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REPORT ON THE 6th ICES TRACE METAL INTERCOMPARISON EXERCISE FOR CADMIUM AND LEAD IN BIOLOGICAL TISSUE

by

G Topping

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International Council for the Exploration of the Sea
Palægade 2-4, 1261 Copenhagen K
Denmark

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SUMMARY

A report has been prepared on the 6th ICES trace metal intercomparison exercise giving details of the preparation and circulation of the 3 reference samples used in this exercise and presenting a detailed interpretation of the results submitted by 52 participants. The exercise demonstrated that all participants could produce comparable data for cadmium at a concentration of ca 1 mg/kg but that some participants did not produce comparable data for lead at a concentration of ca 2 mg/kg. Only a minority of participants produced comparable data for lead analysis at a concentration of ca. 0.5 mg/kg. The author recommends that further improvements in lead analysis are needed and suggests that a group of specialists should be convened to resolve this matter.

INTRODUCTION

During 1971-79, 5 ICES intercomparison exercises were conducted to compare the analytical procedures used for the measurement of trace metals in biological tissues. The participants in these exercises consisted of analysts associated with the ICES fish and shellfish baseline and monitoring programmes, analysts nominated by the Joint Monitoring Group of the Oslo/Paris Commissions and other scientists who had expressed an interest in participating in ICES intercomparison exercises. The collective results of these exercises have shown that for some trace metals (Cu, Zn and Hg) there has been a gradual improvement in the level of agreement between analysts with each successive exercise whereas for cadmium and lead there has been little or no improvement in the level of agreement (Topping and Holden, 1978 and Holden and Topping, 1981). In view of the relatively poor agreement for cadmium and lead at low levels of concentration, i.e., those associated with fish tissue, it was proposed that a further exercise for these metals should be conducted to assess comparability at relatively high residue levels (ICES, 1979). This proposal by the Marine Chemistry Working Group was endorsed by the Council at the Statutory Meeting in October 1979 (C.Res.1979/4:16). This report presents and discusses the results of the 6th ICES trace metal intercomparison exercise.

SELECTION AND PREPARATION OF REFERENCE SAMPLES

It was necessary for this exercise to select a sample, or samples, of biological tissue which contained concentrations of cadmium and lead in the ranges 0.1 - 1.0 mg/kg and 1 - 10 mg/kg respectively.

The choice of tissue for the cadmium reference sample was relatively easy in that a number of shellfish species were known to contain high concentrations of this metal. The tissue eventually selected for this purpose was the white meat of edible crab (Cancer pagurus) since it could be obtained in large quantities relatively easily from local shellfish processors.

By comparison, the selection of suitable material for the lead reference sample was more difficult since there were few tissues with naturally high levels of lead. Two materials, a commercial fish meal and the digestive gland of a lobster (Homarus americanus), were eventually

selected for this purpose, on the basis that they were available in large quantities and that they contained concentrations of lead in the desired range of values.

The white crab meat and the commercial fish meal were processed into a homogeneous dry fine flour as follows: The material was freeze-dried in small batches using a small laboratory freeze-drier. The total freeze-dried material was then repeatedly ground in a hammer mill until a very fine flour was produced.

The digestive gland of the lobster was processed as follows: The material was homogenised, placed in a large beaker and successively extracted with acetone and butanol until all the water was removed. The residual organic solvent was removed from the material by drying in a current of air and then the total sample was ground into a fine powder.

DISTRIBUTION OF THE REFERENCE SAMPLES

Following the circulation of a letter by the ICES General Secretary to all ICES Delegates (31 October 1979), 38 laboratories informed the author of their wish to participate in the 6th ICES exercise. In view of this relatively poor response it was agreed at the 2nd meeting of the ICES Marine Chemistry Working Group (February 1980) that the proposed deadline for this exercise, i.e., 31 March 1980 should be changed to 1 June 1980 in order to allow more analysts to participate in this exercise. It was also agreed that the author should contact the analysts in JMG[1)] laboratories and analysts from other institutes, who had participated in the 5th ICES trace metal intercomparison exercise, with a view to persuading them to participate in this exercise. By the end of February 1980 a total of 71 institutes had informed the author of their wish to participate in the 6th exercise. Each participant was eventually sent 20 g of processed crab meat (Sample 'A'); 20 g of processed fish meal (Sample 'B') and 10 g of processed lobster gland (Sample 'C') together with a list of detailed instructions (Appendix 1) regarding the approach to the analysis of samples and the reporting of data.

RESULTS

Forty-two participants, out of a total of 71 who received the reference samples, submitted the results of their analysis by the new deadline. An additional 3 sets of results were received by the author during the preparation of his preliminary report to the Marine Environmental Quality Committee in October 1980 and these were included in this report (Topping, 1980). A further 7 sets of results were received prior to and during the preparation of the final report.

The names and addresses of the 52 institutes that reported data, together with the names of the analysts associated with these data, are presented in Table 1. The results of the analyses of samples 'A', 'B' and 'C' (mean values and intralaboratory coefficients of variation) are presented in Tables 2, 3 and 4, respectively. A summary of the analytical methods used by participants is presented in Appendix II.

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1) Joint Monitoring Group of the Oslo and Paris Commissions

CADMIUM (Sample 'A')

Mean values of cadmium in the range 0.53 mg/kg to 1.11 mg/kg were reported by 52 participants. The overall mean value and interlaboratory coefficient of variation for these data are 0.80 mg/kg and 17%, respectively. Forty-one laboratories reported data with an individual precision of ≤10% and over half of these produced data with an individual precision of ≤5%. By comparison with previous exercises for cadmium, the level of agreement and individual precision achieved in this exercise are extremely good.

The results of a multiple range test, to test comparability of data which have an acceptable level of precision, i.e., ≤20%, are presented in Figure 1. The results from only 3 laboratories (6, 32 and 38) were excluded from this test. The test shows that significant differences do exist between some of the data reported but that there are a number of groups of laboratories which have reported data which are not significantly different. The biggest of these groups consists of 18 laboratories (Figure 1, Laboratory 8-1a inclusive) which reported mean values in the range 0.72 mg/kg to 0.81 mg/kg. The overall mean value and coefficient of variation for this group of data are 0.77 mg/kg and 3.6%, respectively.

LEAD (Sample 'B')

Mean values of lead in the range 0.22 mg/kg to 7.82 mg/kg were reported by 49 participants. The overall mean value and interlaboratory coefficient of variation for these data are 2.70 mg/kg and 47%, respectively (values from Laboratories 39 and 13b were excluded from the calculation of the overall mean value on the basis that they were outliers). In general, the individual precision reported by laboratories for the analysis of lead in Sample 'B' was poor by comparison with the individual precision reported for cadmium in Sample 'A', i.e., the averages of the intralaboratory coefficients of variation for cadmium and lead analyses were 8.4% and 14.2%, respectively. Similarly, the level of agreement between laboratories reporting lead data is poor by comparison with that obtained for cadmium analysis. It should be noted, however, that the level of agreement of lead analyses for this exercise is better than that obtained in previous ICES intercomparison exercises for lead.

