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Kenichi Fujii

Recommended table for the density of water between 0 °C and 40 °C based on recent experimental reports¹

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Abstract. Experimental results from four recent research reports on the determination of the density/temperature relationship of Standard Mean Ocean Water (SMOW) under a pressure of 101 325 Pa are analysed and a new formula is recommended for metrological applications. This paper determines the formulae of density and relative density, with their uncertainties, in the temperature range 0 °C to 40 °C. The uncertainty estimation of one of the reports included in the analysis has been re-evaluated. Effects on water density due to isotopic mixtures other than SMOW, ambient pressures different from 101 325 Pa, and the presence of dissolved air, are also reviewed.

1. Introduction

1.1 Background

Water is a ubiquitous liquid whose physical properties serve as references in many areas of science (particularly in the fields of oceanography and chemistry). Its density is a widely used reference for determinations of unknown densities and volumes. Tables for the relative density² of water between 0 °C and 40 °C have been deduced from measurements carried out by Thiesen et al. [1] and by Chappuis [2] at the beginning of the twentieth century. Most other tables in the literature [e.g. 3-7] are derived from this early work. Note that the relative density tables given in [1] and [2] are consistent to within 1 part in 10⁶ only in the range of temperatures 0 °C to 16 °C. At 40 °C, the tables have diverged by almost 10 parts in 10⁶.

Once the relative density has been established over a range of temperatures, knowledge of the density at one temperature within the range is sufficient to fix the density over the entire range. The density of water was calculated from the measurements at the BIPM, also carried out by Chappuis [2], which found the maximum density ρ_{\max} of distilled tap water, free of dissolved gases and at a pressure of 101 325 Pa, to be 999.972 kg m⁻³. The density maximum occurs at approximately

4 °C. However, these density measurements were made at a time when the existence of isotopes was unknown and, therefore, the uncertainty from this source alone is insufficient for the most demanding modern use.

By 1965, the problem of water density drew the attention of the Association Internationale pour les Sciences Physiques de l'Océan and its recommendation was adopted by the International Union of Geodesy and Geophysics (IUGG) in 1971 (Resolution 18). The Resolution called for the determination of the density of water, in terms of the International System of Units (SI), at 0 °C and 20 °C and for the determination of the relative density of water between 0 °C and 40 °C.

At the same time, Commission I.4 (Commission on Physico-Chemical Measurements and Standards) of the International Union of Pure and Applied Chemistry (IUPAC) took up the same question. In 1973, IUPAC issued a Recommendation [8] asking for the following:

- that absolute determinations of the density of water, whose isotopic composition is as close as possible to Standard Mean Ocean Water (SMOW) be undertaken with the goal of a final uncertainty no greater than 0.001 kg m⁻³ at two or three well-defined temperatures in the range between 0 °C and 40 °C;

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1. This report was prepared by a Task Group formed by the Working Group on Density, Consultative Committee for Mass and Related Quantities (CCM). The Working Group has accepted the report, which will be submitted for final approval to the International Committee for Weights and Measures (CIPM) at its meeting in October 2001.

2. The term "relative density" refers to the ratio of water density at a given temperature to the maximum density, which occurs near 4 °C. The term "thermal dilatation" is sometimes used to designate a related quantity, which is the ratio of water volume at a given temperature to the volume at 4 °C.

- that the relative density of water between 0 °C and 40 °C be determined with the same relative uncertainty as the density measurements;
- that both the influence on the density of water of its isotopic composition and the influence of dissolved atmospheric gases be determined with uncertainties sufficiently small to allow the density of water to be corrected for these effects.

In addition, while awaiting the results of this programme of work, the Recommendation proposed the use of a provisional table giving the density of SMOW, free of dissolved gases and at atmospheric pressure (101 325 Pa) as a function of temperature between 0 °C and 40 °C. The SMOW in question is the reference standard to which water samples of unknown isotopic composition are compared. The provisional table that was appended to the IUPAC Recommendation is taken from Bigg [5]. However the IUPAC recommendation relies on the work of Girard and Menaché [9] to set the value of the maximum density of SMOW as $\rho_{\max} = 999.975 \text{ kg m}^{-3}$.

The final limitation to the utility of the original determinations of the density of water is the relation between the temperature scale used for those determinations and the temperature scale in use today, the International Temperature Scale of 1990 (ITS-90) [10]. Thiesen et al. and Chappuis measured temperature in terms of the “Échelle Normale” (EN), which was based on the hydrogen thermometer. The progression from the EN to the ITS-90 went through no fewer than three “practical” temperature scales: those of 1927, 1948 and 1968 [10]. Except near 0 °C, differences between these scales and the EN are poorly known, which makes it impossible to compare high-accuracy modern measurements of relative density with those made almost a century ago. In the range from 0 °C to 40 °C, the many tables of water density that are based on the work of Thiesen et al. and Chappuis assume different hypotheses relating the EN to the later temperature scales.

