APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 12, 531–539 (1998)

WORKING METHODS PAPER

Certification of Total Mercury and Methylmercury in an Estuarine Sediment, CRM 580

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Legislation on methylmercury within the European Union (EU), e.g. in food (national regulations) or water (EC Directives), requires that the determinations are of proven quality; thus implies that they should be carried out under strict quality control (QC). One method of achieving good quality control in chemical analysis is to verify the analytical performance of methods by analysing Certified Reference Materials (CRMs). While CRMs of biological matrices (e.g. fish, mussels) are already available, there was a lack of materials for the QC of sediment analysis. This paper describes the preparation of an estuarine sediment reference material, the homogeneity and stability studies and the analytical work performed for the certification of the contents of total mercury and methylmercury. The results of a group of expert laboratories are discussed and the methods used to certify the mass fractions of total mercury (132 ± 3 mg kg^{-1} on a dry mass basis) and methylmercury (75.5 ± 3.7 μg kg^{-1} as CH_3Hg^+ on a dry mass basis) are described.

Appl. Organometal. Chem. **12**, 531–539 (1998)

Keywords: methylmercury; estuarine sediment; certification; (BCR); quality control

Received 16 July 1997; accepted 2 September 1997

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INTRODUCTION

Methylmercury (MeHg) is known to be extremely toxic, which is of particular concern since this compound is widespread in the environment; it originates either from direct release or from the biomethylation of inorganic mercury in biological tissues,[1,2] or it may be produced by abiotic routes.[3] Due to a very effective biomagnification mechanism, food chains are enriched in MeHg, resulting in high levels in top predators (e.g. tuna fish).[4] The lack of knowledge on the toxic impact of MeHg in sediment (e.g. on filter-feeding organisms) and the need to understand better the environmental pathways justify the monitoring of this compound in various matrices (biota, water and sediment). Legislation on MeHg within the European Union, e.g. in food (national regulations) or water (EC Directives), requires that the determinations are of proven quality. The quality control of MeHg determinations was hardly possible at the beginning of the 1990s: this justified the organization of several interlaboratory studies to evaluate and improve the state of the art.[5,6] These improvements made it possible for certified reference materials (CRMs) of fish to be produced, e.g. by the National Research Council of Canada[7] and the BCR (Community Bureau of Reference),[8] which in turn offered laboratories the means to verify the performance of their methods using reliable CRMs. A certification campaign on MeHg in sediment has recently been organized by the International Atomic Energy Agency (IAEA, Vienna), which showed a reasonable agreement between techniques (coefficient of variation between laboratory means of *ca* 14% for a MeHg level of 5.46 μg kg^{-1}) and enabled a CRM to be produced[9]. Upon the request of a

 CCC 0268–2605/98/080531–09 $17.50

consortium of laboratories from different EU and EFTA (European Free Trade Association) Member States, the Measurements and Testing Programme (formerly BCR) has organized an interlaboratory study for the evaluation of the performance of methods for the determination of MeHg in a highly contaminated sediment which was successfully concluded in 1995.[10] The project was pursued by preparation of a sediment candidate reference material (CRM 580) which was certified for its content of total mercury and methylmercury. This paper describes the results of the interlaboratory study, the preparation of the candidate CRM and homogeneity and stability studies, the methods used in the certification and the results of the technical and statistical evaluation.