The results of a multiple range test on the data reported for Sample 'B' are presented in Figure 1. It should be noted that nearly 20% of the data was excluded from this test on the grounds that these data had a precision of ≥20%. The results of this test show that there are some laboratories (47 and 13a) which have produced data which are significantly different from the rest of the data. The remaining laboratories fall into groups (2 or more laboratories) which in themselves do not produce significantly different data. With the exception of 2 groups (12-13a incl. and 18-15 incl.), the groups exhibit a fair degree of overlap with groups on either side of them. The largest of these groups is a group of 11 laboratories (Figure 1, 35 - 5c incl.) which reported mean values in the range 2.52 mg/kg to 2.96 mg/kg. The overall mean value and interlaboratory coefficient of variation for this group are 2.77 mg/kg and 5.9%, respectively.

LEAD (Sample 'C')

Mean values of lead in the range 0.11 mg/kg to 3.20 mg/kg were reported by 32 participants for this sample. The overall mean value and interlaboratory coefficient of variation for these data are 0.75 mg/kg and

71%, respectively (the value of 3.20 mg/kg reported by Laboratory 9 was rejected as an outlier). The average of the intralaboratory coefficients of variation was 22%; this compares with an average value of 14.2% calculated for the data for lead in Sample 'B'. It is clear from the data in Tables 3 and 4 that the level of agreement amongst analysts decreased with decreasing concentrations of lead in the reference samples.

Only 16 of the 32 laboratories were selected for inclusion in the multiple range test. The results of this test (Figure 1) show that 4 of these laboratories (9, 13, 33 and 45) produced data which are significantly different from the rest of the data. The remaining laboratories fall into groups of laboratories which exhibit a large degree of overlap. The largest of these groups (Figure 1, Laboratories 16-5a incl.) produced mean values of lead in the range 0.20 mg/kg to 0.37 mg/kg. The overall mean value and interlaboratory coefficient of variation for these data are 0.30 mg/kg and 17%, respectively.

DISCUSSION

The results of this exercise showed that the majority of participants produced comparable data for cadmium (CV approximately 10%) at a concentration which is typical of that encountered in shellfish monitoring programmes. Unfortunately, the majority of participants do not produce comparable data for lead in the concentration range 0.1 mg/kg to 2 mg/kg, i.e., the range of values normally found in shellfish. In relation to lead analyses, the author recognises that not all participants in this exercise are actually conducting fish and shellfish monitoring programmes and are not associated with the ICES coordinated monitoring programme. It seems relevant under these circumstances to examine the level of agreement amongst those laboratories which are currently conducting monitoring programmes and which also participated in more than one ICES trace metal intercomparison exercise.

An examination of the participants in the 3rd, 5th and 6th exercises for lead reveal that 10 laboratories (3, 4, 15, 19, 24, 30, 34, 36, 45 and 46) participated in all 3 exercises and that these laboratories are associated with the ICES coordinated monitoring programme. The results reported by these laboratories for lead were compared with the results reported by all participants in these exercises (Table 5). The data presented in Table 5 show that the laboratories conducting monitoring programmes achieved a slightly better level of agreement than the group as a whole for exercises 3, 5 and 6b and a much better level of agreement than the group as a whole for exercise 6c.

It is evident from an examination of the lead data that the poor level of agreement amongst laboratories is to a large extent caused by the use of inaccurate analytical procedures rather than due to inhomogeneity in the samples. A test of homogeneity on Sample 'B' carried out in the author's laboratory produced the following mean values and coefficients of variation (CV) for the concentration of lead - 2.52 mg/kg and CV of 4.0% for samples from 10 separate packets of Sample 'B' and 2.51 mg/kg and CV of 3.2% for 10 aliquots of the same packet. (Comparable values for cadmium in Sample 'A' are 0.79 mg/kg and 4.5% and 0.78 mg/kg and 4.6%.)

The accuracy of an analytical procedure is normally estimated by conducting analysis of a standardised material such as the ones prepared by the US National Bureau of Standards (NBS), e.g., orchard leaves. These materials are certified on the basis of the results of analysis by 2 or more independent analysts using 2 or more different analytical procedures (Beckert, 1978). The results from these analyses have to agree within certain limits for the sample to be certified. Unfortunately, the NBS has not yet produced a marine standard reference material for trace metals. The absence of such a standard material means that the author has been unable to comment on the accuracy of trace metal measurements in the ICES intercomparison programme. Fortunately, one of the participants (Laboratory 5) has carried out an 'NBS type standardisation' of these samples by analysing them by 4 different analytical procedures. The methods used were as follows: (a) direct injection of the acid digest into the atomic absorption (AA) furnace (this method is the common one employed by most participants); (b) direct injection of an organic extract (APDC/MIBK) of the acid digest into the AA furnace (this method, or some slight modification of it, has been used by a few participants); (c) inductively coupled plasma atomic emission spectroscopy; and (d) isotope dilution solid source mass spectrometry. The overall mean values and coefficients of variation of lead in Samples 'B' and 'C' derived from techniques (a) - (d) are 2.64 mg/kg and 17% (Sample 'B) and 0.33 mg/kg and 18% (Sample 'C').

If one assumes that the above mean values represent the 'true concentration' of lead in these samples, then 31 participants (Table 3, Nos. 25 - 33 incl.) out of a total of 51 analysing Sample 'B' and 9 participants (Table 4, Nos. 34 - 17 incl.) out of a total of 31 analysing Sample 'C' are producing mean values which fall within 17% of the 'true concentration' of lead in the respective samples. It is interesting to note that of the 9 participants who produced 'accurate' data for Sample 'C' only one of these (No. 23) did not produce 'accurate' data for Sample 'B'. It would appear therefore that ca 60% of the participants who reported results for Sample 'B' have produced accurate lead data for this sample and ca 20% of the participants reported accurate data for Sample 'C'.

An alternative approach to the identification of laboratories with problems of lead analysis has been suggested by Dr John Uthe (personal communication). He states that a Youden plot of the lead data produced by laboratories for Samples 'B' and 'C' (Figure 2) can be informative since it separates laboratories which produce consistently higher or lower values than the median values. He stresses that the plot as used here cannot differentiate between poor laboratories or poor methods but one must question a laboratory which produces either a high 'B' value and low 'C' value or a low 'B' value and high 'C' value.

A breakdown of the analytical results for lead in Samples 'B' and 'C' in relation to the analytical procedures is presented in Table 6. The data in this table show that the analysts incorporating a chelation/extraction step (e.g., APCD/MIBK or Dithizone/$CHCl_3$) in their atomic absorption procedure produced superior data, in terms of comparability, than those employing the more commonly adopted wet digestion/atomic absorption procedure. It is worth noting that the former group of analysts produced a mean value for lead in Sample 'C' which is similar to that obtained by the analyst employing isotope dilution solid source mass spectrometry.

