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International Council for the
Exploration of the Sea

C. M. 1967/C:26
Hydrography Committee

The intercalibration of the methods for silicate determination

Copenhagen 1966

by

Karsten H. Palmork

Institute of Marine Research, Directorate of Fisheries, Bergen, Norway.

The intercalibration of chemical methods which was carried out in Copenhagen 1966, also included the methods in current use for the determination of reactive silicate. The work was carried out onboard four of the participating ships by scientists and technicians from the following five institutes:

1. Fisheries Laboratory, Lowestoft
2. National Institute of Oceanography, Surrey
3. The Institute of Marine Research, Helsinki
4. The Institute of Marine Research, University of Kiel
5. Institute of Marine Research, Bergen

Samples were collected from five different locations on the morning of 30. September and they were analysed during the afternoon and evening of the same day.

Methods:

Three of the participants used a method based on that of Mullin and Riley (1955), modified by Strickland (1965).

Their reagents prepared as follows:

1. Molybdate reagent: 8.0 g ammonium paramolybdate was dissolved in about 600 ml distilled water. 24 ml of concentrated hydrochloric acid made up to 1 liter. Stored in a polythene bottle.
2. Metol-sulphite solution: 12 g of anhydrous sodium sulphite was dissolved in 1 liter of distilled water and 20 g of metol (p-methylaminophenol sulphate) was added and when the metol had dissolved the solution was filtered through a No. 1 Whatman filter paper and stored in a polythene bottle. Lowestoft filtered through a glass fibre paper, Bergen stored the solution in a glass bottle.
3. Oxalic acid solution: A saturated solution of oxalic acid was prepared by shaking 100 g of $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ with 1 liter distilled water and decanted before use.

4. Sulphuric acid solution 50% v/v: 500 ml of concentrated H_2SO_4 (Sp. G. 1.84) was mixed with 500 ml of distilled water and the volume made up to 1 liter.
5. Reducing reagent: 100 ml of metol-sulphite solution was mixed with 60 ml of oxalic acid solution, 60 ml of 50% sulphuric acid was added and the mixture made up to a volume of 300 ml with distilled water. This solution was made for immediate use.

Procedure:

Samples for analyses were between 18-25°C.

10 ml of molybdate solution was added to a dry glass container fitted with a stopper, Lowestoft used polythene bottles, 25 ml of sample was added and the reaction mixture allowed to stand for 10 minutes at least, but not more than 30 minutes. The reducing reagent, 15 ml, was added rapidly with mixing.

After 3 hours, Lowestoft 1 hour, the optical density was recorded at 810 m μ against distilled water on a Unicam Sp. 500 spectrophotometer.

For each sample low in salinity, samples nos. 3, 4 and 14, corrections were made according to Strickland (1965).

Helsinki used the method based on the reaction of silica and molybdate forming β - silicomolybdic acid at pH 1.8. The absorbance of the yellow compound was measured at 350 m μ .

All reagents and distilled water were stored in polyethylene bottles, the reactions were also performed in polyethylene bottles and the reagents were added with nylon syringes of the Krogh type.

The silica content of the distilled water was determined by concentrating a known amount in a platinum dish and analysed for silica.

The reagents were as follows:

reagent A: 1.1 N sulphuric acid

reagent B: 3.7 % ammonium molybdate solution.

Procedure:

35 ml portions were measured with 50 ml measuring cylinder, and 1.0 ml of each of reagent A and B were added while mixing. The absorbance was measured after 20 to 60 minutes in a 10 cm cell, using air as reference, in a Coleman Autoset spectrophotometer, deuterium lamp being the light source. The wavelength was 350 m μ , the band width fixed at 2 millimicrons and with digital reading with maximum 1.750.

Corrections for salinity and phosphate contents of the samples were made according to given tables.

Kiel used the method based on the reduced β - silicomolybdate (Grasshoff 1964). Metol sulphite was used as the reduction reagent. The reduction and formation was performed at pH 2-2.1.

Reagents were prepared as follows:

- a) hydrochloric acid 0.75 N.
- b) 60 g of sodium molybdate in one liter of distilled water.
- c) 20 g of metol and 12 g of sodium sulphite were dissolved and made up to about 3.5 liter with distilled water, and then 36 ml of 5 N sulphuric acid was added and the volum made up to 4 liters. Sodium chloride solutions ~~was~~ ^{were} prepared according to the salt content of the sea water samples.

