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# Review

# The precise measurement of the density of small samples

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The techniques available for measuring the density of small samples (of the order of 10 mg) are reviewed, with special emphasis on those offering high precision (± 0.1% or better). The relative merits of the techniques are examined, sources of error explained and an attempt made to establish a figure of merit.

## 1. Introduction

Density measurements come in three varieties: (1) the ultraprecise measurement of the density of large objects, weighing as much as several kilograms; this is the province of standards laboratories; (2) the approximate measurement (± 1% approximately) of the density of tiny objects, often minute crystals, weighing a small fraction of a milligram, used in the course of crystal structure determination; (3) the precise measurement of the density of small samples (say 1 to 100 mg); this is often done by materials scientists interested in *changes* in density caused by heat-treatments. The interest here lies primarily in sensitivity to small changes, more than in very precise measurement of absolute values. Examples of this third category include examination of radiation effects (where high radioactivity enforces the use of small samples [1] and of the study of the relaxation of metallic glasses [2–4] (where the limitations of physical form restricts the mass of samples). To date, no survey has critically reviewed the problems encountered in this kind of measurement, although Muller's [5] survey has touched on them. This review has been prepared to fill this gap.

## 2. Definitions

Before comparing techniques it is important to define the reference terms used in the comparison. The *sensitivity* is the smallest unit which may be measured, i.e. the limits inherent to the apparatus. The *precision* refers to the reproducibility of a measured value and is often defined as the standard deviation of a single independent determination from the mean of several such determinations. This is usually expressed as a percentage of the density of the specimen. *Accuracy* is the absolute correctness of a measured value with respect to some standard and is therefore more difficult to attain than precision of the same degree. Precision is the parameter most commonly used to define the capacity of a technique in this field.

When comparing the precisions of the various techniques listed it is important to remember that the precision is dependent upon the size of the specimen, the density of the specimen and the number of measurements taken of one particular specimen. Some authors have not stated how precisions were evaluated and therefore the figures quoted should not be taken too literally but instead used as a guide to the value of a technique.

Ultra-high precision may be obtained with little difficulty if large specimens are available; however, if we are limited to using small specimens ($\ll 1\,\text{cm}^3$) then greater sophistication and/or ingenuity is required.

## 3. General precautions

All the techniques reviewed involve immersion of the specimen in a liquid at some stage. Consequently there are two sources of error common to all the techniques. The adherence of air bubbles to

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the surface of the immersed specimen causes an artificial increase in volume and buoyancy. This is amplified in the case of metallic glass foils where the surface area is large with respect to the volume. Immersion liquids should be chosen with low surface tensions (good wetting properties) and low vapour pressures. It is a good idea to distil the liquid before use.

The other common problem is temperature fluctuation. Changes in temperature affect the density measurement because of the different thermal expansion coefficients of the specimen, the immersion liquid and air. Temperature must therefore be carefully controlled or monitored. Corrections can then be made for fluctuations.

## 4. Methods

### 4.1. Displacement methods

In this method the mass of a specimen is measured by simple weighing; the volume is then determined separately by displacement of a liquid. In the simplest form, the rise in the meniscus is noted when a sample is immersed in a half-filled measuring cylinder. Le Chatelier and Bogitch [6] used a 5 mm internal diameter glass cylinder to obtain a precision of ± 0.1% with approximately 2 $cm^3$ of solid. Caley (1930) [7] adapted the system for smaller specimens using 2 mm diameter tubing. A precision of ± 3% was obtained using 30 to 100 mg specimens. More recently, Muller [8] has developed the system by replacing the measuring cylinder with a precision-bore 1 mm diameter glass U-tube. The tube was mounted vertically on a vertical rotating microscope stage with the eyepiece cross-wires focussed on the liquid meniscus. The specimen was then immersed and the angle of tilt necessary to restore the meniscus to its original position on the cross-wires was noted. The precision lay between ± 0.5% and ± 1.0% for 2 to 30 mg specimens. This is the best precision obtained from a displacement technique. The main sources of error specific to the technique are non-uniformity of the bore of the glass tube, evaporation loss of liquid and non-reproducibility of meniscus shape.

A novel method of calibration designed by Blank [9] overcame the bore non-uniformity problem. The displacement vessel was fitted with a capillary side arm which had an upper and lower marker. The apparatus was filled with liquid until the meniscus coincided with the lower marker. Immersion of the specimen caused the meniscus to rise. More liquid was then added from a weight micro-burette until the meniscus coincided with the upper marker. Because the weight of liquid needed to top up the system, the weight of the liquid needed to fill the space between the two markers and the density of the liquid were known, the volume of the specimen could be calculated. Blank obtained precisions similar to Caley's.

Dilatometer attachments which use the displacement principle to measure *in situ* volume changes are now commercially available. The specimen is placed in a cylinder containing an incompressible liquid and a syringe fit piston [10]. Expansion of the specimen pushes the piston via the liquid hence converting a volumetric expansion to a linear displacement which can be monitored by the dilatometer. Precisions obtainable will depend on the specimen size and the precision of the dilatometer.

