Rapport BIPM/85-12

IUPAC Subcommittee on Physicochemical Measurements and Standards

Lyon - August 1985

International Association for the Physical Sciences of the Ocean

Honolulu - August 1985

REDETERMINATION OF WATER DENSITY

by G. Girard
Bureau International des Poids et Mesures
Pavillon de Breteuil - F-92310 Sèvres - France

Water, the metrological liquid above all, is not only a reference material used in most determinations of volume and density, but it is also, in physical oceanography, one of the most fundamental quantities, the knowledge of which is essential to tackle the majority of problems.

The knowledge of its density depends upon a number of factors, most of which are not known with sufficient precision:

a) fundamental value : the accepted value, 999,972 kg.m^{-3}, is the density of air-free water at 4 °C under a pressure of 101 325 Pa, determined between 1895 and 1905, a time when the existence of isotopes was not suspected.

b) the thermal expansion coefficient : the available data between 0 °C and 40 °C are not consistent, particularly above 16 °C.

c) dissolved atmospheric gases : their influence is not sufficiently well known.

d) isotopic composition : this factor was not studied until recently.

e) compressibility : the only factor that is known, around the pressure of one atmosphere, with sufficient precision.

In 1967, M. Menaché drew attention to the fact that for modern requirements, particularly in physical oceanography, there was a need for a better knowledge of the density of water. At that time it was not known to better than 0,01 kg.m^{-3}, due to the cumulation of uncertainties stemming from different parameters. In 1969, the Joint Panel on Oceanographic Tables and Standards (sponsored by International Association for the Physical Sciences of the Ocean (IAPSO), the International Council for the Exploration of the Sea (ICES), UNESCO, and the Scientific Committee on Oceanic Research (SCOR)), prepared a Recommendation that was adopted by IAPSO. The International Union for Geodesy and Geophysics (IUGG) made a Recommendation for a new study of the density of water, the text of which was passed to the Comité International des Poids et Mesures (CIPM).

In the same way, Commission I.4 (Commission on Physicochemical Measurements and Standards) of the International Union of Pure and Applied Chemistry (IUPAC) has been concerned with the same subject since 1965. During its successive meetings, and most particularly in 1969 and 1971, concrete propositions were submitted to this Commission by

Mr. Terrien, at that time Director of BIPM. In 1973, a Recommendation on the redetermination of the density of water and the study of its different factors was issued and sent in 1974 to a number of important metrological and oceanographical laboratories.

In 1975, IAPSO approved the Recommendation of IUPAC in its Resolution N° 8.

Various national laboratories answered this call, and in particular the Commonwealth Scientific and Industrial Research Organization (CSIRO), Division of Applied Physics, Australia, the National Research Laboratory of Metrology (NRLM), Japan, the Istituto di Metrologia G. Colonnetti (IMGC), Italy, and the Bureau International des Poids et Mesures (BIPM), Sèvres (France).

This note aims to inform oceanographic physicists on the progress of the works last recommended by their Association in 1975.

The methods used for the study of all the parameters will be described briefly.

ABSOLUTE VALUE. THERMAL EXPANSION

These two parameters have been studied jointly at CSIRO (Australia) and separately at NRLM (Japan). The study undertaken at IMGC (Italy) concerned only the absolute value of the density of water.

The method used in these three laboratories to determine the absolute value of the density of water consists in measuring, for the same solid body, first its dimensions to determine its volume, then its mass in air, and finally, by the hydrostatic method, its weight submerged in water.

CSIRO (Australia)

A hollow sphere of ULE glass with a low thermal expansion coefficient was used. After making sure its roundness was acceptable, its mean diameter was determined by measurements of 10 different diameters with an interferometer sketched in Figure 1. These measurements were repeated at different temperatures between 6 and 40 °C which allowed the curve of its change of volume to be obtained (see Figure 2).

The mass of the sphere, of about 330 g, was determined to better than 50 µg.

The sphere, suspended from the pan of a balance, was then submerged in the water whose density was to be determined. The weight in water was determined by differential measurement (see Figure 3). These measurements were repeated at different temperatures, between 4 and 40 °C, with several samples of water. The water was either degassed, or in equilibrium with ambient air. The isotopic composition and the content of dissolved atmospheric gases of these samples of water were considered.

Thus the absolute value of the density of water was obtained at several temperatures, and hence its thermal expansion coefficient. Of course, a certain number of corrections were considered in these measurements such as correction of loss of phase in interferometry, compressibility of the sphere, buoyancy of air... and all the necessary precautions were taken in order to eliminate the possible sources of errors.

NRLM (Japan)

The NRLM used three transparent spheres made of fused silica of 85 mm diameter, weighing about 700 g. The measurement of the absolute value of density is divided into four phases:

1. interferometric measurements of the diameter of the spheres;
2. determination of the mass of the spheres;
3. hydrostatic weighings in different samples of water;
4. comparison of these waters to a pure reference water.

1. The out-of-roundness is about 0,2 µm. The interferometer used is very close to the one of Figure 1 but, the spheres being transparent, a change was made to eliminate the parasitic reflections due to the laser beam; 10 diameters were measured.

2. In the measurements of mass, precautions were taken to eliminate the electrostatic forces and special care was taken in the measurement of the parameters for the calculation of the density of air using the CIPM formula.

3. The procedure followed for the hydrostatic weighings is first to degass water at about 75 °C and, when it is partly cooled, to decant it in the container for measurement (see Figure 4), and introduce in it the sphere and the fin. These are intended to slow the spreading of air in water. Twenty five weighings were made in each of the nine samples of water that were used.

4. These samples were then compared to a pure reference water in order to make a correction taking into account the dissolved gases and the isotopic composition. The two samples (measurement water and reference water) were put into two pycnometers placed into a water bath maintained at a constant and uniform temperature. They were compared by the hydrostatic method (see Figure 5).

