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REPORTS ON THE ICES FIRST, SECOND AND THIRD ROUND INTERCALIBRATIONS FOR TRACE METALS IN SEA-WATER

by

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by

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INTRODUCTION

In a report devoted to North Sea pollution (ICES, 1974), attention was drawn to the difficulty in comparing results of trace metal levels in sea-water analysed by different institutes using a variety of techniques.

A meeting of the ICES Working Group on Pollution Baseline and Monitoring Studies in the Oslo Commission and ICNAF areas appointed an analytical sub-group to examine the feasibility of organising an international baseline study of trace metals dissolved in the waters of the ICNAF and Oslo Commission areas of the North Atlantic (ICES, 1975a). The group reported that a project was not feasible until an intercalibration of techniques by participating laboratories had been conducted (ICES, 1975b). A series of exercises was proposed, commencing with an intercalibration of a relatively concentrated standard metal solution, proceeding to the analysis of sea-water and finishing with sea-going exercises.

By the end of 1980 four phases had been completed. This report gives details of the first round, which was concerned with the analyses of concentrated metal solutions, and the third round which involved the analyses of a range of metals in sea-water samples. Both exercises were coordinated by the Fisheries Radiobiological Laboratory, Lowestoft, England.

During the preliminary planning stages, it was decided that the intercalibration of mercury in sea-water should be a separate phase of the project since the storage of water for the analysis of this metal was not compatible with the procedure proposed for other trace metals. Consequently, Round 2 of the programme was devoted to mercury alone and the exercise took place during 1976. This exercise was coordinated by the Marine Research Institute in Reykjavik. The results of this exercise have now been published (Ólafsson 1978), and a summary of the results are included in the second part of this volume.

The results of the fourth round intercalibration, conducted in 1978-1979 by the Bedford Institute of Oceanography, Canada, have been published in Bewers *et al.* (1981).

Participation in the First and Third Round Intercalibrations

The annex lists the participating institutes in these two exercises. Individual laboratories are anonymous in the text and code numbers have been allocated on a system based on the chronological receipt of replies. Organisations participating in both rounds have been assigned the same code numbers for each phase.

Of the 61 participants, 29 took part in both phases, 12 in the first round only and 20 in the third round only. Invitations to participants were extended to all laboratories in ICES member countries, whether or not they had previous experience in the analysis of trace metals in sea-water.

Preliminary accounts of both phases have been prepared (Jones, 1976 and 1977). However, the following report should be taken as the definitive version since it includes results not submitted in time for inclusion in the preliminary reports.

ROUND 1. INTERCALIBRATION FOR TRACE METAL STANDARD SOLUTIONS

INTRODUCTION AND METHOD

This initial phase of the exercise was designed to test standard metal solutions used in routine analyses rather than to intercalibrate analytical techniques.

The test samples consisted of two solutions in which lead and chromium were separated to avoid the precipitation of lead chromate. Solution A contained Hg, Pb, Ni, Co and Fe and Solution B contained Cr, Cu, Cd, Zn and Mn. The samples were prepared by mixing commercially-manufactured standard atomic absorption reagents supplied by Hopkin and Williams. Each reagent was first tested for contamination by the other metals and all were found clear. The samples were distributed early in 1976 and participants were asked to estimate those elements that they routinely measured. Triplicate analyses were requested and it was emphasized that the exercise was a test of standards rather than analytical techniques. Thus, the most direct method available should have been employed and it did not necessarily have to be the same technique that was used for sea-water. Institutes were asked to return unused samples for a stability check.

RESULTS

Participants submitted their data within 6 months of sample distribution. Figure 1 summarises the results in histogram form after the data had been separated into groups of 5% deviation from the expected value. The largest number of observations, apart from those of chromium, fell within ± 5% of the expected value. The maximum number of chromium results occurred in the group -5.1 to -10.0. The distribution of deviation from the expected value was, however, often skewed. The mercury results, for example, showed several values below the expected level whereas many iron results were higher than the medium.

It is difficult to select the acceptable limits of a deviation from the expected values. This exercise involved a concentrated metal standard rather than a sea-water sample of low metal content requiring several manipulative stages during analysis. Thus one may expect a somewhat better accuracy compared with a sea-water intercalibration. However, a limit of ± 10% deviation from the expected value should encompass reasonable analytical error. Out of a total of 326 results, which included all elements, 21% were outside ± 10% of the expected value and 5% were outside the ± 20% limit.

Tables 1 and 2 list the results of the analyses on solutions A and B, respectively, in some detail together with coefficients of variation. The latter only indicates relatively coarse trends since the number of replicate analyses for each element varied. The detailed data substantiate the trends shown in Figure 1. With the exception of mercury, chromium and iron, the total mean metal concentration of all participants was remarkably close to the expected value. The cause of the rather large number of anomalous mercury and chromium values is not apparent. Some, at least, of the high iron values can be explained. Participant 21 subsequently reported that his discrepancy of 20.2% was due to an error in his own standard solution. Participant 30, who analysed his sample using a

graphite furnace, reported that the unknown sample in a perchloric acid matrix showed a much higher sensitivity than his own standard in a chloride matrix. A similar phenomenon may have been responsible for some of the other high results.

For logistic reasons at the organising laboratory, not all samples returned for stability checks could be tested. However, from those analysed there was no evidence of an overall marked deterioration in the stability of any one metal and there was no clear relationship between deviations from the expected values in the results submitted and the check value of the relevant sample.

The coefficient of variation on each set of replicate results reported by the participants was calculated in order to assess the precision of their measurements. This value varied considerably between individual sets of results but the mean value for each metal was fairly constant, falling mainly between 2.0 and 3.0%. Zinc emerged somewhat better with a value of 1.4%.

The coefficient of variation on each metal was also calculated using the mean values reported by the participants. A wide range of "precision" was shown between nickel at 7.2% and iron at 18.6%.

All the mean values above detection limits were subjected to Chauvenet's test to identify outliers. Data were submitted to a maximum of three cycles. The results are shown in Table 3. A total of 22 values were rejected, of which 12 were low and 10 were high values. Using only the data accepted by Chauvenet's test did not materially improve the relationship of the mean value for each metal to the expected value. Indeed, nickel, chromium and zinc came out marginally worse in this respect when compared with the mean values from all the submitted data.

Most of the observations were made by atomic absorption spectroscopy. Thus there are insufficient data to assess the results by different basic analytical techniques. However, in this type of exercise, the method of analysis should not theoretically influence the accuracy of the result.

Some participants used commercially-prepared standard metal reagents in the exercise whereas others prepared their own standard, either by dissolving the metal in acid or preparing a solution of the salt. Tests were made in order to ascertain if the two basic techniques influenced the degree of deviation from the expected value. However, a t-test for two means of a population with unpaired samples was found not to be significant either for individual metals or for all data grouped together.

DISCUSSION

Although the mean value of each metal analysed by the participants was close to the expected concentration, there was a considerable degree of scatter shown. It was somewhat disturbing that 21% of the results were outside ± 10% of the expected value when such relatively high concentrations of metal were being measured. There was little evidence as to the nature of most of these discrepancies and further investigation seemed feasible only by a detailed collaboration with individual participants. Such a process would have been time-consuming and may have delayed the subsequent intercalibration exercise. It was therefore decided to proceed with the programme involving sea-water samples.

ROUND 3. INTERCALIBRATION FOR TRACE METALS IN SEA WATER

INTRODUCTION AND METHOD

This exercise took place during 1977 and was basically concerned with the intercalibration of two frozen sea water samples for the analysis of trace metals.

Two surface sea water samples for Round 3 were collected during January 1977 from the central part of the southern North Sea (51°44' N 02°23' E: Sample A) and from closer inshore off the Netherlands coast (52°03' N 04°04' E: Sample B). The water was filtered through 0.45 µm Millipore membrane filters within a few hours of collection and each sample was bulked in a polyethylene carboy. Several 1 litre aliquots were placed in acid-washed polyethylene bottles and immediately deep frozen. In addition, some samples were run into bottles provided by participating institutes and stored as requested.

Most samples were distributed to participants deep frozen surrounded by dry ice in expanded polystyrene containers. The majority of consignments despatched to overseas institutes were sent by air freight. In most instances this system worked well. A shipping agent was appointed in the United Kingdom to coordinate the transportation and the recipient was alerted in advance in order to expedite customs clearance. The majority of samples were no longer than 48 hours in transit.

Participants were requested to report on those metals of which they had analytical experience. In addition to the sea water, concentrated multi-element standard solutions were distributed as a continuation of Round 1. Analysts were requested to use those standards in addition to their own when determining the metal content of the sea-water samples.

RESULTS

Most of the samples were distributed during February 1977 and the majority of the participating laboratories had responded by September of the same year. A total of 49 institutes submitted data and the results are shown in Table 4. Some laboratories submitted data on mercury levels. These, however, have not been included in view of the general unsuitability of sample storage for analysis of this element coupled with the fact that an intercalibration specifically for mercury was already in progress (Ólafsson, 1978 and Part 2, this volume). Immediately apparent is the wide range of values reported by the participants. Presentation of the data in histogram form (Figure 2) illustrates this feature with a general asymmetric distribution biased towards high values.

It had been anticipated that Sample B would contain an appreciably greater metal concentration than the offshore Sample A. In fact, such a difference is not immediately apparent. The wide range of values makes such a comparison difficult, but a statistical examination of all the data by t-test indicated that only manganese and zinc were significantly ($P = < 0.001$ and < 0.01, respectively) higher in Sample B.

