

Mercury Laboratory Round Robin Project CCME/CEA Project 257-2003 Phase II Third 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 mercury analysis proficiency of laboratories for selected coals used in Canada, 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 third quarter ending December 31 2003.

This third quarter, phase II report demonstrates that Canadian laboratories continue to produce mercury results for coal 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 3	
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 third quarter of Phase II were designated as 20-4 and 23-3. The characteristics of these two coals are listed in Table 2.

ID	Sample 20-4	Sample 23-3
Rank	Medium Volatile A Bituminous	High Volatile A Bituminous
Source	Germany	OPG Kentucky USA
Mercury ng/g dry basis	72	66
Moisture wt %	0.89	1.68
Ash wt % dry basis	7.00	8.52
Sulfur wt % dry basis	0.70	0.92
Chlorine µ/g dry basis	1178	1479

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. The two coals have similar moisture, ash, 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.

For each lab, observations concerning factors that may be affecting results are provided.

Determination of Mercury (Hg) by the CCME/CEA laboratory C3EX

Table Lab C3EX: D 6722 Phase II Third 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
20-4	Germany	Medium Volatile Bituminous Coal	74	75	72	78	72	± 12	± 18	75	5	22
23-3	OPG Kentucky USA	High Volatile A Bituminous Coal	67	68	63	60	66	± 10	± 16	64	8	20

The C3EX average for the German coal agrees with the reference value within the reference CL.

The C3EX average for the OPG Kentucky USA coal agrees with the reference value within the reference CL.

The C3EX 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 **C3EX continues to demonstrate proficiency** in the analysis of mercury.

Observations:

None.

Determination of Mercury (Hg) by the CCME/CEA laboratory C3ER

Table Lab C3ER: D 6722 Phase II Third 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
20-4	Germany	Medium Volatile Bituminous Coal	66	70	66	68	72	± 12	± 18	68	4	22
23-3	OPG Kentucky USA	High Volatile A Bituminous Coal	59	62	60	57	66	± 10	± 16	59	4	20

The C3ER average for the German coal agrees with the reference value within the reference CL.
 The C3ER average for the OPG Kentucky USA coal agrees with the reference value within the reference CL.

The C3ER 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 **C3ER continues to demonstrate proficiency** in the analysis of mercury.

Observations:

The C3ER value for the German coal is 4 ng low while that for the OPG Kentucky USA coal is 7 ng low. This trend towards systematically low results can be attributed to the C3ER calibration.

Determination of Mercury (Hg) by the CCME/CEA laboratory C3EU

Table Lab C3EU: D 6722 Phase II Third 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
20-4	Germany	Medium Volatile Bituminous Coal	72	81	82	77	72	± 12	± 18	78	9	22
23-3	OPG Kentucky USA	High Volatile A Bituminous Coal	82	80	75	73	66	± 10	± 16	77	9	20

The C3EU average for the German coal agrees with the reference value within the reference CL.

The C3EU average for the OPG Kentucky USA coal agrees with the reference value within the expected accuracy.

The C3EU 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 **C3EU continues to demonstrate proficiency** in the analysis of mercury.

Observations:

The C3EU value for the German coal is 6 ng high while that for the OPG Kentucky USA coal is 11 ng high. This trend towards systematically high results can be attributed to the C3EU calibration.

Determination of Mercury (Hg) by the CCME/CEA laboratory C3EL

Table Lab C3EL: D 6722 Phase II Third 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
20-4	Germany	Medium Volatile Bituminous Coal	67	73	73	83	72	± 12	± 18	74	13	22
23-3	OPG Kentucky USA	High Volatile A Bituminous Coal	70	67	69	75	66	± 10	± 16	70	7	20

The C3EL average for the German coal agrees with the reference value within the reference CL.

The C3EL average for the OPG Kentucky USA coal agrees with the reference value within the reference CL.

The C3EL 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 **C3EL continues to demonstrate proficiency** in the analysis of mercury.