In the opinion of the author, further improvement in the accuracy of lead analysis must be achieved by participants for concentrations in the range 0.1 - 2 mg/kg if the results from coordinated monitoring programmes are to be effectively compared. In a recent paper, Holden and Topping (1980) discuss the factors influencing the accuracy of analysis of contaminants (including lead) in tissues and present some guidelines for improvement of methodology in this respect. In relation to lead analysis, the authors consider that an appropriate group of specialists should be convened to consider the following points: (a) the selection of one or two preferred digestion procedures, (b) the elimination of matrix interference, (c) the improvement of blank determinations, (d) the reduction of background contamination, and (e) the most suitable approach to quantification of metals in the final acid digest or organic extract. This evaluation could, in the opinion of the authors, take the form of a specially convened workshop.

In February 1981 the results of this exercise were discussed by the ICES Marine Chemistry Working Group. The Group concluded that further investigative work on the analysis of lead in tissue was necessary in order to improve the comparability of lead data in relation to monitoring programmes. A sub-group was established to make proposals for the necessary analytical studies during the forthcoming year. They accepted the main points made by Holden and Topping (1980) as a basis for their investigations but considered that this work could be conducted in their individual laboratories rather than at a specially convened workshop. The progress made by individuals in these investigations would be periodically communicated by correspondence. A report of the sub-group's findings and recommendations would be made to the parent Working Group at its next meeting in 1982.

CONCLUSIONS

1. The exercise has demonstrated that all participants, including those involved in shellfish monitoring programmes, can produce comparable data for cadmium at a concentration of ca 1 mg/kg dry weight ($\simeq$ 0.2 mg/kg wet weight).

2. The results of the lead intercomparison exercise suggest that the majority of participants could be producing accurate and comparable data at a concentration of ca 2 mg/kg dry weight ($\simeq$ 0.4 mg/kg wet weight) in biological tissue but that only a minority of participants may be capable of producing accurate and comparable data at a concentration of ca 0.5 mg/kg dry weight ($\simeq$ 0.1 mg/kg wet weight) in biological tissue.

3. The author considers that further improvements in the accuracy of lead analysis are needed if the results reported by participants in coordinated monitoring programmes are to be compared.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the help and work of his colleagues, particularly Dr I M Davies who organised the preparation and circulation of Samples 'A' and 'B'. He would also like to thank Dr J Uthe (Environment Canada, Halifax, Nova Scotia) for preparing and circulating Sample 'C' to participants; Dr J Burt (MAFF, Humber Laboratory, Hull, England) for supplying the commercial fish meal used to prepare Sample 'B'; Dr J Edron (NERC Institute of Marine Biochemistry, Aberdeen) for his assistance with the freeze-drying of Samples 'A' and 'B' and Dr R Scott and colleagues (Macaulay Institute of Soil Research, Aberdeen) for their assistance with the final grinding of Samples 'A' and 'B'.

REFERENCES

Beckert, W F. 1978. Mercury, lead, arsenic and cadmium in biological tissue: the need for adequate standard reference materials. UK Dept of Commerce. National Technical Information Service. PB-288-198.

Holden, A V and G Topping. 1980. The future of ICES analytical inter-comparison exercises. ICES, C.M.1980/E:45 (mimeo.).

Holden, A V and G Topping. 1981. Report on further intercalibration analyses in ICES pollution monitoring and base-line studies. ICES, Coop.Res.Rep., No.108.

ICES, 1979. First report of the Marine Chemistry Working Group. ICES, C.M.1979/C:1.

Topping, G. 1980. A summary report on the 6th ICES trace metal inter-comparison exercise for Cd and Pb in biological tissue. ICES, C.M.1980/E:44.

Topping, G and A V Holden, 1978. Report on intercalibration analysis in ICES North Sea and North Atlantic baseline studies. ICES, Coop.Res.Rep., No.80.

TABLE 1

PARTICIPANTS IN 6th ICES INTERCOMPARISON EXERCISE FOR Cd and Pb IN BIOLOGICAL TISSUE

Country	Institute	Lab.No.	Contact or Analyst
AUSTRALIA	Chemistry Division Dept. of Services and Supply 21 Divett Place Adelaide S.A.	1	C S Crisp
	New South Wales State Fisheries 211 Kent Street Sidney N.S.W.	2	R Chvojka
BELGIUM	Ministerie Van Landbouw Instituut voor Scheikundig Onderzoek B 1980 Tervuren Museumlaan 5	3	P Van Boeyweghen
CANADA	Resource Branch Fisheries and Oceans Canada P.O.Box 550 Halifax, N.S.	4	J Uthe
	Division of Chemistry National Research Council Ottawa, Ontario	5	S S Berman
	Université du Québec Institut national de la recherche scientifique Rimouski, Québec	6	D Cossa
DENMARK	National Agency of Environmental Protection Kavalérgaarden 6 DK 2920 Charlottenlund	7	A Jensen
	Ministry of the Environment National Food Institute Mørkhøj Bygade 19 DK 2860 Søborg	8	A Andersen G Rasmussen
	Water Quality Institute Agern Allé 11 DK 2970 Hørsholm	9	M Rauss V B Jensen
GERMAN DEMOCRATIC REPUBLIC	Akademie der Wissenschaften der DDR, Institut für Meereskunde, DDR 253 Rostock-Warnemünde Postschliessfach 38	10	L Brügmann
	Hygiene Institut Rostock Stephansstrasse 18 DDR-25 Rostock	11	G Manthey

Table 1 (ctd)

Country	Institute	Lab.No.	Contact or Analyst
FINLAND	Institute of Marine Research P.O.Box 166 00141 Helsinki 14	12	F Koroleff
	National Board of Waters P.B.250 00101 Helsinki 10	13	Ms K Haapala
FRANCE	Laboratoire Municipal rue de Professeur Vezes, 33000 Bordeaux	14	J G Faugère
	Institut Scientifique et Technique des Pêches Maritimes IPM 3 Pollutions B.P.1049, rue de l'Ile d'Yeu 44037 Nantes Cédex	15	Y Thibaud
FEDERAL REPUBLIC OF GERMANY	Staatliches Veterinäruntersuchungsamt für Fische und Fischwaren Schleusenstrasse 2190 Cuxhaven	16	R Kruse
	Umweltbundesamt Bismarckplatz 1 1000 Berlin 33	17	P Henschel
	Bundesgesundheitsamt Post 33 00 13 1000 Berlin 33	18	K F Becker
	Bundesforschungsanstalt für Fischerei Wüstland 2 2000 Hamburg 55	19	U Harms
	Bundesforschungsanstalt für Getreide- und Kartoffelverarbeitung Am Schützenberg 12 4930 Betmold	20	H D Ocker
	Institut für Meeresforschung 285 Bremerhaven G Am Handelshafen 12	21	M Schulz-Baldes
	Biologische Anstalt Helgoland Wüstland 2 2000 Hamburg 55	22	K R Sperling
ICELAND	Fisheries Laboratory Skúlagata 4 Reykjavik	23	G Arnesen
	Marine Research Institute Skúlagata 4 Reykjavik	24	J Ólafsson

Table 1 (ctd)

