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AN ICES INTERCALIBRATION EXERCISE FOR TRACE METAL STANDARD SOLUTIONS

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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. The nature of such discrepancies were further examined by Duinker *et al* (1975) who reported on an intercalibration exercise between various institutes in Belgium, The Netherlands and the United Kingdom.

A meeting of the ICES Working Group on Pollution Baseline and Monitoring Studies in the Oslo Commission and ICNAF Areas appointed an analytical subgroup 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). They proposed a tripartite programme involving (i) an intercalibration of a relatively concentrated standard metal solution (ii) an intercalibration of actual sea water samples (iii) a multi-research vessel workshop. This report describes the results of the first part of this programme. The aim of the project was primarily to test standard metal solutions used in routine analysis rather than to intercalibrate analytical techniques. The exercise was originally planned to include only those laboratories that may provide an input to future studies in the ICNAF/Oslo Commission area. However requests to participate were received from other institutes. Samples were sent to all who requested them, in view of the obvious scientific value of participation by such an expanded group.

METHODS

The samples consisted of two solutions in which lead and chromium were separated to prevent 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 prepared 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.

Some 45 samples were distributed to participants early in 1976. Analysts were

asked to report on the metal concentration of those elements they routinely measure. Triplicate analyses were requested and it was emphasized that the present exercise was a test of standards rather than analytical technique. Institutes were asked to return unused samples for a stability check. These samples were measured by the atomic absorption flame technique against single element standards prepared from the original Hopkin & Williams reagents. Thus one must assume no deterioration in the original reagents during the approximate 6 month period of the exercise. The whole programme was organised and conducted by the Research Support Group of the Lowestoft Fisheries Laboratory.

By mid July 30 sets of results had been received. Those Institutes which replied are as follows:-

Canada

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

Denmark

Water Quality Institute, Hørsholm.

Federal Republic of Germany

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

Finland

Institute of Marine Research, Helsinki.

France

Institut Scientifique et Technique des Pêches Maritimes, Nantes.

Greenland

Grønlands Fiskeriundersøgelse, Charlottenlund.

Iceland

Hafrannsóknastofnunin, Reykjavik.

Netherlands

Nederlands Instituut voor Onderzoek der Zee, Texel
Rijksinstituut voor Zuivering Afvalwater, Lelystad
TNO Central Laboratorium, Delft.

Norway

Central Institute for Industrial Research, Blindern
Dépt of Chemistry, University of Oslo
Institute for Marine Biology and Limnology, University of Oslo.

Portugal

Centro de Geofísica das Universidades de Lisboa.

UK

Clyde River Purification Board, East Kilbride
Dept of Agriculture and Fisheries for Scotland, Marine Laboratory, Aberdeen
Dept of Oceanography, University of Liverpool
Dept 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, Fisheries Radiobiological
Laboratory, Lowestoft
Southern Water Authority, Brighton
Southern Water Authority, Winchester
Wessex Water Authority, Poole.

USA

Skidaway Institute of Oceanography, University of Georgia.

USSR

Dept of the Baltic Sea Institute, Tallinn.

RESULTS

The results of the exercise are shown in Figure 1 and Tables 1 and 2. The participating laboratories are anonymous and code numbers were allocated in chronological order of receiving the replies. 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, other than those of mercury and chromium, fell within $\pm 5\%$ of the theoretical value. The greatest number of chromium and mercury results occurred in the groups -10.1 to -15.0 and -5.1 to -10.0 respectively. The reason for these anomalies is not absolutely clear. There was a tendency for mercury values reported by cold vapour atomic absorption to be lower than those measured by flame. However, this trend was not statistically significant, probably because of an insufficient number of observations.

It is difficult to select the limits of an acceptable deviation from the expected values. The present exercise involved a concentrated metal standard rather

than a sea water sample of low metal content requiring several manipulative stages during analysis. Hence one may expect a somewhat better accuracy in the present exercise compared with an intercalibration of sea water exercise. However a limit of $\pm 10\%$ deviation from the expected value should encompass acceptable analytical error. Out of a total of 232 results, which included all elements, approximately 20% were outside $\pm 10\%$ of the expected value and 6.5% were outside the $\pm 20\%$ limit.

