Applied Organometallic Chemistry (1989) 3 257–266

0268-2605/89/03308257/$03.50

WORKING METHODS PAPER

An international intercalibration for methylmercury in biological tissue

Y. Thibaud and D. Cossa
Institut Français de Recherche pour l'Exploitation de la Mer, BP 1049, F-44037 Nantes Cedex 01, France

Received 2 November 1988 *Accepted 19 December 1988*

An intercalibration exercise between 13 laboratories from seven countries was conducted for comparing the methylmercury measurement techniques for marine biological tissues. Analyses have been conducted on two sets of samples: a fish muscle and a mussel soft tissue. Most of the participating laboratories performed six replicate analyses, allowing statistical comparisons. Various analytical techniques have been used, including cold vapour atomic absorption spectrophotometry (CVAA), electron capture gas liquid chromatography (GCEC), neutron activation (NAA), and inductively coupled plasma–isotopic dilution mass spectrometry (ICPIDMS). All of these methods offer similar results. They allow us to define consensus values which seem good estimates of the real concentrations. In addition the results show, for most of the participating laboratories, good accuracy and precision in the determination.

Keywords: mercury, methylmercury, intercalibration, biota, analysis

INTRODUCTION

Certain metals occur in marine organisms as relatively stable organometallic compounds. Organic mercurial compounds, especially the most common form, methylmercury, are highly toxic. Thus, it is very important to have accurate data about the amount of this kind of compound in seafood. Since 1971, the International Council for the Exploration of the Sea (ICES) has organized seven intercomparison exercises to test the measurement of trace metals in marine biological tissues. Encouraging results were obtained suggesting the efficiency of such exercises in improving reliability and intercomparability of data produced during monitoring programmes.[1–3] Therefore ICES suggested an intercomparison exercise on the analyses of methylmercury in biological tissues. The Marine Chemistry Working Group of ICES decided to focus the exercise on the measurements of methylmercury in fish muscle and mussel soft tissue. It was carried out in 1987 and restricted to laboratories that had experience with the analysis of methylmercury. The present report describes the results obtained.

EXPERIMENTAL

Sample preparation and distribution

The two sets of samples (fish muscle and mussel soft tissue) were provided by the National Research Council of Canada and came from the remaining stock of the ICES 7/TM/BT intercomparison exercise. Sample E consisted of dog fish muscle; Sample H consisted of soft tissue of blue mussel (*Mytilus edulis*). Their preparation procedure and their trace metal contents have already been described.[3]

After homogenization, the material provided was distributed in 25 g amounts in glass bottles previously cleaned with an acid wash in a clean room and dried at 350°C in an oven. Screw-on plastic caps were fitted with Teflon liners. The bottles were labelled and wrapped hermetically in sealed plastic bags.

The sets of two bottles each (samples E and H) were sent in August 1987 to the participating laboratories. In February 1988 the results were received from 13 laboratories, which are listed in Table 1.

Table 1 List of participating laboratories

Country	Lab. no.	
Canada	1	Drs S. Berman and M. Sin, Division of Chemistry, National Research Council Canada, Montreal Road, Ottawa, Canada KIA OR6
	8	Dr A. Rieger, Department of Fisheries and Oceans, Central and Arctic Region, Freshwater Institute, 501, University Crescent, Winnipeg, Canada R3T 2N6
Denmark	3	Dr. I. Drabaek, Danish Isotope Center, Skelbaekgaede 2, DK-1717 Kbh. V, Denmark
	15	Dr H. U. Riisgard, Institute of Biology, Odense University, Campusvej 55, DK-5230 Odense M, Denmark
France	5	M. R. Flaugnatti, Laboratoire Municipal et Regional, 29, rue Bourg l'Abbé, F-76000 Rouen, France
	18	Dr Y. Thibaud and B. Averty, IFREMER, Centre de Nantes, BP 1049, F-44037 Nantes Cedex 01, France
German Democratic Republic	11	Dr. G. Manthey, BezirksHygieneInspektion und Hygiene-Institut, Stephanstr. 18, DDR-2500 Rostock, GDR
	14	Dr M. Roschig, Arbeits hygienisches Zentrum der Chemischen, Industrie der DDR Betriebspoliklinik, DDR-4220 Leuna, GDR
	20	Dr G. Wolff, Institut für Hochseefischerei Rostock–Marieneche, an der Jägerbäk 2, DDR-2510 Rostock, GDR
German Federal Republic	6	Dr U. Harms, Bundesforschungsanstalt für Fischerei, Labor für Radioökologie der Gewässer, Wüstland 2, D-2000 Hamburg 55, FRG
Norway	9	Dr K. Julsham, Fiskeridinektoratets Ernarings Institute, Lars Hilles gt. 26, PO Box 4285, 5028 Bergen, Norway
Sweden	12	Dr B. Ohlin, Food Research Laboratory, The National Food Administration, Box 622, S-75126 Uppsala, Sweden
	19	Dr B. Westöö, Swedish Environmental Research Institute, PO Box 21060, S-100 31 Stockholm, Sweden

