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A PRELIMINARY REPORT ON THE ICES INTERCALIBRATION OF SEAWATER SAMPLES FOR THE ANALYSIS OF TRACE METALS

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SUMMARY

This exercise formed part of a trace metal intercalibration programme conducted under the auspices of the ICES Working Group on Pollution Baseline and Monitoring Studies. Two samples of sea water (inshore and offshore) were collected from the southern North Sea during January 1977. The water was filtered, subdivided and stored mostly deep frozen. Subsamples were distributed to 65 participants in ICES member countries. Twenty-eight sets of results had been received by July 1977. The range of values reported for most metals was large and coefficients of variation were between 18 and 201%. The analysis of cadmium, lead and nickel showed the greatest variability but the manganese and zinc data showed less variation than the remainder. A group of institutes was selected on the basis of their manganese analysis and it was shown that their coefficient of variation for most metals was better than the group as a whole. A full report on this exercise together with the results of other phases of the programme will be published in the ICES Cooperative Research Report Series. Further programmes of intercalibration are proposed.

INTRODUCTION

During 1975 the ICES Working Group on Pollution Baseline and Monitoring Studies in the Oslo Commission and ICNAF areas appointed a sub-group on Contaminant Levels in Sea Water to examine technical matters relating to the monitoring of trace metals and their analysis. This sub-group proposed a series of intercalibration exercises (ICES, 1975) and the first two phases examined trace metal standard solutions and mercury in sea water. Reports on these projects have been made by Jones (1976) and Ólafsson (1976) respectively. The third phase of this series involves the intercalibration of seawater samples for a variety of metals and this report presents preliminary data on this project.

METHODS

During January 1977 samples of surface sea water were collected in the central part of the southern North Sea (51°44'N 02°23'E: Sample A) and closer inshore off the Netherlands coast (52°03'N 04°04'E: Sample B). The water was filtered through 0.45 µm Millipore membranes within a few hours of collection and each sample was bulked. 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.

In addition to the sea water, concentrated multi-element standard solutions were sent to each participant as a continuation of the first phase of the intercalibration (Jones, 1976). Analysts were requested to use these standards in addition to their own when determining the metal content of the seawater samples.

Samples have been distributed to the following institutes:

Belgium

Free University of Brussels

Canada

Bedford Institute of Oceanography, Dartmouth
Department of the Environment, Victoria

Denmark

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

Federal Republic of Germany

Deutsches Hydrographisches Institut, Hamburg
Gesellschaft für Kernenergieverwertung in Schiffbau und Schiffahrt, Geesthacht
Institut für Meereskunde an der Universitat, Kiel

Finland

Institute of Marine Research, Helsinki

France

Centre National pour l'Exploitation des Océans, Brest (To distribute 15 sets of samples)
Institut Scientifique et Technique des Pêches Maritimes, Nantes

German Democratic Republic

Institut für Meereskunde, Warnemünde

Greenland

Geological Survey, Greenland

Iceland

Hafrannsoknastofnunin, Reykjavik

Netherlands

Instituut voor Bodemvruchtbaarheid, Haren
Nederlands Instituut voor Onderzoek der Zee, Texel
Rijksinstituut voor Zuivering 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

Oddzial Morski IMGW, Gdynia

Portugal

Instituto do Ambiente e Poluicào Aquática, Lisbon

Republic of Ireland

Department of Agriculture and Fisheries, Dublin

UK

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
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

USA

California Institute of Technology
Environmental Protection Agency, Narragansett
Ira Darling Centre, University of Maine
Marine Science Centre, University of Connecticut
National Marine Fisheries Service, Milford

USA (continued)

New England Aquarium, Boston
NOAA, AOML, Miami
Scripps Institute of Oceanography
Skidaway Institute of Oceanography, University of Georgia
Southern California Coastal Water Research Project, El Segundo
University of Delaware
University of Washington
US Environmental Protection Agency, Edison

USSR

Department of the Baltic Sea Institute, Tallinn

RESULTS

By late July 1977 results had been received from 28 of the 65 participants. A detailed analysis of the data will not be made until more results have been received. However, the results submitted so far are presented in Tables 1 and 2. The participating laboratories are anonymous and code numbers were allocated in chronological order of receiving the replies. The statistical analysis of the results at the foot of each table has been calculated using only results above detection limits, but cobalt and mercury have been omitted owing to the small sample number.