Tables 1 and 2 lists the results in detail and includes some simple statistical tests. The lack in uniformity of much of the data, such as the variable number of replicate analyses by different participants and the variation in the total number of elements analysed by each laboratory, means that the results of these tests should only be used to indicate relatively coarse trends.

Apart from mercury, chromium and iron, the total mean metal concentrations of all participants was remarkably close to the expected value, thus substantiating to a large degree the results presented in Table 1. The rather high mean iron value of 157 ppm resulted from a relatively large number of observations in excess of $\pm 20\%$ of the expected value. Private communication with participant number 21 showed the value of $\pm 20.2\%$ for iron to have resulted from an error in his own standard solution.

Of those samples returned for stability checks, 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. Cobalt data on the returned samples are incomplete owing to a lamp failure.

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 2.1 and 2.8. Chromium and zinc emerged somewhat better with values of 1.4 and 1.6 respectively.

The coefficient of variation on each metal was also calculated using the mean values reported by the participants. In this case v showed a wide range of variation between copper at 6.3 and iron at 19.9. The relatively poor uniformity of the iron results was undoubtedly a result of the excessively high values reported by some participants.

Correlation coefficient tests were made between the % discrepancy of each participant from the expected metal value and his coefficient of variation, in order to assess if those results which showed the greatest deviation from the expected values also showed the poorest reproducibility. The test was made for each individual metal (Tables 1 and 2) and also for the mean values of all metals in both solutions A and B (Table 2). The sign of the discrepancy was ignored. The correlation coefficient was probably significant for lead at the 5% level ($r = 0.44$) and somewhat less significant for copper and cadmium ($r = 0.35$ and 0.38 respectively). The remaining metals showed no such correlation. However, the overall test of

correlation based on the mean of all the values was significant at the 1% level ($r = 0.48$). Thus there is some evidence that the larger deviations from the expected values were associated with a lower degree of precision.

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 for either individual metals or all data grouped together.

DISCUSSION

To summarise the findings of the present exercise, the distribution of reported values for most metals fell fairly evenly on either side of the expected value. The exceptions were the distributions for mercury and chromium, which tended to be skewed towards the low side, and iron, where a relatively large group of values were greater than 20% of the expected level. The mercury discrepancy may be related to the technique of measurement. The high iron value may be caused by the removal of the metal from the participants own solution either by precipitation or adsorption. The possibility of such a process should be investigated further. If one takes a deviation of $\pm 10\%$ from the expected value as the limit of acceptance, then the 20% of the returned observations which fell outside the acceptable range should receive further investigation. There was some evidence that the results which showed the largest deviation from the expected value also exhibited the lowest precision of measurement. Such a trend seems a reasonable expectation, although clearly this feature is not the major cause of the discrepancy. Finally, there was no evidence to relate the nature of the participants' own standard solutions with any of the discrepancies concerned.

Most of the observations were made by atomic absorption. Thus there are insufficient data to assess the results by different analytical techniques. Duinker et al (1975) suggested that discrepancies in the intercalibration of sea water samples were related to the method of analysis. However, theoretically there should be no such correlation in this instance, since standards rather than methods were being compared.

Further examination of the discrepancies observed seems only feasible by a detailed collaboration with individual participants. Such a process would be time-consuming and may not necessarily eliminate future errors. It is therefore proposed that arrangements for the next stage of the intercalibration programme should proceed and that frozen sea water samples be distributed during the first part of next year. At the same time it is proposed that a concentrated multi-element standard, similar to the one used in the present exercise, should be distributed. Participants will be asked to analyse the unknown sea water both against their own standard and the one provided. Thus the results of the sea water exercise should provide continuity with the present trial and a more detailed analysis of the present data may then

prove feasible.

SUMMARY

An international intercalibration of standard trace metal solutions was conducted under the auspices of the ICES Working Group on Pollution Baseline and Monitoring Studies in the Oslo Commission and ICNAF Areas. Participants received concentrated standard solutions containing Hg, Pb, Ni, Co, Fe, Cr, Cu, Cd, Zn and Mn and were asked to measure as many metals as possible against their own standard solutions. Measurements were requested by the simplest possible technique since this was not an intercalibration of analytical methods. From a total of 232 results, approximately 20% were outside $\pm 10\%$ of the expected value. Mercury and chromium results tended to be low and several iron values were 20% too high. Remaining deviations were fairly evenly distributed. Various statistical tests were applied to the data and there was an indication that the greatest discrepancies were associated with a low degree of precision. It was proposed that the second stage of the ICES exercise involving the intercalibration of sea water samples should proceed as planned.