RESULTS

The data

The data presented some disparity with respect to the results concerning organic mercury compounds. They included:

(a) total mercury, methylmercury or organic mercury on samples E and H by nine laboratories (3, 6, 8, 9, 11, 12, 14, 18 and 19);
(b) total mercury, organic mercury and methylmercury on sample E and total mercury on sample H by three laboratories (1, 5 and 15);
(c) only methylmercury on samples E and H by laboratory 20.

Most participating laboratories performed six replicates for total mercury, organic mercury or methylmercury. We checked that all results had been expressed as mercury whatever the chemical form was. In addition, all the laboratories measured the water content of the samples as requested. All mercury concentrations are expressed on a dry weight basis.

All analytical data (moisture, total mercury, organic mercury or methylmercury) are given in Table 2. In addition, methylmercury and organic mercury results are presented in Fig. 1 for sample E and Fig. 2 for sample H.

The description of analytical methods used by different laboratories and their detection limits are given in Table 3.

Statistical approach

In order to approach the real concentration in the samples in order to be able to assess the analytical

Table 2 Analytical results

m, average concentration; SD, standard deviation; x, individual results, in μg Hg g^{-1} (dry wt).

Laboratory	Sample	H_2O (%)	Total Hg, $m \pm$ SD (CV) $x_1, x_2, x_3, \ldots x_6$	Methyl Hg, $m \pm$ SD (CV) $x_1, x_2, x_3, \ldots, x_6$	Organic Hg, $m \pm$ SD (CV) $x_1, x_2, x_3, \ldots, x_6$
1	E	2.2	2.2 ± 0.2 (9%) 2.2, 2.1, 2.6, 2.0, 2.0, 2.1	1.1 ± 0.1 (9%) 1.0, 1.1, 1.1, 1.1, 1.0, 1.0, 1.0, 1.1, 1.0, 1.2, 1.0	1.1 ± 0.0 1.1, 1.1, 1.1 0.8 ± 0.1 (13%) 0.8, 1.0, 0.8, 0.8, 0.7
	H	1.8	0.17 ± 0.03 (18%) 0.21, 0.14, 0.17, 0.14, 0.17, 0.16		
3	E	3.5	2.114 ± 0.180 (9%) 1.891, 2.378, 2.052, 2.248, 1.975, 2.139		0.985 ± 0.072 (8%) 0.989, 1.080, 0.929, 1.034, 0.878, 0.998
	H	3.5	0.180 ± 0.009 (5%) 0.180, 0.176, 0.166, 0.184, 0.192, 0.180		0.056 ± 0.004 (7%) 0.050, 0.053, 0.058, 0.056, 0.061, 0.058
5	E	2.7	1.567 ± 0.092 (6%) 1.500, 1.490, 1.680,1.670, 1.600, 1.460	0.908 ± 0.051 (6%) 0.973, 0.850, 0.976, 0.855, 0.900, 0.896	
	H	2.8	0.202 ± 0.011 (5%) 0.192, 0.201, 0.207, 0.200, 0.215, 0.198		
6	E	4.9	2.07 ± 0.04 (2%) 2.08, 2.12, 2.09, 2.07, 2.03, 2.00	1.42 ± 0.05 (4%) 1.45, 1.47, 1.36, 1.46, 1.37, 1.41	
	H	5.1	0.20> ± 0.005 (2%) 0.209, 0.210, 0.213, 0.209, 0.201, 0.214	0.078 ± 0.005 (6%) 0.075, 0.078, 0.086, 0.075, 0.078, 0.073	
8	E	12.9	2.21 ± 0.17 (7.8%) 2.09, 2.41, 2.27, 2.37, 2.16, 1.96		1.43 ± 0.11 (7.4%) 1.32, 1.38, 1.32, 1.55, 1.44, 1.55
	H	5.5	0.18 ± 0.02 (12.4%) 0.17, 0.19, 0.21, 0.20, 0.17, 0.15		0.08 ± 0.033 (41%) 0.11, 0.11, 0.05, 0.11, 0.05, 0.05
9	E	8.0	2.03 ± 0.136 (7%) 2.19, 2.08, 1.91, 1.93, 1.91, 2.18		1.20 ± 0.098 (8%) 1.29, 1.18, 1.01, 1.23, 1.25, 1.21
	H	3.7	0.235 ± 0.014 (6%) 0.206, 0.241, 0.241, 0.244, 0.240, 0.239		0.042 ± 0.021 (50%) 0.010, 0.066, 0.048, 0.054, 0.052, 0.023
11	E	4.4	1.87 ± 0.05 (3%) 1.82, 1.81, 1.84, 1.89, 1.95, 1.89		1.16 ± 0.03 (3%) 1.16, 1.16, 1.19, 1.16, 1.18, 1.11 1.02 ± 0.07 (7%) 1.08, 0.97, 1.05, 1.11, 0.94, 0.97
	H	3.9	0.192 ± 0.005 (3%) 0.185, 0.193, 0.193, 0.193, 0.190, 0.200		0.054 ± 0.003 (6%) 0.056, 0.058, 0.050, 0.054, 0.054, 0.050

