[CONTRIBUTION FROM THE OCEANOGRAPHIC AND CHEMICAL LABORATORIES OF THE UNIVERSITY OF WASHINGTON]

Distribution of Isotopic Water in the Sea

BY HENRY E. WIRTH WITH THOMAS G. THOMPSON AND CLINTON L. UTTERBACK

Gilfillan[1] found that water distilled from sea water had a density 2.3 parts per million greater than water distilled from tap water. This difference was attributed to the presence of an increased concentration of the heavy isotopes of hydrogen and/or oxygen in the sea water. Contrary to his expectation, he found no difference in the density of Atlantic Ocean water at the surface and at 4500 meters. Washburn and Smith's[2] determinations showed that sea water was about 2 parts per million denser than ordinary water. Greene and Voskuyl[3] also found water distilled from sea water collected near Gloucester, Massachusetts, to be 1.8 parts per million denser than water from Cambridge tap water.

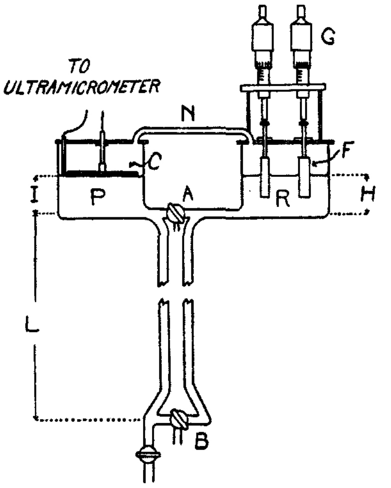

Fig. 1.—Apparatus for the determination of small density differences.

As it was desired to investigate the isotopic composition of water at various depths and at different localities, a sensitive apparatus for directly measuring small differences in density was designed and used in the determination of the density of the waters from the several oceans.

Apparatus and Methods

The apparatus used in the experiments described below was based on the method of communicating tubes, described by Frivold.[4] In this method the difference in density between two liquids can be determined directly from two measurements of distance. A liquid of density d filled the left side of the apparatus (Fig. 1) including the stopcocks A and B, while a liquid of density d_0 filled the right side. If ΔH is the difference in height of the liquid of density d_0 under conditions of hydrostatic equilibrium, first with A open and B closed, then with B open and A closed, and if the height I remains unchanged, then

$$\frac{d - d_0}{d_0} = \frac{\Delta H}{L}$$

where L is the vertical distance between the stopcocks A and B.

The height H was varied to maintain equilibrium and ΔH was measured by means of calibrated silver plated plungers F, controlled by Starrett micrometer heads G.

A brass plate C suspended over the liquid surface formed with this surface a condenser which was part of an ultramicrometer. By means of this instrument a change of less than 1×10^{-6} cm. in the height I could be detected when the distance between the plate and the liquid was approximately 0.5 mm.

The instrument consisted essentially of a beat-frequency oscillator, the frequency of one of its two component oscillating circuits being controlled by the variable capacity of a condenser formed by one of the free surfaces of the liquid and a fixed plane electrode placed parallel to, and at a slight distance above, the liquid surface. The position of the liquid surface was determined by a comparison of the beat frequency of the oscillator with the frequency of an electrically driven tuning fork by the method of audible beats.

Several "ultramicrometers" have been described in the literature, but the most sensitive one, that described by Whiddington,[5] is characterized by unsatisfactory stability. Since this is an undesirable characteristic of an instrument for routine use, the circuit shown in Fig. 2 which combines simplicity with the well-known stability of the dynatron type of oscillator, was adopted and gave satisfactory results.

In this instrument, the oscillating circuits of

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[1] Gilfillan, THIS JOURNAL, **56**, 406 (1934).

[2] Washburn and Smith, *Bur. Standards J. Research*, **12**, 305 (1934).

[3] Greene and Voskuyl, THIS JOURNAL, **56**, 1649 (1934).

[4] Frivold, *Physik. Z.*, **21**, 529 (1920).

[5] R. W. Whiddington, *Phil. Mag.*, **40**, 6, 634 (1920).