INTERLABORATORY STUDIES

Interlaboratory studies were organized within the BCR programme, from 1987, to improve the quality of mercury speciation analyses.[5] The first interlaboratory study dealt with the analysis of solutions containing pure substances (CH_3HgCl in toluene, mixtures of MeHgCl, C_2H_5HgCl and C_6H_5HgCl in toluene, and aqueous solutions of MeHgCl and $HgCl_2$). No systematic errors could be detected in the final determination techniques tested at this stage. A second exercise was undertaken in 1989 on the determination of MeHg in fish extracts (raw extract, raw extract spiked with MeHg, and cleaned extract). Analyses of extracts led to difficulties mainly attributable to a lack of good long-term reproducibility for many laboratories. Capillary GC was found to offer good possibilities, but its use was hampered by the absence of commercially available columns. A third intercomparison was carried out in 1990 dealing with the analysis of toluene extracts and freeze-dried samples of mussel and fish tissues. Sources of discrepancies were detected, the most important one being the inadequacy of the packed chromatographic columns; other sources of error were due to interferences in MeHg determination in mussel tissue. Recommendations were given to use capillary columns at the certification stage and to take the necessary precautions for cleaning up the extracts (e.g. use of cysteine paper to remove impurities by washing repeatedly with toluene while MeHg is immobilized on the cysteine paper). The coefficients of variation (CVs) obtained between laboratories were 17.4% and 13.7% for the mussel and fish samples, respectively; the higher CV obtained for mussels was attributed to the much lower level of MeHg than that in tuna fish ($0.14\ mg\ kg^{-1}$ and $4.33\ mg\ kg^{-1}$ as MeHgCl, respectively). The good agreement of the results obtained in the last trial encouraged the BCR to organize a certification campaign on methylmercury in fish materials containing high levels of mercury (i.e. ranging from 2 to $5\ mg\ kg^{-1}$ of methylmercury). Details of these interlaboratory studies are available elsewhere.[5]

As a follow-up to these studies, there was a project to test the feasibility of preparation and certification of a sediment containing high levels of methylmercury. It included the collection, preparation, homogenization, stabilization by gamma-irradiation, and homogeneity and stability studies of a test material, followed by an interlaboratory study with a group of EU expert laboratories.[10] This interlaboratory project made it possible to confirm the feasibility of preparation of a candidate CRM and to detect and remove some systematic errors in the methods used in the exercise. The CV obtained for the mean of laboratory means was *ca* 16% at a level of $53.1 \pm 8.5\ \mu g\ kg^{-1}$ as MeHg. Besides errors due to an apparent lack of quality control for some laboratories, a systematic bias was suspected to occur in relation to the distillation procedure; hence, recommendations were given that this method be carefully checked by spiking experiments for further use in the certification campaign.[10] The outcome of the technical scrutiny was a clear illustration of the effects and importance of participating in interlaboratory studies; indeed, most of the laboratories from which the data were selected had participated previously in the stepwise interlaboratory programme on MeHg in solutions and biological samples, whereas most of the other laboratories for which sources of error were identified were participating in such an exercise for the first time.[10] This interlaboratory study gave encouragement to the latter laboratories to improve their methods, which were further tested in the course of the certification described in the present paper; the results clearly stressed the importance of method validation, including recovery tests, to obtain accurate results.[11]

PREPARATION OF THE CANDIDATE CRM

Sample preparation

The sediment was collected in 1994 in the Ravenna Lagoon (Italy) close to a petrochemical plant water discharge. A batch of *ca* 250 kg was collected from

a boat, using a grab to retrieve the 30–40 cm top sediment layer. The wet material was sieved to pass apertures of 2 mm and air-dried at 25 °C in a drying chamber. The moisture content was monitored during the drying process; when a constant moisture content was reached (3.5%), the material was manually crushed and sieved again at 2 mm to remove coarse particles (the fraction above 2 mm was discarded). The resulting material was stored in polyethylene bags and transported to the Joint Research Centre of Ispra (Italy).

The material was passed through a hammer mill with tungsten carbide blades, and sieved to pass apertures of 90 μm in order to ensure good homogenization. The < 90 μm fraction was collected in a PVC mixing drum (filled with dry argon) and homogenized for 14 days at about 48 rpm. The bottling procedure was performed manually: a first series of 20 bottles was filled and immediately closed with screw-caps and plastic inserts. Series of 20 bottles were filled successively, alternating with remixing of the powder for 2 min. All bottles were stored at ambient temperature in the dark. Around 1100 bottles were prepared, each containing *ca* 40 g.