The reference water was prepared either by purifying tap-water or by purifying sea-water by triple distillation according to the method of Cox, MacCartney and Culkin. A comparison of these two reference waters showed no significant difference.

After these different successive measurements, we expect to know the absolute value of the density of water with an accuracy better than 1×10^{-6}.

Four hollow bodies were used to study the thermal expansion coefficient of water (two filled with water, two others empty). They were submerged in water and the upthrust they received was measured by the hydrostatic method (see Figure 6). The compressibility of these hollow bodies was determined together with their change in volume according to temperature. The samples of water used were purified by double distillation and their isotopic composition determined in a specialised laboratory. The measurements of the thermal expansion coefficient of water were made between 0 and 44 °C with a precision better than 1×10^{-6}. The results were fitted to an equation of the sixth degree giving the relative density of water according to temperature.

IMGC (Italy)

In this laboratory 9 cm diameter Zerodur spheres were used whose mass was close to 1 kg. This material has a very low thermal expansion coefficient, close to $1 \times 10^{-8}\ \mathrm{K}^{-1}$ and a density of about $2\,500\ \mathrm{kg.m}^{-3}$.

Before measuring their volume, their roundness was verified and curves such as the ones of Figure 7 were obtained.

The volume was calculated according to the measurements of the different diameters in an interferometer whose principle is close to the one of Figure 1. The relative uncertainty on the volume, of about $380\ \mathrm{cm}^3$, is $1{,}1 \times 10^{-6}\,(1\sigma)$.

The determination of the mass of these spheres raises some problems due principally to the air buoyancy correction which is of the order of 400 mg.

The total uncertainty on the density of these spheres is of $1{,}1 \times 10^{-6}$.

The ratios of the volumes of these different spheres was verified by the hydrostatic method using water as the transfer standard (Figure 8). The agreement is very good ($\approx 1 \times 10^{-6}$) between the ratios of the volumes measured by interferometry and by water.

From these bodies whose volume is known, measurements are being made to determine the density of water.

DISSOLVED ATMOSPHERIC GASES

The influence of this parameter on the density of water has been studied at CSIRO, NRLM and BIPM.

CSIRO (Australia)

In this laboratory, the method of a magnetic servo-controlled float was used (see Figure 9). A glass float containing a magnet and properly ballasted is maintained in a steady position located by an optical system. Every deviation from this position produces a current change in a coil, which creates a restoring force on the float. The servo-controlled current gives a measurement of the buoyancy of the float and hence of the density of the liquid in which it is immersed. One can then detect small changes in density.

The degassed water was transfered to the measurement cell. After the necessary time for the readings of position, air was bubbled through the water for about fifteen hours in order that it be air-saturated. A second series of readings was made, and the difference between the currents is a measurement of the change in density. Measurements were made between 3 and 21 °C.

Another series of experiments, in the same range of temperatures, consisted in dissolving separately the principal constituents of air such as oxygen, nitrogen and argon, the procedure of measurement remaining the same.

The result of these measurements shows that if the changes in density observed for each gas are added, taking into account their molar fraction weighting, the same change in density as the one due to air is observed.

NRLM (Japan)

In this laboratory as well, two series of measurements have been made, one with atmospheric air, the other with oxygen, nitrogen, argon and carbon dioxide.

In the first series of measurements, two pycnometers compared by the hydrostatic method in the same way as for the determination of the absolute value of the density of water were used (see page 3 and figure 5). One of these pycnometers is filled with degassed water and the other one with air-saturated water.

The concentration of dissolved air is inferred from that of dissolved oxygen, measured by the Winkler method.

In the second series, the same method of pycnometers was used, one of the pycnometers being always filled with degassed water, while the other one was filled with water saturated with one of the constituent gases of air, above mentionned.

These measurements were repeated at several temperatures between 0,7 °C and 20 °C, but the results can be extrapolated up to 40 °C. Taking into account the partial molar volume of each gas, a formula was obtained giving the difference in density between degassed and saturated water as a function of temperature.

BIPM

At BIPM, this study was undertaken using the apparatus that is used to determine the volume of mass standards by hydrostatic weighing. The variation in upthrust on a body whose volume is known, immersed in water, according to the change in the quantity of dissolved atmospheric gases in this water, was observed. The first weighing was made after degassing, soon after the exposure of the hydrostatic bath to air; the following weighings were spaced over several days during which the content of dissolved atmospheric gases increased whether naturally, or artificially by bubbling. The quantity of dissolved gases was determined on samples taken after every hydrostatic weighing. In a parallel study, it was demonstrated that one could confine oneself to chemical titration of oxygen, for example by the method of Winkler, improved by Carpenter, since the oxygen saturation level of the sample represented satisfactorily its saturation level in dissolved atmospheric gases. Figure 10 shows the observed changes of the density of water according to the content in dissolved atmospheric gases, at 4 and 22 °C.

Figure 11 allows a comparison of the results obtained in the three laboratories, CSIRO, NRLM and BIPM.

ISOTOPIC COMPOSITION

A first theoretical study of the effect of the isotopic composition of water on its density was made in 1965 by M. Menaché who published in 1971 a second, more sophisticated, formula. The isotopic composition of water in oxygen-18 (^{18}O), oxygen-17 (^{17}O) and deuterium (D) is compared with that of a reference water which is taken, by the specialists, as the standard of isotopic composition: Standard Mean Ocean Water now called Vienna-SMOW (V-SMOW).