Whiddington's apparatus are replaced by two dynatron circuits. The beat notes between these two oscillating circuits are amplified and finally made audible by means of head-phones or a loud speaker.

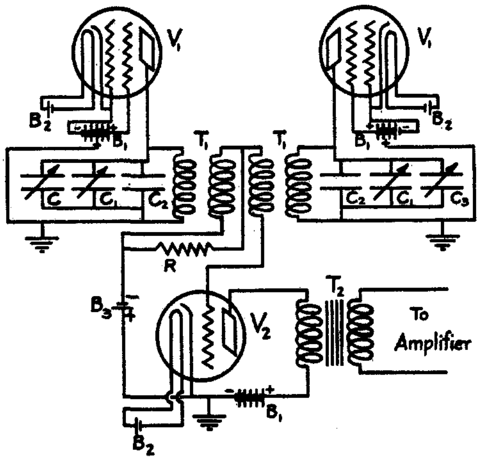

Fig. 2.—Diagram of dynatron circuit. T_1, 175 k. c. tuned transformer; T_2, audiofrequency transformer; C_1, variable condenser with vernier adjustment; C_2, 0.0002 mfd.; C_3, (see Fig. 3); R, 2000 ohms; V_2, RCA 27 tubes; V_1, RCA 224 tubes, selected for their dynatron characteristics.

In Fig. 3 is shown one of the open ends of the manometer. A brass plate 7.5 cm. in diameter was rigidly supported over the surface of the liquid, and together with the liquid surface formed the variable condenser C_3. Any change in the height of the liquid changed the capacity of the condenser and consequently the rate of oscillation of the circuit of which it is part. When a non-conducting liquid, such as distilled water, was used in the apparatus, a piece of aluminum foil about 8.0 cm. in diameter placed on the liquid surface made a satisfactory plate. The ground connection (G, Fig. 2) held the foil in position, and due to surface tension the foil spread out taut and reproduced exactly any fluctuation in the height of the liquid.

To operate, a difference of approximately 1000 oscillations per second was established between the two dynatron circuits by adjustment of the variable condensers C and C_1. This note was compared with that of an electrically driven tuning fork, also operating at 1000 cycles, and the beat between these two used as the basis for measurement. It is believed that a tuning fork makes a better comparison standard than another oscillating circuit (as used by Whiddington) since, due to its greater stability, it permits any fluctuation to be immediately assigned to some factor in the measuring circuit.

The use of an audible indicating device was preferred to the use of a current measurement of the type employed in the instrument described by Olson and Hirst[6] as it freed the visual attention of the observer during certain preliminary manipulations. Also, the adjustments necessary to bring the liquid surface back to its initial position after accidental displacement were facilitated as the direction and approximate distance of this displacement could be inferred from the note of the loud speaker.

With a distance of about 0.05 cm. between the brass plate and the liquid surface, a change of one beat per second was found to be equivalent to a change of 7×10^{-6} cm. in the height of the liquid. Since a change of one-tenth beat per second can be determined with a good stop watch when the loud speaker frequency and fork frequency differ by not more than four beats per second, the instrument was more than sufficiently sensitive for the work. Greater sensitivity could be obtained by decreasing the distance between the plates of condenser C_3, and also by decreasing the fixed capacity C_2. However, this latter would be at a sacrifice of stability in the instrument.

When the apparatus was used as a simple manometer with water as the manometric liquid, differences in pressure of 2×10^{-3} dynes per square centimeter were determined.

The covers to the arms P and R were designed to prevent evaporation from the liquids. A tube N connected the two arms so that the same pressure would be exerted on both liquid surfaces.

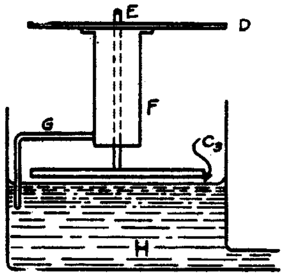

Fig. 3.—Detail of condenser C_3.