Stabilization

The optimal stabilization procedure (by gamma irradiation) investigated on the test material in the interlaboratory study[10] was used on the candidate CRM. The optimal gamma irradiation dose was found to be 8 kGy, which sterilized the sediment without affecting the methylmercury content.[10,12]

Homogeneity tests

The between-bottle homogeneity of the candidate CRM 580 was verified by the determination of total mercury and methylmercury on sample sizes of 50, 100 and 250 mg taken from 20 bottles which were set aside at regular intervals during the whole period of bottling. The within-bottle homogeneity was assessed by 10 replicate determinations of total mercury and methylmercury on sample sizes of 50, 100 and 250 mg taken from one bottle.

Each bottle was shaken manually to eliminate segregation which might have occurred during transport and storage. For the determination of total mercury, 100 mg dry sediment was mineralized by addition of aqua regia. The final determination was performed by cold-vapour atomic absorption spectrometry (CV AAS) after $SnCl_2$ reduction. Methylmercury was determined by capillary gas chromatography (CGC) followed by hydride-generation atomic absorption spectrometry (HG AA). A portion of 0.1–0.5 g dry sediment was extracted by addition of 5 ml of 2.5 M H_2SO_4, followed by addition of 5 ml toluene; after centrifugation, the supernatant was placed in a 10-ml vial containing 4 ml thiosulphate solution. After shaking for 30 s, the toluene layer was discarded and the thiosulphate solution was transferred into a 25-ml beaker and heated on a hotplate (200 °C) to evaporate the solution to 2–3 ml. After cooling, the remaining solution was diluted to 10 ml with water and stored for analysis. An aliquot of this extract was transferred into a purge trap vial and 100 μl of 1% $NaBH_4$ was added to the purged solution. The methylmercury hydride formed was trapped at 120 °C in a CGC column, separated and detected by CV AA. The uncertainties of the methods of final determination were assessed by the analysis of five aliquots from one digest solution (nitric acid for total mercury, toluene for methylmercury). The CV of the method, therefore, does not include the CV introduced by the extraction procedure.

The CVs for total mercury and methylmercury in CRM 580 are presented in Table 1. An *F*-test at a significance level of 0.05 did not reveal significant differences between the within- and between-bottle variances for MeHg and total Hg in the CRM. The within-bottle CV for total mercury is very close to the CV of the method; with respect to methylmercury, the higher value of the within-bottle CV in comparison to the method CV represents the additional uncertainty related to extraction which is not taken into account in the method-CV calculation (analysis of extracts). On the basis of these results, no inhomogeneities in the material were suspected. It was concluded that the material is suitable for use as a CRM and is homogeneous, at an analytical portion of 250 mg and above, for total mercury and methylmercury.

Stability tests

The stability of the total mercury and methylmercury contents was tested to determine the suitability of this material as a candidate CRM. Bottles were kept at -80, $+20$ and $+40$ °C, respectively, over a period of 15 months (starting in October 1995) and total mercury and methylmercury were determined at regular intervals during the storage period.

Tests were made at the beginning of the storage period and after 1, 3, 6, 11 and 15 months. Samples were analysed using the same procedures as for the homogeneity study. Total mercury and methylmer-

Table 1 Within- and between-bottle homogeneity for CRM 580: CV $\pm$ U_{CV} (%)[a]

Intake (mg)	Between-bottle[b]	Within-bottle[c]	Method of final determination[d]
50			
Total Hg	—	4.5 ± 1.2	—
MeHg	—	7.2 ± 2.2	—
100			
Total Hg	—	5.1 ± 1.6	—
MeHg	—	6.2 ± 1.9	—
250			
Total Hg	3.6 ± 0.6	5.0 ± 1.5	4.1 ± 1.3
MeHg	7.2 ± 1.2	5.6 ± 1.8	2.5 ± 0.8

[a] Uncertainty on the CVs: $U_{CV} \approx CV/\sqrt{2n}$.
[b] Single determination on the content of each of 20 bottles.
[c] 10 replicate determinations on the content of one bottle.
[d] 5 replicates of an digest/extract solution.

cury were each determined five times (one replicate analysis in each of five bottles stored at different temperatures) on each occasion of analysis.

Any change with time in the content of a element or compound indicates an instability. Instability would be detected by comparing, on the various occasions of analysis, the contents of different elements or compounds in samples stored at different temperatures with those stored at a low temperature.

