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WORKING METHODS PAPER:

Certification of Methylmercury Compounds Concentration in Marine Sediment Reference Material, IAEA-356

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An intercomparison exercise was organized between seven laboratories using various isolation procedures (extraction, distillation, ion-exchange and alkaline digestion) and detection systems (CV AAS, cold vapour atomic absorption spectroscopy; CV AFS, cold vapour atomic fluorescence spectroscopy; GC, ECD, gas chromatography electron capture detector and HPLC with CV AFS detection) for determination of methylmercury compounds in sediment sample. All certification criteria were fulfilled and therefore the value for total concentration of methylmercury compounds was certified to be 5.46 ng g^{-1}, with a 95% confidence interval from 4.07–5.84 ng g^{-1}. The acceptable range, calculated as two times the confidence interval of the mean is therefore from 4.68–6.23 ng g^{-1}. This is the first sediment reference material ever to be certified for concentration of methylmercury compounds. Comparison of the data obtained by various methodologies has shown that the most critical step is the isolation of methylmercury compounds from binding sites. Acid leaching only cannot release methylmercury compounds quantitatively. Total release of methylmercury compounds could only be achieved by alkaline digestion or distillation. This simple intercomparison exercise has shown that since large numbers of laboratories world-wide are performing methylmercury compound analyses using various improved and specific separation methods and sensitive detection systems, certification of methylmercury compounds in different biological and environmental samples should not be a problem in the future.

Keywords: Methylmercury, marine sediment, certification, reference material, intercomparison

INTRODUCTION

At the International Conference on 'Mercury as a Global Pollutant' (Monterey, CA, June 1992) it was concluded that numerous questions on the biogeochemical cycle of mercury in the natural environment have been answered, but that many gaps still remain in the overall understanding. One very important contribution in the latest research on biogeochemical cycles is the availability of specific and sensitive analytical methods by which it is possible to perform studies under natural conditions. The importance of studies on exposure of humans to mercury through excessive consumption of food (particularly fish) is well known. The methylation of inorganic mercury is a key process in the biogeochemical mercury cycle. Net mercury methylation rates appear to be higher in sediments than in the water column, although the availability of methylmercury compounds formed in sediments to the food chain is

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unknown. Usually methylmercury concentration in sediments does not exceed 1.5% of the total mercury present. However, its concentration is very important in the interpretation of biogeochemical cycles of mercury in the aquatic environment. Mercury and methylmercury in this area of the environment is mainly associated with sulphide and organic substances (especially humic substances, amino acids and proteins).

It is obvious that a good quality assurance programme should be implemented in any of such studies. One way to control the accuracy of the results is by analysing certified reference materials (CRMs). At present there are many CRMs available for total mercury concentration in various matrices (sediment, soil, ash, water and tissues). Unfortunately, only five marine biological CRMs are certified for methylmercury compounds. Four are available from the National Research Council of Canada (NRCC)[1] and one is available from the International Atomic Energy Agency (IAEA).[2] It is likely that these materials are not sufficient to satisfy the quality assurance control requirements in many laboratories performing methylmercury analyses. Therefore, apart from the analyses of CRMs, the accuracy of analytical procedures for determination of methylmercury were tested by intercomparison exercises[3,4] as well as by comparison of the results obtained by various isolation and final measurement procedures.[5,6] In some such studies it has been shown that when speciation of mercury compounds is required with insoluble samples (such as sediments and soils) it is very difficult to estimate the recovery of the isolation procedures. This is due to the fact that added methylmercury is not equivalent to the methylmercury originally present in the sample. It has been shown that conventional methods based on acid leaching of organomercury compounds prior to extraction of methylmercury compounds into an organic solvent is inadequate to release methylmercury compounds quantitatively. Recently it has been shown that total release of methylmercury compounds could so far only be achieved by alkaline digestion[7] or distillation.[7-9]