With the exception of iron, the inshore sample B shows higher mean metal levels than the offshore sample A. The variation in mean concentration between the two samples is an order of magnitude for manganese but much less for the other metals.

Immediately apparent is the very high coefficient of variation for most of the metals, extending up to 200% for lead in sample B. For sample A the coefficient of variation increases in the order Zn → Cu → Fe → Mn → Cr → Cd → Pb → Ni. For sample B the order is Mn → Zn → Fe → Cr → Cu → Cd → Ni → Pb. Thus, for both samples, nickel, lead and cadmium show the worse agreement. The position of the other metals varies somewhat between each set, although zinc shows a relatively 'low' coefficient of variation in both instances.

The lowest coefficient of variation (18%) was for manganese in sample B. A comparison with other metals cannot strictly be made since not all the participants measured each element. A statistical analysis has, however, been made using only the data of those participants who reported manganese values above detection limits for sample B (Table 3). In addition to cobalt and mercury, chromium has also been excluded owing to the small number of reported values. With the exception of iron where the data were common to both sets, coefficients of variation for each

metal were markedly lower than those listed in Tables 1 and 2. The value for manganese in sample B, however, remained the lowest of the set. One may thus infer that the laboratories in this limited group were able to achieve a closer degree of uniformity than the participants as a whole.

Six subsamples from each of samples A and B were analysed during May by the Fisheries Radiobiological Laboratory at Lowestoft. Coefficients of variation on each set of replicates ranged between 9 and 24% for the metals Cd, Cu, Ni and Zn. Thus the wide variability reported throughout the group would not seem attributable to sample inhomogeneity and, as would be expected, a greater degree of precision can be achieved on replicate analyses by one laboratory using a single method.

The analytical methods used in this exercise cover a wide range of techniques. A statistical treatment of the data in relation to the methodology will be made when more data are available.

Several participants, in addition to receiving frozen samples in standard polyethylene bottles, provided their own bottle with specific methods of sample storage. All data from this part of the exercise are now available and the results are given in Table 4. Any difference between the analysis on the standard (MAFF) sample and the sample from the participants own bottle (P) may result from contamination and/or changes during storage in the amount of metal available for analysis. The results in Table 4, however, are inconclusive since there are too many variable factors coupled with insufficient replication.

The multi-element standard solutions distributed to participants were similar to those used for the first phase of the exercise. They contained Co, Fe, Ni, Pb, Cd, Cr, Cu, Mn and Zn in concentrations ranging between 193 and 261 mg l^{-1}. Coefficients of variation reported on the results of the first exercise (Jones, 1976) were an order of magnitude lower than those recorded during the present phase. Thus it will probably be difficult to isolate any features specifically associated with the use of the standard solutions within the present exercise. Moreover, some participants who used electro-chemical methods of analysis experienced difficulty with the multi-element standards owing to interference between one element and another. Details of the results obtained using these standards will be given in the final report.

DISCUSSION

The range of values reported for most of the metals are disturbingly large and are similar to those of a much earlier intercalibration

coordinated by Brewer and Spencer (1970). However, participation in the present exercise was open to all institutes of ICES member countries and some laboratories are relatively new to the analysis of sea water. It is perhaps significant that there were seven established marine institutes within the eight laboratories whose data showed closer agreement than the group as a whole (Table 3).

The use of a common standard metal solution for calibration purposes in such an exercise would seem to have some advantages. However, for reasons already given, a multi-element standard now seems undesirable and should, perhaps, be replaced by several single-element solutions.

The system of distributing deep frozen samples by air freight proved very satisfactory and could form the basis of any future exercise of a similar nature. The appointment of an agent to coordinate air transit is highly recommended.

The two seawater samples used in the present exercise did not differ by a sufficient margin to evaluate the capability of an institute to measure the metal content of 'oceanic' water compared with highly polluted water. Also in most instances there was not a sufficient amount of sample to permit replication of analyses. The sub-group on Contaminant Levels in Sea Water has therefore proposed a fourth exercise (ICES, 1977). Frozen seawater samples will be distributed in sufficient quantity to allow replicate analyses and some water will be enriched with metal in order to assess analyses at high concentration levels. Subsequent exercises will probably involve closely controlled tests in which methods of water collection and storage are compared using a single research vessel.

