

# Mercury Laboratory Round Robin Project CCME/CEA Project 257-2003 Phase II Second 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 second quarter ending September 1 2003.

This second 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.

<b>Table 1 List of Approved CCME/CEA Project 257-2003 Laboratories Phase II QA/QC Quarter 2</b>	
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 second quarter of Phase II were designated as 21-4 and 23-2. The characteristics of these two coals are listed in Table 2.

<b>Table 2 Characteristics of CCME 257-2003 Phase II Second Quarter Samples</b>		
<b>ID</b>	<b>Sample 21-4</b>	<b>Sample 23-2</b>
<b>Rank</b>	<b>High Volatile A Bituminous</b>	<b>Subbituminous</b>
<b>Source</b>	<b>USA KY Pond Creek</b>	<b>TransAlta Sundance</b>
<b>Mercury ng/g dry basis</b>	<b>53</b>	<b>59</b>
<b>Moisture wt %</b>	2.13	9.47
<b>Ash wt % dry basis</b>	8.10	24.31
<b>Sulfur wt % dry basis</b>	0.74	0.24
<b>Chlorine µ/g dry basis</b>	1906	36

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 significantly different 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.

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

Determination of Mercury (Hg) by the CCME/CEA laboratory C2DB

Table Lab C2DB: D 6722 Phase II Second 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
21-4	USA KY Pond Creek	High Volatile A Bituminous Coal	58	60	62	65	53	± 5	± 12	61	7	14
23-2	TransAlta Sundance	Subbituminous Coal	59	64	61	63	59	± 8	± 14	62	4	20

The C2DB average for the USA KY Pond Creek coal agrees with the reference value within the expected accuracy.

The C2DB average for the TransAlta Sundance coal agrees with the reference value within the reference CL

The C2DB 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 **C2DB continues to demonstrate proficiency** in the analysis of mercury.

**Observations:**

None

Determination of Mercury (Hg) by the CCME/CEA laboratory C2DN

Table Lab C2DN: D 6722 Phase II Second 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
21-4	USA KY Pond Creek	High Volatile A Bituminous Coal	53	57	55	56	53	± 5	± 12	55	3	14
23-2	TransAlta Sundance	Subbituminous Coal	61	61	60	61	59	± 8	± 14	61	1	20

The C2DN average for the USA KY Pond Creek coal agrees with the reference value within the reference CL.

The C2DN average for the TransAlta Sundance coal also agrees with the reference value within the reference CL.

The C2DN 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 **C2DN continues to demonstrate proficiency** in the analysis of mercury.

**Observations:**

None

Determination of Mercury (Hg) by the CCME/CEA laboratory C2DS

Table Lab C2DS: D 6722 Phase II Second 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
21-4	USA KY Pond Creek	High Volatile A Bituminous Coal	52	59	59	56	53	± 5	± 12	56	7	14
23-2	TransAlta Sundance	Subbituminous Coal	64	70	66	66	59	± 8	± 14	66	5	20

The C2DS average for the USA KY Pond Creek coal agrees with the reference value within the reference CL.

The C2DS average for the TransAlta Sundance coal agrees with the reference value within the reference CL.

The C2DS 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 **C2DS 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 C2DS exhibited wider precision for the high moisture lignite coal distributed in the first quarter of phase 2. This behaviour is not evident for the high moisture subbituminous coal distributed in the second quarter.

Determination of Mercury (Hg) by the CCME/CEA laboratory C2DI

Table Lab C2DI: D 6722 Phase II Second 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
21-4	USA KY Pond Creek	High Volatile A Bituminous Coal	50	56	51	51	53	± 5	± 12	52	6	14
23-2	TransAlta Sundance	Subbituminous Coal	58	57	73	63	59	± 8	± 14	63	14	20

The C2DI average for the USA KY Pond Creek coal agrees with the reference value within the reference CL.

The C2DI average for the TransAlta Sundance coal agrees with the reference value within the reference CL.

The C2DI 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 **C2DI continues to demonstrate proficiency** in the analysis of mercury.

**Observations:**

None

Determination of Mercury (Hg) by the CCME/CEA laboratory C2DF

Table Lab C2DF: D 6414 Phase II Second 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
21-4	USA KY Pond Creek	High Volatile A Bituminous Coal	49	48	48	51	53	± 5	± 24	49	3	24
23-2	TransAlta Sundance	Subbituminous Coal	50	53	49	44	59	± 8	± 24	49	7	24

The C2DF average for the USA KY Pond Creek coal agrees with the reference value within the reference CL.

The C2DF average for the TransAlta Sundance coal also agrees with the reference value within the expected accuracy.

The C2DF precision value for the USA KY Pond Creek and the TransAlta Sundance coal is well within the ISO 5725-6 limiting precision value.

Based on the criteria and limitations specified in the evaluation criteria, laboratory **C2DF continues to demonstrate proficiency** in the analysis of mercury.

**Observations:**

None.

Determination of Mercury (Hg) by the CCME/CEA laboratory C2DD

Table Lab C2DD: D 6722 Phase II Second 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
21-4	USA KY Pond Creek	High Volatile A Bituminous Coal	54	55	50	51	53	± 5	± 12	53	5	14
23-2	TransAlta Sundance	Subbituminous Coal	61	54	51	56	59	± 8	± 14	55	8	20

The C2DD average for the USA KY Pond Creek coal agrees with the reference value within the reference CL.

The C2DD average for the TransAlta Sundance coal agrees with the reference value within the reference CL.

The C2DD 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 **C2DD continues to demonstrate proficiency** in the analysis of mercury.

**Observations:**

None.

Determination of Mercury (Hg) by the CCME/CEA laboratory C2DY

Table Lab C2DY: Microwave ICPMS Phase II Second 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
21-4	USA KY Pond Creek	High Volatile A Bituminous Coal	69	65	62	63	53	± 5	± 18	65	6	14
23-2	TransAlta Sundance	Subbituminous Coal	56	56	55	61	59	± 8	± 18	57	6	16

The C2DY average for the USA KY Pond Creek coal agrees with the reference value within the expected accuracy.

The C2DY average for the TransAlta Sundance coal agrees with the reference value within the Reference CL.

The C2DY 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 **C2DY continues to demonstrate proficiency** in the analysis of mercury.

**Observations:**

None.

Determination of Mercury (Hg) by the CCME/CEA laboratory C2DM

Table Lab C2DM: D 6414 Phase II Second 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
21-4	USA KY Pond Creek	High Volatile A Bituminous Coal	60	60	60	60	53	± 5	± 24	60	0	24
23-2	TransAlta Sundance	Subbituminous Coal	61	65	65	65	59	± 8	± 24	64	4	24

The C2DM average for the USA KY Pond Creek coal agrees with the reference value within the expected accuracy.

The C2DM average for the TransAlta Sundance coal agrees with the reference value within the reference CL.

The C2DM 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:**

None.