CLERICI SOLUTION FOR THE SPECIFIC GRAVITY DETERMINATION OF SMALL MINERAL GRAINS

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In the identification of minerals, as well as in the determination of their properties, modern methods tend to minimize the amount of material necessary for satisfactory results. In this direction lie the immersion methods of optical investigations and the more recently developed microchemical techniques. Certain cases, however, require the determination of hardness and specific gravity as an adjunct; of these the specific gravity is the more easily and accurately obtained.

Among the more common methods of gravity determination are: (*a*) the suspension, (*b*) the pycnometric, (*c*) the micropycnometric, and (*d*) the immersion methods. The pycnometric method is the most precise of the first three, although micropycnometry (1, 11, 14)* may attain nearly the same degree of accuracy with a considerable reduction in the amount of material required. These advantages also obtain in the case of immersion methods (in which the mineral grains are placed in a liquid medium and the specific gravity of the liquid varied as desired), and in addition the speed of manipulation is greatly increased. This simple technique has had limited application in the past, due to the paucity of liquids of high specific gravity, as well as to their excessive cost, chemical instability, or poisonous nature. The writer believes that most of these defects can be overcome by the use of Clerici solution (sp. gr. approx. 4.32 when saturated at room temperature) in very small quantities, as indicated in the following paragraphs.

PREPARATION AND PROPERTIES OF CLERICI SOLUTION

Strictly speaking, Clerici solution is a mixture of equal parts of thallium formate (HCOOTl) and thallium malonate ($CH_2(COOTl)_2$), dissolved in a minimum amount of water. It is a mobile, odorless liquid, straw-yellow in color. The specific gravity of the saturated solution at 20°C. is $4.324 \pm .002$; this can be increased by heating and dissolving more of the salts to make a more concentrated saturated solution at the higher temperature (2), and decreased by dilution with water.

The solution used by the writer was prepared by dissolving 300 grams of each salt** in 40 cc. of water, warming slightly to hasten the process.

* Numbers in parentheses refer to references cited in the bibliography at the end of this paper.

** Thallium formate and thallium malonate are obtainable as dry salts from the Eastman Kodak Co., Rochester, New York. Prices quoted are $7.00 per 100 grams for the former, $9.00 per 100 grams for the latter.

The resulting solution is not saturated, but can be made so by careful evaporation (heating over a hot plate gives good results) to the point at which a yellow-brown, curdy hydrolysis product begins to form. Filtration gives about 135 cc. of clear, concentrated liquid, ready for use.

Concerning the use of Clerici solution, there are several important features to be considered. (*a*) Evaporation of water with resultant frac-

