007	1.24 g	ICPOES
Lab05	BTG-1	C	254	4/16/2007	4/17/2007	1.24 g	ICPOES
Lab06	BTG-1	A	218	4/2/2007	4/4/2007	1.00 g	ICP-MS
Lab06	BTG-1	B	222	4/2/2007	4/4/2007	1.00 g	ICP-MS
Lab06	BTG-1	C	219	4/2/2007	4/4/2007	1.01 g	ICP-MS
Lab07	BTG-1	A	198	4/17/2007	4/17/2007	1.00 g	ICPMS
Lab07	BTG-1	B	199	4/17/2007	4/17/2007	1.00 g	ICPMS
Lab07	BTG-1	C	206	4/17/2007	4/17/2007	1.00 g	ICPMS
Lab08	BTG-1	A	249	4/20/2007	4/20/2007	1.00 g	ICP/MS
Lab08	BTG-1	B	236	4/20/2007	4/20/2007	1.00 g	ICP/MS
Lab08	BTG-1	C	236	4/20/2007	4/20/2007	1.00 g	ICP/MS
Lab01	BTG-2	A	1650	4/16/2007	4/16/2007	1.00	ICP-MS
Lab01	BTG-2	B	1570	4/16/2007	4/16/2007	1.00	ICP-MS
Lab01	BTG-2	C	1700	4/16/2007	4/16/2007	1.00	ICP-MS
Lab02	BTG-2	A	1835	4/11/2007	4/11/2007	1.00 g	ICP-OES
Lab02	BTG-2	B	1887	4/11/2007	4/11/2007	1.00 g	ICP-OES
Lab02	BTG-2	C	1596	4/11/2007	4/11/2007	1.00 g	ICP-OES
Lab03	BTG-2	A	1800	4/16/2007	4/18/2007	1.005	ICP-OES
Lab03	BTG-2	B	1700	4/16/2007	4/18/2007	1.006	ICP-OES
Lab03	BTG-2	C	1870	4/16/2007	4/18/2007	1.003	ICP-OES
Lab04	BTG-2	A	3065	4/11/2007	4/12/2007	1.00 g	ICP/MS
Lab04	BTG-2	B	3075	4/11/2007	4/12/2007	1.00 g	ICP/MS
Lab04	BTG-2	C	2950	4/11/2007	4/12/2007	1.01 g	ICP/MS
Lab05	BTG-2	A	2190	4/16/2007	4/17/2007	1.23 g	ICPOES
Lab05	BTG-2	B	2340	4/16/2007	4/17/2007	1.23 g	ICPOES
Lab05	BTG-2	C	2210	4/16/2007	4/17/2007	1.23 g	ICPOES
Lab06	BTG-2	A	1690	4/2/2007	4/4/2007	1.01 g	ICP-MS
Lab06	BTG-2	B	1670	4/2/2007	4/4/2007	1.00 g	ICP-MS
Lab06	BTG-2	C	1660	4/2/2007	4/4/2007	1.00 g	ICP-MS
Lab07	BTG-2	A	2210	4/17/2007	4/17/2007	1.00 g	ICPMS
Lab07	BTG-2	B	1370	4/17/2007	4/17/2007	1.00 g	ICPMS
Lab07	BTG-2	C	1570	4/17/2007	4/17/2007	1.00 g	ICPMS

Appendix 4. BC SALM on Barium Spiked Soils Results Table (cont'd).

