

Mercury Laboratory Round Robin Project CCME/CEA Project 257-2003 Phase II First Quarter 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. Phase II seeks to benchmark selected coals used in Canada for mercury, and to provide on-going quality assurance for the duration of this two-year data collection program. During Phase II quarterly samples are to be sent out to the eight CCME/CEA approved laboratories. This report evaluates laboratory performance for the first quarter ending June 1 2003.

This first quarter, phase II report demonstrates that Canadian laboratories continue to produce mercury results for coal with a level of quality consistent with quality assurance and control requirements specified in recognized international standards. All eight laboratories that qualified for Phase 2 met the performance requirements. Table 1 lists the laboratories.

Table 1 List of Approved CCME/CEA Project 257-2003 Laboratories Phase II QA/QC Quarter 1	
CANMET	Ottawa ON
SaskPower	Regina SK
Ontario Power Generation	Toronto ON
University of Ottawa	Ottawa ON
PSC Analytical	Bedford NS
Loring Labs	Calgary AB
Kinetrics	Toronto ON
Maxxam Analytics	Calgary AB

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).

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.

During Phase II laboratories shall analyze quarterly samples over a period of one year. Each quarter consists of a sample pair. One shall be a coal chosen by a Canadian utility, representative of those used for power production in Canada. Another shall be a reference material (RM) coal selected by Quality Associates International®. Both samples have known mercury values established from results provided by the laboratories that take part in the CANSPEX™ (Coal and Ash Sample Proficiency Exchange). Analytical results from the CANSPEX™ community of laboratories have been employed by the National Institute of Standards and Technology (NIST) USA to develop 8 Certified Reference Material (CRM) coals over the past 8 years. Data submitted by CANSPEX™ laboratories was used to establish and/or verify NIST certificate values for ash, sulfur, mercury and chlorine. Results from CANSPEX™ have also been used in certification exercises conducted by the South African Bureau of Standards (SABS), the United States Geological Survey (USGS) and in method validation studies conducted by the International Organization for Standardization (ISO).

The two samples employed in the first quarter of Phase II were designated as 22-3 and 23-1. The characteristics of these two coals are listed in Table 2.

ID	Sample 22-3	Sample 23-1
Rank	High Volatile A Bituminous	Lignite A
Source	United Kingdom Thoresby	Saskatchewan Poplar River
Mercury ng/g dry basis	132	142
Moisture wt %	2.97	12.16
Ash wt % dry basis	19.19	21.33
Sulfur wt % dry basis	1.90	0.92
Chlorine µ/g dry basis	4877	61

The two coals are of completely different rank but have very similar mercury content. Table 2 also lists coal properties that are known to have an impact on the reliable determination of mercury. Although the ash contents are similar, the two coals have significantly different moisture, sulfur and chlorine contents. Selection of the coals in this manner permits the identification of factors that may be affecting the quality of laboratory mercury results.

4 Evaluation of the Performance of Participating Laboratories

Evaluation Criteria

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 3 through 10 present the individual CCME/CEA study laboratory results.

Each laboratory table lists

- The laboratory code
- The method employed by the laboratory
- The sample ID, source and rank
- The four dry basis mercury results calculated from the values reported by the laboratory.
- The 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.

Observations for each lab on factors that may be affecting results are provided where appropriate.

Determination of Mercury (Hg) by the CCME/CEA laboratory C1CM

Table 3 Lab C1CM: D 6722 Phase II First Quarter Mercury Results ng/g dry basis

Sample	Source	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
22-3	United Kingdom Thoresby	High Volatile A Bituminous Coal	142	143	139	141	132	± 4	± 18	141	3	20
23-1	Saskatchewan Poplar River	Lignite Coal	136	129	136	134	142	± 12	± 22	134	7	24

The C1CM average for the United Kingdom, Thoresby coal agrees with the reference value within the expected accuracy.

The C1CM average for the Saskatchewan Polar River coal agrees with the reference value within the reference CL

The C1CM precision value for both coals is well within the ISO 5725-6 limiting precision value.

Based on the criteria and limitations specified in the evaluation criteria, laboratory **C1CM continues to demonstrate proficiency** in the analysis of mercury.

