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**NO. 237**

# Seventh Intercomparison Exercise on Trace Metals in Sea Water

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# 1 Introduction

This is the seventh intercomparison exercise for trace metals in sea water organized by the Marine Chemistry Working Group (MCWG) of the International Council for the Exploration of the Sea (ICES). It is designated as 7/TM/SW.

The MCWG at its annual meeting in March 1995 formulated a proposal to conduct an intercomparison exercise for trace metals in coastal sea water in order to give laboratories from the participating countries an opportunity to assess their capabilities regarding this type of environmental analysis. The last study of this nature (6/TM/SW) carried out by the MCWG involved estuarine waters and took place in 1986 (Berman and Boyko, 1988).

A detailed proposal to collect water in the Kattegat and distribute two samples of sea water to volunteer participants for trace metal analysis was prepared by an *ad hoc* committee consisting of:

| | | |
|---|---|---|
| Dr Britta Pedersen | National Environmental Research Institute (NERI) | Denmark |
| Dr Gert Asmund | National Environmental Research Institute (NERI) | Denmark |
| Dr J.F. Chiffoleau | IFREMER | France |
| Dr Jon Ólafsson | Marine Research Institute (MRI) | Iceland |
| Dr Shier Berman | National Research Council (NRC) | Canada |

The proposal to conduct this intercomparison exercise was accepted by the ICES Council in October 1995.

There were ten designated elements of interest: chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, cadmium and lead. Of these, copper, zinc and cadmium were mandatory in OSPARCOM Joint Monitoring Programme in Europe, while chromium, nickel and arsenic were voluntary.

A preliminary survey had indicated that there was insufficient interest from potential participants in the addition of mercury to the list of analytes. However, the addition of mercury also would have added considerably to the cost of the study because separate samples would have had to be collected and bottled for this single element.

The *ad hoc* committee also agreed that the results of the study should be evaluated by NRC in the same manner that was used for previous MCWG intercomparison exercises coordinated by that laboratory.

# 2 Seawater Collection and Sample Preparation

The samples were collected in the Sound, a channel (strait) between Denmark and Sweden, in August 1996. Both samples were collected at the same position, 55°52′00 N, 12°45′00 E (GEO coordinates). The depth at the sampling station was 52 metres.

The hydrographic conditions in the area are dominated by the large exchange of water between the Baltic Sea and the Kattegat. A northern current of relatively low salinity water of 8 to 9 is transported from the Baltic Sea to the Kattegat and flows over the more saline water in the Kattegat, resulting in a stratification of the water body. It was therefore possible to collect two samples of water of different salinities at the same position.

The sample collection was carried out on board the M/V Aphrodite, supplied by Marin ID, by Britta Pedersen and Gert Asmund of the Danish National Environmental Research Institute along with Alex Mykytiuk and Shier Berman of the Canadian National Research Council (NRC).

The collection equipment had been brought from the NRC laboratory in Ottawa and is the same used in the collection of sea water for NRC's Certified Reference Materials Project. The water was peristaltically pumped aboard the vessel using precleaned silicone tubing, simultaneously filtered through tandem 0.8 µm and 0.45 µm acrylic copolymer filters, and acidified with high purity nitric acid to pH 1.6. The water was delivered directly into sealed, precleaned 50-litre polypropylene carboys. The collected water was never exposed to the atmosphere.

Sample A was collected in the low salinity layer at about 5 m depth and has a salinity of 8, as expected for water from the Baltic Sea. Sample B was collected at about 15 m and has a salinity of 25, as expected for Kattegat water. Two hundred litres of each sample were collected.

The filled carboys were transported to the National Environmental Research Institute laboratories in Roskilde. Each sample was equilibrated overnight in a clean room at the Institute in a 200-litre precleaned polyethylene tank and then peristaltically pumped into precleaned 2-litre polyethylene bottles. One hundred bottles of each sample were prepared.

The total organic carbon (TOC) concentrations of the two samples were not measured, but other samples collected in the same month at the same location contained 4.3 mg $l^{-1}$ TOC in the surface layer and 2.8 mg $l^{-1}$ TOC in the deeper water. There is no reason to believe that the TOC contents of Samples A and B are significantly different from these values. Humic substances constitute a significant part of the organic matter in the Baltic Sea, presumably land derived. These compounds are not found to the same extent in the Kattegat.

# 3 Sample Distribution and the Receipt of Results

By the end of August 1996, fifty-five avowed participants, listed in Annex 1, were each sent a 2-litre bottle of Sample A and a 2-litre bottle of Sample B. They were asked to 'perform five replicate analyses (no more, no less)' for each of the ten elements mentioned above. They were warned that their data may not be used if fewer than five replicate values were submitted. 1 December 1996 was set as the deadline date for the receipt of results.

Participants were also informed that they would receive information from the Marine Laboratory in Aberdeen about one month before the deadline regarding sending in their data. This was done on schedule.

The data collector program was provided by the Marine Laboratory by e-mail, as a spreadsheet file, or by the provision of a diskette to each participating laboratory. All data received, including information regarding analytical methodologies used by the laboratories, were transferred electronically into the database and results received by the Aberdeen Laboratory were acknowledged, by fax or e-mail, within seven to ten days of receipt. Results received after the deadline date were included if received prior to the commencement of the data assessment.

The last results accepted into the database for the draft report were received during the third week of January 1997. However, two additional sets of data were received at about this same time and have been included in this final report.

A draft report was submitted to the meeting of the Marine Chemistry Working Group in Ostende (3–7 March 1997). Some suggestions were made regarding the presentation of the results, the discussion, and the conclusions. Many of these suggestions are incorporated into this final report with the result that there are many changes, including the accepted values for the analytes and the evaluation of the laboratories.

# 4 Results

Forty laboratories (71 percent) submitted data. However, there are 41 sets of data because one laboratory (Labs 4 and 5) provided two sets of values for some of the analytes. This caused some complication in evaluating the data from that laboratory, resulting in a possible distortion of its capabilities.

Because most of the data were submitted by the participants in electronic form, there was a minimum possibility of the Marine Laboratory erring in copying them into the database. This obviated much tedious work by the Marine Laboratory and the data assessor. A spreadsheet containing all the data and another containing the methodologies were produced. These were transmitted to the assessor at NRC.

While working with the data, some obvious typographical errors were discovered. The data assessor took the liberty to correct these, assuming that the prime purpose of the study was to intercompare the laboratories' analytical capabilities rather than their typographic abilities. The raw data, with the few corrections, are listed in Annex 2.

The database produced by the Marine Laboratory had been formatted to allow for three decimal places for the five expected replicate values. This is obviously in excess of that needed for many of the analytes, but we have retained this format in Annex 2. The values are listed as received with respect to significant figures. It is apparent that many of the respondents do not pay much attention to the concept of significant figures.

In spite of the warning mentioned above, many respondents submitted fewer than five replicate values for the analytes. In order to include as many laboratories as possible in the establishment of the accepted values, means, standard deviations and relative standard deviations were calculated wherever there were at least three replicates. This skews the statistics somewhat because the same weight is given to a mean of three replicates as to a mean of five replicates. These means could have been weighted relative to the number of replicates, but the evaluation was too far advanced before the assessor thought of doing this.

Annex 2 contains the results of the above calculations and a 'mean' of other quantitative values if there were fewer than three replicates and if there were also no 'less than' numbers included in the data. The number of replicate quantitative values is listed next to the laboratory number.

Most analytical procedures for trace metals in sea water require a separation of the analyte from the saline matrix. The procedures used by the respondents and the instrumentation used to measure the trace metal concentrations are summarized in Annex 3. A 'Y' in the 'Evaluated' column indicates that the laboratory's results were used in the procedure to establish the accepted trace metal concentration and the associated confidence interval. An '*' beside the laboratory number indicates that the laboratory's mean was rejected as an outlier in this procedure. A number of abbreviations used in this report are listed on the title page of Annex 3.

It was necessary to arrive at an accepted value for each analyte concentration for each unknown sample in order to evaluate laboratory biases. The overall mean concentration for each metal was calculated from the mean of laboratory replicates. These means were assumed to be normally distributed, which may not be a valid assumption at very low concentrations, but for the purpose of this exercise it is felt to be adequate. A successively applied Student *t* test (Miller and Miller, 1988) at the 95 percent confidence level was used to identify outliers and establish accepted values and confidence intervals for each analyte in each sample. See Annex 7 for a rationale and further description of this approach.

The data are plotted on the graphs on the even-numbered pages (4 to 22) where possible, depending on the scaling. Means that were outliers from the accepted concentration are indicated by an asterisk following the laboratory number (e.g., 5*). If a laboratory did not submit quantitative data or submitted fewer than three replicate values, the data were not used in the calculation of the accepted value and the 95 percent confidence interval. These laboratory numbers do not appear on the graphs.

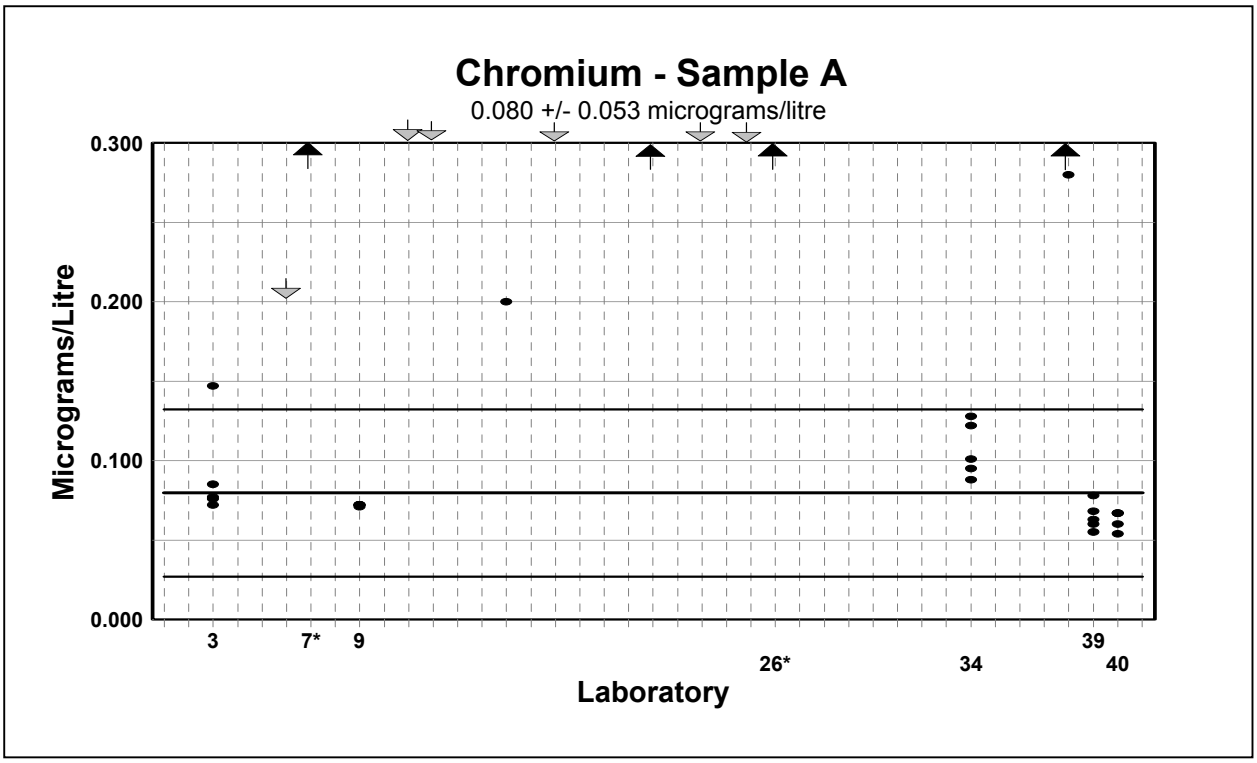
'Less than' values are indicated by a downward grey arrow whose point is at the 'less than' concentration. If that concentration is equal to or higher than the upper limit of the graph, the arrow is at the top boundary of the graph. Some high results that if plotted would distort the clarity of the graph are indicated by an upward black arrow. A thick horizontal line represents the accepted value for a sample analyte. The thinner horizontal lines above and below the accepted value enclose the estimated 95 percent confidence intervals for these values. A short summary of results for each analyte is listed on the page opposite the appropriate graph. All concentrations are expressed in micrograms per litre. The accepted value and the 95 percent confidence interval are shown at the top of each graph.

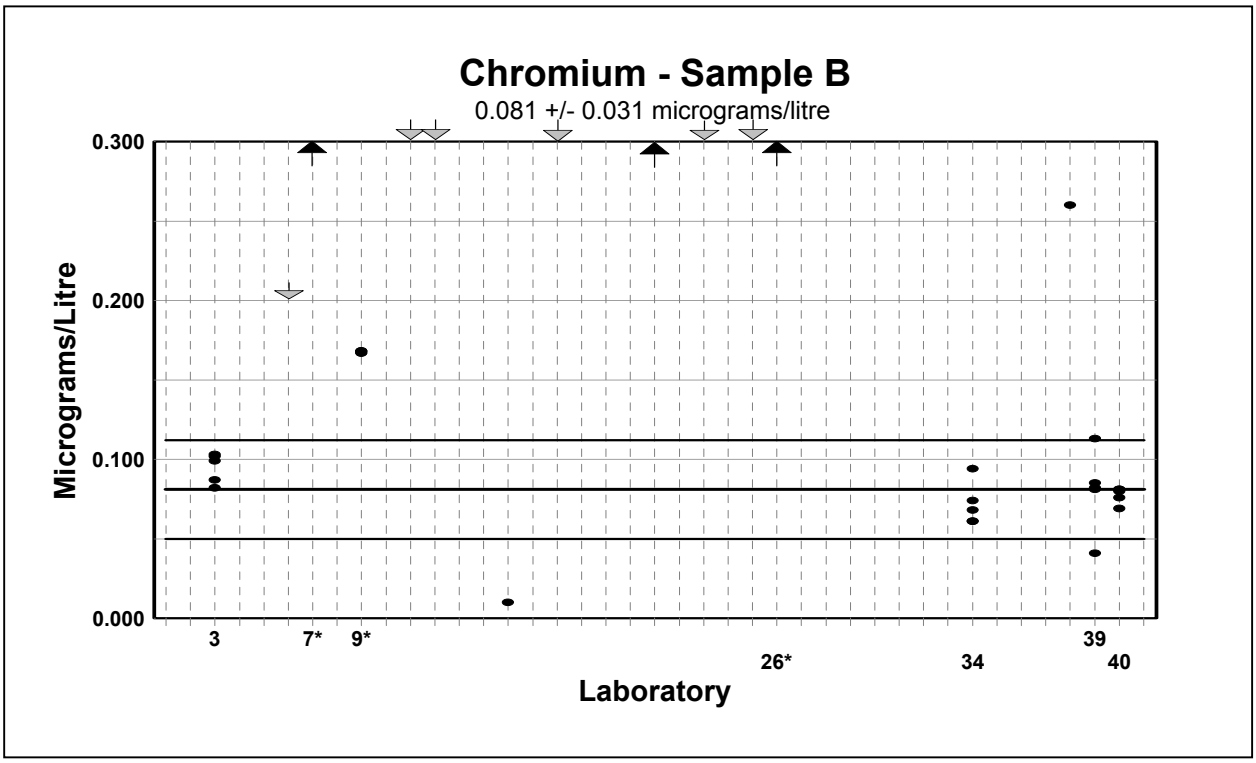
Youden (or two sample) plots (Youden, 1969) have also been included for the two samples. These plots of the laboratory mean for Sample B versus its mean for Sample A can give useful information when the analyte concentrations of the two samples are close to one another. This is the case for almost all of the analytes in this exercise. The laboratory must, of course, have submitted quantitative results for both samples for its values to appear in this plot. Some high data have not been plotted. These are all in the upper right quadrant and are noted on the right of the graph.

If non-systematic or random errors are occurring, the results would be expected to group at random about the intersection of the two accepted values within and out of the 95 percent confidence interval. If, however, systematic errors occur (e.g., a high or low result for both samples), a predominance of points would be expected to group about a line running from the origin through the intersection of the two accepted values with a preponderance of points within the confidence interval and the lower left and upper right quadrants. The latter case is common in intercomparison exercises due to calibration, contamination, blank and arithmetic errors.

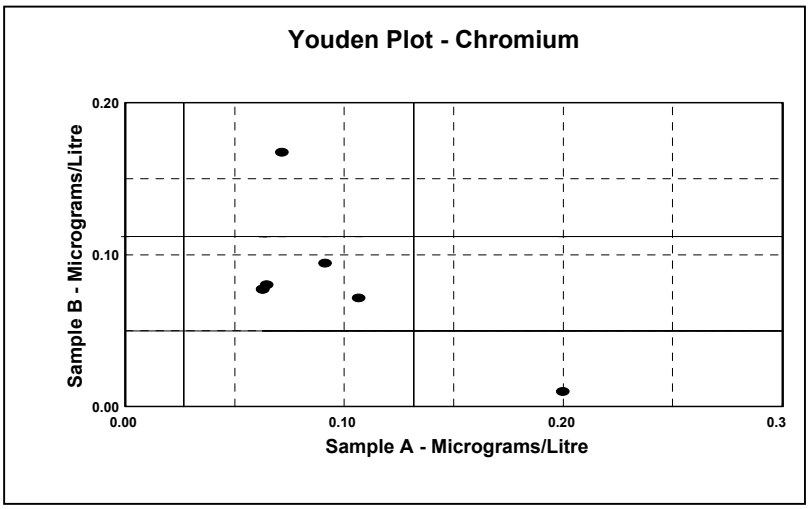
The accepted confidence intervals are indicated by the solid lines.

A brief description of the results for each analyte follows on the next twenty pages.


Chromium - Sample A
0.080 +/- 0.053 micrograms/litre
Micrograms/Litre
0.300
0.200
0.100
0.000
3
7*
9
26*
34
39
40
Laboratory


Chromium - Sample B
0.081 +/- 0.031 micrograms/litre
Micrograms/Litre
0.300
0.200
0.100
0.000
3
7*
9*
26*
34
39
40
Laboratory

Data off scale
Labs 7, 26




| **Chromium** | **Sample A** | **Sample B** |
|---|---|---|
| Results received: | 16 | 16 |
| More than 2 quantitative results: | 7 | 7 |
| Rejected means: | 2 | 3 |
| Accepted value: | 0.080 ± 0.053 | 0.081 ± 0.031 micrograms/litre |

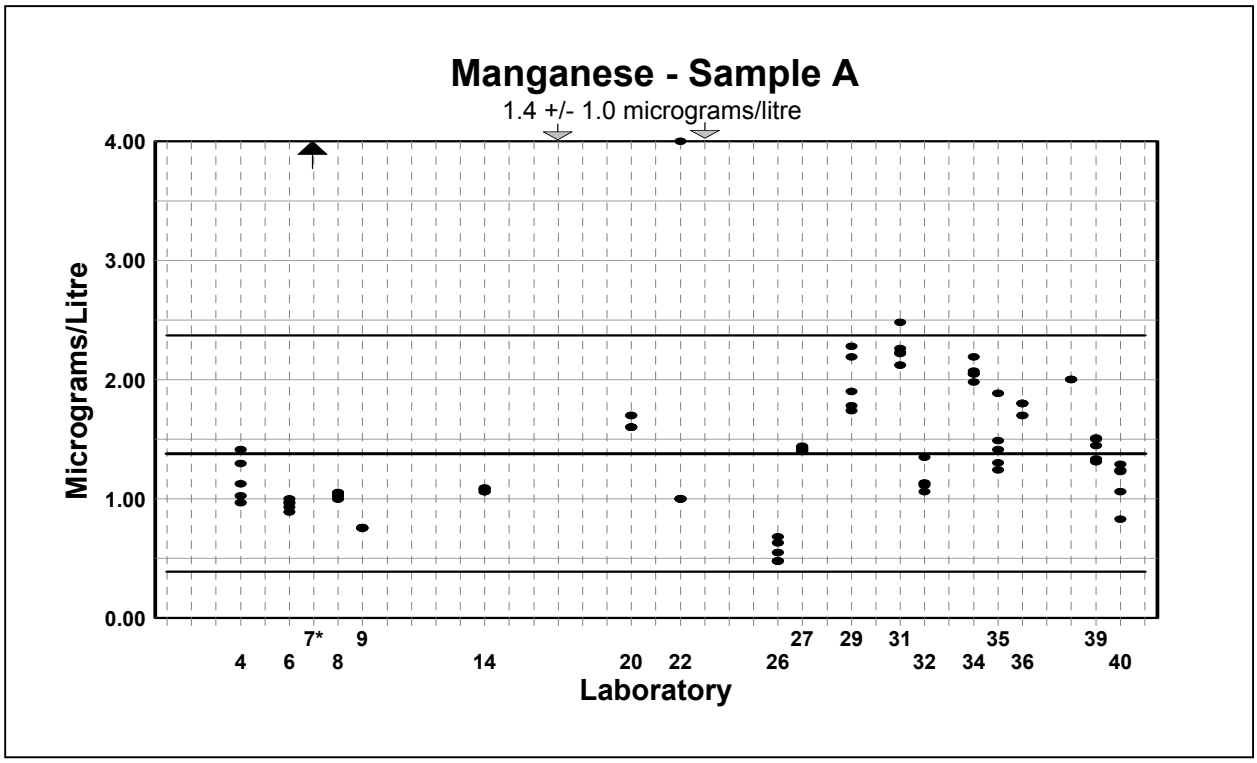
Fewer than twenty percent of the participants produced more than two quantitative results for each sample. More than one-third of the evaluated means were rejected, all high. The accepted values are based on only five and four sets of data, respectively, for the two samples, the least amount of quantitative data in this study.

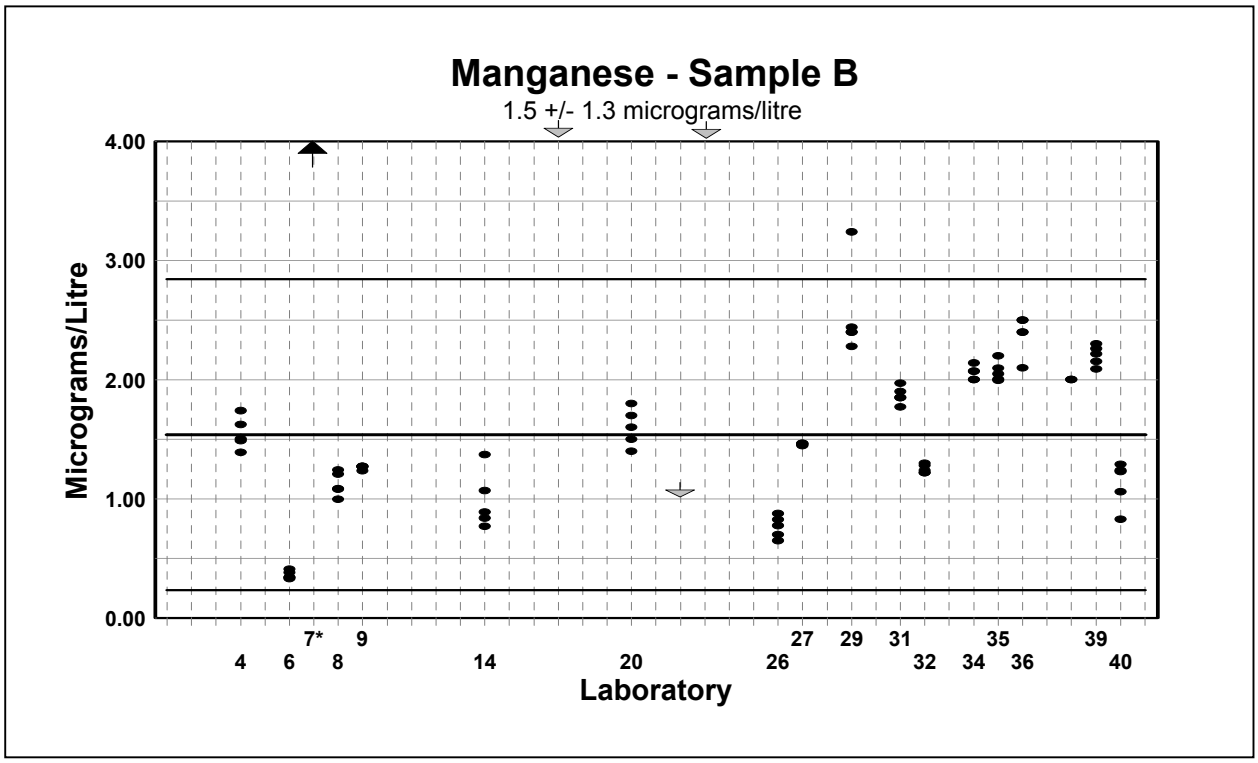
All the accepted sets involved the separation of the chromium from the seawater matrix, usually by a solvent extraction procedure (Labs 3, 34 and probably 9 and 39). One of the laboratories, Lab 34, used a chromatographic separation and another, Lab 40, separated the chromium by precipitation.

All measured the analyte using GFAAS with background correction, except for Lab 40 which used ICPMS.

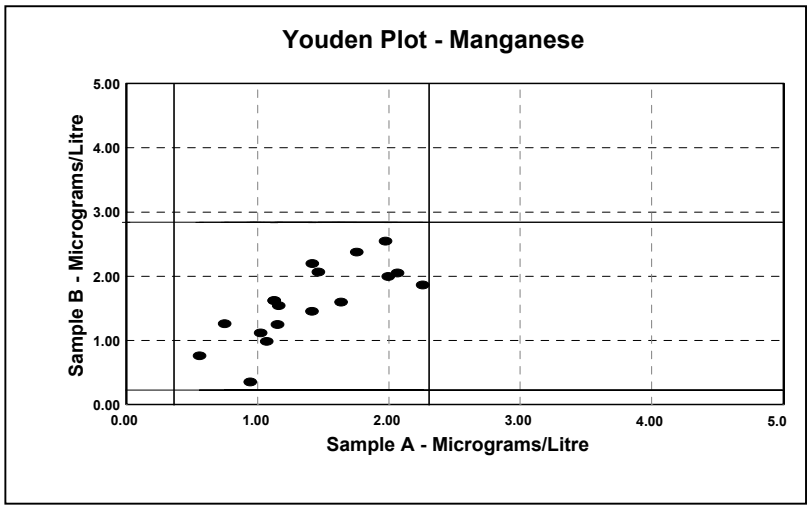
There are insufficient data in the above Youden plot to draw satisfactory conclusions, but systematic errors probably predominate. Two laboratories, Labs 9 and 15, clearly show random errors. The general problems are probably due to contamination, inadequate blank correction, calibration or arithmetic (Lab 9's data for Sample B are exactly twice the accepted value).

The determination of chromium in sea water has a history of causing difficulties, usually due to inefficient extraction procedures. However, the lack of low results in this study obviates this general conclusion.


Manganese - Sample A
1.4 +/- 1.0 micrograms/litre
Micrograms/Litre
4.00
3.00
2.00
1.00
0.00
4 6 7* 8 9 14 20 22 26 27 29 31 32 34 35 36 39 40
Laboratory


Manganese - Sample B
1.5 +/- 1.3 micrograms/litre
Micrograms/Litre
4.00
3.00
2.00
1.00
0.00
4 6 7* 8 9 14 20 26 27 29 31 32 34 35 36 39 40
Laboratory

Data off scale
Lab 7




| **Manganese** | **Sample A** | **Sample B** |
|---|---|---|
| Results received: | 21 | 21 |
| More than 2 quantitative results: | 18 | 17 |
| Rejected means: | 1 | 1 |
| Accepted value: | 1.4 ± 1.0 | 1.5 ± 1.3 micrograms/litre |

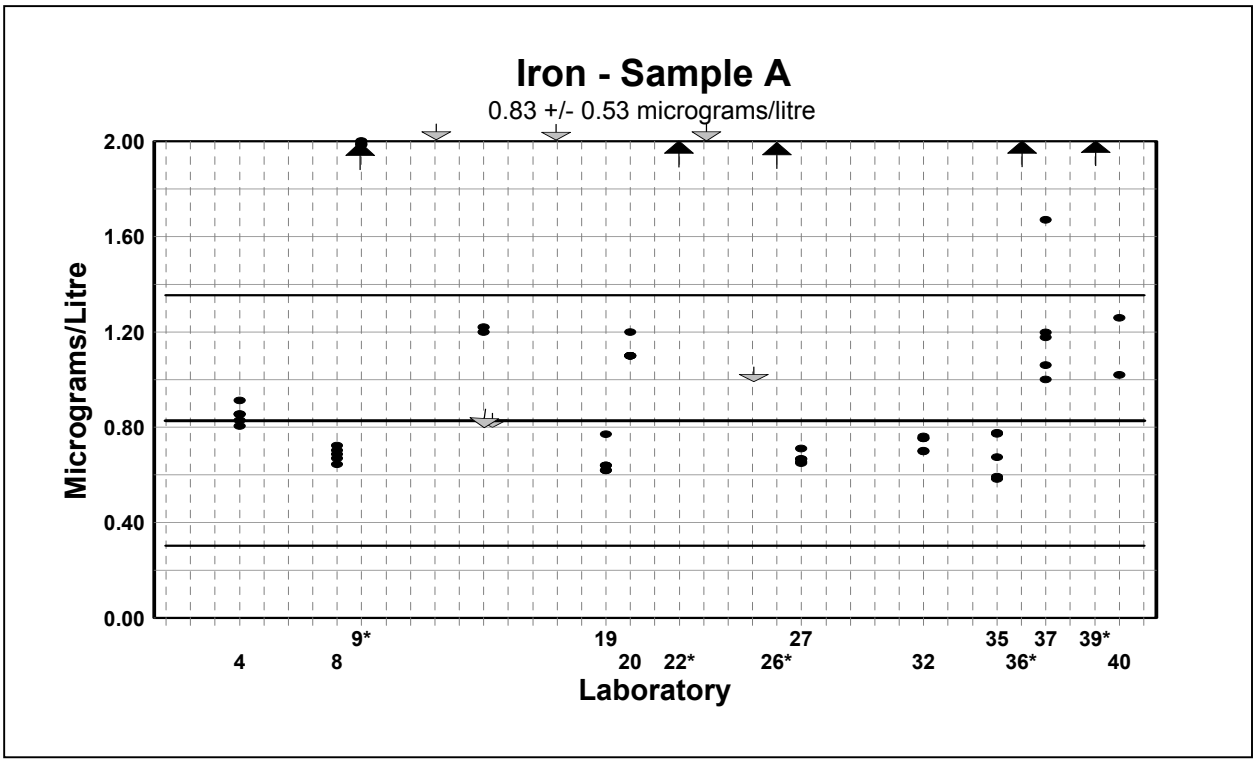
About forty-five percent of the participants produced more than two quantitative results for each sample. Only one mean of those evaluated was rejected for each sample (Lab 7), high in both cases. The accepted values are based on the means of 18 and 17 sets of data, respectively, for the two samples. The 95 percent confidence intervals are large, 71 % and 87 %, respectively, considering the concentrations of manganese.

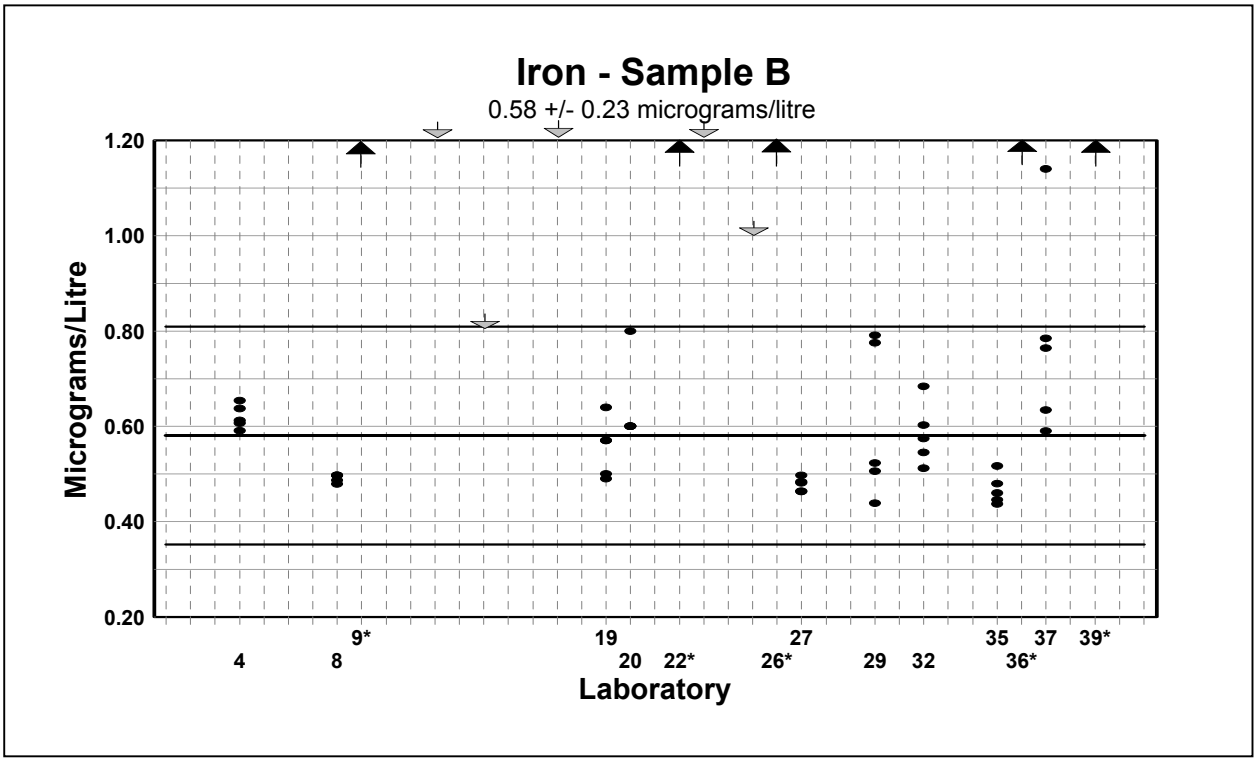
We do not have descriptions of sample preparation procedures from Laboratories 6, 7, 8, 9, 31 and 39, but it is probably safe to assume that all the accepted sets involved the separation of the manganese from the seawater matrix. Most laboratories used a solvent extraction procedure (Labs 4, 14, 20, 22, 26, 27, 29, 32, and 36). Two used a chromatographic separation (Labs 34 and 35) and Lab 40 employed a precipitation method.

Eleven laboratories used GFAAS with some form of background correction to measure the manganese. Some used a matrix modifier, others did not. Five laboratories used ICPAES and two employed ICPMS. One laboratory (Lab 35) used total reflection X-ray fluorescence (TXRF). There are no apparent significant differences which can be attributed to methodologies.

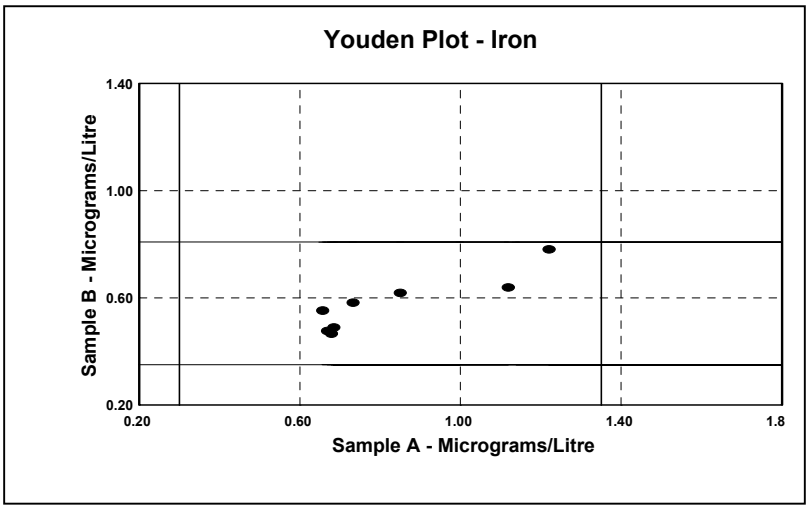
The Youden plot indicates a preponderance of systematic errors. The lack of good interlaboratory variance is probably due to inadequate blank correction and/or calibration errors. (Lab 7's results are five times the accepted mean.)

The determination of manganese in sea water has generally not caused great difficulties, partially due to the relatively high metal concentrations. The relatively large confidence intervals in this study are disappointing.


Iron - Sample A
0.83 +/- 0.53 micrograms/litre
Micrograms/Litre
2.00
1.60
1.20
0.80
0.40
0.00
4
9*
8
19
20
22*
27
26*
32
35
36*
37
39*
40
Laboratory


Iron - Sample B
0.58 +/- 0.23 micrograms/litre
Micrograms/Litre
1.20
1.00
0.80
0.60
0.40
0.20
4
9*
8
19
20
22*
27
26*
29
32
35
36*
37
39*
Laboratory

Data off scale
Labs 9, 22, 26, 36, 39




| **Iron** | **Sample A** | **Sample B** |
|---|---|---|
| Results received: | 19 | 19 |
| More than 2 quantitative results: | 13 | 14 |
| Rejected means: | 5 | 5 |
| Accepted value: | 0.83 ± 0.53 | 0.58 ± 0.23 micrograms/litre |

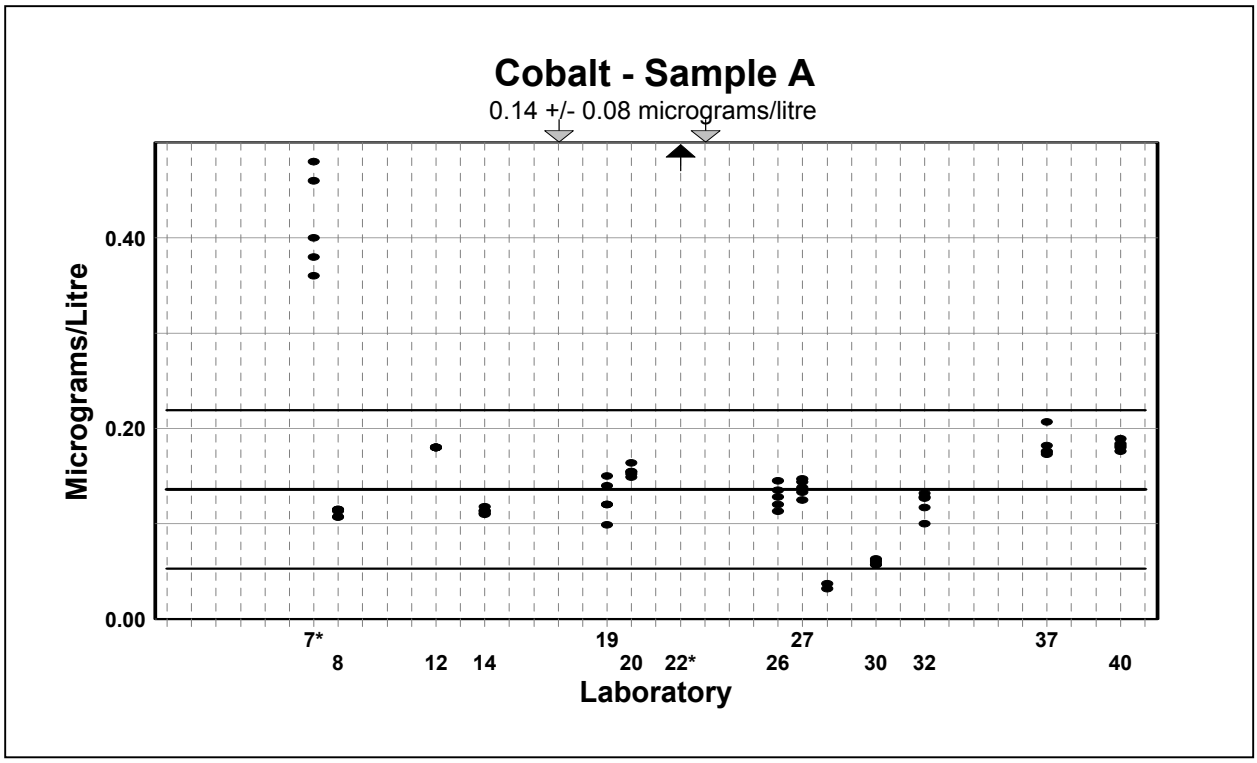
About one-third of the participants produced more than two quantitative results for each sample. Five of the evaluated means were rejected for each sample (Labs 9, 22, 26, 36 and 39), with high results in all cases. The accepted values are based on the means of eight and nine sets of data, respectively, for the two samples. The 95 percent confidence intervals are 64 % and 39 %, respectively.