LAB ID	Sample ID	Rep.	Result	Date Digested	Date Analysed	Weight Digested	Method Instrument
Lab08	BTG-2	A	2015	4/20/2007	4/20/2007	1.00 g	ICP/MS
Lab08	BTG-2	B	1939	4/20/2007	4/20/2007	1.00 g	ICP/MS
Lab08	BTG-2	C	1904	4/20/2007	4/20/2007	1.00 g	ICP/MS
Lab01	BTG-3	A	2420	4/16/2007	4/16/2007	1.00	ICP-MS
Lab01	BTG-3	B	2030	4/16/2007	4/16/2007	1.00	ICP-MS
Lab01	BTG-3	C	2070	4/16/2007	4/16/2007	1.00	ICP-MS
Lab02	BTG-3	A	2307	4/11/2007	4/11/2007	1.00 g	ICP-OES
Lab02	BTG-3	B	2167	4/11/2007	4/11/2007	1.00 g	ICP-OES
Lab02	BTG-3	C	2408	4/11/2007	4/11/2007	1.00 g	ICP-OES
Lab03	BTG-3	A	2800	4/16/2007	4/18/2007	1.001	ICP-OES
Lab03	BTG-3	B	2820	4/16/2007	4/18/2007	1.003	ICP-OES
Lab03	BTG-3	C	2720	4/16/2007	4/18/2007	1.005	ICP-OES
Lab04	BTG-3	A	4303	4/11/2007	4/12/2007	1.01 g	ICP/MS
Lab04	BTG-3	B	3888	4/11/2007	4/12/2007	1.00 g	ICP/MS
Lab04	BTG-3	C	4188	4/11/2007	4/12/2007	1.01 g	ICP/MS
Lab05	BTG-3	A	3070	4/16/2007	4/17/2007	1.23 g	ICPOES
Lab05	BTG-3	B	3060	4/16/2007	4/17/2007	1.24 g	ICPOES
Lab05	BTG-3	C	2800	4/16/2007	4/17/2007	1.25 g	ICPOES
Lab06	BTG-3	A	1920	4/2/2007	4/4/2007	1.00 g	ICP-MS
Lab06	BTG-3	B	1910	4/2/2007	4/4/2007	1.00 g	ICP-MS
Lab06	BTG-3	C	2120	4/2/2007	4/4/2007	1.00 g	ICP-MS
Lab07	BTG-3	A	2480	4/17/2007	4/17/2007	1.00 g	ICPMS
Lab07	BTG-3	B	2270	4/17/2007	4/17/2007	1.00 g	ICPMS
Lab07	BTG-3	C	2100	4/17/2007	4/17/2007	1.00 g	ICPMS
Lab08	BTG-3	A	2484	4/20/2007	4/20/2007	1.00 g	ICP/MS
Lab08	BTG-3	B	2582	4/20/2007	4/20/2007	1.00 g	ICP/MS
Lab08	BTG-3	C	2606	4/20/2007	4/20/2007	1.00 g	ICP/MS
Lab01	BTG-4	A	8430	4/16/2007	4/16/2007	1.00	ICP-MS
Lab01	BTG-4	B	8500	4/16/2007	4/16/2007	1.00	ICP-MS
Lab01	BTG-4	C	6940	4/16/2007	4/16/2007	1.01	ICP-MS
Lab02	BTG-4	A	8517	4/11/2007	4/11/2007	1.00 g	ICP-OES
Lab02	BTG-4	B	8637	4/11/2007	4/11/2007	1.00 g	ICP-OES
Lab02	BTG-4	C	9203	4/11/2007	4/11/2007	1.00 g	ICP-OES
Lab03	BTG-4	A	9260	4/16/2007	4/18/2007	1.006	ICP-OES
Lab03	BTG-4	B	9420	4/16/2007	4/18/2007	1.001	ICP-OES
Lab03	BTG-4	C	9450	4/16/2007	4/18/2007	1.002	ICP-OES
Lab04	BTG-4	A	10600	4/11/2007	4/12/2007	1.02 g	ICP/MS
Lab04	BTG-4	B	10500	4/11/2007	4/12/2007	1.01 g	ICP/MS
Lab04	BTG-4	C	10500	4/11/2007	4/12/2007	1.01 g	ICP/MS
Lab05	BTG-4	A	10000	4/16/2007	4/17/2007	1.24 g	ICPOES
Lab05	BTG-4	B	10300	4/16/2007	4/17/2007	1.23 g	ICPOES
Lab05	BTG-4	C	9740	4/16/2007	4/17/2007	1.24 g	ICPOES
Lab06	BTG-4	A	9770	4/2/2007	4/4/2007	1.00 g	ICP-MS
Lab06	BTG-4	B	9540	4/2/2007	4/4/2007	1.00 g	ICP-MS
Lab06	BTG-4	C	9340	4/2/2007	4/4/2007	1.00 g	ICP-MS

Appendix 4. BC SALM on Barium Spiked Soils Results Table (cont'd).

