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3.2. Determination of the density of solids

By F. M. Richards and P. F. Lindley

3.2.1. Introduction (By P. F. Lindley)

The measurement of the density of a crystal has become a neglected art, and yet, in combination with an accurate knowledge of the unit-cell dimensions, it can provide vital information regarding the total molecular weight of the unit-cell contents. From this quantity, it is usually possible to determine the number of molecules in the unit cell and their individual molecular weights. The equation relating the crystal density (ρ), unit-cell volume (V), and the overall molecular weight is

$$\rho = Mm_a/V,$$

where m_a is the atomic mass unit (1.66057×10^{-24} g) and V is expressed in mm^3. Alternatively,

$$M = 0.602206V\rho,$$

where V is in units of Å^3. The mass per asymmetric unit can be determined by dividing M by the number of asymmetric units, Z (dependent on the space group), and this will normally correspond to the molecular weight. However, the quotient can either be a fraction of the molecular weight (normally $1/2$) when the molecular symmetry permits the molecule to lie on a special position such as a centre of symmetry or a symmetry axis, or a multiple if the asymmetric unit contains more than one molecule. In either case, a special examination of the choice of unit cell and space group should be undertaken to ensure that the *correct* ones have been chosen. Normally, the measured and calculated densities should agree within at least 1.5%; discrepancies greater than this may indicate an incorrect molecular formula (not unknown in preparative chemistry) or the presence of solvent molecules or other additives. Incorrect choice of space group, inappropriate choice of unit cell, and incorrect asymmetric unit contents can all have profound effects on the success of a structure analysis and on the refinement of the resulting structure.

The classical techniques of density measurement are described by Tutton (1922) and by Reilly & Rae (1954). An excellent and detailed review of both the standard and the less common methods is given by Mason (1944), but, because this work can be difficult to obtain, some of the references compiled by this author are cited herein.

3.2.1.1. *General precautions*

Meticulous temperature control is essential for the highest precision. The allowable temperature fluctuation will depend on the thermal coefficient of expansion of the material and on the required accuracy of the measurement. The utmost care must be taken to avoid air bubbles and inclusions. In those techniques that require immersion of the solid in a liquid, it is assumed that no chemical or physical interaction occurs between the liquid and the solid, and that the volume of the liquid displaced represents the true volume of the solid. For most hard crystalline materials, liquids can easily be found for which these assumptions are valid. However, for amorphous powders, porous structures such as zeolites, crystalline proteins, and natural and synthetic fibres, the measured 'density' may depend markedly on the particular liquid chosen and on the details of the method applied. In these cases, *penetration* or *swelling* of the solid will depend on a variety of factors such as interfacial tension, the relation of pore size to molecular dimensions, adsorption, and electrostrictive forces. The structural unit to which the measured density applies may be very difficult to specify. Even with materials not subject to these difficulties, variability in the measured density is frequently found. Such variations may arise from differences in trace impurities or in the previous history of the sample (Johnston & Adams, 1912).

3.2.2. Description and discussion of techniques (By F. M. Richards)

The discussion here will be limited to six general methods, of which at least one may be adapted to the requirements of almost any problem. The method of choice will depend to a large extent on the nature of the material under study. The merits and disadvantages of each method will be discussed.

3.2.2.1. *Gradient tube*

This technique is simple, versatile, and capable of the greatest sensitivity. It is the method of choice except in those cases where immersion liquids with an appropriate density and chemical inertness cannot be found.

Originally devised by Linderstrom-Lang (Linderstrom-Lang, 1937; Linderstrom-Lang & Lanz, 1938) for the determination of the density of aqueous solutions, the procedure has been adapted for the measurement of crystal densities by Low & Richards (1952*a*). For the original solution measurements, a precision of 0.000001 g ml^{-1} was obtained, although no attempt has been made to attain that precision with solids. This technique was apparently developed and used quite independently in the sugar-cane industry [see, for example, Guo & White (1983) and earlier references contained therein].

3.2.2.1.1. *Technique*

When one liquid is layered over another of greater specific gravity, with which it is miscible, a linear gradient of density develops near the interface. Manipulation of a plunger-type stirrer in a vertical tube can extend the gradient over the greater part of the column. In the absence of convection, the process of diffusion in a column of this type is so slow that the gradient will be maintained virtually unchanged for many months.

A crystal introduced into the tube falls until it reaches a level corresponding to its own density, where it will remain stationary. The density gradient may be calibrated either by introducing immiscible liquid drops of known density, or by the use of a micro-Westphal balance designed for the purpose (Richards & Thompson, 1952).

With an adequate thermostat, measurements may be made at any temperature between the freezing and boiling points of the mixtures involved.

Powders and crystals with cavities or inclusions may be ground to a slurry with the lighter column liquid, subjected to reduced pressure to remove trapped air bubbles, and then introduced into the gradient tube. With hygroscopic materials, these operations are carried out in a dry atmosphere. Finely divided material settles rapidly if the tube is centrifuged. Although centrifugation does not markedly affect the gradient, the column should be calibrated after this step.

If such samples are homogeneous, they will form a thin layer after centrifuging. If, on the other hand, some air bubbles or

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