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# Interlaboratory Quality Control Study No. 19

## Total Mercury in Water, Low-Level Concentrations

K.I. Aspila and J.M. Carron

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**REPORT SERIES NO. 62**
*(Résumé en français)*

*INLAND WATERS DIRECTORATE, ONTARIO REGION,*
*WATER QUALITY BRANCH,*
*BURLINGTON, ONTARIO, 1979.*

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# Abstract

Results of an interlaboratory comparison of ten test samples containing mercury between 0.00 and 0.56 μg/L are described. Twenty-seven Canadian laboratories participated. Test samples (100 mL) were preserved with 1% (v/v) $H_2SO_4$ + 0.05% (w/v) $K_2Cr_2O_7$ and distributed in Pyrex glass bottles with Teflon inserts. Because of breakage some participants received additional solutions contained in linear polyethylene bottles. Data were evaluated by the rejection of results greater than two standard deviations from the mean. Using this adjusted data set, precision functions were developed to describe the interlaboratory standard deviations as a function of concentration. Within-run and between-run precision functions for in-laboratory analyses are also described. A number of laboratories have demonstrated that they have significant potential with respect to monitoring mercury in natural samples in the critical environmental range from 0.02 μg/L to 0.20 μg/L Hg.

# Résumé

Le présent rapport renferme les résultats d'une étude interlaboratoire comparative du dosage de dix échantillons, dont la teneur en mercure variait entre 0,00 et 0,56 μg/L de Hg. Vingt-sept laboratoires canadiens ont participé à l'étude. Les échantillons (100 mL), conservés dans une solution $H_2SO_4$ 1% (v/v) + $K_2Cr_2O_7$ 0,05% (p/v), leur étaient parvenus dans des bouteilles «Pyrex» à doublure intérieure «Teflon». Des bouteilles de polyéthylène linéaire ont remplacé celles qui s'étaient cassées en cours de route. Les données qui différaient de la moyenne par une valeur supérieure à deux écarts types ont été rejetées. Pour mesurer la précision des données épurées, on donne des relations exprimant les écarts types entre les laboratoires en fonction de la teneur des échantillons. Des relations analogues sont aussi fournies pour les dosages dans chaque laboratoire, effectués au cours d'un même essai ou de plusieurs. Certains laboratoires ont montré qu'ils étaient capables de doser avec précision le mercure dans des échantillons naturels, dans l'intervalle de 0,02 μg/L à 0,20 μg/L de Hg, qui est critique pour l'environnement.

# Interlaboratory Quality Control Study No. 19
## Total Mercury in Water, Low–Level Concentrations

K.I. Aspila and J.M. Carron

### INTRODUCTION

Interlaboratory quality control study No. 19 was carried out between December 1976 and April 1977. It was prepared to complement a similar study (study No. 16, IWD Report Series No. 53) involving mercury in natural waters. In contrast with study No. 16, Pyrex glass bottles were used as sample containers and the five pairs of water samples had a much lower mercury concentration (0 to 0.56 μg/L Hg). The decisions to change the sample container and to use near-detection limit concentrations of mercury were made after a review of preservation studies (Carron and Agemian, 1977) conducted during the previous year. The use of low concentrations of mercury for interlaboratory testing has significant merit, since it helps to provide quality assurance statements on waters containing mercury at levels similar to those found in many environmental samples. The choice of preservative, 1% (v/v) $H_2SO_4$ + 0.05% (w/v) $K_2Cr_2O_7$, was similar to that of the previous study, since evidence was available supporting its adequacy (Carron and Agemian, 1977; Aspila and Carron, 1978).

As mercury at low-level concentrations has been a controversial parameter with respect to containers, preservation and analysis, a detailed time study analysis was carried out on several of these sample sets before, during and after the study. This procedure was essential in order to present factual evidence on the integrity of test samples provided to participants.

### EXPERIMENTAL DESIGN

Samples for this study were paired and included an unspiked natural water paired with a distilled water blank, and four spiked natural waters, each paired with four very similar standard solutions. The concentrations of these samples are described in Table 1.

The bulk natural water used was tap water that had been collected several months earlier, preserved and stored in an old 50-L polyethylene carboy. Prior to aliquoting the bulk sample for this study, a portion was analyzed and a level of 0.02 μg/L to 0.04 μg/L Hg was found in the preserved bulk sample. The presence of this low-level mercury residue provided a useful natural test sample with a low-level mercury concentration. The residue probably originated from contamination or very slow leaching of mercury from the large storage vessel.

Table 1. Samples Distributed

| Sample | Contents of test sample |
|---|---|
| 1 | Distilled water blank (<0.01 μg/L Hg) |
| 2 | Blank + 0.06 μg/L Hg ($HgCl_2$) |
| 3 | Blank + 0.19 μg/L Hg ($HgCl_2$) |
| 4 | Blank + 0.50 μg/L Hg ($HgCl_2$) |
| 5 | Blank + 0.56 μg/L Hg (as $CH_3HgCl$) |
| 6 | Natural sample x(μg/L Hg) |
| 7 | Natural sample + 0.06 μg/L Hg ($HgCl_2$) |
| 8 | Natural sample + 0.19 μg/L Hg ($HgCl_2$) |
| 9 | Natural sample + 0.50 μg/L Hg ($HgCl_2$) |
| 10 | Natural sample + 0.56 μg/L Hg (as $CH_3HgCl$) |

Pyrex glass bottles of 125-mL capacity (Sovirel®, Pegasus Industrial Specialties Ltd.) were selected for distribution of all test samples. These new, unused bottles were originally washed with hot Chromerge®, tap water and distilled water, and then rinsed with the test sample. Initial monitoring of standards (samples 2 to 5) in these bottles, however, revealed a slight loss of mercury. These test samples were then discarded; the new Pyrex bottles were recleaned and conditioned rigorously by boiling in concentrated nitric acid for several hours followed by a washing with hot Chromerge, tap water and distilled water, and a final rinse with the test sample. The use of hot nitric acid to clean sample containers for mercury is described in the literature (Weiss and Shipman, 1976). Some of the bottles dispatched to participants for the interlaboratory comparison study froze in transit, and the glass bottles broke, resulting in loss of sample. Replacement make-up samples were prepared and dispatched in 125-mL linear polyethylene bottles. These bottles were washed in hot Chromerge, rinsed in tap water, and then rinsed with distilled water and the test sample.

All of the test samples that were prepared for distribution (Table 1) were made sequentially from the lowest concentration to the highest to avoid cross contamination. The fortified natural water samples and corresponding standards in distilled water were prepared simultaneously in bulk at the same concentrations just prior to subdivision.

To ensure the stability of test solutions, mercury concentrates were added to bulk waters (natural and distilled) that were prepared in advance to contain the preservative 1% (v/v) $H_2SO_4$ + 0.05% (w/v) $K_2Cr_2O_7$. The mercury concentrates used for spiking were made from appropriate dilute solutions of mercuric chloride (Fisher Scientific Atomic Absorption Standard) and methyl mercuric chloride (Pfaltz and Bauer Inc., Flushing, N.Y.). Bulk solutions in Pyrex vessels were prepared in 8-L quantities, and after thorough mixing, the samples were transferred to clean Sovirel bottles. The excess solution was stored in glass containers and used later in the make-up samples that were distributed in linear polyethylene bottles.

To identify and confirm the quality of the experimental design, five randomly chosen complete sets of test samples were selected and routinely monitored over a four-month time interval. This monitoring was initiated in advance of sample distribution to participants and then recommenced during the time interval in which the participants analyzed and reported their results. The method for in-house analysis used for monitoring is described in the Water Quality Branch *Analytical Methods Manual* (Department of the Environment, 1974).

## EVALUATION OF DATA

### In-Laboratory Data

Five complete, but randomly selected, test samples were analyzed repetitively over several months. The data accumulated were used to identify both the capabilities of the test method employed and the stability of the test samples.

Within-run standard deviations were calculated on each day that the test samples were monitored. For this study, the within-run (in-laboratory) precision was calculated from five results on the five different bottles, each containing, theoretically, the same solutions. The standard deviation (S.D.) was obtained using the equation

$$S.D. = \left[\Sigma (x_i - \bar{x})^2/(n-1)\right]^{1/2}$$

where $x_i$ is the calculated concentration, $\bar{x}$ is the mean concentration and n is the number of determinations.

Between-run standard deviations were calculated from mean mercury values determined on different days but on the same bottles (Table A-1, Appendix A). These standard deviations were anticipated to be higher than within-run values because each individual mercury value was based on new reference calibrations established each day.