A study of the effects of long-term storage and sample preparation on the stability of methylmercury compounds in sediments[7] and biological sample has already been performed.[10] The results of these studies showed that methylmercury is very stable in most of the matrices studied. In some currently available biological and sediment CRMs certified for total mercury, methylmercury was also determined by a few laboratories using various analytical procedures.[5-7] Very good agreement of the results was obtained for biological samples.[5,6] In addition, methylmercury was shown to be very stable under good long-term storage conditions.[7,10]

The IAEA has been providing an analytical quality control service (AQCS) to its member states since the 1960s. The AQCS programme includes the distribution of reference materials, the organization of intercomparison runs, the provision of training courses for quality assurance and chemical analyses of radioactive (and also partly non-radioactive) measurements of contaminants. For its part the IAEA—Marine Environment Laboratory in Monaco has been organizing intercomparison exercises on trace element analyses in marine biological and sediment samples since 1973. Laboratories (usually more than 100) from all over the world are invited to participate. The data reported are then statistically evaluated and where the consensus median value is very clearly determined and a series of statistical criteria are fulfilled, the sample is issued as a reference material for use in the analytical quality control programme. A sediment intercomparison sample used for the present study has been prepared within a regular Analytical Data Quality Assurance Programme for trace metal analyses in polluted marine sediment. Preliminary measurements have shown that the methylmercury compounds value is relatively high and therefore it was decided to distribute the sample for methylmercury analysis to some laboratories that were willing to participate. The reported results are discussed in the present paper. Since all certifiction criteria were fulfilled, the value for methylmercury was certified. This offers an opportunity for many laboratories to compare their data with the certified value. Results for total mercury analyses are not discussed in this paper, as the value has been certified through a regular large scale intercomparison run.[11]

EXPERIMENTAL

Description of the material

About 30 kg of sediment was collected from a contaminated bay in the Mediterranean. This sediment was deep frozen, freeze dried, ground

Table 1 List of participating laboratories and their analytical methods used for methylmercury compound determinations

Laboratory no.	Institute/company	Laboratory method code	Isolation procedure	Detection technique	DL[a] (ng g^{-1})	References
1	IAEA	1A	Distillation/solvent extraction	GC, ECD	0.6	7, 12
		1B	Alkaline digestion/solvent extraction		0.3	7, 13, 12
		1C	Acid leaching/solvent extraction		0.3	12
2	Brooks Rand, Ltd.	2A	Alakaline digestion/distillation/aqueous phase ethylation	GC, CV, AFS	0.0001	7, 8, 14
		2B	Alkaline digestion/aqueous phase ethylation	GC, CV AFS	0.1	13, 14
3	Frontier Geosciences	3	Distillation/aqueous phase ethylation	GC, CV AFS	0.003	7, 13, 14
4	Research Centre Julich	4A	Distillation/ion exchange	CV AAS	0.1	6, 15, 16
		4B	Acid leaching/anion exchange	CV AAS	0.1	16
5	IVL, Sweden	5	Distillation/aqueous phase ethylation	GC, CV AFS	0.003	7, 8, 14, 17
6	GKSS	6	Acid leaching/solvent extraction	HPLC, CV AFS	0.1	18, 19, 20
7	University of Wisconsin	7	Distillation/aqueous phase ethylation	GC, CV AFS	0.04	7, 8, 14

[a] DL is the detection limit of the method, expressed as three standard deviations of the procedural blank.

and passed through a 250 μm sieve and then thoroughly homogenized. Homogeneity of the material was tested by determining the concentration of selected trace metals in several samples taken randomly from the bulk of the powder. A one-way analysis of the variance indicated that the material could be considered as homogeneous. The water content of the lyophilized material (as determined by drying to a constant weight at 105 °C) was found to be approximately 1.5%. All results reported are expressed on a dry weight basis.

Participating laboratories

An invitation to participate in small scale intercomparison exercises on methylmercury analyses was sent to several laboratories that had reported methylmercury values in sediments. Those that were willing to participate were given a bottle of approximately 50 g of sample. A list of participants and the methods used together with relevant references are given in Table 1. Only a brief description of methods used is given below. As the organizer of this intercomparison exercise, the main purpose of the IAEA laboratory was to verify some of the conclusions drawn regarding the effectiveness of the acid leaching method compared to some other isolation techniques. Therefore, their methods are described more precisely.

