Mercury Laboratory Round Robin Project
CCME/CEA Project 257-2003
Phase 1 CRM/RM Sample Report

1 Overview

The Canadian Council of Ministers of the Environment (CCME) Mercury Canada-wide Standards (CWS) Development Committee (DC), the Canadian Electricity Association (CEA) and Canadian coal-fired electric utilities are working cooperatively to refine the atmospheric mercury (Hg) emissions inventory from this sector for Canada. CCME member regulatory agencies and utility CEA stakeholders are carrying out a multi-year data-gathering program relating to the emission of mercury from utility coal-fired boilers. A laboratory quality assurance assessment program, to evaluate the uncertainty in the analysis and measurement of mercury in coal in Canada, is an integral part of this program.

The mercury laboratory round robin project (CCME/CEA Project 257-2003) is using a multi-stage approach. A commissioning test phase was used at the start (completed Nov/02) to determine each laboratory's capability to analyze a standard coal sample for mercury and other parameters. In Phase I, participating laboratories were sent a number of CRM and RM materials for analysis. Phase II seeks to benchmark selected coals used in Canada for mercury and other coal-specific properties, and to provide on-going quality assurance for the duration of this two-year data collection program.

This Phase 1 report demonstrates that Canadian laboratories can produce mercury results for coal and coal related materials with a level of quality equivalent to any other testing community worldwide. However, the reader is cautioned this report serves only as an indicator of performance. Laboratory competence can only be established and monitored through a properly conducted quality assurance program, which should be verified by an independent audit of the laboratory operations consistent with the requirements of ISO 17025.

2 Organization of the Report

Part 3 describes the samples used in this component of the study. Part 4 is an evaluation of the performance of participating laboratories for the determination of mercury (Hg). Part 5 provides observations on factors that can impact the precision and accuracy of mercury results. Part 6 is an assessment of laboratory optional analysis (ash, sulfur and chlorine). Part 7 lists the names of the laboratories that completed this component of CCME/CEA project 257-2003.

Throughout this report the term "CCME" is used when comparing the results obtained in this study with reference results. The use of "CCME" in this context is as an abbreviation that refers to the results obtained in CCME/CEA Project 257-2003.

3 Samples

The primary objective of CCME/CEA Project 257-2003 is to obtain an indication of the ability of Canadian laboratories to determine mercury (Hg) in a wide range of coal as well as materials derived from, or related to, coal combustion.

The CRM/RM component of the study employed a total of 10 Certified Reference Materials (CRMs) and Reference Materials (RMs).

CRM samples were obtained from the Canadian Certified Reference Materials Program (CCRMP) CANMET, the National Institute of Standards and Technology (NIST), USA, and the South African Bureau of Standards (SABS), Republic of South Africa.

The RM coal samples were employed in an ASTM study and prepared in accordance with ASTM D 2013, *Standard Method of Preparation of Coal Samples for Analysis*. Based on comparisons of measurements made on ash, sulfur and Btu, all RM coal samples were shown to be equivalent in homogeneity to at least one certified reference material (CRM) coal.

In an independent collaborative study conducted through ASTM and EPRI all RM coals were analyzed at the same time by the same group of laboratories for the same test parameters as and concurrent with the following Certified Reference Material (CRM) Coals, NIST SRM 2692b, NIST SRM 1632c and SABS SARM 20. Where certified values were available no significant bias was found for the CRM samples SRM 1632c or SABS SARM 20 when analyzed by the same methods as the RM samples.

Table 1 lists source, type, and composition of each CCME/CEA study sample.

Table 1 CCME/CEA Samples						
Sample Source	**Sample Type**	**CRM/RM ID**	**Mercury (Hg) ng/g**	**Ash wt % dry basis**	**Sulfur wt % dry basis**	**Chlorine µg/g**
CCRMP	**Soil**	**SO-2**	**82**	**88.20**		
NIST	**Fly Ash**	**1633b**	**141**	**97.04**	**0.21**	
CCRMP	**Lake Sediment**	**LKSD-3**	**290**	**90.00**	**0.14**	
ASTM	**High Volatile B Bituminous Coal**	**ES-3**	**37**	**10.33**	**0.57**	**26**
ASTM	**Subbituminous Coal**	**ES-4**	**83**	**7.78**	**0.46**	**95**
NIST	**High Volatile A Bituminous Coal**	**1632c**	**93.8**	**7.16**	**1.46**	**1139**
ASTM	**Lignite Coal**	**ES-5**	**105**	**11.34**	**1.04**	**211**
ASTM	**High Volatile B Bituminous Coal**	**ES-2**	**116**	**11.01**	**4.45**	**465**
NIST	**High Volatile A Bituminous Coal**	**2692b**	**133**	**7.90**	**1.17**	**1593**
SABS	**High Volatile C Bituminous Coal**	**SARM-20**	**250**	**35.98**	**0.51**	

The coal and non-coal samples included in the CRM/RM component of the study cover a wide range of type and composition. The fly ash was selected for inclusion in the study for obvious reasons. The soil and lake sediment were selected as many utilities have monitor sites and effluent ponds associated with their operations.

Mercury (Hg) and moisture are the only mandatory analyses required of the participating laboratories in the CRM/RM component of this study. Analysis of any or all of ash, sulfur and chlorine are optional.

4 Evaluation of the Performance of Participating Laboratories for the Determination of Mercury (Hg)

Of the 14 laboratories that enlisted in the original CCME/CEA 257-2003 commissioning study, 13 elected to take part in the CRM/RM component of the study. Laboratory RMBB reported mercury results for non-coal materials only.

The performance evaluation is presented in two parts.

- Comparison of the community of CCME/CEA laboratory mercury measurements with the mercury measurements used to establish the reference values and confidence limits of the CRM and RM samples employed in this component of the study.
- Evaluation mercury measurements for each laboratory.

Comparison CCME/CEA Study Mercury Values with Reference Mercury Values

Table 2 compares the median value and confidence limit (CL) of the project's mercury results with reference value and reference confidence limit (CL) for each CRM and RM sample as established in an independent certification exercise or Interlaboratory study (ILS).

Comparison of the median of the project's laboratory results with the reference value is of no practical benefit if the confidence interval of the project's measurements is unacceptable.

A CCME CL that is less than or equal to the reference CL is obviously acceptable and is green.

To determine whether a CCME CL greater than the reference CL is acceptable an independent measure of performance, the Horrat CL is employed. The Horrat CL is calculated using the Horwitz function. The Horwitz function is an empirical function that applies over a wide range of concentrations, test materials, analytes and physical principles underlying an analytical procedure.

The Horrat CL is calculated according to the conditions specified in the GeoPT™ *Proficiency Testing Protocol of Operation* appropriate for high precision analysis for pure geological research employing equation 1.

$$CL = t \times ((0.02c^{0.8495})/2) * \sqrt{n}$$

Where both *CL* and *c* are both expressed as mass ratios (e.g. 1 ng/g = 10^{-9})
c is the level or concentration of the mercury (Hg) in the material
t is the t value for the number of laboratories reporting results
n is the number of laboratories.

A CCME CL that is greater than the reference CL but less than or equal to the Horrat CL is also acceptable. A CCME CL meeting this condition is shown in blue.

