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WORLD-WIDE INTERCOMPARISON EXERCISE FOR THE DETERMINATION OF TRACE ELEMENTS AND METHYLMERCURY IN MARINE SEDIMENT IAEA-433

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WORLD-WIDE INTERCOMPARISON EXERCISE FOR THE DETERMINATION OF TRACE ELEMENTS AND METHYLMERCURY IN MARINE SEDIMENT IAEA-433

1. INTRODUCTION

The implementation of accepted quality assurance practices to analytical chemistry is recognized as a prerequisite to producing data with known accuracy and precision. Whether the target analyte is a trace metal or an organic constituent, whether the sample is environmental or food, quality assurance and quality control are the cornerstones to analytical data validation.

Quality assurance and quality control cover a very broad discipline; there are numerous factors and methods that must be employed to validate data and ensure adequate analytical performance. A good QA plan should include both internal performance checks for day-to-day validation, as well as regular external performance evaluations for an independent assessment of analytical proficiency.[1-5] An intercomparison exercise such as the subject study serves as such an independent external assessment.

One of the most basic and routine internal methods of quality control is the concurrent processing of a material similar in matrix to the sample and of known composition, i.e., a reference material, to validate the accuracy of the analytical process. This should be a continuous and regular process, not only to maximize the confidence in a particular data set, but also to maximize the confidence in an analytical process, and indeed, in how the laboratory routinely operates in the longer term.[6,7] Their limited supply keeps representative and appropriate reference materials in high demand; producers of such materials can only prepare a limited quantity of a homogenous sample at one time, and the fabrication process is a rigorous one.

For nearly thirty years the Marine Environmental Studies Laboratory (MESL) of IAEA-MEL has conducted intercomparison exercises that have resulted in the preparation of reference materials (RMs) for the analysis of trace elements and organic compounds as part of its contribution to IAEA's Analytical Quality Control Service, UNEP's Regional Seas Programme, and formerly in association with the IOC Global Investigation of the Pollution in the Marine Environment (GIPME) programme.[8-21]

This report describes the performance of laboratories in one intercomparison exercise conducted during 2003 that was organized for the determination of trace elements and methylmercury in a marine sediment. This study was intended to give laboratories responsible for trace element analyses of marine sediment an opportunity to check their analytical performance. In January 2003, the sample material was prepared and distributed to 182 laboratories world-wide. Results from 103 laboratories in 47 countries were received.

The performance of the participant laboratories is demonstrated by their respective Z-scores, which were calculated based on the accuracy of reported results compared to established reference values.[3,22] This report provides feedback to the individual participants about their performance and should enable them to make appropriate modifications to their laboratory's analytical procedures where necessary. All results were treated as strictly confidential and each laboratory was identified with a code number for anonymity.

The data sets reported by laboratories and the technical and statistical evaluations of the results for each element are given in this report. As statistical and technical criteria for assigning recommended concentrations to a number of elements were fulfilled, the sample can now be used as a Reference Material for quality control of data in the determination of trace elements and methylmercury in sediment samples.

Further information concerning this report and the IAEA quality assurance programme can be obtained by contacting the IAEA-MEL, Marine Environmental Studies Laboratory, 4 quai Antoine 1er, MC 98000, Monaco.

2. SCOPE OF THE INTERCOMPARISON

Each participating laboratory received one sample of lyophilised marine sediment material, accompanied by an information sheet and a report form. The sample originated from the batch of homogenized material prepared as described below. Participants were requested to determine by their routine procedures as many trace elements as possible out of the following 18 elements: Al, As, Cd, Co, Cr, Cu, Fe, Hg (total and methylmercury), Li, Mn, Ni, Pb, Sb, Se, Sn, Sr, V and Zn. The IAEA was also interested in receiving results for any other element(s) which participating laboratories would be willing to determine.

In January 2003, the bottles of sample material were dispatched to 182 laboratories that had expressed interest in participating in this exercise by answering positively to a questionnaire sent out in September 2002. The deadline for returning the results was June 2003, but was later extended to September 2003.

In total, 103 laboratories from 47 countries participated in this intercomparison exercise (Annex III) and reported results for 48 elements. Organomercury results were provided by 11 laboratories.

The UNEP Regional Seas participants included 50 laboratories from 30 countries:

	Number of laboratories	Number of countries
Mediterranean Action Plan	15	10
(On record in MEDPOL region)	*37*	*13*
Kuwait Action Plan	3	3
West and Central Africa Action Plan	2	2
Caribbean Action Plan	3	2
East Asian Seas Action Plan	2	2
South-East Pacific Action Plan	4	3
Eastern African Action Plan	1	1
South Asian Seas Action Plan	6	3
Black Sea Environmental Programme	11	3
South-West Atlantic	3	1

3. DESCRIPTION OF THE MATERIAL

A large quantity of marine sediment was collected in 2002 from the Algerian coast of the Mediterranean Sea for use as an intercomparison material. It was deep-frozen, freeze-dried, then ground and sieved. The particle size fraction <250 µm was homogenized and bottled in clean plastic bottles. After confirming general homogeneity via a pre-test (results not reported here), the samples were rebottled by packing aliquots of approximately 20 g into cleaned, brown borosilicate glass bottles with Teflon lined screw caps and sealed in plastic bags. Approximately 500 bottles were produced.

The average moisture content of the lyophilised sample after bottling, determined by drying to a constant weight at 105°C, was found to be approximately 1.9%. Since the moisture content can vary with the ambient humidity and temperature, it was recommended that the water content of this material be determined in a separate subsample (not used for analysis) by drying to a constant weight (~24 h) at 105°C just prior to analysis. Final results should always be reported on a dry weight basis.

4. HOMOGENEITY TESTS

4.1 Homogeneity study of trace element concentrations

A homogeneity test was conducted after re-bottling the sample material. The between-bottle homogeneity was tested by the determination of the concentration of some typical elements (Mn, Co, Cu, Zn, Hg) on sample intakes of 0.2 g taken from 10 bottles, which were taken directly from the bulk material, specifically for the purpose of this pre-test. The within-bottle homogeneity was assessed by 6 replicate determinations on the re-homogenized content of one bottle.

For the elemental analysis, the samples were mineralised with HNO_3 and HF using a microwave digestion system. Boric acid was later added to dissolve fluorides and neutralize excess HF. The final determination was performed by F-AAS for all elements except Hg, and by SAAS (direct solid sample AAS analysis, also known as AMA) for Hg. The uncertainty of the analytical methods was assessed for each element by 5 replicate measurements on one digest solution.

Table 1. Within- and between- bottle homogeneity for IAEA-433

Element	Within-bottle [1] CV(%)	Between-bottle [2] CV(%)	Method [3] CV(%)
Mn	3.0	2.5	2.5
Co	6.3	5.2	5.9
Cu	2.0	3.7	2.2
Zn	2.0	2.4	2.5
Hg	8.3	8.9	1.1

[1] 6 replicates determinations on the content of one bottle.
[2] Single determinations on the content of 9 bottles.
[3] 6 replicates of a reference material
CV = Coefficient of variation (or relative standard deviation).

The coefficients of variation (CV) obtained for the studied elements (Mn, Co, Cu, Zn and Hg) are presented in Table 1. An F-test at a significance level of 0.05[23,24] was performed for the different metals and did not reveal significant differences between the within- and between-bottle variances, indicating that the heterogeneity observed was relatively consistent, and independent of how the material was distributed. It was concluded that the material was homogeneous for key elements at an analytical portion of 200 mg and above; it was therefore considered suitable for use as an intercomparison sample.

5. STABILITY TESTS

The stability of the sample with respect to several trace metals was tested to determine the suitability of this material as a candidate RM.[24] Five bottles of the IAEA-433 material were stored in the dark at +20 °C, –20 °C and +60 °C, respectively, over a period of 12 months (starting in January 2003) and the measurement of As, Mn, Cu, Zn and total Hg was performed at regular intervals during the storage period. Instability would be detected by noting disparities in the concentrations of different elements between samples stored at different temperatures and those stored at a low temperature at the various occasions of analysis.

Tests were made at the beginning of the storage period and after 3, 6 and 12 months. Samples were prepared and analysed using the same methods described for the homogeneity study, with the additional parameter of As, analysed by GF-AAS. Trace elements were each determined five times (one replicate analysis of five bottles stored at different temperatures) on each occasion of analysis. The samples stored at –20 °C were used as reference for the samples stored at +20 °C and at +60 °C, respectively. The normalized results of the stability study are presented in Table 2. This table gives the ratios (R_T) of the mean values (X_T) of five measurements made at +20 °C and at +60 °C respectively, to the mean value ($X_{-20\,°C}$) of five determinations made on the same day of analysis of samples stored at a temperature of –20°C:

$$R_T = \frac{X_T}{X_{-20°C}} \qquad [1]$$

The uncertainty U_T has been calculated from the coefficient of variation (CV) of 5 measurements obtained at each temperature:

$$U_T = \frac{\sqrt{(CV_T^2 + CV_{-20°C}^2)} * R_T}{100} \qquad [2]$$

In case of ideal stability, the ratios (R_T) should be 1. In practice, however, there are some random variations due to the error on the measurements. The uncertainty in the CVs can account for the deviations observed. No systematic change in concentrations for the different elements was detected during the investigated time period. On the basis of these results, it was concluded that no instability of the material could be demonstrated. This material will continue to be monitored at regular intervals.

Table 2. Normalized results of the stability study for IAEA-433

Element	Time (month)	$R_T \pm U_T$ +20°C	$R_T \pm U_T$ +60°C
As	3	1.000 ± 0.122	0.954 ± 0.098
	6	1.024 ± 0.042	1.000 ± 0.039
	12	0.985 ± 0.026	1.010 ± 0.027
Cu	3	0.983 ± 0.154	1.023 ± 0.152
	6	0.987 ± 0.104	0.995 ± 0.120
	12	1.007 ± 0.027	1.039 ± 0.050
Hg	3	0.970 ± 0.098	0.995 ± 0.057
	6	1.038 ± 0.082	1.070 ± 0.129
Mn	3	1.008 ± 0.088	1.013 ± 0.031
	6	0.997 ± 0.029	1.016 ± 0.031
	12	1.019 ± 0.020	1.031 ± 0.024
Zn	3	1.008 ± 0.091	1.027 ± 0.042
	6	0.977 ± 0.032	1.003 ± 0.026
	12	1.010 ± 0.024	1.020 ± 0.022

[a] R_T = ratio of the mean values (X_T) of five measurements made at +20 °C and +60 °C, respectively, and the mean value ($X_{-20\,°C}$) from five determinations made on the same occasion of analysis on samples stored at temperature of -20 °C (Eqn [1]).

U_T = uncertainty obtained from the coefficient of variation (CV) of five measurements obtained at each temperature (Eqn [2]).

6. ANALYSES AND REPORTING

The participants were requested to analyse the trace metal concentration of the samples by their usual technique. They were requested to make at least three, but preferably six, independent replicate determinations for each element and to report all results on the report form. Also, they should provide a summary of quality control procedures routinely employed within their laboratory and the results for Reference Materials analysed concurrently. Other information requested included the drying procedure and a short description of the analytical method used, as well as the pre-treatment or separation methods (e.g. mineralisation procedure), the instrumental method employed for the quantitative determination, and the way in which calculation of results was performed.

All results were to be reported on a dry-weight basis, and the moisture content of the sediment sample had to be indicated. The concentrations were to be reported as net values (i.e., after correcting for the blanks, etc.), leaving as many significant figures as justified by the precision of the method.

For each element the participants were requested to report the average weight of the sample taken for analysis, the concentration of each independent replicate determination, the arithmetic mean and the standard deviation (s_{n-1}) of the replicate determinations and the detection limit of the method.

7. EVALUATION OF THE RESULTS

7.1. Data Table Terms

Results reported by all the laboratories are presented in Annex I. The terms used in the tables are defined as follows:

(C)RM: The (certified) reference materials used by the laboratories.

Laboratory code: Each laboratory was identified by a code number that remains unchanged throughout the tables.

Method code: A code number, described in Table 3, identifies the analytical method employed. The information given includes the pre-treatment method, the acids used for mineralisation of the samples and the instrumental technique employed.

Detection limit: This value is the detection limit reported by the individual laboratory for each element.

Dry/wet ratio: This value gives the dry/wet ratio as reported by the individual laboratory.

Number of determinations: Number of replicate determinations of a given element performed by a laboratory using the same analytical procedure.

Laboratory mean: Arithmetic mean ($\bar{x}$) computed from all individual results supplied by a laboratory for the determination of a given element. Results given as below the detection limit (DL) or not detectable (ND) are reported with the symbol "<" or ND, respectively.

Standard deviation (Stdev): This is the weighted (n-1) standard deviation (s_{n-1}) of the experimental data given as an absolute value.

Outliers: The statistical model used includes all data; i.e., no data are eliminated as 'outliers'. For this reason, the term is not applicable in this report.

Table 3. Method codification for the intercomparison IAEA-433

The "Method Code No." consists of a numerical code containing a maximum of 4 digits and a letter code as described below:

- 1 or 2 digits for pre-treatment techniques;
- followed by a number from 1 to 16 for the chemicals used (if applicable);
- and a letter code for instrumental methods.

Pre-treatment (digestion) techniques:

- 0 : No pre-treatment

- 1 : Dry ashing
    - 10 : Not specified
    - 11 : Muffle furnace
    - 12 : Plasma (oxygen)

- 2 : Wet ashing
    - 20 : Not specified
    - 21 : Normal pressure (hot plate, open vials)
    - 22 : Pressure decomposition (hot plate, closed bombs)
    - 23 : Microwave oven
    - 24 : Distillation
    - 25 : Solvent extraction
    - 26 : Leaching

- 3 : Fusion

Acids used:

1 : HNO_3, HCl, HF + H_3BO_3
2 : HNO_3, $HClO_4$, HF
3 : HNO_3
4 : HNO_3, HCl, H_2O_2
5 : HNO_3, HCl
6 : HNO_3, HCl, HF
7 : HNO_3, H_2SO_4
8 : H_2SO_4
9 : HNO_3, HF
10 : HNO_3, $HClO_4$
11 : HCl, HF, $HClO_4$
12 : HNO_3, HF, H_2O_2
13 : HF, $HClO_4$
14 : HNO_3, H_2O_2
15 : HNO_3, $HClO_4$, HCl, HF
16 : alkaline digest
17 : HNO_3, $HClO_4$, H_2SO_4
18 : others
19 : HNO_3, HF, $HClO_4$, H_2O_2
20 : HNO_3, HCl, H_2SO_4
21 : HF, HCl
22 : 20 + HF, H_20_2

Table 3. Method codification for the intercomparison IAEA-433 (continued)

Method Code	**Instrumental Method**
A0	Atomic absorption spectrophotometry (AAS), not specified
A1	AAS, flame (F-AAS)
A2	AAS, electrothermal (graphite furnace), no background correction (GF-AAS)
A3	AAS, electrothermal, + Zeeman background correction (ZGF-AAS)
A4	AAS, electrothermal, + Deuterium background correction (GF-AAS)
A5	AAS, electrothermal, + other type background correction (GF-AAS)
A6	AAS, electrothermal, background correction not specified (GF-AAS)
A7	AAS, cold vapour ($SnCl_2$) (CV-AAS)
A8	AAS, hydride generation ($NaBH_4$) (Hydr.-AAS)
A9	AAS, electrothermal, solid analyser
C1	Colorimetry (spectrophotometry)
E0	Emission spectrometry, unspecified
E1	Emission spectrometry, inductively coupled plasma (ICP-AES)
E2	Emission spectrometry, hydride generation
F1	Atomic fluorescence spectrophotometry, cold vapour ($SnCl_2$), (CV-AFS)
F2	Atomic fluorescence spectrophotometry, hydride generation ($NaBH_4$), (Hydr.-AFS)
F3	Gas chromatography (GC) - AFS
F4	HPLC-AFS
M0	Mass spectrometry, unspecified
M1	Mass spectrometry, inductively coupled plasma (ICP-MS)
M2	ICP-MS, hydride generation
N0	Neutron Activation Analysis (NAA), unspecified
N1	NAA, radiochemical (RNAA)
N2	NAA, instrumental (INAA)
P1	Polarography (P)
S1	Gas chromatography, electron capture detection (GC-ECD)
S2	Gas chromatography, atomic emission detection (GC-AED)
S3	Gas chromatography (GC-) ICP-MS
X1	X-ray Fluorescence (XRF)

Z-score: For the assessment of laboratory performance, a Z-score is calculated according to the formula:

$$Z = \frac{(x_i - x_a)}{s_b}$$

where $\mathbf{x_i}$ is the arithmetic mean of the reported value of the analyte concentration in the sample; $\mathbf{x_a}$ is the reference or assigned value; and $\mathbf{s_b}$ is the target standard deviation [3,22].

This score effectively expresses the difference between the mean of the laboratory and the assigned value in units s_b.

- Performance is considered to be acceptable if this difference is less than or equal to two ($|\mathbf{Z}| \leq \mathbf{2}$);
- The results are of questionable quality when: $\mathbf{2} < |\mathbf{Z}| < \mathbf{3}$
- The measurement is regarded as out of the acceptable range when: $|\mathbf{Z}| \geq \mathbf{3}$.

This type of score represents a simple method of giving each participant a normalized performance score for bias. This method of assessing laboratories has been accepted as a standard for ISO/IUPAC.[3]

The selection of the correct target value depends on the monitoring objectives. The criteria used in this report have been set so that laboratories should have at least a relative bias equal to or better than 25% ($2s_b$, s_b=12.5%). A fixed value of s_b has the advantage that the Z-scores derived from it can be compared from round to round to demonstrate general trends for a laboratory or a group of laboratories.

For a few elements, the uncertainty of the assigned concentration was somewhat higher (i.e., up to a factor of 2) than the target precision. Although this factor can be taken into account, the same criteria as used in previous exercises were applied in order to facilitate comparisons with past performance.

Where the methodology or a laboratory performance cannot meet these targets, then action should be taken to improve that situation. It should be recognized that the designated specifications are minimum criteria.

7.2. Statistical and technical evaluation

For each of the data sets in Annex I, the range of determinations, arithmetic mean and standard deviation were compiled for each element, based on the laboratory means. Laboratory means were calculated from the Cofino quantum statistical model.[25] The primary advantage of this model is that all data points are used; outliers are given such an inconsequential weighting factor that they essentially eliminate themselves. Because all data generated were used to calculate the final results, the Cofino model obviated the usual practice of evaluating the data sets for outliers, or considering whether data from a laboratory was usable based on the quality assurance data reported: every value received was used in the model for calculating the final result.

The mean values determined by the Cofino model are based on modal distributions, therefore each data set will have multiple means for the multiple modes found. In evaluating the data, it is therefore necessary to examine the modes while considering the probable idiosyncrasies of a particular digestion procedure, likelihood of contamination or poor recovery of a given element, etc. A common example of a bimodal distribution for which a preference would be given to a particular mode would be in the case of certain refractory elements in sediment: there will often be 2 distributions corresponding to those laboratories that did or did not use HF during sample dissolution. It is therefore conceivable that a secondary mode could more accurately reflect the 'true value' population. For this reason, secondary modes were evaluated for significance for each analyte, however there was never a situation observed for which the secondary mode(s) was found to be more significant than the calculated primary mode.

Although it is common for intercomparison exercises to report the uncertainty range according to 95% confidence limits (per ISO/REMCO N 566 guidelines), there seems to be universal confusion regarding the meaning of this range. These limits are based on n (the number of measurements) with significantly tighter limits for increasing n. The resulting range represents the uncertainty of the mean rather than that of the actual data spread. For example, mean values with coefficients of variation of 30 or 40 percent can have 95% confidence limits of only 5 or 10%, which could imply to many users that the acceptable range of data is much more restrictive than it actually is. For this reason, the recommended value is reported with both the conventional 95% confidence interval, as well as the standard deviation of the first mode's mean.

In addition to the tables of results given in Annex I, the distribution of laboratory means for selected elements is illustrated graphically in Annex II. The laboratory means are plotted in ascending concentration on the y-axis with their corresponding laboratory code noted along the x-axis (S-plots). Error bars represent laboratory means ±1 standard deviation ($\bar{x} \pm s_{n-1}$). The horizontal lines on the figures indicate the limits representing ±1 standard deviation of the calculated mean value from the Cofino statistical model. These graphs are presented for all elements where 6 or more accepted laboratory means exist. Results that have not been validated by appropriate quality control (i.e., no reference material results were reported) are indicated with an 'X' through the middle of the data point.

7.3. Certification criteria

The data for many of the elements is sufficiently well grouped to permit provisional certification of the marine sediment sample as a reference material. Criteria used for obtaining reference values are indicated below:

1. For a given concentration range the relative uncertainty of the overall arithmetic mean (relative standard deviation) does not exceed the following limits:

100 - 500 mg kg^{-1}	± 20%
10 - 100 mg kg^{-1}	± 30%
0.1 - 10 mg kg^{-1}	- 50%; + 60%
<0.1 mg kg^{-1}	- 50%; + 100%

2. The overall mean is based on data obtained by at least two different methods.

3. The overall mean is calculated on the basis of at least the following number of laboratory means: (a) 10; (b) 5; (c) 3.

On the basis of these criteria, three classes (categories) of Reference Material are defined:

Class A: when criteria 1, 2, and 3 (a) are fulfilled.

Class B: when criteria 1, 2, and 3 (b) are fulfilled.

Class C: Information value only
when criteria 1 and 3 (c) are fulfilled.

Table 4. Results of intercomparison exercise IAEA-433 sediment sample (in mg kg^{-1})

Analyte	*n*	Mean *	Std Dev. **	95% Confidence Interval ***	Class
Ag	**9**	**0.133**	**0.009**	**0.127 – 0.139**	**B**
Al	**39**	**78200**	**4200**	**76800 – 79600**	**A**
As	**57**	**18.9**	**1.8**	**18.4 – 19.4**	**A**
Ba	**8**	**268**	**32**	**241 – 295**	**B**
Br	**9**	**67**	**16**	**55 – 79**	**B**
Cd	**67**	**0.153**	**0.033**	**0.145 – 0.161**	**A**
Ce	**7**	**64.5**	**2.8**	**61.9 – 67.1**	**C**
Co	**65**	**12.9**	**1.2**	**12.6 – 13.2**	**A**
Cr	**79**	**136**	**10**	**134 – 138**	**A**
Cs	**8**	**6.40**	**0.44**	**6.03 – 6.77**	**B**
Cu	**89**	**30.8**	**2.6**	**30.2 – 31.4**	**A**
Eu	**6**	**1.18**	**0.07**	**1.11 – 1.25**	**C**
Fe	**72**	**40800**	**1900**	**40300 – 41300**	**A**
Hf	**5**	**3.66**	**0.18**	**3.44 – 3.88**	**C**
Hg	**62**	**0.168**	**0.017**	**0.164 – 0.172**	**A**
MeHg (in µg kg^{-1})§	**9**	**0.172**	**0.073**	**0.117 – 0.227**	**B**
K	**7**	**16600**	**3200**	**13600 – 19600**	**B**
La	**8**	**33.7**	**2.7**	**31.4 – 36.0**	**B**
Li	**25**	**67.0**	**3.9**	**65.4 – 68.6**	**A**
Lu	**4**	**0.361**	**0.039**	**0.299 – 0.423**	**C**
Mg	**19**	**11500**	**900**	**11100 – 11900**	**A**
Mn	**81**	**316**	**16**	**312 – 320**	**A**
Na	**6**	**13500**	**1500**	**11900 - 15100**	**C**
Nd	**5**	**29.2**	**2.2**	**26.5 – 31.9**	**C**
Ni	**72**	**39.4**	**3.1**	**38.7 – 40.1**	**A**
Pb	**84**	**26.0**	**2.7**	**25.4 – 26.6**	**A**
Rb	**8**	**99.9**	**14.2**	**88.1 – 111.7**	**B**
Sb	**26**	**1.96**	**0.18**	**1.89 – 2.03**	**A**
Sc	**6**	**14.6**	**1.1**	**13.4 – 15.8**	**C**
Se	**23**	**0.78**	**0.20**	**0.70 – 0.85**	**A**
Sm	**6**	**5.61**	**0.33**	**5.26 – 5.96**	**C**
Sn	**23**	**2.32**	**0.36**	**2.17 – 2.47**	**A**
Sr	**41**	**302**	**20**	**296 – 308**	**A**
Ta	**6**	**1.03**	**0.09**	**0.94 – 1.12**	**C**
Tb	**5**	**0.696**	**0.092**	**0.582 – 0.810**	**C**
Th	**9**	**9.78**	**0.57**	**9.34 – 10.22**	**B**
U	**6**	**2.45**	**0.24**	**2.20 – 2.70**	**B**
V	**36**	**160**	**11**	**156 – 164**	**A**
Yb	**5**	**2.24**	**0.17**	**2.03 – 2.45**	**C**
Zn	**93**	**101**	**8**	**99 – 103**	**A**
Zr	**4**	**148**	**19**	**118 – 178**	**C**

* Cofino model mean values expressed on a dry-weight basis.
** 1 standard deviation of the mean
*** (mean +/- 95% confidence limit)
§ As inorganic Hg.

The classification of the data is shown in Table 4. It was possible to establish recommended values for 28 elements (19 class "A" and 9 class "B") and information values for 12 elements (class "C"). In addition, a recommended value was established for methylmercury (class "B").

The results that have been classified as information values should be used with caution. In some cases, an information value was assigned because too few results were reported for it to be classified as a recommended value, or because it was determined via only one analytical method. For others, an exceedingly large uncertainty resulted in an information value instead of a recommended value.

The reference sheet for IAEA-433 reference material is presented in Annex IV.

8. RESULTS AND DISCUSSION

8.1. Overview of the results

This exercise included a similar number of participants and analytes measured as the previous intercomparison exercise, IAEA-407, on a fish tissue homogenate.[19] One hundred three laboratories provided 110 sets of data, which included analytical results for a total of 48 elements and methylmercury (Annex I). Z-scores were calculated for 22 elements with class A or B certification, and enough data was available to allow plots for 35 analytes to be made (Annex II).

The largest number of results (≥ 20) was reported for Al, As, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb, Sb, Se, Sn, Sr, V and Zn. For 8 elements only a few results were obtained and reference values could not be calculated. These data are given in Annex I, but are not included in the detailed description or in the figures.

Annex I reports all of the results exactly as they were received. Those results calculated incorrectly by the participant (i.e., the mean and/or standard deviation, based on the individual replicate results provided) are highlighted in grey. Some of the participants reported an inappropriate number of significant figures, with some reporting as many as nine. This was especially common for the larger concentrations; e.g., concentrations >10 000 mg kg^{-1} were often reported with all 5 digits as being significant. Participants should be aware that the number of digits that can be reported is limited by the precision of the method. Only the digits that do not vary plus no more than 2 should be reported.[23] For example, if the result obtained were 123.45 with an uncertainty of 11.2233, the 100's place will not vary, so no more than the 10's and the 1's place can be reported in addition to the 100's; i.e., 123 ± 11 for this example. Results >1000 should be reported with zeros for the insignificant figures, e.g., 12 345 should be reported as 12 300. In general, the instruments involved in these studies can rarely provide precision better than 3 significant figures, and never more than 4 in any case.

A review of Annex II reveals that although there appeared to be some data points that would normally be considered outliers, the degree of agreement between data sets was indeed reasonable for most elements. For example, the coefficients of variation (calculated from all means) were less than 10 % for Ag, Al, As, Co, Cr, Cs, Cu, Fe, La, Li, Mg, Mn, Ni, Sb, Sr, Th, U, V and Zn, and <15 % for Ba, Hg, Pb, and Rb.

8.1.1. Moisture content

It was required that the results be reported on a dry weight basis. The moisture content of sediment can vary dramatically with the ambient humidity. Most laboratories (90%) reported their results for moisture content, with values ranging between 1 and 5 percent, with an average value of just under 2%. The recommended procedure for its determination (i.e., drying at 105°C to constant weight) was generally followed.

8.1.2. Analytical methods

Table 5 represents the frequency of application of instrumental methods. It shows the number of basic techniques employed to analyse each element. The percentage of analytical methods used for determining the reported values is graphically depicted in Figure 1. The wide range of methods employed will permit a statistically valid comparison of the principal methods used, particularly the instrumental methods following sample digestion and the “non-destructive” techniques such as neutron activation analysis and X-ray fluorescence (XRF).

The following inter-study comparisons are being made between the subject study and that of IAEA-405 (conducted in 1999)[10,26] instead of with the most recent study, IAEA-407,[19] due to the obvious similarities between the two sediments, not only in terms of matrix but also in terms of analyte concentrations. Put another way, it is likely that different methods would be used to analyse a fish tissue than to analyse a sediment, therefore the legitimacy of comparing the methods used for such disparate sample types is questionable.

The subject exercise reaffirmed a continued downward trend in the application of F-AAS. Compared to the IAEA-405 intercomparison exercise in which 28.8% of the reported results were obtained using F-AAS, only 17.7% of the results came from F-AAS in this exercise. The primary techniques that saw a significant upward shift were ICP-MS (19.7% compared to 14.5% for IAEA-405), and neutron activation analysis (15.7% compared to 11.4% for IAEA-405). Other methods showing a modest increase in utilization frequency include XRF (7.4% instead of 5.3% for IAEA-405) and newcomer SAAS (AMA) for direct analysis of Hg (just under 1% of total measurements, but 15.4% of the Hg measurements). Most of the other methods saw similar frequency of use as in previous studies. As in previous studies, several laboratories used hydride generation with atomic absorption spectrophotometry (AAS) or atomic fluorescence spectrophotometry (AFS) detection for the determination of As, Sb, Se and Sn.

Most of the laboratories employed wet ashing as the sample pre-treatment procedure that is the preferred method for analysis by AAS and ICP. Among those, a majority used a total decomposition method with a mixture of acids. The effect of the difference of sample treatment and analytical technique on the results will be further discussed in section 8.2.

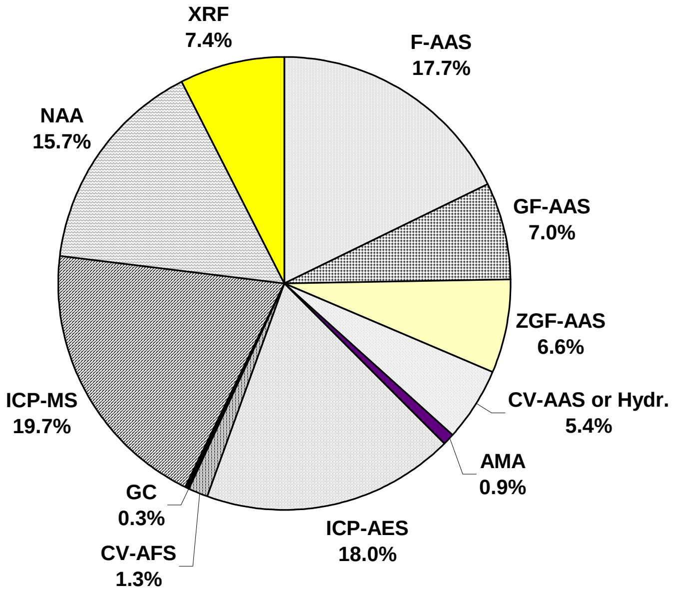

Figure 1: Percentage of the analytical methods used for determining the results collected

Table 5. Frequency of the application of analytical methods used in intercomparison IAEA-433

	A1	A2-A4-A5-A6	A3	A7-A8	A9	E	F	S	M	N	X
	F-AAS	GF-AAS	ZGF-AAS	CV-AAS or Hydr.	SAAS	ICP-AES	CV-AFS	GC	ICP-MS	NAA	XRF
Ag	1	2	1						5		1
Al	7	2	2			14			3	8	2
As		3	5	11		5	2		16	10	5
Ba						1			2	3	1
Be						1			1		
Br										6	2
Ca	1									1	1
Cd	6	19	20			6			19		2
Ce										7	
Co	8	3	5			13			21	10	4
Cr	13	12	8			16			14	9	6
Cs									1	7	
Cu	31	10	9			18			15		5
Eu										6	
Fe	25	2	1			17			10	10	6
Ga										2	
Hf										5	
Hg	2	1		40	10	2	5		2	1	2
MeHg					1		6	4			
K	1									5	1
La									1	7	
Li	6		1			10			8		
Lu										4	
Mg	4					8			4	2	1
Mn	30	3	2			19			14	5	7
Na										6	
Nd										5	
Ni	20	7	6			15			16	1	6
P						1				1	
Pb	21	13	15			10			18		7
Rb										6	1
Sb		1		3		5	1		10	8	3
Sc										6	
Se		1		10		4	2		9	3	1
Sm										6	
Sn		2	2	2		5			12	1	2
Sr	1					16			10	5	8
Ta										6	
Tb										5	
Th						1			1	6	1
Ti											2
U									2	3	1
V		1	2			13			12	3	4
Yb										5	
Zn	39	3	2			19			15	7	7
Zr						1				1	1

F-AAS: flame atomic absorption spectrophotometry; **GF-AAS**: graphite furnace atomic absorption spectrophotometry; **ZGF-AAS**: graphite furnace atomic absorption spectrophotometry with Zeeman background correction; **CV-AAS or Hydr**.: cold vapour atomic absorption spectrophotometry or hydride generation; **SAAS:** Solid Hg Analyser; **ICP-AES**: inductively coupled plasma atomic emission spectrometry; **CV-AFS**: cold vapour atomic fluorescence spectrophotometry; **GC:** Gas Chromatography; **ICP-MS**: inductively coupled plasma mass spectrometry; **NAA**: neutron activation; **XRF:** X-ray fluorescence.

8.1.3. Laboratory performances

The performance for accuracy was assessed by Z-scores, which were calculated for each element individually as indicated in the previous section (see 7.1). Complete results are presented in Annex I. Z-scores were calculated only for selected elements with assigned Recommended (i.e., class "A" or "B") values and are summarized in Table 6. The performance is considered satisfactory if the relative deviation from the recommended value is equal to or better than 25% (**$|Z| \leq 2$**). Z-scores from 2 to 3 indicate that the results are of questionable quality. Z-scores equal to or higher than 3 (shaded cells) indicate that the measurements are inaccurate.

Table 7 summarizes the performance of all laboratories. The proportion of Z-scores falling within $|Z| < 3$ and the number which fall within the band $2 < |Z| < 3$ are given. The percentage of satisfactory Z-scores ($|Z| < 3$) for each laboratory is then used to assign the performance of each laboratory to a group level graded 1 to 4 as follows:

- Group 1 laboratories with $|Z| < 3$ for ≥ 90% of the data;
- Group 2 laboratories with $|Z| < 3$ for 75% to < 90% of the data;
- Group 3 laboratories with $|Z| < 3$ for 50% to < 75% of the data;
- Group 4 laboratories with $|Z| < 3$ for < 50% of the data.

It is encouraging to note that 84% of all values reported were acceptable. Furthermore, 83 of the 110 data sets submitted (75% of all, and representing 76 different laboratories) received either Group 1 or Group 2 classifications. In addition, an impressive 39% of the data sets submitted received acceptable Z-scores for all of the results reported. This performance is a measurable improvement over that obtained during the previous intercomparison exercise on a sediment material (IAEA-405).[10,26] In contrast, 9 laboratories failed as <50% of the results that they reported were determined to be acceptable. Thus ~8% of the laboratories involved in this exercise were unable to produce reliable data for trace metal analyses.

