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Results of Multiyear International Interlaboratory Comparison Program for Mercury in Human Hair

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Abstract. Since 1990, Laboratory Services, First Nations and Inuit Health Branch (Health Canada) conducted an interlaboratory comparison program for mercury in human hair. Laboratory Services initiated this program to compare the performance of participating laboratories, analyzing mercury in human hair samples by a variety of analytical methods and instrumental detection techniques. The results of the quality assurance program, which included 31 participants on four continents, are described. Of the participating laboratories, 92% consistently meet QA/QC performance limits for the determination of Hg in human hair. A variety of analytical methods using different digestion and instrumental techniques gave similar results. The most frequently used instrumental techniques were: CV-AA, CV-AFS, and ICP-MS. A summary of results from 24 rounds is provided. The feedback from this program has assisted some laboratories in improving their results and solving some of their analytical problems.

The neurotoxic effects of mercury (especially methylmercury, MeHg) on humans are very well described in the scientific and medical literature (Dolbec *et al.* 2000; Harada 1995; Steuerwald *et al.* 2000). The most severe effects were seen in Minamata and Niigata, Japan (Harada 1995), where children were born with severe cerebral palsy in a population that consumed mercury-contaminated seafood. Other similar studies on exposed populations from Iraq (Bakir *et al.* 1973), Seychelles Islands (Crump *et al.* 2000), and Faeroe Islands (Grandjean *et al.* 1999) also indicated the occurrence of adverse health effects. A recent review by Mahhafey (2000) summarized the current status of mercury (Hg) exposure and health effects.

Human mercury exposure is measured in terms of biomarkers of an internal dose, *i.e.*, hair or blood mercury concentrations. These biomarkers of an internal dose are often preferred for exposure assessment, but it is still debatable which biomarker relates most closely to the toxic dose, presumably within the fetal brain (Cernichiari *et al.* 1995; Grandjean *et al.* 1997, 1999; JAMA 1999; Jacobson 2001). Each of these surrogate measures has advantages and disadvantages. Cord blood can be considered as near a direct measure of fetal Hg blood concentrations; however it is only available at a single point in time (parturition) and is a value for a range of exposures over mainly the third trimester. Hair is a well-established and widely used matrix for measuring Hg exposure of an individual. Sequential segmental analysis of hair allows one to get information on the pattern of maternal (even fetal) exposure to MeHg over the entire course of the pregnancy (Cernichiari *et al.* 1995; Health Canada 1999). Hair provides a time-based biomarker of exposure. From analytical point of view, it should be considered that the concentration of Hg in hair is at least 150–200 orders of magnitude higher than the corresponding concentration in blood.

An assessment of human exposure to mercury from environmental sources requires reliable determinations of mercury in these matrices. A good quality assurance/quality control program should be implemented in all biological monitoring or health risk–related studies on mercury and its most toxic compounds, namely, MeHg. Otherwise, the results may not be comparable, reliable, or meaningful and may not withstand the scrutiny of regulatory agencies. Moreover, major public health decisions and significant costs are based on these results. For data users in the scientific and regulatory arenas, an accurate estimate of data quality, including statistical uncertainty, is required for health risk assessment and enforcement.

In 1975, the Medical Services Branch (Health Canada) started a biomonitoring program by analyzing Hg in human hair across Canada. Over the past 25 years, more than 50,000 hair samples in more than 500 First Nations communities across Canada were analyzed in this program (Health Canada 1999). As a part of the quality assurance process for the program, in 1990 the laboratory initiated an international interlaboratory comparison program. The primary objective of the program was to allow participating laboratories to gain insight into their own performance and comparability of their results with other laboratories. Since its initiation, the program has conducted 24 interlab comparison exercises for Hg in human hair. Currently, 24 laboratories from eight different countries are registered in the program.

In this article, we describe the background and operation,

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present some of the results obtained, and comment on the future.

Materials and Methods

Methods of Determining Mercury Concentrations in Hair

Human exposure to mercury has been monitored in blood, urine, and hair. Levels of mercury in urine typically measure occupational exposure to inorganic mercury (ACGIH 1996), whereas mercury in blood gives a snapshot of recent exposure (half-life 45 days). Hair mercury concentration reflects both recent and historical exposures, each centimeter representing approximately a month of exposure (Clarkson *et al.* 1988). The determination of mercury in hair is a noninvasive method for human exposure assessment purposes.

