

International Council for the
Exploration of the Sea

Fisheries Improvement Cttee
CM 1975/E: 36

AN APPRAISAL OF 1973 ICES TRACE METAL INTERCALIBRATION EXERCISE

by

G. Topping

Marine Laboratory
Aberdeen, Scotland.



Introduction

The ICES Working Group for the study of the pollution of the North Sea proposed in January 1973 that a second intercalibration exercise should take place that year, and it was agreed that a new reference sample for trace metals should be prepared and circulated by the Marine Laboratory, Aberdeen. It was further agreed that a dilute solution of metal ions of known concentration should also be prepared and circulated with this sample, so that an exact metal standard would be available to all analysts and permitting a true comparison of the procedures adopted by the analysts involved in this exercise. Following the meeting in January 1975, the group agreed that all participants in this exercise should make every effort to submit their data to the convenor by the end of February 1975.

This report represents an appraisal of the results submitted as of February 1975.

Details of Fish Flour Preparation

The fish flour used in this exercise was prepared from freshly caught inshore cod by the MAFF Humber Laboratory in Hull. The details of preparation of this meal are as follows:

- i. Freshly caught cod from an inshore area was stored in ice after capture.
- ii. The fish was filleted but the fillets were not skinned.
- iii. The fillets were then steamed for ca 30 mins and then broken up into small pieces.
- iv. The cooked fish was air dried in a tunnel for ca 24 hrs.
- v. The dried fish was minced and then repeatedly ground in a hammer mill.

Reference solution

The solution of metal ions was prepared from BDH stock standard solutions by dilution, using 1 N HCl as the diluent. The exact composition of this standard is presented at the foot of Table 5.

This paper not to be cited without prior reference to the author

Circulation of Reference Samples

Each analyst or laboratory participating in this exercise received 2 plastic phials, each containing ca 25 gm fish flour, and an additional 2 phials containing ca 20 ml of the reference solution. These samples were accompanied by two circulars (Appendices I and II) giving details of the standard analytical procedure to be adopted by each analyst, and details of the requirements for reporting the results of their analyses. Each analyst was asked to analyse the fish flour by both the standard procedure and the analytical procedure adopted by their laboratory for the forthcoming fish and shellfish baseline study.

RESULTS

A list of participants who submitted data on fish flour and the reference solution is presented in Table 1, and a summary of the individual analytical procedures used by the participants is presented in Table 2.

The results of the fish flour and reference solution analyses are presented in Tables 3, 4 and 5. These eleven sets of data represent the total return of information in an exercise which involved the circulation of over 50 sets of samples and which commenced nearly two years ago. This is a rather disappointing return when one considers how important inter-calibration is in any international cooperative study. Only 8 of the 11 sets of data can be used in any ICES evaluation exercise since the other 3 laboratories do not participate in ICES fish and shellfish baseline studies.

Fish Flour Data

ZINC AND COPPER

In general there was good agreement between the laboratories on the results for zinc and copper, overall coefficient of variations for zinc and copper of 7.2% and 17.2% respectively, indicating a slight improvement in the analysis for copper. Mean value of the individual coefficients of variation for zinc and copper were 4.3% and 6.7% respectively for the standard procedure and 4.8% and 8.1% respectively for the individual procedure (Table 7).

MERCURY

Individual laboratories produced data of a very high precision, as shown by coefficients of variation which fell in the range 1.5% - 6.4% for the individual procedures and 1.0% - 14.9% for the standard procedure (Table 7). Unfortunately for both standard and individual procedures there is a ratio of almost 2 between the highest and lowest reported mean values of mercury in fish flour, and this accounts for the high values of the overall coefficients of variation (Table 6).

There is an indication that the differences in mean values of mercury in fish flour might be related to the true concentrations of standards used by the various laboratories. If this is so, and suitable corrections are applied to individual mean values then the differences between laboratories are significantly reduced. This point will be discussed in detail in the Section dealing with the analysis of the reference solutions.

CADMIUM

The precision of cadmium analysis in this exercise is poor, compared to the analysis of mercury, copper and zinc. Coefficients of variation fall in the range 0.9% - 28.3% (mean 12.8%) for the standard procedure and 5.7% - 20.5% (mean 12.5%) for the individual procedures. In addition, there are significant differences between the mean values returned by the different laboratories. This results in a high overall coefficient of variation for the standard procedure (22.4%) and a very high overall coefficient of variation for the individual procedures (40.3%).

