

Manual of Petroleum Measurement Standards Chapter 11—Physical Properties Data

Section 4—Properties of Reference Materials

Part 1—Density of Water and Water Volumetric Correction Factors for Water Calibration of Volumetric Provers

FIRST EDITION, DECEMBER 2003



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Chapter 11—Physical Properties Data

Section 4—Properties of Reference Materials

Part 1—Density of Water and Water Volumetric Correction Factors for Water Calibration of Volumetric Provers

1 Introduction

This Standard specifies the density of water to be used in all applicable API MPMS Standards. It also specifies the volume correction factor equation for water and demonstrates its use for water calibration of volumetric provers (see API MPMS Chapters 12.2.1, 12.2.3).

2 Scope

This standard is applicable to all API Standards that use the density of water or its volume correction factors.

3 References

- H. Wagenbreth and H. Blanke, "The Density of Water in the International System of Units and in the International Practical Temperature Scale of 1968," *Mitteilungen der Physikalisch-Technischen Bundesanstalt (PTB-Mitt)*, 412–415, June 1971.
- G.S. Kell, *Journal of Chemical Engineering Data*, 1967, 12, 66–69; *ibid*, 1975, 20, 97–105.
- N. Bignell, "The Effect of Dissolved Air on the Density of Water," *Metrologia*, 1983, 19, 57–59.
- J.B. Patterson and E.C. Morris, "Measurement of Absolute Water Density," *Metrologia*, 31, 277–288, 1994.
- M. Tanaka, G. Girard, R. Davis, A. Peuto and N. Bignell, "Recommended table for the density of water between 0°C and 40°C based on recent experimental reports," *Metrologia*, 38, 301–309, 2001.

4 Definitions

4.1 density, absolute: The density of a solid or liquid substance at a specified temperature is the mass of the substance occupying a unit of volume at the specified temperature. Density so defined is sometimes referred to as "true density" or as "density in vacuo." When reporting density, the units of mass and volume used and the temperature of the determination must be stated (for example, grams per millili-

ter at 15°C). Density is assumed to be for water at atmospheric pressure unless otherwise stated.

4.2 volume correction factor (VCF): The density of a liquid at temperature t divided by its density at a chosen reference temperature. Multiplying a liquid's volume measured at temperature t by the VCF provides the volume of the liquid at the chosen reference temperature. Volume Correction Factors are assumed to be for water at atmospheric pressure unless otherwise stated. Certain API MPMS Chapters call this factor CTDW.

5 Implementation Procedures

The implementation procedures below are the standard. Representative density values are presented in the Appendix A for programming verification purposes only.

5.1 ABSOLUTE DENSITY OF WATER

The previous standard (API MPMS 11.2.3, 1984), which this Standard replaces, was based on the internationally accepted work of Wagenbreth and Blanke, which produced a density of 999.012 kg/m³ at 60°F. In 1994, Patterson and Morris published a paper proposing a new equation based on their laboratory data of VSMOW (see Appendix B), which was accepted by the NIST (National Institute of Standards and Technology). In 2001, a review (Tanaka, *et al.*) proposed a new equation regressed from the data of several researchers (including that of Patterson and Morris). Although they are aware of this paper, the NIST at this writing has chosen to continue to accept the work of Patterson and Morris. This Standard is therefore based on that same work, applicable between 1°C and 40°C (see Appendix C).