Comparison of each CCME median value with the reference value is conducted as follows.

A CCME median value that agrees with the reference value within the reference CL is green.

In some cases the CCME median value does not agree with the reference value within the reference CL.

NIST publication 260-100, page 87, provides guidance on comparing sets of measured values when there is reason to believe that the standard deviation of the data sets differs (e.g. different experimental conditions, different laboratories). This is certainly a valid argument for using the NIST approach to compare a CCME median value with the reference value. The comparison is based on a combined confidence limit (CL) calculated according to NIST 260-100, page 88, case II.

A CCME median value that does not agree with the reference value within the reference CL but agrees with the reference value within the combined CL is blue.

A CCME median value that does not agree with the reference value within the combined CL is red.

Table 2 Comparison of CCME/CEA Mercury Values with Reference Mercury Values

Source	Sample	Sample Type	Reference Value	Reference CL	CCME Median	CCME CL	Horrat CL	Combined CL
ASTM	ES-3	High Volatile B Bituminous Coal	37	8	36	3	4	10
ASTM	ES-4	Subbituminous Coal	83	5	86	5	7	8
NIST	1632c	High Volatile A Bituminous Coal	94	4	91	4	7	6
ASTM	ES-5	Lignite Coal	105	9	118	8	8	13
ASTM	ES-2	High Volatile B Bituminous Coal	116	4	120	3	9	6
NIST	2692b	High Volatile A Bituminous Coal	133	4	125	3	10	6
SABS	SARM-20	High Volatile C Bituminous Coal	250	23	244	7	16	27
CCRMP	SO-2	Soil	82	9	83	7	7	12
NIST	1633b	Fly Ash	141	19	144	8	11	23
CCRMP	LKSD-3	Lake Sediment	290	11	277	15	18	19

It is evident from table 2 that ***Canadian laboratories produce mercury results of exceptional quality for coal and coal related materials of exceptional quality.***

9 of the CCME CL values are at least as good as the reference CL.
All of the CCME CL are less than the Horrat research grade CL.

On the other hand, ASTM ES-3, SABS SARM-20, NIST 1633b and CCRMP SO-2 have a reference CL that is greater than the Horrat research grade CL. This serves to emphasize that the CCME measurements for these samples are at least as high quality as those obtained in the certification of the CRM/RM samples.

7 of the CCME median values agree with the reference value within the reference CL.

2 of the CCME median values ASTM ES-5, and CCRMP LKSD-3 agree with the reference value within the combined CL.

1 of the CCME median values that for NIST 2692b does not agree with the reference value within the combined limits.

NIST 2692b warrants further discussion. NIST 2692b has been used extensively in studies conducted by ASTM and ISO. The consensus results obtained for NIST 2692b by laboratories participating in those studies are listed in Table 3 below.

Table 3 NIST 2692b Results From Previous ILS

ILS	Method	Sample Treatment	Consensus ng/g
ASTM	ASTM D 3684	Bomb Combustion	123
ISO	ISO 15237	Bomb Combustion	129
ASTM	ASTM D 6414	Acid Extraction	121
ASTM	ASTM D 6722	Direct Combustion	126

The median of the studies listed in table 3 is 124 ng/g. The CCME study median is 125 ng/g.

None of the CCME/CEA study laboratories employed methods similar to either D 3684 or ISO 15237. The majority of CCME/CEA study laboratories employed methods identical to or similar to ASTM D 6722 or ASTM D 6414.

The median result of laboratories employing D 6722 in the CCME/CEA study is 125 ng/g. This is in excellent agreement with the ASTM D 6722 study result.

The median result of laboratories employing procedures similar to D 6414 in the CCME/CEA study is 124 ng/g. This is also in excellent agreement with the ASTM D 6414 study result.

These results point to an unresolved bias in either the NIST reference value or the procedures employed in the ASTM, ISO and CCME/CEA studies.

Evaluation of Individual Laboratories

<u>Evaluation Criteria</u>

Each CCME/CEA project laboratory is evaluated according to the provisions of ***ISO 5725-6 Accuracy (trueness and precision) of measurement methods Part 6: Use in practice of accuracy values***, **Section 7.2 Evaluation of the use of a measurement method by a laboratory not previously assessed, clause 7.2.3 Measurement method for which a reference material exists.**

Laboratory averages are compared with the reference value for each study material employing two criteria. Laboratory averages are compared with the reference value employing the reference material confidence limit (CL). Laboratory averages are also compared with the reference values employing an expected accuracy calculated according to ISO 5725-6 7.2.1.3. The expected accuracy is calculated as a combination of the multiple laboratory uncertainty of the laboratory method, as derived from a method validation Interlaboratory Study (ILS) and the uncertainty of the reference material.

Laboratory precision is evaluated by comparing laboratory precision with a limiting precision calculated according to ISO 5725-6 7.2.3.2.4. The limiting precision is calculated as a combination of the single laboratory uncertainty of the laboratory method, as derived from a method validation Interlaboratory Study (ILS) and the uncertainty of the reference material.

In instances where a laboratory reported the use of a method that is not supported by data from a method validation Interlaboratory Study (ILS), the Horwitz function as cited in the GeoPT™ *Proficiency Testing Protocol of Operation* was employed to estimate multiple and single laboratory uncertainties.

Tables 4 through 16 present the individual CCME/CEA study laboratory results.

Each laboratory table lists

- The laboratory code.
- The method employed by the laboratory.
- The sample source, sample ID and type.
- The four dry basis mercury results calculated from the values reported by the laboratory.
- The CRM or RM reference value in green as well the reference CL in green.
- The expected accuracy.
- The laboratory average.
- The laboratory precision.
- The limiting precision in blue.

Laboratory precision is determined from the standard deviation of the 4 dry basis mercury values.

A laboratory average that agrees with the reference value within the reference CL is green and can be considered to be free of bias.

A laboratory average that agrees with the reference value within the expected accuracy is blue and indicates the laboratory is proficient in the routine application of the laboratory method.

A laboratory average in red indicates the laboratory is experiencing problems with the determination of mercury for the sample.

Blue laboratory precision indicates laboratory precision is acceptable.

Red laboratory precision indicates laboratory precision is suspect.

The calculations in ISO 5725 Part 6 produce limits within which 95 % of the averages and the precision estimates for a particular laboratory could be expected to fall. Since 10 samples were tested in this component of the study, the mathematical expectation would be that 9.5 of the laboratory averages and 9.5 of the laboratory precision values would fall within the specified conditions. This mathematical condition is clearly impractical. In light of the fact that a complete evaluation of the impact in each laboratory of the uncertainty of moisture determination upon the dry basis mercury results is not possible for the nature of materials under test, a more reasonable expectation would be that 9 of the 10 laboratory averages and 9 of the ten laboratory precision values would fall within the conditions specified. A laboratory meeting these conditions can be considered to be proficient in the analysis of mercury under the conditions and at the time of the conduct of this study.