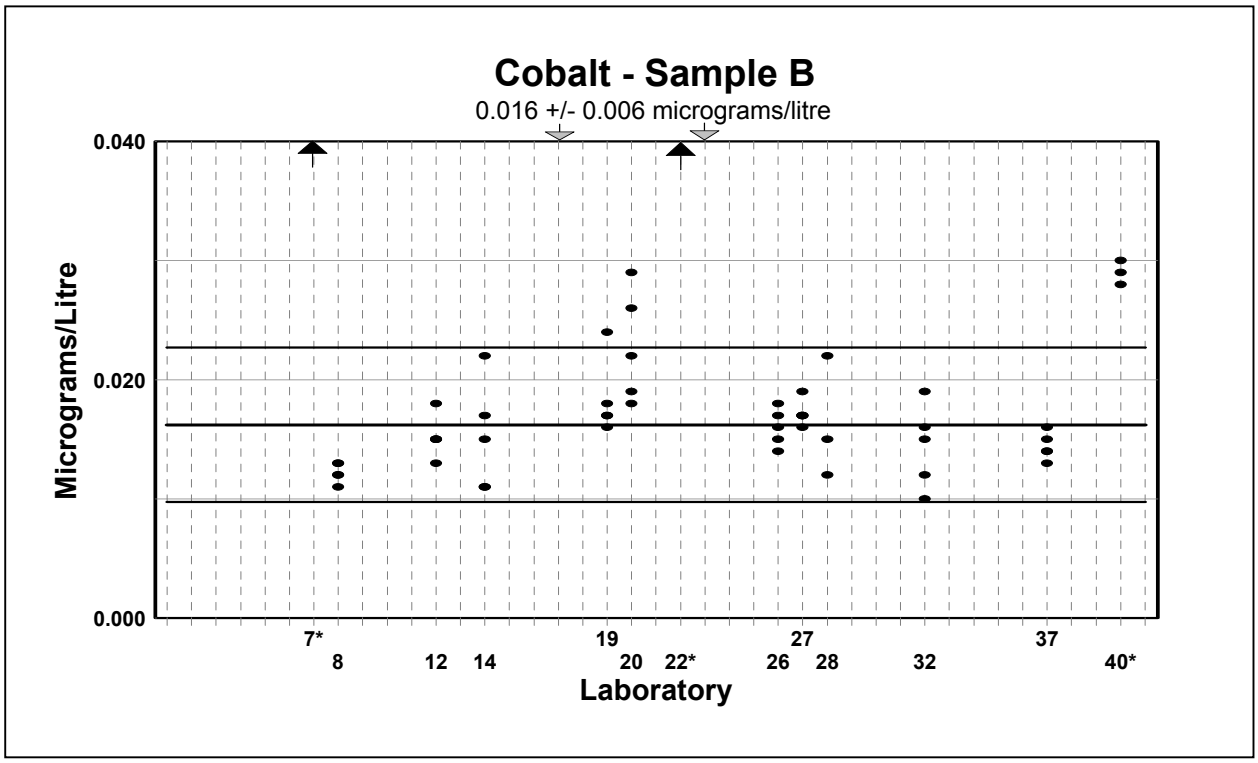
We do not have descriptions of sample preparation procedures from Laboratories 9 and 39. All the accepted sets involved the separation of the iron from the seawater matrix either by solvent extraction (Labs 4, 8, 19, 20, 27, 32 and 37) or chromatography (Lab 35).

Five of the accepted laboratories used GFAAS with some form of background correction to measure the iron. One used a matrix modifier, four did not. One laboratory employed ICPMS, one laboratory used TXRF, and one used ASV. The results of only one of the three laboratories that used ICPAES were accepted. There are no apparent significant differences which can be attributed to methodologies.

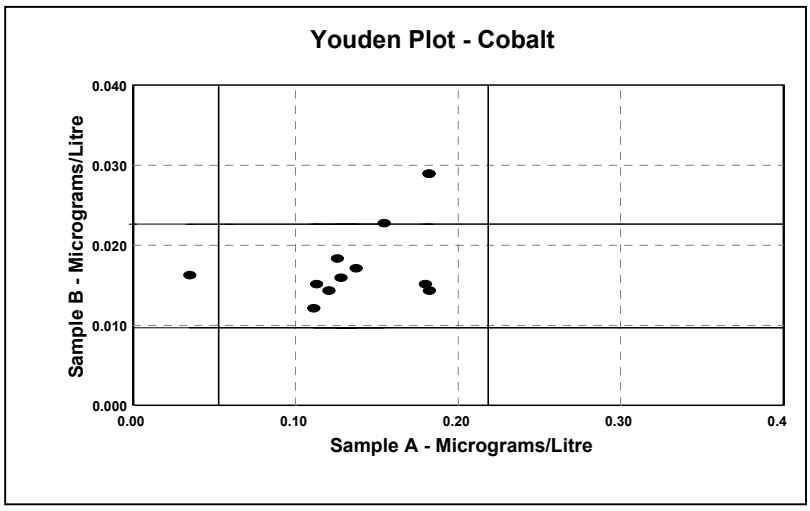
The Youden plot indicates a preponderance of systematic errors. The results of the five rejected laboratories are in the upper right quadrant but are not shown due to the chosen scale. The problems are probably due to contamination, inadequate blank correction and/or calibration errors.

Historically, the determination of iron in sea water has generally not caused great difficulties, partially due to the relatively high metal concentrations, especially in coastal and estuarine waters.


Cobalt - Sample A
0.14 +/- 0.08 micrograms/litre
Micrograms/Litre
0.00
0.20
0.40
7*
8
12
14
19
20
22*
26
27
30
32
37
40
Laboratory


Cobalt - Sample B
0.016 +/- 0.006 micrograms/litre
Micrograms/Litre
0.000
0.020
0.040
7*
8
12
14
19
20
22*
26
27
28
32
37
40*
Laboratory

Data off scale
Labs 7, 22




| **Cobalt** | **Sample A** | **Sample B** |
|---|---|---|
| Results received: | 16 | 15 |
| More than 2 quantitative results: | 13 | 13 |
| Rejected means: | 2 | 3 |
| Accepted value: | $0.14 \pm 0.08$ | $0.016 \pm 0.006$ micrograms/litre |

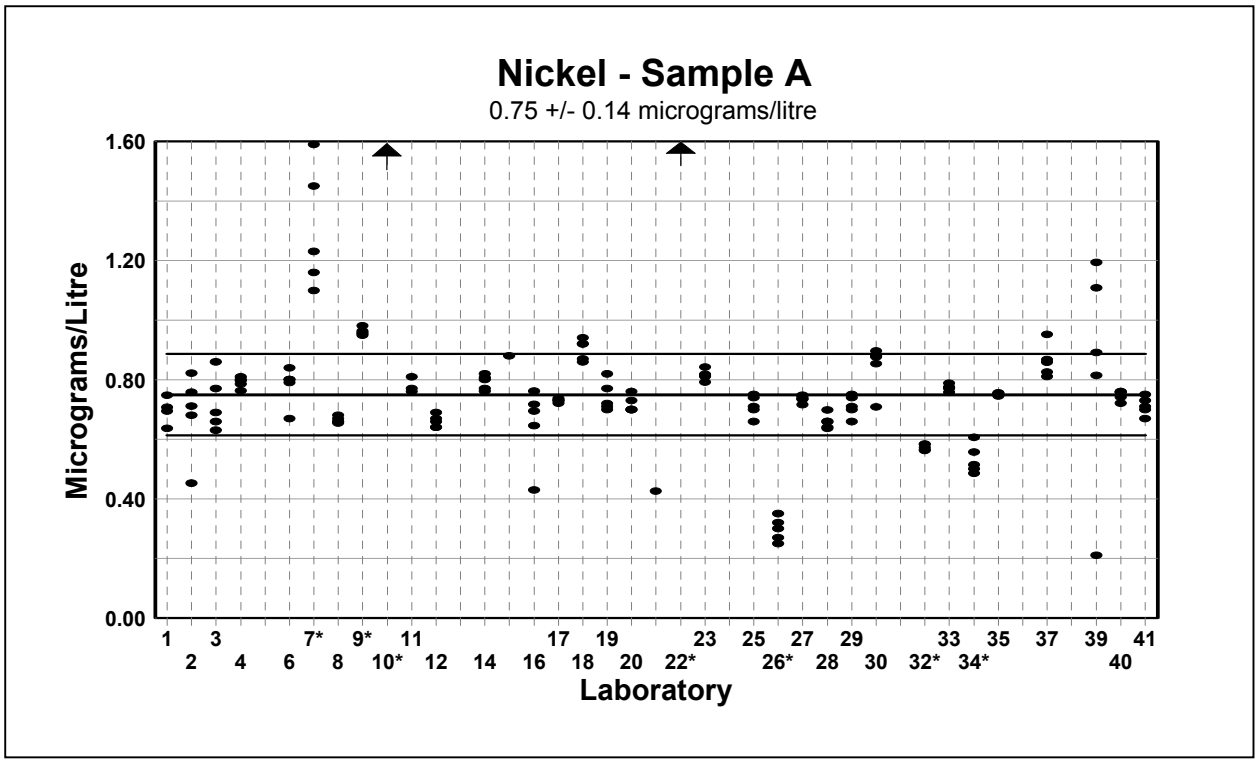
About one-third of the participants produced more than two quantitative results for each sample. Two and three means were rejected for each sample, respectively (Labs 7 and 22, and Labs 7, 22 and 40), with high results in all cases. The accepted values are based on the means of eleven and ten sets of data, respectively, for the two samples. The 95 percent confidence intervals are 57 % and 38 %, respectively.

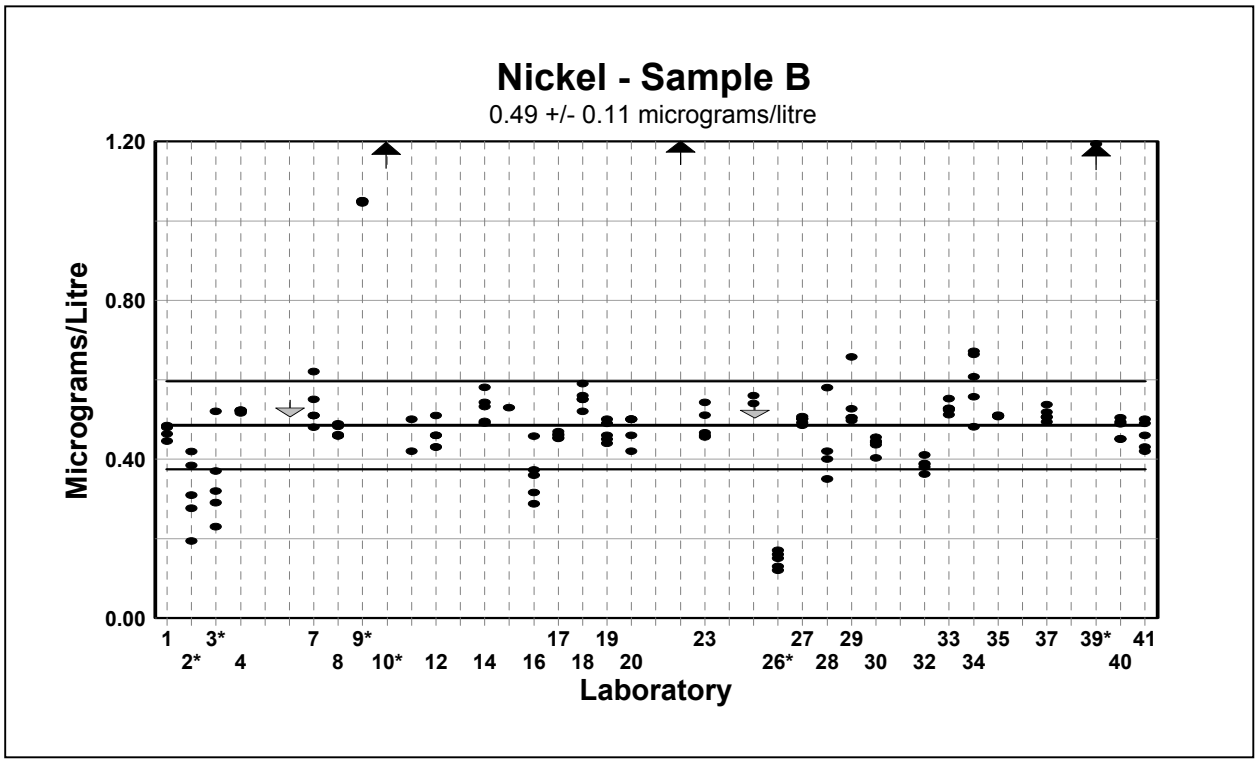
We do not have a description of the sample preparation procedure for Lab 7. All the accepted sets involved the separation of the cobalt from the seawater matrix either by solvent extraction (Labs 8, 12, 14, 19, 20, 26, 27, 30, 32 and 37) or precipitation (Lab 40).

Six of the accepted laboratories used GFAAS with some form of background correction to measure the cobalt. Two used a matrix modifier, four did not. Three laboratories employed ICPMS, one used ICPAES, and another used electrochemical determination. There are no apparent significant differences which can be attributed to methodologies.

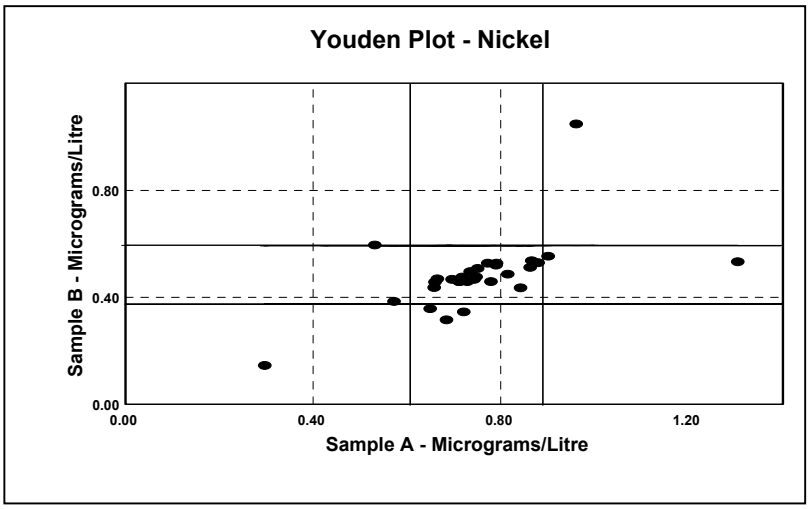
The Youden plot indicates a tendency towards systematic errors, but there are obvious random errors. The results of rejected laboratories are in the upper right quadrant but are not shown due to the chosen scale. The problems are probably due to inadequate blank correction and/or calibration errors.

The determination of cobalt in sea water has generally not caused great difficulties in spite of its relatively low concentration, especially in high salinity waters.


Nickel - Sample A
0.75 +/- 0.14 micrograms/litre
Micrograms/Litre
1.60
1.20
0.80
0.40
0.00
1 3 7* 9* 11 17 19 23 25 27 29 33 35 37 39 41
2 4 6 8 10* 12 14 16 18 20 22* 26* 28 30 32* 34* 40
Laboratory


Nickel - Sample B
0.49 +/- 0.11 micrograms/litre
Micrograms/Litre
1.20
0.80
0.40
0.00
1 3* 7 9* 17 19 23 27 29 33 35 37 39* 41
2* 4 8 10* 12 14 16 18 20 26* 28 30 32 34 40
Laboratory

Data off scale
Labs 10, 22




| **Nickel** | **Sample A** | **Sample B** |
|---|---|---|
| Results received: | 35 | 34 |
| More than 2 quantitative results: | 33 | 29 |
| Rejected means: | 7 | 6 |
| Accepted value: | $0.75 \pm 0.14$ | $0.49 \pm 0.11$ micrograms/litre |

Eighty-three % and 73 % of the laboratories, respectively, produced more than two quantitative results for each sample. Seven means were rejected for Sample A (Labs 7, 9, 10, 22, 26, 32 and 34) and six means for Sample B (Labs 2, 3, 9, 10, 26 and 39). There were a total of eight high results and four low results rejected. The accepted values are based on the means of 26 and 23 sets of data, respectively, for the two samples. The 95 percent confidence intervals are 18 % and 23 %, respectively.

We do not have descriptions of sample preparation procedures for Labs 7, 9, 10, 17, 28 and 39, but we assume that in all probability they used a solvent extraction or a chromatographic technique to separate the nickel from the sea water. Fifty percent of the means from these laboratories were not accepted. The accepted sets for which we know the techniques involved the separation of the nickel from the matrix either by solvent extraction, chromatography or precipitation.

Eleven of the accepted laboratories used GFAAS with some form of background correction to measure the nickel. Some used a matrix modifier, others did not. Five laboratories employed ICPMS. Two of the three laboratories that used ICPAES had problems, as did two of the four laboratories which used electrochemical determinations. One laboratory employed TXRF and another FAAS.

The Youden plot indicates a predominance of systematic errors. Usually the same laboratories have results rejected for both samples, but this was the case for only two of ten laboratories for nickel. Two sets of rejected results are in the upper right quadrant, but are not shown due to the chosen scale. The problems are probably due to contamination, inadequate blank correction and/or calibration errors.

The determination of nickel in sea water has generally not caused great difficulties. This is confirmed here by the relatively large number of respondents and the small confidence intervals.

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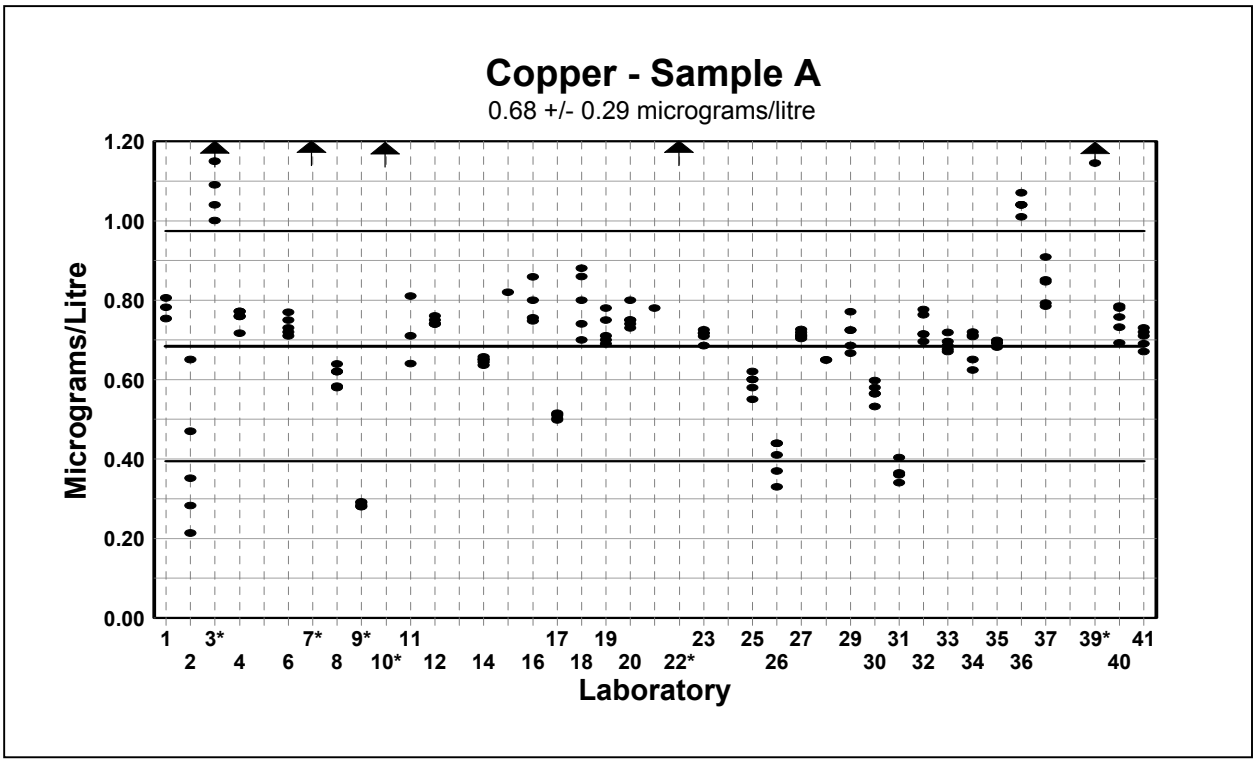
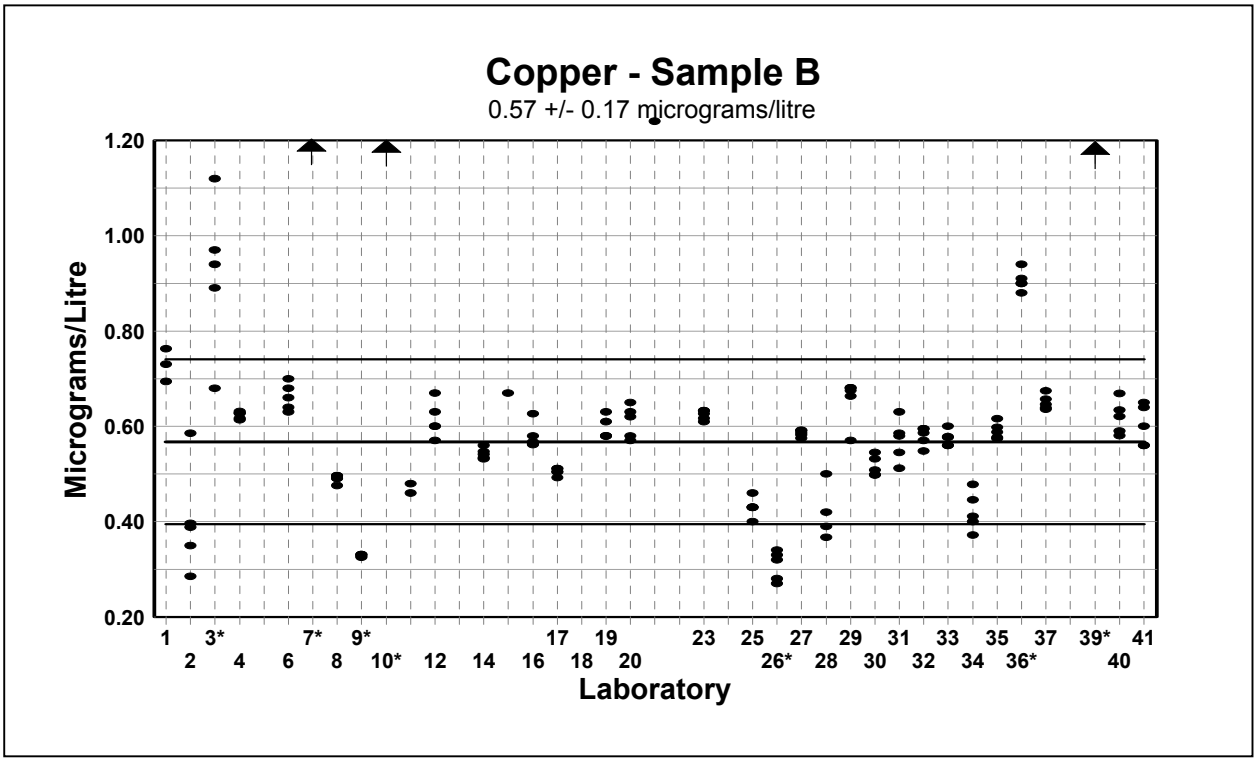
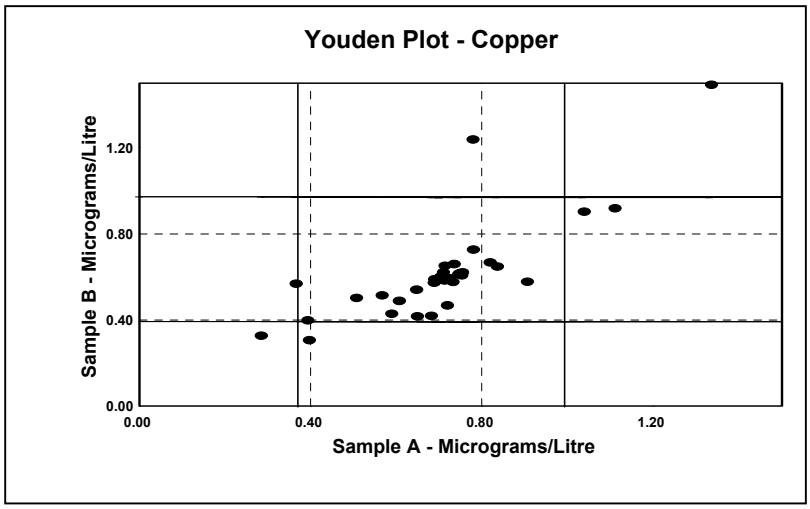

Copper - Sample A
0.68 +/- 0.29 micrograms/litre
Micrograms/Litre
1.20
1.00
0.80
0.60
0.40
0.20
0.00
1 2 3* 4 6 7* 8 9* 10* 11 12 14 16 17 18 19 20 22* 23 25 26 27 29 30 31 32 33 34 35 36 37 39* 40 41
Laboratory


Copper - Sample B
0.57 +/- 0.17 micrograms/litre
Micrograms/Litre
1.20
1.00
0.80
0.60
0.40
0.20
1 2 3* 4 6 7* 8 9* 10* 12 14 16 17 18 19 20 23 25 26* 27 28 29 30 31 32 33 34 35 36* 37 39* 40 41
Laboratory

Data off scale
Labs 7, 10




| **Copper** | **Sample A** | **Sample B** |
|---|---|---|
| Results received: | 37 | 37 |
| More than 2 quantitative results: | 34 | 32 |
| Rejected means: | 6 | 7 |
| Accepted value: | 0.68 ± 0.29 | 0.57 ± 0.17 micrograms/litre |

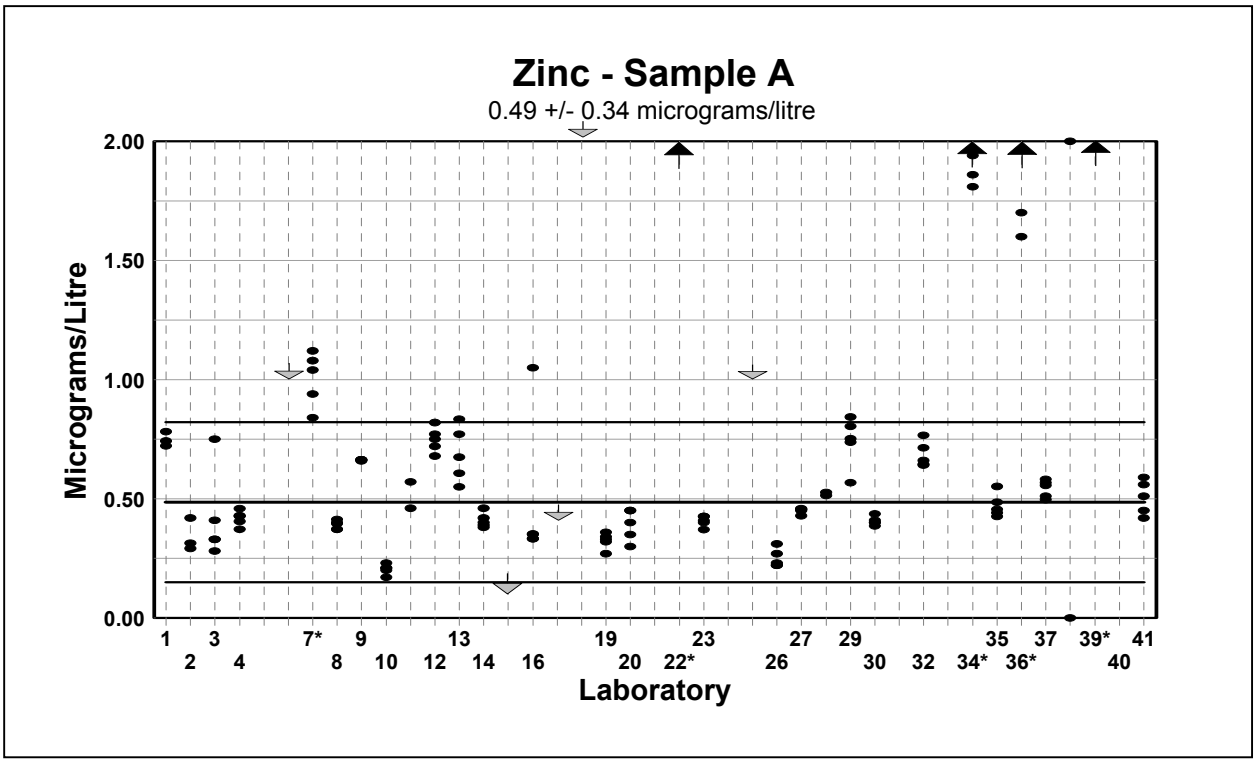
Eighty-five % and 80 % of the laboratories, respectively, produced more than two quantitative results for each sample. Six means were rejected for Sample A (Labs 3, 7, 9, 10, 22 and 39) and seven means for Sample B (Labs 3, 7, 9, 10, 26, 36 and 39). Ten of the thirteen results rejected were high. The accepted values are based on the means of 28 and 25 sets of data, respectively, for the two samples. The 95 percent confidence intervals are 42 % and 30 %, respectively.

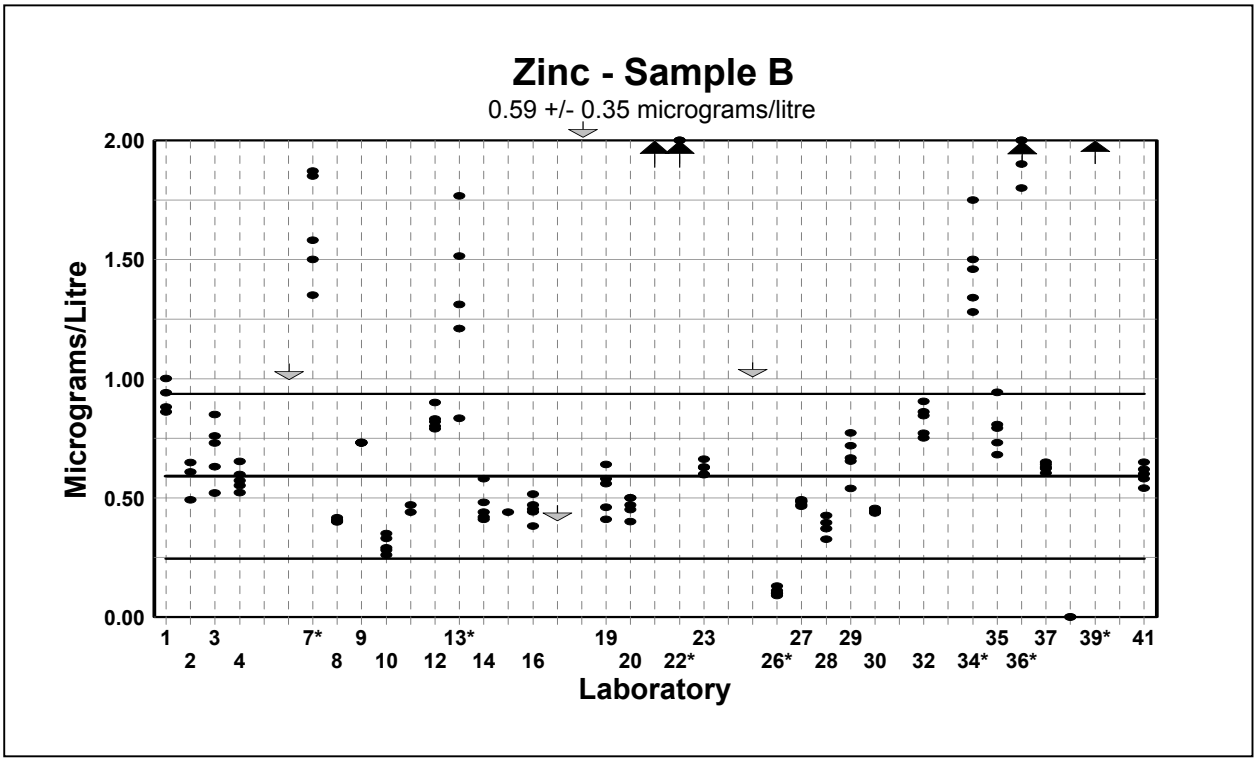
We do not have descriptions of sample preparation procedures for Labs 7, 9, 10, 17, 28 and 39, but we assume that in all probability they used a solvent extraction or a chromatographic technique to separate the copper from the matrix. About 60 percent of the means from these laboratories were not accepted. The accepted sets for which we are sure of the techniques involved the separation of the nickel from the matrix either by solvent extraction, chromatography or precipitation.

Twelve of the accepted laboratories used GFAAS with some form of background correction to measure the copper. Some used a matrix modifier, others did not. Six laboratories used an electrochemical determination. Five laboratories employed ICPMS. Two of the three laboratories that used ICPAES had problems. One laboratory employed TXRF and another FAAS.

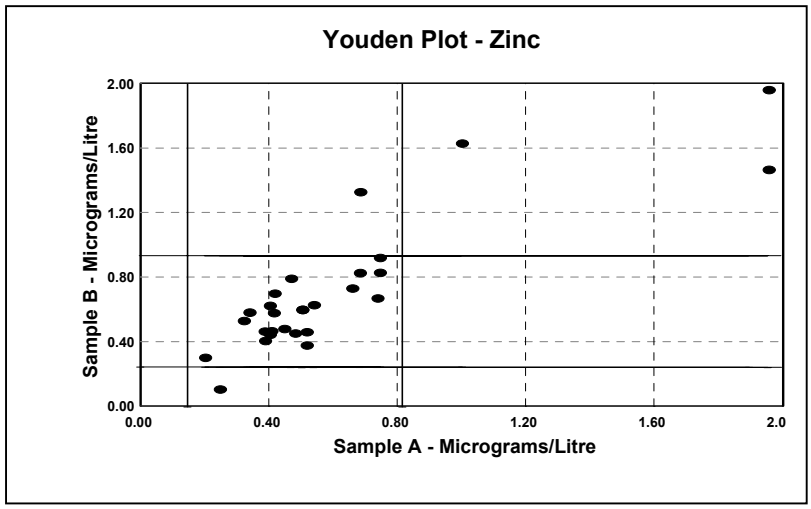
The Youden plot indicates a preponderance of systematic errors. Two sets of rejected results are in the upper right quadrant, but are not shown due to the chosen scale. The problems are probably due to contamination, inadequate blank correction and/or calibration errors.

The determination of copper in sea water has generally not caused great difficulties, as is demonstrated by the relatively large number of respondents and the small confidence intervals.


Zinc - Sample A
0.49 +/- 0.34 micrograms/litre
Micrograms/Litre
2.00
1.50
1.00
0.50
0.00
1 2 3 4 7* 8 9 10 13 12 14 16 19 20 23 22* 27 26 29 30 35 32 37 34* 39* 36* 41 40
Laboratory


Zinc - Sample B
0.59 +/- 0.35 micrograms/litre
Micrograms/Litre
2.00
1.50
1.00
0.50
0.00
1 2 3 4 7* 8 9 10 13* 12 14 16 19 20 23 22* 27 26* 29 28 30 35 32 37 34* 39* 36* 41
Laboratory

Data off scale
Labs 22, 39




| **Zinc** | **Sample A** | **Sample B** |
|---|---|---|
| Results received: | 35 | 35 |
| More than 2 quantitative results: | 27 | 28 |
| Rejected means: | 5 | 7 |
| Accepted value: | $0.49 \pm 0.34$ | $0.59 \pm 0.35$ micrograms/litre |

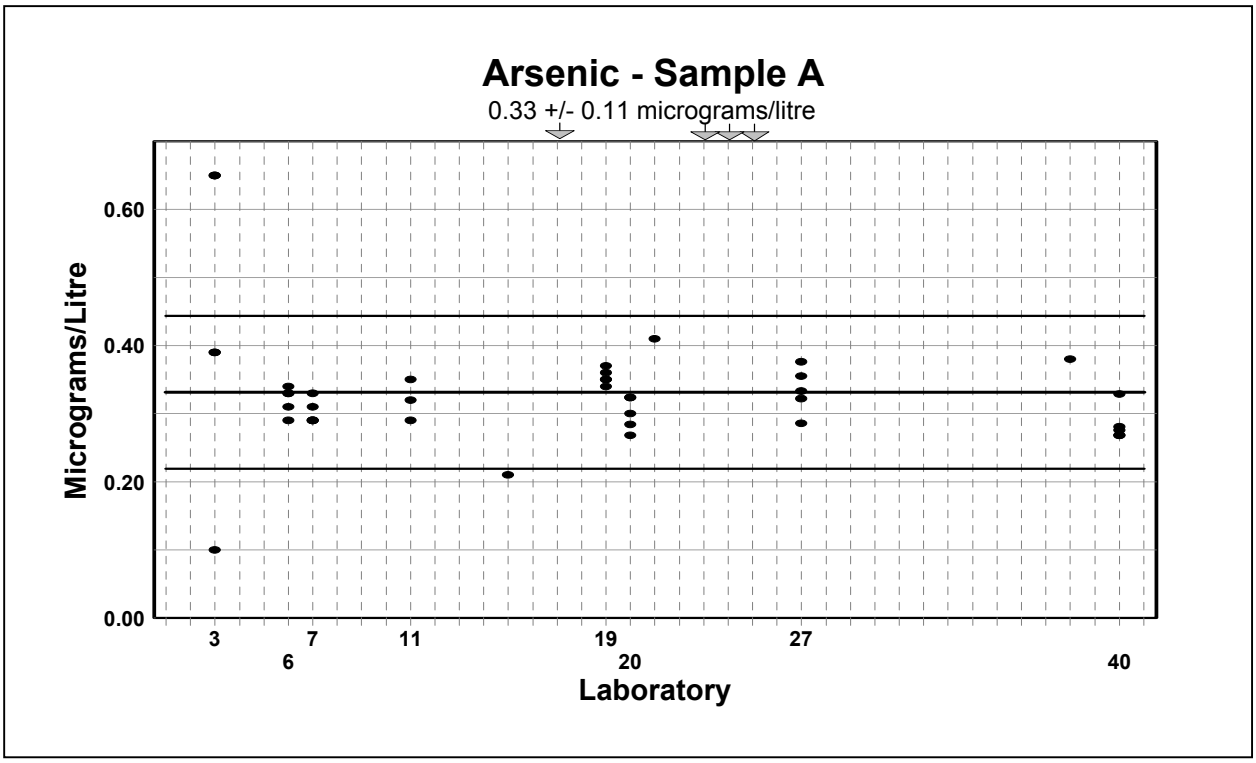
Sixty-five percent of the laboratories produced more than two quantitative results for each sample. Five means were rejected for Sample A (Labs 7, 22, 34, 36 and 39) and seven means for Sample B (Labs 7, 13, 22, 26, 34, 36 and 39). All but one of the thirteen results rejected were high. The accepted values are based on the means of 22 and 21 sets of data, respectively, for the two samples. The 95 percent confidence intervals are 69 % and 59 %, respectively.

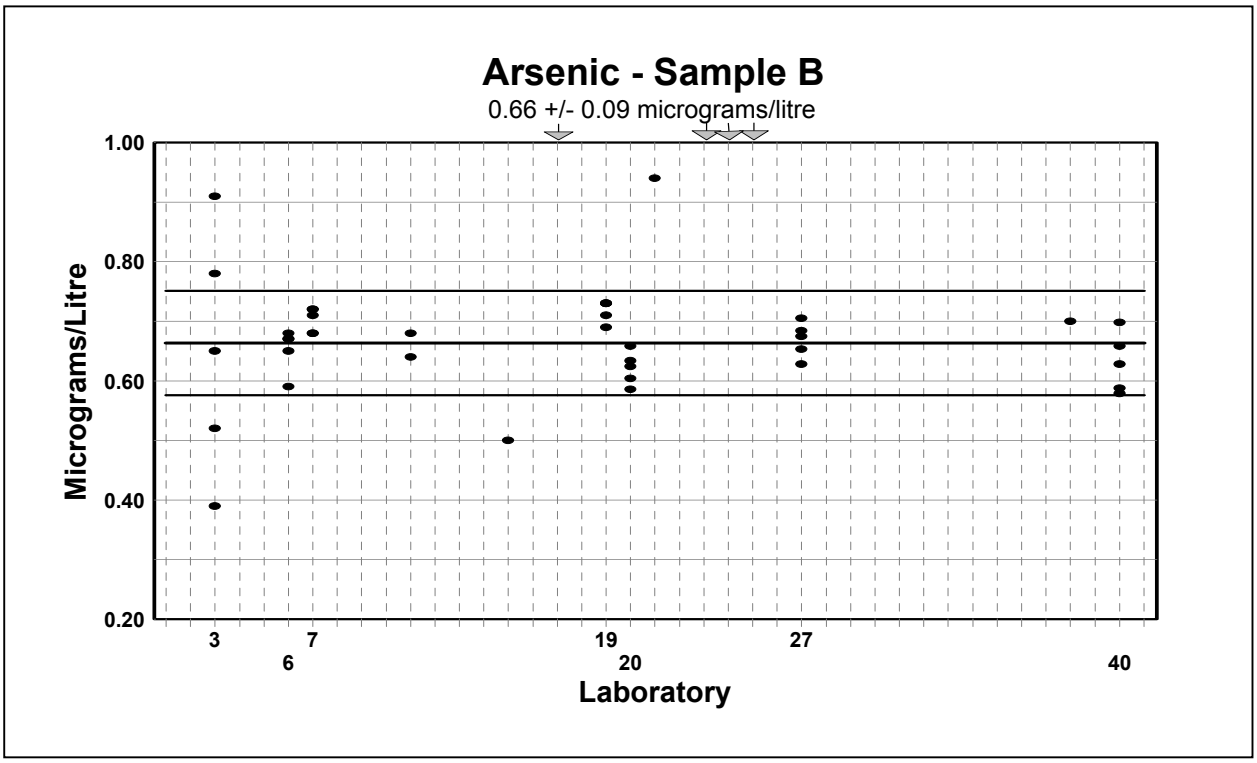
We do not have descriptions of sample preparation procedures for Labs 7, 9, 10, 28 and 39, but we assume that in all probability they used a solvent extraction or a chromatographic technique to separate the zinc from the matrix. About 67 percent of the means from these laboratories were not accepted. The accepted sets for which we are sure of the techniques involved the separation of the zinc from the matrix either by solvent extraction, chromatography or precipitation.