The following equation expresses the density of water as a function of temperature in degrees Celsius:

$$\rho_{tC} = \rho_0 [1 - (A\Delta t + B\Delta t^2 + C\Delta t^3 + D\Delta t^4 + E\Delta t^5)] \quad (1)$$

where

$$\begin{aligned}\rho_{tC} &= \text{density at temperature } t^{\circ}\text{C in kg/m}^3, \\ \rho_0 &= \text{density at temperature } t_0, 999.97358 \text{ kg/m}^3 \\ &\quad (\text{maximum density of water}), \\ \Delta t &= t - t_0, \\ t_0 &= 3.9818^{\circ}\text{C}, \\ A &= 7.0134 \times 10^{-8} \text{ } (^{\circ}\text{C})^{-1}, \\ B &= 7.926504 \times 10^{-6} \text{ } (^{\circ}\text{C})^{-2}, \\ C &= -7.575677 \times 10^{-8} \text{ } (^{\circ}\text{C})^{-3}, \\ D &= 7.314894 \times 10^{-10} \text{ } (^{\circ}\text{C})^{-4}, \\ E &= -3.596458 \times 10^{-12} \text{ } (^{\circ}\text{C})^{-5}.\end{aligned}$$

The following equation expresses the density of water as a function of temperature in degrees Fahrenheit:

$$\rho_{tF} = \rho_0 [1 - (A\Delta t_F + B\Delta t_F^2 + C\Delta t_F^3 + D\Delta t_F^4 + E\Delta t_F^5)] \quad (2)$$

where

$$\Delta t_F = \frac{(^{\circ}\text{F} - 32)}{1.8} - t_0$$

These equations provide the following values:

$$\text{Density at } 60^{\circ}\text{F } (15.5556^{\circ}\text{C}): \quad 999.016 \text{ kg/m}^3$$

$$\text{Density at } 15^{\circ}\text{C } (59^{\circ}\text{F}): \quad 999.102 \text{ kg/m}^3$$

$$\text{Density at } 20^{\circ}\text{C } (68^{\circ}\text{F}): \quad 998.206 \text{ kg/m}^3$$

The output of equation (1) and (2) is rounded to three decimal places for further use.

5.2 VOLUME CORRECTION FACTORS FOR WATER

The volume correction factor equation for water with respect to a chosen reference temperature is the density at temperature t (ρ_{tC}) divided by the density of water at that reference temperature. For 15°C , it is:

$$\text{VCF}_{15^{\circ}\text{C}} = \frac{\rho_{tC}}{999.102} \quad (3)$$

Similarly, the volume correction factor equation for water referenced to 20°C is:

$$\text{VCF}_{20^{\circ}\text{C}} = \frac{\rho_{tC}}{999.206} \quad (4)$$

The volume correction factor equation for water referenced to 60°F is:

$$\text{VCF}_{60^{\circ}\text{F}} = \frac{\rho_{tC}}{999.016} \quad (5)$$

The output of equation (3), (4), and (5) is rounded to no more than 6 decimal places for further use. Although VCFs are assumed to be for water at atmospheric pressure unless otherwise stated, the VCFs for water under pressure are slightly smaller. As this difference is very small, application of such VCFs should be contingent upon agreement of both parties to a transaction after evaluation of the difference.

5.3 WATER VOLUME CORRECTION FACTORS FOR VOLUMETRIC PROVERS

For waterdraw calibrations of volumetric provers, the prover volume is calculated from the volume of the certified volumetric field test measure using a VCF based on the densities of water in the prover (deemed the reference density) and the measure as follows:

$$\text{VCF}_{pt} = \frac{\rho_{mt}}{\rho_{pt}} = \frac{V_p}{V_m}$$

$$V_p = V_m * \text{VCF}_{pt} = V_m * \frac{\rho_{mt}}{\rho_{pt}} \quad (6)$$

where

VCF_{pt} = volume correction factor, prover reference temperature (also called CTDW),

ρ_{mt} = water density at its actual temperature in the test measure,

ρ_{pt} = water density at its actual temperature in the prover,

V_p = prover volume (to be further corrected as indicated in Ch. 12.2.3),

V_m = measure volume (to be further corrected as indicated in Ch. 12.2.3)

The densities ρ_{mt} and ρ_{pt} are calculated from equations (1) or (2). Correction for dissolved air (see Appendix D) is not necessary as we are dealing with a density ratio. V_p , the final result, is rounded to the same number of decimal places as V_m (see Examples). Correction for pressure compressibility is provided in Appendix E.