It is apparent that the levels of trace metals present in the samples were below the detection limits for several laboratories. Participants were asked to provide information on their limits of detection and precision of measurement for each metal. The replies received are listed in Table 5. A variety of methods were used to determine this information and little attempt has been made to standardise the presentation in the table. It is apparent, however, that the limits of detection frequently span three orders of magnitude for many of the metals listed. It is more difficult to make generalised comment on precision in view of the range of forms used to express this parameter.

In most instances the amount of sample available for analysis did not permit replication and thus individual coefficients of variation cannot be assessed. However, the overall variation of each metal in each sample can be calculated and Chauvenet's test can be applied to the data to identify outliers (Table 6). Only values above detection limits have been processed. The range of values reported for each metal spans one and often two orders of magnitude with consequently high coefficients of variation. Manganese and zinc, however, showed

less variability than the other metals. During the period of the exercise, six sub-samples from each of Samples A and B were analysed by the Lowestoft Laboratory. Coefficients of variation on each set of replicates ranged between 9 and 24% for Cd, Cu, Ni and Zn. Thus the wide variability reported throughout the group would not seem attributable to sample inhomogeneity. After the exclusion of data by Chauvenet's test, the range, mean values and the coefficients of variation were reduced. In every case, however, it was the higher values which were excluded and the lower end of each range span remained the same. This feature, coupled with the asymmetric distributions shown in Figure 2, suggests that sample contamination during the analyses must have been a significant cause of error. Moreover, the work of Patterson et al. (1976) would suggest that contamination by lead probably occurred as early as the sample collection stage. For the purpose of the present exercise, such a situation is acceptable provided it did not lead to sample inhomogeneity.

The multi-element standard solutions distributed to participants were similar to those used for the first phase of the exercise and contained Co, Fe, Ni, Pb, Cd, Cr, Cu, Mn and Zn in concentrations ranging between 193 and 261 mg l^{-1}. It soon became apparent, however, that some participants who used electro-chemical methods of analysis experienced difficulty with the multi-element standards owing to interference between one element and another. Moreover, the degree of variability between the reported sea-water values was some order of magnitude greater than the standard solution results. Thus it was decided not to make any study of the data relating to this part of the exercise.

In addition to receiving frozen samples in standard polyethylene bottles, some participants provided their own bottle with specific methods of sample storage. The results of this part of the exercise were rather inconclusive and the number of observations was relatively small. The data from the present exercise are not included in this report since this aspect of the intercalibration was to receive much greater attention in subsequent phases.

The method of sample analysis showed a wide range of techniques (Table 4), but for the elements Pb, Cd, Cu and Zn they can basically be divided into electro-chemical and non-electro-chemical methods. The latter were mainly by atomic absorption spectroscopy. The results have been divided into the above two groups and outliers excluded by Chauvenet's test (Table 7). Mean lead and copper values measured by electro-chemistry were higher than analyses by other techniques whereas for cadmium the situation was reversed. However, none of these trends were statistically significant. Coefficients of variation did not indicate that either of the two basic methods yielded more consistent data than the other.

Since participation in the present exercise was open to all institutes of ICES member countries and some laboratories were relatively new to the analysis of sea-water, a method was sought to identify those more experienced institutes and to see if their performance differed from the remainder. The criterion used for selection was an appropriate entry in the 1977 edition of the FAO International Directory of Marine Scientists. There were 26 institutes in this category (numbers 1, 2, 6, 7, 8, 9, 19, 20, 21, 22, 26, 28, 29, 30, 31, 32, 35, 38, 40, 48, 54, 55, 56, 58, 59 and 60) and 23 participants were not listed. This division into approximately two equal parts makes a comparison of the two sets relatively simple. Table 8 shows the mean metal values with coefficients of variation for those two groups. It is immediately apparent that for most metals the mean value was very much lower for the listed group. The exceptions were for manganese and zinc where the two groups were more comparable; indeed only in Sample B for zinc does the listed set record the lower value. With regard to the degree of variability, 12 out of the 16 paired sets showed a smaller coefficient of variation for the listed institutes. Thus it has been demonstrated that the listed institutes showed less variation as a group and, with the exception of manganese

and zinc, lower mean values than the remainder. It is interesting to note that of the 38 values excluded by the Chauvenet test, 29 were from unlisted participants. There is also evidence to suggest that the listed participants were able to achieve lower limits of detection than the rest. Taking all observations together the listed institutes reported 13 and 6 values below detection for Samples A and B, respectively, whereas the unlisted laboratories recorded 51 and 39 values, respectively.

DISCUSSION

It was clear from this exercise that the concept of a multi-vessel monitoring programme providing trace metal data of acceptable comparability was far from reality. The standard solution (Round 1) intercalibration showed a somewhat unsatisfactory degree of variability, but the sea-water samples were at least an order of magnitude worse.

It was unfortunate that the two sea-water samples did not show a greater difference between one another in trace metal content. Previous experience had generally shown the inshore location of Sample B to have a much higher metal content than on the present occasion. The fact that only the zinc and manganese content of these samples showed a significant difference probably reflects the smaller coefficient of variation with which these metals were measured compared with the remainder (Table 6).

The classification of institutes according to analytical experience must be somewhat arbitrary and it should not necessarily be assumed that all of those laboratories not listed in the FAO publication had no such experience. However, the results shown in Table 8 did indicate the validity of such a separation to a certain extent. It is interesting to note again the relation of zinc and manganese to the remainder of the metals. It appears that the measurement of these elements showed a greater uniformity of results compared with the remaining metals irrespective of the degree of analytical experience.

This exercise did not evaluate the precision of individual measurements since the sample volume generally did not permit replicate analyses. Moreover, since there was little measurable difference in the metal content of the two samples, it was not possible to relate analytical performance to concentration. The general high degree of variability made comparison of data according to analytical technique difficult. However, this round did demonstrate the feasibility of distributing frozen samples by air freight. It also showed that experience in the field of marine analytical chemistry tended to produce more consistent data with less evidence of analytical contamination.

Thus the way was clear for the Fourth Round Intercalibration Exercise and this was conducted during 1978 and early 1979 by the Bedford Institute of Oceanography, Canada. Several samples, some of which were spiked, were distributed to participants in sufficient quantities to allow replicate analyses. Samples were stored both acidified and deep frozen in different types of containers. A report on the exercise has already been prepared (Bewers et al., 1981) and in general there is an improvement in both analytical precision and agreement between laboratories compared with the present round.

The original Sub-Group on Contaminant Levels in Sea Water was incorporated into the newly formed ICES Marine Chemistry Working Group in 1978 and the latter continues to guide the programme of trace metal intercalibration. A fifth round is being planned and will involve a comparison of sampling techniques at sea together with subsequent analyses at a shore-based laboratory.

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ANNEX I

PARTICIPATING INSTITUTES

Canada

Bedford Institute of Oceanography, Dartmouth
Department of the Environment, Victoria
Fisheries Research Board of Canada, Vancouver

Denmark

Danish School of Pharmacy, Copenhagen
Institute of Plant Ecology, University of Copenhagen
Superfos Research Laboratory, Vedbæk
Water Quality Institute, Hørsholm

Federal Republic of Germany

Deutsches Hydrographisches Institut, Hamburg
Institut für Meereskunde an der Universität, Kiel
Max-Planck Institut für Metallforschung, Schwäbisch Gmünd

Finland

Institute of Marine Research, Helsinki

France

Centre d'Etudes Nucléaires de Cadarache
Centre d'Etudes Nucléaires de Grenoble
Centre d'Etudes et de Recherches de Biologie et d'Océanographie Médicale, Nice
Centre Océanologique de Bretagne, Brest
Centre de Recherche de Sédimentologie Marine, Centre Universitaire de Perpignan
Département de Chimie, Université de Bretagne Occidentale, Brest
Faculté de Pharmacie de Marseille
Institut Scientifique et Technique de Pêches Maritimes, Nantes
Laboratoire Départemental d'Hygiène, Caen
Laboratoire d'Océanographie Physique, Villefranche sur Mer
Laboratoire de la ville de Bordeaux
Laboratoire de la ville de Rouen
Musée Océanographique, Monaco
Société d'Etudes et Conseils, Giugues
Station de Recherches Agronomiques et Océanologiques, Ajaccio

German Democratic Republic

Institut für Meereskunde, Warnemünde

Greenland

Geological Survey, Greenland

Iceland

Hafrannsóknastofnunin, Reykjavik

Netherlands

Instituut voor Bodemvruchtbaarheid, Haren

Nederlands Instituut voor Onderzoek der Zee, Texel

Ryksinstituut voor Ziuvering Afvalwater, Lelystad

TNO Central Laboratorium, Delft

Norway

Central Institute for Industrial Research, Blindern

Department of Chemistry, University of Oslo

Institute for Marine Biology and Limnology, University of Oslo

Poland

Institute of Meteorology and Water Management, Gdynia

Portugal

Centro de Geofisica das Universidades de Lisboa

United Kingdom

Clyde River Purification Board, East Kilbride

Department of Agriculture and Fisheries for Scotland, Aberdeen

Department of Oceanography, University of Liverpool

Department of Oceanography, University of Southampton

Institute of Marine Environmental Research, Plymouth

Imperial College of Science and Technology, University of London

Ministry of Agriculture, Fisheries and Food, Lowestoft

Southern Water Authority, Brighton

Southern Water Authority, Winchester

Thames Water Authority, London

University College of Swansea

Wessex Water Authority, Poole

U.S.A.