Total mercury in hair is determined routinely by several approaches. Digestion of hair matrix and manipulation of the Hg oxidation state are typically accomplished by using a variety of acids, bases, and oxidizing agents. A vast array of combinations of strong acids (HCl, H_2SO_4, HNO_3), strong base (NaOH), oxidants (H_2O_2, $KMnO_4$, $K_2S_2O_8$), microwave, and elevated temperatures have been used (Campe *et al.* 1982; Farant *et al.* 1981; Giovanoli-Jakubczak *et al.* 1974; Harada *et al.* 1999). It is generally agreed that oxidative conversion of all forms of mercury in the sample to ionic mercury (Hg^{2+}) is necessary prior to reduction to elemental Hg^0 and its subsequent measurement by various detection techniques. The most common methods used to measure mercury concentrations in hair include cold vapor–atomic absorption spectroscopy (CV-AAS), atomic fluorescence spectroscopy (CV-AFS), and inductively coupled plasma–mass spectrometry (ICP-MS) (Farant *et al.* 1981; Giovanoli-Jakubczak *et al.* 1974; Harada *et al.* 1999). Mercury content in hair has also been measured by neutron activation analysis and X-ray fluorescence (Cernichiari *et al.* 1995).

Inorganic mercury in hair sample is determined by method described by Magos (1971) or a modified version of this method (Farant *et al.* 1981). Briefly the hair sample is digested with 45% sodium hydroxide solution on a hot plate in the presence of cysteine. After binding to cysteine in solution, inorganic mercury (Hg^{2+}) is reduced to elemental mercury Hg^0 by stannous ions (Sn^{2+}) in a strongly basic solution. The Hg^0 produced in the process is partitioned into air by a vacuum that carries the released Hg^0 into cell of a cold-vapor mercury monitor. The concentration of Hg^0 is determined by a Hg monitor at 254 nm (253.7 nm). In this process the organic mercury–cysteine complexes are not reduced to elemental mercury form.

Program Operation and Participation

The primary objective of the program is to allow participating laboratories to gain insight into their own performance and comparability of their results with other laboratories. This external laboratory quality assessment is intended to complement rather than replace internal quality control in participant laboratories. Thus, the frequency of sample distribution was based on human resources and facilities available.

Each year a total of six/nine QC samples were distributed to the participating laboratories in two/three round-robins with three samples per round. Participants are asked to treat the QA/QC samples as if they were routine samples using their routine methods. A report form is sent out with the samples to ensure that all results are reported in the same units. The program is currently available at no cost to any interested laboratory (national or international), although postage and shipment time may create significant problems for participants in some countries. Upon entering the program, each participating laboratory is assigned a code number for identifying results.

The laboratories participating in the program come from quite a diverse background, including academic, commercial, government (regulatory), clinical, and epidemiological laboratories. A list of laboratories that participated in rounds 1–24 is given in Table 1.

Sample Preparation and Homogeneity Tests: QC samples are prepared from hair specimens received in our laboratory from the Canadian population. After the required mercury in hair analysis has been performed, the remaining specimens are used to prepare round-robin samples of various concentrations. A cryogenic grinding freezer mill was used to pulverize and homogenize hair samples. Each batch was thoroughly homogenized and tested for suitability in the interlaboratory study, by analyzing for total mercury (six 10-mg subsamples) using CV-AAS in organizers' laboratories. The sample size distributed to the participants varied from 50 to 200 mg/test/laboratory.

Frequency of Distribution and Operating Schedule: Over the past 11 years, each laboratory received three samples per round, each with a different mercury concentration, on a predetermined schedule. The time period (cycle time) from receipt of sample by participant laboratory to receipt of reports is designed to allow a reasonable time for international participants to receive and analyze their QA/QC samples. The QC samples in each round are accompanied by a results sheet bearing the laboratory's code number and the date by which results must be received by the organizing laboratory. The samples were distributed to the participating laboratories via air or surface mail.

A report form and information sheet were provided with the samples. The information provided to the laboratories includes the consensus mean values and ranges for the previous testing event, further shipping dates and other pertinent information. Participants must submit their data within 3 months of the date of shipment. Many overseas participants fax or e-mail their results to ensure inclusion.