6 Rounding

In many cases the number of decimal places that are to be used is influenced by the source of the data itself. For example, if a container's capacity table is calibrated to the nearest whole barrel, then all subsequent barrel values should be rounded accordingly. Furthermore, calculation standards such as *MPMS* Chapter 12 will specify rounding for each unique application. However, in those cases where there are no other limiting factors, the operator should be guided by Table 1.

Each calculated density shall always be rounded off in one step to three places past the decimal and not rounded in two or more successive steps. Water Volume Correction Factors are rounded to six places past the decimal. When the figure to the right of the last place to be retained is less than 5, the figure in the last place retained should be unchanged.

Table 1—Significant Digits

Units	No. of Decimals
Gallons	xxxx.xx
Barrels	xxx.xx
Cubic Meters	xxx.xxx
Cubic Inches	xxxxx.xxxx
Pounds	xxx.0
Milliliters	xxxxxx.xxx
Liters	xxx.0
Kilograms	xxx.0
VCF	x.xxxxxx
Density kg/m ³	xxx.xxx
Density lb/gal.	xx.xxx
Relative density	x.xxxx
Temperature °F	xxx.x
Temperature °C	xxx.x5
C _{pw}	x.xxxxxx

7 Examples

The following examples are for illustration purposes only. The relevant API *MPMS* chapters (4.9.2, 12.2.4, etc.) govern use and rounding for specific applications.

7.1 PROVER VOLUME, MEASURE TEMPERATURE HIGHER THAN PROVER TEMPERATURE (USC UNITS)

Problem: During a waterdraw, the water in a prover at 80.7°F is transferred into a test measure volume of 11,551.50 cubic in. at 83.0°F. What is the volume of the prover at 80.7°F?

Solution: Use equation (2) to separately calculate the water densities ρ_{mt} and ρ_{pt} :

$$\rho_{mt} = 996.139 \text{ kg/m}^3$$

$$\rho_{pt} = 996.499 \text{ kg/m}^3$$

Their ratio is:

$$\frac{\rho_{mt}}{\rho_{pt}} = 0.999639$$

From equation (6), the prover volume is calculated to be (rounded to the same number of decimal places as the test measure):

$$V_p = V_m * \frac{\rho_{mt}}{\rho_{pt}} = 11,547.3299 \text{ cubic in. @80.7°F}$$

7.2 PROVER VOLUME, MEASURE TEMPERATURE LOWER THAN PROVER TEMPERATURE (USC UNITS)

Problem: During a waterdraw, the water in a prover at 83.0°F is transferred into a test measure volume of 11,551.50 cubic in. at 80.7°F. What is the volume of the prover at 83.0°F?

Solution: Use equation (2) to separately calculate the water densities ρ_{mt} and ρ_{pt} :

$$\rho_{mt} = 996.499 \text{ kg/m}^3$$

$$\rho_{pt} = 996.139 \text{ kg/m}^3$$

Their ratio is:

$$\frac{\rho_{mt}}{\rho_{pt}} = 1.000361$$

From equation (6), the prover volume is calculated to be (rounded to the same number of decimal places as the test measure):

$$V_p = V_m * \frac{\rho_{mt}}{\rho_{pt}} = 11,555.6701 \text{ cubic in. @83.0°F}$$

7.3 VOLUME OF WATER AT 60°F (USC UNITS)

Problem: A tank car contains 21,953 gallons of water at 93.4°F. What is the volume of water at 60°F in the car?

