International Council for
the Exploration of the Sea

C.M.1972/C:21
Hydrography Committee

Report on the ICES/SCOR Nutrient Intercalibration Experiment, September 1972

In the first progress report two years ago preliminary results from 36 laboratories was given. As samples were distributed to 55 institutes several attempts have been made to get the missing results, however, with no greater success. Today are available data from 44 laboratories, and of these 41 sets can be used in the statistical treatment. Most regrettably is, that no data from the Soviet Union are sent in.

Preliminary results for data recieved after 1970 are given in appendix 1.

In a short report to SCOR early this year the evolution of the intercalibration experiment was outlined as follows:

Draft to Table of Content:

- Introduction
- Participating laboratories
- Description of the study
  - Preparation of the samples
  - Analytical methods
  - Glossary of terms
- Results
  - Tabulating of all data including statistics
  - Results in figures
- Discussion and conclusions
- Acknowledgements

The draft to the main Table is given in appendix 2. The data must be arranged as shown, because four batches of samples

with slightly varying concentrations were distributed.

For the Figures it has preliminary been decided to draw them as two sample charts as suggested by Youden (1967).

All data are now tabulated and available for computer treatment. The final arrangement will be discussed during the ICES meeting.

Already now the following general conclusions can be drawn:

PHOSPHATE: The Murphy and Riley Mixed reagent method was used in 28 laboratories, and the same method with ascorbic acid added separately in 8 laboratories. Stannous chloride as the reducing agent was used in 5 experiments.

From the data the relative error of accuracy, equal to the mean error expressed as a percentage of the true value, can be estimated:

At the low level, 0.2 ugat.dm^{-3}, the accuracy is $\pm$15 %, with a predominant negative trend.

At the medium level, 0.9 µgat.dm^{-3}, the accuracy is $\pm$ 6 %, with the same negative trend, and

At the high level, 2.8 ugat.dm^{-3}, the relative error in accuracy is $\pm$ 2 %, with the same trend to negative values.

In very few cases the error was greater than 20 per cent.

Between the various methods no significant difference could be traced.

SILICATE: This nutrient was determined i) by measuring the yellow color of silicomolybdic acid formed, and ii) by reducing the last mentioned complex with methol to a blue complex. Only 6 laboratories used the "yellow" method. Between the to modifications no difference in accuracy was observed.

At the low level, 4.5 µgat.dm^{-3}, the relative error of accuracy was ± 4 %, favoring positive values, at the medium level, 45 µgat.dm^{-3}, the relative error was ± 2.5 %, with no significant trend to positive or negative values, and at the high level, 150 µgat.dm^{-3}, about 6 % in relative error was observed with a trend towards low values.

As in phosphate experiment an error exceeding 10 per cent was observed in few determinations only.

NITRITE: In all laboratories the method based on the classical Griess reaction was used.
At the low level, 0.2 µgat.dm^{-3}, the relative error of accuracy was ± 5 %, at the medium level, 0.9 µgat.dm^{-3}, the error was ca 2.5 %, and at the high level, 1.8 µgat.dm^{-3}, the relative error of accuracy was also ca 2.5 %.

At all levels a slight positive trend was observed.

NITRATE: In 23 laboratories nitrate was reduced in a column filled with copper treated cadmium. Nine laboratories used amalgamated cadmium, 5 laboratories the hydrazine reduction method, in 2 laboratories nitrate was reduced with zinc powder, and in one the old strychnidine method was used. For the three last mentioned methods the data are too few to make a comparation with the Cd-reduction methods possible. A skilled chemist, familiar with these old methods, get good results, however, one must keep in mind that the samples were articifial.

In general the relative error of accuracy has been rather good:
Low level, 0.5 µgat.dm^{-3}, about 2 %,
Medium level, 9.0 µgat.dm^{-3}, about 3 % and at
High level, 30.0 µgat.dm^{-3}, about 3 %.

The percentages given are valid for all laboratories at the low level, but only for about half of the material at the medium and the high level, where the error in many cases exceeded 10 per cent. Several laboratories reported, that

they have had trouble with their columns and a further study of the reduction with cadmium is of urgent need.

In the intercalibration experiment there was an intention to study the effect of phosphate in the determination of silicate and vice versa. The data are available, however, the treatment of the material is complicated because of the fact, that there is definitely silicate in various amounts in the phosphate samples and it is impossible to decide, wheather the response of the silicate reaction to the phasphate samples is due to the phosphate or to the silicate dissolved from the walls of the ampoules. At this moment it seems that this study must be abondoned.

Already in 1970 the Woking Group on chemical analysis of seawater discussed the use of standards from the Sagami Chemical Research Center in Japan for nutrients in future international expeditions, and it was agreed that these standards will form a much more uniform basis for future nutrient analysis.

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Paper C:21, appendix 1.

Preliminary Results, data recieved after 1970.

Continuation of the list given in paper C.M.1970/C:33

Deviation of the mean from the correct value in $\mu gat.dm^{-3}$.

			Low	Medium	High
38.	P	M.R.C.	-0.095	-0.13	-0.03
	Si	Blue	+0.05	-2.6	-16.6
	NO_2		+0.01	+0.02	+0.03
	NO_3	Cd-Cu	+0.05	-0.25	+0.6
39.	P	M.R.M.	-0.025	-0.025	-0.04
	Si	Blue	+0.02	+0.8	-0.1
	NO_2		+0.006	+0.03	+0.03
	NO_3	Cd-Cu	+0.02	-0.01	-1.1
40.	P	M.R.M.	-0.035	-0.07	-0.02
	Si	Blue	+0.09	-0.7	-2.2
	NO_2		+0.04	+0.01	+0.04
	NO_3	Cd-Cu	-0.04	-2.2	-5.3
41.	P	M.R.M.	-0.04	-0.31	-0.38
	Si	Blue	+0.12	-6.6	+10.1
	NO_2		-0.04	-0.03	-0.07
	NO_3	Cd-Cu	-0.05	-0.09	-0.8
43.	P	$SnCl_2$	0.	-0.006	-0.1
	Si	Blue	-0.28	-0.7	-6.1
	NO_2		+0.01	+0.03	+0.02
	NO_3	Strychnidine	-0.17	-0.7	-0.2
44.	P	M.R.M.	-0.065	-0.07	0.
	Si	Blue	+0.1	-0.7	-21.3
	NO_2		-0.01	0.	+0.1
	NO_3	Cd-Cu	-0.04	-0.3	-1.5

Paper C:21, appendix 2.

Draft to the main Table

Phosphate

	Low	Medium	High	Stand.dev. each part. (n-1)	Correlation coefficient
True value	0.270	0.900	3.100		
Lab No. Method Code					
	.	.	.		
	.	.	.		
	.	.	.		
	. mean	. mean	. mean		
	.	.	.		
	.	.	.		
	.	.	.		
	. mean	. mean	. mean		
Total mean					
True value	0.225	0.991	2.860		
Total mean					
Total Standard Deviation					