REFERENCES

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- ICES, 1974. Report of Working Group for the International Study of the Pollution of the North Sea and its effect on living resources and their exploitation. Coop. Res. Rep. int. Coun. Explor. Sea, (39), 191 pp.
- ICES, 1975(a). First Report of the Working Group on Pollution Baseline and Monitoring Studies in the Oslo Commission and ICNAF Areas. ICES C.M. 1975/E:2. 43 pp.
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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. %	v %	check	mean (no. of obs)	Disc. %	v %	check	mean (no. of obs)	Disc. %	v %	check	mean (no. of obs)	Disc. %	v %	check	mean (no. of obs)	Disc. %	v %	check
1 (C) AA					281(3)	-1.7	1.68	292	141(4)	-1.4	3.09	155				143	140(3)	-2.1	3.22	143
2 (C) AA	249(3)	-12.9	4.12	308	300(3)	4.9	0.00	283	138(3)	-3.5	0.83	150	139(3)	-2.8	1.50		124(3)	-13.3	1.68	150
3 (C) AA					273(3)	-4.6	3.17		144(3)	0.7	0.40						142(3)	-0.7	1.22	
4 (C) AA					329(3)	15.0	5.10	286	141(3)	-1.4	4.65	147	140(3)	-2.1	3.57	136	137(3)	-4.2	1.88	134
5 (C) AA					265(3)	-7.3	3.01	286	183(3)	28.0	3.20	151	151(3)	5.6	5.97	136	177(3)	23.8	10.59	140
6 (C) AA	250(2)	-12.6	1.42	293	320(2)	11.9	0.66	286								130	161(2)	12.6	0.88	134
7 (C) AA					282(3)	-1.4	4.46	286	143(3)	0.0	4.50	143	125(3)	-12.6	4.00	130	147(3)	2.8	3.93	131
8 (C) AA									148(2)*	3.5	2.39	147	144(2)	0.7	0.49	136	156(2)*	9.1	0.00	137
9(1)(C) AA1									129(2)	-9.8	1.09	155								
9(2)(C) AA2									133(3)	-7.0	1.15						231(2)	61.5	3.98	
10 (C) AA					299(3)	4.6	3.37	283	145(3)	1.4	0.79	150	143(3)	0.0	0.70		144(3)	0.7	1.75	154
11 (C) AA	281(3)	-1.7	1.48	280	295(3)	3.1	1.46	279	143(3)	0.0	1.40	143	140(3)*	-2.1	1.65	130	146(3)*	2.1	0.0	131
12 (C) AA					295(3)*	3.1	1.87	276	149(3)	4.2	1.55	150					150(3)	4.9	2.69	150
13 (C) AA	254(3)	-11.2	2.02	300	300(3)	4.9	1.00	276	140(3)	-2.1	1.80	148	146(3)	2.1	1.82		143(3)	0.0	4.36	154
14 (C) AA	285(2)	-0.3	2.48		293(3)	2.4	1.77		151(3)	5.6	7.85						146(3)	2.1	1.82	
15 (C) ASV					283(6)	-1.0	6.47	283												154
16 (C) AA	274(3)	-4.2	0.97		284(3)	-0.7	0.61		144(3)	0.7	2.81		139(3)	-2.8	4.34		158(3)	10.5	4.12	
17 (C) AA	251(5)	-12.2	4.71	300	241(4)	-15.7	14.20	270												154
18(1)(C) XRF					266(3)	-7.0	4.19		123(3)	-14.0	7.72		127(3)	-11.2	9.23		130(3)	-9.1	1.60	
18(2)(C) AA	286(3)	0.0	2.99		255(3)	-10.8	2.35		146(3)	2.1	1.58		155(3)	8.4	1.49		143(3)	0.0	1.62	
19 (C) ASV					227(1)	-20.6		287												
20 (C) AA	264(8)	-7.7	2.25	308	292(2)	2.1	1.21	276												
21 (C) AA									155(1)	8.4							172(1)	20.2		
22 (C) AA	248(3)	-13.3	2.40	286	316(2)	10.5	0.45	283												
23 (C) AA	267(1)	-6.6		296	301(3)	5.2	0.00	273	156(3)	9.1	0.72	150	161(3)	12.6	0.36		155(3)	8.4	0.37	150
24 (C) AA	238(1)	-16.8			279(1)	-2.4			145(1)	1.4			142(1)	-0.7			142(1)	-0.7		
25 (C) AA	317(3)	10.8	7.88	282	279(3)	-2.4	1.29	277	146(3)	2.1	1.42	153	181(3)	26.5	1.69		165(3)	15.4	4.57	158
26(2) AA					311(3)	8.7	2.51	280	144(3)	0.7	1.75	155	149(3)	4.2	2.79					
27 (C) ES	240(2)	-16.1	0.00	300																
28 (C) AA	135(3)	-52.8	2.22	286	278(12)	-2.8	1.08	280	145(12)	1.4	2.07	155					143(12)	0.0	2.10	161
29 (C) ?	275(1)	-3.8			282(1)	-1.4			140(1)	-2.1			139(1)	-2.8			259(8)	81.1	7.32	
30 (C) AA																				
Mean	257		2.69	294	286		2.69	281	145		2.51	150	145		2.83	134	157		2.82	145
Mean v	15.0				8.04				7.54				9.08				19.92			
r		0.06				0.44				-0.03				0.12				-0.11		

