NRL Report 6767

The Density-Gradient Column as a Tool for Measuring Sea Water Density

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September 20, 1968

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Washington, D.C.

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ABSTRACT

The possibility of using the density-gradient technique for determining the density of sea water is examined. In this method a water-drop sample falls through a column of immiscible liquid having a vertical density gradient, and the rest position of the drop is noted. The preliminary laboratory work indicates that the density of the water can be determined to at least one part in 10^5, which is adequate for most oceanographic purposes. The importance of standardizing the procedure, and the experimental conditions, is amply demonstrated. Experiments to test the feasibility of the method aboard ship are also planned.

PROBLEM STATUS

This is an interim report; work on the problem continues.

AUTHORIZATION

NRL Problem G04-01
Project RR 104-03-41-5503

Manuscript submitted July 2, 1968.

THE DENSITY-GRADIENT COLUMN AS A TOOL FOR MEASURING SEA WATER DENSITY

INTRODUCTION

Density is one of the most important physical properties of sea water; from an accurate knowledge of the *in situ* density structure over a given region, it is possible to predict the movement of water masses, the formation of currents, and the sea-surface slope. Density is not, however, an isolated property; it is intimately associated with, and dependent upon, salinity, temperature, and pressure; in the open ocean it ranges from a σ of about 24.00 (d = 1.02400) to a σ of about 30.00 (d = 1.0300) (1). The usual method of determining density is by calculation based upon a knowledge of these variables; for most oceanographic purposes it is necessary to know this value correctly to at least one part in the fifth decimal or $\pm 0.01\ \sigma$ units (2).

There are several direct and indirect methods for measuring the density of sea water, some of which are shown in Table 1. Pycnometry, timing of a falling drop, and hydrostatic weighing are not suitable for shipboard use; others, such as stem hydrometry, usually are not sensitive enough for oceanographic purposes (2,3). Also, there is at present no method for measuring density *in situ*, although the proposed vibrating-tube method of Richardson (4) appeared promising. The idea has been abandoned, apparently because of the adverse effects of temperature on the dimensions and properties of the tube (3). A preliminary study has been made here to determine the feasibility of adapting another method, the density-gradient column, for use in determining the density of sea water.

Table 1
Various Approaches to Density Estimations

Direct	Indirect
Pycnometry	Salinity Determinations
	Conductivity Determinations
Hydrometry	Falling Drop (10)
	Vibrating Tube (4)
	Compressibility Float (11)
	Refractive Index by Interferometry (12,13)
	Hydrostatic Weighing

THE DENSITY-GRADIENT COLUMN

In this method a column of liquid having a vertical density gradient is prepared. The sample (a solid or an immiscible liquid) is inserted in the column where it falls until it reaches a level of its own density. The rest position of the sample is compared to the positions of known reference drops. Density is computed on the basis of a linear density gradient. It is a very sensitive tool for measuring densities of both liquids and solids and for measuring phenomena which cause tiny variations in the density of these materials. Introduced by Linderstrom-Lang (5) as a technique for determining the rate of enzymatic hydrolysis of peptides, the density-gradient field has since been employed for

such diverse uses as the measurement of the density of biological fluids, the measurement of the rates of crystallization in plastics, and the analysis of impurities in semiconductor metals (6). Miller and Gasek (7) have thoroughly studied factors controlling "drift"—a phenomenon we shall discuss later; our work touching on this topic should be considered as confirming and supplementing theirs.

The development of a density-gradient column is based on the principle of Fick (8), which states that, when a liquid is layered over a more dense liquid with which it is miscible, a linear density gradient will develop across the interface between the liquids. With a freshly prepared column, careful stirring is usually used to hasten the initial mixing process. The column is then allowed to stand while the gradient smooths out by diffusion. It is desirable that the liquids should have viscosities and vapor pressures as low as possible.

Once the density gradient has been established, it must be calibrated. A theoretical calibration may be derived for a column at various stages of its development on the assumption that it develops according to Fick's diffusion laws; a method for doing this is described (9). A direct method of calibration is simply adding drops of liquids of accurately known density to the column and observing their final rest positions with respect to a reference plane. The rest position of a given drop in the column is that position where the drop has become neutrally buoyant with respect to its surroundings, thus establishing the density of the gradient medium at that point. The density of an unknown is determined by measuring its rest position within the gradient with respect to those of the calibrating drops and relating these values by simple proportion to the densities of the standards. A linear density gradient over the range of drop positions is, of course, implied.