The effect of isotopic composition on the density of natural waters is given in the following formula, valid between 0 and 30 °C.

$$(\rho_{\text{sample}} - \rho_{\text{V-SMOW}})\ 10^3/(\text{kg.m}^{-3}) = 0{,}233\ \delta_{18} + 0{,}0166\ \delta_D \pm 0{,}1$$

$$\text{where } \delta_{18} = \frac{\dfrac{[^{18}O]}{[^{16}O]}\ (\text{sample}) - \dfrac{[^{18}O]}{[^{16}O]}\ (\text{V-SMOW})}{\dfrac{[^{18}O]}{[^{16}O]}\ (\text{V-SMOW})} \cdot 10^3$$

$$\delta_D = \frac{\dfrac{[D]}{[H]}\ (\text{sample}) - \dfrac{[D]}{[H]}\ (\text{V-SMOW})}{\dfrac{[D]}{[H]}\ (\text{V-SMOW})} \cdot 10^3$$

where $[H]$, $[D]$, $[^{16}O]$, $[^{18}O]$ are the concentrations (amount of substance divided by volume) of the different nuclides present in this sample.

This theoretical study has been confirmed by experimental work at BIPM, the final results of which were presented at the IUGG General Assembly in 1975.

The same apparatus as for the study on the influence of dissolved gases was used. The method is the same: the change of buoyancy of the water on the immersed body, of known volume, being due now to the change of the isotopic composition, corresponding to different samples of water.

These samples came from: 1) melted Antarctic ice (one of the lightest of the natural waters), 2) the Mediterranean, 3) BIPM tap-water. After double distillation, the difference between the maximum and minimum densities was found to be 19 x 10^{-3} kg.m^{-3}.

COMPRESSIBILITY

We presently have a formula, proposed by Kell, which is satisfactory for measurements around atmospheric pressure.

VERIFICATION

Comparisons have been undertaken to determine the agreement between these results and those coming from the determination of the density of silicon crystals, obtained at the National Bureau of Standards (U.S.A.) in 1974. The first results show an agreement of the order of 1×10^{-6} in relative value.

CONCLUSION

The above mentionned studies have been completed or are on the way to being completed. They will help to establish a table of the variation in the density of water according to temperature, isotopic composition, content in dissolved atmospheric gases and pressure, in the neighbourhood of natural conditions.

We hope to be able to realize this table of the density of water in the near future and hence give to oceanographic physicists, as well as to others, a single source of data, sufficient for their needs.

BIBLIOGRAPHY

Non-exhaustive list of some bibliographical references giving the methods used and the results obtained.

CSIRO (Australia)

BELL, G.A., CLARKE, A.L. Atomic Masses and Fundamental Constants, *5*, 1976, p. 615 (Plenum Publishing Corporation, New York).

BELL, G.A., PATTERSON, J.B. Proceedings Conf. Precise Measurement Fundamental Constants II, NBS Special Pub. 617, Washington, 1984, p. 445.

BIGNELL, N. *J. Phys. E: Sci. Instr.*, *15*, 1982, p. 378; *Metrologia*, *19*, 1983, p. 57; *J. Phys. Chem.*, *88*, 1984, p. 5409.

NRLM (Japan)

IIZUKA, K., SEINO, S., INAMATSU, T., WATANABE, H., MASUI, R., ITO, T. *Acta IMEKO 1979*, 1979, p. 827.

MASUI, R., SEINO, S., SENDA, O., OKAMOTO, Y. Document presented at the Xth International Conference on the properties of vapor, Moscow, September 1984.

MASUI, R., WATANABE, H. *Japan J. Appl. Phys.*, *17*, 1978, p. 755.

WATANABE, H., IIZUKA, K. Proceedings 8th Symp. Thermophysical Properties, Vol. II, 1981, p. 319 (American Society Mechanical Engineers, New York).

WATANABE, H., IIZUKA, K. *Japan J. Appl. Phys.*, *20*, 1981, p. 1979; *Metrologia*, *21*, 1985, p. 19.

IMGC (Italy)

PEUTO, A., SACCONI, A. et al. Proceedings Conf. Precise Measurement Fundamental Constants II, NBS Special Pub. 617, Washington, 1984, p. 449.

PEUTO, A., PETTORRUSO, S., RASETTI, M. Proceedings Symp. IMEKO TC-8, 1983, p. 305.

PEUTO, A., SACCONI, A. *Fisica e Tecnologia*, *6*, 1983, p. 277.

BIPM

Formule pour la détermination de la masse volumique de l'air humide (1981). *BIPM Proc.-Verb. Com. Int. Poids et Mesures*, *49*, 1981, pp. C1-C15; Equation for the determination of the density of moist air (1981). *Metrologia*, *18*, 1982, pp. 33-40.

GIRARD, G., MENACHE, M. *Metrologia*, *7*, 1971, p. 83; *C.R. Acad. Sci. Paris*, *B*, *274*, 1972, p. 377.

GIRARD, G., COARASA, M.-J. Proceedings Conf. Precise Measurement Fundamental Constants II, NBS Special Pub. 617, Washington, 1984, p. 453.

MENACHE, M. *Metrologia* ,*3*, 1967, p. 58.

