Quality Assurance/Quality Control and Data Process

Asia Pacific Mercury Monitoring Network

Center for Environmental Monitoring and Technology
National Central University

Quality Control

Quality control (QC) tests demonstrating the performance of the modified method, including the following:

- Calibration
- Initial precision and recovery
- Analysis of blanks
- Matrix spike/matrix spike duplicate analysis
- Ongoing precision and recovery
- Quality control sample
- Method detection limit

Analytical Batch

a. Three blanks
b. Five calibration standards
c. Ongoing precision and recovery (OPR)
d. Quality control sample
e. Method blank
f. Seven samples
g. Method blank
h. Three samples
i. Matrix spike/Matrix spike duplicate
j. Four samples
k. Method blank
l. Six samples
m. Matrix spike/Matrix spike duplicate
n. Ongoing precision and recovery

Analytical Batch

Unverified

a. Three blanks
b. Five calibration standards
c. Ongoing precision and recovery (OPR)
d. Quality control sample

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n. Ongoing precision and recovery

Verified

12 hours has elapsed

Contamination Control

The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is metal free and free from any material that may contain mercury

Contamination Control

- Avoiding contamination
- Use a clean environment
- Minimize exposure
- Clean work surfaces
- Wear gloves
- Use metal-free Apparatus
- Avoid sources of contamination

System calibration

1. Bubbler system calibration

- Establish the operating conditions necessary to purge Hg from the bubbler and to desorb Hg from the traps in a sharp peak => The calibration must contain a minimum of 5 non-zero points and the results of analysis of three bubbler blanks.
- Analyze the standards beginning with the lowest concentration and proceeding to the highest.

System calibration

1. Bubbler system calibration

- Prepare and analyze a minimum of 3 bubbler blanks. If the result for any method blank is found to contain > 0.50 ng/L (50 pg) Hg, the system is out of control.
- Calculate the calibration factor (CFx) for Hg in each of the five standards using the mean bubbler-blanksubtracted peak height or area.

System calibration

$$CF_x = \frac{(A_x) - (\overline{A}_{BB})}{(C_x)}$$

Where:

A_x = *peak height or area for Hg in standard*
$\overline{A}_{BB}$ = *mean peak height or area for Hg in bubbler blank*
C_x = *mass in standard analyzed (ng)*

Calculate the mean calibration factor (CFm), SD calibration factor, RSD of the calibration factor,

where RSD = 100 x SD/CFm.

If RSD < 15%, calculate the recovery for the lowest standard using CFm. If the recovery of the lowest standard is in the range of 75-125%, the calibration is acceptable.

System calibration

2. Flow-injection system calibration

- The criteria are similar with the bubbler system calibration. Only difference in repairing the solution.

$$CF_x = \frac{(A_x) - (\overline{A}_{SB})}{(C_x)}$$

Where:

A_x = peak height or area for Hg in standard

$\overline{A}_{SB}$ = mean peak height or area for Hg in calibration blanks

C_x = concentration of standard analyzed (ng/L)

Calibration curve

- Calibration to a range other than 0.5 to 100 ng/L
- There must be a minimum of five non-zero calibration points
- The difference between successive calibration points must be no greater than a factor of 10 and no less than a factor of 2.
- RSD < 15%. The calibration factor for any calibration point at a concentration greater than 100 ng/L must be within ±15% of the average calibration factor for the points at or below 100 ng/L.
- The calibration factor for any point <0.5 ng/L must be within 25% of the average calibration factor for all points.
- Our calibration curve : 0.5, 1, 5, 10, 25, 50 ng/L

Analysis of blanks

- Bubbler blanks

demonstrate that bubbler systems are free from contamination at levels that could affect data quality

- System blanks

demonstrate that flow injection systems are free from contamination at levels that could affect data quality

Analysis of blanks

- Reagent blanks

demonstrate that the reagents used to prepare samples for Hg analyses are free from contamination

- Method blanks

demonstrate that the analytical system is free from contamination that could otherwise compromise sample results

Analysis of blanks

- Field blanks

demonstrate that samples have not been contaminated by the sample collection and transport activities

