

ANNEX VI

REPORT OF SCOR WORKING GROUP 25
ON
NUTRIENT CHEMISTRY

We have taken our objective to be to consider the possibility of bringing about some measure of uniformity in the methods for the analytical determination of the chemical nutrients in sea water and, if we decide that this can and should be done, to recommend active steps which might accomplish it.

The substances which we have considered to be involved are those conventionally included in oceanographic surveys: inorganic phosphate, nitrate, nitrite, silicate and ammonia. We acknowledge that there may well be other substances involved in the productivity of the sea, but the very fact that there is some question as to the nature of their involvement makes them a separate problem, and we have accordingly limited our consideration to the five first mentioned.

We are aware that this is not a new problem and that other groups have faced the same question as far back as 1935 when a committee was established by ICES under the chairmanship of Hermann Wattenberg, to consider the standardization of methods for plankton nutrients. It may be noted that this committee surveyed the methods then available, but came to the conclusion that it was too early to attempt standardization. At the present time there is another committee of ICES, under the chairmanship of Dr. Klaus Grasshoff, with very nearly the same objective. This group consists of eleven active chemists, in as many different European countries, who are continually carrying out analyses of sea water. To make their work more uniform they exchange their experiences by means of a technical information bulletin issued by ICES. The first of these bulletins has just appeared and its preface contains the following statement:

"Marine chemistry is an expanding science, and this implies an increase of research and survey work in this field. The methods and instruments for sea-water analysis are in a developing stage, and they are, in many cases, far from sufficient. Only practical experience and trials can show whether new methods are suitable and represent improvements. Rapid exchange of experience on new methods and instruments, as well as experiences from intercalibration trials, shall also be among the main purposes of this sheet."

Our survey of current methods for sea-water analysis reveals the fact that for the five nutrient substances with which we are concerned, the present methods are almost without exception colorimetric or spectrophotometric. The universal method for phosphate is the old Deniges reaction ("ceruleomolybdate"), the blue color developed by reduction of the phosphomolybdate complex formed when molybdate and sulphuric acid are added to the sample. Modifications consist of changes in the proportions of reagents, the choice of reducing agent, the time, the temperature and the other conditions under which the reaction is carried out.

The determination of nitrite is one of the simplest and most satisfactory methods, consisting of the formation of a highly colored dye by combination of a coupling agent (such as alpha naphthylamine or, now commonly, N-(1-naphthyl)-ethylenediamine) with the diazo compound formed when the nitrite in the sample is combined with sulphanilic acid or sulphanilamide. This description itself suggests the possible modifications.

Nitrate - long a troublesome factor to analyze - is now universally determined by reduction to nitrite and determination as such. The reducing agent, however, and the conditions under which it is used, are matters of critical choice.

Silicate is determined by a method closely related to that for phosphate. Silicate in the sample forms a yellow complex with molybdic acid (ammonium molybdate plus sulphuric acid) which may itself be measured spectrophotometrically or reduced to a more intense blue

colored compound before measurement of color. While there is latitude for some choice of conditions, the principal choice is whether or not to reduce.

For ammonia there are one or two available color reagents, but they are not altogether satisfactory. A recent suggestion is to oxidize to nitrite and measure as such, but there has been little experience with this method. Old methods involve distillation of some kind and are laborious.

There are various means of making the final measurement in each case. Filter photometers measure the intensity of color in a selected narrow band, while spectrophotometers make similar measurements in still narrower bands, approaching single wavelengths. Numerical results can vary somewhat, depending upon the choice between these two types of instruments. Apparently all present makes of spectrophotometers are equally effective, although this has not been positively confirmed.

Older methods of visual color comparison seem to have been entirely abandoned, although they are available as a last resort.

In any survey of methods from the standpoint of precision we must consider the purpose of our analyses and the use to be made of them. In order to distinguish between fertile and non-fertile areas, for example, a method with an accuracy of, say, two per cent might be satisfactory, while much better precision would be necessary if one were interested in "material budgets", particularly in deep water where differences in concentration are slight. We recognize, of course, the difference between precision, the susceptibility of a method to random errors, and accuracy, the deviation from a true value. It is possible that the recommendation of standard methods should depend upon these considerations.