College of Marine Studies, University of Delaware, Lewis, Del.

New England Aquarium, Boston, Mass.

NOAA, AOML, Miami, Fla.

Marine Research Laboratory, University of Connecticut, Noank, Conn.

Skidaway Institute of Oceanography, University of Georgia, Savannah, Ga.

Southern California Coastal Water Research Project, El Segundo, Cal.

US Environmental Protection Agency, Edison, New Jersey

US Environmental Protection Agency, Narragansett, Rhode Island

U.S.S.R.

Department of the Baltic Sea Institute, Tallinn

Table 1 The analysis of metal Solution A

Institute and method	Mercury 286 ppm				Lead 286 ppm				Nickel 143 ppm				Cobalt 143 ppm				Iron 143 ppm			
	Mean (no. of obs.)	Disc. %	Coeffic. var.	Check	Mean (no. of obs.)	Disc. %	Coeffic. var.	Check	Mean (no. of obs.)	Disc. %	Coeffic. var.	Check	Mean (no. of obs.)	Disc. %	Coeffic. var.	Check	Mean (no. of obs.)	Disc. %	Coeffic. var.	Check
1 AA (C)					281 (3)	- 1.7	1.7	292	141 (4)	- 1.4	3.1	155				143	140 (3)	-2.1	3.2	143
2 AA	252(6)	-11.9	3.6	308	300 (6)	4.9	0.0	283	138 (6)	- 3.5	1.1	150	140 (6)	-2.1	2.2		124 (6)	-13.2	1.7	150
3 AA (C)					273 (3)	- 4.6	3.2		144 (3)	0.7	0.4						142 (3)	- 0.7	1.2	
4 AA (C)					326 (9)	14.0	4.0	286	141 (9)	1.4	4.3	147	140 (9)	-2.1	3.1	136	137 (9)	- 4.2	1.9	134
5 AA					265 (3)	- 7.3	3.0	286	183 (3)	28.0	3.2	151	151 (3)	5.6	6.0	136	171 (3)	19.6	0.7	140
6 AA (C)					320 (2)	11.9	0.6	286								130	161 (2)	12.6	0.9	134
7 AA (C)					282 (3)	- 1.4	4.5	286	143 (3)	0.0	4.5	143	125 (3)	-12.6	4.0	130	147 (3)	2.8	3.9	131
8 AA (C)									148 (4)*	3.5	2.6	147	143 (4)	0.0	0.8	136	156 (4)*	9.1	1.1	137
9 AA1 (C)									129 (2)	- 9.8	1.1	155								
AA2									133 (3)	- 7.0	1.1						238 (2)	66.4	3.9	
10 AA					299 (3)	4.6	3.4	283	145 (3)	1.4	0.7	150	143 (3)	0.0	1.0		144 (3)	0.7	1.5	154
11 AA (C)	282 (3)	- 1.4	1.4	280	295 (3)	3.2	1.4	279	143 (3)	0.0	1.4	143	140 (3)	- 2.1	1.7	130	146 (3)*	2.1	0.3	131
12 AA (C)					295 (3)*	3.2	1.9	276	149 (3)	4.2	1.6	150					150 (3)	4.9	2.7	150
13 AA (C)	254 (3)	-11.2	2.0	300	300 (3)	4.9	1.0	276	140 (3)	- 2.1	1.8	148	146 (3)	2.1	1.8		143 (3)	0.0	4.4	154
14 AA	285 (2)	- 0.4	2.5		293 (3)	2.4	1.8		151 (3)	5.9	7.8						146 (3)	2.1	1.8	
15 EC					283 (6)	- 1.0	6.5	283												154
16 AA	274 (3)	- 4.2	1.0		284 (3)	- 0.7	0.6		144 (3)	0.7	2.8		139 (3)	- 2.8	4.4		158 (3)	10.5	4.1	
17 AA (C)	251 (5)	-12.2	4.7	300	241 (4)	-15.7	14.2	270												154
18 XRF (C)					266 (3)	- 7.0	4.2		123 (3)	-14.0	9.2		127 (3)	-11.2	9.2		130 (3)	- 9.1	1.6	
AA (C)	286 (3)	0.0	3.0		255 (3)	-10.8	2.4		146 (3)	2.1	1.6		155 (3)	8.4	1.5		143 (3)	0.0	1.6	
19 EC					247 (2)	-13.8	11.2													
20 AA (C)	264 (8)	- 7.7	2.3	308	293 (2)	2.4	1.2	276												
21 AA (C)									155 (1)	8.4							172 (1)	20.2		
22 AA	248 (3)	-13.3	0.6	286	316 (2)	10.5	0.4	283												
23 AA	267 (1)	- 6.6		296	301 (3)	5.2	0.0	273	156 (3)	9.1	0.7	150	161 (3)	12.6	0.4		155 (3)	8.4	0.4	150
24 AA (C)	288 (1)	-16.8			279 (1)	- 2.4			145 (1)	1.4			142 (1)	- 0.7			142 (1)	- 0.7		
25 AA	317 (3)	10.8	7.8	282	279 (3)	- 2.4	1.4	277	146 (3)	2.1	1.6	153	181 (3)	26.6	1.4		165 (3)	15.4	4.3	158
26 AA					311 (3)	8.7	2.5	280	144 (3)	0.7	1.8	155	149 (3)	4.2	2.8					
27 ES	240 (2)	-16.1	0.0	300																
28 AA (C)	270 (5)	- 5.6	2.2	286	278 (12)	- 2.8	1.1	280	145 (12)	1.4	2.0	155					143 (12)	0.0	2.1	161
29 AA (C)	275 (1)	- 3.8			282 (1)	- 1.4			140 (1)	- 2.1			139 (1)	- 2.8						
30 AA (C)																	259 (8)	81.1	7.4	
31 AA (C)					300	4.9	1.7		150	4.9	3.3						150	4.9	3.3	
32 AA	300 (1)	4.9							150 (1)	4.9			130 (1)	- 9.1						
EC					330 (1)	15.4														
CL																	140 (1)	- 2.1		
33 AA (C)	279 (3)	- 2.4	1.4		287 (3)	0.4	2.4		146 (3)	2.1	1.4		145 (3)	1.4	1.4		143 (3)	0.4	2.0	
34 AA (C)	298 (3)	4.2	1.0		301 (3)	5.2	0.7		150 (3)	4.9	0.0		151 (3)	5.6	0.7		150 (3)	4.9	2.7	
35 AA (C)	210 (3)	-26.6	4.8		310 (3)	8.4	9.7													
36 AA	221 (3)	-22.7	1.7		285 (3)	- 0.4	1.8						142 (3)	- 0.7	1.4		143 (3)	0.0	2.1	
EC									127 (3)	-11.2	2.4									
37 AA (C)	278 (3)	- 2.8	1.8		355 (3)	24.1	1.1		152 (3)	6.3	1.3		151 (3)	5.6	0.7		164 (3)	14.7	1.2	
38 EC (C)					330 (3)	15.4	3.6													
39 AA	293 (3)	2.4	2.0		297 (3)	3.8	1.7		149 (3)	4.2	2.0		150 (3)	4.9	0.7		150 (3)	4.9	0.0	
40 AA (C)	283 (2)	- 1.0			301 (2)	5.2							150 (2)	4.9			147 (2)	2.8		
41 AA	220	-23.1			290	1.4	0.3		158	10.5	0.0		158	10.5	0.6		102	28.3	0.5	
Mean	268		2.4	295	292		2.9	281	145		2.3	151	146		2.3	134	153		2.2	146
Coeffic. var.	10.0				8.1				7.2				8.0				18.6			

Key:- AA = Atomic absorption. EC = Electrochemistry. CL = Colorimetric
AA1 = Direct. XRF = X-ray fluorescence. (C) = Measured against commercial standard except for asterisk
AA2 = Standard addition. ES = Emission spectroscopy. Check = Metal content of returned sub-sample

