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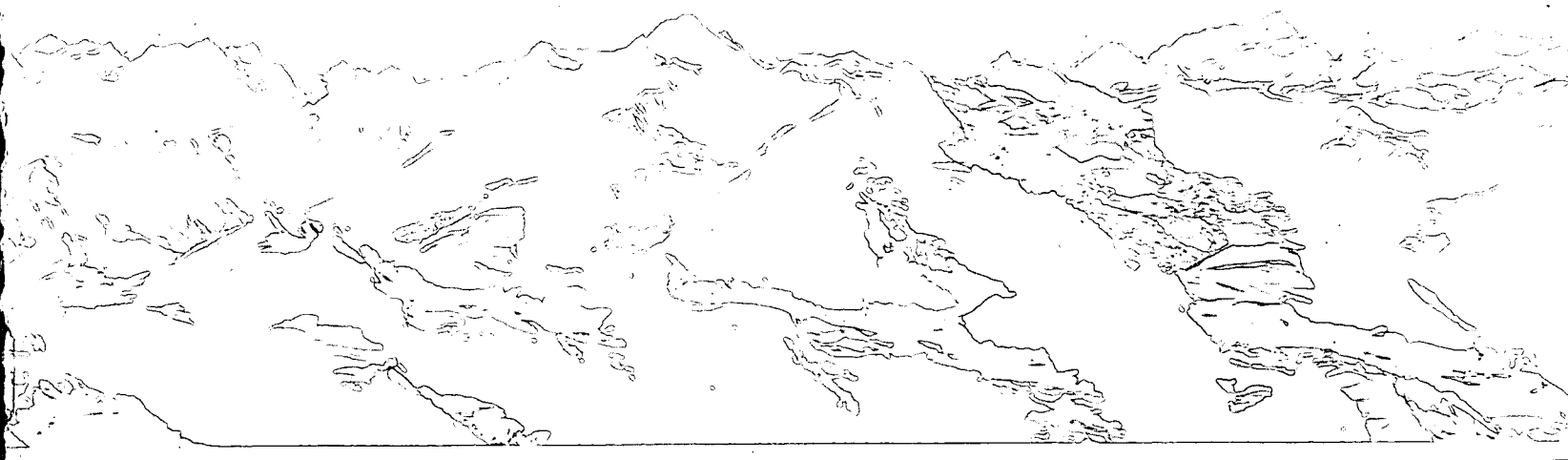
Interlaboratory Quality Control Study No. 26

Arsenic and Selenium in Water

V. Cheam and K. I. Aspila



REPORT SERIES NO. 68

INLAND WATERS DIRECTORATE, ONTARIO REGION
WATER QUALITY BRANCH
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Abstract

An intercomparison study on the determination of arsenic and selenium in water is described. Thirty Canadian laboratories participated, and each analyzed 10 natural, spiked and distilled water samples preserved with 0.2% H_2SO_4 in polyethylene containers. The concentration of both elements ranged from 0 to 1000 μg/L. Pooled analytical data were assessed using several statistical analyses—which included outlying tests, paired sample treatments, and ranking technique—to determine laboratory performance and bias. The majority of participants using the atomic absorption technique via atomization of hydrides produced reliable results. Based on the data from this study, this technique was assessed to be preferable to colorimetry, atomic emission and atomic absorption using graphite atomizer because of its good sensitivity and its capability of analyzing the whole concentration range.

Résumé

On a comparé dans trente laboratoires canadiens les méthodes de dosage de l'arsenic et du sélénium dans l'eau. Chacun des participants a analysé dix échantillons d'eau à l'état naturel, d'eau enrichie en ces éléments et d'eau distillée, conservés avec 0,2 % de H_2SO_4 dans des contenants de polyéthylène. La concentration des deux éléments s'étalait entre 0 à 1000 μg/L. On a analysé les résultats regroupées par diverses méthodes statistiques dont la détermination des résultats aberrants, le traitement d'échantillons jumelés et la technique de rangement des données, en vue d'évaluer le travail des laboratoires et l'erreur systématique. La majorité des participants qui ont utilisé l'absorption atomique par atomisation des hydrures ont obtenu des données fiables. D'après les résultats, cette méthode serait préférée à la colorimétrie, à l'émission atomique et à l'absorption atomique à atomiseur de graphite parce que sa sensibilité est bonne et que sa gamme de mesure correspond à l'intervalle de concentrations analysées.

List of Symbols

n	Number of results used in calculating the group mean ($\bar{x}$)
$\bar{x}$	Mean value, $\bar{x} = \Sigma x_i / n$
S	Standard deviation, $S = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}}$
Sj	Standard deviation of sample j, j = 1 - 10
Sg	Standard deviation using difference and average difference between m paired results, $Sg = 0.886 \sum_{i=1}^{m} \frac{\lvert di - d \rvert}{m}$ where di is algebraic difference between results of sample j + 1 and sample j, and $d = \sum_{1}^{m} \frac{\lvert di \rvert}{m}$
C.V.	Coefficient of variation, C.V. = $(S/\bar{x})\,100$
R	Results with a flag R were statistically determined to be outliers

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INTRODUCTION

Arsenic compounds, trivalent inorganics in particular, have been shown to exhibit high toxicity.[1] Being classified as a national health hazard, arsenic emissions have been regulated by Environment Canada, and new regulation standards will become effective by mid-1980.[2,3] Even though it is shown to be a respiratory and dermal carcinogen,[1] arsenic along with its sister element selenium is suggested to be of nutritional value owing to its electron transfer capability.[4] Arsenic and selenium are therefore interesting elements to investigate. This intercomparison study took place after many laboratories had responded to our questionnaire and had expressed interest in participating in a round-robin study on the analysis of arsenic and selenium in water.

Recently, Dreesen *et al.*[5] reported in an intercomparison study that the complex matrix background is the main cause for the disparity in results of arsenic, molybdenum, and in particular, selenium. They also reported that some of the hydride generation techniques were inadequate in quantitatively generating the hydrides, especially the arsines; this might be due to incomplete liberation of hydrides from generators and to inorganic interferences. The evidence we have accumulated in regard to arsenic and selenium analyses using hydride generation techniques tends to indicate that chemical interferences might play a more important role than suspected.

The above prompts us to communicate this round-robin study, which indicates that the majority of laboratories that used atomic absorption spectrometry to quantify arsenic and selenium via hydrides generated by various devices were capable of reliably analyzing the two elements in many water samples, which were preserved with 0.2% H_2SO_4.

STUDY DESIGN

In order to accommodate every laboratory that had expressed interest in participating in this study a wide range of As and Se concentrations, 0-1000 μg/L, were designed to include all the specified detection limits or lowest concentrations that the laboratories routinely report. As most detection limits are below 50 μg/L (ppb), the design was to have more samples with concentrations below 50 ppb than above—seven samples below and three above.

