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REPORT NO. 34 - TRACE ELEMENT MEASUREMENTS ON SHRIMP HOMOGENATE. RESULTS OF THE WORLDWIDE INTERCOMPARISON RUN MA-A-3/TM AND OF THE MED POL EXERCISE MA(S)MED-86/TM

June 1987

In co-operation with :

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PROGRESS REPORT No. 34

INTERCALIBRATION OF ANALYTICAL METHODS ON MARINE ENVIRONMENTAL SAMPLES

Trace Element Measurements on Shrimp Homogenate

Results of the Worldwide Intercomparison Run

MA-A-3/TM

and of the MEDPOL Exercise

MA(S)MED86/TM

June 1987

International Atomic Energy Agency
Laboratory of Marine Radioactivity
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Prepared in co-operation with UNEP

1. Introduction

The use of marine animals as pollution indicators of coastal sea water has extended during the past years. Mussels, in particular, are frequently used for that purpose since these animals are filter-feeders and can concentrate metals in their tissues from the surrounding sea water (1). Nowadays, other possible bioindicators are under survey, such as shrimps, crabs, fish, etc. All these animals take up metals which are present in their environment. The mechanism of uptake is different for each species but the metal concentrations in the tissues of most marine animals will normally reflect (after a sufficiently long exposure time) the average concentrations of these metals in the surrounding sea water and/or sediment. For these reasons many pollution studies are devoted, nowadays, to the metabolism of trace metals in various marine animals and are not restricted to filter-feeding animals such as mussels (2).

The International Atomic Energy Agency has organized in past years laboratory intercomparisons related to the determination of trace elements in marine environmental materials such as lyophilised mussel tissue (3) and sediment (4). The present intercomparison concerns the determination of trace elements in a homogenized sample of shrimp tissue. This intercomparison had a double aim: first, it was intended to provide laboratories dealing with the analysis of trace elements in marine animals with an opportunity for checking their analytical performance, second, this material could be used later as a reference material since it was expected that the concentration of most elements in this homogeneous sample of shrimp tissue would be determined with a sufficient degree of accuracy. Such a material would enable chemists working in the field of trace element determination in marine animals to check the validity of their results in particular when they apply new methods of analysis.

2. Scope of the intercomparison

Each participating laboratory received a sample of lyophilised shrimp tissue accompanied by an information sheet and a report form. Participants were requested to determine as many as they could from among the following 15 elements: Ag, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, V and Zn. The IAEA, however, expressed its interest in receiving results for any other element(s) which participating laboratories would be willing to determine.

This material was, indeed, used in the framework of two laboratory intercomparisons running simultaneously:

(1) a worldwide intercomparison, called MA-A-3/TM, in which a large number of samples of this material was distributed to laboratories located in many countries in the world.

(2) a regional intercomparison organized in the framework of the MEDPOL-Phase II programme of UNEP and restricted to laboratories located in Mediterranean countries. This intercomparison was named MA(S)MED86/TM.

It appears from recent MEDPOL intercomparisons that the quality of results is, nowadays, about the same for both groups of laboratories (5). It was decided, therefore, to combine the results of the two exercises. By proceeding in this way, more results could be available, which should increase the quality of data evaluation from the statistical point-of-view.

By the end of February 1987, 51 laboratories (out of 75) participating in the worldwide intercomparison and 10 laboratories (out of 32) participating in the MEDPOL intercomparison reported their results. In order to avoid an excessive lag through these laboratories being slow to furnish all the results of this intercomparison, it was decided to issue a provisional report on the basis of the results which were received by the end of February 1987. This procedure could enable the laboratories which have already analysed this material to compare their results with those from other laboratories. It is not possible, however, to recommend definitive consensus values for the concentrations of trace elements in this sample. These values will be established only when all results from participating laboratories are available, i.e. when the definitive report on this intercomparison is established.

3. Description of the material

About 200 Kg of deep-frozen shrimps (Penaeus duorarum) imported from Senegal were collected from a local supplier. Each animal was treated in the following way: the abdomen was separated from the cephalothorax which was discarded. The cuticle was removed and only the muscle was retained. Then, soft tissues were frozen and lyophilised.

