Gravimetric Troubleshooting Checklist

July 14, 2021

This checklist is intended to help metrologists identify potential problems in their gravimetric volume calibrations. It identifies known errors or difficulties that metrologists have had with the gravimetric volume calibration procedures.

Standards

- Appropriate quantity of correct class of mass standards - need enough standards to cover the range of use
- Valid and current calibration certificates make sure densities are selected properly
- Use TRUE MASS values for mass standards in equations – avoid duplicate buoyancy correction bias; make sure certificate has true mass values or perform calculations to obtain true mass
- Make sure magnetism of reference standards is not a problem
- Thermometer calibration and resolution (for water temperature) to at least 0.1 ºC; make sure corrections are used as the water density calculations rely on accuracy to this level (an offset is greater than water density uncertainty!)
- T, P, RH measurements need to be within SOP 2 specifications for air density calculations (use corrections)

Balances

- Be familiar with GMP 10 and good weighing practices (centering, gentle placement, drafts)
- Electronic balance or mass comparators – know the difference, calibration methods, and impact on results (comparators may NOT be used as a calibrated balance with readings without likely errors)
- Appropriate capacity – obtain preliminary estimates of baseline mass of container and estimated mass of water when full (an approximation of mass can be determined using an estimated divisor of 1.003; e.g. 1 L is approximately 1 000 g, but will weigh about 997 g) An estimated value can be determined for your lab and conditions based on performing all calculations except the mass difference in equation 1, section 3.1 in SOP 14.
- Ensure suitable resolution for desired uncertainty; 1 or 2 digits beyond typical repeatability of the process ensures that the balance resolution is not usually a critical factor in the uncertainties (it should be a minor factor in repeatability because the meniscus or delivery/drain/retention effects influence more than resolutions) – ASTM E542 and ISO 4787 both have recommended balance resolutions for balances that normally won't be a concern for a lab that also performs mass calibrations. But, select the balance with the smallest resolution that is available that can also handle the size and configuration of the container and mass
- If using direct reading methods (no longer recommended), the balance must be calibrated with suitable mass standards prior to test AND the correct density for internal weights must be used with the correct apparent mass correction value for the selected balance (older procedures in ASTM E542 and SOP 13 for mechanical balances relied on internal calibrations and used direct readings) - Euramet CG 18 or similar procedure can be used to calibrate the balance and determine contributing uncertainties
- For larger electronic balances (above 5 kg) look for corner loading errors, linearity errors, range of use problems (minimize low end), relative accuracy/calibration errors, repeatability
- Consider air current effects and draft shields (limit movement of people)
- Filling on the pan – discouraged due to drift and hysteresis problems

- Be aware of possible magnetism of leveling pans (bearings in leveling pans), transfer vessels, or standards themselves
- Watch for linearity effects (consider whether Option A, 1 point or Option B, 2 point reference standards is the best approach)
- Zero balance before each reading – per the instructions! To avoid additional drift in the balance readings
- You can track and plot your mass standard values after zeroing (to monitor variability and drift)

Water

- Be familiar with GLP 10 and water quality requirements and evaluations
- Purity of water (do NOT use TAP Water!!! Some labs will not be able to use reverse osmosis (RO) alone)
- Be aware of the age of distilled or deionized water (check expiration date)
- Density testing of water – ensure adequate accuracy (calibration) and resolution of instrument; if testing the density of water, the uncertainty needs to be from a six place density meter (0.000 001 g/cm^3) rather than a five place density meter (0.000 01 g/cm^3); units need to have calibration with standard water samples (watch CRM or SRM dates!)
- Be aware of water temperature gradients – equilibration, handling effects (e.g., necks on flasks or provers will warm or change quicker due to handling)

Meniscus Reading

- Meniscus Reading (See GMP 3); meniscus readers, cameras, microscopes – be aware of what method is specified (Option A, Option B in GMP 3 – some international standards specify something like to Option B for glassware)
- Watch lighting, alignment, use of correct meniscus readers, and visual acuity and effects of glasses (especially bi focal, tri focal, or progressive lenses) and/or magnification
- Types of meniscus and effects of surface tension – test measures or glassware
- Effect of small amounts of water on meniscus and on mass (20 drops is approximately 1 mL or 1 g; get an estimate of 1 drop of water on changing the meniscus and mass) – Observe graduation width and neck diameter effects and compare to the observed process repeatability

