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Important Technical Guidance on Glassware

By Tom Coleman and Georgia Harris

Getting New Glassware into Service

"If it ain't broke, don't break it. If it breaks, it needed replacing anyway." That sounds pretty obvious, right? Well, if you do break it and end up replacing field standard glassware, make sure it gets calibrated! A number of laboratories have reported failure rates on new glassware as high as 50 %. Yes, on new glassware! Most glassware manufacturers are not accredited and there is no system in place to ensure that new glassware complies with specifications and tolerances other than through your laboratory's initial verification. Most glassware manufacturers have good quality control systems in place, but many do not, so do not use test flasks or other liquid measures until they have been verified.

Failures in new glassware are primarily related to flasks being found out of tolerance. Avoiding such errors is critically important to anyone using the glassware to take enforcement action. If the glassware fails, it is important to contact the manufacturer for replacement. Otherwise, a field official must use a correction factor supplied by the laboratory, which can complicate testing, and could result in errors.

For Metrologists:

Glassware Specifications

Glassware specifications and tolerances for weights and measures can be found in documentary standards such as:

NIST Standards (available for free at http://www.nist.gov/labmetrology)

- Handbook 105-2, "Specifications and Tolerances for Reference Standard and Field Standard Weights And Measures, 2. Specifications and Tolerances for Field Standards Measuring Flasks," 1996.

OIML Standards (available for free at http://www.oiml.org)

- International Recommendation No. 43, "Standard Graduated Flasks for Verification Officers," 1976.
- International Recommendation No. 4, "Volumetric Flasks (one mark) in Glass," 1972.

ASTM Standards (available for purchase at http://www.astm.org)

- E 288-94, "Standard Specification for Laboratory Glass Volumetric Flasks," 1994.
- E 438-90, "Standard Specification for Glasses in Laboratory Apparatus," 1992.
- E 542-94, "Standard Practice for Calibration of Laboratory Volumetric Apparatus," 1994.

- E 694-94, "Standard Specification for Laboratory Glass Volumetric Apparatus," 1994.
- E 1272-95, "Standard Specification for Glass Graduated Cylinders," 1995.

Calibration Intervals

Once glassware has had initial testing, subsequent testing based on suitable calibration intervals could be limited to a visual inspection prior to use. It is a good idea to have calibrations conducted at least every ten years to verify that the calibration is still valid and to provide a "current" calibration report if enforcement actions are taken using the glassware. It is extremely difficult to justify calibration intervals longer than ten years.

Calibrating Glassware

Two methods for calibrating glassware are commonly used: 1) volume transfer from automatic pipettes and 2) gravimetric calibration. The two primary standard operating procedures (SOPs) are SOP 16 (volume transfer) and SOP 14 (gravimetric calibration using an electronic balance) (see NIST Handbook 145).

*Special Considerations for SOP 16******

(*****SOP 16, as published in NBS Handbook 145, “Handbook for the Quality Assurance of Metrological Measurements,” 1986, contained an error in the temperature correction formula. Corrections were issued in a Tech Memo in April 1999.)

The correct reference temperature for glassware calibration is 20 °C. The correct V20 equation is as follows:

$$VTD\ 20\ °C = VTDM\ [1 + (t - 20)(a_s - a_x)]$$

Where:

Symbol	Quantity Represented
V_{TD}	Volume to deliver
V_{TDM}	Volume to deliver, as measured
t	Temperature at time of test, °C
a_s	Coefficient of expansion for the standard
a_x	Coefficient of expansion for the test flask

If your laboratory is using the automatic pipettes and burettes provided by NIST as a part of the States Standards Program, they must have calibrations less than ten years old! Calibrations of laboratory standards must be done gravimetrically and can be performed by NIST or by any laboratory that is accredited or recognized for gravimetric calibrations where the uncertainty of the calibration is sufficiently small. Be sure to check the scope on the laboratory’s accreditation/recognition certificate to be sure that the calibration is covered by the scope and that the uncertainty will be sufficiently small. To be recognized by NIST, laboratory staff must have successfully completed Intermediate level training and the Intermediate Laboratory Auditing Program problems, and must have also demonstrated proficiency through round robin testing.