Because the in-house monitoring of test samples involved extensive accumulation of data for the five pairs of test samples, a precision function could be derived by plotting the standard deviation as a function of the calculated mercury content. This precision function was assumed to be linear at these very low concentrations and was mathematically derived from the least squares line.

### Interlaboratory Data

Results received from participants were tabulated and organized into two categories—those obtained for test samples in glass bottles and those from polyethylene bottles. The few results that were provided in duplicate or replicate were averaged to identify one value per laboratory.

Overall mean values and standard deviations were first calculated using the entire population of results on each sample. Data submitted and identified as "less than" values were not used. Data were rejected rather rigorously by removing sequentially all results greater than two standard deviations until no further results were greater than plus or minus two standard deviations in the adjusted population. Precision functions were calculated in the same manner as for the in-house data discussed above.

## RESULTS AND DISCUSSION

### Stability of Test Samples

Test samples randomly selected prior to distribution of this study were routinely monitored before, during and after completion of the interlaboratory study. This monitoring exercise should be recognized as a necessity, since there is always a need to scrutinize the unpredictable behaviour of mercury in test solutions of very low concentrations. Further benefits from this time study were (a) the evaluation of the analytical test method and (b) the provision of data to support the quality of the glass sample containers for low-level mercury and the suitability of the 1% (v/v) $H_2SO_4$ + 0.05% (w/v) $K_2Cr_2O_7$ preservative. Detailed results of in-house analysis of mercury in glass bottles are given in Table A-1. A similar set of data on the plastic bottles is given in Table A-2 and also in a summary format in Table A-3 in Appendix A.

*Estimates of In-Laboratory Precision and Detection Limits*

Precision estimates (standard deviations) were calculated for both within-run and between-run data given in Table A-1. The within-run data are those data obtained within one day and without readjustment of the calibration (Table A-1). It is accepted that these within-run estimates, which utilized five originally identical test samples, may differ from those of the more conventional method of using replicate data from the sample bottle. The difference between these two methods is not expected to be too large, since the test samples were all rather stable. What is more important is the between-run precision estimate on each test sample, especially in its relation to the interlaboratory precision. It should be evident that the very good precision (within-run and between-run) obtained with the selected bottles analyzed during this study implies that interlaboratory data have the potential to be of excellent quality and only differ owing to inadequate methods (sensitivity) or incompatible reference standards.

A detection limit for both within-run and between-run analyses can be derived from the calculated precision data obtained for the entire set of samples. The precision estimates are in a graphical format in Figures 1 and 2. The data in these figures were derived from results given in Table A-1. If a detection limit is defined as two times the standard deviation, then the least squares line calculated for within-run and between-run data implies limits of just less than 0.02 μg/L Hg for both sets of data. It is of interest to note that distilled water standards were analyzed with slightly less precision than the natural waters.

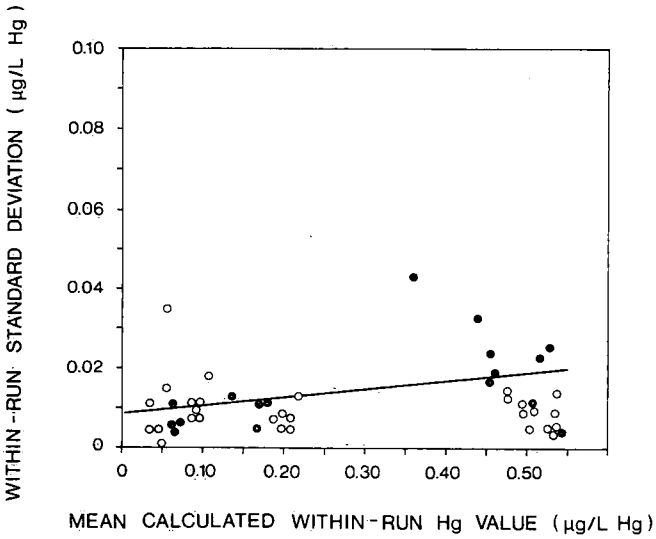


**Figure 1.** The variation of the within-run standard deviation as a function of mean calculated mercury concentrations. Open circles represent results for spiked natural water and closed circles, results for standard solutions. Equation of least squares line is y = 0.00053x + 0.0101.

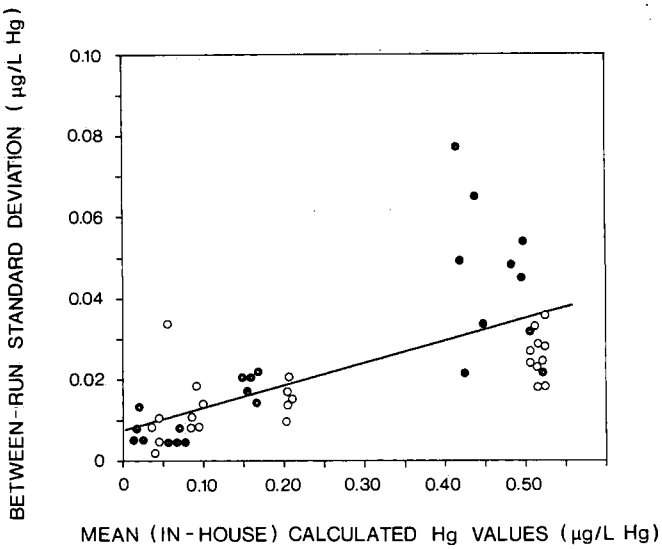


**Figure 2.** The variation of the between-run standard deviation as a function of mean calculated mercury concentrations. Open circles represent results for spiked natural water and closed circles, results for standard solutions. Equation of least squares line is y = 0.035x + 0.0084.

*Accuracy*

The accuracy of test solutions containing low-level concentrations of mercury has always been difficult to establish because of the inherent instability at low concentrations and the ease with which contamination can be introduced. The diversity of preservation procedures is well documented in the literature (Carron and Agemian, 1977). A method of validation through an interlaboratory study is also described (Winters *et al.*, 1977).

For this study, test solutions for mercury analysis were prepared in bulk at low concentrations by an appropriate dilution of a stable laboratory concentrate. Although each solution (after subdivision to test bottles) was assigned "a design value," monitoring over a period of several months revealed slightly different values. This slight difference is evident in Table A-1. No significant impact is attached to the subtle difference between theoretical design values and actual laboratory values, since the calculated values (from in-laboratory monitoring) were confirmed by results of a four-laboratory intercomparison. The four laboratories used equally sensitive methods but with different standards. It is of interest to note that in-laboratory analysis revealed that two different "certified standards" available commercially differed by 15%. This difference made the assignment of a "true value" that much more difficult.

## Results from Participants

Data received from participants are given in Table 2. In several cases where a laboratory provided duplicate data or replicates, only the mean values are given. Note that the data in Table 2 include results for mercury in both glass bottles and plastic bottles. Data from plastic bottles are indicated by *P* following the laboratory numbers.

Mean values and standard deviations for the interlaboratory data are also summarized in Tables 3 and 4. Values excluded in determining the means are followed by *R* in Table 2. Values designated as less than (<) were also excluded. For visual clarity, the raw data are presented as Youden plots in Figures 3 and 4. The methods used by all laboratories are given in an abbreviated format in Table A-4, Appendix A.

Compared with study No. 16 of the report series, laboratories on this occasion provided more compatible data. This was partially because of the excellent stability of the solutions in glass containers.