Statistics

The statistical analysis and evaluation of results were performed at the authors' laboratory. On receipt, analytical results were checked, and any obviously unusual results were discussed with the appropriate laboratory and errors corrected. For each sample, we first calculated the mean (μ) and standard deviation (SD) for all reported values (initial calculation). Then, after excluding results out of the 2 SD range, we determined with the remaining data (final calculation) a new mean (μ_1), standard deviation (SD_2) and coefficient of a variance (CV). The standard statistics and spreadsheet software (Excel 2000, Microsoft, Redmond, WA) were used to examine these data. Each participant received the results for three samples in the form of table and graphical representation with the individual results as well as participants retained (n_2), the corrected mean (μ_1), SD and CV. The consensus mean value for each QC sample was established by the arithmetic mean of results of retained laboratories, after exclusion of results outside $\pm$ 2 SD from the initial mean value.

The results submitted by the laboratories were tested for outliers using Grubb's test (Kelley *et al.* 1991). Grubb's test compares an absolute deviation from the overall mean with the SD, in effect computing a relative deviation. Where results for a sample have a relatively large SD, the relative absolute deviation is not large enough to be flagged as outlier by this test.

Results and Discussion

Program enrollment had steadily increased by 50% in fiscal year 1996 and then stabilized to around 22 participants.

Different quantities of a sample, types of reagents, digestion

Table 1. List of participant laboratories from 1990 to 2000

Participant	Affiliation	Country
Prof. A. C. Barbosa	Laboratorio de Quimica Anilitica Ambiental Univ. de Brasilia	Brazil
Mr. O. Malm	Lab. Radio isotopos EPF, Univ. federal do rio DeJaneiro	Brazil
Prof. Edinaldo de Castro e Silva	Labotatorio de Analises de Metais Depart. de Quimica, Univ. Federal DeMato Grosso	Brazil
M. das Gracas Pires Sablayrolles	Universidade Federal do Para - Campus de Santarem	Brazil
Dr. J-P. Weber	Centre de Toxicologie du Québec	Canada
Mme. I. Rheault	UQAM-Geotop	Canada
Mr. S. Lapierre	Laboratoire de Santé Publique du Québec	Canada
Mr. J. Davidson	Quanta Trace Laboratories Inc.	Canada
Mr. J. R. Downie	Analytical Service Laboratories Ltd.	Canada
Dr. U. Gill	Laboratory Services	Canada
Mr. R. Jornitz	Can Test Ltd.	Canada
Mr. J. E. O. Varon	Insitituto Nacional De Salud	Columbia
Mr. P. Subrt	Laboratory Department	Czech Republic
Dr. P. Grandjean	Odense university, Institute of Environmental Health	Denmark
Mme. A. Nicolas	Toxilabo	France
Dr. T. Suzuki	University of Tokyo	Japan
Ms. V. F. L. Costa	Departamento De Oceanografia E Pescas, Univ. Dos Açores	Portugal
Ms. E. Cernichiari	Analytical Core Facility, Univ. of Rochester School of Medicine	USA
Ms. M. H. Hopper, MA,	Quality Assurance Co-ordinator, Mayo Clinic	USA
Cecilia Arms	State of Florida, Dept. of Health Bureau of Laboratories	USA
Ms. B. K. Trosko	Pharmacology and Toxicology Depart., Michigan State Univ.	USA
Prof. B. J. Presley	Department of Oceanography, Texas A&M University	USA
L. Liang, Ph.D.	Cebam Analytical, Inc.	USA
Ms. Ann Fisher	Doctor's Data	USA
Mr. L. Hart	Great Smokies Diagnostic Laboratory	USA
Dr. N. Bloom	Brooks Rand Ltd.	USA
Dr. T. M. Chandrasekhar	Department of Environmental Protection, State of Florida	USA
Dr. J. A. Dellinger	Medical College of Wisconsin	USA
Dr. P. J. Kostyniak	Toxicology Research Center, Univ. at Buffalo	USA
Mr. J. B. Mann	Dept. of Epidemiology & Public Health, Univ. Miami	USA
Dr. R. Fornes	California State Dept. of Health Services	USA