Determination of Mercury (Hg) by the CCME/CEA laboratory RMBT

Table 4 CCME/CEA Mercury (Hg) Results: RMBT D 6722													
Source	Sample ID	Type	Lab Run 1	Lab Run 2	Lab Run 3	Lab Run 4	Reference Value	Reference CL	Expected Accuracy	Lab Average	Lab Precision	ISO 5725-6 Limiting Precision
ASTM	ES-3	High Volatile B Bituminous Coal	38	38	42	49	37	± 8	± 12	42	10	16
ASTM	ES-4	Subbituminous Coal	75	85	89	77	83	± 5	± 14	81	13	18
NIST	1632c	High Volatile A Bituminous Coal	92	94	96	97	94	± 4	± 14	95	5	18
ASTM	ES-5	Lignite Coal	115	108	111	109	105	± 9	± 20	111	6	22
ASTM	ES-2	High Volatile B Bituminous Coal	126	119	121	121	116	± 4	± 16	122	6	20
NIST	2692b	High Volatile A Bituminous Coal	123	125	127	121	133	± 4	± 18	124	6	20
SABS	SARM-20	High Volatile C Bituminous Coal	241	245	260	243	250	± 23	± 38	247	17	38
CCRMP	SO-2	Soil	87	88	88	89	82	± 9	± 16	88	1	20
NIST	1633b	Fly Ash	146	154	146	146	141	± 19	± 26	148	8	28
CCRMP	LKSD-3	Lake Sediment	278	297	288	284	290	± 11	± 34	287	16	32

8 of the 10 results reported by RMBT agree with the reference value within the reference CL.
The remaining two results agree with the reference value within the expected accuracy.

All of the RMBP precision values are well within the ISO 5725-6 limiting precision value.

Based on the criteria and limitations specified on page 7, laboratory RMBT has demonstrated they are proficient in the analysis of mercury.

Determination of Mercury (Hg) by the CCME/CEA laboratory RMBP

Table 5 CCME/CEA Mercury (Hg) Results: RMBP D 6722												
Source	**Sample ID**	**Type**	**Lab Run 1**	**Lab Run 2**	**Lab Run 3**	**Lab Run 4**	**Reference Value**	**Reference CL**	**Expected Accuracy**	**Lab Average**	**Lab Precision**	**ISO 5725-6 Limiting Precision**
ASTM	ES-3	High Volatile B Bituminous Coal	34	41	34	36	37	± 8	± 12	36	7	16
ASTM	ES-4	Subbituminous Coal	96	98	94	90	83	± 5	± 14	95	7	18
NIST	1632c	High Volatile A Bituminous Coal	95	94	91	93	94	± 4	± 14	93	3	18
ASTM	ES-5	Lignite Coal	103	107	100	103	105	± 9	± 20	103	6	22
ASTM	ES-2	High Volatile B Bituminous Coal	118	116	117	117	116	± 4	± 16	117	2	20
NIST	2692b	High Volatile A Bituminous Coal	116	127	123	122	133	± 4	± 18	122	8	20
SABS	SARM-20	High Volatile C Bituminous Coal	252	260	248	247	250	± 23	± 38	252	12	38
CCRMP	SO-2	Soil	85	84	84	83	82	± 9	± 16	84	2	20
NIST	1633b	Fly Ash	139	140	142	142	141	± 19	± 26	141	2	28
CCRMP	LKSD-3	Lake Sediment	267	273	277	269	290	± 11	± 34	272	9	32

7 of the 10 results reported by RMBP agree with the reference value within the reference CL.
The remaining three results agree with the reference value within the expected accuracy.

All of the RMBP precision values are well within the ISO 5725-6 limiting precision value.

Laboratory RMBP confirmed that they had adhered strictly to the instructions supplied by the project coordinator for analysis of the CRM and RM samples.

Based on the criteria and limitations specified on page 7, laboratory RMBP has demonstrated they are proficient in the analysis of mercury.

Determination of Mercury (Hg) by the CCME/CEA laboratory RMBV

Table 6 CCME/CEA Mercury (Hg) Results: RMBV D 6722													
Source	**Sample ID**	**Type**	**Lab Run 1**	**Lab Run 2**	**Lab Run 3**	**Lab Run 4**	**Reference Value**	**Reference CL**	**Expected Accuracy**	**Lab Average**	**Lab Precision**	**ISO 5725-6 Limiting Precision**
ASTM	ES-3	High Volatile B Bituminous Coal	29	32	33	34	37	± 8	± 12	32	4	16
ASTM	ES-4	Subbituminous Coal	91	96	96	112	83	± 5	± 14	99	18	18
NIST	1632c	High Volatile A Bituminous Coal	93	92	92	88	94	± 4	± 14	91	5	18
ASTM	ES-5	Lignite Coal	106	108	101	100	105	± 9	± 20	104	7	22
ASTM	ES-2	High Volatile B Bituminous Coal	129	117	121	115	116	± 4	± 16	121	12	20
NIST	2692b	High Volatile A Bituminous Coal	124	136	133	128	133	± 4	± 18	130	10	20
SABS	SARM-20	High Volatile C Bituminous Coal	252	256	253	251	250	± 23	± 38	253	4	38
CCRMP	SO-2	Soil	80	80	75	80	82	± 9	± 16	79	5	20
NIST	1633b	Fly Ash	134	133	128	138	141	± 19	± 26	133	8	28
CCRMP	LKSD-3	Lake Sediment	286	271	279	291	290	± 11	± 34	282	17	32

9 of the 10 results reported by RMBV agree with the reference value within the reference CL.

All of the RMBV precision values are within the ISO 5725-6 limiting precision value.

The exception to this high level of performance is the accuracy of ASTM Sample ES-4.

Possible explanations for the performance discrepancy for sample ES-4 are described in Section 5.

Based on the criteria and limitations specified on page 7, laboratory RMBV has demonstrated they are proficient in the analysis of mercury.

Determination of Mercury (Hg) by the CCME/CEA laboratory RMBH

Table 7 CCME/CEA Mercury (Hg) Results: RMBH D 6414												
Source	**Sample ID**	**Type**	**Lab Run 1**	**Lab Run 2**	**Lab Run 3**	**Lab Run 4**	**Reference Value**	**Reference CL**	**Expected Accuracy**	**Lab Average**	**Lab Precision**	**ISO 5725-6 Limiting Precision**
ASTM	ES-3	High Volatile B Bituminous Coal	32	45	35	33	37	± 8	± 22	36	11	22
ASTM	ES-4	Subbituminous Coal	80	78	104	87	83	± 5	± 16	88	23	28
NIST	1632c	High Volatile A Bituminous Coal	86	86	84	87	94	± 4	± 20	86	2	28
ASTM	ES-5	Lignite Coal	117	103	110	100	105	± 9	± 24	108	15	32
ASTM	ES-2	High Volatile B Bituminous Coal	117	120	119	123	116	± 4	± 24	120	5	30
NIST	2692b	High Volatile A Bituminous Coal	126	120	131	132	133	± 4	± 26	127	11	34
SABS	SARM-20	High Volatile C Bituminous Coal	223	224	223	220	250	± 23	± 50	222	4	52
CCRMP	SO-2	Soil	74	73	73	74	82	± 9	± 18	73	1	28
NIST	1633b	Fly Ash	120	133	120	119	141	± 19	± 32	123	13	38
CCRMP	LKSD-3	Lake Sediment	251	251	250	239	290	± 11	± 54	248	12	54

6 of the 10 results reported by RMBH agree with the reference value within the reference CL.
The remaining 4 results agree with the reference value within the expected accuracy.