Lyophilised tissues were first ground in a mixer made of stainless steel and glass only. Then, the coarse powder which was obtained in this way was ground in a porcelain ball mill. The resulting powder was sieved through a 150 µm stainless steel sieve. Only the fraction of the material passing through the sieve was kept.

Homogenization was performed by mixing the entire quantity of powder having a particle size < 150 µm in a stainless steel rotating drum for one week. Then, aliquots of about 25g were packed into glass bottles with plastic screw caps. These bottles were labelled MA-A-3/TM in the case of the worldwide intercomparison, and MA(s)MED86/TM in the case of the MEDPOL intercomparison.

The homogeneity of the material for trace elements was checked by determining the concentrations of some typical trace elements (Zn, Cd, Cu and V) in ten 500 mg-samples taken randomly in the bulk of the powder. The samples were mineralized by wet ashing with nitric acid and perchloric acid. Zinc was determined by flame atomic absorption spectroscopy while the graphite furnace technique was applied to the determination of Cd, Cu and V. Each sample solution was measured 10 times. A one-way variance analysis showed that the variance between samples could be explained by the analytical variance for each element determined. This material was, therefore, considered as homogeneous (at least for a sample weight > 500 mg).

The water content of the lyophilised material as determined by drying to a constant weight at 85°C was found to be 7.3%. Since, however, the moisture content may change with the ambient humidity and temperature, it was recommended that the water content of this material always be determined in a separate sub-sample (not that taken for analysis) by drying for 48 hours at 85°C.

All results were to be reported on a dry-weight basis.

4. Evaluation of results

The data provided by laboratories participating in this intercomparison are presented in Tables 1-13. All results relevant to a given element are grouped in the same table. Only results for trace elements, the determination of which was requested, were reported. Results for additional elements as well as for Ag and Sb, for which not enough data were available, will be reported in the final report on this intercomparison.

The terms used in the tables are defined as follows:

Unit: Units in which the concentration of an element to be determined is expressed. In this intercomparison, all results are expressed in $\mu g.g^{-1}$ (micrograms per gram) or $ng.g^{-1}$ (nanograms per gram) of dry-weight.

Laboratory Code No.: Each laboratory was represented by a code number, which remains unchanged throughout the tables. The numbers, however, do not correspond to the sequence of laboratories in the list of participants given at the end of this report, so that anonymity is preserved. When a laboratory has used two different analytical procedures for the determination of the same element, the results are distinguished as different sets of data by the capital letter A or B added to the code number. The same procedure was applied when the same method for element determination was used in both cases, following different methods of sample pretreatment (e.g., dry ashing and wet ashing).

Method: Participating laboratories were requested to give basic information on the analytical methods which they applied to the determination of trace elements. These methods are described in the tables by a code, namely:

I - NAA:	Neutron activation analysis (instrumental)
R - NAA:	" " " (with radiochemical separations)
AAS:	atomic absorption spectroscopy (without specification)
Flame-AAS	" " " (flame technique)
GF-AAS:	" " " (graphite-furnace technique)
Hydride-AAS:	" " " (hydride generation technique)
CV-AAS	" " " (cold-vapour technique)
AES:	atomic emission spectroscopy (without specification)
ICP-AES:	inductively coupled plasma atomic emission spectroscopy
DCP-AES:	direct current plasma atomic emission spectroscopy
XRF:	X-ray fluorescence
PIXE:	particle-induced X-ray emission
ASV:	polarography or anodic stripping voltammetry
SP:	spectrophotometry, colorimetry

No. of determinations: The number of individual determinations of a given trace element, performed by a laboratory using the same analytical procedure.

Laboratory mean: The arithmetic mean computed from all individual results supplied by a laboratory for the determination of a given trace element.

Coefficient of variation: The ratio (expressed in percent) of the standard deviation of the individual results of determination of a given trace element to the laboratory mean (the standard deviation is computed in the usual way). The coefficient of variation was not computed when less than 3 individual results were reported.

5. Discussion

As already mentioned, the purpose of this preliminary report is to give to participants who reported their results before March 1987 an opportunity to compare data from other laboratories with their own results. The comparison of results given by different methods as well as the establishment of "certified consensus values" were not attempted in the framework of this preliminary study. This will be done with the complete data treatment and the establishment of the final report.