In 1975, the Director of the BIPM accepted responsibility for coordinating international work on water density. Programmes of research were soon begun at the CSIRO (Australia) and the NRLM (Japan) on the density and relative density of water, as well as on the influence of dissolved atmospheric gases. The difference in density, relative to SMOW, as a function of the isotopic composition of water had already been determined at the BIPM in a programme that had begun in 1967. With the creation of the Consultative Committee for Mass and Related Quantities (CCM) of the CIPM, responsibility for coordinating this work passed to the CCM Working Group on Density.

1.2 Results published in the 1990s

Recent progress in materials science and technology has provided metrologists with several new concepts

and tools for the determination of the density of water. Preparation of pure water has been aided by semiconductor technology and preparation of artefacts of known volume (sometimes known as “sinkers”) is now possible using high-precision technology. The four most recent experimental results [11-14] fulfil the programme of work recommended by the IUPAC in 1973. Specifically, we note the following accomplishments:

- Results are reported in terms of the temperature scale now in use (ITS-90).
- Relative density results cover the range of temperatures from 0 °C to 40 °C [11-13].
- Density determinations are reported at a number of different temperatures by one group [13] and at a temperature of 16 °C by a second group [14].
- Density results are corrected to the density of SMOW.
- Results are based on de-aerated water at standard atmospheric pressure (101 325 Pa).
- Results have a claimed relative uncertainty of approximately 1×10^{-6} .

All results have been peer-reviewed and published in *Metrologia*. The authors have, in some cases, provided additional information during the preparation of this report.

We first briefly summarize the new measurements. We then explain in detail the method used to combine these results to arrive at analytical expressions for the density and relative density of water. The maximum density of water and the temperature of this maximum are given explicitly. We then compare the recommended table with two tables based on the earlier work. Finally, we indicate how the density of water changes as a function of isotopic abundances, atmospheric pressure and dissolved air.

2. Results considered in this work

2.1 Relative density measurements of Takenaka and Masui [11]

A cylindrical dilatometer made from fused quartz was filled with a water sample. One surface of the water was sealed by mercury which, in turn, passed through a capillary tube and out of the thermostat. The change in the volume of the water as a function of temperature was determined from the mass of mercury collected in a weighing bottle. The temperature range from 0 °C to 85 °C was studied. Results are given relative to ρ_{\max} . The thermal expansion of the fused quartz cell was determined experimentally by optical interferometry. Measurements were made in four different series totalling 72 data points. Type A relative uncertainties were claimed to be 0.2×10^{-6} for all data

points. Type B relative uncertainties were estimated at 20 °C, 40 °C and 80 °C and a full uncertainty budget was given (Table 3 of [11]). We have assumed that Type A uncertainties are uncorrelated and that Type B uncertainties are correlated for all data within a subset. In the present analysis, the Type B uncertainties throughout the temperature range were estimated by interpolation.

2.2 Relative density measurements of Watanabe [12]

A solid, hollow, artefact made from fused quartz was suspended from a balance and immersed in the water sample. Data were obtained in the temperature range from 0 °C to 44 °C. The thermal expansion of the sinkers was determined by optical interferometry and mechanical measurements on cylinders cut from the sinkers themselves. Four different sinkers were used in the experiment, giving a total of 225 data points. The results are summarized in [12] but the author has provided detailed results for the present analysis. The uncertainties were estimated at six different temperatures spanning the measurement range (Table 3 of [12]).

We have assumed that Type A uncertainties are uncorrelated and that Type B uncertainties are correlated over points in the data subset. A third-order polynomial was used to interpolate uncertainties throughout the temperature range.

2.3 Density measurements of Patterson and Morris [13]

The density was determined from the buoyant force on a hollow sphere of known density which was suspended from a balance and immersed in the sample of water. The sphere was made of ULE (ultra-low-expansion glass); its volume was measured by optical interferometry and its mass was determined by conventional means. Data were obtained at temperatures from 1 °C to 40 °C. The isotopic abundances of the water samples were measured relative to SMOW and the density was corrected to SMOW using the recommendation of Menaché et al. [16] (see Section 5). Nine different water samples were measured, giving a total of 67 data points.

Type A uncertainties are assumed to be uncorrelated and Type B uncertainties correlated. Among the latter, for example, is the uncertainty in the volume measurement of the ULE sphere. For unknown reasons, the densities obtained for one data set were inconsistent with the others; the relative densities inferred from these measurements were however consistent. The authors of [13] included these results for calculation of relative density only. We have thought it prudent not to include these points in our analysis. Furthermore, one of the authors of [13] (EM) has informed us of an erratum that should be included in the present

analysis. The uncertainty of both the mass standards and their correction for air buoyancy were omitted from the published report. The standard uncertainties for weighing should, therefore, be as follows:

- mean standard deviation of balance readings: 40 µg (as reported in [13]);
- standard uncertainty of air buoyancy correction: 27 µg;
- standard uncertainty of mass standards: 60 µg.

These components are uncorrelated and so we add them in quadrature to give a total uncertainty of 77 µg in the weighing, or a relative uncertainty component of 0.334×10^{-6} in the water density. Thus the third column of Table 16 of [13] should read 0.112×10^{-12} rather than 0.031×10^{-12} .