Considerations with SOP 14

If a laboratory chooses not to maintain valid traceability on the automatic pipettes and burettes, a suitable alternative is to gravimetrically calibrate all glassware that is submitted. This approach actually minimizes the number of standards that a laboratory needs to maintain and shortens the traceability hierarchy. One disadvantage is that the staff must have successfully completed the requirements for gravimetric calibrations described above.

To avoid errors in gravimetric calibrations, the most important thing to remember is that the water used in this type of calibration is a standard and must be of suitable purity. Adequate purity can be obtained by using distilled water, deionized (DI) water, or a combination of reverse osmosis (RO) with deionization (DI). Handbook 145, *Good Laboratory Practices*, specifies ASTM Class 4 water, however the ASTM D 1193 standards don't provide any information about density. It is important to monitor the water system and purity (with check standards following the same procedures) because water systems can degrade with time. Most water systems will have a method to measure conductivity and/or resistivity, which is a measure of purity, but is not directly correlated with density. Obviously, if the system indicator shows that service is needed, it is a wise thing to ensure it is performed and verified before calibrations are conducted. The key thing to remember with all gravimetric calibrations is that ORDINARY TAP WATER MUST NEVER BE USED! You might be able to use alternative sources of water if your laboratory invests $20,000 in a 5-place or 6-place density meter, verifies its operation with certified reference standards each time testing is performed, and then tests the water each time a calibration is performed. However, a density meter is not needed if you use a suitable water source to begin with.

For Field Inspectors:

Because flasks are ordinarily calibrated on a "to deliver" basis, they must be "wet down" before using. Immediately before use, fill the volumetric flask or graduate with water. The water should be at the reference temperature of the product being tested. Fill the flask with water to a point slightly below the top graduation on the neck. The flask should be emptied in 30 seconds (± 5 seconds). Tilt the flask gradually so the flask walls are splashed as little as possible as it is emptied. When the main flow stops, the flask should be nearly inverted. Hold the flask in this position for 10 seconds and touch off the drop of water that adheres to the tip. If necessary, dry the outside of the flask. This is called the "wet down" condition. The flask or graduate is then ready to fill with liquid from the package.

When using a volumetric measure that is calibrated "to contain", the measure must be dried before each measurement. Before making additional measurements of a liquid, use water to wash or rinse and prepare the volumetric measure. Between each measurement of liquid from the sample packages, prepare the volumetric measure as described above, dry the outside of the flask, and drain the volumetric measure as described.

If the flask capacity is equal to the labeled volume, pour the liquid into the volumetric measure tilting the package to a nearly vertical position. If the flask capacity is smaller than the package's labeled volume, fill the flask to its nominal capacity graduation. If conducting a volumetric test, drain the container into the volumetric measure for 1 minute after the stream of liquid breaks into drops.

Reading the Meniscus

Position the volumetric measure on a level surface at eye level. For clear liquids, place a material of some dark color outside the flask immediately below the level of the meniscus. Read the volume from the lowest point of the meniscus. For opaque liquids, read the volume from the center top rim of the liquid surface.

Glassware is used to check liquid commodities (e.g., milk, orange juice, soap) and not solid commodities (e.g., rice, M&Ms, salt). Sometimes glassware is used to determine the product density for subsequent package testing by weighing and sometimes it is used to verify the volume for each package being evaluated.

Temperature corrections generally must be made to the correct reference temperatures. Reference temperatures for various products are:

Frozen food labeled by volume (fruit juice)	-18 ºC (0 ºF)
Beer	3.9 ºC (39.1 ºF)
Food that must be refrigerated (milk, dairy products)	4.4 ºC (40 ºF)
Distilled spirits or petroleum	15 ºC (60 ºF)
Unrefrigerated products (unchilled liquids, wine, soft drinks)	20 ºC (68 ºF)

Temperature Effects on the Graduate/Flask

As liquids expand and contract with temperature variations, so does glass! Therefore, to provide a standard for users of volumetric flasks, the manufacturers of graduates state the temperature at which it will be correct. Since room temperature or laboratory temperature is most nearly 20 ºC (68 ºF), the manufacturers have accepted this temperature as their standard.