Table 2. Commonly used methods for determination of total and inorganic mercury

		Reduction Media			
Method	Digestion Media	THg	IHg	Instrumentation	Detection Technique
A	45% NaOH/1% L-cysteine	$SnCl_2/CdCl_2$	$SnCl_2$	LDC mercury monitor	CV-AAS
B	HNO_3 (total Hg determination)			Pharmacia UV detector	
A	45% NaOH/1% L-cysteine		$SnCl_2$		
C	$H_2SO_4/HNO_3/KMnO_4$			4110ZL, FIAS 400	
C	$H_2SO_4/HNO_3/KMnO_4$			Perkin Elmer AA 5000	
A	45% NaOH/1% L-cysteine		$SnCl_2$	Perkin Elmer AA 5001	
D	HNO_3/H_2O_2, microwave	$SnCl_2$		LDC mercury monitor	
A	45% NaOH/1% L-cysteine		$SnCl_2$		
E	$HNO_3/HCl/KMnO_4$	$SnCl_2$		Cetac M-6000A	
F	$H_2SO_4/HNO_3/KMnO_4/K_2S_2O_8$	$SnCl_2$			
F	$H_2SO_4/HNO_3/KMnO_4/K_2S_2O_8$			Varian Spectra 220-AA	
G	$H_2SO_4/KMnO_4/CIH_4NO$	$SnCl_2$		Perkin Elmer Coleman 50A	
H	$HCl/H_2SO_4/HNO_3$	$SnCl_2$		Fluorimeter	CV-AFS
I	$KOH/CH_3OH/BrCL$	$SnCl_2$		Tekran 2500AFS	
J	$KOH/CH_3OH/HCl$		$SnCl_2$		
H	$HCl/H_2SO_4/HNO_3$				
K	HNO_3 in acid bomb			PE ICP/MS 6100	ICP/MS
L	HNO_3, microwave			Perkin Elmer Sciex 5001	
M	Microwave			Perkin Elmer Elan 6000	
N	$H_2SO_4/HNO_3/KMnO_4$, microwave	$SnCl_2/HCl$		FIMS 400 - Perkin Elmer	Hydride generation AA
M	$H_2SO_4/HNO_3/KMnO_4$	$NABH_4$		FIMS	Cold-vapor generation
O	HNO_3/H_2O_2, microwave			Pharmacia Model 100M	Cold-vapor generation

FIAS, Flow injection cold-vapor mercury analysis system; FIMS, flow injection mercury system; CV-AAS, cold-vapor atomic absorption spectrometry; CV-AFS, cold-vapor atomic fluorescence spectrometry; ICP/MS, inductively coupled plasma mass spectrometry.