### 4.2. Pycnometry

Pycnometry is based on the use of commercially available specific gravity bottles (pycnometers). The mass of the specimen is determined by weighing, and its volume is obtained by weighing the liquid displaced from the pycnometer by the specimen.

Four weighings are performed,

$W_1$ = Weight of empty pycnometer,
$W_2$ = Weight of pycnometer + specimen,
$W_3$ = Weight of pycnometer + specimen + liquid
$W_4$ = Weight of pycnometer filled with liquid.

The density of the specimen is then given by

$$\rho_{\text{spec}} = \rho_{\text{liq}} \frac{(W_2 - W_1)}{(W_4 - W_1) - (W_3 - W_2)}. \quad (1)$$

As with the displacement technique, the precision is dependent on the size of the sample. Various authors [11, 12] have adapted the technique to microscale and achieved precisions of ~ ± 0.5% to ± 1.0% for 5 to 100 mg specimens. $W_3$ and $W_4$ weighings can be made to greater precision if the immersion liquid is dense. For this reason Muccigrosso *et al.* [12] used mercury as the immersion liquid in a micropycnometer. By performing 24 determinations on alumina particles (~ 0.01 $cm^3$) a density of 3.481 $g\,cm^{-3}$ and a precision of ± 0.7% was obtained. However, the corrosive nature of mercury will limit the use of this technique.

The major sources of errors in the pycnometer technique are evaporation, loss of liquid and imperfect reproducible filling of the pycnometer. Temperature fluctuations are also important but may be monitored and corrected for.

## 4.3. Comparison with heavy liquids

This technique is one of the most precise available for small specimens as its precision is independent of specimen size. The principle is based upon bringing the specimen into hydrostatic balance with a heavy liquid. The density of the liquid which equals the density of the specimen is then estimated by another technique. The density of bulk liquids can be determined to great accuracy using pycnometry, refractive index measurements or magnetic suspension techniques. In the magnetic suspension technique, a piece of ferrite is magnetically suspended in the liquid: from the strength of the magnetic field and the density of the ferrite the density of the liquid can be determined [13].

Comparison techniques can be subdivided into two categories. In the first, the specimen is immersed in a pure liquid of known density. Depending on whether the specimen floats or sinks, a less dense or more dense miscible liquid is added to bring the specimen into hydrostatic balance with the mixture. The density of the mixture is then determined as described above. Precisions of ± 0.02% have been obtained by this technique since 1931 [14]. More recently, workers have modified the technique, making the final adjustments to the density of the liquid by temperature control [15]. In order to speed up mixing and specimen movement, centrifuging may be used.

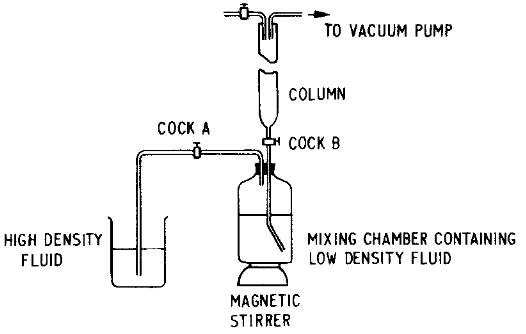


*Figure 1* Mixture density column preparation technique, after Jones [16].

In the second category, a density gradient column is set up. The density of the liquid in the column increases uniformly from top to bottom. When the specimen is immersed in the column it will float at a position where the density of the liquid equals its own. The sensitivity of the technique depends on the gradient of the column, i.e. the difference in density between top and bottom and the length of the column.

Setting up a density gradient column is a difficult procedure. Two approaches have been adopted. The first involves the controlled mixing of two miscible liquids whose densities equal the desired limits for the column. The alternative is to set up a thermal gradient in a homogeneous liquid. Mixture columns are usually set up by allowing the two liquids to diffuse into each other. This is generally a slow process. However, Jones [16] has described a mixing technique by which a column can be set up in 10 min; the apparatus is shown in Fig. 1. When stopcock B is open, liquid is drawn into the column from the mixing chamber; the reduced pressure in the chamber

