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REPORT OF THE SECOND ICES INTERCOMPARISON EXERCISE ON THE DETERMINATION OF TRACE METALS IN SUSPENDED PARTICULATE MATTER

by

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INTRODUCTION

At its meeting in Copenhagen in 1987, the ICES Working Group on Marine Sediments in Relation to Pollution (WGMS) decided to distribute a questionnaire to determine how many laboratories would be interested in participating in an intercomparison exercise on the determination of trace metals in small amounts of suspended matter. According to the responses to the questionnaire, 60 laboratories were interested in participating in such an intercomparison exercise, although several of them expressed conditions for their participation. Later, a further five laboratories expressed interest in participating.

At the WGMS meeting in Savannah in 1989, it was agreed to carry out the first phase of a sequence of intercomparison exercises on the determination of trace metals in suspended particulate matter. Jens Skei, on behalf of the Norwegian Institute of Water Research, accepted the invitation to organize this first phase of the intercomparison exercise.

The laboratories were asked to perform a preliminary exercise using their own standard reference material, certified for trace metals, or any other well-characterized material. They should weigh out a minimum of three sub-samples in the range 1 - 5 mg, and analyze them for the metals for which certified values exist. Once the laboratory had achieved the ability to analyze such small samples, they should notify the coordinator and request the intercomparison material. The deadline for this preliminary exercise was set at 30 June 1989.

PARTICIPATION

The coordinator received positive responses from 29 laboratories, who requested the test samples to participate in the intercomparison exercise. The requests originated from laboratories in Belgium (4), Canada (4), Denmark (2), Finland (1), Færoe Islands (1), France (6), the Federal Republic of Germany (2), the Netherlands (1), Norway (1), Poland (1), Portugal (1), Spain (1), the United Kingdom (2), and the USA (2). On 26 September 1989, the three samples in plastic vials were mailed to the participants along with the guidelines for their analysis.

The initial deadline for receipt of the results by the coordinator was 31 December 1989, but this was later extended to 1 March 1990. In January 1990, the coordinator sent a letter to the participants who had not forwarded results reminding them of the deadline and asking them to confirm that they still intended to submit data for the exercise.

Final results were received from 19 laboratories (Annex 1) located in Belgium (3), Canada (1), Finland (1), France (6), the Federal Republic of Germany (1), the Netherlands (1), Norway (1), Poland (1), Spain (1), the United Kingdom (1), and the USA (2).

A preliminary presentation of the initial statistical analyses of the data was made at the WGMS meeting in Lisbon in April 1990, and a final draft report was presented at the WGMS meeting in Copenhagen in March 1991. This report presents the final results of this intercomparison exercise.

SCOPE OF THE EXERCISE

Studies of particulate matter in sea water involve water sampling, filtration or centrifugation (particulate matter recovery), and chemical analyses. The scope of this intercomparison exercise was defined as the analytical exercise, and the objective was to evaluate the capabilities of the laboratories to analyze small sediment samples (1 - 5 mg) accurately and precisely. The exercise was designed to evaluate the suitability of total digestion of small amounts of marine sediments, and to assess comparability of analytical results among laboratories in ICES member countries.

SAMPLES

As test samples it was decided to use three standard reference materials with certified values for trace metals. Because there is no available material made from suspended matter, three marine sediments were purchased from the National Research Council of Canada:

Sample A	PACS-1
Sample B	MESS-1
Sample C	BCSS-1

Samples B and C are estuarine sediments with low concentrations of trace metals, while Sample A is more concentrated with respect to the same elements. Approximately 5 mg, 15 mg and 20 mg, respectively, of the Samples A, B and C, were weighed in plastic vials and distributed to the participants, who were asked to analyze three aliquots of each sample: 1 mg aliquots of Sample A, 3 mg of Sample B, and 5 mg of Sample C. Each participant was asked to determine metal concentrations in at least three replicate digests for each sediment sample. A total dissolution method using hydrofluoric acid was recommended (Loring and Rantala, (4)), however, it was not specified whether the microwave or boiling water bomb digestion methods should be used. The participants were asked to analyze the samples for aluminium, iron, cadmium, chromium, copper, lithium, manganese, nickel, lead and zinc.

TREATMENT OF RESULTS

A varying number of results have been received for the different metals, and 10 - 14 laboratories out of 19 have submitted results for the high concentration metals, while 8 - 12 laboratories analyzed the metals present in lower concentrations. Only four laboratories have reported results for lithium. In addition, two laboratories have submitted results for cobalt.

The analytical data received from the participants were transferred to a primary data file on the Nord-CX computer at Norwegian Institute for Water Research, Oslo. For each laboratory, the following statistical parameters were calculated to describe the intra-laboratory variations in the results:

- Number of replicates (n);

- Mean values for each element, sample and laboratory (x). The Dixon test for outliers (2) was applied to exclude deviating results;

- The standard deviation (sd) and the relative standard deviation (rsd) of each mean was calculated for n equal to, or greater than, 3.

To provide information on the inter-laboratory variations of the analytical results, the following statistical parameters were calculated for each sediment sample:

- The grand mean calculated from the individual laboratory means;

- The standard deviation and the relative standard deviation of the grand mean;

- Anomalous results may occur due to a gross error, or they may be a part of the population. Individual means beyond $\pm$ 2.325 x standard deviation of the grand mean were rejected. This procedure was repeated twice, to yield an "excluded mean". The results from one laboratory, using a digestion method known to dissolve less than the total of most metals, were excluded before this calculation;

- The standard deviation and the relative standard deviation of the excluded mean;

- The median value calculated from the individual laboratory means.

A summary of the statistical data is provided in Tables 1 - 11 in Annex 3, and the reader is referred to this for the actual values produced by the computer treatment of the data.

To visualize the comparability of the analytical results, the following graphical illustrations have been produced: The mean value for each laboratory has been plotted in a diagram, with the sd given as limits, and this has been repeated for each element and sample. The true (certified) value is given as the horizontal line in the diagram, while the dotted lines represent the confidence limits of the certified value. Some laboratory means deviating strongly from the true value are not shown in the diagrams.

DIGESTION METHODS USED

It was recommended that the method of Loring and Rantala (4) be used for the total digestion of the sediment samples. This method is based on dissolution of the sample with a mixture of hydrofluoric acid and aqua regia. The information received from the participants about the procedures used clearly indicates that the laboratories preferred to use their own routine method for the preparation of the samples, instead of applying the recommended method. The various dissolution techniques which have been used by the participating laboratories are listed in Annex 2.

With the exception of two laboratories, all participants applied a digestion method involving the use of hydrofluoric acid (HF). Eight out of 19 laboratories used the recommended method, with or without some minor modifications (some laboratories used a microwave oven, while others used heating at 110°C for two hours, etc.). We expect that the methods involving hydrofluoric acid in combination with an oxidizing acid (nitric acid is used in most cases) should be comparable with respect to dissolution effectiveness. Therefore, possible differences resulting from different modifications of HF digestion methods are expected to be very small.

One of the two laboratories not using HF employed a method based on dissolution of the sample with nitric acid only, which is known to dissolve only a certain part of most of the metals in the sediment samples, and the results reported for this method have, therefore, been excluded from the statistical calculations. However, the results from this laboratory (No. 6) are included in the diagrams, and the results for the elements cadmium, lead, and zinc are comparable to the corresponding results where the total digestion method has been used. The results for the other metals are lower than the true values, the deviations varying for the different metals and being greatest for the most strongly bound metals.

The other laboratory employed a method based on a technique where the dissolution step is omitted. With this method, the sample is made up in a slurry with glycerine, and sampled directly into the graphite furnace (3). These results proved to be comparable to the corresponding values of the total dissolution method. However, this technique will probably not work easily with small samples collected on filters.

THE ANALYTICAL RESULTS

Aluminium

Aluminium was determined by only 10 laboratories (12 laboratories determined aluminium in sample C). The results are shown in Figures 1 to 3 and Table 1 (in Annex 3). The intra-laboratory arithmetic mean is lower than the certified value in nearly all data sets, and the grand mean of the results is 6 - 12 % lower than the certified value for each of the three samples. The overall relative standard deviation is 11 - 15 %. The relative standard deviation is greater than 10 % for only five intra-laboratory data sets. Thus, the determination of aluminium is fairly precise, despite the systematic low results.

Two laboratories applied the Inductively Coupled Plasma (ICP) emission technique for the determination of aluminium. The other laboratories determined this metal with atomic absorption spectrometry, of which four laboratories used the graphite furnace technique and the other six nitrous oxide/acetylene flame. There is no evidence that the determination step significantly affects these results.

Note: The footnotes in Tables 1, 2, 6 and 8 of Annex 3 give the sample letter, laboratory number, number of replicates, mean value, standard deviation, and relative standard deviation of results rejected by the Dixon test for outliers.

Iron

For this main component, most of the analytical results are lower than the certified value, the recovery being 94 - 96 % on average, after exclusion of deviating intra-laboratory means. The results using nitric acid digestion are too low, and are excluded from the statistical calculations. The results are shown in Figures 4 to 6 and Table 2.

Most of the laboratories used flame atomic absorption spectrometry for the final determination of iron. Four laboratories used a graphite furnace, of which two applied the Zeeman correction. Only one laboratory used ICP for the determination of this element. There are no significant differences between the results determined by the different methods.

The results for iron illustrate some of the problems associated with the small sample size. The intra-laboratory relative standard deviation is less than 10 % for all laboratories for Sample C. For Sample A, where smaller aliquots have been used for the digestion, four laboratories are outside this limit.

Cadmium

For this metal (see Figures 7 to 9 and Table 3) the recoveries, calculated from the grand mean, are greater than 100 %. The generally high recovery of this element and the high standard deviation of some laboratories indicate that contamination may be a serious problem. Additionally, the low concentration may cause problems at the determination step, because of the low instrument signal/noise ratio. All laboratories used the graphite furnace technique for the final measurement, except for one laboratory using ICP/MS (Mass Spectroscopy).

For this metal, the results of the nitric acid decomposition method are comparable to the corresponding values from the total digestion method.

Chromium

Most of the laboratories used graphite furnace for the atomic absorption determination, while three laboratories used ICP or ICP/MS emission methods. The results determined with ICP/MS (laboratory No. 16) are comparatively high. The results are shown in Figures 10 to 12 and Table 4.

The overall recovery for this metal varies from 77 - 85 %, the lowest recovery observed for the metals analyzed in this exercise. The picture is rather different for the three samples, the intra-laboratory standard deviations being far greater for Sample A than for Sample C, with those for Sample B intermediate. This is probably due to the small aliquots of Sample A digested. At the same time, the inter-laboratory relative standard deviation is high for Samples B and C, because none of the low results have been excluded before the statistical calculations. For Sample C, the relative intra-laboratory standard deviation is less than 10 % for all laboratories except two. Larger sample aliquots obviously improve the precision of the analytical results.