To be consistent with previous intercomparison exercises, results reported as below detection limits were not included in assessing laboratory proficiency. It should be noted, however, that ignoring these results necessarily biases laboratory performance on the favourable side. By dismissing all 'less-than' values, data sets containing inaccurate or inappropriately high limits received better overall classifications than if these results had been counted as unacceptable. For example, 6 'less-than' values were reported for Cd. Though the subject sediment is not polluted, the level of Cd present was measurable if the appropriate technique (e.g., GF-AAS or ICP-MS) had been used. It is recognized and appreciated that not all laboratories have a full suite of instrumentation available for measuring every trace metal. However, those laboratories responsible for routinely measuring and reporting Cd in sediment should have the appropriate instrumentation to make this determination. If 'less-than' numbers are routinely reported, project managers should review and verify that those detection limits are indeed meaningful and appropriate, e.g., the limit represents a legitimate pollutant threshold. Just because an analyte is not detected does not mean that contamination of that analyte – even at dangerous levels – does not exist. 'Less-than' results are not always incorrect, though they are never entirely correct either. For this reason, they were not included in determining the reference values, they were not given Z-scores, and they were not included in the percentage of correct results used to classify each data set. However, they are included in the Z-score chart and highlighted in grey to indicate an unacceptable result.

As can be seen in the figures (Annex II), results obtained for Cu, Co, Fe, Mn, Sr V and Zn are generally relatively well clustered around the reference value, with few outlier values. In contrast, the distributions exhibit a modest positive bias (towards high values) for Cd, Hg, and MeHg, and a modest negative bias for Cr and V, with more outlier values reported for these elements.

Out of the 110 data sets received, 13 included no information at all on their quality control procedures as was requested on the report form, and an additional 6 data sets provided either partial or otherwise unusable QC results. Some of those submitting this unverified data indicated that theirs were accredited laboratories. Unfortunately, even if the reported results turned out to be accurate, they are invalid in the absence of quality control data. In order to validate their results, all laboratories should systematically: (1) analyse reagent blanks for the verification of the quality of the purified water and reagents, and to control other possible sources of contamination; (2) analyse standard reference material with a similar matrix and approximately the same concentration level as in the samples being analysed.[6,7] This should be done for each series of analyses (e.g., batch of digested samples), and these digests should be analysed at regular intervals during the measurements.

Laboratories with erroneous results should carefully check their laboratory procedures. Erroneous calibration standards may be a source of bias. For instance, it is important to note that losses can occur in low-concentration working standard solutions, which would result in overestimates of the concentrations of elements in the samples. Thus, they should not be stored for an extended period of time.

High-biased results could originate from contamination during either sample preparation (e.g. mineralisation) or analysis. The laboratories concerned should check the quality of purified water and reagents and try to improve the cleanliness of their working environment, as dust is the most common atmospheric source of contaminants for trace elements in laboratories. Filtration of solution digests should be avoided as it can contaminate samples. Laboratories should also develop an effective scheme for cleaning laboratory-ware that generally includes a soap wash, an acid wash and thorough rinsing with purified water free from trace elements.[27]

Table 6. Z-scores for intercomparison sample IAEA-433: assessment of laboratory performances

Lab Code	Ag	Al	As	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Sb	Se	Sn	Sr	V	Zn
1				<			0.41		-6.86							-3.72						-0.35
2								-0.02					4.15							-1.17		-0.16
3		0.07	0.60	0.26	0.92	0.06	1.54	0.27			-1.42	-0.08	0.89		0.56	0.21			-0.64	0.74	1.19	2.38
4	0.06			1.41	0.50		-1.51	0.61					-0.56		3.68	-0.95						-0.83
5		0.56		13.96	-0.81	-0.14	0.18	0.14	-0.67		0.04	0.40	0.00		0.32	1.20				-1.11	-1.00	0.58
6		0.68	-0.85	<	0.37	0.29	-0.73	0.16	1.29		1.25	0.28	0.08		0.16	1.29	<	-2.54	<	0.48	-0.35	0.32
7			3.61	8.81	-1.07	-0.82	-0.51	-0.19					0.03		-1.90	-1.73				0.42	-2.67	-1.14
8		-0.59	-0.08	1.78		0.15	-0.34	0.47					0.05		1.18	0.22					-2.27	2.48
9				-6.59	21.09	-0.88	-1.28	-0.02	-0.90						5.17	9.03						-0.73
10			-1.19	0.26		-0.28	0.83	0.27	3.14				-0.11									0.11
11		-6.49	-1.06	<	-1.24	-4.76	-0.47	-0.20	1.05		-2.90		-0.84		-1.87	-1.14				-1.99	-3.80	-0.71
12				4.03		2.60	1.84									10.06						-0.74
13									-2.14													
14		-0.35			-2.09	0.65		-0.29	-0.57				0.58		0.85					0.03	0.50	1.43
15				25.99	1.62	0.15	0.93	-0.50	3.10				-0.05		-3.07	-3.79						-0.86
16				5.91	0.31		1.51						0.35			-3.32						-3.61
17				<		-6.99	-2.68						-2.73			-1.88						-2.53
18		-2.74	-0.66	-2.09	-1.16	-1.24	0.40	-0.41	0.10		-1.22	-0.80	-0.93		-1.29	-0.49	-1.81	-2.36	-1.73	-2.81	-1.25	-0.16
19		0.52	-0.21	-1.78	-0.81	0.12	-0.08	-0.17	-1.29				0.28		-0.59	0.37	-0.45	<	18.31	-0.26	0.30	0.63
20				195.40			-1.57	-1.21	17.76				-0.48		4.41	35.70						0.74
21	10.35			11.87	-0.25	-0.29	0.34	0.14	0.48				0.05		0.63	0.15				-0.29		0.40
22				0.37		0.35	-0.21		<				0.00		0.12	-0.92						1.74
23							-1.34		10.38							-0.29						-0.12
24									-0.40													
25		-1.16	-1.48	-0.16	0.04	-0.41	0.10	-0.64	-0.38		-1.19	-0.77	-0.25		-0.55	-0.18	1.18	-2.95	-0.07	-1.38	-0.85	-0.63
26	-1.62	-0.81	-0.04	-0.52	0.31	-0.29	0.08	-0.49	-0.10				0.46		0.10	0.46	0.57	-1.08	1.14		0.00	0.40
27				-7.69	-8.00	-8.00	-5.61	-7.98					-7.08		-7.85	-4.68						-7.48
28a		0.59		-0.68		1.32	-0.21	0.25	0.48				-0.05		0.43	0.62						1.01
28b							0.00		0.62													1.00
29		-3.70	-1.06	-2.77	-0.68	-4.70	-0.83	-0.65	-0.86		-3.28	-0.43	-0.38		-1.26	-1.11	-6.94	1.68	-5.79	-2.91	-5.16	-0.81

|Z| ≤ 2: Performance is considered to be acceptable

2 < |Z| <3: The results are of questionable quality

Shaded areas represent unacceptable results (|Z| ≥ 3 or ‘below detection limit’, i.e., ‘<’)

Table 6. Z-scores for intercomparison sample IAEA-433: assessment of laboratory performances (continued)

Lab Code	Ag	Al	As	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Sb	Se	Sn	Sr	V	Zn
30		0.09	-0.89	-0.47	1.80	2.35	-0.10	-0.37	-2.29		0.12	0.54	-0.30		0.93	-0.15	14.45	-2.23	3.28	0.72	-0.40	0.87
31		-0.32	0.80	7.16	1.49	-1.06	0.44	-0.43	-0.52				0.56		1.56	0.37					-1.15	-0.63
32	-0.24			0.96	-0.73		-1.13	-0.63	0.44				-0.21		-2.22							-0.27
33			0.38		0.99	0.06		0.41	15.33	2.77			3.11	3.24			0.78			0.48		2.85
34		-4.56			0.06	-4.48	-2.37	-1.16	1.14		-3.95		-1.37		-1.77	-4.37	-3.55	1.68		-2.70		-1.67
35		0.34	0.72	-0.16	1.12	0.12	0.62	-0.14	-0.29				0.05		0.39	0.71	0.20		0.31		0.40	0.87
36				-1.31			0.10		-7.21							0.68						0.08
37				-0.31			-0.08	0.16	-0.43				-0.05		0.37	0.80						0.49
38	<		-4.53	<	-2.98	-6.29	-0.73	-0.85	<				-1.34		-1.10	-0.31		<	<	-2.86		-0.55
39			-7.27	783.11	-6.17	-2.54	3.02	-7.96	25.33		-7.74	2.12	-7.69		-6.11	-7.63						6.57
40			-1.27	-0.68	1.98	2.47	0.68						0.30			3.72				-0.19		2.14
41			12.55	0.05		6.35	0.46	-0.49	-0.76				5.18		2.93	1.97		0.95				-0.25
42			-1.74	-1.57	-3.39	1.53	-0.75	0.10	0.33				-0.31		-0.67	-0.40		-0.53				-0.44
43		3.05		0.37		0.12	1.04				0.55		0.66			0.83						
44				3.35			-1.79		-7.19							-1.81						
45			-0.47	0.89	-0.74	0.28	-0.94	0.33					-0.59		0.59	-2.09			0.62			0.72
46		-0.94	2.16	-6.69		0.65	-0.21	0.63	1.38		0.12		-1.44		-2.11	-3.11						-0.08
47	5.23	-0.02		0.89	-0.06	-0.47	-0.03	-0.16	-0.14		0.00		0.53		0.73	1.54						0.63
48									1.05													
49			-1.40	-1.05	1.49	-3.65	0.13		0.76				1.82			2.09		5.28		0.13	-3.73	-0.97
50			-2.38	-0.58	-1.25	-4.60	-0.26		-0.10				-1.04			-2.75		-5.16	-4.10			-0.13
51				0.16			-0.91		-0.62				-0.78		-1.28							
52a			0.08	1.41	2.29	-1.18	-0.60		0.57		-0.25		-1.16		-0.35	0.22	-0.82	-1.51	-0.90	-0.40	-2.15	0.08
52b			0.04	<	1.92	-0.47	-0.73		<				-0.25		-0.28	0.31	<	<	<	-0.45	-0.10	0.24
53	-2.35		0.86	-3.45	2.19	0.88	1.21						5.01		2.23	1.77		-0.01				0.30
54		3.35	-1.40			-4.81	-3.53	-1.14	12.48				0.56		-1.95	-1.97		-4.09				7.00
55				-0.03		-0.38	0.05						-0.49		-2.13	-4.68						-0.23
56		0.27	-0.51	1.25	0.62	-0.29	-0.10	0.19	0.48		-2.34	-0.99	0.00		0.04	-0.28	0.16	-0.90	0.76	-0.13	-0.15	0.08
57		-2.42		10.82		-2.43	3.71	1.67							-2.99	-1.44						
58									-0.38													
59		0.13	-0.21	-2.25	2.67	0.82	1.87	0.33	2.00		5.13		-0.05		-0.30	0.09	<	<	-1.10	0.13	0.40	0.48

|Z| ≤ 2: Performance is considered to be acceptable

2 < |Z| <3: The results are of questionable quality

Shaded areas represent unacceptable results (|Z| ≥ 3 or 'below detection limit', i.e., '<')

Table 6. Z-scores for intercomparison sample IAEA-433: assessment of laboratory performances (continued)

Lab Code	Ag	Al	As	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Sb	Se	Sn	Sr	V	Zn
60			0.47		0.12	-0.53		-7.92		-7.92				-7.92			2.08			-0.21		0.40
61		-5.58	-2.60	23.27	-0.43	-2.80	-1.07	0.12	0.29		-3.97		-0.50		-0.99	0.92	-4.82	-4.29				-0.44
62			-0.85		0.31	-0.59		-0.14	2.24					-0.43			-0.57					0.24
63			-3.36	-1.57			0.49		-1.29													-0.70
64		-0.72	1.50		2.23	-2.70		-0.71					0.06								-1.86	
65			1.19		0.19	-0.01		0.53					-0.46		-1.10		-0.24	18.77		-0.29		0.95
66			1.07	3.50	0.06	-0.74	1.40	-0.06					0.11		-0.23	-0.19		2.30	-0.38	0.36	-0.71	2.19
67						0.59	-0.47	-0.17				0.14	0.28		-0.32	1.29						0.24
68		0.03	0.42			2.47	1.01	0.79				5.55	0.89		2.58	1.91	0.16		3.03	0.21	1.10	0.71
69				-4.75		0.25	-0.52								0.00	0.95						-0.24
70		0.42	0.04	2.46	1.36	-0.29	0.83	0.02	1.24		-0.30	0.47	0.56		-0.24	0.58	-0.24	<		0.26	-0.10	-0.16
71									11.91							-7.23						
72		0.25				0.62	-0.77	-0.09					-1.70			-0.53						-1.44
73a		0.08	1.27	2.46	-0.31	-0.82	-0.52	-0.12	0.24		-1.43	-0.27	0.15		0.12	0.06	0.16	1.58	0.62	-0.20	0.06	0.65
73b		0.08	0.25	0.37	-0.06	-0.24	-0.03	-0.16			-0.36	-0.02	-0.18		-0.06	0.49	-0.69	7.44	2.00	0.03	-0.50	-0.24
74		-0.52	-1.35		-0.12	-0.18		0.33		-0.07		2.62	-0.15	0.46			0.16	-4.40	47.86		-1.20	4.75
75			-0.14		-0.25	-1.43	-1.77															-0.70
76		0.22	0.04		0.93	-0.18	-0.57	-0.24	0.29		2.91	-0.18	-0.78		-0.97	-1.14				-0.16	-1.00	0.08
77			<	563.50	-0.79	-3.95	9.25	-0.38	<		-3.49	-1.90	-1.23		-0.52	<	<	<	24.90	-7.67	-6.37	-0.41
78		1.44	0.51	0.89	0.68	1.16	2.13	0.77	0.57		1.07		1.04		0.89	1.57	0.98	0.24	0.31	1.22	0.56	1.43
79a			-0.51		-0.37	-0.35	-0.73	0.21	-0.38	-0.64			0.10	-0.16	-0.89	-0.31	-0.94			-0.26		-0.55
79b			0.34		-0.37	-0.41		-0.03							-0.49	-0.92						
79c					0.37																	
80	0.06			1.41	0.50		-1.51	0.61					-0.56		3.68	-0.95						-0.83
81		-0.04	1.48	-0.26		0.88	0.47	0.49	0.00				0.30		-0.08	0.52			3.93			0.48
82		-6.30		1.93		-3.53	0.57	2.97	2.95				9.11		-2.92	1.23						-2.53
83	229.89	-7.98	-5.65	54.05	-0.21	-4.30	0.54	0.87	29.38				0.68		5.94	2.34	55.81			1.24	-5.58	1.00
84				2.99			18.81		0.20													0.34
85				54.75			0.94									15.17						
86						1.88							0.48		0.00	-0.03						

|Z| ≤ 2: Performance is considered to be acceptable

2 < |Z| <3: The results are of questionable quality

Shaded areas represent unacceptable results (|Z| ≥ 3 or 'below detection limit', i.e., '<')

Table 6. Z-scores for intercomparison sample IAEA-433: assessment of laboratory performances (continued)

Lab Code	Ag	Al	As	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Sb	Se	Sn	Sr	V	Zn
87a			-2.08				0.74	0.89		-0.55		0.34	-0.83		6.82	0.77						1.28
87b								0.67		-1.25			-0.09			2.42						0.82
88									-0.14													
89				284.81			-4.92	-1.20					1.28			-6.36						0.23
90							0.21						-0.25		0.93	3.38						0.00
91			-0.08		-0.06	0.65		0.06		0.90				0.40			0.41			0.13		0.32
92				11.87	-7.10	-7.37	-5.19	-7.84					-7.66		-0.15							-1.97
93					1.12	0.38	-1.19	-0.60					-1.67		-1.97	1.94				0.90		-2.06
94a			-1.16		-0.92	3.32	-0.27	-0.34					-1.07		0.19	-1.28				-1.01		-0.43
94b					-0.82	-1.86	0.75	-0.89					3.36		1.80	-1.14						0.05
95									-0.86													
96			0.99	-0.16	2.29	-2.39	-5.78		-1.33				-0.39		3.61	4.32	<	<	-3.41		-2.82	-1.09
97				0.52		1.89	-2.69		9.05							-1.68						
98		-0.02	0.34		78.20			0.33				1.44	0.78				1.02	21.65		1.43	0.00	1.35
99				-3.29			-0.31		1.19		-0.59				2.09	0.68						0.40
100				44750			397.19									340.92						342.10
101			2.34		-0.35	0.33	1.09								0.08	0.88				1.24	0.30	0.23
102	0.12	-0.40	-0.63	-0.78	0.62	0.76	0.21	-0.16			0.19		0.18		0.81	-0.22	0.04		-0.34	0.32	0.60	-0.90
103		-0.24	-0.21	-1.88	-0.12	0.88	-0.08	-0.09	-0.19				0.41		0.41	1.17				-0.40	1.10	-0.08

|Z| ≤ 2: Performance is considered to be acceptable

2 < |Z| <3: The results are of questionable quality

Shaded areas represent unacceptable results (|Z| ≥ 3 or ‘below detection limit’, i.e., ‘<’)

Table 7. Overall assessment of the performance of the laboratories: Group Classification

IAEA-433									
LAB No.	No $\lvert Z\rvert<3$	%	No $2<\lvert Z\rvert<3$	GROUP	LAB No.	No $\lvert Z\rvert<3$	%	No $2<\lvert Z\rvert<3$	GROUP
1	2	50%	0	3	32	9	100%	1	1
2	3	75%	0	2	33	8	73%	2	3
3	16	100%	1	1	34	9	64%	2	3
4	8	89%	0	2	35	15	100%	0	1
5	14	93%	0	1	36	4	80%	0	2
6	16	100%	1	1	37	8	100%	0	1
7	10	83%	1	2	38	8	80%	2	2
8	11	100%	2	1	39	2	15%	2	4
9	5	56%	0	3	40	8	89%	2	2
10	7	88%	0	2	41	8	73%	1	3
11	11	79%	1	2	42	11	92%	0	1
12	3	60%	1	3	43	6	86%	0	2
13	1	100%	1	1	44	2	50%	0	3
14	10	100%	1	1	45	11	100%	1	1
15	7	70%	0	3	46	10	83%	2	2
16	3	50%	3	3	47	12	92%	0	1
17	4	80%	4	2	48	1	100%	0	1
18	19	100%	0	1	49	9	75%	1	2
19	15	94%	0	1	50	8	73%	2	3
20	4	50%	0	3	51	5	100%	0	1
21	10	83%	0	2	52a	16	100%	2	1
22	7	100%	0	1	52b	10	100%	0	1
23	3	75%	0	2	53	9	82%	3	2
24	1	100%	0	1	54	5	45%	0	4
25	19	100%	1	1	55	6	86%	1	2
26	17	100%	0	1	56	19	100%	1	1
27	0	0%	0	4	57	5	71%	3	3
28a	10	100%	0	1	58	1	100%	0	1
28b	3	100%	0	1	59	15	94%	3	1
29	13	68%	2	3	60	6	67%	1	3
30	17	89%	3	2	61	10	67%	2	3
31	12	92%	0	1	62	8	100%	1	1

- Group 1 laboratories with $\lvert Z\rvert < 3$ for $\geq 90\%$ of the data;
- Group 2 laboratories with $\lvert Z\rvert < 3$ for 75% to $< 90\%$ of the data;
- Group 3 laboratories with $\lvert Z\rvert < 3$ for 50% to $< 75\%$ of the data;
- Group 4 laboratories with $\lvert Z\rvert < 3$ for $<50\%$ of the data.

Table 7. Overall assessment of the performance of the laboratories (continued)

IAEA-433									
LAB No.	No │Z│<3	%	No 2<│Z│<3	GROUP	LAB No.	No │Z│<3	%	No 2<│Z│<3	GROUP
63	4	80%	0	2	84	3	75%	1	2
64	7	100%	2	1	85	1	33%	0	4
65	9	90%	0	1	86	4	100%	0	1
66	13	93%	2	1	87a	8	89%	1	2
67	8	100%	0	1	87b	5	100%	1	1
68	12	86%	2	2	88	1	100%	0	1
69	5	83%	0	2	89	3	50%	0	3
70	17	100%	1	1	90	4	80%	0	2
71	0	0%	0	4	91	9	100%	0	1
72	7	100%	0	1	92	2	25%	0	4
73a	19	100%	1	1	93	9	100%	1	1
73b	17	94%	1	1	94a	9	90%	0	1
74	11	79%	1	2	94b	7	88%	0	2
75	5	100%	0	1	95	1	100%	0	1
76	15	100%	1	1	96	8	67%	3	3
77	6	46%	0	4	97	4	80%	1	2
78	18	100%	1	1	98	9	82%	0	2
79a	14	100%	0	1	99	6	86%	1	2
79b	6	100%	0	1	100	0	0%	0	4
79c	1	100%	0	1	101	9	100%	1	1
80	8	89%	0	2	102	17	100%	0	1
81	11	92%	0	1	103	14	100%	0	1
82	7	70%	4	3					
83	7	44%	1	4					

- Group 1 laboratories with │Z│ < 3 for ≥ 90% of the data;
- Group 2 laboratories with │Z│ < 3 for 75% to < 90% of the data;
- Group 3 laboratories with │Z│ < 3 for 50% to < 75% of the data;
- Group 4 laboratories with │Z│ < 3 for <50% of the data.

8.2. Laboratory performance for selected trace elements

In order to examine the relative precision and accuracy of different instrumental techniques, the complete data set for selected elements (i.e., all reported laboratory means) was divided into classes corresponding to the different analytical methods and represented as multiple box-and-whisker plots (Figs. 2 to 13; see Table 3 or 5 for method codes/names). Statgraphics software was used for producing these plots. As previously described in 7.2 for the S-plots in Annex II, the dashed horizontal lines in the figures indicate the limits representing ±1 standard deviation of the calculated mean value from the Cofino statistical model. For a method to be displayed on these plots, there must be at least 4 results submitted for the method. For each method, a box encloses the middle 50% of the data (i.e., the 25 and 75 percentiles), the median is represented as a horizontal line and the mean is represented as a point. It should be noted that due to data that would normally be considered outliers, the mean point, and possibly even the median line, may sometimes fall outside the middle 50% box. The whiskers represent the 10 and 90 percentiles, but are only displayed when there are at least 10 measurements in the data set. The number of measurements represented by each data set is reported above the box, or, if present, the 90 percentile whisker.

The graphs clearly demonstrate the robustness of the median (compared to the mean) in the first approximation of a reference value. The graphs consistently show that while the mean may fall anywhere (due to significant influence by outliers), the median is often very close to the recommended value, generally regardless of the data distribution for the method.

The results for some individual elements, all class “A”, are presented here.

8.2.1. Arsenic

This element was analysed using several methods, and there was reasonable overlap observed in results across the methods employed (Fig. 2). Median results were virtually identical between ZGF-AAS, ICP-AES, ICP-MS, NAA, and XRF techniques. Although there was some data overlap observed between the results obtained using hydride generation -AAS, the data spread for this techniques was significantly larger and biased much lower than for the other methods. Both the median and the entire middle 50% of the data for this method showed no overlap with the 1-standard deviation limits. The relatively low values observed for this method could be due to incomplete hydride generation. Possible reasons for this could include an ineffective reducing agent (e.g., not prepared fresh), or perhaps general differences in oxidation states, either within the sample itself, or between the standard and the sample.

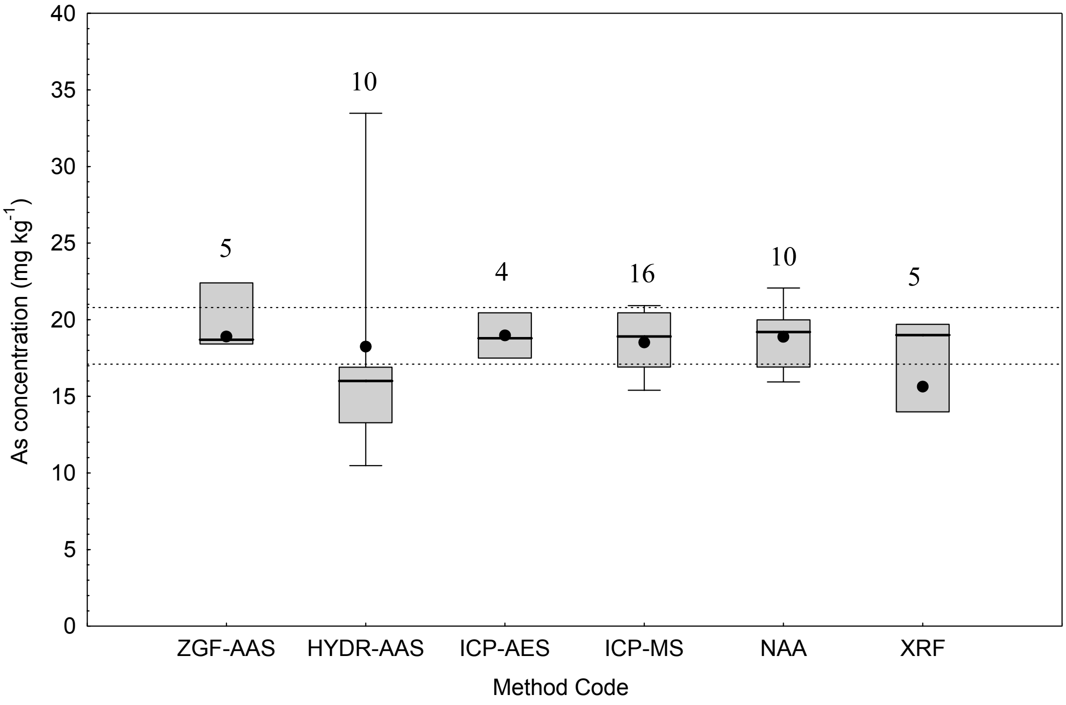

Figure 2. Arsenic results by different methods. (Recommended value: 18.9 mg kg^{-1})

8.2.2. Cadmium

Although the level of cadmium in this sample is relatively low, reasonable agreement was obtained between the different laboratories and the different methods used (see S-plot in Annex III and Fig. 3, next page). The majority of laboratories used AAS techniques (flame or graphite furnace), or ICP-MS. Reported results, especially the median values, are in very close agreement for GF-AAS, ZGF-AAS and ICP-MS. The data spread was much larger, and biased significantly high, in the case of F-AAS. This points out the inadequacy of this method for such low concentration levels (i.e., high detection limit), as was previously noted for the exercise on IAEA-140 sea plant sample,[8,11] IAEA-405 sediment sample,[10,26] and IAEA-407 fish tissue sample.[19] A couple of anomalously high data points also affected the data spread for GF-AAS, however these data did not significantly affect the median. The data spread was much tighter for ZGF-AAS, highlighting the advantages of this feature over deuterium-corrected GF-AAS. The best data set, however, was obtained by ICP-MS; with 19 results, the data spread including the whiskers is approximately the same as the 50% box for GF-AAS, and both the median and mean lie within the 1-standard deviation limits.

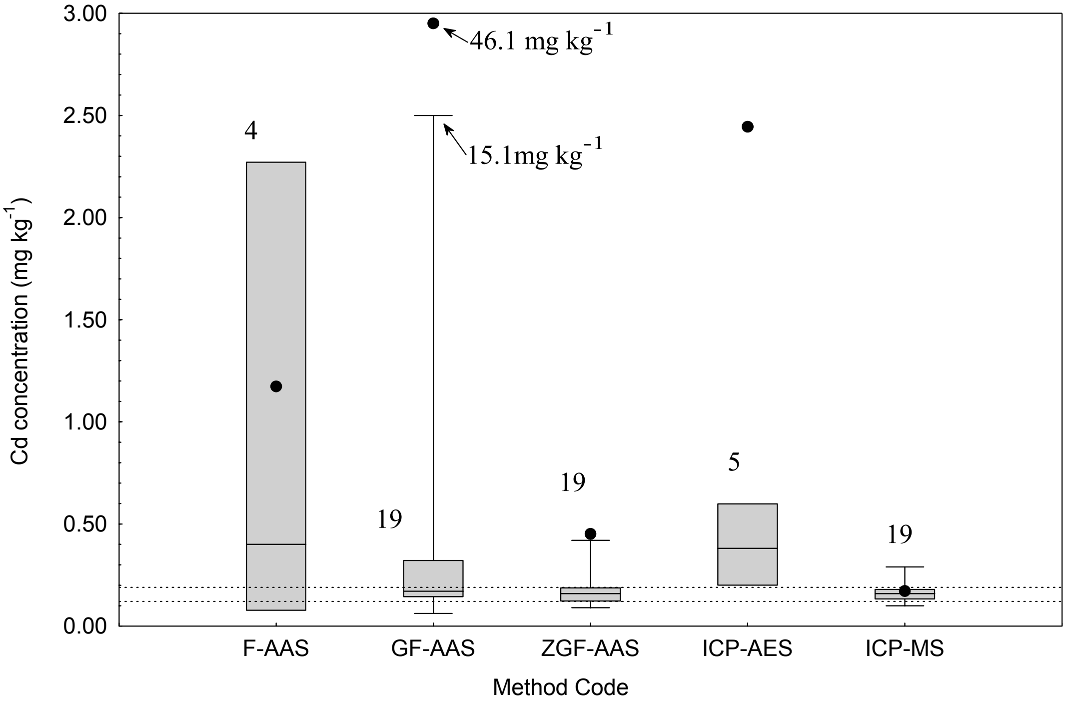

Figure 3. Cadmium results by different methods. (Recommended value: 0.153 mg kg^{-1})

8.2.3. Chromium

Chromium was determined by a variety of analytical techniques, as depicted in Figure 4. Despite the relatively large spread in results compared to most of the other elements, the medians obtained for the different techniques fell within the 1-standard deviation limits, with the exception of those for GF-AAS (high) and ICP-AES (low).

Although good Cr results are certainly attainable by GF-AAS, this element is notoriously difficult to analyse by this technique, even when using Zeeman correction. For this exercise, it appears that Zeeman provided a modest advantage over non-Zeeman results, but neither technique produced a mean inside the standard deviation limits.

This element was determined mainly by AAS (flame or graphite furnace), followed by ICP-AES, ICP-MS, NAA and XRF. The method yielding the best accuracy and reproducibility between laboratories was probably NAA, however there did not seem to be one method that clearly stood out among the others. Results in general tended to be biased on the low side, with the exception of those obtained by GF-AAS. In the case of the destructive analysis methods, a contributing factor to this apparent low bias may have been the digestion method employed. When evaluating the results based on whether or not the dissolution method included hydrofluoric acid, there was a clear difference between the results obtained by those laboratories that used HF and those laboratories that did not (Figure 4). As has been observed and reported in previous intercomparison exercises on sediment,[10,12,13] hydrofluoric acid is required for breaking down the silicate lattice of a sediment matrix. Without HF, the dissolution of sediment will be incomplete, resulting in lower observed concentrations – and a wider range of concentrations – for certain refractory elements, such as chromium.

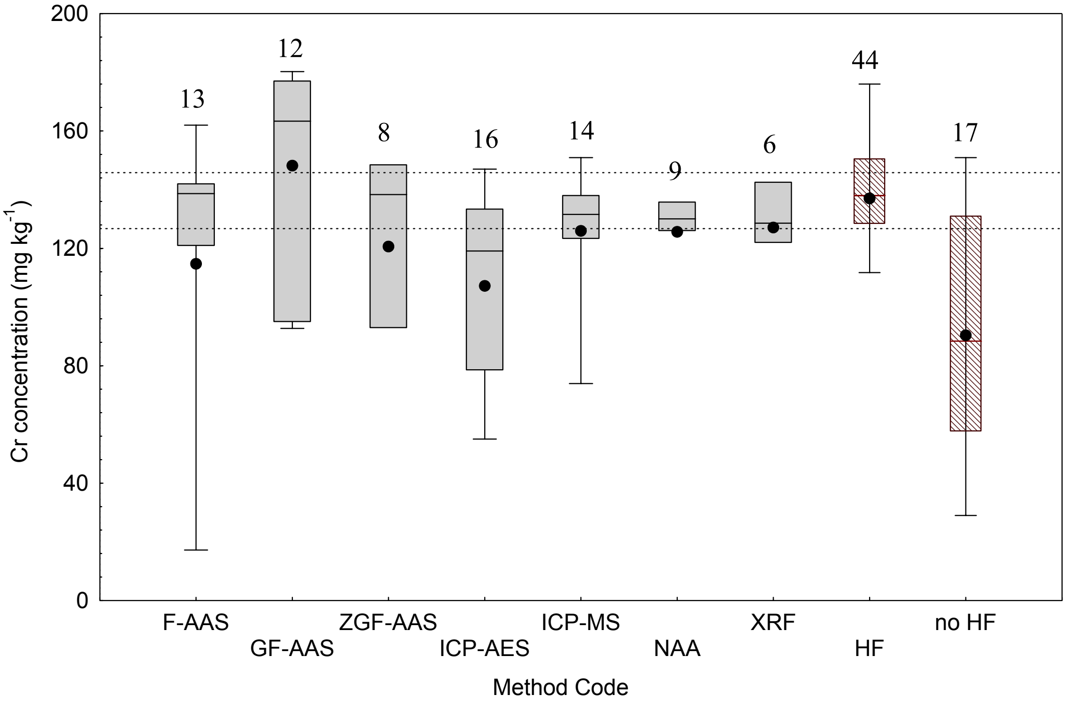

Figure 4. Chromium results by different methods. (Recommended value: 136 mg kg^{-1})

8.2.4. Copper, Cobalt, Nickel and Zinc

These are examples of well-grouped data with generally good agreement between the different analytical methods used (Figs. 5–8). Such well-grouped data are typically obtained for Cu and Zn in intercomparison exercises,[8-10,12,19] however, Cu by GF-AAS proved to be an exception for this exercise. Although the population of this subset consists of only 10 results, the distribution is much wider than for any other method, and indeed much wider than would normally be expected for this technique.

Although the ranges and means varied slightly more for Ni than for Cu, Co and Zn, it is notable that the median value for each technique was very close to the recommended value. The fairly large uncertainty spread observed by GF-AAS and XRF for Ni is probably due to an inadequate number of measurements for both data sets (7 and 6 respectively); however, F-AAS also showed a large distribution range with 20 results. Most of the data was obtained by AAS techniques (flame or graphite furnace), followed by ICP-MS, ICP-AES and XRF.

For cobalt, the data ranges were impressive for all methods; the apparently wide whiskers seen in the case of NAA was due to a couple of outliers, as evidenced by the tight 50 percentile through the middle of the 1-standard deviation limits. For zinc, the only biased method appeared to be NAA, which provided significantly higher concentrations than the other methods, as well as a wider distribution.