Laboratory 1

The IAEA Marine Environment Laboratory has used three various approaches to separate methylmercury compounds from the sediment followed by GC with an electron capture detector (ECD).

- **1A:** The first isolation method is based on distillation[6,7] followed by a solvent extraction method.[12] However, a slight modification was applied. Only approximately 0.5 g of sample was subjected to distillation. The distillate was acidified with 4 ml 4M H_2SO_4(sat.$CuSO_4$) and 4 ml of 4M KBr. Methylmercury bromide was then extracted into 5 ml of toluene. This extraction was repeated twice. Combined toluene extracts were purified by a clean-up step. The organic phase was first equilibrated with 3 ml of aqueous 1% cysteine solution and then back-extracted as methylmercury bromide (after acidification with 1.5 ml of 4M H_2SO_4(sat. $CuSO_4$) and 1.5 ml of 4M KBr) into 1 ml of toluene. In order to reduce possible interfering peaks and to concentrate methylmercury into a smaller volume of toluene the clean-up procedure was repeated as follows. A strip of cysteine-impregnated paper was inserted into the final toluene extract so that all methylmercury was trapped on the paper. The paper was rinsed once with a clean portion of toluene and then dried. The method is precisely described in another paper.[12] After acidification with 0.1 ml 4M

H_2SO_4(sat. $CuSO_4$) and 0.1 ml of 4M KBr, methylmercury bromide was back-extracted into 0.1 ml of toluene. In each separation step the mixture was shaken for 10 min and centrifuged for 10 min at 3000 rpm. A sample of the final extract (2 µl) was then injected on the GC column (column temperature 160 °C, 1.6 m long, 2 mm ID, packed with 5% DEGS on Supelcoport 100–120 mesh). An example of the chromatogram is shown in Fig. 1(A). The recovery of the overall isolation procedure was 68 ± 2% based on the overage of four spiking recovery tests.

- **1B:** The second approach was the same as that described above except that the distillation step was replaced with the alkaline digestion. Approximately 2 g of the sample was digested with 6 ml of 25% KOH in methanol in closed Teflon vials for 3 h at 75 °C. When cooled it was acidified with 5 ml 4M H_2SO_4(sat. $CuSO_4$) and 5 ml of 4M KBr and extracted into 5 ml of toluene. The extraction was repeated twice. The same double clean-up procedure as described above was used. The volume of the final toluene extract was 0.5 ml. The recovery of spiked methylmercury was only 50%. However, it was reproducible so that we could correct the results accordingly. An example of the chromatogram is given in Fig. 1(B).
- **1C:** The third isolation procedure is based on acid leaching of methylmercury from the sediment. Approximately 2 g of the sediment was acidified with 4M H_2SO_4(sat. $CuSO_4$) and 5 ml of 4M KBr. MeHgBr was extracted into 5 ml of toluene. The extraction was repeated twice. A further procedure included the double clean-up step as described above (1A and

