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WORKING METHODS PAPER

An international intercomparison exercise for total mercury in seawater

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Two 30 dm^3 coastal seawater samples were collected in September 1983. One was acidified, homogenized and divided among 50 500-cm^3 glass ampoules. The second was spiked with 612 ng of mercury added as methylmercury chloride, acidified, homogenized and divided among 50 500-cm^3 glass ampoules. All these operations were performed under a mercury-free atmosphere. A single sample from each set was sent to each of 37 laboratories; 21 of them submitted their results of a 'total' mercury concentation determination. The consensus values and their confidence limits are 6.0 ± 1.6 and 24.2 ± 2.8 ng dm^{-3} for the natural and the spiked samples respectively. Eleven laboratories reported reliable quantitative results (within ± 2SD) for the natural (unspiked) sample, and 12 for the spiked sample. In addition, ten laboratories give sets of results within ± 2SD of the consensus values. Storage for up to four months of methylmercury spiked samples with 1.4% nitric acid (0.3 mol dm^{-3}) at room temperature is, alone, an unsuitable treatment for releasing mercury from its monomethyl compounds.

Deux échantillons de 30 dm^3 d'eau de mer côtière ont été prélevés en septembre 1983. L'un d'eux a été acidifié, homogénéisé et réparti dans 50 ampoules de 500 cm^3. L'autre, après ajout de 612 ng de mercure sous forme de chlorure de méthylmercure, a été acidifié, homogénéisé et réparti dans 50 ampoules identiques. Ces opérations ont été effectuées sous atmosphere purgée de mercure. Un lot de chacun des échantillons a été expédié à 37 laboratoires dont 21 ont fourni des résultats concernant la teneur en mercure 'total'. Les valeurs de consensus et leur intervalle de confiance sont respectivement de 6,0 ± 1,6 et 24,2 ± 2,8 ng dm^{-3} pour l'échantillon naturel et le dopé. Onze laboratoires rapportent des résultats quantitatifs fiables (écart < ± 2*s*) pour l'échantillon naturel (sans ajout) et douze pour l'échantillon dopé. De plus, dix laboratoires présentent des paires de résultats groupés à moins de deux écarts type des valeurs de consensus. Le stockage, même pendant quatre mois, d'échantillons d'eau de mer en présence d'acide nitrique (0,3 mol dm^{-3}) est, à lui seul, un traitement insuffisant pour libérer le mercure sous sa forme monométhylée.

Keywords: Intercomparison, mercury, methyl mercury, seawater, analysis

INTRODUCTION

Following the first intercalibration exercise for trace metals,[1] trace mercury determinations in seawaters have received special and separate attention with ICES (International Council for the Exploration of the Sea) during the last several years. The main results of these activities have been summarized by Olafsson in two reports.[2,3] In short, these exercises indicate that serious errors in low-level determinations are systematic, but that for inorganic mercury spiked samples, a majority of the laboratories can obtain good accuracy and precision in recovery.

During the preparatory stage of the fifth intercalibration exercise for trace metals in seawater,

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it was suggested that the general capabilities of laboratories for the entire determination procedure for 'total' mercury – including organomercury decomposition – should be assessed. The results presented here concern the experiment which was designed to evaluate, among participating laboratories, the ability to measure natural and high 'total' mercury levels in seawater.

EXPERIMENTAL DESIGN

The samples were collected in the Saint Lawrence estuary, Canada, during a NAVIMAR UN cruise in September 1983. Two 30-dm^3 seawater samples were collected by pumping from 25 m depth with a peristaltic pump using acid-washed silicon tubing. The 'natural'-level sample was collected at 48° 58.3′N and 67° 54.5′W; its salinity was 30.72‰. The sample to be spiked with methylmercury was collected at 48° 22.1′N and 70° 36.5′W; its salinity was 27.30‰. The spike consisted of 612 ng of mercury as methylmercury chloride in the 30-dm^3 water sample. The exact concentration of the solution added is difficult to assess because of the poor water solubility of methylmercury chloride.