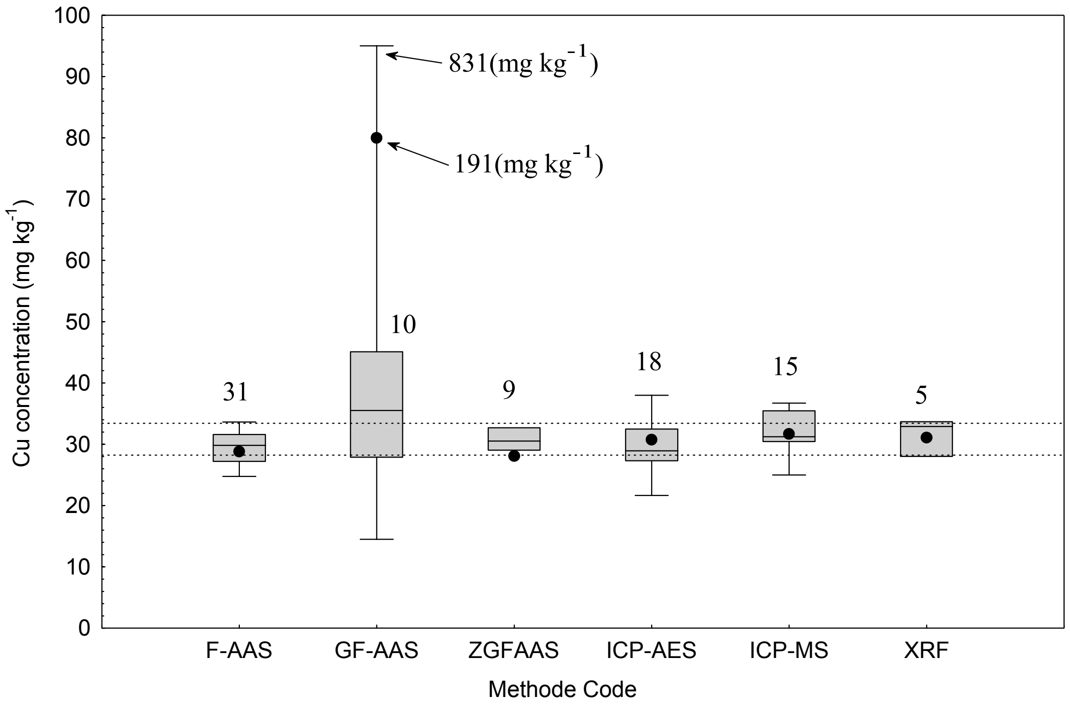

Figure 5. Copper results by different methods. (Recommended value: 30.8 mg kg^{-1})

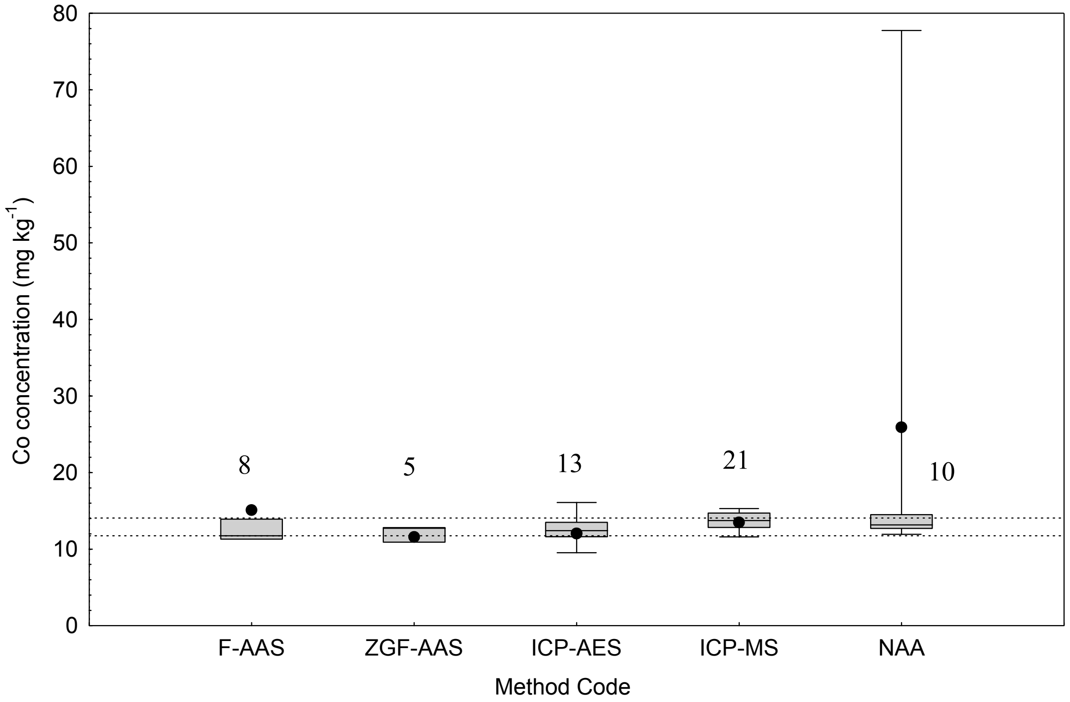

Figure 6. Cobalt results by different methods. (Recommended value: mg kg^{-1})

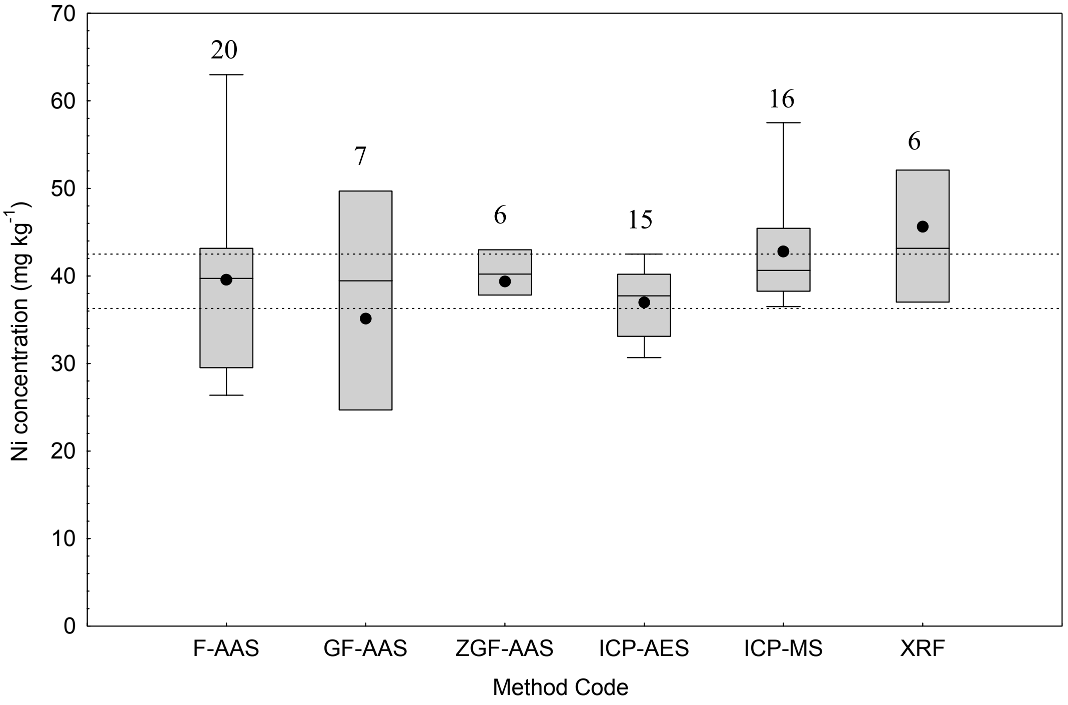

Figure 7. Nickel results by different methods. (Recommended value: 39.4 mg kg^{-1})

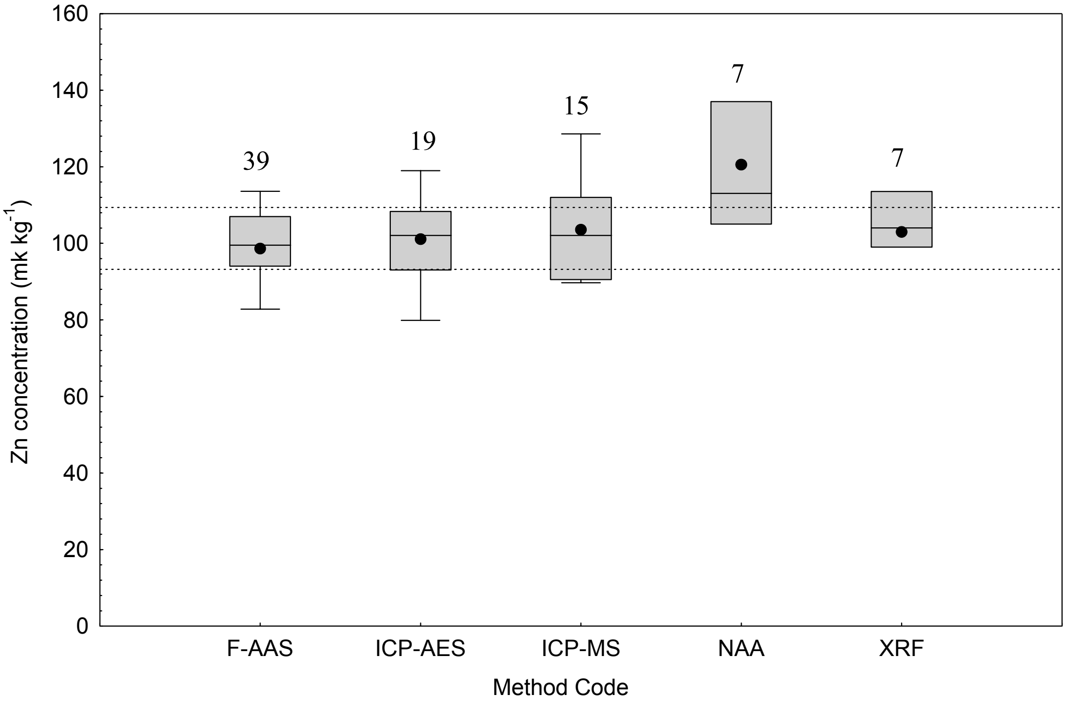

Figure 8. Zinc results by different methods. (Recommended value: 101 mg kg^{-1})

8.2.5. Iron and Manganese

Most of the laboratories used Flame-AAS or ICP-AES to analyse Fe, probably due to its relatively high concentration compared to the other trace metals in the sample. Medians are in good agreement between analytical techniques for both Fe and Mn (inter-technique CV's of <10%; Figs. 9 and 10), and data spreads are also very good. One exception is the data range for

Mn by XRF, which showed a large variation and a high bias. With only 7 results, however, the data set is too small to assess accurately a general limitation with XRF for Mn.

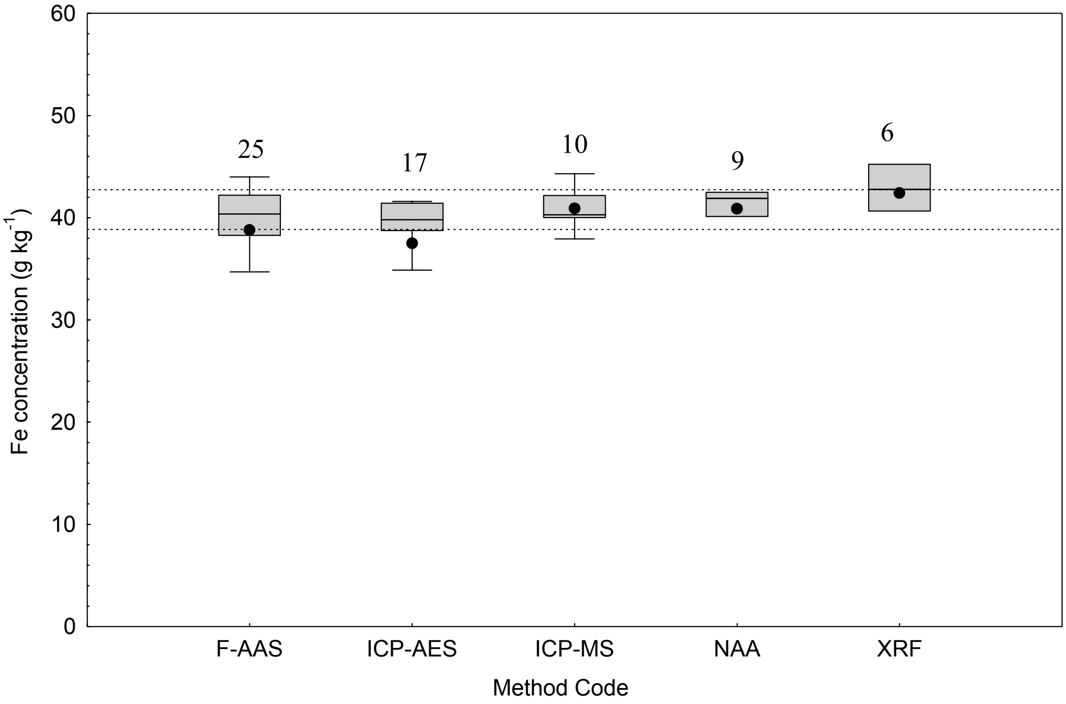

Figure 9. Iron results by different methods. (Recommended value: 40.8 g kg^{-1})

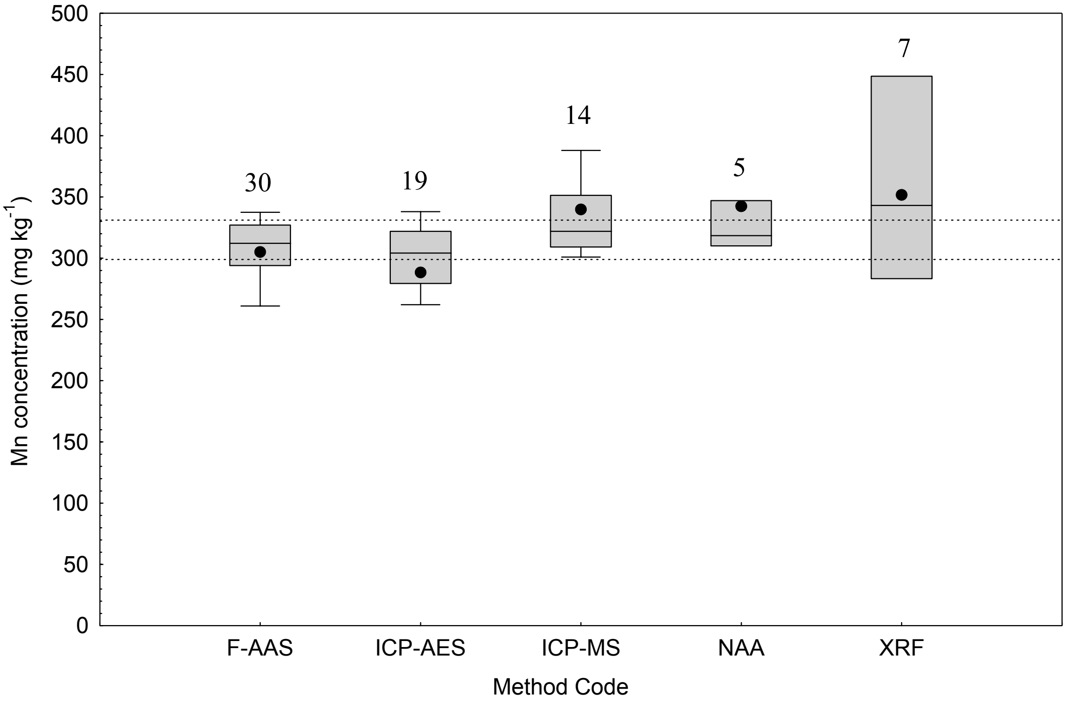

Figure 10. Manganese results by different methods. (Recommended value: 316 mg kg^{-1})

8.2.6. Mercury

The data received are generally in very good agreement (see S-plot in Annex III and Fig. 11). The medians between the 3 techniques displayed are almost identical. For the determination of total Hg, most of the laboratories used a wet digestion procedure employing different mixtures of acid followed by cold vapour techniques, with detection either by AAS or AFS. The majority of laboratories used $SnCl_2$ as the reducing agent, and only a few used $NaBH_4$. There continues to be a significant increase in the use of solid mercury analysers for this exercise: 10 laboratories used the SAAS technique compared to only 7 in the previous exercise (IAEA-407), and only 2 in the exercise before that one (IAEA-405). The values obtained by this technique were very comparable to those obtained by the 2 other techniques.

A few excess results were reported using the CV-AAS technique. High biases are usually due to reagent or labware contamination, however, one would probably expect a greater incidence of contamination for the more sensitive techniques, and CV-AAS is the least sensitive of the 3. On the other hand, it's possible that laboratories that routinely use the more sensitive techniques are more cognizant of potential contamination sources, which could lead to greater care and precautions implemented to prevent contamination from occurring.

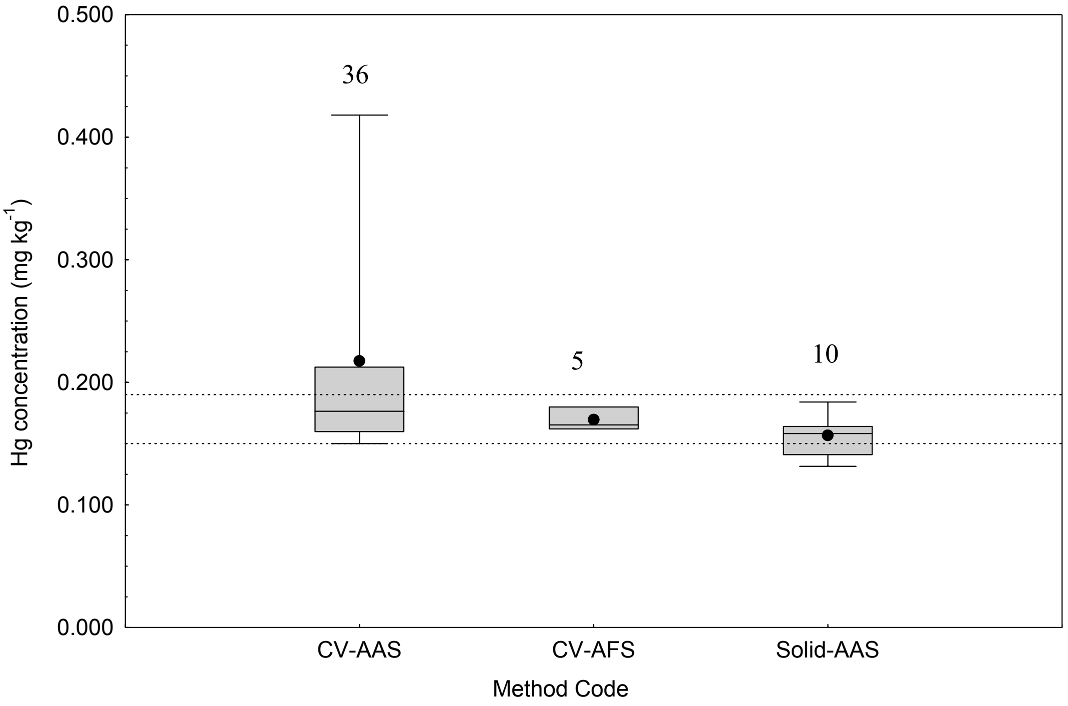

Figure 11. Mercury results by different methods. (Recommended value: 0.168 mg kg^{-1})

8.2.7. Lead

Lead should have been easy to measure in this material, due to its relatively high concentration (26.0 mg kg^{-1}). Contamination, while always a consideration when analysing lead regardless of the concentration, was undoubtedly less of a factor for this exercise. Even so, none of the AAS methods provided impressive data sets with respect to data distribution or mean results, though the medians for both GF-AAS subsets (i.e., with and without Zeeman correction) fell in the middle of the standard deviation limits. Interestingly, the Zeeman set appeared to be biased low, while the GF-AAS set without Zeeman appeared to be biased high.

Perhaps this indicates that there is an interference present that requires correction, but that the Zeeman technique may be over-correcting for this material. Previous intercomparison exercises[10,19] have demonstrated a clear advantage of using Zeeman correction for obtaining Pb results, but most notably when the concentrations were low.

The ICP-MS data set stood out among the others as superior in every respect for measuring Pb. This was also evident for the previous 2 intercomparison exercises. The ICP-AES method also proved to be effective for determining lead, with a reasonably tight and accurate distribution. XRF also yielded an acceptable distribution, though there seemed to be indications of a modest high bias, perhaps owing in part to the limited population of this data set (only 7 results).

Most laboratories reported values of Pb using AAS techniques (flame or graphite furnace), followed by ICP-MS, ICP-AES and XRF.

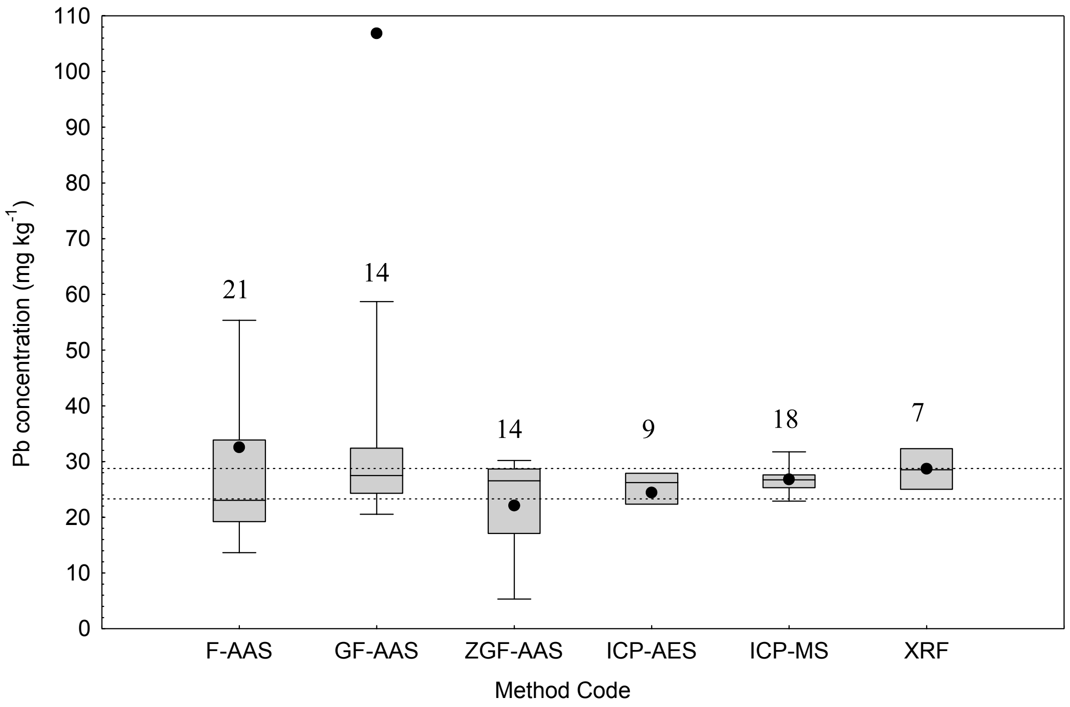

Figure 12. Lead results by different methods. (Recommended value: 26.0 mg kg^{-1})

8.2.8. Strontium

Strontium was analysed by ICP-AES, ICP-MS, NAA and XRF. All data sets provided comparable results with reasonable data ranges (Fig. 13). The only notable observation was the comparatively large 50 percentile data spread and apparent low bias for the ICP-AES analysis. In spite of this, the median obtained by ICP-AES falls right in the middle of the 1-standard deviation limits, indicating that the distribution was probably adversely affected by a few low outliers.

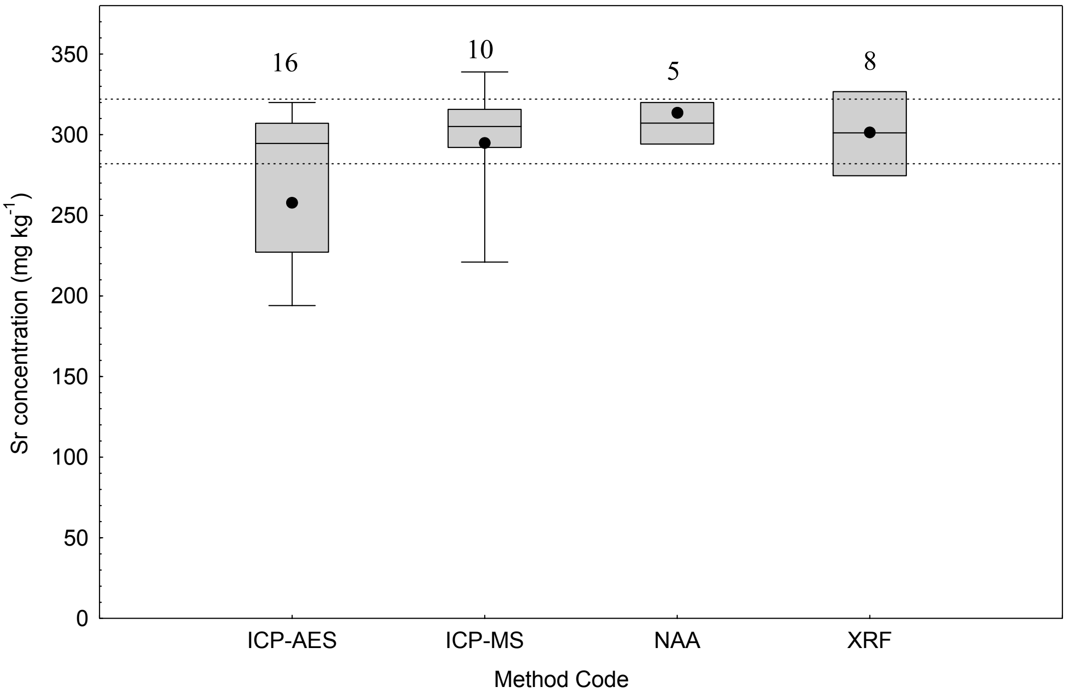

Figure 13. Strontium results by different methods. (Recommended value: 302 mg kg^{-1})

9. METHYLMERCURY

Ten laboratories reported results for methylmercury (MeHg) using various isolation procedures and detection systems, and an additional laboratory employed a method that yielded a result representing all organomercury compounds. A list of the participants with a description of the method used is given in Table 8. The aim of the study was to compare results for methylmercury compounds obtained by different methods. In the very first step, when MeHg was released from the binding sites, two approaches were used: distillation and acid leaching. Further processing included additional separation of organic and inorganic mercury, solvent extraction with or without a clean-up step (using equilibration into aqueous cysteine or thiosulfate solution) and derivatisation by aqueous phase ethylation and GC separation. The detection systems included primarily variations of gas chromatography (GC) combined with atomic fluorescence spectrophotometry (AFS), atomic emission detection (AED), and ICP-time of flight mass spectrometry. Only 2 laboratories used detection methods that did not involve some form of gas chromatography: one used HPLC with AFS, and the other used solid analyser AAS, though the latter provided a result representing total organomercury.

The recommended value is 0.17 µg Hg kg^{-1} with a confidence interval of 0.12 to 0.23 µg kg^{-1}. The results obtained are presented in Annex I. The laboratories' means are also plotted in ascending concentration (Annex II). Ten of the 11 laboratories reporting MeHg results provided mean values above the detection limit; the one 'less-than' result was not included in calculating the reference concentration, nor was the value representing total organomercury.

The 9 valid results varied between 0.1 and 1.4 μg kg^{-1} – a variation of an order of magnitude, undoubtedly owing in large part to the very low concentration present in the subject material.

Four of the five results observed between the 1-standard deviation limits were obtained using essentially the same isolation procedure: acid leaching, extraction in CH_2Cl_2, back-extraction in water, aqueous-phase ethylation, and collection on a Tenax column. The fifth result was a similar procedure, but employed distillation instead of acid leaching + extraction in dichloromethane. The 4 higher results, falling outside the 1-standard deviation limits, used different techniques. While it may be reassuring to see such good agreement between the laboratories that used the same method, it remains unclear which method, if any, provided the most accurate result. A recovery problem with the most common method could have resulted in a reproducible low bias. Alternatively, there could be unaccounted artefacts for the other methods, resulting in varying high biases. Had a more definitive method, such as isotope dilution mass spectrometry, been implemented in this study, perhaps these lingering uncertainties could have been addressed unequivocally. As these more advanced techniques become more common, it is presumed that there will be greater confidence and less uncertainty in the resulting recommended values, even for concentrations as low as that found in this study.

Table 8. List of laboratories and analytical methods used for methylmercury determinations

Lab Code	Isolation Procedure	Detection Technique [a]	Detection Limit ($\mu g\ kg^{-1}$)	RM used
11	Extraction derivatisation	GC-AED	2	-
24	Double extraction to dithizone including back extraction to Na_2S	GC (detection not reported)	1	CRM 580
25	Extraction CH_2Cl_2 (Westoo), Aqueous phase ethylation, Tenax	GC-AFS	0.01	IAEA 405
26	Acid leaching (H_2SO_4/KBr/$CuSO_4$) extraction CH_2Cl_2, Back extraction water, Aqueous phase ethylation, Tenax	GC-AFS	0.00002	IAEA 405
41	Extraction Toluene-HCl, back extraction cysteine chloride	Solid Analyzer AAS (org-Hg)	1	LUTS-1 /TORT-2
48	Leaching HNO_3 (6M) using open microwave oven	PTI-MCGC-ICP-TOFMS	0.06	IAEA 405
56	Dithizone extraction with chloroform, back extraction with sodium thiosulfate	HPLC-AFS	1	CRM 580
70	Acid leaching (H_2SO_4/KBr/$CuSO_4$) extraction with toluene, Grignard	HRGC-MIP-AED	0.5	CRM 580
78	Distillation, aqueous phase ethylation, Tenax	GC-AFS	0.02	IAEA 405
88	Acid leaching (H_2SO_4/KBr/$CuSO_4$) extraction CH_2Cl_2, Back extraction water, Aqueous phase ethylation, Tenax	GC-AFS	0.08	BCR 580
95	Acid leaching (H_2SO_4/KBr/$CuSO_4$) extraction CH_2Cl_2, Back extraction water, Aqueous phase ethylation	Head space GC-AFS	0.05	IAEA 405

[a] **GC**: Gas chromatography; **AFS**: Atomic fluorescence spectrometry; **AAS**: Atomic absorption spectrometry; **PTI-CGC-ICP-TOFMS**: Purge and trap injection coupled to multicapillary gas chromatography and inductively coupled plasma- time of flight-mass spectrometry; **HPLC**: high performance liquid chromatography; **HRGC-MIP-AED**: High resolution gas chromatography coupled with microwave-induced plasma atomic emission spectrometric detection; **AED**: Atomic emission detector

10. RECOMMENDATIONS

Participants are recommended to review their data element-by-element and to "score" each result by evaluating whether its $|Z|$ value is less than or equal to 2. This range is somewhat arbitrary, but is presented as a simple guideline for the user. The precision required for data depends upon its final application – e.g., long-term trend data or that used for geochemical monitoring must be much more precise than that used for "hot spot" pollution monitoring. The use of the Z-scores will help to identify systematic errors in accuracy (e.g.

from calibration errors, reagent contamination or incomplete digestion) and should ultimately improve data quality.

A few laboratories still need to improve their quality control procedures. Intercomparison exercises represent only one aspect of data quality assurance and can only provide occasional indicators of data quality. The most valuable approach is through the regular analysis of standard reference materials, or even in-house working reference materials, and by plotting the resulting data on a quality control chart. This provides continuous feedback to the analyst and is an essential tool for monitoring data quality and assuring acceptable results in future exercises.

11. CONCLUSIONS

The relatively narrow data distributions observed for the results of the IAEA-433 trace metals intercomparison exercise are indicative of accurate analyses and a homogeneous material. Most concentrations are neither exceptionally high nor low for a coastal marine sediment, but all analytes examined were virtually always measurable by the methods employed, which undoubtedly contributed to the reproducibility observed. A class “A” or “B” consensus value could be given to 28 elements and in addition a recommended concentration was established for methylmercury (class “B”). The confidence in the reference values obtained indicate that the sample is suitable for verifying the accuracy and precision of analytical measurements when sediment samples from coastal environments are to be analysed for trace elements. Participants in the intercomparison should therefore retain their samples as a Reference Material.

IAEA-433 Reference Material is now available from the International Atomic Energy Agency (IAEA), AQCS, PO Box 100, A-1400 Vienna, Austria. A full catalogue of available IAEA reference materials is published regularly and can be consulted on the IAEA website: http://www.iaea.org/programmes/aqcs.

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13. REFERENCES

1 H. O. F. Andersson, *Accred. Qual. Assur.*, 1998, **3**, 224.

2 R. Becker, I. Nehls and U. Dorgerloh, *Accred. Qual. Assur.*, 2003, **8**, 150.

3 ISO, *Proficiency testing by interlaboratory comparisons- Part 1: Development and operation of proficiency testing schemes*, Guide 43-1, ISO, 1997.

4 B. King, N. Boley and G. Kannan, *Accred. Qual. Assur.*, 1999, **4**, 280.

5 E. A. Maier, P. Quevauviller and B. Griepink, *Analytica Chimica Acta*, 1993, **283**, 590.

6 J. K. Taylor, *Quality assurance of chemical measurements*, Lewis Publishers Inc., Boca Raton, FL, USA, 1987, 328.

7 IAEA, *Contaminant monitoring programmes using marine organisms: Quality Assurance and Good Laboratory Practice. Reference Methods for Marine Pollution Studies*, 57, IAEA, 1990.

8 M. Coquery, F. P. Carvalho, M. Horvat and S. Azemard, *Report on the world-wide intercomparison exercise IAEA-140 for the determination of trace elements in Fucus sample*, IAEA/AL/139 (IAEA/MEL/64), IAEA, Monaco, 1997.

9 M. Coquery, F. P. Carvalho, S. Azemard and M. Horvat, *Sci. Total Environ.*, 1999, **237** / **238**, 501.

10 M. Coquery, S. Azemard and S. de Mora, *Report on the world-wide intercomparison exercise for the determination of trace elements and methylmercury in estuarine sediment IAEA-405*, IAEA/AL/127 (IAEA/MEL/70), IAEA, Monaco, 2000.

11 M. Coquery, F. P. Carvalho, S. Azemard, M. Bachelez and M. Horvat, *Fresenius. J. Anal. Chem.*, 2000, **366**, 792.

12 M. Coquery, E. J. Wyse, S. Azemard and S. de Mora, *The analytical performance study for ROPME sea area: determination of trace elements in sediment SD-ROPME-3/TM and fish homogenate MA-ROPME-2/TM*, IAEA, Monaco, 2001.

13 M. Horvat, L. Mee and B. Oregioni, *Report on the world-wide and regioinal intercomparison run IAEA-356 trace elements in polluted marine sediment*, IAEA/AL/080 (IAEA/MEL/56), IAEA, Monaco, 1994.

14 M. Horvat, V. Mandic, L. Liang, N. S. Bloom, S. Padberg, Y.-H. Lee, H. Hintelmann and J. Benoit, *Appl. Organometal. Chem.*, 1994, **8**, 533.

15 L. Mee and B. Oregioni, *Report on the world-wide intercomparison of trace elements measurements in marine sediments SD-M-2/TM*, IAEA/AL/053, IAEA, Monaco, 1991.

16 J.-P. Villeneuve, S. J. de Mora, C. Cattini and F. P. Carvalho, *Journal of Environmental Monitoring*, 2000, **2**, 524.

17 J.-P. Villeneuve, S. J. de Mora and C. Cattini, *Environmental Technology*, 2002, **23**, 1203.

18 J.-P. Villeneuve, S. J. de Mora and C. Cattini, *World-wide and regional intercomparison for the determination of organochlorine compounds and petroleum hydrocarbons in sediment sample IAEA-417*, Report IAEA/AL/131, International Atomic Energy Agency, Vienna, 2002.

19 E. J. Wyse, S. Azemard and S. de Mora, *World-wide intercomparison exercise for the determination of trace elements and methylmercury in fish homogenate IAEA-407*, IAEA/AL/144 (IAEA/MEL/72), IAEA, Monaco, 2003.

20 F. P. Carvalho, J.-P. Villeneuve and C. Cattini, *International Journal of Environmental Analytical Chemistry*, 1999, **75**, 315.

21 F. P. Carvalho, J.-P. Villeneuve and C. Cattini, *Trends Anal. Chem.*, 1999, **18**, 656.

22 M. Thompson and R. Wood, *J. Pure. Appl. Chem*, 1993, **65**, 2123.

23 J. C. Miller and J. N. Miller, *Statistics for Analytical Chemistry*, Ellis Horwood Limited, West Sussex, 1993, 233.

24 ISO, *Certification of reference materials - General and statistical principles*, Guide 35, Rev. 1, ISO, 2000.

25 W. P. Cofino, I. H. M. van Stokkum, D. E. Wells, F. Ariese, J.-W. M. Wegener and R. A. L. Peerboom, *Chemometrics and Intelligent Laboratory Systems*, 2000, **53**, 37.