All of the RMBH precision values are within the ISO 5725-6 limiting precision value.

Laboratory RMBH experienced difficulties in the analysis of the CCME/CEA commissioning sample. Upon receipt of the commissioning report the laboratory acted on the recommendations contained in that report. Laboratory RMBH has shown the most improvement in the CRR/RM component of this study.

Based on the criteria and limitations specified on page 7, laboratory RMBH has demonstrated they are proficient in the analysis of mercury.

Determination of Mercury (Hg) by the CCME/CEA laboratory RMBL

Table 8 CCME/CEA Mercury (Hg) Results: RMBL D 6722												
Source	**Sample ID**	**Type**	**Lab Run 1**	**Lab Run 2**	**Lab Run 3**	**Lab Run 4**	**Reference Value**	**Reference CL**	**Expected Accuracy**	**Lab Average**	**Lab Precision**	**ISO 5725-6 Limiting Precision**
ASTM	ES-3	High Volatile B Bituminous Coal	39	31	28	32	37	± 8	± 12	33	9	16
ASTM	ES-4	Subbituminous Coal	83	68	88	84	83	± 5	± 14	81	17	18
NIST	1632c	High Volatile A Bituminous Coal	89	89	94	93	94	± 4	± 14	91	5	18
ASTM	ES-5	Lignite Coal	115	108	127	117	105	± 9	± 20	117	16	22
ASTM	ES-2	High Volatile B Bituminous Coal	120	121	120	119	116	± 4	± 16	120	2	20
NIST	2692b	High Volatile A Bituminous Coal	119	132	128	126	133	± 4	± 18	126	11	20
SABS	SARM-20	High Volatile C Bituminous Coal	232	242	239	241	250	± 23	± 38	238	9	38
CCRMP	SO-2	Soil	84	80	82	79	82	± 9	± 16	81	4	20
NIST	1633b	Fly Ash	141	141	147	145	141	± 19	± 26	144	6	28
CCRMP	LKSD-3	Lake Sediment	257	250	252	255	290	± 11	± 34	253	6	32

7 of the 10 results reported by RMBL agree with the reference value within the reference CL.
2 results agree with the reference value within the expected accuracy.
All of the 10 RMBL precision values are within the ISO 5725-6 limiting precision value.
The RMBL result for sample LKSD-3 is not within the expected accuracy.

The suspect accuracy result for sample LKSD-3 could be attributed to the fact that laboratory RMBL conducted the analysis of the CRM/RM samples using a single calibration over a period of 5 days. Sample LKSD-3 was analyzed on the fifth day. Since this sample is at the extremes of the calibration, a minor drift even if re-slope precautions are taken could lead to a depressed (or elevated) value.

Based on the criteria and limitations specified on page 7, laboratory RMBL has demonstrated they are proficient in the analysis of mercury.

Determination of Mercury (Hg) by the CCME/CEA laboratory RMBI

Table 9 CCME/CEA Mercury (Hg) Results: RMBI D 6722												
Source	**Sample ID**	**Type**	**Lab Run 1**	**Lab Run 2**	**Lab Run 3**	**Lab Run 4**	**Reference Value**	**Reference CL**	**Expected Accuracy**	**Lab Average**	**Lab Precision**	**ISO 5725-6 Limiting Precision**
ASTM	ES-3	High Volatile B Bituminous Coal	38	31	37	31	37	± 8	± 12	34	8	16
ASTM	ES-4	Subbituminous Coal	86	82	96	91	83	± 5	± 14	89	12	18
NIST	1632c	High Volatile A Bituminous Coal	96	95	94	96	94	± 4	± 14	95	2	18
ASTM	ES-5	Lignite Coal	122	116	140	123	105	± 9	± 20	125	21	22
ASTM	ES-2	High Volatile B Bituminous Coal	126	128	126	125	116	± 4	± 16	126	2	20
NIST	2692b	High Volatile A Bituminous Coal	128	133	129	127	133	± 4	± 18	129	5	20
SABS	SARM-20	High Volatile C Bituminous Coal	272	272	273	280	250	± 23	± 38	274	8	38
CCRMP	SO-2	Soil	86	89	87	88	82	± 9	± 16	87	2	20
NIST	1633b	Fly Ash	150	150	151	159	141	± 19	± 26	153	9	28
CCRMP	LKSD-3	Lake Sediment	271	265	265	275	290	± 11	± 34	269	10	32

5 of the 10 results reported by RMBI agree with the reference value within the reference CL.
5 results agree with the reference value within the expected accuracy.
All of RMBI precision values are within the ISO 5725-6 limiting precision value.

The project coordinator conducted an independent analysis of the instrument output results submitted by RMBI. This analysis suggested that 7 of the 10 results reported by RMBI agree with the reference value within the reference limits and the remaining 3 results including that for ES-5 agree with the reference value within the expected accuracy. This points to a potential inconsistency with the RMBI instrument calibration algorithm that underestimates the quality of results produced by RMBI.

Based on the criteria and limitations specified on page 7, laboratory RMBI has demonstrated they are proficient in the analysis of mercury.

Determination of Mercury (Hg) by the CCME/CEA laboratory RMBD

Table 10 CCME/CEA Mercury (Hg) Results: RMBD D 6722												
Source	Sample ID	Type	Lab Run 1	Lab Run 2	Lab Run 3	Lab Run 4	Reference Value	Reference CL	Expected Accuracy	Lab Average	Lab Precision	ISO 5725-6 Limiting Precision
ASTM	ES-3	High Volatile B Bituminous Coal	34	35	43	40	37	± 8	± 12	38	9	16
ASTM	ES-4	Subbituminous Coal	67	68	68	74	83	± 5	± 14	69	6	18
NIST	1632c	High Volatile A Bituminous Coal	85	78	75	84	94	± 4	± 14	81	9	18
ASTM	ES-5	Lignite Coal	113	109	102	101	105	± 9	± 20	106	12	22
ASTM	ES-2	High Volatile B Bituminous Coal	118	115	117	116	116	± 4	± 16	116	3	20
NIST	2692b	High Volatile A Bituminous Coal	120	117	119	115	133	± 4	± 18	118	4	20
SABS	SARM-20	High Volatile C Bituminous Coal	236	227	231	228	250	± 23	± 38	231	9	38
CCRMP	SO-2	Soil	72	62	73	64	82	± 9	± 16	68	10	20
NIST	1633b	Fly Ash	132	132	134	141	141	± 19	± 26	134	9	28
CCRMP	LKSD-3	Lake Sediment	282	286	278	280	290	± 11	± 34	281	7	32

6 of the 10 results reported by RMBD agree with the reference value within the reference CL.
4 results agree with the reference value within the expected accuracy.
All of the RMBD precision values are within the ISO 5725-6 limiting precision value.

Based on the criteria and limitations specified on page 7, laboratory RMBD has demonstrated they are proficient in the analysis of mercury.