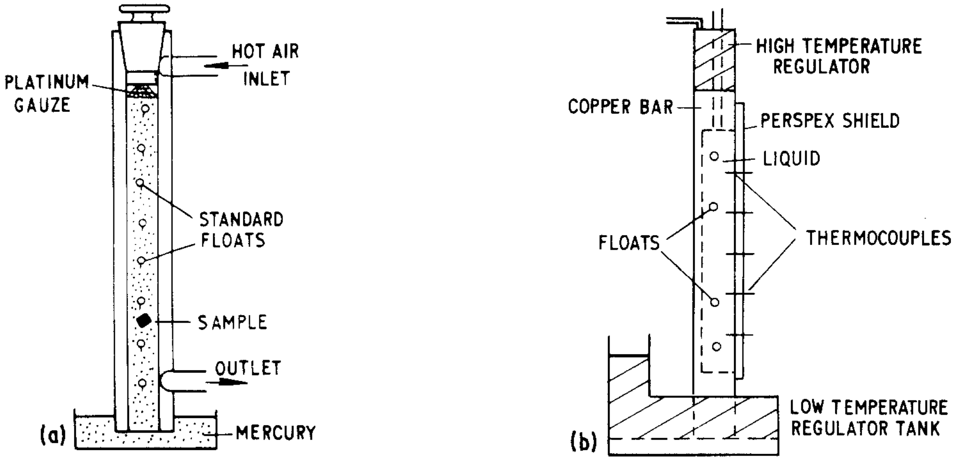
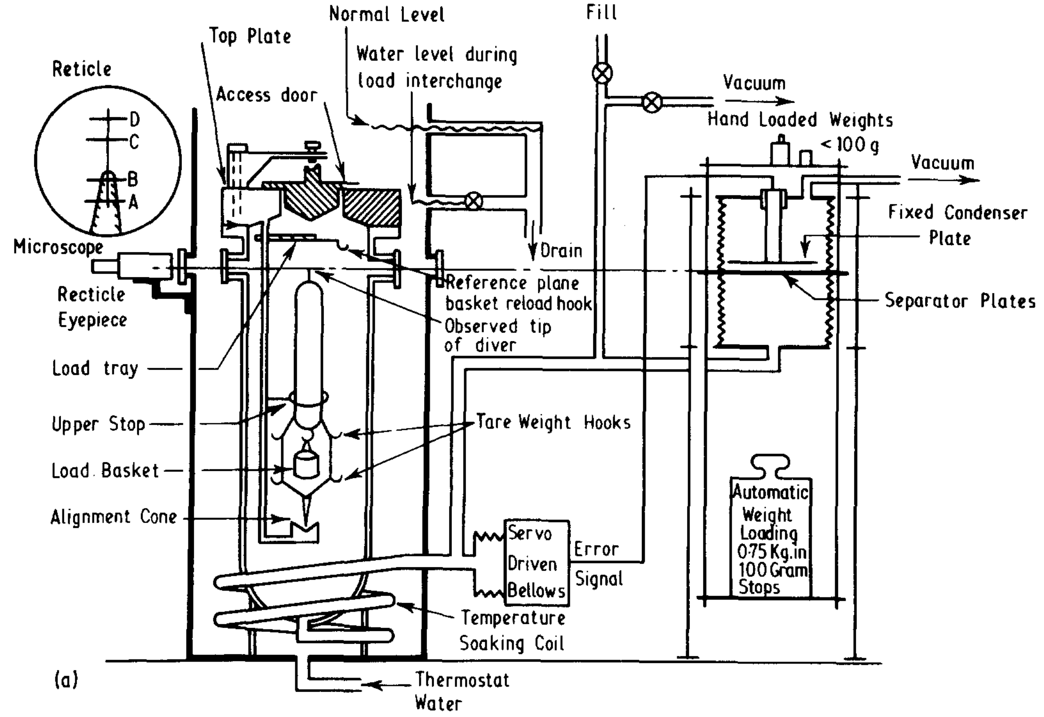


*Figure 2* Thermal gradient density columns, after (a) Moret [17] and (b) Pelsmaeker and Amelinckx [18].



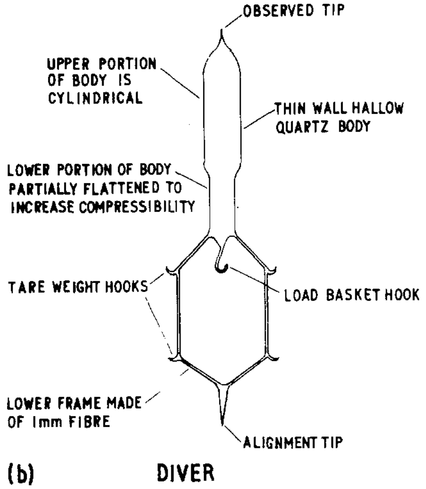


*Figure 3* Cartesian diver device of Bowman and Schoonover [20]. The apparatus consists of a Cartesian diver in a pressure controlled tank.

then causes the high density fluid to flow in via stopcock A, gradually increasing the density of the liquid in the chamber. Density gradients of less than 0.001 g $\mathrm{cm}^{-3}$ per cm have been established using this technique in a 5 cm diameter, 1 metre long column. Thermal gradient columns have been set up in a variety of ways. Moret [17] has used a flow of hot air down an outer jacket (Fig. 2a), while other workers [18] lagged the column in a heavy copper jacket and placed temperature regulators top and bottom (Fig. 2b).

Calibration of both types of column may be carried out in a variety of ways. The simplest is to use a series of calibrated floats; readings between the markers may be calculated by interpolation. Jones [19] has developed a novel approach which uses a hollow glass prism as the column container. The density of the liquid at any given level is calculated from its refractive index, which is measured by the method of minimum deviation. Refractive index generally scales linearly with density.