Provisional "consensus values" for the concentrations of some elements, however, were computed on the basis of the data which were available. No sophisticated test of outlier elimination was used for that purpose, but the following procedure was applied when computing the overall means of the results of trace element determinations. This procedure aimed to remove the influence of doubtful values on the overall mean (these values correspond to a probability level < 0.05 if one considers the set of laboratory means reported for the same element as normally distributed).

(1) Laboratory means given in the form "less than" were not used in the computation of the overall mean and were removed from the set of data.

(2) The arithmetical mean ($\bar{x}_o$) and the standard deviation (S_o) of the remaining laboratory means were computed in the usual way.

(3) Student's factor t_o corresponding to a 0.05 probability level and to the number of results under survey was determined from statistical tables.

(4) The interval $(\bar{x}_o - t_o S_o, \bar{x}_o + t_o S_o)$ was determined.

(5) All laboratory means lying outside this interval were removed from the set of original data.

(6) A new arithmetical mean ($\bar{x}$) and a new standard deviation (S) were computed from the set of the remaining data (n values).

(7) The standard error $S/\sqrt{n}$ was calculated.

(8) Student's factor t corresponding to a 0.05 significance level and to (n - 1) degrees of freedom was determined from statistical tables.

(9) The confidence interval of the overall mean was computed in the usual way, i.e.:

$$\bar{x} - t.S/\sqrt{n} < \mu < \bar{x} + t.S/\sqrt{n}$$

where: μ = theoretical mean of the distribution of results (μ was taken as the "provisional consensus value").

Provisional consensus values are given in Table 14 for ten elements. These values are not certified and should only be considered as estimates of the most probable concentrations of these elements in this material at the present stage of this intercomparison.

No provisional consensus value is given when less than 15 "accepted" results are available, or in the case where the computed error $t.S/\sqrt{n}$ exceeds 50% of the value of the overall mean $\bar{x}$.

In general, results given in Tables 1 - 13 are well grouped, particularly in the case of those elements for which it was possible to derive provisional consensus values. One can, therefore, already say that the quality of results reported by the laboratories participating in this intercomparison is good on the whole. Hence one can expect that the certification of the elements As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Se and Zn will be possible in the case of this shrimp sample, as well as that of additional elements.

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Table 1
Results of intercomparison for arsenic

Unit: Microgram/gram (dry-weight)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
4	R-NAA	3	30.1	5.8%
5	I-NAA	4	28.0	4.2%
6	I-NAA	6	28.3	4.8%
7	ICP-AES	5	29.6	2.9%
11	XRF	-	<1.0	-
14	PIXE	3	32.0	3.1%
18	Hydride-AAS	4	2.30	8.7%
19	Hydride-AAS	4	27.6	4.0%
23	GF-AAS	6	15.9	4.7%
25	Hydride-AAS	6	32.3	3.3%
28	ICP-AES	6	34.3	1.1%
30	ICP-AES	6	32.9	2.3%
36	I-NAA	6	24.0	3.4%
40	Hydride-AAS	3	3.08	9.2%
44	Hydride-AAS	3	4.37	10.3%
45	Hydride-AAS	6	31.8	1.6%
46	GF-AAS	6	31.8	3.7%
54	GF-AAS	6	20.7	5.2%
56	SP	6	21.3	7.4%
59	R-NAA	6	31.5	7.5%
60	GF-AAS	-	<4.0	-

Table 2

Results of intercomparison for cadmium

Unit: Microgram/gram (dry weight)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	AAS	-	<0.06	-
2A	Flame-AAS	2	0.68	-
2B	Flame-AAS	2	0.68	-
4	R-NAA	-	<10.0	-
7	ICP-AES	5	0.56	12.3%
10	GF-AAS	4	0.56	10.5%
11	AAS	-	<0.50	-
12	GF-AAS	-	<0.01	-
14	PIXE	-	<50.0	-
17	DCP-AES	6	0.64	3.7%
19	Flame-AAS	3	0.54	1.9%
20	AAS	3	2.16	12.4%
21	AAS	6	0.68	3.0%
22	Flame-AAS	6	0.55	13.2%
23	GF-AAS	6	0.49	4.4%
24	GF-AAS	4	0.36	5.3%
28	ICP-AES	-	<0.20	-
29	Flame-AAS	6	0.13	12.2%
30	GF-AAS	5	0.86	5.3%
31	ICP-AES	3	0.39	6.8%
32	GF-AAS	5	0.95	4.1%
33	Flame-AAS	6	0.75	10.6%
34	GF-AAS	4	0.56	12.2%
36	I-NAA	-	<19.0	-
38	ASV	6	0.61	6.0%
39	GF-AAS	3	0.64	5.5%
40	GF-AAS	3	0.47	10.8%

