An Apparatus for Determining the Salinity of Sea Water.

By

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Introduction.

The "Hydrographical Tables" of MARTIN KNUDSEN give very complete data correlating the density and salinity of sea water, and it was suggested that an accurate means of determining density would provide an indirect means of determining salinity. An apparatus has been designed on this basis, using the temperature of equilibrium of a glass float in a sample of sea water as an indication of the density of the sample[1]). If a glass float, for example a hollow cylindrical glass bulb, is loaded with mercury so as to have a suitable density, it will float in sea water at ordinary temperatures and sink when the temperature is raised sufficiently. At some intermediate temperature the densities of the sample and of the float will be equal and the float will have no tendency either to rise or sink in the liquid. This temperature we will call the equilibrium temperature of the float. If the density of the float at any temperature and its coefficient of cubical expansion are known, then the determination of the equilibrium temperature of the float in any liquid suffices to determine the density of the liquid at that temperature.

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[1]) This method of determining density is, of course, by no means a new one. See for example "An Instrument for accurate and rapid Density Measurements on board ship" by A. L. THURAS "Jour. Wash. Acad. Sci". 1917, VII, 605, and "A comparison of the Atomic Weights of Silicon from different sources" by Robinson & Smith "Jour. Chem. Soc." 1926, *129*, 1263.

It was desired that the apparatus should be suitable for determining salinities (measured as the total weight of salt in grammes in 1000 gms. of sea water) over a range of salinity from 33 $^0/_{00}$ to 36 $^0/_{00}$ correct to within $\pm$ 0.02 gms. This corresponds to an accuracy of $\pm$ 0.000016 gms/ml in density and $\pm$ 0.05° C. in determination of equilibrium temperature. It was also desired that the apparatus should be suitable for use on light-ships and vessels of the mercantile marine and to this end it was necessary that only the simplest means of heating should be required, that the apparatus should not be affected by the motion of the ship, that not more than 250 ml of sea-water should be required, and that the apparatus should be simple to use. The apparatus designed with a view to fulfilling these requirements forms the subject of this paper.

Description of Apparatus.

The essential part of the apparatus, as constructed for trial, is shown in Fig. 1. It consists of two vertical glass tubes, A and B, about 2.5 cms. in internal diameter and about 22 cms. long, sealed at their lower ends, open at the top and connected by two horizontal cross-pieces C and D. The volume of sea water required is about 150 millilitres which suffices to fill the apparatus to about 1.5 cms. above the top of the connecting limb D. The float E, is placed in the left hand vertical tube which is closed by means of an india-rubber stopper carrying a thermometer. The thermometer scale has a range from 18° C. to 32° C. and is sub-divided into tenths of a degree centigrade, the graduation marks being about 1 mm. apart. The cork closing the limb B has a vertical hole bored centrally through it, and a glass rod F which passes through this hole has a horizontal disc fused at its lower end and serves as a stirrer. The sea water is stirred by raising and lowering F, the diameter of the disc being 2 to 3 mm. less than the internal diameter of the tube B. Two enlargements on the rod F act as stops and limit the motion of the disc to the portion of the tube B lying between the two horizontal connecting tubes C and D.

For preliminary experiments the apparatus was set up as shown in Fig. 2. The apparatus shown in detail in Fig. 1 was held in a retort stand so that it was suspended in a 3000 ml. beaker filled with water, the level of the water in the beaker being well above the level of the liquid surfaces inside the vertical tubes A and B. The water in the beaker was stirred by means of a vertical glass rod bent at its lower end into the form of a hexagon lying in a horizontal plane, and fitting between the walls of the beaker and the apparatus suspended in it.

This arrangement was only intended as a provisional one. A rectangular sheet metal bath having glass windows front and back and provided with a suitable clamp for holding the inner vessel would be more convenient for use at sea. The metal bath could with advantage have a capacity somewhat greater than 3000 ml and so make slow rates of temperature change more easily attainable.

Adjustment of Floats.