Table 2 The analysis of metal Solution B

Institute and method	Chromium 232 ppm				Copper 232 ppm				Cadmium 179 ppm				Zinc 179 ppm				Manganese 179 ppm			
	Mean (no. of obs.)	Disc. %	Coeffic. var.	Check	Mean (no. of obs.)	Disc. %	Coeffic. var.	Check	Mean (no. of obs.)	Disc. %	Coeffic. var.	Check	Mean (no. of obs.)	Disc. %	Coeffic. var.	Check	Mean (no. of obs.)	Disc. %	Coeffic. var.	Check
1 AA (C)	206 (3)	-11.2	2.8	232	214 (4)	- 7.8	3.1	241	175 (4)	- 2.2	3.7	179	180 (4)	0.6	2.8	185	180 (4)	0.6	1.0	183
2 AA	225 (6)	- 3.0	0.6	235	228 (6)	- 1.7	2.3	232	176 (6)	- 1.7	1.1	176	179 (6)	0.0	1.1	182	177 (6)	- 1.1	1.9	179
3 AA (C)	196 (3)	-15.5	3.1		241 (3)	3.9	1.7		186 (3)	3.9	3.0		185 (3)	3.4	1.4		181 (3)	1.1	1.2	
4 AA (C)	214 (9)	- 7.8	3.3	228	240 (9)	3.4	0.0	238	178 (9)	- 0.6	3.2	179	174 (9)	-2.8	4.2	182	186 (9)	3.9	2.5	179
5 AA	229 (3)	- 1.3	2.0	232	236 (3)	1.7	1.7	238	182 (3)	1.7	1.0	179	181 (3)	1.1	1.2	183				
6 AA (C)					254 (2)	9.5	0.6	238	177 (2)	- 1.1	1.2	179	200 (2)	11.7	0.0	183	184 (2)	2.8	1.2	183
7 AA (C)	217 (3)	- 6.5	3.0	228	233 (3)	0.4	7.3	235	177 (3)	- 1.1	1.6	179	176 (3)	-1.7	0.6	183	178 (3)	- 0.6	1.8	183
8 AA					221 (4)	- 4.7	0.6	235	179 (3)	0.0	0.3	179	179 (3)	0.0	0.6	180	186 (4)	3.0	2.2	183
9 AA1 (C)					238 (2)	2.6	3.3	229	167 (2)	- 6.7	1.3	177					166 (3)	- 7.3	6.4	174
AA2 (C)					239 (1)	3.0			166 (2)	- 7.3	11.5						178 (3)	- 0.6	2.2	
10 AA	182 (3)	-21.6	0.2	238	235 (3)	1.3	0.9	232	160 (3)	-10.6	0.4	177	164 (3)	-8.4	1.4	182	127 (3)	-29.1	1.0	179
11 AA (C)	223 (3)	- 3.9	0.0	238	232 (3)	0.0	0.0	235	182 (3)	1.7	2.9	179	181 (3)	1.1	0.9	180	178 (3)*	- 0.6	3.0	183
12 AA (C)	205 (3)	-11.6	0.0	232	242 (3)	4.3	2.4	232	172 (3)	- 3.9	7.8	177	192 (3)	7.3	2.1					
13 AA (C)	232 (3)	0.0	0.9	232	232 (3)	0.0	0.9	225	177 (3)	- 1.1	3.6	177	182 (3)	1.7	0.8	172	180 (3)	0.4	1.4	172
14 AA					230 (3)	- 0.9	0.4		179 (3)	0.0	1.8		175 (3)	-2.2	4.3		180 (3)	0.6	1.9	
15 EC					248 (6)	6.9	16.6	232	158 (6)	-11.7	4.8	177								
16 AA	180 (3)	-22.3	2.0		232 (3)	0.0	1.0		181 (3)	1.1	1.1		178 (3)	-0.5	1.5		180 (3)	0.6	1.7	
17 AA (C)	224 (2)	- 3.4	1.9	238	192 (3)	-17.2	5.2	236	258 (2)	44.1	4.1	183	200 (2)*	11.7	0.7	186				
18 XRF (C)	217 (3)	- 6.5	3.1		217 (3)	- 6.4	5.5		155 (3)	-13.4	4.6		163 (3)	- 8.9	3.4		157 (3)	-12.3	3.7	
AA (C)	214 (3)	- 7.8	0.9		231 (3)	- 0.4	1.4		183 (3)	2.2	0.8		178 (3)	- 0.6	0.9		184 (3)	2.8	0.0	
19 AA (C)					235 (2)	1.3	11.2		183 (2)	2.2	8.9		112 (2)	-37.4	8.2					
20 AA (C)					239 (2)	3.0	0.6	232	183 (2)	2.2	0.4	177								
21 AA (C)	220 (1)	- 5.2			244 (1)	5.2			194 (1)	8.4			192 (1)				185 (1)	3.4		
22 AA					233 (2)	0.4	0.6	245	176 (2)	1.7	1.2	185	184 (2)	2.8	1.9	185				
23 AA	259 (3)	11.6	0.6	232	232 (3)	0.0	0.3		186 (3)	3.9	0.0	177	177 (3)	- 1.1	0.6	179	188 (3)	5.0	0.3	176
24 AA (C)	211 (1)	- 9.1			223 (1)	- 3.9			176 (1)	- 1.7			173 (1)	- 3.4			181 (1)	1.1		
25 AA	218 (3)	- 6.0	1.1	238	237 (3)	2.2	1.4	238	186 (3)	3.9	1.5		176 (3)	- 1.7	1.6	180	167 (3)	- 6.7	0.7	183
26 AA					235 (3)	1.3	1.2	248												
AA					243 (3)	4.7	4.0		167 (3)	- 6.7	4.4		187 (3)	4.4	3.1					
27 ES																				
28 AA (C)					258 (12)	11.2	1.6	238	175 (12)	- 2.2	1.7	181	167 (6)	- 6.7	3.0		169 (12)	- 5.6	1.2	181
29 AA (C)					229 (1)	- 1.3			182 (1)	1.7			175 (1)	- 2.2			175 (1)	- 2.2		
30 AA (C)					279 (8)	20.3	6.4		255 (6)	42.5	6.6						163 (6)	- 8.9	7.0	
31 AA (C)	205	-11.6	2.4		240	3.4	2.1		180	0.6	2.8		180	0.6	2.9		180	0.6	2.8	
32 AA	300	29.3											180	0.6			180	0.6		
EC					230	- 0.9			180	0.6										
CL																				
33 AA (C)	235 (3)	1.3	0.4		237 (3)	2.2	1.3		184 (3)	2.8	1.1		183 (3)	2.2	1.6		182 (3)	1.7	2.8	
34	228 (3)	- 1.7	3.1		237 (3)	2.2	0.8		182 (3)	1.7	1.1		185 (3)	3.4	2.7		185 (3)	3.1	1.6	
35 AA (C)									150 (3)	16.2	13.3		185 (3)	3.3	8.1					
36 AA	200 (3)	-13.8	0.0		225 (3)	- 3.0	2.2		195 (3)	8.9	2.6		197 (3)	10.0	1.5		185 (3)	3.3	2.7	
EC																				
37 AA (C)	214 (3)	- 7.8	0.5		236 (3)	1.7	0.4		186 (3)	3.9	3.3		201 (3)	12.3	1.0		199 (3)	11.2	0.5	
38 EC (C)					155 (3)	-33.2	3.9		187 (3)	4.4	4.8		207 (3)	15.6	1.9					
39 AA	225 (3)	- 3.0	1.3		238 (3)	2.6	0.4		180 (3)	0.6	0.6		181 (3)	1.1	1.6		179 (3)	0.0	0.6	
40 AA (C)					246 (2)	6.0			187 (2)	4.4			185 (3)	3.4			180 (3)	0.6		
41 AA	240	3.4	0.0		270	16.4	0.0		160	-10.6	0.0		198	10.6	0.5		198	10.6	0.5	
Mean	220		1.4	233	234		2.6	236	181		3.0	179	181		2.1	180	178		2.0	180
Coeffic. var.	10.7				8.0				10.9				8.5				7.1			

Key:- AA = Atomic absorption. EC = Electrochemistry. CL = Colorimetric
AA1 = Direct. XRF = X-ray fluorescence. (C) = Measured against commercial standard except for asterisk
AA2 = Standard addition. ES = Emission spectroscopy. Check = Metal content of returned sub-sample

Table 3 Application of Chauvenet's test to trace metal standard solution data

	Hg	Pb	Ni	Co	Fe	Cr	Cu	Cd	Zn	Mn
Concentration (ppm)	286	286	143	143	143	232	232	179	179	179
Mean	268	292	145	146	153	220	234	181	181	178
% diff from mean	- 6.3	2.1	1.4	2.1	7.0	- 5.2	0.9	1.1	1.1	- 0.6
Coefficient variation	10.0	8.1	7.2	8.0	18.6	10.7	8.0	10.8	8.5	7.1
Mean after Chauvenet	268	290	146	144	148	215	234	178	183	180
% diff from mean	- 6.3	1.4	2.1	0.7	3.5	- 7.3	0.9	- 0.6	2.2	0.6
Coefficient variation	10.0	7.2	3.8	6.3	7.0	7.0	3.7	5.1	5.6	4.3
Values rejected (participant)	Nil	355 (37)	123 (18(1)) 127 (36) 129 (9(1)) 183 (5)	181 (25)	102 (41) 238 (9(2)) 259 (30)	259 (23) 300 (33)	155 (38) 192 (17) 258 (28) 270 (41) 279 (30)	150 (35) 255 (30) 258 (17)	112 (19)	127 (10) 157 (18(1))