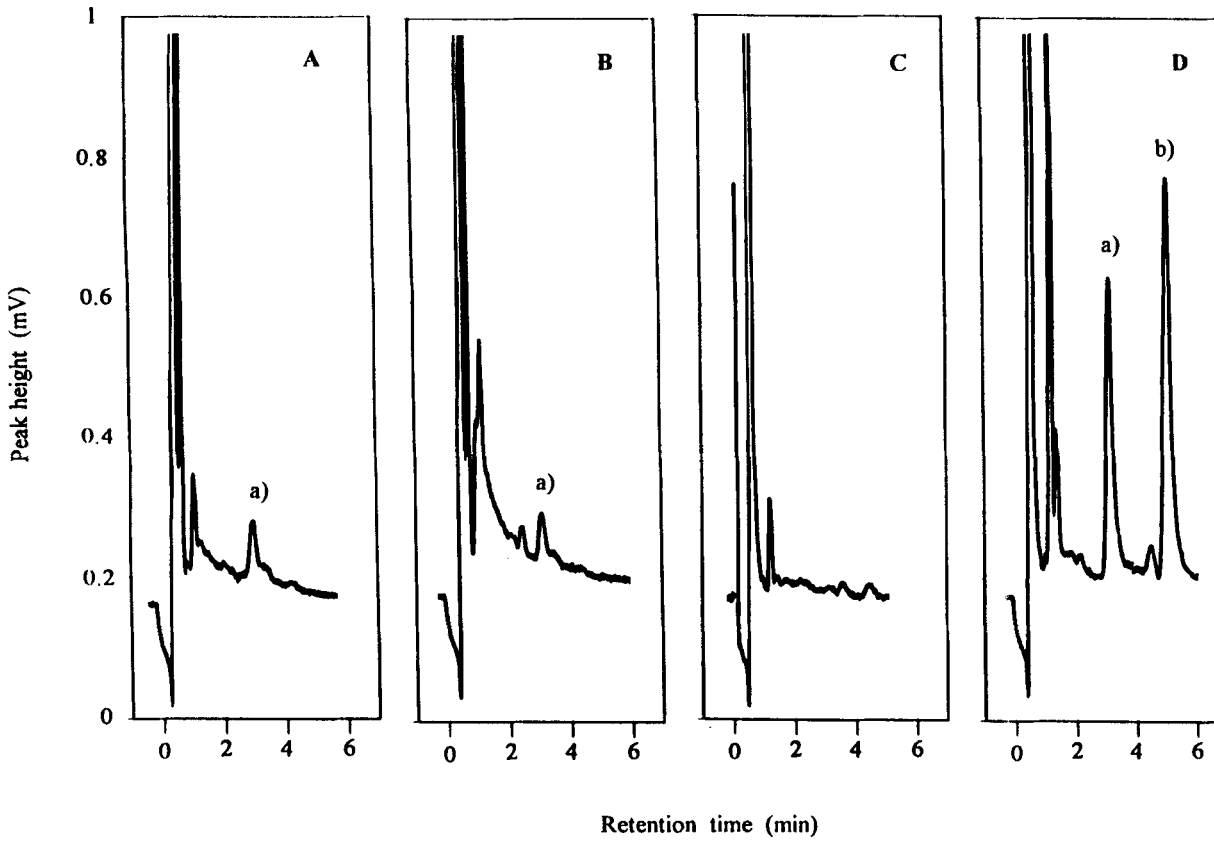

Figure 1 (A) Chromatogram for 2 µl injection from 0.1 ml of the final toluene extract using distillation/solvent extraction procedure. (B) Chromatogram for 2 µl injection from 0.5 ml of the final toluene extract using alkaline digestion and solvent extraction procedure. (C) Chromatogram for 2 µl injection of the blank of the extraction procedure. Chromatogram for 2 µl standard of 0.050 µg MeHgCl ml^{-1} and 0.050 µg EtHgCl ml^{-1}, both expressed as mercury. Glass column: 1.6 m long, 2 mm ID, packed with GP 5% DEGS-PS Supelcoport (100–120 mesh) operated at 160 °C and 40 ml min^{-1} carrier gas-glow rate. (a) Methylmercury; (b) ethylmercury.

1B). The recovery of spiked methylmercury was 74 ± 1% based on four independent spiked runs. Very similar chromatograms as for the method 1B were obtained.

During each set of analysis two or three blanks were also run. An example of the chromatogram of the blank of the extraction procedure is shown in Fig. 1(C).

Laboratory 2

Two different isolation procedures were applied: distillation after alkaline digestion[7] (2A) and alkaline digestion with 25% KOH in methanol[7, 13, 14] (2B). An aliquot was then subjected to aqueous phase ethylation, GC separation and detection by CV AFS.[14] The recovery of spiked methylmercury using the distillation pre-separation was 87.4%.