- Equipment blanks

demonstrate that the sampling equipment is free from contamination

- Bottle blanks

verify the effectiveness of the cleaning procedures

Criteria for Performance

Quality Control Acceptance Criteria for Performance Tests in EPA Method 1631

Table 2

Acceptance Criteria	Section	Limit (%)
Initial Precision and Recovery (IPR)	9.2.2	
Precision (RSD)	9.2.2.3	21
Recovery (X)	9.2.2.3	79-121
Ongoing Precision and Recovery (OPR)	9.5.2	77-123
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	9.3	
Recovery	9.3.4	71-125
Relative Percent Difference (RPD)	9.3.5	24

Initial precision and recovery

To establish the ability to generate acceptable precision and recovery, the laboratory shall perform the following operations

1. Analyze four replicates of the IPR solution (5 ng/L)
2. Using the results of the set of four analyses, compute the average percent recovery (X), and the standard deviation of the percent recovery (s) for Hg
3. Compare s and X with the corresponding limits for initial precision and recovery. (79 – 121% (Accuracy) and 21% RSD (Precision))

Ongoing precision and recovery

To demonstrate that the analytical system is within the performance criteria of this method and that acceptable precision and recovery is being maintained within each analytical batch

Ongoing precision and recovery

Analyze the OPR solution (5 ng/L) prior to the analysis of each analytical. An OPR also must be analyzed at the end of an analytical sequence or at the end of each 12-hour shift

Ongoing precision and recovery

If the recovery is in the range specified, the analytical system is in control and analysis of samples and blanks may proceed. If, however, the concentration is not in the specified range, the analytical process is not in control.

Initial Precision and Recovery (IPR) and Ongoing Precision and Recovery (OPR) solutions

It can be the working Hg standard. Prepare IPR and OPR solutions at a concentration of 5 ng/L Hg in reagent water. IPR/OPR solutions are prepared using the same amounts of reagents used for preparation of the calibration standards.

Matrix spike/matrix spike duplicate analysis

To assess the performance of the Method on a given sample matrix, the laboratory must spike, in duplicate, a minimum of 10% (1 sample in 10) from a given sampling site or, if for compliance monitoring, from a given discharge.

The concentration of the spike in the sample shall be determined as 1–5 times the background concentration of the sample or at 1-5 times the ML in Table

Lowest Ambient Water Quality Criterion for Mercury and the Method Detection Limit and Minimum Level of Quantitation for EPA Method 1631

Metal	Lowest Ambient Water Quality Criterion[1]	Method Detection Limit (MDL) and Minimum Level (ML)	
		MDL[2]	ML[3]
Mercury (Hg)	1.3 ng/L	0.2 ng/L	0.5 ng/L

1. Lowest water quality criterion for the Great Lakes System (Table 4, 40 CFR 132.6). The lowest Nationwide criterion is 12 ng/L (40 CFR 131.36).
2. Method detection limit (40 CFR 136, Appendix B)
3. Minimum level of quantitation (see Glossary)

Matrix spike/matrix spike duplicate analysis

Determine the background concentration (B). Spike two additional sample aliquots with identical amounts of the spiking solution and analyze these aliquots to determine the concentration after spiking (A)

$$\% R = 100 \frac{(A-B)}{T}$$

where:

A = *Measured concentration of analyte after spiking*
B = *Measured concentration of analyte before spiking*
T = *True concentration of the spike*

Matrix spike/matrix spike duplicate analysis

Compare percent recovery (R) with the QC acceptance criteria. If the results of both the spike and the OPR test fall outside the acceptance criteria, the analytical system is judged to be not in control, and the results may not be reported or used for permitting or regulatory compliance purposes

Matrix Spike/Matrix Spike Duplicate (MS/MSD)	9.3	
Recovery	9.3.4	71-125
Relative Percent Difference (RPD)	9.3.5	24

Quality control sample

The laboratory must obtain a QCS from a source different from the Hg used to produce the standards used routinely.

The QCS should be analyzed as an independent check of system performance.

Quality control sample

National Research Council Canada

ORMS-5: Elevated Mercury in River Water

Product documentation

- ORMS-5 (PDF, 150 KB)

ORMS-5 is a river water spiked with inorganic mercury. The material is packaged in 50 ml glass ampoules stabilized with 0.5% BrCl.