Table 4 The analysis of sea water samples A and B, $\mu g\ l^{-1}$

Institute and method	Sample A									Sample B								
	Co	Fe	Ni	Pb	Cd	Cr	Cu	Mn	Zn	Co	Fe	Ni	Pb	Cd	Cr	Cu	Mn	Zn
1 AA (1) A			<0.2	<0.4	<0.06		0.4		3.3			1.1	<0.4	0.12		0.7		10.1
2 AA (2) D (Zn (1) D)	0.13	1.05	0.80	0.71	0.099		0.55	0.39	4.0	0.15	1.80	0.72	0.8	0.078		0.46	9.6	7.8
3 AA (1) B			<0.1	0.7	1.5		3.1	<0.1	2.7			1.3	23	4.4		1.2	7.2	18
6 AA (2) A				0.37	0.07		0.5						0.09	0.11		1.2		
7 AA (1) A (Cd,Pb,Mn (2)A)		3.0		0.51	0.09		0.60	<0.06	9.9		2.6		0.51	0.13		0.6	10.6	10.5
EC pH 1.85				2.0	0.10		0.8						2.2	0.09		0.9		
EC pH 8.1				0.18	0.11		0.4		4.7				0.26	0.12		0.3		4.65
8 AA (2) A	0.17	8.1	0.28		0.13		0.76	1.5	10.8	0.13	5.8	0.69		0.57		0.71	11.6	13.8
9 AA (2) A		4.9	0.5		0.19		0.9	2.2			2.2	1.0		0.10		0.5	13.8	
EC				2.1	0.14				17				1.1	0.09				8
11 AA (1) A	0.2	2.3	0.6	0.8	0.3	0.4	0.6	0.4	4.8	0.4	4.0	1.2	0.6	0.2	0.3	1.0	9.8	9.8
12 AA (1) A		<1	<2.5	<0.5	0.03	< 0.5	<0.5		6.2		<1	<2.5	<0.5	0.14	<0.5	0.7		7.7
CL								<10									<10	
13 AA (2) C (Cd,Pb,Co,Ni (2) A)	<5	(<100)	5	<5	<5	(390)	(80)		<20	<5	(<100)	16	<5	<5	33	(70)		<20
15 EC				0.90	0.18		0.88						0.42	0.087		0.89		
16 AA (2) A	<0.5	<1.0	<1.0	<0.5	<0.1	<10	0.4	<20	6.5	<0.5	<1.0	1.8	<0.5	<0.1	<10	0.80	<20	10.5
19 EC				0.315	0.047		0.49		3.59				0.205	0.080		0.830		3.78
20 EC				0.13	0.03		1.0						0.09	0.13		1.4		
21 AA (2) (Zn (1) A)			0.26		0.020		0.27		7.55			0.95		0.032		0.60		11.6
22 AA (2) (Zn (1) A)					0.2		0.4		8.6					0.3		0.8		11.1
24 AA (1) A			<0.1	2.0	0.05	2.3	0.5		6.0			0.9	0.5	0.15	3.3	0.8		10.0
26 AA (2) B							0.36									0.54		
28 AA (2) A			0.44		0.023		0.22		5.5			1.1		0.17		0.29		15
29 AA (2) A (Zn (1) A)	<0.5			0.74	0.26		0.94		14.8	<0.5			0.74	0.36		1.21		21.8
30 AA (2) A		4.15		0.205	0.095		0.45	1.5			1.2		0.12	0.17		0.63	9.8	
EC									6.2									7.7
31 EC				1.50	0.25		2.1		10.5				0.90	0.20		0.60		7.5
32 EC				1.0	<0.1		1.8		1.7				1.4	<0.1		1.5		37
AA (Ni (1)) (Cr (2)) A			<0.5			<0.3						0.7			<0.3			
CL		<4						3.9			15						12.4	
35 AA (2) A				<0.3	0.02		0.25		6.0				0.3	0.12		0.50		9.5
36 AA (2) A (Zn (1) A)	<0.5	8.0		<0.2	0.3	<0.5	0.6	3.5	17	<0.5	4.0		<0.2	0.2	<0.5	1.2	16	20
37 AA (2) A (Mn (1) A)	<0.5	15	1	<1	<0.2	0.5	<0.5	<1	5	<0.5	35	1	<1	<0.2	1.5	0.5	8.5	8
38 EC				2.35	0.30		1.80		13.90				2.85	0.26		1.15		5.35
39 AA (1) A	<0.2	<0.5	<0.5	<0.5	<0.2	<0.5	<0.5	2	3.5	<0.2	0.7	<0.5	0.7	<0.2	<0.5	0.7	12	12
40 AA (2) A (Zn (1) A)				0.06	0.03		0.25		3.0				0.11	0.08		0.50		7.5
42 AA (?) A				<1	<0.2	<1	0.5	1.3					1	0.35	<1	<0.5	12	
43 AA (?) A				0.45	0.03		2.5		8.0				0.25	0.03		3.0		8.5
44 AA (?) A				<10	<1		<1		9				<10	10		1.0		11
45 EC (Zn AA (?) A)				5.5	1.2		3.1		11.5				3.2	0.5		2.5		24
46 AA (?) A				<0.5	<0.4	<0.5			21				<0.5	<0.5	<0.5			20
47 EC				0.093	0.1		0.99		4.8				0.11	0.088		1.10		11.0
48 AA (2) C		1.1			<0.05		0.46	0.24	10.5		1.7			0.20		1.1	7.5	11
49 PE A			0.35		<0.07	0.63			5.6			1.9		1.2	0.53			14.1
50 AA (1) A				0.15	0.053		0.39						0.11	0.103		0.60		
51 AA (1) B				<1	0.04		1.4		11.6				<1	0.2		0.8		13.3
52 AA (2) C						0.40									0.64			
53 AA (1) A			6.4	1.4	0.2		2.2		2.1			24.2	11.2	1.9		8.8		30.3
54 AA (2) A		0.9		0.7	0.04		0.2				1.6		0.9	0.63		2.0		
55 AA (1) A (Ni,Pb (2) A			0.74	0.49	<0.95		0.52		10.63			1.03	0.38	<0.95		0.92		3.43
56 AA (1) A				0.75	0.17		0.62		7.6				0.54	0.26		0.89		8.4
57 AA (2) A (Zn (1) A)	2.5		6.0	2.9	<0.2		1.0		4.9	3.0		5.4	2.5	<0.2		1.3		10.4
58 AA		1.35	0.19	0.12	0.49	0.09	0.74		5.41		2.23	0.71	0.28	0.084	0.11	2.28		5.90
59 EC				0.18	0.09		1.22		4.72				0.32	0.11		0.90		7.92
60 EC				5.6	0.6		<1.0		22.2				5.0	0.3		<1.0		6.6
61 AA (2) B (Ni,Pb,Zn (1) B)		<0.4	<0.8	<0.8	0.13		<0.2	0.7	5.5		<0.4	<0.8	<0.8	0.09		<0.2	0.8	10.4

Key AA = Atomic absorption. PE = Plasma emission. (1) = Flame. A = Organic extraction. C = Direct injection.
EC = Electrochemistry. CL = Colorimetric. (2) = Furnace. B = Ion exchange resin. D = Coprecipitation.

Table 5 Precision and limits of detection of participants in sea water intercalibration. Values in $\mu g\ l^{-1}$ unless otherwise indicated.

	Co		Fe		Ni		Pb		Cd		Cr		Cu		Mn		Zn	
	Limit det.	Precision	Limit det.	Precision	Limit det.	Precision	Limit det.	Precision	Limit det.	Precision	Limit det.	Precision	Limit det.	Precision	Limit det.	Precision	Limit det.	Precision
1					0.2	0.1	0.4	0.02	0.05	0.03			0.1	0.05			0.2	0.1
2		0.06		0.1		0.08		0.04		0.006				0.06		0.04		
6							0.05	50%	0.03	15%			0.1	30%			3	40%
8	0.037	0.012	1.5	0.5	0.19	0.06							0.068	0.023	0.03	0.01	0.26	0.09
9			0.5	± 16%	0.5	± 16%	0.15	± 28%	0.01	± 16%			0.2	± 3.5%	0.3	± 3.5%	0.2	± 12%
11	1.0	0.5 SD	1.6	1.9 SD	1.0	0.48 SD	0.4	0.21 SD	0.2	0.1 SD			0.5	0.2 SD	2.0	1.0 SD	0.44	0.6 SD
12				± 1.0		± 2.5		± 0.5		± 0.05		± 0.05		± 0.5		± 10		± 0.5
13	5	± 10%	5	± 10%	5	± 10%	5	± 10%	5	± 10%			1	± 10%			20	± 10%
15								16% CV		12% CV				7% CV				
16	0.5	10%	1.0	10%	1.0	10%	0.5	10%	0.1	10%	10	15%	0.2	5%	20	20%	0.5	10%
19							0.01	0.05 SD	0.01	0.005 SD			0.1	0.07 SD			0.1	0.5 SD
20							0.03		0.02				0.2					
21						± 0.2								± 0.06				± 1.1
22									0.01	± 0.1			0.04	± 0.1			0.07	± 0.3
24					0.1	0.1	0.5	0.05	0.05	0.05	0.02	0.1	0.1	0.1			0.1	0.5
26													0.03	8% CV				
28						± 0.05				± 0.01				± 0.06				± 0.75
30			0.2	7% CV			0.03	12% CV	0.02	10% CV			0.2	5% CV	0.1	7% CV	0.3	15% CV
31							0.1		0.05				0.25				0.5	
32			4.0		0.5		0.5		0.1		0.3		0.5		2.0		0.5	
35							0.15		0.02								0.2	
36	0.5		1.0				0.2		0.05		0.5		0.5		1.0		1.0	
37	0.5		1.0		0.5		1.0		0.2		0.5		0.5		1.0		1.0	
39	0.2		0.5		0.5		0.5		0.2		0.5		0.5					
40							0.05		0.03				0.1				3.0	
42							1.0		0.2		1.0		0.5		1.0			
44							10.0		1.0				1.0					
45							0.1		0.1				0.2				5.0	
46			0.5				0.5		0.4									
47							0.005	22% CV	0.005	18% CV				21% CV				13% CV
48			1.6	0.36 SD					0.10	0.02 SD			0.62	0.29 SD	0.61	0.12 SD	0.30	0.43 SD
49					0.15	± 0.2			0.06	± 0.2	0.07	± 0.2					0.6	± 0.2
50							0.04	± 10%	0.005	± 10%			0.02	± 10%				
51							1		0.25				0.4				0.6	
53					25	8.9% SD	40		5				10	17.0% CV			5	2.6% CV
55					0.30	0.6% CV	0.10	6.0% CV	0.95	1.2% CV			0.15	49.4% CV			0.35	3.5%
57	1.2	1.2 SD			1.7	2.7 SD	1.0	1.8 SD	0.2				0.8	1.0 SD			1.2	1.4 SD
58				0.12 SD		0.08 SD		0.04 SD		0.015 SD		0.02 SD		0.48 SD				0.38 SD
59							0.005	± 7%	0.01	± 15%			0.02	± 15%			0.01	± 10%
60							0.5	± 12%	0.1	± 10%			1.0	± 5%			0.5	± 10%
61			0.4		0.8		0.8			± 0.005			0.2			± 0.3		± 0.3

Key SD = Standard deviation.
CV = Coefficient variation.