Observations:

None

Determination of Mercury (Hg) by the CCME/CEA laboratory C1CT

Table 4 Lab C1CT: D 6722 Phase II First Quarter Mercury Results ng/g dry basis

Sample	Source	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
22-3	United Kingdom Thoresby	High Volatile A Bituminous Coal	137	137	134	130	132	± 4	± 18	134	6	20
23-1	Saskatchewan Poplar River	Lignite Coal	133	130	138	143	142	± 12	± 22	136	11	24

The C1CT average for the United Kingdom, Thoresby coal agrees with the reference value within the reference CL.

The C1CT average for the Saskatchewan Polar River coal also agrees with the reference value within the reference CL

The C1CT precision value for both coals is well within the ISO 5725-6 limiting precision value.

Based on the criteria and limitations specified in the evaluation criteria, laboratory **C1CT continues to demonstrate proficiency** in the analysis of mercury.

Observations:

None

Determination of Mercury (Hg) by the CCME/CEA laboratory C1CH

Table 5 Lab C1CH: D 6722 Phase II First Quarter Mercury Results ng/g dry basis

Sample	Source	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
22-3	United Kingdom Thoresby	High Volatile A Bituminous Coal	141	139	137	146	132	± 4	± 18	141	8	20
23-1	Saskatchewan Poplar River	Lignite Coal	130	135	153	135	142	± 12	± 22	138	20	24

The C1CH average for the United Kingdom, Thoresby coal agrees with the reference value within the expected accuracy.

The C1CH average for the Saskatchewan Polar River coal agrees with the reference value within the reference CL

The C1CH precision value for the United Kingdom, Thoresby coal is well within the ISO 5725-6 limiting precision value while that for the Saskatchewan Polar River coal approaches the limiting value.

Based on the criteria and limitations specified in the evaluation criteria, laboratory **C1CH continues to demonstrate proficiency** in the analysis of mercury.

Observations:

Both the accuracy and precision of coal mercury results can degrade significantly as the ash, sulfur, chlorine and moisture content of coal increases. Since the United Kingdom Thoresby coal is significantly higher in sulfur and chlorine than the Saskatchewan Poplar River coal the C1CH precision value for the Saskatchewan Poplar River coal may indicate a calibration and/or instrument stability problem associated with the moisture content of coal.

Determination of Mercury (Hg) by the CCME/CEA laboratory C1CE

Table 6 Lab C1CE: D 6722 Phase II First Quarter Mercury Results ng/g dry basis

Sample	Source	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
22-3	United Kingdom Thoresby	High Volatile A Bituminous Coal	142	146	146	147	132	± 4	± 18	145	4	20
23-1	Saskatchewan Poplar River	Lignite Coal	145	136	139	134	142	± 12	± 22	139	10	24

The C1CM average for the United Kingdom, Thoresby coal agrees with the reference value within the expected accuracy.

The C1CE average for the Saskatchewan Polar River coal agrees with the reference value within the reference CL

The C1CE precision value for both coals is well within the ISO 5725-6 limiting precision value.

Based on the criteria and limitations specified in the evaluation criteria, laboratory **C1CE continues to demonstrate proficiency** in the analysis of mercury.

Observations:

None

Determination of Mercury (Hg) by the CCME/CEA laboratory C1CB

Table 7 Lab C1CB: D 6414 Phase II First Quarter Mercury Results ng/g dry basis

Sample	Source	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
22-3	United Kingdom Thoresby	High Volatile A Bituminous Coal	134	132	131	137	132	± 4	± 26	133	5	34
23-1	Saskatchewan Poplar River	Lignite Coal	153	140	137	159	142	± 12	± 30	147	21	36

The C1CB average for the United Kingdom, Thoresby coal agrees with the reference value within the reference CL.

The C1CB average for the Saskatchewan Polar River coal also agrees with the reference value within the reference CL

The C1CB precision value for the United Kingdom, Thoresby coal is well within the ISO 5725-6 limiting precision value while that for the Saskatchewan Polar River coal approaches the limiting value.

Based on the criteria and limitations specified in the evaluation criteria, laboratory **C1CB continues to demonstrate proficiency** in the analysis of mercury.

Observations:

Both the accuracy and precision of coal mercury results can degrade significantly as the ash, sulfur, chlorine and moisture content of coal increases. Clearly accuracy is not an issue for lab C1CB. In fact lab C1CB continues to produce some of the most accurate results that have been observed to date from any laboratory using ASTM method D 6414, a method that employs an acid extraction.