LAB ID	Sample ID	Rep.	Result	Date Digested	Date Analysed	Weight Digested	Method Instrument
Lab07	BTG-4	A	10100	4/17/2007	4/17/2007	1.00 g	ICPMS
Lab07	BTG-4	B	9330	4/17/2007	4/17/2007	1.00 g	ICPMS
Lab07	BTG-4	C	10000	4/17/2007	4/17/2007	1.00 g	ICPMS
Lab08	BTG-4	A	9406	4/20/2007	4/20/2007	1.00 g	ICP/MS
Lab08	BTG-4	B	9752	4/20/2007	4/20/2007	1.00 g	ICP/MS
Lab08	BTG-4	C	9612	4/20/2007	4/20/2007	1.00 g	ICP/MS

Appendix 5

DRAFT BCMOE SOLUBLE BARIUM METHOD

Soluble Barium by Calcium Chloride Extraction - Prescriptive

Parameter Soluble Barium (CaCl2)

Analytical Method Calcium Chloride extraction

Introduction

This analytical method was prepared for the British Columbia Ministry of Environment by the BCLQAAC Barite Task Group (Mark Hugdahl, Darlene Lintott, John Ashworth and Miles Tindal).

Because of the extremely low aqueous solubility and corresponding low toxicity of barite, the Barite-Barium Issues Sub-Committee recommended that the Province develop and endorse an analytical method for soluble barium for use under the Contaminated Sites Regulation at sites where detailed documentary evidence of barite usage exists. The method is intended to provide quantification of soluble barium species, without extracting insoluble and/or sequestered barite or barium.

This method uses excess calcium ions to encourage displacement of barium from cation exchange sites, and measures the total amount of barium that is dissolved in the pore water together with the barium that can be released through cation exchange.

Method Summary

This method is prescriptive. It must be followed exactly as described. Where minor deviations are permitted, this is indicated in the text.

Samples are dried at low temperature and sieved using a 2-mm (10-mesh) sieve. Solids samples are extracted for 2 hours with 1.0 M $CaCl_2$ at a 10:1 ratio of extraction solvent to solid. The extract is filtered and analyzed for barium using an appropriately sensitive and precise analytical method for barium (ICP-AES, ICP-MS).

MDL and EMS Codes

Analyte	Approx. MDL (units)	EMS Code
Soluble Barium (CaCl2)	0.05 mg/kg	

Matrix Soil, Sediment, Drilling Waste Solids, Waste

Interferences and Precautions

Samples with high petroleum or non-petroleum hydrocarbon content (Oil and Grease) may require specialized sample pre-treatment by solvent extraction.

Sample Handling and Preservation

Collect samples in a clean polyethylene or glass container. No preservation is required.

Stability

Holding and Storage Time: Soils may be stored at room temperature or refrigerated at <6℃ for up to 6 months.

Extracts must be stored at room temperature, and must be analyzed within 7 days of extraction.

Procedure

The samples are prepared and digested using the following procedures. All procedures are mandatory elements, unless otherwise indicated.

1. **Reagents**
   - 1.1. **1.0 M $CaCl_2$.** Volumetrically prepare the extraction solution by dissolving 147.0 g $CaCL_2.2H_20$ per 1L of laboratory grade water.
   - 1.2. **Laboratory Grade Water:** Water free of substances that interfere with the analytical method; equivalent to Type 1 water as set out in the current edition of Standard Methods

(APHA).

