

IMPORTANCE AND SIGNIFICANCE OF INTERCALIBRATION EXERCISE IN MARINE CHEMICAL STUDIES

Tariq Kureishi, Sujata Sanzgiry, Analía Mesquita & R. Sen Gupta
National Institute of Oceanography
Dona Paula, Goa 403 004

INTRODUCTION

The purpose of any intercalibration exercise in marine chemical studies is to assess the ability of the laboratories and personnel to determine accurately concentrations of different constituents in various segments of the marine environment. The need for such an exercise gathers momentum because of the complexity of the behaviour of these constituents and their environmental significance in the marine environment. Further, since the levels to be determined range from nanograms to milligrams i.e., ppt to ppm the alteration in their concentrations could be caused by the analyst at any or all of the following steps.

1. Sampling techniques and gears employed.
2. Storage so as to ensure the stability of the insitu level of the constituent.
3. Processing - To ensure neither loss nor addition of a particular constituent under study.
4. Analytical technique - employment of an accurate, sensitive and reproducible technique.

The intercalibration exercise is therefore designed to permit a check on both precision and accuracy in recovering spikes from a given sample using the various techniques routinely followed by the analysing laboratories. This gives the variations and errors systematic or otherwise, prevalent in the final results supplied by the analyst. Thus one can foresee the role of intercalibration exercise in a coordinated programme where a number of laboratories are independently responsible for collection, interpretation and comparison of data from different areas of study. Even a coordinated effort to put together the concepts, arising from the wealth of data available needs consistency and

reliability. If one has a look at the tremendous volume of data concerning marine chemical constituents one would find a wide variation, which makes the task of a marine scientist even more difficult for a conclusive interpretation. This variation however, need not always arise from the shortcomings of the analysis but could also be a natural phenomenon as well.

Keeping this in view, the International Council for the Exploration of the Seas (ICES) had initiated a series of intercalibration exercises in the early seventies. This was later on taken over by the Intergovernmental Oceanographic Commission (IOC) with the help of United Nations Environment Programmes (UNEP). These exercises were conducted for the various UN action programmes for example in the Baltic and in the Mediterranean and were later extended to other oceanic areas of the world.

Successful international intercomparisons include a work on lead in sea water by Patterson¹, mercury and cadmium by Bugawara², the Baltic trace metals by Kremling³, the ICES sea water intercomparison reported by Jones and Topping⁴, the IOC intercalibration reported by Bewers et. al.^{5,6} the ICES/IOC intercomparison on the determinations of petroleum hydrocarbons⁸.

To cite a few examples of intercalibration exercises related to various kinds of environmental chemical constituents, the results submitted by various participating laboratories have been given in Tables 1-7.

DISCUSSION

Tables 1A and 1B give the results of the determinations of petroleum hydrocarbons of different origin in biological tissues. For this exercise the authors mention a 57% response by the laboratories. This can be considered fairly good taking into account the usually occurring unexpected complications (UOUC), these laboratories develop after their initial commitment to participation. These UOUCs are an integral part of any intercalibration exercise even though such exercises are always voluntary and open to participation, without any stringent strictures on the methodologies to be adopted. One of the conclusions drawn from the above exercise on petroleum hydrocarbons was that published data on hydrocarbons in tissue samples should be cautiously compared. As rightly observed by the authors differences in hydrocarbon between different regions or changes in concentrations over time based or comparisons among data from different laboratories cannot be accepted as real differences unless they are greater than approximately 80-120%. This is evident from the results produced from Tables 1A and 1B.

Table IA - U.V.-Fluorescence Data; Chrysenes Equivalents
(10⁻⁶ g/g dry weight)

Laboratory #	n	ave.	±	s.d.	c.v.
6	3	53.5	±	1.1	2%
8	3	9.63	±	0.35	4%
10	2	27.5	±	0.14	1%
11	1	6.0			—
12	2	12.4	±	1	8%
14	3	103	±	21	20%
17	3	12.8	±	1.7	13%
20	3	8.0	±	1.5	19%
21	3	27.8	±	4.0	14%
22	3	61	±	95	156%
24	2	26.3	±	3.3	13%
25	3	21	±	15	71%
26	3	14.4	±	1.9	13%
29	2	4.38	±	1.4	32%
30	3	45	±	2.5	6%
31	3	9.80	±	5.2	53%
32	2	7.22	±	1.5	21%
37	3	29.5	±	2.8	9%
42	2	11.9	±	3.0	25%
47	2	12.8	±	1.3	10%
48	5	14.1	±	1.5	11%
50	3	6.5	±	1.4	22%
22	\bar{x} = 24	±	24	100%	
Outliers eliminated by t tests (see text)					
18	\bar{x} = 14.6	±	8.2	56%	

Source : ICES/IOC Intercomparison Exercises on the determination of petroleum hydrocarbons in biological tissues (mussel homogenate) - ICES(2/HC/BT).