Table 2 *(continued)*

Laboratory	Sample	H_2O (%)	Total Hg, $m \pm$ SD (CV) $x_1, x_2, x_3, \ldots x_6$	Methyl Hg, $m \pm$ SD (CV) $x_1, x_2, x_3, \ldots, x_6$	Organic Hg, $m \pm$ SD (CV) $x_1, x_2, x_3, \ldots, x_6$
12	E	5.5	2.03 ± 0.098 (5%) 2.06, 2.06, 2.16, 1.86, 2.02, 2.00	0.80 ± 0.05 (6%) 0.77, 0.76, 0.79, 0.80, 0.90, 0.77	
	H	3.2	0.19 ± 0.02 (11%) 0.17, 0.17, 0.18, 0.20, 0.22, 0.20	0.086 ± 0.006 (7%) 0.086, 0.083, 0.095, 0.080, 0.081, 0.091	
14	E	6.0	1.77 ± 0.12 (7%) 1.88, 1.93, 1.66, 1.70, 1.69		1.14 ± 0.17 (15%) 1.29, 1.32, 0.94, 1.05, 1.03
	H	3.6	0.17 ± 0.005 (3%) 0.17, 0.16, 0.17, 0.17, 0.16, 0.16		0.04 ± 0.004 (10%) 0.04, 0.04, 0.04, 0.04, 0.04, 0.03
15	E	3.4	1.853 ± 0.093 (5%) 1.880, 1.922, 1.947, 1.729, 1.745, 1.896		0.862 ± 0.090 (10%) 0.914, 0.878, 0.912, 0.741, 0.763, 0.966
	H	3.7	0.109 ± 0.035 (32%) 0.093, 0.090, 0.100, 0.075, 0.124, 0.172		
18	E	10.2	1.86 ± 0.11 (6%) 1.80, 1.80, 1.81, 1.85, 2.06	1.00 ± 0.02 (2%) 1.02, 1.02, 1.01, 0.97, 1.00, 1.00	
	H	5.5	0.174 ± 0.004 (2%) 0.168, 0.173, 0.180, 0.174, 0.175	0.045 ± 0.003 (7%) 0.048, 0.043, 0.042, 0.047, 0.048, 0.042	
19	E	9.2	2.250 ± 0.113 (5%) 2.460, 2.250, 2.180, 2.260, 2.180, 2.150	0.356 ± 0.043 (12%) 0.350, 0.400, 0.400, 0.310, 0.320	
	H	5.4	0.183 ± 0.0027 (2%) 0.179, 0.183, 0.184, 0.182, 0.185, 0.187	0.0545 ± 0.0024 (2%) 0.056, 0.054, 0.055, 0.058, 0.053, 0.051	
20	E	4.7		0.68 ± 0.036 (5%) 0.73, 0.70, 0.69, 0.69, 0.65, 0.62	
	H	4.1		0.053 ± 0.01 (19%) 0.066, 0.061, 0.057, 0.050, 0.048, 0.040	

