SOP 11

Gravimetric calibration of the volume of a gas loop using mercury

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. Such loops are used together with a valve system to deliver known amounts of pure carbon dioxide to calibrate the coulometer used in the extraction / coulometric procedure for determining 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 mercury and its volume at the calibration temperature is computed from the mass of mercury contained. The volume at another temperature can then be calculated by allowing for the thermal expansion of the tubing.

3. Apparatus

3.1 Analytical balance, capacity 100 g, sensitivity 0.1 mg

3.2 Thermometer accurate to ± 0.2 °C

3.3 Length of 316 stainless steel tubing $^{1}/_{16}$ inch outside diameter, electropolished on the inside and coiled as a loop. The ends of the tubing must be cut perfectly square (Note 1).

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[1] Using $^{1}/_{16}$ inch tubing minimizes the size of the inlet ports in the chromatography valve used with the gas loop as well as errors due to the mercury meniscus. The square ends are needed to ensure that the tubing fits perfectly into the valve ports.

4. Reagents

4.1 Clean mercury (Note 2)

4.2 Acetone (analytical grade)

4.3 Supply of clean, dry, gas

4.4 Source of vacuum

5. Procedure

5.1 Clean the loop prior to weighing

It is essential that the loop be scrupulously clean before the measurement and that it remain that way. This can be achieved as follows: rinse the exterior of the loop and flush the interior of the loop repeatedly with acetone. Then blow the loop dry using clean dry gas. Use gloves or tongs to handle the loop at all times to maintain its cleanliness. If a gas with a density different from air is used to dry the loop (*e.g.* helium), it is important that this gas be flushed out of the tube with laboratory air prior to weighing.

5.2 Weigh the empty loop on an analytical balance

5.3 Fill the loop with mercury prior to reweighing (Note 3)

Immerse one end of the loop in a beaker of clean mercury (Note 4). The other end of the loop should also be maintained below the mercury level. Fill the loop with mercury by sucking it through the loop using a piece of flexible, transparent, plastic tubing (*e.g.* Tygon®) connected to a vacuum pump. Once the stainless steel loop is full, disconnect the plastic tubing from the loop and allow the mercury to continue syphoning through the loop to ensure that no air bubbles remain in the tube.

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[2] Mercury can be cleaned satisfactorily by washing it thoroughly with dilute nitric acid and dilute sodium hydroxide, then rinsing it with copious amounts of deionized water. The mercury is dried by dabbing the excess water off the top using a piece of filter paper then filtering it through a pinhole in a filter paper.

[3] Mercury vapor is potentially hazardous and mercury should be handled appropriately. In particular, efforts should be made to minimize spillage and to contain such spills as occur.

[4] Both the mercury and stainless steel loop must be allowed to equilibrate with the room temperature before starting this procedure.

Once at least one loop volume has siphoned through, close the ends of the loop with the fingertips—wearing disposable plastic gloves—and invert the loop so that the open ends are upward.

Top the loop off with small droplets of mercury which are picked up using a syringe needle. Examine the ends closely to ensure that they are filled correctly (Note 5). Replace the disposable gloves before handling the loop further (Note 6).

Note the temperature of the mercury and weigh the filled loop.

5.4 Empty the loop of mercury

Provided that the loop is scrupulously clean, the mercury will siphon out cleanly. If on reweighing, the loop is still thought to contain mercury, the loop should be blown through with a clean dry gas, taking care to catch the mercury droplets that are blown out. Again, make sure the loop is filled with laboratory air before reweighing.

5.5 Assemble the valve

Once accurate volumes have been obtained for both loops, mount the loops on the valve. It is essential that the stainless steel tubing fit perfectly into the valve ports and that the tubing is held firmly while tightening the fittings.