Solution: Adapting Equation (6):

$$V_{60^{\circ}\text{F}} = V_m * VCF_{60^{\circ}\text{F}} = V_m * \frac{\rho_t}{999.016}$$

The volume $V_{60^{\circ}\text{F}}$ (intermediate results rounded here for display only) is thus:

$$\begin{aligned} V_{60^{\circ}\text{F}} &= V_m * \frac{\rho_{93.4}}{999.016} = V_m * \frac{994.335}{999.016} \\ &= 21953 * 0.995314 \\ &= 21,850 \text{ gallons @ } 60^{\circ}\text{F} \end{aligned}$$

7.4 PROVER VOLUME, MEASURE TEMPERATURE HIGHER THAN PROVER TEMPERATURE (SI UNITS)

Problem: During a waterdraw, the water in a prover at 18.3°C is transferred into a test measure volume of 189,214 milliliters at 21.1°C. What is the volume of the prover at 18.3°C?

Solution: Use equation (1) to separately calculate the water densities ρ_{mt} and ρ_{pt} :

$$\rho_m = 997.972 \text{ kg/m}^3$$

$$\rho_{pt} = 998.541 \text{ kg/m}^3$$

Their ratio is:

$$\frac{\rho_{mt}}{\rho_{pt}} = 0.999430$$

From equation (6), the prover volume is calculated to be (rounded to the same number of decimal places as the test measure):

$$V_p = V_m * \frac{\rho_{mt}}{\rho_{pt}} = 189,106.148 \text{ milliliters @ } 18.3^{\circ}\text{C}$$

7.5 PROVER VOLUME, MEASURE TEMPERATURE LOWER THAN PROVER TEMPERATURE (SI UNITS)

Problem: During a waterdraw, the water in a prover at 21.1°C is transferred into a test measure volume of 189,214 milliliters at 18.3°C. What is the volume of the prover at 21.1°C?

Solution: Use equation (1) to separately calculate the water densities ρ_{mt} and ρ_{pt} :

$$\rho_{mt} = 998.541 \text{ kg/m}^3$$

$$\rho_{pt} = 997.972 \text{ kg/m}^3$$

Their ratio is:

$$\rho_{mt} = 1.000570$$

From equation (6), the prover volume is calculated to be (rounded to the same number of decimal places as the test measure):

$$V_p = V_m * \frac{\rho_{mt}}{\rho_{pt}} = 189,321.852 \text{ milliliters @ } 21.1^{\circ}\text{C}$$

7.6 VOLUME OF WATER AT 15°C (SI UNITS)

Problem: A tank car contains 83,101 liters of water at 34.1°C. What is the volume of water at 15°C in the car?

Solution: Adapting Equation (6):

$$V_{15^{\circ}\text{C}} = V_m * VCF_{15^{\circ}\text{C}} = V_m * \frac{\rho_t}{999.012}$$

The volume $V_{15^{\circ}\text{C}}$ is thus (intermediate results rounded here for display only):

$$V_{15^{\circ}\text{C}} = V_m * \frac{\rho_{34.1}}{999.102} = V_m * \frac{994.338}{999.102}$$