The relationship is shown in the expression

$$d_u = \frac{(d_2 - d_1)(h_1 - h_u)}{(h_1 - h_2)} + d_1 ,$$

where d_1 and d_2 are the densities of the light and heavy calibrating drops, respectively, h_1 and h_2 are the positions of these drops in the gradient, and d_u and h_u are the corresponding values for the unknown.

The range of densities measurable by such a column depends on the respective densities of the "light" and "heavy" components used in preparing the gradient. The sensitivity depends on the length of the gradient and the difference in density of the two column liquids. There are several potential advantages: it is a direct method, offering both sensitivity and speed, and, because the water sample is very small, there is rapid temperature equilibration with the column liquid.

The goal of the preliminary experiments reported here is to explore the precision and sensitivity of the method in the zone of interest to oceanographers, the fifth decimal point of density.

EXPERIMENTAL CONSIDERATIONS

Calibrating Solutions

The standard solutions used for calibrating the density gradients were prepared from analytical-grade NaCl which had been dried for several hours at 110°C. The concentration and density of these solutions is given in Table 2. Their exact densities were

Table 2
Standard-Density Solutions

%NaCl	Density (gm/ml)	Sigma Units
3.5	1.02167 ± 0.00003	21.67
3.7	1.02225 ± 0.00003	22.25
3.95	1.02386 ± 0.00003	23.86
4.2	1.02565 ± 0.00003	25.65
4.4	1.02706 ± 0.00002	27.06

determined by pycnometry; all weighing was done in a constant-temperature (24°C) room, and appropriate corrections were made. The pycnometers were calibrated with degassed distilled water. The solutions were stored in tightly stoppered bottles capped against dust.

Column Components

The column components which were finally adopted for this study were bromobenzene (b.p. 154.9 to 156.9°C d = 1.48531) and kerosene (d = 0.80437). Before use, both liquids were passed through chromatographic columns packed with adsorption-grade aluminum oxide to remove polar impurities. Because of the wide separation in densities of these two organics, they were not used directly in preparing the density-gradient columns. Instead, two mixtures of "high" and "low" density, respectively, were prepared at the extremes of the selected density range from approximately a σ value of 20.00 (d = 1.02000) to a σ value of 28.00 (d = 1.02800) by combining the two liquids in the proper ratios. Each of these mixtures was equilibrated with a 6% aqueous solution of KBr, for a reason to be given later.

Density Columns

The density gradients were prepared in tubes (8) as shown in Fig. 1. Enough of the heavier mixture was poured into the tube to fill it half way; the lighter mixture was carefully layered over the heavier with a syringe bearing a J-shaped delivery tube. An initial gradient was established by gentle mixing with a stirrer having a spiraled wire end. The stirrer was carefully inserted into the column as far as the interface between the components and was then raised and lowered about this position with increasing amplitude until the spiral came to within 1 cm of each bulb. Usually 10 to 15 complete cycles of the stirrer sufficed to establish the initial gradient. The liquids in the bulbs are reservoirs of unmixed column components serving to maintain the gradient. The gradient tube was then stoppered to prevent evaporation and contamination by dust and allowed to stand for 24 hours before it was used.

Since the density gradient can be upset by fluctuations in ambient temperature, all tubes were kept in a constant-temperature bath at 26 ± 0.01°C. Temperature measurements within dummy tubes indicated that the variations were less than 0.001°C. The complete apparatus for making the density measurements is presented in Fig. 2.