2. Sample Preparation.

2.1. Inspect the sample and record any unusual or significant characteristics (i.e. foreign material, metals etc.).
2.2. Remove any obviously foreign material such as vegetation.
2.3. Homogenize the entire sample and subsample a sufficient quantity for drying and analysis. Use appropriate subsampling techniques and quantities to ensure that the sample has been sufficiently represented.
2.4. Dry sub-samples to constant weight at a temperature of <60°C. If no other metals or temperature-sensitive analytes are to be determined using the same sub-sample, a drying temperature of up to 105°C may be used.
2.5. Disaggregate the dried sample by manual or gentle mechanical action.
2.6. Sieve each sample through a 2 mm (10 mesh) sieve. Discard the "greater than 2 mm" fraction.

3. Sample Extraction Procedure

3.1. Accurately weigh 5.0 ± 0.5 g of dry sample into a vessel appropriate for mechanical mixing (i.e. 250 mL glass Erlenmeyer). Include method blanks, duplicates and at least one reference material per batch of samples. Record sample weights to ± 0.01 g.
3.2. Add 50 ± 0.5 mL of 1.0 M $CaCl_2$ extraction solution.
3.3. Extract the mixture for 2 hours ± 15 minutes using a mechanical agitation method such as a shaker table or rotary mixer.
3.4. Filter the extract under gravity or suction, using a filter paper fine enough to yield a clear filtrate. Alternatively extracts can be centrifuged to remove suspended particles.
3.5. Accurately dilute the entire sample with laboratory grade water to the volume required for the analysis. The dilution volume will depend on the analysis technique, the detection limit, and the sample concentration.

4. Sample Analysis for Barium

4.1. Analyze the appropriately diluted extract of samples and QC samples using an appropriate technique for barium, such as ICP-AES or ICP-MS. Report results for soluble barium on a dry weight basis.
4.2. Report any anomalies during extraction and analysis.

Performance Requirements

All laboratories performing this analytical method must conduct validation to confirm that the requirements below are met.

Accuracy and Precision requirements apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples. For Initial Validations, averages of at least 8 spikes or CRMs must be assessed (preferably taken from multiple analytical batches). Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 80% or better for a minimum of 8 clean matrix spikes of barium chloride in clean sand, at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 15% relative standard deviation for a minimum of 8 clean matrix spikes of barium chloride in clean sand, at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements

QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank	One per batch	Less than reported DL
Method Spike or Ref. Material	One per batch	70 – 130% or better
Lab Duplicates	Approximately 5-10%	40% RPD

* Minimum DQOs apply to individual QC samples, not averages, and only at levels above 10x MDL. If any DQOs are exceeded at a frequency of more than ~5%, the laboratory's method should be reviewed in an attempt to improve its performance. Laboratories should report qualified data when DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.

Method Blank: Required. Minimum one per batch or as necessary to ensure contamination control.

Lab Duplicates: Required. Replicate all components of the test from start to finish. Random duplicate selection at an approximate frequency of 5-10% is recommended.

Reference Material or Method Spike: Required. Use of a Clean Matrix Spike of Barium Chloride in sand is strongly recommended. In-house prepared RMs are permitted.

Revision History March 27, 2007

Appendix 5

Round Robin Instructions for Analysis of Barium Soils

INSTRUCTIONS – Analysis of Barium Soils

Introduction

This instruction set relates only to the four (4) Barium Soil samples (BTG-1 to BTG-4) included in this sample submission. This component of the submission is focused on evaluation of methods for soluble and strong acid leachable barium in soil.