Copper

The results for copper are shown in Figures 13 to 15 and Table 5. The recovery is rather different for the three samples, varying from 84 % in Sample A, to 101 and 97 % in Samples B and C, respectively. The relative standard deviation of the grand mean varies from 11 - 26 %. Only two of the laboratory means lie within the confidence limits of the true value of Sample A, while more than half of the laboratory means of Samples B and C are within the confidence limits. The rather large relative standard deviation indicates that contamination may be a problem for the determination of copper in the small sample aliquots used here.

With the exception of two laboratories using emission techniques (ICP and ICP/MS), the participants applied graphite furnace atomic absorption for the determination, of which five used the Zeeman correction. No significant differences between laboratories using different determination techniques are observed.

Manganese

The results are shown in Figures 16 to 18 and Table 6. The overall recovery for manganese is about 97 %. The overall relative standard deviation of the grand mean varies from 6 to 12 %, which may be regarded as acceptable. Unfortunately, the picture is disturbed by the large relative standard deviations at some of the laboratories, especially for Samples A and B. For Sample C, the precision is much better; this may be due to the larger aliquots being digested for this sample. The footnote in Table 6 gives the sample letter, laboratory number, number of replicates, mean value, standard deviation, and relative standard deviation for the outlier rejected by the Dixon test.

Most laboratories used the graphite furnace method for the determination, but five laboratories used flame atomic absorption for this metal. In most cases, the precision is better at the laboratories using graphite furnace rather than flame. Three laboratories used emission techniques; however, these results are rather variable.

Nickel

The results for Sample A (see Figures 19 to 21 and Table 7) are rather different from the others, as the mean recovery is 118 %. Because there are rather small differences between the nickel concentrations in the three samples, the difference observed may be explained by the small amounts being digested of Sample A. The intra-laboratory precision is generally much better for Samples B and C. The large relative standard deviation observed for Sample A may also indicate that there are problems associated with the determination step when analyzing low nickel concentrations.

Two laboratories used ICP or ICP/MS. The other laboratories used the graphite furnace technique, four of which applied the Zeeman correction.

Lead

The overall recovery for lead varies from 92 - 96 % of the certified value; the greatest deviation from the grand mean is observed for Sample C which contains the lowest lead concentration. The deviation therefore seems, at least in part, to be dependent on the lead concentration in the digested sample. The results are shown in Figures 22 to 24 and Table 8; the footnote in Table 8 gives the sample letter, laboratory number, number of replicates, mean values, standard deviations, and relative standard deviations of data rejected by the Dixon test for outliers.

Except for one laboratory using ICP/MS, all the laboratories applied graphite furnace atomic absorption for the determination. The matrix modification as used by laboratories No. 8 and 13 seems to give a rather varying effect.

Zinc

The overall recovery ranges between 90 - 96 % of the certified value for zinc, the greatest deviation being observed for Sample C in which the zinc concentration in the digested solution is the lowest. In spite of this, the best intra-laboratory precision is obtained for this sample, probably due to the larger aliquots digested. Owing to the quite large intra-laboratory relative standard deviations obtained by many of the laboratories, no participant using a total digestion method was excluded from the statistical calculations. The results for zinc are depicted in Figures 25 to 27 and Table 9.

Two laboratories used emission methods (ICP and ICP/MS) for the determination, half of the remaining laboratories used flame atomic absorption, and the other half applied the graphite furnace technique.

GENERAL

Some of the participating laboratories reported that they did not have any experience with methods for the digestion and analysis of very small samples. Accordingly, these participants emphasized the potential uncertainty of the results they submitted. Some laboratories even informed the coordinator that they would not participate in this intercomparison exercise because of their lack of experience in analyzing small samples. Therefore, when the results are evaluated, it is important to bear in mind the rather variable experience the participants have had in analyzing such small samples. On the other hand, it is reasonable to suppose that most of the participating laboratories are representative of the best of those able to analyze small sediment samples. This is supported by the fact that the overall precision and recovery observed for many of the metals may be regarded as acceptable.