Table IB - U.V.-Fluorescence Data;
EPA/API Arabian Light Crude Oil Equivalents

(10⁻⁶ g/g dry weight)

Laboratory #	n	ave.	±	s.d.	c.v.
6	3	358	+	21	4%
8	3	84	±	3.1	4%
11	1	80	—	—	—
10	2	336	+	1.1	.3%
12	2	101	±	0	0
14	3	704	+	134	19%
17	3	56.3	±	2.3	4%
20	3	32	±	5	16%
21	3	116	±	17	15%
22	3	720	±	98	14%
24	2	238	±	30	13%
25	3	70	±	50	71%
26	3	181	±	23	13%
29	2	37.9	±	19	33%
30	3	285	±	36	13%
32	2	29.7	±	.03	.1%
37	3	145	±	27	19%
43	3	658	±	159	24%
47	2	121	±	10	8%
48	5	130	±	19	15%

20 $\bar{x} = 235$ ± 234 98%

No outliers identified by t tests (see text)

The results of the exercise conducted by ICES/SCOR on another important environmental parameter namely chlorinated hydrocarbons, are presented in Table 2. In spite of various problems that arise in reporting data for residual chlorinated hydrocarbons most of the laboratories have reported values close to the true ones. However, variations in results of the individual components do occur. The range of standard deviations and the percentage deviations from the true value are given in Table 2. Significant conclusions have been drawn from this exercise, namely,

- Chromatograms should be asked from the various participants in order a critical evaluation be made.
- Two spiked samples should be distributed so that the reproducibility of the results can be determined.
- Emphasis on a single analysis as is normally the case in biological material.

Table 2: Results of the analyses of maize oil intercalibration Sample 5B.

Laboratory	Reverted values in $\mu\text{g/g}$				Percentage deviation from true values														
	Lab. 1	Lab. 2	Lab. 3	Lab. 4	Lab. 1	Lab. 2	Lab. 3	Lab. 4	Lab. 5	Lab. 6	Lab. 7	Lab. 8	Lab. 9	Lab. 10	Lab. 11	Lab. 12	Lab. 13	Lab. 14	
Lab. 1	74	31	54	-	170	190	244	340	1300	0.47	0.12	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
Lab. 2	74	31	54	86	86	170	210	460	970	0.51	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
Lab. 3	44	24	46	-	64	179	800	2000	1000	-	-	-	-	-	-	-	-	-	-
Lab. 4	-	-	-	-	79	77	96	396	396	-	-	-	-	-	-	-	-	-	-
Lab. 5	-	-	-	-	108	108	108	444	990	-	-	-	-	-	-	-	-	-	-
Lab. 6	34	39	46	-	118	170	390	470	480	0.42	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
Lab. 7	30	48	46	97	97	200	400	500	1100	0.46	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
Lab. 8	34	46	45	103	103	307	148	570	370	0.47	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
True values	55	47	50	500	500	218	500	1000	1000										
Mean	43	48	51	61	118	187	343	490	970										
Standard deviation	4.7	4.7	5.2	21	35	65	54	51	146										
Standard deviation as percentage of mean	11	10	10	36	30	35	16	11	15										

* value omitted.

Source : Cooperative Research Report No. 63.

- d) A realistic samples should be included so that the extraction and fat determination steps could be checked.

In response to a general awareness of the impact of metal contaminants, as well as a growing concern for accurate measurements of trace elements in establishing true baseline levels in seawater and biological tissues, the ICES, IAEA and IOC have conducted several intercomparison exercises during the last decade.

Table 3 summarizes the findings of five intercomparison exercises conducted from 1971-80 by the ICES in biological tissues. In the Table the data submitted by each participating laboratory is clearly identified and consists of ranges of mean values, grand mean values and interlaboratory standard deviations (SD) and coefficients of variation (CV). Although no standard analytical technique was imposed, most of the participants used flame atomic absorption spectrometry (AAS) for the various analysis. However, with the subsequent introduction of heated graphite furnace a number of the analysts switched over to this mode. The cold vapour technique was adopted for mercury.