Observations:

The C3EL value for the German coal is 2 ng high while that for the OPG Kentucky USA coal is 4 ng high. This trend towards slightly high results can be attributed to the C3EL calibration.

Determination of Mercury (Hg) by the CCME/CEA laboratory C3EG

Table Lab C3EG: D 6414 Phase II Third 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
20-4	Germany	Medium Volatile Bituminous Coal	59	61	63	59	72	± 12	± 20	61	4	30
23-3	OPG Kentucky USA	High Volatile A Bituminous Coal	58	60	58	68	66	± 10	± 16	61	9	26

The C3EG average for the German coal agrees with the reference value within the reference CL.

The C3EG average for the OPG Kentucky USA coal agrees with the reference value within the reference CL.

The C3EG 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 **C3EG continues to demonstrate proficiency** in the analysis of mercury.

Observations:

The C3EG value for the German coal is 11 ng low while that for the OPG Kentucky USA coal is 5 ng low. There are two probable causes for this trend.

This trend towards systematically low results can be attributed to the C3EG calibration.

Alternatively all of the mercury present in the coal may not be extracted by the C3EG acid extraction procedure. This tends to be supported by the higher observed difference for the German coal than the OPG Kentucky USA coal. The German coal is a medium volatile coal that contains more refractory carbon compounds than the OPG Kentucky USA coal. These compounds, which can contain mercury, may not be completely decomposed by the acids used in the digestion.

Determination of Mercury (Hg) by the CCME/CEA laboratory C3EV

Table Lab C3EV: D 6722 Phase II Third 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
20-4	Germany	Medium Volatile Bituminous Coal	76	69	74	74	72	± 12	± 18	74	6	22
23-3	OPG Kentucky USA	High Volatile A Bituminous Coal	63	66	58	61	66	± 10	± 16	62	7	20

The C3EV average for the German coal agrees with the reference value within the reference CL.
 The C3EV average for the OPG Kentucky USA coal agrees with the reference value within the reference CL.

The C3EV 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 **C3EV continues to demonstrate proficiency** in the analysis of mercury.

Observations:

None.

Determination of Mercury (Hg) by the CCME/CEA laboratory C3EZ

Table Lab C3EZ: Microwave ICPMS Phase II Third 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
20-4	Germany	Medium Volatile Bituminous Coal	59	65	60	63	72	± 12	± 24	62	6	22
23-3	OPG Kentucky USA	High Volatile A Bituminous Coal	58	56	57	55	66	± 10	± 24	56	3	20

The C3EZ average for the German coal agrees with the reference value within the reference CL.
 The C3EZ average for the OPG Kentucky USA coal agrees with the reference value within the reference CL.

The C3EZ 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 **C3EZ continues to demonstrate proficiency** in the analysis of mercury.

Observations:

The C3EZ value for the German coal is 10 ng low and that for the OPG Kentucky USA coal is also 10 ng low. This trend towards uniformly low results can most likely be attributed to the C3EZ calibration.

Determination of Mercury (Hg) by the CCME/CEA laboratory C3EN

Table Lab C3EN: D 6414 Phase II Third 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
20-4	Germany	Medium Volatile Bituminous Coal	63	58	56	58	72	± 12	± 20	59	7	30
23-3	OPG Kentucky USA	High Volatile A Bituminous Coal	58	56	58	56	66	± 10	± 16	57	3	26

The C3EN average for the German coal agrees with the reference value within the expected accuracy.

The C3EN average for the OPG Kentucky USA coal agrees with the reference value within the reference CL.

The C3EN 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 C3EN value for the German coal is 13 ng low while that for the OPG Kentucky USA coal is 9 ng low. There are two probable causes for this trend.

This trend towards systematically low results can be attributed to the C3EN calibration.

Alternatively all of the mercury present in the coal may not be extracted by the C3EN acid extraction procedure. This tends to be supported by the higher observed difference for the German coal than the OPG Kentucky USA coal. The German coal is a medium volatile coal that contains more refractory carbon compounds than the OPG Kentucky USA coal. These compounds, which can contain mercury, may not be completely decomposed by the acids used in the digestion.