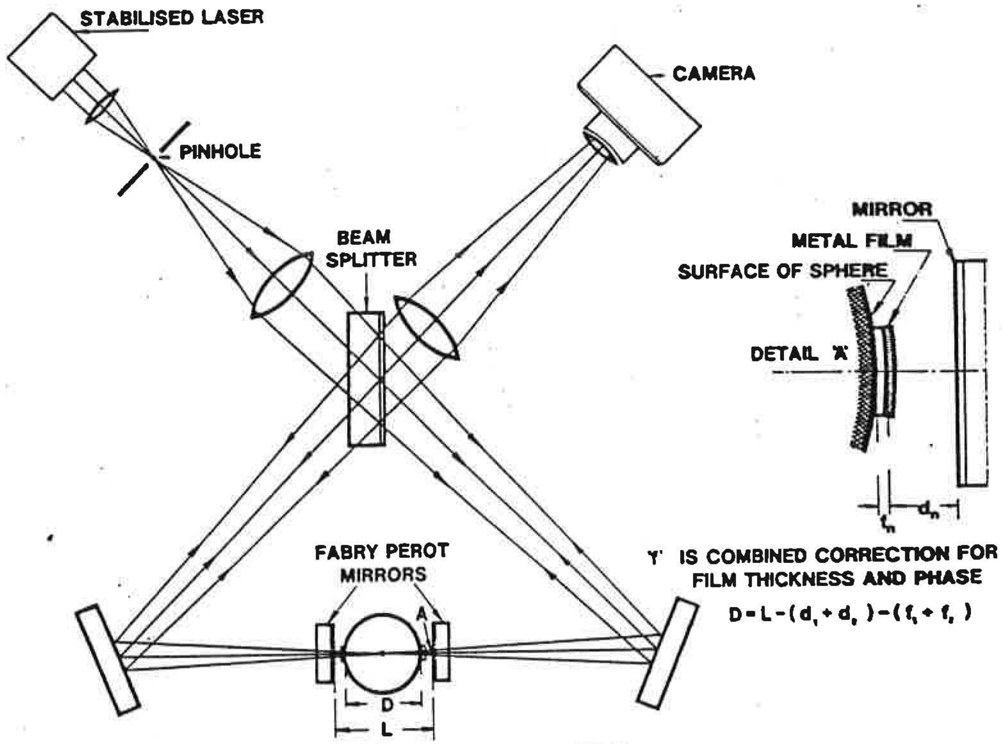
MENACHE, M., BEAUVERGER, C., GIRARD, G. *Ann. Hydrographiques*, *6*, 1978, p. 37.

Miscellaneous

CARPENTER, J.H. Limnol Ocean, 10, 1965, p. 135.
COX, R.A., MacCARTNEY, M.J., CULKIN, F. Deep-Sea Res., 17, 1968, p. 679.
IUPAC Commission I.4. Recommendation for Redetermination of the Absolute Density of Water, 1974.
KELL, G.S. J. Chem. Eng. Data, 15, 1970, p. 119.

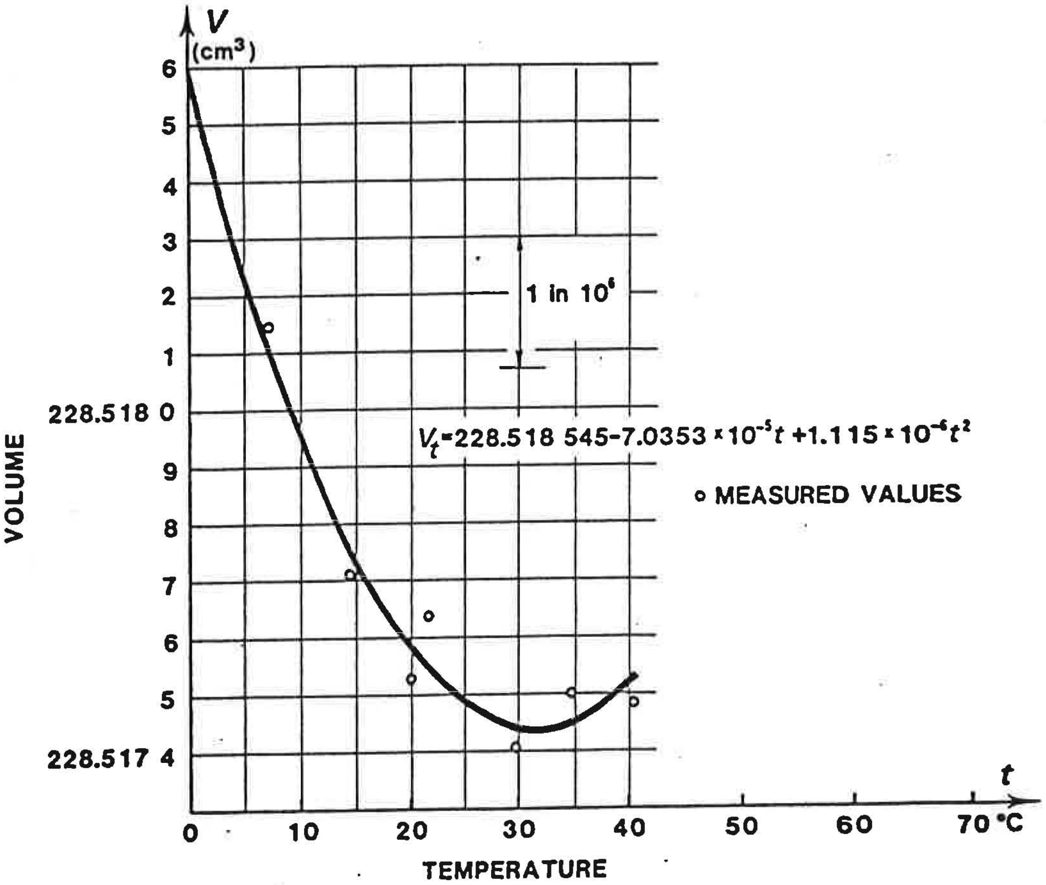
CAPTIONS TO FIGURES

1. Sketch of the interferometer for the measurement of the diameters of a sphere.
2. Variation of the volume of a sphere according to temperature.
3. Principle of the apparatus for a hydrostatic weighing.
4. Sketch of the hydrostatic bath.
5. Hydrostatic weighing for comparative measurement of density.
6. Sketch of the apparatus for the measurement of the thermal expansion coefficient of water.
7. Examples of curves both polar and cartesian, showing the variation in the radius of a sphere.
8. Sketch of the apparatus, balance and hydrostatic weighing.
    1. single-pan 1 kg balance
    2-4. Pt-resistance thermometer
    3. mass standards
    5. rotating and vertically sliding platform
    6. immersed "pan" (stainless-steel suspension)
    7. solid density standard
    8. inner vessel filled with bi-distilled water
9. Magnetic float densimeter.
10. Variation, at 4 and 22 °C, of the density of a sample of water according to the content in dissolved atmospheric gases.
11. Variation of the difference of density between degassed water and saturated water, according to temperature. Results obtained.
    1. NRLM
    2-3. CSIRO
    4. BIPM



