

Mercury Laboratory Round Robin Project CCME/CEA Project 257-2003 Phase II Fourth 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 fourth quarter ending March 31 2004.

This fourth 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. Seven of the 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
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.

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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 fourth quarter of Phase II were designated as II-4-1 and II-4-2. The characteristics of these two coals are listed in Table 2.

Table 2 Characteristics of CCME 257-2003 Phase II Fourth Quarter Samples		
ID	II-4-1	II-4-2
Rank	High Volatile A Bituminous	High Volatile A Bituminous
Source	Venezuela	Venezuela
Mercury ng/g dry basis	73	73
Moisture wt %	2.08	2.08
Ash wt % dry basis	5.44	5.44
Sulfur wt % dry basis	0.67	0.67
Chlorine µ/g dry basis	208	208

The two fourth quarter samples are the same coal. Selecting the samples in this manner permits the evaluation of bottle-to-bottle inhomogeneity as well as within lab calibration drift.

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Table 3 summarizes the laboratory averages and precision for each fourth quarter sample.

Table 3 Fourth Quarter CCME Lab Averages and Precision					
Lab	Reference Value	II-4-1 Average	II-4-2 Average	II-4-1 Precision	II-4-2 Precision
C4FN	73	63	56	4	9
C4FS	73	67	57	7	6
C4FJ	73	72	69	5	3
C4FV	73	71	68	6	5
C4FT	73	72	72	7	7
C4FZ	73	79	75	7	3
C4FI	73	71	74	17	9
C4FO	73	74	75	20	19

Sample II-4-1 and II-4-2 was also distributed to the CANSPEX™ group of laboratories as sample 2003-4. The results from the CANSPEX™ laboratories were used to establish the reference value listed in table 3. The within bottle precision for CANSPEX™ laboratories employing the same methods as the CCME group of laboratories was in the range of 3 to 11 ng/g. Every CCME laboratory except C4FI and C4FO reported precision results within this range. This outcome supports the observation samples II-4-1 and II-4-2 exhibit uniform homogeneity.

Specific comments on laboratory performance are provided in section 4.

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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.

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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.

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Determination of Mercury (Hg) by the CCME/CEA laboratory C4FS

Table Lab C4FS: D 6722 Phase II Fourth 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
II-4-1	Venezuela	High Volatile A Bituminous Coal	71	67	63	66	73	± 11	± 16	67	7	20
II-4-2	Venezuela	High Volatile A Bituminous Coal	61	54	57	55	73	± 11	± 16	57	6	20

The C4FS average for sample II-4-1 agrees with the reference value within the reference CL.

The C4FS average for sample II-4-2 agrees with the reference value within the expected accuracy.

The C4FS precision value for both samples is well within the ISO 5725-6 limiting precision value.

Based on the criteria and limitations specified in the evaluation criteria, laboratory **C4FS continues to demonstrate proficiency** in the analysis of mercury.

Observations:

The C4FS results are on average 11 ng/g low. Adding this to the C4FS results would yield corrected averages of 78 ng/g and 68 ng/g respectively. This suggests calibration drift may have occurred during the analysis of the two CCME samples. This drift could be caused by a number of factors including change in instrument peak profiles with time.

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Determination of Mercury (Hg) by the CCME/CEA laboratory C4FJ

Table Lab C4FJ: D 6722 Phase II Fourth 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
II-4-1	Venezuela	High Volatile A Bituminous Coal	72	76	71	70	73	± 11	± 16	72	5	20
II-4-2	Venezuela	High Volatile A Bituminous Coal	68	68	70	71	73	± 11	± 16	69	3	20

The C4FJ average for both samples agrees with the reference value within the reference CL.

The C4FJ precision value for both samples is well within the ISO 5725-6 limiting precision value.

Based on the criteria and limitations specified in the evaluation criteria, laboratory **C4FJ continues to demonstrate proficiency** in the analysis of mercury.

Observations:

None.

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Determination of Mercury (Hg) by the CCME/CEA laboratory C4FO

Table Lab C4FO: D 6722 Phase II Fourth 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
II-4-1	Venezuela	High Volatile A Bituminous Coal	81	83	68	63	73	± 11	± 16	74	20	20
II-4-2	Venezuela	High Volatile A Bituminous Coal	88	69	77	67	73	± 11	± 16	75	19	20

The C4FO average for both samples agrees with the reference value within the reference CL.

The C4FO precision value for both samples is right on the limit of the ISO 5725-6 limiting precision value.

Based on the criteria and limitations specified in the evaluation criteria, laboratory **C4FO continues to demonstrate proficiency** in the analysis of mercury.

Observations:

Lab C4FO also takes part in the CANSPEX™ program.

CANSPEX™ sample 2003-4 was distributed as II-4-1 and II-4-2

This lab reported an average value of 72 ng/g with a precision of 10 ng/g for sample CANSPEX sample 2003-4.

The lab confirmed that between analysis of the CANSPEX™ sample and CCME II-4-1 and II-4-2 the instrument was returned to the manufacturer for repair.