It is not convenient on board ship to attain equilibrium temperatures by cooling the samples below room temperature, and on the other hand it is desirable not to have to raise the temperature of the sample more than is necessary. In temperate regions samples of sea water will rarely have a temperature higher than 18° C. A change in salinity from 33 $^0/_{00}$ to 36 $^0/_{00}$ corresponds to about 9° C. change in equilibrium temperature. If the float is adjusted so as to have an equilibrium temperature somewhere between 18° C. and 21° C. in sea water of salinity 33 $^0/_{00}$ then it may be used to determine the density of samples having a salinity 36 $^0/_{00}$ without it being necessary to heat them to a higher temperature than about 30° C. Such a float would be suitable for our purpose. The density of sea water of salinity 33 $^0/_{00}$ is 1.023764 gms/ml at 18° C. and 1.022996 gms/ml at 21° C., so that the float will be convenient if at 18° C. it has any density lying between these values, for this will bring its equilibrium temperature in a sea water of salinity 33 $^0/_{00}$ within the range 18° C. to 21° C. The permissible variation in the density of the float at 18° C. is therefore (1.023764—1.022996) gms/ml i. e., 0.000768 gms/ml. The volume of the float used was about 7 ml. so that the permissible variation in density corresponds to a latitude of about 5 milligrammes in adjusting the mass of the float. This is quite a practicable proposition and no difficulty was experienced in obtaining floats suitably adjusted from a hydrometer manufacturer.

Determination of Equilibrium Temperature.

Starting with the apparatus assembled as shown in Fig. 2, with the water in the beaker and the sample in the inner vessel both at room temperature, the float will be at the surface of the liquid in the vertical tube containing the thermometer. A small quantity of hot water is added to the beaker, both inner and outer vessels are stirred and the behaviour of the float after the effects of stirring have subsided is noted. If the float returns to the surface of the sample more hot water is added to

the outer vessel and the stirring and observation of the float repeated. This is continued until the float is seen to remain at the bottom of the sample. The temperature of the sample will then be a little above the equilibrium temperature and the following operations should be carried out repeatedly in the order enumerated:—

1) The water in the outer vessel is stirred.
2) The sample in the inner vessel is stirred.
3) When the motion imparted to the float by the stirring has died out[1]) the float is watched carefully to see whether it rises or sinks.
4) Immediately it has been decided whether the float tends to rise or to sink, the thermometer is read to the nearest 0.01° C.
5) The time is noted as soon as the thermometer reading has been recorded. This is not essential but is useful for indicating the rate at which the temperature is changing.

The above series of observations is repeated until the temperature falls below the equilibrium temperature.

A set of readings with rising temperature may then be obtained by adding hot water to the outer vessel in small quantities at a time so that the temperature slowly rises through the equilibrium temperature. When passing through the equilibrium temperature the rate of change of temperature should not be greater than 0.1° C. per minute.

It is convenient to record the observations as follows:—

						A		B	
Behaviour of Float ..	S	S	S	S	S	S	R	R	R	S
Temperature °C......	21.22	21.19	21.17	21.12	21.10	21.06	21.02	20.99	20.99	21.03
Time from start (Min.)	0	2¼	3¾	5¼	6¾	8¾	10¼	12	15¼	17¼

			C			D	
Behaviour of Float ..	S	S	S	E	R	R	S
Temperature °C......	21.09	21.10	21.08	21.02	20.99	20.99	21.04
Time from start (Min.)	18¾	23	24½	26½	27¾	30¼	32¼

S = Float sinks.   R = Float rises.   E = Float in equilibrium.

The means of the temperatures enclosed in the rectangles marked A, B, C and D, which include temperatures in the immediate neighbourhood of the equilibrium temperature, when the temperature was falling

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[1]) The stirrer in the inner vessel can be used to control the motion of the float. By gently moving the stirrer up and down, as required, the float may be manipulated so as to come steadily to a position about midway between the bottom of the inner vessel and the surface of the sample. After a little practice one is soon able to discriminate between a motion of the float imparted to it by stirring and motion in accordance with the difference in density between the float and the surrounding liquid.

in A and C and rising in B and D, are 21.04° C., 21.01° C., 21.03° C. and 21.01$_5$° C. respectively. The mean of all four values viz., 21.02° C. is taken as the equilibrium temperature.

One passage of the temperature through the equilibrium temperature suffices to determine the latter but it is preferable to obtain two values one with falling and one with rising temperatures to serve as a check on the consistency of the results obtained.

Results obtained with the Apparatus.

1) Determination of Equilibrium Temperatures at the National Physical Laboratory.

The first thing to be ascertained was whether the apparatus was suitable for locating the equilibrium temperature in any sample to a sufficient degree of accuracy. Three observers, normally occupied in testing volumetric glassware, each determined the equilibrium temperature of a float in a salt solution taking two determinations with rising and two with falling temperatures. The mean of each observer's determinations differed from the grand mean by not more than 0.02$_5$° C. not only in the observations just mentioned but also in two other similar sets of observations. Further no individual observation in any one set of observations differed from the final mean of the set by more than 0.05°C. This applied to a total of thirty eight observations in all, each determination by any one observer with rising or falling temperature being counted as an individual observation. The results quoted were the first observations carried out with the apparatus by the observers concerned, so that the degree of accuracy required was achieved without any lengthy experience in the use of the apparatus.