We emphasize that the largest uncertainty component for these measurements is due to the measurement of the apparent mass of the sphere in water. In this case, the published uncertainties are correct. There is a correlation in these uncertainties due to the standard masses but this component is only 0.1×10^{-6} relative to the density of water. Apart from the changes mentioned above, we have used the authors' estimated uncertainties from their Table 16 and have interpolated between temperatures as required.

2.4 Density measurement by Masui, Fujii and Takenaka [14]

Density was determined from the weight in water of a fused quartz sphere. The volume of the sphere had been measured by optical interferometry and its mass determined by conventional means. The density of the working sample of water was compared by a differential method to the density of reference samples whose isotopic abundances had been measured relative to SMOW.³ All density determinations were carried out at a nominal temperature of 16 °C.

Eighteen different working samples and three different spheres were used for the hydrostatic weighing. The density of each working sample was determined in five independent series of measurements and then used to determine the density of each reference sample. The densities of eighteen reference samples of known isotopic abundance were thereby determined, giving a total data set of 90 points. The estimated uncertainties are given in Table 3 of [14]. We have treated the Type B uncertainties in Table 3 as correlated and the Type A uncertainties as uncorrelated.

3. In [14], the authors cite the same correction formula as given in [13]. In fact, a slightly different formula was used. The consequences of this inconsistency are negligible for the present study. Nevertheless, in correcting their results to the density of SMOW, we have used the formula recommended in Section 5. This point was recently brought to light by Dr S. Gupta, now retired from the National Physical Laboratory of India.

3. Procedure for data analysis

The tables for the density and relative density of SMOW at 101 325 Pa are derived from formulae where temperature is the only independent variable. Temperatures in the range 0 °C to 40 °C have been studied in all four reports considered here (Sections 2.1 to 2.4) and all the data points with temperatures in this range are included in the present analysis.

The density of water, ρ , as a function of temperature, t , is expressed by Thiesen's formula using five parameters, a_1 to a_5 , as shown in the following equations.

$$\rho(t, \{a\}) = a_5 \left[1 - \frac{(t + a_1)^2(t + a_2)}{a_3(t + a_4)} \right] \quad (1)$$

$$r(t, \{a\}) = \left[1 - \frac{(t + a_1)^2(t + a_2)}{a_3(t + a_4)} \right]. \quad (2)$$

Equation (1) shows the relationship of density to temperature and (2) shows the relationship of relative density to temperature. The set of parameters a_1, a_2, a_3, a_4, a_5 , is expressed by $\{a\}$. One advantage of the formula is that both the maximum density, a_5 , and the temperature at which this occurs, $-a_1$, are used as parameters. In addition, expression (2) for the relative density allows easier data processing for the present analysis, especially for the data sets described in Sections 2.1 and 2.2, and most of the experimental data points show no significant or systematic deviation from the formula over the temperature range concerned. A polynomial expression to higher order would, of course, provide a closer fit to the data points. However, the present analysis, in which both density and relative density experiments are treated simultaneously, would require a much more complicated coding process in the polynomial expression than Thiesen's expression and would not provide a significant reduction in the uncertainty.

The set $\{a\}$ is determined by analysing the data set described in Section 2. Although (1) and (2) are non-linear in temperature, it should be kept in mind that the maximum differences in density (or relative density) throughout the range 0 °C to 40 °C are less than 1 %. Each data subset (2.1, 2.2, 2.3 and 2.4) has a finite number of data points, expressed either by (temperature, density) or by (temperature, relative density), denoted generally as (x_{ij}, y_{ij}) . Their uncertainties are determined according to the process described in Section 2.

The suffix i corresponds to the i -th data subset, 1 for 2.1 (Takenaka and Masui), 2 for 2.2 (Watanabe), 3 for 2.3 (Patterson and Morris) and 4 for 2.4 (Masui, Fujii and Takenaka), while j is the address of the data point in the data subset, starting from 1 up to the number of the last data point, J_i , in the data subset. The largest data set is $J_2 > 200$. For the others, $J_i < 100$. The data

structure of the hierarchy, in which a set of data points in one report forms a data subset and the set of four data subsets includes all data points for the present analysis, is assumed for simplicity. "Correlation" of the uncertainties means the correlation among the points in a data subset.

The algorithm to find the most probable parameter set, $\{a\}$, and to estimate their uncertainties is started by optimizing the following function, chi-square grand, χ_G^2 . The derivation of the function is presented in Appendix A.

$$\chi_G^2(\{a\}) = \sum_i \left(\sum_j \frac{F_{ij}^2}{\varphi_{ij}^2} - \frac{1}{1 + \sum_j \left(\frac{\psi_{ij}}{\varphi_{ij}} \right)^2} \left\{ \sum_j \frac{\psi_{ij} F_{ij}}{\varphi_{ij}^2} \right\}^2 \right), \quad (3)$$

where $F_{ij} = F(x_{ij}, y_{ij}, \{a\}) = y_{ij} - f(x_{ij}, \{a\})$ is the measure of deviation of each data point from the function, f , which is either ρ for density or r for relative density; x is the temperature, y is the density (or the relative density) and φ and ψ are the uncorrelated and correlated uncertainties due to sources of uncertainties ξ and η for x and y :

