GLP 10

Good Laboratory Practice
for the
Purity of Water

1 Water for volume calibrations.

Water is used in two ways in the metrology laboratory. It may be used as a cleaning fluid. It may also be used as a transfer medium in volume transfer calibrations, or as standard reference material for gravimetric volume calibrations. In each of these cases, the water must be clean; in the case of gravimetric volume calibrations it must be pure, as well.

Dirty water can cause many measurement problems, including depositing residues in a volumetric vessel that could cause volumetric errors or could soil its interior. When in doubt of the cleanliness of the water supply, filters should be attached to the supply lines used.

Cleanliness of water may be achieved by removal of physical contaminating substances, especially by filtration. City water is ordinarily clean but may become dirty from the distribution system and especially from prolonged standing in some kinds of pipes and tubing. Hoses used to transfer water from and into large vessels and tanks may need internal cleaning, as well. Flushing to remove visible contamination is all that is usually required prior to use in volume transfer calibrations or prior to further purification.

2 Clean Water used in Volume Transfer Calibrations

Clean water is all that is necessary when making measurements by volumetric transfer since volumetric comparisons are involved. When the water density value is used in a volume transfer equation, the ratio of the density values of clean water versus pure water is essentially unchanged, despite impurities. The coefficient of expansion for distilled water and pure water are also essentially the same.

Note: the equations used in gravimetric calibrations do not use ratios and systematic errors will result in the calibration relative to impurities in the water. The use of low resolution density meters for evaluating the quality of clean water (instead of using pure water as described) is discouraged for use in gravimetric calibrations.

3 Pure Water used in Gravimetric Volume Calibrations

Pure water is needed for gravimetric volume calibrations. For gravimetric calibrations, filtration systems alone are *not* adequate. Pure water requires the removal of chemical contaminants and this may be achieved by distillation, reverse osmosis, ion exchange systems, or combinations of these systems. The purity of the water from any given system and maintenance requirement is often dependent on the quality of the source water. Source water should be tested to determine the best type of system to meet laboratory needs. Density calculations may be accurate even when appreciable levels of dissolved salts remain in the water. However, since it is very difficult to know what type and quantity of salts are tolerable before density is affected, it is prudent to use the best system practical within budgetary constraints.

4 Water Quality Specifications and Purification Methods

Water that has electrical conductivity of ≤ 5 µS/cm is recommended as adequate for gravimetric calibration purposes. Such water may be produced by distillation, ion exchange, continuous electrodeionization reverse osmosis, electrodialysis, or a combination thereof, followed by polishing with a 0.45 µm membrane filter. The type of systems recommended here will typically provide water quality that meets Type I specifications and are relatively inexpensive for smaller quantities.

The ASTM D-1193[1] specifications for conductivity and resistivity are noted in Table 1. Alternatively, a similar ISO 3696 standard[2] may be used.

Table 1. Conductivity and resistivity specifications for water from ASTM D-1193.

	Type I	Type II	Type III	Type IV
Electrical conductivity, max, µS/cm at 298 K (25 °C)	0.056	1.0	0.25	5.0
Electrical resistivity, min, MΩ·cm at 298 K (25 °C)	18	1.0	4.0	0.20

Conductivity or resistivity (along with other water quality measurements) are often used to assess the water quality used in cooling towers, boilers, relative humidity systems, micro and nanoelectronic systems and in pharmaceuticals, to ensure water of sufficient purity and to minimize corrosion or build-up within such systems.

Conductivity and resistivity measurements do not have a direct correlation to water density, which is the critical attribute of concern for gravimetric volume calibrations. However, conductivity or resistivity measurements are a good indicator of water quality and whether the system is in good operating condition or needs service. Conductivity is simply the reciprocal of resistivity. For water quality specifications and assessment purposes, conductivity is usually measured in microSiemens per centimeter (µS/cm) and resistivity is usually measured in megaohms-centimeter (MΩ·cm), both usually at a reference temperature of 25 ºC. Conductivity is greatly influenced by temperature and is not linear. However, this is not a major concern for typical laboratory applications requiring pure water. Either a meter or indicator light should be included in laboratory systems to monitor water quality output. Standard reference materials are available to test conductivity and resistivity units. But, because the measurement values are used to assess quality, but not used to perform corrections to volume calibrations, traceable calibrations of the units are not essential.