Procedure:

Kiel was using the Technicon Auto Analyzer system as described by Grasshoff (1965).

Table 1 gives the instrumentation of the participants, the wavelengths and cuvettes used for taking the measurements. The preparing of the standards were the same for all the participants, namely by fusing a weighed amount with sodium carbonate untill clear and to dissolve the melt in distilled water. Bergen used a standard supplied by Lowestoft for the Norwestland III cruise 1963, which had been kept in the refridgerator in a screw capped polythene bottle.

Results of the intercalibration:

Standards from the different participants have been analysed for control by Helsinki, partly by Kiel and partly by Lowestoft. The results are listed in Table 2. Each participant analysed samples in triplicate from five different stations.

Table 3 gives the results of the intercalibration trials with standard deviations of each participant and of each station. The standard deviation, (Table 3), is based on the formula

$$S = \sqrt{\frac{1}{n} \left[\sum_{i=1}^n x^2 - \frac{1}{n} \left(\sum_{i=1}^n x \right)^2 \right]}$$

The precision is given as two standard deviations, as prescribed by Strickland.

Standard deviations were also made excluding the Kiel values for Kattegat and Øresund and the Helsinki values for Kattegat and North Sea surface.

An attempt was made to find a significant correlation between the grand mean silicate content of each sample and the participants deviations from this mean. The calculations were performed using the following formula:

$$r = \frac{\sum_{i=1}^n x_i y_i - n \bar{x} \bar{y}}{n S_x S_y}$$

The results are given in Table 4. The Table also shows the difference between mean values of each participant and grand mean in $\mu\text{g. atoms SiO}_3\text{-Si/l}$ and the probability.

Concluding remarks:

Four of the participants have used the reduced β -silicomolybdate as bases for their determinations and the fifth participant has used not reduced β -silicomolybdate. Having standard deviations of the magnitude shown in Table 3 and Fig. 1 and extreme values shown in Fig. 1, it is naturally to look at the results obtained by the reduced β -modification alone. If we do so, we find that for samples nos. 1, 4 and 10, the standard deviation will decrease. However, regarding the four participants using manual analysis techniques, leaving the auto analyser out, we get a small decrease in standard deviation for the samples nos. 4 and 14, one with high, the other with low silicate content.

Looking at the three participants using the method based on the reduced β -silicomolybdate and manual analyses with the same model of instrument, we get an over-all decrease in standard deviation.

The statistical handling of the results as listed in Table 3 and Table 4, do not indicate a significant difference.

At this stage, having had only one silicate intercalibration, which gave a rather unclear picture, it is not possible to come to a final conclusion and the methods for the determination of reactive silicate have to be further considered in the Subcommittee for chemical analyses of sea water.

References

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Table 1. The participants instrumentation.

Participant	Instrument	Wavelength or filter	Cuvette length in cm
Lowestoft	Unicam SP. 500	810 m μ	1 and 4
N. I. O.	Unicam SP. 500	810 m μ	1.4 and 10
Bergen	Unicam SP. 500	810 m μ	1
Helsinki	Coleman Autoset Spectrophotomet	350 m μ	2.5 and 10
Kiel	Technicon Auto-analyzer	Filter I 651 (660 m μ)	1.5

Table 2. Control of standards.

A.				B.			
Source of standard	Analyst			Source of standard	Analyst		
	Helsinki	Kiel	Lowestoft		Helsinki	Kiel	Lowestoft
Denmark	3.94	20.82	8.00	Denmark	0.99	1.02	1.00
	3.87	20.08	8.05				
	3.88	19.94	8.05				
Kiel	10.12			Kiel	1.01		
	10.20						
	9.94						
N I O	20.16	10.44		N I O	1.00	1.01	
	20.30	10.44					
	20.36	10.49					
Lowestoft	5.01			Lowestoft	1.00		
	5.02						
	4.92						
Bergen	4.90			Bergen	0.98		
	4.86						
	4.92						
Helsinki		35.79		Helsinki	1.00		
		35.33					
		35.56					

(A) Recorded values.