LEAD

The precision of lead analysis is found to be similar to that for copper, zinc and mercury analyses, i.e. coefficients of variation of laboratories fall in the range 3.2% - 10% (mean 6.7%) for the standard procedure and 6.1% - 15.8% (mean 9.7%) for the individual procedures. There are, however, significant differences between mean values of lead in fish flour reported by the different laboratories and this results in poor overall coefficients of variation for both the standard procedure (60.2%) and the individual procedures (27%).

Reference solution

The results of the individual analyses of the reference solutions are presented in Table 5 with the overall mean values tabulated in Table 6. These results indicate that there are significant differences between the standards used by individual laboratories and that these differences might well account for a major portion of the differences produced in the fish flour analysis. It is convenient to illustrate this point by examining the mercury data in a little more detail.

The concentration of mercury in fish flour determined by the individual methods range from 0.47 ppm - 0.83 ppm. Similarly the levels of mercury in the reference solution range from 0.10 ppm - 0.18 ppm (it is interesting to see that no laboratory returned levels less than the true value of 0.10 ppm).

A plot of the individual levels of mercury in fish flour and mercury in the reference solution (Fig. 1) suggests that there might be a linear relationship between these sets of data. By applying a factor to each of the individual mercury values for the fish flour, the entire picture of the results is changed (Table 8). The factor for each laboratory is obtained by dividing the true value of mercury in the reference solution by the measured value of mercury in the reference solution. The range of mean levels of mercury in fish flour obtained by this procedure, 0.47 - 0.65 ppm is a significant improvement over the range of mean levels previously submitted, 0.47-0.83 ppm. However a note of caution must be sounded here, since this approach assumes that the mercury reference solution remained unchanged during the period in which it was in circulation. I believe the results obtained indicate that this assumption is correct, but there is a need to confirm this point in the third ICES intercalibration exercise.

I have proposed that the next fish flour reference sample should be accompanied by a small volume (10 ml) of the Marine Laboratory's stock metal solution (1000 ppm), enclosed in individual plastic phials, so that all participants can refer to the same standards for this exercise.

I have also proposed that dilute mercury standards should be made up according to a standard procedure, to avoid losses due to volatilization and adsorption. I believe this is essential since all of the participants

in this exercise had a different approach to preservation and storage of mercury standards (Table 9) which could account for the observed differences in mercury standards.

SUMMARY

1. The results of the analyses of copper, zinc, mercury, lead and cadmium in fish flour by a number of laboratories indicate that individual laboratories can produce analytical data of an acceptable precision for all these metals. However, when overall means and standard deviations are calculated for these data the overall precision is shown to be good for copper and zinc, poor for mercury and very poor for lead and cadmium.

2. The results of the analyses of the circulated reference solution by these same laboratories indicates that different standards are employed by each laboratory, and that these differences in standard solutions could be responsible for the poor interlaboratory comparability.

CONCLUSIONS

In general the results presented here indicate that there has been an improvement in interlaboratory analyses since the first ICES intercalibration exercise. In my opinion, however, the analyses of mercury, lead and cadmium must be improved even further if the Working Group is to consider comparing data for these metals in future ICES studies. Stronger efforts must be made to improve these analyses as soon as possible. As a first priority I believe we should satisfy ourselves that the standards we use are both accurate and stable over the period of their use in the laboratory. I have therefore made two proposals concerning standards which members of the group have accepted and will implement during the third ICES intercalibration exercise.

RECOMMENDATIONS

1. A stock standard solution (1000 ppm) of each metal to be analysed should be circulated with the next round of ICES reference samples. The strength of this standard should ensure that the standard remains constant during its period of circulation. This standard should either be used by each participating laboratory in place of their own standard solutions or be compared to their own standards in order to produce a correction factor for each metal analysed.

2. Dilute standards should be prepared and used according to a standard procedure, to avoid losses by adsorption (Cu, Zn, Hg, Pb, Cd) and by volatilization (Hg). (Appendix 3).