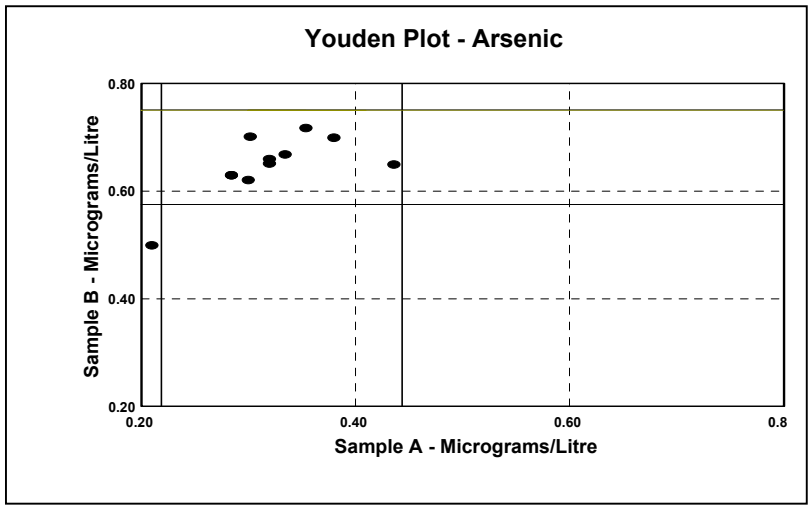
Ten of the accepted laboratories used GFAAS with some form of background correction to measure the zinc. Some used a matrix modifier, others did not. Two of the five laboratories that used an electrochemical determination were successful. Four laboratories employed ICPMS. Two of the three laboratories that used ICPAES had problems. One laboratory employed TXRF and four used FAAS.

The Youden plot indicates a preponderance of systematic errors. The problems are probably due to contamination, inadequate blank correction and/or calibration errors, and even poor arithmetic.

The determination of zinc in sea water has generally not caused great difficulties. Instrument sensitivities are high, but the techniques are prone to contamination and blank problems due to the ubiquitous nature of zinc.


Arsenic - Sample A
0.33 +/- 0.11 micrograms/litre
Micrograms/Litre
0.00
0.20
0.40
0.60
3
6
7
11
19
20
27
40
Laboratory


Arsenic - Sample B
0.66 +/- 0.09 micrograms/litre
Micrograms/Litre
0.20
0.40
0.60
0.80
1.00
3
6
7
19
20
27
40
Laboratory




| **Arsenic** | **Sample A** | **Sample B** |
|---|---|---|
| Results received: | 15 | 15 |
| More than 2 quantitative results: | 8 | 7 |
| Rejected means: | 0 | 0 |
| Accepted value: | 0.33 ± 0.11 | 0.66 ± 0.09 micrograms/litre |

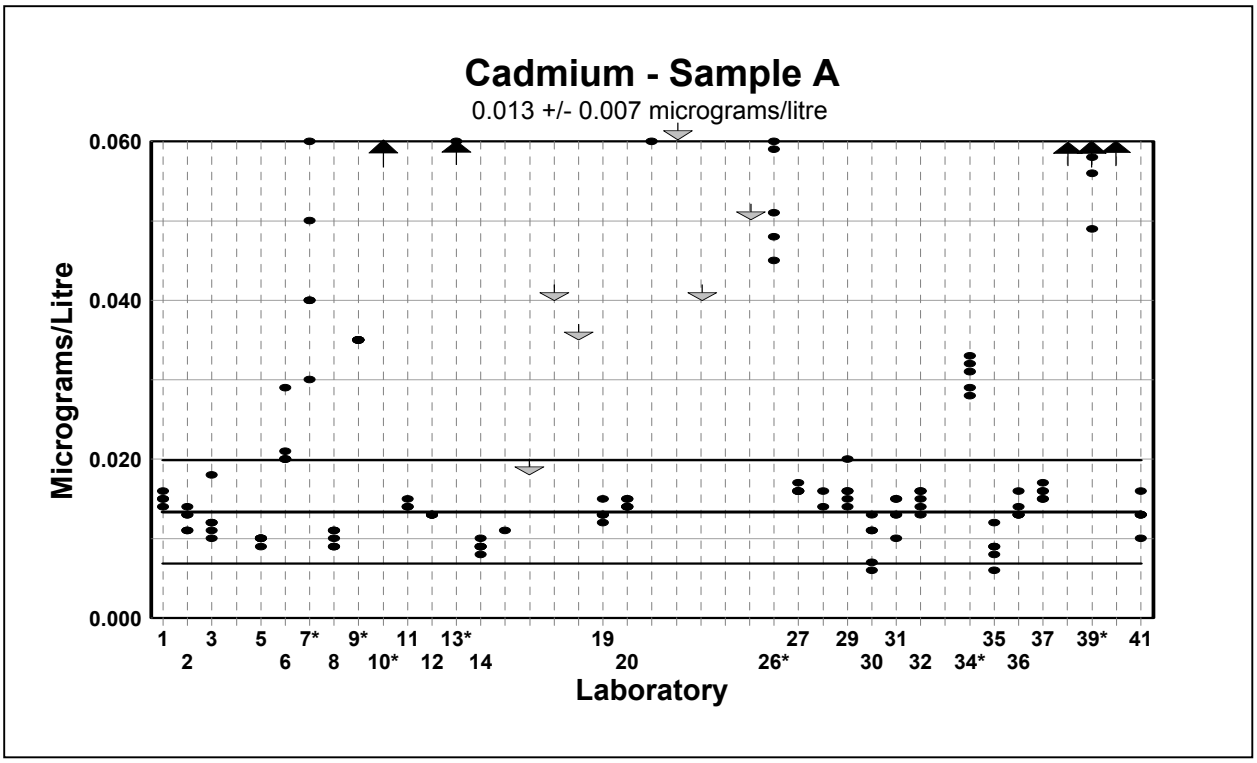
A small number (about 20 percent) of the laboratories produced more than two quantitative results for each sample. However, no means were rejected for either sample. The accepted values are based on the means of only eight and seven sets of data, respectively, for the two samples. The 95 percent confidence intervals are 33 % and 14 %, respectively.

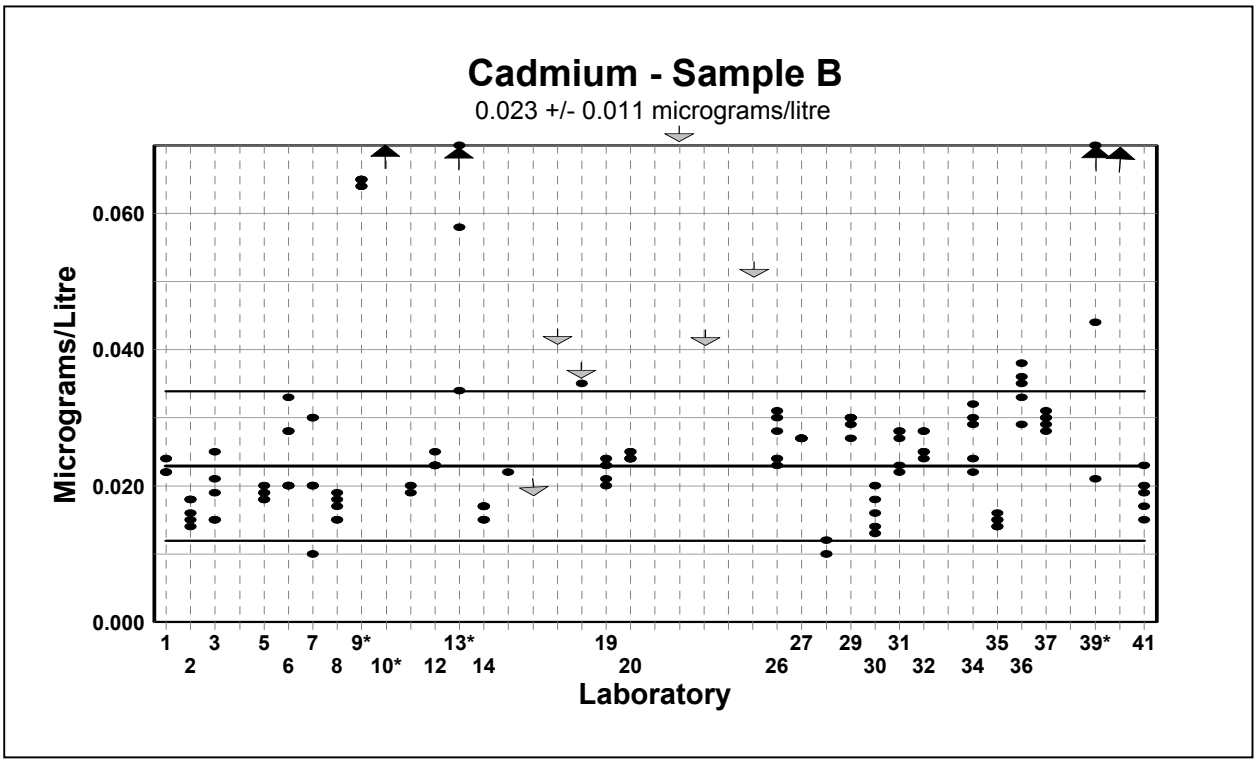
There are no detailed descriptions of sample preparation procedures for most of the laboratories. Separations of the analyte from the matrix are not necessary for arsenic in many cases. All but one of the accepted laboratories used a hydride generation procedure. Lab 40 precipitated the analyte with APDC. Measurements were made by most laboratories using hydride generation and FAAS. One laboratory used HG-atomic fluorescence, another HG-ICPAES and a third HG-ICPMS. Lab 40 used ICPMS to directly estimate the arsenic in the digested precipitate.

All laboratories that submitted quantitative data for arsenic did well, except for the poor precision of Lab 3.

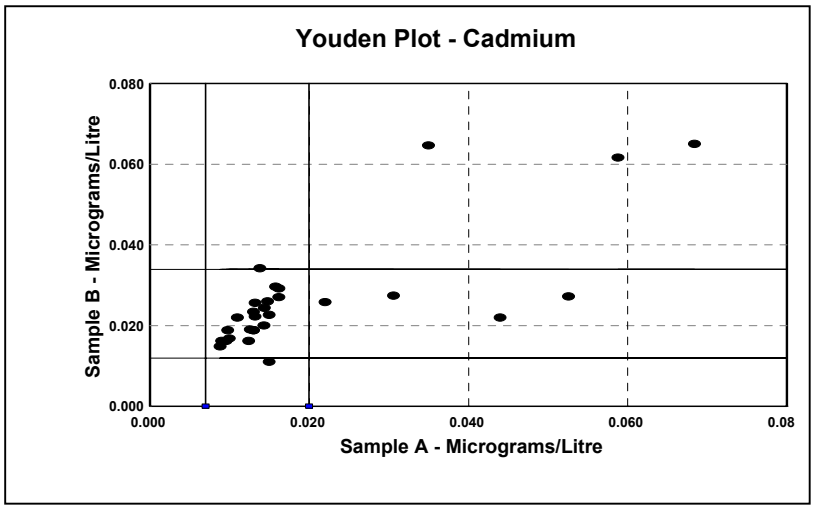
The Youden plot contains too few results to be very informative, but shows a tendency to systematic errors.

Historically, the determination of arsenic in sea water has generally not caused great difficulties. Considering the ease of the analysis, it is surprising that so few laboratories analysed the samples for arsenic.


Cadmium - Sample A
0.013 +/- 0.007 micrograms/litre
Micrograms/Litre
0.060
0.040
0.020
0.000
1 3 5 7* 9* 11 13* 19 27 29 31 35 37 39* 41
2 6 8 10* 12 14 20 26* 30 32 34* 36
Laboratory


Cadmium - Sample B
0.023 +/- 0.011 micrograms/litre
Micrograms/Litre
0.060
0.040
0.020
0.000
1 3 5 7 9* 13* 19 27 29 31 35 37 39* 41
2 6 8 10* 12 14 20 26 30 32 34 36
Laboratory

Data off scale
Lab 10




| **Cadmium** | **Sample A** | **Sample B** |
|---|---|---|
| Results received: | 38 | 36 |
| More than 2 quantitative results: | 27 | 26 |
| Rejected means: | 7 | 4 |
| Accepted value: | $0.013 \pm 0.007$ | $0.023 \pm 0.011$ micrograms/litre |

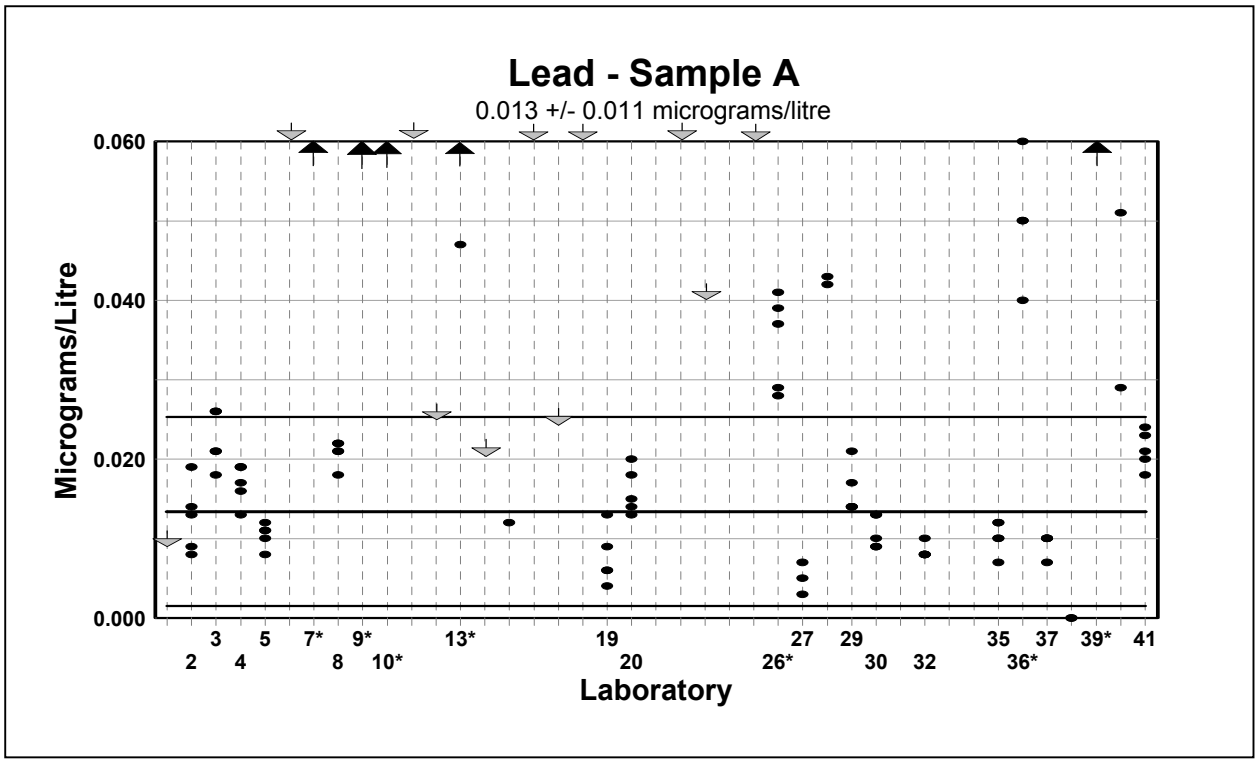
About 65 percent of the laboratories produced more than two quantitative results for each sample. Seven means were rejected for Sample A (Labs 7, 9, 10, 13, 26, 34 and 39) and four means for Sample B (Labs 9, 10, 13 and 39). All of the eleven results rejected were high. The accepted values are based on the means of 20 and 22 sets of data, respectively, for the two samples. The 95 percent confidence intervals are 49 % and 48 %, respectively.

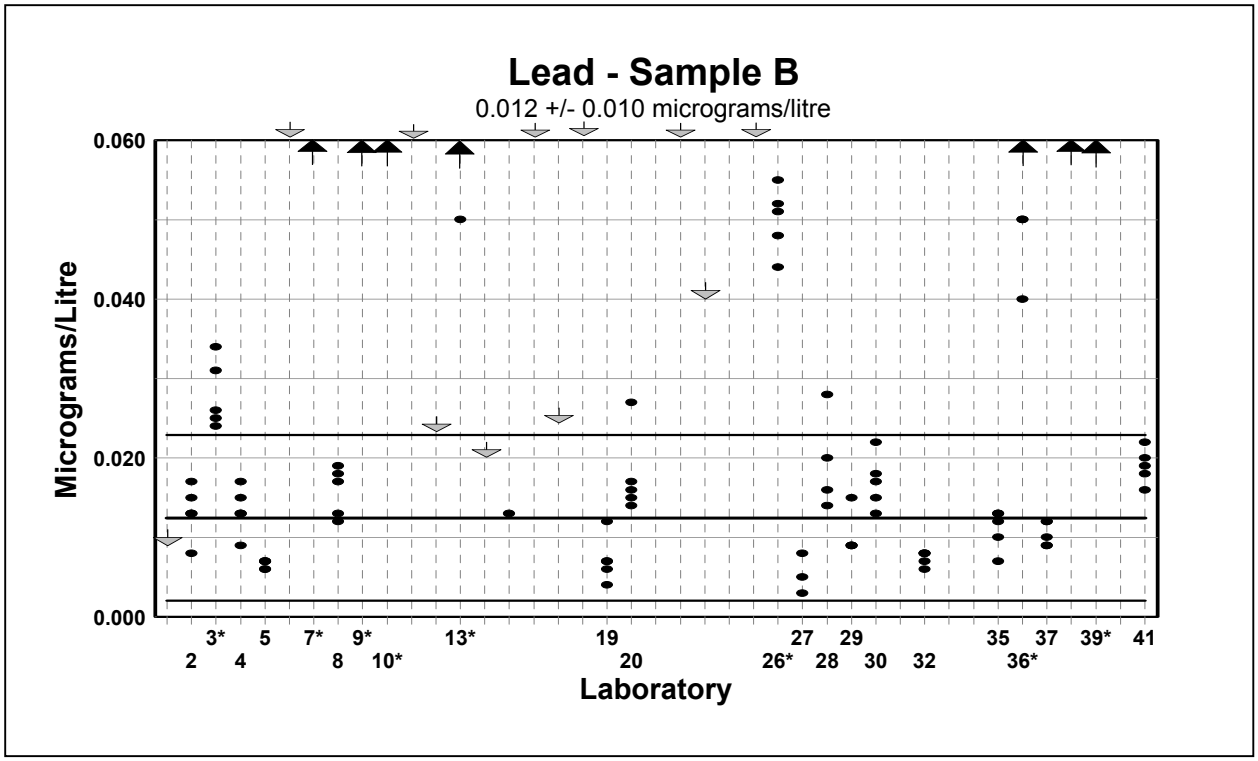
We do not have descriptions of sample preparation procedures for Labs 5, 7, 9, 30, 31 and 39, but we assume that in all probability they used a solvent extraction or a chromatographic technique to separate the cadmium from the matrix. About 45 percent of the means from these laboratories were not accepted. The accepted sets for which we are sure of the techniques involved the separation of the cadmium from the matrix either by solvent extraction, chromatography or precipitation.

Twelve of the accepted laboratories used GFAAS with some form of background correction to measure the cadmium. Some used a matrix modifier, others did not. Four laboratories used an electrochemical determination. Three laboratories employed ICPMS. One laboratory employed TXRF. None used ICPAES or FAAS.

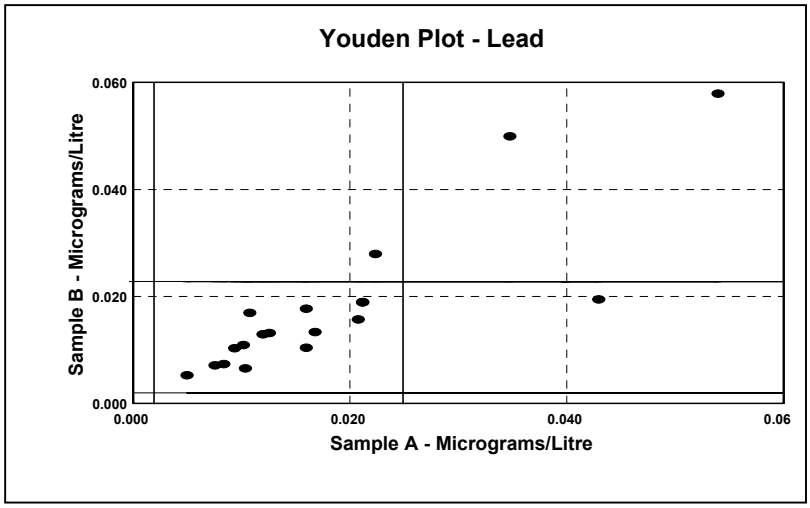
The Youden plot indicates a preponderance of systematic errors, but also some random behaviour. It appears to be more difficult for some laboratories to analyse Sample A than Sample B. Most problems are probably due to contamination, inadequate blank correction and/or calibration errors.

The determination of cadmium in sea water has generally not caused great difficulties, as is demonstrated by the relatively large number of respondents and the small confidence intervals, considering the low concentrations.


Lead - Sample A
0.013 +/- 0.011 micrograms/litre
Micrograms/Litre
0.060
0.040
0.020
0.000
3 5 7* 9* 13* 19 27 29 35 37 39* 41
2 4 8 10* 20 26* 30 32 36*
Laboratory


Lead - Sample B
0.012 +/- 0.010 micrograms/litre
Micrograms/Litre
0.060
0.040
0.020
0.000
3* 5 7* 9* 13* 19 27 29 35 37 39* 41
2 4 8 10* 20 26* 28 30 32 36*
Laboratory

Data off scale
Labs 7, 13, 39




| **Lead** | **Sample A** | **Sample B** |
|---|---|---|
| Results received: | 35 | 35 |
| More than 2 quantitative results: | 21 | 22 |
| Rejected means: | 7 | 8 |
| Accepted value: | $0.013 \pm 0.011$ | $0.012 \pm 0.010$ micrograms/litre |

Just over 50 percent of the laboratories produced more than two quantitative results for each sample. Seven means were rejected for Sample A (Labs 7, 9, 10, 13, 26, 36 and 39) and eight means for Sample B (Labs 3, 7, 9, 10, 13, 26, 36 and 39). All of the fifteen results rejected were high. The accepted values are based on the means of fourteen sets of data for each of the two samples. The 95 percent confidence intervals are 86 % and 84 % for the samples, the highest in this study.

We do not have descriptions of sample preparation procedures for Labs 5, 7, 9, 10, 28, 30 and 39, but we assume that in all probability they used a solvent extraction or a chromatographic technique to separate the lead from the matrix. About 55 percent of the means from these laboratories were not accepted. The accepted sets for which we are sure of the techniques involved the separation of the lead from the matrix either by solvent extraction, chromatography or precipitation.

Ten laboratories used GFAAS with some form of background correction to measure the lead. Five of these were accepted. Some used a matrix modifier, others did not. Four successful laboratories used ICPMS and another three laboratories employed an electrochemical determination. There were no accepted results employing ICPAES. One laboratory used TXRF. None used FAAS.

The Youden plot indicates a preponderance of systematic errors. Most problems are probably due to contamination, inadequate blank correction and/or calibration errors.

The determination of lead in sea water has long been a cause of great difficulties. This is again demonstrated by the large number of rejected results (the highest in this study) and the large confidence intervals. Because of the inherently low lead concentrations, laboratory contamination is usually the major problem.

# 5 Discussion

The intent of this exercise was to assess the capability of participating laboratories to determine selected trace metals in a coastal sea water. This is best measured through an evaluation of their accuracy and, to some extent, their intralaboratory precision.

An accepted mean and a 95 percent confidence interval for each trace metal were calculated from the submitted data for each of the two unknown samples. An implication of this approach is that the accuracy evaluation of a laboratory's performance for a particular trace metal in a particular matrix is relative to the performances of all accepted laboratories. Thus, we get an indication of the type of comparability we may expect if the accepted group were to analyse similar materials.

In our experience, there always appears to be a group of participating laboratories that are competent to analyse the sea waters for each of the trace metals designated in this study and it is possible to establish an accepted value for the mean concentration along with an appropriate 95 percent confidence interval. The confidence interval may at times be larger than one may desire, but it does describe the uncertainty within the accepted group of laboratories.

A system to evaluate laboratory performance for the individual elements in the seawater samples was established using the following criteria:

E Excellent accuracy: all replicate values are within the established confidence interval.

G Good accuracy: the mean of the replicates is within the established confidence interval but one or more of the replicates is outside; a 'less than' value has been reported that is not less than the lower confidence limit and not three times greater than the accepted mean.

L Low results: the mean of the replicates is less than the lower confidence limit; a 'less than' value reported is less than the lower confidence limit.

H High results: the mean of the replicates is greater than the upper confidence limit; a 'less than' reported is greater than a factor of three above the accepted or certified value.

S Good precision: the intralaboratory precision is within the criteria for precision listed below in Table 1.

P Poor precision: the intralaboratory precision is not within the criteria for precision listed below in Table 1.

Results from laboratories which did not submit at least three replicates for a trace metal were also evaluated according to the above criteria for accuracy, receiving a G if the results were within the confidence interval. There was, of course, no assessment of precision.

The 'less than' values are considered to yield valid information provided that they meet the criteria listed above.

**Table 1.** Criteria for intralaboratory precision evaluation.

| Analyte Concentration | Expected RSD |
|---|---|
| ≤0.5 micrograms litre$^{-1}$ | ± 20 percent |
| >0.5 micrograms litre$^{-1}$ | ± 10 percent |

Tables of this assessment are tabulated in Annex 4.

Z-scores were calculated in all instances where quantitative values were submitted. For the purpose of this evaluation, we set a tolerable bias of ± 12.5 percent of the accepted value.

$$Z = \frac{X_C - C_A}{0.125\, C_A}$$

where $C_A$ is the accepted value, and

$X_C$ is the laboratory's mean value.

Thus, a Z-score of ≤2 indicates that the laboratory's mean was within 25 percent of the accepted trace metal concentration. The Z-scores are listed in Annex 4.

Charts of the Z-scores are displayed in Annex 5. The solid boundary lines in these charts represent the Z = ± 2 region. The cut-off range for the charts is Z = ± 5. It is apparent from these data that for all the trace metals, except arsenic, large high errors predominate over large low errors. This is probably indicative of contamination and a lack of proper blank controls and calibration procedures in these laboratories.

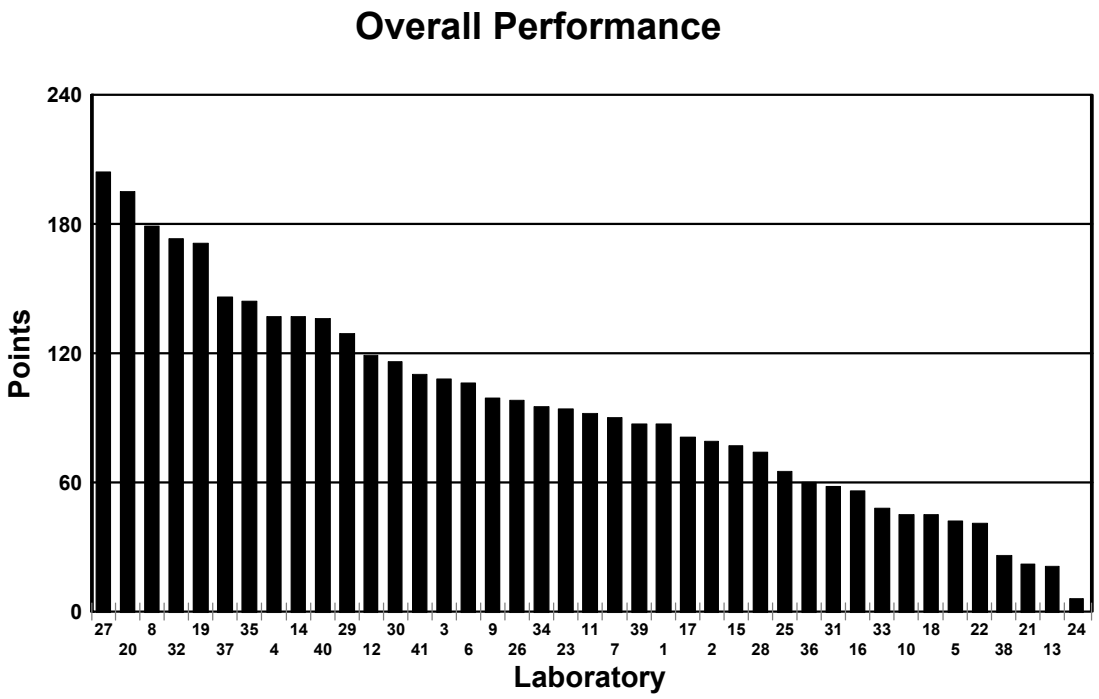
A proper and reliable assessment of the laboratories' performance is very difficult to carry out and a correct approach can be the subject of some philosophical discussion.

A point system was devised in order to begin to assess and differentiate the laboratories' performances. This system is based on the evaluation of the laboratories shown in Annex 4.

For example, a laboratory with an E-S rating and a Z-score ≤2 was awarded 12 points, the maximum. A laboratory with a G-S rating and a Z-score >2 but ≤4 was awarded 7 points. A laboratory with a G rating received 3 points, and so on. An H or L rating received 1 point, the minimum.

This system results in a maximum possible score of 240 for a laboratory which has successfully analysed both samples for all ten trace metals. The results of this assessment are shown below in Figure 1.

**Figure 1.** Overall performance based on analysis of both samples for all ten trace metals.




The outcome is disappointing. Only twelve laboratories (27 percent of the total) earned over 120 points, half of the possible score. On further examination, the reason for this becomes obvious. None of the participants, for whatever reasons, produced quantitative results for all ten analytes. Also, laboratories with only one or two quantitative results received no points for intralaboratory precision.

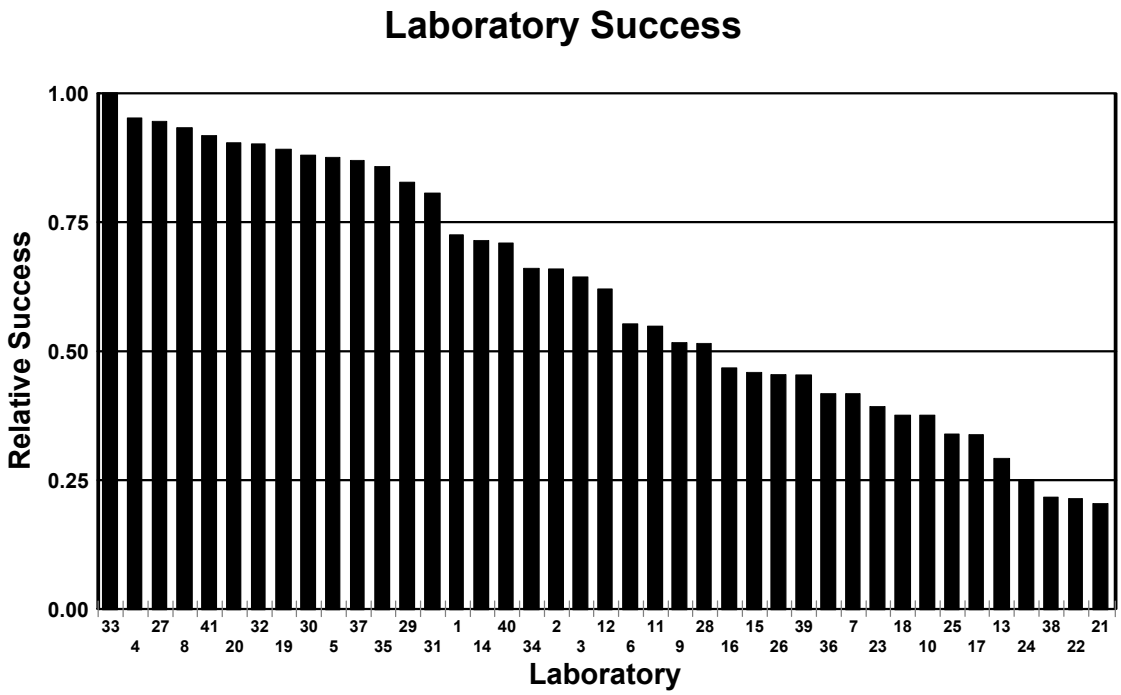
A review of the results shows that a relatively large number of laboratories submitted no data or only qualitative data for a large number of the trace metals. This is shown in Table 2. In this table, an analyte is considered reported even if only one of the two samples was analysed. More often than not, the qualitative data were 'less than' values, indicating that the laboratory's procedure was not sufficiently sensitive to produce quantitative results.

Instead of the possible (and expected) 820 sets of quantitative results, we received, *in toto*, only 421 sets from the 41 respondents, including 38 sets containing only one or two results.

It was felt that a fairer method of evaluation might be to look at the results only in terms of the analyses attempted. If, for example, a laboratory reported results for only five trace metals, there would be 120 possible points rather than the 240 target shown in Figure 1. That laboratory's relative success would be the ratio of its awarded score divided by 120.

The results of this approach are shown in Figure 2. Figure 2 apparently provides a better picture of the laboratories' achievements. Or does it?

**Figure 2.** Relative performance of each laboratory based on the number of analyses actually performed.




The laboratories are distributed into the four quartiles, with 14 in upper quartile and 11 in the next highest quartile (61 percent *in toto*). The 'winner' here is Lab 33, totally successful in all its analyses. But Lab 33 analysed the samples for only two trace metals. Is this laboratory more competent than Lab 20, which did a rather good job of analysing the samples for nine of the ten trace metals?

Have good laboratories been penalized because they tried to conform to the ground rules of this exercise and provide data for trace metals for which they have little or no analytical experience?

Also, those sets of results with less than three replicate values have had no points awarded above for variance.

This intercomparison exercise is sponsored by the Marine Chemistry Working Group of ICES and is, in that context, primarily directed at monitoring laboratories in the ICES Member Countries.

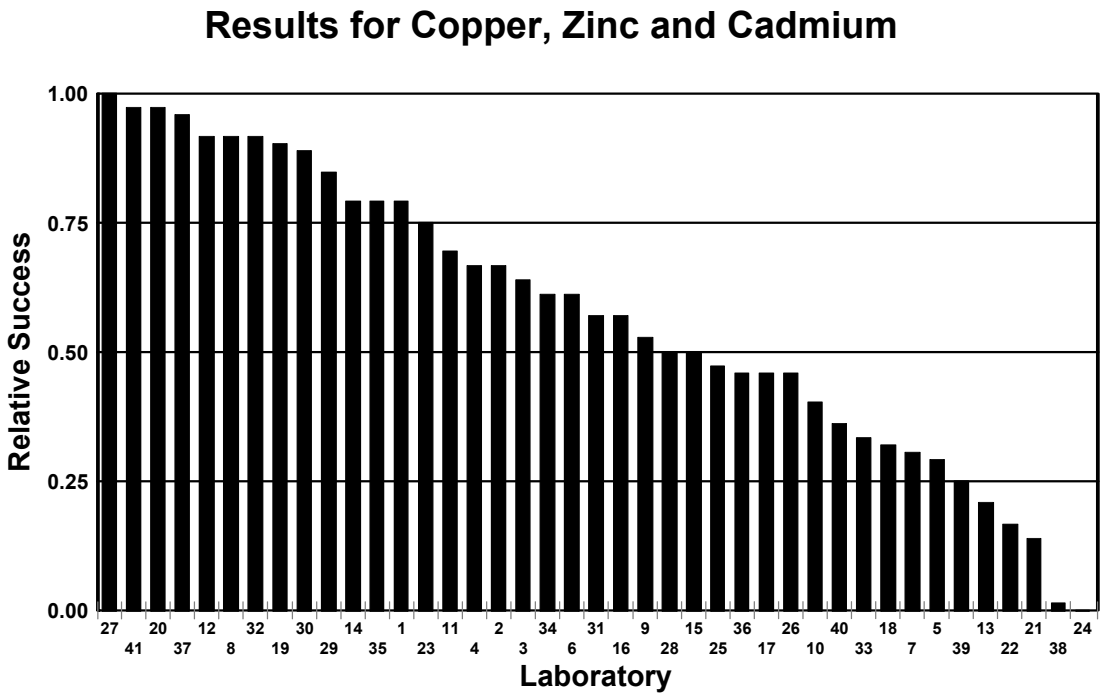
**Table 2.** Number of trace metals determined and sets of quantitative results received for each laboratory.

| Lab. No. | Number of Analytes | Quantitative Results |
|---|---|---|
| 23 | 10 | 3 |
| 17 | 10 | 2 |
| 7 | 9 | 9 |
| 20 | 9 | 9 |
| 26 | 9 | 9 |
| 27 | 9 | 9 |
| 40 | 9 | 9 |
| 14 | 9 | 6 |
| 8 | 8 | 8 |
| 9 | 8 | 8 |
| 19 | 8 | 8 |
| 32 | 8 | 8 |
| 39 | 8 | 8 |
| 22 | 8 | 6 |
| 6 | 8 | 5 |
| 12 | 8 | 5 |
| 25 | 8 | 2 |
| 3 | 7 | 7 |
| 29 | 7 | 7 |
| 35 | 7 | 7 |
| 37 | 7 | 7 |
| 15 | 7 | 7 |
| 11 | 7 | 5 |
| 4 | 6 | 6 |
| 21 | 6 | 6 |
| 28 | 6 | 6 |
| 30 | 6 | 6 |
| 34 | 6 | 6 |
| 36 | 6 | 6 |
| 38 | 6 | 6 |
| 2 | 5 | 5 |
| 10 | 5 | 5 |
| 41 | 5 | 5 |
| 1 | 5 | 4 |
| 16 | 5 | 3 |
| 18 | 5 | 2 |
| 13 | 3 | 3 |
| 31 | 3 | 3 |
| 5 | 2 | 2 |
| 33 | 2 | 2 |
| 24 | 1 | 0 |

The great majority of the participants are European, working within the Conventions of the Oslo and Paris Commissions (OSPARCOM). The Joint Monitoring Group of OSPARCOM (whose programme has subsequently been revised) has designated four trace metals as mandatory in its seawater monitoring programmes: copper, zinc, cadmium, and mercury. Chromium, nickel, and arsenic are designated as voluntary analytes.

Figure 3 illustrates combined individual laboratory success for the three trace metals copper, zinc, and cadmium.

**Figure 3.** Combined individual laboratory success for copper, zinc, and cadmium.




Fourteen laboratories are in the upper quartile whose minimum requirement is an E-S evaluation with a Z-score less than 4 or an E-P evaluation with a Z-score less than 2. Another eleven laboratories are in the second quartile.

In all, only 25 laboratories (61 percent of the respondents) are in the upper two quartiles. To achieve this a laboratory need have only a G-S evaluation and a Z-score of less than 4 for each trace metal. That is, the laboratory mean is within the calculated confidence interval and is within 50 percent of the accepted value for the trace metal concentration. The fact that more than one-third of the respondent laboratories could not or did not demonstrate this for these three common analytes is disappointing to the authors and should be a source of concern to the laboratories and to those who organize monitoring programmes.

The following laboratories did not submit quantitative results for one or more of the three Joint Monitoring Group trace metals:

| | |
|---|---|
| Copper: | Labs 13, 24, 38 |
| Zinc: | Labs 6, 17, 24, 25, 31, 33, 38, 40 |
| Cadmium: | Labs 16, 17, 18, 22, 23, 24, 25, 33 |

Labs 4 and 5 are not included in the above listing because they are essentially one laboratory and between the two entities submitted results for all three metals. It is also obvious from the data that this laboratory is quite competent to analyse sea water for these metals.

The prime judgement factor has to be accuracy. This can be demonstrated for each laboratory through its Z-score for each of the metals for which quantitative results were submitted. The laboratory Z-scores are presented in Annex 6. Z-scores greater than ± 4 (i.e., biases greater than 50 percent from the accepted values) are off scale in these diagrams.