(B) Recorded values divided by theoretical values.

Table 3. Results of the silicate intercalibration trials.

Sample no.	$\mu\text{g atoms SiO}_3\text{-Si/l}$					Stand. deviat. of each particip.	Precision of each particip.
	1	3	4	10	14		
Location Analyst	Kattegat 70 m	Gulf of Bothnia 150 m	Gotland Deep 120 m	North Sea surface	Øresund surface		
Lowestoft	9.01 8.91 9.01	73.15 73.15 73.15	68.43 68.43 67.92	6.24 6.11 6.11	17.23 17.38 17.33	± 0.368	± 0.736
Mean	8.98	73.15	68.26	6.15	17.31		
N I O	9.70 10.50 10.2	74.12 73.35 -	69.00 69.90 70.18	7.30 7.60 8.10	18.39 18.49 18.49	± 0.351	± 0.702
Mean	10.1	73.74	69.70	7.67	18.46		
Kiel	11.45 11.45 11.45	75.09 75.41 75.52	69.67 69.88 69.88	8.49 8.36 8.48	12.43 12.58 12.43	± 0.102	± 0.204
Mean	11.45	75.34	69.81	8.44	12.48		
Helsinki	6.73 6.83	73.92 73.79	67.52 67.65	4.87 4.82	16.50 16.14	± 0.009	± 0.018
Mean	6.78	73.85	67.58	4.85	16.32		
Bergen	9.00 8.90 8.70	74.50 74.50 74.50	68.00 69.10 68.90	6.10 6.00 6.80	16.60 17.00 17.20	± 0.291	± 0.582
Mean	8.87	74.50	68.67	6.30	16.93		
Total mean $\mu\text{g atoms SiO}_3\text{-Si/l}$	9.42	74.17	68.89	6.81	16.30	(A)	
Standard deviation	± 1.457	± 0.81	± 0.882	± 1.217	± 2.109		
Precision $\mu\text{g atoms SiO}_3\text{-Si/l}$	± 2.91	± 1.62	± 1.76	± 2.43	± 4.22		
Grand mean $\mu\text{g atoms SiO}_3\text{-Si/l}$	9.33	74.17	68.89	7.14	17.34	(B)	
Standard deviation	± 0.609	± 0.81	± 0.882	± 0.987	± 0.774		
Precision $\mu\text{g atoms SiO}_3\text{-Si/l}$	± 1.22	± 1.62	± 1.76	± 1.97	± 1.55		

(A) All values included.