$$\begin{aligned} \psi_{ij}^2 &= \zeta_i^2 F_{z_{ij}}^2, \\ \varphi_{ij}^2 &= F_{x_{ij}}^2 \xi_{ij}^2 + F_{y_{ij}}^2 \eta_{ij}^2, \end{aligned} \quad (4)$$

where the subscripts x, y and z indicate the derivative of the function F at the data point (x_{ij}, y_{ij}) . The variable z is used to deduce either x or y (F , in general), commonly over all the data points in a single data subset. For example, the buoyancy force is calculated from a balance reading and a mass standard whose value is known through prior calibration. Consequently, y is directly obtained from the reading of the balance and the uncertainty of one reading is uncorrelated to that of any other reading, while z is the calibrated value of the mass standard, whose uncertainty, ζ , is common to all the data points in a single data subset.

In the first stage of optimization, one has to calculate F_{ij} according to the published data, x_{ij}, y_{ij} and z_i . Then the uncertainties φ_{ij} and ψ_{ij} must be entered into (3). (Normally, each author has already combined z_i with y_{ij} and the uncertainties in x and z with those of y .) In practice, the following five equations are solved in terms of the parameters

$$\begin{aligned} \frac{\partial \chi_G^2}{\partial a_1} &= 0, & \frac{\partial \chi_G^2}{\partial a_2} &= 0, & \frac{\partial \chi_G^2}{\partial a_3} &= 0, \\ \frac{\partial \chi_G^2}{\partial a_4} &= 0, & \frac{\partial \chi_G^2}{\partial a_5} &= 0. \end{aligned} \quad (5)$$

To optimize χ_G^2 , the following series expansion by a_K is useful:

$$\chi_G^2 = \chi_G^2(\{a_0\}) - 2 \sum_K \beta_{K0}(a_K - a_{K0}) + \sum_{KL} \alpha_{KL0}(a_K - a_{K0})(a_L - a_{L0}) + \dots, \quad (6)$$

where $\{a_0\}$ is the initial guess of $\{a\}$ and the first optimization of $\{a\}$ is given by matrix analysis of β and α . Then the new parameter set $\{a\}$ replaces $\{a_0\}$ in (6), yielding an updated optimization. This iteration is repeated until no significant decrease in chi-square grand is observed.

The least-squares calculations of χ_G^2 use the standard Marquardt method [15] with some modifications introduced for the present analysis. These are:

- (a) As mentioned above, the variable y changes only slightly over the temperature range. Therefore, an initial scaling is desirable in order to reduce computation errors. Consequently, each datum y is converted to $(1-y) \times 10^4$, for $i = 1$ and 2 (relative density), and to $(1000 - y) \times 10$, for $i = 3$ and 4 (density). Both scaled variables then fall between 0 and 100 in the temperature range 0 °C to 40 °C.
- (b) In the calculation of the curvature matrix, α_{KL0} , in (6), the second derivative of the function r , which is normally neglected for simplicity despite being mathematically necessary, has to be correctly included in the coding.

Once the optimization is completed, chi-square grand must be evaluated in order to test the consistency of the data system consisting of whole data points, uncertainties and the formula with the optimized $\{a\}$. For example, if the data are consistent, then the optimized value of chi-square grand must be less than the total number of data points (N) minus the number of parameters in the fit (P). If this condition is not achieved, indicating inconsistency among the data sets, the data system must be modified by some means, for example, by adjusting all uncertainties. In the present adjustment, all uncertainties are multiplied by a single number, specified by the square root of the ratio of optimized chi-square grand to $N - P$. One can apply other kinds of testing criterion and adjust either the data points or their uncertainties in other ways. However, the present method guarantees that the optimized $\{a\}$ is determined solely by the experimental data and their claimed uncertainties. The uncertainties in the parameter set $\{a\}$ are calculated from the covariance matrix, $[\alpha]^{-1}$, which is a by-product of the optimization analysis:

$$\langle \Delta a_K \Delta a_L \rangle = [\alpha_{KL}]^{-1}. \quad (7)$$

The uncertainties in the formula are calculated from the uncertainties in $\{a\}$ and the derivatives of the formula

for the parameters:

$$\langle \Delta f(t) \Delta f(t) \rangle = \sum \Sigma f_K(t) f_L(t) \langle \Delta a_K \Delta a_L \rangle. \quad (8)$$

4. Results of analysis

The number of data points, N , used in the present analysis in the temperature range 0 °C to 40 °C, is 569 ($N = 569$). These were used to fit five parameters ($P = 5$). The convergence of the iteration is considered successful when the value of chi-square grand changes by less than 0.001. The final chi-square was 2213, which divided by $N - P$ is 3.92. This factor is used to arrive at final uncertainties, as described above.