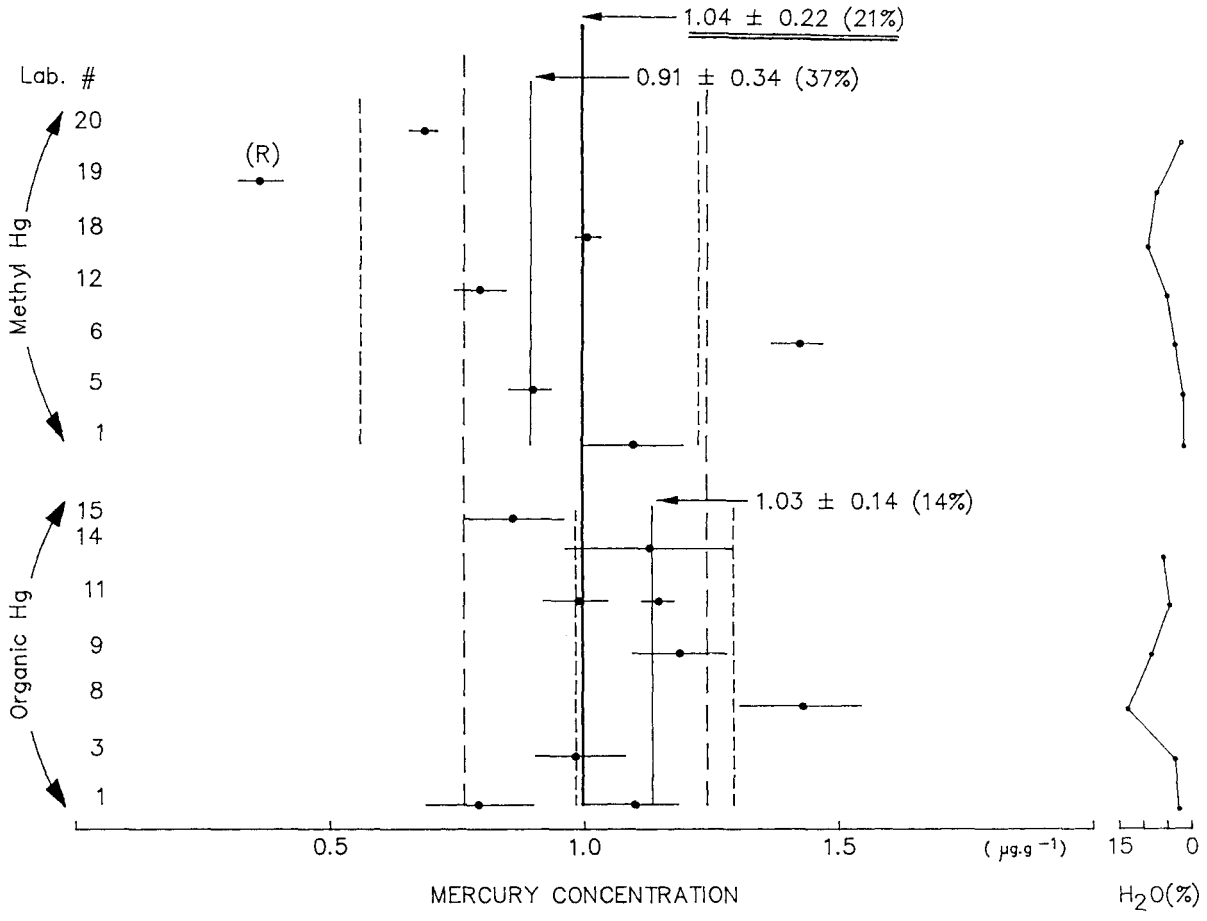

Figure 1 Sample E (dog fish). (R), rejected value for the calculation of the overall (methylmercury + organic mercury data) consensus value.

capabilities of the participating laboratories, a simple statistical treatment has been performed. After testing the normality of the distribution of the data, we applied *t*-tests, with 95% confidence limits, to the different data series: average values were rejected until the obtaining of homogeneous sets of data; discarded data are considered as outlying values. This approach is similar to the one used in the recent ICES intercalibration exercises.[3]

Water content

Moisture determinations vary from 2.2 to 12.9% for sample E and from 1.8 to 5.5% for sample H. Such variations can result from a lack of standardized methods for the measurement of water content and/or real discrepancies from one sample to another. This last hypothesis is very unlikely because of the procedure used for the preparation of the samples.

Total mercury

Laboratory data for total mercury are within 2 standard deviations (SD) around the means determined during the ICES 7/TM/BT exercise.[3] The overall averages ± SD are 1.99 ± 0.21 $\mu g\ g^{-1}$ (dry wt) and 0.18 ± 0.03 $\mu g\ g^{-1}$ (dry wt) for samples E and H respectively. These averages are close to the consensus value determined by Berman and Boyko[3] during the ICES 7/TM/BT exercise: 1.95 ± 0.38 $\mu g\ g^{-1}$ (dry wt) for sample E and 0.17 ± 0.04 $\mu g\ g^{-1}$ (dry wt) for sample H.

