IMPROVED TECHNIQUE IN MICROPYCNOMETRIC DENSITY DETERMINATION

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The uncertainties in measuring the volume of a liquid in a pcynometer[1] are largely overcome if the pycnometer is filled just full, as determined by reflecting light from the meniscus of the filling liquid when the meniscus is flat across the top of the pycnometer. For a large pycnometer other factors than volume may be of major importance, but for a micropycnometer, reproducibility of volume, and accuracy of weighing are the chief considerations.

A micropycnometer of this type may be made from a thick-walled capillary tube, for which the length and bore can be made to suit the material of the test sample. The one here used was about 5 cm. long, 4 mm. wide, and 1.6 mm. bore, with a volume of 0.1110_7 cm.^{3}. The inside of the closed end was thoroughly rounded but not bulged. The open end was ground flat and polished. To prevent chipping, the end of the capillary was filled with plaster of Paris and a fine abrasive used from the start. A plaster cast around the end of the capillary aided in obtaining a smooth flat surface, although extreme flatness was not required. The pycnometer was cleaned so as to avoid at the top any extraneous surface effects. It was then almost filled with water, and was suspended vertically on the balance.

A long, narrow source of light, such as a slit in a screen in front of a diffuse light, which would be equivalent to a width of an inch or less at about 20 feet, was arranged horizontally to reflect from the top of the pycnometer at a glancing angle of about 10°. If the slit could have been behind the balance the adjustment would have been easy, but the slit was between the balance and an overhead light, and had to be reflected by an adjustable mirror just behind the pycnometer in the balance case. The slit illuminated the top of the pycnometer evenly, and the liquid was evenly illuminated when it just filled the pycnometer, but when the meniscus was significantly curved the reflection of the slit in it was narrowed.

The reflections should be watched through the glass door of the balance case while weighings are being made. A little magnification and a fixed point of observation are desirable. A reading telescope (or microscope) with a working distance of 6 to 10 inches is best, but a reading glass fixed, and covered except for a small aperture, may be used.

[1] (a) Bannister, F. A., and Hey, M. H., *Min. Mag.*, **25,** 30–34 (1938); (b) Winchell, H., *Am. Mineral.*, **23,** 805 (1938).

Temperatures in the balance case should be known within a few tenths of a degree.

A droplet of water was added to make the meniscus slightly convex, and the meniscus was observed as the water evaporated. The top of the pycnometer now looked bright, and a bright, narrow, curved line crossed the meniscus. This line slowly straightened, then it rapidly widened till it covered the whole meniscus, and then quickly narrowed. The pycnometer was full at the instant the surfaces of both meniscus and pycnometer were completely illuminated. Observations were repeated with weights adjusted and the balance swinging so that evaporation was accompanied by a shift of the zero, and finally, while the change from convexity to concavity was in progress a record was made of the swings with respect to the time at which flatness occurred.

The capacity of this pycnometer was so small that only rough temperature control was required. Water changes volume one part in a thousand in the intervals 4—16—25—29°.

The sensitiveness and speed of the balance, and the rate of evaporation of the liquid are factors in the accuracy. The humidity of the balance case can be controlled somewhat. After calibration with the water the density of other liquids may be found, but if some other wetting liquid is required its density may first be found by some other method.

Careful cleaning (as with nitric and chromic acids), drying in a vacuum, and weighing of the pycnometer between fillings are essential.

The micropycnometer is most useful for small amounts of liquid, and small volumes of heavy substances. However, to test the accuracy of fillings and weighings, standard quartz was used here. The percentage accuracy of density determinations is about the same for equal volumes of material of different densities. Because the fullness can be determined with methylene iodide as accurately as weighings can be made on an ordinary analytical balance (in this case to about 0.00003 g.) the accuracy in this type of pycnometer is about in proportion to the density of the liquid used in the calibration and immersion. The following changes in the formula and explanation below apply when other liquids than water are used: for specific gravity, "relative density"; and for water, "liquid."

$$\text{Sp. gr.} = \frac{\text{Weight of the sample}}{(\text{wt. of sample} + \text{wt. of pyc. full of water}) - \text{wt. of pyc. filled with sample and water}}.$$

This is reduced to density, g./cm.^{3}, by multiplying by the weight of 1 cm.^{3} of water at the temperature of observation. At 16° = 0.999_0, at 21° = 0.998_0, at 25° - 0.997_1, at 29° 0.996_0.

Density, g./cm.,[3] was determined on small quantities of clear quartz: on 0.0325_8 g. $= 2.649_8$; on 0.0223_0 g. $= 2.649_1$. For a milky quartz the value was 2.633.

The only weights not compensated here are of (1) the crystals (numerator) and (2) water displaced (denominator).

The volume found with single weighings of water for a pycnometer of 0.6 mm. bore was 0.0332_6 at 26.5°, and 0.0332_0 at 27.7°. The calculated difference is 0.00001. The determination of the moment at which the pycnometer was full was decidedly more accurate than the weighings. There appears to be no advantage in using a small-bore pycnometer, which is difficult to fill, unless a microbalance is used with it.

The change of density over this range per 1° C. for toluene[2] is 0.0009; methylene iodide,[3] 0.0027; 1,1,2,2-tetrabromoethane,[4] 0.0022; for bromoform,[1a] 0.0021.

Slowly volatile liquids can be brought to the level of the surface of the pycnometer by a change of temperature or by transferring liquid by means of a small bristle. Liquids that creep are not suitable for accurate density determination by this method, but the capillary may be almost filled and the temperature raised, or a droplet added by means of a bristle.

The following technique in filling a pycnometer in both micro- and macro-pycnometric methods has been found quite simple and practical. The pycnometer containing the sample[5] is suspended in a desiccator and first evacuated. The desiccator is provided with a separatory funnel containing the displacement liquid. The end of the funnel is a finely drawn capillary and projects into the pycnometer a short distance above the sample.

By means of the stopcock in the funnel, the vacuum in the desiccator is gradually lowered to that of the vapor pressure of the liquid. This enables particles freed from adsorbed air to be first thoroughly wetted by the liquid. By careful manipulation in lowering the pressure in the desiccator, enough liquid is admitted to cover the sample entirely.

In other cases this technique, which assures reproducibility, can be used to eliminate the various errors in the measurement of a liquid in a capillary.

[2] Computed from unpublished measurements by John S. Burlew.

[3] Timmermans, J., et Mme. Hennaut-Roland, *Jour. chim. phys.*, **29**, 529 (1932).

[4] Walden, P., and Swinne, R., *Zeits. phys. Chem.*, **82**, 281 (1913).

[5] Whenever possible each individual grain of the sample should be first positively identified as such by at least one of its physical characteristics. Handling the individual particles or minute crystals with tweezers with fine points of celluloid, or a medicine dropper with an extremely fine and flexible drawn end, moistened with the displacement liquid, was found very convenient.