The only minor setback that occurred was breakage due to freezing of some test solutions in glass bottles while in transit. The laboratories that received broken bottles

**Table 2. Laboratory Results Provided by Participants**

| Laboratory number | Sample number (results in μg/L Hg) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| 44 | <0.1 | <0.1 | 0.1 | 0.3 | 0.3 R | <0.1 | <0.1 | 0.2 | 0.4 | 0.4 |
| 9 | 0.005 | 0.058 | 0.177 | 0.487 | 0.510 | 0.018 | 0.095 | 0.215 | 0.522 | 0.518 |
| 11 | <0.05 | <0.05 | <0.05 | 0.22 R | 0.33 | <0.05 | 0.07 | 0.17 | 0.55 | 0.63 |
| 28 | 0.52 | 0.95 R | 0.50 R | 0.58 | 0.55 | <0.25 | <0.25 | 0.35 R | 0.55 | 0.50 |
| 34 | 0.08 | 0.09 | 0.21 | 0.49 | 0.57 | 0.06 | 0.11 | 0.21 | 0.55 | 0.62 |
| 43 | <0.07 | 0.09 | 0.13 | 0.45 | 0.49 | <0.07 | 0.10 | 0.21 | 0.53 | 0.55 |
| 47 | <0.05 | <0.05 | 0.14 | 0.45 | 0.50 | <0.05 | <0.05 | 0.18 | 0.50 | 0.48 |
| 50 | <0.02 | 0.07 | 0.20 | 0.52 | 0.59 | <0.02 | 0.09 | 0.22 | 0.55 | 0.59 |
| 8 | 0.4 | <0.2 | 0.3 R | 0.5 | 0.2 R | 0.3 | 0.3 R | 0.3 R | 0.5 | <0.2 R |
| 5 | <0.02 | 0.04 | 0.15 | 0.43 | 0.53 | <0.02 | 0.06 | 0.17 | 0.47 | 0.59 |
| 30 P | 0.01 | 0.04 | 0.13 | 0.41 | 0.47 | 0.01 | 0.05 | 0.19 | 0.49 | 0.51 |
| 54 | 0.19 | 0.04 | <0.02 | 0.72 R | 0.41 | 0.40 | 0.83 R | 0.97 R | 0.84 R | 0.49 |
| 58 | <0.1 | 1.8 R | 2.1 R | 1.1 R | 1.6 R | 1.8 | 1.1 R | 2.1 R | 2.6 R | 0.4 |
| 2 | <0.05 | 0.056 | 0.124 | 0.386 | 0.460 | 0.058 | 0.088 | 0.160 | 0.462 | 0.498 |
| 51a | <0.10 | <0.10 | <0.10 | 0.40 | 0.45 | <0.10 | <0.10 | <0.10 | 0.40 | 0.65 |
| 51b | <0.01 | <0.01 | 0.17 | 0.57 | 0.41 | <0.01 | <0.01 | 0.15 | 0.62 | 0.62 |
| 53 P | <0.10 | <0.10 | 0.12 | 0.33 | 0.44 | <0.10 | <0.10 | 0.17 | 0.44 | 0.55 |
| 1 | <0.02 | 0.048 | 0.158 | 0.480 | 0.536 | <0.02 | 0.068 | 0.18 | 0.493 | 0.498 |
| 13 | <0.20 | <0.20 | 0.25 | 0.64 | 0.64 | <0.20 | <0.20 | 0.25 | 1.2 R | <0.2 R |
| 46 P | <0.05 | 0.15 | 0.10 | 0.50 | 0.40 | 0.08 | 0.10 | 0.15 | 1.10 R | 0.60 |
| 6 P | 0.10 | 0.10 | 0.15 | 0.45 | 0.60 | 0.10 | 0.15 | 0.20 | 0.55 | 0.60 |
| 29 P | 0.00 | 0.03 | 0.10 | 0.39 | 0.47 | 0.03 | 0.08 | 0.19 | 0.50 | 0.15 R |
| 39 P | 0.16 | 0.12 | 0.13 | 0.34 | 0.36 | 0.04 | 0.07 | 0.18 | 0.47 | 0.14 R |
| 14a | <0.05 | 0.058 | 0.175 | 0.493 | 0.515 | – | – | – | – | 0.587 |
| 14b P | <0.05 | 0.055 | 0.118 | 0.250 | 0.328 | 0.062 | 0.100 | 0.233 | 0.582 | 0.519 |
| 10 P | 0.05 | 0.25 | 0.30 R | 0.55 | 0.25 | 0.25 | 0.10 | 0.35 R | 0.65 | 0.60 |
| 60 P | 0.06 | 0.15 | 0.12 | 0.22 | 0.16 | 0.06 | 0.11 | 0.20 | 0.46 | 0.20 |
| Design level | 0.00 | 0.06 | 0.19 | 0.50 | 0.56 | x | x + 0.06 | x + 0.19 | x + 0.50 | x + 0.56 |
| Glass only | | | | | | | | | | |
| n | 18 | 9 | 12 | 15 | 15 | 18 | 8 | 12 | 14 | 16 |
| $\bar{x}$ | – | 0.061 | 0.165 | 0.478 | 0.499 | – | 0.085 | 0.193 | 0.507 | 0.539 |
| S.D. | – | 0.019 | 0.041 | 0.084 | 0.079 | – | 0.017 | 0.029 | 0.061 | 0.078 |
| Plastic only | | | | | | | | | | |
| n | 9 | 8 | 8 | 9 | 9 | 9 | 8 | 8 | 8 | 6 |
| $\bar{x}$ | – | 0.112 | 0.121 | 0.382 | 0.386 | – | 0.095 | 0.189 | 0.518 | 0.563 |
| S.D. | – | 0.073 | 0.017 | 0.109 | 0.131 | – | 0.030 | 0.024 | 0.071 | 0.043 |

P–Laboratories that received test samples contained in linear polyethylene bottles.

were given make-up samples in polyethylene. Data from these make-up samples were not as precise and accurate as the data from the glass containers. This is not so much a reflection of the capability of the laboratory than of the instability of mercury in the polyethylene. In-house data (Tables A-2 and A-3) on six complete sets of test samples in the plastic bottles confirm this variation. The more unstable samples were the distilled water standards. These same standards in glass (Figs. 1 and 2) had similar, but much less pronounced, behaviour.

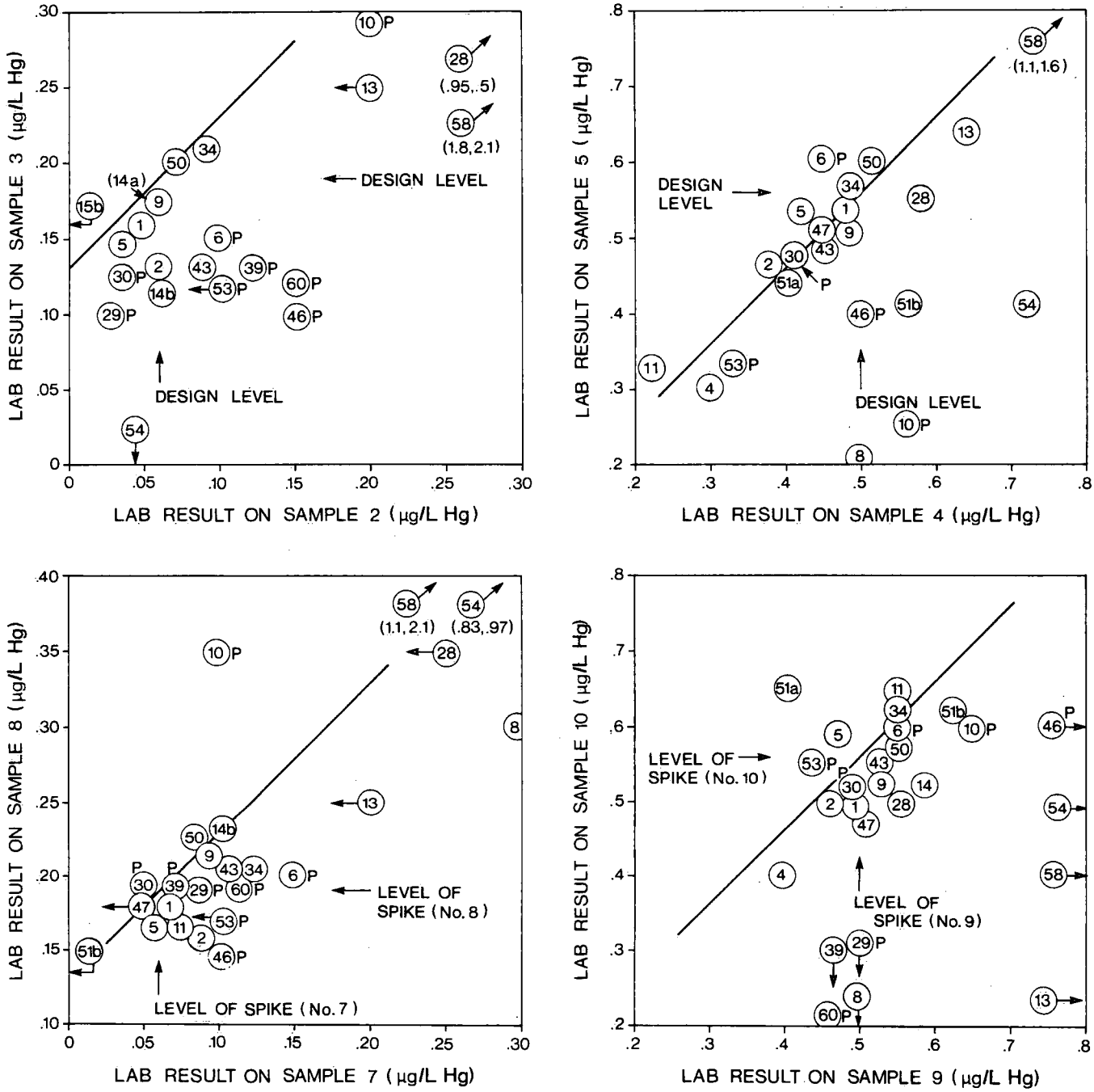


**Figure 3. Youden plots for paired natural samples and paired standards. The design level identifies concentration in standards and the level of spike, concentration in spiked natural water.**

It should be emphasized that although the glass containers in this study were better than the plastic containers, this difference should not be considered a serious problem, since earlier storage studies (Carron and Agemian, 1977) on a wide variety of plastic containers have shown that linear polyethylene is quite adequate. In fact, the utilization of linear polyethylene for the make-up samples was based on such evidence.