The samples stored at -80 °C were used as reference for the samples stored at $+20$ °C and at $+40$ °C respectively. Table 2 gives the ratios (R_T) of the mean values (X_T) of five measurements made at $+20$ °C and $+40$ °C, respectively, to the mean values ($X_{-80\,°C}$) of five determinations made on the same occasion of analysis of samples stored at a temperature of -80 °C:

$$R_T = X_T / X_{-80\,°C} \quad [1]$$

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

$$U_T = (CV_T{}^2 + CV_{-80\,°C^2})^{1/2} \cdot R_T/100 \quad [2]$$

In the case of ideal stability, the ratios R_T should be 1. In practice, however, there are some random variations due to the error on the measurement. In almost all cases, $R_T - U_T \leq 1 \leq R_T + U_T$ for both total mercury and methylmercury. The uncertainty in the CV can account for the deviations observed. On the basis of these results, it was concluded that no instability of the material could be demonstrated.

METHODS USED IN THE CERTIFICATION

After a preparatory meeting in which all the requirements for certifying reference materials were reviewed, two bottles of the candidate CRM were shipped to each of the participating laboratories (see Acknowledgements). Each laboratory that took part in the certification exercise was requested to perform six independent replicate determinations on at least two different bottles of the CRM on different days. The results were statistically evaluated, presented in the form of bar charts and discussed at a technical meeting with all the participants. A brief description of the methods used is given below; additional details on these methods may be found in the certification report.[12]

Laboratory 01

A subsample of 200 mg was digested with a HNO_3/NaCl mixture, followed by gold preconcentration and determination of total Hg by CV AA.

Laboratory 02

Total Hg was determined by cold-vapour atomic fluorescence spectrometry (CV AF) after pressurized digestion with H_2SO_4 for 6–8 h at 100 °C, addition of BrCl, reduction with $SnCl_2$ and gold preconcentration. For MeHg, a CRM subsample of 200 mg was pretreated by addition of H_2SO_4/KCl, water–steam distillation, and ethylation with $NaBEt_4$ in acetate buffer solution. The recovery ($98 \pm 6\%$) was verified by spiking the CRM before

Table 2 Normalized results of the stability study

Species	Time (months)	$R_T \pm U_T$[a] 20 °C	$R_T \pm U_T$[a] 40 °C
Total Hg	1	1.06 ± 0.07	1.01 ± 0.09
	3	1.10 ± 0.05	1.04 ± 0.03
	6	0.96 ± 0.04	0.98 ± 0.04
	11	1.02 ± 0.03	1.10 ± 0.06
	15	1.06 ± 0.07	1.00 ± 0.03
Methylmercury	1	1.05 ± 0.10	1.13 ± 0.08
	3	1.00 ± 0.06	1.14 ± 0.06
	6	0.99 ± 0.06	1.05 ± 0.08
	11	0.98 ± 0.09	0.99 ± 0.07
	15	1.07 ± 0.15	1.09 ± 0.14

[a] R_T = ratio of the mean values (X_T) of five measurements made at +20 °C and +40 °C, respectively, and the mean value ($X_{-80\ °C}$), from five determinations made on the same occasion of analysis on samples stored at a temperature of −80 °C (Eqn [1]).
U_T = uncertainty obtained from the coefficient of variation (CV) of five measurements obtained at each temperature (Eqn [2]).

distillation (standard additions). Separation was by CGC, followed by CV AF detection.

Laboratory 03

Total Hg was determined by CV AA after pressurized digestion with H_2SO_4/HNO_3, reduction with $SnCl_2$ and gold preconcentration. For MeHg, a CRM subsample of 2000 mg was pretreated by addition of HCl and toluene, back-extraction with cysteine acetate, and re-extraction into toluene. The recovery (88 ± 5%) was assessed by two spikings of a CRM (PACS-1). Separation was by CGC, followed by electron capture detection.