Finally, the density ρ of de-aerated SMOW at a pressure of 101 325 Pa and at a temperature t expressed in terms of the ITS-90 is given as

$$\rho = a_5 \left[1 - \frac{(t + a_1)^2(t + a_2)}{a_3(t + a_4)} \right],$$

where

$$\begin{aligned} a_1/^{\circ}\text{C} &= -3.983\,035 \pm 0.000\,67 \\ a_2/^{\circ}\text{C} &= 301.797 \\ a_3/^{\circ}\text{C}^2 &= 522\,528.9 \\ a_4/^{\circ}\text{C} &= 69.348\,81 \\ a_5/(\text{kg m}^{-3}) &= 999.974\,950 \pm 0.000\,84 \end{aligned}$$

and uncertainties are given with a coverage factor $k = 2$. The full precision of the parameters should be used in determining density or relative density from (1) or (2), respectively. The associated uncertainties of these parameters are of interest only in the two cases where the parameter has physical significance. Note, for example, that $-a_1$ is the temperature of maximum density and a_5 is the density of SMOW under one atmosphere at this temperature.

Uncertainties in the recommended density table are calculated according to (8) and have been fitted with a fourth-order polynomial. Uncertainties in density are then given by

$$\begin{aligned} \langle \Delta \rho(t)^2 \rangle^{1/2}/(10^{-3} \text{ kg m}^{-3}) &= \\ 0.8394 - 0.001\,28 \times t + 0.000\,110 \times t^2 - \\ 0.000\,006\,09 \times t^3 + 0.000\,000\,116 \times t^4. \end{aligned}$$

Uncertainties in relative density are given by

$$\begin{aligned} \langle \Delta r(t)^2 \rangle^{1/2}/10^{-6} &= \\ 0.0715 - 0.022\,050 \times t + 0.002\,857\,48 \times t^2 - \\ 0.000\,117\,5515 \times t^3 + 0.000\,001\,568\,52 \times t^4. \end{aligned}$$

Table 1 gives the densities, relative densities and their uncertainties based on the results of this fit, and Figures 1 and 2 show the observed density and relative density, respectively, for SMOW compared with the result of the fit.

Table 1. Recommended table for density and relative density of de-aerated Standard Mean Ocean Water (SMOW) at 101 325 Pa. Expanded uncertainties are given ($k = 2$).

Temp./ °C	Density/ (kg m ⁻³)	Uncer- tainty/ (10 ⁻³ kg m ⁻³)	Relative density	Uncer- tainty/10 ⁻⁹
0	999.8428	0.84	0.999 867 872	92
1	999.9017	0.84	0.999 926 700	56
2	999.9429	0.84	0.999 967 956	30
3	999.9672	0.84	0.999 992 209	12
4	999.9749	0.84	0.999 999 998	0
5	999.9668	0.84	0.999 991 833	9
6	999.9431	0.84	0.999 968 197	17
7	999.9045	0.84	0.999 929 547	24
8	999.8513	0.83	0.999 876 317	31
9	999.7839	0.83	0.999 808 920	37
10	999.7027	0.83	0.999 727 745	44
11	999.6081	0.83	0.999 633 164	51
12	999.5005	0.83	0.999 525 532	57
13	999.3801	0.83	0.999 405 183	62
14	999.2474	0.83	0.999 272 437	66
15	999.1026	0.83	0.999 127 600	70
16	998.9459	0.83	0.998 970 962	72
17	998.7778	0.83	0.998 802 799	74
18	998.5984	0.83	0.998 623 377	75
19	998.4079	0.83	0.998 432 947	75
20	998.2067	0.83	0.998 231 751	75
21	997.9950	0.83	0.998 020 019	76
22	997.7730	0.83	0.997 797 972	76
23	997.5408	0.83	0.997 565 819	77
24	997.2988	0.83	0.997 323 764	78
25	997.0470	0.83	0.997 071 998	80
26	996.7857	0.83	0.996 810 708	82
27	996.5151	0.83	0.996 540 070	83
28	996.2353	0.83	0.996 260 255	85
29	995.9465	0.83	0.995 971 426	86
30	995.6488	0.83	0.995 673 739	88
31	995.3424	0.83	0.995 367 345	89
32	995.0275	0.83	0.995 052 388	90
33	994.7041	0.84	0.994 729 007	93
34	994.3724	0.84	0.994 397 336	99
35	994.0326	0.84	0.994 057 503	108
36	993.6847	0.84	0.993 709 630	124
37	993.3290	0.85	0.993 353 838	147
38	992.9654	0.86	0.992 990 241	177
39	992.5941	0.87	0.992 618 947	214
40	992.2152	0.88	0.992 240 065	260

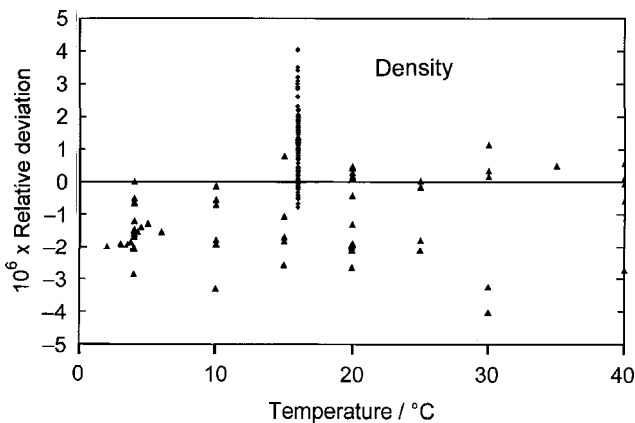


Figure 1. Deviations of the observed values from the recommended values for the density of SMOW. The large triangles show the data of Patterson and Morris and the small diamonds those of Masui, Fujii and Takenaka.