Comparison with heavy liquids is therefore a very powerful tool for determining the density of small samples. Precisions of up to ± 0.002% have been achieved using density columns. However, a major problem arises when specimens are denser than 4 g $\mathrm{cm}^{-3}$, in that it is impossible to find suitable miscible and transparent immersion liquids. Therefore, the technique is of little use for metallic specimens. It may be possible to set up a thermal gradient column using mercury; even then it would be difficult to find the stable position of the specimen, except perhaps by X-ray analysis, $\gamma$-ray radiography or ultrasonics. The technique would be limited to those materials which do not react with mercury.

## 4.4. Other flotation methods

The necessity of using a dense weighing liquid to achieve hydrostatic balance with the specimen may be overcome if the specimen is attached to a suitably buoyant float. Two novel techniques have been based on this principle.

Bowman and Schoonover [20] have described an ultra-precise technique based on the Cartesian diver principle. Their apparatus is shown in Fig. 3. The immersion liquid was water, thermostatically held at 4° C. This temperature was chosen to provide minimum convection currents and maximum mechanical damping. The fused quartz diver (Fig. 3b) had a positive buoyancy of about 5 g. The specimen plus tare weights bring the system into hydrostatic balance with the liquid. The principle of the technique is simple. Where a hollow compressible body such as the diver is immersed in a liquid and the pressure in the liquid is increased, the buoyancy of the body will decrease or increase, respectively, depending on whether the compressibility of the diver is greater or less than that of the liquid. From the applied pressure required to maintain a stationary diver position or constant diver velocity it is possible to calculate the weight of the specimen in the liquid. Bowman and Schoonover [20] calibrated the system against two standard samples. If the weight of the specimen in liquid and the density of the liquid is known and the mass of the specimen is determined by weighing, then the density can be calculated by Archimedes' principle. The system is ideal for measuring changes in density; calibration is then unnecessary. Bowman and Schoonover give details of the pressure-controlling apparatus and the necessary calculations. A precision of ± 0.000 02% was reported for a series of density determinations on a 2 g silicon crystal and a 0.005% change in density was easily monitored when a 250 mg ceramic crystal underwent a structural change.

Franklin and Spal [21] have described another technique innovated by Bowman and Schoonover which, although less precise than the Cartesian diver, is easier to set up. The apparatus is shown in Fig. 4. Two immiscible liquids of differing density are contained in a cylinder. A thin wire is attached to a float in the upper liquid and reaches down into the lower liquid. A hook at the bottom of the wire holds a pan which contains the specimen and tare weights. The float is made sufficiently buoyant in the upper liquid so that by itself it would float. The wire, pan, tare weights and specimen are denser than the lower liquid and therefore exert a downward force. This force diminishes as the wire passes from the less dense upper liquid into the lower liquid, i.e. when the float descends.

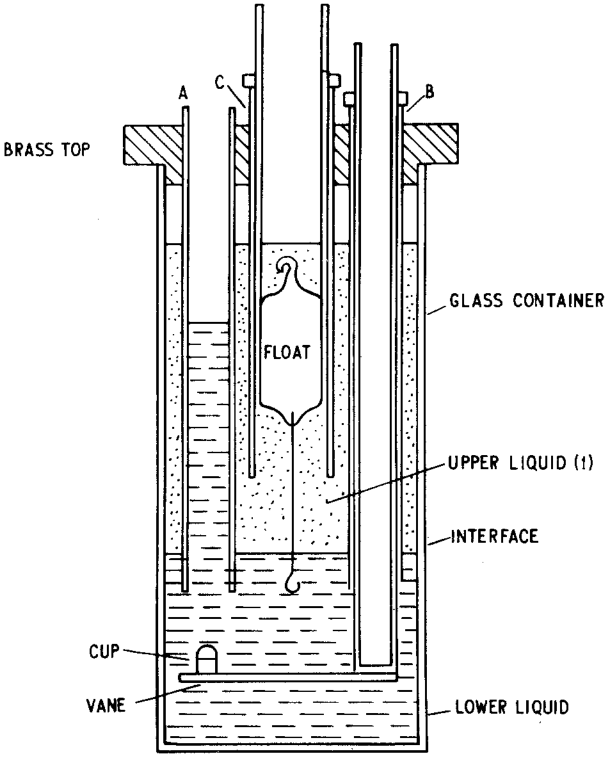


*Figure 4* Franklin and Spal [21] float apparatus.

With a suitable choice of tare weights it is possible to achieve a stable equilibrium position. If the experiment is repeated using a standard of known density, the difference between the specimen's and standard's equilibrium positions reflects the difference in upthrust experienced by them. When their masses are determined by weighing, the density of the specimen relative to the standard may be calculated using Archimedes' principle. Franklin and Spal [21] have described the necessary experimental procedures and calculations. A precision of ± 0.03% was achieved using 40 mg specimens. This technique has a source of error not present in the Cartesian diver technique, that is, the surface tension forces on the suspension wire at the liquid–liquid interface.

