A NEW MICROPYCNOMETER FOR THE DETERMINATION OF DENSITIES OF HEAVY SOLIDS

Horace Winchell, *Harvard University, Cambridge, Mass.*

Abstract

A constant volume quartz-glass pycnometer is described which has been found experimentally capable of giving results with a probable error of about 1.0%, using .03 to .04 cc. of material with a specific gravity of 4.0 to 7.5, and weighing on an ordinary chemical balance accurate to 0.0001 gram.

Introduction

Various micropycnometric methods have been described in the literature (Bannister, 1938; Syromyatnikov, 1935; Hauptmann, 1934; Retgers, 1899). The present method utilized a pycnometer about the size of that used by Retgers (1899), who employed benzol as the displacement fluid and closed his pycnometer by means of a glass plate covering the opening. Wulff and Heigl (1931) have used toluene as the displacement fluid. Syromyatnikov (1935) described a micropycnometer similar to that of Retgers. Bannister (1938) analyzed the systematic errors of the pycnometric method and concluded that Syromyatnikov's method is not as accurate as claimed because the error, due to temperature uncertainty, is probably large. While temperature errors are often serious in larger pycnometers, in the micropycnometer of this type they are small compared with certain other errors, as will be shown later.

One of the difficulties in the application of methods like that of Bannister (1938) is the requirement that weighings be made on a microbalance. Such an instrument is not often easily available. Bannister used a centrifuge to wet the sample and to remove air bubbles. This method does not seem to give as consistent results with the pycnometer here described as the method of boiling under reduced pressure.

Micropycnometer

Figure 1 is a vertical section of a small-volume quartz-glass pycnometer made for the writer by the Macalaster Bicknell Company of Cambridge, Mass. The volume of the instrument is 0.1319 cc., as measured with the liquid meniscus opposite a scratch on the capillary tube; this scratch should, of course, completely circle the tube to allow the elimination of parallax errors (Ellsworth, 1928). A volume of 0.1 cc. is probably near the optimum for the smallest quantities of material consistent with the specified accuracy.

Experience of this investigation shows that the smallest internal diameter large enough to permit escape of bubbles when boiling under reduced pressure is 3.0 mm., as indicated in the figure. Toluene is used as the displacement fluid because its low surface tension facilitates the escape of bubbles.
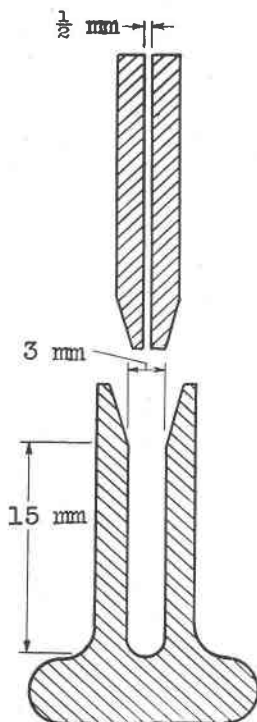

FIG. 1. Quartz-Glass Micropycnometer

PROCEDURE

The procedure adopted for use with this instrument is described below. One determination requires about an hour for an experienced operator.

1. Carefully selected material is powdered fine enough to pass a 1 mm. mesh; the very fine powder (about 130 mesh and smaller) is removed unless only a very small amount of material is available.

2. The weight of the clean, dry pycnometer is recorded in a form like that shown in Table 1; this is W_1.

3. The weight of the pycnometer, $\frac{1}{2}$ to $\frac{2}{3}$ full of the prepared sample, is recorded as W_2. $W_2 - W_1$ is the weight of the sample.

4. Toluene of known density (previously calibrated in a large Ellsworth-type pycnometer) is introduced, filling the pycnometer almost full. The contents are stirred with a capillary glass rod, removing most of the bubbles, and piling the grains along one side of the pycnometer tube, which is placed in a slanting position under a bell jar. The pressure is reduced until the liquid boils. Stirring and boiling may be repeated several times.

5. While the instrument is returning to room temperature after the boiling treatment, additional toluene is added, filling it to the top; the stopper is inserted, filling the capillary opening and forcing liquid out through it. Excess toluene is removed with filter paper. The weight, W_3, is determined at the instant when the evaporation has brought the meniscus down opposite the scratch on the outside of the capillary. Several trials are usually necessary for this operation; the pycnometer must be refilled with toluene for each trial.

6. The temperature in the balance case is recorded opposite t.

7. The pycnometer is washed in acetone, dried by blowing out with compressed air, and weighed again. Its contents can be washed on a filter paper, dried, and later used as desired.

CALCULATION OF SPECIFIC GRAVITY

The data necessary for calculating the specific gravity of the powder are now at hand. The specific gravity of the toluene may be calculated from $s = a - bt$, where s = specific gravity of the toluene, a = specific gravity at 0°, b = the density coefficient, and t = the observed temperature. The constants a and b should be determined for each new lot of toluene; a is, in general, near 0.8810, b near 0.0010.