The results of the intercalibration programme to date, which will include the tests of standards, the mercury exercise and the above frozen seawater project together perhaps with an earlier exercise between Belgium, Netherlands and the United Kingdom (Duinker, Elskens and Jones, 1975), will be presented in the ICES Cooperative Research Report Series. In addition, an abbreviated version will probably be published in a journal of wider distribution.

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Table 1 The analysis of sample A ($\mu g\ l^{-1}$)

Institute and method	Co	Fe	Ni	Pb	Cd	Cr	Cu	Mn	Zn	Hg
1. AA (2) A		4.1		0.20			0.45	1.5	8.6	
EC									6.2	
2. AA (1) A (Mn*)		<1.0	<2.5	<0.5	0.03	< 0.5	<0.5	<10	5.6	
3. AA (1) A	0.2	2.3	0.6	0.8	0.3	0.4	0.6	0.4	4.8	
4. EC (Hg AA (3))				0.18	0.09		1.22		4.72	38.6
5. AA (2) A	<0.5	<1.0	<1.0	<0.5	<0.1	<10	0.4	<20	6.5	
6. EC				5.6	0.6		<1.0		22.2	
7. AA (2) A (Zn (1) A)				0.37	0.07		0.5		5.5	0.15
8. EC				0.315	0.047		0.49		3.59	
9. AA (2) B							0.36			
10. AA (1) A (Cd, Pb Mn (2) A)		3.0		0.51	0.09		0.6	< 0.06	9.9	
EC pH 8.1				0.18	0.11		0.4		4.7	
EC pH 1.85				2.0	0.10		0.8			
11. AA (2) A		4.9	0.5		0.19		0.9	2.2		
EC				2.1	0.14				17	
12. EC				0.90	0.18		0.88			
13. AA (1) A			<0.1	2.0	0.05	2.3	0.5		6.0	
14. AA (2) B (Ni, Pb and Zn (1) B)		<0.4	<0.8	<0.8	0.13		<0.2	0.7	5.5	
15. AA (?) A	<5		5	<0.5	<0.5					
16. EC				0.09	0.10		0.99		4.8	

Table 1 (cont)

Institute and method	Co	Fe	Ni	Pb	Cd	Cr	Cu	Mn	Zn	Hg
17. EC				0.13	0.03		1.0			
18. AA (2) C		1.1			<0.05		0.5	0.24	11	
19. AA (1) A			<0.2	<0.4	<0.05		0.3		2.9	
20. PE			0.35		<0.07	0.63			5.6	
21. AA (2) B				0.15	0.053		0.39			
22. AA (2) D	0.13	1.05	0.80	0.71	0.099		0.55	0.39	4.0	
23. AA (2) A	0.17	8.1	0.28		0.13		0.76	1.5	10.8	
24. AA (?) B				<1	0.04		1.4		11.6	
25. AA (?) A			0.44		0.023		0.22		5.5	
26. AA (2) C						0.40				
27. AA (1) A			6.4	1.4	0.2		2.2		2.1	
28. AA (2) A			0.26		0.020		0.27		7.55	
$\bar{X}$		3.51	1.63	1.04	0.12	0.93	0.70	0.99	7.36	
S		2.48	2.34	1.37	0.12	0.92	0.44	0.75	4.59	
V%		71	144	132	100	99	63	76	62	

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

Table 2 The analysis of sample B ($\mu g\ l^{-1}$)

Institute and method	Co	Fe	Ni	Pb	Cd	Cr	Cu	Mn	Zn	Hg
1. AA (2) A		1.2		0.12	0.17		0.63	9.8	7.6	
EC									7.7	
2. AA (1) A (Mn*)		<1.0	<2.5	<0.5	0.14	0.5	0.7	<10	15.2	
3. AA (1) A	0.4	4.0	1.2	0.6	0.2	0.3	1.0	9.8	9.8	
4. EC (Hg AA (3)				0.32	0.11		0.90		7.92	27.5
5. AA (2) A	<0.5	<1.0	1.8	<0.5	<0.1	<10	0.8	<20	10.5	
6. EC				5.0	0.3		<1.0		6.6	
7. AA (2) A (Zn (1) A)				0.09	0.11		1.2		11.8	0.07
8. EC				0.205	0.080		0.83		3.78	
9. AA (2) B							0.54			
10. AA (1) A (Cd, Pb Mn (2) A)		2.6		0.51	0.13		0.6	10.6	10.5	
EC pH 8.1				0.26	0.12		0.3		4.65	
EC pH 1.85				2.2	0.09		0.9			
11. AA (2) A		2.2	1.0		0.10		0.5	13.8		
EC				1.1	0.09				8	
12. EC				0.42	0.087		0.89			
13. AA (1) A			0.9	0.5	0.15	3.3	0.8		10.0	
14. AA (2) B (Ni, Pb and Zn (1) B)		<0.4	<0.8	<0.8	0.09		<0.2	9.8	10.4	
15. AA (?) A	<5		16	<5	<5					
16. EC				0.11	0.09		1.10		11.0	

