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Distilled Water for Relative Density Standard

by

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Introduction

The figures usually quoted as "density" of sea water are specific gravities. That is, they are ratios between the density of the water concerned and that of pure water at 4°C, where its density is greatest. Since specific gravity is a ratio, it is a pure number without units; it is hence incorrect to quote any units when referring to specific gravity values, or to specific volumes defined as reciprocals of specific gravity. Many oceanographers have mistakenly quoted units of g/cm^3 for specific gravity, and cm^3/g for specific volume. This is wrong, because the density of pure water at 4°C is not exactly 1 g/cm^3, but probably about 0·99997 g/cm^3. More frequently units of g/ml. have been quoted. The litre was, until recently, defined as the volume of 1 kg. of water at 4°C, so that to quote units of g/ml. for a specific gravity, while somewhat misleading, did not introduce any numerical error. This is no longer so, as the litre has now been re-defined (from Oct. 1964) as a cubic decimetre, and the millilitre and cubic centimetre are synonymous. (See Pollack, 1961, and Cox, 1963).

It is very rarely that specific gravity of sea water is measured directly. Almost always the specific gravity is computed from <u>in situ</u> temperature and chlorinity or salinity determined by silver titration or by measurement of conductivity or refractive index. Various tables and nomograms exist for computing specific gravity, but most, indeed probably all, are based on measurements by Forch, Knudsen and Sørensen (1902). The measurements were precise and careful, and form a sound basis for all subsequent work on sea water densities. Unfortunately, despite their care, the authors had no knowledge of one vital fact (since it was not discovered until years later) that water is not a single substance.

We know today that neither hydrogen nor oxygen, as they exist in nature, is a single substance. All natural hydrogen contains a small proportion of heavy hydrogen, deuterium, with an atomic weight of 2 instead of the usual 1, and oxygen contains a small proportion of atoms of weight 18, instead of the usual 16. This means that natural water is a little heavier than pure $H_2^1O^{16}$, since $H_2^2O^{16}$ and $H_2^1O^{18}$ are both considerably more dense than normal water. This in itself would not be of any consequence, were the proportions of these heavy isotopes constant (as is true within measurable limits with most other natural elements). With water, however, it is possible by simple distillation to concentrate the heavy isotopes in the tail fractions, as the heavier molecules are less volatile. The proportions of H^2 and O^{18} in water are thus not constant, since water is contunually subject to distillation in the natural processes of evaporation and precipitation. Water taken from various sources (rain, snow, rivers, ocean) differs significantly in isotopic ratio. These differences affect the density; water from the sea is reported to be about 1·5 p.p.m. heavier than rain water (Wirth, Thompson and Utterback, 1935).

Forch, Knudsen and Sørensen (1902) say nothing about the source of the water they used as reference for specific gravity; this point would not appear, to them, to be of any importance. It is reasonable to suppose that it was distilled from tap water in the usual way. We have no knowledge of the type of still used, or of the number of distillations. Consequently we have no means of "recovering" the true density of their standard.

A similar difficulty arises when studying the last attempt to measure the absolute density of water (GUILLAUME, 1910). Here three competant workers, in difficult laboratories, could not agree on the results to nearer than 5 p.p.m., although they each considered their results should have been within 1 p.p.m. Again nothing is said regarding the source on preparation of the water, except that it was "repeatedly re-distilled using a silver condenser". The figure 1·000028, quoted in the literature as the conversion factor between the litre and dm^3, is an average value based on these determinations, not necessarily reliable to better than 5 p.p.m.

In the recent work on the relationships between salinity, conductivity, refractive index and density of sea water [Cox, Culkin, Greenhalgh and Riley (1962)], the problem arose of the water to use as reference for the specific gravity measurements. Preliminary results showed that pure water distilled from sea water was significantly denser than when distilled from tap water. Measurements on samples distilled from various regions (Antarctic, Pacific, Atlantic, Mediterranean) showed apparent variations, deep water being denser and Antarctic surface water lighter than the mean, with a range of about 20 p.p.m. These results, however, are suspect, as the apparatus may not have been entirely reliable.