The purpose of the study was to find out the capability and compatibility of participating laboratories; a comparison of laboratory performance, bias and methodology was to be made. The study was also designed so that the results on each sample could be treated individually, then paired with those of another sample having similar composition and concentration at three different levels (2, 10 and 60 ppb—Table 1), and finally combined with those of all other samples. The three levels were chosen to be higher than the three general categories of detection limits (1, 5 and 50 μg/L) and therefore permit most laboratories to participate at least in a meaningful paired samples study. Youden[6] has shown that the paired samples technique is statistically preferable to duplicate analysis, and when graphically presented, the results can be easily interpreted.

Table 1. Description of Samples*

Sample	Contents	Concentration (μg/L)
1	Blank (distilled water)	0
2	Hamilton Harbour water	x
3	Hamilton Harbour & spike	x + 1.0
4	Hamilton Harbour & spike	x + 5.0
5	Hamilton Harbour & spike	x + 10.0
6	Hamilton Harbour & spike	x + 11.0
7	Hamilton Harbour & spike	x + 30.0
8	Hamilton Harbour & spike	x + 60.0
9	Hamilton Harbour & spike	x + 66.0
10	Concentrate (distilled water)	1000 of As and Se

* The spike added to the Hamilton Harbour water had by design the arsenic and selenium at equal concentrations.
All samples contained 0.2% (v/v) H_2SO_4 as a preservative.
In-house analyses placed a value of x = 1.12 μg Se/L and 1 μg As/L.

The design value for each of the samples 2-9 was equal to the sum of background value (from sample 2) and spike. Prior to distribution, the background concentrations were determined to be 1.12 ppb Se and 1 ppb As, but the median in sample 2 was used as the representative background value to compute the errors and recoveries.

EXPERIMENTAL

Chemicals

Both selenium dioxide, SeO_2 (ultrapure, lot #021077), and arsenic pentoxide, As_2O_5 (anhydrous, ultrapure, lot #060976), were purchased from Ventron Corp., Alfa Products, and used to make stocks of 1000 mg/L. The stocks were preserved with 0.2% (v/v) H_2SO_4 (Baker Analysed Reagent).

Sample Preparation

All containers were soaked with 10% H_2SO_4 overnight and then with 0.2% H_2SO_4 for several weeks before use.

One hundred litres of an intermediate concentrate containing both As and Se at 1000 μg/L was prepared in a 25-gal polyethylene barrel by appropriately diluting the stocks with deionized distilled water. This concentrate and all other test samples were preserved with 0.2% H_2SO_4. Sample 1 was deionized distilled water subsampled from the bulk used to make the concentrate. Sample 2 was from the bulk of Hamilton Harbour water (45 gal), which was used to prepare samples 3-9. Samples 3-9 were prepared by spiking an appropriate amount of concentrate into 30 L of Hamilton Harbour water to give the concentrations shown in Table 1. The samples were then subdivided into 250-mL polyethylene bottles. A few participants, upon request, were provided with larger volumes, 1 or 2 L.

Arsenic and Selenium Analysis

Participants had a free choice of analytical methods but were instructed to take the concentrate (sample 10) as a known containing 1000 μg As, Se/L and use it to establish calibration curves for analysis of samples 1-9. This should eliminate the type of bias that is normally caused by the use of different standards. Next, all laboratories were requested to take the concentrate sample 10 as an unknown and determine its concentration in duplicate using their own standards.

Since the study covers such a wide range of concentrations, it is almost certain that no participant has ever encountered either of the extremes during routine analysis. Consequently, hoping that it would help to explain some deviant results, we requested the laboratories to give their working detection limits and, if any, the dilution or concentration factor for each sample before it was analyzed. Indeed, many samples were diluted before analysis, and sample 9, which contained 66 μg/L, had to be diluted 10 times by a few laboratories.

Brief outlines of methodology were also requested from the participants. The analytical methods can be broadly grouped into (a) hydride generation techniques, which refer to the atomic absorption determinations of hydrides generated by various devices; (b) colorimetry, referring to spectrophotometric determinations on coloured complexes of arsenic and selenium; (c) atomic absorption determinations using graphite furnace atomizer (HGA); and atomic emissions analyses using Inductively Coupled Argon Plasma Emission Spectrophotometer.

The participants were allowed 1½ months to complete the analysis.

DATA EVALUATION

All the data received were summarized in Tables 2 and 5 and were treated by three main evaluation procedures in order to identify with confidence the performance and capability of each participant. First, each sample was analyzed for outliers and unacceptable individual results, then paired samples were evaluated to determine the unacceptable pairs, and finally the samples were altogether assessed for outlying laboratories by a ranking technique.[6] We believe that this use of combined evaluation procedures fairly assesses each participant's capability and thereby provides a confident answer to the question often asked by laboratory managers, "How did my lab do?"

Before the median, mean and other statistics were calculated, some data were screened out as follows:

(a) data submitted as experimental only,

(b) since there was a wide range of concentrations and detection limits, and since some laboratories reported results below their detection limits, the following data were taken as experimental only: those for the samples having design values significantly lower than the specified detection limits. For example, if the detection limit or the lowest concentration that a laboratory routinely reports is 10 μg/L, its data for samples 1-4, whose design values are 0-5 μg/L, were considered experimental only,

(c) data which were statistically determined to be outliers[7] and were flagged with "R".

The medians were determined after steps a and b, whereas the other statistics were determined after step c. Greenberg's criteria of acceptability, [8,9] as well as the one we adapt from them, were used to determine the unacceptable individual or paired results. The ranking was performed on raw data of samples 4 to 9 to avoid dealing with the many "less than" results for samples 2 and 3.

Table 2. Selenium Results (ppb, μg/L)