Country	Institute	Lab.No.	Contact or Analyst
IRELAND	Fisheries Research Centre Abbotstown Castleknock Co. Dublin	25	D O'Sullivan
NETHERLANDS	Food Inspection Department Prinsegracht 50 2512 9A The Hague	26	A J K Haneveld
	Institute for Fishery Products TNO Dokweg 37 1976 CA IJmuiden	27	J Luten
	Rijks-Kwaliteitsinstituut Voorland-Entuinbouwprodukten Postbus 230 6700 AE Wageningen	28	W G de Ruig
NORWAY	Hermetikkindustriens Kontrol-institutt P.O.Box 329 N-4001 Stavanger	29	B Uppstad
	Fiskeridirektoratets Vitamin-institutt Lars Hillesgt 26 P.O.Box 187 N-5001 Bergen	30	K Julshamn
	Norwegian Institute for Water Research P.O.Box 333 Blindern Oslo	31	H Hovind
	Sentralinstituttet for Industriell Forskning P.O.Box 350 Blindern Oslo	32	P Paus B Enger
POLAND	Institute of Meteorology and Water Management Maritime Branch Waszyngtona 42 81-342 Gdynia	33	Ms A Brzezinska
PORTUGAL	Instituto Nacional de Investigação das Pescas Avenida Brasilia 1400 Lisbon	34	Ms C Lima
SPAIN	Laboratorio Oceanográfico P.O.Box 22 San Pedro del Pinatar Murcia	35	J Guerro

Table 1 (ctd)

Country	Institute	Lab.No.	Contact or Analyst
SWEDEN	The National Swedish Environment Protection Board Research Laboratory S-170 11 Drottningholm	36	Ms E Sköld
	The National Swedish Environment Protection Board Research Laboratory Box 1302 S-171 25 Solna	37	H Borg
UNITED KINGDOM	Albright and Wilson Ltd. P.O.Box 15 Whitehaven Cumbria, England	38	K Wolstenholme
	ICI Brixham Laboratory Freshwater Quarry Overgang Brixham Devon, England	39	D Taylor
	Clyde River Purification Board Rivers House Murray Road East Kilbride Scotland	40	T Leatherland
	Marine Biological Association Laboratory Citadel Hill Plymouth Devon, England	41	G Bryan
	North West Water Authority Rivers Division Warrington Lancashire, England	42	M Horne
	Severn Trent Water Authority Stoke Bardolph Nottingham, England	43	D Wood
	Department of Agriculture for Northern Ireland, Fisheries Research Laboratory, 38 Castleroe Road, Coleraine, Co. Londonderry Northern Ireland	44	J G Parker
	Department of Agriculture and Fisheries for Scotland Marine Laboratory P.O.Box 101, Victoria Road Aberdeen AB9 8DB, Scotland	45	J M Pirie

Table 1 (ctd)

Country	Institute	Lab.No.	Contact or Analyst
	MAFF Fisheries Laboratory Remembrance Avenue Burnham-on-Crouch Essex CM0 8HA, England	46	D Lawson
	Welsh Water Authority Directorate of Scientific Services Ponthir Treatment Works Ponthir Gwent, Wales	47	C Pattinson
	Forth River Purification Board Colinton Dell House West Mill Road Colinton Edinburgh, Scotland	48	A Griffiths
USA	National Marine Fisheries Service 212 Rogers Avenue Milford Connecticut 06516	49	R Greig
	US Dept. of Commerce NOAA, National Marine Fisheries Service South East Fisheries Center P.O.Box 12607 Charleston South Carolina 29412	50	Ms M Sanders
	Marine Science Institute University of Connecticut Avery Point Groton Connecticut 06340	51	S Y Feng
AUSTRALIA (ctd)	Government Chemical Laboratories 30 Plain Street Perth Western Australia 6000	52	D Tranthim-Fryer

TABLE 2

RESULTS OF THE ANALYSIS OF CADMIUM IN SAMPLE 'A' (mg/kg dry wt)

Lab No	Mean Value	CV*	Lab No	Mean Value	CV*
36	0.53	4.7	41	0.80	3.3
31	0.56	6.4	28	0.80	5.6
16	0.58	2.9	11	0.80	-
21	0.60	7.0	1b	0.81	0.4
51	0.61	14.3	1a	0.81	1.0
25	0.64	7.2	6	0.81	23.2
4	0.68	2.8	44	0.82	5.0
24	0.68	4.2	47	0.83	6.6
5b	0.68	13.4	5d	0.83	10.2
7a	0.68	6.8	30	0.85	9.4
7b	0.70	4.2	42	0.87	7.3
2	0.71	4.7	33	0.87	3.9
34	0.72	8.1	40	0.87	12.1
8	0.72	5.2	20	0.89	3.9
10	0.72	-	17	0.93	4.5
32	0.73	27.3	50	0.93	8.9
5a	0.73	9.8	13	0.94	3.4
43	0.73	5.5	48	0.95	6.6
49	0.74	14.7	12	0.95	4.9
3	0.74	3.4	14	0.96	3.0
29	0.75	3.3	19	0.99	4.4
5c	0.76	7.3	35	0.99	7.0
18	0.77	4.1	46	1.01	3.5
37	0.77	17.0	38	1.02	71.5
52	0.77	0.6			
15	0.78	11.4	39	1.03	14.6
22	0.79	3.9	27	1.05	8.2
9	0.79	3.3	23	1.11	16.4
45	0.79	4.3			

*CV = Coefficient of Variation

a, b, c and d refer to results obtained by different analytical methods.

TABLE 3

RESULTS OF THE ANALYSIS OF LEAD IN SAMPLE 'B' (mg/kg dry wt)

Lab No	Mean Value	CV*	Lab No	Mean Value	CV*
18	0.22	12.9	11	2.7	-
51	0.31	19.0	43	2.80	20.3
23	0.51	14.1	48	2.81	4.4
15	0.74	18.2	1b	2.89	4.2
			17	2.89	15.5
16	1.16	3.3	5d	2.89	4.6
49	1.22	23.1	10	2.9	-
35	1.30	14.4	38	2.90	29.8
24	1.59	9.2	1a	2.93	2.7
21	1.61	6.0	36	2.94	17.0
31	1.68	9.4	5c	2.95	17.9
			52	2.96	14.3
25	1.92	21.0	28	3.03	7.1
13b	1.98	20.0	8	3.18	20.0
9	1.99	13.1	50	3.25	24.3
19	2.04	6.1	45	3.28	7.3
4	2.10	10.0	27	3.37	10.3
2	2.14	11.6	33	3.44	5.1
20	2.18	6.9	14	3.55	5.8
5a	2.20	13.6	41	3.58	12.1
30	2.35	26.8	42	3.66	21.1
37	2.40	40.5	12	3.93	17.7
32	2.50	27.3	29	4.02	9.0
34	2.52	10.0	40	4.50	20.7
5b	2.52	12.0	47	4.65	11.5
6	2.60	19.4	39	6.08	31.8
3	2.62	7.4	13a	7.82	9.8
46	2.65	5.9			
26	2.67	15.5			

*CV = Coefficient of Variation

a, b, c and d refer to results obtained by different analytical method.