I have proposed that the next fish flour reference sample should be accompanied by a small volume (10 ml) of the Marine Laboratory's stock metal solution (1000 ppm), enclosed in individual plastic vials, so that all participants can refer to the same standards for this exercise.

I have also proposed that dilute mercury standards should be made up according to a standard procedure, to avoid losses due to volatilization and adsorption. I believe this is essential since all of the participants

APPENDIX I

ICES WORKING GROUP FOR THE STUDY OF THE POLLUTION OF THE NORTH SEA:
INTERCALIBRATION EXERCISE

You will remember that at the last meeting of the analysts (15 - 17 January 1973 at Charlottenlund), associated with the above study group, it was agreed that a further intercalibration exercise for trace metals and organochlorine compounds, on the lines of the one conducted in 1972, would be most valuable in providing comparative data for the laboratories participating in the overall study of the North Sea. It was agreed that the two reference samples for trace metals would consist of a fish flour - whose trace metal content was lower than 1972 reference sample and an acidic solution of known metal content.

I am pleased to inform you that the trace metal reference samples are now ready and that you should receive them soon after you receive this communication. I must apologise for the considerable delay in dispatching these samples but unfortunately a breakdown in the hammer mill grinder, which was used for the final grinding of the fish meal to the fine flour, delayed the sample preparation by a number of weeks.

May I take this opportunity of reminding participants of the following points, which were agreed at the meeting in January 1972, regarding analyses and the reporting of the results.

1. The fish flour should be analysed by the analytical procedure adopted by you for the base line survey of trace metals in 1972 and also by the 'standard method' discussed at the last meeting - details of this 'standard method' will be sent with the samples.
2. All analyses should be carried out 6 times and the full results together with mean values, standard deviations and details of the analytical method should be sent to myself and to Dr J E Portmann, Fisheries Laboratory, Remembrance Avenue, Burnham-on-Crouch, Essex, CM0 8HA, England.

I look forward to hearing from you in the near future.

Yours sincerely

APPENDIX II

I.C.E.S. TRACE METAL INTERCALIBRATION EXERCISE

SEPTEMBER 1973

Please find enclosed samples of fish flour and standard metal solution in IN acid. Both samples have been duplicated to allow for variations in methodology and in the event of accidental spillages. The fish flour sample should be analysed by your normal analytical procedure and also by the 'Standard Method' outlined below.

"Standard Method"

The fish flour (ca 3 gm) should be weighed without further drying into a 100-150 ml flat bottomed silica flask and treated with 20 ml concentrated nitric acid (Aristar or similar grade). The flask should be covered with a silica bubble stopper and allowed to stand for 1 hour at room temperature. Transfer the flask to a hot plate having a surface temperature of ca 140°C and allow the acid to reflux for ca 12 hours. The bubble stopper should then be removed and the solution slowly evaporated to a volume of 2-3 ml. After cooling, the solution and washings should be transferred to a 25 ml graduated flask and diluted to the mark using distilled water.

The solution should be centrifuged to remove any suspended matter and then examined for trace metals using standard atomic absorption techniques, correcting for non-atomic absorption using background correction.

[Please analyse for as many trace metals as possible, but include Cu, Zn, Pb, Cd and Hg.]

The results should be reported as outlined in my recently circulated letter.

APPENDIX III

Proposals for the preparation and storage of working standards

MERCURY STANDARD

1. Stock solutions (1000 ppm) should be made up in 1N H_2SO_4 or HCl and stored in glass bottles. Fresh stock solutions should be prepared every 6 months or when the level of the solution in the container falls below the halfway mark.

2. Working solutions. This should be prepared daily by dilution using 1N H_2SO_4 together with sufficient 6% $KMnO_4$ solution to produce a distinct pink colour in the final solutions. Please check the mercury content of your Potassium Permanganate solution as this can contain very high levels of mercury. In practice solution should be prepared immediately before use and should only have a bench life of ca 2 hrs.

OTHER STANDARDS

1. Stock solutions (1000 ppm) should be made up in 1N acid and can be stored in other glass or plastic bottles. Fresh solutions should be prepared every 6 months or when the level of the solution in the container falls below the halfway mark.