26 E. Wyse, M. Coquery, S. Azemard and S. de Mora, *Journal of Environmental Monitoring*, 2004, **6**, 48.

27 IAEA, *Reagent and laboratory-ware clean-up procedures for low-level contaminant monitoring*, 65, IAEA, 1995.

ANNEX I

Data report of the individual laboratory results sorted by element

IAEA-433

Note: all results reported as received. Those calculated incorrectly by participant are highlighted in grey.

SILVER (Ag) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
4	0.134	0.008	5	0.05	215-M1	MESS3
21	0.305	0.050	6	0.02	3212-M1	CRM277
26	0.106	0.00673	5	0.005	221-A2	MESS3
32	0.12896	0.00313	5	0.008	202-A5	QTM058MS
38	<20		4		235-A1	
47	0.22	0.03	6	0.04	226-A3	MESS3
53	0.094	0.009	5	0.00000261	233-M1	PACS2
80	0.134	0.008	5	0.05	215-M1	MESS3
83	3.955	0.82990963	6	0.05	0-X1	
102	0.135	0.004	5	0.0002	238-M1	MESS2

ALUMINIUM (Al) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
3	78847	3634	6	0.3	222-M1	405
5	83660	570	3		212-E1	SRM1646
6	84817	1738	6	50	225-E1	MESS3
8	72400	4200	6	10	236-A3	BCSS1
11	14800	420	6	15	231-E1	WQB3
14	74777	2537	6	0.76	11-E1	PACS1
18	51420	3792	6	500	2111-E1	IAEA405
19	83320	5744	6	184	231-E1	MESS2
25	66887	4660	6	2	226-M1	IAEA405
26	70317	1074	6	1.43	221-M1	MESS3
28	84000	1900	6	0.00018	226-A1	MESS2
29	42000	920	6	0.5	2314-E1	Priority PollutnT
30	79100	1100	6	1000	216-E1	GBW07303
31	75100	1200	6		212-E1	MESS3
34	33620	13400	6	0.5	2225-E1	
35	81500	1700	3	76	222-M0	MESS2
43	108000	2000	6	0.30	236-A3	MESS3
46	69000	4640	6	20	236-A1	QTM58MS
47	78000	3000	6	2000	226-A1	MESS3
54	110900	6900	3	1	238-A1	
56	80800	3680	6	0.5	2312-M1	MESS3
57	54500	5100	6	0.00317	236-A6	MESS3
59	79500	580	3	10	231-E1	
61	23665	3707	6	40	235-E1	IAEA-405
64	71194.14	540.30	6	0.10	0-N2	IAEA-405
68	78470	1188	6		0-X1	SARM69
70	82300	564	6	50	234-E1	BCSS1
72	80600	6698	6		231-A1	IAEA-405
73a	79000	2500	6	2.5	212-E1	IAEA-405
73b	79000	4000	4	15	236-M1	Soil 2509-83
74	73100	3000	6	3200	0-N2	IAEA-SL1
76	80358	957	6	0.4	219-E1	IAEA-SL1
78	92240	6909	6	27	226-M1	MESS3
81	77800	2000	6	15	236-A1	BCR 277
82	16584	1437	6		229-A5	Taifun 2500-83
83	149.94	9.53	6	0.05	0-X1	
98	78000	1690	4	2.59E-07	0-N0	SRM1646
102	74300	4500	5	0.002	238-M1	MESS2
103	75840	619	5		238-A1	MESS2

ARSENIC (As) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
3	20.32	0.51	6	0.01	222-M1	IAEA 05
6	16.9	0.3	6	0.1	225-A8	MESS3
7	27.42	1.32	6	0.013	215-A4	BCSS1
8	18.7	1.0	6	0.100	236-A3	BCSS1
10	16.1	1.5	6	0.030	231-A8	TORT2
11	16.4	0.2	6	6.000	235-E1	WQB3
18	17.35	0.876	6	0.5	2111-F2	IAEA405
19	18.4	0.3	6	1.1	231-M1	IAEA405
25	15.4	1.3	6	0.0002	226-M1	IAEA405
26	18.8	0.235	6	0.188	2212-M1	MESS3
29	16.4	0.32	6	0.02	2314-M1	Priority PollutnT
30	16.8	0.23	6	0.7	215-A8	GBW07303
31	20.8	1.5	6		212-M1	MESS3
33	19.8	1.30	5	3.5	0-N2	IAEA405
35	20.6	0.8	3	0.080	222-M0	MESS2
38	8.2	0.68	4		235-A8	
39	1.73	0.10	6		215-A4	
40	15.9	0.9	6	0.003	2319-A8	BCSS1
41	48.54	1.23	6	0.05	239-A8	SDM2TM
42	14.8	0.7	8	0.05	215-M1	MESS3
45	17.8	0.4	6	1.0	235-A7	MESS3
46	24	3.02	4	0.05	236-A3	QTM58MS
49	15.6	0.53	6	0.03	2214-M1	MESS1
50	13.27	0.52	6	0.02	233-A8	PACS2
52a	19.1	0.5	6	1.1	234-M1	BRM#03
52b	19	0.9	6	2	0-X1	CRM277
53	20.92	0.27	5	0.0000043	233-M1	PACS2
54	15.6	2.7	6	0.50	238-A8	
56	17.7	0.18	6	0.1	2312-M1	MESS3
59	18.4	0.2	3	0.5	231-A8	
60	20	1.5	6	1	0-N0	1633A
61	12.76	0.194	6	8.83	235-A8	IAEA-405
62	16.9	0.3	6	0.60	0-N0	SRM 2704
63	10.97	0.32	4	0.5	223-A3	IAEA-405
64	22.44	1.10	6	0.01	0-N2	IAEA-405
65	21.7	1.1	6	0.4	0-N2	BIL1
66	21.42	1.116	6		232-M1	IAEA-405
68	19.9	0.6	6		0-X1	SARM69
70	19	0	6	1	234-M1	BCSS1
73a	21.9	0.4	6	0.5	212-E1	IAEA-405
73b	19.5	1.8	8	0.5	236-M1	Soil 2509-83
74	15.7	1.9	6	5.3	0-N2	IAEA-SL1
75	18.57	0.89	6	2.33	2314-E1	PACS2
76	19.0	0.507	5	6	219-E1	IAEA-SL1
77	<D.L.		6	0.25	2114-E1	
78	20.1	1.6	6	0.25	226-F2	MESS3
79a	17.7	0.7	6	0.050	0-N0	SOIL7
79b	19.7	0.5	6	1.000	0-X0	SOIL7
81	22.4	0.6	6	0.005	236-A3	BCR 277
83	5.55833333	0.70323301	6	0.05	0-X1	
87	13.98	16.19	6	7.84	0-X1	IAEA/LS-3
91	18.7	0.3	6	1.400	0-N0	SOIL7
94	16.17	0.66	6	0.025	0-N0	IAEA356
96	21.25	0.77	5	0.5	235-A6	

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
98	19.7	0.3	6	2.75E-08	0-N0	SRM1646
101	24.43	0.90	3			
102	17.4	0.5	5	0.01	238-M1	MESS2
103	18.4	0.4	6		238-A3	MESS2

BARIUM (Ba) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
33	313	5	3	30	0-N2	SOIL-5
60	279	27	6	30	0-N0	1633A
62	274	22	6	58	0-N0	SRM 2704
66	236	4	6		232-M1	IAEA-405
76	205	3.65	6	0.02	219-E1	IAEA-SL1
83	343.3705	13.0919846	6	0.05	0-X1	
101	278.53	3.91	3			
102	227	15	5	0.0002	238-M1	MESS2

BERYLLIUM (Be) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
19	2.13	0.03	6	0.1	231-M1	MESS2
76	1.784	0.045	6	0.02	219-E1	IAEA-SL1

BROMINE (Br) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
33	83.9	8.8	6	25	0-N2	IAEA405
60	67.5	4	6	1	0-N0	1633A
62	70	3	6	0.5	0-N0	SRM 2704
74	54	7	6	10	0-N2	IAEA-SL1
79	81	3.5	6	0.1	0-N0	SOIL7
91	67.1	0.67	6	1.6	0-N0	SOIL7
93	53.3	6.8	6	5.5	0-X0	SDN1/2
101	73.23	0.15	3			
87	50.07	71.31	0	4.48	0-X1	IAEA/LS-3

CALCIUM (Ca) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
87a	52811	5853.07	6	1651	0-X1	IAEA/LS-3
87b	56673	1008.29	3	14.37	2020-A1	
91	63800	3000	6	13000	0-N0	SOIL7

CADMIUM (Cd) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
1	<DL	<DL		0.1000	226-A1	SDM2/TM
3	0.158	0.007	6	0.002	222-M1	IAEA405
4	0.180	0.005	5	0.050	215-M1	MESS3
5	0.42	0.03	3		212-A3	SRM1646
6	NA	NA	6	0.1	225-A1	MESS3
7	0.322	0.0061	6	0.0004	215-A4	BCSS1
8	0.187	0.080	6	0.010	236-A3	BCSS1
9	0.027	0.0008	6	1.00E-05	2315-A4	SRM2976
10	0.158	0.010	6	0.020	231-A3	TORT2
11	<0.3			0.300	235-E1	
12	0.230	0.020	2		226-A2	BCSS1
15	0.65	0.062	6	0.200	222-A1	IAEA405
16	0.266	0.004	4	19.0E-6	236-A3	SRM1646
17	<1.2			1.200		
18	0.113	0.016	6	0.10	2111-E1	IAEA405
19	0.119	0.009	6	0.038	231-M1	MESS2
20	3.89	0.999	3	0.07	3205-A1	
21	0.380	0.030	6	0.02	3212-M1	RCM277
22	0.16	0.025	6	0.04	226-A3	IAEA405
25	0.15	0.02	6	0.001	226-M1	IAEA405
26	0.143	0.00413	6	0.0587	2212-M1	MESS3
27	0.006		3		2018-A1	
28	0.14	0.006	5	0.00025	226-A3	MESS2
29	0.10	0.002	6	0.01	2314-M1	Priority PollutnT
30	0.144	0.006	6	0.05	216-A4	GBW07303
31	0.29	0.01	6		212-M1	MESS3
32	0.17134	0.01359	5	0.0080	202-A4	QTM058MS
35	0.15	0.01	3	0.018	222-M0	MESS2
36	0.128	0.0165	6	0.003	233-A6	
37	0.147	0.0085	6	0.003	235-A1	
38	<1				235-A3	
39	15.13	0.30	6		215-A4	
40	0.14	0.01	6	0.01	2319-A4	BCSS1
41	0.154	0.018	6	0.001	239-A4	SDM2/TM
42	0.123	0.020	7	0.05	215-M1	MESS3
43	0.160	0.010	6	0.02	236-A3	MESS3
44	0.217	0.005	6	0.01	226-A3	IAEA405
45	0.170	0.020	5	0.05	235-A4	PACS2
46	0.025	0.007	3	10.00	226-A3	QTM58MS
47	0.17	0.01	6	0.01	226-A3	MESS3
49	0.133	0.005	6	0.01	2214-M1	MESS1
50	0.142	0.008	6	0.009	233-A3	PACS2
51	0.156	0.016	6	0.003	235-A4	144R
52a	0.18	0.02	6	0.02	234-A3	LGC6139
52b	n.d.			2	0-X1	CRM277
53	0.087	0.015	4	0.0000012	233-M1	PACS2
55	0.1525	3.76	6	0.0529	239-A3	IAEA-405
56	0.177	0.006	6	0.05	2312-M1	MESS3
57	0.36	0.04	6	0.000111	236-A6	MESS3
59	0.11	0.01	3	0.05	231-A3	
61	0.598	0.128	6	0.833	235-E1	IAEA-405
63	0.123	0.013	4	0.02	223-A3	IAEA-405
66	0.22	0.008	6		232-M1	IAEA-405
69	0.0621	0.0072	4	0.030	212-A4	IAEA-405

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
70	0.2	0	6	0.1	234-M1	BCSS1
73a	0.20	0.02	6	0.05	212-E1	IAEA-405
73b	0.160	0.03	7	0.04	236-M1	Soil 2509-83
77	10.93	0.46	6	0.025	2114-E1	
78	0.17	0.03	6	0.12	226-M1	MESS3
80	0.18	0.005	5	0.05	215-M1	MESS3
81	0.148	0.009	6	0.0002	236-A3	BCR 277
82	0.19	0.01	6		229-A5	Taifun 2500-83
83	1.18666667	0.50277894	6	0.050	0-X1	
84	0.210141	0.015463	6		223-A4	BCSS1
85	1.20	0.10	4	0.010	236-A5	IAEA-405
89	5.60	0.5141	4		2111-A3	QTM022MS
92	0.38	0.08	6		232-E1	MESS1
96	0.15	0.01	5	0.100	235-A6	
97	0.163	0.010	5	0.033	236-A2	BCSS1
99	0.09	0.02	6	0.05	233-A3	MESS2
100	856				205-A2	
102	0.138	0.003	5	0.0002	238-M1	MESS2
103	0.117	0.007	6		238-A3	MESS2

CERIUM (Ce) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
33	71.5	0.4	2	1.0	0-N2	SOIL5
60	63.4	2	6	10	0-N0	1633A
62	64	2	6	0.4	0-N0	SRM 2704
65	64.5	0.9	6	0.6	0-N2	BIL1
74	73.0	6.0	6	3.8	0-N2	IAEA-SL1
79	64	2.6	6	0.2	0-N0	SOIL7
91	71.4	0.57	6	0.91	0-N0	SOIL7

COBALT (Co) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
3	14.38	0.15	6	0.002	222-M1	IAEA405
4	13.7	0.32	5	0.05	215-M1	MESS3
5	11.6	0.4	3		212-E1	SRM1646
6	14	1	6	2	225-E1	MESS3
7	11.17	0.363	6	0.010	215-A1	BCSS1
9	46.90	0.66	6	0.05	2315-A1	
11	10.9	0.1	6	0.200	235-E1	WQB3
14	9.53	1.04	6	0.89	11-E1	PACS1
15	15.52	0.561	6	3.500	222-A1	IAEA405
16	13.400	0.180	4	96.0E-6	236-A3	SRM1646
18	11.03	0.333	6	1.0	2111-M1	IAEA405
19	11.6	0.4	6	0.02	231-M1	MESS2
21	12.5	0.43	6	0.1	3212-M1	CRM277
25	12.96	1.09	6	0.02	226-M1	IAEA405
26	13.4	0.243	6	0.0129	2212-M1	MESS3
27	0.00		3		2018-A1	
29	11.8	0.46	6	0.01	2314-M1	Priority PollutnT
30	15.8	0.23	6	0.5	216-A4	GBW07303
31	15.3	0.5	6		212-M1	MESS3
32	11.73	0.78	5	2.4	202-A1	QTM058MS
33	14.5	0.7	6	2.0	0-N2	IAEA405

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
34	13.00	1.17	6	0.2	225-E1	
35	14.7	0.5	3	0.02	222-M0	MESS2
38	8.1	0.22	4		235-A3	
39	2.95	0.09	6		215-A4	
40	16.1	1.2	6	0.5	2319-E1	BCSS1
42	7.43	0.17	8	0.05	215-M1	MESS3
45	11.7	0.5	6	5.0	235-A1	MESS3
47	12.8	0.6	6	0.2	226-A3	MESS3
49	15.3	0.32	6		2214-M1	MESS3
50	10.88	0.49	6	0.24	233-A3	PACS2
52a	16.6	0.8	6	2.5	234-M1	LGC6139
52b	16	0.9	6	5	0-X1	CRM277
53	16.43	0.27	5	0.0000094	233-M1	PACS2
56	13.9	0.31	6	0.1	2312-M1	MESS3
59	17.2	0.50	6	1	231-E1	
60	13.1	0.8	6	0.7	0-N0	1633A
61	12.2	0.229	6	6.83	235-E1	IAEA-405
62	13.4	0.4	6	0.10	0-N0	SRM 2704
64	16.50	2.10	6	0.20	0-N2	IAEA-405
65	13.2	0.2	6	0.05	0-N2	BIL1
66	13.0	0.26	6		232-M1	IAEA-405
70	15.1	0.2	6	0.1	234-M1	BCSS1
73a	12.4	0.42	6	0.25	212-E1	IAEA-405
73b	12.8	0.3	7	0.01	236-M1	Soil 2509-83
74	12.7	1.9	6	1.7	0-N2	IAEA-SL1
75	12.50	1.21	5	0.11	239-E1	PACS2
76	14.4	0.326	6	0.2	219-E1	IAEA-SL1
77	11.63	1.09	6		2114-E1	
78	14.0	0.7	6	0.35	226-M1	MESS3
79a	12.3	0.8	6	2	2121-A1	SOIL-7
79b	12.3	0.4	6	0.05	0-N0	SOIL7
79c	13.5	0.4	6	2	0-X0	SOIL7
80	13.7	0.32	5	0.05	215-M1	MESS3
83	12.5666667	0.3369669	6	0.05	0-X1	
91	12.8	0.13	6	0.13	0-N0	SOIL7
92	1.45	0.25	6		232-E1	MESS1
93	14.7	1.7	6	12	0-X0	SDN1/2
94a	11.41	0.43	6	0.05	239-A1	SDM2/TM
94b	11.58	0.77	6	0.02	0-N0	IAEA356
96	16.59	0.54	5	0.1	235-A6	
98	139	1	6	5.15E-08	0-N0	SRM1646
101	12.33	1.92	3			
102	13.9	0.9	5	0.002	238-M1	MESS2
103	12.7	0.6	6		238-A3	MESS2

CHROMIUM (Cr) mg kg^{-1}

Lab code	**Lab. Mean**	**Stdev**	**Number Determination**	**Det. Limit**	**Method**	**RM**
3	137.1	2.1	5	0.1	222-M1	IAEA405
5	133.7	2.1	6		212-E1	SRM1646
6	141	1.8	6	2.000	225-E1	MESS3
7	122	3.52	6	10	0-X1	BCSS1
8	138.5	5.0	5	0.050	236-A3	BCSS1
9	121.0	2.2	6	0.06	2315-A1	
10	131.3	3.5	6	3.000	231-A1	TORT2
11	55	3	6	5.000	235-E1	WQB3
12	180.25	13.96	6		226-A4	BCSS1
14	147	12.5	6	1.710	11-E1	PACS1
15	138.6	1.8	6	5.0	222-A1	IAEA405
17	17.2	2.0	6	8.000	233-A1	
18	115.0	1.789	6	1.0	2111-E1	IAEA405
19	138	8.4	6	4.0	231-M1	MESS2
21	131	3.1	6	2	3212-E1	CRM277
22	142	8.2	6	10	222-A1	IAEA405
25	129	9	6	0.2	226-M1	IAEA405
26	131	1.83	4	0.07	2212-M1	MESS3
27	0.00		6		2018-A1	
28	158.5	4.2	6	0.005	226-A2	MESS2
29	56.1	6.05	6	0.03	2314-M1	Priority PollutnT
30	176	4.2	5	4	216-A2	GBW07303
31	118	8.3	6		212-M1	MESS3
33	137	2	3	10	0-N2	IAEA405
34	59.84	12.55	4	0.2	225-E1	
35	138	3	5	0.2	222-M0	MESS2
38	29	1.9	6		235-A1	
39	92.75	0.63	6		215-A4	
40	178	7	3	0.02	2319-A4	BCSS1
41	244.00	23.40	6	0.05	239-A4	SDM2/TM
42	162	12	6	4.5	215-A1	MESS3
43	138	2	6	0.07	236-A3	MESS3
45	140.8	3.5	6	10	235-A1	MESS3
46	147	1.50	6	2	226-A1	QTM58MS
47	128	7	5	0.2	226-A3	MESS3
49	73.9	5.6	2		2214-M1	BCR277
50	57.78	1.51	6	1.63	233-A3	PACS2
52a	116	0.8	6	3	234-E1	LGC6139
52b	128	1.2	6	5	0-X1	CRM277
53	150.9	7.4	6	0.000026	233-M1	PACS2
54	54.3	16.6	6	1	238-A3	
55	129.567	2.14	6	0.0078	239-A1	IAEA-405
56	131	1.3	5	0.2	2312-M1	MESS3
57	94.61	2.88	6	0.00932	236-A6	MESS3
59	150	2.1	3	1	231-E1	
60	127	6	6	10	0-N0	1633A
61	88.37	5.75	6	8.00	235-E1	IAEA-405
62	126	3	6	1.00	0-N0	SRM 2704
64	90.13	4	6	0.30	0-N2	IAEA-405
65	135.8	2.6	6	1.2	0-N2	BIL1
66	123.4	2.08	6		232-M1	IAEA-405
67	146	6	6	0.385	232-A3	IAEA-405
68	178	4	5		0-X1	SARM69
69	140.2	1.51	6	7.1	212-A1	IAEA-405

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
70	131	2	6	1	234-E1	BCSS1
72	146.6	20.5	8		231-A4	IAEA-405
73a	122.1	2.2	6	0.25	212-E1	IAEA-405
73b	132	6	6	0.25	236-M1	Soil 2509-83
74	133	14	6	8.4	0-N2	IAEA-SL1
75	111.74	11.41	6	0.45	239-E1	PACS2
76	133	2.29	6	0.08	219-E1	IAEA-SL1
77	68.79	1.79	5	0.05	2114-E1	
78	155.7	7.9	6	2.6	226-M1	MESS3
79a	130	14	6	0	0-N0	SOIL7
79b	129	3	8	2	0-X0	SOIL7
81	151	3	3	0.2	236-A3	BCR 277
82	76	7	6		229-A5	Taifun 2500-83
83	62.865	6.62630113	6	0.050	0-X1	
86	168	2	6	1.108	226-A4	MESS1
91	147	1.3	6	1.4	0-N0	SOIL7
92	10.75	0.72	3		232-E1	MESS1
93	142.5	6.9	6	16.4	0-X0	SDN1/2
94a	192.52	4.80	5	0.05	239-A1	SDM2/TM
94b	104.42	4.61	3	0.04	0-N0	IAEA356
96	95.38	1.22	6	0.1	235-A6	
97	168.19	3.97	6	0.004	236-A2	BCSS1
101	141.67	1.46	6			
102	149	7	4	0.002	238-M1	MESS2
103	151	4.5	6		238-A3	MESS2

CAESIUM (Cs) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
33	6.32	0.65	4	2.0	0-N2	IAEA405
60	5.92	0.35	6	0.20	0-N0	1633A
62	6.5	0.3	6	0.15	0-N0	SRM 2704
65	6.8	0.2	6	0.1	0-N2	BIL1
66	6.00	0.31	6		232-M1	IAEA-405
74	7.0	0.6	6	1.5	0-N2	IAEA-SL1
79	6.3	0.36	6	0.100	0-N0	SOIL7
91	6.55	0.14	6	0.38	0-N0	SOIL7

COPPER (Cu) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
1	32.38	5.60	6	0.310	226-A1	SDM2/TM
3	36.72	0.29	6	0.0600	222-M1	IAEA405
4	25.0	0.7	5	0.1	215-M1	MESS3
5	31.5	0.8	3		212-E1	SRM1646
6	28	0.63	6	2.000	225-E1	MESS3
7	28.82	0.369	6	0.100	215-A1	BCSS1
8	29.5	2.4	6	0.07	236-A3	BCSS1
9	25.88	0.196	6	0.030	2315-A1	2976
10	34.0	1.2	6	3.000	231-A1	TORT2
11	29	1	6	7	235-E1	WQB3
12	37.90	3.45	2		226-A2	BCSS1
15	34.38	1.057	6	1.5	222-A1	IAEA405
16	36.6	0.64	4	4.40E-05	236-A3	SRM1646
17	20.5	1.5	2	4	233-A1	

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
18	32.33	0.484	6	1.0	2111-E1	IAEA405
19	30.5	0.3	6	0.1	231-M1	MESS2
20	24.76	0.999	5	0.02	3205-A1	
21	32.1	0.55	6	0.5	3212-E1	CRM277
22	30	1.2	6	5.0	226-A1	IAEA405
23	25.66	0.6075	6	0.2	225-A1	JSD2
25	31.2	1.0	6	0.03	226-M1	IAEA405
26	31.1	0.327	6	0.13	2212-M1	MESS3
27	9.2		3		2018-A1	
28a	30.0	0.2	6	0.008	226-A1	MESS2
28b	30.8	0.1	5	0.008	223-A1	MESS2
29	27.6	0.76	6	0.02	2314-M1	Priority PollutnT
30	30.4	0.53	6	3	216-A4	GBW07303
31	32.5	1.5	6		212-E1	MESS3
32	26.45	0.91	5	1.6	202-A1	QTM058MS
34	21.66	1.68	6	0.2	225-E1	
35	33.2	0.6	3	0.4	222-M0	MESS2
36	31.2	0.4416	6	6	233-A1	
37	30.5	0.37	6	0.1	235-A1	
38	28	1.89	4		235-A1	
39	42.43	1.51	6		215-A4	
40	33.4	3.7	6	0.6	2319-E1	BCSS1
41	32.59	2.53	6	1.00	239-A1	SDM2/TM
42	27.9	0.3	7	3.5	215-A1	MESS3
43	34.8	1.3	6	0.17	236-A3	MESS3
44	23.9	1.5	6	0.311	226-A1	IAEA405
45	27.2	0.5	6	1	235-A1	MESS3
46	30	0.469	6	1	226-A1	QTM58MS
47	30.7	0.8	6	0.400	226-A3	MESS3
49	31.3	0.62	6		2214-M1	MESS1
50	29.80	1.68	6	0.42	233-A1	PACS2
51	27.3	1.1	6	0.1	235-E1	144R
52a	28.5	0.5	6	3	234-E1	LGC6139
52b	28	1.3	6	2	0-X1	CRM277
53	35.46	0.80	5	0.0000013	233-M1	PACS2
54	17.2	4.2	5	1	238-A3	
55	30.9834	0.33	6	0.004	239-A1	IAEA-405
56	30.4	0.56	6	0.1	2312-M1	MESS3
57	45.07	3.37	6	0.0155	236-A6	MESS3
59	38.0	0.3	3	2	231-E1	
61	26.68	0.955	6	6.33	235-E1	IAEA-405
63	32.7	3.3	4	1.5	223-A3	IAEA-405
66	36.2	4.36	6		232-M1	IAEA-405
67	29.0	0.4	6	0.112	232-A3	IAEA-405
68	34.7	0.7	6		0-X1	SARM69
69	28.8	0.577	4	4.0	212-A1	IAEA-405
70	34	1	6	2	234-E1	BCSS1
72	27.85	1.63	6		231-A4	IAEA-405
73a	28.8	0.10	6	0.25	212-E1	IAEA-405
73b	30.7	2.0	7	0.25	236-M1	Soil 2509-83
75	23.98	2.14	6	0.28	239-E1	PACS2
76	28.6	0.305	6	0.08	219-E1	IAEA-SL1
77	66.43	0.47	6	0.05	2114-E1	
78	39.0	2.0	6	0.49	226-M1	MESS3
79	28	1.5	6	0.5	2121-A1	SOIL-7

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
80	25.0	0.7	5	0.1	215-M1	MESS3
81	32.6	1.3	6	0.01	236-A1	BCR 277
82	33	1	6		229-A5	Taifun2500-83
83	32.8783333	2.89385844	6	0.05	0-X1	
84	103.232	12.997	6		223-A4	BCSS1
85	34.4	0.40	6	2	236-A1	IAEA-405
87	33.63	0.58	3	8.07	2020-A1	IAEA/LS-1
89	11.85	0.8436	6		2111-A3	QTM022MS
90	31.6	0.85	6	4	225-A1	IAEA405
92	10.81	0.30	6		232-E1	MESS1
93	26.2	11.0	6	2.5	0-X0	SDN1/2
94a	29.75	0.82	6	0.02	239-A1	SDM2/TM
94b	33.70	1.5	6	2.5	0-X1	IAEA356
96	8.55	0.37	5	0.1	235-A6	
97	20.45	0.33	5	0.022	236-A2	BCSS1
99	29.6	2.7	6	2.5	233-A1	MESS2
100	1560				205-A2	
101	35.00	0.44	3			
102	31.6	2.4	5	0.002	238-M1	MESS2
103	30.5	0.4	6		238-A3	MESS2

EUROPIUM (Eu) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
33	1.24	0.02	4	0.1	0-N2	
60	1.18	0.07	6	0.05	0-N0	1633A
62	1.13	0.03	6	0.03	0-N0	SRM 2704
65	1.28	0.02	6	0.02	0-N2	BIL1
74	1.1	0.1	6	0.2	0-N2	IAEA-SL1
91	1.18	0.032	6	0.05	0-N0	SOIL7

IRON (Fe) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
2	40717	388	6	75	0-X1	IAEA405
3	42189	573	6	2	222-M1	IAEA405
4	43900	1040	5	0.1	215-M1	MESS3
5	41500	500	3		212-E1	SRM1646
6	41600	780	6	50	225-E1	MESS3
7	39825	227	6	30	215-A1	BCSS1
8	43200	1500	6	10	236-A3	BCSS1
9	40685	484	6	0.06	2315-A1	SRM2976
10	42200	900	6	7	231-A1	TORT2
11	39800	1100	6	90	235-E1	WQB3
14	39318	1582	6	0.10	11-E1	PACS1
15	38265	1575	5	15	222-A1	IAEA405
18	38720	891	6	10	2111-E1	IAEA405
19	39941	556	6	479	231-E1	MESS2
20	34613	0.999	5	0.35	3205-A1	
21	41500	550	6	500	3212-E1	CRM277
25	37546	1124	6	0.6	226-M1	IAEA405
26	38300	1205	6		2212-M1	MESS3
27	113.4		3		2018-A1	
28	42100	600	6	0.00002	226-A1	MESS2

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
29	37500	390	6	1.0	2314-E1	Priority PollutnT
30	38900	650	6	1000	216-C1	GBW07303
31	38600	300	6		212-E1	MESS3
32	37614	690	5	2.4	202-A1	QTM058MS
33	42900	1500	6	10000	0-N2	IAEA-405
34	34880	1160	6	0.5	225-E1	
35	40100	1600	3	140	222-M0	MESS2
37	41621	346	6	0.08	235-A1	
38	36456	567	4		235-A1	
39	215.9	2.69	6		215-A4	
41	38300	2480	6	1	239-A1	SDM2/TM
42	41292	2889	8	5.5	215-A1	MESS3
45	42500	910	6	1000	235-A1	
46	44000	639	6	50	226-A1	QTM58MS
47	40000	1000	6	1000	226-A1	MESS3
54	35000	2900	5	0.5	238-A1	
56	41800	1220	6	0.5	2312-M1	MESS3
57	49300	1300	6	0.000254	236-A1	MESS3
59	42500	500	3	5	231-E1	
60	417	22	6	20	1633A	I
61	41426	1712	6	42.5	235-E1	IAEA-405
62	40100	600	6	100	0-N0	SRM 2704
64	37188.05	372.06	6	50.00	0-N2	IAEA-405
65	43500	600	6	100	0-N2	BIL1
66	40490	296.7	6		232-M1	IAEA-405
67	39932	1131	6	954	232-A1	IAEA-405
68	44823	340	6		0-X1	SARM69
70	40900	366	6	50	234-E1	BCSS1
72	40353	2275	5		231-A1	IAEA-405
73a	40171	515	6	15	212-E1	IAEA-405
73b	40000	1000	8	10	236-M1	Soil 2509-83
74	42500	2900	6	100	0-N2	IAEA-SL1
76	39590	275	6	0.6	219-E1	IAEA-SL1
77	38860	6800	6	50	2114-E1	
78	44722	2454	6	245	226-M1	MESS3
79a	41900	1200	6	5.0	0-N0	SOIL7
79b	40633	1180	6	100.0	0-X0	SOIL7
80	43900	1040	5	0.1	215-A1	MESS3
81	43300	1800	6	100	236-A1	BCR 277
82	55978	4502	6		229-A5	Taifun 2500-83
83	45233.3333	592.171146	6	0.05	0-X1	
87a	45347.29	2287.29	0	89.1	0-X1	IAEA/LS-3
87b	44239.49	1012.00	0	11.76	2020-A1	IAEA/LS-1
89	34710	620.4	6		2111-A1	QTM022MS
91	41100	410	6	130	0-N0	SOIL7
92	804	34	6		232-E1	MESS1
93	37735	606	6	24	0-X0	SDN1/2
94a	39060	1130	6	0.05	239-A1	SDM2/TM
94b	36286	840	6	10	0-N0	IAEA356
98	42500	179	6	5.29E-06	0-N0	SRM1646
102	40000	1300	5	0.002	238-M1	MESS2
103	40360	2274	5		238-A1	MESS2

GALLIUM (Ga) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
33	25.9	0.9	6	2.5	0-N2	SOIL-5
74	32	8	6	7	0-N2	IAEA-SL1

HAFNIUM (Hf) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
33	4.42	0.04	2	0.1	0-N2	IAEA-405
60	3.54	0.31	6	0.02	0-N0	1633A
62	3.6	0.2	6	0.11	0-N0	SRM 2704
74	3.70	0.13	6	0.93	0-N2	IAEA-SL1
91	3.71	0.053	6	0.27	0-N0	SOIL7
33	4.42	0.04	2	0.1	0-N2	IAEA-405

MERCURY (Hg) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
1	0.0240	0.0120	6	0.005	226-A7	SDM2/TM
5	0.154	0.012	3		212-A7	SRM1646
6	0.195	0.0094	6	0.005	225-A7	MESS3
9	0.149	0.0083	6	5.00E-05	2315-A1	SRM2976
10	0.234	0.013	6	0.010	231-A7	TORT2
11	0.190	0.030	6	0.010	0-A9	WQB3
13	0.123	0.005	6	0.002	0-A9	COPT-3
14	0.156	0.005	6	0.0005	0-A9	CRM141R
15	0.233	0.010	6	0.050	225-A7	IAEA405
18	0.170	0.015	6	0.05	2111-A7	IAEA405
19	0.141	0.009	6	0.005	231-M1	MESS2
20	0.54	0.001	5	0.00007	3205-A7	
21	0.178	0.007	6	0.005	0-A9	CRM277
22	<0.02	0.0	3	<0.02	227-A7	IAEA405
23	0.386	0.017	3	0.025	227-A7	JSD2
24	0.159593	0.007719	6	0.00034	2117-A7	
25	0.16	0.01	6	0.0001	0-A9	IAEA405
26	0.166	0.0127	6	0.005	221-A7	MESS3
28a	0.178	0.0145	5	0.005	223-A1	MESS2
28b	0.181	0.013	3	0.0004	205-F1	MESS2
29	0.15	0.005	6	0.01	2314-A7	Priority PollutnT
30	0.12	0.01	6	0.01	216-A7	GBW07303
31	0.157	0.007	6		212-A9	MESS3
32	0.17728	0.00606	3	0.00009	202-A7	QTM058MS
33	0.490	0.040	4	1.0	0-N2	
34	0.192	0.013	6	0.005	227-A7	
35	0.162	0.006	3	0.001	225-F1	MESS2
36	0.017	0.00176	6	0.003	233-A8	
37	0.159	0.0059	6	0.00001	0-A9	
38	<0.5		4		235-A7	
39	0.7	0.07	6		215-A7	
41	0.152	0.009	6	0.001	239-A7	SDM2/TM
42	0.175	0.010	7	0.06	2120-A7	MESS3
44	0.017	0.001	4	0.238	226-A7	IAEA405
46	0.197	0.026	6	0.001	226-A7	QTM58MS
47	0.165	0.004	5	0.001	226-A7	MESS3