TABLE 4

RESULTS OF THE ANALYSIS OF LEAD IN SAMPLE 'C' (mg/kg dry wt)

Lab No	Mean Value	CV*	Lab No	Mean Value	CV*
51	0.11	27.2	30(1)	0.69	36.5
16	0.20	8.6	36	0.71	20.9
34	0.27	9.9			
28	0.28	14.4	12	0.73	17.8
5b	0.29	11.7	14	0.74	5.1
20	0.29	42.6	24	0.79	25.4
19	0.30	3.8	21	0.82	12.5
23	0.34	13.6	32	0.85	13.9
5d	0.35	18.4	40	0.92	14.3
5a	0.37	12.7	35	0.99	52.4
37	0.38	20.5	15	1.18	20.8
11(1)	0.39	-	45(1)	1.18	15.5
17	0.45	9.0	42	1.30	95.1
46	0.52	21.8	29(2)	1.32	26.1
31	0.53	25.3	45(2)	1.43	10.3
50	0.53	36.2	29(1)	1.43	36.8
13b	0.57	18.3	33	2.14	7.3
4	0.57	21.1	13a	2.72	12.7
11(2)	0.61	-	9	3.20	18.1
30(2)	0.63	30.4			
41	0.68	23.2			

*CV = Coefficient of Variation

a, b, c and d refer to results obtained by different analytical methods.

(1) and (2) refer to the results of the analysis of two separate samples of 'C'.

TABLE 5

Comparison of the analysis of Cd by selected* participants and all participants in the 3rd, 5th and 6th ICES intercomparison exercises.

Exercise	Participants Number	Accepted Concentration Range (mg/kg)	Mean (mg/kg)	CV+	Values Omitted
3	All (21)	0.16 - 3.00	1.10	77	One high value
	Selected (10)	0.16 - 2.1	0.79	75	One high value
5	All (33)	0.018 - 0.71	0.21	72	All (7) values and 2 high values
	Selected (10)	0.018 - 0.45	0.18	70	One high value
6b	All (52)	0.22 - 4.65	2.53	38	Two high values
	Selected (10)	0.74 - 3.28	2.28	30	None
6c	All (39)	0.11 - 3.20	0.82	81	None
	Selected (10)	0.30 - 1.30	0.70	47	None

*Laboratory Nos (Exercise 6) - 3, 4, 15, 19, 24, 30, 34, 36, 45 and 46.

+CV = Coefficient of Variation

TABLE 6

Results of the analysis of lead in Samples 'B' and 'C' in relation to analytical techniques

Technique	No of analysts	Mean value (µg/g)	CV*	No of analysts	Mean Value (µg/g)	CV*
Wet digestion/ AAS+	30	2.71	58	24	0.92	86
Dry ashing/AAS	9	2.84	24	3	0.70	76
Wet digestion/ chelation-extraction/AAS	7	2.57	14	2	0.30	2
IDSSMS++	1	2.89	5**	1	0.35	18

*inter laboratory coefficient of variation based on mean values submitted by analysts
**intra laboratory coefficient of variation based on six replicate analyses
+Atomic Absorption Spectrometry
++Isotope dilution solid source mass spectrometry

FIGURE 1 RESULTS OF MULTIPLE RANGE TESTS*

SAMPLE A - CADMIUM

Lab. No.	36	31	16	21	51	25	4	24	5b	7a	7b	2	34	8	5a	43	49	3	29	5c	18	52	37	15	22	9	45	41	28	1b	1a	44	5d	47	30	42	33	40	20	17	50	13	48	12	14	19	35	46	39	27	23
Mean	0.53	0.56	0.58	0.60	0.61	0.64	0.68	0.68	0.68	0.68	0.70	0.71	0.72	0.72	0.73	0.73	0.74	0.74	0.75	0.76	0.77	0.77	0.77	0.78	0.79	0.79	0.79	0.80	0.80	0.81	0.81	0.82	0.83	0.83	0.84	0.87	0.87	0.87	0.89	0.93	0.93	0.94	0.95	0.95	0.96	0.99	0.99	1.01	1.03	1.05	1.11
No.	6	6	6	6	18	14	6	6	6	6	4	6	6	6	6	9	6	6	6	6	17	6	6	6	6	6	6	6	6	6	6	6	6	6	9	6	6	6	6	6	6	3	6	6	6	6	6	6	6	6	6

SAMPLE B - LEAD

Lab. No.	18	51	23	15	16	35	24	21	31	13b	9	19	4	2	20	5a	34	5b	6	3	46	26	43	48	1b	17	5d	1a	36	5c	52	28	8	45	27	33	14	41	12	29	47	13a
Mean	0.22	0.31	0.51	0.74	1.16	1.30	1.59	1.61	1.68	1.98	1.99	2.04	2.10	2.14	2.18	2.20	2.52	2.52	2.60	2.62	2.65	2.67	2.80	2.81	2.89	2.89	2.89	2.93	2.94	2.95	2.96	3.03	3.18	3.28	3.37	3.44	3.55	3.58	3.93	4.02	4.65	7.82
No.	18	18	6	6	6	6	6	6	6	3	6	6	6	6	6	5	6	6	6	6	6	6	9	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	5	3

SAMPLE C - LEAD

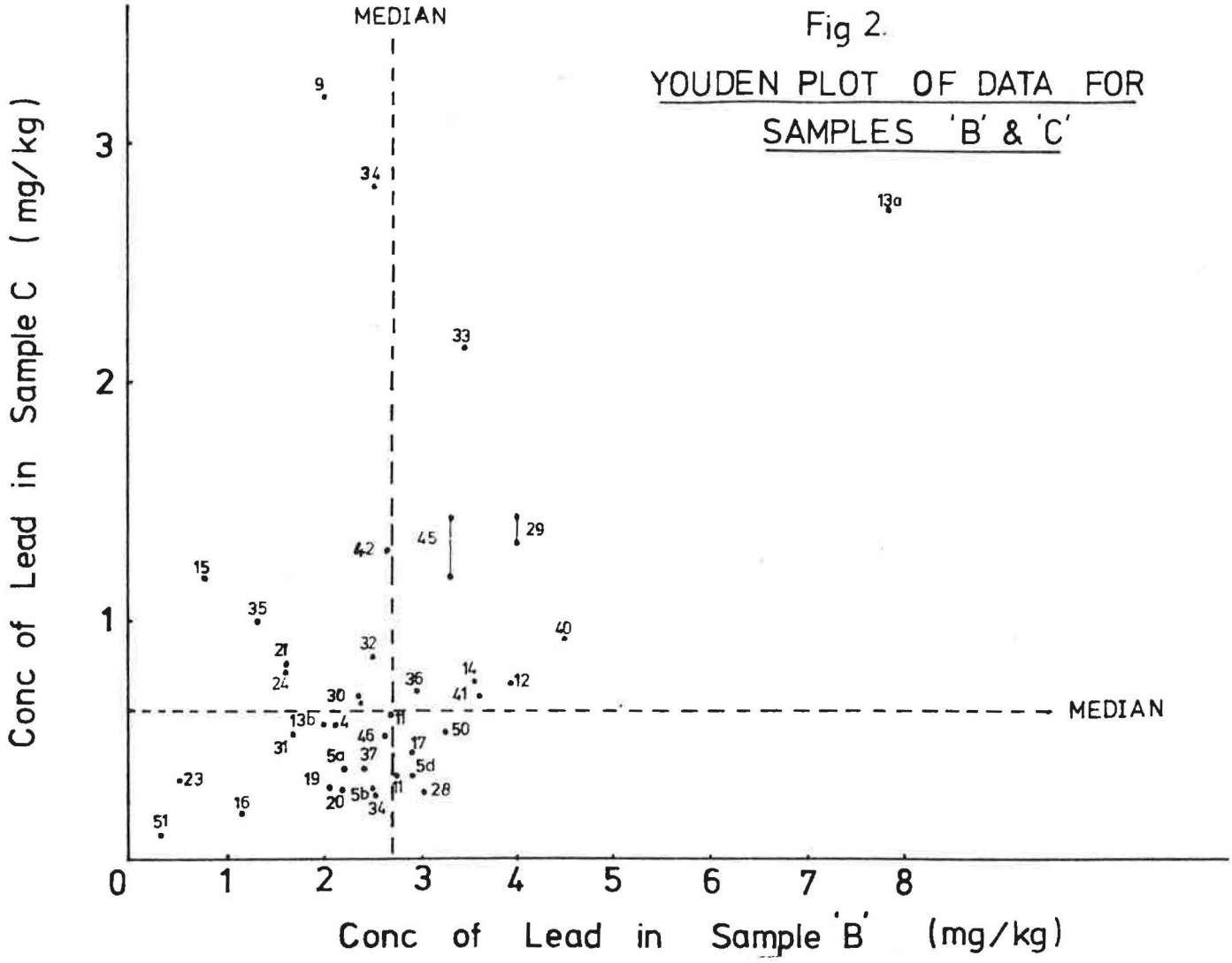
Lab. No.	16	34	28	5b	19	23	5d	5a	17	13b	12	14	21	32	40	45(1)	45(2)	33	13a	9
Mean	0.20	0.27	0.28	0.29	0.30	0.34	0.35	0.37	0.45	0.57	0.73	0.74	0.82	0.85	0.92	1.18	1.43	2.14	2.72	3.19
No.	6	6	6	6	6	6	6	6	6	6	6	6	6	4	6	6	6	6	2	4