When testing milk, the ideal situation would be for the temperature of the milk to be 4.4 ºC (40 ºF) and the glass of a flask or graduate to be 20 ºC (68 ºF). Since the glass will assume the temperature of the product with which it is filled, this is impossible. What is the effect? Assuming that a 32-fluid ounce glass graduate will maintain a 20 ºC (68 ºF) temperature when being filled with 4.4 ºC (40 ºF) milk, the volume would be correct when the milk reaches the line on the graduate indicating that amount (32 fluid ounces).

However, as the glass cools, it contracts and as it shrinks, the milk will rise in the neck of the graduate and it will indicate more than 32 fl oz. In a study conducted by NIST, it was found that a graduate marked "To Deliver (TD) - 68 degrees F" when cooled to 4.4 ºC (40 ºF) would contract 2.37 minims on a 32-fl oz graduate. Therefore, when the graduate is used at a temperature of 4.4 ºC (40 ºF), the packager need only provide 15,357.63 minims to indicate 32 fl oz, rather than 15,360. And who is the benefactor? It is the packager who benefits when the graduate is used at a temperature lower than 20 ºC (68 ºF).

Conclusion: While 2.37 minims (temperature effect on the graduate) is an immeasurable amount in the field, it should not be considered a factor in his/her field inspection. Since the temperature of milk is an important consideration, the weights and measures official should determine that temperature when determining the density of a specific volumetric quantity, following NIST Handbook 133, Checking the Net Content of Packaged Goods procedures. It is not necessary that the milk be exactly 4.4 ºC (40 ºF) if the official is aware of the variables involved. However, if the data were to be used as evidence in a court action, the milk must be measured and the volume determined at 4.4 ºC (40 ºF).

If you are taking enforcement action on packages and using glassware as one of the standards, be sure that:

1. Glassware has been calibrated properly by an appropriate laboratory and it complies with applicable specifications and tolerances.
2. You have equipment that is working properly and is calibrated (e.g., thermometer, scale, weights).
3. You follow Handbook 133 and only use glassware to test liquid commodities sold by volume.
4. You are familiar with how to correctly read a meniscus.
5. You perform calculations (e.g., temperature corrections) completely, accurately, and in accordance with procedures.

ALL Applications

There are a number of items that are important for both the calibration and application processes.

1. Glassware must be clean. Typically, hot, low-sudsing soap and water can be used, followed by several rinses with high-purity water. If needed, stronger solvents such as acetone or ethanol may be used, but suitable safety precautions need to be followed when using chemicals. We do not recommend the use of acids such as chromic acid except when suitable safety precautions are followed; chromic acid requires the use of hoods and special safety clothing and eye/face protections along with hazardous waste disposal practices.
2. It is critical that the meniscus be read properly. Reading the meniscus is one of the largest sources of error in calibrating or using glassware. Instructional methods are in Handbook 145, GMP 3 and in Handbook 133.
3. Proper pour/drain times must be used correctly. Flasks are calibrated with a 30-second pour and 10-second drain at 5 to 10 degrees from vertical. They must be used in the same way or your test results will be incorrect.

4. "To contain" and "to deliver" flasks must be selected and used properly. "To-deliver" flasks used to measure product delivery must have a proper wet-down. If a "to-contain" flask is used, it must be completely dry between tests. Hence, "to-deliver" flasks are usually used with suitable wet downs.
5. Thermometers used in calibration and field applications must have sufficient resolution, accuracy, and traceability. For calibrations, the thermometers must have a 0.1 °C resolution and calibration reports are required. For field applications, the resolution must be 0.x °C and calibration is essential for good temperature corrections, especially when regulatory action may be taken.

If you have any questions regarding the use of glassware in field testing, contact Tom Coleman at 301-975-4868 or at t.coleman@nist.gov. Questions regarding the calibration of glassware should be directed to Georgia Harris at 301-975-4014 or at gharris@nist.gov.