SOP 11

Gravimetric calibration of the volume of a gas loop using water

1. Scope and field of application

This procedure describes how to calibrate the volume of a length of stainless steel tubing coiled as a loop based on the procedures of Wilke *et al.* (1993). Typically, two loops are installed onto an 8-port chromatography valve to calibrate the coulometer used in the determination of total dissolved inorganic carbon in sea water (SOP 2). This procedure is capable of achieving a reproducibility of about 0.01% (1 relative standard deviation). A procedure is also detailed for computing the volume of the loop, in the valve assembly, at temperatures different from the calibration temperature.

2. Principle

The loop is weighed empty and full of water and its volume at the calibration temperature is computed from the mass of water contained. The volume at another temperature can then be calculated by allowing for the thermal expansion of the tubing.

3. Apparatus

- Length of 316 stainless steel tubing $^1/_8$ inch (~ 0.3 cm) outside diameter, electropolished on the inside, and coiled as a loop. The ends of the tubing must be cut perfectly square[1]. Typically, two calibration loops have lengths designed to deliver a volume of pure CO_2 that brackets the anticipated CO_2 content of the sea water samples. If the sea water sample size is approximately 29 ml, then a typical carbon yield (S = 35, C_T = 2000 μmol kg^{-1}) is about 700 μg C. Ideal nominal loop volumes would then be 1.25 and 1.75 ml yielding about 500 and 800 μg C, respectively.
- 8-port chromatography valve (*e.g.*, 8UWP, Valco Instruments Co. Inc. (VICI®)),
- Analytical balance, capacity 300 g, sensitivity 0.1 mg,
- Constant temperature bath capable of maintaining 25 ± 0.1°C,
- 100 ml syringe and clean Teflon® tubing to connect the syringe to the loop/valve assembly,
- Helium leak detector (*e.g.*, Gow-Mac Instrument Co., Bethlehem, PA, U.S.A.) or an alternative method for ensuring a proper seal between the loops and the chromatography valve.

[1] The square ends are needed to ensure that the tubing fits properly into the valve ports.

4. Reagents

- Helium supply,
- Ultra-pure water (*e.g.*, distilled and then deionized) degassed by sparging with He at > 200 ml min^{-1} for 30 minutes,
- Dry compressed N_2 gas,
- Methanol (analytical grade).

5. Procedure

5.1 Clean the loop and valve assembly prior to weighing. It is essential that they be scrupulously clean before the measurement and that they remain that way. Rinse the exterior of the loop and flush the interior of the loop repeatedly with deionized water, then with methanol. Dry the loop overnight by flushing with N_2 gas. Use gloves or tongs to handle the loop at all times to maintain cleanliness.

5.2 Carefully connect the loops to the ports of the chromatography valve using either Hastalloy (ZF2HC, VICI®) or gold plated (ZF2GP, VICI®) ferrules.

5.3 Leak test the loop/valve assembly by pressurizing the system to ~ 250 kPa with helium and checking for leaks using the helium leak detector.

5.4 Place the valve along with loose port plugs (ZC2, VICI®) into an open Ziploc freezer bag and dry in a vacuum oven at < 95 kPa at ambient temperature until a constant weight can be determined. Reseal the bag as you remove it from the oven to minimize moisture contamination.

5.5 Determine the dry weight by quickly removing the valve from the Ziploc and weighing on the balance. Take the average of five weights as the "dry weight" of the assembly.

5.6 Once the dry weight is determined, secure the ports for the second loop using the port plugs and attach the syringe and tubing to the remaining two ports.

5.7 Place the container of ultra-pure water and the valve assembly double bagged in Ziplocs® (valve assembly must be kept scrupulously dry) into the constant temperature bath for 1 hour until thermally equilibrated.

5.8 Flush and fill the loop with ultra-pure degassed water using the syringe, then manually switch the valve as smoothly and quickly as possible to isolate the fluid path. The temperature of the water should be controlled.

5.9 Remove the valve from the bath, disconnect tubing and flush non-isolated valve pathways with N_2, flush with two 50 ml methanol rinses, then purge with N_2 for 30–45 minutes at 200 ml min^{-1}. Ensure that all exposed parts are dry.

5.10 Weigh the valve assembly five times to determine the "full weight".

5.11 Remove port plugs and rinse with methanol, dry with N_2, turn valve to original position and return valve and plugs to vacuum oven.

5.12 Weigh the dried valve assembly at ½-hour intervals until a constant weight is obtained. If the difference between the dry weight and the final weight is < 0.0007 g, then the calibration result is considered valid.

6. Calculation and expression of results

6.1 The volume (V) of water, in milliliters, is calculated by correcting the mass of water (M_a), determined as the difference between the full weight and the dry weight, to the weight under vacuum (buoyancy correction) and dividing the result by the density (d) of water[2] at 25°C:

$$V = \left[M_a \cdot (0.0012/d - 0.0012/8.000) + M_a\right]/d \quad (1)$$

where 0.0012 g cm^{-3} is the density of moist air at standard temperature and pressure and 8.000 g cm^{-3} is the density of stainless steel weights in air.

6.2 The thermal expansion of the tubing being used must be taken into account in order to convert the volume measured at one temperature (t_1) to an alternate temperature (t_2). For 316 stainless steel, the coefficient of linear expansion (α_l) is about 1.73 × 10^{-5} K^{-1} (Weast, 1975). The coefficient of volumetric expansion,

$$\alpha_v = (1+\alpha_l)^3 - 1 \approx 3 \cdot \alpha_l, \quad (2)$$

is used to calculate the volume at the alternate temperature,

$$V(t_2) = V(t_1)\left[1 + \alpha_V (t_2 - t_1)\right]. \quad (3)$$

7. Quality assurance

The following points should be noted:

- The weights for the stainless steel tubing (dry) obtained at each measurement should agree with each other to ± 1 mg. This confirms that the tubing is being cleaned and dried adequately before each weighing.
- Measurements of the volume of the stainless steel tubing made on different days should agree with each other when corrected to a standard temperature.
- The ratio of measured loop volumes from a pair of loops should agree with the ratio of the amounts of CO_2 gas delivered, as determined by the coulometer.

8. Bibliography

Weast, R.F. 1975. CRC Handbook of Chemistry and Physics, 56th edition, Chemical Rubber Company.

Wilke, R.J., Wallace, D.W.R. and Johnson, K.M. 1993. Water-based, gravimetric method for the determination of gas sample loop volume. *Anal. Chem.* **65**: 2403–2406.

[2] The formula given for the water density in Chapter 5 is for air-saturated water. However, the error induced by using this formula with helium-sparged water is negligible.