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
48	0.19	0.02	5	0.00059	233-S3	IAEA405
49	0.184	0.027	6	0.030	2214-M1	BCR 277
50	0.166	0.006	6	0.001	233-A7	PACS2
51	0.155	0.018	6	0.01	235-A7	144R
52a	0.18	0.02	6	0.01	234-A7	LGC6139
52b	n.d.			2	0-X1	CRM277
54	0.43	0.1	6	0.05	238-A7	
56	0.178	0.003	6	0.1	235-A7	LGC 6135
58	0.160	0.00383	6	0.002	227-F1	MESS2
59	0.21	0.01	3	0.05	231-A7	
61	0.174	0.019	6		235-A8	IAEA-405
62	0.215	0.003	6	0.115	224-A7	SRM 2704
63	0.141	0.006	6	0.001	0-A9	GSO 2509-83
70	0.194	0.009	6	0.004	234-A7	BCSS1
71	0.4181	0.014245	3		2312-A7	
73a	0.173	0.014	6	0.05	212-A7	IAEA-405
76	0.174	0.008	5	0.02	219-E1	IAEA-SL1
77	<D.L.		6	0.20	2114-E1	
78	0.18	0.01	6	0.003	226-F1	MESS3
79	0.16	0.005	6	0.01	2110-A7	IAEA-336
81	0.168	0.008	6	0.0002	236-A7	BCR 277
82	0.23	0.010	4		229-A5	Taifun 2500-83
83	0.785	0.08757854	6	0.05	0-X1	
84	0.17224	0.01643	6		223-A7	BCSS1
88	0.165	0.0187	3	0.00035	227-F1	MESS3
95	0.150	0.004	6	0.002	?-A7	IAEA405
96	0.140		5	0.100	0-A9	
97	0.358	0.033	6	0.024	237-A7	IAEA405
99	0.193	0.021	6	0.02	233-A7	MESS2
103	0.164	0.009	5		0-A9	MESS2

METHYLMERCURY Reported as µg Hg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
11	<2		6	2.0	25S2	
24	1.04	0.08	6	0.1	25S	CRM580
25	0.180	0.040	6	0.01	25F3	
26	0.105	0.0086	6	0.00002	25F3	IAEA405
41	5.00	1.16	6	1	25-A9	TORT2
48	0.507	0.088	5	0.0601	233-S3	IAEA405
56	1.40	0.10	6	1	F4	CRM580
70	0.812	0.196	6	0.5	25S0	CRM580
78	0.109	0.020	3	0.020	24F3	IAEA405
88	0.206	0.005	3	0.08	25-F3	BCR580
95	0.20	0.03	6	0.05	25-F3	IAEA405

POTASSIUM (K) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
33	22400	1900	6	5.0	0-N2	IAEA-405
60	171	330	6	30	0-N0	1633A
74	16500	2800	6	3000	0-N2	IAEA-SL1
79	15300	800	6	100	0-N0	SOIL7
87a	15500.14	4837.55	0	2487	0-X1	IAEA/LS-3
87b	14031.28	451.59	0	6.31	2020-A1	IAEA/LS-1
91	18500	720	6	4400	0-N0	SOIL7

LANTHANUM (La) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
33	36.9	0.4	6	5.0	0-N2	IAEA-405
60	32.2	2.8	6	1	0-N0	1633A
62	30.8	0.5	6	0.24	0-N0	SRM 2704
65	34.4	0.5	6	0.03	0-N2	BIL1
66	29.7	0.7	6		232-M1	IAEA-405
74	35.4	3.7	6	9.9	0-N2	IAEA-SL1
79	35	2	6	0.05	0-NO	SOIL7
91	33.4	0.13	6	0.29	0-N0	SOIL7

LITHIUM (Li) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
3	55.1	1.7	6	0.005	222-M1	IAEA405
5	67.3	1.5	3		212-E1	SRM1646
6	78	1	6	2	225-E1	MESS3
11	42.7	0.9	6	0	235-E1	WQB3
18	56.77	1.922	6	1.0	2111-A1	IAEA405
25	57	2	6	0.04	226-M1	IAEA405
29	39.5	4.40	6	0.02	2314-M1	Priority PollutnT
30	68	2.8	6	1	216-E1	GBW07303
34	33.89	7.27	6	0.2	225-E1	
39	2.212	0.09	6		215-A1	
43	71.6	3.7	6	0.06	236-A3	MESS3
46	68	0.644	6	0.5	226-A1	QTM58MS
47	67	2	4	15	226-A1	MESS3
52a	64.9	0.5	6	3	234-E1	LGC6139
56	47.4	0.62	6	0.1	2312-M1	MESS3
59	110	2	3	5	231-E1	
61	33.78	2.31	6		235-E1	IAEA-405
70	64.5	3.0	6	0.2	234-M1	BCSS1
73a	55.0	1.4	6	0.015	212-E1	IAEA-405
73b	64	5	6	0.012	236-M1	Soil 2509-83
76	91.4	2.76	6	0.02	219-E1	IAEA-SL1
77	37.80	0.53	6	0.05	2114-A1	
78	76.0	5.4	6	0.25	226-M1	MESS3
99	62.1	0.9	6	2.5	233-A1	MESS2
102	68.6	1.3	5	0.0002	238-M1	MESS2

LUTETIUM (Lu) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
33	0.41	0.04	2	0.1	0-N2	IAEA-405
60	0.350	0.032	6	0.05	0-N0	1633A
62	0.35	0.02	6	0.07	0-N0	SRM 2704
74	0.35	0.05	6	0.07	0-N2	IAEA-SL1

MAGNESIUM (Mg) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
3	11410	170	6	0.100	222-M1	IAEA405
5	12100	100	3		212-E1	SRM1646
6	11933	186	6	50	225-E1	MESS3
18	10380	1102	6	10	2111-E1	IAEA405
25	10412	253	6	0.5	226-M1	IAEA405
29	10900	250	6	0.5	2314-E1	Priority PollutnT
30	12300	450	6	400	216-E1	GBW07303
39	14585	93.1	6		215-A1	
56	10100	440	6	0.2	2312-M1	MESS3
67	11729	189	6	293	232-A1	IAEA-405
68	19520	500	6		0-X1	SARM69
70	12200	55	6	50	234-E1	BCSS1
74	15300	2200	6	12600	0-N2	IAEA-SL1
73a	11142	180	6	13	212-E1	IAEA-405
73b	11500	1100	6	5	236-M1	Soil 2509-83
76	11272	455	6	0.04	219-E1	IAEA-SL1
77	8790	1340	6	50	2114-A1	
87	12021.33	323.17	6	2.07	2020-A1	
98	13600	1120	4	15.8	0-N0	SRM1646

MANGANESE (Mn) mg kg^{-1}

Lab code	Lab Mean	Stdev	Number Determination	Det. Limit	Method	RM
2	480	60	6	113	0-X1	IAEA 405
3	351.3	8.1	6	0.01	222-M1	IAEA 405
4	294	3.8	5	0.1	215-M1	MESS3
5	316	6.8	3		212-E1	SRM1646
6	319	8.07	6	1	225-E1	MESS3
7	317.07	1.115	6	0.1	215-A1	BCSS1
8	318	5	6	0.05	236-A3	BCSS1
10	311.7	4.7	6	5	231-A1	TORT2
11	283	6	6	0	235-E1	WQB3
14	339	31.8	6	0.82	11-E1	PACS1
15	314.04	14.51	6	0.6	222-A1	IAEA 405
16	330.0	4.66	4	0.01	236-A1	SRM1646
17	208.1	13.1	2	2.8		
18	279.3	7.312	6	1.0	2111-E1	IAEA405
19	327	21	6	0.2	231-M1	MESS2
20	297.18	0.999	6	0.14	3205-A1	
21	318	3.5	6	1	3212-E1	CRM277
22	316	3.8	6	3.0	226-A1	IAEA405
25	306	13	6	0.004	226-M1	IAEA405
26	334	5.66	6	0.0556	2212-M1	MESS3

[redacted]

Lab code	Lab Mean	Stdev	Number Determination	Det. Limit	Method	RM
90	306.3	5.57	6	3	225-A1	IAEA405
92	13.54	1.65	6		232-E1	MESS1
93	250	15.8	6	13	0-X0	SDN1/2
94a	273.55	9.51	6	0.02	239-A1	SDM2/TM
94b	448.62	14.80	6	18	0-X1	IAEA356
96	300.65	1.64	5	0.02	235-A1	
98	347	5	4	3.49E-08	0-N0	SRM1646
102	323	15	5	0.002	238-M1	MESS2
103	332	4.9	5		238-A1	MESS2

MOLYBDENUM (Mo) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
60	2.89	0.48	6	1	0-N0	1633A
101	2.23	0.51	3			

SODIUM (Na) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
33	19000	1100	6	5.0	0-N2	SOIL-5
60	138	10	6	10	0-N0	1633A
62	12790	248	6	190	0-N0	SRM 2704
74	14300	2100	6	0.4	0-N2	IAEA-SL1
79	13250	243	6	1	0-N0	SOIL7
91	14200	100	6	34	0-N0	SOIL7

NEODYMIUM (Nd) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
60	28.0	3.7	6	4	0-N0	1633A
62	29	2	6	2	0-N0	SRM 2704
65	28.7	1.3	6	3	0-N2	BIL1
74	30.0	3.0	6	6.0	0-N2	IAEA-SL1
91	30.1	0.84	6	2.7	0-N0	SOIL7

NICKEL (Ni) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
3	42.16	1	6	0.02	222-M1	IAEA 405
4	57.5	2.1	5	0.1	215-M1	MESS3
5	41.0	0.6	3		212-E1	SRM1646
6	40.2	1.33	6	2.000	225-E1	MESS3
7	30.025	0.583	6	0.015	215-A1	BCSS1
8	45.2	1.2	6	0.08	236-A3	BCSS1
9	64.85	0.459	6	0.100	2315-A1	SRM2976
11	30.2	0.3	6	0.800	235-E1	WQB3
14	43.6	4.020	6	3.090	11-E1	PACS1
15	24.28	1.94	5	3.3	222-A1	IAEA 405
18	33.07	0.344	6	1.0	2111-E1	IAEA 405
19	36.5	1.4	6	0.4	231-M1	MESS2
20	61.12	0.999	2	0.15	3205-A1	
21	42.5	0.82	6	1	3212-E1	CRM277
22	40	1.3	6	5.0	222-A1	IAEA 405

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
25	36.7	2.0	6	0.05	226-M1	IAEA 405
26	39.9	0.539	6	0.0491	2212-M1	MESS3
27	0.73		3		2018-A1	
28	41.5	0.7	5	0.019	223-A1	MESS2
29	33.2	1.10	6	0.01	2314-M1	Priority PollutnT
30	44.0	0.86	6	1	216-A4	GBW07303
31	47.1	2.2	6		212-M1	MESS3
32	28.46	0.58	5	1.6	202-A1	QTM058MS
34	30.68	3.52	6	0.4	225-E1	
35	41.3	1.3	3	0.04	222-M0	MESS2
37	41.2	1.4	6	0.04	235-A1	
38	34	1.290	4		235-A1	
39	9.3	0.2	6		215-A4	
41	53.82	6.16	6	0.10	239-A4	SDM2/TM
42	36.1	0.4	8	2.8	215-A1	MESS3
45	42.3	1.2	6	5.0	235-A1	MESS3
46	29	0.679	6	2	226-A1	QTM058MS
47	43	2	6	0.2	226-A3	MESS3
51	33.1	1.0	6	0.3	235-E1	144R
52a	37.7	0.4	6	4	234-E1	LGC6139
52b	38	0.6	6	2	0-X1	CRM277
53	50.39	0.85	5	0.0000046	233-M1	PACS2
54	29.8	6.600	5	1	238-A3	
55	28.8871	1.96	6	0.0204	239-A1	IAEA-405
56	39.6	0.69	6	0.1	2312-M1	MESS3
57	24.66	2.62	6	0.0116	236-A6	MESS3
59	37.9	0.7	3	2	231-E1	
61	34.52	1.3	6	10.16	235-E1	IAEA-405
65	34	3	6	14	0-N2	BIL1
66	38.26	1.53	6		232-M1	IAEA-405
67	37.8	0.8	5	0.534	232-A3	IAEA-405
68	52.1	0.5	6		0-X1	SARM69
69	39.4	0	4	16.2	212-A1	IAEA-405
70	38.2	1.1	6	0.5	234-M1	BCSS1
73a	40.0	1.5	6	0.25	212-E1	IAEA-405
73b	39.1	1.6	7	0.12	236-M1	Soil 2509-83
76	34.6	0.246	6	0.6	219-E1	IAEA-SL1
77	36.84	3.16	6	0.20	2114-E1	
78	43.8	1.9	6	0.27	226-M1	MESS3
79b	37	2.0	6	2	0-X0	SOIL7
79	35	1.6	6	2	2121-A1	SOIL-7
80	57.5	2.1	5	0.1	215-M1	MESS3
81	39.0	1.900	6	0.005	236-A3	BCR 277
82	25	3	6		229-A5	Taifun 2500-83
83	68.6466667	1.51051867	6	0.05	0-X1	
86	39.4	0.8	6	0.322	226-A4	MESS1
87	72.99	1.68	5	10.58	2020-A1	IAEA/LS-1
90	44.0	0.85	6	8	225-A1	IAEA405
92	38.65	3.29	6		232-E1	MESS1
93	29.7	8.0	6	8.5	0-X0	SDN1/2
94a	40.32	1.62	6	0.04	239-A1	SDM2/TM
94b	48.26	6.99	6	7	0-X1	IAEA356

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
96	57.19	0.89	5	0.1	235-A1	
99	49.7	1.2	6	0.2	233-A2	MESS2
101	39.80	0.17	3			
102	43.4	6.3	4	0.002	238-M1	MESS2
103	41.4	1.1	6		238-A3	MESS2

PHOSPHORUS (P) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
33	1220	90	6	100	0-N2	SOIL5
76	738	11.0	6	6	219-E1	IAEA-SL1

LEAD (Pb) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
1	13.91	6.54	6	0.560	226-A1	SDM2/TM
3	26.69	0.19	6	0.03	222-M1	IAEA 405
4	22.9	0.56	5	0.05	215-M1	MESS3
5	29.9	2.7	3		212-E1	SRM1646
6	30.2	1.17	6	2	225-A1	MESS3
7	20.39	0.771	6	1.000	215-A1	BCSS1
8	26.7	0.8	6	0.07	236-A3	BCSS1
9	55.34	3.29	6	0.0001	2315-A1	
11	22.3	0.4	6	3.000	235-E1	WQB3
12	58.7	2.97	2		226-A4	BCSS1
15	13.67	1.07	5	2.500	222-A1	IAEA 405
16	15.2	0.5	4	0.006	236-A3	SRM1646
17	19.9	3.4	2	10	233-A1	
18	24.40	0.190	6	5.0	2111-E1	IAEA 405
19	27.2	0.6	6	0.01	231-M1	MESS2
20	142.01	0.998	4	0.41	3205-A1	
21	26.5	1.73	6	0.5	3212-M1	CRM277
22	23	1.0	6	5.0	226-A1	IAEA 405
23	25.05	0.4980	6	0.5	225-A1	JSD2
25	25.4	1.6	6	0.01	226-M1	IAEA 405
26	27.5	0.423	6	0.0348	221-M1	MESS3
27	10.8		3		2018-A1	
28	28.0	0.6	6	0.0002	226-A3	MESS2
29	22.4	1.30	6	0.01	2314-M1	Priority PollutnT
30	25.5	0.35	6	0.2	216-A4	GBW07303
31	27.2	0.8	6		212-M1	MESS3
34	11.79	1.69	6	0.4	225-E1	
35	28.3	0.9	3	0.06	222-M0	MESS2
36	28.2	0.645	5	0.030	233-A6	
37	28.6	0.85	6	0.004	235-A3	
38	25	0.96	4		235-A3	
39	1.2	0.1	6		215-A4	
40	38.1	1.2	6	0.02	2319-A4	BCSS1
41	32.39	2.29	6	0.01	239-A4	SDM2/TM
42	24.7	0.7	8	4.0	215-A1	MESS3
43	28.7	0.5	6	0.3	236-A3	MESS3
44	20.124	0.466	6	0.120	226-A3	IAEA405

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
45	19.2	1.2	6	10.0	235-A1	MESS3
46	15.9	0.719	6	2	226-A1	QTM058MS
47	31.0	0.4	6	0.4	226-A3	MESS3
49	32.8	0.60	6		2214-M1	MESS1
50	17.07	2.45	6	5.33	233-A3	PACS2
52a	26.7	0.8	6	3.5	234-M1	LGC6139
52b	27	0.8	6	0.2	0-X1	CRM277
53	31.74	1.03	5	0.00000040	233-M1	PACS2
54	19.6	2.5	5	0.8	238-A3	
55	10.7838	1.04	6	0.0184	239-A1	IAEA-405
56	25.1	0.35	6	0.1	2312-M1	MESS3
57	21.32	5.31	6	0.00000354	236-A6	MESS3
59	26.3	0.5	3	2	231-E1	
61	28.99	1.537	6	8.33	235-E1	IAEA-405
66	25.39	1.80	6		232-M1	IAEA-405
67	30.2	0.7	5	0.178	232-A3	IAEA-405
68	32.2	0.3	6		0-X1	SARM69
69	29.1	3.71	4	0.6	212-A4	IAEA-405
70	27.9	0.2	6	0.1	234-E1	BCSS1
71	2.48649	0.257422	3		2312-A3	
72	24.29	1.17	6		231-A4	IAEA-405
73a	26.2	0.5	6	0.25	212-E1	IAEA-405
73b	27.6	2.2	7	0.12	236-M1	Soil 2509-83
76	22.3	0.847	6	4	219-E1	IAEA-SL1
77	<D.L		6	0.25	2114-E1	
78	31.1	1.8	6	0.13	226-M1	MESS3
79a	25	0.4	6	1	0-X0	SOIL7
79b	23	0.8	6	2	2121-A1	SOIL-7
80	22.9	0.56	5	0.05	215-M1	MESS3
81	27.7	1.2	6	0.01	236-A1	BCR 277
82	30	3	6		229-A5	Taifun 2500-83
83	33.6116667	1.72246819	6	0.05	0-X1	
85	75.3	1.68	4	2.0	236-A1	IAEA-405
86	25.9	0.86	6	0.045	226-A4	MESS1
87a	28.50	15.50	0	15.1	0-X1	
87b	33.85	0.59	0	23.43	2020-A1	IAEA/LS-1
89	5.32	1.4147	6		2111-A3	QTM022MS
90	37.0	0.70	6	8	225-A1	IAEA405
93	32.3	4.1	6	4.3	0-X0	SDN1/2
94a	21.84	1.08	6	0.06	239-A1	SDM2/TM
94b	22.31	1.25	6	5	0-X1	IAEA356
96	40.04	0.82	5	0.1	235-A1	
97	20.55	0.60	5	0.014	236-A2	BCSS1
99	28.2	3.2	6	0.2	233-A3	MESS2
100	1134				205-A2	
101	28.87	0.57	3			
102	25.3	0.5	5	0.0002	238-M1	MESS2
103	29.8	0.3	6		238-A3	MESS2

RUBIDIUM (Rb) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
33	120	1.5	2	5.0	0-N2	SOIL5
60	81	7	6	10	0-N0	1633A
62	95	3	6	4.5	0-N0	SRM 2704
74	98	25	6	32	0-N2	IAEA-SL1
79a	113.3	7.39	6	1	0-N0	SOIL7
79b	97	1.3	6	1	0-X0	SOIL7
91	105	1.2	6	5.9	0-N0	SOIL7
101	109.00	0.20	3			

ANTIMONY (Sb) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
6	NA	NA	6	20	225-E1	MESS3
18	1.517	0.058	6	0.5	2111-F2	IAEA405
19	1.85	0.09	6	0.1	231-M1	MESS2
25	2.25	0.27	6	0.0003	226-M1	IAEA405
26	2.10	0.0167	6	0.0257	2212-M1	MESS3
29	0.26	0.06	6	0.02	2314-M1	Priority PollutnT
30	5.5	0.43	6	0.2	215-A8	GBW07303
33	2.15	0.09	3	2.0	0-N2	IAEA-405
34	1.09	0.22	6	0.06	225-A8	
35	2.01	0.05	3	0.028	222-M0	MESS2
52a	1.76	0.11	6	0.12	234-M1	LGC6139
52b	ND			2	0-X1	CRM277
56	2.00	0.04	6	0.1	2312-M1	MESS3
59	<5		3	5	231-E1	
60	2.47	0.36	6	0.1	0-N0	1633A
61	0.78	0.189	6	5.33	235-A8	IAEA-405
62	1.82	0.09	6	0.20	0-N0	SRM 2704
65	1.90	0.12	6	0.05	0-N2	BIL1
68	2.0	0.2	6		0-X1	SARM69
70	1.9	0.1	6	0.1	234-E1	BCSS1
73a	2.0	0.19	6	0.5	212-E1	IAEA-405
73b	1.79	0.13	6	0.025	236-M1	Soil 2509-83
74	2.0	0.2	6	1.8	0-N2	IAEA-SL1
77	<DL		6	0.10	2114-E1	
78	2.2	0.2	6	0.06	226-M1	MESS3
79	1.73	0.07	6	0.02	0-N0	SOIL7
83	15.6333333	3.43272875	6	0.05	0-X1	
91	2.06	0.066	6	0.20	0-N0	SOIL7
96	<0.1		6	<0.1	235-A6	
98	2.21	0.03	5	6.77E-09	0-N0	SRM1646
102	1.97	0.04	5	0.0002	238-M1	MESS2

SCANDIUM (Sc) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
33	15.8	0.8	6	1.0	0-N2	IAEA-405
60	12.6	0.6	6	0.4	0-N0	1633A
62	14.6	0.2	6	0.01	0-N0	SRM 2704
74	14.4	1.8	6	0.4	0-N2	IAEA-SL1

79	14.3	0.38	6	0.002	0-N0	SOIL7
91	15.1	0.06	6	0.020	0-N0	SOIL7

SELENIUM (Se) mg kg^{-1}

Lab code	**Lab. Mean**	**Stdev**	**Number Determination**	**Det. Limit**	**Method**	**RM**
6	0.53	0.052	6	0.100	225-A8	MESS3
18	0.548	0.015	6	0.5	2111-F2	IAEA405
19	<1.24		6	1.24	231-M1	MESS2
25	0.49	0.05	6	0.0001	226-M1	IAEA405
26	0.672	0.0151	6	0.007	2212-A8	MESS3
29	0.94	0.10	6	0.07	2314-M1	Priority PollutnT
30	0.56	0.02	6	0.04	215-A8	GBW07303
34	0.94	0.39	6	0.06	225-A8	
38	<0.8		4		235-A8	
41	0.869	0.144	6	0.020	239-A8	SDM2/TM
42	0.726	0.089	7	0.05	215-M1	MESS3
49	1.29	0.05	6	0.1	2214-M1	BCR277
50	0.276	0.050	6	0.013	233-A8	PACS2
52a	0.63	0.03	6	0.05	234-A8	LGC6139
52b	n.d.		6	2	0-X1	CRM277
53	0.776	0.108	3	0.00012	233-M1	PACS2
54	0.38	0	6	0.5	238-A8	
56	0.69	0.06	6	0.5	2312-M1	MESS3
59	<5		3	5	231-E1	
61	0.36	0.024	6	12.5	235-A8	IAEA-405
65	2.6	0.2	6	1.0	0-N2	BIL1
66	1.00	0.035	6		232-M1	IAEA-405
70	<1	0	6	1	234-E1	BCSS1
73a	0.93	0.11	6	0.5	212-E1	IAEA-405
73b	1.5	0.3	8	0.025	236-M1	Soil 2509-83
74	0.35	0.04	6		0-N2	IAEA-SL1
77	<D.L.		6	0.30	2114-E1	
78	0.8	0.2	6	0.14	226-F2	NIST-2709
96	<0.2		5	<0.2	235-A6	
98	2.88	0.13	6	4.03E-08	0-N0	SRM1646

SAMARIUM (Sm) mg kg^{-1}

Lab code	**Lab. Mean**	**Stdev**	**Number Determination**	**Det. Limit**	**Method**	**RM**
60	5.64	0.39	6	1	0-N0	1633A
62	5.3	0.4	6	0.10	0-N0	SRM 2704
65	5.72	0.11	6	0.02	0-N2	BIL1
74	5.5	0.2	6	0.3	0-N2	IAEA-SL1
79	6.26	0.31	6	0.01	0-N0	SOIL7
91	5.48	0.026	6	0.06	0-N0	SOIL7

TIN (Sn) mg kg^{-1}

Lab code	**Lab. Mean**	**Stdev**	**Number Determination**	**Det. Limit**	**Method**	**RM**
3	2.135	0.025	6	0.003	222-M1	IAEA405
6	<5		6	5	225-E1	MESS3
18	1.817	0.252	6	1.0	2111-E1	IAEA405
19	7.63	2.08	6	1.3	231-M1	MESS2

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
25	2.3	0.3	6	0.0004	226-M1	IAEA405
26	2.65	0.0273	6	0.117	2212-M1	MESS3
29	0.64	0.05	6	0.01	2314-M1	Priority PollutnT
30	3.27	0.11	6	0.2	216-A4	GBW07303
35	2.41	0.10	6	0.160	222-M0	MESS2
38	<0.8		4		235-A3	
45	2.5	0.4	6	1.0	235-A7	PACS2
50	1.13	0.43	6		233-A8	PACS2
52a	2.1	0.16	6	0.15	234-M1	LGC6139
52b	N.D		6	2	0-X1	CRM277
56	2.54	0.07	6	0.1	2312-M1	MESS3
59	2.0	0.1	3	0.5	231-E1	
66	2.21	0.200	6		232-M1	IAEA-405
68	3.2	0.2	6		0-X1	SARM69
73a	2.5	0.15	6	0.5	212-E1	IAEA-405
73b	2.9	0.2	7	0.025	236-M1	Soil 2509-83
74	16.2	2.0	6	1.3	0-N2	IAEA-SL1
77	9.54	2.03	6	0.30	2114-E1	
78	2.41	0.31	3	0.75	226-M1	MESS3
81	3.46	0.31	6	0.002	236-A3	BCR 277
96	1.33	0.16	5	1	235-A6	
102	2.22	0.22	5	0.0002	238-M1	MESS2

STRONTIUM (Sr) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
2	258	7	6	7	0-X1	IAEA 405
3	329.8	2.0	6	0.004	222-M1	IAEA 405
5	260	5	3		212-E1	SRM1646
6	320	7.89	6	1	225-E1	MESS3
7	317.7	0.516	6	20	0-X1	BCSS1
11	227	3	6	0.1	235-E1	WQB3
14	303	24	6	0	11-E1	PACS1
18	195.8	4.553	6	1.0	2111-E1	IAEA 405
19	292	16.0	6	0.4	231-M1	MESS2
21	291	10.3	6	2	3212-E1	CRM277
25	250	6	6	0.02	226-M1	IAEA 405
29	192	10.5	6	0.1	2314-M1	Priority PollutnT
30	329	3.6	6	3	216-E1	GBW07303
33	320	24	2	50	0-N2	
34	200.0	14.4	6	0.2	225-E1	
38	194	11.8	4		235-E1	
40	295	22	6	0.12	2319-E1	BCSS1
49	307	8	6		2214-M1	MESS1
52a	287	3	6	0.5	234-E1	LGC6139
52b	285	2.6	6	2	0-X1	CRM277
56	297	2.4	6	0.1	2312-M1	MESS3
59	307	1	3	5	231-E1	
60	294	22	6	30	0-N0	1633A
65	291	34	6	50	0-N2	BIL1
66	315.7	2.69	6		232-M1	IAEA-405
68	310	3	6		0-X1	SARM69
70	312	3	6	1	234-E1	BCSS1
73a	294.5	12.4	6	0.25	212-E1	IAEA-405
73b	303	8	7	0.12	236-M1	Soil 2509-83
76	296	1.80	4	0.02	219-E1	IAEA-SL1
77	12.35	4.27	6	0.05	2114-E1	
78	348	18	6	0.08	226-M1	MESS3
79	292	4.2	6	1	0-X0	SOIL7
83	348.781667	4.9941943	6	0.05	0-X1	
91	307	13	6	60	0-N0	SOIL7
93	335.8	49.9	6	66	0-X0	SDN1/2
94	263.78	6.62	6	1.2	0-X1	IAEA356
98	356	15	6	1.75E-06	0-N0	SRM1646
101	348.87	1.18	3			
102	314	18	5	0.002	238-M1	MESS2
103	287	5.7	4		238-A1	MESS2

TANTALUM (Ta) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
60	0.99	0.09	6	0.05	0-N0	1633A
62	1.00	0.08	6	0.08	0-N0	SRM 2704
65	1.13	0.04	6	0.03	0-N2	BIL1
74	1.1	0.1	6	0.8	0-N2	IAEA-SL1
79	1.01	0.08	6	0.1	0-N0	SOIL7
91	0.99	0.04	6	0.13	0-N0	SOIL7

TERBIUM (Tb) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
33	0.71	0.06	2	0.1	0-N2	IAEA-405
60	0.68	0.08	6	0.04	0-N0	1633A
62	0.7	0.1	6	0.11	0-N0	SRM 2704
74	0.98	0.17	6	0.74	0-N2	IAEA-SL1
91	0.65	0.04	6	0.17	0-N0	SOIL7

THORIUM (Th) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
33	10.4	0.3	3	1.0	0-N2	IAEA-405
60	8.9	0.7	6	0.5	0-N0	1633A
62	9.2	0.2	6	0.45	0-N0	SRM 2704
66	5.63	0.80	6		232-M1	IAEA-405
74	10.1	0.4	6	0.6	0-N2	IAEA-SL1
76	4.93	0.193	6	0.2	219-E1	IAEA-SL1
79a	10.2	0.94	6	0.01	0-N0	SOIL7
79b	9.6	0.3	6	1	0-X0	SOIL7
91	9.8	0.16	6	0.30	0-N0	SOIL7

TITANIUM (Ti) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
83	4698.33333	91.742393	6	0.05	0-X1	
87	3243.33	1307.40	0	442	0-X1	IAEA/LS-3

URANIUM (U) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
60	2.80	0.20	6	0.2	0-N0	1633A
62	2.5	0.1	6	0.3	0-N0	SRM 2704
66	2.23	0.07	6		232-M1	IAEA-405
79	2.3	0.1	6	1	0-X0	SOIL7
91	2.7	0.2	6	1.4	0-N0	SOIL7
102	2.13	0.04	4	0.0002	238-M1	MESS2

VANADIUM (V) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
3	183.7	1.9	6	0.03	222-M1	IAEA 405
5	140	1	3		212-E1	SRM1646
6	153	1.63	6	5	225-E1	MESS3
7	106.7	0.816	6	10	0-X1	BCSS1
8	114.7	3.8	6	1.5	236-A3	BCSS1
11	84	2	6	2	235-E1	WQB3
14	170	13.7	6	2	11-E1	PACS1
18	135.0	0.569	6	1.0	2111-E1	IAEA 405
19	166	10.1	6	1.0	231-M1	MESS2
25	143	12	6	0.1	226-M1	IAEA 405
26	160	1.76	6	0.237	2212-M1	MESS3
29	56.8	7.18	6	0.01	2314-M1	Priority PollutnT
30	152	1.0	6	2	216-E1	GBW07303
31	137	1.9	6		212-E1	MESS3
35	168	5	6	0.62	222-M0	MESS2
49	85.4	6.15	6		2214-M1	MESS1
52a	117	0.7	6	4	234-E1	LGC6139
52b	158	1.4	6	10	0-X1	CRM277
56	157	1.9	6	0.2	2312-M1	MESS3
59	168	2	3	2	231-E1	
64	122.74	3.30	6	0.10	0-N2	IAEA-405
66	145.9	5.36	6		232-M1	IAEA-405
68	182	7	6		0-X1	SARM69
70	158	1	6	1	234-E1	BCSS1
73a	161.2	5.5	6	0.25	212-E1	IAEA-405
73b	150	6	8	0.025	236-M1	Soil 2509-83
74	136	15	6	70	0-N2	IAEA-SL1
76	140	3.50	6	0.1	219-E1	IAEA-SL1
77	32.56	3.77	6	0.05	2114-E1	
78	171.1	9.4	6	0.39	226-M1	MESS3
83	48.4866667	6.84792134	6	0.05	0-X1	
96	103.59	1.10	5	0.4	235-A6	
98	160	5	4	1.72E-08	0-N0	SRM1646
101	165.90	0.82	3			
102	172	12	5	0.002	238-M1	MESS2
103	182	2	6		238-A3	MESS2

TUNGSTEN (W) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
60	2.28	0.29	6	0.5	0-N0	1633A

YTTRIUM (Y) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	CRM
79	21	0.7	6	1	0-X0	SOIL7

YTTERBIUM (Yb) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
33	3.22	0.11	2	0.5	0-N2	IAEA-405
62	1.96	0.03	6	0.20	0-N0	SRM 2704
65	2.16	0.07	6	0.05	0-N2	BIL1
74	2.3	0.2	6	1.1	0-N2	IAEA-SL1
91	2.4	0.041	6	0.34	0-N0	SOIL7

ZINC (Zn) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
1	96.63	18.11	6	1.04	226-A1	SDM2/TM
2	99	9	6	31	0-X1	IAEA 405
3	131	27	6	0.30	222-M1	IAEA 405
4	90.5	2.0	5	0.05	215-M1	MESS3
5	108.3	1.5	3		212-E1	SRM1646
6	105	3.27	6	1	225-E1	MESS3
7	86.65	0.924	6	0.10	215-A1	BCSS1
8	132.3	4.5	6	6.0	236-A3	BCSS1
9	91.80	3.08	6	0.01	2315-A1	SRM2976
10	102.4	1.0	6	1.0	231-A1	TORT2
11	92	2	6	0.8	235-E1	WQB3
12	91.68	3.73	2		226-A1	BCSS1
14	119	10.8	6	1.49	11-E1	PACS1
15	90.1	9.2	5	0.50	222-A1	IAEA 405
16	55.4	2.0	4	0.02	236-A1	SRM1646
17	69.1	3.0	6	1.1	233-A1	
18	98.97	4.000	6	1.0	2111-E1	IAEA 405
19	109	2.5	6	4.0	231-M1	MESS2
20	110.36	0.999	6	0.0001	3205-A1	
21	106	1.4	6	2	3212-E1	CRM277
22	123	4.9	6	1.0	226-A1	IAEA 405
23	99.47	1.3494	6	0.2	225-A1	JSD2
25	93	3	6	0.001	226-M1	IAEA 405
26	106	1.22	6	1.02	2212-M1	MESS3
27	6.53		3		2018-A1	
28a	113.8	4.6	6	0.003	226-A1	MESS2
28b	113.6	1.3	5	0.003	223-A1	MESS2
29	90.8	2.11	6	0.5	2314-M1	Priority PollutnT
30	112	1.5	6	1	216-E1	GBW07303
31	93.0	2.3	6		212-E1	MESS3
32	97.58	2.52	5	0.32	202-A1	QTM058MS
33	137	3	4	30	0-N2	
34	79.90	6.38	6	0.5	222-E1	
35	112	3	6	2.1	222-M0	MESS2
36	102	2.8	6	12	233-A1	
37	107.2	1.1	6	0.1	235-A1	
38	94	3.16	4		235-A1	
39	184	1.96	6		215-A4	
40	128	4	6	0.11	2319-E1	BCSS1
41	97.79	3.03	6	1.00	239-A1	SDM2/TM
42	95.4	5.4	8	2.9	215-A1	MESS3
45	110.1	3.4	6	10.0	235-A1	MESS3