It must be remembered that there cannot be reliable accuracy without good precision.

# 6 Comparison with the Sixth Round Intercomparison Exercise

An examination of the report for the Sixth Round Intercalibration Exercise for Trace Metals in Estuarine Water (6/TM/SW) (Berman and Boyko, 1988) would indicate that there is not much to be gained by attempting a direct comparison of the results of the two studies. The concentrations of the trace metals in the estuarine waters were from two to twenty times higher than those encountered in this exercise.

Also, that work was carried out in 1986, ten years earlier. The advances in the reliability of analytical procedures for the determination of trace metals in sea water since then have been dramatic. However, the separation procedures which were used by the participants have, surprisingly, not changed much over the past decade. But laboratory practices and quality assurance measures are now much improved. The enhanced reliability of electrothermal ionization techniques such as graphite furnace atomic absorption spectrometry, the most widely used trace metal measurement tool, and the improvement of electrochemical methods have contributed much to laboratory capabilities. The development and commercialization of the inductively coupled plasma mass spectrometer, available only in research laboratories in 1986, is one of the decade's major advances in trace metal analysis and is obviously being employed now in a number of marine laboratories.

There is no doubt that the general capabilities of the marine laboratories with respect to the analysis of sea water for trace metals are much improved. For example, in 1986 twenty-eight participants submitted quantitative results for copper in one of the samples. The accepted value was $4.2 \pm 0.4$ µg per litre. Twelve results were rejected. In this study thirty-two participants submitted quantitative results for copper in one of the samples whose accepted value is only $0.6 \pm 0.2$ µg per litre. Seven results were rejected. Similar improvements may be seen for all the analytes common to both studies.

# 7 Conclusions

The capability of many marine (and other) laboratories to analyse sea water for trace metals has improved over the past decade.

There exists among the respondent laboratories a group of twelve (Labs 4(5), 8, 12, 14, 19, 20, 27, 29, 32, 35, 37 and 40) which has demonstrated an ability to competently analyse sea water for at least six of the trace metals of interest in this exercise.

Another twelve laboratories (Labs 1, 2, 3, 6, 9, 11, 28, 30, 31, 33, 34 and 41) analysed the sea water for fewer trace metals and generally did well for their selected analytes.

Based on their Z-scores ($Z \leq 4$ for at least one of the samples), Labs 2, 4(5), 8, 11, 12, 14, 15, 19, 20, 27, 28, 29, 30, 32, 35, 37 and 41 appear to be competent regarding the analysis of the samples for the three trace metals, copper, zinc and cadmium.

However, the majority of the respondent laboratories has not demonstrated an ability to analyse adequately both samples for all these three trace metals.

There is a number of competent procedures for the extraction of trace metals from sea water. This study could not discern significant differences in the efficacy of these separation methods. (It is, however, disturbing to note that some laboratories, involved in environmental work, use 1,1,2-trichloro-1,2,2-trifluorethane, a high level ozone-depleting chemical solvent, in their trace metal extraction procedures. There are alternate adequate extraction solvents, as demonstrated in this study.)

Also, there is a number of reliable instrumental methods for the measurement of trace metal concentrations after extraction from sea water. This study could not distinguish significant differences in the proficiency of these instrumental procedures, although those laboratories using ICPAES seemed to have more problems than others.

It is not necessary to extract arsenic from the matrix. The hydride generation procedure along with flame atomic absorption spectrometry measurement appears to work well. It is surprising that so few laboratories analysed the samples for this metalloid.

Many laboratories do not appear to be using procedures of adequate sensitivity for the analysis of the sea waters for trace metals. This is puzzling because their reported procedures are often not much different from those of laboratories

producing good quantitative results. We suggest that laboratories with problems consult with their more capable colleagues regarding their analytical procedures.

Laboratory contamination and/or poor control of reagent blanks and/or improper calibration procedures appear to be major sources of error in many laboratories. Some laboratories reported extremely high values for Samples A and B which were essentially uncontaminated waters. Arithmetic errors are suspected in some cases.

Clean facilities, equipment, and reagents are a prerequisite for the successful analysis of sea water for trace metals. Good laboratory practices are essential.

The 95 percent confidence intervals are, in general, relatively smaller for Sample B. This may be related to the lower total organic carbon content of this sea water, resulting in more efficient extraction of the trace metals. Also, the high salinity may be a factor.

The amount of information submitted regarding procedures seems to be proportional to the laboratory's ability to produce good results. Many of the laboratories that did not do well also did not describe their procedures well.

# 8 References

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# 9 Acknowledgments

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# ANNEX 1

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Samples were sent to the following laboratories, but no results were received.

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NR = no results

# ANNEX 2

# Data

# Chromium

## Sample A

### 0.080 ± 0.053 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | 5 | 0.085 | 0.147 | 0.077 | 0.072 | 0.076 | 0.091 | 0.031 | 0.344 |
| 4 | | | | | | | | | |
| 5 | | | | | | | | | |
| 6 | | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | | | |
| 7* | 5 | 0.870 | 0.810 | 0.860 | 1.060 | 0.760 | 0.872 | 0.114 | 0.131 |
| 8 | | | | | | | | | |
| 9 | 5 | 0.072 | 0.072 | 0.072 | 0.072 | 0.071 | 0.072 | 0.000 | 0.006 |
| 10 | | | | | | | | | |
| 11 | | <0.3 | <0.3 | <0.3 | | | | | |
| 12 | | <5 | <5 | <5 | <5 | <5 | | | |
| 13 | | | | | | | | | |
| 14 | | | | | | | | | |
| 15 | 1 | 0.200 | | | | | 0.200 | | |
| 16 | | | | | | | | | |
| 17 | | <0.35 | <0.35 | <0.35 | <0.35 | <0.35 | | | |
| 18 | | | | | | | | | |
| 19 | | | | | | | | | |
| 20 | | | | | | | | | |
| 21 | 1 | 16.400 | | | | | 16.400 | | |
| 22 | | | | | | | | | |
| 23 | | <2 | <2 | <2 | <2 | <2 | | | |
| 24 | | | | | | | | | |
| 25 | | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | | | |
| 26* | 5 | 2.200 | 2.250 | 2.050 | 2.040 | 2.700 | 2.248 | 0.269 | 0.120 |
| 27 | | | | | | | | | |
| 28 | | | | | | | | | |
| 29 | | | | | | | | | |
| 30 | | | | | | | | | |
| 31 | | | | | | | | | |
| 32 | | | | | | | | | |
| 33 | | | | | | | | | |
| 34 | 5 | 0.101 | 0.128 | 0.095 | 0.122 | 0.088 | 0.107 | 0.017 | 0.163 |
| 35 | | | | | | | | | |
| 36 | | | | | | | | | |
| 37 | | | | | | | | | |
| 38 | 2 | 0.460 | 0.280 | | | | 0.370 | | |
| 39 | 5 | 0.068 | 0.078 | 0.063 | 0.055 | 0.060 | 0.065 | 0.009 | 0.135 |
| 40 | 5 | 0.054 | 0.060 | 0.067 | 0.067 | 0.067 | 0.063 | 0.006 | 0.093 |
| 41 | | | | | | | | | |

## Sample B

### 0.081 ± 0.031 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | 5 | 0.082 | 0.103 | 0.102 | 0.099 | 0.087 | 0.095 | 0.010 | 0.100 |
| 4 | | | | | | | | | |
| 5 | | | | | | | | | |
| 6 | | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | | | |
| 7* | 5 | 1.250 | 0.950 | 1.140 | 0.930 | 1.030 | 1.060 | 0.135 | 0.127 |
| 8 | | | | | | | | | |
| 9* | 5 | 0.168 | 0.168 | 0.167 | 0.167 | 0.168 | 0.168 | 0.001 | 0.003 |
| 10 | | | | | | | | | |
| 11 | | <0.3 | <0.3 | | | | | | |
| 12 | | <5 | <5 | <5 | <5 | <5 | | | |
| 13 | | | | | | | | | |
| 14 | | | | | | | | | |
| 15 | 1 | 0.010 | | | | | 0.010 | | |
| 16 | | | | | | | | | |
| 17 | | <0.35 | <0.35 | <0.35 | <0.35 | <0.35 | | | |
| 18 | | | | | | | | | |
| 19 | | | | | | | | | |
| 20 | | | | | | | | | |
| 21 | 1 | 11.500 | | | | | 11.500 | | |
| 22 | | | | | | | | | |
| 23 | | <2 | <2 | <2 | <2 | <2 | | | |
| 24 | | | | | | | | | |
| 25 | | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | | | |
| 26* | 5 | 2.250 | 2.670 | 2.350 | 2.740 | 2.650 | 2.532 | 0.217 | 0.086 |
| 27 | | | | | | | | | |
| 28 | | | | | | | | | |
| 29 | | | | | | | | | |
| 30 | | | | | | | | | |
| 31 | | | | | | | | | |
| 32 | | | | | | | | | |
| 33 | | | | | | | | | |
| 34 | 5 | 0.068 | 0.061 | 0.094 | 0.061 | 0.074 | 0.072 | 0.014 | 0.191 |
| 35 | | | | | | | | | |
| 36 | | | | | | | | | |
| 37 | | | | | | | | | |
| 38 | 2 | 0.320 | 0.260 | | | | 0.290 | | |
| 39 | 5 | 0.085 | 0.082 | 0.113 | 0.081 | 0.041 | 0.080 | 0.026 | 0.319 |
| 40 | 5 | 0.081 | 0.069 | 0.076 | 0.081 | 0.080 | 0.077 | 0.005 | 0.066 |
| 41 | | | | | | | | | |

# Manganese

## Sample A

### 1.4 ± 1.0 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | 5 | 1.413 | 1.125 | 1.024 | 0.969 | 1.294 | 1.165 | 0.186 | 0.159 |
| 5 | | | | | | | | | |
| 6 | 5 | 1.000 | 0.970 | 0.960 | 0.930 | 0.890 | 0.950 | 0.042 | 0.044 |
| 7* | 5 | 6.000 | 6.100 | 6.800 | 6.520 | 6.120 | 6.308 | 0.339 | 0.054 |
| 8 | 5 | 1.054 | 1.021 | 0.996 | 1.025 | 1.047 | 1.029 | 0.023 | 0.022 |
| 9 | 5 | 0.753 | 0.756 | 0.755 | 0.754 | 0.755 | 0.755 | 0.001 | 0.002 |
| 10 | | | | | | | | | |
| 11 | | | | | | | | | |
| 12 | | | | | | | | | |
| 13 | | | | | | | | | |
| 14 | 5 | 1.080 | 1.060 | 1.060 | 1.090 | 1.080 | 1.074 | 0.013 | 0.012 |
| 15 | | | | | | | | | |
| 16 | | | | | | | | | |
| 17 | | <20 | <20 | <20 | <20 | <20 | | | |
| 18 | | | | | | | | | |
| 19 | | | | | | | | | |
| 20 | 5 | 1.600 | 1.700 | 1.600 | 1.600 | 1.700 | 1.640 | 0.055 | 0.033 |
| 21 | | | | | | | | | |
| 22 | 5 | 1.000 | 4.000 | 1.000 | 1.000 | 1.000 | 1.600 | 1.342 | 0.839 |
| 23 | | <10 | <10 | <10 | <10 | <10 | | | |
| 24 | | | | | | | | | |
| 25 | | | | | | | | | |
| 26 | 5 | 0.480 | 0.550 | 0.630 | 0.680 | 0.475 | 0.563 | 0.091 | 0.161 |
| 27 | 5 | 1.395 | 1.409 | 1.428 | 1.415 | 1.440 | 1.417 | 0.017 | 0.012 |
| 28 | | | | | | | | | |
| 29 | 5 | 1.900 | 1.780 | 2.190 | 2.280 | 1.740 | 1.978 | 0.244 | 0.123 |
| 30 | | | | | | | | | |
| 31 | 5 | 2.230 | 2.480 | 2.260 | 2.120 | 2.220 | 2.262 | 0.133 | 0.059 |
| 32 | 5 | 1.060 | 1.349 | 1.129 | 1.132 | 1.113 | 1.157 | 0.111 | 0.096 |
| 33 | | | | | | | | | |
| 34 | 5 | 2.070 | 2.190 | 2.050 | 2.050 | 1.980 | 2.068 | 0.076 | 0.037 |
| 35 | 5 | 1.301 | 1.487 | 1.886 | 1.412 | 1.241 | 1.465 | 0.254 | 0.173 |
| 36 | 5 | 1.800 | 1.700 | 1.800 | 1.700 | 1.800 | 1.760 | 0.055 | 0.031 |
| 37 | | | | | | | | | |
| 38 | 2 | 2.000 | 2.000 | | | | 2.000 | | |
| 39 | 5 | 1.334 | 1.511 | 1.447 | 1.312 | 1.500 | 1.421 | 0.093 | 0.065 |
| 40 | 5 | 0.830 | 1.230 | 1.290 | 1.240 | 1.060 | 1.130 | 0.189 | 0.167 |
| 41 | | | | | | | | | |

## Sample B

### 1.5 ± 1.3 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | 5 | 1.622 | 1.488 | 1.739 | 1.391 | 1.502 | 1.548 | 0.134 | 0.087 |
| 5 | | | | | | | | | |
| 6 | 5 | 0.380 | 0.330 | 0.340 | 0.340 | 0.410 | 0.360 | 0.034 | 0.094 |
| 7* | 5 | 7.400 | 7.200 | 7.400 | 6.900 | 7.000 | 7.180 | 0.228 | 0.032 |
| 8 | 5 | 1.242 | 1.081 | 1.207 | 1.083 | 0.996 | 1.122 | 0.101 | 0.090 |
| 9 | 5 | 1.236 | 1.270 | 1.272 | 1.271 | 1.271 | 1.264 | 0.016 | 0.012 |
| 10 | | | | | | | | | |
| 11 | | | | | | | | | |
| 12 | | | | | | | | | |
| 13 | | | | | | | | | |
| 14 | 5 | 1.070 | 1.370 | 0.890 | 0.770 | 0.840 | 0.988 | 0.241 | 0.244 |
| 15 | | | | | | | | | |
| 16 | | | | | | | | | |
| 17 | | <20 | <20 | <20 | <20 | <20 | | | |
| 18 | | | | | | | | | |
| 19 | | | | | | | | | |
| 20 | 5 | 1.800 | 1.400 | 1.700 | 1.500 | 1.600 | 1.600 | 0.158 | 0.099 |
| 21 | | | | | | | | | |
| 22 | | <1 | <1 | <1 | <1 | <1 | | | |
| 23 | | <10 | <10 | <10 | <10 | <10 | | | |
| 24 | | | | | | | | | |
| 25 | | | | | | | | | |
| 26 | 5 | 0.875 | 0.825 | 0.650 | 0.700 | 0.775 | 0.765 | 0.091 | 0.119 |
| 27 | 5 | 1.465 | 1.460 | 1.452 | 1.448 | 1.465 | 1.458 | 0.008 | 0.005 |
| 28 | | | | | | | | | |
| 29 | 5 | 2.400 | 2.400 | 2.280 | 3.240 | 2.440 | 2.552 | 0.389 | 0.153 |
| 30 | | | | | | | | | |
| 31 | 5 | 1.900 | 1.850 | 1.970 | 1.850 | 1.770 | 1.868 | 0.074 | 0.039 |
| 32 | 5 | 1.220 | 1.300 | 1.220 | 1.280 | 1.240 | 1.252 | 0.036 | 0.029 |
| 33 | | | | | | | | | |
| 34 | 5 | 2.000 | 2.140 | 2.070 | 2.000 | 2.070 | 2.056 | 0.059 | 0.028 |
| 35 | 5 | 1.996 | 2.050 | 2.095 | 2.004 | 2.199 | 2.069 | 0.083 | 0.040 |
| 36 | 5 | 2.500 | 2.100 | 2.400 | 2.400 | 2.500 | 2.380 | 0.164 | 0.069 |
| 37 | | | | | | | | | |
| 38 | 2 | 2.000 | 2.000 | | | | 2.000 | | |
| 39 | 5 | 2.259 | 2.153 | 2.216 | 2.300 | 2.090 | 2.204 | 0.084 | 0.038 |
| 40 | 5 | 1.720 | 1.120 | 1.340 | 2.020 | 1.930 | 1.626 | 0.385 | 0.237 |
| 41 | | | | | | | | | |

# Iron

## Sample A

### 0.83 ± 0.53 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | 5 | 0.829 | 0.856 | 0.806 | 0.912 | 0.854 | 0.851 | 0.040 | 0.046 |
| 5 | | | | | | | | | |
| 6 | | | | | | | | | |
| 7 | | | | | | | | | |
| 8 | 5 | 0.724 | 0.670 | 0.687 | 0.703 | 0.644 | 0.686 | 0.031 | 0.045 |
| 9* | 5 | 1.984 | 1.988 | 2.001 | 1.998 | 1.991 | 1.992 | 0.007 | 0.004 |
| 10 | | | | | | | | | |
| 11 | | | | | | | | | |
| 12 | | <5 | <5 | <5 | <5 | <5 | | | |
| 13 | | | | | | | | | |
| 14 | 5 | 1.200 | <0.8 | <0.8 | 1.220 | <0.8 | | | |
| 15 | | | | | | | | | |
| 16 | | | | | | | | | |
| 17 | | <20 | <20 | <20 | <20 | <20 | | | |
| 18 | | | | | | | | | |
| 19 | 5 | 0.620 | 0.620 | 0.640 | 0.640 | 0.770 | 0.658 | 0.063 | 0.096 |
| 20 | 5 | 1.200 | 1.100 | 1.100 | 1.100 | 1.100 | 1.120 | 0.045 | 0.040 |
| 21 | | | | | | | | | |
| 22* | 5 | 17.000 | 12.000 | 10.000 | 26.000 | 3.000 | 13.600 | 8.562 | 0.630 |
| 23 | | <10 | <10 | <10 | <10 | <10 | | | |
| 24 | | | | | | | | | |
| 25 | | <1 | <1 | <1 | <1 | <1 | | | |
| 26* | 5 | 7.380 | 6.380 | 6.530 | 6.950 | 6.580 | 6.764 | 0.403 | 0.060 |
| 27 | 5 | 0.649 | 0.666 | 0.711 | 0.667 | 0.655 | 0.670 | 0.024 | 0.036 |
| 28 | | | | | | | | | |
| 29 | | | | | | | | | |
| 30 | | | | | | | | | |
| 31 | | | | | | | | | |
| 32 | 5 | 0.753 | 0.754 | 0.698 | 0.702 | 0.762 | 0.734 | 0.031 | 0.042 |
| 33 | | | | | | | | | |
| 34 | | | | | | | | | |
| 35 | 5 | 0.772 | 0.674 | 0.593 | 0.777 | 0.583 | 0.680 | 0.093 | 0.137 |
| 36* | 5 | 2.600 | 2.700 | 3.000 | 2.700 | 3.100 | 2.820 | 0.217 | 0.077 |
| 37 | 5 | 1.670 | 1.061 | 1.001 | 1.198 | 1.178 | 1.222 | 0.264 | 0.216 |
| 38 | | | | | | | | | |
| 39* | 5 | 6.918 | 5.929 | 6.353 | 5.811 | 6.002 | 6.203 | 0.448 | 0.072 |
| 40 | 2 | 1.020 | 1.260 | | | | 1.140 | | |
| 41 | | | | | | | | | |

## Sample B

### 0.58 ± 0.23 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | 5 | 0.591 | 0.654 | 0.637 | 0.612 | 0.607 | 0.620 | 0.025 | 0.040 |
| 5 | | | | | | | | | |
| 6 | | | | | | | | | |
| 7 | | | | | | | | | |
| 8 | 5 | 0.497 | 0.479 | 0.497 | 0.487 | 0.497 | 0.491 | 0.008 | 0.017 |
| 9* | 5 | 2.606 | 2.607 | 2.610 | 2.598 | 2.605 | 2.605 | 0.004 | 0.002 |
| 10 | | | | | | | | | |
| 11 | | | | | | | | | |
| 12 | | <5 | <5 | <5 | <5 | <5 | | | |
| 13 | | | | | | | | | |
| 14 | | <0.8 | 0.820 | 0.920 | <0.8 | <0.8 | | | |
| 15 | | | | | | | | | |
| 16 | | | | | | | | | |
| 17 | | <20 | <20 | <20 | <20 | <20 | | | |
| 18 | | | | | | | | | |
| 19 | 5 | 0.640 | 0.570 | 0.490 | 0.500 | 0.570 | 0.554 | 0.061 | 0.110 |
| 20 | 5 | 0.800 | 0.600 | 0.600 | 0.600 | 0.600 | 0.640 | 0.089 | 0.140 |
| 21 | | | | | | | | | |
| 22* | 5 | 4.000 | 4.000 | 9.000 | 4.000 | 2.000 | 4.600 | 2.608 | 0.567 |
| 23 | | <10 | <10 | <10 | <10 | <10 | | | |
| 24 | | | | | | | | | |
| 25 | | <1 | <1 | <1 | <1 | <1 | | | |
| 26* | 5 | 5.830 | 6.150 | 5.580 | 5.950 | 5.880 | 5.878 | 0.206 | 0.035 |
| 27 | 5 | 0.463 | 0.481 | 0.464 | 0.484 | 0.497 | 0.478 | 0.014 | 0.030 |
| 28 | | | | | | | | | |
| 29 | 5 | 0.791 | 0.775 | 0.506 | 0.523 | 0.439 | 0.607 | 0.164 | 0.230 |
| 30 | | | | | | | | | |
| 31 | | | | | | | | | |
| 32 | 5 | 0.684 | 0.574 | 0.545 | 0.603 | 0.512 | 0.584 | 0.066 | 0.112 |
| 33 | | | | | | | | | |
| 34 | | | | | | | | | |
| 35 | 5 | 0.446 | 0.517 | 0.437 | 0.460 | 0.480 | 0.468 | 0.032 | 0.068 |
| 36* | 5 | 1.900 | 2.100 | 2.100 | 2.100 | 2.600 | 2.160 | 0.261 | 0.121 |
| 37 | 5 | 0.590 | 0.764 | 0.634 | 1.140 | 0.785 | 0.783 | 0.216 | 0.276 |
| 38 | | | | | | | | | |
| 39* | 5 | 6.494 | 6.272 | 6.918 | 5.801 | 5.910 | 6.279 | 0.453 | 0.072 |
| 40 | | | | | | | | | |
| 41 | | | | | | | | | |

# Cobalt

## Sample A

### 0.14 ± 0.08 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | | | | | | | | | |
| 5 | | | | | | | | | |
| 6 | | | | | | | | | |
| 7* | 5 | 0.480 | 0.360 | 0.380 | 0.460 | 0.400 | 0.416 | 0.052 | 0.124 |
| 8 | 5 | 0.115 | 0.115 | 0.107 | 0.107 | 0.113 | 0.111 | 0.004 | 0.037 |
| 9 | | | | | | | | | |
| 10 | | | | | | | | | |
| 11 | | | | | | | | | |
| 12 | 5 | 0.180 | 0.180 | 0.180 | 0.180 | 0.180 | 0.180 | 0.000 | 0.000 |
| 13 | | | | | | | | | |
| 14 | 5 | 0.114 | 0.111 | 0.113 | 0.118 | 0.110 | 0.113 | 0.003 | 0.028 |
| 15 | | | | | | | | | |
| 16 | | | | | | | | | |
| 17 | | <20 | <20 | <20 | <20 | <20 | | | |
| 18 | | | | | | | | | |
| 19 | 5 | 0.140 | 0.120 | 0.120 | 0.099 | 0.150 | 0.126 | 0.020 | 0.158 |
| 20 | 5 | 0.155 | 0.164 | 0.152 | 0.149 | 0.154 | 0.155 | 0.006 | 0.036 |
| 21 | | | | | | | | | |
| 22* | 5 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 0.000 | 0.000 |
| 23 | | <10 | <10 | <10 | <10 | <10 | | | |
| 24 | | | | | | | | | |
| 25 | | | | | | | | | |
| 26 | 5 | 0.135 | 0.113 | 0.145 | 0.120 | 0.128 | 0.128 | 0.013 | 0.098 |
| 27 | 5 | 0.125 | 0.138 | 0.133 | 0.144 | 0.147 | 0.137 | 0.009 | 0.064 |
| 28 | 2 | 0.037 | 0.032 | | | | 0.035 | | |
| 29 | | | | | | | | | |
| 30 | 5 | 0.057 | 0.060 | 0.062 | 0.063 | 0.057 | 0.060 | 0.003 | 0.046 |
| 31 | | | | | | | | | |
| 32 | 5 | 0.128 | 0.127 | 0.117 | 0.100 | 0.132 | 0.121 | 0.013 | 0.107 |
| 33 | | | | | | | | | |
| 34 | | | | | | | | | |
| 35 | | | | | | | | | |
| 36 | | | | | | | | | |
| 37 | 5 | 0.207 | 0.175 | 0.173 | 0.182 | 0.176 | 0.183 | 0.014 | 0.077 |
| 38 | | | | | | | | | |
| 39 | | | | | | | | | |
| 40 | 5 | 0.176 | 0.180 | 0.182 | 0.189 | 0.184 | 0.182 | 0.005 | 0.026 |
| 41 | | | | | | | | | |

## Sample B

### 0.016 ± 0.006 micrograms/litre

| Lab | n | | | | | | Mean | SD | |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | | | | | | | | | |
| 5 | | | | | | | | | |
| 6 | | | | | | | | | |
| 7* | 5 | 0.700 | 1.070 | 0.800 | 1.100 | 0.950 | 0.924 | 0.172 | 0.186 |
| 8 | 5 | 0.012 | 0.013 | 0.012 | 0.013 | 0.011 | 0.012 | 0.001 | 0.069 |
| 9 | | | | | | | | | |
| 10 | | | | | | | | | |
| 11 | | | | | | | | | |
| 12 | 5 | 0.015 | 0.015 | 0.015 | 0.013 | 0.018 | 0.015 | 0.002 | 0.118 |
| 13 | | | | | | | | | |
| 14 | 5 | 0.022 | 0.011 | 0.015 | 0.017 | 0.011 | 0.015 | 0.005 | 0.303 |
| 15 | | | | | | | | | |
| 16 | | | | | | | | | |
| 17 | | <20 | <20 | <20 | <20 | <20 | | | |
| 18 | | | | | | | | | |
| 19 | 5 | 0.024 | 0.018 | 0.017 | 0.017 | 0.016 | 0.018 | 0.003 | 0.174 |
| 20 | 5 | 0.018 | 0.019 | 0.026 | 0.022 | 0.029 | 0.023 | 0.005 | 0.204 |
| 21 | | | | | | | | | |
| 22* | 5 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 0.000 | 0.000 |
| 23 | | <10 | <10 | <10 | <10 | <10 | | | |
| 24 | | | | | | | | | |
| 25 | | | | | | | | | |
| 26 | 5 | 0.014 | 0.015 | 0.018 | 0.016 | 0.017 | 0.016 | 0.002 | 0.099 |
| 27 | 5 | 0.016 | 0.017 | 0.019 | 0.017 | 0.017 | 0.017 | 0.001 | 0.064 |
| 28 | 3 | 0.012 | 0.015 | 0.022 | | | 0.016 | 0.005 | 0.314 |
| 29 | | | | | | | | | |
| 30 | | | | | | | | | |
| 31 | | | | | | | | | |
| 32 | 5 | 0.015 | 0.010 | 0.012 | 0.019 | 0.016 | 0.014 | 0.004 | 0.244 |
| 33 | | | | | | | | | |
| 34 | | | | | | | | | |
| 35 | | | | | | | | | |
| 36 | | | | | | | | | |
| 37 | 5 | 0.013 | 0.014 | 0.014 | 0.016 | 0.015 | 0.014 | 0.001 | 0.079 |
| 38 | | | | | | | | | |
| 39 | | | | | | | | | |
| 40* | 3 | 0.029 | 0.030 | 0.028 | | | 0.029 | 0.001 | 0.034 |
| 41 | | | | | | | | | |

# Nickel

## Sample A

### 0.75 ± 0.14 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 4 | 0.707 | 0.695 | 0.748 | 0.637 | | 0.697 | 0.046 | 0.066 |
| 2 | 5 | 0.681 | 0.453 | 0.711 | 0.822 | 0.758 | 0.685 | 0.140 | 0.205 |
| 3 | 5 | 0.660 | 0.860 | 0.690 | 0.630 | 0.770 | 0.722 | 0.093 | 0.129 |
| 4 | 5 | 0.801 | 0.797 | 0.785 | 0.763 | 0.810 | 0.791 | 0.018 | 0.023 |
| 5 | | | | | | | | | |
| 6 | 5 | 0.800 | 0.800 | 0.790 | 0.840 | 0.670 | 0.780 | 0.064 | 0.083 |
| 7* | 5 | 1.100 | 1.230 | 1.590 | 1.160 | 1.450 | 1.306 | 0.207 | 0.158 |
| 8 | 5 | 0.681 | 0.655 | 0.660 | 0.660 | 0.670 | 0.665 | 0.010 | 0.016 |
| 9* | 5 | 0.950 | 0.981 | 0.955 | 0.958 | 0.963 | 0.961 | 0.012 | 0.012 |
| 10* | 5 | 9.330 | 9.180 | 9.510 | 9.270 | 9.440 | 9.346 | 0.132 | 0.014 |
| 11 | 3 | 0.810 | 0.770 | 0.760 | | | 0.780 | 0.026 | 0.034 |
| 12 | 5 | 0.670 | 0.640 | 0.640 | 0.660 | 0.690 | 0.660 | 0.021 | 0.032 |
| 13 | | | | | | | | | |
| 14 | 5 | 0.819 | 0.807 | 0.771 | 0.801 | 0.762 | 0.792 | 0.024 | 0.031 |
| 15 | 1 | 0.880 | | | | | 0.880 | | |
| 16 | 5 | 0.645 | 0.761 | 0.695 | 0.718 | 0.430 | 0.650 | 0.130 | 0.200 |
| 17 | 5 | 0.721 | 0.731 | 0.738 | 0.727 | 0.732 | 0.730 | 0.006 | 0.009 |
| 18 | 5 | 0.920 | 0.940 | 0.860 | 0.920 | 0.870 | 0.902 | 0.035 | 0.039 |
| 19 | 5 | 0.700 | 0.720 | 0.710 | 0.770 | 0.820 | 0.744 | 0.050 | 0.068 |
| 20 | 5 | 0.760 | 0.730 | 0.700 | 0.700 | 0.700 | 0.718 | 0.027 | 0.037 |
| 21 | 1 | 0.426 | | | | | 0.426 | | |
| 22* | 3 | 7.000 | 4.000 | 3.000 | | | 4.667 | 2.082 | 0.446 |
| 23 | 5 | 0.818 | 0.842 | 0.792 | 0.813 | 0.811 | 0.815 | 0.018 | 0.022 |
| 24 | | | | | | | | | |
| 25 | 5 | 0.710 | 0.660 | 0.740 | 0.750 | 0.700 | 0.712 | 0.036 | 0.050 |
| 26* | 5 | 0.300 | 0.320 | 0.350 | 0.250 | 0.270 | 0.298 | 0.040 | 0.133 |
| 27 | 5 | 0.716 | 0.742 | 0.748 | 0.735 | 0.735 | 0.735 | 0.012 | 0.016 |
| 28 | 5 | 0.637 | 0.660 | 0.698 | 0.640 | 0.660 | 0.659 | 0.024 | 0.037 |
| 29 | 5 | 0.768 | 0.789 | 0.962 | 0.897 | 0.919 | 0.867 | 0.077 | 0.091 |
| 30 | 5 | 0.708 | 0.897 | 0.876 | 0.854 | 0.880 | 0.843 | 0.077 | 0.091 |
| 31 | | | | | | | | | |
| 32* | 5 | 0.572 | 0.565 | 0.562 | 0.584 | 0.583 | 0.573 | 0.010 | 0.018 |
| 33 | 5 | 0.758 | 0.771 | 0.776 | 0.773 | 0.788 | 0.773 | 0.011 | 0.014 |
| 34* | 5 | 0.514 | 0.500 | 0.557 | 0.486 | 0.607 | 0.533 | 0.049 | 0.092 |
| 35 | 5 | 0.745 | 0.755 | 0.755 | 0.749 | 0.752 | 0.751 | 0.004 | 0.006 |
| 36 | | | | | | | | | |
| 37 | 5 | 0.952 | 0.826 | 0.867 | 0.859 | 0.811 | 0.863 | 0.055 | 0.064 |
| 38 | | | | | | | | | |
| 39 | 5 | 0.814 | 1.108 | 1.194 | 0.891 | 0.211 | 0.844 | 0.386 | 0.458 |
| 40 | 5 | 0.758 | 0.742 | 0.721 | 0.758 | 0.760 | 0.748 | 0.017 | 0.022 |
| 41 | 5 | 0.710 | 0.700 | 0.730 | 0.670 | 0.750 | 0.712 | 0.030 | 0.043 |

## Sample B

### 0.49 ± 0.11 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 4 | 0.484 | 0.445 | 0.463 | 0.479 | | 0.468 | 0.018 | 0.038 |
| 2* | 5 | 0.194 | 0.384 | 0.276 | 0.309 | 0.419 | 0.316 | 0.089 | 0.282 |
| 3* | 5 | 0.230 | 0.290 | 0.320 | 0.520 | 0.370 | 0.346 | 0.110 | 0.317 |
| 4 | 5 | 0.523 | 0.523 | 0.520 | 0.521 | 0.516 | 0.521 | 0.003 | 0.006 |
| 5 | | | | | | | | | |
| 6 | | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | | | |
| 7 | 5 | 0.510 | 0.510 | 0.550 | 0.620 | 0.480 | 0.534 | 0.054 | 0.101 |
| 8 | 5 | 0.489 | 0.459 | 0.459 | 0.482 | 0.461 | 0.470 | 0.014 | 0.031 |
| 9* | 5 | 1.045 | 1.048 | 1.050 | 1.051 | 1.049 | 1.049 | 0.002 | 0.002 |
| 10* | 5 | 9.500 | 9.350 | 9.580 | 9.430 | 9.600 | 9.492 | 0.104 | 0.011 |
| 11 | 2 | 0.500 | 0.420 | | | | 0.460 | | |
| 12 | 5 | 0.430 | 0.430 | 0.460 | 0.510 | 0.460 | 0.458 | 0.033 | 0.071 |
| 13 | | | | | | | | | |
| 14 | 5 | 0.581 | 0.491 | 0.543 | 0.532 | 0.495 | 0.528 | 0.037 | 0.070 |
| 15 | 1 | 0.530 | | | | | 0.530 | | |
| 16 | 5 | 0.287 | 0.316 | 0.373 | 0.458 | 0.359 | 0.359 | 0.065 | 0.182 |
| 17 | 5 | 0.454 | 0.452 | 0.460 | 0.462 | 0.469 | 0.459 | 0.007 | 0.015 |
| 18 | 5 | 0.550 | 0.590 | 0.520 | 0.560 | 0.550 | 0.554 | 0.025 | 0.045 |
| 19 | 5 | 0.460 | 0.450 | 0.490 | 0.500 | 0.440 | 0.468 | 0.026 | 0.055 |
| 20 | 5 | 0.500 | 0.500 | 0.500 | 0.420 | 0.460 | 0.476 | 0.036 | 0.075 |
| 21 | | | | | | | | | |
| 22 | 5 | 30.000 | 7.000 | 25.000 | 40.000 | <4 | | | |
| 23 | 5 | 0.543 | 0.456 | 0.511 | 0.466 | 0.460 | 0.487 | 0.038 | 0.078 |
| 24 | | | | | | | | | |
| 25 | | <0.5 | 0.560 | 0.540 | <0.5 | <0.5 | | | |
| 26* | 5 | 0.130 | 0.160 | 0.150 | 0.120 | 0.170 | 0.146 | 0.021 | 0.142 |
| 27 | 5 | 0.485 | 0.501 | 0.492 | 0.507 | 0.501 | 0.497 | 0.009 | 0.017 |
| 28 | 4 | 0.420 | 0.400 | 0.580 | 0.350 | | 0.438 | 0.099 | 0.227 |
| 29 | 5 | 0.504 | 0.497 | 0.504 | 0.657 | 0.527 | 0.508 | 0.068 | 0.128 |
| 30 | 5 | 0.403 | 0.442 | 0.445 | 0.436 | 0.455 | 0.436 | 0.020 | 0.045 |
| 31 | | | | | | | | | |
| 32 | 5 | 0.389 | 0.410 | 0.380 | 0.387 | 0.362 | 0.386 | 0.017 | 0.045 |
| 33 | 5 | 0.512 | 0.527 | 0.528 | 0.523 | 0.552 | 0.528 | 0.015 | 0.028 |
| 34 | 5 | 0.664 | 0.557 | 0.607 | 0.671 | 0.481 | 0.596 | 0.079 | 0.133 |
| 35 | 5 | 0.509 | 0.509 | 0.507 | 0.509 | 0.511 | 0.509 | 0.001 | 0.003 |
| 36 | | | | | | | | | |
| 37 | 5 | 0.506 | 0.506 | 0.494 | 0.537 | 0.518 | 0.512 | 0.016 | 0.032 |
| 38 | | | | | | | | | |
| 39* | 5 | 2.393 | 1.475 | 1.193 | 2.011 | 1.918 | 1.798 | 0.470 | 0.261 |
| 40 | 5 | 0.489 | 0.450 | 0.494 | 0.504 | 0.451 | 0.478 | 0.025 | 0.053 |
| 41 | 5 | 0.460 | 0.420 | 0.500 | 0.490 | 0.430 | 0.480 | 0.035 | 0.077 |

# Copper

## Sample A

### 0.68 ± 0.29 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 3 | 0.754 | 0.782 | 0.806 | | | 0.781 | 0.026 | 0.033 |
| 2 | 5 | 0.651 | 0.470 | 0.352 | 0.283 | 0.214 | 0.394 | 0.172 | 0.437 |
| 3* | 5 | 1.040 | 1.280 | 1.150 | 1.000 | 1.090 | 1.112 | 0.109 | 0.098 |
| 4 | 5 | 0.772 | 0.759 | 0.759 | 0.717 | 0.772 | 0.756 | 0.023 | 0.030 |
| 5 | | | | | | | | | |
| 6 | 5 | 0.750 | 0.770 | 0.710 | 0.730 | 0.720 | 0.736 | 0.024 | 0.033 |
| 7* | 5 | 2.080 | 1.970 | 1.880 | 1.720 | 1.950 | 1.920 | 0.133 | 0.069 |
| 8 | 5 | 0.639 | 0.583 | 0.580 | 0.620 | 0.620 | 0.608 | 0.026 | 0.042 |
| 9* | 5 | 0.281 | 0.292 | 0.290 | 0.280 | 0.285 | 0.286 | 0.005 | 0.019 |
| 10* | 5 | 8.400 | 8.550 | 8.340 | 8.260 | 8.480 | 8.406 | 0.114 | 0.014 |
| 11 | 3 | 0.810 | 0.710 | 0.640 | | | 0.720 | 0.085 | 0.119 |
| 12 | 5 | 0.740 | 0.740 | 0.740 | 0.760 | 0.750 | 0.746 | 0.009 | 0.012 |
| 13 | | | | | | | | | |
| 14 | 5 | 0.652 | 0.657 | 0.636 | 0.644 | 0.650 | 0.648 | 0.008 | 0.012 |
| 15 | 1 | 0.820 | | | | | 0.820 | | |
| 16 | 5 | 0.756 | 0.859 | 0.800 | 0.748 | 1.370 | 0.907 | 0.263 | 0.290 |
| 17 | 5 | 0.515 | 0.513 | 0.510 | 0.498 | 0.502 | 0.508 | 0.007 | 0.014 |
| 18 | 5 | 0.880 | 0.740 | 0.700 | 0.860 | 0.800 | 0.796 | 0.077 | 0.096 |
| 19 | 5 | 0.700 | 0.710 | 0.690 | 0.750 | 0.780 | 0.726 | 0.038 | 0.052 |
| 20 | 5 | 0.800 | 0.740 | 0.750 | 0.730 | 0.750 | 0.754 | 0.027 | 0.036 |
| 21 | 1 | 0.780 | | | | | 0.780 | | |
| 22* | 5 | 9.000 | 10.000 | 7.000 | 9.000 | 9.000 | 8.800 | 1.095 | 0.124 |
| 23 | 5 | 0.717 | 0.709 | 0.686 | 0.717 | 0.725 | 0.711 | 0.015 | 0.021 |
| 24 | | | | | | | | | |
| 25 | 5 | 0.600 | 0.580 | 0.550 | 0.600 | 0.620 | 0.590 | 0.026 | 0.045 |
| 26 | 5 | 0.440 | 0.410 | 0.440 | 0.330 | 0.370 | 0.398 | 0.048 | 0.120 |
| 27 | 5 | 0.704 | 0.719 | 0.726 | 0.708 | 0.712 | 0.714 | 0.009 | 0.012 |
| 28 | 2 | 0.650 | 0.650 | | | | 0.650 | | |
| 29 | 5 | 0.724 | 0.686 | 0.724 | 0.667 | 0.771 | 0.714 | 0.040 | 0.056 |
| 30 | 5 | 0.598 | 0.580 | 0.532 | 0.565 | 0.565 | 0.568 | 0.024 | 0.043 |
| 31 | 4 | 0.404 | 0.365 | 0.340 | 0.360 | | 0.367 | 0.027 | 0.073 |
| 32 | 5 | 0.715 | 0.714 | 0.763 | 0.776 | 0.696 | 0.733 | 0.035 | 0.047 |
| 33 | 5 | 0.719 | 0.676 | 0.670 | 0.696 | 0.686 | 0.689 | 0.019 | 0.028 |
| 34 | 5 | 0.651 | 0.720 | 0.708 | 0.712 | 0.624 | 0.683 | 0.043 | 0.063 |
| 35 | 5 | 0.692 | 0.692 | 0.699 | 0.684 | 0.682 | 0.690 | 0.007 | 0.010 |
| 36 | 5 | 1.010 | 1.040 | 1.070 | 1.040 | 1.040 | 1.040 | 0.021 | 0.020 |
| 37 | 5 | 0.909 | 0.785 | 0.851 | 0.846 | 0.792 | 0.837 | 0.050 | 0.060 |
| 38 | | | | | | | | | |
| 39* | 5 | 1.241 | 1.593 | 1.145 | 1.286 | 1.418 | 1.337 | 0.174 | 0.130 |
| 40 | 5 | 0.732 | 0.785 | 0.780 | 0.757 | 0.692 | 0.749 | 0.038 | 0.051 |
| 41 | 5 | 0.720 | 0.690 | 0.710 | 0.670 | 0.730 | 0.704 | 0.024 | 0.004 |