Table 6 The mean concentration and range of values of each metal above detection limit analysed in sea water Samples A and B together with the coefficient of variation and application of Chauvenet's test.

	Co		Fe		Ni	
	All	After Chauv.	All	After Chauv.	All	After Chauv.
Sample A						
Mean $\mu g\ l^{-1}$ (No. obs.)	0.70 (4)	0.18 (3)	4.53 (11)	3.50 (10)	1.74 (13)	1.74 (13)
Range $\mu g\ l^{-1}$	0.13-2.5	0.13-0.2	0.9-15	0.9-8.1	0.19-6.4	0.19-6.4
Coefficient variation %	156	21	96	79	135	135
Institutes excluded		57		37		Nil
Sample B						
Mean $\mu g\ l^{-1}$ (No. obs.)	0.92 (4)	0.23 (3)	5.99 (13)	2.53 (11)	3.43 (18)	1.07 (15)
Range $\mu g\ l^{-1}$	0.13-3.0	0.13-0.4	0.7-35	0.7-5.8	0.7-24.2	0.7-1.9
Coefficient variation %	151	66	158	59	184	34
Institutes excluded		57		32,37		13,53,57

Table 6 continued

	Pb		Cd		Cr	
	All	After Chauv.	All	After Chauv.	All*	After Chauv.
Sample A						
Mean $\mu g\ l^{-1}$	1.16 (30)	0.77 (27)	0.21 (37)	0.12 (33)	0.72 (6)	0.40 (5)
Range $\mu g\ l^{-1}$	0.06-5.6	0.06-2.35	0.02-1.5	0.02-0.3	0.09-2.3	0.09-0.6
Coefficient variation %	121	88	148	75	110	49
Institutes excluded		42,57,60		3,42,58,60		24
Sample B						
Mean $\mu g\ l^{-1}$	1.92 (33)	0.77 (30)	0.40 (42)	0.21 (39)	1.06 (6)	0.61 (5)
Range $\mu g\ l^{-1}$	0.09-23	0.09-2.85	0.03-4.4	0.03-0.63	0.11-3.3	0.11-1.5
Coefficient variation %	228	100	197	92	113	87
Institutes excluded		3,53,60		3,49,53		24

*Excluding Institute No. 13

Table 6 continued

	Cu		Mn		Zn	
	All*	After Chauv.	All	After Chauv.	All	After Chauv.
Sample A						
Mean $\mu g\ l^{-1}$ (No. obs.)	0.93 (40)	0.08 (35)	1.60 (11)	1.60 (11)	7.98 (41)	7.28 (39)
Range $\mu g\ l^{-1}$	0.2-3.1	0.2-1.8	0.4-3.9	0.4-3.9	1.7-22.2	1.7-17
Coefficient variation %	83	60	77	77	62	54
Institutes excludes		3,31,42 43,53		Nil		46,60
Sample B						
Mean $\mu g\ l^{-1}$ (No. obs.)	1.16 (44)	0.83 (39)	10.75 (14)	10.35 (13)	11.93 (41)	10.47 (38)
Range $\mu g\ l^{-1}$	0.2-3.1	0.2-1.4	7.2-16	7.2-13.8	3.43-37	3.43-20
Coefficient variation %	113	36	22	19	57	41
Institutes excluded		42,43,53 54,58		36		32,42,53

*Excluding Institute No. 13

Table 7 Comparison of electrochemical methods of sea water analysis with other techniques

	Pb		Cd		Cu		Zn	
	Electrochem.	Others	Electrochem.	Others	Electrochem.	Others	Electrochem.	Others
Sample A								
Mean $\mu g\ l^{-1}$ (No. obs)	0.98 (11)	0.54 (15)	0.13 (10)	0.21 (24)	1.15 (10)	0.56 (25)	7.46 (9)	6.60 (28)
Coefficient variation %	90	64	64	149	50	51	69	43
Sample B								
Mean $\mu g\ l^{-1}$ (No. obs)	0.91 (12)	0.55 (16)	0.16 (12)	0.20 (26)	0.95 (10)	0.82 (30)	6.94 (9)	11.19 (28)
Coefficient variation%	97	93	60	80	36	42	31	34

Table 8 Sea water intercalibration comparing "listed" and "unlisted" participants.

	Co		Fe		Ni	
	Unlisted	Listed	Unlisted	Listed	Unlisted	Listed
Sample A						
Mean $\mu g\ l^{-1}$ (No. obs.)	1.35 (2)	0.15 (2)	8.43 (3)	3.07 (8)	3.23 (6)	0.46 (7)
Coefficient variation %	120	19	75	83	89	52
Sample B						
Mean $\mu g\ l^{-1}$ (No. obs.)	1.70 (2)	0.14 (2)	10.93 (4)	3.79 (9)	5.97 (9)	0.89 (9)
Coefficient variation %	108	10	148	116	141	20

Table 8 continued

	Pb		Cd		Cr	
	Unlisted	Listed	Unlisted	Listed	Unlisted*	Listed
Sample A						
Mean $\mu g\ l^{-1}$ (No. obs.)	1.49 (10)	1.00 (20)	0.32 (13)	0.15 (24)	0.85 (5)	0.09 (1)
Coefficient variation %	111	129	149	98	103	
Sample B						
Mean $\mu g\ l^{-1}$ (No. obs.)	3.55 (12)	0.91 (21)	1.30 (15)	0.19 (25)	1.25 (5)	0.11 (1)
Coefficient variation %	193	129	206	77	98	

*Excluding Institute No. 13

Table 8 continued

	Cu		Mn		Zn	
	Unlisted*	Listed	Unlisted	Listed	Unlisted	Listed
Sample A						
Mean $\mu g\ l^{-1}$ (No. obs.)	1.36 (13)	0.79 (27)	1.58 (6)	1.62 (6)	7.54 (18)	8.35 (23)
Coefficient variation %	75	72	78	83	65	60
Sample B						
Mean $\mu g\ l^{-1}$ (No. obs.)	1.58 (17)	0.89 (27)	10.76 (7)	10.76 (7)	13.83 (18)	10.26 (23)
Coefficient variation %	125	54	27	19	45	69

*Excluding Institute No. 13

Figure 1. Results of trace metal standard solution intercalibration in histogram form.