The overall results of this study as evident from the table showed a progressive improvement in the analysis of Cu, Zn and Hg by the participating laboratories especially those who took part in all the five intercomparison exercises, thereby suggesting that analytical data produced by these laboratories for the above mentioned metals in fish and shellfish tissues are comparable. The Pb and Cd data reported by most of the analysts were poor in terms of comparability and accuracy especially at low concentrations, where the range of values covered more than one order of magnitude.

In 1982 the IOC/GEMSI conducted an Intercomparison Exercise for trace metals in biological tissues and standard solutions in which the NIO was the only participant from India. The results of the analyses as submitted in a report to the participants⁶ are presented in Tables 4A-E. For each metal the mean values, standard deviation, coefficient of variation together with the true metal concentrations in the aqueous solutions and the consensus values in the ICES reference materials have been included, and discussed individually.

Copper. (Table. 4A)

All the results of the copper analysis show that the concentrations reported, 720-960 µg/m³, are in excess of the true concentration 700 µg/ml. Small deviations in the range + 30 µg/ml were attributed to errors in dilution, as well as preparation of the standard solution by the

authors⁹. Deviations in excess of 750 µg/ml were probably due to the inaccuracy of the working standards. For the ICES reference materials DP/UT and DP/TW the mean values and the standard deviations excluding the outliers are 4.1; 1.6 µg/g dry wt. (CV 39%) and 1.8; 0.09 µg/g dry wt. (CV 50%) which compare well with the ICES analytical results of these samples i.e. 3.8±0.7 dry wt. (CV 18%) and 1.8±0.7 dry wt. (CV 39%) except for the coefficient of variation reported for UT which is twice that reported by the ICES.

Zinc (Table 4 B)

The results in the table indicate the significant spread of zinc values 474-818 µg/l in CZ1 standard solution. Out of twenty three laboratories sixteen reported values more than +5% outside the true values, two reported values 30% higher than the true value and one reported a value 25% too low. For the ICES reference materials DP/UT and DP/TW the mean values and the standard deviations reported by twenty two laboratories 41.7±6.4 (CV 15%) and 20.8±7.4 (CV 35%) compare well with the ICES reported value. of Pb data.

Mercury (Table 4C)

Only three laboratories submitted acceptable data i.e. 5% deviation from the true value in the mercury standard solution. The mean values and the standard deviations for the reference materials DP/UT, DP/TW and DP/EP which were spiked with different concentrations, compare well with the consensus value except for DP/EP which had a low concentration of mercury 0.06 ± 0.03, and the mean reported value is twice the ICES value. An interesting observation made, that though 50% of the participants produced acceptable data for one or more samples which ranged from 0.04 - 0.8 µg/g only 25% produced acceptable results for all three samples.

Lead (Table 4D)

As seen from the table only six laboratories submitted acceptable values for the standard solution VP2 i.e. 5% deviation from the true value. Three laboratories produced 30% higher values and one value was 50% the true value. However for the reference materials disappointing results were observed as seen from the difference between the ICES consensus value and the reported value. The poor performance of the analysts with the DP/SS sample which was spiked with a very high concentration of Pb 2.5 ± 0.2 µg/g dry wt. was viewed with much concern by the organizers of the inter-calibration exercise. There is little doubt that only a systematic evaluation of the lead analysis and the adoption of a recommended analytical procedure will lead to a significant improvement in the accuracy and comparability.

Table 3 Summary of the results of the analysis of reference materials distributed in the ICES metal intercomparison exercise (1971-1980)