The British Columbia Ministry of Environment is currently developing matrix numerical soil standards for barium. Because of the extremely low aqueous solubility and corresponding low toxicity of barite, the Barite-Barium Issues Sub-Committee is recommending that the Province develop and endorse an analytical method for soluble barium for use under the Contaminated Sites Regulation at sites where detailed documentary evidence of barite usage exists. The BCLQAAC Technical Subcommittee was tasked with the development and validation of a suitable analytical method for the determination of soluble barium in soils and solids. The BC CSR soluble barium method has been developed. The primary objective of this round robin is to evaluate interlaboratory precision of the proposed soluble barium method.

Current numerical soil standards for barium require analysis of soil by the BC SALM method for strong acid leachable barium. This round robin also includes analysis of the enclosed samples for barium to evaluate interlaboratory precision for the anticipated new version of the BC SALM method.

Drafts of both the new BC soluble barium method and the anticipated new revision of the BC MOE – SALM method have been included with the instruction set and must be followed strictly.

General Instructions

The samples designated for this study are labeled as follows:

BTG-1
BTG-2
BTG-3
BTG-4

Sample Handling and Storage

The samples have been processed and stabilized such that degradation should be minimal at room temperature (i.e. 20℃).

These samples have been prepared by spiking soils with soluble and insoluble barium, at relatively high concentrations. All normal safety precautions applicable to the handling of potentially hazardous materials should be observed.

Preparation and Analytical Methodology – BC Soluble Barium Method

4. Refer to the attached draft method for Soluble Barium by Calcium Chloride Extraction for a detailed description of the required methodology.
5. Prepare a 1.0 M $CaCl_2$ extraction solution as described in the Reagents section of the Soluble Barium method;
6. Weigh out triplicate 5.0 g $\pm$ 0.5 g subsamples from each of the sample bottles provided (BTG1 through BTG4);
7. Continue processing according to Sample Extraction Procedure steps 1 through 5, and Sample Analysis for Barium, steps 1 and 2 in the Soluble Barium method.

Preparation and Analytical Methodology – BCMOE - SALM Barium

1. Weigh out triplicate 1.00 – 1.25 gram subsamples from each of the sample bottles provided (BTG-1 through BTG-4);
2. Add 5.0 $\pm$ 0.1 mL of HCl and 5.0 $\pm$ 0.1 mL of HNO_3 to each of the sub-samples;
3. Continue processing according to Section Procedure d) Sample Digestion Procedure step 1 through 8 of the attached draft method (BCMOE – SALM in Soil. Version 2.0draftB).
8. Analyze the extract for barium using appropriate analytical techniques.

SPECIAL NOTES:

- Please extract all sub-samples in one batch and include all routine QA/QC
- Please use the most appropriate and sensitive technique (avoid reporting <DL) to analyze for barium.

WARNING:
The new draft BCMOE SALM reference method must be followed as written.

Reporting Requirements

Please use the electronic file that will be provided to you by email to report the data. This file is an MS Excel spreadsheet with protection applied to specific cell ranges. There should be no need to unprotect these ranges. However if the participant does require protection to be turned off, or if you have any questions related to reporting of data, please contact James R. Downie at the contact information below.

Please include summaries of any applicable data qualifiers in the fields provided within the data sheet.

Once the data file has been completed please email or courier the file on disk to:

James (Jamie) R. Downie
692 Cedar Drive
Heriot Bay, BC V0P 1H0
Canada
250-830-3732
Jamie.Downie@JRD Consulting.ca

DATA IS DUE AT THE ABOVE COORDINATES ON OR BEFORE

2007 April 20

Material sent to you and left over from this study is provided to you free of charge in appreciation for the time and effort you have provided to this project.

All data reported during this project will be kept in strict confidence. The association between Laboratory IDs and reported results will only be known to James R. Downie (of the JRD Consulting Company) for the purposes of data analysis. Participating labs will be listed in the final published report. Data sets will be reported anonymously in the final published report.

Once again, thank-you for agreeing to participate in this study. Any questions regarding the instructions, sample issues or barium analytical methods may be directed to the following:

Darlene Lintott
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Edmonton, AB
780-438-5525 ext 281
Darlene.Lintott@norwestlabs.com