Table 2 (continued)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
41	GF-AAS	6	0.48	5.1%
44	GF-AAS	3	0.61	26.8%
46	GF-AAS	6	0.50	3.3%
48A	GF-AAS	1	0.58	-
48B	GF-AAS	1	0.68	-
51	GF-AAS	6	0.93	1.5%
52	GF-AAS	5	0.72	12.4%
53	GF-AAS	3	0.68	8.4%
54	GF-AAS	6	0.31	9.4%
55	GF-AAS	6	1.03	7.7%
56	GF-AAS	6	0.78	5.4%
57	GF-AAS	6	0.74	13.3%
58	ASV	6	0.35	8.8%
59	R-NAA	5	0.65	4.2%
60	GF-AAS	4	1.04	3.2%
61	GF-AAS	6	0.78	4.6%

Table 3

Results of intercomparison for cobalt

Unit: Nanogram/gram (dry weight)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	AAS	-	<300.0	-
4	R-NAA	-	<6900.0	-
5	I-NAA	4	56.0	17.2%
8	I-NAA	5	63.4	17.1%
9	I-NAA	6	48.8	4.0%
10	GF-AAS	-	<50.0	-
11A	AAS	6	750.0	7.3%
11B	XRF	-	<100.0	-
14	PIXE	-	<5000.0	-
17	DCP-AES	6	118.5	3.4%
18	AAS	-	<1000.0	-
20	AAS	3	616.7	42.7%
26	I-NAA	5	60.0	20.4%
27	GF-AAS	6	593.3	6.4%
29	Flame-AAS	6	201.7	3.7%
30	GF-AAS	-	<80.0	-
31	ICP-AES	-	<100.0	-
33	Flame-AAS	6	550.0	29.9%
36	I-NAA	6	40.7	14.6%
37	I-NAA	4	101.0	26.7%
40	GF-AAS	3	46.7	12.4%
42	I-NAA	5	44.8	28.9%
54	GF-AAS	-	<1500.0	-
59	I-NAA	4	65.5	15.1%
60	GF-AAS	-	<200.0	-

Table 4

Results of intercomparison for chromium

Unit: Microgram/gram (dry-weight)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	AAS	-	<0.15	-
2A	GF-AAS	2	0.45	-
2B	GF-AAS	2	0.46	-
4	R-NAA	-	<11.0	-
5	I-NAA	4	0.72	27.4%
6	I-NAA	6	0.58	39.3%
7	ICP-AES	5	0.75	3.2%
8	I-NAA	5	0.66	12.0%
9	I-NAA	6	0.46	5.7%
11A	AAS	6	0.95	5.8%
11B	XRF	-	<1.5	-
12	GF-AAS	3	1.16	3.8%
14	PIXE	-	<1.0	-
16	Flame-AAS	6	1.88	6.6%
17	DCP-AES	6	0.96	27.6%
20	AAS	3	4.17	117.8%
22	Flame-AAS	-	<1.4	-
23	GF-AAS	6	1.78	26.1%
26	I-NAA	4	1.47	10.6%
27	GF-AAS	6	2.43	12.1%
29	Flame-AAS	6	2.20	7.0%
30	GF-AAS	6	0.77	7.5%
31	ICP-AES	3	0.42	4.8%
33	Flame-AAS	-	.<0.25	-
40	GF-AAS	3	1.45	8.7%
42	I-NAA	5	0.36	8.5%
44	GF-AAS	3	9.60	14.5%

Table 4 (continued)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
46	GF-AAS	6	0.29	16.8%
54	GF-AAS	6	0.53	6.5%
55	GF-AAS	6	0.71	81.9%
56	GF-AAS	6	2.65	11.7%
57	GF-AAS	6	0.79	5.2%
59	I-NAA	4	0.51	23.3%
60	GF-AAS	4	0.43	7.9%