The apparatus was kept in an air-bath at 25 ± 0.02°. It was further insulated so that the temperature of the vertical tubes remained constant to within ±0.001° after temperature equilibrium was attained.

The distance L between the stopcocks was 164.8 cm. The free surface area of arm R was 54.07 sq. cm. The cross sectional area of the plunger used for the measurement was 0.5026 sq.

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(6) A. R. Olson and L. L. Hirst, THIS JOURNAL, **51**, 2378 (1929).

cm. From these values and the density of water at 25° the factor by which the measured change in height on the micrometer carrying the plunger must be multiplied to give $d - d_0$ was calculated to be 5.623×10^{-5}. As the micrometer read to 2×10^{-4} cm., equivalent to 2×10^{-6} cm. in the height ΔH, the apparatus was sensitive to differences in density of the order of 1×10^{-8}.

Pure water was prepared from sea water and from laboratory tap water by the method used by Gilfillan,[1] except that four distillations were made alternately from alkaline permanganate and phosphoric acid solutions. This was done to decrease further the possiblity of contamination of the water by volatile substances from the sea water; 500-ml. samples were used, and 125 ml. was discarded with the four residues and the first portion of the final distillate. This distillate was saturated with air previous to the density determination so that no uncertainty would be introduced due to an unknown concentration of dissolved air in the samples.

The laboratory tap water was derived from Cedar River. A single 20-liter sample of this water was collected and used as the standard.

To avoid systematic error, the difference in density between ordinary distilled water, which was always retained in the left portion of the apparatus, and water distilled from tap water was determined. The latter was replaced by water distilled from sea water, and the difference in density again determined. From these two values the difference in density between the water from sea water and water from tap water was calculated.

Results

The differences in density between water distilled from twenty-one samples of sea water from various localities and water distilled from tap water are given in Table I. The values obtained on the water from the Mediterranean Sea, Red Sea and Indian Ocean, with one exception, were very uniform, averaging 1.34×10^{-6}. The one exception, at 4000 meters in the Indian Ocean, was one of the highest values found. No surface sample from this station was available. Low

TABLE I

ISOTOPIC COMPOSITION OF WATER FROM VARIOUS LOCALITIES

Sample number	Location	Depth in meters	Chlorinity (grams per kilogram)	$d - d_0$ at 25°
1	0°4.1′ S., 79°43.2′ E. (Indian Ocean)	0	19.5	1.30×10^{-6}
2	7°38.5′ N., 55°43.3′ E. (Indian Ocean)	1500	19.4	1.30
3	12°9.0′ S., 119°53.1′ E. (Indian Ocean)	0	19.3	1.35
4	12°9.0′ S., 119°53.1′ E. (Indian Ocean)	2000	19.2	1.39
5	36°38′ N., 12°56′ E. (Mediterranean)	0	20.7	1.32
6	36°38′ N., 12°56′ E. (Mediterranean)	900	21.4	1.36
7	22°56.7′ N., 37°11.5′ E. (Red Sea)	0	22.1	1.36
8	22°56.7′ N., 37°11.5′ E. (Red Sea)	900	22.5	1.38
9	1°6′ S., 94°56′ E. (Indian Ocean)	4000	19.2	1.67
10	48°59′ S., 114°13′ E. (Antarctic Ocean)	0	18.8	1.01
11	48°59′ S., 114°13′ E. (Antarctic Ocean)	3200	19.2	1.22
12	7°45.5′ S. 131°24′ W., (Pacific Ocean)	0		1.45
13	7°45.5′ S. 131°24′ W., (Pacific Ocean)	4500		1.38
14	177°59′ W., 51°8′ N. (Pacific Ocean)	0	18.2	1.00
15	177°59′ W., 51°8′ N. (Pacific Ocean)	1200	19.2	1.29
16	178°22′ W., 52°15′ N. (Bering Sea)	0	18.5	1.42
17	178°22′ W., 52°15′ N. (Bering Sea)	700	18.9	1.00
18	178°22′ W., 52°15′ N. (Bering Sea)	2700	19.4	1.26
19	57°22′ N., 19°47′ E. (Baltic Sea)	0	3.8	0.33
20	57°22′ N., 19°47′ E. (Baltic Sea)	150	6.4	0.53
21	65°58′ N. (Baltic Sea)	0	1.3	0.21

