

INFORMATION ON THE SYMPOSIUM ON INTERCOMPARISON OF METHODS
FOR HYDROCHEMICAL ANALYSES

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by

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During the period from 20 March to 12 April 1962, the Symposium was conducted at the Black Sea Experimental Research Station of the Institute of Oceanology of the Academy of Sciences of the USSR for intercomparison of methods of hydrochemical analyses being used by oceanographical institutions of the Soviet Union.

The reason for conducting this Symposium was the existence of considerable discrepancies between results of various hydrochemical determinations in the ocean. It is known that the first such intercomparison was carried out in September 1961 with the participation of the research vessel VITYAZ in the Hawaii region during the Tenth Pacific Science Congress. The problem of intercomparison of hydrochemical analyses was further discussed at the First Session of the IOC and at the Fifth Session of the Scientific Committee on Oceanic Research (SCOR). Both IOC and SCOR recommended that similar tests be conducted on national as well as on international levels.

During the Symposium the parallel determination of chlorinity, dissolved oxygen and phosphates from the same freshly gathered samples were carried out. These analyses were made according to the procedures and with the apparatus and standard solutions currently in use by each particular institution in its expeditions and at its coastal stations. The results obtained during these tests were discussed with a view to determining the possibilities of further standardization, perfecting of methods of analyses and sample collection and using new apparatus for hydrochemical determinations in oceanography.

The following institutions took part in this work:

- (1) State Oceanographic Institute;
- (2) Institute of Oceanology, Academy of Sciences;
- (3) Black Sea Experimental Research Station of the Institute of Oceanology;
- (4) Marine Hydrophysical Institute;
- (5) Institut für Meereskunde, German Democratic Republic.

Representatives of other institutions, including Sabastopol Biological Station, took part in the discussion of results.

Water samples were taken from various depths with standard metal Nansen bottles as well as with five litre plastic Nansen bottles from the research vessel AKADEMIK SHIRSHOV at a distance of eight to ten miles from the shore where the
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depth ranged from 1500-1700 meters. Only fixation of samples for subsequent oxygen determination was made aboard ship. Samples for chlorinity and phosphates were collected into glass bottles and delivered to the shore station without any conservation for subsequent analyses. Phosphates were determined 1-2 hours after collection of the samples from Nansen bottles. Dissolving of the sediment and further titration of samples for oxygen determination was done 3-6 hours after collection of the samples and chlorinity determination on the samples' reaching room temperature but not later than 24 hours after collection.

The methods of determination were mostly the same and corresponded to the Manual for Marine Hydrochemical Investigations (Moscow 1959) and to the Instruction for Standard Hydrochemical Determination in the Sea under the programme of IGY. There were, however, some variations in the methods used. For example, the Institute of Oceanology and the Marine Hydrophysical Institute used for the oxygen fixation automatic pipettes and the State Oceanographic Institute used conventional pipettes. There are some differences in the quantity of acid being added for the dissolving of sediment, etc. The Marine Hydrophysical Institute used specially designed photoelectric colorimeter with optical cuvettes 30 cm. in length. The same institute used during determination of large phosphate concentrations (more than 2.5-3.0 mg. atoms per litre) samples diluted with dephosphated sea water. A major deviation from the standard Knudsen method for chlorinity determination was introduced by the German Democratic Republic, the scientists of which used for titration a solution of AgNO_3 which is twice as concentrated (73.75 grams per litre) as standard. Accordingly, the burettes used by German scientists for chlorinity determination have their scale in ordinary and not double millilitres. The same refers to all other measuring glasses. The results of chlorinity, oxygen and phosphate determinations could be summarized as follows:

1. Chlorinity

Altogether 134 determinations were made on 30 samples. Variations in repeated titrations by the same analyst did not exceed 0.02-0.03% Cl. The mean square difference between the results of parallel titrations by analysts from different institutions was found to be 0.012% Cl. The maximum difference of determinations on the same sample was 0.10% Cl. Variations in the results of chlorinity titration as a rule did not exceed the value of the smallest interval of the burette scale (all burettes used were cylinder burettes without a ball).