6. Calculation and expression of results

6.1 Volume of the tubing used as the loop

The weight of the mercury contained is computed from the difference between the filled and empty loop weights:

$$w(\mathrm{Hg}) = w(\text{filled loop}) - w(\text{empty loop}) \quad .$$

The mass of mercury contained is computed from the weight, correcting for air buoyancy (see SOP 21). The volume of the loop at the temperature of weighing is given by the expression

$$V(t) = m(\mathrm{Hg}) / \rho(\mathrm{Hg}) \quad .$$

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5 One method of achieving this is to use two small transparent plastic weighing boats which are used to flatten and observe the mercury meniscus.

6 Small droplets of mercury adhering to the outside of the loop are a significant cause of contamination and must be avoided. This is a precaution to help achieve this.

The density of mercury over the range 0 – 40 °C is given by:

$$\rho(\text{Hg}) = 13.5955\left(1-\alpha_V(\text{Hg})\left(\frac{t}{°\text{C}}\right)\right)\ \text{g}\cdot\text{cm}^{-3} \quad ;$$

where t is the temperature. The volumetric coefficient of expansion

$$\alpha_V(\text{Hg}) = \left(181792 + 0.175\left(\frac{t}{°\text{C}}\right) + 0.035116\left(\frac{t}{°\text{C}}\right)^2\right)\times 10^{-9}$$

Weast (1975). The temperature of the mercury, t, must be known to within 0.5 °C to achieve an accuracy of better than 1 part in 10^4.

6.2 Volume in the valve configuration

The volume of the coiled tubing is not the only contribution to the volume of a loop on a chromatography valve. Although it is possible to plumb an eight port chromatography valve so that the path through the valve rotor is not part of the loop (see Annexe A to SOP 2), allowance needs to be made for the volume of the valve inlet ports. This information is typically available from the manufacturer.

6.3 Volume at an alternate temperature

The thermal expansion of the tubing being used must be taken into account to convert volume measured at one temperature (t) to a standard or alternate temperature (θ). For 316 stainless steel the coefficient of linear expansion α_l is about $1.73 \times 10^{-5}\ \text{K}^{-1}$ (Weast, 1975). The coefficient of volumetric expansion,

$$\alpha_V = (1+\alpha_l)^3 - 1 \approx 3\,\alpha_l \quad ,$$

is used to calculate the volume at the alternate temperature:

$$V(\theta) = V(t)\,\{1 + \alpha_V\,(\theta - t)\} \quad .$$

6.4 Example calculation

The following data were used for this calculation:

weighing conditions
$\rho(\text{air}) = 0.0012\ \text{g}\cdot\text{cm}^{-3}$ (Note 7),
$\rho(\text{weights}) = 8.0\ \text{g}\cdot\text{cm}^{-3}$,
calibration temperature = 23.0 °C ,

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7 This value is appropriate to measurements of moderate accuracy made at sea level pressure (1 atm) and at normal laboratory temperatures (~20 °C). For a more accurate value see SOP 21, equation (1).

w(Hg) = 15.0000 g ,
ρ(Hg, 23.0 °C) = 13.5386 g·cm^{-3} ,
V(inlet port) = 1.6×10^{-4} cm^3 ,
temperature of use θ = 30.0 °C .

6.4.1 Correct weight of mercury to mass:

m(Hg) = 14.9991 g .

6.4.2 Compute volume of stainless steel tubing at t = 23.0 °C:

$V(t)$ = 1.10791 cm^3 .

6.4.3 Compute volume of loop at t = 23.0 °C (*i.e.* including two inlet ports):

V(loop, t) = 1.10823 cm^3 .

6.4.4 Compute volume of loop at θ = 30.0 °C:

V(loop, θ) = 1.10863 cm^3 .

7. Quality asurance

The following points should be noted:

- The weights for the stainless steel tubing (empty of mercury) obtained at each measurement should agree with each other to ± 1 mg. This confirms that the tubing is being cleaned 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.

References

Weast, R. F. (1975) *CRC Handbook of chemistry and physics*, 56th edition, Chemical Rubber Company.