Key:- AA Atomic Absorption; AA1 direct; AA2 Standard addition; ASV Anodic stripping voltametry; XRF X-ray fluorescence; ES emission spectroscopy
 (C) Institute used commercially prepared standard to determine unknown except for metals with asterisk
 v Coefficient of variation, and correlation coefficient
 check - metal content of returned subsample

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				All metals Solutions A&B	
	Mean (No. of obs)	Disc. %	v %	check	Mean (No. of obs)	Disc. %	v %	check	Mean (No. of obs)	Disc. %	v %	check	Mean (No. of obs)	Disc. %	v %	check	Mean (No. of obs)	Disc. %	v %	check	Mean Disc. %	Mean v %
1 (C) AA	206(3)	-11.2	2.76	232	214(4)	-7.8	3.12	241	175(4)	-1.7	3.66	179	180(4)	0.6	2.81	185	180(4)	0.6	1.89	183	3.4	2.78
2 AA	225(3)	-3.0	0.44	235	228(3)	-1.7	2.63	232	177(3)	-1.1	1.18	176	178(3)	-0.6	1.42	182	177(3)	-1.1	2.28	179	4.5	1.61
3 (C) AA	196(3)	-15.5	3.10		241(3)	3.9	1.73		186(3)	3.0	2.95		185(3)	3.3	1.36		181(3)*	1.1	1.15		4.1	1.89
4 (C) AA	214(3)	-7.8	3.71	228	240(3)	3.4	0.00	238	178(3)	-0.6	3.61	179	174(3)	-2.8	4.47	182	186(3)	3.0	2.76	179	4.5	3.31
5 AA	229(3)	-1.3	1.97	232	236(3)	1.7	1.71	238	182(3)	1.3	0.95	179	181(3)	1.1	1.15	183					8.8	3.54
6 (C) AA					254(2)	9.5	0.56	238	176(2)	-1.7	1.20	179	200(2)	11.7	0.00	183	184(2)	2.8	1.15	183	9.0	0.84
7 (C) AA	217(3)	-6.5	2.96	228	233(3)	0.4	7.30	235	177(3)	-1.1	1.63	179	176(3)	-1.7	0.65	183	178(3)	-0.6	1.80	183	3.0	3.47
8 (C) AA					221(2)*	-4.7	0.64	235	179(3)*	0.0	0.32	179	179(3)*	0.0	0.56	180	186(2)*	3.0	2.66	183	3.0	1.01
9(1) (C) AA1					238(2)	2.6	3.27	229	166(2)	-7.2	1.28	177					166(3)	-7.3	6.44	174	6.7	3.02
9(2) (C) AA2					239(1)	3.0			165(2)	-7.8	11.57						178(3)	-0.6	2.25		20.0	4.73
10 AA	182(3)	-21.6	0.32	238	234(3)	0.9	1.08	232	160(3)	-10.6	0.36	177	164(3)	-8.4	1.27	182	126(3)	-29.6	0.91	179	8.6	1.17
11 (C) AA	223(3)	-3.9	0.00	228	232(3)	0.0	0.00	235	182(3)	1.7	2.91	179	181(3)	1.1	0.85	180	178(3)*	-0.6	2.83	183	1.6	1.26