Element	Exercise	No. of Participants	Range of Mean Values submitted ($\mu\text{mol kg}^{-1}$)	Grand Mean ($\mu\text{mol kg}^{-1}$)	S.D.*	C.V.*	Outliers (or Qualifications)
Copper	1	6	175 - 316	267	47	18	None
	2a	7	130 - 159	144	11	8	None
	3	10	61 - 89	60	11	18	None
	4a	16	46 - 63	28	11	39	<6 as 6
Zinc	1	6	597 - 1220	1010	216	21	None
	2a	7	352 - 490	413	54	11	None
	3	21	428 - 811	581	97	18	None
	4a	36	199 - 566	352	61	18	None
Mercury	1	7	0.45 - 3.5	0.80	0.7	31	One high value (3.5) omitted
	2a	8	3.0 - 6.2	3.5	0.35	10	None
	3	16	3.7 - 6.3	4.7	0.3	10	One high value (6.3) omitted
	4a	33	0.25 - 1.9	1.05	0.35	33	None
	4b	34	0.03 - 1.3	0.4	0.13	56	All < values (two) and two high values (1.05 and 1.25) omitted
	4c	34	0.03 - 1.3	0.4	0.13	56	All < values (two) and two high values (1.05 and 1.25) omitted
Cadmium	1	5	9.8 - 22.3	15.1	6.2	41	None
	2a	7	0.18 - 9.8	6.6	2.6	43	One < value omitted
	3	31	0.19 - 18.8	0.7	0.3	79	All < values (four) omitted
	4a	33	0.03 - 8.6	0.19	0.26	87	All < values (five) and four high values (2.5, 2.8, 3.5 and 5.8) omitted
Lead	2a	32	4.3 - 9.9	7.1	5.8	17	None
	1	6	4.8 - 43.2	26.4	16.3	62	None
	4a	5	6.2 - 14.4	8.6	2.4	28	One < value omitted
	3	21	0.73 - 19.2	5.3	4.3	82	One high value (19.2) omitted
	4a	32	0.96 - 36.0	1.0	0.7	71	All < values (seven) and two high values (13.4, 36.0) omitted
	5b	32	1.06 - 37.4	13.0	6.1	47	Two high values (29.3 and 37.4) omitted
Arsenic	5c	32	0.33 - 15.4	3.6	2.5	71	One high value (15.4) omitted
	4a	16	6.7 - 275	198	56	28	Three low values (6.7, 8.4 and 21.5) omitted

* SD = interlaboratory standard deviation
 * CV = interlaboratory coefficient of variation

Source: G. Topping.

Cadmium (Table 4 E)

The results illustrated in the table indicate that only 4 laboratories submitted acceptable data i.e. (5% deviation from the true value. However the response to the analysis of the reference material DP/TW which had a very low concentration of the metal 0.005 µg/g dry wt. the range of values were 0.01 - 0.85. For DP/UT which had a higher spike of Cadmium 0.04±0.06, six laboratories produced

TABLE 4A Results of the analysis of copper in marine reference materials

Laboratory No	DP/UT µg/dry wt	DP/TW µg/dry wt	VPZ standard solution µg/ml
1	*	*	*
2	2.47/2.38	6.28/6.18	962/963
3	8.16/7.58	2.08/1.95	938
4	*	*	*
5	2.5/2.3	1.3/1.3	890/900
6	3.6/4.0	1.7/1.7	724/720
7	3/3	1/1	782/798
8	3.6/3.6	1.5/1.5	798/798
9	*	*	*
10	4.42/4.40	2.70/2.65	800/794
11	4.3/3.6	1.53/1.50	763/770
12	8.27/8.42	4.70/4.65	950/930
13	11.0/5.7	1.63/1.68	770/767
14	2.7/2.6	1.0/1.2	890/885
15	*	*	*
16	5.02/4.94	1.67/1.61	850/840
17	4.27/4.13	1.88/1.91	830/830
18	3.2/3.0	1.4/1.1	820/810
19	4.13/3.33	1.67/1.66	760/770
20	4.9/5.3	2.5/2.1	734/730
21	4.9/4.9	3.0/2.9	720/720
22	4.3/5.0	2.0/2.2	785/795
23	*	*	776/772
24	1.73/1.90	0.96/1.39	770/766
25	2.49/3.52	0.54/0.61	765/780
26	3.78/3.55	2.67/2.13	820/825

Range of values reported	1.73-11.0	0.54-6.28	720-963
Mean value (SD) CV (outliers)	4.12 (1.64) 40%	1.85 (0.88) 48%	810 (68) 8%
	11.0	6.28, 6.18	none

Probable value based on results of ICES exercises

	3.8 ± 0.7	1.8 ± 0.7	True conc = 700 µg/ml
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* No results submitted
SD = Standard Deviation
CV = Coefficient of Variation

Source : Report on IOC/GEMS/ Intercomparison Exercise for Metals In Biological Tissue.

acceptable data. An interesting fact observed was that two of these laboratories were unable to report acceptable data for DP/IR a sample with relatively high concentration of cadmium.

Table-5.

This table depicts a comparison of results of inter-comparison exercises using reference materials over a period of five exercises. It shows that the various participants in both IAEA and the ICES intercomparison exercises achieved a similar level of performance in the analysis of five trace elements and it also highlighted that the problems associated with the analysis of Cd and Pb are experienced on a global basis.

