A new micro-pyknometric method for the specific gravity of heavy solids; with a note on the accuracy of specific gravity determinations.

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THE determination of the specific gravity of a solid which is only available in small quantity has always been a difficult problem in cases where the suspension method fails, either because the solid is too dense, or because it dissolves in or reacts with the heavy liquids available. It is hoped that the following method will be found a useful addition to the numerous methods which have been proposed from time to time to meet such cases. References to most of these methods are given at the end of the paper. Neither the new method nor any one of the older ones is universally applicable, and the best method for any particular case will depend on many circumstances.

In the new method, a straight capillary tube of silica-glass, 9 cm. in length, 0·5 mm. in bore, and with walls 0·75 mm. thick, closed at one end and as perfectly cylindrical as possible[1] serves as the pyknometer. This is calibrated by determining the weight of bromoform it holds when filled (by the aid of a fine glass capillary tube and a centrifuge) to several different heights; the length of the column of liquid at each filling is determined after weighing, the tube being placed in a beaker of water at room-temperature along with a delicate thermometer for a few minutes to attain a known temperature and then measured with a travelling microscope. The weighings are made on the micro-balance; the pyknometer is never more than half filled with bromoform, when evaporation errors have been shown to be negligible. From these calibration data and the expansion coefficient of bromoform, the weight of bromoform held by the tube at any given temperature and height of filling may be calculated.

[1] In the tubes now in use, the weight of bromoform per 1 cm. of tube does not vary by more than about 0·2 % from part to part of the tube.

The expansion coefficient of bromoform does not appear to have been determined hitherto. A figure of sufficient accuracy for our purpose was obtained by determining the specific gravity of a sample of bromoform at two temperatures, using the silica-glass pyknometer designed by H. V. Ellsworth (1928). From the results, $d_{20\cdot8}^{20\cdot8} = 2\cdot8670$ and $d_{20\cdot8}^{32\cdot4} = 2\cdot8425$ (both not corrected to vacuum), the apparent coefficient of thermal expansion of bromoform in silica-glass is found to be 0·00074 per 1° C.

The use of the calibrated pyknometer in a specific gravity determination closely follows the usual macro-method. The solid, preferably in as coarse (but non-porous) fragments as will enter the tube, is weighed into the pyknometer. This operation is greatly facilitated by the use of a small filling device turned out of 'perspex' resin in the form of a funnel with its apical aperture about 0·3 mm. in diameter and a support for the pyknometer tube.

If the material is in the form of large smooth crystal fragments, it will often be satisfactory to fill with bromoform, using the glass capillary and centrifuge, and then evacuate to remove residual air bubbles (satisfactory results were so obtained with galena); but with a fine powder any attempt at evacuation after addition of the bromoform has always led to ejection of some of the solid. It is therefore necessary when fine powder is used to support the pyknometer in a wide tube which can be evacuated, and introduce the bromoform after thorough evacuation through a capillary tube projecting a short way into the mouth of the pyknometer, while maintaining the vacuum. In either case, the bromoform column should preferably not extend more than 5 mm. beyond the solid.

The pyknometer plus solid is weighed and the length of the bromoform (plus solid) column measured as in the calibration, after bringing to a known temperature. All the data for the calculation of the specific gravity are now available except the specific gravity of the bromoform. This must be determined in the usual way at fairly frequent intervals, as it varies for different samples and for the same sample after exposure to light and air.

The accuracy of the determinations has been found to be reasonably good. As in all other methods of specific gravity determination in which a liquid displacement medium is used, the presence of air bubbles is often one of the most important sources of error. This error may reach several per cent., and it is difficult to suppress entirely; probably most determinations, by this or other methods, suffer to the extent of at least

0·1 %, the values being always low. It is usual in macro-pyknometric determinations to accept the highest value found as the most accurate for this reason, and the same procedure must be followed when the micro-pyknometer is used.

While this source of error, as well as those due to inclusions in the material and the adsorption of air or vapours on the surface of the pyknometer or the material, must be accounted as of unknown magnitude, there are several sources of error, the probable magnitude of which can be approximately calculated.

If the balance weighs to $\pm\delta W$ grams, the effective volume V c.c. of the pyknometer is reproducible to $\pm\delta V$ c.c., and the temperature can be determined to $\pm\delta t°$ C., the probable percentage error introduced by these uncertainties into the determination of the specific gravity S of W grams of a solid, using a displacement liquid of specific gravity σ and coefficient of expansion α is approximately $\pm 100\delta S/S = \pm(\delta W/S + 2\delta W/\sigma + \delta V + \alpha V\delta t)200S/W\%$.