The formula for calculating the specific gravity of the powder can be expressed by

$$S = \frac{s(W_2 - W_1)}{W_2 + sv - W_3}$$

where S = specific gravity of the powder (unknown)

      s = specific gravity of the toluene = $a - bt$ as already defined

   W_1 = weight of the pycnometer, empty

   W_2 = weight of the pycnometer with powder

   W_3 = weight of the pycnometer with powder and liquid

    v = volume of the pycnometer; previously determined using water or bromoform

The form shown in Table 1 facilitates making orderly calculations to which future reference can be made.

TABLE 1. FORM FOR CALCULATION OF DENSITY

Sphalerite, Santander			
W_2	5.9814	$sv+W_2$	6.0944
W_1	5.8272	W_3	6.0622
W_2-W_1	0.1542	$sv+W_2-W_3=D$	0.0322
t	24.5°C.	$\log(W_2-W_1)$	9.1881–10
s	0.8566	$\log s$	9.9328–10
sv	0.1130	$\text{colog } D$	1.4921
W_2	5.9814	$\log S$	0.6130
		S	4.1020

ACCURACY OF THE METHOD

Differentiating the equation and dividing by S, the relative error in the results may be obtained. This can be simplified to the following inequality:

$$\frac{dS}{S} < \frac{dW_1}{W_2-W_1} + \frac{dW_2+dW_3}{W_2+sv-W_3} + \frac{(W_2-W_1)ds}{(W_2+sv-W_3)s}$$

Assuming $dW=.0001$ gram, and $ds=.0002$,[1] we can evaluate the right side of the inequality for any trial. Using the example in Table 1 we find the first term is .00065, the second, .00621, and the third, .00059.

TABLE 2. TRIAL DENSITY DATA

	1* Pyrite	2 Sphalerite, Santander	3 Galena, Joplin
Number of trials	4	6	7
Highest specific gravity	5.11	4.16	7.69
Lowest specific gravity	4.23	3.95	7.60
Average specific gravity	4.60	4.09	7.64
Probable error of average	0.30	0.02	0.01
Probable error of 1 trial	0.60	0.05	0.02
Probable error of 1 trial	13.04%	1.22%	0.26%
Calculated maximum error (see text)	1.25%	0.71%	0.70%
Average weight of sample	0.1128 g.	0.1545 g.	0.2852 g.
Calculated specific gravity (x-ray data)	4.99	4.08	7.57

* Column 1 states results obtained using the method of centrifuging to remove air bubbles. Columns 2 and 3 state results using the method of boiling under reduced pressure, without the use of the centrifuge.

[1] As already stated, $s=a-bt$; therefore $ds=\pm bdt$. Hence, if the temperature is correct to 0.2°, $ds=.0002$.

The sum of these is .00745, of which the part due to temperature uncertainty is .00059, or less than .1 of the whole uncertainty. Even with a temperature uncertainty of .5°, this term is .00118 in a total of .00804.

It should be noted that the second term of this inequality contains the weight of the liquid in the pycnometer as part of the numerator, and the weight of liquid displaced by the powder as the denominator. This explains the advantage of using a micropycnometer nearly full of powder rather than a macropycnometer containing the same amount of powder in a relatively much larger container.

The above evaluation of the "maximum" error does not take account of air bubbles trapped in the powdered material by the liquid. To evaluate this added uncertainty, a series of trials on pyrite, sphalerite, and galena gave results indicated in Table 2. The data for pyrite were obtained using a centrifuge for the elimination of air bubbles from the pycnometer. The data for sphalerite and galena were obtained using the procedure outlined above.

For pyrite the probable error determined experimentally[2] is many times that calculated as a maximum for the conditions of the experiment, but for sphalerite and galena the probable error is very near that maximum (see Table 2). Therefore, the air bubbles were probably more successfully eliminated in the sphalerite and galena trials than in the pyrite trials. The consistency of the results is a recommendation for the procedure by which these results were obtained. Experiments using a more accurate balance might show a corresponding increase in accuracy; at present a probable error of 1% is assigned to any single random determination, or a correspondingly smaller probable error to the average of several such determinations.

[2] If n observations of a quantity are represented by $x_1, x_2, \cdots, x_n$, and their mean by $\bar{x}$, and their respective deviations from $\bar{x}$ by d_i, then the probable error of any individual determination is

$$0.6745 \sqrt{\frac{\sum d_i^2}{n-1}}$$

and the probable error of the mean, $\bar{x}$, is

$$0.6745 \sqrt{\frac{\sum d_i^2}{n(n-1)}}.$$

Charles Palache, made possible the pursuit of these experiments. Professor Palache's interest and encouragement greatly augmented the writer's patience during the early experiments on the design of the pycnometer.

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