$$= 83,101 * 0.995232$$

$$= 82,705 \text{ liters @ } 15^{\circ}\text{C}$$

APPENDIX A—REPRESENTATIVE DENSITY VALUES

°F	°C	kg/m ³	°F	°C	kg/m ³
33	0.6	999.878	69	20.6	998.089
34	1.1	999.907	70	21.1	997.970
35	1.7	999.930	71	21.7	997.847
36	2.2	999.949	72	22.2	997.721
37	2.8	999.962	73	22.8	997.592
38	3.3	999.970	74	23.3	997.460
39	3.9	999.974	75	23.9	997.325
40	4.4	999.972	76	24.4	997.187
41	5.0	999.965	77	25.0	997.046
42	5.6	999.954	78	25.6	996.902
43	6.1	999.938	79	26.1	996.755
44	6.7	999.918	80	26.7	996.605
45	7.2	999.893	81	27.2	996.453
46	7.8	999.863	82	27.8	996.297
47	8.3	999.829	83	28.3	996.139
48	8.9	999.791	84	28.9	995.978
49	9.4	999.748	85	29.4	995.814
50	10.0	999.702	86	30.0	995.648
51	10.6	999.651	87	30.6	995.479
52	11.1	999.596	88	31.1	995.307
53	11.7	999.537	89	31.7	995.133
54	12.2	999.474	90	32.2	994.956
55	12.8	999.407	91	32.8	994.776
56	13.3	999.336	92	33.3	994.594
57	13.9	999.262	93	33.9	994.409
58	14.4	999.184	94	34.4	994.222
59	15.0	999.102	95	35.0	994.032
60	15.6	999.016	96	35.6	993.840
61	16.1	998.927	97	36.1	993.645
62	16.7	998.834	98	36.7	993.448
63	17.2	998.738	99	37.2	993.249
64	17.8	998.638	100	37.8	993.047
65	18.3	998.535	101	38.3	992.842
66	18.9	998.429	102	38.9	992.635
67	19.4	998.319	103	39.4	992.426
68	20.0	998.206	104	40.0	992.215

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APPENDIX B—REFERENCE STANDARD WATER

The Patterson & Morris equation (1) is based on the isotopic composition of VSMOW (Vienna Standard Mean Ocean Water). VSMOW is so named because it is distributed by the IAEA (International Atomic Energy Agency) headquartered in Vienna.

It should be noted that water obtained from other sources does not have the same isotopic composition and thus has slightly different densities. Evaporation or distillation shifts the isotopic composition as molecules with heavier isotopes of hydrogen and/or oxygen have slightly higher boiling points. Conversely, rain or snow tends to slightly concentrate molecules with the heavier isotopes, leaving more of the

lighter molecules in the air. The result is that fresh water varies widely in isotopic composition around the earth. However, the isotopic composition of deep ocean water is reasonably constant everywhere.

VSMOW is expensive and of limited availability. Current commercially available densitometers using water as a reference density standard are not sensitive enough to measure the density difference between distilled fresh water and VSMOW.

This effect need not be considered when doing prover waterdraws, as density ratios are used.

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APPENDIX C—TANAKA VS PATTERSON EQUATION

The Tanaka equation has a 1 σ (Sigma) uncertainty of ± 0.00083 at 60°F (15.556°C). This means that the calculated density of water of 999.01692 most likely lies between 999.01775 and 999.01609. Listing the values and rounding to 3 places past the decimal provides:

$$999.01775 \text{ =====> } 999.018$$

$$999.01692 \text{ =====> } 999.017$$

$$999.01609 \text{ =====> } 999.016$$

Likewise, the Patterson equation has a 1 σ uncertainty of ± 0.00064 at 60°F. Listing the values and rounding to 3 places past the decimal provides:

$$999.01666 \text{ =====> } 999.017$$

$$999.01602 \text{ =====> } 999.016$$

$$999.01538 \text{ =====> } 999.015$$

When compared at reference temperature, the results of the two equations are extremely close. The difference is for all practical purposes insignificant. Thus, the API will continue to use the Patterson equation until it can be shown that the true density of water lies entirely outside Patterson's 1 σ uncertainty value (i.e., the uncertainty ranges do not overlap).

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APPENDIX D—CORRECTION FOR DISSOLVED AIR

The density of water is normally assumed to be air-free. Distilled water can be made air-free by purging with helium or applying a vacuum. However, this is often not possible in the field. The correction for dissolved air most commonly used is one proposed by N. Bignell for the difference between air-free and air-saturated water. Between 0°C and 25°C (32°F to 77°F) the difference is described by:

$$C_{air} = s_0 + s_1 t \quad (D.1)$$

where

$$C_{air} = \text{density correction, kg/m}^3$$

SI Units

$$s_0 = -4.612 \times 10^{-3}$$

$$s_1 = 1.06 \times 10^{-4}$$

$$t = ^\circ\text{C}$$

USC Units

$$s_0 = -4.612 \times 10^{-3}$$

$$s_1 = 5.89 \times 10^{-5}$$

$$t = ^\circ\text{F} - 32$$

This correction is added to the density calculated by equation (1) or (2). Although the equation applies up to 25°C (77°F), it can be reasonably extended to 37.8°C (100°F). In any event, the change in density due to saturated air is minor, from -0.004 kg/m³ at 4°C (39.2°F) to -0.001 kg/m³ at 37.8°C (100°F).