For the new method, assuming an accuracy of weighing $\delta W = 0{\cdot}002$ mg., of temperature 0·1° C., and of measurement of the bromoform column 0·002 cm., the error using 15 mg. of material of specific gravity 4 and with the bromoform meniscus 4 cm. from the closed end of a pyknometer tube holding 7·5 mg. of bromoform per cm. will be $\pm(0{\cdot}03 + 0{\cdot}07 + 0{\cdot}27 + 0{\cdot}04) = \pm 0{\cdot}4$ %. Allowing for the errors of unknown magnitude, an accuracy of 0·5 % should be and is attainable with 5 to 15 mg. of material. It may be noted that the greatest single error in this case is due to errors of measurement of the length of the bromoform column, and is independent of the displacement liquid used.

These figures may be compared with the accuracy attainable in other methods of specific gravity determination. F. V. Syromyatnikov (1935) claims an accuracy of 0·3 % for his micro-pyknometer method, using 40 mg. of a solid of specific gravity 4, and working with an ordinary balance, and a much greater accuracy with a micro-balance. This figure, however, takes account only of the errors of weighing. The volume error of his pyknometer is uncertain, while the temperature error, also uncertain, must be very large since there is no proper control or measurement of the temperature. It is probable that about ± 1 % is a more accurate estimate of the accuracy of this method; the use of a micro-balance would not assist much, since the largest single error is certainly the temperature error.

In one of the most accurate forms of the macro-pyknometric method, that of H. V. Ellsworth (1928), the attainable accuracy, calculated from

the above formula, using the exceptionally large amount of 12 grams of a solid of specific gravity 4 and bromoform as displacement liquid, taking the volume of the pyknometer as 8 c.c. and the individual errors $\delta W = 0{\cdot}1$ mg., $\delta V = 0{\cdot}2$ c.mm., $\delta t = 0{\cdot}1°$ C., is $\pm(0{\cdot}002+0{\cdot}005+0{\cdot}013+0{\cdot}039) = \pm 0{\cdot}06\%$, the greatest single error being due to the temperature effect. In this case, the error due to air bubbles, of unknown magnitude but probably not less than 0·1%, is much more serious than the errors of known magnitude, but when less material is available, the latter may become important. It may be noted that, contrary to a common assumption, there is no advantage gained by using a dense displacement liquid; the liquid chosen should have a low surface tension, low expansion coefficient, and low volatility, but its density is almost immaterial.

The micro-volumenometer of H. Hauptmann and G. E. R. Schulze (1934), using a gas as displacement fluid, is claimed to have an accuracy of about 1 % for volumes down to 0·01 c.c. This is inadequate for general use, but should prove valuable for highly reactive solids.

The accuracy attainable in a specific gravity determination by the method of hydrostatic weighing is difficult to assess; with suitably large specimens it can be very accurate, probably $\pm 0{\cdot}1$ % or even better. The greatest source of error is usually the surface tension effect, reducing the accuracy of the weighings. The method has been applied on a semi-micro scale by P. Wulff and A. Heigl (1931), who claim an accuracy of 0·1 % with suitable material in portions of 0·5 gram; it would hardly be suitable for much smaller amounts of material.

The attainable accuracy in the suspension method is often higher than in the pyknometric, if the observer has sufficient patience in adjusting the specific gravities of solid and liquid, the density of the liquid is determined with a good pyknometer, and the temperatures are measured with adequate accuracy. With the Ellsworth pyknometer the specific gravity of the liquid may be measured to an accuracy of about $\pm 0{\cdot}0003$, and if the temperature of comparison of liquid and solid is measured to 0·1° C. and a correction made for temperature changes, an accuracy of $\pm 0{\cdot}003$ may be attained for solids for which a suitable suspension liquid can be found.

Where the use of a float is necessary the accuracy is reduced. If a solid fragment of specific gravity S and weight W, combined with a float of specific gravity s and weight F remains suspended in a liquid of specific gravity σ, $S = \sigma+(\sigma - s)F/W$. If both σ and s can be determined with an accuracy of $\pm 0{\cdot}003$, and if s is about 2·3 while σ is near

3·3, the error due to the determination of s and σ is $\pm 0{\cdot}003(1 + 2F/W) = \pm 0{\cdot}003\{1+2(S-\sigma)/(\sigma - s)\}$, which for a solid of specific gravity 4·3 is 0·009 or 0·2 %, and for one of specific gravity 7·3 is 0·027 or 0·4 %. If the float and the solid fragment can be weighed on the micro-balance, this accuracy should be approachable, though the method is by no means simple; but if only an ordinary balance is available a further error is introduced due to inaccuracies in the determination of F and W. The attainable accuracy in the suspension method, using a float and the micro-balance, should thus approach that of the new micro-pyknometric method, but the latter is probably the more convenient in practice.

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