2. Working solutions This should be prepared daily by dilution using 1N acid.

Table 1

LABORATORY/INSTITUTE PARTICIPATING IN 1973/1974 ICES INTERCALIBRATION EXERCISE

Participants in Baseline Survey

<u>No.</u>	<u>Country</u>	<u>Institute</u>	<u>Reporting analyst</u>
1	Sweden	Staten naturvårdsverk Undersöknings laboratoriet Drottningholm	O. Lindgren
2	France	Institute Scientifique et Technique des Pêches Maritime, Nantes.	Y Thibaud
3	Germany	Bundesforschungsanstalt für Fischerei Isotopenlaboratorium Hamburg	U Harms
4	Belgium	Ministerie van Landbouw Institut voor Scheikundig Onderzoek Tervuren	P Herman
5	England	Ministry of Agriculture, Fisheries and Food, Fisheries Laboratory, Burnham	J Portmann
6	Scotland	Department of Agriculture and Fisheries for Scotland, Marine Laboratory, Aberdeen	G Topping
7	Iceland	Hafrannsóknastofnunin Marine Research Institute, Reykjavik	J Olafsson
8	Netherlands	Netherlands Institute for Fishery Investigation, IJmuiden	P Hagel
<u>Other Analysts</u>			<u>Analyst</u>
9	Dept of Agriculture and Fisheries for Scotland Freshwater Fisheries Laboratory, Pitlochry		L Caines
10	Marine Biological Association of the United Kingdom, Plymouth		G Bryan
11	Deutsches Hydrographisches Institut Hamburg		D Schmidt

Table 2

Summary of the Individual Analytical Techniques Employed by Laboratories

Lab. No	Mercury	Other Metals
1	Wet digestion with $\text{HNO}_3/\text{HClO}_4$ at 70°C overnight. Cold vapour analysis using IRD Mercurimeter.	Wet digestion with $\text{HNO}_3/\text{HClO}_4$ at 70°C . A.A. using Perkin Elmer 303 with background correction.
2	Wet digestion with $\text{HNO}_3/\text{H}_2\text{SO}_4$ $50-60^\circ\text{C}$ for 2 hrs followed by KMnO_4 solution. Cold vapour analysis.	Wet digestion with $\text{HNO}_3/\text{HClO}_4$ AA using air acetylene flame.
3a	Dry decomposition using Schöniger flask combustion followed by cold vapour analysis.	Wet digestion with $\text{HNO}_3/\text{HClO}_4$ using "Bethge" apparatus. Zn, Cu, measured using standard AA technique. Cd and Pb measured using flameless AA - graphite tube furnace. Mn, Co and Ni measured using x-ray fluorescence.
3b	Wet digestion using "Bethge" apparatus - $\text{HNO}_3/\text{H}_2\text{SO}_4$ followed by $\text{HNO}_3/\text{HClO}_4$. Cold vapour analysis; Jarrell Ash mercury analysis kit.	Wet digestion using $\text{HNO}_3/\text{HClO}_4$. Cd and Pb determined by HGA-72 (Perkin Elmer).
4	Wet digestion $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 + \text{KMnO}_4$ Cold vapour analysis.	Dry combustion at 450°C for Cu, Pb and Zn. Flameless AA for Cu and Pb. Flame AA for Zn. Wet digestion for Cd. Flameless AA for Cd. [Perkin Elmer 303]
5	Wet digestion $\text{H}_2\text{SO}_4/\text{HNO}_3$ at 140°C + Potassium persulphate. Cold vapour analysis.	Wet digestion, Cu, Zn, Cd and Cr by flame AA using background connector. Pb extracted with APDC and MIBK - followed by flame AA.
6	Dry combustion at $900^\circ-1000^\circ\text{C}$ followed by absorption in $\text{KMnO}_4/\text{H}_2\text{SO}_4$ Cold vapour analysis.	Wet digestion using $\text{HNO}_3/\text{HClO}_4$. Flame AA for Cu, Cd, Pb and Zn using I.L.251. (background correction incorporated into double beam system)
7	Atomic Absorption Newsletter (1971). 10, p 101-103 [H_2O_2 replaced by ascorbic acid] Flameless AA following amalgamation procedure using gold.	
9	Wet digestion with $\text{HNO}_3/\text{H}_2\text{SO}_4$ using air condenser. Cold vapour analysis.	Wet digestion with $\text{HNO}_3/\text{HClO}_4$ followed by flame AA Perkin Elmer.
10.		Wet digestion using HNO_3 followed by flame AA - Perkin Elmer 306.
11.		Wet digestion using HNO_3 followed by flameless AA using HGA 74 - Perkin Elmer 300.