Table 2 (cont)

Institute and method	Co	Fe	Ni	Pb	Cd	Cr	Cu	Mn	Zn	Hg
17. EC				0.11	0.23		1.4			
18. AA (2) C		1.7			0.20		1.1	7.4	11	
19. AA (1) A		1.2		<0.4	0.10		0.6		9.0	
20. PE		1.9			1.2	0.52			14	
21. AA (2) B				0.11	0.103		0.6			
22. AA (2) D	0.15	1.80	0.72	0.80	0.078		0.46	9.6	7.8	
23. AA (2) A	0.13	5.8	0.69		0.57		0.71	11.6	13.8	
24. AA (?) B				<1	0.2		0.8		13.3	
25. AA (?) A			1.1		0.17		0.29		15	
26. AA (2) C						0.66				
27. AA (1) A			24.2	11.2	1.9		8.8		30.3	
28. AA (2) A			0.95		0.032		0.60		11.6	
$\bar{X}$		2.76	4.31	1.39	0.25	1.06	1.08	10.30	10.89	
S		1.61	7.59	2.80	0.40	1.26	1.63	1.84	5.10	
V%		58	176	201	160	119	151	18	47	

Key: AA = Atomic absorption
EC = Electrochemistry
PE = Plasma emission
(1) = Flame
(2) = Furnace
(3) = Cold vapour

A = Organic extraction
B = Ion exchange resin
C = Direct injection
D = Coprecipitation
* = Colorimetric

Table 3 A statistical analysis of trace metal data from Institutes reporting manganese values

Sample A

	Fe	Ni	Pb	Cd	Cu	Mn	Zn
$\bar{X}$ µg l^{-1}	3.51	0.55	0.56	0.16	0.62	0.99	7.80
S	2.48	0.22	0.27	0.08	0.16	0.75	2.97
V%	71	40	48	50	26	76	38

Sample B

	Fe	Ni	Pb	Cd	Cu	Mn	Zn
$\bar{X}$ µg l^{-1}	2.76	0.90	0.51	0.19	0.71	10.30	10.13
S	1.61	0.24	0.29	0.16	0.25	1.84	2.10
V%	58	27	57	84	35	18	21

Table 4 The metal content of samples ($\mu g\ l^{-1}$) stored in MAFF polyethylene bottles and the participant's (P) own bottle

Institute sample and bottle		Co		Fe		Ni		Pb		Cd		Cr		Cu		Mn		Zn	
		MAFF	P	MAFF	P	MAFF	P	MAFF	P	MAFF	P	MAFF	P	MAFF	P	MAFF	P	MAFF	P
1 Quartz frozen	A																	6.2	2.9
2 Poly-ethylene acidified and unfrozen	A			<1.0	4.5	<2.5	<2.5	<0.5	<0.5	0.03	<0.02	<0.5	<0.5	0.5	0.6	<10	<10	5.6	5.2
	B			<1.0	5.0	<2.5	<2.5	<0.5	<0.5	0.14	0.08	<0.5	<0.5	0.7	0.6	<10	<10	15.2	9.3
8 Poly-ethylene unfrozen	A							0.315	0.494	0.047	0.063			0.49	0.49			3.59	4.80
	B							0.205	0.220	0.080	0.099			0.83	0.63			3.78	4.66
23 Poly-ethylene acidified and unfrozen	A	0.17	<0.037	8.1	4.3	0.28	0.38			0.13	0.072			0.76	0.44	1.5	0.36	10.8	6.0
	B	0.13	0.10	5.8	4.2	0.69	1.04			0.57	0.098			0.71	0.73	11.6	12.1	13.8	13.5