The determination of mercury on many analyzers can be carried out by accumulating instrument response as peak height or peak area. Acceptable within lab precision for standards and control samples but unacceptable precision for test samples can occur for analyzers that are calibrated to accumulate instrument response in peak height mode. This is because the release of mercury from some coals may not yield consistent peak height.

Since the time of repair the consistency of the instrument peak height profile may have deteriorated.

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Determination of Mercury (Hg) by the CCME/CEA laboratory C4FT

Table Lab C4FT: D 6722 Phase II Fourth 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
II-4-1	Venezuela	High Volatile A Bituminous Coal	72	76	71	68	73	± 11	± 16	72	7	20
II-4-2	Venezuela	High Volatile A Bituminous Coal	74	67	75	71	73	± 11	± 16	72	7	20

The C4FT average for both samples agrees with the reference value within the reference CL.

The C4FT precision value for both samples is well within the ISO 5725-6 limiting precision value.

Based on the criteria and limitations specified in the evaluation criteria, laboratory **C4FT continues to demonstrate proficiency** in the analysis of mercury.

Observations:

None.

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Determination of Mercury (Hg) by the CCME/CEA laboratory C4FI

Table Lab C4FI: D 6414 Phase II Fourth 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
II-4-1	Venezuela	High Volatile A Bituminous Coal	68	83	63	69	73	± 11	± 18	71	17	30
II-4-2	Venezuela	High Volatile A Bituminous Coal	79	68	76	74	73	± 11	± 18	74	9	30

The C4FI average for both samples agrees with the reference value within the reference CL.

The C4FI precision value for both samples is within the ISO 5725-6 limiting precision value.

Based on the criteria and limitations specified in the evaluation criteria, laboratory **C4FI continues to demonstrate proficiency** in the analysis of mercury.

Observations:

C4FI exhibits higher precision for II-4-1 than II-4-2. Examination of the lab's results for the previous three quarters indicates this situation occurred for one other sample. The method employed by lab C4FI involves acid extraction of mercury from the sample. This step can increase opportunities for memory effects or contamination. Procedures for treating and conducting blank checks on extraction vessels to minimize contamination or memory effects can improve precision.

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Determination of Mercury (Hg) by the CCME/CEA laboratory C4FN

Table Lab C4FN: D 6722 Phase II Fourth 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
II-4-1	Venezuela	High Volatile A Bituminous Coal	66	62	61	63	73	± 11	± 16	63	4	20
II-4-2	Venezuela	High Volatile A Bituminous Coal	59	52	52	60	73	± 11	± 16	56	9	20

The C4FN average for sample II-4-1 agrees with the reference value within the reference CL.

The C4FN average for sample II-4-2 fails to meet the expected accuracy requirements.

Based on the criteria and limitations specified in the evaluation criteria, laboratory C4FN has generated a deficiency in the analysis of mercury.

Observations:

Lab C4FN also takes part in the CANSPEX™ program.

CANSPEX™ sample 2003-4 was distributed as II-4-1 and II-4-2.

The reference value for CANSPEX™ sample 2003-4 is 73 ± 11 ng/g.

C4FN reported an average value of 94 ng/g for sample 2003-4.

C4FN reported an average of 60 ng/g for CCME sample II-4-1 and II-4-2.

The difference between the two results is 34 ng/g well outside the reference value limits.

CANSPEX™ sample 2003-3 was distributed in the third quarter as sample 23-3.

The reference value for CANSPEX™ sample 2003-3 is 66 ± 11 ng/g.

C4FN reported an average of 66 ng/g for CANSPEX™ sample 2003-3.

C4FN reported 62 ng/g for CCME sample 23-3.

The difference between the two results is 4 ng/g well within the reference value limits.

This indicates the lab C4FN instrument is no longer in a stable state of control.

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Determination of Mercury (Hg) by the CCME/CEA laboratory C4FV

Table Lab C4FV: Microwave ICPMS Phase II Fourth 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
II-4-1	Venezuela	High Volatile A Bituminous Coal	72	69	67	74	73	± 11	± 24	71	6	20
II-4-2	Venezuela	High Volatile A Bituminous Coal	71	67	69	65	73	± 11	± 24	68	5	20

The C4FV average for both samples agrees with the reference value within the reference CL.

The C4FV precision value for both samples is well within the ISO 5725-6 limiting precision value.

Based on the criteria and limitations specified in the evaluation criteria, laboratory **C4FV continues to demonstrate proficiency** in the analysis of mercury.

Observations:

None.

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Determination of Mercury (Hg) by the CCME/CEA laboratory C4FZ

Table Lab C4FZ: D 6414 Phase II Fourth 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
II-4-1	Venezuela	High Volatile A Bituminous Coal	76	76	82	82	73	± 11	± 18	79	7	30
II-4-2	Venezuela	High Volatile A Bituminous Coal	76	76	73	76	73	± 11	± 18	75	3	30

The C4FZ average for both samples agrees with the reference value within the reference CL.

The C4FZ precision value for both samples is well within the ISO 5725-6 limiting precision value.

Based on the criteria and limitations specified in the evaluation criteria, laboratory **C4FI continues to demonstrate proficiency** in the analysis of mercury.

Observations:

None.