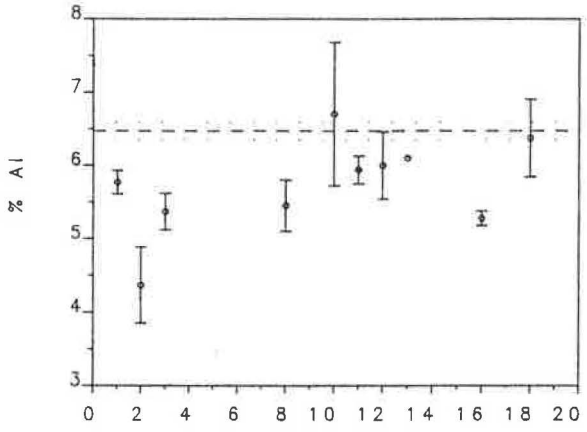

Fig. 1 Results for Al, sample A

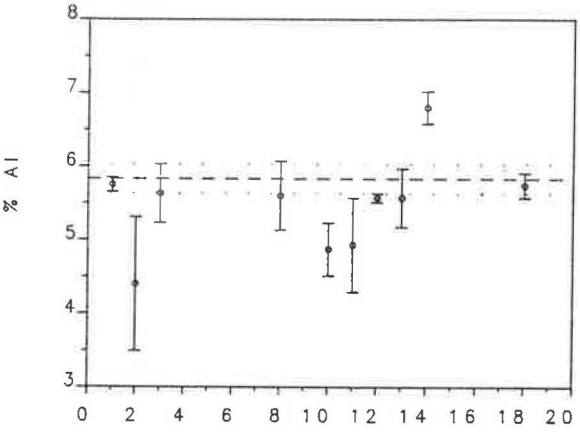

Fig. 2 Results for Al, sample B

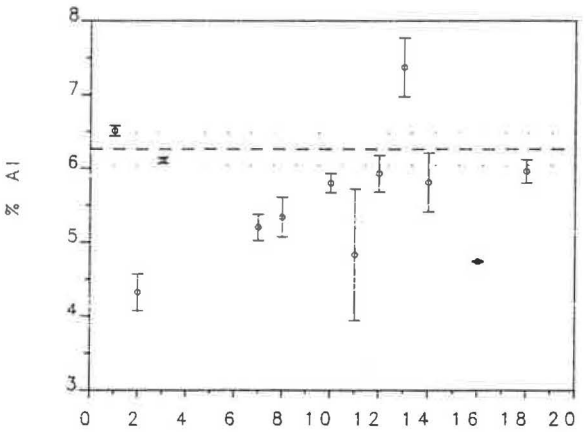

Fig. 3 Results for Al, sample C

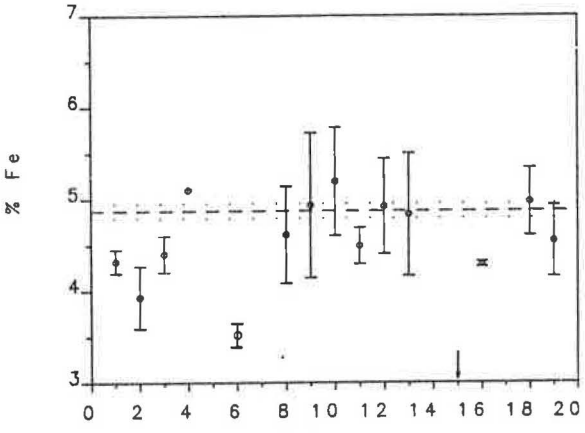

Fig. 4 Results for Fe, sample A

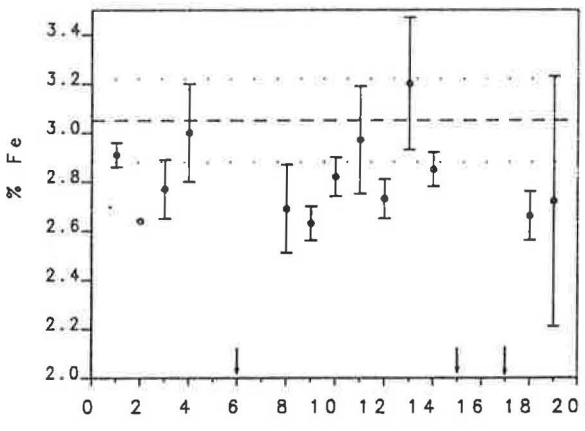

Fig. 5 Results for Fe, sample B

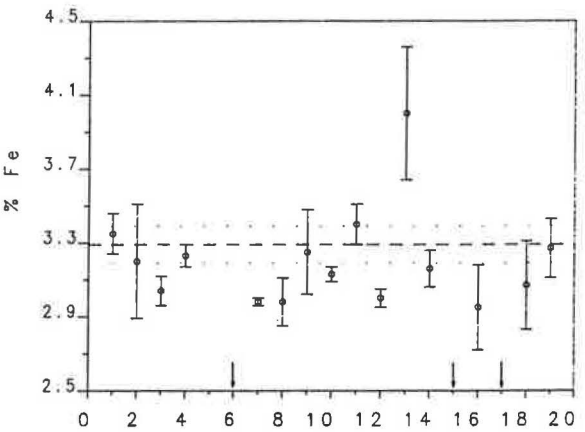

Fig. 6 Results for Fe, sample C

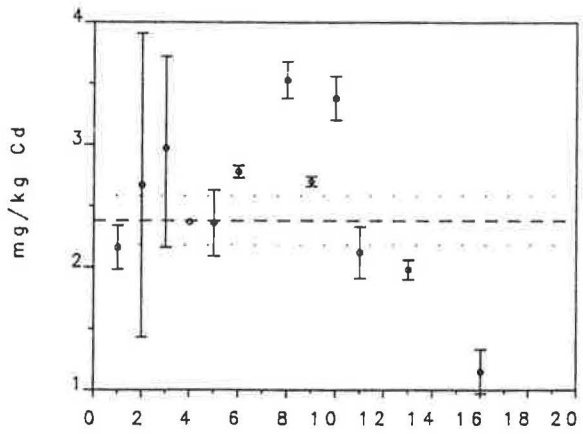

Fig. 7 Results for Cd, sample A

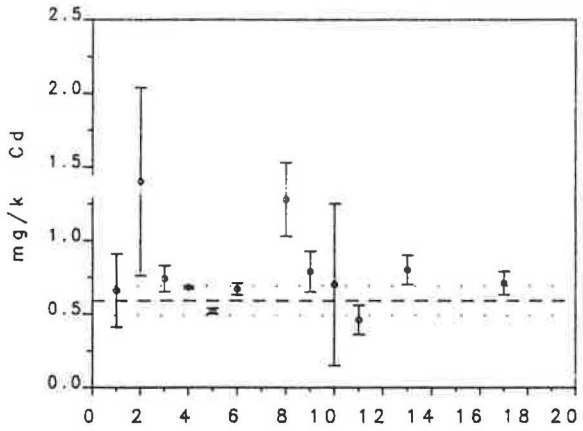

Fig. 8 Results for Cd, sample B

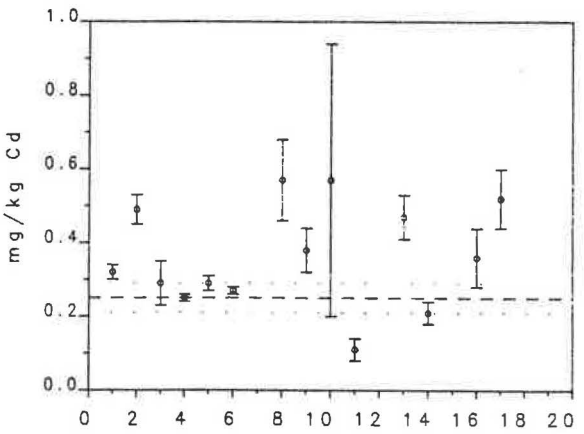

Fig. 9 Results for Cd, sample C

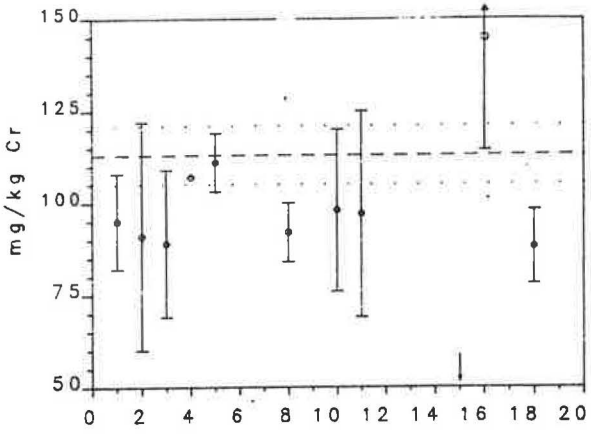

Fig. 10 Results for Cr, sample A

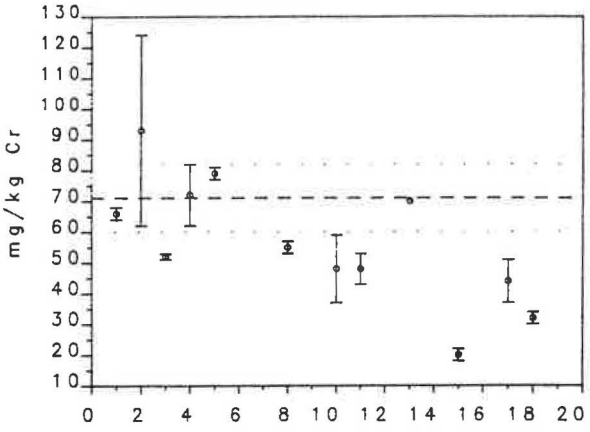

Fig. 11 Results for Cr, sample B

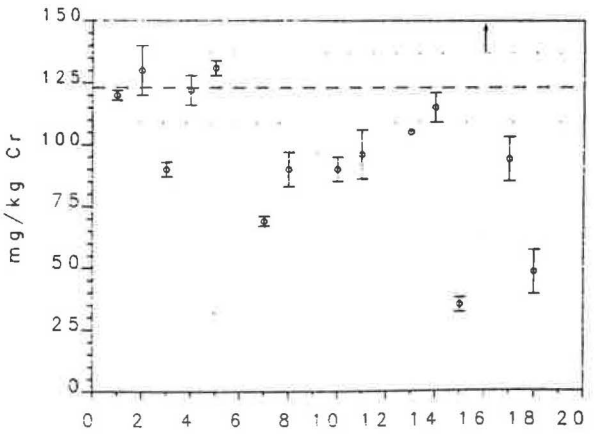

Fig. 12 Results for Cr, sample C

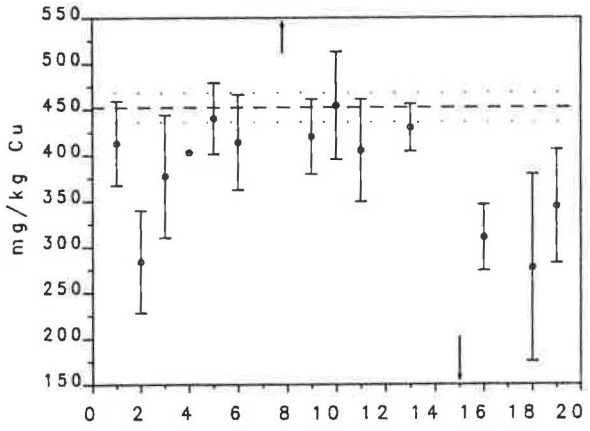

Fig. 13 Results for Cu, sample A

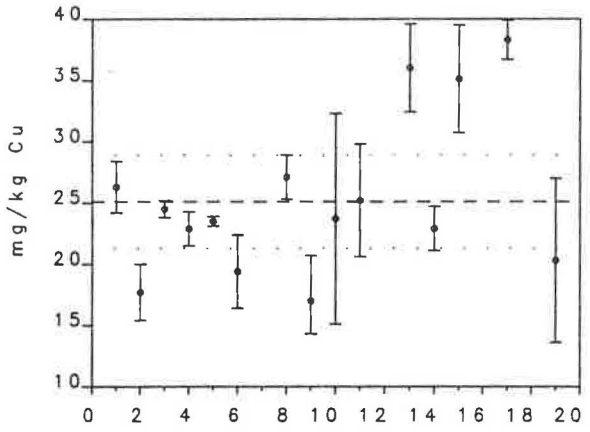

Fig. 14 Results for Cu, sample B

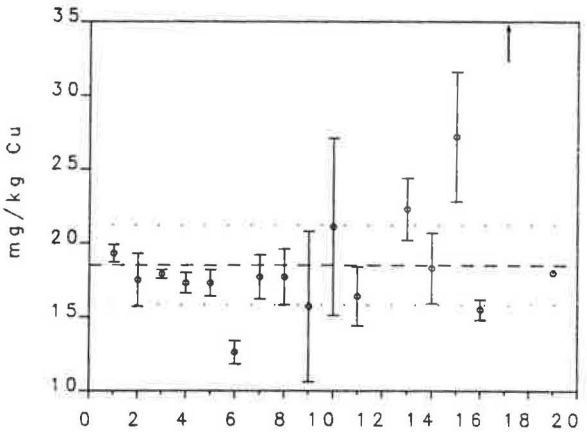

Fig. 15 Results for Cu, sample C

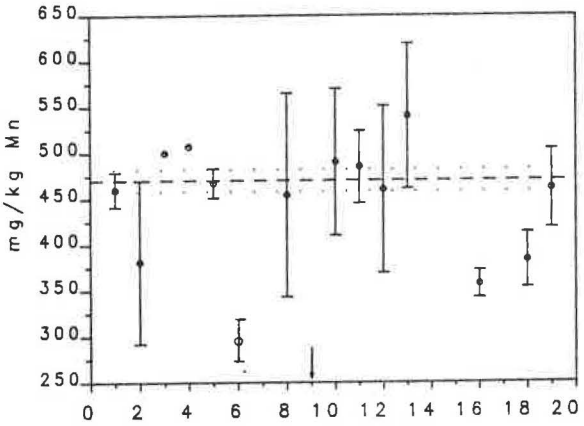

Fig. 16 Results for Mn, sample A

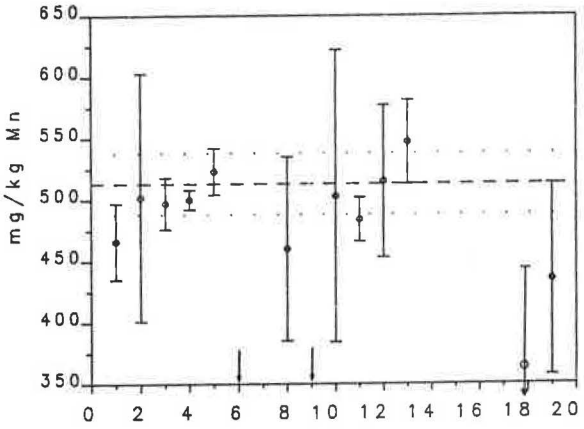

Fig. 17 Results for Mn, sample B

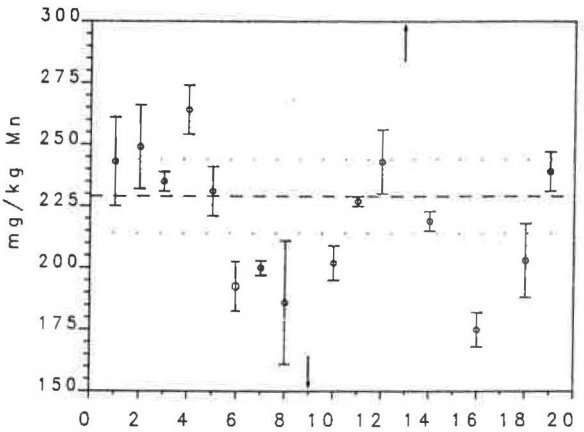

Fig. 18 Results for Mn, sample C

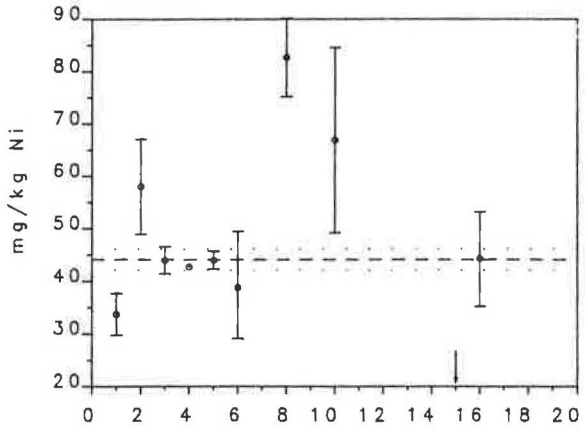

Fig. 19 Results for Ni, sample A

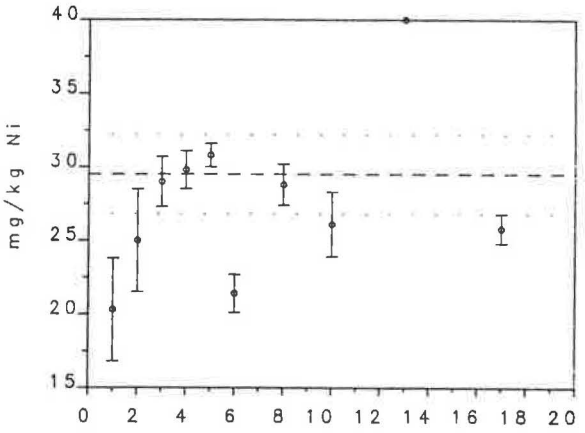

Fig. 20 Results for Ni, sample B

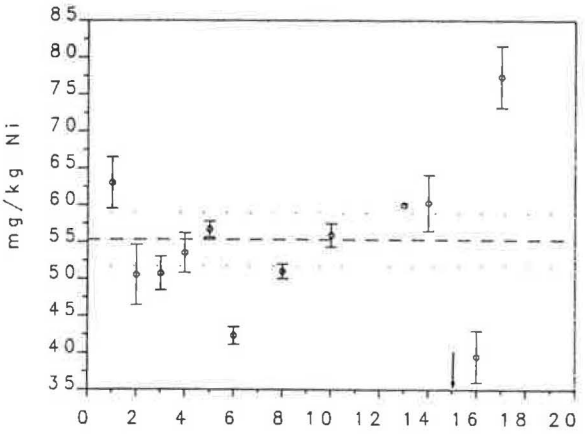

Fig. 21 Results for Ni, sample C

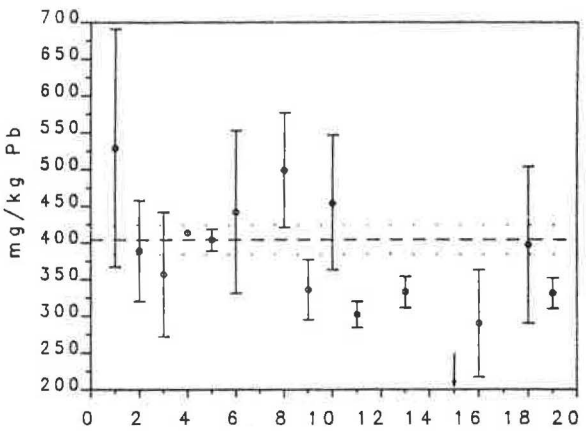

Fig. 22 Results for Pb, sample A

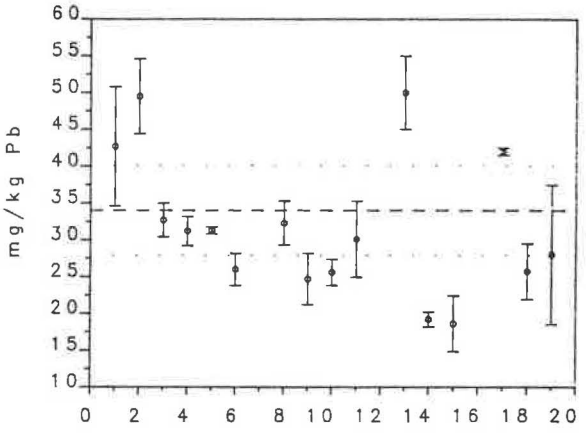

Fig. 23 Results for Pb, sample B

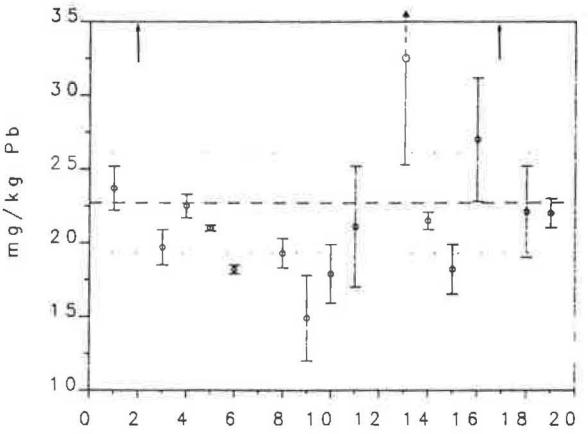

Fig. 24 Results for Pb, sample C

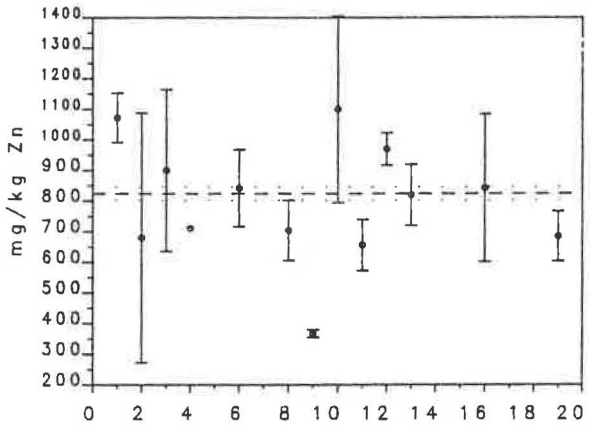

Fig. 25 Results for Zn, sample A

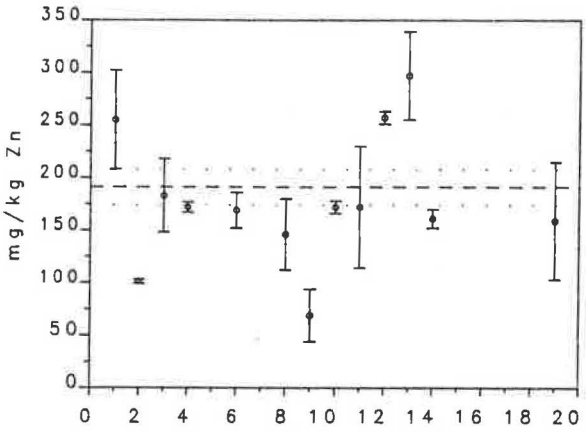

Fig. 26 Results for Zn, sample B

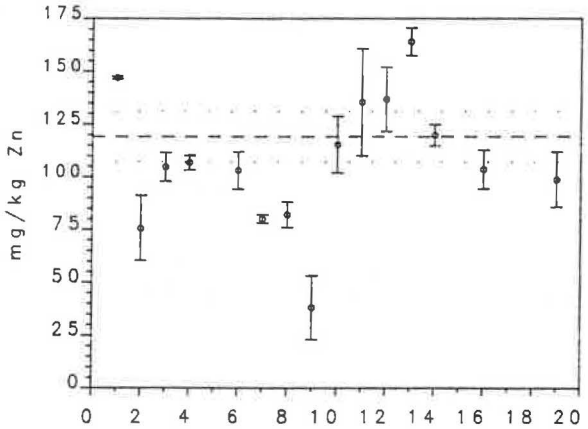

Fig. 27 Results for Zn, sample C

Table A. Recoveries calculated from the "excluded" grand mean.

Metal	A (%)	B (%)	C (%)
Al	88.7	94.2	90.4
Fe	95.5	93.8	95.4
Cd	104.6	133.9	148.0
Cr	85.3	79.6	77.5
Cu	84.1	100.8	97.3
Mn	97.2	96.3	96.9
Ni	117.8	96.3	101.6
Pb	95.8	94.7	91.6
Zn	96.1	93.7	90.5

The recoveries calculated for each element and sample are based on the excluded grand means of the results submitted by the participating laboratories, the outliers having been rejected (see Table A). The dominating trend is that the recovery is too low for most of the elements, the deviation from the certified value varies from element to element, and is more than 20 % in the worst case (chromium in Sample C). The occurrence of several low results is probably due to suppression by matrix elements.

On the other hand, for cadmium (Samples A, B and C) and nickel (Sample A), the recoveries observed are too high. This may be due to contamination or blank problems when analyzing low concentrations of these metals in small samples.

The hydrofluoric acid digestion method should bring the total amount of the sample into solution. Nevertheless, the average recovery for most of the elements is less than 100 %, which may indicate a loss of material in some step of the analytical procedure. Most likely this is not due to loss of material during the digestion (or, in some procedures, the heating to dryness), since this effect is not observed when larger sample quantities are digested. Most laboratories reported - in the preliminary exercise carried out before this intercomparison - that they observed recoveries close to 100 % when they were digesting mg samples of standard reference materials.