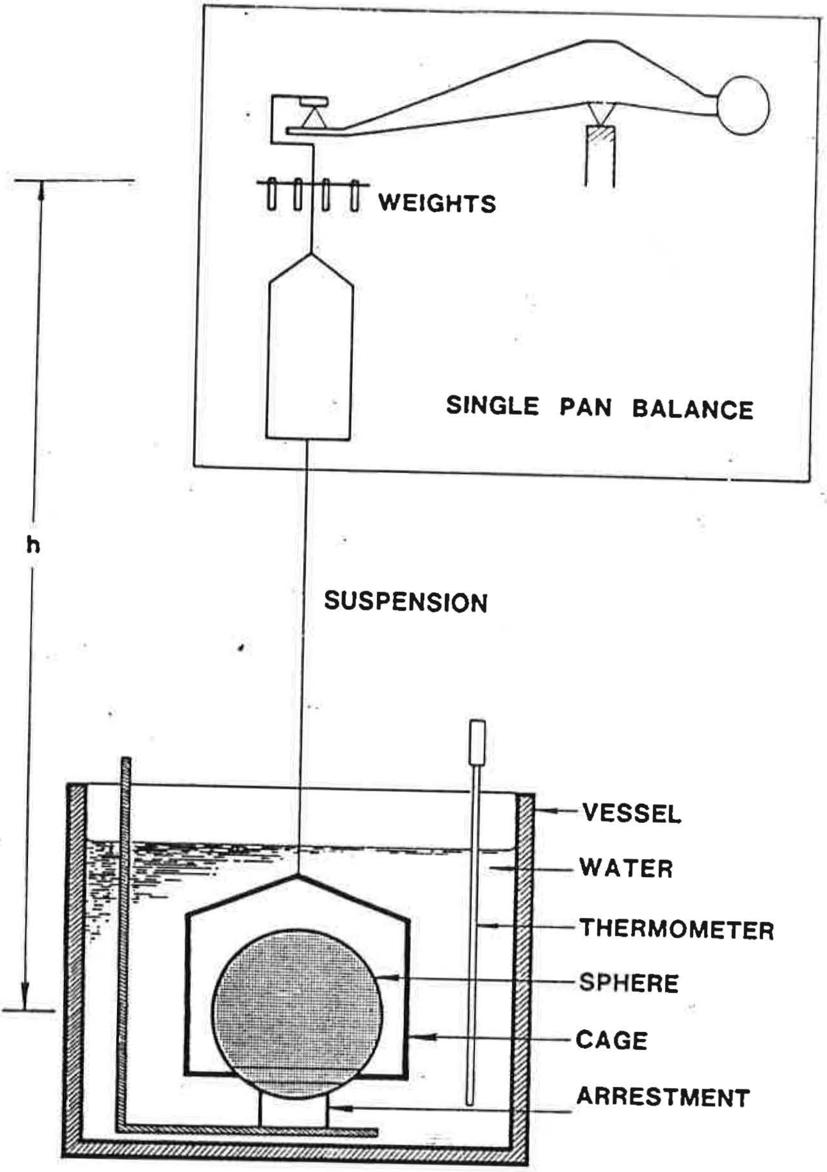
MEASUREMENT OF SPHERE

Fig. 1 .- CSIRO



VOLUME OF ULE SPHERE

Fig. 2.- CSIRO



PRINCIPLE OF EXPERIMENT