* refers to laboratories whose coefficient of variation are $\leq$ 20%.

KEY Laboratories that are underscored by the same line have produced data which are not significantly different.

Fig 2.

YOUDEN PLOT OF DATA FOR SAMPLES 'B' & 'C'



APPENDIX I

6th ICES TRACE METAL INTERCOMPARISON EXERCISE FOR BIOLOGICAL TISSUE

Instructions for the analysis of the three ICES reference materials

1. Sample 'A' should be analysed for Cd only.

2. Sample 'B' and 'C' should be analysed for Pb only.

3. The samples should be analysed by the methods currently in use in your Laboratory.

4. Each sample should be analysed 6 times using separate 1 g * aliquots. Replicate analyses should be spread over a number of days ie 2 replicates on each of 3 days.

5. Blank determinations should be made with each set of replicates.

6. The results should be expressed on a dry weight basis. The dry weight determination should be carried out on separate samples of the reference material.

   The results should be reported to 3 significant figures.

7. Your analytical methods should be calibrated using working standards prepared in accordance with instructions given in the last ICES intercomparison exercise.

   *The level of Cd and Pb in these samples is thought to be in the following ranges - 0.5 - 2 ppm for Cd and 1 - 5 ppm for Pb. A sample size of $\leq$ 1 g is therefore sufficient to meet the requirements of most analytical methods for these two metals.

On completion of this exercise each participant should send me the following:

1. Six individual results for each sample together with blank values and calculated detection limits.

2. A brief summary of the analytical procedure.

3. The make and model number of the instrumentation used on the procedures.

4. A copy of all recorder data (where relevant).

APPENDIX II

SUMMARY OF ANALYTICAL METHODS USED BY PARTICIPANTS IN ICES 6th METAL INTERCOMPARISON EXERCISE

Laboratory No.	Cadmium	Lead
1	a) 1 g digested with $HNO_3/HClO_4$. Dilute to volume with 10% $HClO_4$. Aspirate directly into flame (Varian 575). Standards in 10% $HClO_4$.	Digestion as per Cd. Standard addition procedure. Varian 575.
	b) Extract 5 ml digest (pH 3.7) with 1% APDC and 1% DDDC with 5 ml MIBK. Aspirate as above. Blank 0.001 ppm	Blank 0.005-0.02 ppm
2	Sample digested with 30 ml $HNO_3/HClO_4$ (6:1) to dryness. Dissolve in 10 ml HNO_3 (20%). Standards as per ICES instructions. Varian AA5 (bg correction). Blank 0.07-0.2 ppm	As per Cd Blank 0.7 ppm Blank 0.7 ppm
3	0.5 g dry ashed at 450°C (Pt crucible). Dissolved in 2.5 ml HNO_3 and 1 ml H_2O_2 (30%). Reflux for 3/4 mins. Cool and dilute to 50 ml with water. Standards - dilution of stock standards (1 ppm). IL 751 furnace. No information on blanks.	As per Cd
4	0.5 g digested with 4 ml H_2SO_4/HNO_3 (1:1) in 50 ml Folin-Wu tube. The digest was cooled and diluted to 25 ml with double distilled water (DW). Standard addition procedure. PE Model 403 (D_2 corr.) HGA-74, Model 2100 controller. AS-1 sampler and Model 056 recorder. Blank - none detectable.	As per Cd except 5 ml HNO_3 added as digestion acid. Blank 0.08 µg (Sample C) 0.125-0.15 µg (Sample B)
5	(1) 1 g sample digested with $HNO_3/HClO_4$ to dryness. Dissolved in dilute HNO_3. Matrix modifier added. Standard addition procedure. Varian AA-5 (bg correction) fitted with PE HGA 2200, AS-1 sampler. Blank <0.01 ppm	As per Cd Blanks 0.02 ppm 0.04 ppm
	(2) Extraction with MIBK following chelation with APDC. Determination by furnace AAS following back extraction into dilute HNO_3. Blank 0.02 ppm	Blanks 0.02-0.05 ppm 0.07 ppm
	(3) Prepare solutions as per (1). Measurement by inductively coupled plasma-atomic emission spectroscopy (custom built). Blank 0.02 ppm	