The two samples were successively homogenized with 1.4% nitric acid (0.3 mol dm^{-3}) (Baker, suitable for mercury determination) in a 35-dm^3 polypropylene container with magnetic stirring. The contribution of nitric acid to the mercury concentration of the samples is around 1 ng dm^{-3}. Total mercury concentration measurements performed on board by laboratory No 5 after acidification and homogenization gave ≤ 5 ng dm^{-3} for the two collected samples and 22 ± 2 ng dm^{-3} for the spiked sample. Fifty 500-cm^3 glass ampoules of each sample were filled in a glove box under a mercury-free atmosphere, then sealed. The 'natural'-level ampoules were assigned numbers 1 to 50 and the spiked sample ampoules numbers 51 to 100, according to their order of filling.

SAMPLE DISTRIBUTION AND RESULTS RECEIVED

The list of laboratories which received one set of two ampoules ('natural' and spiked samples) and returned results is given in Table 1. The samples were shipped to the participants within three weeks after the cruise, i.e. before the end of October 1983. A deadline for receiving the results was initially set for 31 December 1983, then it was postponed until 1 February 1984. Only 20 sets of data are taken into account in the present report because one laboratory did not express its results in concentration units.

CLEANING PROCEDURE

The glass ampoules were initially heated at 450°C for 24 h, then cleaned by the following procedure. They were filled with a mixed solution of 0.1% $KMnO_4$, 0.1% $K_2S_2O_8$ and 1% H_2SO_4, and heated to 80°C for 3 h; they were then cooled to room temperature, and 2 cm^3 of 12% $NH_2OH.HCl$ was added. This procedure was repeated before rinsing the ampoules with low-mercury water (tapwater). Plastic ware was soaked in hot 5% HCl for three days, rinsed, then filled with 1% HNO_3 for three more days and finally rinsed with tapwater.

HOMOGENEITY VERIFICATION

Laboratory 20 received five sets of two ampoules. These samples were selected according to their filling rank in order to detect potential changes in the total mercury concentrations during the filling operation. The results are shown in Table 2. From the measurements, it can be concluded that there is no such systematic trend in the total mercury concentration between the first and last ampoules filled. However, on the basis of an analysis of variance performed on the concentrations measured on the spiked samples, the concentrations are not identical in every ampoule (Table 2). The small differences in the data reported, 0.7 (unspiked) and 2.2 ng dm^{-3} (spiked) (Table 2), may be due to a heterogeneity in the mercury concentration of the samples distributed. However, although laboratory 20's results show no systematic differences between the samples, these measurements cannot ensure the absence of individual biased samples in the overall sample set.

Table 1 Participant laboratories

Laboratory no.	Participants	Address
3	P Yeats J Dalziel	Atlantic Oceanographic Laboratory, Bedford Institute of Oceanography, P.O. Box 1006, Dartmouth, N.S. B2Y 4A2, Canada
4	I Drabaek	Danish Isotope Center, Skelbaekgade 2, DK 1717, Copenhagen, V, Denmark
5	D Cossa J Langis	Centre Champlain des Sciences de la Mer, C.P. 15500 901, Cap Diamant, G1K 7Y7 Québec, (Québec) Canada
7	P C Head	North West Water, Dawson House, Great Sankey, Warrington WA5 3LW, UK
8	M J Beard	Southern Water Area Resource Laboratories, Southampton Road, Otterbourne, Winchester SO21 2DP, UK
9	S Blake	Water Research Centre, Henley Road, Medmenham, Marlow, Bucks SL7 2HD, UK
10	A Griffiths W Collett	Forth River Purification Board, Colinton Dell House, West Mill Road, Colinton, Edinburgh EH13 0PH, UK
11	A J Bates	Anglian Water Authority, Lincolnshire River Division, 50 Wide Bargate, Boston, Lincs PE21 6SA, UK
12	B Enger L Madsen	Central Institute for Industrial Research, P.B. 350, Blindern, Oslo 3, Norway
13	M P Bertenshaw	Severn–Trent Water Authority, Lower Severn Division, Malvern Laboratory, 141 Church Street, Malvern, Worcs WR14 2AN, UK
14	D W Jennings M Davies	Thames Water, Rivers House, Crossness Works, Abbey Wood, London SE2 9AQ, UK
15	I Gustavsson	The National Swedish Environment Protection Board, Laboratory for Coastal Research, PO Box 8043, S 750 08 Uppsala, Sweden
17	A Iverfeldt	Chalmers University of Technology, Department of Inorganic Chemistry, S 412 96 Göteborg, Sweden
18	G Decadt	Faculteit Wetenshappen, Analytische Scheikunde, Pleinlaan 2, B-1050 Bruxelles, Belgium
20	J Ólafsson	Marine Research Institute, PO Box 390, Skulagata 4, Reykjavik, Iceland
23	D Schmidt P Freimann	Deutsches Hydrographisches Institut, Postfach 2 20, 2000 Hamburg 4, FRG
24	J L Martin A M Le Guellec	Centre Océanologie de Bretagne, BP 337, 29273 Brest-Cedex, France
25	P Courau	Laboratoire de Physique et Chimie Marines, Université P. et M. Curie, 06230 Villefranche-sur-Mer, France
35	A J N Haig	Clyde River Purification Board, Rivers House, Murray Road, East Kilbride, Glasgow G75 0LA, UK
37	N Bloom	Department of Marine Sciences, University of Connecticut, Avery Point, CT 06340, USA