Table 3

RESULTS OF FISH FLOUR ANALYSES*

USING THE STANDARD METHOD

Lab No	Metal Concentration mg/kg									
	Hg	Cu	Zn	Cd	Pb	Cr	Mn	Co	Ni	Fe
1	a	0.655	10.05	23.88	0.403	1.4	0.05	-	-	-
	b	0.017	0.64	0.29	0.055	-	-	-	-	-
	c	0.65-0.68	9.2-10.7	23.5-24.1	0.35-0.48	1.4	-	-	-	-
3	a	-	8.7	29.5	0.55	3.0	-	2.7	<0.5	3.1
	b	-	0.6	2.1	0.08	0.17	-	0.2	-	0.29
	c	-	-	-	-	-	-	-	-	-
4	a	0.83	9.86	27.42	0.47	0.25	-	-	-	-
	b	0.008	0.79	0.063	0.133	0.008	-	-	-	-
	c	0.82-0.84	9.16-10.67	27.35-27.50	0.34-0.59	0.24-0.26	-	-	-	-
5	a	0.47	10.1	23	<0.2	2.5	~0.3	-	-	-
	b	0.07	0.5	2	-	.2	-	-	-	-
	c	0.37-0.58	9.7-10.8	21-25	<0.2	2.3-2.9	~0.3	-	-	-
6	a	0.62	9.9	25.7	0.39	2.0	-	-	-	-
	b	0.03	0.4	0.9	0.03	0.2	-	-	-	-
	c	0.58-0.65	9.5-10.4	24.4-26.9	0.37-0.43	1.7-2.1	-	-	-	-
7	a	0.485	-	-	-	-	-	-	-	-
	b	0.037	-	-	-	-	-	-	-	-
	c	0.45-0.551	-	-	-	-	-	-	-	-
9	a	0.45	9.2	27.0	0.4	2.4	-	-	-	-
	b	0.03	0.4	1.4	-	-	-	-	-	-
	c	0.41-0.48	8.9-9.9	25.5-28.5	0.4	2.3-2.4	-	-	-	-
10	a	-	9.97	27.7	0.43	1.84	-	2.07	-	2.15 74.2
	b	-	0.60	0.4	0.05	0.13	-	0.15	-	0.37 14.7
	c	-	-	-	-	-	-	-	-	-
11	a	-	7.6	24.2	0.332	-	0.132	-	-	2.5 62.0
	b	-	1.0	1.8	0.003	-	0.034	-	-	0.5 6.7
	c	-	6.4-8.4	20.8-27.5	0.323-0.342	-	0.098-0.166	-	-	1.8-3.2 56-70