## Sample B

### 0.57 ± 0.17 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 3 | 0.763 | 0.694 | 0.730 | | | 0.729 | 0.035 | 0.047 |
| 2 | 5 | 0.585 | 0.285 | 0.388 | 0.350 | 0.396 | 0.401 | 0.112 | 0.279 |
| 3* | 5 | 1.120 | 0.970 | 0.680 | 0.940 | 0.890 | 0.920 | 0.159 | 0.173 |
| 4 | 5 | 0.628 | 0.627 | 0.631 | 0.614 | 0.617 | 0.623 | 0.007 | 0.012 |
| 5 | | | | | | | | | |
| 6 | 5 | 0.630 | 0.660 | 0.680 | 0.700 | 0.640 | 0.662 | 0.029 | 0.043 |
| 7* | 5 | 1.630 | 1.700 | 1.460 | 1.730 | 1.540 | 1.612 | 0.112 | 0.070 |
| 8 | 5 | 0.491 | 0.491 | 0.496 | 0.476 | 0.496 | 0.490 | 0.008 | 0.017 |
| 9* | 5 | 0.327 | 0.325 | 0.330 | 0.331 | 0.331 | 0.329 | 0.003 | 0.008 |
| 10* | 5 | 7.270 | 7.080 | 7.340 | 7.100 | 7.320 | 7.222 | 0.123 | 0.017 |
| 11 | 2 | 0.460 | 0.480 | | | | | | |
| 12 | 5 | 0.630 | 0.670 | 0.570 | 0.600 | 0.600 | 0.614 | 0.038 | 0.062 |
| 13 | | | | | | | | | |
| 14 | 5 | 0.534 | 0.547 | 0.560 | 0.532 | 0.541 | 0.543 | 0.011 | 0.021 |
| 15 | 1 | 0.670 | | | | | 0.670 | | |
| 16 | 5 | 0.567 | 0.626 | 0.562 | 0.564 | 0.580 | 0.580 | 0.027 | 0.046 |
| 17 | 5 | 0.492 | 0.511 | 0.505 | 0.504 | 0.511 | 0.505 | 0.008 | 0.015 |
| 18 | | <0.65 | <0.66 | <0.65 | <0.65 | <0.65 | | | |
| 19 | 5 | 0.580 | 0.580 | 0.630 | 0.610 | 0.580 | 0.596 | 0.023 | 0.039 |
| 20 | 5 | 0.630 | 0.650 | 0.620 | 0.580 | 0.570 | 0.610 | 0.034 | 0.056 |
| 21 | 1 | 1.240 | | | | | 1.240 | | |
| 22 | | <1 | <1 | <1 | <1 | <1 | | | |
| 23 | 5 | 0.610 | 0.617 | 0.633 | 0.626 | 0.633 | 0.624 | 0.010 | 0.016 |
| 24 | | | | | | | | | |
| 25 | 5 | 0.400 | 0.460 | 0.430 | 0.430 | 0.430 | 0.430 | 0.021 | 0.049 |
| 26* | 5 | 0.270 | 0.330 | 0.320 | 0.340 | 0.280 | 0.308 | 0.031 | 0.101 |
| 27 | 5 | 0.575 | 0.591 | 0.582 | 0.592 | 0.586 | 0.585 | 0.007 | 0.012 |
| 28 | 4 | 0.367 | 0.390 | 0.420 | 0.500 | | 0.419 | 0.058 | 0.138 |
| 29 | 5 | 0.570 | 0.663 | 0.681 | 0.675 | 0.681 | 0.654 | 0.048 | 0.073 |
| 30 | 5 | 0.498 | 0.545 | 0.499 | 0.532 | 0.508 | 0.516 | 0.021 | 0.041 |
| 31 | 5 | 0.512 | 0.585 | 0.630 | 0.580 | 0.545 | 0.570 | 0.044 | 0.078 |
| 32 | 5 | 0.548 | 0.595 | 0.595 | 0.586 | 0.570 | 0.579 | 0.020 | 0.035 |
| 33 | 5 | 0.577 | 0.560 | 0.578 | 0.560 | 0.600 | 0.575 | 0.016 | 0.029 |
| 34 | 5 | 0.400 | 0.411 | 0.446 | 0.372 | 0.478 | 0.421 | 0.041 | 0.098 |
| 35 | 5 | 0.588 | 0.616 | 0.577 | 0.598 | 0.574 | 0.591 | 0.017 | 0.029 |
| 36* | 5 | 0.880 | 0.940 | 0.910 | 0.900 | 0.900 | 0.906 | 0.022 | 0.024 |
| 37 | 5 | 0.636 | 0.646 | 0.639 | 0.674 | 0.657 | 0.650 | 0.015 | 0.024 |
| 38 | | | | | | | | | |
| 39* | 5 | 1.335 | 1.618 | 1.580 | 1.411 | 1.528 | 1.494 | 0.118 | 0.079 |
| 40 | 5 | 0.581 | 0.621 | 0.590 | 0.669 | 0.634 | 0.619 | 0.035 | 0.057 |
| 41 | 5 | 0.600 | 0.560 | 0.650 | 0.640 | 0.560 | 0.602 | 0.043 | 0.071 |

# Zinc

## Sample A

### 0.49 ± 0.34 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 3 | 0.782 | 0.722 | 0.742 | | | 0.749 | 0.031 | 0.041 |
| 2 | 3 | 0.292 | 0.313 | 0.420 | | | 0.342 | 0.069 | 0.201 |
| 3 | 5 | 0.330 | 0.750 | 0.410 | 0.280 | 0.330 | 0.420 | 0.190 | 0.453 |
| 4 | 5 | 0.459 | 0.372 | 0.427 | 0.405 | 0.429 | 0.418 | 0.032 | 0.077 |
| 5 | | | | | | | | | |
| 6 | | <1 | <1 | <1 | <1 | <1 | | | |
| 7* | 5 | 1.120 | 1.040 | 0.940 | 0.840 | 1.080 | 1.004 | 0.113 | 0.113 |
| 8 | 5 | 0.395 | 0.400 | 0.413 | 0.372 | 0.372 | 0.390 | 0.018 | 0.046 |
| 9 | 5 | 0.663 | 0.663 | 0.659 | 0.662 | 0.663 | 0.662 | 0.002 | 0.003 |
| 10 | 5 | 0.210 | 0.200 | 0.170 | 0.230 | 0.210 | 0.204 | 0.022 | 0.107 |
| 11 | 2 | 0.570 | 0.460 | | | | 0.520 | | |
| 12 | 5 | 0.770 | 0.720 | 0.680 | 0.750 | 0.820 | 0.748 | 0.053 | 0.070 |
| 13 | 5 | 0.550 | 0.770 | 0.606 | 0.833 | 0.675 | 0.687 | 0.116 | 0.169 |
| 14 | 5 | 0.400 | 0.460 | 0.380 | 0.390 | 0.420 | 0.410 | 0.032 | 0.077 |
| 15 | | <0.1 | | | | | | | |
| 16 | 5 | 0.352 | 0.352 | 0.332 | 0.332 | 1.050 | 0.484 | 0.317 | 0.655 |
| 17 | | <0.4 | <0.4 | <0.4 | <0.4 | <0.4 | | | |
| 18 | 5 | 3.900 | <2.5 | 3.000 | 2.600 | <2.5 | | | |
| 19 | 5 | 0.270 | 0.340 | 0.360 | 0.330 | 0.320 | 0.324 | 0.034 | 0.104 |
| 20 | 5 | 0.450 | 0.450 | 0.400 | 0.350 | 0.300 | 0.390 | 0.065 | 0.167 |
| 21 | | | | | | | | | |
| 22* | 5 | 10.000 | 11.000 | 4.000 | 3.000 | 3.000 | 6.200 | 3.962 | 0.639 |
| 23 | 5 | 0.408 | 0.426 | 0.371 | 0.400 | 0.425 | 0.406 | 0.023 | 0.055 |
| 24 | | | | | | | | | |
| 25 | | <1 | <1 | <1 | <1 | <1 | | | |
| 26 | 5 | 0.220 | 0.310 | 0.230 | 0.270 | 0.220 | 0.250 | 0.039 | 0.157 |
| 27 | 5 | 0.456 | 0.459 | 0.456 | 0.451 | 0.429 | 0.450 | 0.012 | 0.027 |
| 28 | 2 | 0.514 | 0.526 | | | | 0.520 | | |
| 29 | 5 | 0.803 | 0.38 | 0.751 | 0.567 | 0.843 | 0.740 | 0.106 | 0.143 |
| 30 | 5 | 0.436 | 0.386 | 0.409 | 0.400 | 0.400 | 0.406 | 0.019 | 0.046 |
| 31 | | | | | | | | | |
| 32 | 5 | 0.766 | 0.642 | 0.645 | 0.661 | 0.714 | 0.686 | 0.053 | 0.078 |
| 33 | | | | | | | | | |
| 34* | 5 | 2.230 | 1.860 | 1.810 | 1.960 | 1.940 | 1.960 | 0.163 | 0.083 |
| 35 | 5 | 0.426 | 0.442 | 0.551 | 0.455 | 0.486 | 0.472 | 0.049 | 0.105 |
| 36* | 5 | 2.100 | 2.200 | 1.600 | 2.200 | 1.700 | 1.960 | 0.288 | 0.147 |
| 37 | 5 | 0.581 | 0.510 | 0.557 | 0.567 | 0.497 | 0.542 | 0.037 | 0.068 |
| 38 | 1 | 2.000 | | | | | 2.000 | | |
| 39* | 5 | 17.506 | 19.341 | 18.191 | 17.811 | 19.002 | 18.370 | 0.780 | 0.042 |
| 40 | | | | | | | | | |
| 41 | 5 | 0.510 | 0.420 | 0.590 | 0.450 | 0.560 | 0.506 | 0.072 | 0.142 |

## Sample B

### 0.59 ± 0.35 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 4 | 0.881 | 0.861 | 0.941 | 1.000 | | 0.921 | 0.063 | 0.068 |
| 2 | 3 | 0.609 | 0.647 | 0.491 | | | 0.582 | 0.081 | 0.140 |
| 3 | 5 | 0.520 | 0.630 | 0.730 | 0.760 | 0.850 | 0.698 | 0.127 | 0.182 |
| 4 | 5 | 0.653 | 0.572 | 0.552 | 0.521 | 0.598 | 0.579 | 0.050 | 0.086 |
| 5 | | | | | | | | | |
| 6 | | <1 | <1 | <1 | <1 | <1 | | | |
| 7* | 5 | 1.850 | 1.580 | 1.870 | 1.500 | 1.350 | 1.630 | 0.226 | 0.138 |
| 8 | 5 | 0.402 | 0.405 | 0.416 | 0.399 | 0.406 | 0.406 | 0.006 | 0.016 |
| 9 | 5 | 0.731 | 0.731 | 0.731 | 0.729 | 0.733 | 0.731 | 0.001 | 0.002 |
| 10 | 5 | 0.290 | 0.260 | 0.350 | 0.280 | 0.330 | 0.302 | 0.037 | 0.123 |
| 11 | 2 | 0.470 | 0.440 | | | | 0.460 | | |
| 12 | 5 | 0.820 | 0.900 | 0.830 | 0.790 | 0.800 | 0.828 | 0.043 | 0.052 |
| 13* | 5 | 1.766 | 1.312 | 1.514 | 0.833 | 1.210 | 1.327 | 0.348 | 0.263 |
| 14 | 5 | 0.480 | 0.410 | 0.580 | 0.420 | 0.440 | 0.466 | 0.069 | 0.148 |
| 15 | 1 | 0.440 | | | | | 0.440 | | |
| 16 | 5 | 0.469 | 0.516 | 0.381 | 0.442 | 0.452 | 0.452 | 0.049 | 0.108 |
| 17 | | <0.4 | <0.4 | <0.4 | <0.4 | <0.4 | | | |
| 18 | | <2.5 | <2.5 | <2.5 | <2.5 | <2.5 | | | |
| 19 | 5 | 0.460 | 0.410 | 0.640 | 0.560 | 0.580 | 0.530 | 0.093 | 0.176 |
| 20 | 5 | 0.400 | 0.500 | 0.500 | 0.450 | 0.470 | 0.464 | 0.042 | 0.090 |
| 21 | 1 | 18.300 | | | | | 18.300 | | |
| 22* | 5 | 5.000 | 3.000 | 2.000 | 3.000 | 2.000 | 3.000 | 1.225 | 0.408 |
| 23 | 5 | 0.627 | 0.597 | 0.599 | 0.662 | 0.629 | 0.623 | 0.027 | 0.043 |
| 24 | | | | | | | | | |
| 25 | | <1 | <1 | <1 | <1 | <1 | | | |
| 26* | 5 | 0.110 | 0.130 | 0.100 | 0.100 | 0.090 | 0.106 | 0.015 | 0.143 |
| 27 | 5 | 0.465 | 0.485 | 0.472 | 0.492 | 0.484 | 0.480 | 0.011 | 0.023 |
| 28 | 4 | 0.370 | 0.395 | 0.326 | 0.425 | | 0.379 | 0.042 | 0.111 |
| 29 | 5 | 0.773 | 0.719 | 0.666 | 0.539 | 0.654 | 0.670 | 0.087 | 0.130 |
| 30 | 5 | 0.445 | 0.442 | 0.445 | 0.436 | 0.455 | 0.445 | 0.007 | 0.015 |
| 31 | | | | | | | | | |
| 32 | 5 | 0.861 | 0.771 | 0.751 | 0.845 | 0.904 | 0.826 | 0.064 | 0.077 |
| 33 | | | | | | | | | |
| 34* | 5 | 1.750 | 1.500 | 1.460 | 1.340 | 1.280 | 1.466 | 0.182 | 0.124 |
| 35 | 5 | 0.807 | 0.792 | 0.681 | 0.732 | 0.942 | 0.791 | 0.098 | 0.124 |
| 36* | 5 | 2.100 | 2.000 | 1.800 | 2.000 | 1.900 | 1.960 | 0.114 | 0.058 |
| 37 | 5 | 0.622 | 0.629 | 0.603 | 0.640 | 0.649 | 0.629 | 0.018 | 0.028 |
| 38 | | | | | | | | | |
| 39* | 5 | 28.121 | 19.343 | 25.817 | 20.161 | 23.500 | 23.388 | 3.711 | 0.159 |
| 40 | | | | | | | | | |
| 41 | 5 | 0.540 | 0.650 | 0.600 | 0.620 | 0.580 | 0.598 | 0.041 | 0.089 |

# Arsenic

## Sample A

### 0.33 ± 0.11 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | 5 | 0.100 | 0.390 | 0.650 | 0.390 | 0.650 | 0.436 | 0.228 | 0.524 |
| 4 | | | | | | | | | |
| 5 | | | | | | | | | |
| 6 | 5 | 0.290 | 0.340 | 0.330 | 0.310 | 0.330 | 0.320 | 0.020 | 0.062 |
| 7 | 5 | 0.330 | 0.290 | 0.310 | 0.290 | 0.290 | 0.302 | 0.018 | 0.059 |
| 8 | | | | | | | | | |
| 9 | | | | | | | | | |
| 10 | | | | | | | | | |
| 11 | 3 | 0.350 | 0.290 | 0.320 | | | 0.320 | 0.030 | 0.094 |
| 12 | | | | | | | | | |
| 13 | | | | | | | | | |
| 14 | | | | | | | | | |
| 15 | 1 | 0.210 | | | | | 0.210 | | |
| 16 | | | | | | | | | |
| 17 | | <1 | <1 | <1 | <1 | <1 | | | |
| 18 | | | | | | | | | |
| 19 | 5 | 0.370 | 0.340 | 0.350 | 0.350 | 0.360 | 0.354 | 0.011 | 0.032 |
| 20 | 5 | 0.300 | 0.324 | 0.324 | 0.268 | 0.284 | 0.300 | 0.025 | 0.082 |
| 21 | 1 | 0.410 | | | | | 0.410 | | |
| 22 | | | | | | | | | |
| 23 | | <1 | <1 | <1 | <1 | <1 | | | |
| 24 | | <1 | <1 | <1 | <1 | <1 | | | |
| 25 | | <1 | <1 | <1 | <1 | <1 | | | |
| 26 | | | | | | | | | |
| 27 | 5 | 0.376 | 0.286 | 0.355 | 0.333 | 0.322 | 0.334 | 0.034 | 0.102 |
| 28 | | | | | | | | | |
| 29 | | | | | | | | | |
| 30 | | | | | | | | | |
| 31 | | | | | | | | | |
| 32 | | | | | | | | | |
| 33 | | | | | | | | | |
| 34 | | | | | | | | | |
| 35 | | | | | | | | | |
| 36 | | | | | | | | | |
| 37 | | | | | | | | | |
| 38 | 1 | 0.380 | | | | | 0.380 | | |
| 39 | | | | | | | | | |
| 40 | 5 | 0.329 | 0.268 | 0.276 | 0.268 | 0.281 | 0.284 | 0.026 | 0.090 |
| 41 | | | | | | | | | |

## Sample B

### 0.66 ± 0.09 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | 5 | 0.780 | 0.650 | 0.520 | 0.910 | 0.390 | 0.650 | 0.206 | 0.316 |
| 4 | | | | | | | | | |
| 5 | | | | | | | | | |
| 6 | 5 | 0.650 | 0.670 | 0.680 | 0.670 | 0.590 | 0.652 | 0.036 | 0.056 |
| 7 | 5 | 0.720 | 0.680 | 0.680 | 0.710 | 0.720 | 0.702 | 0.020 | 0.029 |
| 8 | | | | | | | | | |
| 9 | | | | | | | | | |
| 10 | | | | | | | | | |
| 11 | 2 | 0.680 | 0.640 | | | | 0.660 | | |
| 12 | | | | | | | | | |
| 13 | | | | | | | | | |
| 14 | | | | | | | | | |
| 15 | 1 | 0.500 | | | | | 0.500 | | |
| 16 | | | | | | | | | |
| 17 | | <1 | <1 | <1 | <1 | <1 | | | |
| 18 | | | | | | | | | |
| 19 | 5 | 0.690 | 0.730 | 0.730 | 0.730 | 0.710 | 0.718 | 0.018 | 0.025 |
| 20 | 5 | 0.658 | 0.634 | 0.604 | 0.624 | 0.586 | 0.621 | 0.028 | 0.045 |
| 21 | 1 | 0.940 | | | | | 0.940 | | |
| 22 | | | | | | | | | |
| 23 | | <1 | <1 | <1 | <1 | <1 | | | |
| 24 | | <1 | <1 | <1 | <1 | <1 | | | |
| 25 | | <1 | <1 | <1 | <1 | <1 | | | |
| 26 | | | | | | | | | |
| 27 | 5 | 0.653 | 0.675 | 0.705 | 0.684 | 0.628 | 0.669 | 0.030 | 0.044 |
| 28 | | | | | | | | | |
| 29 | | | | | | | | | |
| 30 | | | | | | | | | |
| 31 | | | | | | | | | |
| 32 | | | | | | | | | |
| 33 | | | | | | | | | |
| 34 | | | | | | | | | |
| 35 | | | | | | | | | |
| 36 | | | | | | | | | |
| 37 | | | | | | | | | |
| 38 | 1 | 0.700 | | | | | 0.380 | | |
| 39 | | | | | | | | | |
| 40 | 5 | 0.579 | 0.658 | 0.628 | 0.588 | 0.698 | 0.630 | 0.049 | 0.078 |
| 41 | | | | | | | | | |

# Cadmium

## Sample A

### 0.013 ± 0.007 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 4 | 0.015 | 0.015 | 0.016 | 0.014 | | 0.015 | 0.001 | 0.054 |
| 2 | 5 | 0.011 | 0.013 | 0.011 | 0.013 | 0.014 | 0.012 | 0.001 | 0.108 |
| 3 | 5 | 0.011 | 0.018 | 0.012 | 0.012 | 0.010 | 0.013 | 0.003 | 0.248 |
| 4 | | | | | | | | | |
| 5 | 5 | 0.010 | 0.010 | 0.009 | 0.010 | 0.010 | 0.010 | 0.000 | 0.046 |
| 6 | 5 | 0.020 | 0.020 | 0.020 | 0.021 | 0.029 | 0.022 | 0.004 | 0.179 |
| 7* | 5 | 0.060 | 0.040 | 0.030 | 0.050 | 0.040 | 0.044 | 0.011 | 0.259 |
| 8 | 5 | 0.009 | 0.009 | 0.011 | 0.011 | 0.010 | 0.010 | 0.001 | 0.100 |
| 9* | 5 | 0.035 | 0.035 | 0.035 | 0.035 | 0.035 | 0.035 | 0.000 | 0.000 |
| 10* | 5 | 0.114 | 0.120 | 0.098 | 0.110 | 0.125 | 0.113 | 0.010 | 0.091 |
| 11 | 3 | 0.015 | 0.014 | 0.014 | | | 0.014 | 0.001 | 0.040 |
| 12 | 5 | 0.013 | 0.013 | 0.013 | 0.013 | 0.013 | 0.013 | 0.000 | 0.000 |
| 13* | 5 | 0.062 | 0.060 | 0.083 | 0.068 | 0.069 | 0.068 | 0.009 | 0.132 |
| 14 | 5 | 0.009 | 0.010 | 0.009 | 0.009 | 0.008 | 0.009 | 0.001 | 0.079 |
| 15 | 1 | 0.011 | | | | | 0.110 | | |
| 16 | | <0.018 | <0.018 | <0.018 | <0.018 | <0.018 | | | |
| 17 | | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | | | |
| 18 | | <0.035 | <0.035 | <0.035 | <0.035 | <0.035 | | | |
| 19 | 5 | 0.013 | 0.013 | 0.015 | 0.012 | 0.013 | 0.013 | 0.001 | 0.083 |
| 20 | 5 | 0.014 | 0.014 | 0.014 | 0.015 | 0.015 | 0.014 | 0.001 | 0.038 |
| 21 | 1 | 0.060 | | | | | | | |
| 22 | | <2 | <2 | <2 | <2 | <2 | | | |
| 23 | | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | | | |
| 24 | | | | | | | | | |
| 25 | | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | | | |
| 26* | 5 | 0.059 | 0.060 | 0.048 | 0.045 | 0.051 | 0.053 | 0.007 | 0.127 |
| 27 | 5 | 0.016 | 0.016 | 0.017 | 0.016 | 0.016 | 0.016 | 0.000 | 0.028 |
| 28 | 2 | 0.016 | 0.014 | | | | 0.015 | | |
| 29 | 5 | 0.020 | 0.016 | 0.015 | 0.014 | 0.016 | 0.016 | 0.002 | 0.141 |
| 30 | 5 | 0.011 | 0.013 | 0.007 | 0.006 | 0.011 | 0.010 | 0.003 | 0.309 |
| 31 | 5 | 0.015 | 0.013 | 0.010 | 0.015 | 0.013 | 0.013 | 0.002 | 0.155 |
| 32 | 5 | 0.015 | 0.013 | 0.016 | 0.014 | 0.016 | 0.015 | 0.001 | 0.088 |
| 33 | | | | | | | | | |
| 34* | 5 | 0.033 | 0.029 | 0.028 | 0.031 | 0.032 | 0.031 | 0.002 | 0.068 |
| 35 | 5 | 0.008 | 0.006 | 0.012 | 0.009 | 0.009 | 0.009 | 0.002 | 0.246 |
| 36 | 5 | 0.013 | 0.014 | 0.013 | 0.016 | 0.013 | 0.014 | 0.001 | 0.094 |
| 37 | 5 | 0.016 | 0.015 | 0.017 | 0.016 | 0.015 | 0.016 | 0.001 | 0.053 |
| 38 | 1 | 0.110 | | | | | | | |
| 39* | 5 | 0.056 | 0.064 | 0.058 | 0.067 | 0.049 | 0.059 | 0.007 | 0.120 |
| 40 | 1 | 0.102 | | | | | 0.102 | | |
| 41 | 5 | 0.013 | 0.013 | 0.010 | 0.016 | 0.013 | 0.013 | 0.002 | 0.163 |

## Sample B

### 0.023 ± 0.011 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 3 | 0.022 | 0.022 | 0.024 | | | 0.023 | 0.001 | 0.051 |
| 2 | 5 | 0.018 | 0.016 | 0.014 | 0.015 | 0.018 | 0.016 | 0.002 | 0.110 |
| 3 | 5 | 0.015 | 0.025 | 0.019 | 0.021 | 0.015 | 0.019 | 0.004 | 0.223 |
| 4 | | | | | | | | | |
| 5 | 5 | 0.018 | 0.018 | 0.019 | 0.020 | 0.019 | 0.019 | 0.001 | 0.045 |
| 6 | 5 | 0.028 | 0.028 | 0.033 | 0.020 | 0.020 | 0.026 | 0.006 | 0.220 |
| 7 | 5 | 0.010 | 0.020 | 0.030 | 0.030 | 0.020 | 0.022 | 0.008 | 0.380 |
| 8 | 5 | 0.015 | 0.017 | 0.015 | 0.019 | 0.018 | 0.017 | 0.002 | 0.106 |
| 9* | 5 | 0.065 | 0.065 | 0.065 | 0.064 | 0.064 | 0.065 | 0.001 | 0.008 |
| 10* | 5 | 0.106 | 0.095 | 0.110 | 0.101 | 0.099 | 0.102 | 0.006 | 0.058 |
| 11 | 2 | 0.020 | 0.019 | | | | 0.020 | | |
| 12 | 5 | 0.023 | 0.023 | 0.025 | 0.023 | 0.023 | 0.023 | 0.001 | 0.038 |
| 13* | 5 | 0.058 | 0.077 | 0.070 | 0.034 | 0.086 | 0.065 | 0.020 | 0.310 |
| 14 | 5 | 0.015 | 0.017 | 0.017 | 0.015 | 0.017 | 0.016 | 0.001 | 0.068 |
| 15 | 1 | 0.022 | | | | | 0.022 | | |
| 16 | | <0.018 | <0.018 | <0.018 | <0.018 | <0.018 | | | |
| 17 | | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | | | |
| 18 | 5 | 0.035 | <0.035 | <0.035 | <0.035 | <0.035 | | | |
| 19 | 5 | 0.021 | 0.024 | 0.020 | 0.023 | 0.023 | 0.022 | 0.002 | 0.074 |
| 20 | 5 | 0.024 | 0.024 | 0.024 | 0.025 | 0.025 | 0.024 | 0.001 | 0.022 |
| 21 | | | | | | | | | |
| 22 | | <2 | <2 | <2 | <2 | <2 | | | |
| 23 | | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | | | |
| 24 | | | | | | | | | |
| 25 | | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | | | |
| 26 | 5 | 0.024 | 0.023 | 0.028 | 0.030 | 0.031 | 0.027 | 0.004 | 0.131 |
| 27 | 5 | 0.027 | 0.027 | 0.027 | 0.027 | 0.027 | 0.027 | 0.000 | 0.000 |
| 28 | 2 | 0.012 | 0.010 | | | | 0.011 | | |
| 29 | 5 | 0.030 | 0.029 | 0.030 | 0.030 | 0.027 | 0.029 | 0.001 | 0.045 |
| 30 | 5 | 0.014 | 0.013 | 0.018 | 0.020 | 0.016 | 0.016 | 0.003 | 0.177 |
| 31 | 5 | 0.028 | 0.027 | 0.028 | 0.022 | 0.023 | 0.026 | 0.003 | 0.113 |
| 32 | 5 | 0.028 | 0.024 | 0.028 | 0.025 | 0.025 | 0.026 | 0.002 | 0.072 |
| 33 | | | | | | | | | |
| 34 | 5 | 0.032 | 0.029 | 0.022 | 0.030 | 0.024 | 0.027 | 0.004 | 0.154 |
| 35 | 5 | 0.014 | 0.015 | 0.015 | 0.016 | 0.014 | 0.015 | 0.001 | 0.057 |
| 36 | 5 | 0.029 | 0.033 | 0.035 | 0.038 | 0.036 | 0.034 | 0.003 | 0.100 |
| 37 | 5 | 0.030 | 0.030 | 0.029 | 0.031 | 0.028 | 0.030 | 0.001 | 0.039 |
| 38 | | | | | | | | | |
| 39* | 5 | 0.092 | 0.021 | 0.044 | 0.081 | 0.070 | 0.062 | 0.029 | 0.468 |
| 40 | 1 | 0.283 | | | | | 0.283 | | |
| 41 | 5 | 0.017 | 0.015 | 0.020 | 0.019 | 0.023 | 0.019 | 0.003 | 0.161 |

# Lead

## Sample A

### 0.013 ± 0.011 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | <0.009 | <0.009 | <0.009 | <0.009 | | | | |
| 2 | 5 | 0.008 | 0.019 | 0.014 | 0.013 | 0.009 | 0.013 | 0.004 | 0.349 |
| 3 | 5 | 0.026 | 0.021 | 0.026 | 0.018 | 0.021 | 0.022 | 0.004 | 0.157 |
| 4 | 5 | 0.017 | 0.019 | 0.016 | 0.013 | 0.019 | 0.017 | 0.002 | 0.148 |
| 5 | 5 | 0.012 | 0.010 | 0.008 | 0.011 | 0.011 | 0.010 | 0.002 | 0.146 |
| 6 | | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | | | |
| 7* | 5 | 0.410 | 0.320 | 0.320 | 0.390 | 0.290 | 0.346 | 0.051 | 0.148 |
| 8 | 5 | 0.018 | 0.022 | 0.021 | 0.022 | 0.021 | 0.021 | 0.002 | 0.079 |
| 9* | 5 | 0.111 | 0.119 | 0.112 | 0.118 | 0.118 | 0.116 | 0.004 | 0.033 |
| 10* | 5 | 0.460 | 0.500 | 0.420 | 0.470 | 0.460 | 0.462 | 0.029 | 0.062 |
| 11 | | <0.1 | <0.1 | <0.1 | | | | | |
| 12 | | <0.025 | <0.025 | <0.025 | <0.025 | <0.025 | | | |
| 13* | 5 | 0.047 | 0.098 | 0.066 | 0.172 | 0.190 | 0.115 | 0.064 | 0.555 |
| 14 | | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | | | |
| 15 | 1 | 0.012 | | | | | 0.012 | | |
| 16 | | <0.161 | <0.161 | <0.159 | <0.159 | <0.161 | | | |
| 17 | | <0.024 | <0.024 | <0.024 | <0.024 | <0.024 | | | |
| 18 | | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | | | |
| 19 | 5 | 0.013 | 0.009 | 0.006 | 0.006 | 0.004 | 0.008 | 0.004 | 0.461 |
| 20 | 5 | 0.014 | 0.015 | 0.018 | 0.020 | 0.013 | 0.016 | 0.003 | 0.182 |
| 21 | | | | | | | | | |
| 22 | | <2 | <2 | <2 | <2 | <2 | | | |
| 23 | | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | | | |
| 24 | | | | | | | | | |
| 25 | | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | | | |
| 26* | 5 | 0.037 | 0.029 | 0.028 | 0.041 | 0.039 | 0.035 | 0.006 | 0.170 |
| 27 | 3 | 0.007 | 0.005 | 0.003 | | | 0.005 | 0.002 | 0.400 |
| 28 | 2 | 0.043 | 0.042 | | | | 0.043 | | |
| 29 | 5 | 0.021 | 0.017 | 0.014 | 0.014 | 0.014 | 0.016 | 0.003 | 0.193 |
| 30 | 5 | 0.009 | 0.013 | 0.010 | 0.013 | 0.009 | 0.011 | 0.002 | 0.190 |
| 31 | | | | | | | | | |
| 32 | 5 | 0.008 | 0.008 | 0.008 | 0.008 | 0.010 | 0.008 | 0.001 | 0.106 |
| 33 | | | | | | | | | |
| 34 | | | | | | | | | |
| 35 | 5 | 0.012 | 0.010 | 0.010 | 0.012 | 0.007 | 0.010 | 0.002 | 0.201 |
| 36* | 5 | 0.040 | 0.050 | 0.070 | 0.050 | 0.060 | 0.054 | 0.011 | 0.211 |
| 37 | 5 | 0.010 | 0.010 | 0.010 | 0.010 | 0.007 | 0.009 | 0.001 | 0.143 |
| 38 | | | | | | | | | |
| 39* | 5 | 0.875 | 1.000 | 1.212 | 1.115 | 1.300 | 1.100 | 0.168 | 0.153 |
| 40 | 2 | 0.029 | 0.051 | | | | | | |
| 41 | 5 | 0.020 | 0.023 | 0.024 | 0.021 | 0.018 | 0.021 | 0.002 | 0.113 |

## Sample B

### 0.012 ± 0.010 micrograms/litre

| Lab | n | | | | | | Mean | SD | RSD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | <0.009 | <0.009 | <0.009 | <0.009 | | | | |
| 2 | 5 | 0.013 | 0.017 | 0.015 | 0.008 | 0.013 | 0.013 | 0.003 | 0.254 |
| 3* | 5 | 0.025 | 0.026 | 0.034 | 0.031 | 0.024 | 0.028 | 0.004 | 0.154 |
| 4 | 5 | 0.009 | 0.013 | 0.017 | 0.013 | 0.015 | 0.013 | 0.003 | 0.221 |
| 5 | 5 | 0.007 | 0.007 | 0.006 | 0.006 | 0.007 | 0.007 | 0.001 | 0.083 |
| 6 | | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | | | |
| 7* | 5 | 0.280 | 0.190 | 0.150 | 0.160 | 0.160 | 0.188 | 0.054 | 0.285 |
| 8 | 5 | 0.018 | 0.013 | 0.012 | 0.019 | 0.017 | 0.016 | 0.003 | 0.197 |
| 9* | 5 | 0.151 | 0.149 | 0.149 | 0.151 | 0.151 | 0.150 | 0.001 | 0.007 |
| 10* | 5 | 0.390 | 0.330 | 0.440 | 0.410 | 0.380 | 0.390 | 0.041 | 0.104 |
| 11 | | <0.1 | <0.1 | | | | | | |
| 12 | | <0.025 | <0.025 | <0.025 | <0.025 | <0.025 | | | |
| 13* | 5 | 0.199 | 0.198 | 0.198 | 0.098 | 0.050 | 0.149 | 0.070 | 0.472 |
| 14 | | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | | | |
| 15 | 1 | 0.013 | | | | | 0.013 | | |
| 16 | | <0.161 | <0.161 | <0.159 | <0.159 | <0.16 | | | |
| 17 | | <0.024 | <0.024 | <0.024 | <0.024 | <0.024 | | | |
| 18 | | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | | | |
| 19 | 5 | 0.012 | 0.007 | 0.006 | 0.007 | 0.004 | 0.007 | 0.003 | 0.410 |
| 20 | 5 | 0.017 | 0.014 | 0.016 | 0.015 | 0.027 | 0.018 | 0.005 | 0.296 |
| 21 | | | | | | | | | |
| 22 | | <2 | <2 | <2 | <2 | <2 | | | |
| 23 | | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | | | |
| 24 | | | | | | | | | |
| 25 | | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | | | |
| 26* | 5 | 0.044 | 0.048 | 0.055 | 0.052 | 0.051 | 0.050 | 0.004 | 0.084 |
| 27 | 3 | 0.003 | 0.005 | 0.008 | | | 0.005 | 0.003 | 0.472 |
| 28 | 4 | 0.014 | 0.016 | 0.020 | 0.028 | | 0.020 | 0.006 | 0.318 |
| 29 | 4 | 0.009 | 0.009 | 0.015 | 0.009 | | 0.011 | 0.003 | 0.286 |
| 30 | 5 | 0.017 | 0.013 | 0.022 | 0.015 | 0.018 | 0.017 | 0.003 | 0.199 |
| 31 | | | | | | | | | |
| 32 | 5 | 0.008 | 0.007 | 0.008 | 0.008 | 0.006 | 0.007 | 0.001 | 0.121 |
| 33 | | | | | | | | | |
| 34 | | | | | | | | | |
| 35 | 5 | 0.010 | 0.007 | 0.012 | 0.013 | 0.013 | 0.011 | 0.003 | 0.232 |
| 36* | 5 | 0.050 | 0.040 | 0.080 | 0.050 | 0.070 | 0.058 | 0.016 | 0.283 |
| 37 | 5 | 0.012 | 0.012 | 0.009 | 0.010 | 0.009 | 0.010 | 0.002 | 0.146 |
| 38 | 1 | 0.400 | | | | | | | |
| 39* | 5 | 2.617 | 2.252 | 2.971 | 2.121 | 2.100 | 2.412 | 0.375 | 0.155 |
| 40 | | | | | | | | | |
| 41 | 5 | 0.018 | 0.020 | 0.019 | 0.016 | 0.022 | 0.019 | 0.002 | |

# ANNEX 3

## Sample Preparation and Analyte Measurement



**Abbreviations**

| | |
|---|---|
| APDC | Ammonium pyrolidine dithiocarbamate |
| ASV | Anodic stripping voltammetry |
| $CCl_4$ | Carbon tetrachloride |
| $CHCl_3$ | Chloroform |
| DDC | Dibenzyldithiocarbamate |
| FAAS | Flame atomic absorption spectrometry |
| GFAAS | Graphite furnace atomic absorption spectrometry |
| HDME | Hanging drop mercury electrode |
| HG | Hydride generation |
| ICPAES | Inductively coupled plasma atomic emission spectrometry |
| ICPMS | Inductively coupled plasma mass spectrometry |
| MeOH | Methanol |
| MIBK | Methylisobutylketone |
| NaDDC | Sodium dibenzyldithiocarbamate |
| TTE | 1,1,2-trichloro-1,2,2-trifluoroethane |
| TXRF | Total reflection X-ray fluorescence spectrometry |
| Y | The results are used to establish the accepted concentration and confidence interval. |
| * | An * after the laboratory number indicates that the laboratory's mean was rejected as an outlier. |
| ? | No information was given by the laboratory. |

**METHODOLOGY - Chromium**

| Lab | Evaluated | Sample Preparation | Analyte Measurement |
|---|---|---|---|
| 3 | Y | Solvent extraction: APDC/MIBK | GFAAS: Zeeman background correction; matrix modifier |
| 6 | | ? | GFAAS: Zeeman background correction; matrix modifier |
| 7* | Y | None described | GFAAS: Zeeman background correction; matrix modifier |
| 9* | Y | None described | GFAAS: $D_2$ background correction; matrix modifier |
| 11 | | Solvent extraction: ? | GFAAS: $D_2$ background correction; no matrix modifier |
| 12 | | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: No background correction; no matrix modifier |
| 15 | | None described | ? |
| 17 | | None described | GFAAS: Zeeman background correction; matrix modifier |
| 21 | | None described | GFAAS: Zeeman background correction; no matrix modifier |
| 23 | | None described | ? |
| 25 | | Digestion: $HNO_3$<br>Solvent extraction: APDC/? | GFAAS: Zeeman background correction; matrix modifier |
| 26* | Y | Digestion: $HNO_3$<br>Solvent extraction: NaDDC/$CHCl_3$ | ICPAES |
| 34 | Y | Chromatographic separation | GFAAS: $D_2$ background correction; no matrix modifier |
| 38 | | Digestion: $HNO_3$ | GFAAS: Zeeman background correction; matrix modifier |
| 39 | Y | None described | ? |
| 40 | Y | Precipitation: APDC<br>Filtration and acid digestion | ICPMS |