TABLE 4B Results of the analysis of zinc in marine reference materials

Laboratory No	DP/UT µg/g dry wt	DP/TW µg/g dry wt	CZ1 Standard solution µg/ml
1	43/40	22/19	635/615
2	56.3/55.9	37.8/38.1	816/818
3	40.6/40.8	25.1/27.9	710
4	*	*	*
5	41/40	24/24	650/670
6	42.6/39.4	21.4/20.7	610/615
7	50/51	22/22	670/667
8	31.4/32.0	15.4/16.3	579/579
9	*	*	*
10	45.4/45.3	23.6/23.3	<0.025
11	45.5/43.4	22.9/22.9	589/592
12	42.7/43.0	25.9/26.5	810/780
13	53.9/40.8	21.0/21.9	644/649
14	38/36	0.05/0.05	775/775
15	*	*	*
16	39.8/40.2	21.4/21.0	700/718
17	37.3/37.6	21.0/20.8	650/650
18	43.8/43.5	23.6/22.9	688/685
19	38/41	22/23	670/680
20	44/47	24/23	605/625
21	44/42	22/21	610/590
22	39.0/39.5	20.5/19.7	620/670
23	*	*	644/657
24	40.2/39.9	21.9/22.3	618/640
25	52.5/36.0	5.9/6.0	624/616
26	27.4/25.3	15.9/14.7	477/474
Range of values reported,	25.3-56.3	0.05-38.1	474-818
Mean (SD) CV	41.7 (6.4) 15%	20.8 (7.4) 35%	654 (75) 11%
outliers	none	none	<0.025
Probable value based on results of ICES exercises	38 ± 6	23 ± 4	True conc = 600 µg/ml

* No results submitted SD = Standard Deviation CV = Coefficient of Variation

TABLE 14C Results of the analysis of mercury in marine reference materials

Laboratory No	DP/UT µg/g dry wt	DP/TW µg/g dry wt	DP/EP µg/g dry wt	HG3 Standard solution µg/ml
1	2.2/2.2	0.55/0.5	0.23/0.29	277/278
2	ND	ND	ND	1.26
3	ND	ND	ND	300/300
4	0.91/0.93	0.30/0.21	0.23/0.23	270
5	1.25/1.31	0.26/0.62	1.03/5.41	370/360
6	1.3/1.2	0.24/0.21	0.04/0.03	528/547
7	0.60/0.59	0.12/0.11	0.07/0.07	290/295
8	ND	0.22/0.22	0.046/0.045	248/252
9	1.94/1.68	0.76/0.87	0.14/0.15	315/315
10	ND	ND	ND	266/267
11	ND	ND	ND	260/265
12	0.90/0.85	0.15/0.20	0.03/0.03	268/269
13	ND	ND	ND	290/295
14	0.91/0.90	0.20/0.20	0.048/0.045	267/271
15	0.97/0.95	0.21/0.21	0.050/0.048	260/250
16	0.82/0.80	0.18/0.15	0.027/0.027	273/283
17	0.55/0.49	0.044/0.044	0.18/0.18	0.278/0.285
18	1.03/1.05	0.22/0.22	0.05/0.05	0.278-547
19	1.12/1.19	0.10/0.11	0.035/0.036	282 (29) 10%
20	1.04/0.97	0.26/0.21	0.09/0.09	1.26, 3.1, 3.0, 0.285, 0.278
21	0.77/0.70	0.21/0.21	0.13/0.20	True conc 250 µg/ml
22	0.67/0.79	0.19/0.17	0.055/0.055	CV = Coefficient of Variation
23	0.80/0.83	0.20/0.18	0.24/0.24	
24	0.64/0.66	0.044-0.87	0.027-3.41	
25	0.49-2.2	0.23 (0.15) 62%	3.41	
26	1.01 (0.44) 41%	0.87	0.06 ± 0.03	
Mean (SD) CV				
outliers				
Probable value based on results of ICES exercises	0.85 ± 0.06	0.21 ± 0.07	0.06 ± 0.03	
* No results submitted	ND = Not Detected	SD = Standard Deviation		