Table 5

Results of intercomparison for copper

Unit: Microgram/gram (dry-weight)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	ICP-AES	6	21.5	6.4%
2A	Flame-AAS	2	20.0	-
2B	Flame-AAS	1	23.8	-
4	R-NAA	3	24.3	7.3%
7	ICP-AES	5	24.3	0.9%
10	Flame-AAS	4	21.9	0.4%
11A	AAS	6	37.5	1.5%
11B	XRF	3	26.5	3.9%
13	R-NAA	6	21.9	10.9%
14	PIXE	3	23.3	6.5%
15	Flame-AAS	6	19.4	1.8%
16	Flame-AAS	6	26.8	1.1%
17	DCP-AES	6	23.1	1.6%
18	AAS	6	24.7	8.0%
19	Flame AAS	3	22.8	5.8%
20	AAS	3	9.5	45.8%
21	AAS	6	20.3	5.2%
22	Flame-AAS	6	22.7	2.3%
23	Flame-AAS	6	20.9	1.8%
24	GF-AAS	6	20.6	1.9%
25	Flame-AAS	4	23.0	6.1%
26	I-NAA	5	60.0	36.3%
27	GF-AAS	6	18.5	3.0%
28	ICP-AES	6	22.6	2.1%
29	Flame-AAS	6	20.5	5.0%
30	ICP-AES	6	25.4	2.0%
31	ICP-AES	3	22.0	4.5%

Table 5 (continued)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
32	Flame-AAS	5	23.0	2.2%
33	Flame-AAS	6	18.5	2.0%
34	GF-AAS	5	22.4	5.6%
35	Flame-AAS	6	23.7	8.3%
36	I-NAA	-	<89.0	-
40	ICP-AES	3	23.2	3.8%
43	AAS/AES	1	22.4	-
44	GF-AAS	3	16.3	7.9%
46	GF-AAS	6	20.2	8.9%
48A	GF-AAS	1	20.1	-
48B	GF-AAS	1	20.6	-
49	Flame-AAS	1	17.7	-
50A	Flame-AAS	4	21.9	5.5%
50B	Flame-AAS	4	21.2	3.0%
51	GF-AAS	6	21.7	1.1%
52	GF-AAS	4	29.3	1.7%
53	Flame-AAS	3	23.4	0.7%
54	Flame-AAS	6	22.0	0.0%
56	GF-AAS	6	21.8	7.6%
57	GF-AAS	6	21.1	6.1%
58	ASV	6	21.2	5.1%
59	R-NAA	6	21.6	7.7%
60	GF-AAS	4	21.7	1.3%
61	Flame-AAS	6	19.9	1.7%

Table 6

Results of intercomparison for iron

Unit: Microgram/gram (dry-weight)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	AAS	6	41.7	5.6%
2A	Flame-AAS	2	58.1	-
2B	Flame-AAS	1	59.5	-
4	R-NAA	-	<2000.0	-
5	I-NAA	4	48.0	10.6%
6	I-NAA	6	61.6	8.2%
7	ICP-AES	5	64.0	6.0%
8	I-NAA	5	70.4	5.5%
9	I-NAA	6	58.0	2.7%
10	Flame-AAS	4	58.9	0.5%
11A	AAS	6	47.3	0.9%
11B	XRF	3	52.3	9.2%
12	Flame-AAS	3	54.1	5.6%
14	PIXE	3	34.7	13.0%
15	Flame-AAS	6	48.4	3.6%
17	DCP-AES	6	58.6	2.2%
19	Flame-AAS	3	58.6	2.4%
20	AAS	3	58.8	15.2%
21	AAS	6	60.8	4.3%
22	Flame-AAS	6	46.7	5.9%
23	Flame-AAS	6	52.1	8.1%
24	GF-AAS	5	54.9	4.2%
25	Flame-AAS	4	64.7	12.4%
26	I-NAA	4	39.0	19.3%
27	GF-AAS	5	140.6	14.0%
28	ICP-AES	6	41.6	5.0%
29	Flame-AAS	6	64.6	2.3%