Because dried sediments are known to be hygroscopic, the samples were tested for their water content. Different sample amounts, varying from 5 to 100 mg for each sediment sample, were dried at 105°C for one hour. The average weight losses are given in Table B. No significant differences were observed for different sample sizes. The possible time effect of drying the samples was further tested for 24 hours, but the loss of weight increased by only 0.2 - 0.4 % as a result of increasing the drying time from one to 24 hours. Thus, the low recoveries cannot be explained by increased uptake of water by the sediments during freight and storage in the plastic vials.

Table B. Average weight losses for Samples A, B and C when dried for one hour at 105°C. Five samples with weights varying from 10 to 100 mg were used.

Sample	x	s
A	2.3%	0.09
B	1.0%	0.15
C	0.9%	0.17

The standard reference materials used for this intercomparison exercise were homogenized before certification, and the size distribution of the particulate fraction will give us an idea about the inhomogeneity problem. About 50 mg of the samples were suspended in 1000 ml of water, and a Coulter Counter was used to determine the number of particles of different size fractions. These results are presented in Figures 29 to 32. The ordinate axis is logarithmic because of the great amount of particles of small sizes compared to the larger particles. Two of the samples were filtered through a 95 μm filter to avoid clogging problems in the instrument. This was particularly necessary for Sample A, where a visible amount of particulate matter was retained on the filter. Samples B and C could be counted without filtration. To test this, Sample C was counted both before and after filtration, and the difference was very small. This should indicate that practically all particles in Samples B and C are less than 100 μm in size. Inhomogeneity may thus be a problem for Sample A, especially when the digested aliquots are very small.

Outliers in a data set may be due to sediment inhomogeneities; in this case the analyst cannot do anything to prevent this source of error other than increasing the sample amount analyzed. Sediments and suspended matter are known to be inhomogeneous by nature, and this manifests itself most clearly when very small fractions are analyzed. The quality of the results is, therefore, directly dependent on the homogeneity of the sample.

There is no general indication that the quality of the measurements decrease with the decreasing weight fraction analyzed, except for the metals having the lowest concentrations and in cases where inhomogeneity becomes a problem. For the precise determination of these elements, it may be necessary to use larger sub-samples. The sediment samples used here are very homogeneous. Therefore, it is possible to determine the low concentration elements within acceptable accuracy limits, even with the small amounts of sub-samples used in this exercise. Generally, the accurate weighing of samples smaller than 5 mg requires very sensitive balances which are properly calibrated and controlled daily, because the weighing of small samples will be highly influenced by errors in the balance.

In Figure 28, the recoveries of different metals in Sample C by laboratory No. 4 are plotted against the sub-sample weight. Using iron as a reference element, Figure 28 shows that the fluctuations in the concentrations as a function of sample weight are closely correlated for the elements chromium, manganese, lead and zinc, while cadmium, copper and, in part, nickel are exceptions. Good correlation may indicate that the main error lies in the weight determination of such small amounts. This may well be connected to the transfer of the weighed sub-sample into the teflon bombs and, thus, is not truly a homogeneity problem.