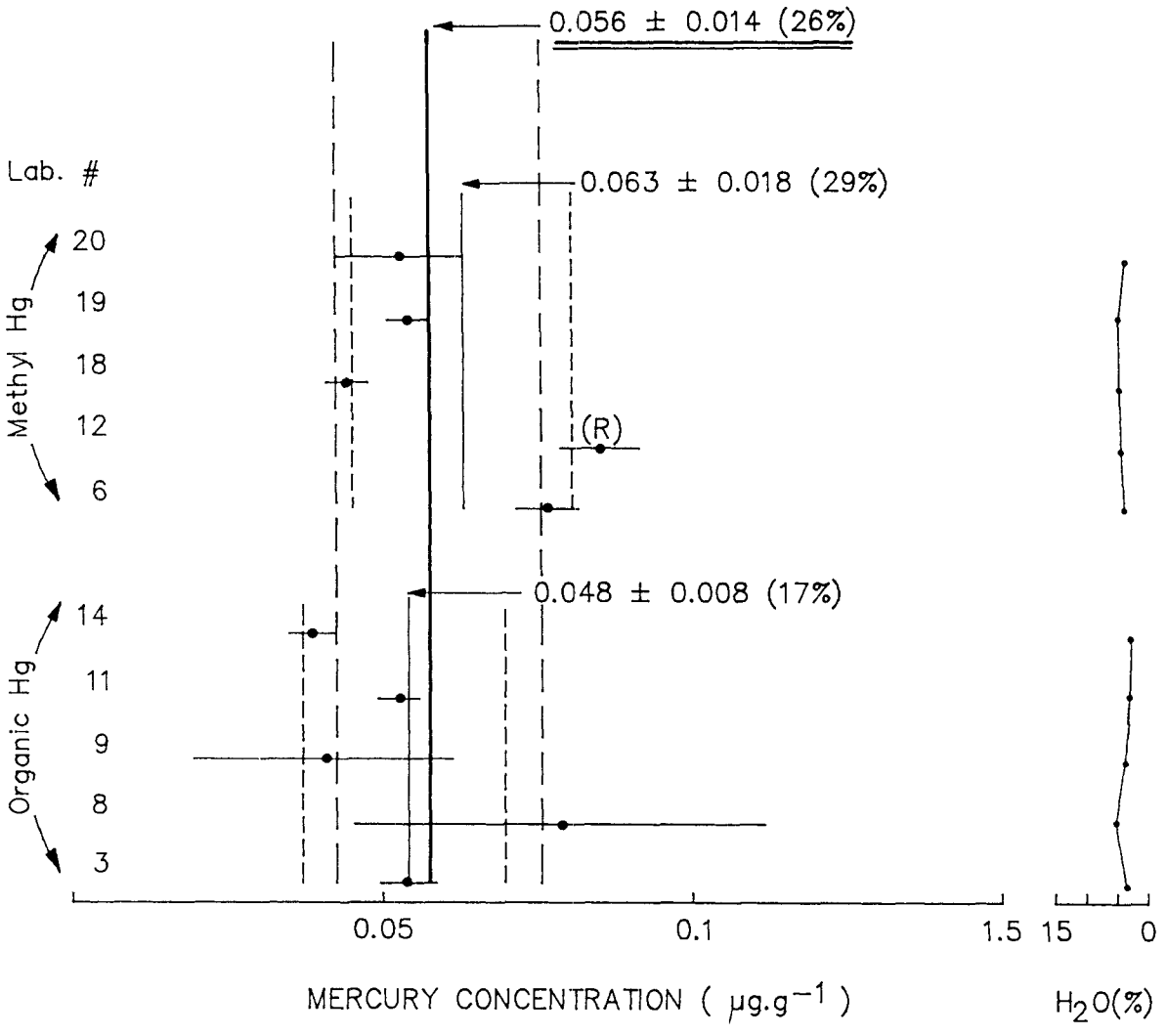

Figure 2 Sample H. (R) rejected value for the calculation of the overall (methylmercury + organic mercury data) consensus value.