TABLE 4D Results of the analysis of lead in marine reference samples

Laboratory No	DP/UT µg/g dry wt	DP/TW µg/g dry wt	DP/SS µg/g dry wt	VPZ Standard solution µg/ml
1	9.6/7.3	10/7.0	10/11	408/380
2	7.7/7.5	1.96/2.01	5.96/5.78	352/352
3	0.31/0.32	0.31/0.12	0.36/1.07	851
4	*	*	*	*
5	0.13/0.22	<0.02	0.47/0.52	380/360
6	7.0/7.1	<5.8	11.2/11.4	315/320
7	4/4	4/3	7/6	306/300
8	0.5/0.5	0.3/0.3	0.8/0.8	330/336
9	*	*	*	*
10	<0.5	<0.5	<0.5	328/325
11	0.32/0.39	0.37/0.30	0.21/0.19	314/316
12	1.10/1.12	0.52/0.47	1.64/1.66	240/251
13	0.69/2.1	0.32/0.22	3.7/1.9	320/310
14	0.9/0.9	0.6/0.5	5.8/6.1	410/395
15	*	*	*	*
16	0.58/0.52	ND	2.85/2.84	363/367
17	<0.26	<0.27	1.85/1.89	359/362
18	<0.2	<0.2	0.56/0.58	340/350
19	<0.36	<0.36	3.7/4.5	330/340
20	6	3/2	15/14	303/299
21	1.11/0.90	0.64/0.38	3.10/3.90	310/310
22	<0.12	<0.12	0.42/0.40	130/130
23	*	*	*	333/333
24	0.37/0.35	0.34/0.29	0.74/0.92	390/396
25	0.48/0.50	0.30/0.31	1.49/1.50	340/321
26	2.37/2.64	ND	5.85/4.78	308/318
Range of values reported	0.13-9.6	0.12-10	0.19-15	130-851
Mean (SD) CV	2.41 (2.86) 120%	1.19 (1.61) 135%	3.91 (3.98) 101%	327 (56) 17%
outliers	all < values	all < values and 10 µg/g	<0.5	851
Probable value based on results of ICES exercises	0.5-1.0	0.02-0.05	2.5 ± 0.2	True conc = 300 µg/ml
* No results submitted	ND = Not Detected	SD = Standard Deviation	CV = Coefficient of Variation	

TABLE 4E Results of the analysis of cadmium in marine reference samples

Laboratory No	DP/UT µg/g dry wt.	DP/TW µg/g dry wt.	DP/IE µg/g dry wt.	CZ1 Standard solution µg/ml
1	*	*	*	*
2	0.64/0.62	0.65/0.60	0.65/0.64	326/324
3	0.09/0.07	0.45/0.16	0.89/0.75	427
4	*	*	*	*
5	0.1/0.1	0.04/0.06	1.2/1.2	530/540
6	0.67/0.77	0.52/0.422	1.18/1.16	405/407
7	<0.2	<0.2	0.6/0.7	360/368
8	ND	ND	0.5/0.6	441/441
9	*	*	*	*
10	0.25/0.22	0.022/0.020	1.93/1.93	465/456
11	0.057/0.061	0.031/0.024	0.62/0.61	394/393
12	0.018/0.021	0.47/0.32	0.44/0.42	625/595
13	0.066/0.079	0.012/0.027	0.39/0.55	438/442
14	<0.1	<0.1	1.3/1.3	520/525
15	0.047/0.043	*	0.79/0.80	*
16	ND	ND	0.72/0.75	479/479
17	<0.11	<0.11	0.77/0.77	450/450
18	<0.1	<0.1	0.60/0.62	448/448
19	<0.15	<0.15	0.93/0.98	460/450
20	0.6/0.7	0.2/0.3	1.1/1.1	405/405
21	0.10/0.17	0.01/0.01	0.72/0.67	390/400
22	0.13/0.15	<0.015	0.60/0.64	320/325
23	*	*	*	430/425
24	0.15	0.047/0.035	1.5/1.5	549/516
25	0.035/0.038	0.08/0.07	0.83/0.84	429/420
26	ND	ND	0.98/0.95	355/345
Range of values reported	0.018-0.77	0.01-0.65	0.39-1.93	320-625
Mean (SD) CV	0.22 (0.25) 112%	0.19 (0.21) 112%	0.87 (0.32) 37%	438 (71) 16%
outliers	all < values	all < values	1.93	none
Probable value based on results of ICES exercises	0.08 ± 0.06	0.005 - 0.010	0.80 ± 0.14	True conc = 400 µg/ml

CV = Coefficient of Variation

ND = Not Detected SD = Standard Deviation

* No results submitted

ANALYSIS OF TRACE METALS IN BIOLOGICAL REFERENCE MATERIALS

Table 5 Comparison of results of intercomparison exercises using marine reference materials