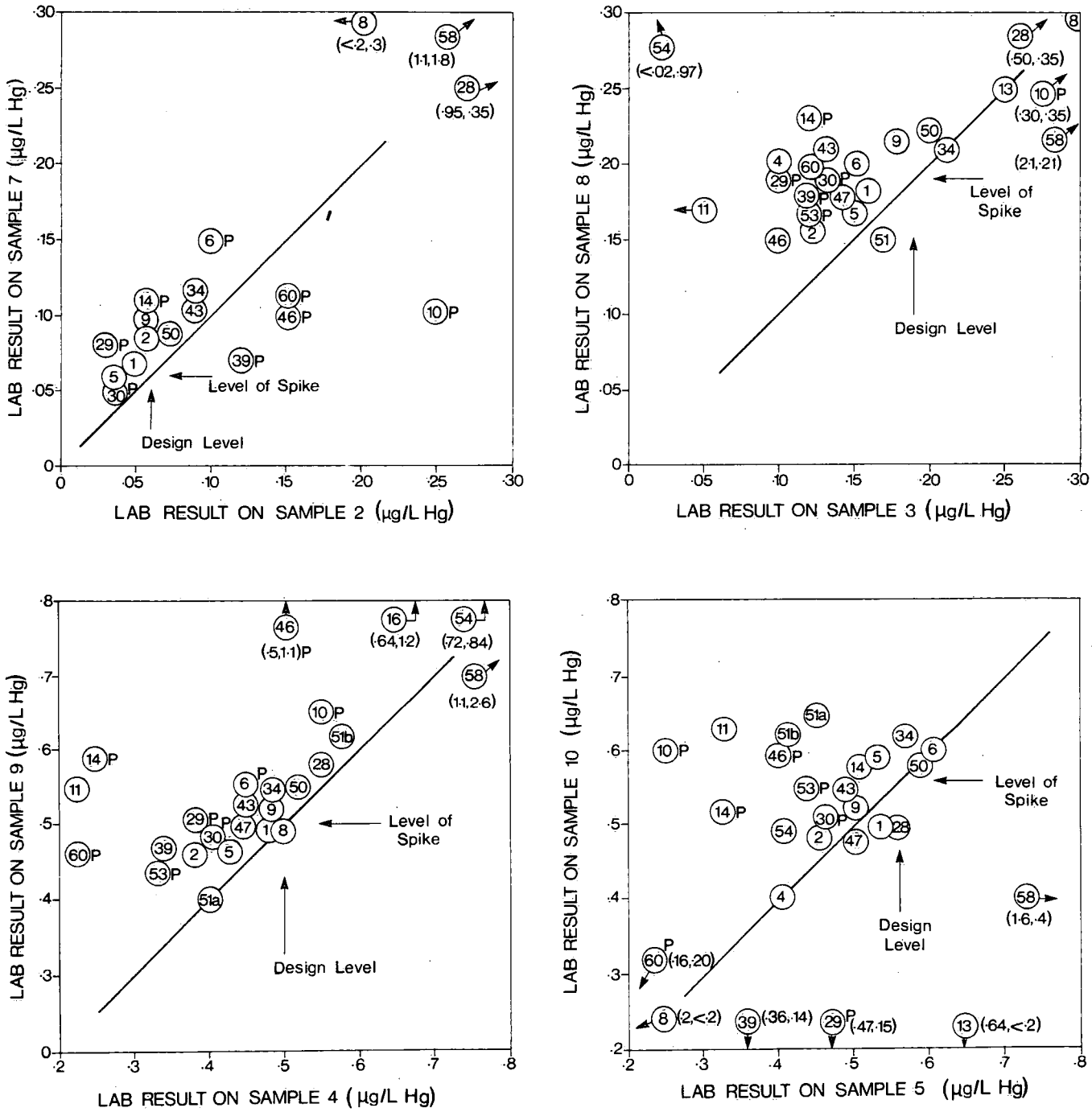


**Figure 4. Youden plots for paired samples containing similar concentrations of mercury (spiked natural waters versus standard solutions).**

## Comparison of Interlaboratory Data

### *General*

Four specific laboratories with recognized capabilities in low-level mercury analysis and with methods known to be similar to those described in the Water Quality Branch *Analytical Methods Manual* (Department of the Environment, 1974) were requested to provide replicate data on all test samples. These data are summarized in Table 3 and Figure 5. Although two of the four laboratories estimated values of <0.05 μg/L Hg for the sample blank (No. 2), scrutiny of the instrument chart paper recordings provided by these laboratories indicated a capability of detecting

Table 3. Comparison of Hg Data from Four Laboratories Which Provided Replicate Within-Run Analyses on All Test Samples

| Sample number | Statistics | Laboratory number 9 (glass) | 1 (glass) | 2 (glass) | 14 (glass) | 14 (plastic) | Mean interlaboratory standard deviation* (μg/L Hg) | Mean in-laboratory within-run standard deviation* (μg/L Hg) | Design level (μg/L Hg) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $\bar{x}$ | 0.005 | <0.02 | <0.05 | <0.05 | <0.05 | (<0.05)† | | 0.00 |
| | S.D. | 0.008 | – | – | – | – | | | |
| | n | 6 | 5 | 5 | 6 | 6 | | | |
| 2 | $\bar{x}$ | 0.058 | 0.048 | 0.056 | 0.058 | 0.055 | (0.055) | | |
| | S.D. | 0.004 | 0.005 | 0.009 | 0.008 | 0.006 | 0.005 | 0.006 | 0.06 |
| | n | 6 | 5 | 5 | 6 | 6 | | | |
| 3 | $\bar{x}$ | 0.177 | 0.158 | 0.124 | 0.175 | 0.118 | (0.159) | | |
| | S.D. | 0.010 | 0.005 | 0.006 | 0.012 | 0.004 | 0.025 | 0.008 | 0.19 |
| | n | 6 | 5 | 5 | 6 | 6 | | | |
| 4 | $\bar{x}$ | 0.478 | 0.480 | 0.386 | 0.493 | 0.250 | (0.462) | | |
| | S.D. | 0.008 | 0.012 | 0.009 | 0.019 | 0.006 | 0.051 | 0.012 | 0.50 |
| | n | 6 | 5 | 5 | 6 | 6 | | | |
| 5 | $\bar{x}$ | 0.510 | 0.536 | 0.460 | 0.515 | 0.328 | (0.505) | | |
| | S.D. | 0.009 | 0.009 | 0.010 | 0.022 | 0.008 | 0.032 | 0.012 | 0.56 |
| | n | | | | | | | | |
| 6 | $\bar{x}$ | 0.018 | <0.02 | 0.058 | | 0.062 | (<0.05) | | |
| | S.D. | 0.004 | – | 0.008 | Broken | 0.004 | – | 0.006 | x |
| | n | 6 | 5 | 5 | | 6 | | | |
| 7 | $\bar{x}$ | 0.095 | 0.068 | 0.088 | | 0.100 | (0.084) | | |
| | S.D. | 0.008 | 0.005 | 0.005 | Broken | 0.009 | 0.014 | 0.006 | x + 0.06 |
| | n | 6 | 5 | 5 | | 6 | | | |
| 8 | $\bar{x}$ | 0.212 | 0.180 | 0.160 | | 0.233 | (0.184) | | |
| | S.D. | 0.004 | 0.007 | 0.007 | Broken | 0.010 | 0.026 | 0.006 | x + 0.19 |
| | n | 6 | 5 | 5 | | 6 | | | |
| 9 | $\bar{x}$ | 0.522 | 0.493 | 0.462 | | 0.582 | (0.492) | | |
| | S.D. | 0.013 | 0.013 | 0.005 | Broken | 0.026 | 0.030 | 0.010 | x + 0.50 |
| | n | 6 | 5 | 5 | | 6 | | | |
| 10 | $\bar{x}$ | 0.518 | 0.498 | 0.498 | 0.587 | 0.519 | (0.525) | | |
| | S.D. | 0.012 | 0.008 | 0.010 | 0.014 | 0.032 | 0.042 | 0.011 | x + 0.56 |
| | n | 6 | 5 | 5 | 6 | 6 | | | |

* No data from plastic bottles were used to calculate mean in-laboratory or between-laboratory standard deviations.
† Values in parentheses are the average of the interlaboratory results.