Table 2 Homogeneity verification (analyses performed by laboratory 20).

Sample	Ampoule number	Total mercury concentration (ng dm^{-3})		
		Data	Mean	SD
Natural-level	3	4.0	–	–
	13	4.0	–	–
	25	3.8	–	–
	36	4.5	–	–
	47	4.1	–	–
Spike	53	25.6, 24.4, 24.3	24.8	0.7
	63	22.3, 24.1, 23.2	23.2	0.9
	75	23.4, 22.5, 22.0	22.6	0.7
	86	22.3, 23.1, 22.5	22.6	0.4
	97	25.2, 24.6, 24.7	24.8	0.3

Analysis of variance on the spiked sample concentrations: $F_{\text{obs.}} = 5.33$, $F_{0.05} = 3.48$ and $F_{0.01} = 5.99$.

CONCENTRATION OF TOTAL MERCURY IN THE SAMPLES

A brief description of the analytical methods used among the participants is given in Table 3. The results reported, together with means and standard deviations, are presented in Table 4. In order to test the normality of the frequency distributions, we used a graphic analysis of the data ('droite de Henry'). The cumulative frequencies, excluding the non-numerical (≤ detection limit) results, are illustrated in Fig. 1. Laying out in line of the points means a normal distribution. The changes of slopes observed for the two sets of data show that neither the natural seawater nor the spiked samples results are normally distributed. The curvatures were used as criteria to exclude outliers. The limits chosen are 10.7 and 31.7 ng dm^{-3} for the natural and the spiked sample respectively (Fig. 1). After discarding outlying values, the two sets of data were found to have distributions not different from normal distribution using a Kolmogorov–Smirnov goodness-of-fit test.[4] The overall means (consensus values) and their confidence limits (95%) are 6.0 ± 1.6 and 24.2 ± 2.8 ng dm^{-3} for the natural and the spiked samples respectively. For the natural samples eight laboratories gave results within ± one standard deviation (SD = 2.4 ng dm^{-3}) of the mean and 11 within ± 2SD. For the spiked samples eight laboratories gave results within ± one standard deviation (SD = 4.4 ng dm^{-3}) of the mean and 12 within ± 2SD. In addition, ten laboratories gave pairs of results (natural and spiked samples) within ± 2SD of the consensus values.

The coefficient of variation (CV) is 18% for the spiked samples and higher (39%) for the natural samples. However, the slight change of slope observed after the sixth result (Fig. 1) indicates that the large CV of the natural samples set is mainly due to the highest results. Indeed, when the six laboratories which gave the lowest results only are taken into account, the CV is 12% and the consensus value is lowered to 4.2 ng dm^{-3}.

RELEASE OF MERCURY FROM ITS ORGANIC COMPOUNDS

The 'reactive' mercury concentrations obtained by tin(II) characterization without chemical or photochemical treatment for the release of mercury from its organic compounds are presented in Table 5. It can be seen that the reactive mercury concentrations in the natural level (unspiked) samples were not significantly different from the total mercury concentrations shown in Table 4. In contrast, reactive mercury concentrations in the spiked samples were lower than those obtained after an oxidizing pretreatment.