The ideal solution to these problems would be a series of direct determinations of absolute density of a suitable range of sea water samples. The absolute accuracy required, for the preparation of new tables, is about 1 p.p.m. (0·001 in σ_t). Unfortunately such direct determinations are not practicable. The only known methods for absolute density determinations involve either weighing the liquid in a container (a hollow cube or cylinder) of precisely determined volume, or weighing a solid object of known size immersed in the liquid. Both these methods were used by the National Physical Laboratory in the determination of the density of mercury. Similar methods could serve for an absolute determination on pure water, and the N.P.L. would like to do this, if funds can be found to support the work. It is an indication of the magnitude of the problem that N.P.L. estimate the time required for this measurement as two or three years, and the cost as £30,000. Measurements on sea water, however, present two additional problems. Firstly, pure water can be measured at 4°C where the temperature coefficient of density is zero. Temperature control is thus not very critical. Sea water, unfortunately, has no temperature of maximum density, so a very good thermostat is needed. Secondly, if pure water evaporates a little, the effect on the density is negligible. Not so, however, with sea water. If a sea water sample is allowed to equilibrate with its own volume of dry air, its density will be significantly increased. These additional restrictions make the direct determination of density of sea water, to the accuracy needed, impracticable at present.

The alternative is to adopt a "standard-density water" as a reference for relative density (specific gravity) measurements. Clearly the important qualities of this standard are that it shall be readily reproduced and defined so that another worker, perhaps years later and in another country, can be sure he has water of the same density. It would also seem to be best to have a reasonable approximation to "average water", so that the standard will represent the mean composition of the water in the world. Finally, we would like to know the absolute density of our standard, so that if and when desirable we can convert our specific gravity ratios to absolute units.

Over 97% of the water on earth is in the sea, so it is quite obvious that water taken directly from the sea will be nearer to a true sample than rain water, which has already undergone a fractionation process. The choice of precise location for the collection of the water is more difficult. The most uniform bodies of water in the world seem to be the deep water of the N. Pacific Ocean, and the deep water of the Mediterranean Sea. Both these water masses are exceptionally homogeneous in temperature and salinity, and the residence time of the water is certainly hundreds and probably thousands of years. The deep Pacific water is much greater in bulk, but we think the deep Mediterranean water, particularly from the Western basin, is probably more uniform. Probably there is little or nothing to choose between them and they would be used interchangeably. Our final choice was influenced by immediate availability - we had a large sample of deep Mediterranean water, but only small samples of Pacific water, and it would have taken some time and trouble to get more.

The work described below, then, was done on a single sample of about 20 litres of water from the Mediterranean. It was collected in December 1963 by R.R.S. "Discovery" from 1500 m. depth at approximately 38°N 5°E and stored in a high density polyethylene container until used. Before distillation, the salinity was 38·40‰. From this sample, over sixty tubes of distilled water have been extracted, each containing between 250 and 300 ml. of water.

The guiding principles of the distillation process used are to recover the highest possible proportion of the water in the original sea water, adding as little extra water as possible, and yielding water pure enough that its density would not be significantly affected by the remaining dissolved material.

Experimental procedure

If sea water is distilled to dryness without precautions, the distillate is considerably contaminated with hydrogen chloride. This comes from the thermal hydrolysis of the unstable magnesium chloride in the residue, which decomposes to leave a basic salt of uncertain composition. In addition, some water is left in the residue as water of crystallisation.

Both these troubles can be greatly reduced by adding to the sea water an excess of sodium fluoride before distillation. This process precipitates calcium, magnesium and strontium as stable insoluble and anhydrous fluorides (Guntz and Kocher, 1952, Morris and Riley, 1965) after which the water can be distilled off without much decomposition, and negligible water-loss. The sea water, therefore, was first distilled in a Pyrex still, with excess fluoride.

The first distillate contained about 10 p.p.m. of chloride, traces of silicate and fluoride, and an appreciable but not determined amount of volatile organic matter. To remove the organic material, small amounts of concentrated sulphuric acid and potassium permanganate were added, and the water re-distilled. A little silver sulphate was also added, in the hope that this would "fix" the chloride as insoluble silver chloride. This hope was not entirely fulfulled, as the strongly acid permanganate in the closing stages of the distillation oxidised some at least of the chloride to chlorine which came over with the distillate. The second distillate thus contained carbon dioxide and traces of chloride, hypochlorite and sulphate. It was slightly acid (pH 5).

The second distillate was now made slightly alkaline with sodium hydroxide and again distilled in a silica apparatus. The water condensing in this third distillation was almost free from impurity, with a specific resistance at 20°C of about 0·7 x 10^6 ohms cm $^{-1}$. The usual value quoted for "conductivity water" in equilibrium with air is about 1·1 x 10^6 ohms cm $^{-1}$. Normal laboratory distilled water is typically 0·3 x 10^6 ohms cm $^{-1}$.

The overall recovery of the three-stage process was always over 99%, and usually over 99·5%. It is apparent that there can be very little change in isotope ratios in this process. In order that other workers can, if required, reproduce,this process as closely as possible, full details are given below.

Experimental details

The stills used in the first two stages of the distillation are shown in Fig. One. The two stills are identical in design, except that the second stage still used an internal-coil condenser (5 in Fig. One) while the first stage had a double-surface condenser (3). The spiral condenser has a small advantage in that its hold-up volume is rather less, but the effect is probably insignificant. The procedure was as follows.