$\bar{x}$–Within-run mean value (μg/L Hg).
S.D.–Within-run standard deviation (μg/L Hg).
n–Number of determinations.

<0.02 μg/L Hg. In fact, an interpolation of a precision function for either within-run or between-run data indicates these laboratories indeed have a capability of quantitating mercury to at least 0.02 μg/L Hg. It is of interest to note that when laboratory No. 14 provided mercury data from both glass and plastic containers, a significant difference for distilled water standards was observed between the samples stored in glass and plastic containers. The results for spiked natural samples in plastic, however, were very similar to the data from glass bottles. The same conclusion is evident from all the other laboratories that received plastic bottles (Table 2).

A summary comparison of in-laboratory data, the special four-laboratory intercomparison, and the overall national results is given in Table 4. An effective visual

**Table 4. Summary of Data on Test Samples**

| Sample number | Statistics | In-house within-run statistics* (glass) | In-house between-run statistics† (glass) | Interlaboratory data‡ (glass) | National data¶ (glass) | National data (plastic) | Design level (μg/L Hg) |
|---|---|---|---|---|---|---|---|
| 1 | $\bar{x}$ | 0.014 | 0.014 | <0.05 | – | – | 0.00 |
| | S.D. | – | – | – | – | – | |
| | n | | | – | – | – | |
| 2 | $\bar{x}$ | 0.064 | 0.064 | 0.055 | 0.061 | 0.112 | 0.06 |
| | S.D. | 0.0065 | 0.005 | 0.005 | 0.019 | 0.073 | |
| | n | 4(20) | 5(20) | 4 | 9 | 8 | |
| 3 | $\bar{x}$ | 0.162 | 0.162 | 0.159 | 0.165 | 0.121 | 0.19 |
| | S.D. | 0.010 | 0.019 | 0.025 | 0.041 | 0.071 | |
| | n | 4(20) | 5(20) | 4 | 12 | 8 | |
| 4 | $\bar{x}$ | 0.429 | 0.429 | 0.462 | 0.478 | 0.382 | 0.50 |
| | S.D. | 0.026 | 0.050 | 0.051 | 0.084 | 0.109 | |
| | n | 4(20) | 5(20) | 4 | 15 | 9 | |
| 5 | $\bar{x}$ | 0.501 | 0.501 | 0.505 | 0.499 | 0.386 | 0.56 |
| | S.D. | 0.018 | 0.041 | 0.032 | 0.079 | 0.131 | ($CH_3HgCl$) |
| | n | 4(20) | 5(20) | 4 | 15 | 9 | |
| 6 | $\bar{x}$ | 0.044 | 0.044 | <0.05 | – | – | x |
| | S.D. | 0.015 | 0.016 | – | – | – | |
| | n | 6(30) | 5(30) | – | – | – | |
| 7 | $\bar{x}$ | 0.090 | 0.090 | 0.084 | 0.085 | 0.095 | x + 0.06 |
| | S.D. | 0.011 | 0.012 | 0.014 | 0.017 | 0.030 | |
| | n | 6(30) | 5(30) | 3 | 8 | 8 | |
| 8 | $\bar{x}$ | 0.202 | 0.203 | 0.184 | 0.193 | 0.189 | x + 0.19 |
| | S.D. | 0.009 | 0.015 | 0.026 | 0.029 | 0.024 | |
| | n | 6(30) | 5(30) | 3 | 12 | 8 | |
| 9 | $\bar{x}$ | 0.511 | 0.511 | 0.492 | 0.507 | 0.518 | x + 0.50 |
| | S.D. | 0.008 | 0.026 | 0.030 | 0.061 | 0.071 | |
| | n | 6(30) | 5(30) | 3 | 14 | 8 | |
| 10 | $\bar{x}$ | 0.513 | 0.513 | 0.525 | 0.539 | 0.563 | x + 0.56 |
| | S.D. | 0.013 | 0.027 | 0.042 | 0.071 | 0.043 | ($CH_3HgCl$) |
| | n | 6(30) | 5(30) | 4 | 16 | 6 | |

* Within-run S.D. is the average calculated within-run variation in results for five identical bottles monitored either four or six different times over three months.

† Between-run S.D. is the average between-day variation in Hg content measured for five different bottles either four or six different times over three months.

‡ Interlaboratory data obtained from Table 3 for four laboratories.

¶ All laboratories.

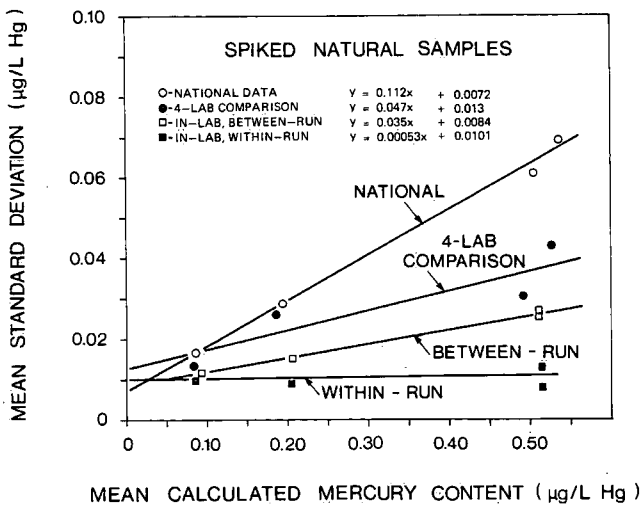


**Figure 5. Comparison of precision functions for various data sets.**

comparison is presented in Figure 5 in which the standard deviation is plotted as a function of the mean calculated mercury concentrations. These precision functions are quite valuable, since in using them a data interpreter (or an environmental manager) can quickly determine the confidence one can place on a data set obtained from a single laboratory or from several laboratories. Caution is necessary, since these functions are applicable only to that data set derived using Pyrex glass containers and the 1% (v/v) $H_2SO_4$ + 0.05% (w/v) $K_2Cr_2O_7$ preservative.

*Youden Plots*

For visual clarity, the laboratory results are presented in Youden plots in Figures 3 and 4. The horizontal axis identifies the laboratory results for one sample, and the vertical axis, the corresponding laboratory results for another sample. Youden plots are used successfully for intercomparison studies when the samples in the pair have similar composition and both have been analyzed with similar precision. In Figure 3, this usual format differs slightly for some of the paired sample plots. An excellent discussion of the application of Youden plots is available in the literature (U.S. Department of Commerce, 1969; Cheeseman, 1974; Youden and Steiner, 1975).

In Figures 3 and 4, the circles identify the paired results, and the number within each circle is the laboratory identification code. The single line drawn in each plot is of slope equal to 1 and is drawn through the pair of design levels (sample 2 vs 3 and 4 vs 5) and through the level of the spike (sample 7 vs 8 and 9 vs 10). Circled laboratory numbers with arrows indicate either less than values or results that are beyond the co-ordinates of the graph. If all of the laboratories were to exhibit only a small random error, if the design levels were totally accurate and consistent with all laboratory standards and if the natural water were absolutely free from mercury, then a cluster of results would appear near the line and surround the theoretical design values (or spike values). This desirable situation, of course, was not achieved, since the samples were realistic and the various laboratories did differ in capability.

The two sets of Youden plots (Figs. 3 and 4) are informative in visually summarizing the data from Table 2. Outliers that were designated by *R* in Table 2 are in most cases distinctly off the co-ordinates of the graph and separated from the cluster of well-controlled laboratories. Caution in interpretation is necessary, since all of the Youden plots involve a group of data from plastic bottles. These laboratory results are identified by *P* and are more scattered, and if not blocked off, their presence can visually misinform the reader.