.....

APPENDIX E—CORRECTION FOR COMPRESSIBILITY

The density of de-aerated water has been given at a pressure of 101.325 kPa (14.696 psi or one atmosphere). Water is slightly compressible, so a correction must be made for pressures other than atmospheric. Based on the work by Kell, the density at one atmosphere should be multiplied by a correction factor C_{pw} (which we will call C_{pw}):

$$C_{pw} = 1 + (k_0 + k_1 t + k_2 t^2) \Delta p \quad (\text{E.1})$$

where

Metric Units

$$\Delta p = p - 101325$$

$$p = \text{absolute pressure in Pa (Pascals)}$$

$$k_0 = 5.074 \times 10^{-10}$$

$$k_1 = -3.26 \times 10^{-12}$$

$$k_2 = 4.16 \times 10^{-14}$$

$$t = \text{temperature in } ^\circ\text{C}$$

US Customary Units

$$\Delta p = p - 14.696$$

$$p = \text{pressure in psia (pounds per square in. absolute)}$$

$$k_0 = 3.4984 \times 10^{-6}$$

$$k_1 = -1.2487 \times 10^{-8}$$

$$k_2 = 8.85253 \times 10^{-11}$$

$$t = ^\circ\text{F} - 32$$

C_{pw} should be rounded to 6 decimal places for further use.

Example

Problem: Evaluate the difference between the VCF for water at 95°F and 100 psia and the VCF for water at 95°F and atmospheric pressure.

Solution: Use equation (E.1) to separately calculate the correction factors $C_{100\text{psi @ } 60^\circ\text{F}}$ and $C_{100\text{psi @ } 95^\circ\text{F}}$.

$$C_{100\text{psi @ } 60^\circ\text{F}} = 1.000275$$

$$C_{100\text{psi @ } 95^\circ\text{F}} = 1.000261$$

Use equation (2) to calculate the water densities $\rho_{60^\circ\text{F}}$ and $\rho_{95^\circ\text{F}}$ at atmospheric pressure.

$$\rho_{60^\circ\text{F}} = 999.016 \text{ kg/m}^3$$

$$\rho_{95^\circ\text{F}} = 994.032 \text{ kg/m}^3$$

Multiply each density by its corresponding C_{pw} to get the density at that temperature and pressure.

$$\rho_{60^\circ\text{F @ } 100\text{psia}} = 999.016 * 1.000275 = 999.291 \text{ kg/m}^3$$

$$\rho_{95^\circ\text{F @ } 100\text{psia}} = 994.032 * 1.000261 = 994.291 \text{ kg/m}^3$$

The VCF at 95°F and 100 psia ($\text{VCF}_{95^\circ\text{F @ } 100 \text{ psi}}$) is thus:

$$\text{VCF}_{95^\circ\text{F @ } 100 \text{ psi}} = \frac{994.291}{999.291} = 0.994996$$

Compare this to the VCF at 95°F and one atmosphere (14.696 psi)

$$\text{VCF}_{95^\circ\text{F}} = \frac{994.032}{999.016} = 0.995011$$

The importance of the VCF difference (0.000015) depends on the quantities involved.

For 25,000 gallons, it is 0.375 gallons.

For 100,000 barrels, it is 1.5 barrels.

Similar calculations show that for the same temperatures at 500 psia, the VCF difference amounts to 7.4 barrels for a 100,000 barrel transfer. If the water remains at 500 psia but cools to 32°F, the difference is 13.6 barrels.

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