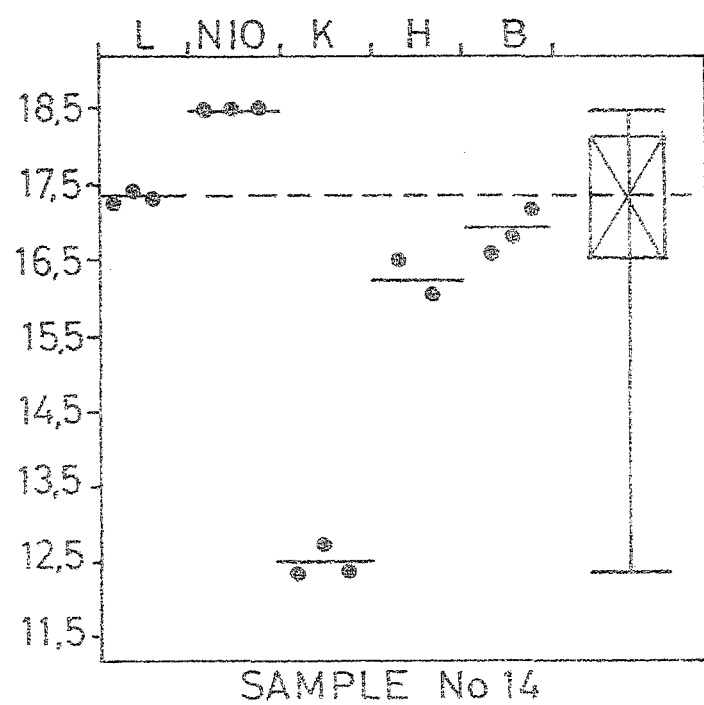
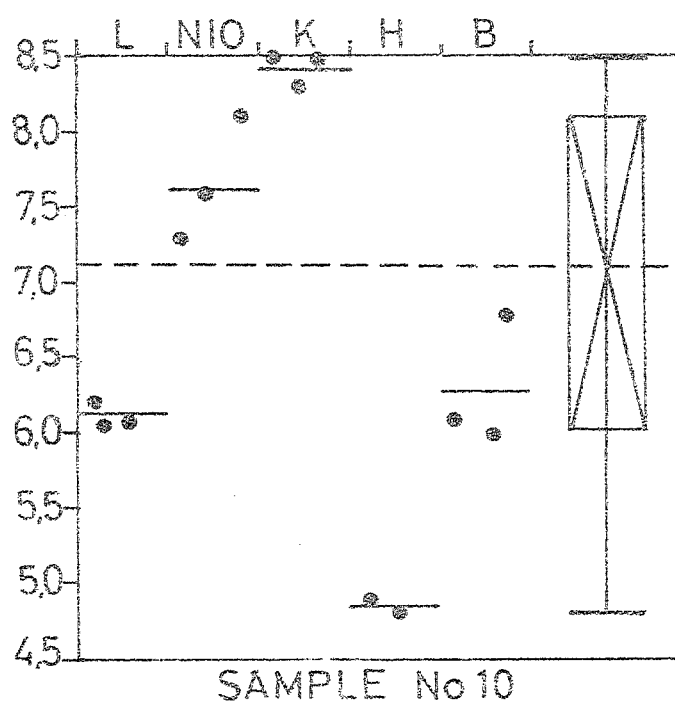
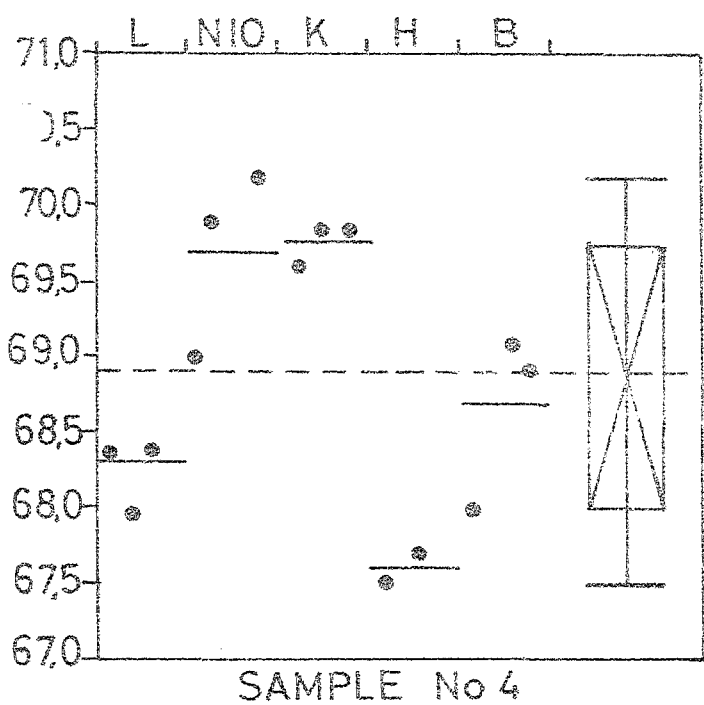
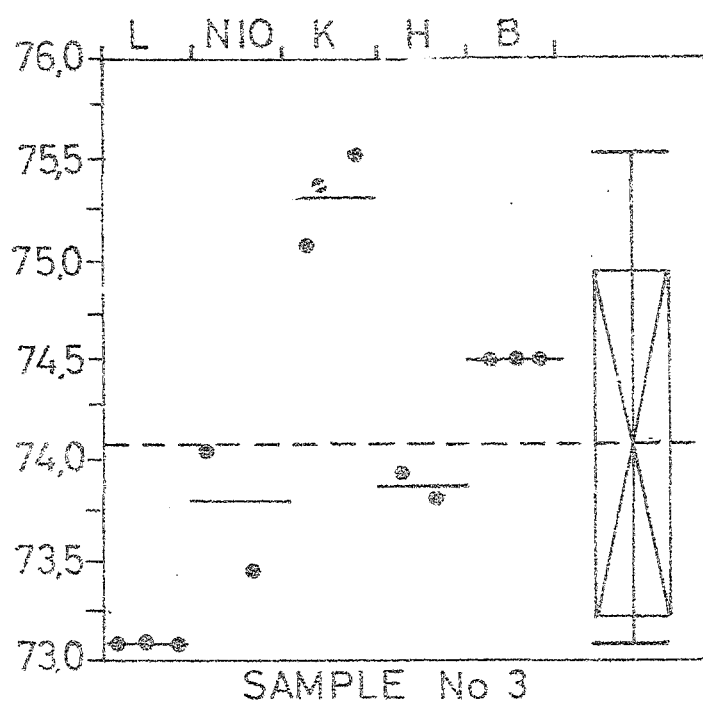
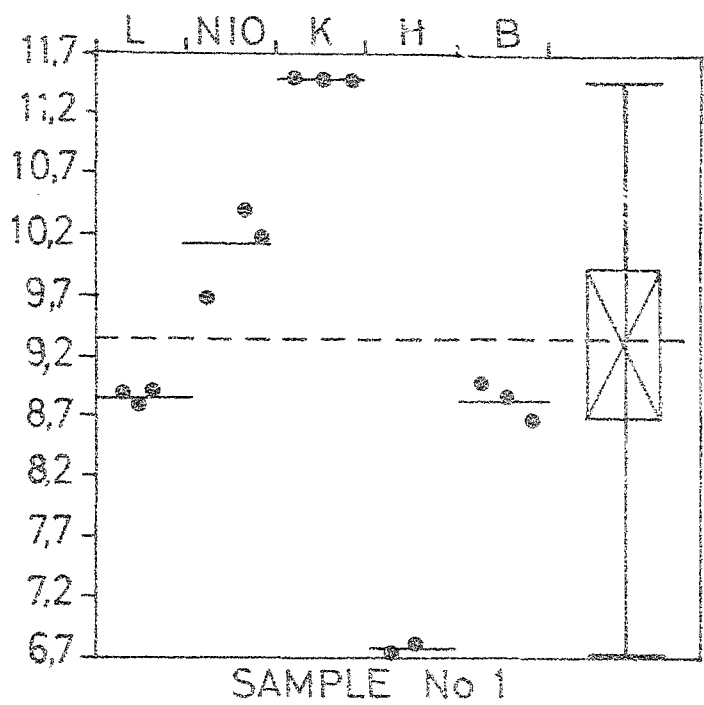
(B) Kiel (Kattegat and Øresund)