In fact, we have observed that the samples used for this intercomparison exercise are rather troublesome to transfer to the teflon bomb after weighing. This is obviously due to static electric effects, and for very small samples this may be a rather serious problem. Some of the very small particles of the sample are observed to disappear when transferring it from the balance to the teflon bomb, and are therefore not digested. This may be an explanation for the systematically low results observed for most of the elements, and this kind of error will be increasingly more serious for decreasing weights of samples. To avoid, or at least reduce, this kind of problem, an ionization source may be used during weighing.

A comparison between two digestion methods that both use hydrofluoric acid and aqua regia, but one uses boric acid to bind the excess of hydrofluoric acid, and the other employs evaporation to remove excess acid, indicates that evaporation methods that volatilize silicon result in a simpler matrix and may give better recoveries for the measured elements. However, possible interferences caused by matrix elements (e.g., boric acid) during measurement with AAS can be removed by further dilution of the extracted samples.

There is practically no information in the returns submitted by the participants to indicate whether contamination is considered as a serious problem or not. Neither is any information given as to whether the laboratories are using clean laboratory conditions for such samples. Contamination of the sample due to the laboratory conditions usually manifests itself for more than one element, and is often seen in the blanks. This might, at least in part, explain the high recoveries observed for some of the low concentration elements. Such poor results are expected for concentrations close to the detection limit. The error should then increase with decreasing sample weight, which should focus our attention on a problem relevant to the analysis of suspended particulate matter: What is the smallest sample weight giving acceptable results? The information collected indicates that the small sample amounts used here may represent this limit, especially for the low concentration metals. When analyzing less homogeneous samples, it is probably necessary to increase the sub-sample weight.

One laboratory used the nitric acid extraction method and indicated that the results for most of the elements were expected to be too low. However, the results demonstrate that elements such as cadmium, zinc and, in part, lead are extracted rather efficiently from the sediments. For the total determination of the other elements, it is necessary to use an efficient digestion method based on the use of hydrofluoric acid.

It is not possible to point out any significant connection between the determination method used and the reported results. Obviously, the analytical method is important when the element concentration is close to the detection limit. The high recoveries observed for cadmium and nickel are probably due to such factors. Matrix modification does not seem to improve the results in these cases. Determinations with ICP and ICP/MS seem to create some problems, while Zeeman corrected graphite furnace results are, in most cases, good.

Excellent results are reported for cadmium, chromium, copper, manganese, nickel and lead, with the slurry technique (laboratory No. 5). Unfortunately, no results are available for the important metals aluminium, iron and zinc. This method is suitable for the determination of trace or minor constituents, usually in the ppm or ppb range. Only in some instances can major components be quantified by this technique.

Suspended particulate matter will generally be much more inhomogeneous than the homogenized sediments used for this first exercise. Even the homogenized samples used here were reported to be too heterogeneous, and had to be finely ground to improve the sample homogeneity, before slurrying in glycerine medium. For small samples collected on a filter, therefore, this slurry technique will not be easy to use because great problems may arise when the particulate material is transferred from the filter before determination. Alternatively, the filter itself must be homogenized together with the sample.

CONCLUSIONS

Nitric acid extraction alone is not effective enough for total trace metal determinations. Hydrofluoric acid must be used in combination with some other oxidizing acid.

Slurry sampling gives results comparable to those of the total digestion methods for some elements in sediment samples. However, problems associated with the transfer of the particulate matter from the filter to the digestion vessel will probably remain as a technical limitation of this method.

The nature of the samples (including inhomogeneities) is probably the major limitation in the accurate determination of metal concentrations in a few milligrams of suspended material or sediments. Sample size

is a dominant problem, especially when determining elements at low concentrations. Thus, 1 mg of sample may be enough for the determination of the primary elements, while larger amounts may be necessary for trace elements.

The natural samples to be used in the next step of this intercomparison exercise may contain more inhomogeneous material than the samples used here. The precision must be expected to be poorer than in this exercise and the digestion of larger sample aliquots will probably be necessary. In addition, there will be problems related to water sampling, filtration or centrifuging processes, storage and preservation of the samples.

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Figure 28. Homogeneity and recovery test for sample C.

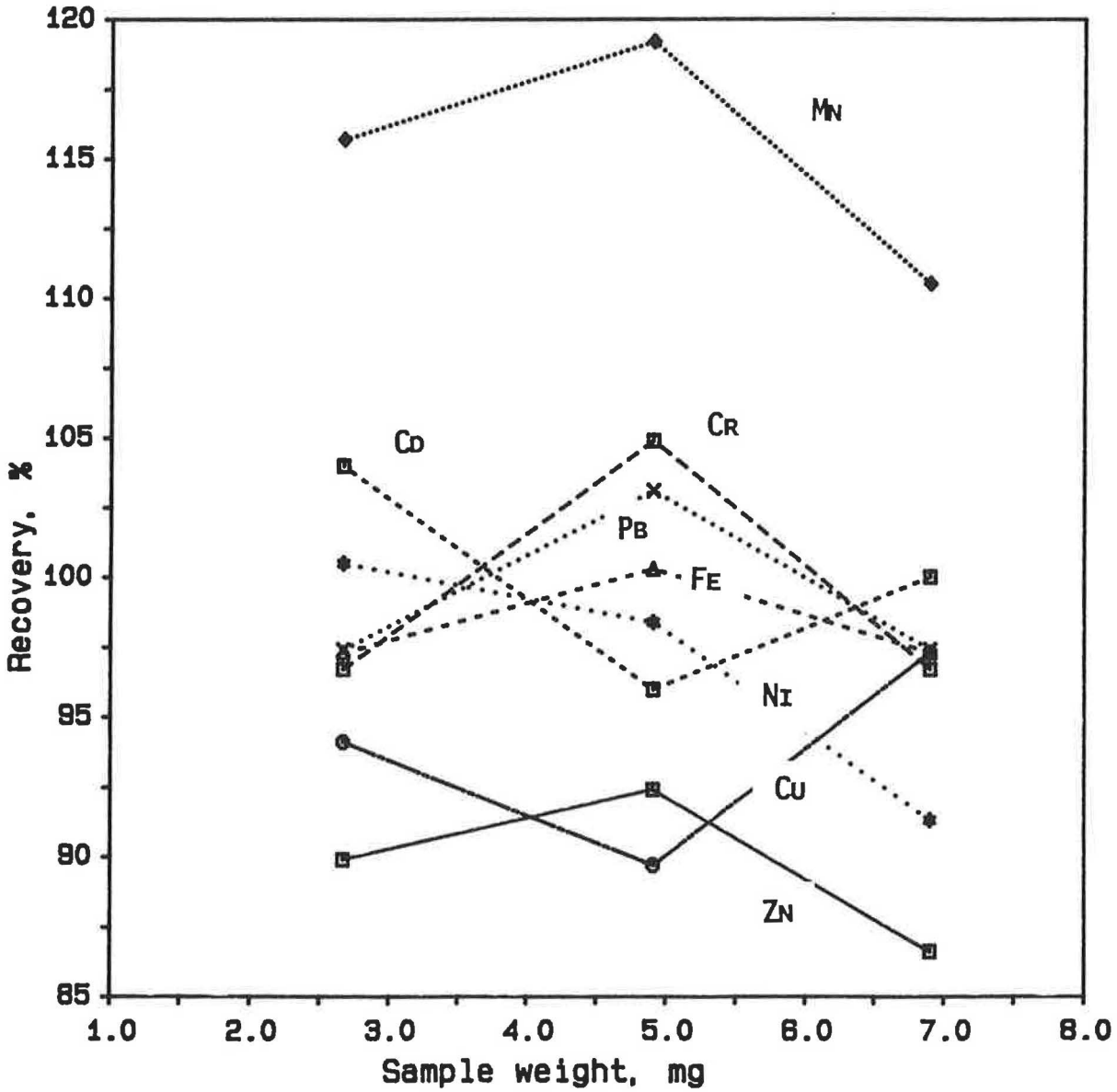


FIGURE 29. PARTICULATE FRACTION DISTRIBUTION OF SAMPLE A (PACS).

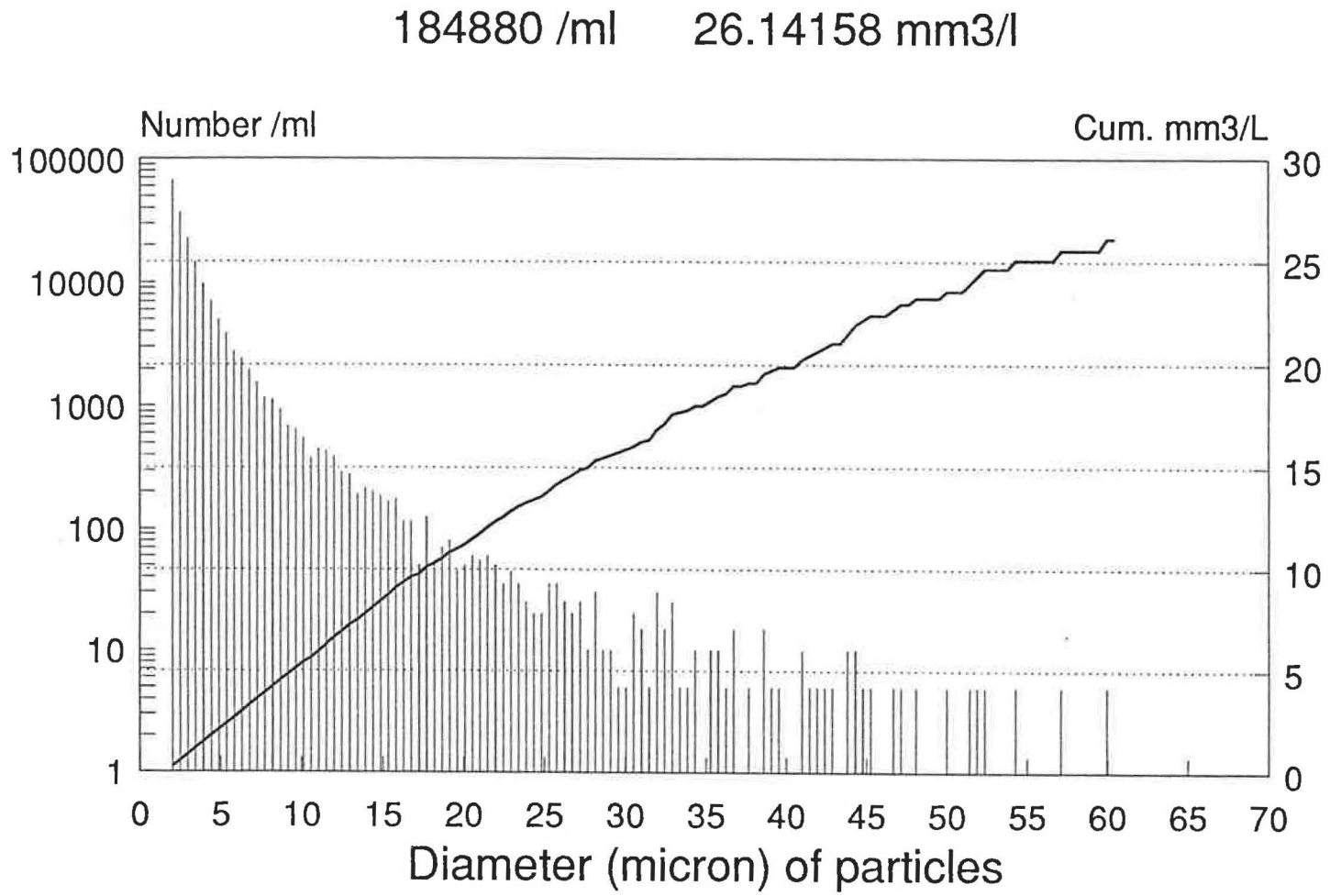


FIGURE 30. PARTICULATE FRACTION DISTRIBUTION OF SAMPLE B (MESS).