In Figure 4, the four Youden plots represent corresponding concentrations with data from the standard solutions plotted against the spiked natural sample. In all of the plots the natural sample clearly has a slightly higher value than the standards (i.e., most data lie above the line of slope 1). This confirms that the natural sample did contain approximately 0.02 µg/L to 0.04 µg/L Hg.

The improved precision obtained with the natural waters compared with the distilled water standards is apparent in Tables 2, 3 and 4 but more visually evident in Figure 4. The distribution of data along the y-axis (natural sample) is much less pronounced than on the x-axis (standards). Again, caution in interpretation is needed, since much of this spread is caused by the plastic bottles exhibiting possible contamination at the low levels (e.g., sample 2 in Figure 4) combined with instability (or loss) of mercury at the higher levels. Subjective evaluations such as those made on the Youdon plots mentioned above should be made carefully and possibly only after rejection of all the data from those laboratories that had the majority of their data rejected.

Many analysts ponder the reasons for rejection and whether a specific method was responsible for deviant results. One generalization, which is somewhat obvious, is that several laboratories with insensitive methods (i.e., detection limits from 0.1 µg/L to 0.2 µg/L Hg) were analyzing so close to their detection limit that they had inherent difficulties in estimating concentrations. Some were not prepared to quantitate in the range from 0.0 to 0.2 µg/L Hg. Five laboratories, 13, 39, 46, 54 and 60 (Table A-4, Appendix A), indicated no persulphate was used in the predigestion and oxidation prior to cold vapour quantitation.

If losses were to occur because of incomplete oxidation, it would be recognized by low recovery of the methyl mercury used in samples 5 and 10 (Tables 1 and 2). Laboratory No. 60 is distinctly low on both, whereas the others are low on only one or the other. Poor internal precision and possible laboratory bias from standards prevent any definite statement. The reader may draw his own conclusions on methods used and quality of data provided. Although it was not the intent of this study to evaluate or compare methods rigorously, it is fairly evident that the automated methods such as those used by the Water Quality Branch (Department of the Environment, 1974) and similar methods used by several other laboratories were very precise and consistent in providing compatible and relatively accurate results. One major caution pertinent to all methods or to any analysis is that an excellent method handled by inexperienced or unqualified laboratory personnel can always provide very poor results.

From observation of the behaviour of test samples and from discussion with participants during the study, it became apparent that all laboratories engaged in low-level mercury analysis should make the routine monitoring of internal controls a top priority. To achieve accuracy in the range from 0.00 to 0.10 μg/L Hg, laboratories must have intimate knowledge of the stability of the test samples and details on the level of contaminants as well as on the employment of accurately prepared standards. Other containers or different preservatives can be utilized, but as this study and the preliminary work have clearly indicated, much effort and in-house scrutiny are required to maintain control of the data successfully.

## SUMMARY

This interlaboratory comparison on analysis of mercury in water, conducted among twenty-seven laboratories, has clearly demonstrated that a significant number of laboratories have potential with respect to precisely monitoring low-level mercury in the range from 0.02 μg/L to 0.20 μg/L. Ten test samples (two blanks, four spiked natural waters and four standards) were preserved in 1% (v/v) $H_2SO_4$ + 0.05% (w/v) $K_2Cr_2O_7$ and provided to participants in Pyrex bottles with Teflon seals. Because of some bottle breakage in transit, several laboratories were given additional test samples in linear polyethylene bottles. All data received were screened for outliers, and the adjusted data were used to estimate in-laboratory and between-laboratory linear precision functions (standard deviation versus calculated mercury concentrations). The interlaboratory precision function on natural samples that were contained in glass and analyzed by the acceptable laboratories indicates a limit of detection from 0.01 μg/L to 0.02 μg/L Hg. Detailed in-laboratory data from sensitive methods confirm this estimated limit.

## ACKNOWLEDGMENTS

The cooperation of the participating laboratories listed in Appendix B has been greatly appreciated.

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# Appendix A

# Analytical Results for Study No. 19

# Analytical Results for Study No. 19

Table A-1. Preservation Data on Five Random Sets Chosen from Study No. 19 (solutions contained in Pyrex bottles)

| Date analyzed | Sample number | Solutions a | b | c | d | e |
|---|---|---|---|---|---|---|
| Nov 8 | 1 (Blank) | 0.03 | 0.03 | 0.01 | 0.01 | 0.01 |
| Nov 19 | | 0.02 | 0.03 | 0.02 | 0.04 | 0.02 |
| Nov 30 | | 0.01 | 0.02 | 0.01 | 0.02 | 0.03 |
| Dec 10 | | 0.02 | 0.02 | 0.02 | 0.01 | 0.01 |
| Jan 20 | | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Feb 10 | | 0.01 | 0.02 | 0.01 | 0.01 | 0.02 |
| Mar 30 | | <0.01 | <0.01 | 0.01 | <0.01 | <0.01 |
| Nov 8 | 2 (0.06 μg/L Hg) | | | | | |
| Nov 19 | | | | | | |
| Nov 30 | | 0.07 | 0.05 | 0.06 | 0.06 | 0.08 |
| Dec 10 | | 0.07 | 0.06 | 0.07 | 0.06 | 0.07 |
| Jan 20 | | 0.07 | 0.06 | 0.06 | 0.06 | 0.06 |
| Feb 10 | | 0.06 | 0.06 | 0.06 | 0.06 | 0.07 |
| Mar 30 | | 0.06 | 0.06 | 0.06 | 0.06 | 0.07 |
| Nov 8 | 3 (0.19 μg/L Hg) | | | | | |
| Nov 19 | | | | | | |
| Nov 30 | | 0.16 | 0.16 | 0.16 | 0.18 | 0.18 |
| Dec 10 | | 0.16 | 0.16 | 0.16 | 0.17 | 0.17 |
| Jan 20 | | 0.16 | 0.13 | 0.13 | 0.13 | 0.14 |
| Feb 10 | | 0.19 | 0.18 | 0.18 | 0.17 | 0.16 |
| Mar 30 | | 0.17 | 0.16 | 0.17 | 0.18 | 0.18 |
| Nov 8 | 4 (0.50 μg/L Hg) | | | | | |
| Nov 19 | | | | | | |
| Nov 30 | | 0.43 | 0.45 | 0.45 | 0.47 | 0.47 |
| Dec 10 | | 0.45 | 0.46 | 0.42 | 0.45 | 0.47 |
| Jan 20 | | 0.40 | 0.40 | 0.35 | 0.30 | 0.34 |
| Feb 10 | | 0.42 | 0.48 | 0.46 | 0.44 | 0.47 |
| Mar 30 | | 0.47 | 0.47 | 0.46 | 0.48 | 0.50 |
| Nov 8 | 5 (0.56 μg/L Hg) | | | | | |
| Nov 19 | | | | | | |
| Nov 30 | | 0.51 | 0.49 | 0.50 | 0.52 | 0.51 |
| Dec 10 | | 0.53 | 0.54 | 0.54 | 0.53 | 0.53 |
| Jan 20 | | 0.49 | 0.42 | 0.42 | 0.46 | 0.43 |
| Feb 10 | | 0.54 | 0.48 | 0.53 | 0.52 | 0.52 |
| Mar 30 | | 0.51 | 0.46 | 0.50 | 0.51 | 0.52 |
| Nov 8 | 6 (Natural blank, x μg/L Hg) | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| Nov 19 | | 0.05 | 0.03 | 0.04 | 0.12 | 0.06 |
| Nov 30 | | 0.04 | 0.03 | 0.03 | 0.04 | 0.04 |
| Dec 10 | | 0.05 | 0.08 | 0.04 | 0.04 | 0.05 |
| Jan 20 | | 0.05 | 0.02 | 0.03 | 0.03 | 0.03 |
| Feb 10 | | 0.04 | 0.03 | 0.03 | 0.03 | 0.04 |
| Mar 30 | | 0.06 | 0.03 | 0.03 | 0.03 | 0.03 |