The laboratory has also provided total mercury results which were obtained by HNO_3/H_2SO_4 digestion in closed Teflon vials and determined by $SnCl_2$ reduction and single stage gold amalgamation CV AFS[21] detection.

Laboratory 3

The methylmercury value was obtained by pre-separation of methylmercury by distillation,[7] followed by aqueous phase ethylation,[13] GC separation and detection by CV AFS.[7, 13] The recovery of the spiked methylmercury was 90.9 ± 5.1% based on three independent runs. Total mercury was obtained after digestion of the sediment by hot aqua regia, $SnCl_2$ reduction, double amalgamation and CV AFS detection.[22]

Laboratory 4

Two methods were used for the isolation of methylmercury.

- **4A:** The first is based on the distillation of methylmercury from approximately 0.2 g of the sample.[6, 15] Inorganic mercury from the distillate was removed by anion exchange resin.[15, 16]

  Methylmercury was destroyed by UV oxidation and measured as Hg^{2+} by $SnCl_2$ reduction, gold amalgamation and CV AAS detection.[16] Recovery of the spiked methylmercury was 80%. In order to confirm the methylmercury concentration obtained, subaliquots of two distillates prior to UV irradiation were subjected to aqueous phase ethylation with $NaB(C_2H_5)_4$, collection on a packed GC column at −194 °C, separation at 120 °C on a GC column, decomposition of separated compounds by pyrolysis and detection by CV AAS.[23] Very similar results were obtained which proved that the organic mercury in the distillates corresponded to methylmercury.
- **4B:** The second method is based on acid leaching by 6M HCl, anion-exchange separation of organic and inorganic mercury, UV irradiation and measurement of organic mercury as Hg^{2+} by $SnCl_2$ reduction, gold amalgamation and CV AAS detection.[16] The recovery of spiked methylmercury was more than 98%.

Total mercury was determined after acid digestion with 10 ml conc. HNO_3 at 150 °C for 8 h in closed quartz vessels.[16] Mercury was then measured by $SnCl_2$ reduction, gold amalgamation and CV AAS detction.

Laboratory 5

This laboratory used the same methods as Laboratories 2 and 3.[7, 8, 14, 17] The reported recovery for spiked methylmercury was 82%.

Laboratory 6

Methylmercury was extracted with HCl followed by subsequent extraction with toluene. This step was repeated twice. The clean-up step included back-extraction of methylmercury into aqueous thiosulphate solution. About 25 µl of this solution was injected onto an octadecylsilane HPLC column (200 × 3 mm i.d.). Mercury compounds were separated by isocratic elution with a methanol/water mixture (30:70, modified with 0.1 mM 2-mercaptoethanol) and, after convertion to elemental mercury in an oxidation/reduction interface, on-line detected by CV AFS. The method is precisely described elsewhere.[18, 19, 20]

Laboratory 7

The same analytical method as in Laboratories 2, 3 and 5 was used.

RESULTS AND DISCUSSION

As mentioned earlier, the overview of participating laboratories and methods used is given in Table 1. Various separation techniques were used. In the very first step, when methylmercury was released from the binding sites, three approaches were used: distillation, alkaline digestion and acid leaching. Further processing included additional separation using anion exchange separation of organic and inorganic

Table 2 Results for methylmercury compounds determined by various analytical methods used by participating laboratories

Laboratory no.[a]	Laboratory/method code	Methylmercury composition concentration (ng g^{-1})	n[b]	Total Hg (μg g^{-1})	n
1	1A	5.20 ± 0.61	6	6.87 ± 0.35	8
	1B	5.94 ± 0.71	4		
	1C	3.66 ± 0.37	4		
2	2A	5.87 ± 0.20	5	6.69 ± 0.27	3
	2B	6.83 ± 0.50	5		
3	3	5.28 ± 0.29	6	6.18 ± 0.33	3
4	4A	6.15 ± 0.56	5	6.34 ± 0.27	3
	4B	5.97 ± 0.65	9		
5	5	5.02 ± 0.19	5	n.r.[c]	
6	6	3.87 ± 0.46	5	n.r.	
7	7	4.74 ± 0.54	16	n.r.	