**METHODOLOGY - Manganese**

| Lab | Evaluated | Sample Preparation | Analyte Measurement |
|---|---|---|---|
| 4 | Y | Solvent extraction: NaDDC/($CHCl_3$/MeOH) | GFAAS: Zeeman background correction; matrix modifier |
| 6 | Y | None described | GFAAS: Zeeman background correction; no matrix modifier |
| 7* | Y | None described | GFAAS: Zeeman background correction; matrix modifier |
| 8 | Y | None described | GFAAS: Zeeman background correction; matrix modifier |
| 9 | Y | None described | GFAAS: $D_2$ background correction; matrix modifier |
| 14 | Y | Solvent extraction: ?/TTE<br>Back extraction: $HNO_3$ | ICPMS |
| 17 | | None described | ICPMS |
| 20 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | ICPAES |
| 22 | Y | Solvent extraction: APDC/? | ICPAES |
| 23 | | Digestion | ICPAES |
| 26 | Y | Digestion: $HNO_3$<br>Solvent extraction: NaDDC/$CHCl_3$ | ICPAES |
| 27 | Y | Solvent extraction: APDC/?<br>Back extraction: acid | GFAAS: $D_2$ background correction; matrix modifier |
| 29 | Y | Solvent extraction: APDC/DDC/Freon<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction |
| 31 | Y | None described | GFAAS: Zeeman background correction; matrix modifier |
| 32 | Y | Solvent extraction: APDC/DDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; no matrix modifier |
| 34 | Y | Chromatographic separation | GFAAS: $D_2$ background correction; no matrix modifier |
| 35 | Y | Chromatographic separation: NaDDC/($CHCl_3$/MeOH) | TXRF |
| 36 | Y | Solvent extraction: NaDDC/$CCl_4$ | GFAAS: $D_2$ background correction; no matrix modifier |
| 38 | | Digestion: $HNO_3$ | ICPAES |
| 39 | Y | None described | ? |
| 40 | Y | Precipitation: APDC<br>Filtration and acid digestion | ICPMS |

**METHODOLOGY - Iron**

| Lab | Evaluated | Sample Preparation | Analyte Measurement |
|---|---|---|---|
| 4 | Y | Solvent extraction:NaDDC/($CHCl_3$/MeOH) | ASV |
| 8 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; no matrix modifier |
| 9* | Y | None described | GFAAS: $D_2$ background correction; matrix modifier |
| 12 | | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: No background correction; no matrix modifier |
| 14 | | Solvent extraction: ?/TTE<br>Back extraction: $HNO_3$ | ICPMS |
| 17 | | None described | HDME |
| 19 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; no matrix modifier |
| 20 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | ICPAES |
| 22* | Y | Solvent extraction: APDC/? | ICPAES |
| 23 | | Digestion | ICPAES |
| 25 | | Digestion: $HNO_3$<br>Solvent extraction: APDC/? | GFAAS: Zeeman background correction; no matrix modifier |
| 26* | Y | Digestion: $HNO_3$<br>Solvent extraction: NaDDC/$CHCl_3$ | ICPAES |
| 27 | Y | Solvent extraction: APDC/?<br>Back extraction: acid | GFAAS: $D_2$ background correction; matrix modifier |
| 29 | Y | Solvent extraction: APDC/DDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction |
| 32 | Y | Solvent extraction: APDC/DDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; no matrix modifier |
| 35 | Y | Chromatographic separation: NaDDC/($CHCl_3$/MeOH) | TXRF |
| 36* | Y | Solvent extraction: NaDDC/$CCl_4$ | GFAAS: $D_2$ background correction; matrix modifier |
| 37 | Y | Solvent extraction: APDC/DDC/$CHCl_3$<br>Back extraction: $HNO_3$ | ICPMS |
| 39* | Y | None described | ? |
| 40 | | Precipitation: APDC<br>Filtration and acid digestion | ICPMS |

**METHODOLOGY - Cobalt**

| Lab | Evaluated | Sample Preparation | Analyte Measurement |
|---|---|---|---|
| 7* | Y | None described | GFAAS: Zeeman background correction; matrix modifier |
| 8 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; no matrix modifier |
| 12 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: No background correction; no matrix modifier |
| 14 | Y | Solvent extraction: ?/TTE<br>Back extraction: $HNO_3$ | ICPMS |
| 17 | | None described | ICPMS |
| 19 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; no matrix modifier |
| 20 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; matrix modifier |
| 22* | Y | Solvent extraction: APDC/? | ICPAES |
| 23 | | Digestion | ICPMS |
| 26 | Y | Digestion: $HNO_3$<br>Solvent extraction: NaDDC/$CHCl_3$ | ICPAES |
| 27 | Y | Solvent extraction: APDC/?<br>Back extraction: acid | GFAAS: $D_2$ background correction; matrix modifier |
| 28 | | None described | ASV |
| 30 | Y | UV irradiation | HDME |
| 32 | Y | Solvent extraction: APDC/DDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; no matrix modifier |
| 37 | Y | Solvent extraction: APDC/DDC/$CHCl_3$<br>Back extraction: $HNO_3$ | ICPMS |
| 40* | Y | Precipitation: APDC<br>Filtration and acid digestion | ICPMS |

**METHODOLOGY - Nickel**

| Lab | Evaluated | Sample Preparation | Analyte Measurement |
|---|---|---|---|
| 1 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: No background correction; no matrix modifier |
| 2* | Y | None | ASV |
| 3 | Y | Solvent extraction: APDC/MIBK | GFAAS: Zeeman background correction; no matrix modifier |
| 4 | Y | Solvent extraction: NaDDC/($CHCl_3$/MeOH) | ASV |
| 6 | Y | Solvent extraction: APDC/MIBK | GFAAS: Zeeman background correction; no matrix modifier |
| 7* | Y | None described | HMDE |
| 8 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; no matrix modifier |
| 9* | Y | None described | GFAAS: $D_2$ background correction; no matrix modifier |
| 10* | Y | None described | GFAAS: Zeeman background correction; matrix modifier |
| 11 | Y | Solvent extraction: ? | GFAAS: $D_2$ background correction; no matrix modifier |
| 12 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: No background correction; no matrix modifier |
| 14 | Y | Solvent extraction: ?/TTE<br>Back extraction: $HNO_3$ | ICPMS |
| 15 | | None described | ? |
| 16 | Y | Solvent extraction: APDC/$CHCl_3$ | FAAS |
| 17 | Y | None described | HMDE |
| 18 | Y | Digestion<br>Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: No background correction; no matrix modifier |
| 19 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; no matrix modifier |
| 20 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | ICPAES |
| 21 | | Solvent extraction: APDC/$CHCl_3$<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; matrix modifier |
| 22* | Y | Solvent extraction: APDC/? | ICPAES |
| 23 | Y | Digestion | ICPMS |
| 25 | Y | Digestion: $HNO_3$<br>Solvent extraction: APDC/? | GFAAS: Zeeman background correction; no matrix modifier |
| 26* | Y | Digestion: $HNO_3$<br>Solvent extraction: NaDDC/$CHCl_3$ | ICPAES |
| 27 | Y | Solvent extraction: APDC/?<br>Back extraction: acid | GFAAS: $D_2$ background correction; matrix modifier |
| 28 | Y | None described | ASV |
| 29 | Y | Solvent extraction: APDC/DDC/Freon<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction |
| 30 | Y | UV irradiation | HMDE |
| 32* | Y | Solvent extraction: APDC/DDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; no matrix modifier |

**Nickel** (continued)

| Lab | Evaluated | Sample Preparation | Analyte Measurement |
|---|---|---|---|
| 33 | Y | | |
| 34* | Y | Chromatographic separation | GFAAS: $D_2$ background correction; no matrix modifier |
| 35 | Y | Chromatographic separation: NaDDC/($CHCl_3$/MeOH) | TXRF |
| 37 | Y | Solvent extraction: APDC/DDC/$CHCl_3$<br>Back extraction: $HNO_3$ | ICPMS |
| 39* | Y | None described | ? |
| 40 | Y | Precipitation: APDC<br>Filtration and acid digestion | ICPMS |
| 41 | Y | Solvent extraction: APDC/DDC/TTE<br>Back extraction: $HNO_3$ | ICPMS |

## METHODOLOGY - Copper

| Lab | Evaluated | Sample Preparation | Analyte Measurement |
|---|---|---|---|
| 1 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; no matrix modifier |
| 2 | Y | None | ASV |
| 3* | Y | Solvent extraction: APDC/MIBK | GFAAS: Zeeman background correction; matrix modifier |
| 4 | Y | Solvent extraction: NaDDC/($CHCl_3$/MeOH) | ASV |
| 6 | Y | Solvent extraction: APDC/MIBK | GFAAS: Zeeman background correction; no matrix modifier |
| 7* | Y | None described | GFAAS: Zeeman background correction; matrix modifier |
| 8 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; no matrix modifier |
| 9* | Y | None described | GFAAS: $D_2$ background correction; no matrix modifier |
| 10* | Y | None described | GFAAS: Zeeman background correction; matrix modifier |
| 11 | Y | Solvent extraction: ? | GFAAS: $D_2$ background correction; no matrix modifier |
| 12 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: No background correction; no matrix modifier |
| 14 | Y | Solvent extraction: ?/TTE<br>Back extraction: $HNO_3$ | ICPMS |
| 15 | | None described | ? |
| 16 | Y | Solvent extraction: APDC/$CHCl_3$ | FAAS |
| 17 | Y | None described | HDME |
| 18 | Y | Digestion<br>Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: No background correction; no matrix modifier |
| 19 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; no matrix modifier |
| 20 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | ICPAES |
| 21 | | Solvent extraction: APDC/$CHCl_3$<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; matrix modifier |
| 22* | Y | Solvent extraction: APDC/? | ICPAES |
| 23 | Y | Digestion | ICPMS |
| 25 | Y | Digestion: $HNO_3$<br>Solvent extraction: APDC/? | GFAAS: Zeeman background correction; no matrix modifier |
| 26* | Y | Digestion: $HNO_3$<br>Solvent extraction: NaDDC/$CHCl_3$ | ICPAES |
| 27 | Y | Solvent extraction: APDC/?<br>Back extraction: acid | GFAAS: $D_2$ background correction; matrix modifier |
| 28 | Y | None described | ASV |
| 29 | Y | Solvent extraction: APDC/DDC/Freon<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction |
| 30 | Y | UV irradiation | HDME |
| 31 | Y | None described | ASV |

**Copper** (continued)

| Lab | Evaluated | Sample Preparation | Analyte Measurement |
|---|---|---|---|
| 32 | Y | Solvent extraction: APDC/DDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; no matrix modifier |
| 33 | Y | Solvent extraction: APDC/DDC/?<br>Back extraction: acid | GFAAS: Zeeman background correction; no matrix modifier |
| 34 | Y | Chromatographic separation | GFAAS: $D_2$ background correction; no matrix modifier |
| 35 | Y | Chromatographic separation: NaDDC/($CHCl_3$/MeOH) | TXRF |
| 36 | Y | Solvent extraction: NaDDC/$CCl_4$ | GFAAS: $D_2$ background correction; no matrix modifier |
| 37 | Y | Solvent extraction: APDC/DDC/$CHCl_3$<br>Back extraction: $HNO_3$ | ICPMS |
| 39* | Y | None described | ? |
| 40 | Y | Precipitation: APDC<br>Filtration and acid digestion | ICPMS |
| 41 | Y | Solvent extraction: APDC/DDC/TTE<br>Back extraction: $HNO_3$ | ICPMS |

**METHODOLOGY - Zinc**

| Lab | Evaluated | Sample Preparation | Analyte Measurement |
|---|---|---|---|
| 1 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | FAAS |
| 2 | Y | None | ASV |
| 3 | Y | Solvent extraction: APDC/MIBK | GFAAS: Zeeman background correction; matrix modifier |
| 4 | Y | Solvent extraction: NaDDC/($CHCl_3$/MeOH) | ASV |
| 6 | | Solvent extraction: APDC/MIBK | HMDE |
| 7* | Y | None described | HDME |
| 8 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; no matrix modifier |
| 9 | Y | None described | GFAAS: $D_2$ background correction; no matrix modifier |
| 10 | Y | None described | GFAAS: Zeeman background correction; matrix modifier |
| 11 | | Solvent extraction: ? | FAAS: $D_2$ background correction; no matrix modifier |
| 12 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: No background correction; no matrix modifier |
| 13* | Y | Solvent extraction: APDC/DDC/TTE | FAAS: $D_2$ background correction |
| 14 | Y | Solvent extraction: ?/TTE<br>Back extraction: $HNO_3$ | ICPMS |
| 15 | | None described | ? |
| 16 | Y | Solvent extraction: APDC/$CHCl_3$ | FAAS: background correction |
| 17 | | None described | HDME |
| 18 | | Digestion<br>Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: $D_2$ background correction; no matrix modifier |
| 19 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; matrix modifier |
| 20 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | ICPAES |
| 21 | | Solvent extraction: APDC/$CHCl_3$<br>Back extraction: $HNO_3$ | FAAS: $D_2$ background correction |
| 22* | Y | Solvent extraction: APDC/? | ICPAES |
| 23 | Y | Digestion | ICPMS |
| 25 | | Digestion: $HNO_3$<br>Solvent extraction: APDC/? | GFAAS: Zeeman background correction; no matrix modifier |
| 26* | Y | Digestion: $HNO_3$<br>Solvent extraction: NaDDC/$CHCl_3$ | ICPAES |
| 27 | Y | Solvent extraction: APDC/?<br>Back extraction: acid | GFAAS: $D_2$ background correction; matrix modifier |
| 28 | Y | None described | ASV |
| 29 | Y | Solvent extraction: APDC/DDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction |

**Zinc** (continued)

| Lab | Evaluated | Sample Preparation | Analyte Measurement |
|---|---|---|---|
| 30 | Y | UV irradiation | HMDE |
| 32 | Y | Solvent extraction: APDC/DDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; no matrix modifier |
| 34* | Y | Chromatographic separation | GFAAS: $D_2$ background correction; no matrix modifier |
| 35 | Y | Chromatographic separation: NaDDC/($CHCl_3$/MeOH) | TXRF |
| 36* | Y | Solvent extraction: NaDDC/$CCl_4$ | GFAAS: $D_2$ background correction; no matrix modifier |
| 37 | Y | Solvent extraction: APDC/DDC/$CHCl_3$<br>Back extraction: $HNO_3$ | ICPMS |
| 38 | | Digestion: $HNO_3$ | ICPAES |
| 39* | Y | None described | ? |
| 41 | Y | Solvent extraction: APDC/DDC/TTE<br>Back extraction: $HNO_3$ | ICPMS |

**METHODOLOGY - Arsenic**

| Lab | Evaluated | Sample Preparation | Analyte Measurement |
|---|---|---|---|
| 3 | Y | None described | HG-FAAS |
| 6 | Y | Digestion (?) | HG-FAAS |
| 7 | Y | Digestion (?) | HG-FAAS |
| 11 | Y | Digestion with aqua regia | HG-ICPAES |
| 15 | | None described | ? |
| 17 | | None described | HG-FAAS |
| 19 | Y | Digestion (?); Chromatographic separation | HG-Atomic fluorescence |
| 20 | Y | None described | HG-FAAS |
| 21 | | None described | HG-FAAS |
| 23 | | Digestion (?) | Electrochemical detection |
| 24 | | None described | HG-FAAS |
| 25 | | Digestion (?) | HG-FAAS |
| 27 | Y | None described | HG-ICPMS |
| 38 | | Digestion with aqua regia | HG-FAAS |
| 40 | Y | Precipitation: APDC<br>Filtration and acid digestion | ICPMS |

**METHODOLOGY - Cadmium**

| Lab | Evaluated | Sample Preparation | Analyte Measurement |
|---|---|---|---|
| 1 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: No background correction; no matrix modifier |
| 2 | Y | None | ASV |
| 3 | Y | Solvent extraction: APDC/MIBK | GFAAS: Zeeman background correction; matrix modifier |
| 5 | Y | None described | ASV |
| 6 | Y | Solvent extraction: APDC/MIBK | GFAAS: Zeeman background correction; matrix modifier |
| 7* | Y | None described | HDME |
| 8 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; matrix modifier |
| 9* | Y | None described | GFAAS: $D_2$ background correction; matrix modifier |
| 10* | Y | None described | GFAAS: Zeeman background correction; matrix modifier |
| 11 | Y | Solvent extraction: ? | GFAAS: $D_2$ background correction; no matrix modifier |
| 12 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: No background correction; no matrix modifier |
| 13* | Y | Solvent extraction: APDC/DDC/TTE | GFAAS: $D_2$ background correction; matrix modifier |
| 14 | Y | Solvent extraction: ?/TTE<br>Back extraction: $HNO_3$ | ICPMS |
| 15 | | None described | ? |
| 16 | | Solvent extraction: APDC/$CHCl_3$ | FAAS |
| 17 | | None described | HDME |
| 18 | | Digestion<br>Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: $D_2$ background correction; no matrix modifier |
| 19 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; matrix modifier |
| 20 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; matrix modifier |
| 21 | | Solvent extraction: APDC/$CHCl_3$<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; matrix modifier |
| 22 | | Solvent extraction: APDC/? | ICPAES |
| 23 | | Digestion | ICPMS |
| 25 | | Digestion: $HNO_3$<br>Solvent extraction: APDC/? | GFAAS: Zeeman background correction; matrix modifier |
| 26* | Y | Digestion: $HNO_3$<br>Solvent extraction: NaDDC/$CHCl_3$ | ICPAES |
| 27 | Y | Solvent extraction: APDC/?<br>Back extraction: acid | GFAAS: $D_2$ background correction; matrix modifier |
| 28 | | None described | ASV |
| 29 | Y | Solvent extraction: APDC/DDC/Freon<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction |
| 30 | Y | None described | Glassy carbon electrode |

**Cadmium** (continued)

| Lab | Evaluated | Sample Preparation | Analyte Measurement |
|---|---|---|---|
| 31 | Y | None described | ASV |
| 32 | Y | Solvent extraction: APDC/DDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; matrix modifier |
| 34* | Y | Chromatographic separation | GFAAS: $D_2$ background correction; no matrix modifier |
| 35 | Y | Chromatographic separation: NaDDC/($CHCl_3$/MeOH) | TXRF |
| 36 | Y | Solvent extraction: NaDDC/$CCl_4$ | GFAAS: $D_2$ background correction; no matrix modifier |
| 37 | Y | Solvent extraction: APDC/DDC/$CHCl_3$<br>Back extraction: $HNO_3$ | ICPMS |
| 38 | | Digestion: $HNO_3$ | GFAAS: Zeeman background correction; matrix modifier |
| 39* | Y | None described | ? |
| 40 | | Precipitation: APDC<br>Filtration and acid digestion | ICPMS |
| 41 | Y | Solvent extraction: APDC/DDC/TTE<br>Back extraction: $HNO_3$ | ICPMS |

**METHODOLOGY - Lead**

| Lab | Evaluated | Sample Preparation | Analyte Measurement |
|---|---|---|---|
| 1 | | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: No background correction; no matrix modifier |
| 2 | Y | None | ASV |
| 3 | Y | Solvent extraction: APDC/MIBK | GFAAS: Zeeman background correction; matrix modifier |
| 4 | Y | Solvent extraction: NaDDC/($CHCl_3$/MeOH) | ASV |
| 5 | Y | None described | ? |
| 6 | | Solvent extraction: APDC/MIBK | GFAAS: Zeeman background correction; no matrix modifier |
| 7* | Y | None described | HDME |
| 8 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; no matrix modifier |
| 9* | Y | None described | GFAAS: $D_2$ background correction; matrix modifier |
| 10* | Y | None described | GFAAS: Zeeman background correction; matrix modifier |
| 11 | | Solvent extraction: ? | GFAAS: $D_2$ background correction; no matrix modifier |
| 12 | | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: No background correction; no matrix modifier |
| 13* | Y | Solvent extraction: APDC/DDC/TTE | GFAAS: $D_2$ background correction; matrix modifier |
| 14 | | Solvent extraction: ?/TTE<br>Back extraction: $HNO_3$ | ICPMS |
| 15 | | None described | ? |
| 16 | | Solvent extraction: APDC/$CHCl_3$ | FAAS |
| 17 | | None described | HDME |
| 18 | | Digestion<br>Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: $D_2$ background correction; no matrix modifier |
| 19 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; matrix modifier |
| 20 | Y | Solvent extraction: APDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: Zeeman background correction; matrix modifier |
| 22 | | None described | ICPAES |
| 23 | | Digestion | ICPMS |
| 25 | | Digestion: $HNO_3$<br>Solvent extraction: APDC/? | GFAAS: Zeeman background correction; no matrix modifier |
| 26* | Y | Digestion: $HNO_3$<br>Solvent extraction: NaDDC/$CHCl_3$ | ICPAES |
| 27 | Y | Solvent extraction: APDC/?<br>Back extraction: acid | ICPMS |
| 28 | Y | None described | ASV |
| 29 | Y | Solvent extraction: APDC/DDC/TTE<br>Back extraction: $HNO_3$ | GFAAS: $D_2$ background correction |
| 30 | Y | None described | Glassy carbon electrode |

**Lead** (continued)

| Lab | Evaluated | Sample Preparation | Analyte Measurement |
|---|---|---|---|
| 32 | Y | Solvent extraction: APDC/DDC/TTE<br>Back extraction: $HNO_3$ | ICPMS |
| 35 | Y | Chromatographic separation: NaDDC/($CHCl_3$/MeOH) | TXRF |
| 36* | Y | Solvent extraction: NaDDC/$CCl_4$ | GFAAS: $D_2$ background correction; no matrix modifier |
| 37 | Y | Solvent extraction: APDC/DDC/$CHCl_3$<br>Back extraction: $HNO_3$ | ICPMS |
| 38 | | Digestion: $HNO_3$ | GFAAS: Zeeman background correction; matrix modifier |
| 39* | Y | None described | ? |
| 40 | | Precipitation: APDC<br>Filtration and acid digestion | ICPMS |
| 41 | Y | Solvent extraction: APDC/DDC/TTE<br>Back extraction: $HNO_3$ | ICPMS |

# ANNEX 4

# Laboratory Evaluations



**Abbreviations**

A system to evaluate laboratory performance for the individual elements was established using the following criteria:

| | |
|---|---|
| E | Excellent accuracy: all replicate values are within the established confidence interval. |
| G | Good accuracy: the mean of the replicates is within the established confidence interval but one or more of the replicates is outside; a 'less than' value has been reported that is not less than the lower confidence limit and not three times greater than the accepted mean. |
| L | Low results: the mean of the replicates is less than the lower confidence limit; a 'less than' value has been reported that is less than the lower confidence limit. |
| H | High results: the mean of the replicates is greater than the upper confidence limit; a 'less than' value has been reported that is greater than a factor of three above the accepted or certified value. |
| S | Good precision: the intralaboratory precision is within the criteria for precision listed in Table 1. |
| P | Poor precision: the intralaboratory precision is not within the criteria for precision listed in Table 1. |

# Evaluation for Chromium

| Lab | Mean A | Z A | Sample A | Mean B | Z B | Sample B |
|---|---|---|---|---|---|---|
| 1 | | | | | | |
| 2 | | | | | | |
| 3 | 0.091 | 1.19 | E-P | 0.095 | 1.34 | E-S |
| 4 | | | | | | |
| 5 | | | | | | |
| 6 | | | G | | | G |
| 7 | 0.872 | 79.7 | H-S | 1.060 | 96.7 | H-S |
| 8 | | | | | | |
| 9 | 0.072 | –0.78 | E-S | 0.168 | 8.55 | H-S |
| 10 | | | | | | |
| 11 | | | G | | | G |
| 12 | | | H | | | H |
| 13 | | | | | | |
| 14 | | | | | | |
| 15 | 0.200 | 12.1 | H | 0.010 | –7.01 | L |
| 16 | | | | | | |
| 17 | | | G | | | G |
| 18 | | | | | | |
| 19 | | | | | | |
| 20 | | | | | | |
| 21 | 16.400 | 1641 | H | 11.5 | 1128 | H |
| 22 | | | | | | |
| 23 | | | H | | | H |
| 24 | | | | | | |
| 25 | | | H | | | H |
| 26 | 2.248 | 218 | H-S | 2.532 | 242 | H-S |
| 27 | | | | | | |
| 28 | | | | | | |
| 29 | | | | | | |
| 30 | | | | | | |
| 31 | | | | | | |
| 32 | | | | | | |
| 33 | | | | | | |
| 34 | 0.107 | 2.74 | E-S | 0.072 | –0.93 | E-S |
| 35 | | | | | | |
| 36 | | | | | | |
| 37 | | | | | | |
| 38 | 0.370 | 29.2 | H | 0.290 | 20.6 | H |
| 39 | 0.065 | –1.48 | E-S | 0.080 | –0.06 | E-P |
| 40 | 0.063 | –1.67 | E-S | 0.077 | –0.36 | E-S |
| 41 | | | | | | |

# Evaluation for Manganese

| Lab | Mean A | Z A | Sample A | Mean B | Z B | Sample B |
|---|---|---|---|---|---|---|
| 1 | | | | | | |
| 2 | | | | | | |
| 3 | | | | | | |
| 4 | 1.2 | –1.2 | E-P | 1.5 | 0.1 | E-S |
| 5 | | | | | | |
| 6 | 1.0 | –2.5 | E-S | 0.4 | –6.1 | G-S |
| 7 | 6.3 | 28.6 | H-S | 7.2 | 29.3 | H-S |
| 8 | 1.0 | –2.0 | E-S | 1.1 | –2.2 | E-S |
| 9 | 0.8 | –3.6 | E-S | 1.3 | –1.4 | E-S |
| 10 | | | | | | |
| 11 | | | | | | |
| 12 | | | | | | |
| 13 | | | | | | |
| 14 | 1.1 | –1.8 | E-S | 1.0 | –2.9 | E-P |
| 15 | | | | | | |
| 16 | | | | | | |
| 17 | | | H | | | H |
| 18 | | | | | | |
| 19 | | | | | | |
| 20 | 1.6 | 1.5 | E-S | 1.6 | 0.3 | E-S |
| 21 | | | | | | |
| 22 | 1.6 | 1.3 | G-P | | | G |
| 23 | | | H | | | H |
| 24 | | | | | | |
| 25 | | | | | | |
| 26 | 0.6 | –4.7 | E-P | 0.8 | –4.0 | E-P |
| 27 | 1.4 | 0.2 | E-S | 1.5 | –0.4 | E-S |
| 28 | | | | | | |
| 29 | 2.0 | 3.5 | E-S | 2.6 | 5.3 | G-S |
| 30 | | | | | | |
| 31 | 2.3 | 5.1 | H-S | 1.9 | 1.7 | E-S |
| 32 | 1.2 | –1.3 | E-S | 1.3 | –1.5 | E-S |
| 33 | | | | | | |
| 34 | 2.1 | 4.0 | E-S | 2.1 | 2.7 | E-S |
| 35 | 1.5 | 0.5 | E-P | 2.1 | 2.8 | E-S |
| 36 | 1.8 | 2.2 | E-S | 2.4 | 4.4 | E-S |
| 37 | | | | | | |
| 38 | 2.0 | 3.6 | G | 2.0 | 2.4 | G |
| 39 | 1.4 | 0.2 | E-S | 2.2 | 3.5 | E-S |
| 40 | 1.1 | –1.4 | E-P | 1.6 | 0.5 | E-P |
| 41 | | | | | | |

# Evaluation for Iron

| Lab | Mean A | Z A | Sample A | Mean B | Z B | Sample B |
|---|---|---|---|---|---|---|
| 1 | | | | | | |
| 2 | | | | | | |
| 3 | | | | | | |
| 4 | 0.85 | 0.2 | E-S | 0.62 | 0.5 | E-S |
| 5 | | | | | | |
| 6 | | | | | | |
| 7 | | | | | | |
| 8 | 0.69 | –1.4 | E-S | 0.49 | –1.2 | E-S |
| 9 | 1.99 | 11.3 | H-S | 2.61 | 27.9 | H-S |
| 10 | | | | | | |
| 11 | | | | | | |
| 12 | | | | | | |
| 13 | | | H | | | H |
| 14 | | | G | | | G |
| 15 | | | | | | |
| 16 | | | | | | |
| 17 | | | H | | | H |
| 18 | | | | | | |
| 19 | 0.66 | –1.6 | E-S | 0.55 | –0.4 | E-P |
| 20 | 1.12 | 2.8 | E-S | 0.64 | 0.8 | E-P |
| 21 | | | | | | |
| 22 | 13.60 | 123.5 | H-P | 4.60 | 55.4 | H-P |
| 23 | | | H | | | H |
| 24 | | | | | | |
| 25 | | | G | | | G |
| 26 | 6.76 | 57.4 | H-S | 5.88 | 73.0 | H-S |
| 27 | 0.67 | –1.5 | E-S | 0.48 | –1.4 | E-S |
| 28 | | | | | | |
| 29 | | | | 0.81 | 0.4 | E-P |
| 30 | | | | | | |
| 31 | | | | | | |
| 32 | 0.73 | –0.9 | E-S | 0.58 | 0.0 | E-P |
| 33 | | | | | | |
| 34 | | | | | | |
| 35 | 0.68 | –1.4 | E-P | 0.47 | –1.6 | E-S |
| 36 | 2.82 | 19.3 | H-S | 2.16 | 21.8 | H-P |
| 37 | 1.22 | 3.8 | G-P | 0.78 | 2.8 | G-P |
| 38 | | | | | | |
| 39 | 6.20 | 52.0 | H-S | 6.28 | 78.5 | H-S |
| 40 | 1.14 | 3.0 | G | | | |
| 41 | | | | | | |

# Evaluation for Cobalt

| Lab | Mean A | Z A | Sample A | Mean B | Z B | Sample B |
|---|---|---|---|---|---|---|
| 1 | | | | | | |
| 2 | | | | | | |
| 3 | | | | | | |
| 4 | | | | | | |
| 5 | | | | | | |
| 6 | | | | | | |
| 7 | 0.42 | 16.5 | H-S | 0.924 | 447.9 | H-S |
| 8 | 0.11 | –1.4 | E-S | 0.012 | –2.0 | E-S |
| 9 | | | | | | |
| 10 | | | | | | |
| 11 | | | | | | |
| 12 | 0.18 | 2.6 | E-S | 0.015 | –0.5 | E-S |
| 13 | | | | | | |
| 14 | 0.11 | –1.3 | E-S | 0.015 | –0.5 | E-P |
| 15 | | | | | | |
| 16 | | | | | | |
| 17 | | | H | | | H |
| 18 | | | | | | |
| 19 | 0.13 | –0.6 | E-S | 0.018 | 1.1 | G-S |
| 20 | 0.15 | 1.1 | E-S | 0.023 | 3.2 | H-S |
| 21 | | | | | | |
| 22 | 2.00 | 109.6 | H-S | 1.000 | 485.4 | H-S |
| 23 | | | H | | | H |
| 24 | | | | | | |
| 25 | | | | | | |
| 26 | 0.13 | –0.5 | E-S | 0.016 | –0.1 | E-S |
| 27 | 0.14 | 0.1 | E-S | 0.017 | 0.5 | E-S |
| 28 | 0.04 | –5.9 | L | 0.016 | 0.1 | E-P |
| 29 | | | | | | |
| 30 | 0.06 | –4.5 | E-S | | | |
| 31 | | | | | | |
| 32 | 0.12 | –0.9 | E-S | 0.014 | –0.9 | E-P |
| 33 | | | | | | |
| 34 | | | | | | |
| 35 | | | | | | |
| 36 | | | | | | |
| 37 | 0.18 | 2.7 | E-S | 0.014 | –0.9 | E-S |
| 38 | | | | | | |
| 39 | | | | | | |
| 40 | 0.18 | 2.7 | E-S | 0.029 | 6.3 | H-S |
| 41 | | | | | | |

# Evaluation for Nickel

| Lab | Mean A | Z A | Sample A | Mean B | Z B | Sample B |
|---|---|---|---|---|---|---|
| 1 | 0.70 | –0.6 | E-S | 0.47 | –0.3 | E-S |
| 2 | 0.68 | –0.7 | G-P | 0.32 | –2.8 | L-P |
| 3 | 0.72 | –0.3 | E-S | 0.35 | –2.3 | L-P |
| 4 | 0.79 | 0.4 | E-S | 0.52 | 0.6 | E-S |
| 5 | | | | | | |
| 6 | 0.78 | 0.3 | E-S | | | G |
| 7 | 1.31 | 5.9 | H-P | 0.53 | 0.8 | E-S |
| 8 | 0.67 | –0.9 | E-S | 0.47 | –0.3 | E-S |
| 9 | 0.96 | 2.3 | H-S | 1.05 | 9.3 | H-S |
| 10 | 9.35 | 91.8 | H-S | 9.49 | 148.5 | H-S |
| 11 | 0.78 | 0.3 | E-S | 0.46 | –0.4 | G |
| 12 | 0.66 | –1.0 | E-S | 0.46 | –0.4 | E-S |
| 13 | | | | | | |
| 14 | 0.79 | 0.5 | E-S | 0.53 | 0.7 | E-S |
| 15 | 0.88 | 1.4 | G | 0.53 | 0.7 | G |
| 16 | 0.65 | –1.1 | G-P | 0.36 | –2.1 | G-P |
| 17 | 0.73 | –0.2 | E-S | 0.46 | –0.4 | E-S |
| 18 | 0.90 | 1.6 | H-S | 0.55 | 1.1 | E-S |
| 19 | 0.74 | –0.1 | E-S | 0.47 | –0.3 | E-S |
| 20 | 0.72 | –0.3 | E-S | 0.48 | –0.2 | E-S |
| 21 | 0.43 | –3.5 | L | | | |
| 22 | 4.67 | 41.8 | H-P | 20.40 | 412.5 | H-P |
| 23 | 0.82 | 0.7 | E-S | 0.49 | 0.0 | E-S |
| 24 | | | | | | |
| 25 | 0.71 | –0.4 | E-S | | | G |
| 26 | 0.30 | –4.8 | L-P | 0.15 | –5.6 | L-P |
| 27 | 0.74 | –0.2 | E-S | 0.50 | 0.2 | E-S |
| 28 | 0.66 | –1.0 | E-S | 0.44 | –0.8 | G-P |
| 29 | 0.87 | 1.3 | G-S | 0.51 | 0.9 | G-P |
| 30 | 0.84 | 1.0 | G-S | 0.44 | –0.8 | E-S |
| 31 | | | | | | |
| 32 | 0.57 | –1.9 | L-S | 0.39 | –1.6 | G-S |
| 33 | 0.77 | 0.3 | E-S | 0.53 | 0.7 | E-S |
| 34 | 0.53 | –2.3 | L-S | 0.60 | 1.8 | G-P |
| 35 | 0.75 | 0.0 | E-S | 0.51 | 0.4 | E-S |
| 36 | | | | | | |
| 37 | 0.86 | 1.2 | G-S | 0.51 | 0.4 | E-S |
| 38 | | | | | | |
| 39 | 0.84 | 1.0 | G-P | 1.80 | 21.6 | H-P |
| 40 | 0.75 | –0.0 | E-S | 0.48 | –0.1 | E-S |
| 41 | 0.71 | –0.4 | E-S | 0.48 | –0.4 | E-S |

# Evaluation for Copper

| Lab | Mean A | Z A | Sample A | Mean B | Z B | Sample B |
|---|---|---|---|---|---|---|
| 1 | 0.78 | 1.1 | E-S | 0.73 | 2.3 | G-S |
| 2 | 0.39 | –3.4 | G-P | 0.40 | –2.4 | G-P |
| 3 | 1.11 | 5.0 | H-S | 0.92 | 5.0 | H-P |
| 4 | 0.76 | 0.8 | E-S | 0.62 | 0.8 | E-S |
| 5 | | | | | | |
| 6 | 0.74 | 0.6 | E-S | 0.66 | 1.3 | E-S |
| 7 | 1.92 | 14.5 | H-S | 1.61 | 14.7 | H-S |
| 8 | 0.61 | –0.9 | E-S | 0.49 | –1.1 | E-S |
| 9 | 0.29 | –4.7 | L-S | 0.33 | –3.4 | L-S |
| 10 | 8.41 | 90.3 | H-S | 7.22 | 93.8 | H-S |
| 11 | 0.72 | 0.4 | E-P | 0.47 | –1.4 | G |
| 12 | 0.75 | 0.7 | E-S | 0.61 | 0.7 | E-S |
| 13 | | | | | | |
| 14 | 0.65 | –0.4 | E-S | 0.54 | –0.3 | E-S |
| 15 | 0.82 | 1.6 | G | 0.67 | 1.4 | G |
| 16 | 0.91 | 2.6 | G-P | 0.58 | 0.2 | E-S |
| 17 | 0.51 | –2.1 | E-S | 0.50 | –0.9 | E-S |
| 18 | 0.80 | 1.3 | E-S | | | G |
| 19 | 0.73 | 0.5 | E-S | 0.60 | 0.4 | E-S |
| 20 | 0.75 | 0.8 | E-S | 0.61 | 0.6 | E-S |
| 21 | 0.78 | 1.1 | G | 1.24 | 9.5 | H |
| 22 | 8.80 | 94.9 | H-P | | | G |
| 23 | 0.71 | 0.3 | E-S | 0.62 | 0.8 | E-S |
| 24 | | | | | | |
| 25 | 0.59 | –1.1 | E-S | 0.43 | –1.9 | E-S |
| 26 | 0.40 | –3.3 | G-P | 0.31 | –3.7 | L-P |
| 27 | 0.71 | 0.3 | E-S | 0.59 | 0.2 | E-S |
| 28 | 0.65 | –0.4 | G | 0.42 | –2.1 | G-P |
| 29 | 0.71 | 0.4 | E-S | 0.85 | 1.2 | E-S |
| 30 | 0.57 | –1.4 | E-S | 0.52 | –0.7 | E-S |
| 31 | 0.37 | –3.7 | L-S | 0.57 | 0.0 | E-S |
| 32 | 0.73 | 0.6 | E-S | 0.58 | 0.2 | E-S |
| 33 | 0.69 | 0.1 | E-S | 0.57 | 0.1 | E-S |
| 34 | 0.68 | –0.0 | E-S | 0.42 | –2.1 | G-S |
| 35 | 0.69 | 0.1 | E-S | 0.59 | 0.3 | E-S |
| 36 | 1.04 | 4.2 | H-S | 0.91 | 4.8 | H-S |
| 37 | 0.84 | 1.8 | E-S | 0.65 | 1.2 | E-S |
| 38 | | | | | | |
| 39 | 1.34 | 7.6 | H-P | 1.49 | 13.1 | H-S |
| 40 | 0.75 | 0.8 | E-S | 0.62 | 0.7 | E-S |
| 41 | 0.70 | 0.2 | E-S | 0.80 | 0.5 | E-S |

# Evaluation for Zinc

| Lab | Mean A | Z A | Sample A | Mean B | Z B | Sample B |
|---|---|---|---|---|---|---|
| 1 | 0.75 | 4.3 | E-S | 0.92 | 4.5 | G-S |
| 2 | 0.34 | –2.4 | E-P | 0.58 | –0.1 | E-P |
| 3 | 0.42 | –1.1 | E-P | 0.70 | 1.5 | E-P |
| 4 | 0.42 | –1.1 | E-S | 0.58 | –0.2 | E-S |
| 5 | | | | | | |
| 6 | | | G | | | G |
| 7 | 1.00 | 8.5 | H-P | 1.63 | 14.1 | H-P |
| 8 | 0.39 | –1.6 | E-S | 0.41 | –2.5 | E-S |
| 9 | 0.66 | 2.9 | E-S | 0.73 | 1.9 | E-S |
| 10 | 0.20 | –4.6 | E-P | 0.30 | –3.9 | E-P |
| 11 | 0.52 | 0.6 | G | 0.46 | –1.8 | G |
| 12 | 0.75 | 4.3 | E-S | 0.83 | 3.2 | E-S |
| 13 | 0.69 | 3.3 | E-P | 1.33 | 10.0 | H-P |
| 14 | 0.41 | –1.2 | E-S | 0.47 | –1.7 | E-P |
| 15 | | | L | 0.44 | –2.0 | G |
| 16 | 0.48 | 0.0 | G-P | 0.45 | –1.9 | E-P |
| 17 | | | G | | | G |
| 18 | | | H | | | H |
| 19 | 0.32 | –2.7 | E-P | 0.53 | –0.8 | E-P |
| 20 | 0.39 | –1.6 | E-P | 0.46 | –1.7 | E-S |
| 21 | | | | 18.30 | 240.0 | H |
| 22 | 6.20 | 94.1 | H-P | 3.00 | 32.6 | H-P |
| 23 | 0.41 | –1.3 | E-S | 0.62 | 0.4 | E-S |
| 24 | | | | | | |
| 25 | | | G | | | G |
| 26 | 0.25 | –3.9 | E-P | 0.11 | –6.6 | L-P |
| 27 | 0.45 | –0.6 | E-S | 0.48 | –1.5 | E-S |
| 28 | 0.52 | 0.6 | G | 0.38 | –2.9 | E-P |
| 29 | 0.74 | 4.2 | G-P | 0.67 | 1.1 | E-S |
| 30 | 0.41 | –1.3 | E-S | 0.44 | –2.0 | E-S |
| 31 | | | | | | |
| 32 | 0.69 | 3.3 | E-S | 0.83 | 3.2 | E-S |
| 33 | | | | | | |
| 34 | 1.96 | 24.3 | H-S | 1.47 | 11.9 | H-P |
| 35 | 0.47 | –0.2 | E-P | 0.79 | 2.7 | E-P |
| 36 | 1.96 | 24.3 | H-P | 1.96 | 18.6 | H-S |
| 37 | 0.54 | 0.9 | E-S | 0.63 | 0.5 | E-S |
| 38 | | | | | | |
| 39 | 18.37 | 294.6 | H-S | 23.39 | 308.9 | H-P |
| 40 | | | | | | |
| 41 | 0.51 | 0.3 | E-P | 0.60 | 0.1 | E-S |