Since the United Kingdom Thoresby coal is significantly higher in sulfur and chlorine than the Saskatchewan Poplar River coal the C1CB precision value for the Saskatchewan Poplar River coal is most likely associated with the moisture content of the coal. CANSPEX™ labs using the ASTM D 6414 procedure have reported that low rank, high moisture coals exhibit a tendency to foam either when the acid extraction medium is added or when the chemicals required to convert and release the mercury are added to the digestate. This characteristic is thought to lead to more erratic within lab results.

Determination of Mercury (Hg) by the CCME/CEA laboratory C1CU

Table 8 Lab C1CU: D 6722 Phase II First Quarter Mercury Results ng/g dry basis

Sample	Source	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
22-3	United Kingdom Thoresby	High Volatile A Bituminous Coal	140	138	134	144	132	± 4	± 18	139	8	20
23-1	Saskatchewan Poplar River	Lignite Coal	127	123	117	120	142	± 12	± 22	122	9	24

The C1CU average for the United Kingdom, Thoresby coal agrees with the reference value within the expected accuracy.

The C1CU average for the Saskatchewan Polar River coal agrees with the reference value within the expected accuracy.

The C1CU p precision value for both coals is well within the ISO 5725-6 limiting precision value.

Based on the criteria and limitations specified in the evaluation criteria, laboratory **C1CU continues to demonstrate proficiency** in the analysis of mercury.

Observations:

Both the accuracy and precision of coal mercury results can degrade significantly as the ash, sulfur, chlorine and moisture content of coal increases. Since the United Kingdom Thoresby coal is significantly higher in sulfur and chlorine than the Saskatchewan Poplar River coal the accuracy of the C1CU values may indicate a calibration problem associated with the moisture content of coal.

Determination of Mercury (Hg) by the CCME/CEA laboratory C1CN

Table 9 Lab C1CN: Microwave ICPMS Phase II First Quarter Mercury Results ng/g dry basis

Sample	Source	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
22-3	United Kingdom Thoresby	High Volatile A Bituminous Coal	123	121	119	124	132	± 4	± 34	122	5	28
23-1	Saskatchewan Poplar River	Lignite Coal	113	119	122	116	142	± 12	± 36	118	8	30

The C1CN average for the United Kingdom, Thoresby coal agrees with the reference value within the expected accuracy.

The C1CN average for the Saskatchewan Polar River coal agrees with the reference value within the expected accuracy.

The C1CN precision value for both coals is well within the ISO 5725-6 limiting precision value.

Based on the criteria and limitations specified in the evaluation criteria, laboratory **C1CN continues to demonstrate proficiency** in the analysis of mercury.

Observations:

Both the accuracy and precision of coal mercury results can degrade significantly as the ash, sulfur, chlorine and moisture content of coal increases. Lab C1CN has a tendency to low recovery of mercury for these two samples. Lab C1CN employs a nitric acid digestion procedure with heating in a microwave. Both of these coals are relatively high in ash content. The Saskatchewan Poplar River sample, which has the lowest recovery, has the highest ash content. In addition the ash of the Poplar River sample contains a significant amount of calcium carbonate, which would react to neutralize the nitric acid employed to digest the coal. Increasing the amount of nitric acid in the digestion step in proportion to the ash content of the coal may improve recovery.

Determination of Mercury (Hg) by the CCME/CEA laboratory C1CW

Table 10 Lab C1CW: D 6414 Phase II First Quarter Mercury Results ng/g dry basis

Sample	Source	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
22-3	United Kingdom Thoresby	High Volatile A Bituminous Coal	152	152	158	158	132	± 4	± 26	155	7	34
23-1	Saskatchewan Poplar River	Lignite Coal	169	169	163	176	142	± 12	± 30	169	11	36

The C1CW average for the United Kingdom, Thoresby coal agrees with the reference value within the expected accuracy.

The C1CW average for the Saskatchewan Polar River coal agrees with the reference value within the expected accuracy.

The C1CW precision value for both coals is well within the ISO 5725-6 limiting precision value.

Based on the criteria and limitations specified in the evaluation criteria, laboratory **C1CN continues to demonstrate proficiency** in the analysis of mercury.

Observations:

The lab C1CW recovery for both coals is high by almost exactly the same amount, **23 ng/g** for the United Kingdom, Thoresby coal and **27 ng/g** for the Saskatchewan Polar River coal. This is a strong indication that the C1CW mercury calibration is biased.