First stage

1(a) All the glassware is thoroughly cleaned, and dried at 110°C in an oven.

(b) The 2 l. flask (1) and the receiver are weighed to 0·01 g. Approx. 1 l. of sea water is introduced into (1), and the flask re-weighed to determine the weight of water.

(c) 10 g anhydrous sodium fluoride is added to (1) together with a few scraps of broken porcelain to reduce bumping. The still is assembled at once, to obviate evaporation of the water.

(d) The heating mantle is turned full on, and the water distilled. The condenser-water flow must be enough that the condensate is cold. The mantle temperature should be about 310°C during the greater part of the distillation.

(e) Towards the end of distillation, the mantle temperature rises. When this temperature approaches 450°, the variable ratio transformer is adjusted so that the final temperature does not exceed this figure, which is the makers' recommended maximum working temperature of the mantle.

(f) When distillation has ceased, and water is no longer dripping into the receiver, a filter pump is connected to the outlet of the adapter (4) and the apparatus briefly evacuated to a pressure of about 1 cm of mercury. A small additional volume of water will condense, representing the majority of the water vapours from the flask (1) and splash head (2).

(g) The receiver is removed, stoppered, and weighed, to determine the weight of distillate.

Second stage

2(a) The apparatus is cleaned and dried, and t receiver (6) weighed.

(b) To the distillate from stage 1, contained in a 2 l. flask, is added 0·5 ml. concentrated sulphuric acid, 1·0 ml. 5% potassium permanganate and 1·0 ml. 1% silver sulphate, with some broken porcelain. The permanganate and silver should be dissolved in distilled sea water, from a preliminary trial distillation.

(c) The heating mantle is turned on, and the water distilled as in 1(d) and 1(e).

(d) As soon as heavy white fumes of sulphuric acid appear, turn off the heat and allow the fumes to subside. Then evacuate as in 1(f).

(e) Weigh the distillate, as in 1(g).

The still for stage 3 is shown in figure Two. A small pad of loosely packed glass wool is pushed into the wide part of the silica condenser (2) above the B24 joint, to reduce carry-over of spray.

Third stage

3(a) The still is cleaned and dried, and the receiver weighed.

(b) The distillate from stage 2 is transferred to the silica flask (1) and a small quantity of A.R. sodium hydroxide added, (three or four pellets) and swirled until dissolved.

(c) The water is tested with litmus paper, to confirm that it is alkaline.

(d) The water is distilled, using a moderate bunsen flame, so that the distillate condenses in about 50% of the length of the water jacket, and the condensate is cool,

(e) When distillation ceases, the apparatus is quickly evacuated to c. 1 cm mercury. If any water is visible in the upper part of the condenser, "brush" this with the bunsen flame, to evaporate this water.

(f) The specific resistance of the distillate is checked with a conductivity probe. The resistance should be approaching 10^6 ohm cm $^{-1}$. Weigh the distillate.

The overall recovery of water should be over 99%. Thus for each 1000 g sea water taken, final condensate should weigh over 954 g
(1000 g less 38 g salt, plus 2 g water, less 1%)
After distillation, the water was transferred to clean, dry ampoules of the type used for Standard Sea Water, and sealed.

Conclusion

No apology is made for what might seem unnecessary detail in this description. The whole object of this report is to make possible exact duplication of the procedure, should other workers wish to prepare similar water.

Arrangements have been made for two independent laboratories, in Denmark and the United States, to determine the isotopic ratios in the water. It is also hoped to prepare similar distilled water from the deep Pacific water, and to compare this with our Mediterranean water, both in isotope ratios and in density. When the N.P.L. determines the absolute density of water, we hope that at least some of their measurements will be on the water prepared as described in this report.

Most of the remaining conductivity shown by this water is certainly due to dissolved carbon dioxide. No attempt has been made to keep the water air-free. It has been shown by several observers (see Dorsey, 1940) that the effect of saturating water with air, compared with air-free water, is to reduce the density by at most 3 p.p.m., and usually less. This being,so, to avoid ahe serious problems inherent in handling and transferring of air-free water, it seems best to use the water in equilibrium with air, always allowing adequate time for equilibration at the temperature at which it is to be used. Should it be decided later to use the water air-free, the air can readily be removed by re-distillation *in vacuo*.