Table A-1. Continued

| Date analyzed | Sample number | Solutions a | b | c | d | e |
|---|---|---|---|---|---|---|
| Nov 8 | 7 (x + 0.06 μg/L Hg) | 0.10 | 0.10 | 0.08 | 0.08 | 0.09 |
| Nov 19 | | 0.10 | 0.09 | 0.09 | 0.10 | 0.10 |
| Nov 30 | | 0.09 | 0.08 | 0.08 | 0.09 | 0.10 |
| Dec 10 | | 0.09 | 0.13 | 0.10 | 0.09 | 0.12 |
| Jan 20 | | 0.10 | 0.08 | 0.07 | 0.08 | 0.08 |
| Feb 10 | | 0.08 | 0.08 | 0.08 | 0.08 | 0.11 |
| Mar 30 | | 0.10 | 0.08 | 0.08 | 0.08 | 0.09 |
| Nov 8 | 8 (x + 0.19 μg/L Hg) | 0.20 | 0.20 | 0.20 | 0.20 | 0.18 |
| Nov 19 | | 0.22 | 0.21 | 0.21 | 0.22 | 0.21 |
| Nov 30 | | 0.19 | 0.19 | 0.20 | 0.20 | 0.20 |
| Dec 10 | | 0.21 | 0.23 | 0.22 | 0.20 | 0.23 |
| Jan 20 | | 0.20 | 0.18 | 0.18 | 0.18 | 0.18 |
| Feb 10 | | 0.20 | 0.20 | 0.21 | 0.22 | 0.22 |
| Mar 30 | | 0.20 | 0.20 | 0.21 | 0.21 | 0.20 |
| Nov 8 | 9 (x + 0.50 μg/L Hg) | 0.51 | 0.51 | 0.50 | 0.50 | 0.50 |
| Nov 19 | | 0.53 | 0.53 | 0.54 | 0.54 | 0.53 |
| Nov 30 | | 0.49 | 0.49 | 0.49 | 0.51 | 0.49 |
| Dec 10 | | 0.52 | 0.53 | 0.53 | 0.52 | 0.53 |
| Jan 20 | | 0.49 | 0.46 | 0.47 | 0.48 | 0.46 |
| Feb 10 | | 0.53 | 0.52 | 0.54 | 0.54 | 0.55 |
| Mar 30 | | 0.50 | 0.50 | 0.53 | 0.54 | 0.50 |
| Nov 8 | 10 (x + 0.56 μg/L Hg) | 0.52 | 0.52 | 0.50 | 0.50 | 0.51 |
| Nov 19 | | 0.54 | 0.53 | 0.54 | 0.53 | 0.54 |
| Nov 30 | | 0.49 | 0.48 | 0.49 | 0.49 | 0.51 |
| Dec 10 | | 0.53 | 0.54 | 0.53 | 0.53 | 0.55 |
| Jan 20 | | 0.50 | 0.47 | 0.48 | 0.48 | 0.46 |
| Feb 10 | | 0.52 | 0.53 | 0.49 | 0.54 | 0.56 |
| Mar 30 | | 0.50 | 0.50 | 0.54 | 0.52 | 0.53 |

Note: (1) All results are in micrograms per litre mercury.
(2) Data from standard solutions 2, 3, 4 and 5 are absent for November 8 and 19 because new test samples were made (originals discarded).
(3) Within-run standard deviations (see Table 4 and Fig. 1) were calculated from rows of data.
(4) Between-run standard deviations (see Table 4 and Fig. 2) were calculated from the data in columns (between days).

Table A-2. In-House Time Study (data for Hg in six different polyethylene bottles)

| Set number | Date analyzed | Sample number (μg/L Hg) 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 77-01-17 | 0.01 | 0.06 | 0.12 | 0.40 | 0.41 | 0.03 | 0.08 | 0.18 | 0.48 | 0.47 |
| | 77-02-10 | 0.03 | 0.07 | 0.12 | 0.40 | 0.40 | 0.04 | 0.10 | 0.20 | 0.52 | 0.49 |
| | 77-03-30 | 0.02 | 0.07 | 0.12 | 0.40 | 0.38 | 0.05 | 0.10 | 0.20 | 0.51 | 0.45 |
| 2 | 77-01-17 | 0.01 | 0.10 | 0.15 | 0.39 | 0.46 | 0.03 | 0.08 | 0.18 | 0.46 | 0.47 |
| | 77-02-10 | 0.02 | 0.10 | 0.07 | 0.22 | 0.40 | 0.03 | 0.08 | 0.20 | 0.52 | 0.48 |
| | 77-03-30 | 0.01 | 0.08 | 0.10 | 0.27 | 0.43 | 0.03 | 0.08 | 0.19 | 0.50 | 0.44 |
| 3 | 77-01-17 | 0.01 | 0.09 | 0.12 | 0.38 | 0.46 | 0.03 | 0.08 | 0.17 | 0.48 | 0.48 |
| | 77-02-10 | 0.02 | 0.12 | 0.10 | 0.40 | 0.45 | 0.03 | 0.10 | 0.19 | 0.50 | 0.48 |
| | 77-03-30 | 0.01 | 0.03 | 0.10 | 0.40 | 0.42 | 0.04 | 0.08 | 0.18 | 0.50 | 0.44 |
| 4 | 77-01-17 | 0.01 | 0.05 | 0.12 | 0.40 | 0.46 | 0.03 | 0.08 | 0.18 | 0.48 | 0.49 |
| | 77-02-10 | 0.01 | 0.06 | 0.06 | 0.41 | 0.46 | 0.04 | 0.10 | 0.20 | 0.52 | 0.50 |
| | 77-03-30 | 0.02 | 0.05 | 0.13 | 0.35 | 0.44 | 0.04 | 0.09 | 0.20 | 0.52 | 0.49 |
| 5 | 77-01-17 | 0.01 | 0.05 | 0.10 | 0.40 | 0.48 | 0.04 | 0.08 | 0.18 | 0.47 | 0.49 |
| | 77-02-10 | 0.02 | 0.06 | 0.04 | 0.36 | 0.42 | 0.03 | 0.09 | 0.20 | 0.50 | 0.53 |
| | 77-03-30 | 0.01 | 0.05 | 0.03 | 0.34 | 0.36 | 0.04 | 0.08 | 0.19 | 0.52 | 0.52 |
| 6 | 77-01-17 | 0.01 | 0.05 | 0.12 | 0.39 | 0.48 | 0.04 | 0.08 | 0.18 | 0.48 | 0.48 |
| | 77-02-10 | 0.02 | 0.05 | 0.08 | 0.30 | 0.46 | 0.04 | 0.08 | 0.20 | 0.54 | 0.58 |
| | 77-03-30 | 0.01 | 0.04 | 0.08 | 0.26 | 0.44 | 0.03 | 0.08 | 0.19 | 0.51 | 0.55 |
| Original value* | | 0.01 | 0.05 | 0.15 | 0.47 | 0.53 | 0.06 | 0.09 | 0.19 | 0.51 | 0.53 |
| Design level | | 0.00 | 0.06 | 0.19 | 0.50 | 0.56 | x | x + 0.06 | x + 0.19 | x + 0.50 | x + 0.56 |

*Calculated on bulk samples prior to subsampling into plastic bottles.

Table A-3. Mean In-House Data on Test Samples Contained in Plastic Bottles

| Date analyzed | Statistics | Sample number (μg/L Hg)* 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 77-01-17 | $\bar{x}$ | <0.01 | 0.067 | 0.122 | 0.393 | 0.458 | 0.035 | 0.080 | 0.180 | 0.475 | 0.48 |
| | S.D. | – | 0.023 | 0.016 | 0.0082 | 0.026 | 0.006 | 0.0 | 0.006 | 0.0084 | 0.0089 |
| 77-02-10 | $\bar{x}$ | ~0.02 | 0.077 | 0.078 | 0.348 | 0.432 | 0.036 | 0.092 | 0.198 | 0.517 | 0.511 |
| | S.D. | – | 0.027 | 0.029 | 0.075 | 0.029 | 0.005 | 0.009 | 0.004 | 0.015 | 0.042 |
| 77-03-30 | $\bar{x}$ | ~0.01 | 0.053 | 0.093 | 0.338 | 0.412 | 0.038 | 0.085 | 0.192 | 0.510 | 0.482 |
| | S.D. | – | 0.019 | 0.036 | 0.063 | 0.038 | 0.0075 | 0.0085 | 0.008 | 0.009 | 0.0462 |
| Original value† | | 0.01 | 0.05 | 0.15 | 0.47 | 0.53 | 0.06 | 0.09 | 0.19 | 0.51 | 0.53 |
| Design value | | 0 | 0.06 | 0.19 | 0.50 | 0.56 | x | x + 0.06 | x + 0.19 | x + 0.50 | x + 0.56 |
| National data‡ | $\bar{x}$ | – | 0.112 | 0.121 | 0.382 | 0.386 | – | 0.095 | 0.189 | 0.518 | 0.563 |
| | S.D. | – | 0.073 | 0.017 | 0.109 | 0.109 | – | 0.030 | 0.024 | 0.071 | 0.042 |
| | n | 9 | 8 | 8 | 9 | 9 | 9 | 8 | 8 | 8 | 6 |

* Mean values for January, February and March results. Refer to the mean values of six different bottles (Table A-2).
† Calculated on bulk samples prior to subsampling into polyethylene bottles.
‡ See Table 4.