Thus we can assert that 1.4% nitric acid (0.3 mol dm^{-3}) alone is unsuitable for the release of mercury from its monomethyl compound even after four months' storage. As shown by results of laboratories 17 and 18, sodium borohydride may be a valuable reagent for direct vaporization of total mercury without any pretreatment. However, according to one of us (PC, unpublished results) attention must be paid to operational conditions and against deactivation of the gold traps by gaseous interference from borohydride.

CONCLUSIONS

The two sets of samples distributed during this intercalibration have been checked for homogeneity. The maximum differences observed from one sample to another are 0.7 ng dm^{-3} for the natural unspiked set and 2.2 ng dm^{-3} for the spiked sample set.

The consensus values and their confidence limits (95%) are 6.0 ± 1.6 and 24.2 ± 2.8 ng dm^{-3} for the natural and the spiked samples respectively.

Excluding the non-numerical results (≤ detection limit), and discarding the outlying values, there remain 11 and 12 laboratories out of 20 for natural level and spiked samples respectively which gave reliable results, i.e. within ± 2SD of the overall means (consensus values). In addition, ten laboratories gave results within ± 2SD, for both samples.

Storage for up to four months of seawater samples with 1.4% nitric acid (i.e. 0.3 mol dm^{-3}) alone, at room temperature, is inadequate for the release of mercury from its monomethyl form.

Table 3 Analytical methods used by the participant laboratories and their performances

Laboratory no.	Pretreatment	Preconcentration	Detection[a]	Reducing agent	Reproducibility[b]	Detection limit (ng dm^{-3})
3	None	Au	CV AA	$SnCl_2$	±0.11 ng dm^{-3}	0.2[c]
4	HNO_3/H_2SO_4/heat	Distillation and electrodeposition on Au	NA	–	10–20%	1–3
5	Br/20°C/15 min	None	CV AA	$SnCl_2$	10–27%	3
7	$K_2S_2O_8$/140°C/15 min	None	CV AA	$NaBH_4$	ND	40
8	$K_2S_2O_8$/80°C/4 h	Au	CV AA	$SnCl_2$	1.3–4%	10
9	Br_2	Au	CV AA	$SnCl_2$	6%	5
10	$KMnO_4/H_2SO_4$[d]	$KMnO_4$	CV AA	$SnCl_2$	15%	8
11	$K_2S_2O_8$	None	CV FE	$SnCl_2$	4.5%	50
12	$KMnO_4/H_2SO_4$	None	CV AA	$SnCl_2$	30%	10
13	$K_2S_2O_8$	$KMnO_4$	CV FE	$SnCl_2$	7%	1.6
14	Br_2	Br_2	CV FE	–	8–16%	10
15	UV/1 h	–	DPASV	–	ND	3
17	None	Au	PE	$NaBH_4$	5%	0.02
18	None	Au	CV AA	$NaBH_4$	1%	0.2
20	UV/1 h	Au	CV AA	$SnCl_2$	±0.4 ng dm^{-3}	0.3
23	UV/2 h	Au	CV AA	$SnCl_2$	4%	0.5
24	$KMnO_4$	Au	CV AA	$SnCl_2$	ND	1
25	$KMnO_4$	Au	CV AA	$SnCl_2$	ND	0.3
35	Br_2	Br_2	CV FE	$SnCl_2$	12%	3–4
37	Br_2	Au	CV AA	$SnCl_2$	10%	0.1

[a] AA, atomic absorption spectrophotometry; CV, cold vapour; FE, fluorescence emission; PE, plasma emission; NA, neutron activation; DPASV, differential pulse anodic stripping voltametry; UV, ultra-violet irradiation. [b] ND, not determined. [c] Characteristic concentration. [d] This test is no longer used by this laboratory for this mercury analysis.