Table 1: Certified quantity value

Element	pg/g
Hg	26.2 ± 1.3

The certified value was derived gravimetrically and corroborated with two methods of analysis: cold vapour isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS) and flow injection cold vapour atomic absorption spectrometry (CV-AAS). The certified value is the unweighted mean of the results ± the expanded (k=2) uncertainty (U_{CRM}). The results generated by each of these methods were judged to be independent.

The expanded uncertainty in the certified value is equal to $U_{CRM} = ku_c$, where u_c is the combined standard uncertainty calculated according to the JCGM Guide and k is the coverage factor. It is intended that U_{CRM} encompasses the uncertainty of every factor that reasonably contributes to the total uncertainty of the measurand. A coverage factor k=2 is used to give an uncertainty interval that contains roughly 95% of the underlying distribution. The value of u_c is determined from the combined uncertainties of the methods (u_{char}) as well as uncertainties associated with homogeneity (u_{hom}).

Intended use

This CRM is intended for the calibration of instruments and evaluation of methods for the determination of mercury.

Date of issue: September 2011
Date of expiry: September 2021
Revised: March 2016 (editorial update)

▸ Report a problem or mistake on this page

Date modified: 2016-12-13

Method Detection Limit

To establish the ability to detect Hg, the laboratory shall achieve an MDL that is less than or equal to the MDL (0.16 ng/L @ NCU)

Lowest Ambient Water Quality Criterion for Mercury and the Method Detection Limit and Minimum Level of Quantitation for EPA Method 1631

Metal	Lowest Ambient Water Quality Criterion[1]	Method Detection Limit (MDL) and Minimum Level (ML)	
		MDL[2]	ML[3]
Mercury (Hg)	1.3 ng/L	0.2 ng/L	0.5 ng/L

1. Lowest water quality criterion for the Great Lakes System (Table 4, 40 CFR 132.6). The lowest Nationwide criterion is 12 ng/L (40 CFR 131.36).
2. Method detection limit (40 CFR 136, Appendix B)
3. Minimum level of quantitation (see Glossary)

Data Analysis and Calculations

Calculations for the bubbler system

$$[Hg]\ (ng/L) = \frac{A_s - \overline{A}_{BB}}{CF_m \times V}$$

where:

A_s = peak height (or area) for Hg in sample

$\overline{A}_{BB}$ = peak height (or area) for Hg in bubbler blank

CF_m = mean calibration factor (Section 10.2.2.5)

V = Volume of sample (L)

We can use this formula to calculate for concentration of Hg in method blanks, field blanks, and reagent blanks

Data Analysis and Calculations

Calculations for the flow-injection system

$$[Hg]\ (ng/L) = \frac{(A_s - \overline{A}_{SB})}{CF_m} \times \frac{V_{std}}{V_{sample}}$$

where:

A_s = peak height (or area) for Hg in sample

$\overline{A}_{SB}$ = mean peak height (or area) for Hg in system blanks

CF_m = mean calibration factor (Section 10.3.2.6)

V_{std} = volume (mL) used for standards – volume (mL) reagent used in standards

V_{sample} = volume (mL) of sample – volume (mL) reagent used in sample

Data Worksheet (instrument output)