Methylmercury and organic mercury

Because of the important differences in analytical approach, a distinction, as a first step of evaluation, between data expressed as methylmercury and those expressed as organic mercury is needed. The first group (methylmercury) refers to data obtained by gas liquid chromatography with electron capture detection (GC EC) after chemical treatments comparable with those initially proposed by Westöö.[4,5] The second group (organic mercury) refers to data obtained by other methods: separation and/or selective reduction of organic forms of mercury as mercury(0) (Hg^0) and measurement by cold vapour atomic absorption spectrophotometry (CV AA), neutron activation analysis (NAA) or inductively coupled plasma and isotopic dilution mass spectrometry (ICP IDMS).

Each data group was normally distributed ($P < 0.05$) around average values with standard deviations given in Table 4. Whatever the sample (E or H) there is no statistically significant difference (t-test, $P = 0.05$) between methylmercury and organic mercury averages. This observation tends to indicate that methylmercury constitutes the only organic form of mercury present in the two samples studied. This conclusion is supported by the observation of

Table 3 Analytical methods

Laboratory	Hg species analysed	Treatment	Detection	Detection limit	Reference
1	Total Hg	Acid digestion	CV AA	0.1 $\mu g\ g^{-1}$	*a*
	Methyl Hg	Extraction with C_6H_6 after HCl treatment; concentration of the solution by evaporation	GC EC	0.1 $\mu g\ g^{-1}$	—
	Organic Hg	Extraction with C_6H_6 after HCl treatment; re-extraction in cysteine; acid digestion	CV AA	0.1 $\mu g\ g^{-1}$	—
		As above + isotopic dilution	ICP IDMS	0.1 $\mu g\ g^{-1}$	—
3	Total Hg	Acid digestion after irradiation, distillation and electrolysis on gold	NAA	1 $ng\ g^{-1}$	*b*
	Organic Hg	Extraction with $C_6H_5CH_3$ after $CuSO_4$ and NaBr treatment; re-extraction with cysteine and $C_6H_5CH_3$	NAA	1 $ng\ g^{-1}$	*c*
5	Total Hg	Acid digestion	CVAA	0.01 $\mu g\ g^{-1}$	—
	Methyl Hg	Extraction with C_6H_6 after HCl treatment	GC EC	0.05 $\mu g\ g^{-1}$	*d,e*
6	Total Hg	Acid digestion	CV AA	0.6 $ng\ g^{-1}$	*f*
	Methyl Hg	Extraction with $C_6H_5CH_3$ after HCl treatment; re-extraction with cysteine and $C_6H_5CH_3$	GC EC	5 $ng\ g^{-1}$	*g*
8	Total Hg	Acid digestion	CV AA	0.01 $\mu g\ g^{-1}$	*h*
	Organic Hg	Treatment with acid solution of $CuSO_4$, NaBr and extraction in CH_2Cl_2; acid digestion	CV AA	0.01 $\mu g\ g^{-1}$	—
9	Total Hg	Acid digestion	CV AA	0.05 $\mu g\ g^{-1}$	—
	Organic Hg	Difference between total Hg ($SnCl_2/CdCl_2$) and inorganic Hg ($SnCl_2$ in alkaline solution)	CV AA	0.05 $\mu g\ g^{-1}$	*i*
10	Total Hg	Acid digestion	CV AA	0.025 $\mu g\ g^{-1}$	—
11	Total Hg	Reduction in alkaline solution (stannite); distillation; concentration on gold	CV AA	0.1 $ng\ g^{-1}$	*j*
	Organic Hg	Difference between total Hg and inorganic Hg; distillation; concentration on gold	CV AA	0.1 $ng\ g^{-1}$	*j*
	Organic Hg	Alkaline digestion; trapping of organic Hg in cysteine solution; reduction; concentration on gold	CV AA	5 $ng\ g^{-1}$	*k*
12	Total Hg	Acid digestion	CV AA	0.06 $\mu g\ g^{-1}$	*l*
	Methyl Hg	Extraction with $C_6H_5CH_3$ after HCl, NaBr treatment; re-extraction with cysteine and $C_6H_5CH_3$	GC EC	0.06 $\mu g\ g^{-1}$	—
14	Total Hg	Alkaline reduction with stannite; distillation; concentration on gold	CV AA	0.1 $ng\ g^{-1}$	*j*
	Organic Hg	Difference between total Hg and inorganic Hg; distillation; concentration on gold	CV AA	0.1 $ng\ g^{-1}$	—

cont.