# Evaluation for Arsenic

| Lab | Mean A | Z A | Sample A | Mean B | Z B | Sample B |
|---|---|---|---|---|---|---|
| 1 | | | | | | |
| 2 | | | | | | |
| 3 | 0.44 | 2.5 | G-P | 0.65 | –0.2 | G-P |
| 4 | | | | | | |
| 5 | | | | | | |
| 6 | 0.32 | –0.3 | E-S | 0.65 | –0.1 | E-S |
| 7 | 0.30 | –0.7 | E-S | 0.70 | 0.5 | E-S |
| 8 | | | | | | |
| 9 | | | | | | |
| 10 | | | | | | |
| 11 | 0.32 | –0.3 | E-S | 0.66 | 0.0 | G |
| 12 | | | | | | |
| 13 | | | | | | |
| 14 | | | | | | |
| 15 | 0.21 | –2.9 | G | 0.50 | –2.0 | G |
| 16 | | | | | | |
| 17 | | | G | | | G |
| 18 | | | | | | |
| 19 | 0.35 | 0.5 | E-S | 0.72 | 0.7 | E-S |
| 20 | 0.30 | –0.8 | E-S | 0.62 | –0.5 | E-S |
| 21 | 0.41 | 1.9 | G | 0.94 | 3.3 | H |
| 22 | | | | | | |
| 23 | | | G | | | G |
| 24 | | | G | | | G |
| 25 | | | G | | | G |
| 26 | | | | | | |
| 27 | 0.33 | 0.1 | E-S | 0.67 | 0.1 | E-S |
| 28 | | | | | | |
| 29 | | | | | | |
| 30 | | | | | | |
| 31 | | | | | | |
| 32 | | | | | | |
| 33 | | | | | | |
| 34 | | | | | | |
| 35 | | | | | | |
| 36 | | | | | | |
| 37 | | | | | | |
| 38 | 0.38 | 1.2 | G | 0.70 | 0.4 | G |
| 39 | | | | | | |
| 40 | 0.28 | –1.1 | E-S | 0.63 | –0.4 | E-S |
| 41 | | | | | | |

# Evaluation for Cadmium

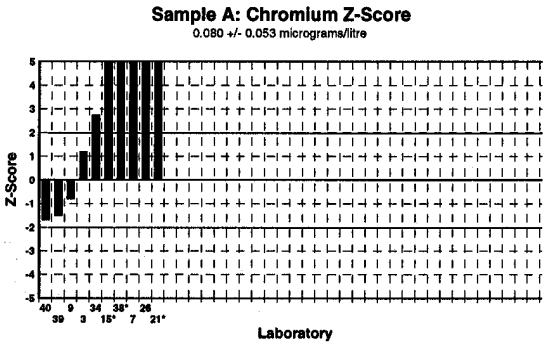
| Lab | Mean A | Z A | Sample A | Mean B | Z B | Sample B |
|---|---|---|---|---|---|---|
| 1 | 0.015 | 0.98 | E-S | 0.023 | –0.08 | E-S |
| 2 | 0.012 | –0.6 | E-S | 0.016 | –2.3 | E-S |
| 3 | 0.013 | –0.5 | E-P | 0.019 | –1.4 | E-P |
| 4 | | | | | | |
| 5 | 0.010 | –2.1 | E-S | 0.019 | –1.4 | E-S |
| 6 | 0.022 | 5.2 | H-S | 0.026 | 1.0 | E-P |
| 7 | 0.044 | 18.4 | H-P | 0.022 | –0.3 | G-P |
| 8 | 0.010 | –2.0 | E-S | 0.017 | –2.1 | E-S |
| 9 | 0.035 | 13.0 | H-S | 0.065 | 14.6 | H-S |
| 10 | 0.113 | 59.9 | H-S | 0.102 | 27.7 | H-S |
| 11 | 0.014 | 0.6 | E-S | 0.020 | –1.0 | G |
| 12 | 0.013 | –0.2 | E-S | 0.023 | 0.2 | E-S |
| 13 | 0.068 | 33.0 | H-S | 0.065 | 14.7 | H-P |
| 14 | 0.009 | –2.6 | H-P | 0.016 | –2.3 | E-S |
| 15 | 0.011 | –1.4 | G | 0.022 | –0.3 | G |
| 16 | | | G | | | G |
| 17 | | | G | | | G |
| 18 | | | G | | | G |
| 19 | 0.013 | –0.1 | E-S | 0.022 | –0.2 | E-S |
| 20 | 0.014 | 0.6 | E-S | 0.024 | 0.5 | E-S |
| 21 | 0.060 | 39.9 | H | | | |
| 22 | | | H | | | H |
| 23 | | | G | | | G |
| 24 | | | | | | |
| 25 | | | H | | | G |
| 26 | 0.053 | 23.5 | H-S | 0.027 | 1.5 | E-S |
| 27 | 0.016 | 1.7 | E-S | 0.027 | 1.4 | E-S |
| 28 | 0.015 | 1.0 | G | 0.011 | –4.2 | G |
| 29 | 0.016 | 1.7 | E-S | 0.029 | 2.2 | E-S |
| 30 | 0.010 | –2.3 | E-P | 0.016 | –2.3 | E-S |
| 31 | 0.013 | –0.1 | E-S | 0.026 | 0.9 | E-S |
| 32 | 0.015 | 0.9 | E-S | 0.026 | 1.1 | E-S |
| 33 | | | | | | |
| 34 | 0.031 | 10.3 | H-S | 0.027 | 1.6 | E-S |
| 35 | 0.009 | –2.7 | E-P | 0.015 | –2.8 | E-S |
| 36 | 0.014 | 0.3 | E-S | 0.034 | 4.0 | G-S |
| 37 | 0.016 | 1.5 | E-S | 0.030 | 2.3 | E-S |
| 38 | 0.110 | 57.9 | H | | | |
| 39 | 0.059 | 27.2 | H-S | 0.062 | 13.5 | H-P |
| 40 | 0.102 | 53.1 | H | 0.283 | 89.9 | H |
| 41 | 0.013 | –0.2 | E-S | 0.019 | –1.4 | E-S |

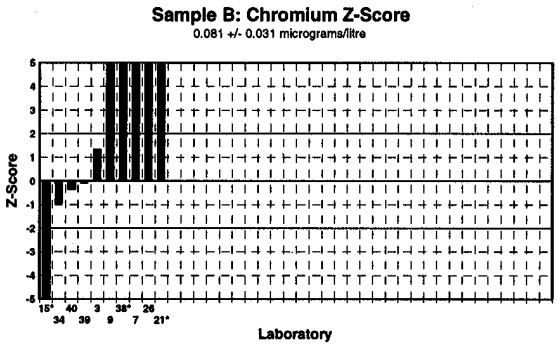
# Evaluation for Lead

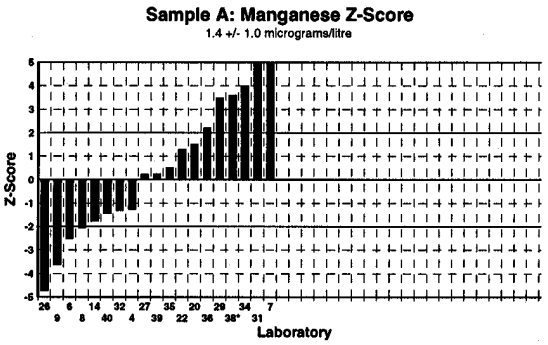
| Lab | Mean A | Z A | Sample A | Mean B | Z B | Sample B |
|---|---|---|---|---|---|---|
| 1 | | | G | | | G |
| 2 | 0.013 | –0.4 | E-P | 0.013 | 0.5 | E-P |
| 3 | 0.022 | 5.5 | E-S | 0.028 | 10.0 | H-S |
| 4 | 0.017 | 2.1 | E-S | 0.013 | 0.6 | E-P |
| 5 | 0.010 | –1.7 | E-S | 0.007 | –3.8 | E-S |
| 6 | | | H | | | H |
| 7 | 0.346 | 200.0 | H-S | 0.188 | 112.9 | H-P |
| 8 | 0.021 | 4.5 | E-S | 0.016 | 2.2 | E-S |
| 9 | 0.116 | 61.5 | H-S | 0.150 | 88.6 | H-S |
| 10 | 0.462 | 269.8 | H-S | 0.390 | 242.8 | H-S |
| 11 | | | H | | | H |
| 12 | | | G | | | G |
| 13 | 0.115 | 60.9 | H-P | 0.149 | 87.6 | H-P |
| 14 | | | G | | | G |
| 15 | 0.012 | –0.8 | G | 0.013 | 0.4 | G |
| 16 | | | H | | | H |
| 17 | | | G | | | G |
| 18 | | | H | | | H |
| 19 | 0.008 | –3.4 | E-P | 0.007 | –3.4 | E-P |
| 20 | 0.016 | 1.6 | E-S | 0.018 | 3.4 | G-P |
| 21 | | | | | | |
| 22 | | | H | | | H |
| 23 | | | G | | | G |
| 24 | | | | | | |
| 25 | | | H | | | H |
| 26 | 0.035 | 12.9 | H-S | 0.050 | 24.2 | H-S |
| 27 | 0.005 | –5.0 | E-P | 0.005 | –4.6 | E-P |
| 28 | 0.043 | 17.9 | G | 0.020 | 4.5 | G-P |
| 29 | 0.016 | 1.6 | E-S | 0.011 | –1.2 | E-S |
| 30 | 0.011 | –1.5 | E-S | 0.017 | 2.9 | E-S |
| 31 | | | | | | |
| 32 | 0.008 | –2.9 | E-S | 0.007 | –3.2 | E-S |
| 33 | | | | | | |
| 34 | | | | | | |
| 35 | 0.010 | –1.9 | E-S | 0.011 | –0.9 | E-P |
| 36 | 0.054 | 24.5 | H-P | 0.058 | 29.3 | H-P |
| 37 | 0.009 | –2.3 | E-S | 0.010 | –1.3 | E-S |
| 38 | | | | 0.400 | 249.3 | H |
| 39 | 1.100 | 653.6 | H-S | 2.412 | 1543.5 | H-S |
| 40 | 0.040 | 16.0 | H | | | |
| 41 | 0.021 | 4.7 | E-S | 0.019 | 4.2 | E-S |

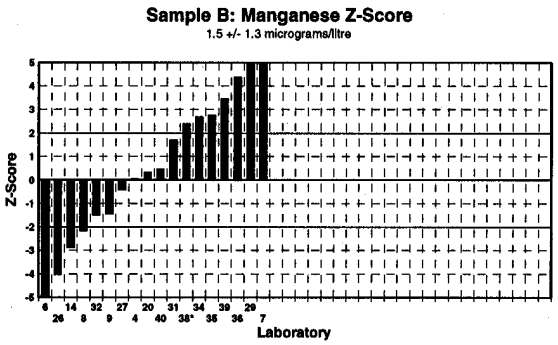
# ANNEX 5

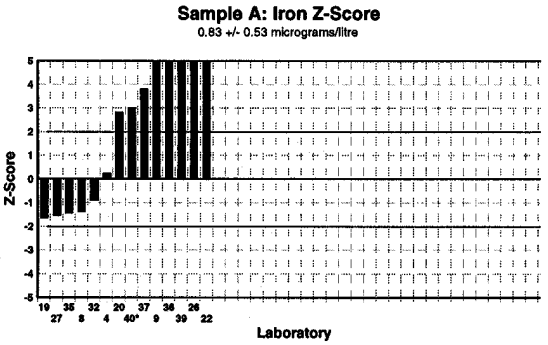
## Trace Metal Z-Scores

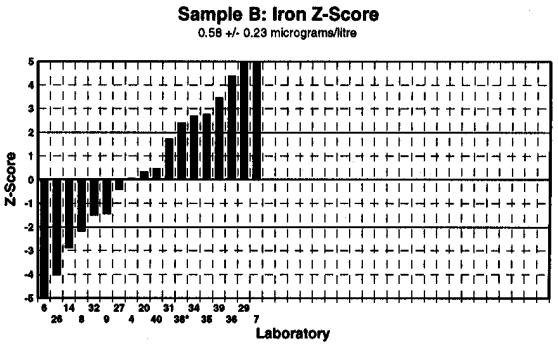


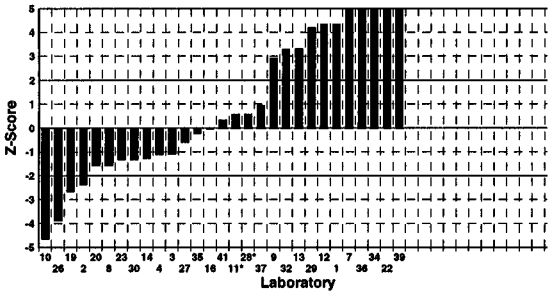



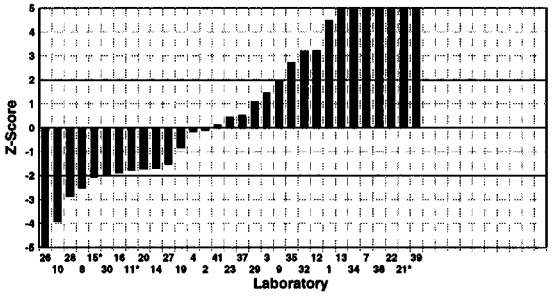
**Sample A: Zinc Z-Score**

0.49 +/- 0.34 micrograms/litre



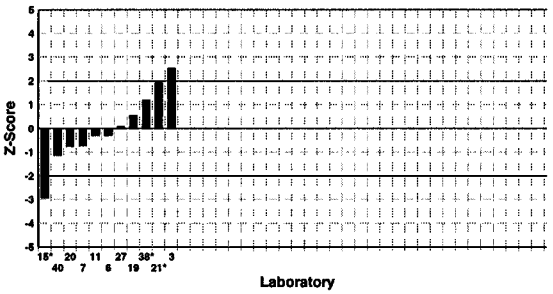

**Sample B: Zinc Z-Score**

0.59 +/- 0.35 micrograms/litre



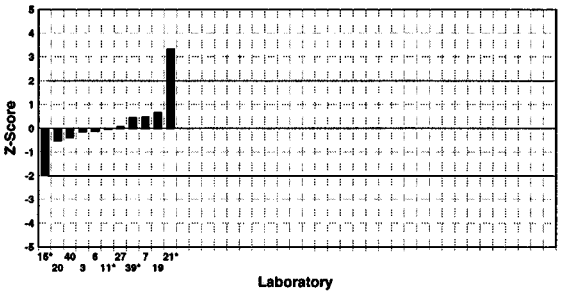

**Sample A: Arsenic Z-Score**

0.33 +/- 0.11 micrograms/litre



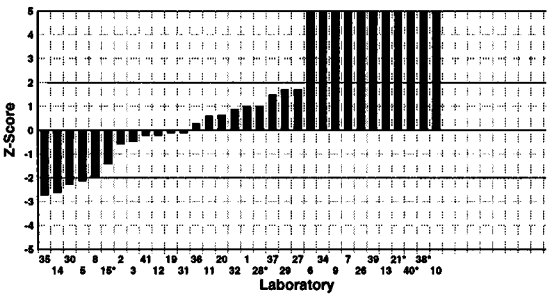

**Sample B: Arsenic Z-Score**

0.66 +/- 0.09 micrograms/litre



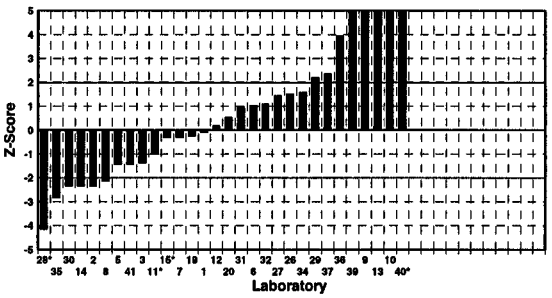

**Sample A: Cadmium Z-Score**

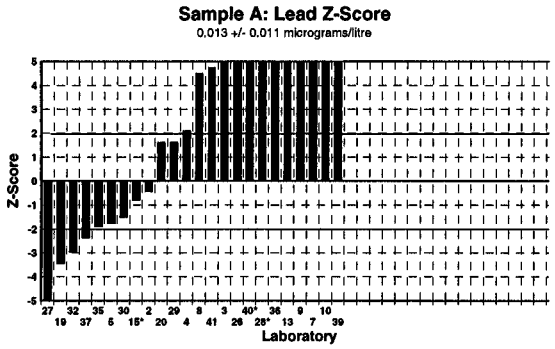
0.013 +/- 0.007 micrograms/litre

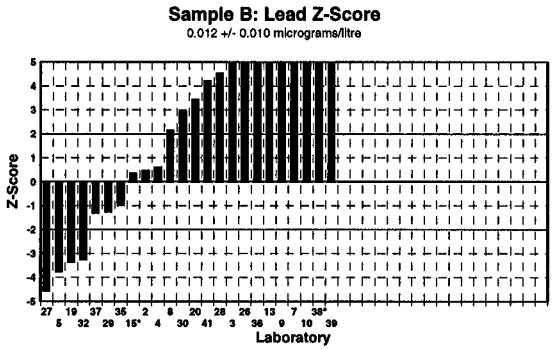



**Sample B: Cadmium Z-Score**

0.023 +/- 0.011 micrograms/litre

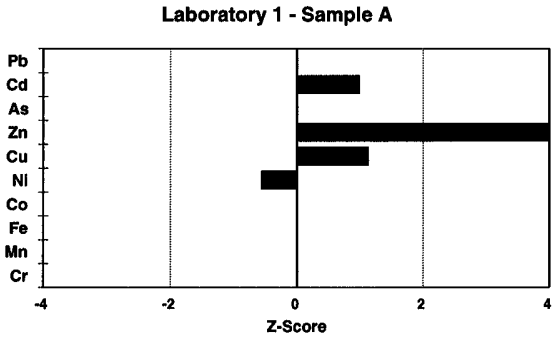


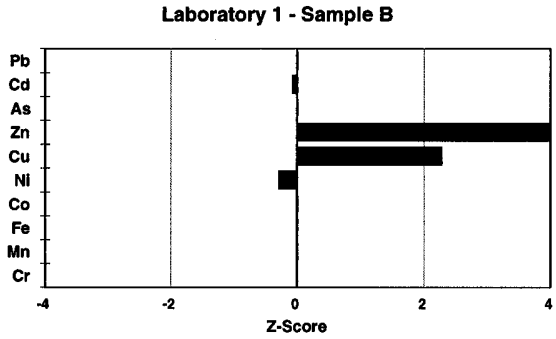

Sample A: Lead Z-Score
0.013 +/- 0.011 micrograms/litre
Z-Score
Laboratory

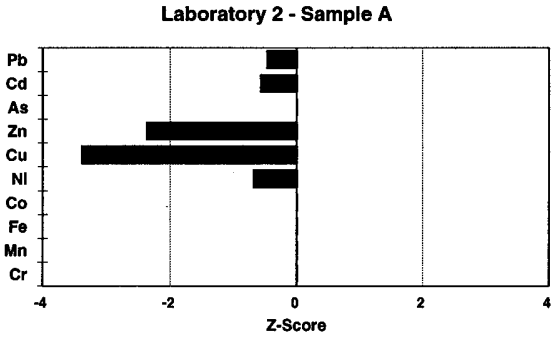

Sample B: Lead Z-Score
0.012 +/- 0.010 micrograms/litre
Z-Score
Laboratory

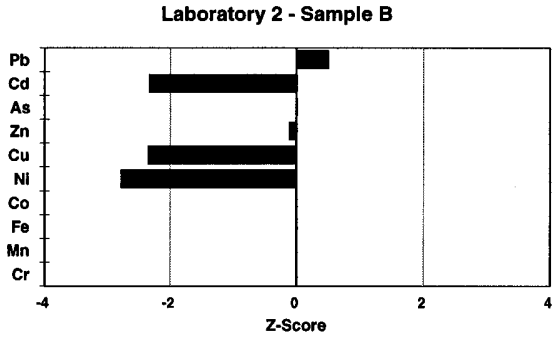
# ANNEX 6

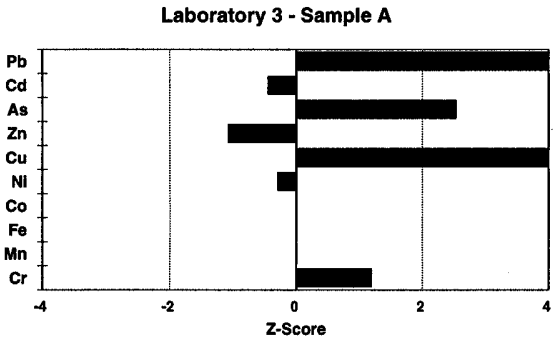
## Laboratory Z-Scores

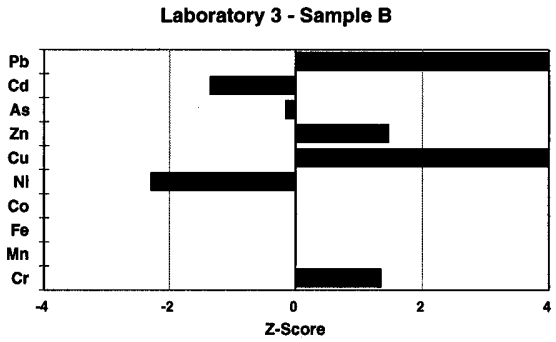


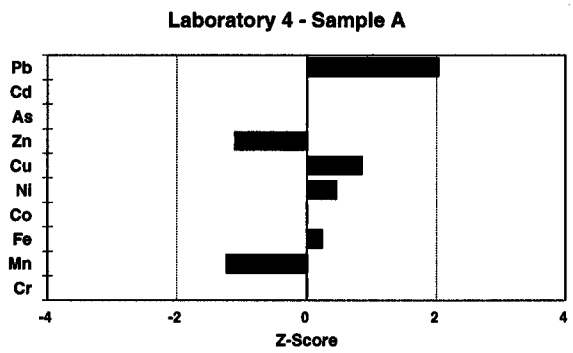

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Pb
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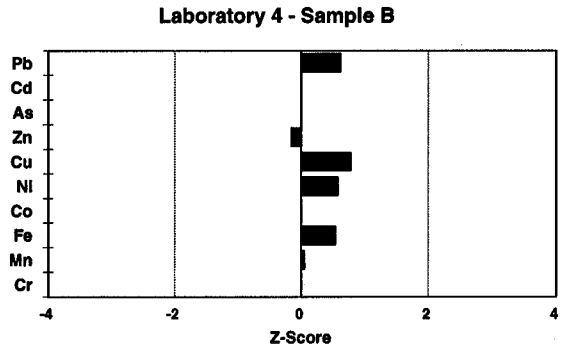
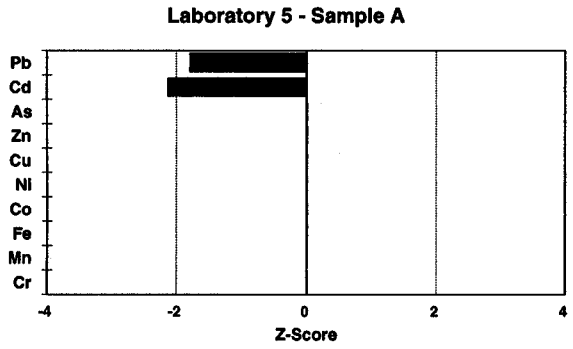
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 4 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score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As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
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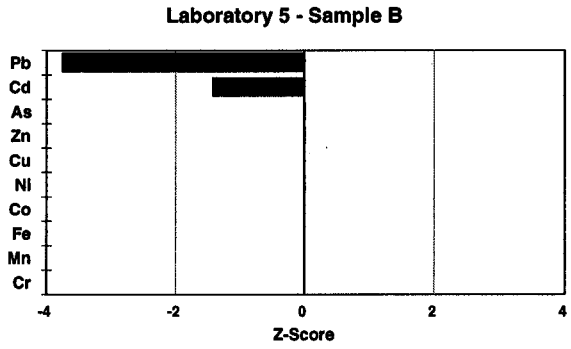
0
2
4
Z-Score


Laboratory 5 - Sample B
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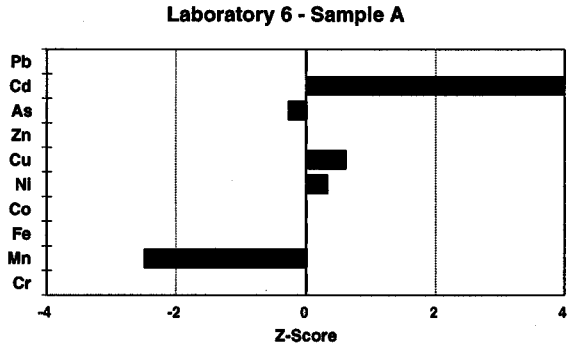
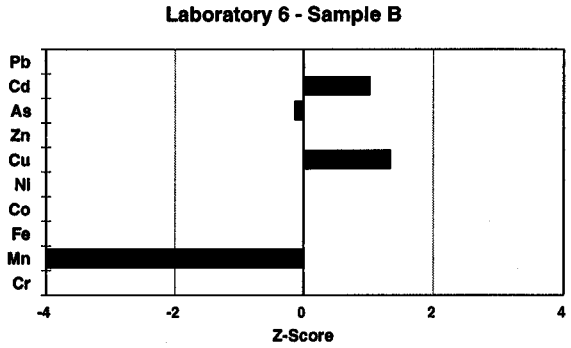
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 6 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 6 - Sample B
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As
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Cu
Ni
Co
Fe
Mn
Cr
-4
-2
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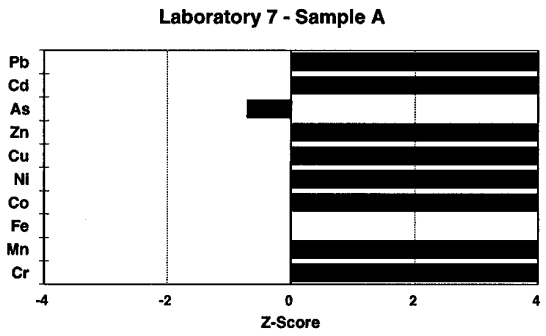
2
4
Z-Score


Laboratory 7 - Sample A
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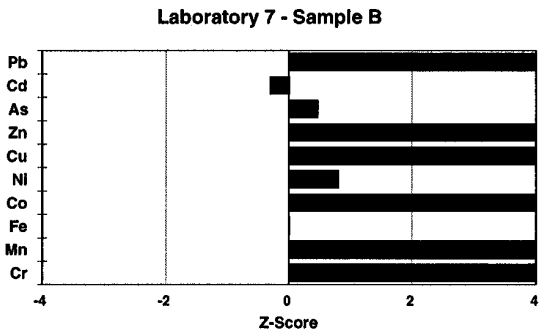
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 7 - Sample B
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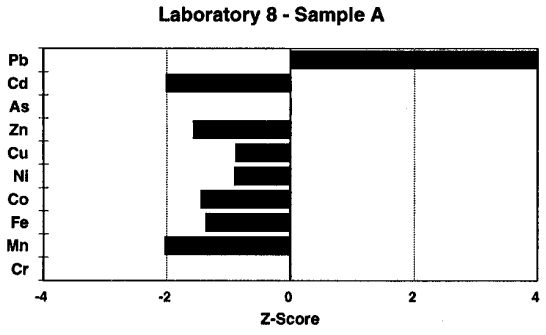
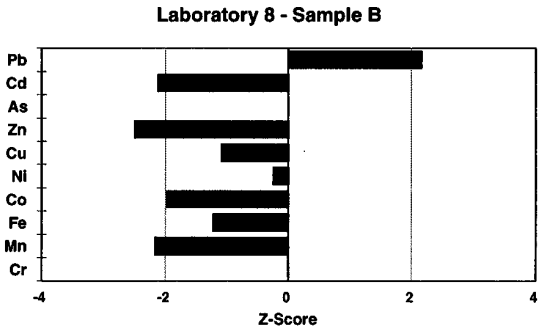
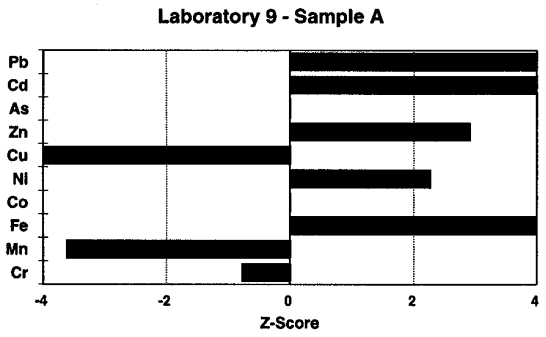
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 8 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 8 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 9 - Sample A
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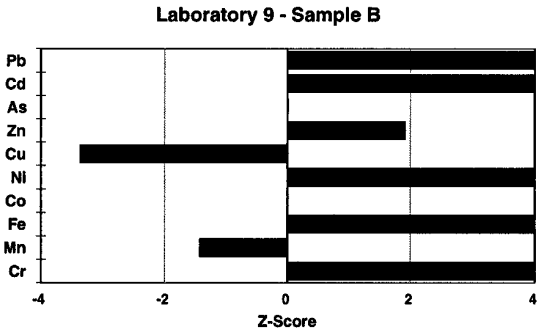
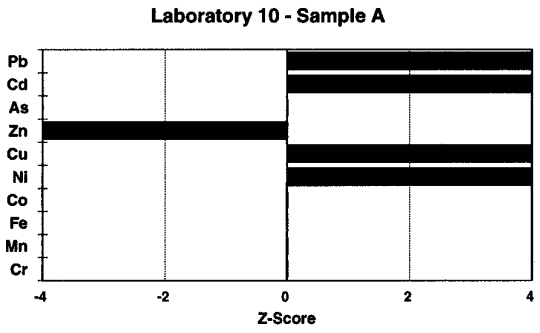
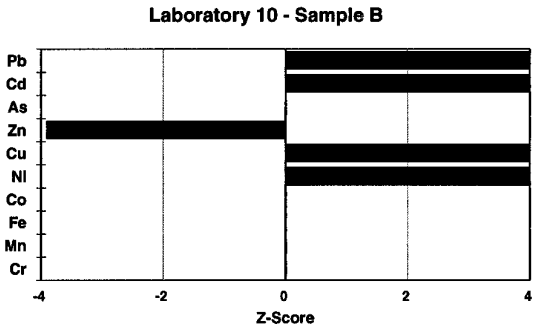
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 9 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 10 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 10 - Sample B
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As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
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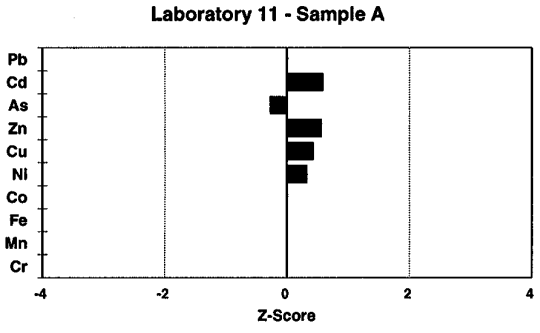
4
Z-Score


Laboratory 11 - Sample A
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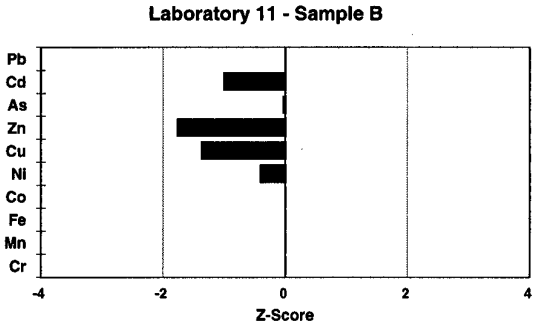
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score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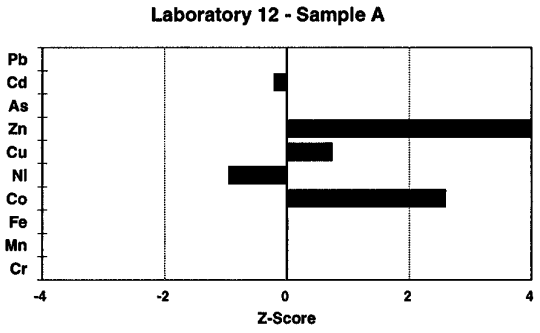
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score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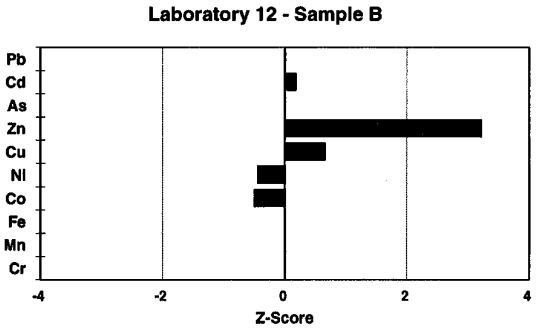
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 12 - Sample B
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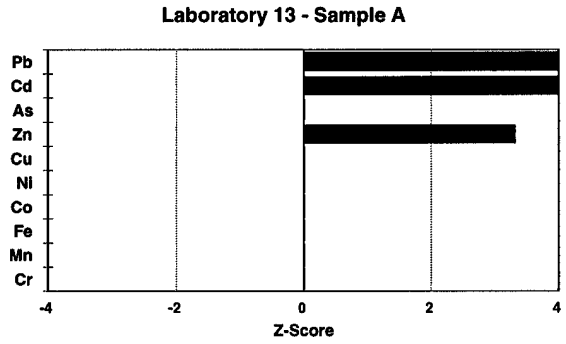
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score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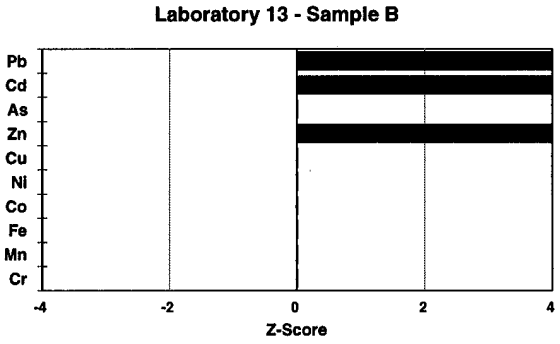
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score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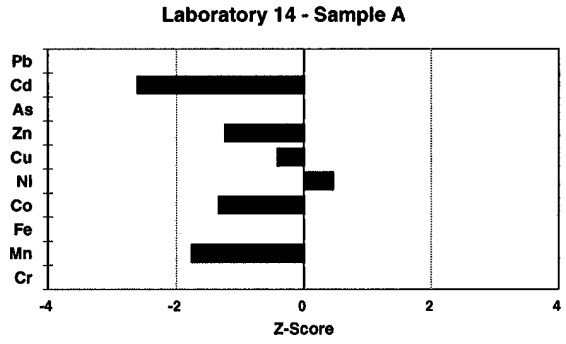
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 14 - Sample A
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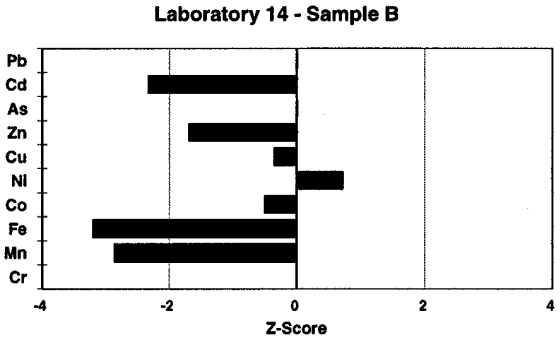
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 14 - Sample B
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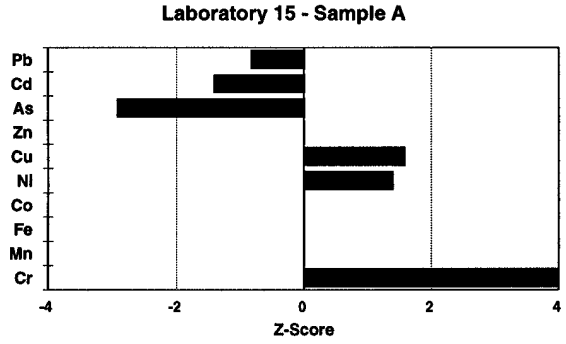
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 15 - Sample A
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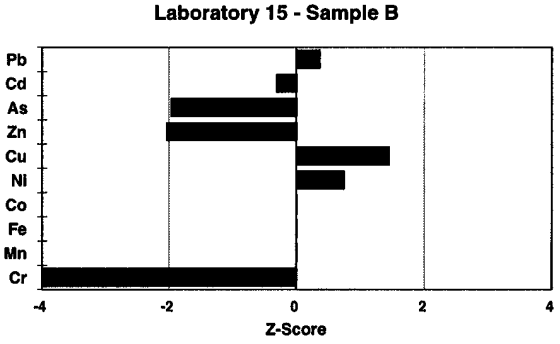
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 15 - Sample B
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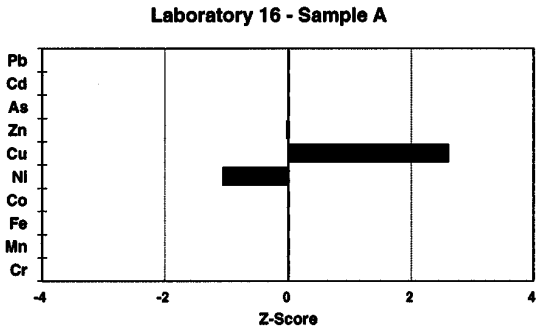
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 16 - Sample A
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As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
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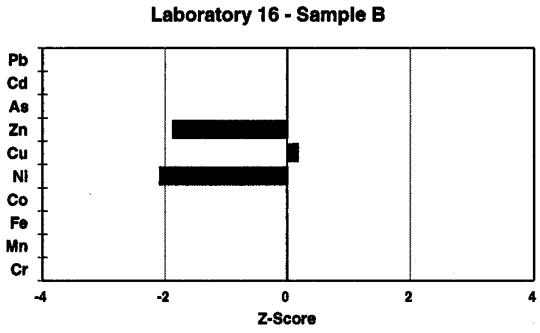
2
4
Z-Score