12 (C) AA	205(3)	-11.6	0.00	232	242(3)	4.3	2.38	232	172(3)	-3.9	7.81	177	192(3)	7.3	2.10	179					5.6	2.63
13 (C) AA	232(2)	0.0	0.90	232	232(3)	0.0	0.90	225	177(3)	-1.1	3.63	177	182(3)	1.7	0.84	179	180(3)	0.6	1.40	172	2.4	1.87
14 AA					230(3)	-0.9	0.43		179(3)	0.0	1.79		174(3)	-2.8	4.35		180(3)	0.6	1.92		1.9	2.80
15 ASV					248(3)	6.9	21.45	232	158(6)	-11.7	4.84	177									6.5	10.92
16 AA	180(3)	-22.4	1.95		232(3)	0.0	1.00		181(3)	1.1	1.09		178(3)	-0.6	1.49		180(3)	0.6	1.67		4.4	2.00
17 (C) AA	224(2)	-3.4	1.89	238	192(3)	-18.1	5.24	236	257(2)	43.6	4.13	183	200(2)*	11.7	0.71	186					17.4	5.19
18(1) (C) XRF	217(3)	-6.4	0.71		217(3)	-6.4	5.50		155(3)	-13.4	4.52										9.6	4.78
18(2) (C) AA	214(3)	-7.8	0.93		231(3)	-0.4	1.39		183(3)	2.2	0.84		178(3)	-0.6	0.00		184(3)	2.8	0.00		3.5	1.80
19 ASV					216(1)	-6.9		241	171(1)	-4.5		181	118(1)	-34.1		179					16.4	
20 (C) AA					239(2)	3.0	0.59	232	182(2)	1.7	0.39	177									3.6	1.11
21 (C) AA	220(1)	-5.2			244(1)	5.2			194(1)	8.4			192(1)	7.3			185(1)	3.4			8.8	
22 AA					233(2)	0.4	0.61	245	175(2)	-2.2	1.21	185	184(2)	2.8	1.92	185					7.6	1.32
23 AA	259(3)	-11.6	0.59	232	232(3)	0.0	0.25	232	186(3)	3.9	0.00	177	177(3)	-1.1	0.65	179	188(3)	5.0	0.31	176	6.3	0.36
24 (C) AA	211(1)	-9.0			223(1)	-3.9			176(1)	-1.7			173(1)	-3.3			181(1)	1.1			4.1	
25 AA	218(3)	-6.0	0.95	238	237(1)	2.1	1.29	238	186(3)	3.9	1.61	181	175(3)	-2.2	1.44	180	167(3)	-6.7	0.60	183	7.8	2.26
26(1) AA					235(3)	1.3	1.23	248													1.3	1.23
26(2) AA					243(3)	4.7	3.93		167(3)	-6.7	4.41		187(3)	4.5	3.13						4.9	3.09
27																						0.00
28 (C) AA					258(12)	11.2	1.55	238	175(12)	-2.2	1.71	181	167(12)	-6.7	2.99	180	169(12)	-5.6	1.18	181	10.3	1.86
29 (?) ?					229(1)	-1.3			182(1)	1.7			175(1)	-2.2			175(1)	-2.2			2.2	
30 (C) AA					279(8)	20.3	6.43		255(6)	42.5	6.57						163(6)	-8.9	7.04		38.2	6.84
Mean	215		1.45	233	234		2.66	236	181		2.82	179	178		1.63	182	176		2.12	180	7.5	2.71
Mean v	8.43				6.32				12.02				8.55				7.42					
r		0.08				0.35				0.38				-0.05				0.04				0.48