Lab code*	Method code†	Detection limit (from lab)‡	Samples§ 1	2	3	4	5	6	7	8	9	10	
01	Hydride	0.5	<0.5	1.4	2.6	6.4	12.6	12	31	59	72	960	980
04	Hydride	0.20	<0.2	1.10	2.00	6.00	10.9	12.0	32.5	60.0	67.0	–	–
09	Hydride	0.10	<0.1	1.4	2.4	6.3	12	12	30	61	68	945	1000
14	Hydride	0.1	<0.1	1.2	2.3	6.5	11	13	30	60	70	1000	980
19	Hydride	0.2	<0.2	1.3	2.1	6.6	12	12	34	56	62	1000	–
47	Hydride	1.0	<1	1	2	6	12	14	39	76	91R	1000	840
47d	Hydride	1.0	<1	<1	1.R	5	11	12	30	60	62	1000	948
50	Hydride	1.0	0	0.9	2.1	6.3	11.1	8.2R	29.1	60.2	68.2	1045	1075
51a	Hydride	2.0	<2	<2	2	7	10	13	34	61	71	1000	–
51b	Hydride	0.2	<0.1	1.2	2.4	6.2	10.8	12.2	34	61	70	1060	1050
51c	Hydride	0.1	<0.1	1.1	2.4	5.9	11.5	12.8	31.5	65	74	950	950
57	Hydride	1.0	2.6	3.6R	4.6R	8.6R	13.3	14.8	35	63	67.6	1000	1017
74	Hydride	1000	<100	<100	<100	<100	<100	<100	<100	<100	<100	1000±500	1000±500
87	Hydride	0.5	0.5	1.5	2.6	7.8	13.5	14	40.0	75	75	1000	–
89	Hydride	1.0	<1.0	1.5	2.1	6.6	11	11	29	61	64	1050	950
90	Hydride	10	<5	<5	<5	5.6	10.7	11.4	29.1	58.9	67.5	1080	–
52E	Colour	5.0	<5	~5	8	10	11	15	35	61	80	1000	995
58	Colour	1.0	<1	<1	2	5	3R	4R	23	48	67	918	868
10	Plasma	50	<50	<50	<50	<50	<50	<50	48	86R	101R	1030	–
15	HGA	50	<50	<50	<50	<50	<50	<50	<50	<50	<50	1100	900

	Samples§ 1	2	3	4	5	6	7	8	9	10
Design values, ppb	0	1.25	2.25	6.25	11.25	12.25	31.25	61.25	67.25	1000
Median values, ppb	–	1.25	2.1	6.3	11.05	12.0	31.25	61.0	68.2	1000
$\bar{x}$, Mean values, ppb	–	1.24	2.23	6.21	11.56	12.59	31.95	61.57	68.35	990.2
S, Standard deviation, ppb	–	0.20	0.23	0.71	0.99	1.08	4.12	6.54	3.84	59.51
C.V., coefficient of variation	–	16.1	10.3	11.4	8.6	8.6	12.9	10.6	5.6	6.0
Mean error, ppb	–	–	0.02	0.04	0.31	0.34	0.70	0.32	1.10	9.81
Relative mean error(%)	–	–	0.9	0.6	2.8	2.8	2.2	0.5	1.6	1.0
Recovery (%)	–	–	99	99	103	103	102	101	102	99

* Lab 47 = samples analyzed as they were; Lab 47d = samples analyzed digested; Lab 52E = results from Lab 52 are experimental only.
† "Colour" refers to colorimetric determination on the selenium complexes in solution. "Hydride" refers to atomic absorption determination on hydrogen selenide gas generated by various devices. "HGA" = Graphite furnace.
‡ The number given is the lowest concentration in ppb that each laboratory routinely reports.
§ Results with a flag R were determined to be outliers. Results outside the interval of $\bar{x} \pm 2S$ are underlined.

RESULTS AND DISCUSSION

Selenium Determinations

All selenium results are given in Table 2 along with the median, mean, standard deviation, coefficient of variation, mean error, relative mean error and recovery values. After the evaluation of individual results on each sample, the analytical results determined to be outliers were flagged with "R", and those determined to be unacceptable (outside the interval of mean ±2 standard deviations [8,9]) were underlined.

The paired results were then treated by graphical evaluation (Figs. 1-3). Greenberg *et al.*[8] defined the results' acceptability based on the medians and standard deviation of the joint paired results. This standard deviation, here referred to as Sg, is calculated from the difference and average difference between the paired results. The points which are outside the circle whose centre is the intersection of the medians and whose radius is 2.448 Sg are considered unacceptable. Applying this definition to our study, we see that the results determined by Grubbs' procedures to be outliers are indeed outside the circles—Lab 57 in Figure 1, Labs 50 and 58 in Figure 2, and Labs 47 and 10

in Figure 3. In addition to these, there are a few more results outside the circles which were determined not to be outliers—Labs 1 and 87 in Figure 1, Labs 57 and 87 in Figure 2, and Labs 58 and 87 in Figure 3. From these observations, it appears that Greenberg's definition results in a somewhat stricter screening than Grubbs', although one deals with paired and the other with single samples results.

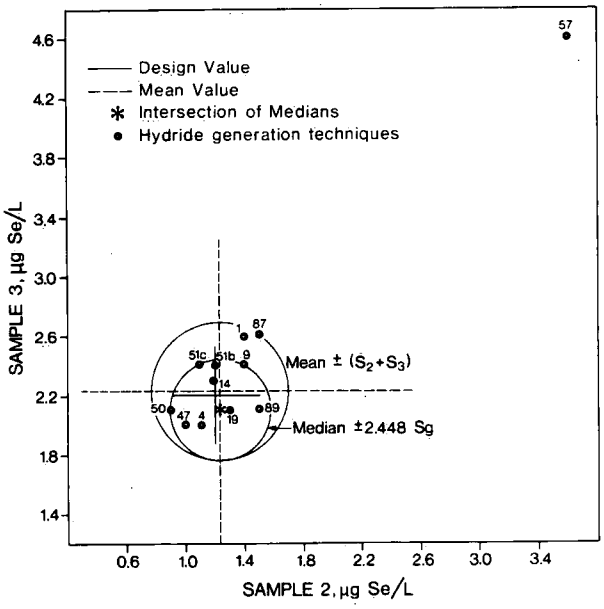

Figure 1. Selenium paired sample plot for samples 2 and 3.

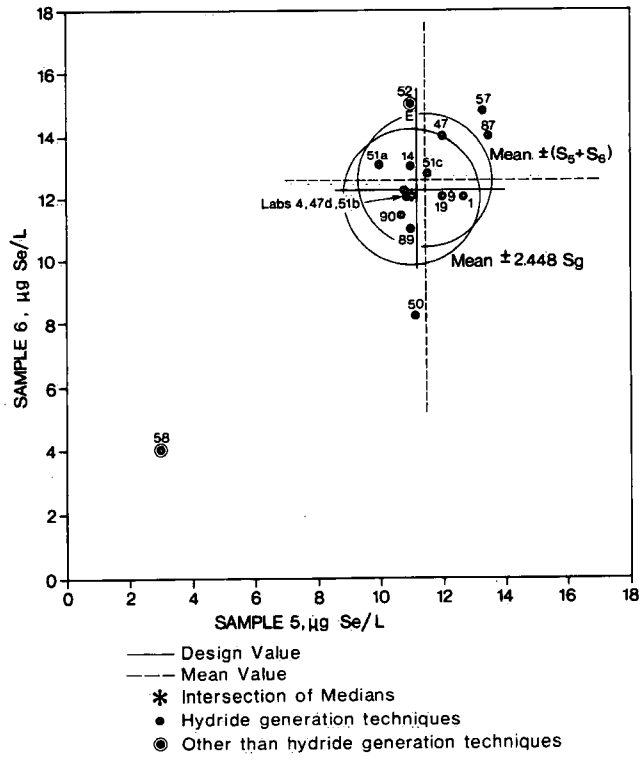

Figure 2. Selenium paired sample plot for samples 5 and 6.