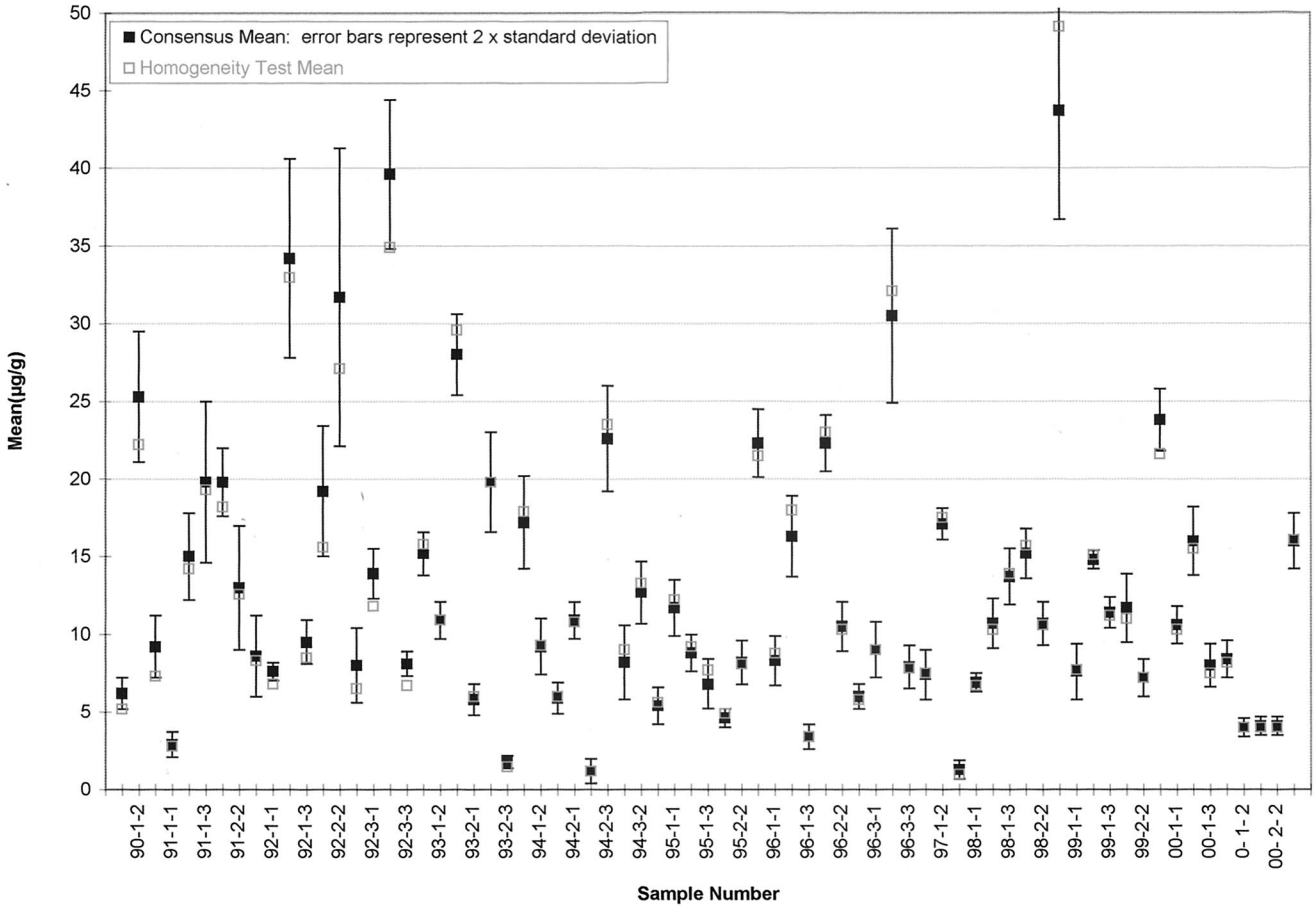

Fig. 1. Consensus mean versus homogeneity mean values for total mercury

media, and reduction procedures are used by the participating laboratories. Commonly employed analytical methods for the determinations of Hg in hair are represented in Table 2. Analytical methods used to determine Hg (total and inorganic forms) by the participating laboratories can be categorized into various combinations of sample preparation techniques and instrumental detection. The sample preparation techniques can be grouped into hot plate, microwave, and other techniques. Ninety-one percent of participating laboratories use hot plate digestion techniques; the majority of these laboratories use a 45% NaOH, $HNO_3/H_2SO_4/KMnO_4$ (EPA method 245.6), HNO_3/HCl, HNO_3, HNO_3/H_2O_2 digestion, and other digestion techniques. Fifty-four percent of participants use CV-AAS, 12% ICP-MS, and 12% AFS detection technique methods for determining mercury content in the QC samples.

The results of homogeneity tests of the prepared QA/QC samples for mercury determinations were compared with consensus mean values. Figure 1 shows the consensus mean values along with error bars and mean values obtained from homogeneity tests. In 24 round-robin studies conducted from 1990–2000, $>$ 90% of the times consensus mean for THg in QC samples produced are in agreement with homogeneity mean values.

Laboratory results are acceptable if they fall within the mercury in hair program performance range limits. Results falling outside the performance range are designated unsatisfactory and need further improvements in the analytical methodology used. The laboratory is proficient if the following occurs: (1) All results have been reported and all are designated as acceptable for the two rounds (six samples) in a year, or (2) three-fourths or more of the results reported in the rounds/year are designated as acceptable. On the other hand, if a particular laboratory does not report values for the Hg in hair on the round being evaluated, the laboratory is not rated. Laboratory performance summary results for the period 1990–2000, providing the number of successful laboratories are given in Table 3.

Acceptable results on all three specimens in a given set, reflect a steady performance over time. A large majority of participants obtained acceptable results as defined by the program acceptability criteria on an individual specimen. Currently, $>$ 90% of the participating laboratories report their results. Of all participating laboratories, only 4–6% had unacceptable results (outliers) on all samples in 5 out of 24 rounds.

