MINERALOGICAL MAGAZINE, DECEMBER 1979, VOL. 43, PP. 556-7

Sources of error in density determinations by the 'swimming' method

BECAUSE of the difficulty of obtaining material completely free from inclusions a precision better than 0.005 is rarely attainable with natural minerals; since the difference between the volume-expansion coefficients of the usual heavy liquids and those of most minerals is at most 0.002 per °C, if the densities of mineral and liquid have been perfectly matched in a determination by the sink-swim method at T °C, then if the temperature of the liquid is allowed to change by as much as 2 °C before the density of the liquid is determined, the resultant error will only be 0.004.

Thus an adequate precision, say ± 0.003, does not necessarily call for precise temperature regulation, but it is necessary to ensure that matching of liquid and mineral is not falsified by currents in the liquid; these may arise not only from thermal convection, but also from imperfect mixing after the addition of diluent or heavy liquid and from an unsuitable choice of diluent. Such currents are particularly dangerous when a centrifuge is used to speed up settling of minute crystals, as proposed by Bernal and Crowfoot (1934). Hendricks (1933) had also proposed the use of a centrifuge for a different purpose—to attain greater accuracy, of the order of ± 0.0002, when using sizable crystals, *c.* $\frac{1}{2}$ mm. Curiously, the centrifuge has been little used for either purpose, perhaps because neither paper gives full experimental details.

In a properly sited and constructed balance room, temperature variations over 24 hrs. should never exceed 2 °C, and if all necessary materials and apparatus (including the centrifuge if one is to be used) are brought into the balance room overnight, thermal effects may normally be neglected (though the temperature at which the measurements were made should always be reported).

If the mixture is not adequately stirred after each addition, not only may density-gradient currents mislead the observer, but a false result may easily be reached, since homogeneity is only slowly approached by diffusion; the danger of a false result is greatest when a centrifuge is used to accelerate the rise or fall of the mineral, for it may separate the liquid into layers of different density. To take an extreme example, suppose a mineral with D 3.25 has been observed to float in a mixture with D 3.27; if 1 % of a diluent with D 1.0 is added, the bulk density of the mixture will be 3.247, and the crystals should just sink, but if the mixture is inadequately stirred and then centrifuged it *could* separate into approximately equal layers of D 3.260 and 3.234, with the crystals suspended at the interface. We conclude that if after adequate standing or centrifuging the crystals are not at the bottom or at the surface of the liquid, mixing has been inadequate and should be repeated.

When one of the aqueous heavy liquids is in use, water is, of course, the appropriate diluent, but in the last stages of matching it is useful to prepare as diluent a mixture only a little weaker than the current mix, so helping to avoid overshooting and easing mixing.

For the organic heavy liquids it is common practice to use toluene as diluent, a choice probably dictated by its low boiling point, making recovery of the heavy component by distillation simple. Toluene is, however, a most unfortunate choice: its vapour pressure at room temperature is high (see Table I), and evaporation of toluene from the surface of the mixture leads to density currents that can be much more serious than any thermal currents (for which they are often mistaken, if noticed). Ethylene dibromide is a better diluent; though its boiling point is only 20 °C higher than that of toluene, its vapour pressure at room temperature is only half that of the latter, and its higher density means that local evaporation of the same weight would affect the local density less and so give rise to weaker density currents. But perhaps the best diluent is diphenyl ether, the vapour pressure of which at room temperature is negligible; as it is a solid, mixtures with about 10 % of acetylene tetrabromide and with about 10 % methylene iodide should be made for use to dilute these two heavy liquids.

For good results, it is best to start with a liquid a little denser than the crystals and dilute it till the crystals just sink in the well-stirred mixture; for very small crystals a centrifuge may be desirable to speed settling, and a hand-lens or low-power microscope may be necessary to locate the crystals. The density of this mixture is determined, then heavier liquid is added (with good stirring) till the crystals just float, and the new density determined. We now have upper and lower limits for the density of the

TABLE I. *Physical constants of some organic liquids*

	D_4^{20}	B. Pt.	V. P.*	α†	n_D^{20}
Toluene	0.8669	111 °C	29	0.00110	1.4961
Diphenylether‡	1.0748	258	< 1	—	—
Carbon tetrachloride	1.594	76.5	120	0.00124	1.4601
Ethylene dibromide	2.175	131	15	0.00215‖	1.5387
Bromoform	2.890	149	7	—	1.5976
Acetylene tetrabromide§	2.965	234	< 1	—	1.6353
Methylene iodide	3.325	182	3	0.0022	1.7425

* Vapour pressure at 20 °C in millibars (1 mm Hg = 1.333 mbar).
† Volume-expansion coefficient.
‡ Melting point 27 °C.
§ Syn. 1.1.2.2-Tetrabromethane.
‖ P. G. Embrey, priv. comm.

crystals, and the operations can be repeated to give closer bracketing as desired.

The densities of the mixtures are usually determined by weighing a calibrated bob in them, though for some purposes a determination of the refractive index and reference to a graph will suffice. (Merwin [1911] proposed this method and gave a graph for Rohrbach's solution; graphs for most other heavy-liquid mixtures are available.) When a bob is used it should be calibrated by weighing it in air and in one or more liquids of known specific gravity (water and acetylene tetrabromide are suitable; volatile liquids such as carbon tetrachloride may give trouble through the heavy vapour falling on to the balance pan). A small glass bulb partly filled with mercury or other dense solid and with a glass ring at the top should be provided with a suspension of very fine tungsten wire ending in a loop; with a suitable hook the bob can then be raised and lowered in the liquid, acting as a stirrer. With wire of 23 μm diameter both surface tension effects and variations in the length of wire immersed can be neglected, while the tensile strength is adequate if handled with reasonable care (P. G. Embrey, priv. comm.).

When the determination is complete, the mineral can be most conveniently recovered by diluting the liquid till the mineral sinks (if an organic heavy liquid is in use, a volatile diluent, carbon tetrachloride or toluene, is preferable here), then siphoning off most of the liquid, using a capillary siphon with a turned-up tip; the crystals are then washed with water, or water followed by acetone, or toluene, carbon tetrachloride, etc., as most appropriate. With small crystals the use of a centrifuge helps to avoid loss.

Methylene iodide is best recovered by vacuum distillation, using an efficient fractionation column; the other organic heavy liquids may be recovered similarly, but are hardly worth the cost.

REFERENCES

Bernal (J. D.) and Crowfoot (D.), 1934. *Nature*, **134**, 809–10.
Hendricks (S. B.), 1933. *J. Opt. Soc. Am.* **23**, 299–307.
Merwin (H. E.), 1911. *Am. J. Sci.*, ser. 4, **32**, 425–32.

[*Manuscript received 20 August 1979*]

British Museum (Natural History)
Cromwell Rd., London SW 7

M. H. HEY