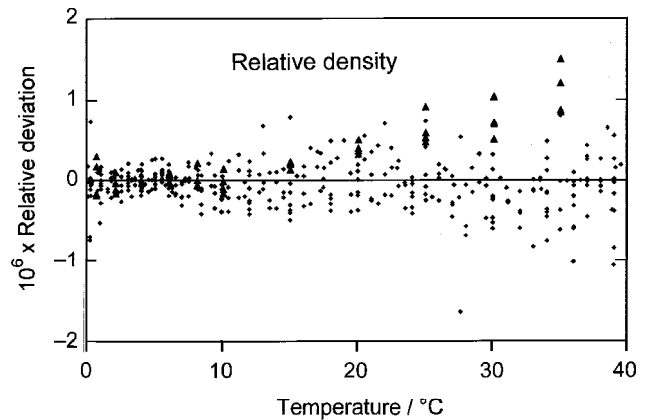


Figure 2. Deviations of the observed values from the recommended values for the relative density table of SMOW. The large triangles show the results of Takenaka and Masui and the small diamonds those of Watanabe.

5. Correction factors to be applied to the density of SMOW

5.1 Isotopic abundance

Most users of water as a density standard rely on tap water instead of SMOW. Thus a_5 must be changed in this case. Based on the work of Girard and Menaché [16], the following correction may be applied:

$$a'_5 = a_5 + 0.233\delta_{18} + 0.0166\delta_D,$$

where a'_5 is the modified parameter. The quantities δ_{18} and δ_D are defined by the relations⁴

$$\delta_{18} = [r_{18}(\text{sample})/r_{18}(\text{SMOW}) - 1] \times 10^3$$

and

$$\delta_D = [r_D(\text{sample})/r_D(\text{SMOW}) - 1] \times 10^3,$$

where r_{18} is the amount-of-substance ratio [¹⁸O]/[¹⁶O] and r_D is the amount-of-substance ratio [D]/[H]. A value of $a'_5 = 999.972 \text{ kg m}^{-3}$ is often assumed, as this was the value found by Chappuis for tap water [2].

5.2 Dissolved air

The density of water has been given under the assumption that the water is air-free. Bignell [17] has determined the difference in density, $\Delta\rho$, between air-free and air-saturated water. Between 0 °C and 25 °C this difference can be described by the following formula:

$$\Delta\rho/(\text{kg m}^{-3}) = s_0 + s_1t,$$

4. The ratios $r_{18}(\text{SMOW})$ and $r_D(\text{SMOW})$ refer to samples of SMOW available from the International Atomic Energy Agency [16]. This material, sometimes called “V-SMOW”, served as the reference for all density data considered in this report.

where

$$s_0/(10^{-3} \text{ kg m}^{-3}) = -4.612$$

and

$$s_1/(10^{-3} \text{ kg m}^{-3} \text{ } ^\circ\text{C}^{-1}) = 0.106.$$

To the precision given, the coefficients s_i are unaffected by expressing the temperature in terms of the ITS-90 instead of the IPTS-68, which was used by Bignell.

5.3 Compressibility

The density of de-aerated water has been given at a pressure p of 101 325 Pa (one atmosphere). Since water is slightly compressible, a small correction may be required under typical laboratory conditions. Based on the work of Kell [4] in 1975, the density at one atmosphere must be multiplied by a factor

$$[1 + (k_0 + k_1t + k_2t^2)\Delta p],$$

where

$$\Delta p/\text{Pa} = p/\text{Pa} - 101\,325$$

$$k_0/(10^{-11} \text{ Pa}^{-1}) = 50.74$$

$$k_1/(10^{-11} \text{ Pa}^{-1} \text{ } ^\circ\text{C}^{-1}) = -0.326$$

$$k_2/(10^{-11} \text{ Pa}^{-1} \text{ } ^\circ\text{C}^{-2}) = 0.004\,16.$$

This pressure coefficient interpolates tabulated points given by Kell and agrees with his values to within 0.3 % in the range $0 \text{ } ^\circ\text{C} \leq t \leq 40 \text{ } ^\circ\text{C}$. To the precision given, the coefficients k_i are unaffected by transposing Kell's table, originally expressed in terms of the IPTS-68, to the ITS-90.

5.4 Purity

Tables for the density of water assume that the water is chemically pure. Methods of achieving the required purity without changing the isotopic composition of water have been well documented, for example [18, 19].

6. Discussion and comparison with other tables

There is satisfactory consistency among the relative density data [11, 13]. The results of [13] and [14] allow the density to be fixed in kg m^{-3} at a given temperature. When this is done, one notes a small systematic difference (about 0.001 kg m^{-3}) depending on whether the results of [13] or [14] are used. This is reflected by the fact that the original ratio of chi-square grand to $N - P$ is about 4. Our approach has been to enlarge the uncertainties in order to make this ratio one. Briefly, we have averaged over the discrepancies and increased our final uncertainty to take this into account. The recommended table for density has an expanded uncertainty ($k = 2$) of less than 0.0009 kg m^{-3} throughout the temperature range. The recommended table for relative density has an expanded

uncertainty ($k = 2$) of less than 3×10^{-7} throughout the temperature range and less than 1×10^{-7} between $0 \text{ } ^\circ\text{C}$ and $34 \text{ } ^\circ\text{C}$. These results will, therefore, satisfy many of the current needs of metrology.