2. Dissolved oxygen

There were altogether 178 determinations on 52 samples. Collection of Samples was made by the analysts of various organizations simultaneously into two oxygen bottles from each Nansen bottle. The range of oxygen concentration was from 0.1-0.65 mg-atoms/l. The results of 90 parallel determinations by the same institution are given in the following table:

Value of difference of parallel determinations of oxygen micro-gram atoms per litre	0	1	2	3	4	5	More than 5	
Number of cases	18	26	19	10	6	1	10	

If one excludes differences greater than 0.005 mg-atoms/l, then the mean square difference of parallel determinations will be found equal to 0.0019 mg-atoms/l. The differences greater than 0.005 mg-atoms/l could be excluded since they are evidently connected with some unspecified matter capable of absorbing iodine (suspension or plankton?) which had inadvertently got into one of the bottles. In this case titration of samples from this particular bottle gave relatively low results.

The mean square difference between the results of the analyses made by different organizations (average of two parallel determinations) was found to be 0.0049 mg-atoms/l. The following differences were obtained in 64 cases:

Differences in micro-gram atoms/l	0	1	2	3	4	5	6	7	8	9	10	More than 10
Number of cases	8	9	6	5	7	4	3	4	4	5	2	7

The mean square differences between determinations of different organizations was found to be greater than the mean square difference of determinations by the same institution, not only because of the diversion in methods and chemicals used, but also probably due to some additional absorbing of oxygen by water during collecting of samples from Nansen bottles. The change of oxygen concentration in the water kept in the Nansen bottle during the collection of samples i.e. during 10-15 minutes, should be taken into account. It was observed that in many cases the highest oxygen concentrations were related to the samples taken from the Nansen bottles in the last turn. If this possibility is taken into account then an average accuracy of oxygen determination (provided the sample is taken from the Nansen bottle immediately) should be estimated as 1.5-2 times less than the observed mean square difference of 0.0049 mg-atoms/l.

3. Phosphates

Altogether 120 determinations were done on 26 samples. Phosphate concentrations ranged from 0.1 to 5.5 micro-gram atoms/l. Repeatability of parallel determinations by the same analyst and also by analysts of different institutions depended upon the order of phosphate concentration in the sample. The least deviations in both cases were observed in the concentration range from 1.0 to 2.0 micro-gram atoms/l. The average difference in this range amounted to 5%. The maximum absolute differences up to 0.4 micro-gram atoms/l were received for the high phosphate concentrations (more than 4.0 micro-gram atoms/l which amounted to a relative error of 10% of concentration. The first reason for this is a greater speed in the change of coloration of the solution when phosphate concentration is high and the second reason is the low accuracy of coloration comparison when intensity of colour is strong. When phosphate concentrations were very small, the absolute differences were also small (0.02-0.05 micro-gram atoms/l) but relative error rose to 20% of determined concentration. This was due to increased importance of any impurity of chemicals used or inaccuracy of corrections for de-phosphated water when comparison was made between very slightly coloured solutions.

On average, analysts of the State Oceanographic Institute obtained higher values of phosphates concentration for the same sample than analysts of the

Marine Hydrophysical Institute. Visual determinations done by the Institute of Oceanology and photoelectric colorimeter measurements by the Marine Hydrophysical Institute gave rather close results which fall between the results of the State Oceanographic Institute and the visual determinations of the Marine Hydrophysical Institute.

The number of communications concerning accuracy and repeatability of hydrochemical determinations, also the use of new apparatus (conductivity salinometers, refractometers, photoelectric colorimeters, polarographs for oxygen determinations, etc.) were discussed at the Symposium. The possibility of certain changes in hydrochemical characteristics of samples during their contact with Nansen bottle walls was also discussed in connexion with putting into practice of new Nansen bottles made of chemical-resistant materials.

A number of recommendations was approved on the basis of these discussions and analyses of results obtained. In particular, it was recommended that similar intercomparison tests be conducted on a wider scale involving comparison of methods and their subsequent standardization between all oceanographic organizations.

The Symposium pointed out that one of the important sources of errors during hydrochemical analyses is analyst's fatigue. Therefore it was recognized that it is urgently necessary to work out reasonable norms for conducting hydrochemical determinations under field conditions. The Symposium stressed the importance of further work to be done in order to perfect and strictly reglement all methods of analysis and also to improve sampling procedures particularly using Nansen bottles made out of materials not affecting hydrochemical characteristics.

The Symposium noted that in some cases existing instructions and manuals for conducting hydrochemical determinations in the sea were out of date or insufficiently complete in detail.

In conclusion, the Symposium approved a number of particular recommendations concerning standardization and improvement of repeatability in analyses of chlorinity, oxygen and phosphates.