Table 4 Mercury concentrations reported by participating laboratories (ng dm^{-3})

Laboratory no.	Natural-level sample				Spiked sample			
	Data	Mean	SD	(*n*)	Data	Mean	SD	(*n*)
3	9.1, 9.5	9.3	0.3	(2)	ND	–	–	–
4	8, 6	7	1.4	(2)	26, 31	29	4	(2)
5	4.6, 4.6, 4.9, 4.1	4.6	0.3	(4)	27.7, 28.7, 28.4, 27.7, 28.9, 28.4	28.3	0.5	(6)
7	≤40, ≤40, ≤40, ≤40, ≤40, ≤40	–	–	–	≤40, ≤40, ≤40, ≤40, ≤40, ≤40	–	–	–
8	50[a]	–	–	–	243[a]	–	–	–
9	9.7, 11.7	10.7	1.4	(2)	17.8, 18.2, 15.4	17.1	1.5	(3)
10	≤8	–	–	–	≤8	–	–	–
11	81, 94	88[a]	9	(2)	90, 115	103[a]	18	(2)
12	20[a]	–	–	–	80[a]	–	–	–
13	52[a]	–	–	–	72[a]	–	–	–
14	Not given	38.2[a]	5.4	(8)	Not given	43.9[a]	6.2	(14)
15	≤3, ≤3, ≤3	–	–	–	18, 25, 13	19	6	(3)
17	3.5, 3.9, 4.4, 3.5, 4.7	4.0	0.5	(5)	29.4, 26.6, 27.2, 28.6, 29.1	28.2	1.1	(5)
18	Not given				24.2, 24.6, 24.3	24.4	0.21	(3)
20	See Table 2	4.1	0.3	(5)	See Table 2	23.6	1.2	(15)
23	5.1, 4.6	4.9	0.4	(2)	22, 20, 22, 23	22	1	(4)
24	6.4, 8.0, 8.2	7.5	1.0	(3)	36, 25, 34	31.7	5.9	(3)
25	4.9, 4.3, 3.9, 3.9	4.3	0.5	(4)	21.8, 22.9, 21.0, 20.8	21.6	1.0	(4)
35	6.5	–	–	–	23.5, 24.2	23.9	0.5	(2)
37	2.8, 3.6, 4.0	3.5	0.6	(3)	22.7, 20.3, 21.1	21.4	1.2	(3)

[a] Data rejected. *n*, number of determinations. ND, not determined.

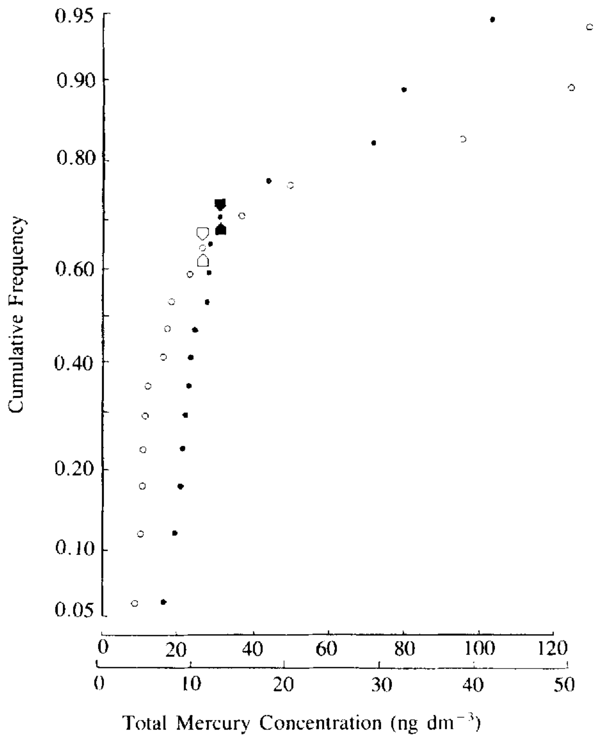

Figure 1 Graphic test illustrating the frequency distributions of the mean given by participating laboratories. ●, Spiked samples; ○, natural samples. Arrows indicate limits chosen to exclude outliers.

Table 5 Mercury concentrations (ng dm^{-3}) obtained without treatment for the release of mercury from its organic compounds

Laboratory no.	Natural-level samples			Spiked samples		
	Mean	SD	(*n*)	Mean	SC	(*n*)
3	9.3	0.3	(2)	8.3	1.6	(2)
5	4.6	–	(1)	7.6	0.5	(2)
17	3.8	0.2	(5)	ND	–	–
24	7.6	0.2	(3)	10.8	1.7	(3)
25	ND	–	–	6.4	0.3	(3)

ND, not determined.

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