Table 3 (*continued*)

Laboratory	Hg species analysed	Treatment	Detection	Detection limit	Reference
15	Total Hg	Alkaline digestion; reduction with $SnCl_2$, then with $NaBH_4$	CV AA	0.04 $\mu g\ g^{-1}$	*m*
	Organic Hg	Alkaline digestion; reduction with $NaBH_4$ after reduction by $SnCl_2$	CV AA	0.04 $\mu g\ g^{-1}$	*m*
	Methyl Hg	Extraction with $C_6H_5CH_3$ after acidic treatment with NaBr; re-extraction with cysteine and C_6H_6	GC EC	5 $ng\ g^{-1}$	—
18	Total Hg	Acid digestion	CV AA	5 $ng\ g^{-1}$	—
	Methyl Hg	Extraction with $C_6H_5CH_3$ after $CuSO_4$ and NaBr treatment; re-extraction with $Na_2S_2O_3$ and $C_6H_5CH_3$	GC EC	0.02 $\mu g\ g^{-1}$	*n*
19	Total Hg	Acid destruction after irradiation, distillation, electrolysis	NAA	0.3 $ng\ g^{-1}$	—
	Methyl Hg	Extraction with $C_6H_5CH_3$ after acidic treatment with NaBr; re-extraction with cysteine and C_6H_6	GC EC	5 $ng\ g^{-1}$	—
20	Methyl Hg	Extraction with $C_6H_5CH_3$ after acidic treatment with KBr; re-extraction with cysteine and $C_6H_5CH_3$	GC EC	0.01 $\mu g\ g^{-1}$	*o*

Abbreviations: CV AA, cold vapour atomic absorption spectrophotometry; NAA, neutron activation analysis; GC EC, gas–liquid chromatography–electron capture detector; ICP IDMS, inductively coupled plasma–isotope dilution mass spectrometry.

REFERENCES TO TABLE 3

a. MacPherson, H B, Mykytink, A P, Berman, S S and Russel, D S Acid digestion, cold-vapour AAS. *Can. J. Spectrosc.*, 1982, 27: 132

b. Drabaek, I, Carlsen V and Just L *J. Radioanal. Nucl. Chem. Lett.*, 1986, 103: 249

c. Drabaek, I and Carlsen, S G *Intern. J. Environ. Anal. Chem.*, 1984, 17: 231

d. Hight, S C and Capar, S G Electron capture gas–liquid chromatography determination of methyl mercury in fish and shellfish: collaborative study. *J. Assoc. Off. Anal. Chem.*, 1983, 66: 1121

e. Alvarez, G H, Hight, S C and Capar, S G Evaluation of electron capture gas chromatographic method for the determination of methyl mercury in freezer-case seafoods. *J. Assoc. Off. Anal. Chem.*, 1984, 67: 715

f. Harms, U Contribution to the trace analysis of mercury at the ng/g level. *Z. Lebensm. Unters. Forsch.*, 1981, 118

g. Hight, S C and Corcoran, M T Rapid determination of methyl mercury in fish and shellfish: method development, *J. Assoc. Off. Anal. Chem.*, 1987, 70: 24

h. Hendzel, M R and Jamieson D M Determination of mercury in fish. *Anal. Chem.*, 1976, 48: 926

i. Magos, L and Clarkson, T W Atomic absorption determination of total, inorganic, and organic mercury in blood. *J. Assoc. Off. Anal. Chem.*, 1972, 55: 966

j. Manthey, G and Berge, H Methode zur differenzierten Bestimmung von anorganisch und organisch gebundenem Quecksilber in Lebensmitteln, Wasser und biologischen Materialien. *Die Nahrung*, 1980, 24: 413

k. Collett, D L, Fleming, D E and Taylor, G Determination of alkylmercury in fish by steam distillation and cold-vapour atomic absorption spectrophotometry. *Analyst*, 1980, 105: 897

l. Pearce, I D, Brooks, R R and Reeves, R D *J. Assoc. Off. Anal. Chem.*, 1976, 59: 655

m. Riisgard, H U and Famme, P Distribution and mobility of organic and inorganic mercury in flounder, *Platichtys flesus*, from a chronically polluted area. *Toxicological and Environmental Chemistry*, 1988 (in press)

n. Uthe, J F, Solomon J and Grift, B Rapid semimicro method for the determination of methyl mercury in fish tissue. *J. Assoc. Off. Anal Chem.*, 1972, 55: 583

o. James, T *J. Assoc. Off. Anal. Chem.*, 1983, 66: 1289

Table 4 Summary results: methylmercury and organic mercury concentrations in $\mu g\ g^{-1}$ (dry weight)