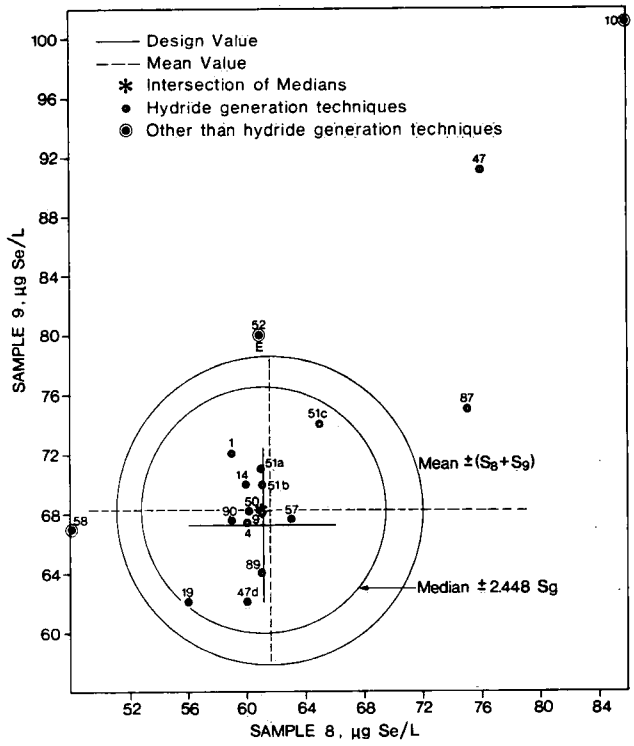

Figure 3. Selenium paired sample plot for samples 8 and 9.

An attempt is made here to adapt the acceptability criterion of mean ± 2 standard deviations to this study and use it to evaluate the paired results. Since our paired samples are indeed very similar in concentration and composition, it seems reasonable to use the average of their standard deviations given in Table 2 as the representative standard deviation for both samples. This average multiplied by 2 is the same as the sum of the paired standard deviations and is taken as the acceptability limit. Now, if one draws in each of the three figures (Figs. 1-3) a circle having this sum as its radius and the intersection of the means as its centre, one sees that the new circles are in general slightly larger than, but close to the first ones. This means that the number of acceptable results also increases accordingly. In this case, two results (Labs 1 and 87 in Fig. 1) become acceptable, whereas the others in Figures 2 and 3 remain unchanged. Thus, the use of the sum of standard deviations derived from two very similar samples as an acceptability criterion seems to be capable of isolating the unacceptable results when compared to the criterion defined by Greenberg *et al.*[8] (Table 4).

In Figures 1-3, a visual comparison between the hydride evolution techniques (solid circles) and others can be readily made. Figure 1 shows only the data for hydride methods, as they are the most sensitive. One out of the 12 pairs is assessed unacceptable. Figure 2 shows two non-hydride methods as well; both are, however, outside the acceptability limit, keeping in mind that Lab 52E is

experimental only and is almost within the limit. On the other hand, 12 out of 15 hydride pairs are within the acceptability circle, indicating that hydride techniques perform well and better than the other techniques. The same observation is repeated with Figure 3, in which 3 out of 3 non-hydride pairs are unacceptable, compared with only 2 out of 15 hydrides.

The data were further evaluated by a ranking procedure originally outlined by Youden[6] but slightly modified, as we chose to assign the rank of 1 to the lowest analytical result and the rank of n to the highest results in each sample of n results. Rules for tie results and critical values can be found in reference 6. Table 3 gives the ranked results for each of the samples 4 to 9 and the overall laboratory scores. The laboratories producing scores outside the critical or acceptable range, in this case 20-88, are assessed to have pronounced biases. Lab 87, scoring 94.5, is biased high, and Lab 58, scoring 10, is biased low. A score inside the range but near the limits, 20 or 88, indicates that overall the results in samples 4-9 tend to be low or high, respectively. To cite an example, Lab 57, scoring 83.5, is expected to have reported high results, which it did (Table 2). This is further confirmed by the analysis for outliers and unacceptable results summarized in Table 4.

It should be recognized that the ranking process above is particularly useful in identifying laboratory bias but not necessarily its precision. Clearly, a laboratory could have a score right in the middle of acceptable range, yet have some results ranked high and others ranked low. The present emphasis, however, is that the existence of pronounced biases for some laboratories has been demonstrated, but the cause of these biases could only be speculated. Certainly, the difference in standards could not be the cause because every participant was provided with and instructed to use the same concentrate standard, which we used to prepare the samples. There are two possible causes for the high systematic error of Lab 87, based on the acceptable performance of some other laboratories which used similar analytical methods and provided the same type of information to our questionnaire. The possible causes might be the high temperature, 1000°C, of the quartz tube atomizer and the type of hydride evolution apparatus, MHS-1. For example, Labs 1, 9 and 14 operated the quartz tube at 850°C, and Lab 90 at 750°C. Also, Labs 51b and 51c used MHS-10 as hydride generator, and Lab 89 used Varian MLS-5. The low systematic error in Lab 58 could not very well be blamed on the colorimetric determination procedure because Lab 52E used the same procedure and almost consistently produced high results (Table 2), with a high score of 83, which is closer to the upper limit of 88 (Table 3).

Table 3. Selenium Ranked Results and Laboratory Scores According to Youden Ranking Techniques.[6]

Lab no.	Ranked results on samples 4-9						Lab score
	4	5	6	7	8	9	
01	10	15	7	8	4	13	57
04	5.5	5	7	10	6	4.5	38
09	8.5	13	7	6	11	8	53.5
14	11	7.5	12.5	6	6	10.5	53.5
19	12.5	13	7	12	2	1.5	48
47	5.5	13	14.5	16	17	17	83
47d	1.5	7.5	7	6	6	1.5	29.5
50	8.5	10	2	3.5	8	9	41
51a	14	2	12.5	12	11	12	63.5
51b	7	4	10	12	11	10.5	54.5
51c	4	11	11	9	15	14	64
57	16	16	16	14.5	14	7	83.5
87	15	17	14.5	17	16	15	94.5*
89	12.5	7.5	3	2	11	3	39
90	3	3	4	3.5	3	6	22.5
52E	17	7.5	17	14.5	11	16	83
58	1.5	1	1	1	1	4.5	10*

* Scores outside the acceptable range, 20-88.

The results of all evaluation procedures are summarized in Table 4, the upper portion of which lists the laboratories having one or more possible suspect results, whereas the bottom portion lists the laboratories with all results assessed acceptable. It is worthwhile noting that the ten participants in the bottom portion all used hydride evolution techniques. Since overall acceptable performance is realized only by the laboratories using hydride methods and not by the laboratories using other methods, indications are that the atomic absorption analysis of Se by atomizing hydrogen selenides is a superior technique for analysis of water samples preserved with 0.2% H_2SO_4. However, it must be recognized that a fair comparison between methods would require that the number of laboratories using one type of method be approximately equal to that using another type of method. In this study, there were 15 hydride and four non-hydride methods (Table 2).