Keys:- AA Atomic Absorption; AA1 direct; AA2 Standard addition; ASV Anodic stripping voltametry; XRF X-ray fluorescence; ES emission spectroscopy
 (C) Institute used commercially prepared standard to determine unknown except for metals with asterisk
 v Coefficient of variation, and correlation coefficient.
 check - metal content of returned subsample

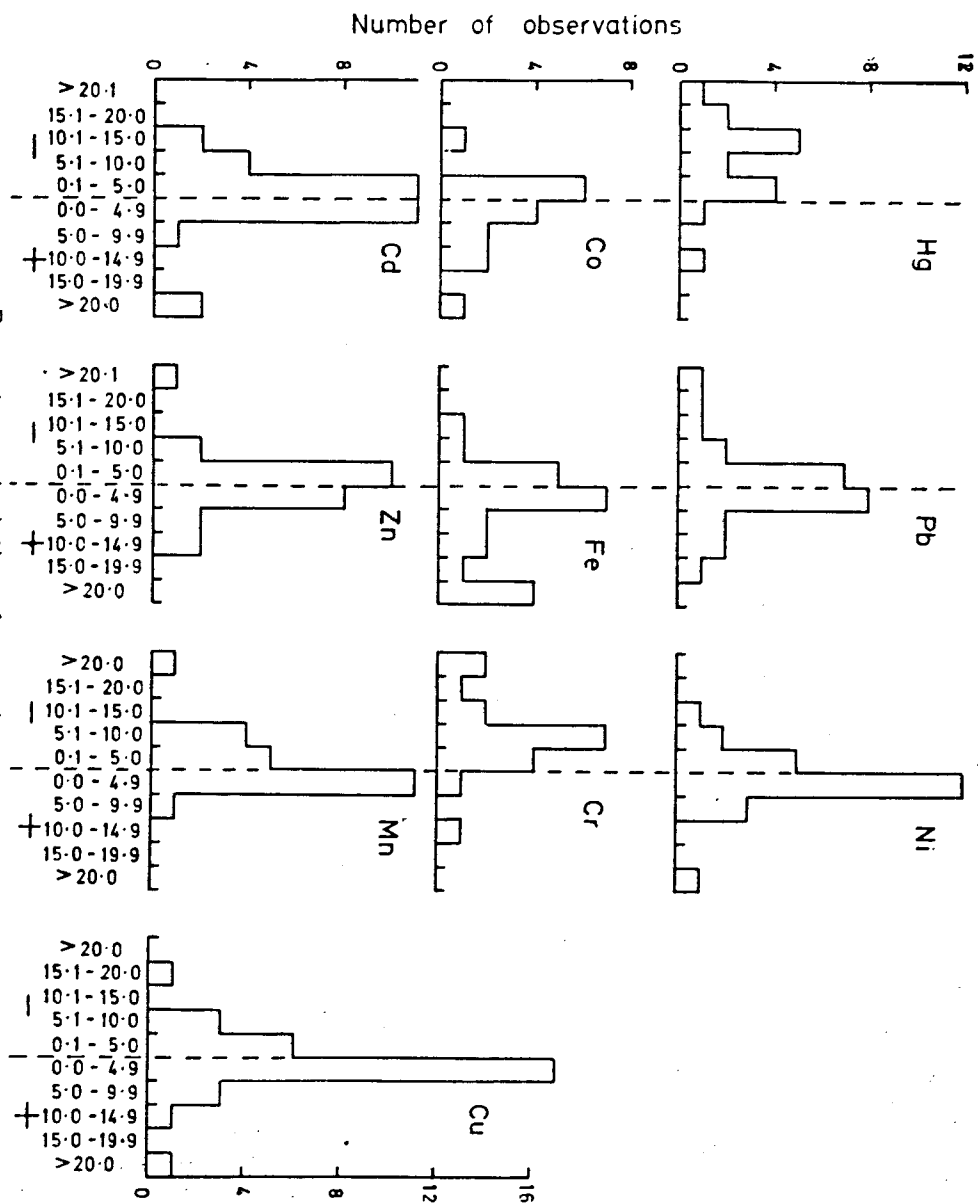


Figure 1. Results of trace metal intercalibration exercise in histogram form