The observations were all taken in the same sample. The mean of the results obtained in the first series including one set of determinations by each observer was 28.11° C., in the second series 28.11° C. and in the third series 28.13° C. The observations were carried out on two successive days and twenty six hours elapsed between the first and last observation the sample remaining in the apparatus throughout this period. The small change in equilibrium temperature over this long period shows that there is no fear of any change in salinity during the course of an ordinary observation of equilibrium temperature.

These preliminary results indicated that the apparatus might be expected to function satisfactorily and the Government Chemist, Sir Robert Robertson, kindly arranged for the apparatus to be tried at the Government Laboratory in conjunction with their titrations of samples of sea water.

2) Results obtained at the Government Laboratory.

At the Government Laboratory the equilibrium temperature was determined in a series of nine samples of sea water of which the salinity was determined by titration. The salinities ranged from 33.2 $^0/_{00}$ to 35.6 $^0/_{00}$ and from the results obtained a graph was drawn correlating salinity and equilibrium temperature. The salinity of seventeen more samples was determined by observing the equilibrium temperature of the float in each sample and obtaining the salinity from the graph constructed on the basis of the first nine samples. The salinity of each sample was also determined by titration. Reporting on the results obtained Sir Robert Robertson wrote:—

"Of the seventeen samples examined one gave a result 0.04 below the mean titration value, one was 0.03 above and another 0.025 below. The others either agreed exactly in the second decimal place or differed by not more than 0.02 from the value obtained by titration.

The apparatus has thus been found to work well with samples of salinity 33.0 to 35.5 $^0/_{00}$.

As far as can be judged from Laboratory experiments, the apparatus appears to be suitable for the purpose for which it was designed, and it is capable of giving results of the accuracy indicated above in the hands of a careful worker."

3) Results obtained on Cruise XI (1925) on board the "George Bligh".

Dr. RUSSELL kindly arranged for observations to be made with the apparatus at sea on the Ministry of Agriculture & Fisheries research vessel "George Bligh". A beaker was used for the outer bath as in the experiments on shore, but, as stated previously, this arrangement is only a provisional one. A float, Nr. 3, was used for which the National Physical Laboratory furnished the data given in Table I.

The table was prepared by determining the equilibrium temperature of the float in a series of salt solutions in which the equilibrium temperature of a "standard float" was also determined. The "standard float" was one for which equilibrium temperatures had been determined at the Government Laboratory in samples of sea water of known salinity determined by titration.

Salinities were determined on board ship by observing the equilibrium temperature and obtaining the salinity from the above table. Duplicate samples were preserved in sampling bottles for subsequent analysis at the Government Laboratory. Salinities were determined by

Table I.

The Table gives the salinities (i. e., total weight of salt in grammes in 1000 grammes of sea water) corresponding to the tabulated equilibrium temperatures.

° C.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
20	32.81	32.84	32.87	32.90	32.93	32.96	32.99	33.02	33.05	33.08
21	33.11	33.14	33.17	33.21	33.24	33.27	33.30	33.33	33.36	33.40
22	33.43	33.46	33.49	33.53	33.56	33.59	33.63	33.66	33.69	33.73
23	33.76	33.79	33.83	33.86	33.90	33.93	33.97	34.00	34.04	34.07
24	34.11	34.14	34.18	34.21	34.25	34.28	34.32	34.36	34.39	34.43
25	34.47	34.50	34.54	34.58	34.62	34.65	34.69	34.73	34.77	34.80
26	34.84	34.88	34.92	34.96	35.00	35.04	35.08	35.11	35.15	35.19
27	35.23	35.27	35.31	35.35	35.39	35.43	35.47	35.52	35.56	35.60
28	35.64	35.68	35.72	35.76	35.80	35.85	35.89	35.93	35.97	36.02
29	36.06	36.10	36.14	36.19	36.23	36.27	36.32	36.36	36.41	36.45

means of the apparatus by three observers (Messrs. J. N. CARRUTHERS, J. R. LUMBY and V. STOTT) during a cruise from Lowestoft to Sylt thence to Bridlington and back from there to Lowestoft. The results obtained at sea are given in Table II.

Table II.