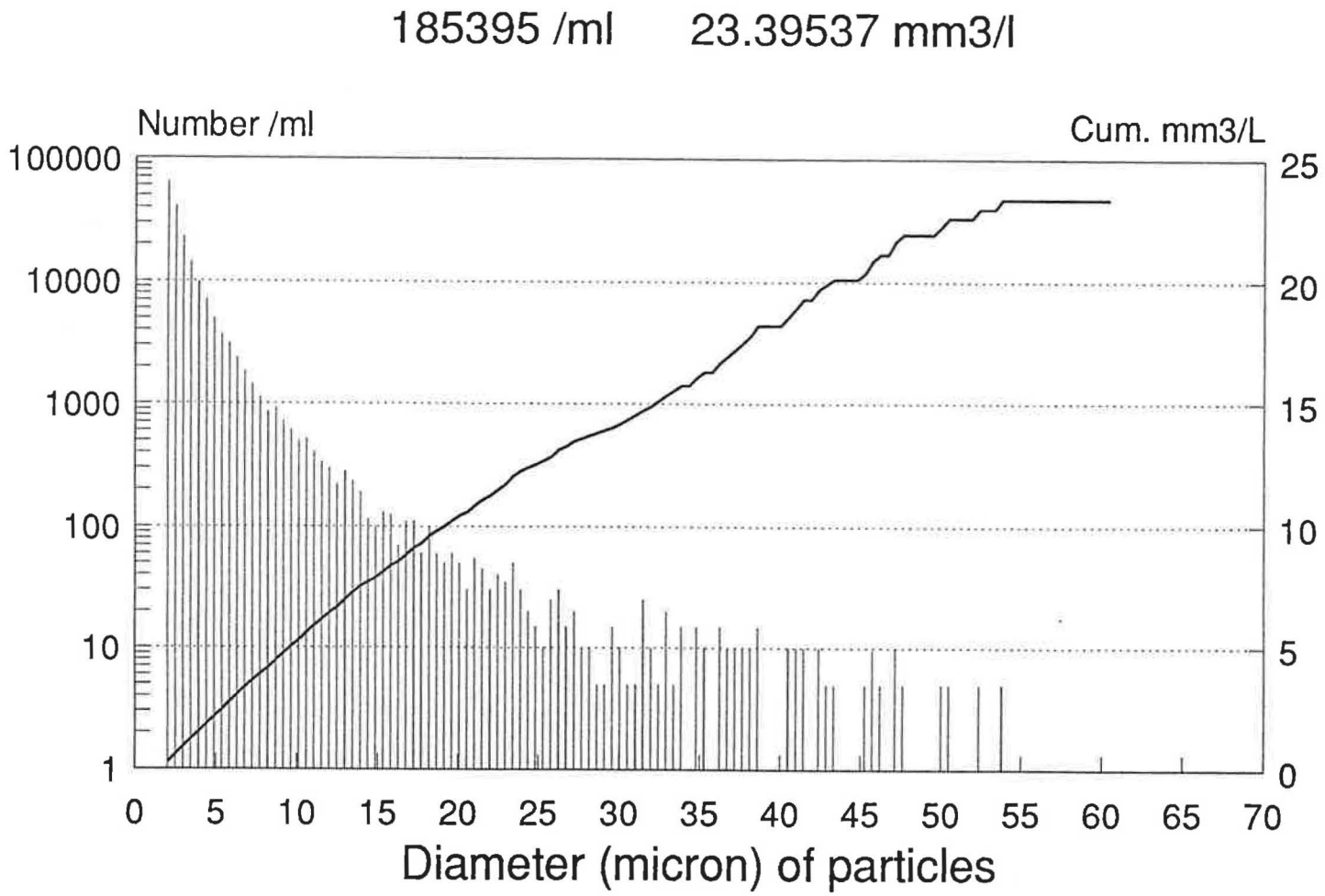
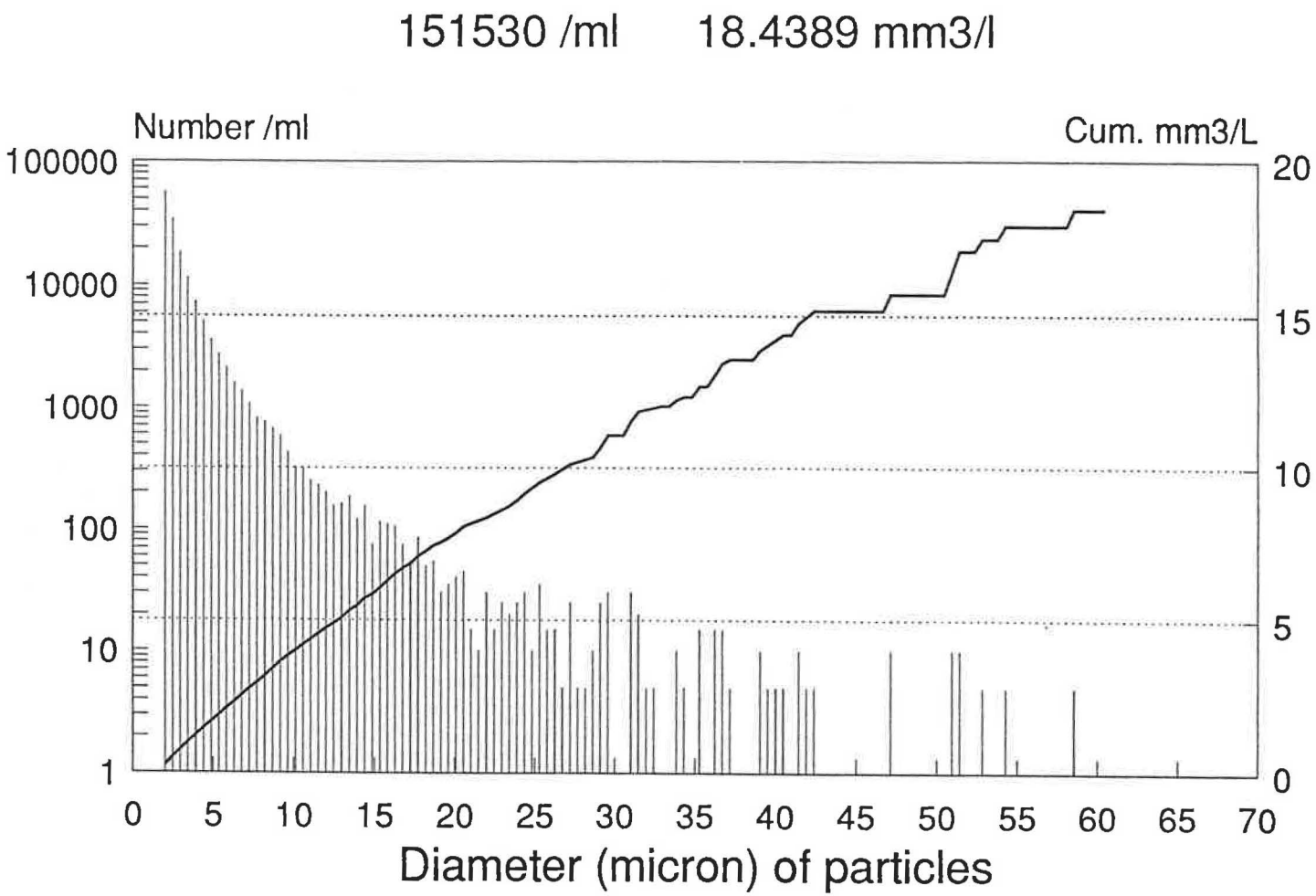


FIGURE 31. PARTICULATE FRACTION DISTRIBUTION OF SAMPLE C (BCSS).



ANNEX 1

LIST OF PARTICIPANTS

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ANNEX 2

PRETREATMENT METHOD

Lab.no.	Description of method and reference
1.	1 ml aqua regia and 1 ml HF digested in teflon bombs in 45 seconds in microwave oven (700 W). Transferred to 0.5 g H_3BO_3 in a polypropylene bottle (1, 4).
2.	HF and aqua regia in teflon bombs for two hours at 110°C. Addition to H_3BO_3 (1, 5).
3.	Aqua regia/HF/$HClO_4$ in a beaker for two hours (6).
4.	Pressure wet ashing with 2 ml HNO_3 and 100 μl HF for two hours at 180°C. Evaporation to dryness and redissolution in HNO_3.
5.	Direct sampling of slurry made by ultrasonic mixing of sediment in glycerine medium (3), after finely grinding the sample.
6.	Nitric acid digestion on hot plate (7).
7.	Recommended method (4).
8.	Total decomposition with 1 ml HNO_3 and 0.4 ml HF in teflon bomb submerged in boiling water for two hours. Evaporation to dryness, and treatment with H_2O_2 and HNO_3.
9.	Digestion in a mixture of HF, HNO_3 and $HClO_4$ in teflon beakers. Evaporation to near dryness and redissolution in water.
10.	Digestion in 250 μl HNO_3, 750 μl HCl and 2 ml HF in teflon bomb, evaporation to dryness and redissolution in HNO_3.
11.	Digestion in HNO_3/HF/$HClO_4$ mixture in teflon microwave vessel (8).
12.	Recommended method (4).
13.	Dissolution in HF/$HClO_4$ in teflon dish. The cake was dissolved in HCl and water to 10 ml.
14.	Recommended method (4).
15.	$HClO_4$/HF wet digestion for 4 hours.
16.	Wet digestion with HNO_3/HF in a teflon bomb in boiling water bath for 4 hours.
17.	Recommended method (4).
18.	Recommended method (4).
19.	Recommended method (4).