	Methylmercury	Organic mercury	Methylmercury + organic mercury
Sample E			
All data (taking into account the average value of each participating laboratory)			
Range	0.356–1.42	0.80–1.43	0.356–1.43
Average ± SD	0.91 ± 0.34	1.08 ± 0.19	1.00 ± 0.27
Number of data	7	9	16
(Lab. nos)	(1, 5, 6, 12, 18, 19, 20)	(1, 3, 8, 9, 11, 14, 15)	(1, 3, 5, 6, 8, 9, 11, 12, 14, 15, 18, 19, 20)
Data taken into account for the consensus value (after *t*-tests)			
Range	0.356–1.42	0.80–1.20	0.68–1.43
Average ± SD	0.91 ± 0.34	1.03 ± 0.14	1.04 ± 0.22
Number of data	7	8	15
(Lab. nos)	(1, 5, 6, 12, 18, 19, 20)	(1, 3, 9, 11, 14, 15)	(1, 3, 5, 6, 8, 9, 11, 12, 14, 15, 18, 20)
Sample H			
All data (taking into account the average value of each participating laboratory)			
Range	0.045–0.086	0.040–0.080	0.040–0.086
Average ± SD	0.063 ± 0.018	0.054 ± 0.016	0.059 ± 0.017
Number of data	5	5	10
(Lab. nos)	(6, 12, 18, 19, 20)	(3, 8, 9, 11, 14)	(3, 6, 8, 9, 11, 12, 14, 18, 19, 20)
Data taken into account for the consensus values (after *t*-tests)			
Range	0.045–0.086	0.040–0.056	0.040–0.080
Average ± SD	0.063 ± 0.018	0.048 ± 0.008	0.056 ± 0.014
Number of data	5	4	9
(Lab. nos)	(6, 12, 18, 19, 20)	(3, 9, 11, 14)	(3, 6, 8, 9, 11, 14, 18, 19, 20)

chromatograms of laboratory 18 according to which neither sample E nor sample H presents any trace of ethylmercury or phenylmercury. In addition, none of the other participating laboratories using GC EC methods reported the presence of organic form of mercury other than the methyl one.

Consequently it is justifiable to calculate overall averages irrespective of the methods used which should be considered as consensus values for methylmercury: 1.04 ± 0.22 $\mu g\ g^{-1}$ (dry wt) for sample E and 0.056 ± 0.014 $\mu g\ g^{-1}$ (dry wt) for sample H, with coefficients of variation (CV = SD/m) of 21 and 26% for samples E and H respectively (m = mean).

On the basis of the results it is possible to calculate methylmercury:total mercury ratios of 0.52 for sample E and 0.31 for sample H.

CONCLUSIONS

The *t*-test procedure used in the previous ICES intercalibration exercises[3] has allowed four consensus values to be defined for methylmercury in the two samples studied. Although involving a small number of participating laboratories, these consensus values seem good estimates of the real concentrations. This opinion is backed up by the multiplicity of the analytical methods used (GC EC, CV AA, NAA, ICP IDMS).

Allowing that all the organic mercury is methylmercury, none of these methods leads to average values significantly different from the overall average for sample E and also sample H. Conversely, it is not possible to point out one type of method as offering better results than another.

It can be stated that, compared with the results of other intercomparison exercises, the overall variability of the results of this first exercise on methylmercury in biological tissue is relatively small. This clearly appears from Figs 2 and 3 and is evidence for the competence of the participating laboratories.

One further step to improve comparability of results would be the measurement of methylmercury in samples with the assistance of certified reference material for methylmercury.

Acknowledgement Thanks are due to participants for having made this ICES 1/CH3HG/BT exercise successful.

REFERENCES

1. Topping, G and Holden, A V *Report on Intercalibration Analysis in ICES North Sea and North Atlantic Baseline Studies*, ICES, Coop. Res. Report No. 80, 1978
2. Topping, G *Report on the 6th ICES Trace Metal Intercomparison Exercise for Cadmium and Lead in Biological Tissue*, ICES, Coop. Res. Report No. 111, 1982
3. Berman, S S and Boyko, V. J *ICES Seventh Round Intercalibration for Trace Metals in Biological Tissue*, ICES 7/TM/BT (Part 2) Report to the Marine Chemistry Working Group, 1987
4. Westöö, G *Acta Chem. Scand.*, 1966, 20: 2131
5. Westöö, G *Acta Chem. Scand.*, 1967, 21: 1790