Determination of Mercury (Hg) by the CCME/CEA laboratory RMBU

Table 11 CCME/CEA Mercury (Hg) Results: RMBU D 6414												
Source	**Sample ID**	**Type**	**Lab Run 1**	**Lab Run 2**	**Lab Run 3**	**Lab Run 4**	**Reference Value**	**Reference CL**	**Expected Accuracy**	**Lab Average**	**Lab Precision**	**ISO 5725-6 Limiting Precision**
ASTM	ES-3	High Volatile B Bituminous Coal	28	30	31	32	37	± 8	± 22	30	4	22
ASTM	ES-4	Subbituminous Coal	82	88	95	87	83	± 5	± 16	88	11	28
NIST	1632c	High Volatile A Bituminous Coal	78	81	96	93	94	± 4	± 20	87	18	28
ASTM	ES-5	Lignite Coal	138	120	125	124	105	± 9	± 24	127	15	32
ASTM	ES-2	High Volatile B Bituminous Coal	99	116	100	128	116	± 4	± 24	111	28	30
NIST	2692b	High Volatile A Bituminous Coal	130	128	122	124	133	± 4	± 26	126	7	34
SABS	SARM-20	High Volatile C Bituminous Coal	237	241	257	241	250	± 23	± 50	244	18	52
CCRMP	SO-2	Soil	93	99	100	100	82	± 9	± 18	98	7	28
NIST	1633b	Fly Ash	136	144	146	170	141	± 19	± 32	149	29	38
CCRMP	LKSD-3	Lake Sediment	335	318	290	330	290	± 11	± 54	318	40	54

4 of the 10 results reported by RMBU agree with the reference value within the reference CL.
6 results agree with the reference value within the expected accuracy.
All of the RMBU precision values are within the ISO 5725-6 limiting precision value.

Based on the criteria and limitations specified on page 7, laboratory RMBU has demonstrated they are proficient in the analysis of mercury.

Determination of Mercury (Hg) by the CCME/CEA laboratory RMBJ

Table 12 CCME/CEA Mercury (Hg) Results: RMBJ Microwave ICP-MS												
Source	**Sample ID**	**Type**	**Lab Run 1**	**Lab Run 2**	**Lab Run 3**	**Lab Run 4**	**Reference Value**	**Reference CL**	**Expected Accuracy**	**Lab Average**	**Lab Precision**	**ISO 5725-6 Limiting Precision**
ASTM	ES-3	High Volatile B Bituminous Coal	37	39	41	39	37	± 8	± 14	39	4	14
ASTM	ES-4	Subbituminous Coal	85	83	80	85	83	± 5	± 24	83	4	18
NIST	1632c	High Volatile A Bituminous Coal	81	86	83	84	94	± 4	± 26	84	4	20
ASTM	ES-5	Lignite Coal	124	117	112	121	105	± 9	± 28	119	11	22
ASTM	ES-2	High Volatile B Bituminous Coal	114	105	116	109	116	± 4	± 30	111	10	24
NIST	2692b	High Volatile A Bituminous Coal	124	122	120	122	133	± 4	± 34	122	3	28
SABS	SARM-20	High Volatile C Bituminous Coal	219	209	212	205	250	± 23	± 60	211	12	48
CCRMP	SO-2	Soil	68	69	69	68	82	± 9	± 24	68	1	20
NIST	1633b	Fly Ash	169	180	173	187	141	± 19	± 40	177	15	34
CCRMP	LKSD-3	Lake Sediment	224	233	224	234	290	± 11	± 62	229	11	48

2 of the 10 results reported by RMBJ agree with the reference value within the reference CL.
8 results agree with the reference value within the expected accuracy.
All 10 of the RMBJ precision values are within the ISO 5725-6 limiting precision value.

Based on the criteria and limitations specified on page 7, laboratory RMBJ has demonstrated they are proficient in the analysis of mercury.

Determination of Mercury (Hg) by the CCME/CEA laboratory RMBF

Table 13 CCME/CEA Mercury (Hg) Results: RMBF Microwave CVAAS												
Source	**Sample ID**	**Type**	**Lab Run 1**	**Lab Run 2**	**Lab Run 3**	**Lab Run 4**	**Reference Value**	**Reference CL**	**Expected Accuracy**	**Lab Average**	**Lab Precision**	**ISO 5725-6 Limiting Precision**
ASTM	ES-3	High Volatile B Bituminous Coal	30	24	25	35	37	± 8	± 14	28	10	14
ASTM	ES-4	Subbituminous Coal	88	69	67	79	83	± 5	± 24	76	20	18
NIST	1632c	High Volatile A Bituminous Coal	86	83	86	80	94	± 4	± 26	84	6	20
ASTM	ES-5	Lignite Coal	112	103	112	142	105	± 9	± 28	118	34	22
ASTM	ES-2	High Volatile B Bituminous Coal	109	111	105	98	116	± 4	± 30	105	12	24
NIST	2692b	High Volatile A Bituminous Coal	122	116	121	108	133	± 4	± 34	117	13	28
SABS	SARM-20	High Volatile C Bituminous Coal	240	239	254	238	250	± 23	± 60	243	15	48
CCRMP	SO-2	Soil	75	74	77	74	82	± 9	± 24	75	3	20
NIST	1633b	Fly Ash	136	130	173	134	141	± 19	± 40	144	40	34
CCRMP	LKSD-3	Lake Sediment	278	285	281	263	290	± 11	± 62	277	19	48

Laboratory RMBF informed the project coordinator they are participating in the CCMECEA study as a means to assess the suitability of an in-house method they have developed for the analysis of mercury. The laboratory RMBF is a modified version of EPA 245.5 that exposes the sample to a more aggressive digestion environment through the use of microwave energy.

Table 13 shows that three of the laboratory RMBF values are within the reference sample CL.
The remaining 7 results are within acceptable accuracy.
7 of the ten precision values are the ISO 5725-6 limiting precision value.
3 of the precision values, those for samples ES-4, ES-5 and 1633b are suspect.

The RMBF modification of EPA 245.5 achieves acceptable recovery of mercury from both coal and non-coal materials. However there appear to be factors affecting the precision of the method that prevent laboratory RMBF from meeting the proficiency requirements detailed on page 7.

Determination of Mercury (Hg) by the CCME/CEA laboratory RMBW

Table 14 CCME/CEA Mercury (Hg) Results: RMBW D 6414

Source	Sample ID	Type	Lab Run 1	Lab Run 2	Lab Run 3	Lab Run 4	Reference Value	Reference CL	Expected Accuracy	Lab Average	Lab Precision	ISO 5725-6 Limiting Precision
ASTM	ES-3	High Volatile B Bituminous Coal	46	52	49	49	37	± 8	± 22	49	5	22
ASTM	ES-4	Subbituminous Coal	144	141	142	121	83	± 5	± 16	137	21	28
NIST	1632c	High Volatile A Bituminous Coal	99	91	96	96	94	± 4	± 20	95	7	28
ASTM	ES-5	Lignite Coal	180	180	155	160	105	± 9	± 24	169	26	32
ASTM	ES-2	High Volatile B Bituminous Coal	121	126	124	125	116	± 4	± 24	124	5	30
NIST	2692b	High Volatile A Bituminous Coal	121	122	126	128	133	± 4	± 26	124	7	34
SABS	SARM-20	High Volatile C Bituminous Coal	333	355	335	299	250	± 23	± 50	331	46	52
CCRMP	SO-2	Soil	91	92	86	90	82	± 9	± 18	90	5	28
NIST	1633b	Fly Ash	133	133	130	132	141	± 19	± 32	132	3	38
CCRMP	LKSD-3	Lake Sediment	303	303	304	294	290	± 11	± 54	301	10	54

4 of the 10 results reported by RMBW agree with the reference value within the reference CL.
3 results agree with the reference value within the expected accuracy.
All of the RMBW precision values are within the ISO 5725-6 limiting precision value.