Environment/Facility

1. Ensure the SOP is followed: 18 °C to 23 °C, Stable to ± 1 °C / 1 h, during the calibration (this is a precision mass calibration), Air and water temperature and stability - minimize uncertainty of CCE and weighing convection currents (close to lab specs for both air and water)
2. RH limits are 40 % to 60 % (this procedure is using balances and manufacturer’s specs are 40 % to 60 %). Make sure humidity is stable to ± 10 % / 4 h (this is a precision mass calibration); this will impact potential evaporation and static; Relative Humidity affects: evaporation, condensation, surface adsorption on transfer vessel or container - especially problematic if direct reading balance values on a calibrated balance
3. If an environment is stable within limits and process is relatively quick (less than an hour), the before/after environmental readings can be done once before all runs and once after all runs (rather than before and after each run)
4. Air currents have the same influence on balances as precision mass calibrations; in cases where the draft shield can’t be used or doors completely closed, be especially attentive to draft effects; lack of thermal equilibration can also cause convection currents
5. Ensure that proper equipment is available for safely moving transfer vessel to and onto balance

(protect staff, equipment, and standards)

Containers (Unknown Standards)

1. Design – do the specification evaluations and evaluate conformity needs (customer requests or legal applications)
2. Note whether container is of a To Contain (TC) or To Deliver (TD) design
3. Evaluate graduations (if present) and select the correct meniscus reading tools for each
4. Cleanliness and Contamination. If metal: look for corrosion, air entrapment, retention; If glassware: look for clean draining and limited retention; If calibrating glassware to contain – verify "dry" condition (step 2.7.6 – dry neck); watch filling on neck wetness on inside/outside for consistency; if to deliver flask – it will have a wet neck so do not dry it (step 2.8.5)
5. Record ALL identification information: serial numbers, drain times, Class (A or B) for glassware, cubical coefficient of expansion (is it labeled correctly?), brand names like Pyrex or Lurex are T1CA borosilicate, note correct reference temperature and make sure customer doesn't need calibration to alternative reference temperatures
6. Be aware of static effects on flasks due to handling (wiping outside of flask can cause static),
7. Match units of CCE and reference temperatures (e.g., / °C and °C to cancel units properly)
8. Inspect valves, drain tubes (SVP), stopcocks for leaking and smooth operations (perform several conditioning runs to exercise valves and/or stopcocks)
9. Inspect for leaks and cracks
10. Make sure containers are equilibrated in the lab (just like precision mass calibrations); equilibrate flasks, provers, or containers water to minimize convection current effects
11. TC glassware – dry conditions; surface may have moisture that is not visible and not to the dry base weight

Transfer Vessels

1. Ensure that stable material is selected with lids/covers (non-magnetic, non-static)
2. Ensure safe handling and movement and gentle setting on balance using good weighing techniques
3. Ensure vessels are temperature equilibrated (minimize convection currents)

Procedure/Calculations

1. Think about *Mise en place* – that is: organize the workspace for best workflow, handling, recording and ensure everything that is needed is set out ahead of time
2. Select the correct methods based on unknown standard to be calibrated (e.g., burette, pipette, slicker plate standard)
3. Use a validated spreadsheets/software and pay attention to data entry
4. Be alert for rounding differences/errors
5. Uncertainty of equations is not the same as the uncertainty of measurements! Equations: air density (0.0012 mg/cm^3), water density (0.000010 g/cm^3).(Use CIPM air density equation, Option B in SOP 2; use Tanaka, et al water density equation in GLP 10 both published in *Metrologia*) – Make sure recommended equations from SOP 2 and GLP 10 are used in your lab spreadsheets!
6. Z values in E-542; use calculations not tables!! 2021 draft of E542 provides tables only for verifying spreadsheets
7. E-542 used to be a "direct reading" procedure with mechanical balances that <u>required</u> calibrations; errors will be incorporated in readings if not corrected. SOP 14 calibrates the balance at the time of use, in the range of use with calibrated reference mass standards
8. Prevent slopped/dripping or evaporated water (use lid or cover) – recall the mass of 1 drop of

water!

9. Consider water retention in drain valves, stopcocks, proper drain times, water in neck on “to contain” flasks in hose between prover and transfer vessel – minimize or stabilize.
10. Ensure water is air saturated and in equilibrium with atmospheric conditions, (no off-gassing).
11. Use correct pour/drain times (e.g., 30 s ± 5 s); drain angle 10° to 15° Consider the impact of non-standard delivery and drain