Method

Drops of the NaCl solutions were introduced into the columns with a micrometer syringe equipped with a 27-gauge stainless steel hypodermic needle. The syringe was rinsed several times with the solution to be used and was then filled completely and a small drop expelled and removed from the needle just prior to inserting it through the

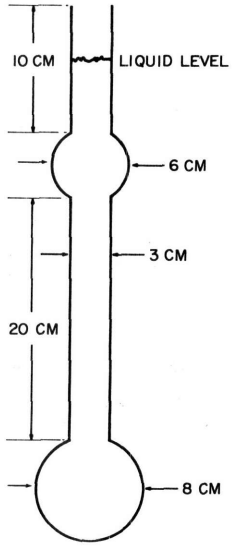

Fig 1 - Density-gradient tube

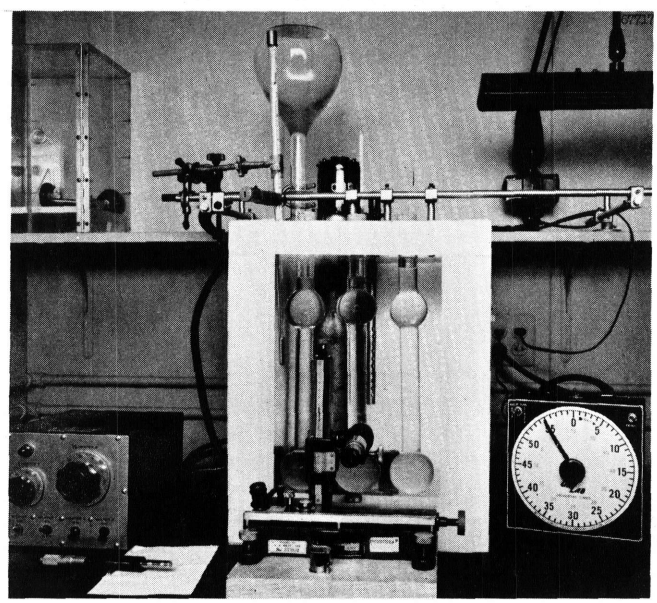

Fig. 2 - Apparatus for the density measurements

air/liquid interface. With the needle below the surface, a drop of the desired volume, usually 1.0 μl, was expelled. The drop would adhere until the needle was withdrawn through the interface, at which time the drop would break free and begin to descend through the gradient. For position-time studies, this event constituted zero time.

Drops no longer needed could be effectively removed from the column by collecting them on the oxidized end of a long copper wire, or they could be pushed to the tube wall, to which they would adhere. When done carefully, removal of the drops did not seem to upset the density gradient.

EXPERIMENTAL RESULTS

Time-Position Curves

Several experiments were performed to determine the behavior of the liquid drops as a function of their volumes, their densities, and time. A typical curve obtained from such data is shown in Fig. 3. The position-time curves of the drops can be divided into two parts. The first portion of the curve is one in which the rate of fall is decreasing and reflects, primarily, the effect of gravity as the drop approaches neutral buoyancy. In the second portion of the curve the rate is constant. This rate is referred to as "drift" and is thought to be caused by a transfer of water from the drop to the surrounding medium (evaporation) which causes a progressive increase in its density. Miller and Gasek (7) found that drift increases with the surface/volume ratio of the drop, that it increases with solute concentration, and that it depends on the nature of the column components. Presaturation of these components with water or a salt solution will reduce drift; dry column components will increase it. Initially we used a chlorobenzene-xylene system; however, it had to be abandoned in favor of the bromobenzene-kerosene system because of the severe drift problem encountered. With the latter systems, equilibration of the column components with a solution of 6% KBr was found effective in reducing drift to a negligible level.