The duplicate results on the concentrate (sample 10) have not a single outlier and are quite comparable, producing excellent statistics (Table 2). At this high concentration, all laboratories seem to be compatible and capable of determining reliable data. At the other extreme of concentration, for Se as well as for As, no attempt was made to treat the results on sample 1 (distilled water), since most of these are "less than" values as expected.

Arsenic Determinations

Table 5 gives the data for arsenic and the calculated statistics. For each sample, the analytical results determined to be outliers are flagged with "R", and those outside the limit of two standard deviations are underlined. Figure 4

Table 4. Evaluation Summary on Se Results in Samples 2-9

Lab No.*	Method†	No. outliers[7] in samples 2-9	No. unacceptable individual results in samples 2-9	No. unacceptable paired results		Lab score (acceptable range = 20-88)
				Greenberg *et al*[8]	St. dev. sum	
1	H	0 out of 8	0 out of 8	1 out of 3	0 out of 3‡	57
10	NH, plasma	2 out of 2	3 out of 3	1 out of 1	1 out of 1	not enough data
15	NH, HGA	–	–	1 out of 1	1 out of 1	not enough data
47	H	1 out of 8	2 out of 8	1 out of 3	1 out of 3	83
50	H	1 out of 8	1 out of 8	1 out of 3	1 out of 3	41
52E	NH, colour	–	5 out of 8	3 out of 3	3 out of 3	83
57	H	3 out of 8	4 out of 8	2 out of 3	2 out of 3	83.5
58	NH, colour	2 out of 7	4 out of 8	2 out of 2	2 out of 2	10
87	H	0 out of 8	2 out of 8	3 out of 3	2 out of 3	94.5
47d	H	1 out of 8	1 out of 8	1 out of 3	1 out of 3	29.5
4,9, 14	H	0	0	0	0	38, 53.5, 53.5
19	H	0	0	0	0	48
51a, 51b	H	0	0	0	0	63.5, 54.5
51c	H	0	0	0	0	64
89,90	H	0	0	0	0	39, 22.5
1‡	H					57

* Laboratories with one or more possible suspect results are grouped in the upper portion of the table, and laboratories with all results acceptable are grouped below.

† H = hydride generation techniques (atomic absorption). NH = non-hydride methods, other than H.

‡ We consider all results reported by Lab 1 as acceptable in spite of the one unacceptable paired result determined by the method of Greenberg *et al*.

illustrates the statistics on samples 2 and 3 with the acceptability limits, which are defined and discussed above. First of all, it clearly indicates that all non-hydride methods, being well outside the limiting circles, were not sensitive enough to analyze low levels of arsenic. On the other hand, all but two hydride evolution techniques produced acceptable results at the 1 ppb level. All the unacceptable results fell in the first quadrant basically along the 45° line, which implies that there were systematic errors (biased high) responsible for those high results.[6]

The paired results of Labs 43b and 50 would be considered unacceptable according to the definition using medians and Sg, but would be acceptable under our evaluation using the mean and standard deviations sum (Fig. 4).

Figure 5 shows the two types of circles for samples 5 and 6. The circle with 2.448 Sg as radius is slightly larger than the other, but the unacceptable pairs are the same, that is, Labs 58, 56, 52E, 43a, 46, 2 and 56E. The points representing these labs are in the first and third quadrants, an indication that there are some systematic factors resulting in too high or too low results. At this level of 10 ppb As, the non-hydride methods perform better than the 1 ppb level; 4 pairs out of 10 are acceptable. However, all but one hydride pair, 18 out of 19, are acceptable.

In Figure 6, dealing with As concentration of 60 ppb, a further improvement in performance is observed for the non-hydride techniques, 8 out of 11 making the acceptable limit defined by the sum of standard deviations. However, according to Greenberg's definition, only 4 out of 11 would be acceptable. Under this same definition, 16 out of 19 hydride pairs are acceptable.

The ranking procedure discussed and used above for selenium results is used here to evaluate the arsenic data.

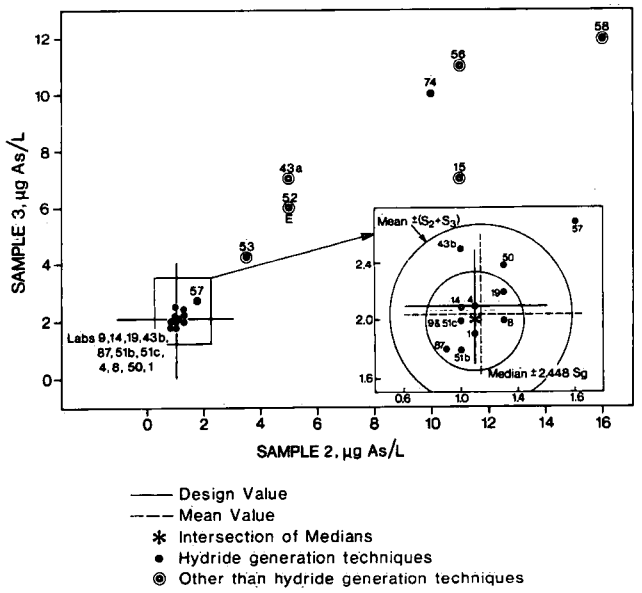

Figure 4. Arsenic paired sample plot for samples 2 and 3.

Table 5. Arsenic Results (ppb, μg/L)