Table 6 (continued)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
30	ICP-AES	5	60.2	2.5%
31	ICP-AES	3	56.0	1.8%
35	Flame-AAS	6	54.9	9.4%
36	I-NAA	6	54.2	10.6%
37	I-NAA	4	85.7	14.5%
40	ICP-AES	3	60.3	1.3%
42	I-NAA	5	82.3	19.3%
43	AAS/AES	1	52.4	-
46	GF-AAS	6	48.9	10.0%
50A	Flame-AAS	4	53.4	5.2%
50B	Flame-AAS	4	47.6	6.9%
54	Flame-AAS	6	49.2	3.7%
59	I-NAA	4	54.9	5.8%
60	GF-AAS	4	64.2	3.8%

Table 7

Results of intercomparison for mercury

Unit: Microgram/gram (dry-weight)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
2	CV-AAS	2	0.07	-
3	CV-AAS	5	1.57	1.6%
4	R-NAA	-	<1.0	-
8	I-NAA	5	2.70	5.9%
11	XRF	-	<1.0	-
12	CV-AAS	3	3.03	9.9%
13	R-NAA	6	1.32	4.4%
14	PIXE	-	<3.0	-
16	CV-AAS	6	1.90	0.9%
18	CV-AAS	4	1.11	3.1%
19	CV-AAS	3	1.92	0.5%
22	CV-AAS	6	1.88	2.9%
23	CV-AAS	6	1.96	2.2%
26	I-NAA	4	0.30	8.2%
29	CV-AAS	6	1.39	4.8%
30	CV-AAS	5	2.00	2.1%
31	CV-AAS	3	1.70	5.9%
36	I-NAA	6	13.0	5.2%
38	CV-AAS	6	1.87	2.3%
39	CV-AAS	3	1.60	2.2%
40	CV-AAS	3	1.85	6.0%
42	R-NAA	5	0.42	14.4%
44	CV-AAS	3	1.93	13.0%
49	CV-AAS	1	1.42	-
50A	CV-AAS	3	1.86	4.2%
50B	CV-AAS	3	2.13	6.2%

Table 7 (continued)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
51	CV-AAS	6	2.75	3.2%
52	CV-AAS	6	2.51	3.5%
53	CV-AAS	3	2.09	2.5%
54	CV-AAS	6	2.27	5.3%
55	CV-AAS	6	1.48	9.0%
56	CV-AAS	6	2.00	5.7%
57	CV-AAS	6	2.10	2.4%
58	CV-AAS	6	2.58	1.5%
59	R-NAA	6	1.90	4.9%
60	AAS	4	1.78	5.6%

Table 8

Results of intercomparison for manganese

Unit: Microgram/gram (dry-weight)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	ICP-AES	6	3.67	22.3%
2A	Flame-AAS	2	3.38	-
2B	Flame-AAS	2	4.14	-
4	R-NAA	3	5.55	6.3%
6	I-NAA	5	3.34	7.0%
7	ICP-AES	5	4.00	2.5%
9	I-NAA	6	3.72	5.2%
10	Flame-AAS	4	3.82	0.4%
11A	AAS	6	2.20	19.9%
11B	XRF	-	<4.0	-
14	PIXE	3	3.73	8.2%
15	Flame-AAS	6	3.34	5.2%
16	Flame-AAS	6	2.74	15.3%
17	DCP-AES	6	4.37	2.9%
19	Flame-AAS	3	4.33	1.3%
20	AAS	3	5.41	4.8%
21	AAS	6	3.83	19.6%
22	Flame-AAS	6	3.85	2.2%
23	Flame-AAS	6	3.23	7.9%
24	GF-AAS	5	4.23	6.3%
26	I-NAA	6	4.99	15.6%
27	GF-AAS	4	5.53	8.3%
28	ICP-AES	6	3.32	2.3%
29	Flame-AAS	6	3.90	2.3%
30	ICP-AES	6	4.41	0.9%
31	ICP-AES	3	3.20	6.3%
33	Flame-AAS	6	4.43	2.6%

Table 8 (continued)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
34	GF-AAS	4	7.14	5.3%
35	Flame-AAS	6	3.59	6.8%
36	I-NAA	-	<11.3	-
40	ICP-AES	3	4.46	5.7%
42	I-NAA	5	4.84	19.5%
43	AAS/AES	1	3.96	-
44	Flame-AAS	3	0.70	0.0%
45	GF-AAS	6	11.0	11.1%
46	GF-AAS	6	3.43	10.0%
47	I-NAA	6	3.99	5.0%
50A	Flame-AAS	4	4.04	2.3%
50B	Flame-AAS	4	3.36	5.4%
54	Flame-AAS	6	4.00	0.0%
59	R-NAA	6	3.82	1.7%
60	GF-AAS	4	3.76	4.0%