Fig. 3.- CSIRO

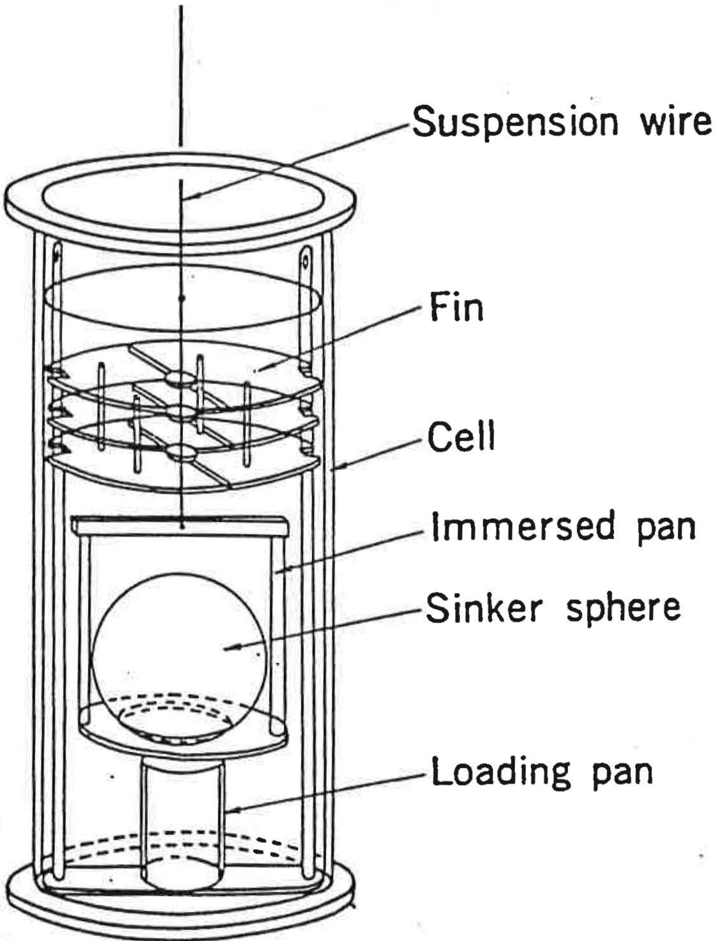


Fig. 4.- NRLM

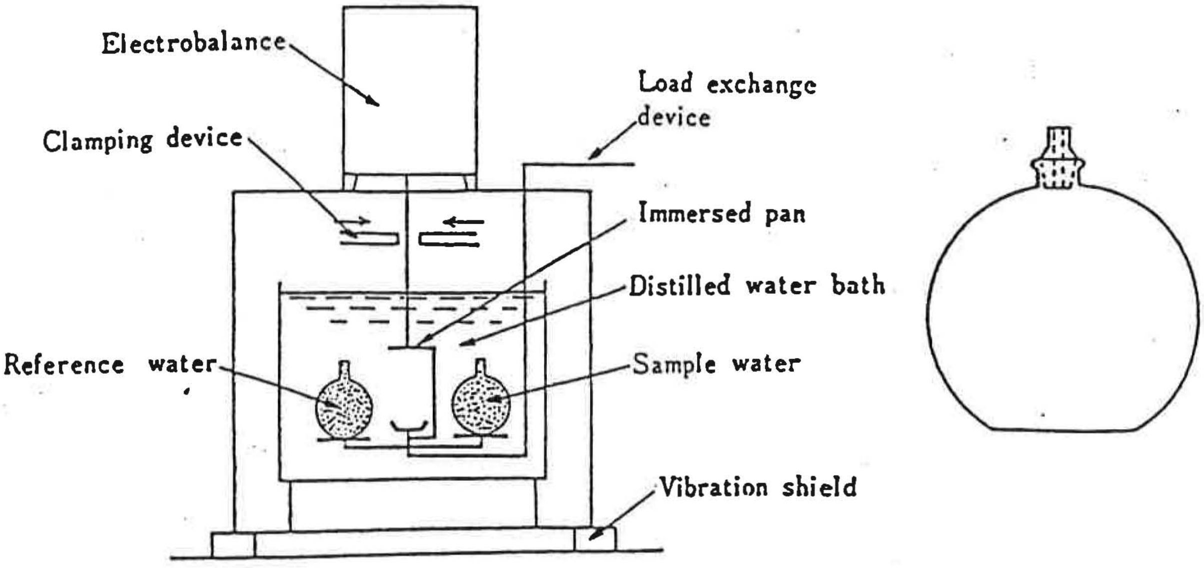


Fig. 5.- NRLM

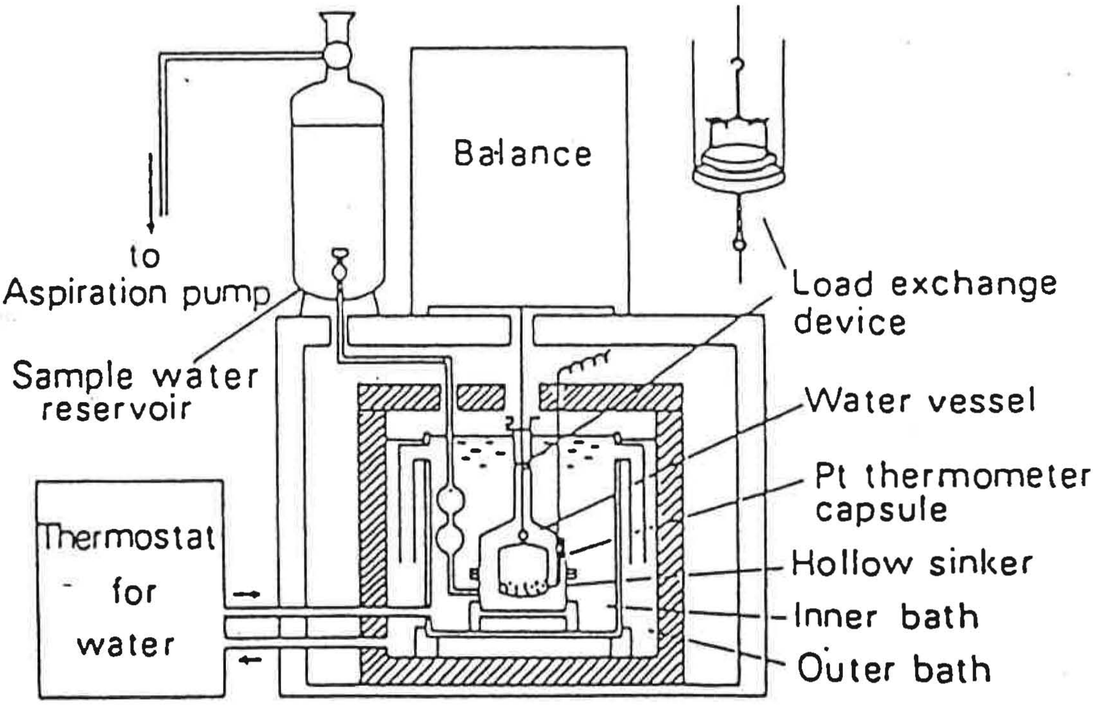