Most manufacturers of systems at this level indicate that the resulting water will meet Type I specifications. The ASTM standard D 1193 also specifies design qualifications, installation qualifications, operational qualifications, and performance qualifications. In

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[1] ASTM D 1193 - (06)2018, Standard Specification for REAGENT WATER, ASTM, http://www.astm.org, 1916 Race St., Philadelphia, PA 19103.

[2] ISO 3696:1995 Water for Analytical Laboratory Use. Specification and Test Methods.

addition, D 1193 specifies that preventive maintenance shall be performed on a regular basis and not less than once per year. Sales literature will usually specify whether the equipment will provide water of the designated quality. Additionally, many manufacturers will provide a source water quality test and recommend a system to meet the purity and volume requirements of the laboratory.

A cartridge-type ion-exchange system is recommended for its simplicity and ease of operation. It can operate intermittently (on demand) and requires little or no maintenance except for change of cartridges, the need for which will be indicated. A relatively small system (2 L/h to 30 L/h) is adequate for laboratories calibrating glassware and test measures up to and including 20 L (5 gal) standards. It may be used on demand or to fill a small (20 L to 40 L) storage bottle to assure a continuous supply of calibration water.

There are two broad types of ion-exchange systems. Pressure cartridge systems (PCS) operate directly from line pressure (up to 700 kPa) and need no special operation precautions. The less expensive type operates from the water line through a needle valve to produce a specified flow through the cartridge(s). In this system, the outlet must not become blocked or turned off to prevent the water pressure from building up and bursting the cartridge. It is common practice to plumb directly from the output of this cartridge to a storage tank without using a valve in between. The unit is operated by simply turning the shut-off valve located at the water supply.

5 Water Density Measurements

Water density may be measured with a five- or six-place oscillation-type density meter calibrated using suitable standard reference materials that are representative of the range of use. These systems typically measure the density at a specific reference temperature (generally 20 ºC). However, density meters are generally not needed if an appropriate water purification system is used that includes a way to measure conductivity or resistivity and where outside validation of water quality has been obtained. If a density meter is used to determine actual density of water as a calibration medium in instances where water is not of the purity specified by this GLP for gravimetric calibrations, accuracy and traceability of the measurement results must be verified.

One method that may be used in the laboratory for monitoring water over time is to maintain a quality assurance reference flask (QARF) that is calibrated at any time a gravimetric calibration is performed. If the results of a proficiency test (interlaboratory comparison) that is conducted at the same time are found acceptable, one can assume that the quality of the water was acceptable on that day. In this way, the reference value for the flask may be monitored over time. Glassware is unlikely to change with use of pure water; thus, significant changes on a control chart for a QARF indicate other problems that may need to be investigated such as water quality or other changes in the calibration system or process.

Exposure of pure water in storage to air will likely cause degradation in the conductivity and/or resistivity measurements. However, pure water has been stored for over a year with little degradation in the density quality (if/when storage containers and lines are clean and that there is no bacterial growth, algae, or other contamination).

Temperature equilibrium is a critical factor in the density stability of water. This is especially important for large volumes. Water temperatures must be stable throughout the container with thermal gradients minimized to the extent possible and applicable. Temperature accuracy is as important as purity for a correct density determination. If water is coming straight from the tap through the purification system into the prover, the temperature may fluctuate appreciably. Therefore, it is important to store an adequate volume of water needed to complete a calibration that is either already purified or ready to enter the system.

6 Water Density Calculations

Water density tables (see Table 9.8 in NISTIR 6969) or calculations are required for most gravimetric calculations. For use in computer programs (most often spreadsheets), the use of calculations is preferred to the use of look-up tables.