Laboratory 04

A CRM subsample of 500 mg was extracted by supercritical fluid extraction with CO_2; the extract was eluted with toluene, followed by Grignard derivatization (n-butylmagnesium chloride). The recovery (57 ± 6%) was verified by a single addition of MeHg to the CRM. Separation was by CGC, followed by microwave-induced plasma–atomic emission spectrometric (MIP AE) detection.

Laboratory 05

Total Hg was determined by CV AA after pressurized digestion with H_2SO_4/HNO_3 in a microwave oven, and reduction with $SnCl_2$. For MeHg, a CRM subsample of 250 mg was pretreated by addition of H_2SO_4/NaCl, water–steam distillation, addition of acetate buffer and complexation with sodium pyrrolidine dithiocarbamate. The recovery (103 ± 7%) was verified by spiking the CRM before distillation and equilibrating overnight (standard additions). Separation was by high-performance liquid chromatography (HPLC) after preconcentration on a C_{18} column, and was followed by CV AA detection.

Laboratory 06

A CRM subsample of 500 mg was digested with HNO_3 in a microwave oven, which was followed by a derivatization with $NaBEt_4$, and cryogenic trapping. The recovery (95–100%) was verified by spiking the CRM before extraction and cross-checking with the reference material (RM) used in the intercomparison. Separation was by packed-column gas chromatography, followed by quartz-furnace atomic absorption spectrometric (QF AA) detection.

Laboratory 07

Total Hg was determined by CV AA after pressurized digestion with HNO_3/HCl and reduction with $SnCl_2$.

Laboratory 08

Total Hg was determined by CV AA after digestion with HNO_3 for 4 h at 80 °C, and reduction with $SnCl_2$. For MeHg, a CRM subsample of 1000 mg was pretreated by addition of HCl and toluene, back-extraction with thiosulphate, addition of acetate buffer, complexation and on-line oxidation (after HPLC) and reduction with $SnCl_2$. The recovery (103 ± 2%) was verified by spiking the

CRM before extraction. Separation was by HPLC, followed by CV AF detection.

Laboratory 09

Total Hg was determined by inductively coupled plasma–mass spectrometry (ICP MS) after microwave digestion with HNO_3 and reduction with $SnCl_2$.

Laboratory 10

Total Hg was determined by CV AA after digestion with HNO_3 for 4 h at 80 °C and reduction with $SnCl_2$. For MeHg, a CRM subsample of 500 mg was pretreated by addition of HCl and extraction into toluene. The recovery (80%) was verified by spiking the RM used in the intercomparison. Separation was by CGC, followed by electron capture detection.

Laboratory 11

Total Hg was determined by CV AA after microwave digestion with HNO_3/HCl and reduction with $SnCl_2$. For MeHg, a CRM subsample of 200 mg was pretreated by addition of H_2SO_4/HCl, water–steam distillation and $NaBEt_4$ derivatization. The recovery (80%) was verified by spiking the CRM before distillation. Separation was by CGC, followed by CV AA detection.

Laboratory 12

Total Hg was determined by CV AA after digestion with H_2SO_4/HCl and reduction with $SnCl_2$. For MeHg, a CRM subsample of 200 mg was pretreated by addition of H_2SO_4/NaCl, toluene extraction, addition of thiosulphate solution and $NaBEt_4$ derivatization. The recovery (85%) was verified by standard additions. Separation was by CGC, followed by CV AA detection.

Laboratory 13

Total Hg was determined by CV AA after digestion with HNO_3 for 3 h under reflux and addition of H_2O_2. For MeHg, a CRM subsample of 250 mg was pretreated by addition of HCl, toluene extraction, clean-up with cysteine solution and back-extraction into toluene. The recovery ($96 \pm 2\%$) was assessed by spiking a CRM extract. Separation was by CGC, followed by CV AA detection.

Laboratory 14

Total Hg was determined by ICP MS after microwave digestion with HNO_3/HCl. For MeHg, a CRM subsample of 200 mg was pretreated by addition of H_2SO_4/HCl, water–steam distillation, addition of acetate buffer solution, (SPDC) complexation, toluene extraction, UV irradiation and $NaBH_4$ reduction after HPLC. The recovery ($104 \pm 6\%$) was verified by standard additions at three spiking levels on wet sediment after equilibration for 5 h. Separation was by HPLC, followed by ICP MS detection.