Fig. 6.- NRLM

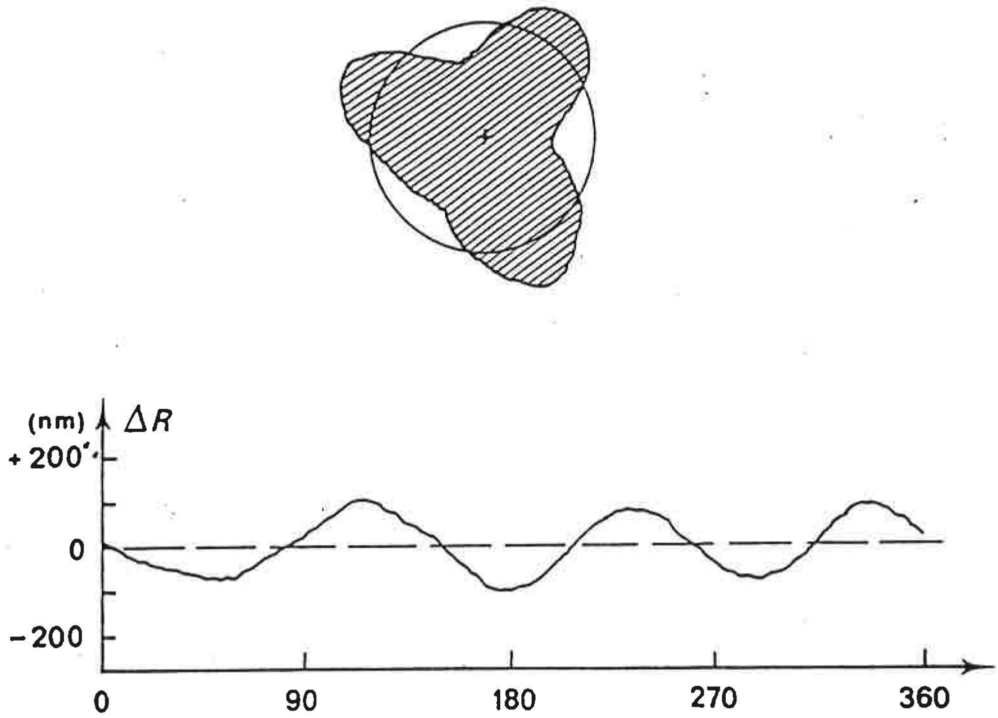


Fig. 7.- IMGC

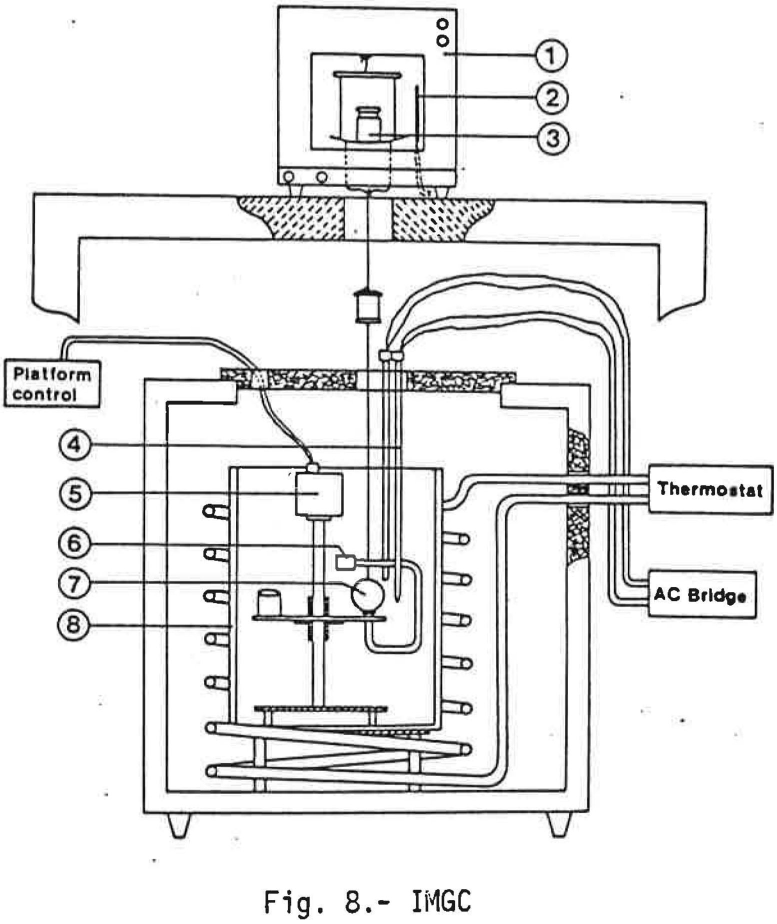


Fig. 8.- IMGC