Element	Marine Reference Material	No. of Participants	Range of values $\mu\text{mol kg}^{-1}$	Mean $\mu\text{mol kg}^{-1}$	SD	CV	Reference
Copper	Fish flesh	64	7.9-226	70.7	37.7	53	IAEA (1980)
	Fish flesh	20	42.4-89.5	59.7	11.0	18	Topping and Holden (1978)
	Fish flesh	36	6.3-62.8	28.3	11.0	39	Holden and Topping (1981)
Zinc	Sea plant	67	51.8-675	198	50.2	26	IAEA (1978)
	Copepod	56	70.7-256	121	23.6	19	IAEA (1978)
	Fish flesh	74	61.2-3121	505	122	26	IAEA (1980)
	Fish flesh	21	428-811	581	92	16	Topping and Holden (1978)
	Fish flesh	36	199-566	352	61	18	Holden and Topping (1981)
	Sea plant	75	22-3443	979	260	27	IAEA (1978)
Mercury	Copepod	86	64.3-3779	2433	367	15	IAEA (1978)
	Fish flesh	52	0.9-17.5	2.5	0.7	29	IAEA (1980)
	Fish flesh	16	3.4-6.3	4.3	0.3	7	Topping and Holden (1978)
	Fish flesh	33	0.27-1.85	1.05	0.4	33	Holden and Topping (1981)
	Fish flesh	34	0.05-1.25	0.3	0.2	50	Holden and Topping (1981)
Cadmium	Sea plant	75	0.25-28	1.7	0.7	43	IAEA (1978)
	Copepod	43	0.20-18	1.4	0.7	48	IAEA (1978)
	Fish flesh	41	0.18-9.8	1.5	2.3	150	IAEA (1980)
	Fish flesh	21	0.27-16.0	0.71	0.53	75	Topping and Holden (1978)
	Fish flesh	35	0.05-8.8	0.29	0.24	87	Holden and Topping (1981)
	Crab meat	52	4.7-9.9	7.1	1.2	17	Topping (1982)
Lead	Sea plant	46	1.0-214	6.2	6.2	96	IAEA (1978)
	Copepod	43	3.0-26.7	6.7	1.7	26	IAEA (1978)
	Fish flesh	33	0.68-24.5	3.8	2.9	71	IAEA (1980)
	Fish flesh	21	0.77-19.2	3.3	4.3	82	Topping and Holden (1978)
	Fish flesh	32	0.10-36.0	1.0	0.7	71	Holden and Topping (1981)
Lobster liver	Fish meal	52	1.06-37.4	13.0	6.1	47	Topping (1982)
	Fish meal	32	0.53-15.4	3.6	2.5	71	Topping (1982)

NATIONAL INTERCALIBRATION EXERCISE

With a growing emphasis on meaningful data of various marine constituents an intercomparison exercise was conducted in 1984 by the NIO/DOD/SCOR for National laboratories in nutrient as well as trace metals. The NIO has made a concerted effort in coordinating as well as assessing a wealth of data arising from several institutions engaged in marine environmental studies within the country and in order to have a quality check on the data it was therefore felt that a National Intercalibration Exercise involving laboratories which undertook these analysis be conducted.

Aqueous standard solutions of three different concentrations for each nutrient i.e. phosphate, nitrate and silicate, and reference materials procured from the IAEA -MA-M-2TM was despatched to 17 participants with suitable instructions. Results have been received, so far, from only 7 laboratories for the nutrients and from 3 laboratories for heavy metals.

As seen from Table 6 the response to the National trace metal intercomparison exercise was very poor. Only three laboratories sent in the results with the UOUCs (usually occurring unexpected complications) forming the bulk of the non reporters. Although the UOUCs form an integral part of any intercalibration, but such a large percentage hampers statistical treatment of the data, and therefore no meaningful conclusion could be drawn, thus defeating the very purpose of the intercalibration exercise. However a slightly better response was received to the nutrient exercise with forty one percent of the laboratories reporting results.

Table 7 illustrates the values reported by seven of the participants, together with the range of mean values observed, the mean values as well as the true value for each of the nutrients. For the purpose of this paper the results of each of the nutrients have been discussed separately.

Phosphate

The overall mean values reported for the three standard solutions P/A, P/B and P/C were in good agreement with the true values as seen from the table. However a close look at the range of values reveals the wide spread of values reported i.e. 0.4-3.46 for 1 $\mu\text{g}/\text{L}$, 0.6-4.35 for 2 $\mu\text{g}/\text{L}$ and 1-5.83 for 3 $\mu\text{g}/\text{L}$.