Laboratory 15

Total Hg was determined by CV AA after digestion with HNO_3 for 4 h at 80 °C and reduction with $SnCl_2$.

TECHNICAL AND STATISTICAL DISCUSSION

All the results found acceptable after both the technical and statistical evaluation are presented in Figs 1 and 2. Each set of results is identified by the code number of the laboratory.

Technical discussion

Total mercury

Two sets of low results were rejected owing to the suspicion of mercury losses; the laboratories concerned had experienced the same difficulty in the interlaboratory study and were encouraged to investigate the source of error leading to biased results. The certified value is mainly based on results obtained by CV AA as final determination (except one set by CV AF spectrometry and two sets by ICP MS); however, the pretreatment techniques were widely different from one laboratory to another.

Methylmercury

As mentioned previously, the determination of MeHg in sediment is susceptible to a range of possible sources of error that have to be carefully controlled, e.g. incomplete extraction, incomplete derivatization or distillation, interferences in detection etc.

The first aspect considered in the technical discussion was related to the verification of

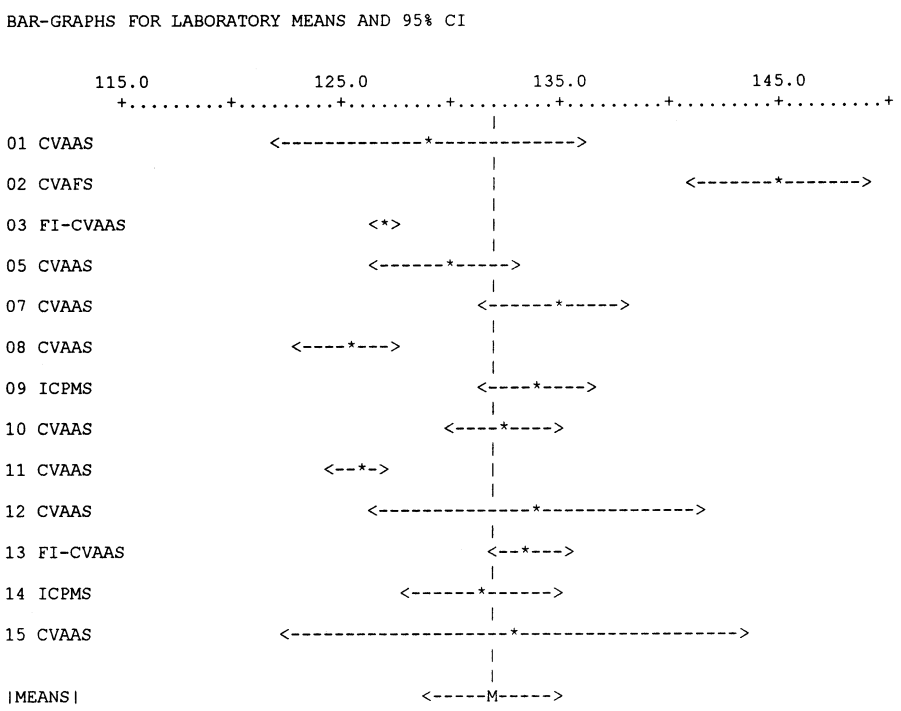

Figure 1 Total mercury (mg kg^{-1} as Hg): laboratory means and 95% confidence intervals.

calibrants. Most of the participants verified their calibrant using alternative calibrant solutions, other participants preferred to check their techniques using a certified reference material of sediment (such as the one produced by the IAEA[9]).