Table 3 presents the Hg interlaboratory data for total and inorganic mercury in hair for 24 rounds over 10 years as submitted by international and Canadian participants. The information on estimated consensus mean Hg value for each sample in a given round and SD, along with minimum and maximum values for a given sample, are provided. So far, it is shown that the results obtained by 95% of the participating

Table 3. Summary of consensus mean, standard deviation, and RSD values in rounds 1–24

Sample Code[a]	No. of Labs Rated	Acceptable Labs (N)	Mean	SD	RSD	Range	Sample Code[a]	No. of Labs Rated	Acceptable Labs (N)	Mean	SD	RSD	Range
90-1-1	10	10	7.1	2.0	0.3	5.3–11.3	99-1-3		17	11.4	0.9	0.1	9.7–13.7
90-1-2		9	25.3	2.1	0.1	21.9–27.5	99-2-1	16	15	11.9	1.5	0.1	9.7–15.7
90-1-3		10	10.5	3.0	0.3	7.5–16.6	99-2-2		15	7.4	0.9	0.1	6.1–9.6
91-1-1	10	10	2.9	0.4	0.1	2.1–3.3	99-2-3		13	23.8	1.0	0.0	22.0–25.1
91-1-2		10	14.5	2.2	0.2	9.5–17.6	00-1-1	18	17	10.9	0.9	0.1	9.4–13.0
91-1-3		10	19.8	2.6	0.1	17.1–25.0	00-1-2		17	15.9	1.6	0.1	11.7–18.6
91-2-1	12	12	17.9	3.9	0.2	9.7–21.8	00-1-3		18	8.2	0.8	0.1	6.9–10.1
91-2-2		11	13.0	2.0	0.2	9.2–15.2	0-1-1	19	16	8.4	0.6	0.1	7.31–9.59
91-2-3		12	8.6	1.3	0.1	6.1–10.3	0-1-2		18	3.9	0.8	0.2	1.81–5.26
92-1-1	11	10	7.6	0.3	0.0	7.1–8.0	00-2-1	19	19	4.1	0.3	0.1	3.7–4.6
92-1-2		11	34.2	3.2	0.1	29.9–38.7	00-2-2		19	4.2	0.4	0.1	3.7–5.4
92-1-3		11	9.5	0.7	0.1	8.4–10.4	00-2-3		19	15.9	1.0	0.1	13.6–17.8
92-2-1	12	12	19.2	2.1	0.1	15.6–22.0	IHg						
92-2-2		12	31.7	4.8	0.2	25.8–41.0	91-2-1	7	6	3.2	1.4	0.4	2.0–5.7
92-2-3		12	8.3	1.6	0.2	6.2–11.8	91-2-2	6	5	1.9	0.6	0.3	1.3–2.8
92-3-1	11	11	13.2	1.6	0.1	10.0–15.3	91-2-3	7	6	1.4	0.4	0.3	0.9–2.1
92-3-2		10	39.6	2.4	0.1	36.1–43.7	92-1-1	6	6	1.3	0.3	0.2	1.0–2.0
92-3-3		11	8.0	1.0	0.1	6.9–10.1	92-1-2		6	5.1	1.2	0.2	4.2–7.2
93-1-1	16	16	15.4	1.2	0.1	13.4–18.0	92-1-3		6	1.2	0.4	0.3	0.8–1.9
93-1-2		16	10.8	0.8	0.1	9.0–11.8	92-2-1	7	6	2.3	0.6	0.2	1.7–3.3
93-1-3		15	28.0	1.3	0.0	25.4–30.0	92-2-2		7	4.2	1.5	0.4	2.7–7.3
93-2-1	17	16	5.7	0.8	0.1	3.9–7.1	92-2-3		6	1.0	0.2	0.2	0.7–1.4
93-2-2		14	19.8	1.6	0.1	17.1–22.2	92-3-1	8	8	2.4	0.5	0.2	1.7–3.1
93-2-3	16	15	2.0	0.4	0.2	1.5–2.9	92-3-2		8	6.1	0.8	0.1	5.1–7.7
