[CONTRIBUTION NO. 228 FROM THE WOODS HOLE OCEANOGRAPHIC INSTITUTION]

The Helium–Neon Content of Sea Water and its Relation to the Oxygen Content[1]

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One of the most widely discussed topics in the field of oceanography at the present time is the cause and significance of the "oxygen minimum zone." The vertical distribution of oxygen in the deeper parts of the ocean shows a minimum concentration at a depth which varies with the location, generally between 200 and 1000 meters. This minimum may be very pronounced, as in parts of the Pacific where there is virtually no oxygen. In the Atlantic the minimum zone is seldom less than 30% saturated, and in the far north and south there is sometimes no minimum.

Some time ago there were reported analyses of the helium–neon content of sea water,[3] the outstanding feature of which was an apparent minimum of the helium–neon mixture coinciding with the oxygen minimum in the same water. The significance of this was discussed briefly and some possible explanations suggested. All of these explanations, however, are in rather serious conflict with other oceanographic evidence. In view of this, as well as the limited number of observations made at that time, we have undertaken to repeat the work, on water from a variety of different locations, and with certain improvements in the analytical method.

The details of the technique are described in the references in the earlier paper, but briefly it consists of boiling the dissolved gas out of the water sample under reduced pressure, adsorption on charcoal at the temperature of liquid air, and measurement of the non-adsorbable residue (helium and a constant fraction of the neon) by means of a McLeod gage. High vacuum technique is used throughout, and great care must be exercised in flushing out the line with pure electrolytic oxygen, removing traces of hydrogen by repeatedly passing over hot palladium.

Slight modifications in the original method consisted of increasing the size of the water sample to about 300 ml., an addition to the line to permit flushing the gas out of the boiling flask by means of oxygen, instead of depending entirely upon water vapor, and a graphic method of calculating results from the McLeod gage readings.

Because of the extremely small size of the gas sample measured (less than 10^{-5} ml.) a capillary of about 0.1 mm. diameter must be used in the McLeod gage. To eliminate the effect of capillary depression upon the mercury level a series of readings was taken for each measurement, at different pressures. When these are plotted graphically the slope obtained is a measure of the volume of gas trapped. This practice largely overcame the great variability in capillary depression which was observed from time to time. It was impossible to determine a constant factor for a given tube. Electrodeless discharge in the capillary, for the purpose of testing the residual gas for hydrogen, was found to change the glass surface so much as to make the tube practically useless.[4]

Water samples were collected in the routine manner at sea, by means of reversing water bottles, and stored in glass citrate bottles, completely filled, to prevent exposure to the air. A method of doing this has been described.[5] From these the water was introduced into the boiler by direct mercury displacement, with only momentary and non-turbulent exposure to the air, a major improvement over the earlier method of pouring from the storage bottle.

The oxygen determinations were made by the routine Winkler method, on shipboard, immediately after collecting the samples.

The results are given in Table I. The five stations chosen present a complete array of conditions, in regard to the oxygen minimum. Four are in the Atlantic and one in the Pacific, the latter being almost entirely depleted of oxygen at a depth of about 600 meters. One of the Atlantic stations, 3113, is in the Sargasso Sea, south of the Gulf Stream; two others somewhat to the north. The oxygen minimum at these three varies from 200 to 900 meters. The last station, 2822CG, shows no oxygen minimum whatever.

In none of these is there any consistent relation between the oxygen and the helium–neon content, nor indeed any regular variation in the latter. We can only conclude that the earlier results, based upon a few observations at only two stations, were in some way fortuitous.

We were also unable to notice any significant difference between the solubility of the helium–neon mixture in sea water at 6 and at 23°, or in normal sea water diluted to half its original salinity, the figures obtained in these three respective cases being 16.9, 16.4, and 17.6.