Lab code*	Method code†	Detection Limit (from lab)‡	Samples § 1	2	3	4	5	6	7	8	9	10	
02	Colour	5	<5	<5	<5	6	8	11	28	50	63	920	940
15	Colour	20	ND	11	7	5	14	12	22	57	44R	925	950
43a	Colour	5	Nil	5	7	9	15	15	35	60	70	900	890
43b	Colour	1	Nil	1	2.5	7	11	12	–	–	–	–	–
52E	Colour	5	<5	~5	6	7	14	16	37	62	75	995	1004
53	Colour	2	<1.2	3.5R	4.2R	6.9	10.1	13.3	22.5	50.1	69.2	1025	980
56E	Colour	10	<5	<5	<5	<5	7	7	28	61	69	930	–
58	Colour	5	11	16	12	11R	17R	25R	38	76	72	980	990
94	Colour	5	<5	<5	<5	8	13	13	36	64	73	1100	960
01	Hydride	0.5	0.5	1.1	1.9	6.4	11.6	13	30	58	70	920	970
04	Hydride	0.2	<0.2	1.10	2.10	6.60	11.50	12.80	32.20	64	71	–	–
08	Hydride	1.0	<1.0	1.3	2.0	6.3	11.8	12.4	32.3	69.6	82.0	1154	925
09	Hydride	0.1	<0.1	1.0	2.0	6.5	12	14	33	68	68	882	–
14	Hydride	0.1	<0.1	1.0	2.1	6.0	10	11	28	60	65	1000	1000
19	Hydride	0.2	<0.2	1.3	2.2	6.1	11	12	34	66	67	1000	–
34	Hydride	2	<2	<2	2.5	6.0	11.0	12.0	28.5	58.0	60.0	907	872
46	Hydride	1.0	<0.4	<0.4	1.6	4.5	8.5	11.6	37	58	71	950	900
47	Hydride	1.0	<1	<1	1	5	10	11	30	67	72	1000	750
47d	Hydride	1.0	<1	<1	2	6	12	12	32	56	66	1000	800
50	Hydride	1.0	<0.5	1.3	2.4	7.2	12.2	13.3	33.1	66.8	69.6	870	834
51a	Hydride	2.0	<2	<2	2	6	10	12	28	54	57	975	–
51b	Hydride	1.0	<0.2	1.0	1.8	5.9	9.8	12	32	63	71	980	990
51c	Hydride	0.2	<0.2	1.0	2.0	6.5	12.2	13.0	31	61	72	920	880
57	Hydride	1.0	1.2	1.8	2.7	6.6	12.4	13.2	32.2	62.8	67.1	852	850
74	Hydride	100	9±6	10±6	10±6	<10	12±6	15±6	32±7	63±9	46±8	1030±80	970±80
87	Hydride	0.5	<0.5	0.9	1.8	7.0	10.5	14.0	35.0	70.0	70.0	830	–
89	Hydride	4.0	<4	<4	<4	7	13	13	33	60	64	960	1040
90	Hydride	10	<5	<5	<5	5.2	9.5	10.8	28.5	52.6	64.6	990	970
26	HGA	5	18	<5	5	12R	14	12	30	51	62	1030	1020
56	HGA	10	0	11	11	17	22R	21R	45R	80	87	987	1026
10	Plasma	1.0	<50	<50	<50	<50	<50	<50	56R	79	88	–	1100

	Samples § 1	2	3	4	5	6	7	8	9	10
Design values, ppb	0	1.1	2.1	6.1	11.1	12.1	31.1	61.1	67.1	1000
Median values, ppb	–	1.1	2.0	6.5	11.55	12.6	32.0	61.0	69.6	970.0
$\bar{x}$, Mean values, ppb	–	1.15	2.04	6.48	11.25	12.48	31.17	62.29	69.67	952.5
S, standard deviation, ppb	–	0.25	0.39	0.93	1.65	1.06	3.86	8.13	7.18	77.83
C.V., coefficient of variation	–	21.7	19.1	14.4	14.7	8.5	12.4	13.0	10.3	8.2
Mean error, ppb	–	–	0.06	0.38	0.15	0.38	0.07	1.19	2.57	47.5
Relative mean error (%)	–	–	2.9	6.2	1.4	3.1	0.2	2.0	3.8	4.7
Recovery (%)	–	–	97	106	101	103	100	102	104	95

* Lab 43a = standard colorimetric determinations of As; 43b = low level determinations by enrichment procedures; Labs 52E and 56E = provided experimental results only; Lab 47 analyzed samples as they were, whereas 47d analyzed samples digested; Labs 51a, 51b, and 51c are three different laboratories.

† "Colour" refers to colorimetric determination on the arsenic complexes in solution. "Hydride" refers to atomic absorption determination on arsine gas generated by various devices. "HGA" = atomic absorption determination on solutions containing As and Se using graphite furnace atomizer.

‡ The number given is the lowest concentration in ppb that each laboratory routinely reports.

§ Results with a flag R were determined to be outliers. Results outside the interval of $\bar{x} \pm 2S$ are underlined.

The ranking results are summarized in the last column under laboratory score in Table 6. Three scores are outside the critical or acceptable range, which is 29-145. The score 26.5 (Lab 2) is indicative that the analytical results are in general low, and this can easily be verified by referring to Table 5 and Figures 4-6. Labs 56 and 58, scoring 167 and 158, did report several high analytical results (Table 5), which were assessed unacceptable under various procedures (Table 6) and which can be checked visually in Figures 4-6.

Nine laboratories analyzed As by the silver diethyldithiocarbamate method (colorimetric determinations). Even though 8 out of these 9 laboratories have one or more possible suspect results (upper portion of Table 6), some useful points should be mentioned about the method. Basically, all but 3 laboratories (Labs 2, 94 and 43b) utilized the method as outlined in "Standard Methods".[10] These 3 laboratories used some additional steps, which overall seem to produce better data. Lab 2 autoclaved the samples and standards with potassium persulphate prior to the reduction step; this laboratory was assessed (Table 6) to have no outliers, none of the unacceptable individual results and one unacceptable pair, which was just outside the acceptability limit (Fig. 5). Even though this laboratory has a ranking score outside the critical range, the score is just below the low limit (26.5 versus 29). All this implies that the laboratory is capable of producing acceptable individual results, but that the results are constantly on the low end of the acceptable range. This in itself illustrates the need to use several combined evaluation procedures to properly assess laboratory performances. But the point to be made here is that the oxidation step introduced into the method seems to produce fairly good data compared with other data which were generated from the basic method and which have at least two outliers and unacceptable individual results combined (Table 6).

Laboratory 94 also used an additional oxidation step with perchloric, sulphuric and nitric acids; this laboratory produced results that were assessed acceptable, except for one result on sample 4 that was just outside the upper end of the acceptable range, 7.41 ppb against 8 ppb (Tables 5 and 6). Laboratory 43b, using an enrichment procedure by coprecipitation of As with ferric hydroxide at pH 7-8[11] to

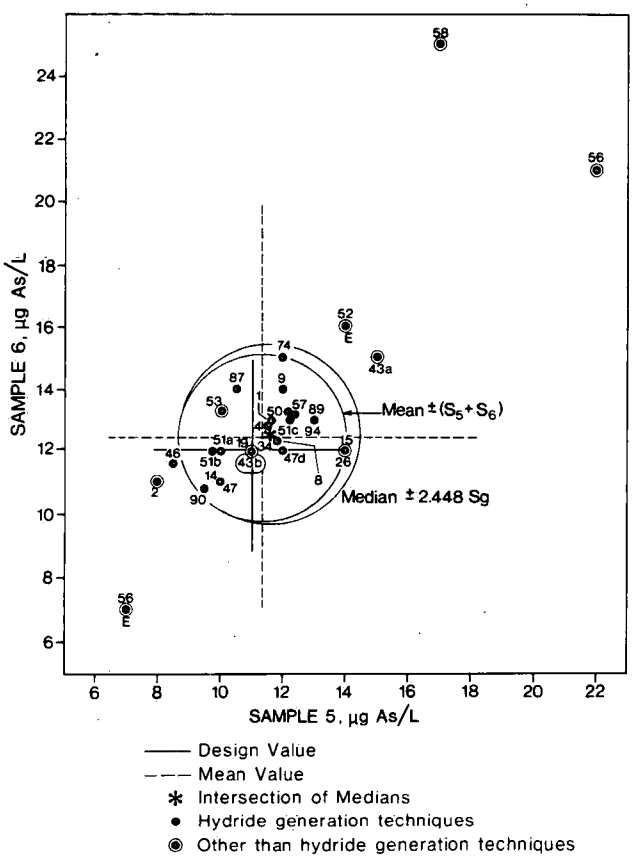

Figure 5. Arsenic paired sample plot for samples 5 and 6.