For the same reasons that led the IUPAC to call for a redetermination of the density of water, it is difficult to make direct comparisons with work carried out in the early twentieth century. That is, comparison of these results with the early relative density measurements is complicated by uncertainties in the temperature scale in use a hundred years ago. Of course, several tables of water density based on the work of Chappuis and Thiesen et al. are in common use. As an aid to users, comparisons with two of these tables are given in Appendix B.

The maximum density of water is independent of temperature scale and, therefore, a useful conclusion can be drawn. Girard and Menaché had predicted that the maximum density of SMOW at one atmosphere is $999.975 \text{ kg m}^{-3}$. The prediction, now confirmed, was based on their measurements of the relative density between tap water from the BIPM and SMOW and the assumption that the isotopic composition of the tap water had not changed since the time of Chappuis.

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Appendix A

Least-squares approach and “chi-square grand”

Table A1 shows the hierarchy in data structure of the present analysis.

The uncertainties in quantities x , y and z are assumed to characterize the statistical distribution of observed quantities as follows. The expected value of the measurand x_{ij} is X_{ij} , and the probability of observing x_{ij} is expressed by the Gaussian distribution equation, with mean X_{ij} , and standard deviation ξ_{ij} :

$$\begin{aligned} \text{Prob}(x_{ij})dx_{ij} &= N\left(\frac{(x_{ij} - X_{ij})}{\xi_{ij}}\right)dx_{ij} \\ &= \left(\frac{1}{\sqrt{2\pi\xi_{ij}^2}}\right)e^{-(x_{ij} - X_{ij})^2/2\xi_{ij}^2}dx_{ij}. \end{aligned}$$

Table A1. Hierarchy in data structure of present analysis.

	(i, j)	x_{ij}	y_{ij}	z_i	φ_{ij}	ψ_{ij}
Data Subset 1	(1,1)	x_{11}	y_{11}	z_1	φ_{11}	ψ_{11}
	(1,2)	x_{12}	y_{12}	z_1	φ_{12}	ψ_{12}
	(1, J_1)	x_{1J_1}	y_{1J_1}	z_1	φ_{1J_1}	ψ_{1J_1}
Data Subset 2	(2,1)	x_{21}	y_{21}	z_2	φ_{21}	ψ_{21}
	(2,2)	x_{22}	y_{22}	z_2	φ_{22}	ψ_{22}
	(2, J_2)	x_{2J_2}	y_{2J_2}	z_2	φ_{2J_2}	ψ_{2J_2}
Data Subset 3	(3,1)	x_{31}	y_{31}	z_3	φ_{31}	ψ_{31}
	(3,2)	x_{32}	y_{32}	z_3	φ_{32}	ψ_{32}
	(3, J_3)	x_{3J_3}	y_{3J_3}	z_3	φ_{3J_3}	ψ_{3J_3}
Data Subset 4	(4,1)	x_{41}	y_{41}	z_4	φ_{41}	ψ_{41}
	(4,2)	x_{42}	y_{42}	z_4	φ_{42}	ψ_{42}
	(4, J_4)	x_{4J_4}	y_{4J_4}	z_4	φ_{4J_4}	ψ_{4J_4}

(A1)

The same is assumed for y_{ij} , with mean Y_{ij} and standard deviation η_{ij} , and for z_i , with mean Z_i and standard deviation ζ_i . The relationship $Y_{ij} + Z_i = f(X_{ij}, \{a\})$ or, equivalently, $F(X_{ij}, Y_{ij}, Z_i, \{a\}) = Y_{ij} + Z_i - f(X_{ij}, \{a\}) = 0$ holds for the true values, X_{ij} , Y_{ij} and Z_i , with f being the function expressed by (1) and (2), whose parameter set $\{a\}$ is to be optimized. Then the likelihood that X_{ij} is the value of the measurand x_{ij} is expressed by (A1) with dX_{ij} instead of dx_{ij} and the same is true for Y_{ij} and Z_i . By combining all these likelihoods, one can compute the likelihood L having the value set (X_{ij}, Y_{ij}, Z_i) , keeping $F(X_{ij}, Y_{ij}, Z_i, \{a\}) = 0$. In mathematical notation,

$$L(\{a\}) \prod_K da_K \times \int \exp\left(-\frac{1}{2} \sum_i \left\{ \sum_j \left[\frac{(X_{ij} - x_{ij})^2}{\xi_{ij}^2} + \frac{(Y_{ij} - y_{ij})^2}{\eta_{ij}^2} \right] + \frac{(Z_i - z_i)^2}{\zeta_i^2} \right\}\right) \times \prod_{ij} \delta[F(X_{ij}, Y_{ij}, Z_i, \{a\})] dX_{ij} dY_{ij} dZ_i. \quad (A2)$$