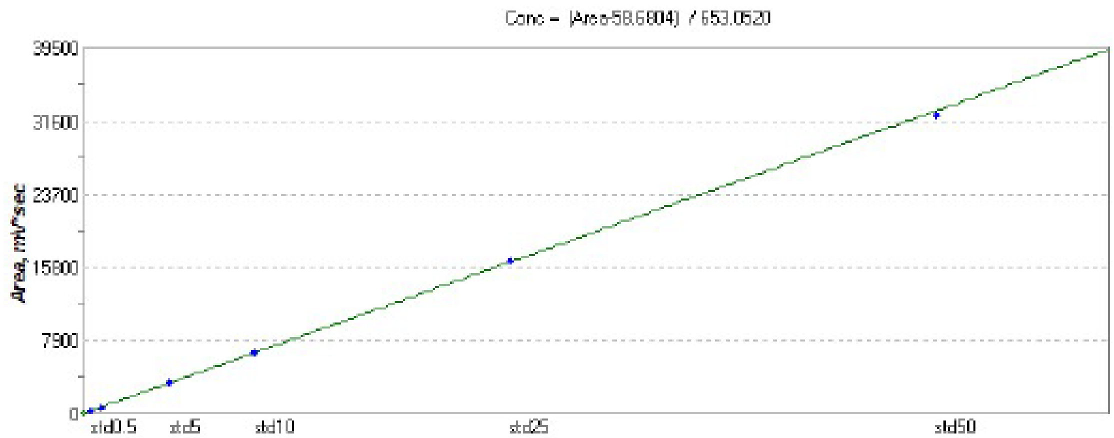
WS00000006*

TotalMercury	**Operator:**		**BlankSub:**	58.6804	**Calib Eqn:**	Conc = (Area-58.6804) / 653.05	**Run Date:** 2017-04-17	**Blank SD:**	5.2322
EPA1631	**Worksheet:**	WS00000006	**CalibFactor:**	653.0520	**Status:**	QC Warnings:1/QC Errors:0	**Run Time:** 00:00:00	**Blank RSD%:**	8.9164
	MethodRev:	2008-05-12	**R:**	0.9999	**R?**	0.9999		**CF SD:**	13.1908
	Description:	IMPORT WS00000105.TWZ WS00000105						**CF RSD%:**	2.0199

	Sample/ID	Location	Rinse	Dilute	Blank	Conc (ppt)	MB%	FinalConc	Rec%	QA	RawData	RunEnd	Peak (Raw)	Control (etf)	Flags	RunCount	Comment
1	Clean				0.00	0.53					3279-1.RAW	11:18:14	343.21	cleandry	OK	1	
2	DIW	a1			58.68	0.00					3280-1.RAW	11:21:52	27.38	invial	OK	1	
3	DIW	a2			58.68	0.00					3281-1.RAW	11:25:30	24.62	invial	OK	1	
4	DIW	a3			58.68	0.00					3282-1.RAW	11:29:08	26.66	invial	OK	1	
5	CalBlank	a4			0.00	0.10					3283-1.RAW	11:32:46	64.12	invial	OK	1	
6	CalBlank	a5			0.00	0.09					3284-1.RAW	11:36:24	58.23	invial	OK	1	
7	CalBlank	a6			0.00	0.08					3285-1.RAW	11:40:01	53.69	invial	OK	1	
8	std0.5 ppt	a7			58.68	0.49			97.41		3286-2.RAW	12:56:41	376.75	invial	OK	2	
9	std1 ppt	a8			58.68	1.03			103.30		3287-1.RAW	11:56:21	733.27	invial	OK	1	
10	std5 ppt	a9			58.68	5.01			100.15		3288-1.RAW	11:59:59	3328.95	invial	OK	1	
11	std10 ppt	a10			58.68	9.97			99.73		3289-1.RAW	12:03:37	6571.65	invial	OK	1	
12	std25 ppt	a11			58.68	25.21			100.83		3290-2.RAW	13:10:58	16520.96	invial	OK	2	
13	std50 ppt	a12			58.68	49.29			98.57		3291-1.RAW	12:10:53	32245.63	invial	FB	1	
14	wash				58.68	0.00					3292-2.RAW	12:52:40	19.51	invial	OK	2	
15	OPR5	A13			58.68	4.82			96.49		3293-1.RAW	13:47:01	3209.48	invial	OK	1	
16	OPR5	A14			58.68	4.88			97.62		3294-1.RAW	13:50:40	3246.33	invial	OK	1	
17	OPR5	A15			58.68	5.06			101.30		3295-1.RAW	13:54:17	3366.29	invial	OK	1	

QC Report (instrument output)