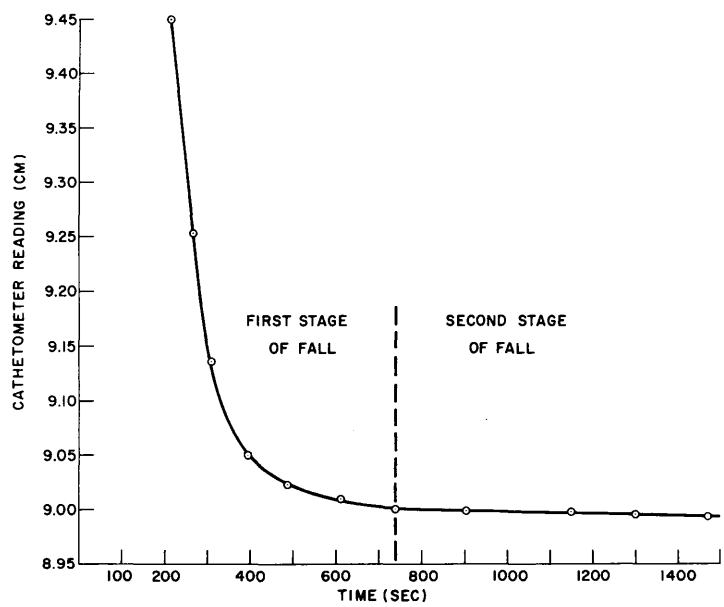

Fig. 3 - Time-position curve of a falling drop

From the results of preliminary experiments it was concluded that a drop would reach a position of neutral buoyancy in the column and be at equilibrium with its surroundings in about 15 minutes; so for density measurements an arbitrary time of 25 minutes was set for observing the rest positions.

Effect of Drop Size

Several experiments were performed to determine the effect of drop size on the position of neutral buoyancy of a drop in the gradient column. Drops of the 4.4% standard NaCl solution with volumes of 1.0 μl, 2.5 μl, and 5.0 μl were used in this study. A typical result is shown in Fig. 4.

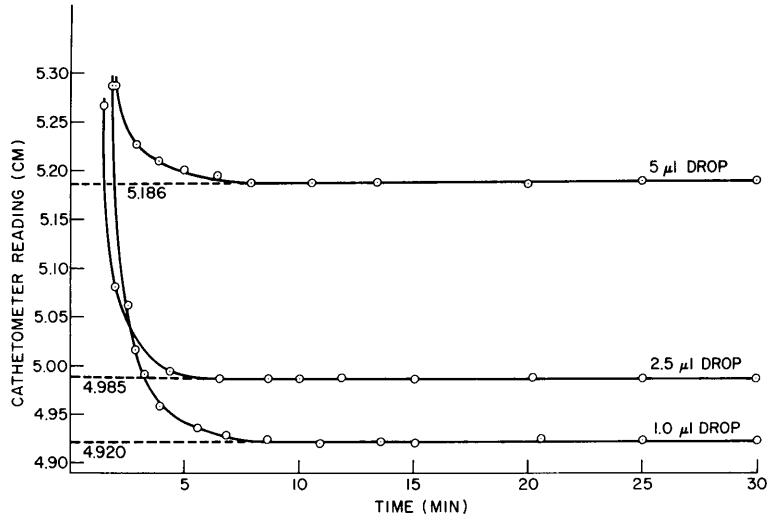

Fig. 4 - Influence of drop size on the rest position

Intuitively, one would expect that any influence attributable to the size of the drop would manifest itself as an increase in drag on the drop as it sought its level of neutral buoyancy, and ultimately all drops of the same density would arrive at the same position in the gradient column. However, larger drops came to rest higher in the column than smaller drops of the same initial density. There are perhaps two possible explanations for the phenomenon. The first is the difference in vapor pressure of the water in the different-size drops. The small drop, with the shorter radius of curvature, and hence the higher vapor pressure, would lose water until the vapor pressure between the drop and the medium immediately surrounding it became equal. The larger drop, with its increased radius and lower vapor pressure, would lose proportionately less water to its immediate surroundings, undergo a smaller increase in density, and take up a higher position in the column. A second possibility is that bromobenzene, heavy and slightly more water soluble than kerosene, equilibrates more rapidly with the smaller drop. The latter seems more reasonable to the authors, though Miller and Gasek (7) appear to reject any preferential transfer of bromobenzene into the sample drop.

Presaturation of the column components with a salt solution of the proper vapor pressure would help to minimize any evaporative changes a drop might undergo while in the gradient field; as stated previously, a solution of 6% KBr was found to be effective for the purpose. The effect attributed to the difference in size of the drops was eliminated by standardizing upon a 1.0-μl drop. A drop of this size allows fast temperature equilibration with the surrounding medium and does not require much space, so that crowding in the gradient column is avoided.