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
46	100	0.759	6	0.50	226-A1	QTM058MS
47	109	2	6	6	226-A1	MESS3
49	88.8	4.65	6	1.5	2214-M1	MESS1
50	99.4	2.6	6	1.5	233-A1	PACS2
52a	102	0.6	6	2	234-E1	LGC6139
52b	104	0.9	6	2	0-X1	CRM277
53	104.8	3.6	5	0.0002010	233-M1	PACS2
54	189.4	29.8	6	1	238-A1	
55	98.0459	1.11	6	0.0014	239-A1	IAEA-405
56	102	1.4	6	0.2	2312-M1	MESS3
59	107	0.6	3	2	231-E1	
60	106	9	6	10	0-N0	1633A
61	95.48	2.01	6	9.66	235-E1	IAEA-405
62	104	5	6	2.8	0-N0	SRM 2704
63	92.2	3.0	4	1.0	223-A3	IAEA-405
65	113	7	6	7	0-N2	BIL1
66	128.6	4.95	6		232-M1	IAEA-405
67	104	2	6	2.31	232-A1	IAEA-405
68	110	1	6		0-X1	SARM69
69	98.0	1.0	3	1.0	212-A1	IAEA-405
70	99	1	6	2	234-E1	BCSS1
72	82.8	6.0	6		231-A1	IAEA-405
73a	109.2	4.2	6	0.5	212-E1	IAEA-405
73b	98	10	7	1.8	236-M1	Soil 2509-83
74	161	31	6	14	0-N2	IAEA-SL1
75	92.16	5.23	5	0.30	239-E1	PACS2
76	102	2.83	6	0.4	219-E1	IAEA-SL1
77	95.78	2.77	6	0.05	2114-E1	
78	119	7.0	6	3.60	226-M1	MESS3
79	94	2.1	6	1	2121-A1	SOIL-7
80	90.5	2.0	5	0.05	215-M1	MESS3
81	107	3	6	0.05	236-A1	BCR 277
82	69	5	6		229-A5	Taifun 2500-83
83	113.573333	2.90674847	6	0.05	0-X1	
84	105.33	2.412	6		223-A1	BCSS1
87a	117.14	30.54	0	21.5	0-X1	IAEA/LS-3
87b	111.39	6.00	0	6.21	2020-A1	
89	103.86	3.61213	6		2111-A1	QTM022MA
90	101	3.52	6	3	225-A1	IAEA405
91	105	2.5	6	6.9	0-N0	SOIL7
92	76.1	2.0	6		232-E1	MESS1
93	75.0	4.5	6	5.2	0-X0	SDN1/2
94a	95.54	1.65	6	0.008	239-A1	SDM2/TM
94b	101.65	7.03	6	5	0-X1	IAEA356
96	87.29	0.75	5	0.1	235-A1	
98	118	2	6	2.98E-07	0-N0	SRM1646
99	106	11	6	5.00	233-A1	MESS2
100	4420				205-A2	
101	103.90	0.36	3			
102	89.7	6.1	5	0.002	238-M1	MESS2
103	100	3	5		238-A1	MESS2

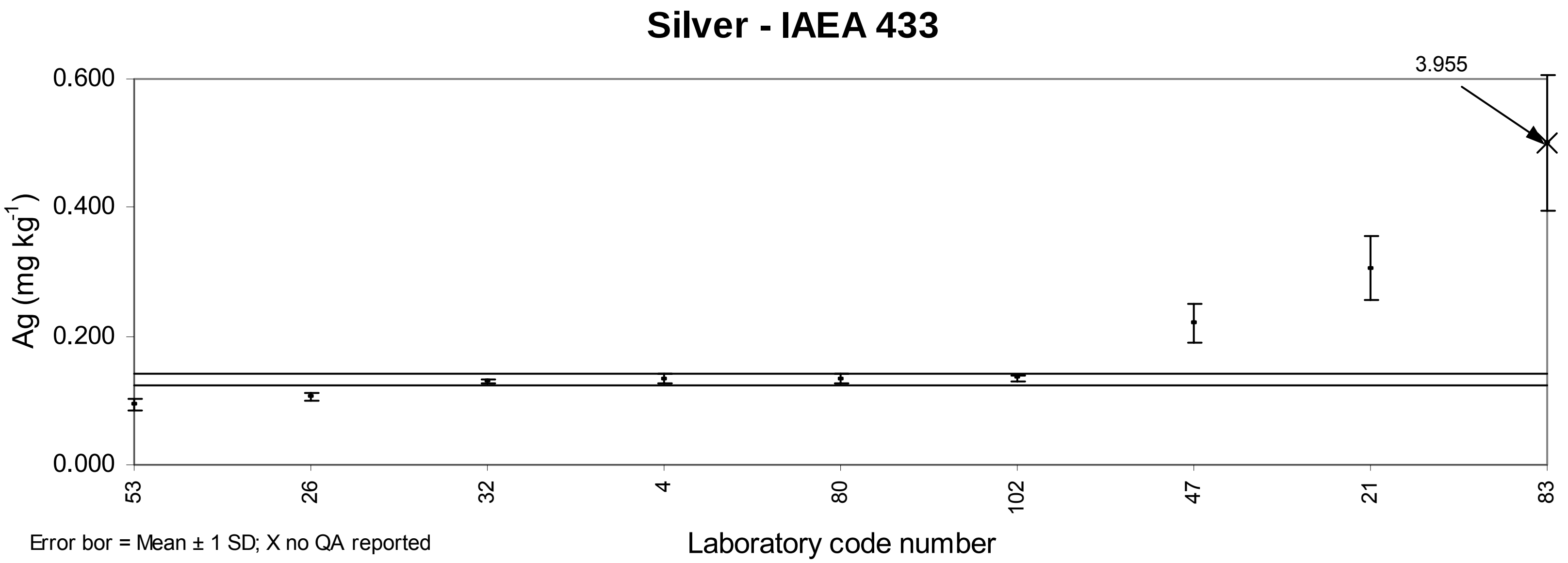
ZIRCONIUM (Zr) mg kg^{-1}

Lab code	Lab. Mean	Stdev	Number Determination	Det. Limit	Method	RM
60	162	26	6	20	0-N0	1633A
76	20.7	1.61	6	0.6	219-E1	IAEA-SL1
79	138	2.2	6	1	0-X0	SOIL7
101	147.70	0.46	3			

ANNEX II

Graphical presentation of results sorted by element

IAEA-433



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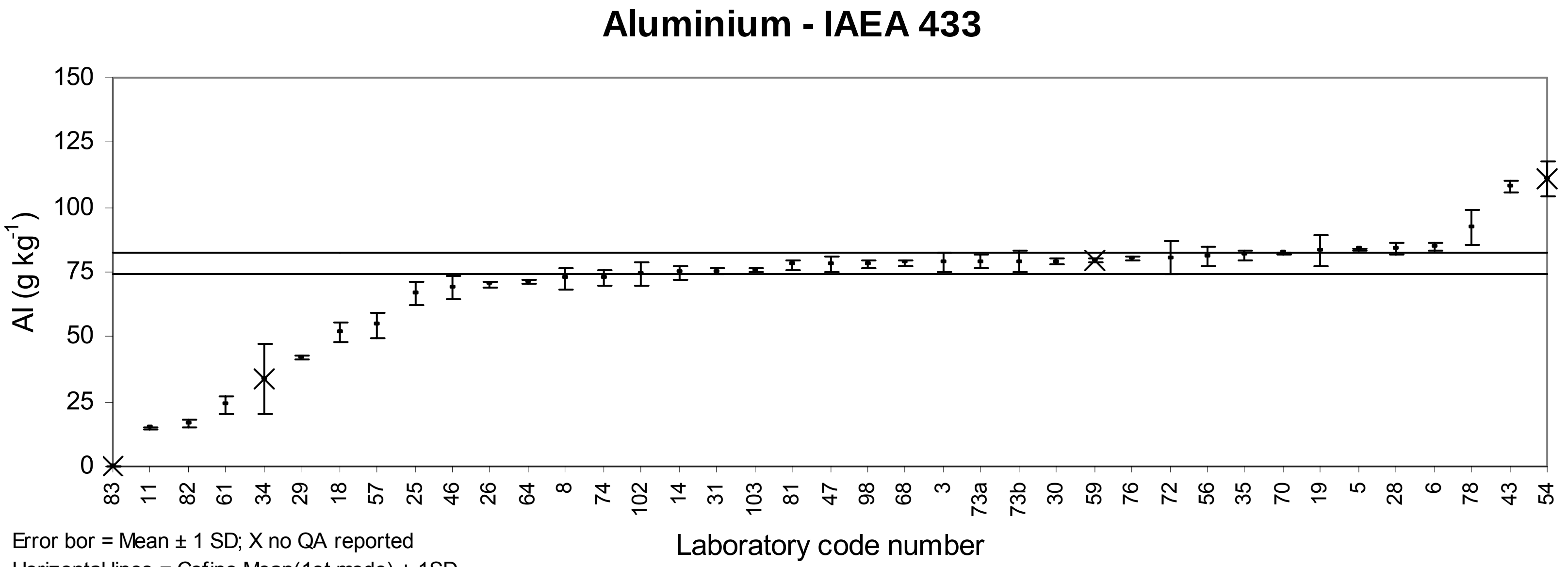

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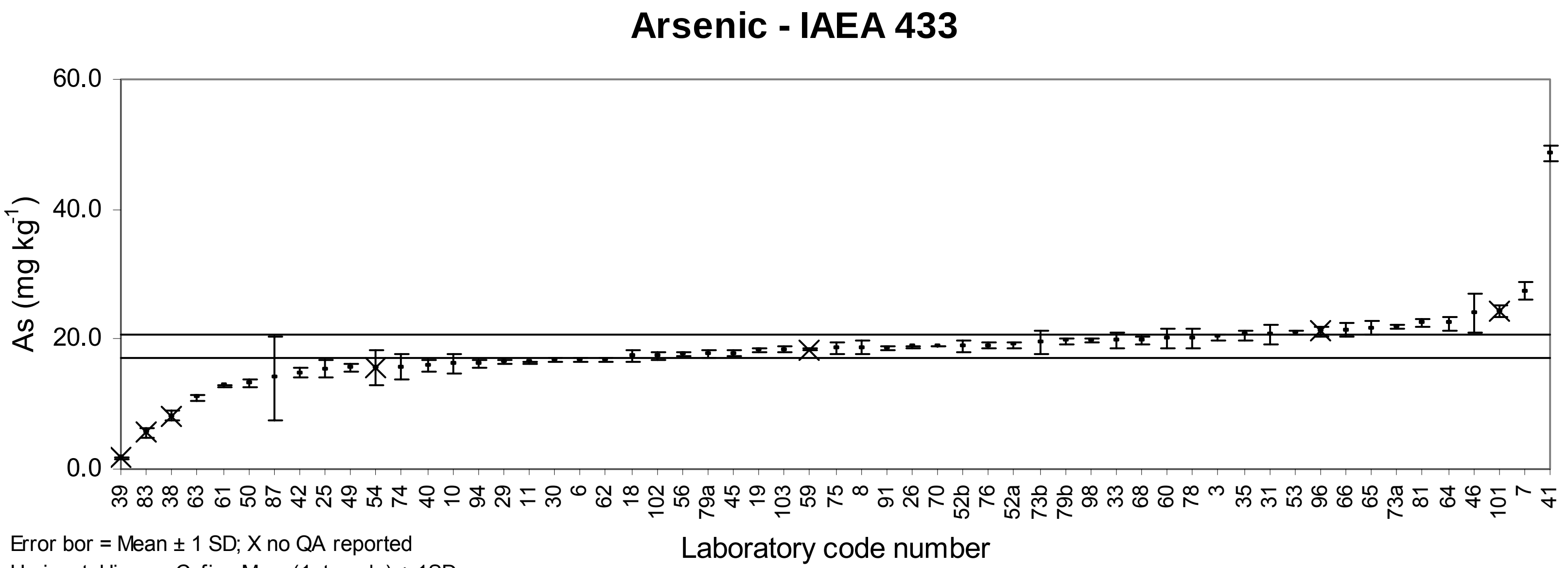

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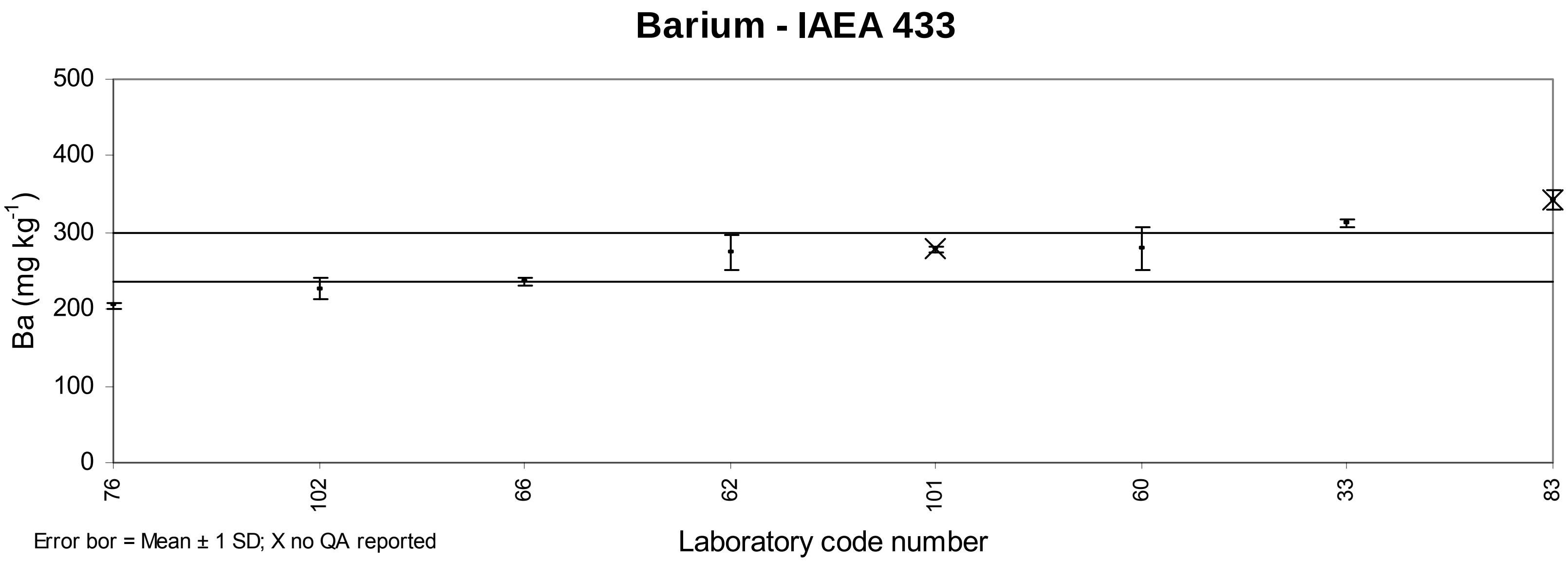

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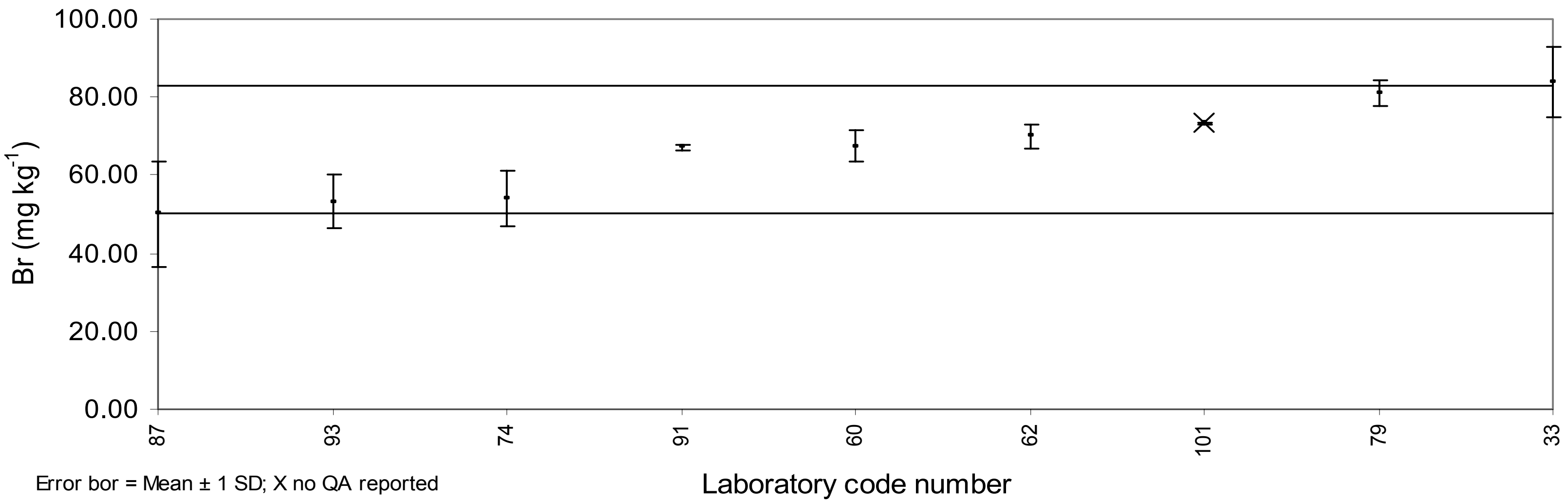
Bromine - IAEA 433



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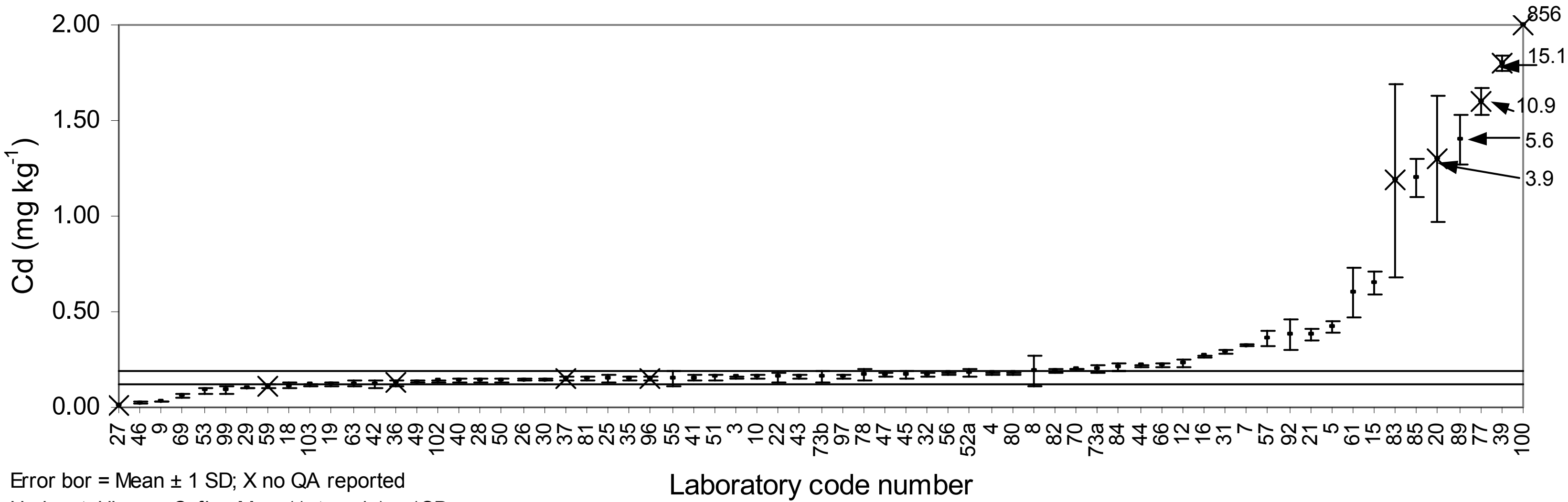
Cadmium - IAEA 433



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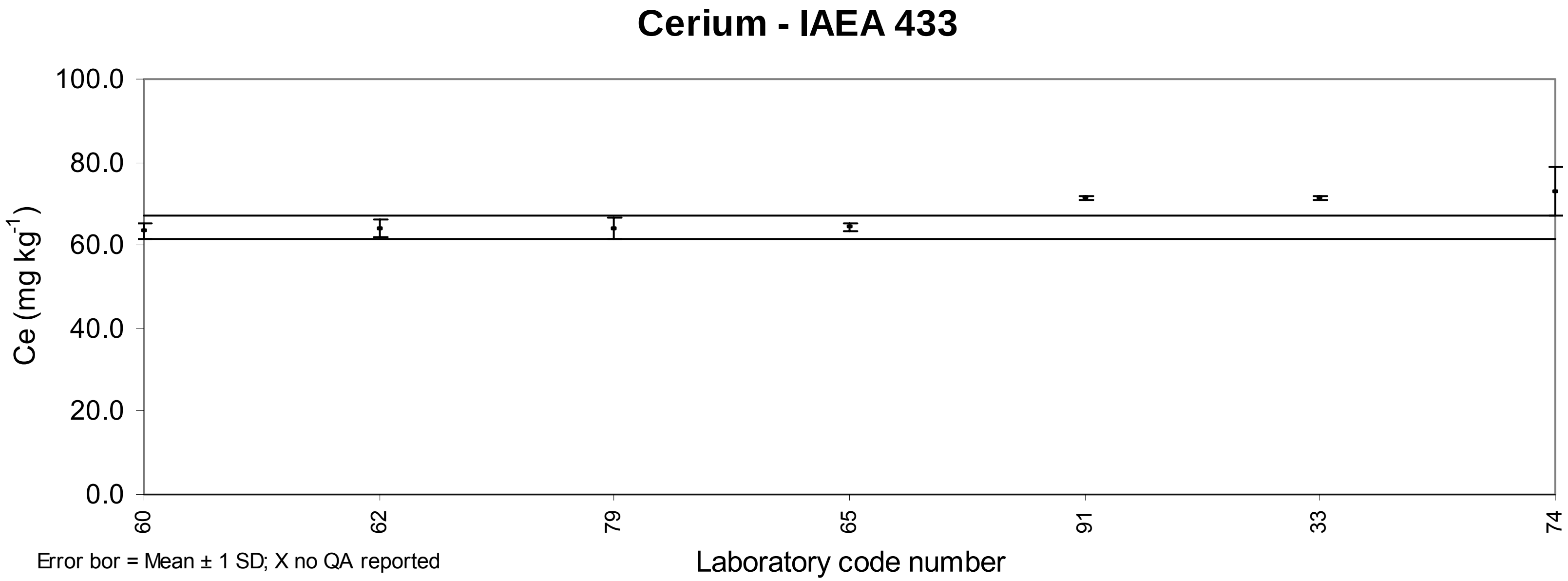

Cerium - IAEA 433

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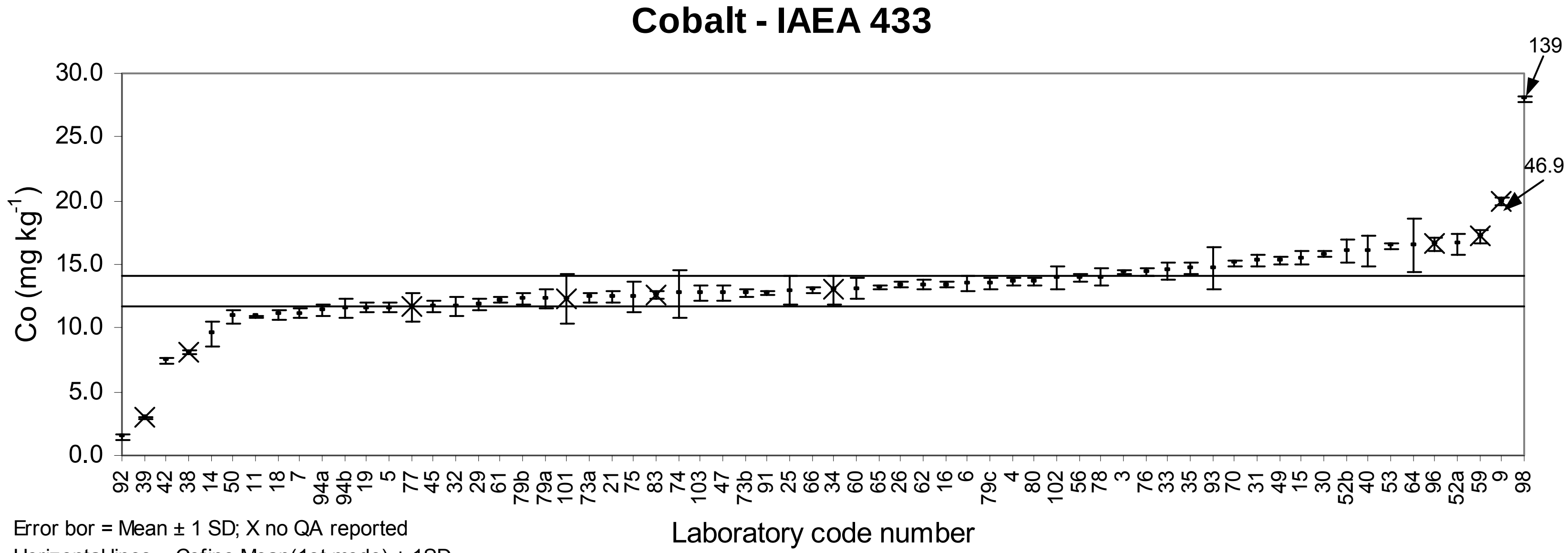

Cobalt - IAEA 433

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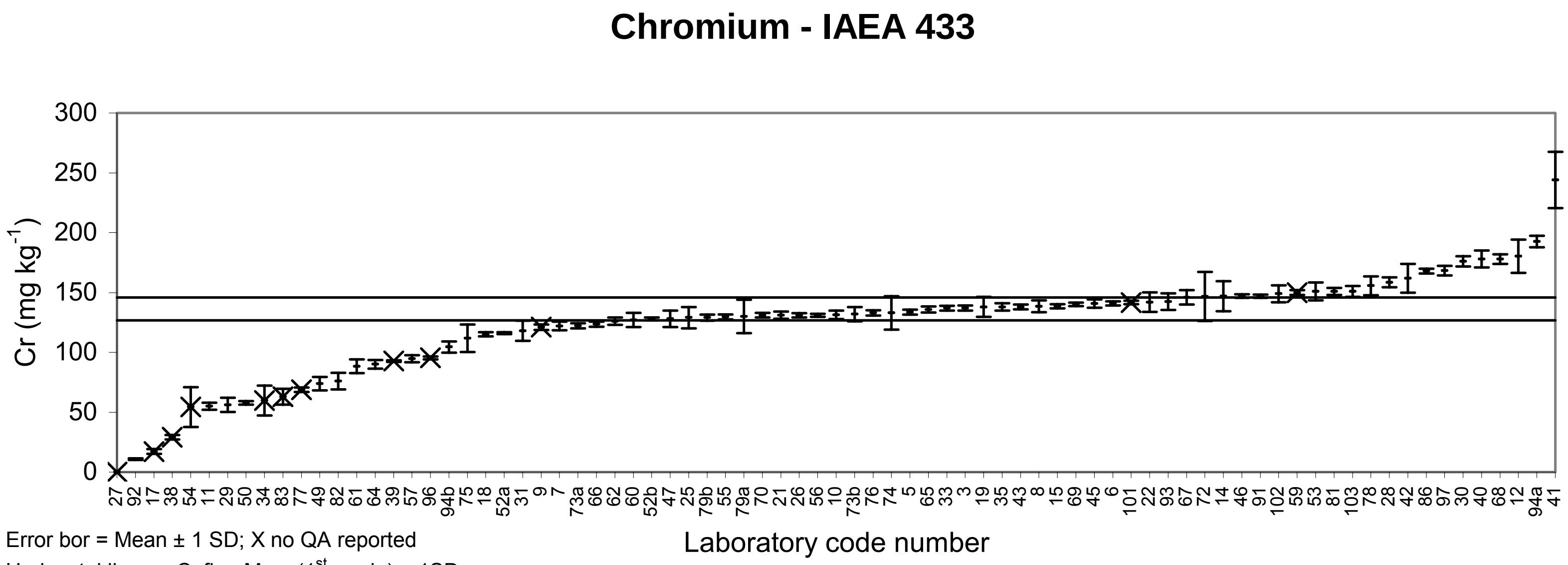

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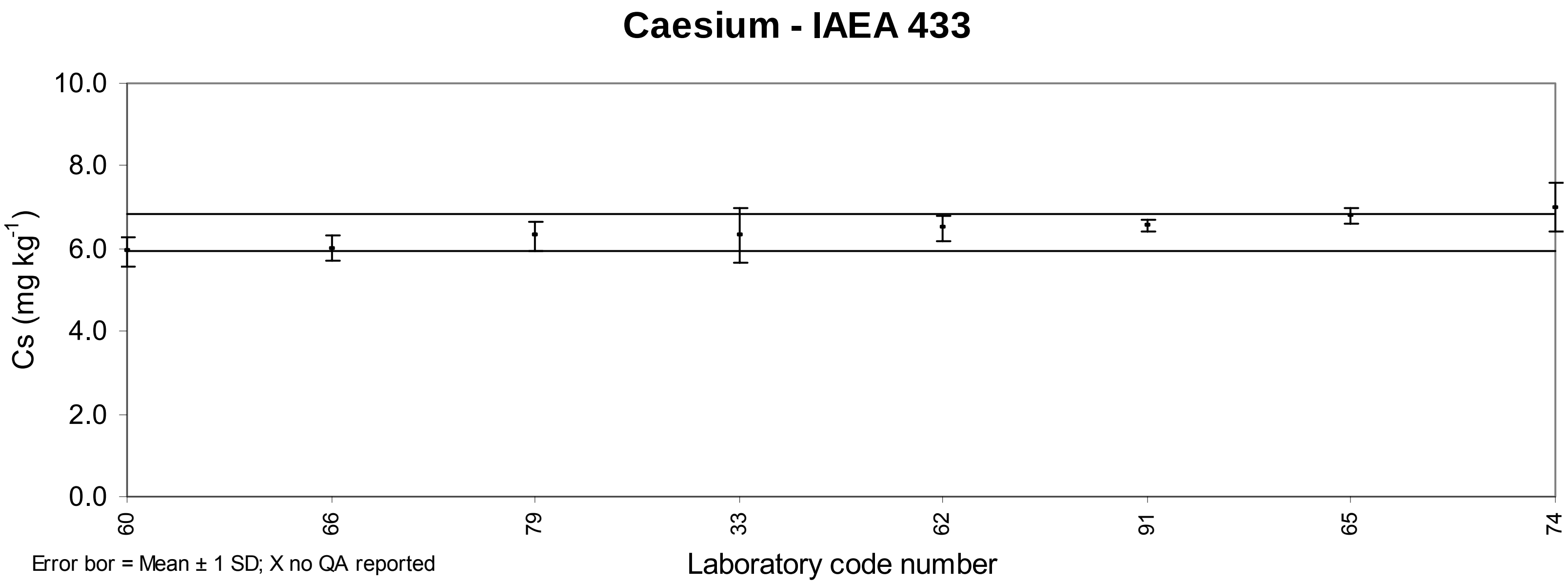

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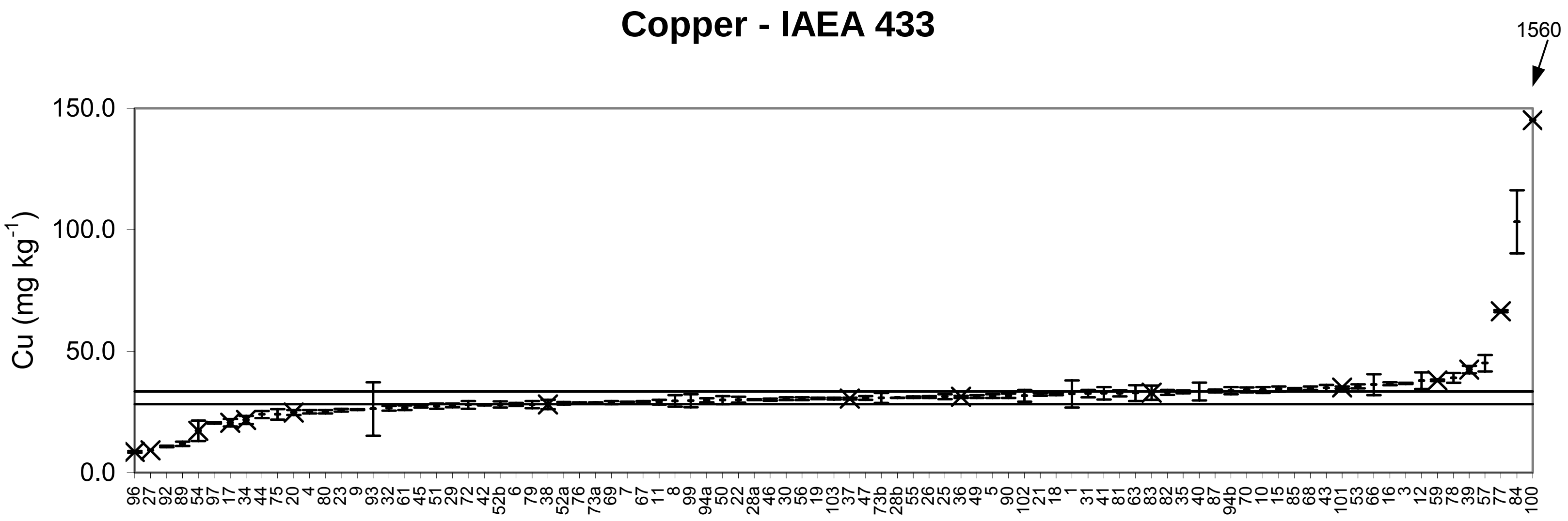

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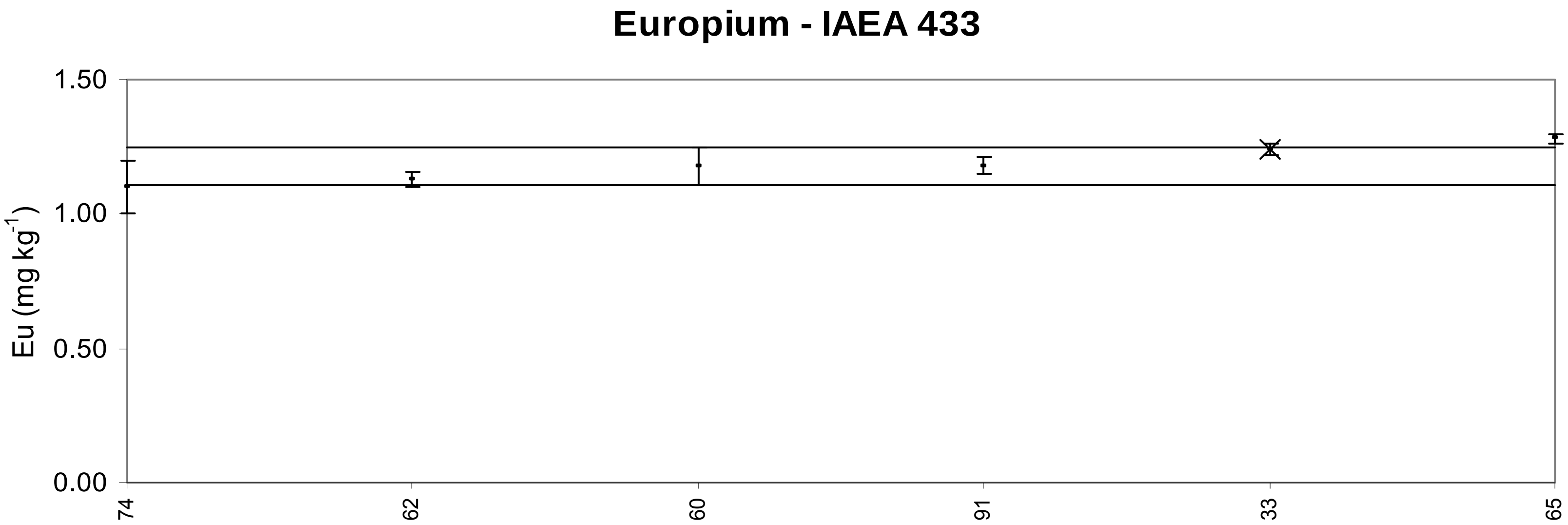