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Figure One: Pyrex stills for stages one and two of distillation

	Quickfit and Quartz catalogue No.
1) 2-l. round bottom flask, B24/29 socket.	FR2L/3M
2) Splash head, vertical delivery, B24/29.	SH7/53
3) Double surface condenser, 15 cm. B24/29 socket and core.	C5/13
4) Receiver adaptor, vertical delivery, B24/29 joints.	RA13/33
5) Internal spiral condenser, 20 cm. B24/29 joints.	C6/13
6) 1-l. flat bottom flask, B24/29 socket.	FF1L/3MF
7) Heating mantle, 2l. size, 450 watts.	
8) Variable-ratio transformer 500 VA.	
9) Labjack, for adjusting heating mantle.	
10) Fibreglass insulation. Shown in place on second still, but used on both stills.	

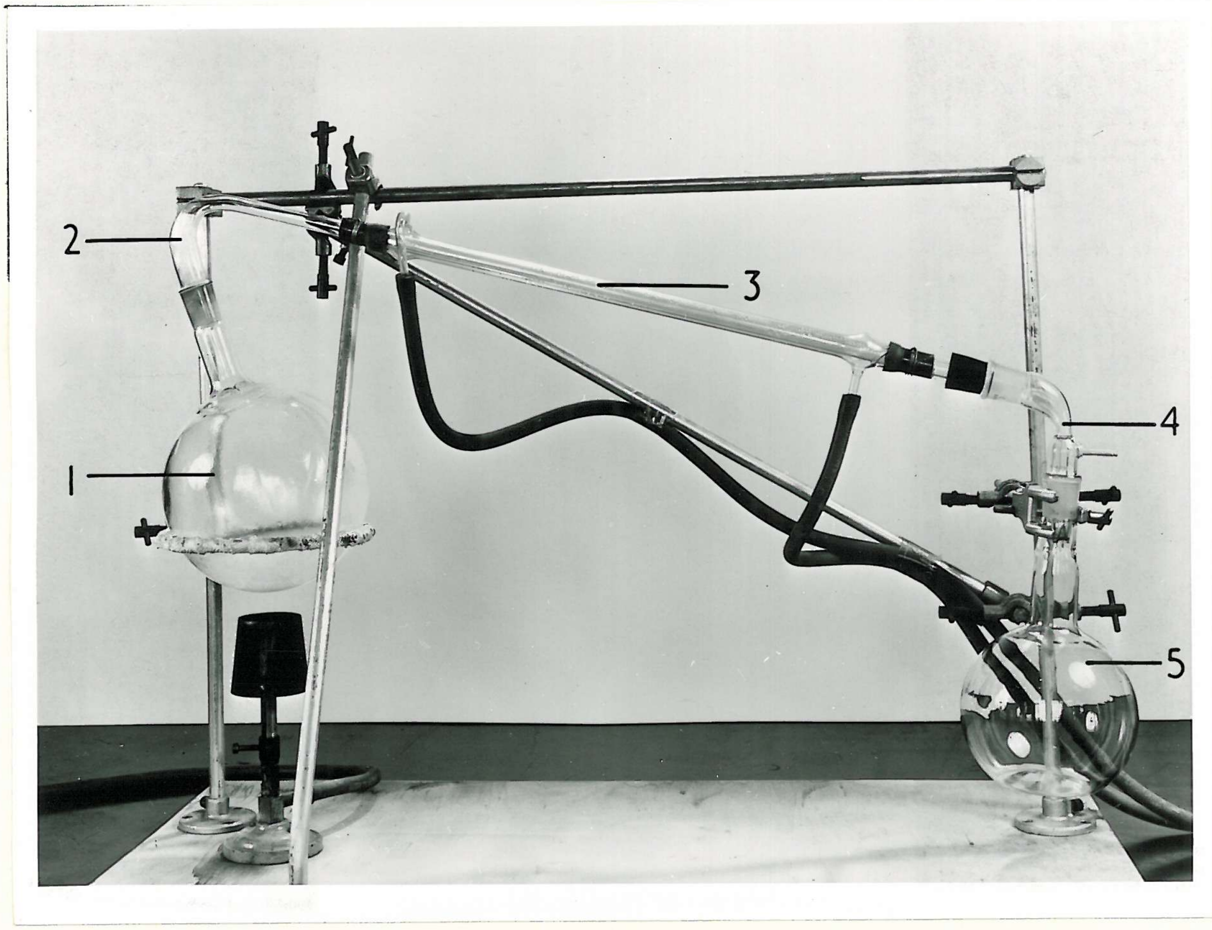

Figure Two: Silica still for stage three of distillation

1) 2-l. transparent silica flask with B24/29 socket.
2) Transparent silica condenser, 65 cm., bore 1 cm.
3) Pyrex water jacket.
4) Angled vacuum reciever, Q & Q RA3/33
5) 1-l. flat botton pyrex flask Q & Q FF1L/2MF.