Samples 1–9 collected by the Snellius Expedition.
Samples 10–11 collected by the British Australia New Zealand Antarctic Expedition.
Samples 12–13 collected by the Dana Expedition.
Samples 14–18 collected by Mr. Clifford A. Barnes (First Aleutian Island Expedition, U. S. Navy).
Samples 19–21 collected by Thalassological Institute, Helsingfors.

values were found for samples from the Antarctic Ocean, North Pacific Ocean, and Bering Sea. The average of the seven samples from these locations was 1.17×10^{-6}.

The very low values found in the Baltic Sea were attributed to the effect of dilution by fresh water, which is very marked as shown by the low chlorinities of the samples.

Table II presents the results obtained on a series of samples taken at various depths from a single station in the Pacific Ocean ninety miles due west of Cape Flattery. The average for the 13 samples was 1.47×10^{-6}, as compared to a general average of 1.37×10^{-6} for all ocean waters investigated.

The values of the density differences in Table II fall in four distinct groups. In the region from 0 to 50 m. inclusive, the average value was 1.54×10^{-6}; from 100 to 600 m., it was 1.29×10^{-6}; from 800 to 1800 m., it was 1.63×10^{-6}; while a single low value of 1.12×10^{-6} was found at 2000 m. These deviations fall well outside the experimental error as indicated by the average difference between duplicates given in Table II. This vertical distribution of density is in general agreement with the distribution of dissolved oxygen in the same region as reported by Thompson, Thomas and Barnes.[7] These authors found that the dissolved oxygen content decreased with depth to 800 m., was uniformly low to 1800 m., and increased with depth below 1800 m. The zone of minimum oxygen content between 800 and 1800 m. corresponds to the zone of maximum density difference as given in Table II, whereas the region between 100 and 600 meters shows low values for the density difference and higher values for the oxygen content.

If the differences in density are plotted against depth as circles whose radii are 0.1×10^{-6}, it is apparent that the centers of these circles for the samples taken at the first three depths lie on the 1.5×10^{-6} line, six other circles are tangent to this line, four from above and two from below. Three other circles lie well below this line and one well above. It seems obvious that any inherent error would be unidirectional and that any observational errors would appear as random deviations. The facts of physical significance are that for samples taken from 100 to 600 meters inclusive, the differences in densities are lower than for samples taken from 0 to 50 meters inclusive and from 800 to 1800 meters inclusive, as also is the value for the sample taken at 2000 meters. While no quantitative agreement is proposed between the oxygen values and these density differences, nevertheless, the regions of high oxygen are exactly those of low density differences, and the regions of low oxygen content are exactly those of relatively high density differences.

That a correlation exists between these facts and the properties of the Bering Sea waters may be seen by a comparison of them with the results obtained from samples 16, 17, and 18 of Table I. While but three depths were sampled in Bering Sea, sufficient data exist to indicate the similarity. The density difference and oxygen content values of sample 16 are quite comparable with those of the surface sample of Table II. Sample 17 was taken above the zone of minimum oxygen and shows a density difference a little lower than the 600-meter sample of Table II. The 2000-meter sample of Table II was taken from about 200 meters below the zone of minimum oxygen, while sample 18 was taken from about 1200 meters below this zone in Bering Sea. The density difference obtained for sample 18 was definitely slightly greater than that of the 2000-meter sample of Table II, while its oxygen content was correspondingly less than that of this same 2000-meter sample.

The apparent discrepancy between the data above discussed and those of samples 14 and 15, does not actually exist. This statement is based on a detailed study made for the Hydrographic

TABLE II

VERTICAL DISTRIBUTION OF ISOTOPIC WATER

Latitude: 48°18.5′ North; Longitude: 127°05′ West. Samples collected by M. S. "Catalyst" of the University of Washington Oceanographic Laboratories.