Table 9

Results of intercomparison for nickel

Unit: Microgram/gram (dry-weight)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	AAS	-	<0.03	-
2A	Flame-AAS	2	3.03	-
2B	Flame-AAS	2	2.38	-
4	R-NAA	-	<17.0	-
7	ICP-AES	5	1.72	4.9%
10	GF-AAS	4	0.56	6.2%
11A	AAS	6	2.53	20.4%
11B	XRF	-	<1.0	-
14	PIXE	-	<2.0	-
17	DCP-AES	6	0.62	20.4%
18	AAS	-	<5.0	-
19	Flame-AAS	3	0.55	9.9%
20	AAS	3	0.57	30.7%
22	Flame-AAS	-	<1.3	-
23	GF-AAS	6	0.80	24.0%
24	GF-AAS	4	0.59	4.2%
27	GF-AAS	6	2.13	7.7%
29	Flame-AAS	6	0.38	8.5%
30	ICP-AES	5	3.54	3.1%
31	ICP-AES	3	0.40	2.5%
33	Flame-AAS	6	1.24	42.4%
40	GF-AAS	3	0.67	8.7%
44	GF-AAS	3	2.33	40.7%
46	GF-AAS	5	0.72	2.9%
54	Flame-AAS	6	3.67	14.1%
60	GF-AAS	-	<0.8	-

Table 10

Results of intercomparison for lead

Unit: Microgram/gram (dry-weight)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
2A	Flame-AAS	2	2.81	-
2B	Flame-AAS	1	2.63	-
11A	AAS	6	1.93	5.3%
11B	XRF	3	15.1	5.3%
12	GF-AAS	-	<0.01	-
14	PIXE	-	<3.0	-
16	Flame-AAS	6	0.38	13.6%
17	DCP-AES	6	0.33	7.5%
19	Flame-AAS	3	0.13	7.7%
20	AAS	3	0.88	43.9%
22	Flame-AAS	-	<1.7	-
23	GF-AAS	6	0.51	24.5%
29	Flame-AAS	6	2.12	10.5%
31	ICP-AES	3	0.36	11.3%
32	GF-AAS	5	4.95	4.2%
33	Flame-AAS	-	<0.50	-
34	GF-AAS	4	0.14	7.7%
38	ASV	-	<1.0	-
39	GF-AAS	3	0.54	7.4%
40	GF-AAS	3	0.30	33.3%
41	GF-AAS	6	0.20	11.5%
44	GF-AAS	-	<0.30	-
45	GF-AAS	6	41.9	2.5%

Table 10 (continued)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
46	GF-AAS	-	<0.15	-
51	GF-AAS	6	0.82	7.2%
53	GF-AAS	-	<0.24	-
54	GF-AAS	6	0.71	2.5%
55	GF-AAS	6	0.86	32.9%
56	GF-AAS	6	0.81	10.6%
57	GF-AAS	6	0.41	9.9%
58	ASV	1	0.53	-
60	GF-AAS	-	<0.10	-

Table 11

Results of intercomparison for selenium

Unit: Microgram/gram (dry-weight)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
4	R-NAA	-	<23.0	-
5	I-NAA	4	1.88	8.7%
6	I-NAA	6	1.74	7.9%
7	ICP-AES	5	2.80	23.1%
8	I-NAA	5	2.12	2.1%
9	I-NAA	6	1.82	4.8%
11	XRF	-	<2.0	-
12	Hydride-AAS	3	3.59	42.0%
14	PIXE	1	1.60	-
26	I-NAA	5	1.95	12.1%
36	I-NAA	6	1.54	10.2%
41	GF-AAS	6	1.76	5.1%
42	R-NAA	5	3.65	11.8%
45	Hydride-AAS	6	0.38	4.2%
46	GF-AAS	6	1.66	5.4%
47	I-NAA	6	1.91	10.0%
54	GF-AAS	6	10.8	13.2%
59A	I-NAA	4	2.05	8.5%
59B	R-NAA	6	1.90	4.8%
60	GF-AAS	-	<15.0	-