Discussions arose on the verification of the

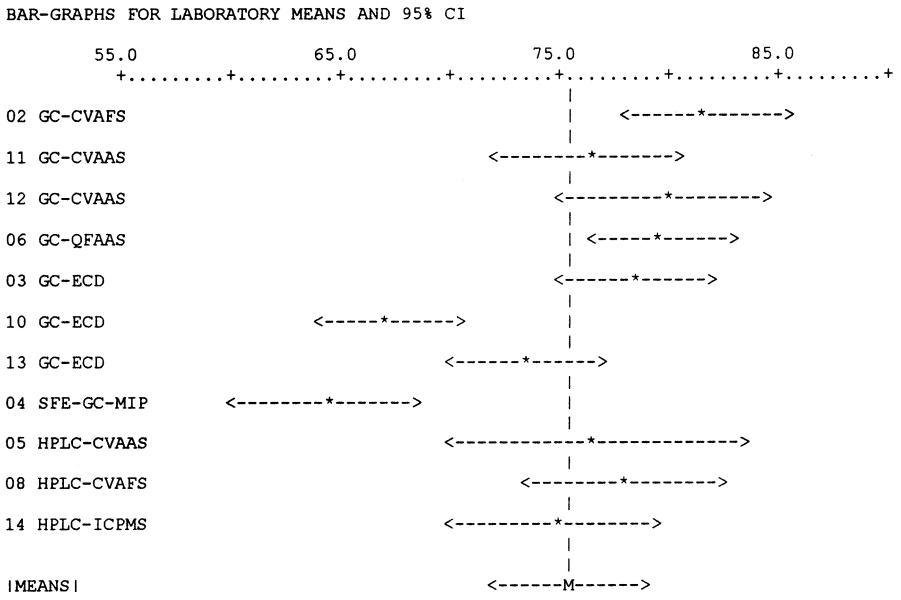

Figure 2 Methylmercury (μg kg^{-1} as MeHg): laboratory means and 95% confidence intervals.

extraction recoveries. At present, there is no standardized procedure for checking the extraction efficiency; the brief summaries (above) of the methods used show that they differed widely from one laboratory to another. The participants recognized that it would be necessary to find the most suitable recovery test so as to propose a standardized procedure in order to avoid possible discrepancies; the technique which was most supported was standard addition (e.g. three levels on wet sediment), equilibrating the spiked mixture overnight.

High results were observed with a technique involving distillation and UV destruction (separation of MeHg by water–steam distillation, removal of inorganic mercury by anion-exchange resin, decomposition of MeHg to ionic mercury by UV irradiation and detection by CV AA). Although the results were confirmed by HPLC, it was suspected that this technique did not remove all the inorganic mercury. This doubt had already been expressed at the first interlaboratory study[10] and the set was not accepted for certification.

The careful verification of the efficiency of distillation procedures (as recommended in the interlaboratory study) demonstrated that this method was in good agreement with alternative techniques using various types of extractions. This is shown in Fig. 2 where the results of laboratories using distillation (Labs 02, 11, 05 and 14) are in good agreement with the other sets of results. Doubts recently expressed on distillation-based procedures at the Conference 'Mercury as a Global Pollutant'[13] should therefore be considered with caution since distillation-based techniques prove to be accurate when applied with a thorough quality control.

Another set of high results was also rejected. The results were obtained by hexane extraction, derivatization with $NaBEt_4$, CGC separation and MIP–AE spectrometry detection (CGC–MIP). Although this technique was recognized as being suitable for MeHg determination, it appeared that its application in the laboratory was not sufficiently under control to produce accurate results.

Laboratory 04 experienced problems of elution from the column which justified the first data in the set to be withdrawn. The SFE technique gave a rather low recovery, which was nevertheless accepted for certification. The laboratory had submitted a second set of data obtained by distillation and CGC–MIP which was on the low side; the efficiency of the distillation was shown to be much lower (70%) than that of the other laboratories using the same technique, which justified withdrawal of the data.

One laboratory used a biological CRM for calibration which could obviously not be accepted for certification. The set of data was rejected.