The RMBW results for samples ES-4, ES-5 and SARM-20 are not within the expected accuracy. RMBW produces a range in quality of results. The results for NIST 1632c, NIST 2692b, ASTM ES-3, ASTM ES-2 and the 3 non-coal materials are of very high to exceptional quality. Those for ASTM ES-4, ASTM ES-5, and SARM-20 are suspect. Most other laboratories had very little trouble with the precision of SARM-20. The project coordinator divided the summed reference values for these 3 samples by the summed reported results to obtain an average correction factor. The corrected results are ES-4 94 ng/g, ES-5 116 ng/g and SARM-20 228 ng/g all of which are acceptable.

There appear to be inconsistencies in application of D 6414 that prevent laboratory RMBW from meeting the proficiency requirements detailed on page 7.

Determination of Mercury (Hg) by the CCME/CEA laboratory RMBA

Table 15 CCME/CEA Mercury (Hg) Results: RMBA INAA

Source	Sample ID	Type	Lab Run 1	Lab Run 2	Lab Run 3	Lab Run 4	Reference Value	Reference CL	Expected Accuracy	Lab Average	Lab Precision	ISO 5725-6 Limiting Precision
ASTM	ES-3	High Volatile B Bituminous Coal	48	46		40	37	± 8	± 14	45	9	14
ASTM	ES-4	Subbituminous Coal	74	56	71	70	83	± 5	± 24	68	16	18
NIST	1632c	High Volatile A Bituminous Coal	101	88	101	103	94	± 4	± 26	98	13	20
ASTM	ES-5	Lignite Coal	138	144	142	123	105	± 9	± 28	137	19	22
ASTM	ES-2	High Volatile B Bituminous Coal	134	117	133	103	116	± 4	± 30	122	29	24
NIST	2692b	High Volatile A Bituminous Coal	99	104	182	148	133	± 4	± 34	133	78	28
SABS	SARM-20	High Volatile C Bituminous Coal	220	234	240	262	250	± 23	± 60	239	35	48
CCRMP	LKSD-3	Lake Sediment	236	287	246	225	290	± 11	± 62	248	54	48

RMBA reported that one of the results for sample ES-3 and all of the results for sample SO-2 and 1633b were less than the measurement capability of the INAA procedure used.

3 of the 8 measurable results reported by RMBA agree with the reference value within the reference CL. 4 results agree with the reference value within the expected accuracy.

The RMBA result for, ES-5 is not within the expected accuracy.

Five of the 8 RMBA precision values are within the ISO 5725-6 limiting precision value.
The two samples with the highest imprecision are CRMs from two recognized sources. It would appear there are factors specific to the handling and measurement of Hg by INAA that prevent laboratory RMBA from meeting the proficiency requirements detailed on page 7.

Determination of Mercury (Hg) by the CCME/CEA laboratory RMBB

Table 16 CCME/CEA Mercury (Hg) Results: RMBB D 6414

Source	Sample ID	Type	Lab Run 1	Lab Run 2	Lab Run 3	Lab Run 4	Reference Value	Reference CL	Expected Accuracy	Lab Average	Lab Precision	ISO 5725-6 Limiting Precision
CCRMP	SO-2	Soil	125	156	125	135	82	± 9	± 16	135	29	28
NIST	1633b	Fly Ash	172	152	172	172	141	± 19	± 30	167	20	38
CCRMP	LKSD-3	Lake Sediment	297	297	297	297	290	± 11	± 50	297	0	54

RMBB elected to report results for the non-coal materials only.

One sample is within the reference CL. Another sample is within the expected accuracy while yet another produces unacceptable accuracy. Not only is the precision of sample SO-2 suspect but also the precision of 0 for sample LKSD-3 is highly unlikely.

Laboratory RMMB produced insufficient results to meet the proficiency requirements detailed on page 7.

5 Factors Affecting Accuracy and Precision of Mercury (Hg) Results

Certain coals have a tendency to explode and scatter when ignited. This characteristic referred to as "sparking" is a function of the composition and distribution of mineral matter in coal as well as the physical association and distribution of moisture within the coal matrix.

When a sample of this type is ignited in a procedure requiring combustion, it sparks. As a result combustion may not proceed in a uniform fashion for each test portion. Many combustion analyzers can be calibrated on the basis of peak height or peak area. The tendency is to defer to the use of peak height. However, in the case of a coal that does not burn in a uniform fashion the instrument peak response for the same weight may exhibit significant variability. In fact it is entirely possible that the instrument response could consist of a series of peaks with variable heights. This behavior would severely compromise the use of peak height and also presents significant challenges to the use of peak area. Most integrators commence and terminate peak measurements by comparing the peak signal to a stable baseline signal. If the instrument peak response is such that the signal generated produces two entirely distinct peaks, it is possible the instrument would terminate analysis after integrating only one of the peaks.

All coal samples employed in the CCME/CEA study were prepared using procedures and equipment that grinds the coal to pass 60 mesh (250 µ), thoroughly mixes the sample and then distributes the material in a sufficiently large number of increments per bottle to obtain a representative sample. Consequently there is the tendency to conclude sample homogeneity would be uniform and should not be an issue. However, despite the fact all coals were prepared in the same fashion, the coals may not be uniformly homogeneous. The problem arises from the fact that different coals will exhibit an entirely different minus 60 mesh size consist. For example the minus 60 mesh material from one coal might be 10 % minus 400 mesh (37 µ), 25 % minus 200 mesh (74 µ), 45 % minus 100 mesh (150 µ) and 20 % minus 60 (250 µ) while the minus 60 mesh size consist of another coal may be entirely different. The particle size distribution of the minus 60 mesh size consist coupled with nature and distribution of the moisture and mineral matter associated with a coal can significantly impact not only the combustion behavior of a coal but also chemical digestion of a coal.

The immediate reaction to this problem is to grind all coals to the point where they would be uniformly homogeneous. This approach suffers from two very significant drawbacks. The first is that most processes for grinding coal to ultra-fine particle sizes generate heat and consequently would lead to the loss of mercury from the sample. The other is that grinding low rank coals to ultra-fine particle sizes radically increases the overall sample surface area making moisture control and measurement very difficult.

Past studies have shown samples ASTM ES-4 and ASTM ES-5 may not be as homogeneous as other materials used in this study. This is supported by the fact that the majority of the precision values reported for these samples in the CCME/CEA study are near or in excess of the limiting ISO 5725-6 precision value.