Standard Curve **IMPORT WS00000105.TWZ WS00000105** **WS00000006***



	Valid	Parameter	Value	Unit	SD	RSD(%)	Rec%	TheorConc. ng/L	CalcConc. ng/L
1		Blank	58.6804	Area	5.2322	8.9164			
2		Blank Conc	0.0899	ng/L	0.0080	8.9164		0.0000	0.0899
3		CalBlank	64.1216	Area				0.0000	0.0982
4		CalBlank	58.2338	Area				0.0000	0.0892
5		CalBlank	53.6859	Area				0.0000	0.0822
6		std0.5	376.7525	Area			97.4109	0.5000	0.4871
7		std1	733.2664	Area			103.2974	1.0000	1.0330
8		std5	3328.9530	Area			100.1535	5.0000	5.0077
9		std10	6571.6500	Area			99.7313	10.0000	9.9731
10		std25	16520.9628	Area			100.8329	25.0000	25.2082
11		std50	32245.6327	Area			98.5739	50.0000	49.2870

Operator: 1 2017/5/16

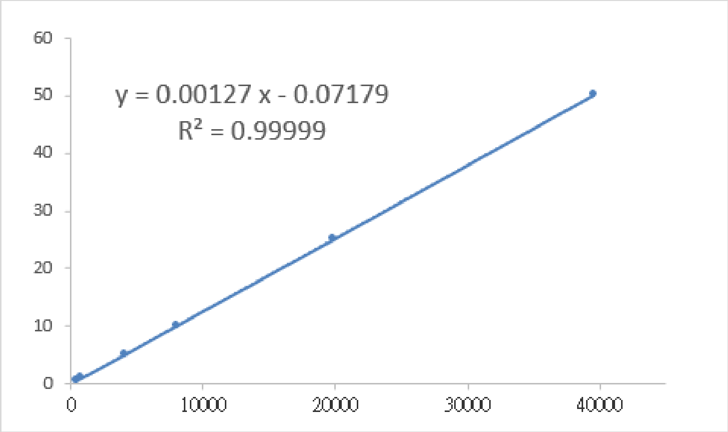
Data Report

採樣日期:			分析日期:	2019/05/30	
採樣者:			分析者:	Albee	
樣品:			地點:		
儀器	2600-IVS				
offset:	0.1042-0.1140		flow:	74.9-79.6	ml/min

(1)檢量線 (1ppb 為5/28配置)

Sigma-Aldrich

	NO.	conc. (ppt)	Area	Area-Area$_{diw}$	peak/conc	
	1	Clean	108.45			
	2	diw	11.86			
	3	diw	9.58			
	4	diw	8.37			
0.05	5	ClBlank	38.51			
0.05	6	ClBlank	37.01	37.29	0.05	
0.05	7	ClBlank	36.34			
0.52	8	0.5	458.17	420.88	841.77	
0.99	9	1	836.86	799.57	799.57	805.76
5.03	10	5	4092.73	4055.45	811.09	18.94
9.89	11	10	8003.02	7965.73	796.57	2.35
24.66	12	25	19909.50	19872.21	794.89	
49.07	13	50	39572.22	39534.93	790.70	
		WASH	10.36			



(2) On-going precision and recovery (OPR)

	NO.	conc. (ppt)	Area	Area-Area$_{diw}$	peak/conc	Check 5 ppt
5.05	1	5	4105.88	4068.59	813.72	100.32%
4.94	2	5	4014.37	3977.08	795.42	98.07%
4.94	3	5	4018.86	3981.57	796.31	98.18%
	average			4046.37		
	SD			51.59		
	RSD(%)			1.27%		

(3)Quality control sample (QCS) **Fluka**

	NO.	conc. (ppt)	Area	Area-Area$_{diw}$	peak/conc	Check 5 ppt
5.04	1	5	4100.41	4063.12	812.62	100.19%