Both techniques are comparison methods, i.e. the density of the specimen is compared with a standard. If the standard has a well defined density, the absolute density of the specimen may be calculated. Both techniques are ideal for measuring relative changes, in which case calibration is unnecessary. The complexity of the pressure controlling system in the Cartesian diver method will limit the technique's use.

## 4.5. Hydrostatic weighing

### *4.5.1. Theory*

Hydrostatic weighing is the best known density measuring technique. In this method, the apparent weight $\bar{W}$ of a specimen is measured in two different media, e.g. air and liquid. The apparent weight of the specimen in each case is given by

$$\bar{W}_{\mathrm{air}} = g(M_{\mathrm{x}} - \rho_{\mathrm{air}} V_{\mathrm{x}}) \qquad (2)$$

$$\bar{W}_{\mathrm{liq}} = g(M_{\mathrm{x}} - \rho_{\mathrm{liq}} V_{\mathrm{x}}) \qquad (3)$$

where $g$ is the acceleration due to gravity, $\rho_{\mathrm{air}}$ is the density of air, $\rho_{\mathrm{liq}}$ is the density of the weighing liquid and $M_{\mathrm{x}}$ and $V_{\mathrm{x}}$ are the true mass and volume of the specimen, respectively. A simultaneous solution of Equations 2 and 3 may be used to calculate the density of the specimen, $\rho_{\mathrm{x}}$.

$$\rho_{\mathrm{x}} = \frac{\bar{W}_{\mathrm{air}}\rho_{\mathrm{liq}} - \bar{W}_{\mathrm{liq}}\rho_{\mathrm{air}}}{\bar{W}_{\mathrm{air}} - \bar{W}_{\mathrm{liq}}}. \qquad (4)$$

If the specimen is small, $\bar{W}_{\mathrm{liq}}\rho_{\mathrm{air}}$ will become very small and negligible compared with errors in the determination. In this case

$$\rho_{\mathrm{x}} = \frac{W_{\mathrm{air}}\rho_{\mathrm{liq}}}{(\bar{W}_{\mathrm{air}} - \bar{W}_{\mathrm{liq}})}. \qquad (5)$$

Weighing in air is a simple procedure; however, weighing in liquid is more complex.

Bowman and Schoonover [22] have outlined the major factors influencing the precision of hydrostatic weighing. For relatively large specimens (more than 1 g) the major factors are non-reproducibility of surface tension forces associated

TABLE I* Some important properties and characteristics of cantilever, spring and beam microbalances

| Considerations | Balance type | | | |
|---|---|---|---|---|
| | Cantilever | Spring | Beam, knife edge | Beam, torsional |
| Response to small change in mass | Bending of a beam | Stretching of a spring | Rotation of beam at primary fulcrum | Rotation of beam at primary fulcrum |
| Capacity | 10 to 0.1 mg | Variable depending on helix size; 0.01 to 10 g, but see LPR | 200 g | 5 g |
| Approximate minimum mass resolution | 10 to 100 ng | 100 ng | 500 ng | 1 ng |
| Range of load to precision ratio (LPR) | $10^3$ to $10^5$ | $10^4$ to $10^6$ | $10^8$ or less | $2 \times 10^8$ or less |
| Typical operation: | | | | |
| Manual | Optical lever | Optical lever for vertical displacement | Riders in a bell jar | Moving coil ammeter |
| Usual calibration method | Standard weights | Standard weights | Standard weights | Standard weights |
| Range | Variable; limited to beam deflection; typically 1 to 10 mg | Variable; limited by size of helix; typically 1 to 10 mg | Largest of all balances, 200 g | Variable |
| Virtues | Simple design | Simple design | Rugged | Good LPR; possible automation |

*Modified from Czanderna and Wolsky [23].