## INFORMATION REQUESTED IN QUESTIONNAIRE SUBMITTED TO PARTICIPANTS

1. Sample Handling

   (i) Volume of subsample (mL) used in analysis for mercury in the test samples provided.

   Number—Identifies volume in millilitres.
   Yes—Means entire 100- to 115-mL sample used.
   No—Means a portion of sample used.

2. Analytical Detection System

   (i) Detection limit (μg/L Hg) indicated by participants.
   (ii) *O* means cold vapour detection cell was open (continuous flow); *C* means cold vapour detection cell was sealed.
   (iii) Path length of absorption cell (cm).
   (iv) Instrumentation used for detection of mercury vapour.

3. Preservatives and Containers

   (i) Acids and oxidants used by participants in their routine programs.
   (ii) Sample containers used by participants for collection or storage of routine test samples.

4. Chemical System Employed

   (i) Yes—Means chemical oxidation and reduction were automated (i.e., Technicon system or equivalent).
   (ii) Oxidants employed in treating test sample:
   a = $H_2SO_4$
   b = $KMnO_4$
   c = $K_2S_2O_8$
   d = $K_2Cr_2O_7$
   e = $HNO_3$ + HCl

   (iii) Reductants employed in production of Hg vapour:
   f = $Sn^{+2}$ (as chloride or sulphate)
   g = hydroxylamine
   h = hydrazine

Table A-4. Analytical Methods Summary

| Laboratory number | Response* | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 (i) | 2(i) | 2(ii) | 2(iii) | 2(iv) | 3(i) | 3(ii) | 4(i) | 4(ii) | 4(iii) |
| 4 | 10 | 0.1 | O | 29 | Pharmacia | $HNO_3 + K_2Cr_2O_7$ | Polypropylene | Yes | a,c | f |
| 9 | 4 | 0.05 | O | 30 | Pharmacia | $H_2SO_4$ | Polypropylene | Yes | a,b,c | f,g |
| 11 | No | 0.05 | O | 30 | Pharmacia | $HNO_3 + K_2Cr_2O_7$ | Pyrex | Yes | a,b,c | f,g |
| 28 | 100 | 0.25 | O | 12 | Varian | $HNO_3 + K_2Cr_2O_7$ | Plastic† | No | a,b,c | f,g |
| 34 | 50 | 0.05 | O | 30 | Pharmacia | $HNO_3 + KMnO_7$ | Glass,‡ Teflon | No | a,b,c | f,g |
| 43 | 75 | 0.05 | O | 30 | Pharmacia | $HNO_3 + K_2Cr_2O_7$ | Polyethylene¶ | No | a,b,c | f |
| 47 | No | 0.05 | O | 15 | Perkin-Elmer 303 | $HNO_3 + Au^{+3}$ | Polypropylene, polyethylene | No | a,b,c | f,g |
| 50 | Yes | 0.02 | C | 30 | Pharmacia | $KMnO_4$ | Glass‡ | No | a,b,c | f,g |
| 8 | 40 | 0.2 | C | 14 | Perkin-Elmer 403 | $H_2SO_4$ | Polyethylene¶ | No | a | f |
| 5 | No | 0.05 | | 30 | Pharmacia | $H_2SO_4$ | Polyethylene¶ | Yes | a,b,c | g |
| 30 P | Yes | 0.02 | C | 25 | Varian | $HNO_3$ | Polyethylene¶ | No | a,b,c | f,g |
| 54 | No | 0.02 | C | 30 | Pharmacia | $HNO_3$ | Nalgene** | No | b | f |
| 58 | Yes | 0.10 | C | – | Coleman | $HNO_3$ | Glass‡ | No | a,b | f,g |
| 2 | 4 | 0.05 | O | 30 | Pharmacia | $H_2SO_4$ | Polypropylene | Yes | a,b,c | f,g |
| 51a | Yes | 0.01-0.05 | O | 30 | Pharmacia | $HNO_3 + K_2Cr_2O_7$ | Pyrex | No | a,b,c | f |
| 51b | Yes | 0.10 | O | 30 | Pharmacia | $HNO_3 + K_2Cr_2O_7$ | Pyrex | No | UV | f |
| 53 P | 100 | 0.10 | O | 15 | Instrumentation Laboratories | $HNO_3$ | Polypropylene | No | a,b,c | f |
| 1 | 4 | 0.05 | O | 30 | Pharmacia | $H_2SO_4$ | | Yes | a,b,c | f,g |
| 13 | 100 | 0.2 | C | 15 | Jarrell-Ash | $HNO_3 + K_2Cr_2O_7$ | Polyethylene¶ | No | b,c | f,g,h |
| 46 P | No | 0.05 | O | 10 | Beckman | $H_2SO_4$ | Glass,‡ Teflon | No | a,b | f |
| 29 P | 100 | 0.03 | C | 10 | Perkin-Elmer 303 | Immediate analysis | | No | a,b,c | f,g |
| 14a | 4 | 0.05 | O | 30 | Pharmacia | $HNO_3 + K_2Cr_2O_7$ | Teflon | Yes | a,b,c | f,g |
| 14b P | 4 | 0.05 | O | 30 | Pharmacia | $HNO_3 + K_2Cr_2O_7$ | Teflon | Yes | a,b,c | f,g |
| 10 P | 100 | 0.05 | O | | Pharmacia | $HNO_3$ | Plastic† | No | a,b,c | f,g |
| 60 P | Yes | 0.02 | O | – | Spectro Products HG-2 | $H_2SO_4$ | Polyethylene¶ | No | a,b | f,g |
| 39 P | 50 | 0.05 | C | – | Pharmacia | $HNO_3$ | Polyethylene¶ | No | a,b | f |
| 6 P | 50 | 0.05 | – | | Beckman | $HNO_3$ | Plastic† | No | e | f |

* Refer to information requested in questionnaire submitted to participants.
† Unspecified material.
‡ Type not identified.
¶ Grade of plastic named (not product).
** Product name (unspecified plastic).

P–Laboratories that received test samples contained in linear polyethylene bottles.

# Appendix B

# List of Participants

# List of Participants

*Fisheries and Environment Canada, Environmental Management Service*

Atlantic Region, Water Quality Branch Laboratory (Moncton)

Ontario Region, Water Quality Branch, Inorganic Laboratory (Burlington)

Pacific and Yukon Region, Water Quality Branch Laboratory (Vancouver)

Western Region, Water Quality Branch Laboratory (Calgary)

*Fisheries and Environment Canada, Environmental Protection Service*

Atlantic Region, Environmental Services Branch (Halifax)

*Fisheries and Environment Canada, Fisheries and Marine Service*

Fisheries Services Laboratory (West Vancouver)

*Provincial Government Laboratories*

Alberta Department of the Environment, Pollution Control Laboratory (Edmonton)

British Columbia Ministry of the Environment, Environmental Laboratory (Vancouver)

British Columbia Research Council, Division of Applied Biology (Vancouver)

Manitoba Department of Mines, Resources and Environmental Management, Environmental Protection Branch (Winnipeg)

Ministère des Richesses naturelles du Québec, Complexe scientifique (Ste-Foy)

Ontario Ministry of the Environment, Thunder Bay Regional Laboratory (Thunder Bay)

Ontario Ministry of the Environment, Inorganic Trace Contaminants Section (Rexdale)

Saskatchewan Department of Public Health, Provincial Laboratories (Regina)

Service de la protection de l'environnement, Complexe scientifique (Ste-Foy)

*Municipal Government Laboratories*

Ville de Montréal, Travaux publiques, Division des eaux et de l'assainissement (Montreal)

*Industrial and Consulting Laboratories*

Aluminum Company of Canada Ltd., Arvida Analytical Centre (Arvida, Quebec)

Barringer Research Ltd. (Rexdale, Ontario)

Beak Consultants Ltd. (Mississauga, Ontario)

Beak Consultants Ltd. (Richmond, British Columbia)

Chemex Labs Ltd. (North Vancouver, British Columbia)

Chemical and Geological Laboratories (Edmondon, Alberta)

Cominco Ltd. (Trail, British Columbia)

Enviroclean Ltd. (London, Ontario)

Renewable Resources Consulting Services Ltd. (Edmonton, Alberta)

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