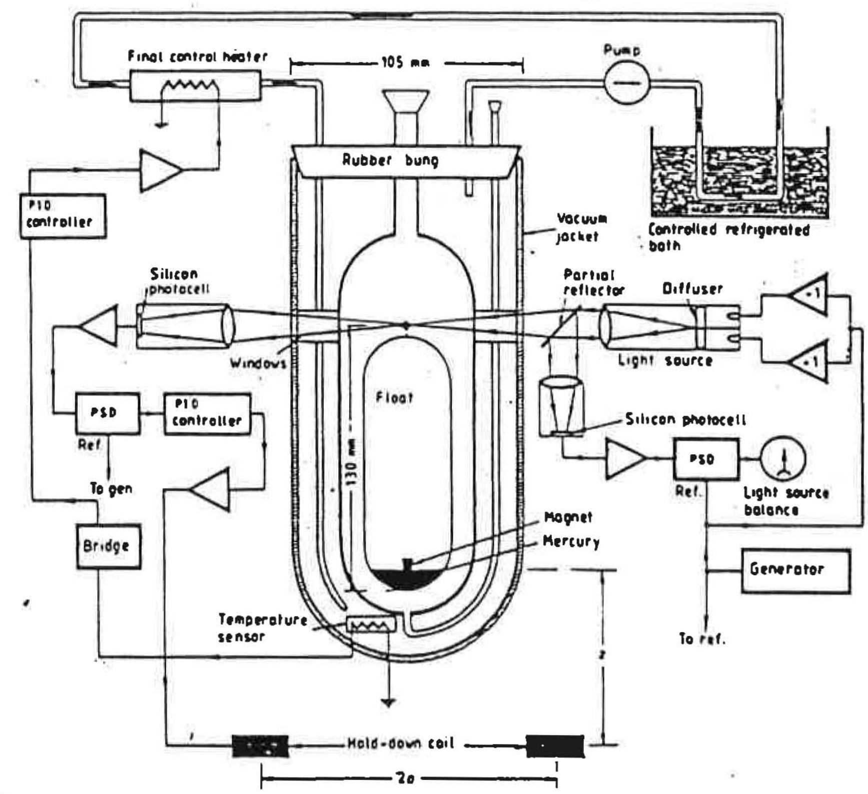


Fig. 9.- CSIRO

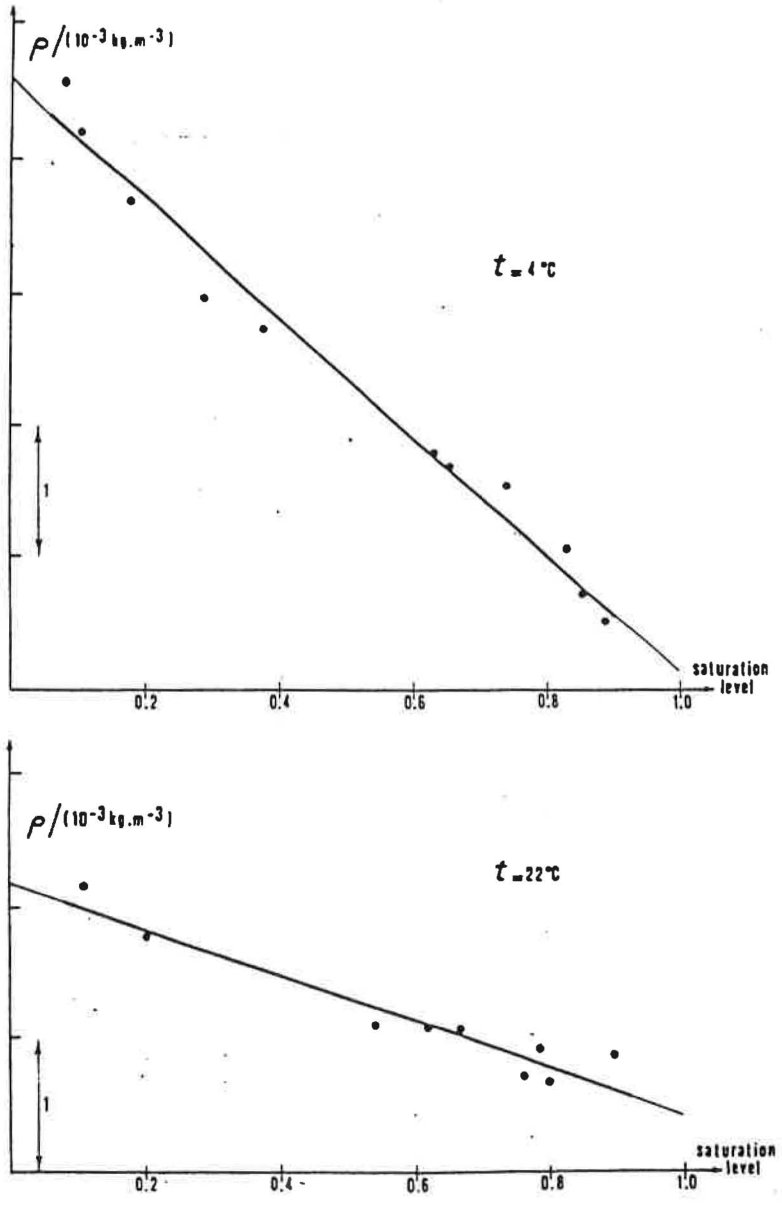


Fig. 10.- BIPM

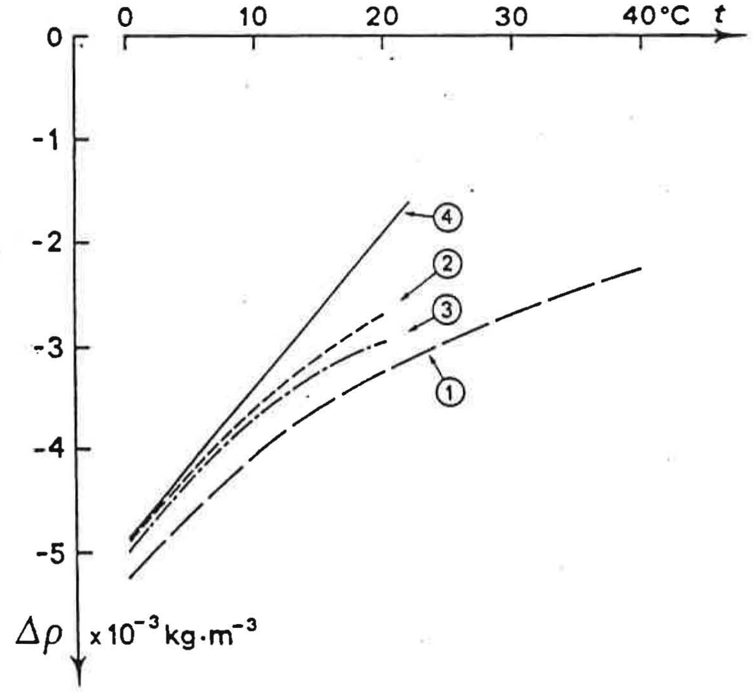


Fig. 11