Statistical discussion

The sets of results accepted after technical scrutiny have been submitted to the following statistical tests: the Kolmogorov–Smirnov–Lilliefors tests to assess the conformity of the distributions of individual results and of laboratory means to normal distributions; the Nalimov test to detect 'outlying' values in the population of individual results and in the population of laboratory means; the Bartlett test to assess the overall consistency of the variance values obtained in the participating laboratories; the Cochran test to detect 'outlying' values in the laboratory variances (s_i^2); and a one-way analysis of variance (*F*-test) to compare and estimate the between- and the within-laboratory components of the overall variance of all individual results. All these tests are described in the certification report.[12]

The estimates of the within-laboratory standard deviation (s_W) and the between-laboratory standard deviation (s_B), as derived from one way analysis of variance, demonstrate that the between-laboratory variation was not significant. For reasons of uniformity, it was decided to base the certification on the laboratory means rather than on all the individual results.

The sets of results found acceptable on technical and statistical grounds are represented in the form of bar charts in Figs. 1 and 2. In the figures the length of a bar corresponds to the 95% confidence interval of the laboratory mean. The certified values were calculated as the arithmetic means of the laboratory means (taking into account the number of sets accepted for certification after both statistical and technical scrutiny); this value is featured as a vertical dotted line on the bar charts (the uncertainty is given by the half-width of the 95% confidence interval).

It was verified that the population of results accepted for certification had a normal distribution, before the 95% confidence interval of the means of means was calculated (Kolmogorov–Smirnov–Lilliefors tests). In addition, no outlying mean values were detected (Nalimov test). The set of variances was not homogeneous for total Hg; as different methods were used, each having a different repeatability and reproducibility, this was not

Table 3 Certified mass fractions of total mercury and methylmercury in CRM 580

Component	Certified value	Uncertainty	Unit	p[a]
Total Hg	132	3	mg kg^{-1}	13
MeHg	75.5	3.7	μg kg^{-1}	11

[a] p = number of accepted sets of results.

surprising and it was fully acceptable. No outlying variances were detected.

CERTIFIED VALUES

The certified values (unweighted mean of p accepted sets of results) and their uncertainties (half-width of the 95% confidence intervals) are given in Table 3 as mass fractions (based on dry mass). Total mercury and methylmercury are certified as mass fractions of Hg (mg kg^{-1} as Hg) and CH_3Hg^+ (μg kg^{-1} as MeHg), respectively.

AVAILABILITY

CRM 580 is available from the Institute for Reference Materials and Measurements (IRMM), Retieseweg, B-2440 Geel (Belgium), along with a certification report describing the material preparation, homogeneity and stability studies, techniques used in the certification, technical and statistical evaluation of the results and all individual results.[12]

Acknowledgments This certification has been carried out under the EC Contract MAT1-CT93-0046 coordinated by the Studio di Ingegneria Ambientale (Milano, Italy). The sample preparation was carried out by the Joint Research Centre of Ispra (Italy) and Ecoconsult (Gavirate, Italy). The homogeneity and stability studies were performed by the Presidio Multizonale di Prevenzione's laboratories of La Spezia and Venezia (Italy). The following laboratories participated in the certification and are gratefully acknowledged:

ENEA, Divisione Chimica Ambientale (Roma, Italy);
GKSS Forschungszentrum (Geesthacht, Germany);
Kernforschungsanlage, Inst. Angewandte Physikalische Chemie (Jülich, Germany);
Presidio Multizonale di Prevenzione, Lab. Chimico (La Spezia, Italy)
Presidio Multizonale di Prevenzione, Sezione Chimico Ambientale (Venezia, Italy);
rivo-dlo (Ijmuiden, The Netherlands);
Service Central d'Analyse, CNRS (Vernaison, France);
Swedish Environmental Research Institute (Gøteborg, Sweden);
Universität Bayreuth, Inst. für Terrestrische Ökosystemforschung (Bayreuth, Germany);
Universität Heidelberg, Institut für Sedimentforschung (Heidelberg, Germany);
Université de Bordeaux I, Lab. Photochimie Moléculaire (Talence, France);
Univ. de Santiago de Compostela, Depto. Química Analítica (Santiago, Spain);
University of Umeå, Dept. of Analytical Chemistry (Umeå, Sweden);
Vrije Universiteit Amsterdam, Inst. voor Milieuvraagstukken (Amsterdam, The Netherlands);
Vrije Universiteit Brussel, Lab. Analytical Chemistry (Brussels, Belgium).

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