Helsinki (Kattegat and North Sea surface excluded).

Table 4. The correlation between the grand mean silicate content of each sample and the participants deviations from this mean.

Sample		Grand mean µg atoms SiO ₃ -Si/l	Difference between mean values of each participants and grand mean µg atoms SiO ₃ -Si/l.				
Number	Locality		Kiel	Helsinki	Lowestoft	N I O	Bergen
1	Kattegat 70 m	9.33	+2.12	±2.55	±0.35	+0.77	±0.46
3	Gulf of Bothnia 150 m	74.17	+1.17	±0.32	±1.02	±0.43	+0.33
4	Gotland 120 m	68.89	+0.92	±1.33	±0.63	+0.81	±0.22
10	North Sea surface	7.14	+1.30	±2.29	±0.99	+0.53	±0.84
14	Øresund surface	17.34	±4.86	±1.02	±0.03	+1.12	±0.41
		Correlation coefficient	+0.199	+0.753	±0.408	±0.566	+0.546
		Probability	>0.8	>0.1	>0.4	>0.3	>0.3

* Total means of participants, excluding Kiel (Kattegat and Øresund) and Helsinki (Kattegat and North Sea surface) samples.



L = LOWESTOFT
 NIO = NATIONAL INST. OF OCEANOGR
 K = KIEL
 H = HELSINKI
 B = BERGEN

--- EXTREME
 --- STANDARD DEV.
 --- EXTREME
 --- MEAN VALUES
 --- GRAND MEAN

FIGURE 1. RESULTS OF SILICATE INTERCALIBRATION COPENHAGEN 1966