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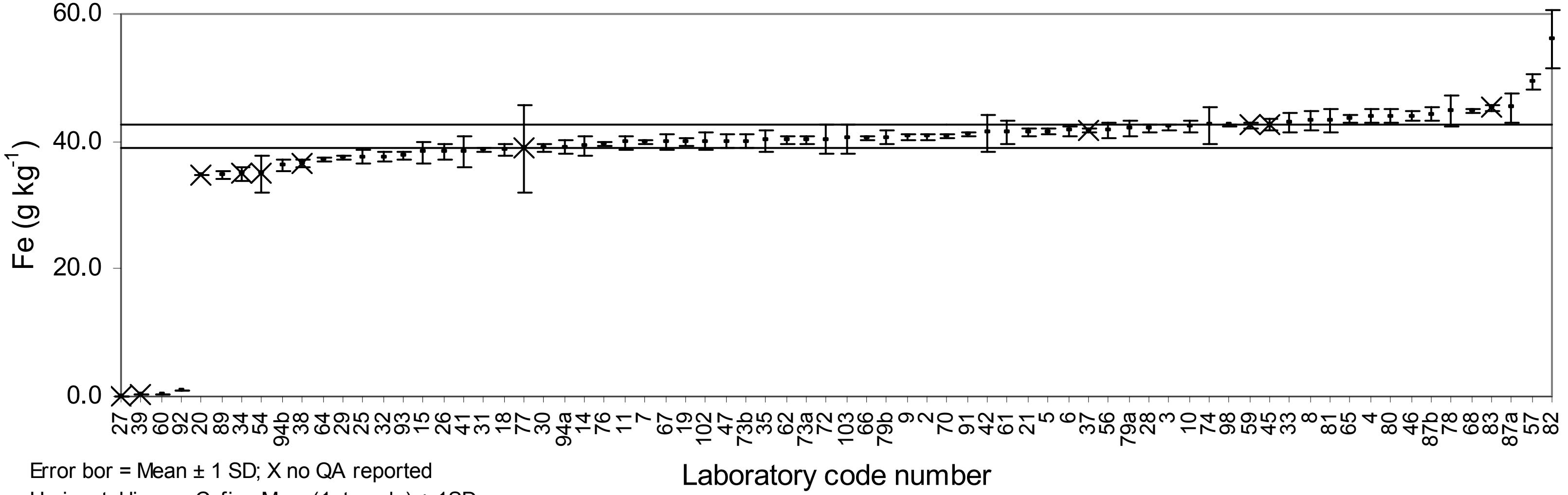
Iron - IAEA 433



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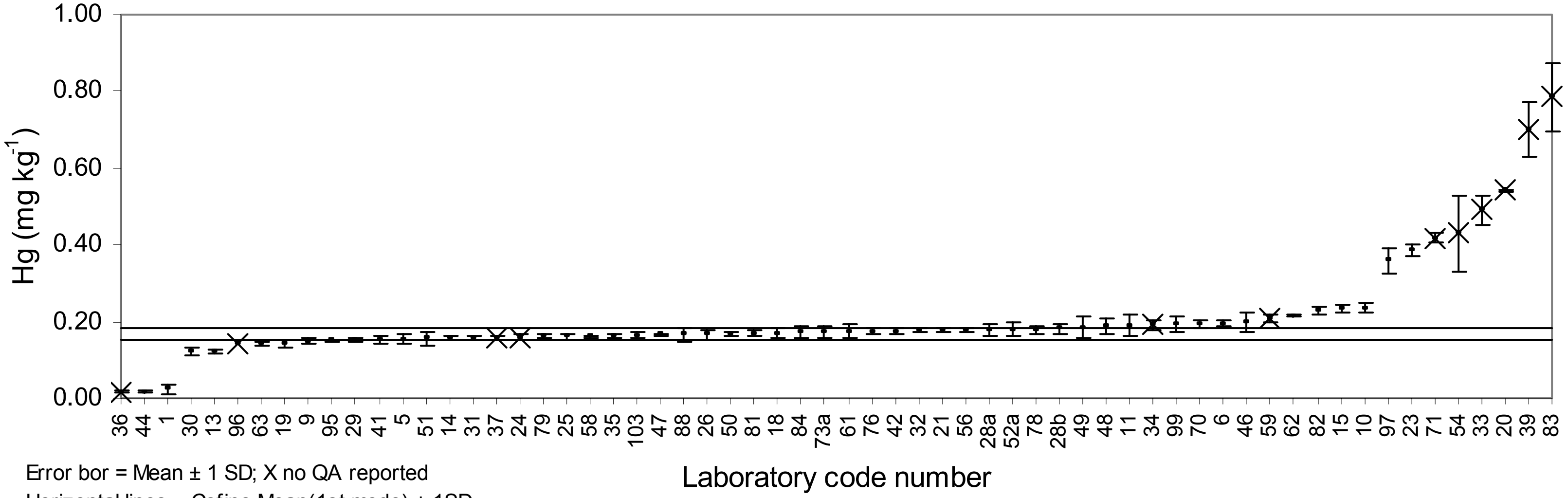
Mercury - IAEA 433



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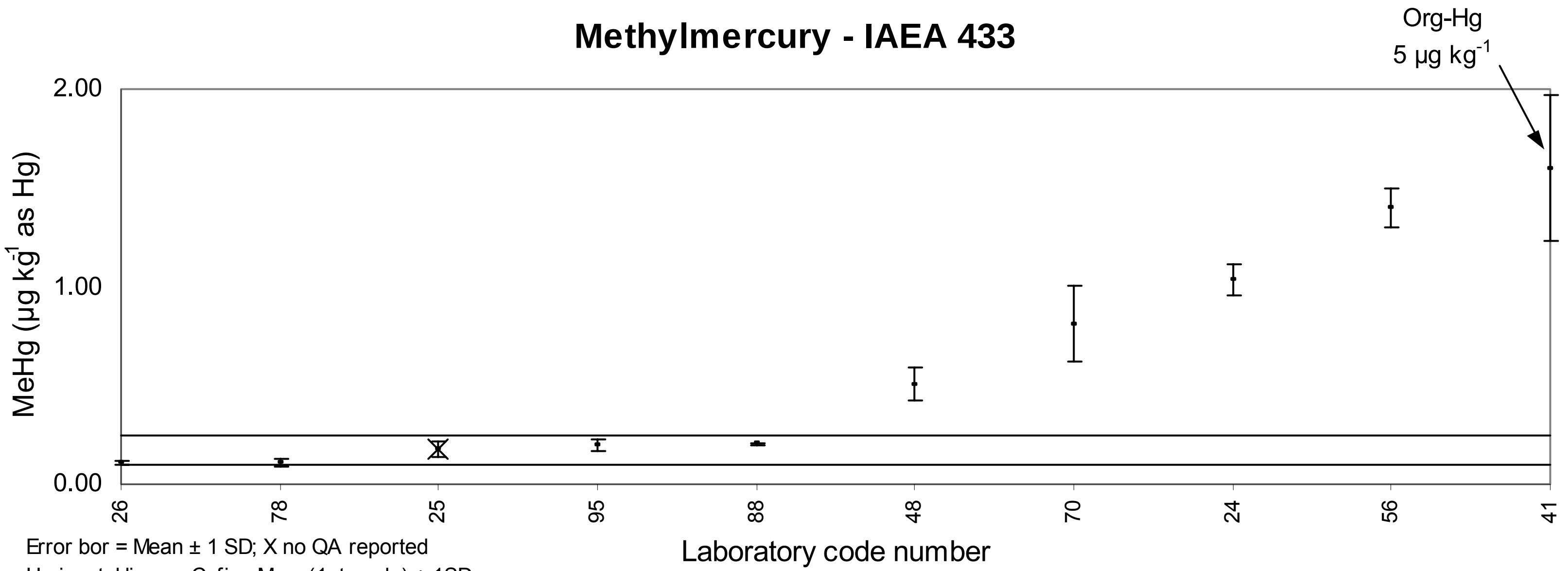

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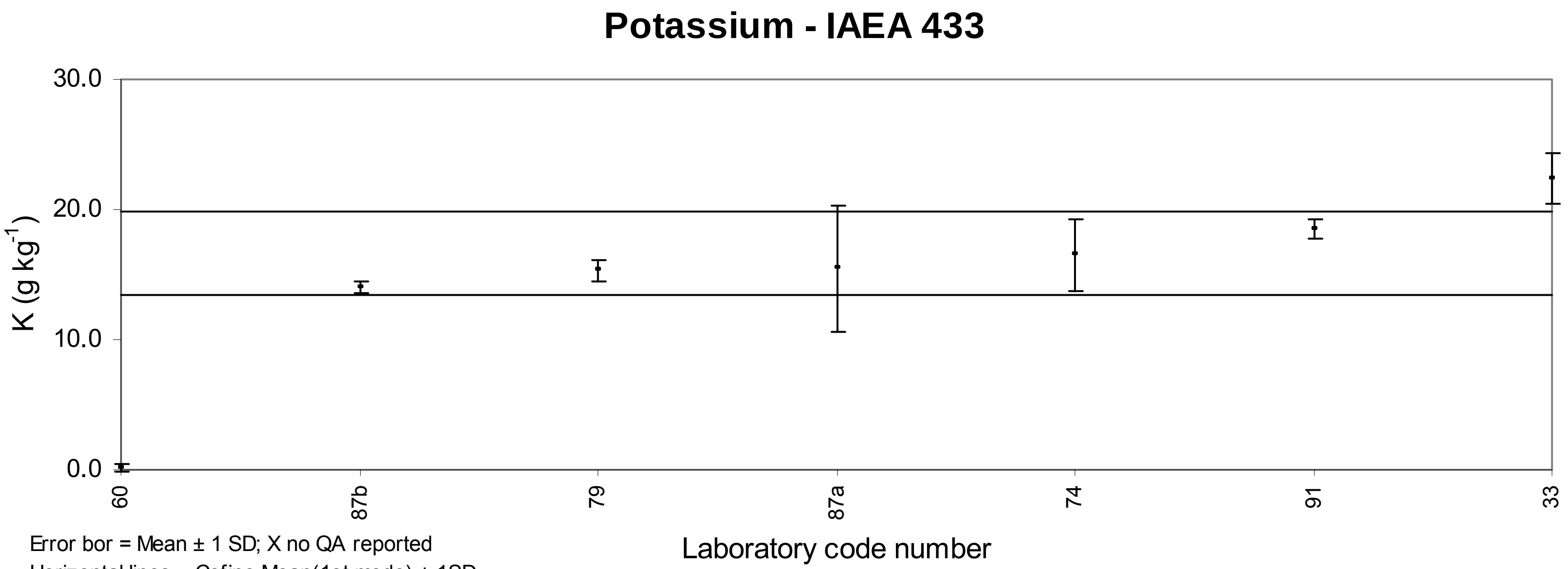

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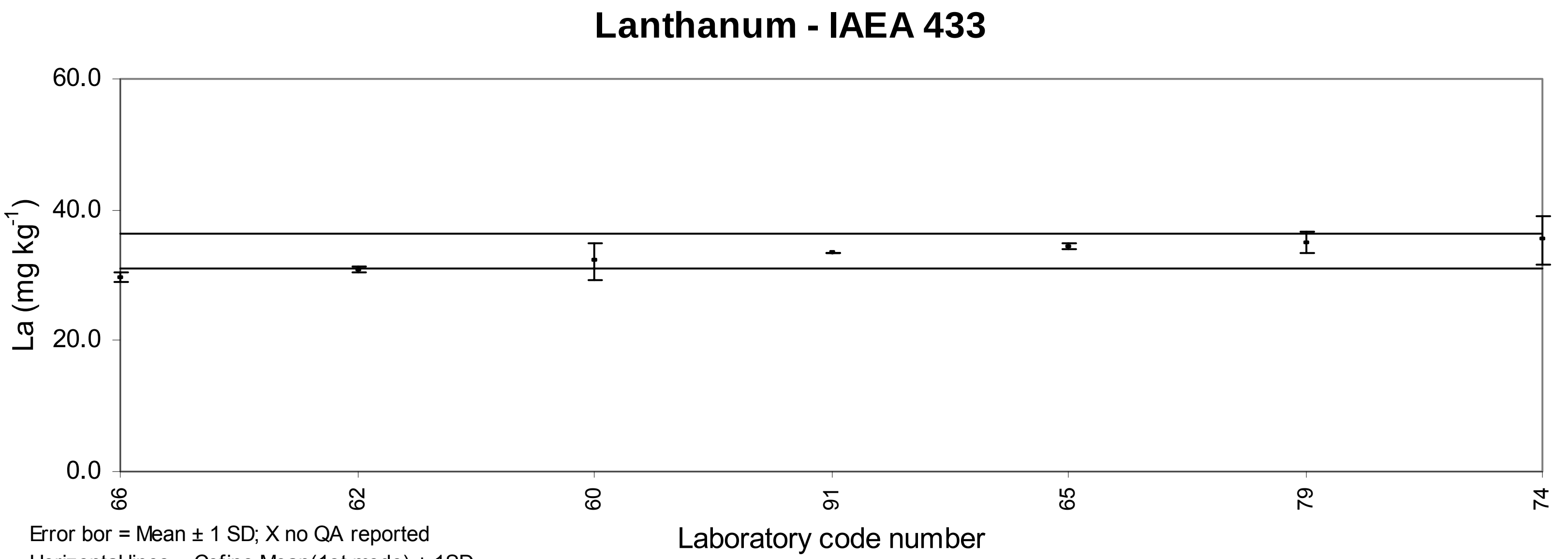

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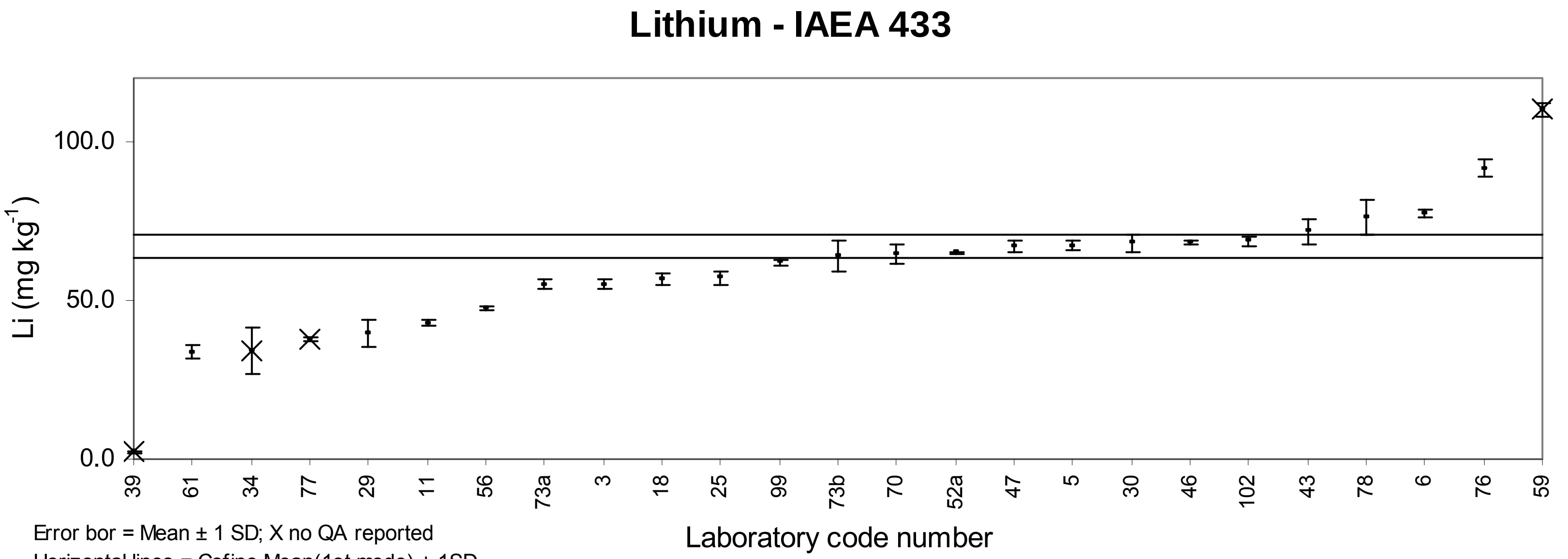

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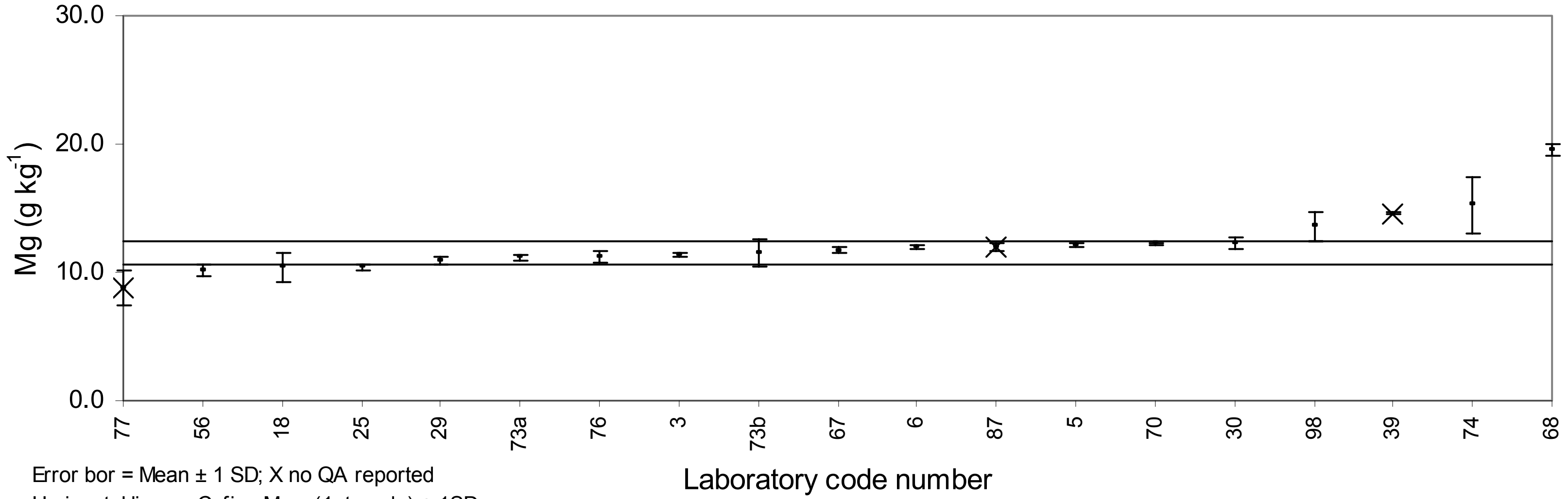
Magnesium - IAEA 433



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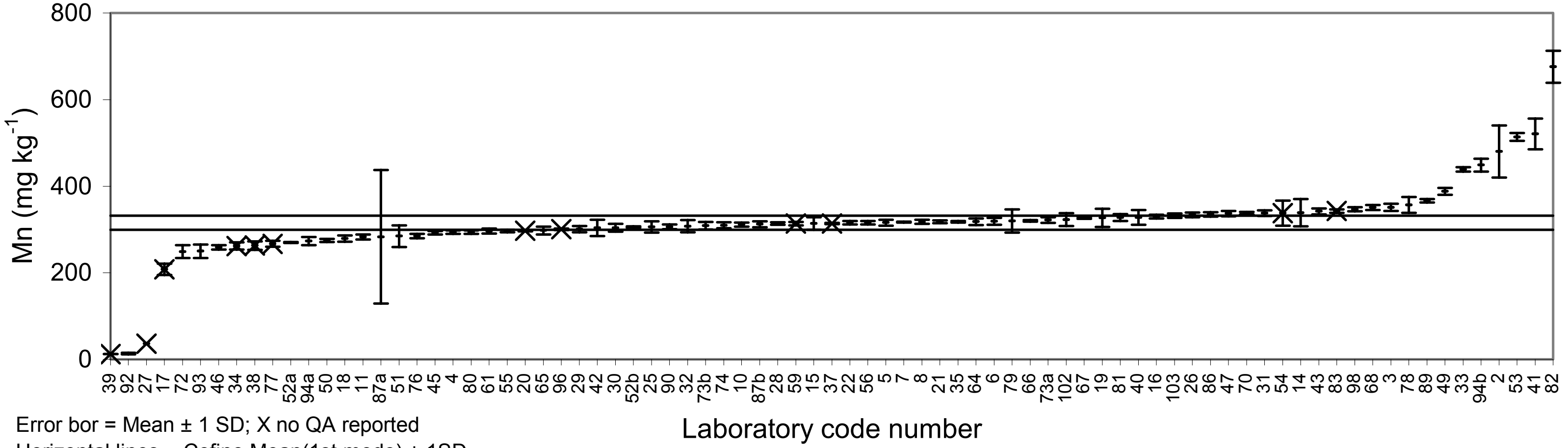
Manganese- IAEA 433



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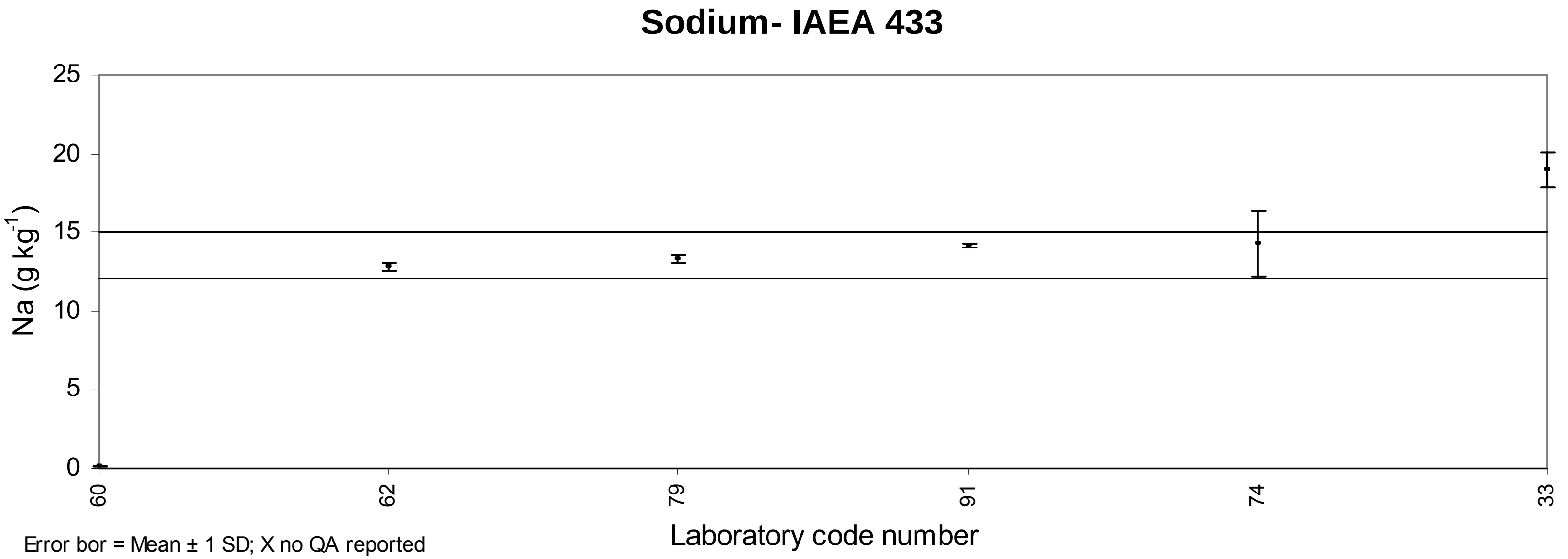

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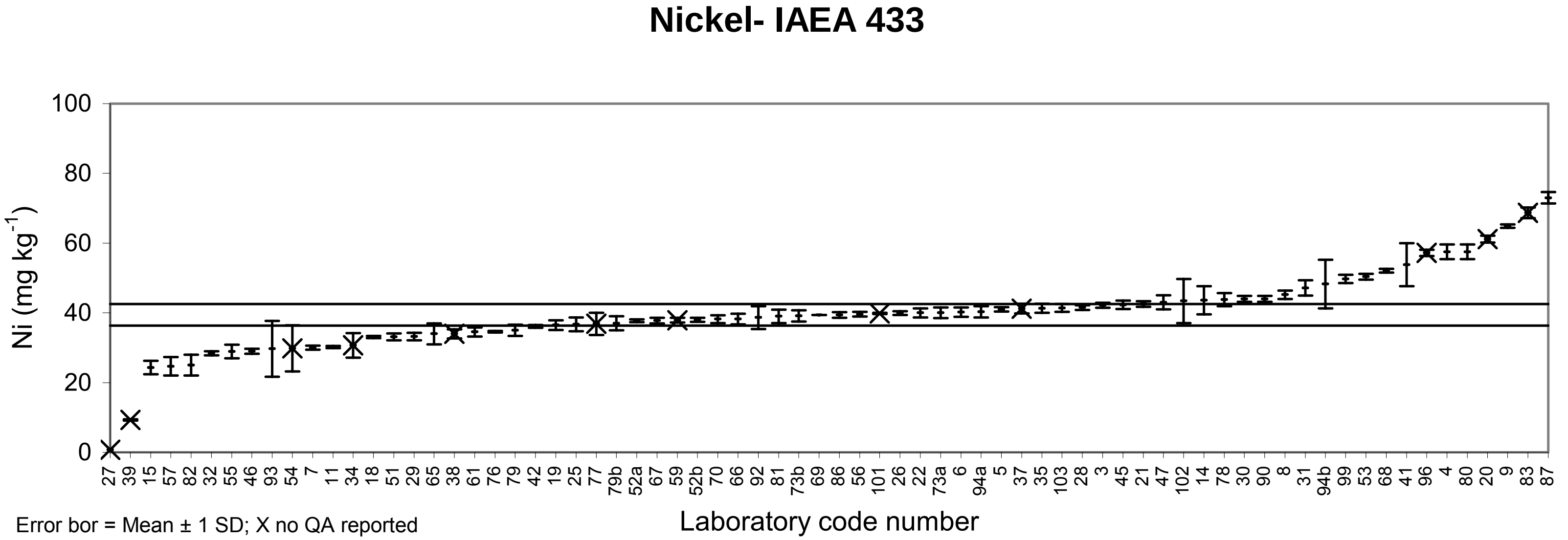

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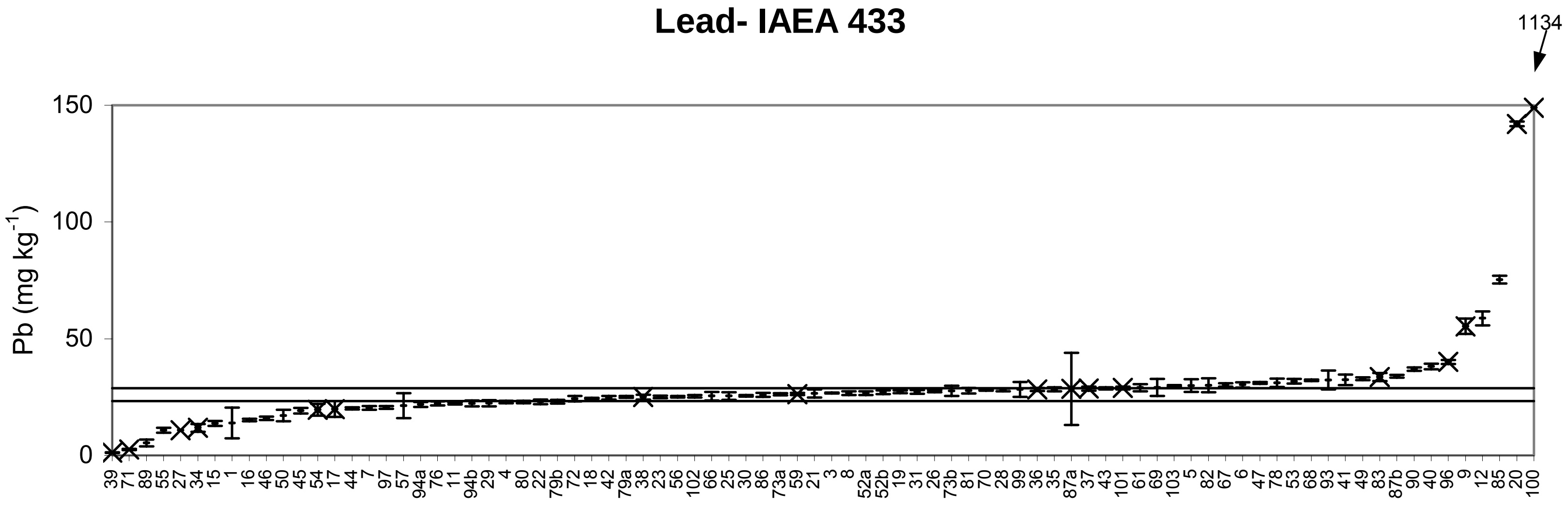

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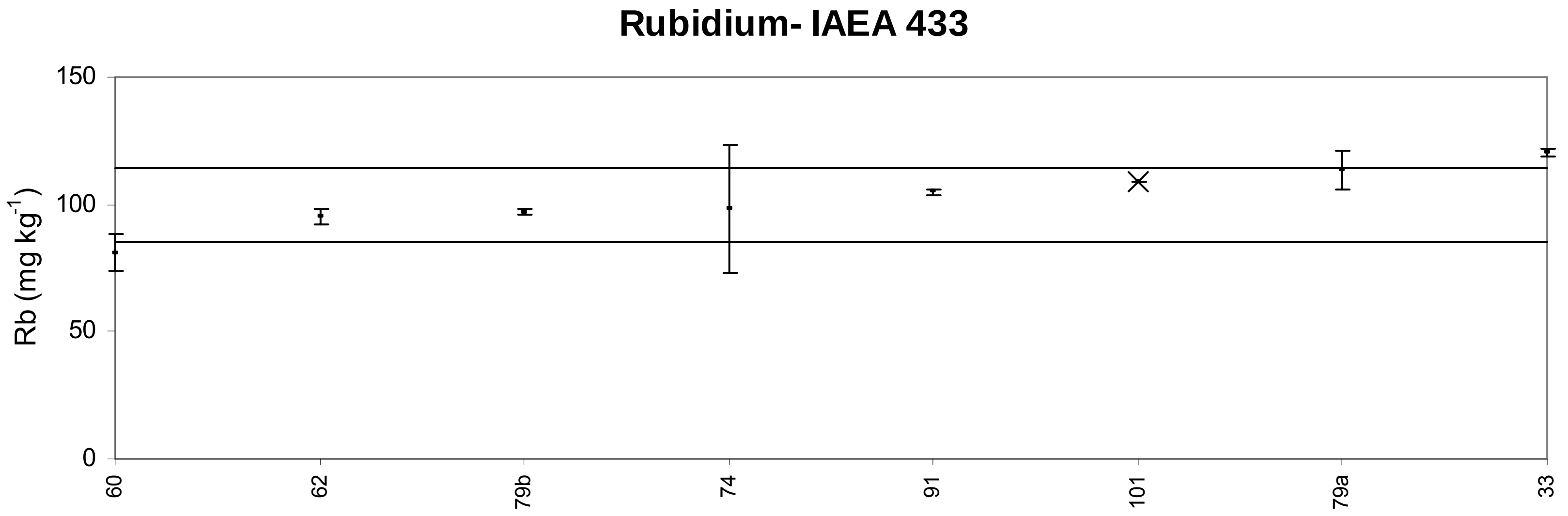

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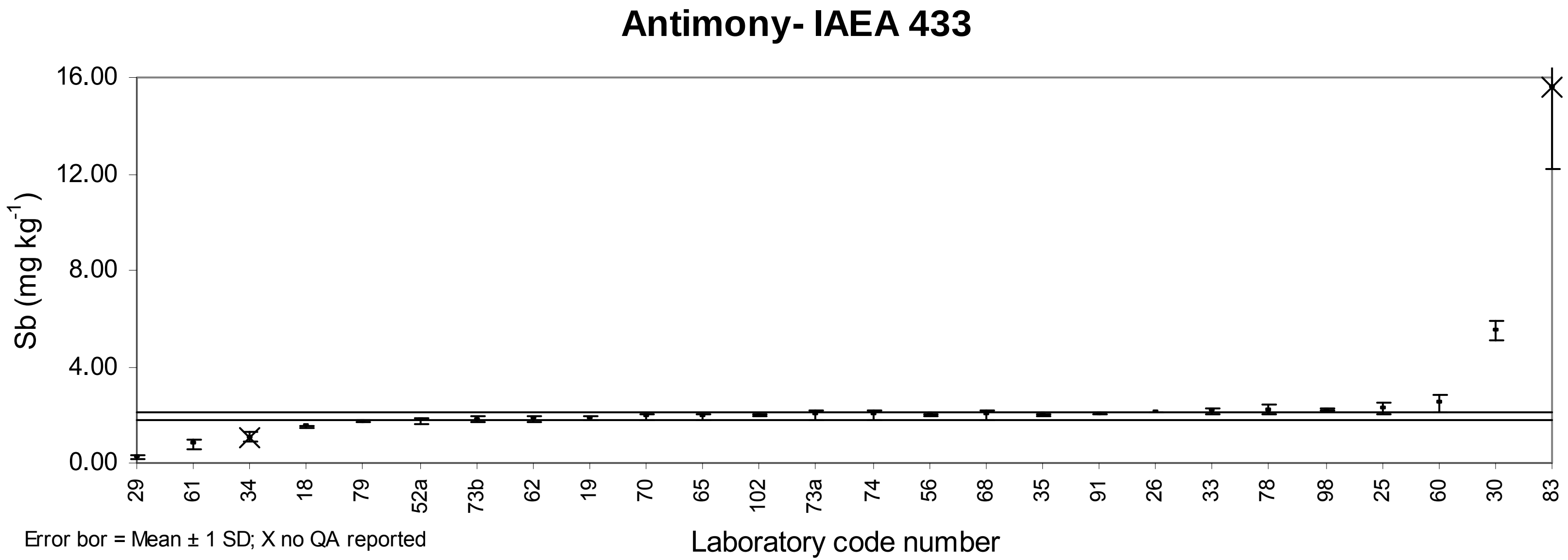