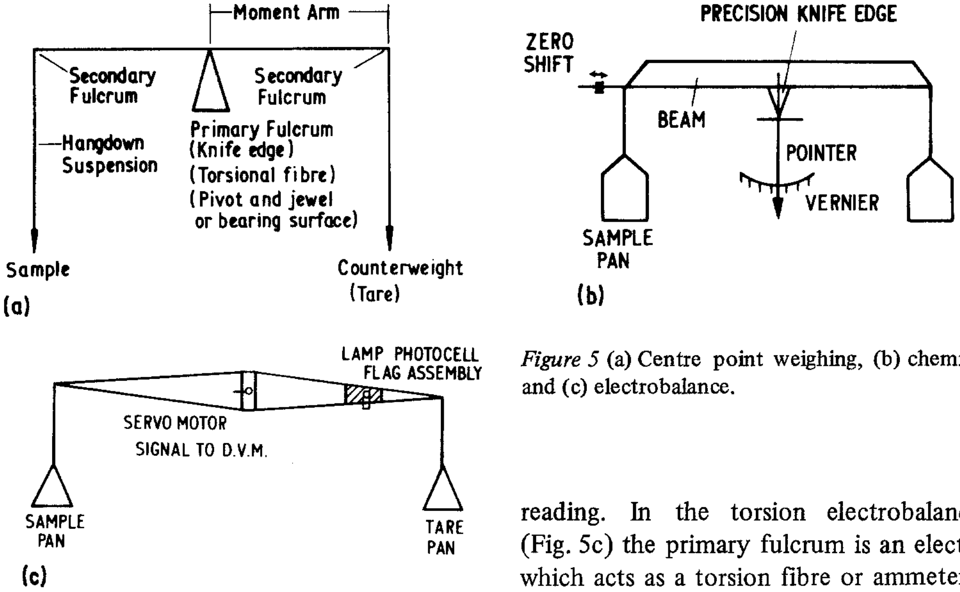


*Figure 5* (a) Centre point weighing, (b) chemical balance and (c) electrobalance.

with the meniscus formed around the suspension wire at the air–liquid interface, the variability of buoyant forces on the immersed specimen due to entrapped gas and fluctuation of temperature. Bowman and Schoonover have described precautions to minimize these problems. However, if the specimens are small then the sensitivity of the weighing balance becomes the limiting factor in precision. For this reason it is worthwhile to examine the merits of various designs of balance.

### *4.5.2. Micro-balances*

Czanderna and Wolsky [23] have recently reviewed the operation and sensitivities of various types of microbalance. Table I reproduces some of their findings. The desirability of a large capacity and a large load-to-precision ratio makes beam balances an obvious choice. Commercial availability then limits the choice to beam-knife edge (mechanical chemical balance) and beam-torsional (electroforce balance) designs. Fig. 5a is a schematic diagram showing the principle of centre-point balancing designs. In the chemical balance design (Fig. 5b) the primary fulcrum is a precision-made knife edge, about which moments are symmetrical when the weighing pans are empty. When a specimen is placed on the specimen pan, calibrated counter weights are placed on the other pan to balance the beam. Any deviation of the beam from horizontal is measured by a pointer and vernier. The true weight of the specimen therefore equals the counter weights plus the calibrated vernier reading. In the torsion electrobalance design (Fig. 5c) the primary fulcrum is an electric motor which acts as a torsion fibre or ammeter. Because of the absence of a precision pivot the system is assymmetric. The torque put on the fulcrum by placing a specimen on the sample pan is compensated by an electromagnetic force. Unlike the operation of the mechanical balance, the beam does not settle to an equilibrium position; instead any deviation of the beam from horizontal causes a photoelectric or magnetic inductive sensor to energize the moving coil and hence restore the beam to its original position. The restoring voltage is then displayed in calibrated force units on a digital voltmeter, If the sample weight exceeds the capacity of the restoring force, coarse tare weights may be used as counterweights to achieve an on-scale reading. The tare weights can then be calibrated by substituting a suitable calibrated weight for the specimen.

Until recently, the knife edge balance was the favoured design; however, a variety of electrobalances has now become commercially available and the many advantages offered by this design have led to an almost complete takeover in applications concerned with small specimens. As applied to hydrostatic weighing, the advantages are greater sensitivity, rapid stabilization of readings, the possibility of direct computer control and data analysis and a permanently horizontal beam. The permanently horizontal beam means that the suspension wire will not oscillate up and down at the liquid–air interface and hence not disturb the surface tension forces. Offsetting these advantages, the mechanical balance has a much larger capacity (200 g as opposed to 5 g) and greater robustness. The price of both types of balance is around £3000. For absolute precision the electrobalance is the better device.

### *4.5.3. Weighing liquids and suspension systems*

The factors governing the choice of immersion liquid have been discussed earlier: these are low surface tension, low vapour pressure and chemical inertness. Added to these in the case of hydrostatic weighing are high density, high viscosity and low and well-defined coefficients of thermal expansion. Use of a dense liquid increases precision by amplifying $(\bar{W}_{\text{air}} - \bar{W}_{\text{liq}})$, while low thermal expansion and high viscosity cut down convection currents in the liquid. Water and diethyl phthalate have achieved the greatest popularity. Water has a well-defined density and low thermal expansion coefficient but a high surface tension. Ideally it is desirable for the liquid to have a low surface tension, so that the liquid will flow up the sides of the suspension wire at the air–liquid interface and give a reproducible zero contact angle. In this way surface tension forces can be kept constant. If water is used as the weighing liquid a few drops of wetting agent must be added. However this will affect the density and expansion coefficient of the water. Bowman and Schoonover [22] have outlined the corrections that should be made to water density for temperature fluctuation and dissolved air. Diethyl phthalate is more viscous, denser ($1.118\,\text{g cm}^{-3}$ at 20° C) and has a lower surface tension than water. The combination of high density and low surface tension is rare and this combined with non-volatility makes diethyl phthalate preferable to other heavy organic liquids. Whichever liquid is used it should be distilled and kept under a partial vacuum.