* a= mean value b= standard deviation c= range of values

Table 4
RESULTS OF FISH FLOUR ANALYSES*
USING THE INDIVIDUAL METHODS

Lab No	Hg	Cu	Zn	Cd	Pb	Cr	Mn	Co	Ni	Fe
1	a	0.662	8.63	26.87	1.12	<3	0.60	-	-	-
	b	0.043	1.60	1.34	0.23	-	0.14	-	-	-
	c	0.62-0.73	6.8-11.4	25.7-29.5	0.9-1.4	-	0.4-0.8	-	-	-
2	a	0.75	9.5	24.8	0.7	-	-	-	-	-
	b	0.04	0.9	1.8	0.1	-	-	-	-	-
	c	0.71-0.81	8.4-11.1	22.1-27.6	0.5-0.9	-	-	-	-	-
3(i)	a	0.47	10.0	31.1	0.49	2.6	-	2.6	0.04	3.5
	b	0.03	0.6	1.6	0.05	0.16	-	0.17	0.005	0.30
	c	-	-	-	-	-	-	-	-	-
(ii)	a	0.73	-	-	0.43	1.74	-	-	-	-
	b	0.05	-	-	0.04	0.08	-	-	-	-
	c	-	-	-	-	-	-	-	-	-
4	a	0.83	8.62	27.12	0.73	1.26	-	-	-	-
	b	0.038	0.539	0.426	0.111	0.178	-	-	-	-
	c	0.79-0.87	8.08-9.41	26.68-27.58	0.58-0.82	1.06-1.42	-	-	-	-
5	a	0.63	10.1	23	<.2	2.5	~.3	-	-	-
	b	0.03	.5	2	-	0.2	~.3	-	-	-
	c	0.60-0.67	9.7-10.8	21-25	<.2	2.3-2.9	~.3	-	-	-
6	a	0.65	9.6	25.6	0.35	1.9	-	-	-	-
	b	0.04	0.2	1.0	0.02	0.3	-	-	-	-
	c	0.60-0.70	9.4-9.8	23.8-26.6	0.33-0.37	1.7-2.3	-	-	-	-
7	a	0.717	-	-	-	-	-	-	-	-
	b	0.011	-	-	-	-	-	-	-	-
	c	0.702-0.732	-	-	-	-	-	-	-	-
8	a	0.6	8.3	32	1.1	-	-	-	-	-
	b	-	-	-	-	-	-	-	-	-
	c	-	-	-	-	-	-	-	-	-
9	a	0.53	10.9	31.6	0.5	<5.0	-	-	-	-
	b	0.02	1.0	0.7	-	-	-	-	-	-
	c	0.49-0.56	9.8-12.4	30.8-32.9	0.4-0.6	<5.0	-	-	-	-

* a = mean value b = standard deviation c = range of values

Table 5

Results of Reference Solution Analyses*

Lab No	Metal concentration ug/ml									
	Hg	Cu	Zn	Cd	Pb	Cr	Mn	Co	Ni	Fe
1 a	0.110	0.460	0.548	0.201	0.340	1.365	-	-	-	-
b	0.004	0.018	0.001	0.004	0.009	0.028	-	-	-	-
c	0.104-0.112	0.440-0.476	0.547-0.550	0.195-0.206	0.330-0.350	1.320-1.395	-	-	-	-
2 a	0.14	0.4	0.53	0.12	-	-	-	-	-	-
b	0.005	0.03	0.04	0.007	-	-	-	-	-	-
c	0.13-0.15	0.33-0.45	0.47-0.60	0.11-0.13	-	-	-	-	-	-
3 a	0.10	0.50	0.54	0.07	0.07	-	-	-	-	-
b	0.008	0.02	0.04	0.01	0.02	-	-	-	-	-
c	-	-	-	-	-	-	-	-	-	-
4 a	0.18	0.392	0.608	0.061	0.249	-	-	-	-	-
b	0.004	0.012	0.036	0.0006	0.0055	-	-	-	-	-
c	0.18-0.19	0.375-0.408	0.573-0.669	0.060-0.062	0.240-0.256	-	-	-	-	-
5 a	0.124	0.48	0.50	0.15	0.49	-	-	-	-	-
b	-	-	-	-	-	-	-	-	-	-
c	-	-	-	-	-	-	-	-	-	-
6 a	0.10	0.40	0.51	0.10	0.23	-	-	-	-	-
b	0.01	0.02	0.01	0.01	0.03	-	-	-	-	-
c	-	-	-	-	-	-	-	-	-	-
7(i)a	0.125	-	-	-	-	-	-	-	-	-
b	0.002	-	-	-	-	-	-	-	-	-
c	-	-	-	-	-	-	-	-	-	-
(ii)a	0.149	-	-	-	-	-	-	-	-	-
b	0.002	-	-	-	-	-	-	-	-	-
c	-	-	-	-	-	-	-	-	-	-
9 a	0.12	0.4	1.0	0.1	0.3	-	-	-	-	-
b	-	-	-	-	-	-	-	-	-	-
c	-	-	-	-	-	-	-	-	-	-
11 a	-	0.415	0.375	0.120	-	0.822	5.1	-	0.008	7.8
b	-	0.034	0.041	0.005	-	0.003	0.3	-	-	0.47
c	-	0.366-0.448	0.320-0.407	0.117-0.127	-	0.820-0.825	4.7-5.5	-	-	-
True Values	0.10	0.40	0.50	0.10	0.30	1.0	5.0	-	-	8.0