Table 12

Results of intercomparison for vanadium

Unit: Microgram/gram (dry-weight)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
1	AAS	-	<0.75	-
2A	GF-AAS	2	0.45	-
2B	GF-AAS	2	0.67	-
11	AAS	-	<4.0	-
14	PIXE	-	<1.0	-
17	DCP-AES	6	0.16	11.5%
26	I-NAA	4	0.40	17.2%
31	ICP-AES	3	0.18	5.6%
40	GF-AAS	3	0.37	41.7%
47	I-NAA	6	0.16	10.9%
48A	GF-AAS	1	0.80	-
48B	GF-AAS	1	0.83	-
59	R-NAA	4	0.11	3.7%
60	GF-AAS	4	1.18	9.8%
61	GF-AAS	6	15.7	1.4%

Table 13

Results of intercomparison for zinc

Unit: Microgram/gram (dry-weight)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
2	Flame-AAS	2	79.9	-
4	R-NAA	3	107.4	16.2%
5	I-NAA	4	69.0	3.8%
6	I-NAA	6	63.8	5.5%
7	ICP-AES	5	66.9	2.1%
8	I-NAA	5	69.2	2.3%
9	I-NAA	6	64.8	3.6%
10	Flame-AAS	4	73.1	0.3%
11A	AAS	6	46.1	1.8%
11B	XRF	3	54.2	1.7%
12	Flame-AAS	3	59.0	0.4%
13	R-NAA	6	61.8	6.6%
14	PIXE	3	61.3	0.9%
15	Flame-AAS	6	65.1	1.1%
16	Flame-AAS	6	76.9	2.7%
17	DCP-AES	6	74.6	1.7%
18	AAS	6	69.2	7.8%
19	Flame-AAS	3	73.1	3.9%
20	AAS	3	47.4	30.7%
21	AAS	6	69.3	2.5%
22	Flame-AAS	6	67.2	1.5%
23	Flame-AAS	6	71.6	2.8%
24	Flame-AAS	6	69.4	3.1%
25	Flame-AAS	4	70.5	4.4%
26	I-NAA	5	43.4	15.5%

Table 13 (continued)

Laboratory Code No.	Method	No. of Determinations	Laboratory Mean	Coefficient of Variation
27	Flame-AAS	6	131.8	5.6%
28	ICP-AES	6	56.9	1.2%
29	Flame-AAS	6	66.7	2.7%
30	ICP-AES	6	48.4	4.8%
31	ICP-AES	3	64.7	7.0%
32	Flame-AAS	5	61.3	3.1%
33	Flame-AAS	6	1.02	5.7%
35	Flame-AAS	6	64.6	5.2%
36	I-NAA	6	59.7	7.0%
40	Flame-AAS	3	64.9	0.4%
42	I-NAA	5	73.1	9.1%
43	AAS/AES	1	67.6	-
44	Flame-AAS	3	76.0	6.0%
46	GF-AAS	6	61.0	3.1%
49	Flame-AAS	1	62.8	-
50A	Flame-AAS	4	68.4	6.6%
50B	Flame-AAS	4	61.5	5.8%
51	Flame-AAS	6	66.2	2.0%
53	Flame-AAS	3	74.5	1.5%
54	Flame-AAS	6	65.6	1.0%
56	Flame-AAS	6	86.0	2.5%
57	Flame-AAS	6	77.8	4.6%
58	ASV	6	65.0	6.7%
59A	I-NAA	4	67.8	6.7%
59B	R-NAA	3	59.5	8.4%
60	Flame-AAS	4	67.3	0.9%

Table 14

Provisional consensus values for the concentrations of some elements (not certified)

Element	Number of Accepted Results	Concentration* ± confidence interval
As	19	24.3±5.1
Cd	35	0.63±0.07
Cr	27	1.11±0.36
Cu	47	22.0±0.7
Fe	39	55.9±3.3
Hg	32	1.79±0.24
Mn	38	4.03±0.29
Ni	19	1.50±0.55
Se	16	2.02±0.42
Zn	48	65.7±2.5

*All values are expressed in $\mu g.g^{-1}$ of dry weight.

Confidence intervals are given for a significance level $\alpha = 0.05$

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