6.1 Air-free water density calculation

The following equation provides the density for air-free water and is recommended for use between 0 °C and 40 °C.[3] This equation provides results in kg/m^3. Therefore, divide by 1000 to convert the value to g/cm^3.

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

where:

a_1 = -3.983 035 °C

a_2 = 301.797 °C

a_3 = 522528.9 °C^2

a_4 = 69.348 81 °C

a_5 = 999.974 950 kg/m^3

t_w = the temperature of the water in °C.

In Excel Format, where, G8 is the cell with the water temperature in °C and calculated water density is given as kg/m^3, the equation will look like this:

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[3] 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).

$$=999.97495\times(1-(((\mathrm{G8}-3.983035)^2\times(\mathrm{G8}+301.797))/(522528.9\times(\mathrm{G8}+69.34881))))$$

Eqn. (2)

6.2 Air-saturation correction for water density calculation

Pure water that is used in the laboratory is generally air-saturated, so the density must be corrected. The impact is approximately between 1 and 4 parts per million (or several times the uncertainty of the water density calculation). To adjust the air-free water density in Equation 1 between 0 °C and 40 °C to air-saturated water (the standard laboratory condition), use the following equation,

$$\Delta\rho / kg\ m^{-3} = s_0 + s_1 t \qquad \text{Eqn. (3)}$$

where,

$S_0/(10^{-3}\ \mathrm{kg\ m^{-3}}) = {}^{-}4.612$

and

$S_1/(10^{-3}\ \mathrm{kg\ m^{-3}\ {}^\circ C^{-1}}) = 0.106$.

In Excel Format:

= (-4.612+0.106*G8)

where, G8 is the cell with the Celsius temperature. (Add this value to the density. Air-saturated water density will be less than air-free water density.)

Note: The units in Equation 2 are 10^{-3} kg/m^3 or “parts per million,” so divide by 1 000 000 to find the change to the water density in g/cm^3.

6.3

The following air-saturated water density calculation is recommended for laboratory use with Eqn. 1 and Eqn. 3 combined as follows, taking care to match units.

$$\rho_w = \frac{a_5\left[1-\frac{\left((t+a_1)^2(t+a_2)\right)}{a_3(t+a_4)}\right]}{1000} + \frac{s_0+s_1 t}{1000000}\ \mathrm{g/cm^3} \qquad \text{Eqn. (4)}$$

7 Uncertainty in Water Density Values

The uncertainty in water density given by the references for the equation itself may be calculated using Eqn. 3. The calculated uncertainty for all the values in the example data shown below is 0.000 000 83 g/cm^3. The uncertainty in water density associated with temperature measurements and temperature gradients must be included in addition to this factor.

$$u(\rho_w) = 0.8394 - 0.00128\times t + 0.000110\times t^2 - 0.00000609\times t^3 + 0.000000116\times t^4\ (10^{-3}\ \mathrm{kg/m^3})$$

Eqn. (5)

7.1 Example Data

Table 2. Example data for water density calculations.

Temperature (°C)	**Air-Free Water Density (g/cm^3)**	**Correction for Air Saturation (g/cm^3)**	**Air-Saturated Water Density (g/cm^3)**
10	0.999 702 70	-0.000 003 55	0.999 699 15
15	0.999 102 57	-0.000 003 02	0.999 099 55
20	0.998 206 75	-0.000 002 49	0.998 204 26
25	0.997 047 02	-0.000 001 96	0.997 045 06

8 Non-mandatory References

ASTM D 1125–2014, Standard Test Method for Electrical Conductivity and Resistivity of Water, ASTM, http://www.astm.org, 1916 Race St., Philadelphia, PA 19103.

ISO 15212-1:1998, Oscillation-type density meters – Part 1: Laboratory instruments, ISO, 1998.

ISO 15212-2:2002, Oscillation-type density meters - Part 2: Process instruments for homogeneous liquids, 2002.