In addition to the factors cited above, the composition of mineral components and refractory carbon compounds for all samples used in this study can lead to incomplete extraction of mercury and/or erratic mercury results.

The CCME/CEA commissioning test report pointed out that EPA 245.5, a procedure based on chemical digestion, did not obtain acceptable recovery of mercury from coals employed in a previous ASTM and EPRI study**. Laboratory RMBF confirmed that not only did EPA 245.5 fail to achieve acceptable recovery of mercury from carbonaceous materials but also the recovery of mercury could be erratic.**

To achieve complete digestion of refractory carbonaceous material and dissolution of all mineral components procedures have been developed that subject the samples to an aggressive digestion environment conducted under elevated pressures. ASTM D 6414 is such a procedure, as are most of those based on the use of microwave energy.

6 Performance of CCME/CEA Laboratories Optional Analysis: Ash, Sulfur and Chlorine

Evaluation Criteria

The decision of a laboratory to report results for ash, sulfur and or chlorine in the CRM/RM component of the CCME/CEA 257-2003 study is entirely voluntary.

This reports makes use of the Horrat CL as the basis for evaluating laboratory results for Ash, Sulfur and Chlorine. The Horrat CL is calculated using the Horwitz function. The Horwitz function is an empirical algorithm that applies over a wide range of concentrations, test materials, analytes and physical principles underlying an analytical procedure.

Because the laboratories conducting these optional tests have quite different measurement needs and resources they were not required to adhere to a specific standard or protocol. This supports the use of the Horrat CL as the basis for evaluating laboratory results for Ash, Sulfur and Chlorine.

The Horrat CL is calculated according to the conditions specified in the GeoPT™ *Proficiency Testing Protocol of Operation* appropriate for high precision analysis for pure geological research employing equation 1.

$$CL = t \times ((0.02c^{0.8495})/2) * \sqrt{n} \qquad (1)$$

Where both CL and c are both expressed as mass ratios (e.g. 1 ng/g = 10^{-9})
c is the level or concentration of the test parameter in the material
t is the t value for the number of laboratories reporting results
n is the number of laboratories.

Evaluation of laboratory performance is made only for those materials for which a reference value is available from an independent certification program or ILS.

The calculations are carried out as follows.

The median of all of the CCME laboratory values is calculated.
A grand median of the reference value and the CCME median value is determined.
The Horrat CL is calculated from this grand median.
The maximum of the CCME median and reference value is specified as Max
The minimum of the CCME median and reference value is specified as Min.
Two sets of limits are calculated for each sample, Research Limits and Applied Limits.
The Research limits are calculated as Max + Horrat CL and Min-Horrat CL.
The Applied limits are calculated as Max + 2 *x* Horrat CL and Min -2 *x* Horrat CL.

The Research limits represent what can be expected in high precision analysis.
The Applied limits represent what can be expected in the routine application of a properly controlled method.

Each optional analysis table lists

- The parameter name and parameter measurement units.
- The sample source, sample ID and type.
- The reference value.
- The CCME median value.
- The Horrat CL in green.
- The Horrat Research Limits in green.
- The Horrat Applied Limits in blue.

If the reference value agrees with the CCME median value within the Horrat CL then both values can be considered to be free of bias and both are in green.

If the reference value does not agree with the CCME median value within the Horrat CL then one or both of the values is biased and both are in black.

A laboratory value that falls within the Horrat Research limits is green and indicates the laboratory is capable of producing high precision unbiased test results.

A laboratory value that falls within the Horrat Applied limits is blue and indicates the laboratory is proficient in the routine application of the laboratory method.

A laboratory value that falls outside the Horrat Applied limits is black and indicates the laboratory may produce biased results with respect to the testing community at large.

Table 17 Evaluation of the Performance of CCME/CEA Laboratories for the Determination of Ash										
Source	NIST	ASTM	NIST	ASTM	ASTM	ASTM	SABS	CCRMP	CCRMP	NIST
Sample ID	1632c	ES-4	2692b	ES-3	ES-2	ES-5	SARM-20	SO-2	LKSD-3	1633b
Type	Coal hvAb	Coal subA	Coal hvAb	Coal hvBb	Coal hvBb	ligA	Coal hvCb	Soil	Lake Sediment	Fly Ash
Reference Value	7.16	7.78	7.90	10.33	11.01	11.34	35.98	88.20	90.00	97.04
CCME Median	7.15	7.87	7.90	10.36	10.88	11.04	36.01	88.62	89.41	97.14
Horrat CL	±0.04	±0.04	±0.04	±0.05	±0.06	±0.06	±0.14	±0.31	±0.31	±0.63
Horrat Research Limits	7.20 7.11	7.91 7.74	7.94 7.86	10.41 10.28	11.07 10.82	11.40 10.98	36.15 35.84	88.93 87.89	90.31 89.10	97.77 96.41
Horrat Applied Limits	7.24 7.07	7.95 7.70	7.98 7.82	10.46 10.23	11.13 10.76	11.46 10.92	36.29 35.70	89.24 87.58	90.62 88.79	98.40 95.78
RMBB	7.07	7.65	7.90	10.14	4.62	11.02	35.90	88.70	89.34	97.35
RMBD	7.02	7.51	7.73	10.11	10.68	10.94	35.98	87.80	89.13	97.15
RMBF	7.15	7.87	7.82	10.25	10.77	11.55	36.01	88.69	89.24	97.14
RMBH	7.12	7.61	7.90	10.38	10.88	11.04	36.20	88.78	89.62	97.06
RMBI	7.33	7.90	8.10	10.35	10.94	11.63	36.06	89.89	90.29	96.89
RMBJ	6.95	7.69	7.85	10.23	10.72	10.95	35.79	88.15	89.37	96.95
RMBL	7.23	7.82	7.92	10.38	11.00	11.45	35.92	88.58	89.41	97.13
RMBP	7.26	7.90	7.97	10.36	10.89	10.25	36.06	88.62	89.46	97.14
RMBU	7.12	8.61	7.88	10.83	10.95	12.24	37.55	19.51	91.21	97.29
RMBV	7.19	8.27	8.07	10.36	10.94	11.67	36.49	88.68	89.88	97.31
RMBW	7.38	8.11	8.24	10.92	10.88	10.93	35.88	88.26	88.97	97.06

The performance of each laboratory is self evident from the results in Table 17.
Discussion of individual performance would require more detailed information concerning the methods used in each laboratory.

It is clear from table 17 that laboratory values for the non-coal materials SO-2, LKSD-3 and 1633b tend to achieve better overall agreement with the reference value than the results for the coal samples. The results in table 17 can be used to identify material properties that can impact the amount of ash generated on heating of a sample.

Normally a laboratory using a coal method heats the sample under conditions that ensure complete decomposition of all organic components without allowing the sample to ignite and in such a way that the interaction between sulfur oxides and reactive mineral components is minimized. If these conditions are not met the amount of ash generated can be variable and/or biased.

This rather short explanation accounts for the results as they appear in table 17.

Sample 1633b consists primarily of non-reactive mineral matter, contains little or no organic material or sulfur. As a consequence it would be expected that this material would yield highly consistent results.

Although sample LKSD-3 also contains very little organic material and sulfur, it contains mineral components that include water of crystallization. These components may not completely decompose unless this sample is heated an adequate amount of time. This could explain the high value in Table 17 for this sample.