Station	Observers			Mean
	A	B	C	
A	33.95	33.95	33.96	33.95
6	34.25	34.26	34.25	34.25
7	32.89	32.87	32.88	32.89
	. .	. .	32.90	. .
13	34.89	*34.96*	*34.88*	34.91
14	34.94	34.92	34.96	34.94
19	*34.26*	34.21	34.21	34.23
	34.24	. .	34.23	. .
B (a)	33.92	33.90	33.90	33.91
	33.91	. .	33.91	. .
B (b)	33.89	33.89	33.87	33.88
C (a)	33.87	. .	33.86	33.86
C (b)	33.86	33.85	. .	33.85

Only the three observations given in italics out of a total of thirty three observations differ from the mean value for the sample by more than $0.02\ ^0/_{00}$. The results of the determination of the salinities of duplicates

of the above samples at the Government Laboratory are given in Table III in which the mean results from Table II are also given for comparison. No duplicate sample was taken for analysis at station A.

Table III.

Station	Salinity from equilibrium temperature of float (1)	Salinity by Titration (2)	Difference (1) — (2)
6	34.25	34.24	+ 0.01
7	32.89	32.82	+ 0.07
13	34.91	34.86	+ 0.05
14	34.94	34.86	+ 0.08
19	34.23	34.15	+ 0.08
B (a)	33.91	33.87	+ 0.04
B (b)	33.88		+ 0.01
C (a)	33.86	33.84	+ 0.02
C (b)	33.85		+ 0.01

If the values of the salinity obtained by each method are correct within $\pm$ 0.02 $^0/_{00}$ then the differences in the last column should not exceed $\pm$ 0.04 $^0/_{00}$ and in general should be less than this. Four of the differences exceed 0.04 $^0/_{00}$ so that one would not feel safe in substituting determinations by the new apparatus for the established titration method without further investigation. All the differences in the last column are positive which suggests a constant error the elimination of which would bring the two sets of results into closer agreement. It was not possible however to assign a definite reason for the presence of any constant error.

For the determinations marked B (b) and C (b) the sample was placed in a sample bottle of the usual type having an air tight stopper. The bottle was placed in warm water, temperature 30° C., and shaken to release air bubbles from the sea water. The sample was then transferred to the apparatus for determination of the equilibrium temperature. This was done because in previous determinations trouble had been experienced through the formation of air bubbles on the float. This necessitated interrupting the observations to remove the bubbles by withdrawing the float from the sample. No trouble with bubbles was experienced when the samples were first warmed as described and the agreement between the results B (a) and B (b) and between C (a) and C (b) indicates that the method employed for preliminary heating of
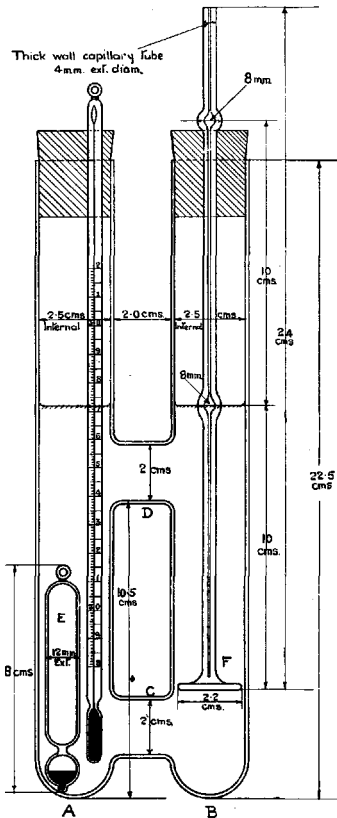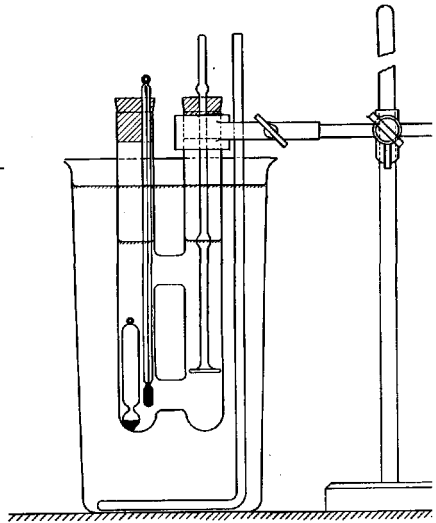
Fig. 1.

Fig. 2.

the sample does not change the salinity as samples B (a) and C (a) were identical with B (b) and C (b) the only difference in procedure being that the samples B (a) and C (a) were not warmed before the determination of the equilibrium temperature. It is, of course, desirable for other reasons to keep the float quite clean, e. g. by washing in a soap solution and then thoroughly rinsing before use, and this also helps to keep the float free from bubbles.