94-1-1	16	16	17.2	1.5	0.1	15.1–20.0	92-3-3		8	1.2	0.3	0.3	0.7–1.7
94-1-2		16	9.1	1.0	0.1	6.7–11.0	93-1-1	11	11	2.0	0.7	0.3	0.7–3.1
94-1-3		16	6.0	0.6	0.1	5.2–7.4	93-1-2		11	1.6	0.5	0.3	0.7–2.5
94-2-1	15	15	10.4	1.3	0.1	7.7–11.9	93-1-3		11	4.8	1.4	0.3	1.9–7.0
94-2-2		14	1.2	0.4	0.3	0.4–1.9	93-2-1	10	9	1.2	0.3	0.2	0.8–1.7
94-2-3		15	22.6	1.7	0.1	19.3–25.7	93-2-2		10	3.0	0.7	0.2	2.1–4.4
94-3-1	19	19	8.4	1.4	0.2	5.8–11.8	93-2-3		9	1.0	0.3	0.3	0.8–1.6
94-3-2		18	12.7	1.0	0.1	11.1–14.7	94-1-1	8	8	3.0	1.0	0.3	1.6–4.5
94-3-3		18	5.4	0.6	0.1	4.3–6.6	94-1-2		8	1.8	0.4	0.2	1.3–2.3
95-1-1	20	20	11.1	1.5	0.1	7.3–13.1	94-1-3		8	1.4	0.3	0.2	1.0–1.9
95-1-2		20	8.8	1.2	0.1	5.7–11.0	94-2-1	9	8	1.5	0.5	0.3	0.9–2.1
95-1-3		19	6.8	0.8	0.1	5.4–8.3	94-2-2	7	7	0.4	0.2	0.4	0.2–0.7
95-2-1	18	17	4.8	0.8	0.2	2.8–6.6	94-2-3	8	7	3.4	0.6	0.2	2.5–4.3
95-2-2		15	8.2	0.7	0.1	7.2–9.4	94-3-1	10	10	1.4	0.5	0.4	0.6–2.5
95-2-3		17	21.7	3.3	0.2	13.4–29.6	94-3-2		10	1.7	0.5	0.3	0.7–2.4
96-1-1	21	20	8.5	1.1	0.1	6.9–11.1	94-3-3		9	0.8	0.3	0.4	0.2–1.1
96-1-2		18	16.6	1.6	0.1	13.8–20.9	95-1-1	10	10	1.6	0.4	0.3	0.6–2.1
96-1-3		19	3.3	0.7	0.2	1.6–4.6	95-1-2	9	8	1.4	0.2	0.2	1.1–1.7
96-2-1	20	20	22.8	2.3	0.1	16.8–27.2	95-1-3		9	1.2	0.3	0.2	0.9–1.7
96-2-2		19	10.4	1.0	0.1	7.9–12.1	95-2-1	8	8	0.6	0.2	0.3	0.4–0.9
96-2-3	19	18	6.0	0.6	0.1	4.5–7.0	95-2-2		8	1.3	0.2	0.2	1.0–1.7
96-3-1	22	21	8.9	1.0	0.1	6.8–10.4	95-2-3		8	3.4	0.7	0.2	2.0–4.3
96-3-2	23	20	30.5	2.8	0.1	25.2–35.7	96-1-1	11	11	1.1	0.3	0.3	0.7–1.9
96-3-3		22	7.7	1.0	0.1	5.3–9.3	96-1-2		11	2.3	1.0	0.4	0.7–4.5
97-1-1	22	22	7.7	1.0	0.1	5.9–10.0	96-1-3	10	9	0.7	0.2	0.3	0.1–0.9
97-1-2		22	17.1	2.2	0.1	12.1–22	96-2-1	11	11	3.0	0.7	0.2	2.4–4.5
97-1-3	21	20	1.4	0.4	0.3	0.9–2.3	96-2-2		11	1.6	0.4	0.3	1.0–2.3
98-1-1	22	22	6.9	1.4	0.2	4.0–10.2	96-2-3		11	0.9	0.3	0.3	0.5–1.3
98-1-2		22	10.7	2.2	0.2	5.4–15.9	96-3-1	9	8	1.4	0.1	0.1	1.2–1.5
98-1-3		22	13.7	3.0	0.2	6.1–21.1	96-3-2		9	4.2	0.8	0.2	3.2–5.8
98-2-1	19	19	14.9	1.5	0.1	11.5–17.7	96-3-3		9	1.3	0.2	0.1	1.1–1.6
98-2-2		17	10.8	1.1	0.1	8.5–13.7	97-1-1	9	8	1.0	0.3	0.3	0.6–1.5
98-2-3		19	42.4	7.9	0.2	22.6–55.8	97-1-2		8	2.2	0.6	0.3	1.3–3.0
99-1-1	18	17	7.6	0.9	0.1	5.9–9.1	97-1-3	6	6	0.6	0.3	0.5	0.3–1.1
99-1-2		18	14.9	0.9	0.1	12.8–17.2	98-1-1	7	7	1.2	0.2	0.2	1.0–1.5