This brief survey will indicate that at least for the first four of the nutrient substances there is in each case no very fundamental difference in method, but only in rather minor details. However, unless the details are agreed upon results will vary, sometimes considerably. Even when different workers carry out analyses upon the same material by ostensibly identical methods there is sometimes discrepancy in their results which cannot be explained. Reasons for such behavior must be found.

It is our considered opinion that for the nutrients nitrate, nitrite, inorganic phosphate and silicate the development of methods is now sufficiently advanced to offer a hope for uniformity. We do not feel justified as yet, however, in recommending in any case a single, detailed method for exclusive and universal use. This is more particularly true for ammonia, for which available methods are still too uncertain. This situation may well improve, however.

We note a statement in the ICES information bulletin above cited:

"Experience has shown that the single solution method by Murphy and Riley is the best and most suitable phosphate analysis method for routine work at sea".

While this may very well be true, it is nevertheless the opinion of two workers, and others accustomed to some other modification may think it too optimistic. What we need is agreement on such a conclusion.

We therefore suggest and recommend an intercalibration or intercomparison experiment on a large scale, similar to smaller ones which have already been carried out. Uniform samples (probably standard nutrient solutions now available from Japanese sources and whose stability has been proven) should be analyzed independently by a considerable number of institutions, each using its own method. Results might not be conclusive, but at least we would have better information than we now have. If such sample material as this were used it would

not be necessary to collect all workers together or to carry out the project at sea. It must be admitted that certain points in the field procedure would not thus be covered, such as the technique of taking the samples from the sea. Uniformity on these points might well be accomplished by other means.

We believe that further progress toward the standardization of methods, including the planning and administration of an intercalibration experiment such as we have suggested, can only be carried out by an organized group of qualified chemists active in this field. The subcommittee of ICES, already referred to, is in this regard the best qualified one with which we are familiar, although its interest includes other aspects of sea-water chemistry than the analytical determination of nutrients. Since it seems unnecessary and impractical to duplicate the effort, we recommend that SCOR support the activity of this group and ask it to undertake a more intense study and intercomparison of the methods for determination of nutrients, in the hope that such a study may lead to the choice of standardized or recommended methods. We also suggest that SCOR urge its national committees and associated institutes to give increased attention to this important problem and to cooperate in the activities of the ICES group.

We would call attention to the availability of stable standard solutions of all the principal nutrients (from Japan). We believe that the use of these or similar standard solutions is a desirable step in the direction of uniformity of methods.

We issue a strong caution that whatever steps are taken toward uniformity there should be no implied restraint on the search for improvements. Analytical techniques are improving rapidly and it may very well happen that new developments in column or gas chromatography, spectrometry, or radiochemistry, for example, will open up new opportunities and more sensitive methods. Automation of analytical methods is developing rapidly and will become more important in large oceanographic operations; provision for this must be made in any directions for analytical procedures.

Finally, we feel that this Working Group has done the exploratory work expected of it and we recommend that it be discharged and the problem be further pursued in the manner suggested.

N.W. Rakestraw

ANNEX VII

SELECTED RECOMMENDATIONS FROM 8th MEETING
OF
IOC BUREAU AND CONSULTATIVE COUNCIL

LONDON, 10-14 JUNE 1968

8.4 The Bureau, having considered together with the Consultative Council perspectives of further development of the IOC in the light of the proposals made by the Secretary-General of the United Nations under Resolution 2172 (XXI), came to the conclusion that thorough preparatory work is needed in order to formulate in detail the required framework of the future administrative arrangements for the work of the broadened IOC and of its Secretariat. The Bureau decides that this work could best be done by a small group of consultants consisting of the Bureau itself and representatives from SCOR, ACMRR, UNESCO, FAO and WMO. This group should meet in September - October 1968 and produce the appropriate proposals for consideration by the 9th Meeting of the Bureau and Consultative Council in early 1969. These proposals should be made available to the Bureau and Consultative Council not later than 15 November 1968.