Density Measurements

The density of a simulated unknown was determined by using three of the standard salt solutions, with the one of intermediate density selected to play the role of the "unknown" One-μl drops were used, and their relative position in the column was measured after 25 min. The experimentally determined density of the "unknown" drop was then compared to its known density. In another analysis of the same data, the best straight line through the points was computed by the method of least squares, and the standard error of the estimate was calculated. Results from six runs are presented in Table 3.

Table 3
Measurements on Known-Density Solutions

Exp. No.	Column	Known Density (σ units by Pycnometer)	Drop Position (cm)	Density of Middle Drop: Obs. (σ units)	Density of Middle Drop: "Error" (σ units)	Least-Squares Line: Slope (σ units / cm)	Least-Squares Line: Std. Error of Estimate (σ units)
1	A	22.25	8.080				
		23.86	6.879	23.92	+0.06	-1.449	0.04
		25.65	5.634				
6	A*	21.40	33.69				
		22.25	29.38	22.47	+0.22	-0.2711	0.12
		23.86	23.83	23.36	-0.50		
		25.65	17.78				
2	B	23.86	9.016				
		25.65	7.227	25.64	-0.01	-1.022	0.03
		27.14	5.808				
3	B†	23.86	4.315				
		25.65	2.077	25.67	+0.02	-0.809	0.02
		27.14	0.261				
4	C	22.25	5.543				
		23.86	3.816	23.80	-0.06	-0.894	0.025
		25.65	1.744				
5	C*	22.25	32.59				
		23.86	26.78	23.86	±0.00	-0.2778	0.00
		25.65	20.35				

*Column had aged an additional 4 months.
†Column had aged an additional 3 months.

There were runs in which agreement was not as good, but in most of these cases there was some obvious reason. The authors believe that it will be possible to determine routinely the density of a sample of sea water to 1 part in 10^5, or 0.01 σ units.

FUTURE DEVELOPMENTS

A serious problem not yet studied is that of the effect of ship motion upon the density gradient. Gimbaling or single-point suspension of the thermostatted gradient tube would probably take care of roll and pitch, especially if the apparatus were located near the center of gravity of the ship. Pounding of the ship's hull against the water and vibration must also be coped with. Sea trials will be conducted to determine the extent of this problem and to explore possible solutions.

SUMMARY

A means for determining the density of sea water using a density-gradient field has been described. Preliminary experiments indicate that an accuracy of one part in 10^5 (0.01 σ units) is attainable, adequate for most present-day oceanographic purposes. In addition to the accuracy of this method, it also provides a rapid, direct measure of density with a very small water sample. Small sample size provides the added advantage of rapid temperature equilibration between the drops and the column components with which they are in direct contact.

The size of the drops was found to have an influence upon their position of neutral buoyancy in the density gradient; this variable was controlled by selecting drops of 1.0-μl volume as the standard for all measurements. Also, position-time studies indicate that

the gravity effect on the drops is usually negligible within 15 min; any shift in drop position after that may be attributed to the evaporation of water from the drop into the organic medium (drift). Drift has to be reduced to insignificance by presaturation of the column components with 6% KBr. A time limit of 25 min was set for making density determinations. This length of time is considered sufficient to allow a drop to equilibrate with its environment.

Field trials still need to be performed to determine the effect of ship's motion upon the density gradient. By suitable suspension of the gradient tube and its thermostat, it is hoped, the ship's motion will not interfere with the operation of the column.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the technical assistance of Linda Green and Timothy Flaherty.

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Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Naval Research Laboratory Washington, D.C. 20390	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

THE DENSITY-GRADIENT COLUMN AS A TOOL FOR MEASURING SEA WATER DENSITY

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

An interim report on one phase of the problem; work on other phases continues.

5. AUTHOR(S) *(First name, middle initial, last name)*

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6. REPORT DATE September 20, 1968	7a. TOTAL NO. OF PAGES 11	7b. NO. OF REFS 13
8a. CONTRACT OR GRANT NO. NRL Problem G04-01 b. PROJECT NO. RR 104-03-41-5503 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6767 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*	

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Department of the Navy (Office of Naval Research), Washington, D.C. 20360

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DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

Security Classification

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Sea water						
Density determination						
Water-drop sample						
Density-gradient column						
Oceanography						

DD FORM 1 NOV 65 1473 (BACK)
(PAGE 2)

Security Classification