The 19.51 results for sample SO-2 is an obvious measurement error. The degree of agreement of results for sample SO-2 is very similar to that for LKSD-3. These two samples are similar in composition except that SO-2 does contain a significantly greater amount of organic matter. Under normal conditions of heating, this organic matter would be expected to decompose well before reactions with the mineral constituents could occur.

The results for the coals are much more variable. The sample yielding the best overall agreement is SARM-20, which is low in sulfur content, and contains relatively inert mineral components. As long as this sample is heated in such a way that it does not ignite consistent results should be obtained.

The rest of the coal materials exhibit a variety of degrees of agreement. The sulfur content and mineral composition of these coals is such that if they are allowed to ignite, the ash results could be highly variable. If the sample ignites, conversion of organic sulfur to sulfur oxides is likely to occur in concert with decomposition of the mineral components. Should the mineral matter contain significant quantities of alkali and alkaline earth compounds then reaction and recombination of sulfur oxides with these materials can proceed in an unpredictable way. The presence of such mineral components is normal in subbituminous and lignite coal (ES-4, ES-5) and most likely accounts for the discrepancy between the CCME median and reference value as well as the spread in agreement of laboratory results.

The results for ES-2 are a function of the amount (~4.5 %) and distribution of sulfur in the coal. This coal contains significant amounts of pyrite (Fe_xS_y) and sulfates (M_xSO4_y). Although the sulfate compounds should remain stable under controlled conditions of heating, the decomposition of the pyrites can and does proceed in a very complex way that can result in the elimination of sulfur from the sample or the recombination with other mineral components present in the sample. This could certainly account for the discrepancy between the CCME median and Reference value.

The results for ES-3, 1632c and 2692b appear to be as much a function of laboratory bias across all coal types as a function of specific coal properties. For example the results for RMBD and RMBJ tend to be low across all materials tested.

Table 18 Evaluation of the Performance of CCME/CEA Laboratories for the Determination of Sulfur									
Source	NIST	ASTM	NIST	ASTM	ASTM	ASTM	SABS	CCRMP	NIST
Sample ID	1632c	ES-4	2692b	ES-3	ES-2	ES-5	SARM-20	LKSD-3	1633b
Type	Coal hvAb	Coal subA	Coal hvAb	Coal hvBb	Coal hvBb	ligA	Coal hvCb	Lake Sediment	Fly Ash
Reference Value	1.46	0.46	1.17	0.57	4.45	1.04	0.51	0.14	0.21
CCME Median	1.51	0.46	1.18	0.58	4.35	1.06	0.55	0.17	0.21
Horrat CL	±0.02	±0.01	±0.01	±0.01	±0.03	±0.01	±0.01	±0.01	±0.01
Horrat Research Limits	1.53 1.44	0.47 0.45	1.19 1.16	0.59 0.56	4.48 4.32	1.07 1.03	0.56 0.50	0.18 0.13	0.22 0.20
Horrat Applied Limits	1.55 1.42	0.48 0.44	1.20 1.15	0.60 0.55	4.51 4.29	1.08 1.02	0.57 0.49	0.19 0.12	0.23 0.19
RMBB	1.60	0.43	1.46	1.08	4.84	1.38	1.04	0.17	0.20
RMBH	1.51	0.40	1.08	0.54	4.83	1.02	0.55	0.15	0.21
RMBI	1.50	0.46	1.21	0.57	4.30	1.04	0.53	0.17	0.20
RMBJ	1.40	0.46	1.16	0.59	4.04	1.07	0.57	0.16	0.20
RMBL	1.48	0.48	1.19	0.58	4.40	1.03	0.55	0.17	0.21
RMBP	1.56	0.45	1.15	0.58	4.20	1.08	0.52	0.17	0.21

In most cases, the sulfur results generated by a laboratory using a coal method are affected by the extent to which the laboratory method accounts for the three dominant forms, organic sulfur, pyrites and sulfates normally present in coal and whether the laboratory follows the basic fundamentals of good laboratory practice as they relate to instrument calibration. If the laboratory method does not address the former then it is virtually impossible to implement the latter over a wide range of coal quality.

Most methods employed for the determination of sulfur in a coal laboratory rely on the conversion of all forms of sulfur to sulfur oxides. A critical factor that can affect the recovery of the sulfur oxides that are formed is the presence of alkali and alkaline mineral components in the coal. These mineral components can react with the sulfur oxides to form insoluble sulfates or sulfates that require elevated temperatures to ensure complete decomposition.

With these observations in mind it is possible to offer explanations for performance of the CCME/CEA laboratories based on the known distribution of organic sulfur, pyrites and sulfates in the CCME/CEA project samples.

Sample 1633b contains little or no organic sulfur or pyrites. The sulfur in this sample is present as soluble sulfates that readily decompose on heating. Although sample LKSD-3 likely contains some significant amount of organic sulfur, which could react with the alkali and alkaline mineral components in this material, the sulfates formed would be soluble and decompose on heating.

All of the coals listed in table 18 contain organic sulfur, pyrites and sulfates in varying amounts. SARM-20 and ES-5 have completely different mineral compositions with respect to alkali and alkaline earth content. The agreement among the CCME/CEA laboratories for these two coals indicates that the CCME/CEA laboratory methods appear to take into account the presence of different forms of sulfur in coal. This suggests that laboratories whose results do not agree within the Horrat Applied Limits are experiencing problems with equipment calibration.

Table 19 Evaluation of the Performance of CCME/CEA Laboratories for the Determination of Chlorine

Source	NIST	ASTM	NIST	ASTM	ASTM	ASTM
Sample ID	1632c	ES-4	2692b	ES-3	ES-2	ES-5
Type	Coal hvAb	Coal subA	Coal hvAb	Coal hvBb	Coal hvBb	ligA
Reference Value	1139	95	1593	26	465	211
CCME Median	1096	88	1593	26	443	196
Horrat CL	±21	±2	±28	±1	±10	±5
Horrat Research Limits	1160 1075	97 86	1621 1565	27 25	475 433	216 191
Horrat Applied Limits	1180 1055	100 83	1649 1537	28 24	484 424	221 186
RMBA	1092	88	1593	30	435	172
RMBH	1096	74	1623	22	443	196
RMBT	1121	116	1570	26	450	209

It appears all three laboratories are proficient in the analysis of chlorine down to approximately 400 µg/g. The performance of the laboratories is less consistent with respect to the Horrat limits in the range of 20 µg/g to 400 µg/g.

7 CCME/CEA Project 257-2003 laboratories

CCME/CEA Project 257-2003 Laboratories	
CANMET	Ottawa ON
SaskPower	Regina SK
Ontario Power Generation	Toronto ON
University of Ottawa	Ottawa ON
PSC Analytical	Bedford NS
Dalhousie University	Halifax NS
University of New Brunswick RPC	Fredericton NB
Loring Labs	Calgary AB
Alberta Research Council	Vegreville, AB
Kinetrics	Toronto ON
Leco	St. Joseph's MI USA
Becquerel Labs	Mississauga ON
Maxxam Analytics	Calgary AB