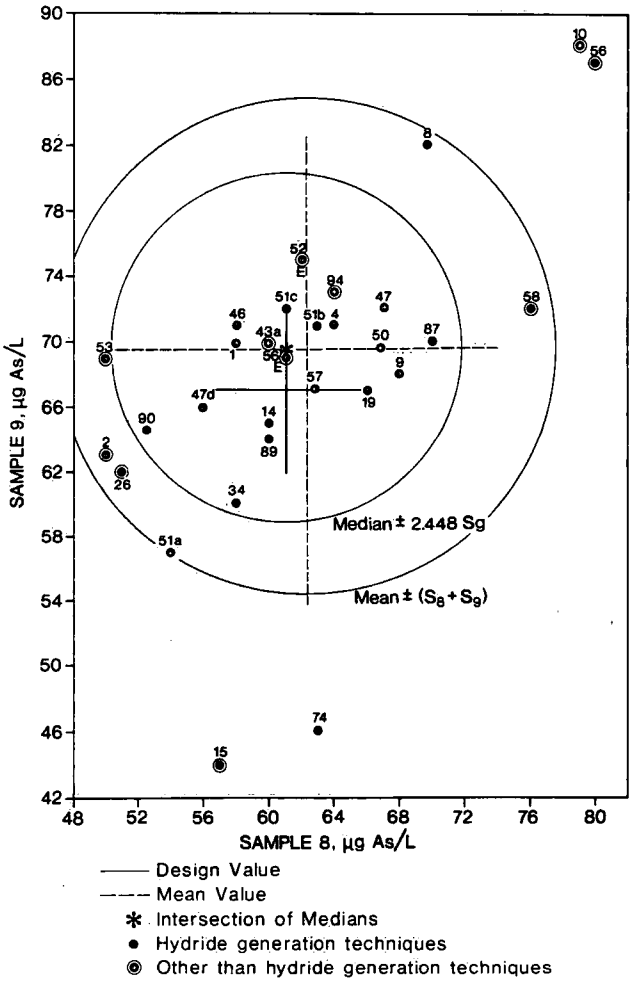

Figure 6. Arsenic paired sample plot for samples 8 and 9.

Table 6. Evaluation Summary on As Results in Samples 2-9

Lab No.*	Method†	No. outliers in samples 2-9	No. unacceptable individual results	No. unacceptable paired results		Lab score (acceptable range = 29-145)
				Greenberg *et al*[8]	St. dev. sum	
2	NH, colour	0	0 out of 8	2 out of 2	1 out of 2	26.5
8	H	0	0 out of 8	1 out of 3	0 out of 3‡	112.0
10	NH, plasma	1	3 out of 3	1 out of 1	1 out of 1	not enough data
15	NH, colour	1	4 out of 8	2 out of 3	2 out of 3	46.0
26	NH, HGA	1	2 out of 8	1 out of 2	0 out of 2	78.0
43a	NH, colour	0	5 out of 8	2 out of 3	2 out of 3	127.5
46	H	0	2 out of 8	1 out of 2	1 out of 2	63.5
51a	H	0	0 out of 8	1 out of 2	0 out of 2‡	37.5
52E	NH, colour	–	3 out of 8	2 out of 3	2 out of 3	138.5
53	NH, colour	2	3 out of 8	2 out of 3	1 out of 3	67.5
56	NH, HGA	3	8 out of 8	3 out of 3	3 out of 3	167.0
56E	NH, colour	–	2 out of 5	1 out of 2	1 out of 2	37.0
57	H	0	1 out of 8	1 out of 3	1 out of 3	102.0
58	NH, colour	3	5 out of 8	3 out of 3	2 out of 3	158.0
74	H	–	4 out of 8	2 out of 3	2 out of 3	not applicable
94	NH, colour	0	1 out of 8	0 out of 2	0 out of 2‡	131.5
47	H	0	1 out of 8	1 out of 3	1 out of 3	70.0
1,4	H	0	0	0	0	81.5, 101.5
9, 14	H	0	0	0	0	111, 44.5
19,34	H	0	0	0	0	78.5, 50.0
43b	NH, colour	0	0	0	0	not enough data
47d	H	0	0	0	0	64.5
50, 51b	H	0	0	0	0	121, 73
51c, 87	H	0	0	0	0	101, 120
89, 90	H	0	0	0	0	97.5, 29.5
8‡, 51a‡	H					112, 37.5
94‡	NH, colour					131.5

* Laboratories with one or more possible suspect results are grouped in the upper portion of the table, and laboratories with all results considered acceptable are grouped below.

† H = hydride generation techniques (atomic absorption). NH = non-hydride methods, other than H.

‡ We consider all results reported by Labs 8, 51a, and 94 acceptable as an overall performance.

analyze the first six samples, has none of its data flagged with outliers or unacceptable results. On the other hand, its counterpart Lab 43a, using the standard method[10] as is, has all five corresponding results evaluated unacceptable. Also, Lab 58, which used the method without modification, is flagged with three outliers, five unacceptable individual results, two unacceptable pairs, and a ranked score outside the acceptable range. This seems to indicate that the additional enrichment or oxidation step incorporated into the original method helped upgrade the As determinations.

The other analyses were made by atomic emission (Inductively Coupled Argon Plasma, ICAP), by atomic absorption with heated graphite atomizer (HGA), and by atomic absorption with various hydride evolution devices. Many analytical results produced by ICAP and HGA are assessed suspect (upper part of Table 6), whereas those generated by hydride evolution methods are mostly acceptable (bottom part of Table 6). Fifteen out of nineteen participants who used hydride techniques have all their results considered acceptable and are grouped at the bottom of Table 6 along with two (out of nine) laboratories utilizing colorimetric procedures. Overall then, the As determination via atomization of arsines generated by various devices is a preferred technique for the analysis of our water samples.