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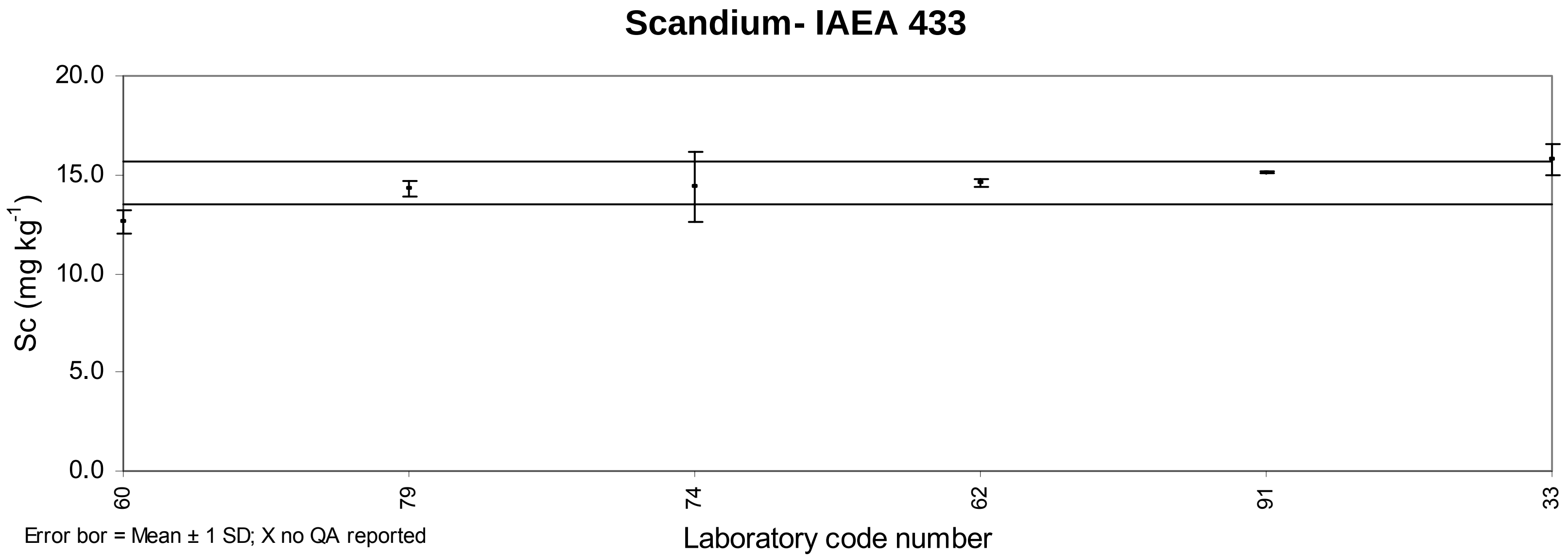

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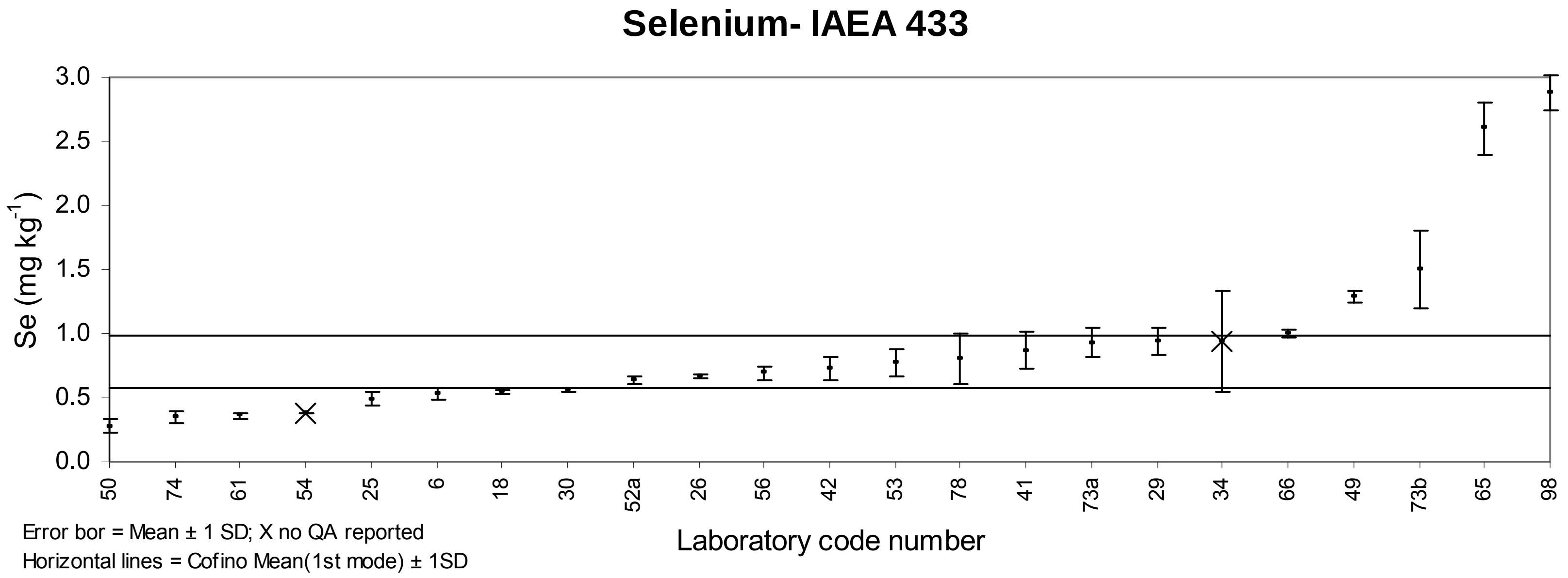

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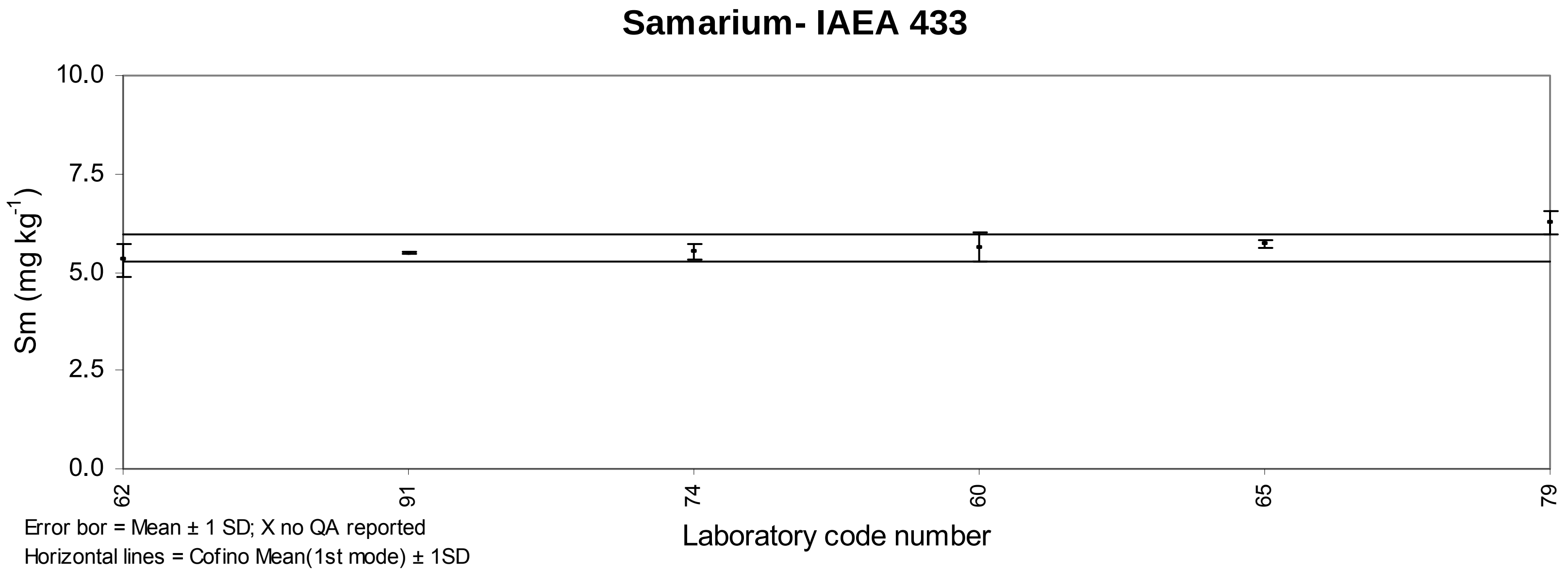

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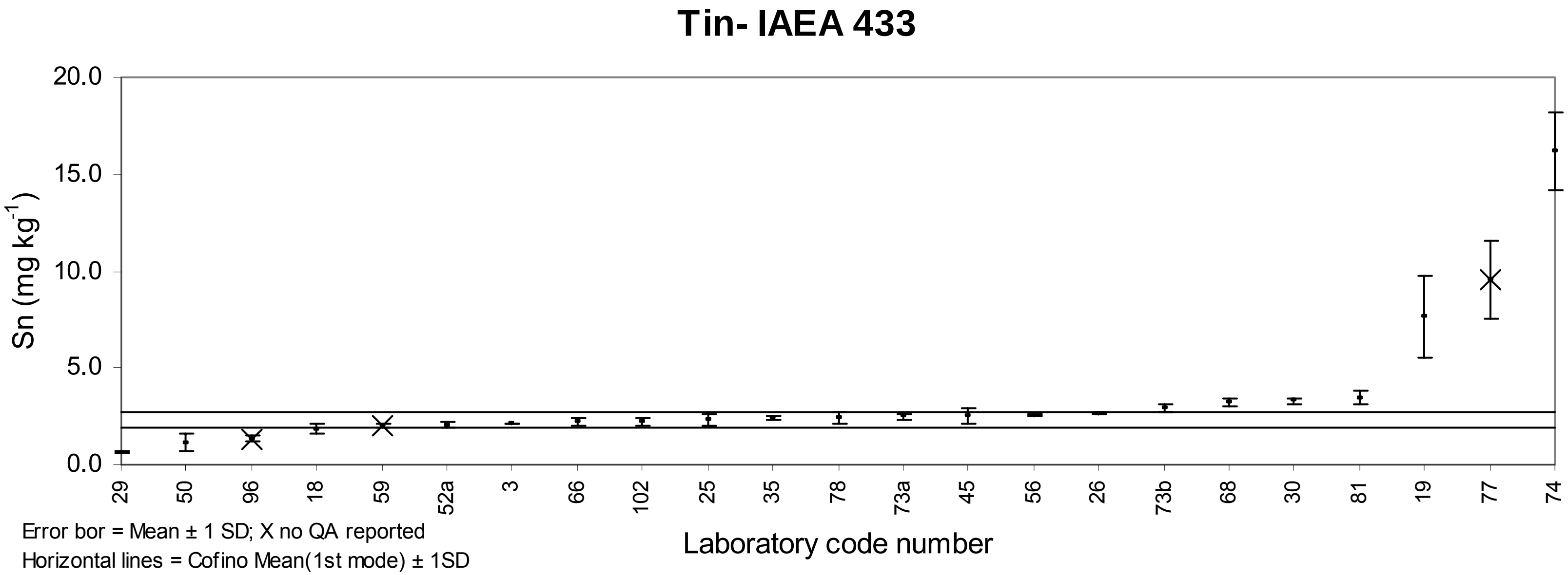

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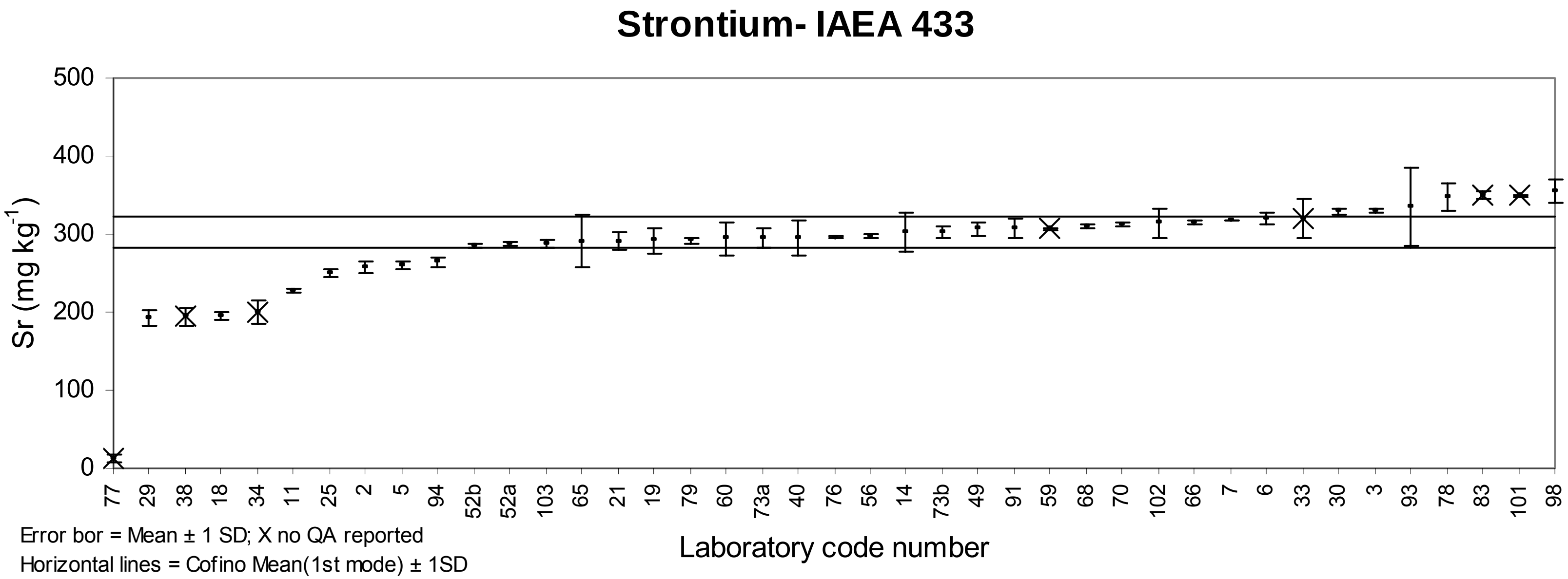

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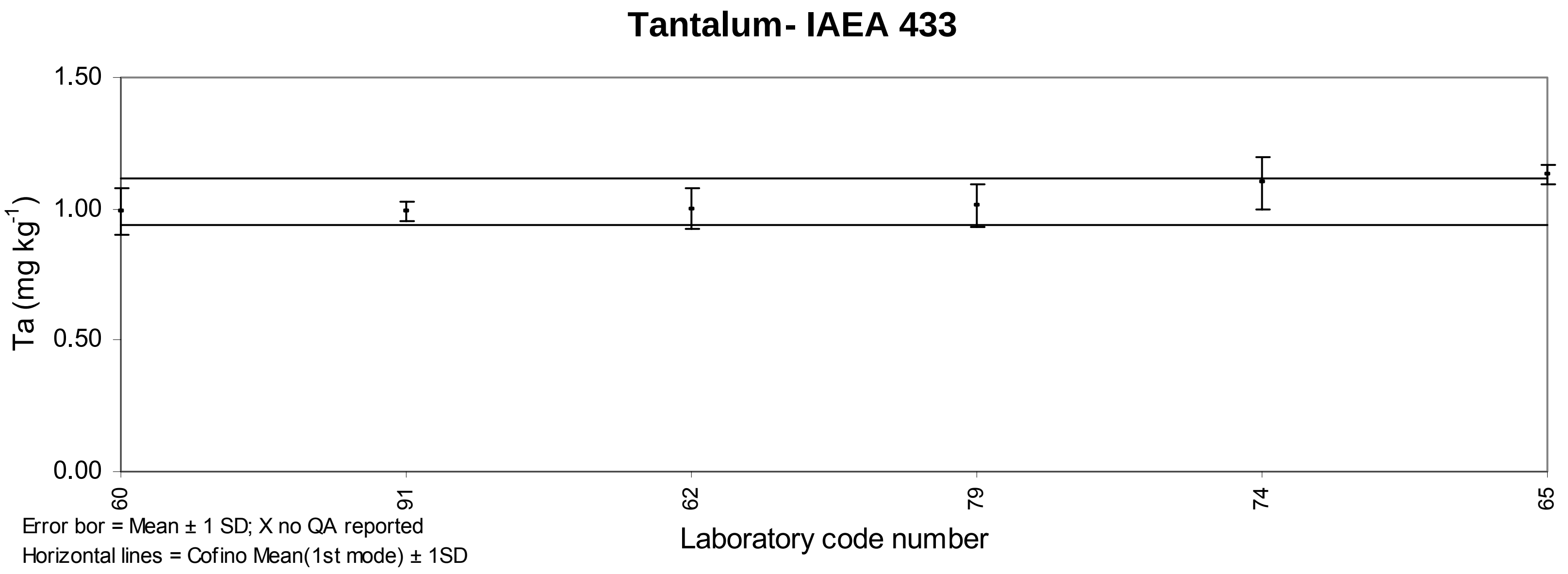

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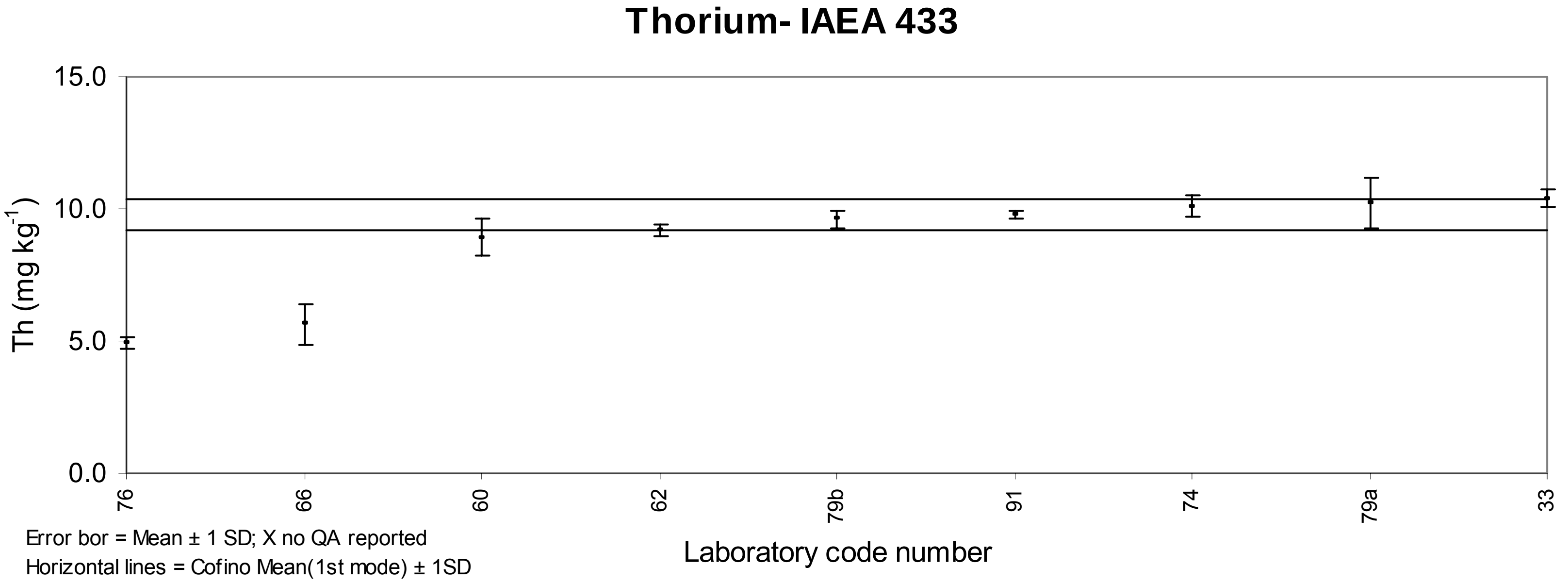

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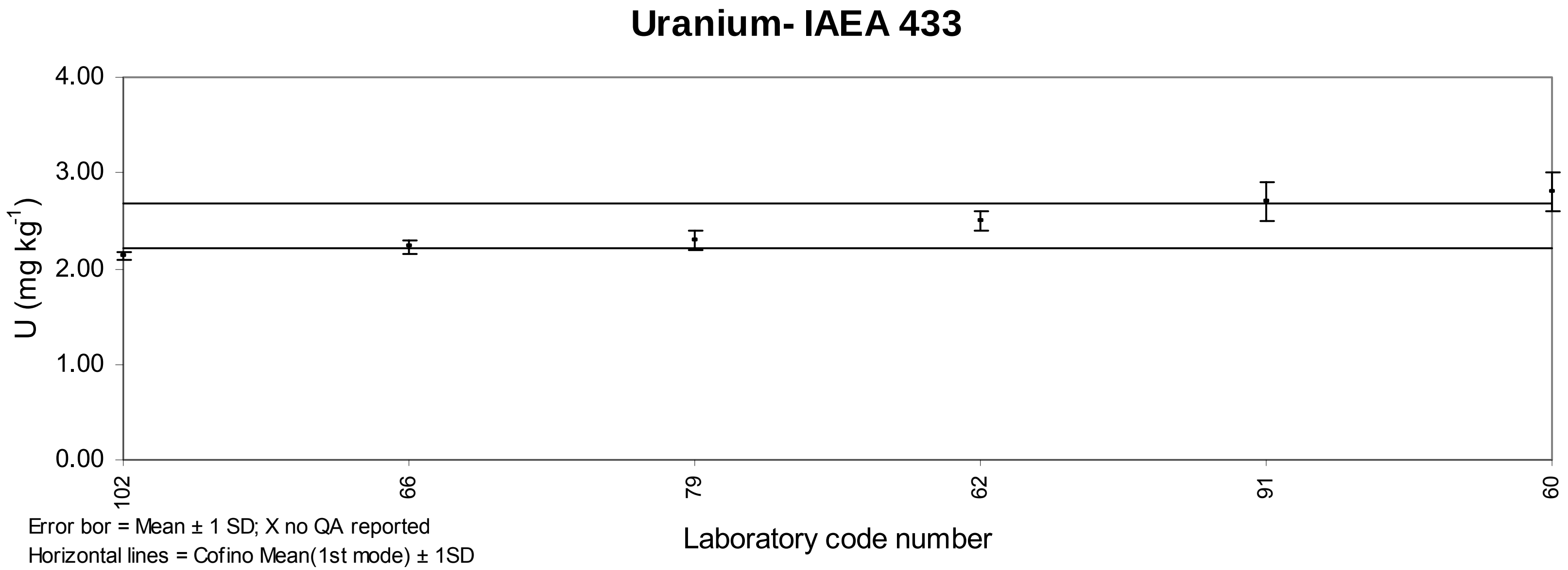

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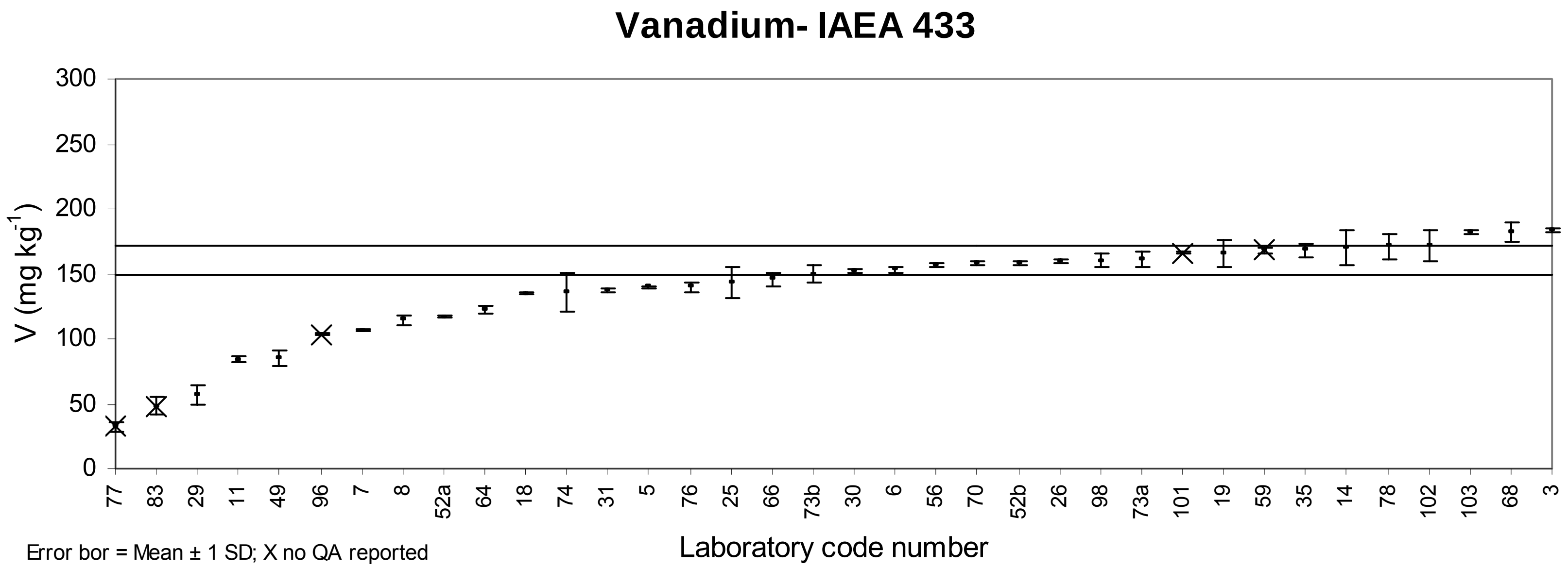

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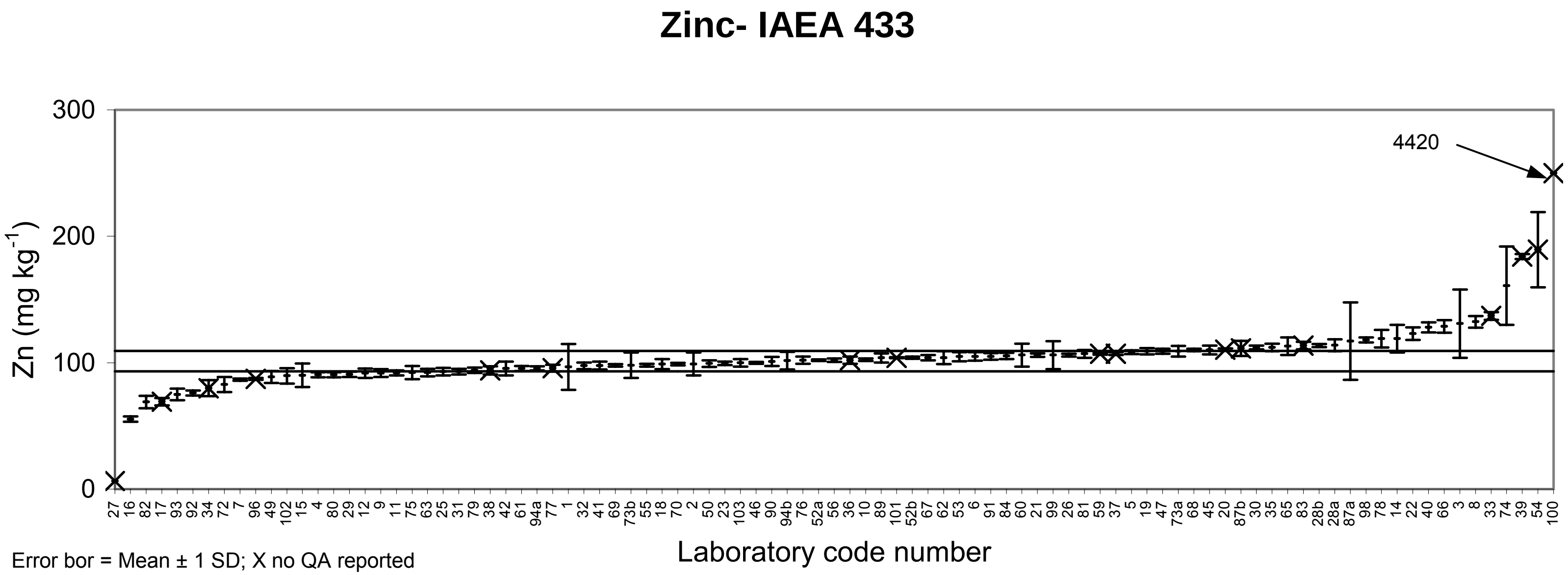

Error bor = Mean ± 1 SD; X no QA reported
Horizontal lines = Cofino Mean(1st mode) ± 1SD

ANNEX III

List of participants

IAEA-433

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ANNEX IV

Reference Sheet for IAEA-433 Marine Sediment

International Atomic Energy Agency
Analytical Quality Control Services
Wagramer Strasse 5, P.O. Box 100, A-1400 Vienna, Austria

REFERENCE SHEET

REFERENCE MATERIAL

IAEA-433

TRACE ELEMENTS AND METHYLMERCURY IN MARINE SEDIMENT

Date of issue: 23 July 2004

Recommended values: Trace Elements

(Based on dry weight)

Element	Concentration [1] (mg kg^{-1})	Std Deviation [2] (mg kg^{-1})	95% Confidence Interval [3] (mg kg^{-1})	*n* [4]
Silver	0.133	0.009	0.127 – 0.139	9
Arsenic	18.9	1.8	18.4 – 19.4	57
Barium	268	32	241 – 295	8
Bromine	67	16	55 – 79	9
Cadmium	0.153	0.033	0.145 – 0.161	67
Cobalt	12.9	1.2	12.6 – 13.2	65
Chromium	136	10	134 – 138	79
Caesium	6.40	0.44	6.03 – 6.77	8
Copper	30.8	2.6	30.2 – 31.4	89
Mercury	0.168	0.017	0.164 – 0.172	62
Lanthanum	33.7	2.7	31.4 – 36.0	8
Lithium	67.0	3.9	65.4 – 68.6	25
Manganese	316	16	312 – 320	81
Nickel	39.4	3.1	38.7 – 40.1	72
Lead	26.0	2.7	25.4 – 26.6	84
Rubidium	99.9	14.2	88.1 – 112	8
Antimony	1.96	0.18	1.89 – 2.03	26
Selenium	0.78	0.20	0.70 – 0.85	23
Tin	2.32	0.36	2.17 – 2.47	23
Strontium	302	20	296 – 308	41
Thorium	9.78	0.57	9.34 – 10.2	9
Uranium	2.45	0.24	2.20 – 2.70	6
Vanadium	160	11	156 – 164	36
Zinc	101	8	99 – 103	93
MeHg [5]	0.17	0.07	0.12 – 0.23	9

[1] Mean values expressed on a dry-weight basis.
[2] 1 standard deviation of the mean.

[3] 95% Confidence Interval, μ, defined as $\bar{x} \pm t(\frac{s}{\sqrt{N}})$, where t is the Student's t value.

[4] Number of accepted laboratory means which were used to calculate the Recommended values and confidence intervals about the mean values.

[5] Concentration reported as μg Hg kg^{-1}

Recommended values: Matrix and Minor Constituents

(Based on dry weight)

Element	Concentration [1] (g kg^{-1})	Std Deviation [2] (g kg^{-1})	95% Confidence Interval [3] (g kg^{-1})	*n* [4]
Aluminium	**78.2**	**4.2**	**76.8 – 79.6**	**39**
Iron	**40.8**	**1.9**	**40.3 – 41.3**	**72**
Potassium	**16.6**	**3.2**	**13.7 – 19.6**	**7**
Magnesium	**11.5**	**0.9**	**11.1 – 12.0**	**19**

Information values

(Based on dry weight)

Element	Concentration [1] (mg kg^{-1})	Std Deviation [2] (mg kg^{-1})	95% Confidence Interval [3] (mg kg^{-1})	*n* [4]
Cerium	**64.5**	**2.8**	**61.9 – 67.1**	**7**
Europium	**1.18**	**0.07**	**1.11 – 1.25**	**6**
Hafnium	**3.66**	**0.18**	**3.44 – 3.88**	**5**
Lutetium	**0.361**	**0.039**	**0.299 – 0.423**	**4**
Sodium	**13500**	**1500**	**12000 – 15100**	**6**
Neodymium	**29.2**	**2.2**	**26.5 – 31.9**	**5**
Scandium	**14.6**	**1.1**	**13.4 – 15.8**	**6**
Samarium	**5.61**	**0.33**	**5.26 – 5.96**	**6**
Tantalum	**1.03**	**0.09**	**0.94 – 1.12**	**6**
Terbium	**0.696**	**0.092**	**0.582 – 0.810**	**5**
Ytterbium	**2.24**	**0.17**	**2.03 – 2.45**	**5**
Zirconium	**148**	**19**	**118 – 178**	**4**

[1] Mean values expressed on a dry-weight basis.

[2] 1 standard deviation of the mean.

[3] 95% Confidence Interval, μ, defined as $\bar{x} \pm t(\frac{s}{\sqrt{N}})$, where t is the Student's t value.

[4] Number of accepted laboratory means which were used to calculate the reference values and confidence intervals about the mean values.

Establishment of reference values

The values listed above were established on the basis of results submitted by laboratories that had participated in an international intercomparison exercise organized in 2003. The details concerning the criteria for qualification as recommended or information value can be found in the "Report on the world-wide intercomparison exercise for the determination of trace elements and methylmercury in marine sediment IAEA-433" [1]. This report is available free of charge upon request.

Intended use

This material is intended to be used as a reference material for the measurement of trace elements and methylmercury (MeHg) in sediment samples. It can also be used as a quality control material for the assessment of analytical procedures, in the elaboration and validation of analytical methods, and for educational purposes.

Origin and preparation of the material

A large quantity of marine sediment was collected in 2002 off the Algerian coast of the Mediterranean Sea for use as an intercomparison material. It was deep-frozen, freeze-dried, then ground and sieved. The particle size fraction <250 μ was homogenized and bottled in clean plastic bottles. After verifying the homogeneity of the sample material (see below), the samples were rebottled by packing aliquots of approximately 20 g into cleaned, brown borosilicate glass bottles with Teflon lined screw caps and sealed in plastic bags. Approximately 500 bottles were produced.

Homogeneity

Extensive homogeneity tests were carried out on this material in order to ensure its suitability as an intercomparison sample. A homogeneity pre-test was conducted before bottling the sample material. The between-bottle homogeneity was tested by the determination of the concentration of some typical elements (Mn, Co, Cu, Zn, Hg) on sample intakes of 0.2 g taken from 10 bottles, which were taken directly from the bulk material, specifically for the purpose of this pre-test. The within-bottle homogeneity was assessed by 6 replicate determinations on the re-homogenized content of one bottle. The uncertainty of the analytical methods was assessed for each element by 5 replicate measurements on one digest solution.

An F-test at a significance level of 0.05 was performed for the different metals and did not reveal significant differences between the within- and between-bottle variances, indicating that the heterogeneity observed was relatively consistent, and independent of how the material was distributed. It was concluded that the material was homogeneous for the elements tested at an analytical portion of 200 mg and above; it is therefore suitable for use as an intercomparison sample [1].

Stability tests

The stability of several trace metals was tested to determine the suitability of this material as a candidate RM. Five bottles of the IAEA-433 material were stored in the dark at +20 °C, –20 °C and +60 °C, respectively, over a period of 12 months (starting in January 2003) and the measurement of As, Mn, Co, Cu, Zn and total Hg was performed at regular intervals during the storage period. On the basis of these results, it was concluded that no instability of the material could be demonstrated [1].

Dry weight determination

The average moisture content of the lyophilised sample after bottling, determined by drying to a constant weight at 105°C, was found to be 1.9 %. Since the moisture content can vary with the ambient humidity and temperature, it is recommended that the water content of this material be determined in a separate subsample (not used for analysis) by drying to a constant weight (~24 hours) at 105°C just prior to analysis. Final results should always be reported on a dry weight basis.

Instructions for use

The recommended minimum sample size for analysis is 200 mg. Analysts are reminded to take appropriate precautions in order to avoid contaminating the remaining material in the bottle. The bottle should be thoroughly mixed by shaking before use and tightly resealed immediately after use. The material should be stored in the dark and kept below 25 ºC.

Legal disclaimer

The IAEA makes no warranties, expressed or implied, with respect to the data contained in this reference sheet and shall not be liable for any damage that may result from the use of such data.

Reference

[1] Wyse, E. J., S. Azemard and S. J. de Mora, 2004. Report on the world-wide intercomparison exercise for the determination of trace elements and methylmercury in marine sediment IAEA-433. IAEA/AL/147, IAEA/MEL/75, IAEA, pp. 113.

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