Data Report

NO.	Name	Area	Area-Area$_{dlw}$	Hg(ppt)	Hg(ppt)
	MBlank	54.72	17.43	0.02	0.02
1	sample1	156.04	118.75	0.15	0.15
2	sample2	10877.56	10840.28	13.77	13.45
3	sample3	11725.83	11688.54	14.84	14.51
4	sample4	11440.31	11403.02	14.48	14.15
5	sample5	9698.40	9661.11	12.27	11.99
6	sample6	6931.87	6894.58	8.76	8.56
7	sample7	10301.63	10264.34	13.04	12.74
	MBlank	55.86	18.57	0.02	0.02
8	sample8	11841.63	11804.34	14.99	14.65
9	sample9	11319.59	11282.30	14.33	14.00
10	sample10	3264.63	3227.34	4.10	4.01
	Matrix spike Add 5 ppt 250 ul(sample10)	7200.51	7163.22	9.10	8.89
	Matrix spike Add 5 ppt 250 ul(sample10)	7158.45	7121.16	9.04	8.84
	QA&QC				
	Matrix spike Add 5 ppt 250 ul(sample10)	98%	75-125		v
	Matrix spike Add 5 ppt 250 ul(sample10)	97%	75-125		v
11	sample11	9613.20	9575.91	12.16	11.88
12	sample12	8245.81	8208.52	10.42	10.19
13	sample13	13708.38	13671.09	17.36	16.97
14	sample14	7491.18	7453.89	9.47	9.25
	MBlank	53.59	16.30	0.02	0.02
15	sample15	3201.04	3163.76	4.02	3.93

Repeat sample

14	sample14-Dup	7528.06	7490.77	9.51	9.30
	QA&QC				
	sample14-Dup	0.49%	±20	v	

Bottle blank

NO.	Name	Area	Area-Area$_{dlw}$	Hg(ppt)	Hg(ppt)
1	bottle blank	63.21	25.92	0.03	0.03
2	bottle blank	97.14	59.85	0.08	0.07

On-going precision and recovery (OPR)

NO.	conc. (ppt)	Area	Area-Area$_{dlw}$	Check 5 ppt
1	5	4050.64	4013.35	98.96%

Data Report

Site	Sample	Date	Date	Date	Sample	Conc.	Operator Remark	Laboratory Notes
Site ID	21	07/28/2015	08/04/2015	08/17/2015	Sample	**5.95**		
Site ID	Blank 1&2	07/28/2015		08/17/2015	Sample	**0.44**		
Site ID	22	08/04/2015	08/11/2015	10/22/2015	Sample	**12.34**		
Site ID	23	08/11/2015	08/18/2015	10/22/2015	Sample	**9.59**		
Site ID	24	08/18/2015	08/25/2015	10/22/2015	Sample	**5.85**		
Site ID	25	08/25/2015	09/01/2015	10/22/2015	Sample	**6.65**		
Site ID	26	09/01/2015	09/08/2015	10/22/2015	Sample	**8.98**		
Site ID	27	09/08/2015	09/15/2015	10/22/2015	Sample	**5.22**		
Site ID	28	09/15/2015	09/22/2015	10/22/2015	Sample	**2.92**		
Site ID	29	09/22/2015	09/29/2015	10/22/2015	Sample	**3.47**		
Site ID	30	09/29/2015	10/06/2015	10/22/2015	Sample	**2.80**		
Site ID	31	10/06/2015	10/13/2015	10/22/2015	Sample	**3.70**		
Site ID	32	10/13/2015	10/20/2015	02/02/2016	Sample	**1.66**		Low sample amount, dilution is required.
Site ID	33	11/10/2015	11/17/2015	02/02/2016	Sample	**6.49**		Low sample amount, dilution is required.
Site ID	34	11/17/2015	11/24/2015	02/02/2016	Sample	**6.03**		
Site ID	35	11/24/2015	12/01/2015	02/02/2016	Sample	**3.12**		
Site ID	36	12/01/2015	12/08/2015	02/02/2016	Sample	**1.55**		
Site ID	37	12/08/2015	12/15/2015	02/02/2016	Sample	**2.67**		
Site ID	38	12/15/2015	12/22/2015	02/02/2016	Sample	**2.22**		
Site ID	39	12/22/2015	12/29/2015	02/02/2016	Sample	**1.50**		
Site ID	40	12/29/2015	01/05/2016	02/02/2016	Sample	**2.13**		
Site ID	41	01/05/2016	01/12/2016	02/02/2016	Sample	**13.17**		Low sample amount, dilution is required.
Site ID	42	01/12/2016	01/19/2016	02/02/2016	Sample	**0.88**		
Site ID	43	01/19/2016	01/26/2016	06/21/2016	Sample	**6.53**		

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Asia Pacific Mercury Monitoring Network

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