[a] See Table 1. [b] Number of independent determinations. [c] Value not reported.

mercury, derivatization by aqueous phase ethylation and GC separation and solvent extraction with a clean up step using equilibration into aqueous cysteine or thiosulphate solution and back-extraction into organic solvent. Additionally, several detection systems were used: CV AAS, GC combined with CV AFS, CV AAS and ECD detector and HPLC with CV AFS detector. This study therefore really represents an intercomparison of various analytical methods. The results obtained are shown in Table 2. However, some laboratories also reported total mercury values which are also reported in Table 2. The value for total mercury was certified on the basis of the results reported in the world-wide intercomparison exercise[11] and the certified value is 7.35 μg g^{-1} with a 95% confidence interval from 6.65–7.93 μg g^{-1}. The acceptable range, calculated as two times the confidence interval of the median, is from 5.77–8.33 μg g^{-1}. All values reported by participating lboratories are within the acceptable range.

The laboratory method mean values are plotted in ascending concentration values in Fig. 2. As evident, results reported vary between 3.66 and 6.83 ng g^{-1}. Although initially it appears that results are in good agreement, close examination of the results obtained by various methods have shown that differences can be related to the methods used. The results obtained by acid leaching followed by solvent extraction (Laboratory/method code 1C and 6) are lower than other reported results. This can be explained by the fact that acid leaching alone cannot release methylmercury compounds from the sediment quantitatively, which is in agreement with recently published studies.[6,7] Even with the addition of copper(II) ions quantitative release of methylmercury could not be achieved. Laboratory 1 has released methylmercury by H_2SO_4(sat.$CuSO_4$) and KBr, while Laboratory 6 has used 6 M HCl only. The final results are almost the same. Laboratory 1 has applied the same extraction procedure to distillates and alkaline digested samples and the values obtained were much higher, 5.20 and 5.94, respectively. This clearly supports the conclusions drawn in other papers[6,7] that when sediments rich in organic matter are to be analysed, acid leaching releases only a certain fraction of methylmercury. Addition of copper(II) ions can increase the amount of methylmercury but not quantitatively. Similar conclusions were also reported from a methodological comparison study performed by Padberg *et al.*[4,9,15] for organic rich soil and sediment samples.

The highest result reported in this study was provided by Laboratory 2 using alkaline digestion followed by aqueous phase ethylation, room temperature pre-collection on Carbotrap, GC separation and CV AFS detection.[13,14] It has been shown that when a sample with high concentration of inorganic mercury is analysed using the above procedure a spurious formation of ethylmethylmercury is formed.[7,8] This might certainly be a problem with a quality of ethylating reagent. Since the sediment sample IAEA-356 contains a relatively high inorganic mercury concentration it can be concluded that a higher methylmercury value was obtained due to this effect.

Interesting results were obtained by

Laboratory 4 which applied a non-specific measurement of methylmercury. This means that methylmercury was measured as inorganic mercury after decomposition of methylmercury by UV irradiation. As already mentioned in the experimental section, the presence of methylmercury in the distillate was confirmed by derivatization of methylmercury into its volatile ethylmethylmercury derivative and measured by GC and CV AAS detection.[22] The second method which is based on acid leaching and separation of organic and inorganic mercury has been shown to be very unspecific for determination of methylmercury compounds in samples such as sediments soils and organic rich water samples .[4,6,8,12] Usually it resulted in too high an organic mercury value. However, in this intercomparison the result obtained compares well with the rest of the results. It is believed that the value obtained does not correspond to methylmercury since the preseparation was performed by 6 M HCl which, as mentioned above, is not able to release methylmercury from this sample quantitatively. This is a typical example in which a good agreement of the result obtained by a non-specific method may be misleading. A good agreement on one complex environmental sample, such as the sediment used in the present intercomparison, does not necessarily mean that the method in general gives accurate results.