The choice of an optimum suspension wire is also very important. Variability in the downward surface tension force associated with the meniscus surrounding the point of penetration of the water surface by the suspension wire has been a major limitation in the reproducibility of hydrostatic measurements. The problem is magnified when the specimen is made smaller, as the surface tension force becomes a greater fraction of the specimen weight. The magnitude of this force when water is used as the weighing liquid is about $70 \times 10^{-5}\,\text{J cm}^{-1}$ length of wire circumference. Wires should therefore be made as fine as possible. Experiments have tried various coatings as an attempt to induce the liquid to flow up the sides of the wire by capillary action and hence create a reproducible zero contact angle. Nichrome wires have been electrodeposited with gold and platinum and thin silica coatings have been deposited by vacuum evaporation. Bowman and Schoonover [22] have suggested a novel method of producing straight wires with good surface finishes. A nichrome wire is put under tension and electrically heated to cherry red temperature in a $10^{-5}$ torr vacuum for 1 h. On cooling, the resultant oxide coat flakes off due to differential contraction and leaves a clean surface. Wires 20 $\mu$m thick produced by this technique performed better than coated fibres. Cawthorne and Sinclair [1] achieved excellent results using a 20 $\mu$m thick quartz fibre which had been cleaned in concentrated caustic potash in ethanol solution.

### *4.5.4. Techniques for determining absolute densities*

Bowman and Schoonover [22] have achieved a precision of 0.0001% in determining the density of a 10 g silicon crystal using a mechanical balance with 1 $\mu$g sensitivity and water as the weighing liquid. They performed two independent series of weighings in air and in liquid. From the average weight in air and average weight in liquid they calculated the density. Corrections were made for the effects of temperature fluctuation, barometric pressure and humidity. Belin and Pellegrin [24] used a similar system but controlled the water temperature to $\pm 3 \times 10^{-3}$ ° C. They achieved a precision of 0.002% in the density of a 5 g PbSe semiconductor sample. The samples were smaller in terms of both mass and volume than those of Bowman and Schoonover and fewer precautions were taken. As a result the precision is worse.

More recently, Cawthorne and Sinclair [1] developed a simplified system to rapidly determine the density of 30 mg irradiated stainless steel specimens. The experimenters were limited to small samples by the radioactivity of the material. The system utilized an electrobalance with 0.1 $\mu$g sensitivity; again the weighing liquid was water. The sequence of weighings used is shown in Fig. 6. The density of the sample is given by

$$\rho_{\text{s}} = \frac{A - N}{A - W}(\rho_{\text{water}} - \rho_{\text{air}}) + \rho_{\text{air}} \qquad (6)$$

where $N$ is the empty weighing system, $A$ is the specimen in air and $W$ is the specimen in liquid.

The technique is rapid and simple. As the

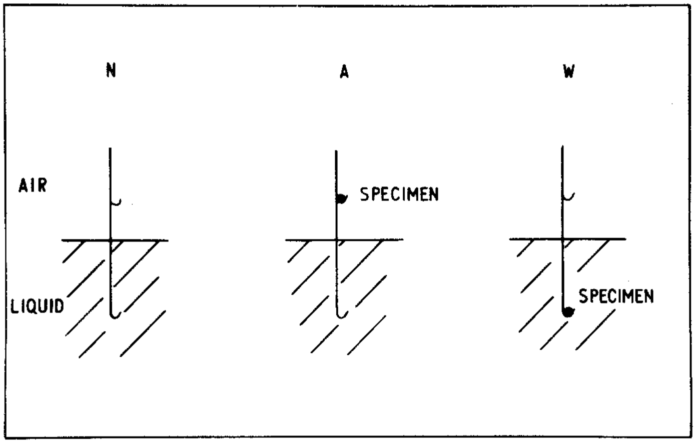


*Figure 6* Hydrostatic weighing technique of Cawthorne and Sinclair [1]. $N$ is the empty weighing system, $A$ is the specimen in air and $W$ is the specimen in liquid.

suspension system remains in the same position during all three weighings, the surface tension force on the wire should be constant. This assumes that the specimen is placed on the upper and lower stirrups without disturbing the meniscus. The system also avoids the need to zero and calibrate the balance. Thus

$$\rho_s = \frac{(KA-C)-(KN-C)}{(KA-C)-(KW-C)}(\rho_{\text{water}}-\rho_{\text{air}})+\rho_{\text{air}} \qquad (7)$$

where $K$ is the calibration error, that is, if each milligram of true weight reads 1.1 mg due to an expansion of the force scale, $K$ will equal $^1/_{1.1}$. It can be seen that $K$ divides out of the above expression; $C$ is a zero shift and subtracts out.

A precision of ± 0.04% was achieved for the 30 mg samples. Allowing for the size of the specimen, this precision is similar to that obtained by Bowman and Schoonover [22]. Because the precision of a determination is dependent on the mass of the specimen, it is reasonable to multiply the precision of the determination by the mass of the specimen to define a figure of merit to compare systems.