Table 3. Continued

Sample Code[a]	No. of Labs Rated	Acceptable Labs (N)	Mean	SD	RSD	Range
98-1-2		7	1.6	0.3	0.2	1.2–2.2
98-1-3		7	2.1	0.3	0.1	1.6–2.4
98-2-1	7	7	1.9	0.4	0.2	1.0–2.4
98-2-2		7	1.7	0.5	0.3	1.0–2.5
98-2-3		7	6.4	1.4	0.2	4.4–9.0
99-1-1	6	6	1.4	0.4	0.3	0.8–1.9
99-1-2		6	2.3	0.3	0.1	1.9–2.8
99-1-3		6	1.9	0.4	0.2	1.4–2.5
99-2-1	5	5	2.1	0.7	0.3	1.4–3.2
99-2-2	6	6	1.5	0.4	0.3	0.9–2.1
99-2-3		5	3.3	0.5	0.2	2.6–3.9
00-1-1	6	6	2.0	0.7	0.3	1.3–3.2
00-1-2		5	2.4	0.4	0.1	2–2.5
00-1-3		6	1.9	0.6	0.3	1.2–2.7
0-1-1	6	6	2.0	0.5	0.2	1.4–2.7
0-1-2		4	0.6	0.2	0.3	0.4–0.8
00-2-1	5	5	0.6	0.3	0.4	0.3–1.0
00-2-2		5	0.7	0.3	0.4	0.3–1.0
00-2-3		5	2.4	0.6	0.3	1.5–3.1

[a] Year-round number-sample number.

Table 4. Results compared for two samples with similar concentrations for 13 laboratories

	All Laboratories in a Round		Laboratories Participated in Both Rounds	
Calculation	S 00-1-1	S 94-3-1	S 00-1-1	S 94-3-1
Initial[a]				
n1	19	19	13	13
X1	8.1	8.4	7.7	8.5
SD1	1.8	1.4	1.7	1.5
CV1, %age	22.2	16.7	22.1	17.6
Final[b]				
n2	16	18	11	12
X2	8.4	8.2	8.3	8.2
SD2	0.6	1.2	0.5	1.2
CV2, %age	7.1	14.6	6	14.6

[a] All values.
[b] After excluding results outside ± 2 SD range.

laboratories using different analytical techniques agree well with the consensus mean values.

Table 4 compares results for two QC sample numbers, S94-3-1 and S00-1-1, used for Hg deteminations in years 1994 and 2000, respectively. A total of 13 laboratories carried the mercury determination in both samples. For initial calculations, the mean values for X_1 were 8.5 and 7.7 μg/g, and the CV_1 value were 17.6% and 22.1%, respectively, for sample A and sample B. Final calculations for the remaining data (11 labs) after excluding results out of 2 SD range, in the same way yield: 8.3 and 8.2 μg/g for X_2 and 14.6% and 6% for CV_2 for S94-3-1 and S00-1-1, respectively. From this data we observe that for the final calculation, CV_2 evolved from 14.6% to 6%, a 2.4-fold improvement of the CV_2, thus substantiating the usefulness of the QA/QC program over time.

Conclusion

Various authors from the participating laboratories have cited their performance results in this interlaboratory program in their publications on mercury in hair (Dolbec *et al.* 2000; Boischio *et al.* 2000; Davis *et al.* 1994). The results from the program indicate that there is a wide range of performance quality in the experienced laboratories in this pool. The ranges of results for individual samples indicate the need for replicate samples to determine the statistical uncertainty of the data from analyses of low and high concentration. Overall, the results of this comparison program are encouraging. There is relatively good agreement on concentrations of Hg species in concentrations that are relevant to biomonitoring in humans.

Data presented in this publication may be considered indicative of current interlaboratory performance by the laboratories routinely engaged in determining Hg in hair. It is hoped that the results provided are of some assistance to the participating laboratories in assessing the effectiveness of their analytical methodologies and the comparative reliability of their results.

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