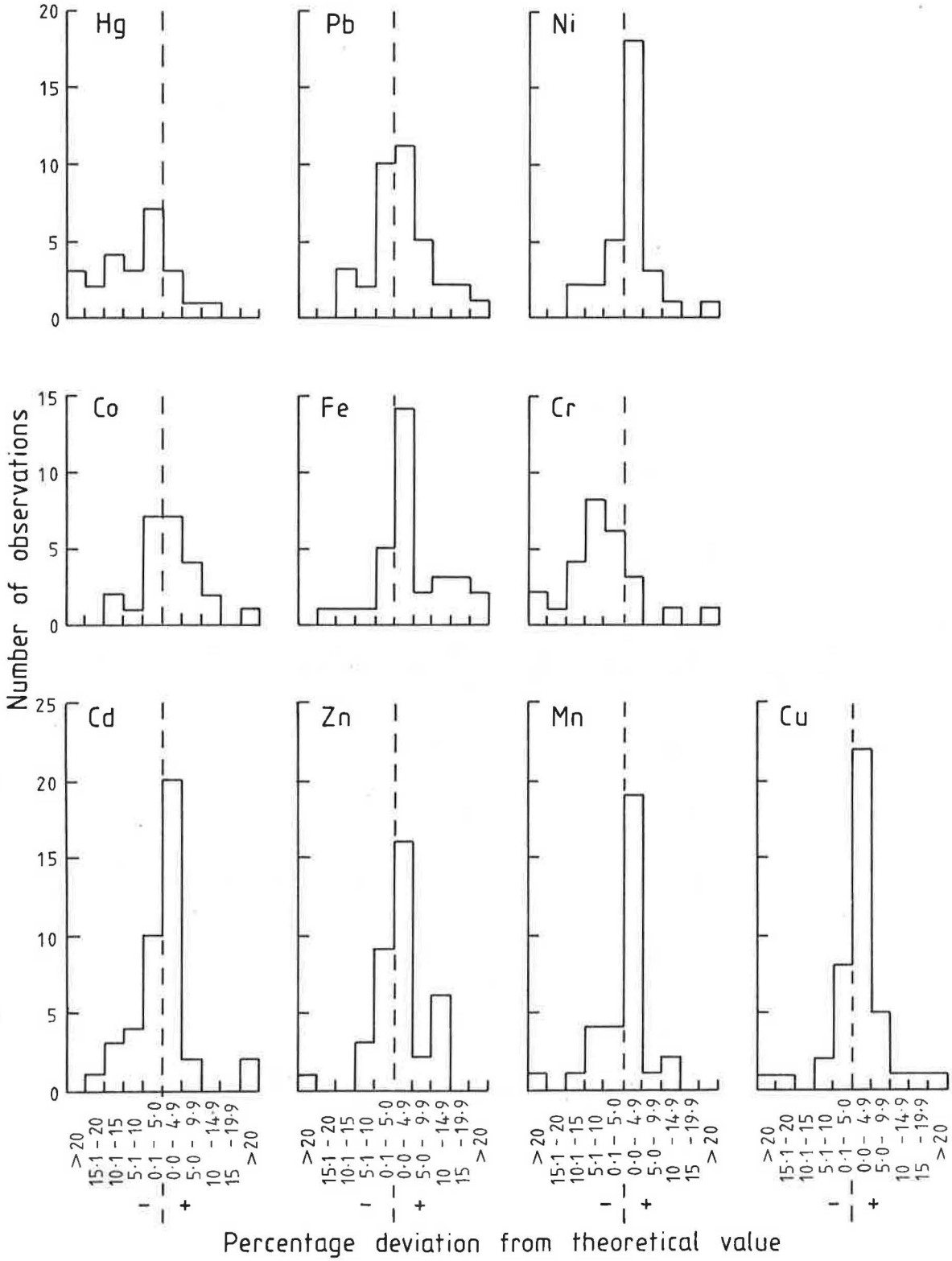
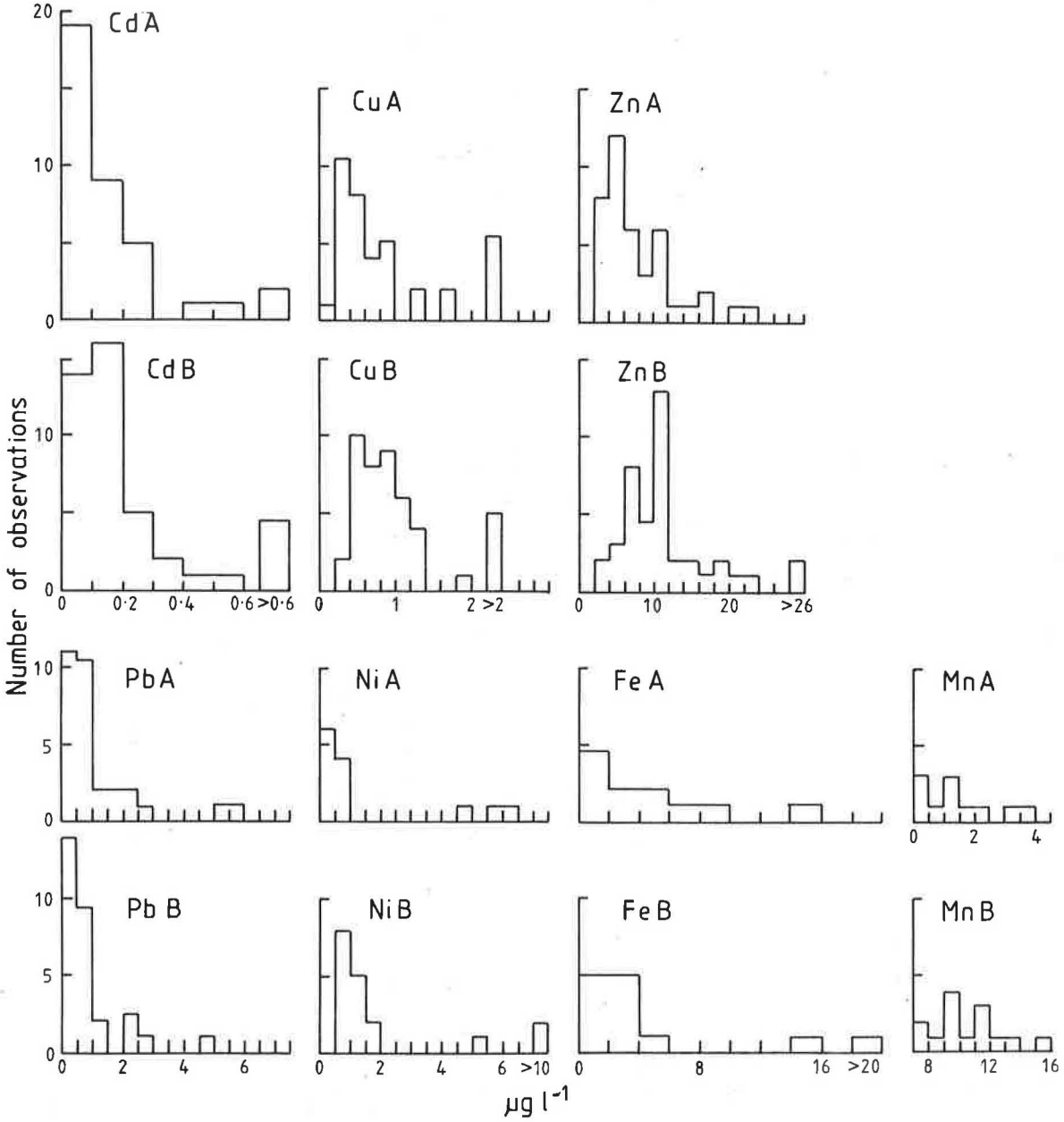


Figure 2. Results of sea-water samples A and B intercalibration in histogram form (excluding cobalt and chromium).



A SUMMARY REPORT ON THE 1976 INTERCALIBRATION OF MERCURY IN SEA WATER

(SECOND ROUND INTERCALIBRATION)

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INTRODUCTION

At the first meeting of the Sub-Group on Contaminant Levels in Sea Water in May 1975 it was decided to organize a series of intercalibration exercises on trace metals, beginning first with the distribution of concentrated multi-element standards (Jones, 1976) followed later by the distribution of sea water samples. The mercury in sea water intercalibration exercise took place in 1976 as the second round in the series of intercalibrations on trace metals in sea water. The results were submitted to the ICES Statutory Meeting that year and later reported on in the open literature (Ólafsson, 1976, 1978).

THE SAMPLES

In the above-cited reports (Ólafsson, 1976, 1978) there are detailed descriptions of the sample preparation. The intercalibration set consisted of two 500 ml samples of natural acidified sea water and one 500 ml sample of acidified seawater spiked with 132 ng l^{-1} of inorganic mercury. In choosing the size of the spike, two objectives were kept in mind: (a) that it should exceed the total natural mercury concentration by at least an order of magnitude, and (b) that very sensitive methods would still be required for accurate determination. The sample containers were 500 ml glass-stoppered Pyrex bottles which had been repeatedly washed with warm nitric acid and mercury-free distilled water. The samples were sent to the participating laboratories (listed in Table 1) in April 1976 and at the request of one laboratory (B) sea water was collected in their special irradiation ampoules concurrently with the sampling for the exercise. Simultaneously with the preparation of the samples, the mercury and "total" mercury after U.V. irradiation (Armstrong et al., 1966) in the natural sea water sample and the mercury, after equilibration, in the spiked sample were determined by cold-vapour atomic absorption after preconcentration by amalgamation on gold (Ólafsson, 1974).

RESULTS

Analytical methods

Most participating laboratories gave an adequate description of their analytical procedures. A brief outline of the methods used is given in Table 2. (The order of laboratories does not correspond to that in Table 1.) It will be seen that one laboratory employed neutron activation whilst all the others used the cold-vapour atomic absorption procedure, one supplementing it with atomic emission. Two basic versions of the cold-vapour technique were used, a closed system where the mercury vapour circulates between the sample vessel and the spectrophotometer cell, and an open system where the mercury vapour is carried through the spectrophotometer cell in a small volume of carrier gas. The latter system can give greater sensitivity than the former, but it also requires a careful control of operating

parameters such as gas flow if reproducible results are to be obtained. Several of the participants have increased the sensitivity by preconcentration prior to the atomic absorption. The laboratories using the cold-vapour atomic absorption technique have generally preceded the measurements with an oxidation step, most commonly treatment with acid permanganate. The oxidation may bring about the break-down of organo-mercury complexes to a degree which depends on the strength of the oxidizing agent.

The sea water sample

The sea water sample was found after collection to have a low mercury concentration (Table 3, lab. A). The values reported showed a wide distribution, ranging from 4.48 to 100 ng l^{-1}. Three laboratories, F, H and I, found the concentration to be below their limits of detection and the information submitted from two other laboratories, J and K, suggested that their results are close to their limits of detection. Statistical examination of the data reveals a very poor agreement for the group as a whole. Considering that the higher values are most likely caused by either contamination or interference, all values > 10 ng l^{-1} were excluded. This leaves only six results, which limits statistical examination. The coefficient of variation is, however, much more reasonable in this case.

In addition to the data in Table 3, laboratory B reported two results for the sea water collected directly in their special ampoules. These were 13 ± 4 ng l^{-1} and 3 ± 2 ng l^{-1}.

The spiked sample

As can be seen from Table 4, the mercury concentration when the intercalibration samples were bottled was 131 ng l^{-1} as determined by cold-vapour atomic absorption. It is worth noting that the results of B, the only laboratory using neutron activation, agree very well with this value. The reported concentrations range from 100 to 300 ng l^{-1}, but as expected the level of variation is much lower here than with the unspiked sample and, when the four values exceeding 200 ng l^{-1} are excluded, the coefficient of variation is reduced to 22.8%.