The apparatus shown in Fig. 1 was used for samples A, 6, 7 and 13 but for the remaining samples an alternative form of apparatus shown in Fig. 3 was used. The construction of this apparatus is clear from the diagram and the method of use was the same as with the original form. It will be seen that equally good results were obtained with both forms of apparatus. The float can be more easily controlled in the original form of apparatus and it is a slight advantage to have the stirrer and

thermometer in separate corks as in Fig. 1 rather than to have both in the same cork which has also to carry the central tube as shown in Fig. 3. There is less lag between the temperature of the outer bath and of the sample with the original form of apparatus than with the concentric form.

4) Results obtained on Cruise F (1927) on board the "George Bligh".

Observations were made on board the "George Bligh" by the same three observers as on the previous cruise, on a run from Lowestoft to the Varne Light Vessel and during a period of about two days whilst the ship was at anchor near the Varne for the purpose of current measurements.

Fig. 3.

The results obtained are given in Table IV the salinities being obtained from the equilibrium temperatures by means of Table I.

Only the three values in italics out of a total of twenty observations differ from the mean value by more than 0.02 $^o/_{oo}$, and none of the values in the second column differ by more than 0.02 $^o/_{oo}$ from the corresponding values in the third column of the table.

The salinities of duplicates of all the samples were subsequently determined by titration at the Government Laboratory. The results together with the mean values from Table IV are given in Table V.
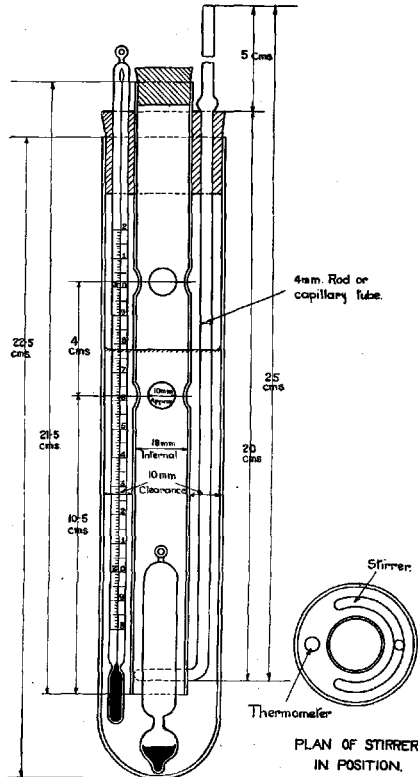
Table IV.

Sample Number	Observers			Mean
	A	B	C	
31	33.54	33.56	. .	33.55
32	34.19	34.19	*34.23*	34.20
33	35.02	35.01	. .	35.01
34	*35.00*	. .	*35.08*	35.04
35	34.86	34.87	. .	34.86
36	34.90	34.88	34.87	34.88
37	34.91	34.90	34.89	34.90
38	34.84	34.84	34.87	34.85

Table V.

Sample Number	Salinity from equilibrium temperature of float (1)	Salinity by Titration (2)	Difference (1) — (2)
31	33.55	33.51	+ 0.04
32	34.20	34.23	— 0.03
33	35.01	35.00	+ 0.01
34	35.04	34.99	+ 0.05
35	34.86	35.00	— 0.14
36	34.88	34.83	+ 0.05
37	34.90	34.98	— 0.08
38	34.85	34.85	0.00

Two of the differences in the last column i. e., those for samples Nos. 35 and 37 are considerably in excess of the value 0.04 $^o/_{oo}$ corresponding to accuracy within $\pm$ 0.02 $^o/_{oo}$ in both methods. Both positive and negative differences occur, as compared with only positive differences in the results of the earlier cruise (Table III).

Conclusion.

The outstanding advantage of the float method is that only one observation, and that a simple determination of temperature, is necessary to obtain the salinity of a sample. The equilibrium of the float is very sensitive to small changes in density and given a slowly changing temperature in the neighbourhood of the equilibrium temperature this can be determined with considerable precision. Satisfactory temperature control

can be obtained by adding hot or cold water to the outer bath as may be necessary, and no thermostatic control is required.

The agreement between results obtained with the apparatus and salinities determined by titration was quite satisfactory when the comparison was made at the Government Laboratory where the same sample could be used for both methods and both determinations could be made within a short space of time.

The agreement between results obtained with the apparatus on board ship and the salinities determined some weeks later on duplicate samples by titration at the Government Laboratory was not so satisfactory. Notwithstanding this it was thought that a description of the apparatus and an account of the experiments carried out might prove of interest and so this note has been written.

I am much indebted to Sir Robert Robertson for kindly having experiments with the apparatus conducted at the Government Laboratory, to Dr. E. S. RUSSELL for arranging for the observations on board the "George Bligh" and to Mr. J. R. LUMBY for his interest and help in this part of the work.