* a = mean value b = standard deviation c = range of values

Table 6

Means, Standard Deviations (s.d.) and Coefficients of Variation (c.v.)
of all samples from all institutes

Fish flour

Metal	Reference solution	Standard method	Individual method
Mercury	.122	.585	.667
s.d.	.029	.140	.117
c.v.	23.8%	23.9%	17.5%
Lead	.274	1.66	2.00
s.d.	.065	1.00	.54
c.v.	23.7%	60.2%	27%
Copper	.428	9.34	9.54
s.d.	.041	1.05	1.17
c.v.	9.5%	11.2%	12.2%
Zinc	.552	25.8	27.9
s.d.	.086	2.5	2.7
c.v.	15.6%	9.7%	9.7%
Cadmium	.110	.424	.617
s.d.	.045	.095	.249
c.v.	41%	22.4%	40.3%

Table 7

COEFFICIENTS OF VARIATION OF INDIVIDUAL METAL ANALYSIS OF FISH FLOUR

USING (a) STANDARD METHOD (b) INDIVIDUAL METHOD

LAB NO	MERCURY		COPPER		ZINC		CADMIUM		LEAD	
	a	b	a	b	a	b	a	b	a	b
1	2.6	6.4	6.4	18.5	1.2	5.0	13.6	20.5	-	-
2	-	5.3	-	9.5	-	7.2	-	14.3	-	-
3	-	6.4	6.9	6.0	7.1	5.1	14.5	10.2	5.6	6.1
4	1.0	4.6	8.0	6.2	0.2	1.6	28.3	15.1	3.2	14.1
5	14.9	4.8	4.9	4.9	8.7	8.7	-	-	8.0	8.0
6	4.8	6.1	4.0	2.1	3.5	4.0	7.7	5.7	10.0	15.8
7	7.6	1.5	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-
9	6.6	3.8	4.3	9.2	5.2	2.2	-	-	-	-
10	-	-	6.0	-	1.4	-	11.6	-	7.0	-
11	-	-	13.0	-	7.4	-	0.9	-	-	-
Mean Value	6.2	5.1	6.7	8.6	4.3	4.8	12.8	12.5	6.7	9.7

Table 8 Comparison of 'normalised' mean values of mercury in fish meal with original mean values submitted by individual laboratories.

Lab No.	Original mean values		'Normalised' values	
	Standard Procedure	Industrial Procedure	Standard Procedure	Individual Procedure
1	0.65	0.66	0.60	0.60
2	N.A.	0.75	N.A.	0.54
3	N.A.	0.47	N.A.	0.47
4	0.83	0.83	0.46	0.46
5	0.47	0.63	0.38	0.53
6	0.62	0.65	0.62	0.65
7	0.48	0.72	0.35	0.52
9	0.45	0.53	0.38	0.44

Table 9

Preparation of Mercury Standards

<u>Lab No</u>	<u>Stock Solution</u>	<u>Intermediate Solution</u>	<u>Daily or Working Solution</u>
1	1000 ppm B.D.H. standard solution	10 ppm (0.1N HCl) weekly	0.1 ppm (0.1N HCl) daily
2	100 ppm. Prepared in laboratory using HgCl_2 every 4 months. 5% conc. HNO_3	1.0 ppm 5% HNO_3 daily	0.1-1.0 ppm 5% conc HNO_3 daily
3	1000 ppm "Merck Titrisol" 1N HNO_3 every 3 months		0.004 ppm daily
4	500 ppm Prepared in laboratory 1N H_2SO_4 (+ KMnO_4) every month		0.02 ppm NH_2SO_4 (+ KMnO_4) daily/weekly
5	1000 ppm Prepared in laboratory 5% conc. HNO_3 ~6 months	10 ppm 5% conc. HNO_3 monthly	0.1 ppm 5% HNO_3 daily
6	1000 ppm BDH 1N HCl 6 months		10 ppm 0.0 1N HCl (+ KMnO_4) daily
7	100 ppm 1N HNO_3 1 month		0.02 ppm In HNO_3 1-5 days
8	1000 ppm 0.1N HCl 1 year		0.1 ppm 0.1N HCl every 2 hours
9	1000 ppm BDH 1N HCl		0.002-0.010 ppm 10% H_2SO_4 / 40% HNO_3 weekly

