International Council for the
Exploration of the Sea

C.M. 1963
No. 133
Hydrographical Committee

The Progress of the Standard Sea Water Investigations 1962-63

by

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A year ago we had established the general principles that there are significant variations in conductivity/chlorinity ratios; that conductivity is very closely related to density at 0°C; that the relationship between chlorinity and density is much less close; and that in consequence if the objective is density measurement, then it is better to measure conductivity than chlorinity as the primary measurement. The special Unesco committee (on which ICES is represented by Messrs. Hermann and Cox) has recommended in its first report (Unesco NS/9/114B of 4 Dec. 1962) that as soon as practicable standard sea water should be certified in conductivity as well as chlorinity. The committee has also recommended the re-definition of salinity as a function of density, and has indicated how the new definition shall be established. For anyone who has not seen this report, copies may be obtained free of charge from the Director, Office of Oceanography, Unesco, Paris VII.

It was very welcome to receive a letter, at the recent second meeting of the Unesco committee in California, from the Academy of Sciences in Moscow. This letter informed the committee that the Antarctic Institute had been investigating chlorinity, conductivity and density of assorted water samples, and confirmed in all respects the major conclusions reached in the British work. We are hoping in due course to hear more details, and to meet the Russian workers concerned.

Although the collection of water samples has continued (including some very welcome Arctic and Black Sea samples from the USSR, and Arctic samples from Canada) most of our work in the last year has been in two fields; firstly, to standardise our present relative measurement of conductivity and density in absolute units, secondly chemical analysis of our samples to try and explain the variations on the basis of the chemical composition.

On the chemical analysis I will not say much here, as my colleague Dr. Culkin will present a second paper covering this field. I will only say that we can explain part, but not yet all, of our variations in chlorinity/conductivity ratio on a basis of changes in the relative proportions of the major ions.

The absolute conductivity apparatus has been seriously delayed by shortage of funds. This will be a relatively expensive instrument, and our Institute has had to outfit our new ship and maintain the expensive Indian Ocean expedition. However we now have promises of financial help from Unesco and IAPO, and will go ahead with this equipment as rapidly as possible. The urgency of this has been increased by the results of checks made on the various batches of standard sea water. Using batches P31 and P33 as standards, we have been checking the conductivity of each new batch, and have found some small variations in the conductivity/chlorinity ratio. The largest variation we have found is in batch P37, where the conductivity is low, relative to the chlorinity, by an amount equivalent to a salinity variation of 0.005‰. An American scientist, Dr. Kilho Park, has made similar checks on a wider range of standard water batches. On the recent batches his results are in fairly close agreement with ours, but in some earlier batches he finds bigger varaiations. These results will shortly be published. Thus it become an urgent and important matter that the standard sea water service shall have this equipment available, so that there shall be no further doubt of the reliability of the standard water as a conductivity reference.

The absolute density apparatus has been finished, and a number of measurements completed. The first measurements of sigma-0 of sea water gave values rather higher than those in Knudsen's tables, relative to the chlorinity. The difference is in the range 0.02 to 0.05 in sigma-0. This corresponds well with some measurements by Thompson and Wirth (J. du Conseil, 1931) where certain Pacific samples averaged 0.03 high.

In the calibration of our apparatus we use pure water at 4°C as reference, this being (by definition) of density 1 g/ml. Having experienced some difficulty in repeating the calibrations, we have prepared pure water samples from different sea waters, by distillation, and have found apparently considerable variations in density between them (of the order of 20 parts per million, 0.02 in sigma). There is still some doubt whether these variations are real, or whether the apparatus is in some way giving misleading values. If the variations are real they probably represent variations in relative proportions of hydrogen-1 and hydrogen-2, and of oxygen-16 and oxygen-18. Such variations are known to cause significant differences in density between natural waters from various sources, at least to an extent of several parts per million, but the magnitude of the variations we find in sea water seem rather large.

However, the existence of variations in density of pure water presents a basic problem. At present sigma-0 is a ratio, the density of the water at 0° divided by that of pure water at 4°C. Hence it cannot be determined directly to a greater precision than we know the density of pure water.

There appear to be two possible approaches. One is to attempt to standardise our densities in absolute units, the gramme and centimetre. This is an axtremely tricky operation, (probably impossible in our present state of knowledge) with sea water, or any other solution in a volatile liquid. This is because if you allow a solution to evaporate, you change its density. But it is possible, though difficult, with pure water. Such determinations were last made about sixty years ago by the Bureau International des Poids et Mesures in Paris, and resulted in the figure 1.000027 for the volume of the litre in cubic decimetres. We understand the Bureau are contemplating further work on this subject, and hope with their co-operation we can ultimately define our water densities in absolute units. The alternative is to select some large uniform body of sea water (suggestions have been the Western Mediterranean deep water and the N.Pacific deep water) and define the density of pure water distilled from this, under controlled conditions, as zero at 4°C. We are proceeding at the moment with this idea, as it seems to be the best we can do fairly quickly.

This work, and its implications, were studied firstly at the recent meeting of the Unesco committee on the equation of state of sea water, and then in open meeting of IAPO at Berkeley, California during August, 1963. The committee is issuing a report, which will be distributed as before by the office of oceanography, Unesco, to all interested organisations. On the recommendation of the committee, IAPO debated and finally adopted a resolution, which is set out below.

Resolution of IAPO, adopted August 22nd,1963

Concerning the work of the joint panel of experts on the equation of state of sea water

(1) IAPO adopts the report and recommendations of the first meeting of the above panel (NS/9/114B of 4 December 1962, issued by UNESCO) together with the additional report of the panel prepared at its second meeting (NS/9/114B of 18 August 1963) clarifying the proposed redefinition of salinity and specifying additional measurements still to be undertaken.

(2) IAPO considers that the panel has successfully accomplished its task within its terms of reference, as outlined in the Resolution of the Hydrographical Committee of ICES, and that therefore these terms of reference should be redefined.

IAPO Recommends

(3) that the Panel, to be called hereafter the "joint ICES/IAPO/SCOR/UNESCO Panel of Experts on Oceanographic Tables and Standards", be requested.

a) to carry out all the necessary preparatory work for publishing new oceanographic tables

b) to advise on the certification of the standard sea water

c) to advise on such further investigations as may be desirable.

(4) that for these new tasks the composition of the Panel be reconsidered by the sponsoring organizations; additional members might be required to advise on the nature of the tables and on the appropriate computor techniques.

(5) that the International Bureau of Weights and Measures be informed of the work of the panel, and be invited to send an observer to the next meeting.

(6) that the date of the next meeting of the Panel be determined by the Director, Office of Oceanography, UNESCO, after due consultation with the members of the Panel.

(7) that the UNESCO Office of Oceanography be asked to continue financial support of this important work, covering further meetings of the Panel and necessary items of measuring equipment.

(8) that the Intergovernmental Oceanographic Commission should be approached and asked to inquire among its members whether any of their institutions are in a position to contribute towards this work.

I would like the Hydrographical Committee to consider these recommendations, in particular items 2, 3 and 4. Possibly the committee might think it appropriate to pass a resolution endorsing part or all of the IAPO resolution; the joint panel would certainly like to hear any views on recommendation 4.