### 4.5.5. Techniques for determining changes in density

The basis of this technique is to weigh a specimen against a dummy (standard) in air and liquid before and after the specimen has been subjected to a treatment which alters its density.

The change in density is given by

$$\frac{\Delta\rho}{\rho} = -\frac{\Delta V}{V} = -\frac{\Delta \bar{W}_{\text{liq}}}{\rho_{\text{liq}}V} \qquad (8)$$

where $V$ is volume and $\Delta V$ is change in volume.

The advantages of this system lie in its symmetry, i.e. any change in temperature etc. which affects the dummy in the same way and the fact calibration and tare weights need not be used.

Bell [25] described a system using a mechanical balance and a temperature-controlled diethyl phthalate bath. Temperature stability was within 0.01° C. The specimen and dummy were made of the same material and matched in weight to 1 part in $10^4$. A precision of 0.001% (as a fraction of the specimen's density) was achieved using a 141 g specimen with a density of $\sim 7.8\,\text{g cm}^{-3}$. Density changes of 0.01% were monitored with ease.

Sezaki and Kuhlmann-Wilsdorf [26] used a similar technique to measure the change in density upon cold-working of a 50 g aluminium sample. Again a mechanical balance and diethyl phthalate were used. Unlike Bell, they did not attempt to rigorously control the temperature of the weighing bath but instead they measured the temperature difference between the specimen and the dummy while readings were being taken. By accurate temperature monitoring, Sezaki and Kuhlmann-Wilsdorf improved the precision to 0.0001%.

Ratcliff [27] simplified the technique by weighing the specimen and dummy alternatively on a single-pan mechanical balance. In this case the temperature was not monitored, but any change in immersed weight of the dummy between weighings was used to calibrate temperature changes: that is, any change in the density of the dummy was assumed to be due to temperature changes and this was backed-off from the apparent density change observed in the specimen due to the extrinsic treatment. Aluminium and magnesium specimens weighing between 30 and 40 g were measured to a precision of 0.001 to 0.0001%. These techniques have not been extended to smaller specimens.

## 5. Summary

The precision of density measuring techniques has increased considerably in the last 20 years. The interest in point defects in crystals led to an advance in the 1960s. High precision flotation techniques were developed to cope with single crystals a few milligrams in weight. Density columns were ideal for specimens whose density was equal to that of heavy organic liquids. However, for more dense materials novel techniques were developed using calibrated floats to increase the buoyancy of the specimen.

More recently, the problem of void-swelling in nuclear materials has led to the need to measure the densities of highly irradiated and therefore very small specimens (~ 30 mg). This, together with the development of the ultra-high precision electrobalance, has brought about refinements in the hydrostatic weighing technique. For specimens as small as 30 mg the sensitivity of the balance becomes the predominant factor governing the precision of the technique. Modern commercial electrobalances are an order of magnitude more sensitive than mechanical balances as well as being faster and more stable. The system used by Cawthorne and Sinclair [1] is rapid, easy to use and gives excellent precision.

Table II compares the precisions that may be obtained using the reviewed techniques. For metallic specimens weighing between 10 and 20 mg, the Cartesian diver, Franklin and Spal [21] float and hydrostatic weighing methods will all give excellent precision. For ultimate precision the Cartesian diver is the best system; however, the complexity of the pressure controlling apparatus will limit its use. The Franklin and Spal [21] float method and hydrostatic weighing give a similar precision. It is likely that hydrostatic weighing will find more applications because only one piece of specialist equipment, i.e. an electrobalance, is required to perform the measurement.

Displacement and micropycnometry techniques are ideal for rapid determinations of intermediate precision but are unsuitable for ultra-high precision work. As yet no system has been developed for measuring the densities of submilligram specimens to any degree of precision. This is one area where much effort is still required.

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TABLE II Comparison of the precisions of various techniques

| Technique | Capacity | Mass of sample used in test (mg) | Precision (%) | Figure of merit: Normalized precision (Precision × mass) (% × mg) |
|---|---|---|---|---|
| Displacement | Milligrams → kilograms | 30 | 1 | 30 |
| Micropycnometry | Milligrams → grams | 40 | 0.7 | 28 |
| Density gradient column | Milligrams → grams | any | 0.002 | (For a 40 mg sample) 0.08 |
| Cartesian diver | Milligrams → grams | 2000 | 0.000 02 | 0.04 |
| Franklin & Spal float | Milligrams | 30 | 0.03 | 0.9 |
| Hydrostatic weighing Bowman, mechanical balance | Milligrams → 200 grams | 10 000 | 0.0001 | 1.0 |
| Hydrostatic weighing Cawthorne, electrobalance | Milligrams → 1 gram | 30 | 0.04 | 1.2 |
|  |  |  |  | A low figure is good |

Note: Table II is a summary of precisions quoted in the text. Because different specimen sizes have been compared, a rough *figure of merit* has been formulated to aid comparison. However this figure does not allow for the effect of the density of the sample and the number of experimental measurements made; it is only a guide to the reader.

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