Fig. 1a

The relationship between the mean concentration of mercury in fish flour and the mean concentration of mercury in the reference solution - Individual Procedure

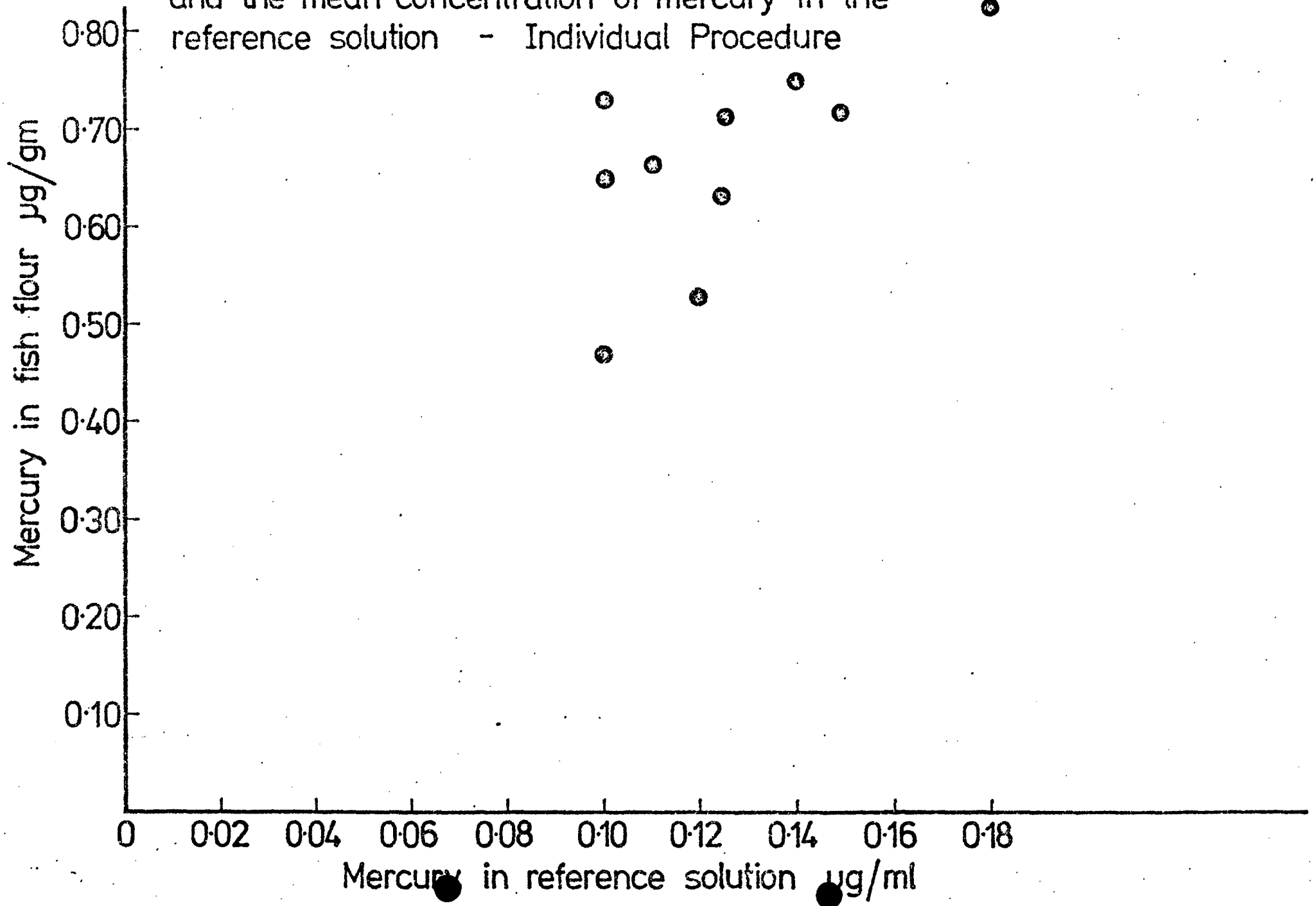


Fig. 1b The relationship between the mean concentration of mercury in fish flour and the mean concentration of mercury in the reference solution - Standard Procedure