Laboratory 16 - Sample B
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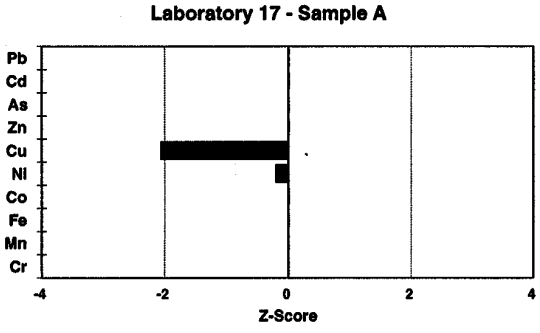
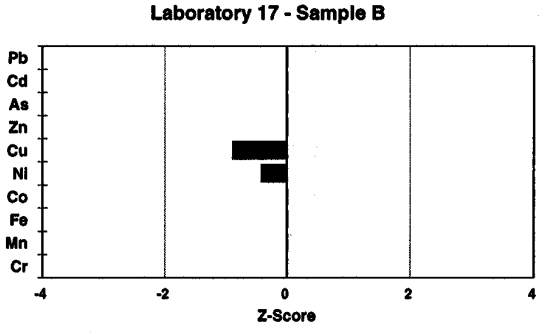
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 17 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 17 - Sample B
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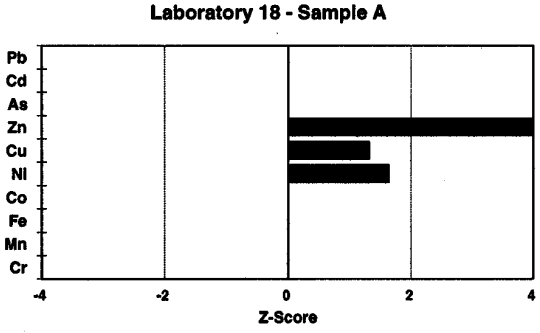
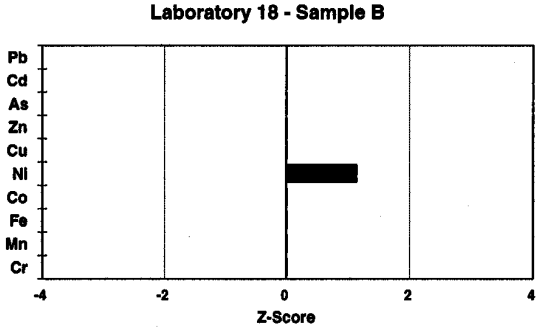
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 18 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 18 - Sample B
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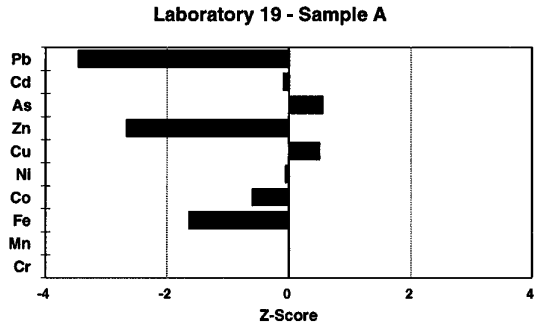
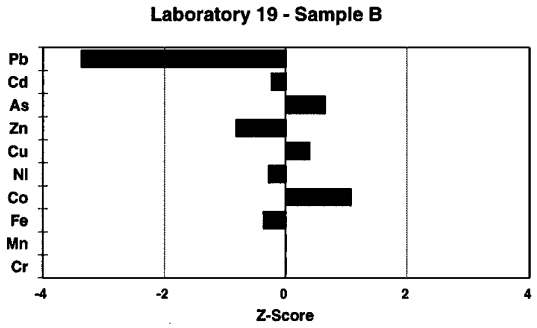
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 19 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 19 - Sample B
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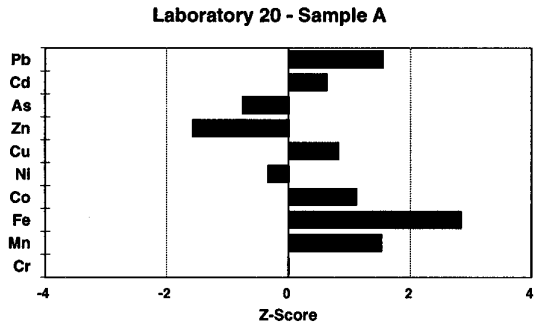
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 20 - Sample A
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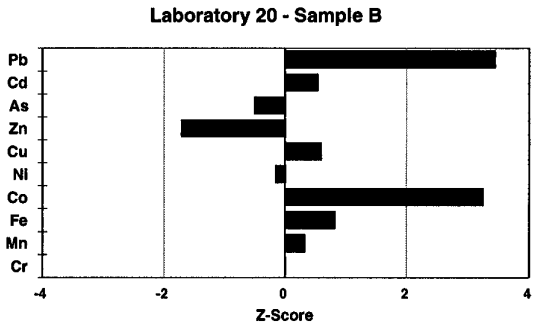
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 20 - Sample B
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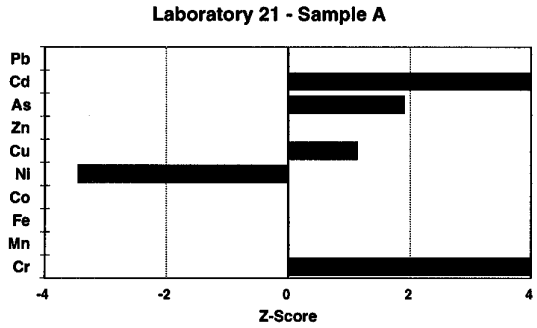
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 21 - Sample A
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As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
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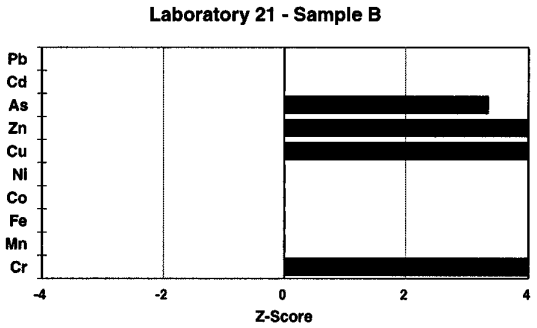
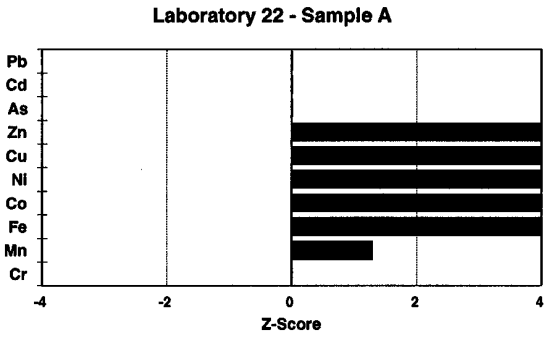
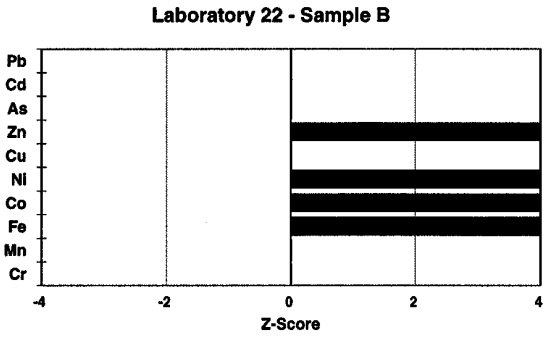
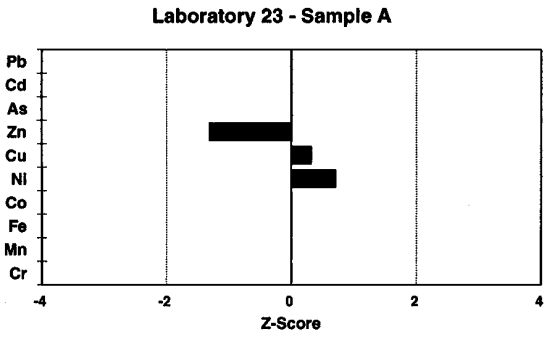
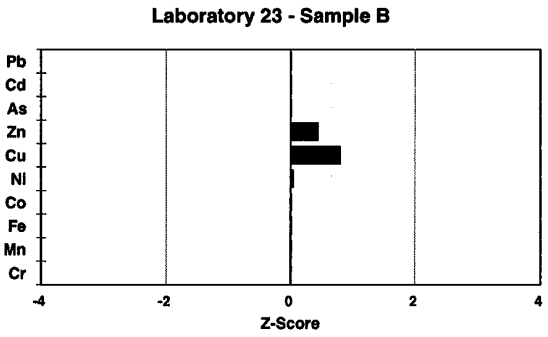
2
4
Z-Score

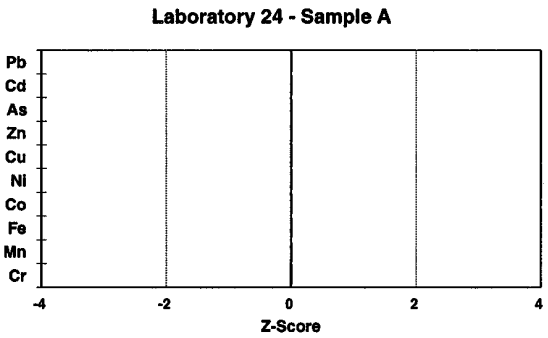

Laboratory 21 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

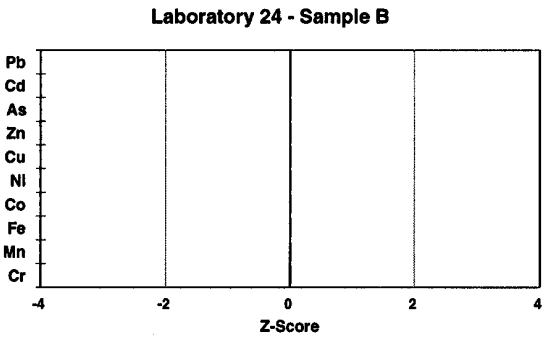

Laboratory 22 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

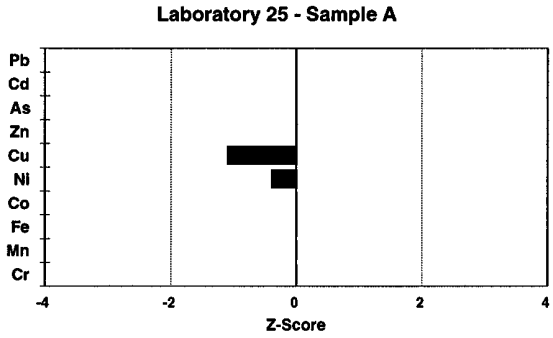

Laboratory 22 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

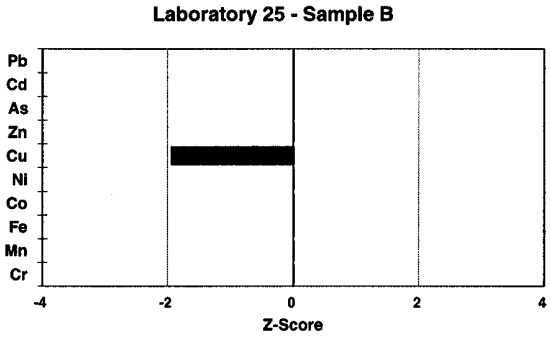

Laboratory 23 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

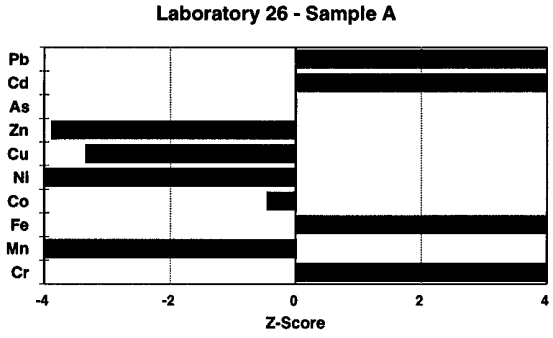

Laboratory 23 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

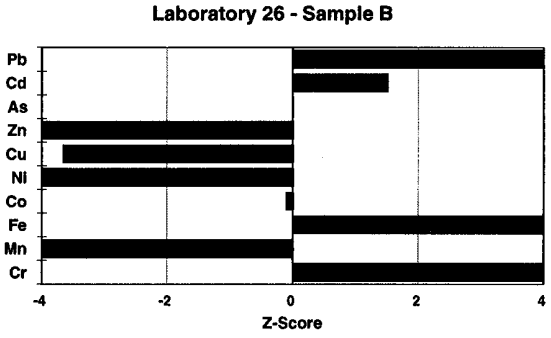

Laboratory 24 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

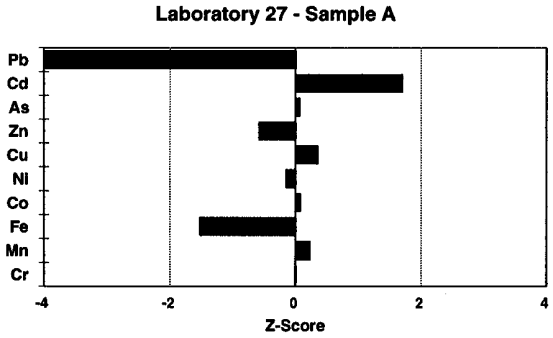

Laboratory 24 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

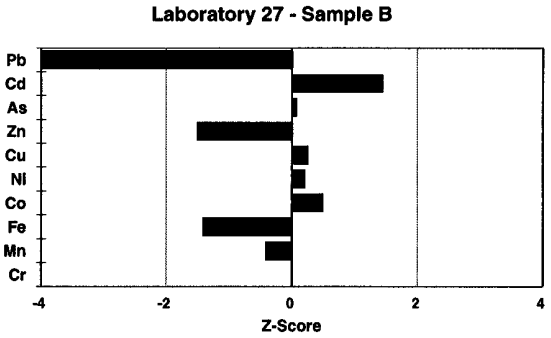

Laboratory 25 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

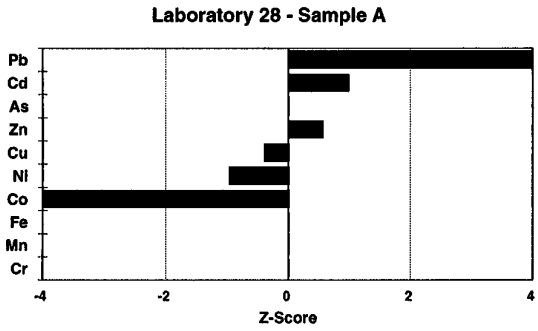

Laboratory 25 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

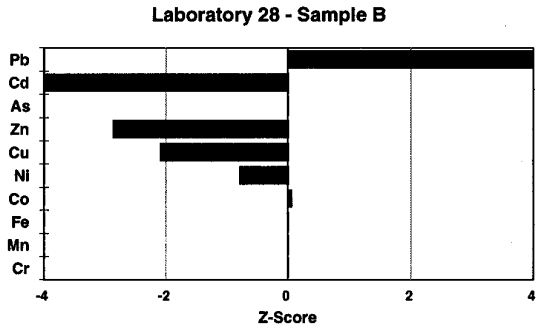

Laboratory 26 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

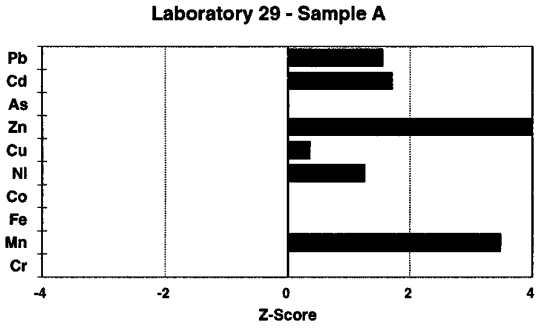

Laboratory 26 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

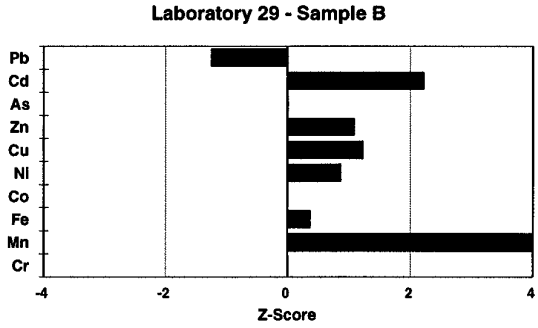

Laboratory 27 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

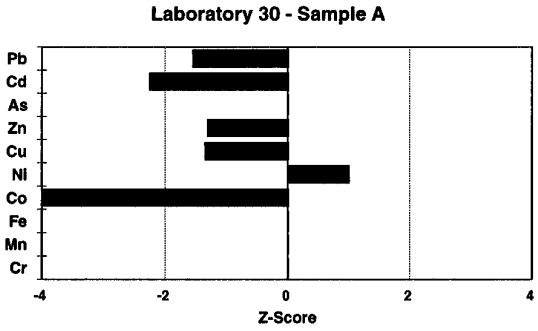

Laboratory 27 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

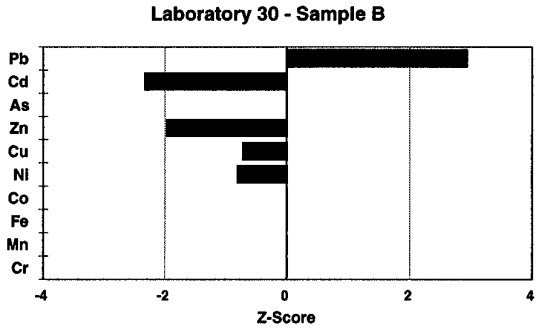

Laboratory 28 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

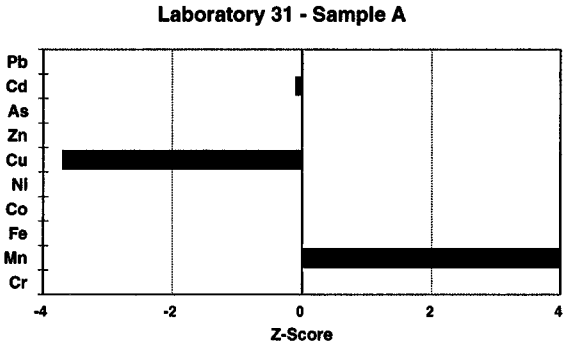

Laboratory 28 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

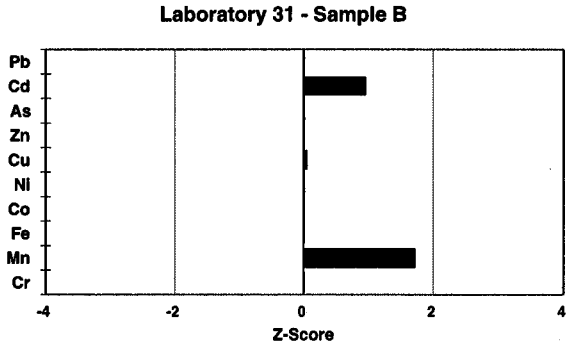

Laboratory 29 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

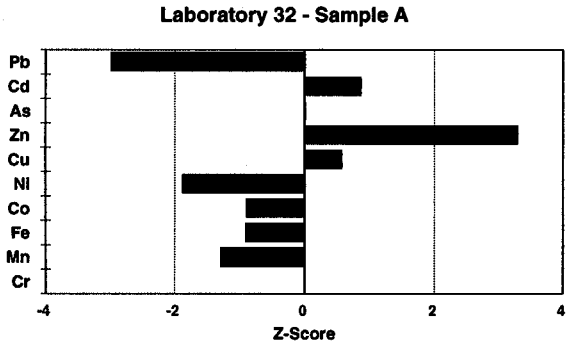

Laboratory 29 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

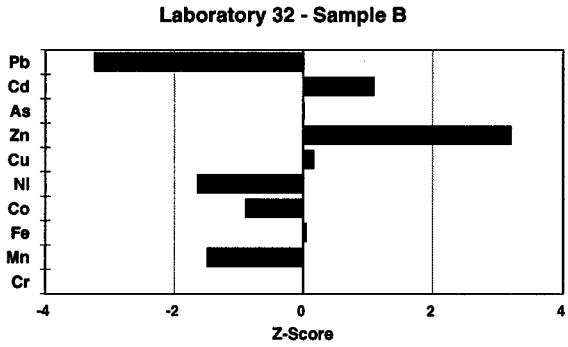

Laboratory 30 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

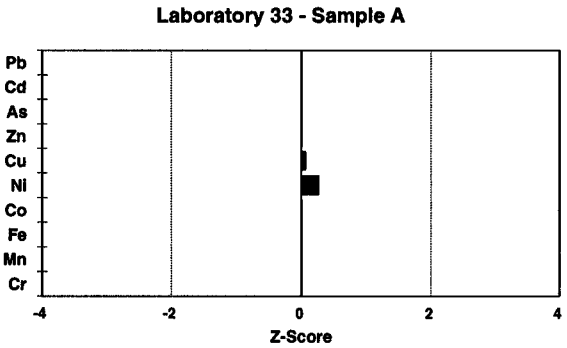

Laboratory 30 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

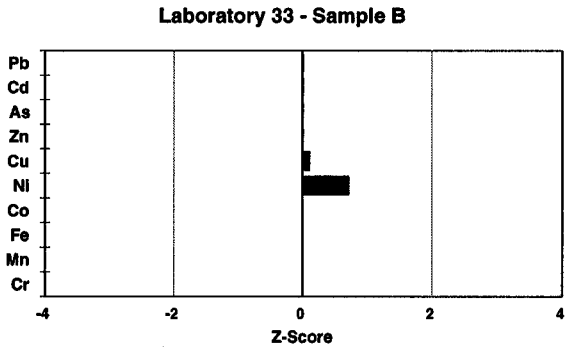

Laboratory 31 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

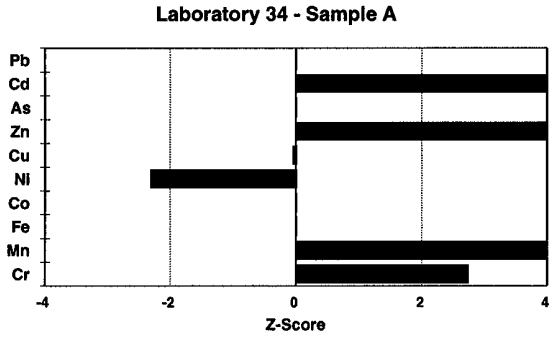

Laboratory 31 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

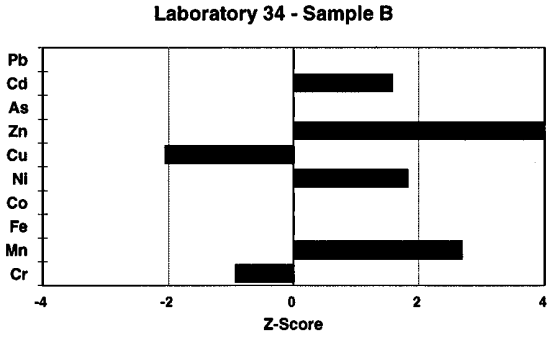

Laboratory 32 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

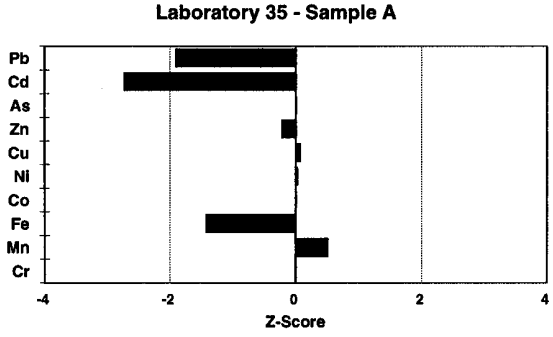

Laboratory 32 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

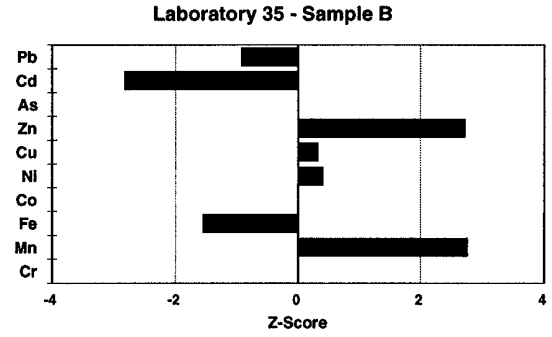

Laboratory 33 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

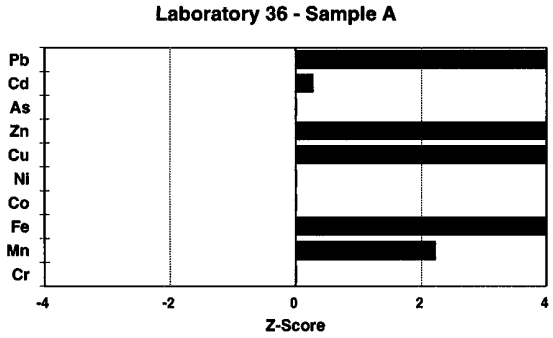

Laboratory 33 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

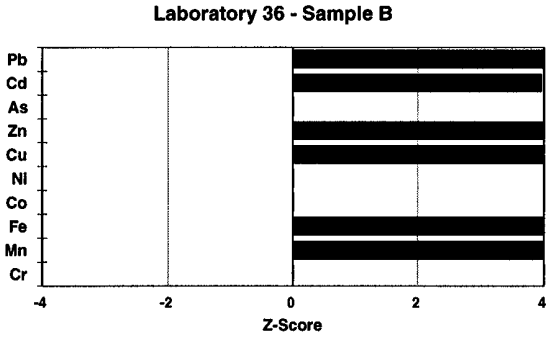

Laboratory 34 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

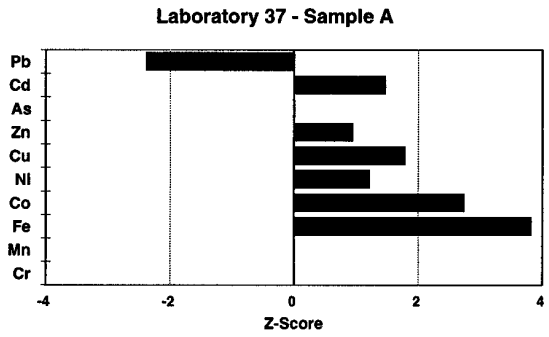

Laboratory 34 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

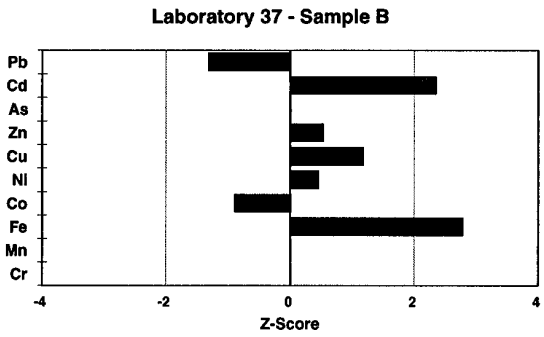

Laboratory 35 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

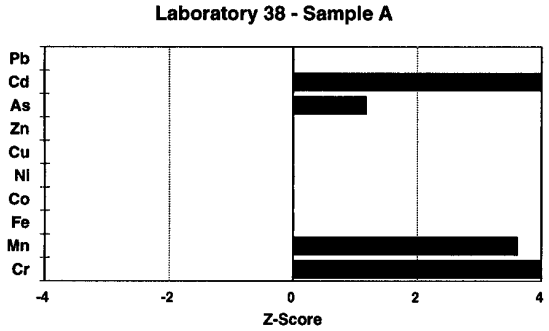

Laboratory 35 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

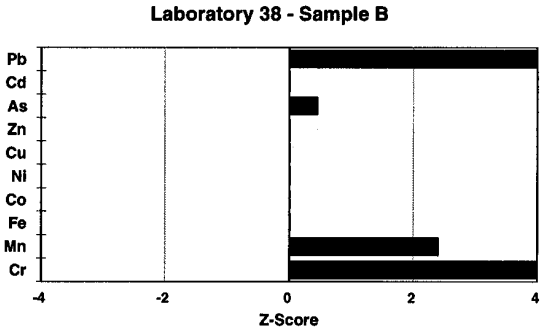

Laboratory 36 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

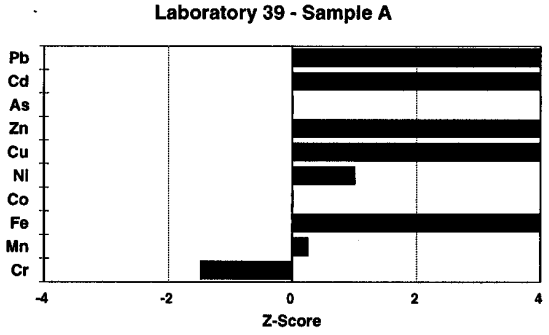

Laboratory 36 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

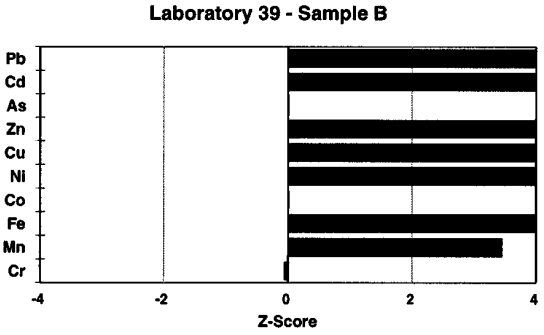

Laboratory 37 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

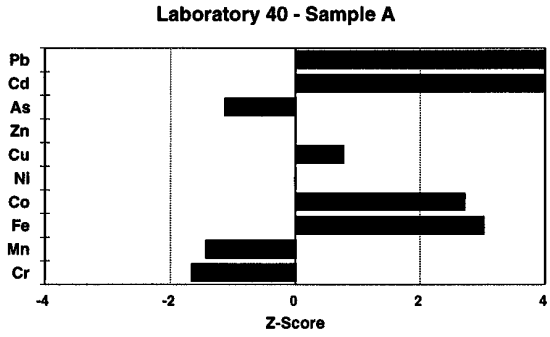

Laboratory 37 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

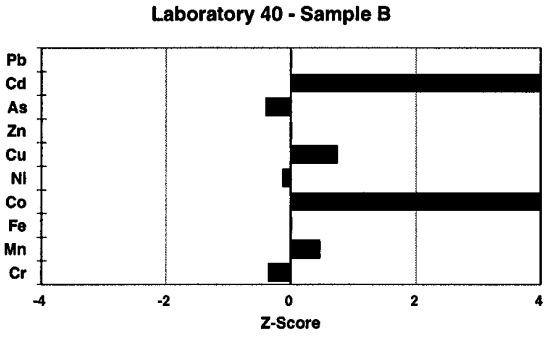

Laboratory 38 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

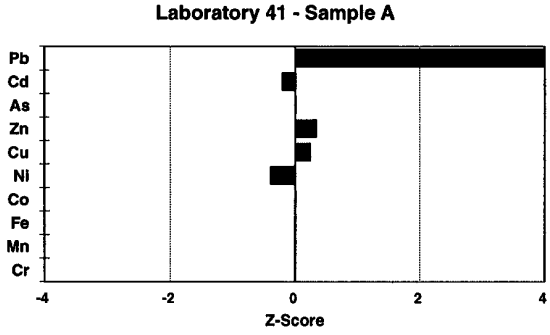

Laboratory 38 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

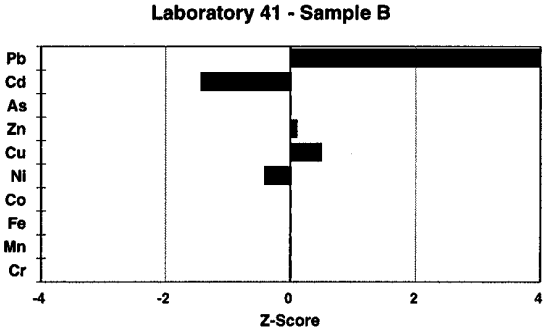

Laboratory 39 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 39 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 40 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 40 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 41 - Sample A
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score


Laboratory 41 - Sample B
Pb
Cd
As
Zn
Cu
Ni
Co
Fe
Mn
Cr
-4
-2
0
2
4
Z-Score

# ANNEX 7

## Comments on the Evaluation of Intercomparison Study Results

The purpose of an intercomparison study is to provide the participating laboratories and the intercomparison study organizers with a means of objectively assessing the reliability of results produced by those laboratories. There are three parameters which are assessed most frequently: 1) accuracy, 2) intralaboratory precision, and 3) interlaboratory precision. These are discussed below.

## 1 Accuracy

The assessment of **accuracy** is usually the most important goal of an ICES intercomparison study. This is an estimate of the **bias** of the participating laboratory with respect to the **assigned value** for the concentration of the analyte. In the best of cases, the assigned value will have been predetermined by the coordinator and will be a practical estimate of the true value of the concentration of the analyte in the matrix. In some instances, this is not possible and the assigned value will be a consensus value established by the coordinator by a **critical evaluation** of the set of results returned by the participants.

The assigned value cannot be merely the consensus value of the participants because there may not be a consensus, or the consensus may be biased due to widespread use of faulty methodology.

The **bias** is equal to $(x - X)$ where

$x$ is the analyte concentration determined by the participant, and

$X$ is the analyte concentration value assigned by the coordinator.

The **relative bias** is $(x-X)/X$. The relative bias is usually used as the measure of accuracy rather than the absolute bias.

If the user community is able to estimate the precision $s$ needed in order to ensure proper data interpretation, the quotient $z = (x - X)/s$ is a very valuable indicator. If $z$ exceeds 2 there is less than a five percent probability that the laboratory can produce reliable data.

## 2 Intralaboratory Precision

This is an estimate of the **repeatability** of a procedure within the individual participating laboratory. Repeatability for a particular analyte concentration can be assessed by the analysis of replicate samples and is usually described by the **standard deviation ($s$)** of a single determination. The computation is simple:

$$s = \sqrt{\frac{\sum_{x=1}^{N} (x_i - \bar{x})^2}{N-1}}$$

where $x_i$ is the determined concentration of an individual replicate,

$x$ is the determined mean of the replicate analyses, and

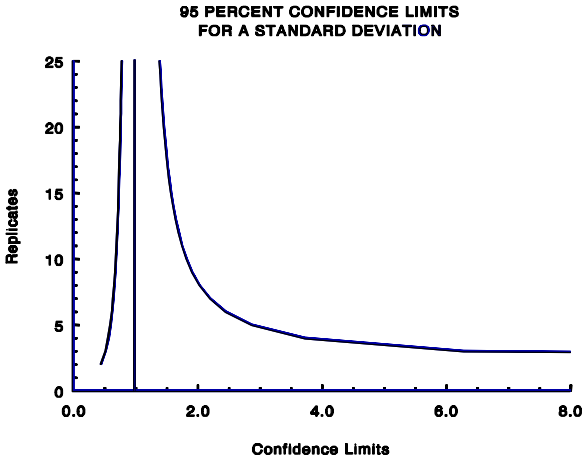
$N$ is the number of replicate analyses.

The **relative standard deviation (RSD)** is $s/x$. This number is often multiplied by 100 to yield the **percent standard deviation**.

An estimate of the repeatability can also be calculated from a set of samples of different analyte concentrations. This is done by a linear regression procedure and yields an overall value of the standard deviation for the range of concentrations tested.

The calculation of the intralaboratory precision is usually done in intercomparison exercises but, except for identifying a laboratory with serious precision problems, is of limited value. An intercomparison study is usually a snapshot in time and only provides an estimate of the true standard deviation. The number of replicate samples analysed is usually rather small and the errors in this estimate can be very large as indicated in Figure 1, below.

**Figure 1**




The confidence limits for the estimation of a standard deviation are not symmetrical and are surprisingly large for small numbers of replicates (Crow *et al*., 1960). The standard deviation calculated from the results of five replicate analyses has a 95 percent confidence interval ranging from 0.6 to 2.4 times its calculated value. The probability of a 'bad' result is quite high. Also, it is obvious that studies based on only one or two measurements may produce misleading results.

A far superior estimate of the standard deviation for a particular analytical procedure is acquired from long-term control chart data maintained by any laboratory employing good laboratory practices.

# 3 Interlaboratory Precision

This is an estimate of the **reproducibility** of submitted analyte concentrations between the participating laboratories. If there is acceptable accuracy and intralaboratory precision, then the interlaboratory precision can be used to determine whether a cooperative project is feasible between the set of laboratories. It is usually described by a standard deviation and the calculation is identical to that shown above but here

$x_i$ is the determined concentration of an analyte from a single participating laboratory,

$x$ is the assigned value for the analyte concentration, and

$N$ is the total number of laboratories whose results are being intercompared.

Other information may be acquired from an intercomparison study, such as the efficacy of various analytical procedures. Also, the distribution of laboratory results about the assigned values could lead to a better understanding of the causes of laboratory bias.

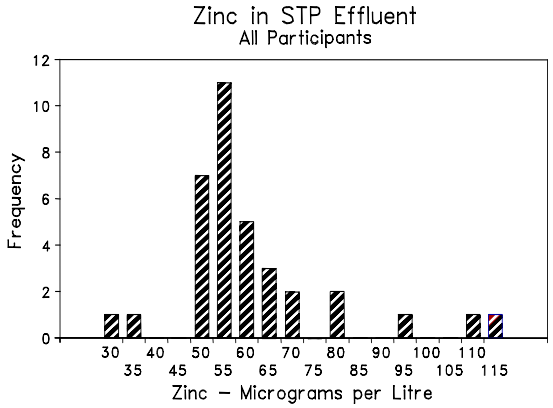
There may be a tendency to try to describe the population of results by a rigorous multivariate model which assumes that the determined values of the analyte concentrations are interdependent. This is a difficult concept for an experienced analytical chemist to accept. The response is, that if this is indeed the case, the analytical procedures are inadequate. However, it is possible that a portion of the population is distorting the distribution. If the former is true, then this area of analysis has severe problems. If the latter is true, then it would be best to find a means of isolating the group whose results may be of an acceptable calibre from the group which is distorting the distribution.

Experiences over the last decade with respect to the analysis of trace metals in various matrices indicate that, as long as the analyte concentrations are above their quantitative limits of determination (at least twice the limit of detection), a group of competent laboratories will produce a set of results homogeneously distributed about a mean which is seldom significantly different from the assigned value. There is no basic reason to believe that organic analytes would produce

a dissimilar distribution. The fundamental problem is that, at the current state of the practice of analytical chemistry, the quantitative analysis of materials for trace organic constituents is a much more difficult and challenging task.

Figure 2 is an example taken from a recent intercomparison study regarding the determination of thirteen trace metals in sewage treatment plant (STP) effluents (Berman and Willie, 1991). Thirty-five sets of zinc concentrations were submitted by the participants for this sample. The distribution of their mean values is shown in the diagram. The consensus mean is 59.3 micrograms zinc per litre. Aside from what is probably a high biased mean, the group cannot distinguish concentration differences from between 29 to 115 micrograms zinc per litre. The standard deviation cannot be used to calculate this range.

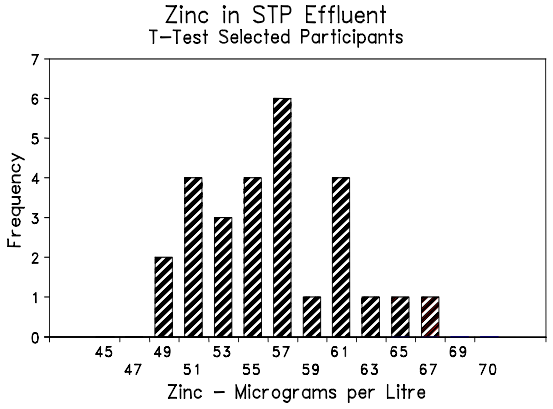
**Figure 2**




The distribution is obviously skewed towards the higher concentrations and does not appear to be normally distributed. However, what we have here are some quite good laboratories and some poor laboratories. The poor laboratories generally produce high results in trace analysis because they do not have their blanks and contamination under control. They also may produce both high and low results because of poor calibration techniques, improper instrument usage, poor choice of methods and poorly trained staff. The problem is to find a relatively simple method to separate the underachievers from the good performers (i.e, get rid of the outliers).

There are many suggestions on how to do this. ISO/REMCO, for example, supports a procedure based on the successive application of the Cochran test and the Grubbs tests (Horowitz, 1988). The QUASIMEME programme uses robust statistics. At the National Research Council, we prefer a more statistically transparent method involving the successive application of a *t*-test at the 95 percent confidence level to isolate what we believe is a fair approximation of a normal distribution. The results of this procedure on the population of Figure 2 are shown in Figure 3.

**Figure 3**




Eight laboratories were eliminated from the distribution in this example, a larger than usual number. The excluded mean is 55.7 ± 9.8 micrograms zinc per litre. The mean is no longer biased and the range of indiscrimination is reduced to 36 to 75 micrograms zinc per litre with 95 percent confidence.

This method may not be statistically rigorous. One or two laboratories may have been rejected (or accepted) when they should not have been. However, we have found that this type of evaluation of the results is readily understandable to the participants and to the user community of the data, most of whom have a rather unsophisticated understanding of even elementary statistics.

The main purpose of the study has been achieved. A subset of the participants has been identified as a homogeneous group and its performance has been characterized. The organizers of the study and the user community are aware of the possible consequences of using any one of the participants in a future project. They are also aware of the limitations on the quality of the data which can be produced by the group as a whole or any subset of laboratories they may choose from this group. This knowledge should be incorporated in their planning. They should be wary of any laboratory, regardless of reputation, which has not participated in an intercomparison study or which has not been accredited through some harmonized proficiency testing programme related to their project interests.

The participating laboratories have gained in that they are aware of their own capabilities, based on an objective assessment. The 'rejected' laboratories must examine their procedures in order to improve their capabilities, seeking outside advice if necessary. The others must also continually seek to improve. The range of indiscrimination between many laboratories is still too large to produce the necessary quality of data for various environmental projects.

# 4 References

Crow, E.L., Davis, F.A., and Maxfield, M.W. 1960. Statistics manual. Dover Publications, New York.

Berman, S., and Willie, S. 1991. MOE/CAEAL Pre MISA laboratory assessment of sewage treatment plant effluents for trace metals. Ontario Ministry of the Environment Report PIBS 1741.

Horowitz, W. 1988. Protocol for the design, conduct and interpretation of collaborative studies. Journal of Pure and Applied Chemistry, 60: 855–864.