Distillation was used by six laboratories as a pre-separation technique. In most laboratories small sample weights (less than 0.50 g) were taken for distillation, since their final detection systems were relatively very sensitive. At the IAEA laboratory larger sample weights were taken in order to achieve a necessary concentration of methylmercury in the final extract. Initially about 2 g of sample was distilled. The recovery of spiked mercury was extremely low (<5%). With smaller sample weights a significant improvement in the recovery of spiked methylmercury was obtained. For example, spiking recovery increased from ~10% for 1.5 g of the sample to 75% for 0.5 g of the sample. It is therefore important to note that when separating methylmercury from this sediment by distillation, sample weights should not exceed 0.5 g. Experiments on the effect of sample weight on spiking recovery have already been performed in earlier studies on various environmental and biological samples.[6,7] Such strong interference of the sample weight had not been observed. This further suggests that when analysing such complex matrices as the present sediment, precautions in many respects are necessary.

The consensus value for total methylmercury

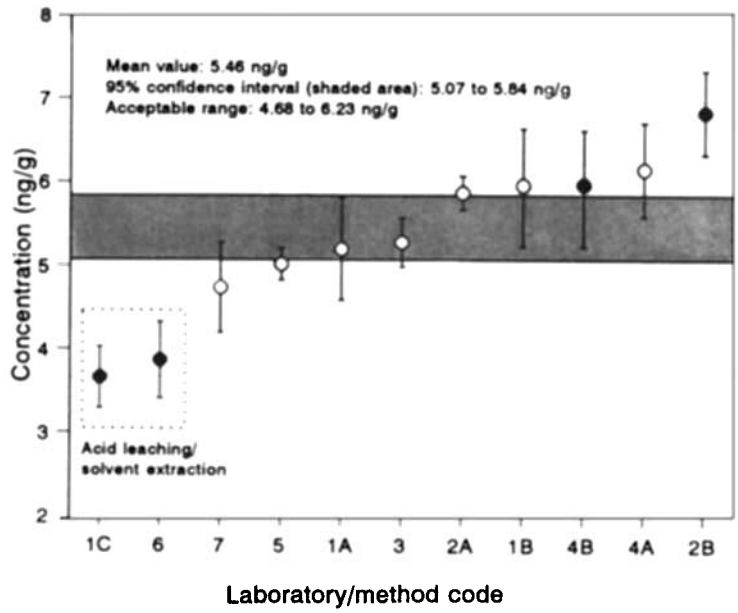

Figure 2 The laboratory method mean values for methylmercury compounds (calculated as mercury) plotted in ascending concentration on the *y*-axis and their respective laboratory method codes noted along the *x* axis. The respective standard deviations (SD) of the means are shown as error bars. Shaded area represents the 95% confidence interval. The solid points indicate results that were not included in the calculation of the concensus value (see text for the explanation).

compounds was therefore calculated taking into account the results obtained by Laboratory code methods 1A, 1B, 2A, 3, 4A, 5 and 7, excluding the results obtained by acid leaching and solvent extraction (1C, 6), alkaline digestion (2B) followed by aqueous phase ethylation and unspecific anion exchange separation and CV AAS detection (4B). Results obtained by those methods are, however, extremely important since they confirm the conclusions of previously published studies.[4,6-8,9,15]

CONCLUSIONS

The value for total methylmercury compounds in reference material IAEA-356 has been certified. It can be concluded that a good sample in terms of representing a 'difficult' matrix chosen. The intercomparison of the results obtained by well experienced laboratories have confirmed conclusions drawn by previous studies that when dealing with the analyses of complex matrices such as sediments, a careful evaluation of the results is necessary, particularly when using non-specific analytical methods. There is a need to organize similar intercomparison exercises on different kinds of sample matrices with various methylmercury concentrations. This will be of great help for both well experienced laboratories and those that have just started with such analyses.

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