ANNEX 3

Table 1. Aluminium. Intra-laboratory means (in %), standard deviation (sd) and relative standard deviation (rsd). n is number of replicates from each participant. The inter-laboratory median (M), grand mean (X), standard deviation (SD) and relative standard deviation (RSD) are also given, in addition to the true value (T). N is the number of results used for calculation of the grand mean.

Lab No.	Sample A				Sample B				Sample C			
	n	Mean	sd	rsd	n	Mean	sd	rsd	n	Mean	sd	rsd
1	3	5.77	0.16	2.8	3	5.75	0.10	1.7	3	6.51	0.07	1.1
2	3	4.37	0.52	11.9	3	4.40	0.91	20.7	3	4.32	0.25	5.8
3	3	5.37	0.25	4.7	3	5.63	0.40	7.1	3	6.11	0.04	0.7
7									3	5.20	0.18	3.5
8	3	5.45	0.35	6.4	3	5.60	0.47	8.4	3	5.34	0.27	5.1
10	5	6.70	0.98	14.6	4	4.87	0.36	7.4	4	5.80	0.13	2.2
11	3	5.94	0.19	3.2	3	4.93	0.64	13.0	3	4.83	0.89	18.4
12	3	6.00	0.46	7.7	3	5.57	0.06	1.1	3	5.93	0.25	4.2
13	2	6.10			3	5.57	0.40	7.2	3	7.37	0.40	5.4
14					3	6.80	0.22	3.2	3	5.81	0.40	6.9
16	3	5.28	0.10	1.9					2	4.74		
18	3	6.37	0.53	8.3	3	5.74	0.17	3.0	3	5.96	0.16	2.7
N	10				10				12			
M	5.86				5.59				5.81			
X	5.74				5.49				5.66			
SD	0.66				0.65				0.84			
RSD	11.4				11.8				14.8			
T	6.47 ± 0.12				5.83 ± 0.20				6.26 ± 0.22			

Table 2. Iron. Intra-laboratory means (in %), standard deviation (sd) and relative standard deviation (rsd). n is the number of replicates from each participant. The inter-laboratory median (M), excluded mean (X), standard deviation (SD) and relative standard deviation (RSD) are also given, in addition to the true value (T). N is the number of results used for calculation of the grand mean. Results in parentheses are excluded from the statistical calculations.

Lab No.	Sample A				Sample B				Sample C			
	n	Mean	sd	rsd	n	Mean	sd	rsd	n	Mean	sd	rsd
1	3	4.32	0.13	3.0	3	2.91	0.05	1.7	3	3.35	0.11	3.3
2	3	3.93	0.34	8.7	2	2.64			3	3.20	0.31	9.7
3	3	4.40	0.20	4.5	3	2.77	0.12	4.3	3	3.04	0.08	2.6
4	1	5.10			3	3.00	0.20	6.7	3	3.23	0.06	1.9
6	3	(3.53)	0.12	3.4	3	(1.98)	0.09	4.5	3	(1.95)	0.04	2.1
7									3	2.98	0.02	0.7
8	3	4.61	0.53	11.5	3	2.69	0.18	6.7	3	2.98	0.13	4.4
9	2	4.93			4	2.63	0.07	2.7	3	3.25	0.23	7.1
10	4	5.19	0.59	11.4	4	2.82	0.08	2.8	4	3.13	0.04	1.3
11	3	4.49	0.20	4.5	3	2.97	0.22	7.4	3	3.40	0.11	3.2
12	3	4.92	0.52	10.6	3	2.73	0.08	2.9	3	3.00	0.05	1.7
13	3	4.83	0.67	13.9	3	3.20	0.27	8.4	3	(4.00)	0.36	9.0
14					3	2.85	0.07	2.5	3	3.16	0.10	3.2
15	3	(1.61)	0.13	8.1	3	(1.08)	0.11	10.2	3	(1.61)	0.10	6.2
16	3	4.29	0.03	0.7					2	2.95		
17					3	(1.57)	0.03	1.9	3	(2.52)	0.10	4.0
18	3	4.97	0.38	7.6	3	2.66	0.10	3.8	3	3.07	0.24	7.8
19	3	4.54	0.39	8.6	3	2.72	0.51	18.8	3	3.27	0.16	4.9
N	13				13				14			
M	4.61				2.77				3.15			
X	4.65				2.86				3.14			
SD	0.36				0.20				0.15			
RSD	7.7				7.0				4.8			
T	4.87 ± 0.08				3.05 ± 0.17				3.29 ± 0.10			

Rejected by Dixons test for outliers: Sample A, no. 10: 5 5.50 1.01 18.4
Sample B, no. 2: 3 3.27 1.09 33.3

Table 3. Cadmium. Intra-laboratory means (in mg/kg), standard deviation (sd) and relative standard deviation (rsd). n is number of replicates from each participant. The inter-laboratory median (M), excluded mean (X), standard deviation (SD) and relative standard deviation (RSD) are also given, in addition to the true value (T). N is the number of results used for calculation of the grand mean. Results in parentheses are excluded from the statistical calculations.

Lab No.	Sample A				Sample B				Sample C			
	n	Mean	sd	rsd	n	Mean	sd	rsd	n	Mean	sd	rsd
1	3	2.16	0.18	8.3	3	0.66	0.251	38.0	3	0.32	0.015	4.7
2	3	2.68	1.23	45.9	3	1.40	0.642	45.9	3	0.49	0.035	7.1
3	3	2.97	0.81	27.3	3	0.74	0.089	12.0	3	0.29	0.057	19.7
4	1	2.37			3	0.68	0.010	1.5	3	0.25	0.010	4.0
5	3	2.36	0.27	11.4	3	0.52	0.018	3.5	3	0.29	0.021	7.2
6	3	(2.78)	0.05	1.8	3	(0.67)	0.044	6.6	3	(0.27)	0.006	2.2
8	3	3.53	0.15	4.2	3	1.28	0.250	19.5	3	0.57	0.107	18.8
9	3	2.70	0.04	1.5	4	0.79	0.139	17.6	2	0.38		
10	4	3.38*	0.18	5.3	3	0.70	0.552	78.9	4	0.57	0.374	65.6
11	3	2.12	0.21	9.9	3	0.46	0.103	22.4	3	0.11	0.030	27.3
13	3	1.98	0.08	4.0	3	0.80	0.100	12.5	3	0.47	0.058	12.3
14									3	0.21	0.025	11.9
16	3	1.15	0.18	15.7					2	0.36		
17					3	0.71	0.082	11.5	3	0.52	0.078	15.0
N	11				11				13			
M	2.37				0.72				0.36			
X	2.49				0.79				0.37			
SD	0.67				0.29				0.14			
RSD	26.9				36.7				37.8			
T	2.38 ± 0.20				0.59 ± 0.10				0.25 ± 0.04			

* One extreme value is excluded.

Table 4. Chromium. Intra-laboratory means (in mg/kg), standard deviation (sd) and relative standard deviation (rsd). n is the number of replicates from each participant. The inter-laboratory median (M), grand mean or excluded mean (X), standard deviation (SD) and relative standard deviation are also given, in addition to the true value (T). N is the number of results used for calculation of the grand mean. Results in parentheses are excluded from the statistical calculations.

Lab No.	Sample A				Sample B				Sample C			
	n	Mean	sd	rsd	n	Mean	sd	rsd	n	Mean	sd	rsd
1	3	95.0	13.1	13.8	3	65.7	1.5	2.3	3	119.7	2.1	1.8
2	3	91.3	31.1	34.1	3	92.9	31.4	33.8	3	130.3	9.7	7.4
3	3	88.8	20.3	22.9	3	52.0	0.9	1.7	3	89.7	2.5	2.8
4	1	107.0			3	72.3	10.3	14.2	3	122.3	5.8	4.7
5	3	111.0	7.5	6.8	3	78.8	2.2	2.8	3	131.3	3.2	2.4
7									3	69.3	2.1	3.0
8	3	91.7	8.1	8.8	3	55.0	2.0	3.6	3	90.0	7.0	7.8
10	5	97.9	22.0	22.5	4	48.2	11.4	23.7	4	90.0	4.5	5.0
11	3	96.7	28.2	29.2	3	48.3	5.0	10.4	3	95.6	10.5	11.0
13					1	70.0			1	105.0		
14									3	115.0	5.6	4.9
15	3	(23.5)	5.5	23.4	3	19.8	2.0	10.1	3	34.8	3.4	9.8
16	3	(146.7)	30.6	20.9					2	(205.0)		
17					3	43.8	7.2	16.4	3	93.7	8.7	9.3
18	3	88.3	10.2	11.6	3	31.6	2.0	6.3	3	47.6	8.9	18.7
N	9				12				14			
M	95.0				53.5				94.7			
X	96.4				56.5				95.3			
SD	7.9				20.5				29.1			
RSD	8.2				36.3				30.5			
T	113 ± 8				71 ± 11				123 ± 14			

Table 5. Copper. Intra-laboratory means (in mg/kg), standard deviation (sd) and relative standard deviation (rsd). n is the number of replicates from each participant. The inter-laboratory median (M), excluded mean (X), standard deviation (SD) and relative standard deviation (RSD) are also given, in addition to the true value (T). N is the number of results used for calculation of the grand mean. Results in parentheses are excluded from the statistical calculations.

Lab No.	Sample A				Sample B				Sample C			
	n	Mean	sd	rsd	n	Mean	sd	rsd	n	Mean	sd	rsd
1	3	413	45.7	11.1	3	26.3	2.1	8.0	3	19.3	0.6	3.1
2	3	284	56.3	19.8	3	17.7	2.3	13.0	3	17.5	1.8	10.3
3	3	377	66.6	17.7	3	24.5	0.7	2.9	3	17.9	0.3	1.7
4	1	403			3	22.9	1.4	6.1	3	17.3	0.7	4.0
5	3	440	39.0	8.9	3	23.5	0.4	4.3	3	17.3	0.9	5.2
6	3	(414)	51.6	12.5	3	(19.4)	3.0	15.5	3	(12.6)	0.8	6.3
7									3	17.7	1.5	8.5
8	3	(612)	79.5	13.0	3	27.1	1.8	6.6	3	17.7	1.9	10.7
9	3	420	41.0	9.8	4	17.0	3.7	21.8	3	15.7	5.1	32.5
10	5	454	58.6	12.9	4	23.7	8.6	36.3	4	21.1	6.0	28.4
11	3	405	56.4	13.9	3	25.2	4.6	18.3	3	16.4	2.0	12.2
13	3	430	26.4	6.1	3	36.0	3.6	10.0	3	22.3	2.1	9.4
14					3	22.9	1.8	7.9	3	18.3	2.4	13.1
15	3	(67)	8.2	12.2	3	35.1	4.4	12.5	3	(27.2)	4.4	16.2
16	3	310	36.0	11.6					2	15.5		
17					3	38.3	1.6	4.2	3	(54.4)	2.1	3.9
18	3	277	101.8	36.8								
19	3	344	62.4	18.1	3	20.3	6.7	33.0	3	18.0	0.0	0.0
N	12				14				14			
M	404				24.1				17.7			
X	380				25.3				18.0			
SD	61.4				6.5				1.9			
RSD	16.2				25.7				10.6			
T	452 ± 16				25.1 ± 3.8				18.5 ± 2.7			

Table 6. Manganese. Intra-laboratory means (in mg/kg), standard deviation (sd) and relative standard deviation (rsd). n is number of replicates from each participant. The inter-laboratory median (M), excluded mean (X), standard deviation (SD) and relative standard deviation (RSD) are also given, in addition to the true value (T). N is the number of results used for calculation of the grand mean. Results in parentheses are excluded from the statistical calculations.