Matrix and Chemical Interferences

In a recent intercomparison study,[5] it was concluded that the disparity of results on selenium and arsenic was caused mainly by the complex matrix of groundwater samples and perhaps to a lesser extent by interference from inorganic ions and incomplete liberation of hydrides. In that study, the water samples had high specific conductance with values ranging up to 20 000 μmhos/cm. Also, the concentrations of test samples with acceptable analysis were equally high, 832 to 1309 μg Se/L and 106 to

676 μg As/L. Faced with these high concentrations of Se and As, many collaborators of this present study, who diluted our samples containing 60 μg As, Se/L 10 times to be within their working range, would certainly have diluted most of the above groundwater samples by 100 times before analysis. This dilution factor would then have reduced the background matrix substantially to a complexity level comparable to that of the Hamilton Harbour water used in this study. This Harbour water had a specific conductance of 511 μmhos/cm along with a high complexing capacity, which is indicative of high organic content.[12] The evaluation results of this round-robin study showed that most hydride methods were capable of producing acceptable analytical data on all samples, including the undiluted Hamilton Harbour solutions (spiked with 1-11 ppb As and Se), and hence were capable of satisfactorily liberating the hydrides. It seems reasonable to assume that the hydride methods would also, through dilution, be capable of handling the groundwater samples in spite of their complex matrix background. The reported[5] inadequacy of the hydride methods may have been caused not by the complex matrix alone or incomplete liberation of hydrides, but perhaps by some specific inorganic ions as well.

Significant nitrate interferences on selenium and arsenic analyses have been reported for manual and automated hydride generation techniques.[13,14] Our laboratory has encountered interferences on inorganic As and in particular Se analyses when using some automated hydride evolution methods [15-17] to analyze water samples which had been acidified with HNO_3. Consequently, for As and Se, our monthly inter-regional quality control samples are not preserved with this acid but instead they are kept at 4°C until analysis. Low-temperature preservation is adequate but impractical according to Cheam and Agemian,[16,17] who found that 0.2% (v/v) H_2SO_4 preservative (a) does not interfere with the three hydride evolution manifolds;[15-17] (b) inhibits algae growth; and (c) stabilizes As and Se species at room temperature for at least 4 months. Furthermore, Goulden[18] recommended not nitric but phosphoric and sulphuric acids as preservatives for atomic absorption determinations of Se and As, respectively. Hence, based on the above discussions on dilution effect, chemical interference and superior performance of the hydride generation atomic absorption methods in our study, and since nitric acid was used by Dreesen *et al.* to acidify their round-robin samples, it is possible that this chemical, along with the complex matrix, might have contributed more significantly than suspected to the observed difficulty with hydride methods.[5]

Precision Functions

For arsenic, the standard deviation can be satisfactorily expressed in terms of concentrations up to 70 μg/L as:

$$S(As) = 0.149 + 0.113 \text{ (concentration)}$$

with a root mean square deviation (RMSD)[19] of 0.6 ppb As. For selenium, the linear expression is:

$$S(Se) = 0.30 + 0.078 \text{ (concentration)}$$

with an RMSD of 1.1 ppb Se. Note, however, that a better fit for the results of this round-robin study is the following equation giving a smaller RMSD of 0.4 ppb Se:

$$S(Se) = 0.478 - 0.0679 \text{ (concn)} + 0.009867(\text{concn})^2 - 0.0001\,184\,(\text{concn})^3.$$

This polynomial expression of third degree also gives good fits to both As and Se relative standard deviations, better than the linear or quadratic form.

CONCLUSIONS

1. More than 50 per cent of participants used the atomic absorption technique via atomization of hydrides to determine selenium and arsenic in water samples; 80% atomize the selenides and 60%, the arsines.

2. In this study, the superiority of the hydride methods was indicated by their capability of producing more reliable results than the other methods including colorimetry, atomic emission, and atomic absorption using graphite atomizer.

3. An enrichment or oxidation step, incorporated prior to the reduction step of the original colorimetric method for arsenic,[10] seems necessary to upgrade the As determinations.

4. Some laboratories performed acceptably at one concentration level but not necessarily so at another level. It follows that the performance of a laboratory cannot be satisfactorily assessed on the basis of a single pair of similar samples, much less on a single sample.

5. The acceptability limit defined by the sum of standard deviations of two very similar samples is slightly more "liberal" than that defined by Greenberg *et al.*[8] and results in 10 more acceptable pairs in 6 paired sample plots.

6. The various evaluation procedures reinforce each other to give confidence in the final assessment of the capability and performance of participants. For selenium and arsenic determinations in several water samples preserved with 0.2% H_2SO_4, 70% and 80% respectively, of the laboratories using hydride evolution methods performed remarkably well (Tables 4 and 6).

ACKNOWLEDGMENTS

The participation of the laboratories listed in the Appendix is gratefully acknowledged.

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FUTURE INTERLABORATORY STUDIES

Lee, H.B. and A.S.Y. Chau. Interlaboratory quality control study No. 27: polychlorinated biphenyls in naturally contaminated dry sediments.

Aspila, K.I. and Haig Agemian. Interlaboratory quality control study No. 28: arsenic and selenium in soils and sediments.

Cheam, V. and A.S.Y. Chau. Interlaboratory quality control studies Nos. 29 and 30: Major ions in water.

APPENDIX

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

- Air Pollution Technology Centre (Ottawa)
- Atlantic Region, Environmental Services Branch (Halifax)
- Northwest Region, Environmental Services Branch (Edmonton)

Health and Welfare Canada, Medical Services Branch

- Occupational Health Unit (Ottawa)

Provincial Government Laboratories

- Alberta Department of the Environment, Pollution Control Laboratory (Edmonton)
- British Columbia Research Council, Division of Applied Biology (Vancouver)
- Manitoba Department of Mines, Resources and Environmental Management, Environmental Protection Branch (Winnipeg)
- Ontario Ministry of the Environment, Thunder Bay Regional Laboratory (Thunder Bay)
- Ontario Ministry of the Environment, Inorganic Trace Contaminants Section (Rexdale)
- Ontario Ministry of Natural Resources, Geoscience Laboratories (Toronto)
- Saskatchewan Department of Public Health, Provincial Laboratories (Regina)
- Service de la protection de l'environnement, Complexe scientifique (Ste-Foy)

Industrial and Consulting Laboratories

- Acres Consulting Services (Niagara Falls, Ontario)
- Beak Consultants Ltd. (Mississauga, Ontario)
- CAN TEST Ltd. (Vancouver, British Columbia)
- Chemex Labs Ltd. (Calgary, Alberta)
- Chemical and Geological Laboratories (Edmonton, Alberta)
- Domtar Ltd. (Senneville, Quebec)
- Enviroclean Ltd. (London, Ontario)
- Noranda Mines Ltd. (Noranda, Quebec)
- Powell Analytical Consulting & Services (Calgary, Alberta)
- Shell Canada Resources Ltd. (Calgary, Alberta)

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