Depth in meters	Chlorinity (grams per kilogram)	$d - d_0$ at 25°	Difference between duplicates
0	17.5	1.56×10^{-6}	...
25	17.8	1.56	0.21×10^{-6}
50	17.9	1.51	.14
100	18.4	1.19	.01
200	18.8	1.44	.03
400	18.9	1.36	.07
600	19.0	1.19	.27
800	19.0	1.67	.11
1000	19.1	1.58	.17
1400	19.2	1.58	.12
1600	19.2	1.63	.10
1800	19.2	1.67	.19
2000	19.2	1.12	.00
	Average	1.47×10^{-6}	0.12×10^{-6}

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(7) James Johnstone Memorial Volume, University of Liverpool, 1934, pp. 202-234.

Office of the United States Navy by one of us. The surface water, sample 14, had a temperature considerably lower than that of the samples taken farther northward in Bering Sea. Dynamical calculations indicate that this water originated somewhere in the Asiatic region, while that of the other is from the eastward.

The precision of measurements reported in this paper are illustrated in Table II. Of the thirteen samples reported in this table, the difference in density between exact duplicates in two cases is 0.2×10^{-6}; in six others, it is 0.1×10^{-6}; while in four cases, the difference between exact duplicates is 0.0 to 10^{-6}. This is an average difference between exact duplicates of 0.1×10^{-6}.

Several determinations of the density of water taken from East Sound, Washington, a region unusually rich in diatom flora, indicate a possible relationship between biological processes and density differences; the data are presented in Table III.

TABLE III

ISOTOPIC COMPOSITION OF WATER FROM EAST SOUND, SAN JUAN ARCHIPELAGO

Sample no.	22	23
Location	Mouth of the Sound	Middle of the Sound
Depth in meters	0	0
Chlorinity, grams per kilogram	16.1	16.1
$d - d_0$ at 25°	0.82×10^{-6}	0.79

The values of $d - d_0$ obtained were much lower than for any taken from the station in the Pacific Ocean even when account is taken of the fresh water dilution which has reduced the chlorinity to 16 parts per thousand. Since the sea water of East Sound was originally derived from the Pacific Ocean, it is apparent that some process other than dilution is in operation.

Partial fractionation of water on evaporation from the surface of the ocean would be expected to increase the measured difference in density. This factor, coupled with the lack of vertical circulation which is unique for the waters of the North Pacific Ocean,[7] probably accounts for the high values for the density difference found between the surface and 100 m. for the Pacific Ocean station. The low values found for the northern and southern ocean waters were probably caused by little evaporation coupled with some biological activity.

Acknowledgment.—The authors wish to express their appreciation to Mr. Paul M. Higgs for advice in the construction of portions of the apparatus.

Summary

1. An apparatus for measuring small differences in density has been described. The sensitivity is of the order of 10^{-8}, but determinations are reported only to 10^{-7}.
2. The average difference in density between water distilled from sea water and that distilled from tap water was found to be 1.37×10^{-6} for thirty-one samples of ocean water investigated.
3. Waters from the different depths of the Indian Ocean, Red Sea, and Mediterranean Sea were very uniform, with the exception of one sample taken at 4000 meters in the Indian Ocean, which showed a greater density difference, 1.67×10^{-6}.
4. Waters of the Baltic showed very low density differences varying from 0.2 to 0.5×10^{-6}. These low values were attributed to the marked dilution of the Baltic by land drainage.
5. The two samples from the Antarctic Ocean showed a density difference that was less than that of the Indian Ocean, 1.0×10^{-6} at the surface and 1.2×10^{-6} at 3200 meters.
6. At a station in the Northeast Pacific where thirteen samples were secured simultaneously at different depths from the surface to 2000 meters, density differences were observed that varied from 1.12×10^{-6} to 1.67×10^{-6}.
7. A region in the San Juan Archipelago, noted for its abundant fauna and flora, yielded waters of very low density differences and of the order of 0.8×10^{-6}.

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