Although the results obtained from the water of the Pacific are higher than all the others, we do not think this represents a real difference. These determinations were made several months after the others, with a different McLeod capillary and a number of other conditions altered. Nevertheless, although they probably cannot be compared

(1) This work was made possible by a grant from the Elizabeth Thompson Science Fund.

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(3) Urry, THIS JOURNAL, **57**, 657 (1935).

(4) In the earlier work a spectroscopic examination was regularly made, by means of an electrodeless discharge in the capillary, after the measurements had been taken. This necessitated a frequent change of capillary.

(5) Rakestraw and Emmel, *Ind. Eng. Chem., Anal. Ed.*, **9**, 344 (1937).

TABLE I

	Depth, meters	Temp., °C.	Oxygen ml./l.	He–Ne ml./l. × 10^{-5}
	0	18.28	5.15	18.5
	5	18.31	5.15	14.1
Station 3025	25	17.97	5.05	15.2
35°-55′N	62	17.93	5.17	15.2
67°-39′W	166	17.92	5.15	15.2
Apr. 7, 1938	333	17.63	4.90	15.6
	622	15.62	4.10	15.9
	912	9.55	3.60	15.9
	1772	3.86	5.88	16.5
	2959	3.16	6.15	17.8
	0	...	4.92	13.5
	24	20.78		16.3
	47	17.78	4.80	15.9
Station 3105	95	14.68	4.10	16.6
39°-20′N	189	14.27	4.58	17.4
70°-32′W	284	12.16	3.40	16.6
July 14, 1938	378	9.10	3.21	15.4
	474	6.83	4.07	15.4
	568	5.41	4.78	15.6
	663	4.76		15.2
	717	4.47	5.59	15.9
	986	4.04	5.98	17.2
	1702	3.46	6.10	14.8
	0	26.14	4.75	13.3
	21	25.81	4.76	13.1
	85	14.85	3.99	15.0
Station 3113	171	9.18	3.14	14.3
37°-01′N	260	7.03	3.94	
74°-21′W	389	5.55	4.73	12.4
Aug. 2, 1938	435	4.88	5.25	13.9
	555	4.55	5.54	15.4
	722	4.19	5.84	
	1055	3.80	6.14	17.9
	1388	3.55	6.24	12.8
	95	3.54	6.64	15.4
Station 2822CG	286	3.28	6.63	16.1
57°-25′N	531	3.22	6.67	15.0
48°-47′W	898	3.18	6.68	15.6
July 26, 1938	1953	3.26	6.58	14.8
	3072	2.46	6.30	14.8
	10	16.39	5.66	17.3
Pacific station	25	14.67	5.93	20.5
32°-34′N	74	10.75	3.91	16.8
117°-28′W	199	8.83	2.11	16.9
Nov. 9, 1938	298	7.98	1.25	16.9
	503	6.11	0.32	16.8
	607	5.41	.26	18.9
	808	4.48	.48	16.8
	979	4.07	.49	17.3
	1121	3.69	.69	16.9

with those from the other stations, they clearly indicate a regular and consistent distribution at this particular station. This view is confirmed by the fact that at this stage two samples of sea water saturated with air at 23 and 24° showed helium–neon contents of 19.1 and 18.7, respectively, higher than the solubility measurements made earlier.

Occasionally, in the earlier part of this work, a determination yielded an impossibly low result, compared with a duplicate. This was sometimes the case even with water saturated with air. Although we never located the reason for this with complete certainty, it seemed to be connected with the process of letting the gas into the adsorption line from the boiling flask. After every movement at this point had been standardized, and especially after provision had been made for washing the gas into the line with excess oxygen, no trouble of this sort was experienced. It is possible that this was the cause of the two or three unusually low values in the previous investigation, leading to the assumption of a helium–neon minimum.

Summary

A repetition of earlier work, under more suitable and representative conditions, shows the sea to be practically saturated with helium and neon at all depths, with no evidence of any depth of minimum concentration, and hence no relation to the depth of oxygen minimum.

RECEIVED AUGUST 17, 1939