Laboratory No.	Cadmium	Lead
5 (ctd)	(4) Following addition of stable isotopes to sample, it is digested with $HNO_3/HClO_4$. Separation by chelax 100 and then evaporate to dryness on the end of a pure Ag electrode. Isotope ratios are measured with AEI MS-702 solid source mass spectrograph using photographic detection. Blank 0.01 ppm	Blank 0.04 ppm 0.12 ppm
6	Digestion with HNO_3 in teflon bomb. Measurement by furnace. Standard addition. No data on blanks.	As per Cd
7	1 g digested with $HNO_3/HClO_4$ (10:1) to near dryness. Dissolve in HNO_3 (0.24N), dilute to 100 ml. PE Model 5000, furnace (Model 500) with AS-1 (by correction). Standards in dilute acid. Blanks 0.02-0.06 ppm	No data
8	As per 5th ICES exercise but with background correction. Blank < detection limit.	As per Cd < dl - 0.6 ppm
9	1 g digested with 50 ml suprapur HNO_3 (1:1). Dilute to 100 ml. Standards prepared as per sample procedure. PE Model 603. HGA 76B and AS-1. Blank 0.006 ppm	As per Cd Blank 0.07 ppm
10	0.5 g dry ashed in covered silica beaker at 450°C. Residue digested in 2 ml HNO_3/HCl (1:3). Dissolved in dilute HNO_3 → 100 ml with water. Analysis by ASV (PAR Model 174 17) and glassy carbon Hg-film electrode. Blank 0.006 ppm	As per Cd Blank 0.015 ppm
11	No information available	
12	~ 1 g digested with 10 ml HNO_3 (MERCK) in 100 ml SOVIREL bottle. Cool, evap. to dryness and add 50 ml distilled water. PE Model 300, HGA 72 (bg correction). No information on preparation of standards or blanks.	As per Cd
13	Digestion with HNO_3. Dilute sample to 25 ml. PE 603 (flame) or 400 (flameless). (Analysis of fish standards of NBS gave correct results by this method.) Results by flameless gave lowest results. No information on blanks.	As per Cd
14	1 g digested with HNO_3/H_2SO_4 (5:1) (as per Gorsuch, 1970). Digest diluted with water to 100 ml. PE 420 (D_2 correction) - EDL used with HGA 500. Blank values 0.02 ppm Standards in 5% H_2SO_4	10 ml aliquot of digest extracted with 5 ml 1% DDDC in $CHCl_3$. Organic solution aspirated directly. Blanks 0.1 ppm

Laboratory No.	Cadmium	Lead
15	0.6-1.5 g digested with HNO_3/H_2SO_4 (20:3) H_2O_2 added to eliminate HNO_3. Dilute to 50 ml with water. Standard addition. IL 151 with furnace model 555 (D_2 correction). Blank < dl	As per Cd Blanks 0.2 ppm
16	50-250 mg digested with 0.5-2.5 ml $HNO_3/HClO_4$ (3:1) in teflon beaker (closed) until dryness. Dilute with HNO_3 (1:1,000 dil). PE 400 HGA 76B AS-1. Blank 0.06 mg	As per Cd Blank 2.5 ng
17	Digestion with HNO_3 (30%) in autoclave. Dilute to 50 ml. PE 300 HGA 72 (D_2 corr.). Standards prepared as per ICES instructions. Blanks 0.1 ppm	As per Cd Blank 0.4 ppm Blank 0.3 ppm
18	Digestion with HNO_3/H_2SO_4 (Bethge). Extract with dithizone/$CHCl_3$ (pH 9.2). Back extract with 0.5 N HNO_3 PE 400, HGA 74, AS-1. Blank values 20 pg/20 µl	As per Cd Blank 180 pg/20 µl
19	0.1 g digested with 0.7 ml HNO_3 (PTFE vials) in stainless steel bomb. Sample solution transferred with 2-3 ml DW into 10 ml quartz tube. Extracted with 1.5 ml dithizone (pH 8.5) in toluene. Back extracted with 1 ml HCl (0.5N). PE 420 (D_2) HGA 76. Standards prepared in HCl (0.5N). Blanks 0.0005 ppm	As per Cd Blanks 0.005 ppm
20	Dry ash (0.5 g-1 g) at 450°C. Dissolve in conc. HCl and evap. to dryness. Dissolve in 1N HCl. Extract with dithizone/$CHCl_3$, back extract with 0.1N HCl. Furnace technique (model not specified). Standards in 0.1N HCl. Blanks 0.004-0.007 ppm	As per Cd Blanks 0.013-0.023 ppm
21	0.1 g digested with 1 ml HNO_3 in glass tube. on Al block with addition of 0.2 ml $HClO_4$ - near dryness. Dissolve in dil. acid. PE 300 SG (D_2) HGA 766 AS-1 (EDL). No information on standards. Blanks 0.05 ppm	As per Cd Blanks 0.1 ppm
22	60-80 mg digested in 4 ml Beckman vials as per method described in literature. Flameless AA. Blank 0.008 ppm	As per Cd Blank < 0.12 ppm

Laboratory No.	Cadmium	Lead
23	Sample refluxed with 50% HNO_3. Dilution with water. PE 403 HGA 70 (D_2) Blank < 0.0005 ppm	As per Cd Blank < 0.0003 ppm
24	0.25 g digested with 2.5 ml HNO_3 in silica tubes. Dilute to 20 ml. Standard addition. Varian Techtron AA6 CRA 90 ASD 53 sampler (bg correction). Blank 0.002 ppm	As per Cd Blank 0.002 ppm
25	Dry ash sample at 450°C. Dissolve residue in 1 ml HNO_3, dilute to 12 ml with water. Add 1 ml 10% NH_4NO_3 and dilute to 25 ml. PE 360 HGA 76 (bg correction). No information on blanks. Standards made up in 4% HNO_3	As per Cd
26	Non-destructive X-ray analysis. Standards were made by addition of pure chemicals to cellulose powder.	
27	0.2 g digested with 5 ml 65% HNO_3 and 2 ml DW. Evap. until 0.5 ml remains. Add 10 ml DW and 10 ml acetone. Varian 1100 Cardon rod (bg correction). Standard addition procedure. Blank values 0.074-0.102 ppm	As per Cd Blanks 0.18-0.73 ppm
28	1 g digested with 5 ml HNO_3 using Tecator destruction device. Add 2.5 ml $HClO_4$ and take to dryness. Dissolve in 0.5 ml conc. HCl, 5 ml H_2O and 5 ml acetate buffer (pH 3.5). Analysis by differential pulse ASV (Metrohom Polarecord E506). Blanks 0.001-0.006 ppm	As per Cd Blanks 0.014-0.030 ppm
29	Dry ashing at 450°C in vycor crucible. Dissolve ash in few drops 35% HCl and 65% HNO_3. Dilute to 25 ml using DW. Extract with APDC/MIBK at pH 2.8. Evap. extract to dryness, dissolve residue in 1 ml HNO_3 (65%) and dilute to 10 ml with DW. PE 403. Blank values ≡ DW blanks	As per Cd