The results reported for nitrate aqueous standards N/A, N/B and N/C are fairly poor, with increasing nitrate concentrations namely 10 $\mu\text{g}/\text{L}$ - 30 $\mu\text{g}/\text{L}$. For N/A and N/B none of the reported values were $\pm 5\%$ of the true value

Table 6 : Results of National Intercomparison Exercise on the determination of heavy metals in mussel tissue - MA - M - 2TM (Exercise conducted by NIO/DOD/SCOR)

Laboratory No.	Element analysed in ug/gm (Mean conc. \pm std. dev.)							
	Ca	Co	Cu	Fe	Pb	Hg	Ni	Zn
1	2.16 \pm 0.38	3.14 \pm 0.71	6.91 \pm 0.19	246.25 \pm 12.60	9.89 \pm 1.80	1.67 \pm 0.08	5.35 \pm 0.33	152.5 \pm 8.4
2			8.39 \pm 0.24			1.12 \pm 0.06		282.5 \pm 7.7
3			0.65 \pm 0.03			1.40 \pm 0.14	1.99 \pm 0.14	1.99

Table 7 : Results of Indian National Inter calibration exercise on the Determination of Nutrients in Sea Water. (Exercise conducted by NIO/DOD/SCOR)

Laboratory No.	Phosphate (µg-D/1)			Nitrate (µg-N/1)			Silicate (µg-Si/1)		
	P/A	P/B	P/C	N/A	N/B	N/C	%	B/B	S/C
1	0.40	0.66	1.0	-	-	-	100.0	77.11	35.00
2	3.66	4.35	5.83	17.66	16.56	37.83	65.69	137.75	171.50
3	0.96	1.59	2.15	18.69	23.14	29.38	106.57	-	150.07
4	0.99	1.05	-	8.17	17.48	17.73	75.28	-	151.87
5	1.40	2.18	3.22	0.02	0.04	0.05	101.0	145.0	201.0
6	1.0	1.9	2.91	9.1	18.0	24.5	98.0	148.0	196.0
7	1.25	2.05	2.68	12.60	-	-	86.8	149.3	193.7

Range of values reported: 0.4 - 3.66 - 4.35 - 5.83 - 17.66 - 18.69 - 23.14 - 29.38 - 37.83 - 106.57 - 149.3 - 201

Mean: 1.38 ± 0.81 - 2.09 ± 1.03 - 2.96 ± 1.46 - 11.04 ± 6.29 - 17.04 ± 9.14 - 21.89 ± 12.73 - 83.26 ± 27.78 - 119.63 ± 46.52 - 156.70 ± 65.00

True value: 1.0 - 2 - 3 - 10 - 20 - 30 - 100 - 200 - 300

i.e. equivalent to 0.5 and 1 $\mu\text{g}/\text{L}$ for 10 and 20 $\mu\text{g}/\text{L}$ respectively. Two laboratories for N/A values (30% of the true value and the rest of the values were 75% too high. The rest of the values reported for N/B were (30% of the reference value). As observed from the table only one of the reported value was +5% of the relevant N/C value while all the rest lie in the (30% of the true value range).

In general, the silicate values reported deviated most from the true value with the percentage error ranging from 16.5 for the 100 $\mu\text{g}/\text{L}$ standard to 52% for the 300 $\mu\text{g}/\text{L}$ standard.

It was however felt that the differences observed in the nutrient analysis could

- a) Reflect the inaccuracy of the individual laboratory's working standards.
- b) Errors arising from faulty instrumentation.
- c) Errors in calculations rather than faulty standards. Thus only a concerted effort from all the participating National laboratories as well as the subsequent intercomparison exercises might improve the accuracy and the comparability of the data.

CONCLUSION

The various Intercalibration Exercises conducted both Internationally and on the National front in marine chemical constituents, highlight the range of differences that occur in the analysis of these constituents, due to simple errors in dilution to the preparation and storage of working standards, faulty instrumentation, unsuitable methodologies and sometimes even miscalculations. This has brought about a general awareness about the various pitfalls encountered at every stage of analysis. The identification of these significant differences will subsequently lead to the adoption of a common procedure which will ensure an improved comparability of data. The most significant achievement of these exercises is that most of the analysts are convinced about the importance of regular participation and continuation of intercomparison exercises in relation to the harmonization of the methods leading to a general improvement in the accuracy and comparability of data as well as the immense help these exercises have been to analysts with limited experience. The interpretation of data from various laboratories into a coherent set requires an assessment of the data reported and thus there is a need for more and frequent intercomparison exercises.

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