The normalization factor for the likelihood is not given, so the equation describes only a proportional relationship. The integral in terms of dX_{ij} , dY_{ij} is converted to the integral by dF_{ij} with $F_{ij} = F(X_{ij}, Y_{ij}, Z_i, \{a\})$ and expressed as follows, after the integration by dZ_i :

$$\propto \exp\left\{-\frac{1}{2} \sum_i \left[\sum_j \frac{F_{ij}^2}{\varphi_{ij}^2} - \frac{1}{1 + \sum_j (\psi_{ij}/\varphi_{ij})^2} \left\{ \sum_j \frac{\psi_{ij} F_{ij}}{\varphi_{ij}^2} \right\}^2 \right]\right\}, \quad (A3)$$

where

$$\begin{aligned} \psi_{ij}^2 &= \zeta_i^2 F_{zij}^2, \\ \varphi_{ij}^2 &= F_{xij}^2 \xi_{ij}^2 + F_{yij}^2 \eta_{ij}^2. \end{aligned} \quad (A4)$$

Optimization of the following likelihood function, chi-square grand, by adjusting $\{a\}$ gives the most likely $\{a\}$:

$$\chi_G^2 = \sum_i \left(\sum_j \frac{F_{ij}^2}{\varphi_{ij}^2} - \frac{1}{1 + \sum_j (\psi_{ij}/\varphi_{ij})^2} \left\{ \sum_j \frac{\psi_{ij} F_{ij}}{\varphi_{ij}^2} \right\}^2 \right). \quad (A5)$$

The chi-square grand is proven positive definite and, in the absence of correlated uncertainties, tends to the conventional expression of chi-square:

$$\chi^2 = \sum_i \left(\sum_j \frac{F_{ij}^2}{\varphi_{ij}^2} \right). \quad (A6)$$

Appendix B

Comparison with other tables

Several tables of water density have been advocated and widely used during the last twenty years. Consequently, it is interesting to see how their values compare with the present table.

IUPAC

As mentioned in the Introduction, the IUPAC had recommended that a table due to Bigg should be used until a synthesis was made of more recent work. This table was last published with temperatures expressed in the IPTS-68 and with the assumption that the maximum density of SMOW is $999.975 \text{ kg m}^{-3}$ [8]. In order to compare this table with the present work, we have expressed temperatures in the ITS-90 using the recommended formula [20]. Figure 3 shows the result. The relative deviations with respect to the present work do not exceed 1.6×10^{-6} .

PTB

Spieweck and Bettin (SB) at the Physikalisch-Technische Bundesanstalt (PTB) have published two tables expressed in the ITS-90 [21, 22]. These are, as is the table of Bigg, recalculations of work carried out early in the twentieth century. The maximum density in these tables is given as $999.972 \text{ kg m}^{-3}$, ultimately derived from the work of Chappuis based on tap

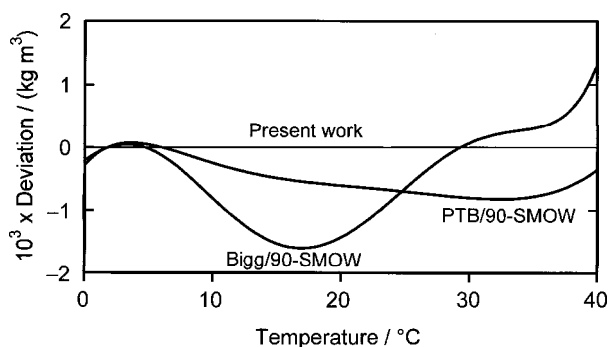


Figure 3. Comparison of density formulae. Bigg/90-SMOW are the provisional values for the density of SMOW as recommended by IUPAC. The IUPAC recommendation has been expressed in terms of the ITS-90 and normalized so that the maximum density is $999.975 \text{ kg m}^{-3}$. PTB/90-SMOW is the most recent table recommended by the PTB [20], but normalized to give $999.975 \text{ kg m}^{-3}$ as the maximum density. The line of zero deviation represents the present analysis.

water at the BIPM. We therefore add 0.003 kg m^{-3} to the densities given in references [21, 22] in order to compare the results with our own, which are given in terms of SMOW. In [21], SB used two different hypotheses regarding the older data (see equations (3) and (4) of [21]). The table of water density published in [19] was derived from (3) and differs in relative value from the present work by no more than 3.1×10^{-6} . In a second publication [22], SB cite (4) only and show a density table based on this polynomial. The differences between SB's (4) and the present work are no greater than 0.8×10^{-6} (see Figure 3).

Others

Other density tables are in wide use [23] but express results to only five significant figures. As would be expected from the analyses given above, such tables are consistent with the present work, although less precise.

The International Association for the Properties of Water and Steam (IAPWS) in 1995 released a set of formulae for the thermophysical properties of water, although an archival description of the formulation is still in preparation. Nevertheless, the IAPWS formulation has already been implemented in user-friendly software [24, 25] where it is seen that the agreement with densities given in Table 1 is within 0.001 kg m^{-3} .

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