Laboratory No.	Cadmium	Lead
30	0.1 g digested with 2 ml $HNO_3/HClO_4$ (1:1 v/v Merck Supra puris) in 10 ml capped vials (SOVIREL). Solution diluted to 10 ml with DW. 1 ml aliquot evap. to dryness in Pt crucible under IR lamp. Dissolve residue to 1 ml HNO_3 (5%) in acid washed plastic tubes. PE 403, HGA-76, AS-1. Blank values 0.004 µg	As per Cd Blank 0.09 µg
31	1 g digested with 25 ml HNO_3 (50% Merck suprapur) in SOVIREL flasks. Dilute to 100 ml with DDW. PE 560, HGA 500. Blank values 0.02-0.05 ppm	As per Cd Blank value 0.1-0.2 ppm
32	a) Samples dry ashed at 450°C in vitrosil vessel. Residue dissolved in HNO_3. b) Samples were wet digested with HNO_3/H_2SO_4. The solution from both procedures were extracted with APDC/MIBK and then aspirated directly into flame AA. PE 303. Blank values < 0.1 ppm	As per Cd Blank values < 0.2 ppm
33	0.5 g was digested with 10 ml HNO_3 (5N, suprapure, Merck) in teflon bomb (home-made). Samples diluted to 25 ml with tri-DW. Standards prepared in 2N HNO_3 by diluting stock solutions. Beckman 1272, Massman furnace. No data for blanks.	As per Cd
34	0.5 g was dry ashed at 450°C. Treat ash with 2.5 ml HNO_3 and 1 ml H_2O_2 (Merck grade). Reflux and dilute to 50 ml. Standards prepared daily by dilution of stock standards (Merck) with HNO_3 (5%) PE 400, HGA 500, AS-1. No data for blanks.	As per Cd
35	Samples digested with HNO_3, refluxed, evaporated to 2-3 ml and diluted to 25 ml with DDW. Cd analysed by flame. Blank 0.01 ppm. Model 603 (D_2)	As per Cd Pb measured by furnace - HGA-76B Blank values 0.01 ppm
36	0.2 g digested with 3 ml HNO_3 taken to near dryness and 2 ml H_2O_2 added. Solution diluted to 10 ml. Method of standard addition PE 305B, HGA-74, AS-1. No data for blanks.	As per Cd

Laboratory No.	Cadmium	Lead
37	0.1-0.2 g digested with HNO_3, taken to near dryness and H_2O_2 (30%) added. Re-heated until fats are oxidised. Dilute with double DW (quartz). Method of standard addition. PE 305B, AGA-74. Blank value 0.02-0.04 ppm	As per Cd Blank value ~ 0.2 ppm
38	1 g digested with HNO_3/H_2SO_4. Dilute to 50 ml with DW. Extract with APDC/methylpentan-2-one. Aspirate extract into flame. Pye Unicam SP9/800. Standards made up in 20% H_2SO_4. Blank value < dl	As per Cd Blank value < dl
39	Samples digested with HNO_3 (Aristar)in glass flasks. Dilute with DW. Aspirate directly into flame PE 460. Standards made up in dil. acid. Blank value 0.04 ppm	As per Cd Measurement by furnace PE HGA 76-B, AS-1
40	Sample digested with $HNO_3/HClO_4$. Dilute to volume with DW. Standards made up in dil. acid. IL251. Blank value 0.01-0.02 ppm	As per Cd Blank value 0.1 ppm
41	1 g digested with 20 ml HNO_3 (Aristar). Evap. to dryness, residue dissolved in 10 ml HCl (1N). Flame AA analysis. PE 603. Blank value 0.02 ppm	As per Cd Blank value 0.09-0.15 ppm
42	0.5 g dry ashed in pyrex beaker at 450°C. Residue treated with 1 ml HNO_3 and 5 ml H_2O_2, gently heated, cooled and diluted to 25 ml with DW. Flame AAS. IL 251. Blank value 0.04-0.10 ppm	As per Cd Blank value 0.10-0.60 ppm
43	1 g digested in 6 ml HNO_3 (Ultrar) in 80 ml pyrex tube in Techne DB heating unit. After cooling, solution was diluted to 25 ml. IL 251 (bg correction). No information on standards preparation. Blank values 0.006-0.009 ppm	As per Cd Blank value < dl
44	1 g dry ashed at 420°C. Treat with 2 ml HCl (50%) and evap. to dryness. Residue dissolved in 10 ml HCl (0.1N). Standard addition procedure. PE 403. Blank values < detection limit	As per Cd Residue dissolved in 5 ml HCl Blank values 0.27-0.61 ppm
45	2 g was digested with 20 ml HNO_3 (Analar). Evap. to 5 ml and dilute to 25 ml. Standard addition procedure. PE 603, HGA-76, AS-1 (D_2). Blank value < 0.0005 ppm	As per Cd Blank value < 0.02 ppm

Laboratory No.	Cadmium	Lead
46	1-2 g digested with 10 ml HNO_3 (1:1) in 50 ml covered beaker. H_2O_2 added; increase temperature and heat until 1-2 ml volume. Dilute to 20 ml with HNO_3 (1N). Flame AA. IL 257 (fitted with high performance package). Standards in acid. Blank values 0.05 ppm	As per Cd Blank values 0.2 ppm Sample 'C' quantified using PE 306, HGA 78, AS-1. Blank value 0.03 ppm
47	1 g digested with 15 ml HNO_3 (Aristar) in 50 ml pyrex flask with air condenser. Dilute to 25 ml with HNO_3 (0.1N). Flame AA. PE 5000 (bg correction). Blank value 0.06-0.18 ppm	As per Cd Blank value < 0.25-1.42 ppm
48	1 g digested with 80 ml HNO_3 (Aristar) in PTFE beaker until brown fumes cease to evolve. Add 10 ml HNO_3 (1N), take to dryness. Dissolve residue in 10 ml HNO_3 (1N) Flame AAS IL 151. Blank value 0.05-0.2 ppm	As per Cd Blank value 0.12-0.17 ppm
49	Sample digested in 10 ml HNO_3 (quartz distilled) in 50 ml pyrex beaker (previously clean by heating with HNO_3) (25%). Evaporate to dryness, add 5 ml HNO_3 and repeat evaporation. Add 1 ml HNO_3 and H_2O_2 (>5 ml). Evap. to dryness and dissolve in dilute HNO_3 to 10 ml volume. PE 560. Furnace 2100. No information preparation of standards. Blank value < 0.05 ppm	As per Cd Blank value 0.2-0.3 ppm
50	1 g was digested with 4 ml H_2SO_4 (0.7N) in Vycor crucible to char stage. Dry ashed at 500°C (quartz lined furnace). Dissolved in HNO_3/HCl (5% v/v) and made up to 10 ml volume. Flame AA IL 751. Blank value 0.07 ppm	0.1 g was digested with 2 ml $HNO_3/HClO_4/H_2SO_4$ (24:24:1) in test tube at 300°C. Add 5 ml high purity water. Samples analysed by ASV. (ESA Model 2014). Standards as per ICES instructions. Blank value 0.05 ppm
51	0.5 g was digested with 25 ml HNO_3. (JT Baker Ultrex grade) in 25 ml acid cleaned volumetric flasks (50°C). Solution was diluted to 25 ml with DDW, filtered and stored in poly-ethylene bottles. Standards prepared in dil. acid. PE 5000, HGA 500, AS-1. Blank value ~ 0.06 ppm	As per Cd Blank value ~ 0.05 ppm
52	1-2 g was digested in 10 ml $HNO_3/HClO_4$ (3:1). Solution made up to 25 ml. Add 10 ml of NaAc (1M) to 20 ml of solution. Adjust pH to 4 and extract Cu, Fe, Ni and Zn with 10 ml and 5 ml of 2% oxial in $CHCl_3$. Add 2 ml of APDC (2%) to aqueous layer and extract with 10 ml, 5 ml and 5 ml, respectively, of $CHCl_3$. Evap. extracts and take up residue in 4 ml of MEK. Compare with standards taken through procedure. Techtron Model AA3. Blank value 0.014 ppm	As per Cd Blank 0.79 ppm

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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