Changes with time

Sufficient numbers of samples of the spiked sea water were retained to follow any changes that would take place in the mercury concentration during the time of the intercalibration. The results of this storage test are shown in Table 5. There is a statistically insignificant change with time and it may be concluded that loss of mercury with storage should not have affected the results of the intercalibration.

The data in Table 4 show no general trend, decrease or increase with time. One laboratory, G, reported a sharp decrease in the concentration of the spiked sample during the time of analysis, when the concentration decreased towards the original value. It seems possible that the drift observed has been unrelated to the concentration in the sample.

Two laboratories, B and C, obtained significantly different results for the duplicate samples of the unspiked sample. The most probable explanation for this seems to be contamination, the source of which is unknown.

CONCLUSION

This exercise indicated that some 5 of the participating laboratories had methods sensitive and accurate enough to determine mercury in unpolluted sea water with a reasonable agreement. It further suggested that at the level of 130 ng l^{-1}, as might be encountered in highly polluted sea water, 11 or possibly 12 out of

the 14 participants could be expected to be able to determine the mercury concentration. Systematic positive errors seemed to be important in many of the laboratories.

In the time that has elapsed since this exercise was carried out, a second intercalibration for mercury in sea water has been conducted (ICES, 1981). For low level determinations this latter exercise did show a considerably better agreement between laboratories, and it furthermore elucidated the errors that are most likely to affect determinations of mercury in sea water.

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Table 1. List of participants

C W Baker	MAFF, Fisheries Radiobiological Laboratory, Hamilton Dock, Lowestoft, Suffolk, England.
J M Bewers and P A Yeats	Atlantic Oceanographic Laboratory, Bedford Institute of Oceanography, Dartmouth, Nova Scotia, B24 4A2, Canada.
P H A Hoogweg	Rijksinstituut voor Zuivering Afvalwater, Postbox 17, Lelystad, Netherlands.
K O Jensen	Isotopcentralen, Skelbækgade 2, DK-1717, Copenhagen, Denmark
W K Johnson and C S Wong	Ocean and Aquatic Sciences, Department of the Environment, Ocean Chemistry Division, 211 Harbour Road, Victoria, B.C. V9A 3S2 Canada.
F Koroleff	Institute of Marine Research, P.O. Box 166, 00141 Helsinki 14, Finland.
C Murphy	State Laboratory, Upper Merrion Street, Dublin, 2, Ireland.
J Ólafsson	Marine Research Institute, Skúlagata 4, Reykjavik, Iceland.
D O'Sullivan	Department of Agriculture and Fisheries, Fisheries Division, 3 Cathal Brugha Street, Dublin 1, Ireland.
P E Paus	Central Institute for Industrial Research, Forskningsveien 1, Blindern, Oslo, Norway.
S J Spijk	Central Laboratory T.N.O., Postbox 217, Delft, Netherlands.
Y Thibaud	Institut Scientifique et Technique des Pêches Maritimes, Rue de I'lle-d'Yeu, B.P. 1049, 44037 Nantes Cedex, France.
G Topping	DAFS, Marine Laboratory, P.O. Box 101, Victoria Road, Torry, Aberdeen AB9 8DB, Scotland.
P Tschöpel	Max-Planck-Institut für Metallforschung, Laboratorium für Reinststoffe, Katharinenstrasse 17, 7070 Schwäbische Gmünd, Federal Republic of Germany.

Table 2

Laboratory	Outline of method
A	Oxidative treatment: U.V. irradiation, HNO_3. Determination: Cold vapour atomic absorption after preconcentration by amalgamation on gold. Open system.
B	Determination: Neutron activation. Radiochemical separation is concluded with electrolytic deposition of mercury on gold foil.
C	Oxidation: Potassium dichromate. Determination: Cold vapour atomic absorption, without preconcentration. Open system.
D	Oxidation: $KMnO_4/H_2SO_4$ few minutes. Determination: Cold vapour atomic absorption after preconcentration by SnII reduction, aeration and collection of the mercury in $KMnO_4/H_2SO_4$ solution. Open system.
E	Oxidation: $HNO_3/KMnO_4/K_2S_2O_8$, 80°C, 2 hrs. Determination: Cold vapour atomic absorption without preconcentration. Open system.
F	Oxidation: Autoclaved with HNO_3 added. Determination: Cold vapour atomic absorption/emission after preconcentration on gold.
G	Oxidation: Boiling with ammonium persulphate. Determination: Cold vapour atomic absorption after preconcentration by amalgamation on gold. Open system.
H	Oxidation: Bromine vapour. Determination: Cold vapour atomic absorption without preconcentration. Open system.
I	Oxidation: $KMnO_4/H_2SO_4$. Determination: Cold vapour atomic absorption without preconcentration. Open system.
J	Determination: Cold vapour atomic absorption, closed system. Preconcentration by dithizone extraction into carbon tetrachloride. Back extraction into aqueous phase after destruction of the dithizone and mercury dithizonate with $KMnO_4/H_2SO_4$ solution.
K	Oxidation: $KMnO_4/H_2SO_4$. Determination: Cold vapour atomic absorption without preconcentration. Closed system.
L	Oxidation: $KMnO_4/HNO_3/H_2SO_4$, 2 hrs. room temperature. Determination: Cold vapour atomic absorption without preconcentration.

Laboratory	Outline of method
M	Oxidation: Bromine vapour. Determination: Cold vapour atomic absorption without preconcentration.
N	Oxidation: $HNO_3/H_2SO_4/KMnO_4$. Determination: Cold vapour atomic absorption, semi-automated, without preconcentration. Open system.

Table 3. Reported mercury concentrations in unspiked sea water samples

Lab.	Sample	Hg ng l^{-1}	Days from collection	Hg ng l^{-1} unoxidized	
A		4.48 ± 0.4	2	1.40 ± 0.4	
B	a	* 31 ± 3	19		Contamination?
	b	6 ± 3	19		
C	a		88	10.5 ± 1.0	
	a		90	11.2 ± 0.7	
	b		88	4.0 ± 0.6	
	b		90	3.9 ± 1.1	
	a	*19.7 ± 2.4	90		Contamination?
	b	8.5 ± 0.9	90		
D	a	5.0	~ 60		3.0 ng l^{-1} Obtained additionally by rinsing sample bottles with $KMnO_4/H_2SO_4$ solution
	b	5.9	~ 60		1.0 ng l^{-1}
E	a	*34	13		Estimated precision ± 10 ng l^{-1}
	b	*42	13		Unusually high blanks
F	a	<50	14		
	b	<50	14		
G	a	9.5	60	6	Detection limit 2 ng l^{-1}
H	a	<50	21		
	b	<50	21		
I	a	<20	14		
	b	<20	14		
J	a	*14	27		Close to the limit of detection
	b	*15	27		
K	a	*50	20		Close to the limit of detection
	b	*50	20		
L	a	*55	29		Estimated precision ± 12%
M	a	*30	13		Estimated precision ± 20 ng l^{-1}
	b	*30	13		
N	a	*60	70		
	a	*100	77		
	b	*80	70		
	b	*90	77		
All reported results	$\bar{x}$	35.2			
	s	29			
	c.v	82.3%			
Results marked* excluded	$\bar{x}$	6.56			
	s	2.0			
	c.v.	30.4%			

$\bar{x}$: mean
s : standard deviation
c.v. : coefficient of variation

Laboratory B later reanalysed their a and b samples and obtained 11 ng l^{-1} and 7 ng l^{-1}, respectively. The initial value of 31 ng l^{-1} obtained for sample a was attributed to laboratory contamination.

Table 4. Reported mercury concentrations in spiked sea water samples

Lab.	Hg ng l^{-1}	Days from preparation	Hg ng l^{-1} unoxidized	
A	131 ± 1.7	0		
B	131 ± 7 121 ± 7	16 16		
C	 114 ± 6	88 90 90	97.7 ± 3.6 84.9 ± 4.9	
D	106 106	~ 60 ~ 60		8.0 ng l^{-1} Obtained additionally by rinsing sample bottles with $KMnO_4/H_2SO_4$ solution Received two aliquots of spiked sample
E	167	10		Estimated precision ± 10 ng l^{-1} Unusually high blanks
F	*250	11		
G	*220 170	58 58 + 6 hrs 61 64	210 170 160 150	
H	110	18		Estimated precision ± 14 ng l^{-1}
I	100	11		
J	140	24		
K	140	17		
L	*300	26		Estimated precision ± 12%
M	200	10		Estimated precision ± 20 ng l^{-1}
N	*220 180	67 74		
All reported results $\bar{x}$	161	$\bar{x}$: mean		
All reported results s	57	s : standard deviation		
All reported results c.v.	35.2%	c.v. : coefficient of variation		
Results marked* excluded $\bar{x}$	137			
Results marked* excluded s	31			
Results marked* excluded c.v.	22.8%			

Table 5. Concentration of mercury in the spiked sea water sample

Date	04.04.1976	22.05.1976	13.07.1976
Concentration ng l^{-1}	131 ± 1.7	134 ± 2.3	134 ± 3.1
No. of determinations	10	3	3

All determinations 132 ± 2.7 ng l^{-1}.

Indication of spine colours

Reports of the Advisory Committee on Fishery Management	Red
Reports of the Advisory Committee on Marine Pollution	Yellow
Fish Assessment Reports	Grey
Pollution Studies	Green
Others	Black

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