Lab No.	Sample A				Sample B				Sample C			
	n	Mean	sd	rsd	n	Mean	sd	rsd	n	Mean	sd	rsd
1	3	460	18.7	4.1	3	466	31.2	6.7	3	243	18.3	7.5
2	3	381	89.0	23.4	3	502	101.1	20.1	3	249	17.2	6.9
3	2	500			3	497	20.8	4.2	3	235	4.0	1.7
4	1	507			3	500	8.1	1.6	3	264	10.1	3.8
5	3	467	16.4	3.5	3	523	19.1	3.7	3	231	10.0	4.3
6	3	(290)	22.0	7.6	3	(293)	30.7	10.5	3	(192)	9.0	4.7
7									3	200	3.2	1.6
8	3	454	111.1	24.5	3	460	74.7	16.2	3	186	24.9	13.4
9	2	(106)			4	(133)	16.5	12.4	3	(71)	5.8	8.2
10	5	490	80.2	16.5	4	503	119.1	23.7	4	202	7.4	3.7
11	3	485	39.1	8.1	3	484	18.3	3.8	3	227	2.1	0.9
12	3	460	91.2	19.8	3	515	62.4	12.1	3	243	12.6	5.2
13	3	540	79.4	14.7	3	547	34.1	6.2	3	(322)	13.3	4.1
14									3	219	4.0	1.8
16	3	357	15.3	4.3					2	175		
18	3	383	30.3	7.9	3	(365)	84.4	23.1	3	203	15.0	7.4
19	3	461	42.5	9.2	3	435	78.1	18.0	3	239	8.0	3.3
N	13				11				14			
M	461				500				229			
X	457				494				222			
SD	53.6				31.3				26.2			
RSD	11.7				6.3				11.8			
T	470 ± 12				513 ± 25				229 ± 15			

Rejected by Dixons test for outliers: Sample A, No. 3: 3 367 115.5 20.4

Table 7. Nickel. Intra-laboratory means (in m/kg), standard deviation (sd) and relative standard deviation (rsd). n is the number of replicates from each participant. The inter-laboratory median (M), excluded mean (X), standard deviation (SD) and relative standard deviation (RSD) are also given, in addition to the true value (T). N is the number of results used for calculation of the grand mean. Results in parentheses are excluded from the statistical calculation.

Lab No.	Sample A				Sample B				Sample C			
	N	Mean	sd	rsd	N	Mean	sd	rsd	N	Mean	sd	rsd
1	3	33.7	4.0	11.9	3	20.3	3.5	17.2	3	63.0	3.5	5.6
2	3	58.0	9.1	15.7	3	25.0	3.5	14.0	3	50.5	4.1	8.1
3	3	44.0	2.6	5.9	3	29.0	1.7	5.9	3	50.7	2.3	4.5
4	1	42.7			3	29.8	1.3	4.4	3	53.5	2.7	5.0
5	3	44.0	1.7	3.9	3	30.8	0.8	2.6	3	56.7	1.1	1.9
6	3	(38.8)	10.7	27.6	3	(21.4)	1.3	6.1	3	(42.3)	1.2	2.8
8	3	82.7	7.5	9.1	3	28.8	1.4	4.9	3	51.0	1.0	2.0
10	5	66.9	17.7	26.5	4	26.1	2.2	8.4	4	55.9	1.6	2.9
13					1	40.0			1	60.0		
14									3	60.3	3.8	6.3
15					3	(3.0)	0.9	30.0	3	(16.8)	1.8	10.7
16	3	44.3	9.1	20.5					2	39.5		
17					3	25.8	1.0	3.9	3	77.4	4.2	5.4
N	8				9				11			
M	44.0				28.8				55.9			
X	52.0				28.4				56.2			
SD	16.1				5.4				9.5			
RSD	31.0				19.0				16.9			
T	44.1 ± 2.0				29.5 ± 2.7				55.3 ± 3.6			

Table 8. Lead. Intra-laboratory means (in mg/kg), standard deviation (sd) and relative standard deviation (rsd). n is the number of replicates from each participant. The inter-laboratory median (M), excluded mean (X), standard deviation (SD) and relative standard deviation (RSD) are also given, in addition to the true value (T). N is the number of results used for calculation of the grand mean. Results in parentheses are excluded from the statistical calculations.

Lab No.	Sample A				Sample B				Sample C			
	n	Mean	sd	rsd	n	Mean	sd	rsd	n	Mean	sd	rsd
1	3	529	162	30.6	3	42.7	8.1	19.0	3	23.7	1.5	6.3
2	3	389	69	17.7	3	49.5	5.1	10.3	3	(41.7)	9.1	21.8
3	3	357	85	23.8	3	32.7	2.3	7.0	3	19.7	1.2	6.1
4	1	414			3	31.2	2.0	6.4	3	22.5	0.8	3.6
5	3	404	15	3.7	3	31.3	0.5	1.6	3	21.0	0.2	1.0
6	3	(442)	111	25.1	3	(26.0)	2.2	8.5	3	(18.2)	0.3	1.6
8	3	499	78	15.6	3	32.3	3.0	9.3	3	19.3	1.0	5.2
9	2	336	41	12.2	4	24.7	3.5	14.2	3	14.9	2.9	19.5
10	5	454	91	20.0	3	25.6	1.8	7.0	4	17.9	2.0	11.2
11	3	302	18	6.0	3	30.1	5.2	17.3	3	21.1	4.1	19.4
13	3	333	21	6.3	3	50.0	5.0	10.0	3	(32.7)	6.8	20.8
14					3	19.2	1.0	5.2	3	21.5	0.6	2.8
15	3	(29)	1.4	4.8	3	18.6	3.8	20.4	3	18.2	1.7	9.3
16	2	290							2	27.0		
17					3	42.0	0.5	1.2	3	(75.7)	3.8	5.0
18	3	397	107	27.0	3	25.7	3.8	14.8	3	22.1	3.1	14.0
19	3	331	21	6.3	3	28.0	9.5	33.9	3	22.0	1.0	4.5
N	13				15				13			
M	389				31.2				21.1			
X	387				32.2				20.8			
SD	73.3				9.8				3.0			
RSD	18.9				30.4				14.4			
T	404 ± 20				34.0 ± 6.1				22.7 ± 3.4			

Rejected by Dixons test for outliers: Sample A, no. 16: 3 500 365 73.0
Sample B, no. 10: 4 32.1 13.1 40.8

Table 9. Zinc. Intra-laboratory means (in mg/kg), standard deviation (sd) and relative standard deviation (rsd). n is the number of replicates from each participant. The inter-laboratory median (M), excluded mean (X), standard deviation (SD) and relative standard deviation are also given, in addition to the true value (T). N is the number of results used for calculation of the grand mean. Results in parentheses are excluded from the statistical calculations.

Lab No.	Sample A				Sample B				Sample C			
	n	Mean	sd	rsd	n	Mean	sd	rsd	n	Mean	sd	rsd
1	3	1072	81	7.6	3	255	47.4	18.6	3	147.0	0.6	0.4
2	3	680	408	60.0	3	101	1.7	1.7	3	75.7	15.5	20.5
3	3	900	265	29.4	3	183	35.1	19.2	3	104.7	6.8	6.5
4	1	711			3	172	4.6	2.7	3	106.7	3.5	3.3
6	3	(842)	126	15.0	3	(169)	17.2	10.2	3	(103.0)	8.9	8.6
7									3	80.0	2.0	2.5
8	3	704	99	14.1	3	146	34.4	23.6	3	82.0	6.1	7.4
9	2	367			4	69	24.8	35.9	3	38.0	15.1	39.7
10	5	1100	305	27.7	4	172	6.3	3.7	4	115.3	13.4	11.6
11	3	656	84	12.8	3	172	58.0	33.7	3	135.3	25.4	18.8
12	3	970	53	5.5	3	257	5.8	2.3	3	136.7	15.3	11.2
13	3	820	99	12.1	3	297	41.6	14.0	3	164.0	6.6	4.0
14					3	161	8.5	5.3	3	119.7	5.1	4.3
16	3	843	242	28.7					2	103.5		
19	3	685	82	12.0	3	159	56.1	35.3	3	98.7	13.1	13.3
N	12				12				14			
M	766				172				105.7			
X	792				179				107.7			
SD	204				64.6				32.7			
RSD	25.8				36.1				30.4			
T	824 ± 22				191 ± 17				119 ± 12			

Table 10. Lithium. Intra-laboratory means (in mg/kg), standard deviation (sd) and relative standard deviation (rsd). n is the number of replicates from each participant. The inter-laboratory median (M), grand mean (X), standard deviation (SD) and relative standard deviation (RSD) are also given. N is the number of results used for calculation of the grand mean.

Lab No.	Sample A				Sample B				Sample C			
	n	Mean	sd	rsd	n	Mean	sd	rsd	n	Mean	sd	rsd
1	3	43.0	7.0	16.3	3	49.7	3.2	6.4	3	46.7	3.2	6.9
7									3	36.6	2.1	5.7
8	3	25.7	1.7	6.6	3	37.3	3.6	9.6	3	36.6	2.7	7.4
10	5	54.1	14.4	26.6	4	47.5	3.1	6.5	4	51.5	2.4	4.7
N	3				3				4			
M	43.0				47.5				41.7			
X	40.9				44.8				42.9			
SD	14.3				6.6				7.5			
RSD	35.0				14.7				17.5			

Table 11. Cobalt. Intra-laboratory means (in mg/kg), standard deviation (sd) and relative standard deviation (rsd). n is the number of replicates from each participant. The true value (T) is also given.

Lab No.	Sample A				Sample B				Sample C			
	n	Mean	sd	rsd	n	Mean	sd	rsd	n	Mean	sd	rsd
4	1	19.5			3	11.5	0.6	5.2	3	11.7	1.0	8.5
9					3	14.1	1.7	12.1	2	13.4		
T	17.5 ± 1.1				10.8 ± 1.9				11.4 ± 2.1			