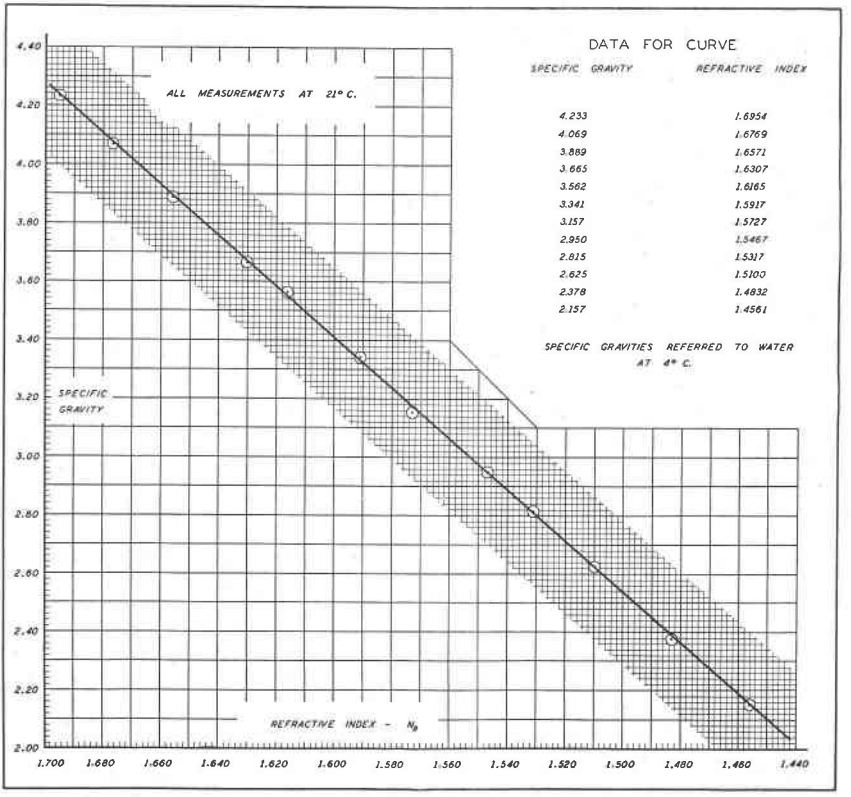

FIG. 1. Relation between specific gravity and refractive index of Clerici solution at 21°C.

tional crystallization of thallium malonate must be avoided. Because of the higher molecular weight of this salt, its loss from solution lowers the specific gravity and refractive index of the saturated liquid. (*b*) Although the solution appears to be stable and inert toward all water-insoluble minerals at ordinary temperatures, it may react with sulfides (12) or with magnetite (13) if exposed to them for long periods when hot. (*c*) Its extremely poisonous and corrosive nature necessitates careful handling. (*d*) The high cost of the solution is somewhat offset by the ease with which it can be recovered and reconcentrated. Careful water-washing of

all grains and receptacles, followed by evaporation of the washings gives at least 99% recovery of concentrated liquid.

As shown by Vassar (12), a straight-line relationship exists between the refractive index and specific gravity of Clerici solution. Because solutions made up of unequal parts of thallium formate and thallium malonate were used in previous index-gravity determinations (12), it was considered advisable to make a similar study of solutions containing equal parts of the two salts. Such solutions are most easily reproduced, now that the dry thallium salts are obtainable on the market. Specific

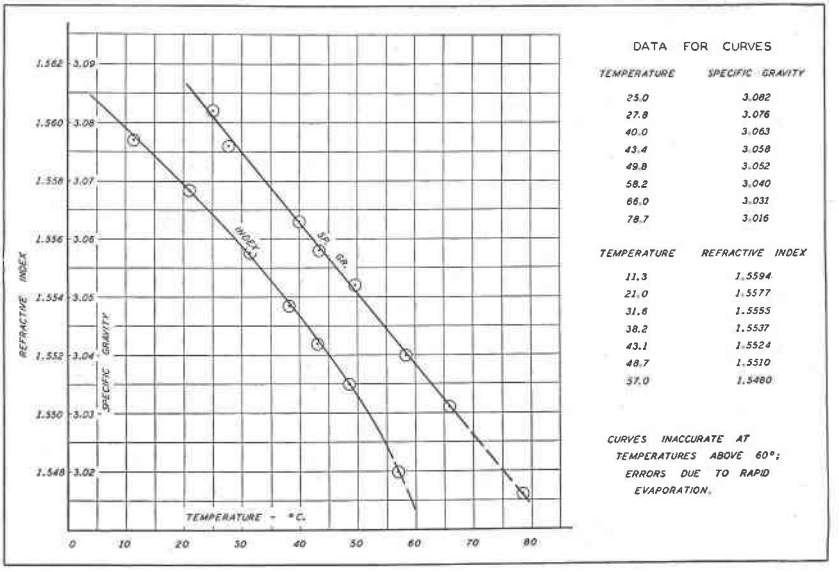

FIG. 2. Temperature-specific gravity and temperature-refractive index curves for a sample of moderately concentrated Clerici solution.

gravities at various concentrations were obtained with a Westphal balance at controlled temperature, and the corresponding refractive indices determined at the same temperature. In spite of changes due to evaporation, the results checked to within 0.01 g./cc. in specific gravity and 0.003 in index. Figure 1 shows the relations involved.

Two samples of specific gravity approximately 3.1 were tested for variation of index and gravity with temperature. Although the curves as plotted (Fig. 2) are approximations, they show the general relations and furnish the data for temperature variation constants:

$$\frac{dN}{dT} = -0.00025/\text{degree C.}$$

$$\frac{d\ sp.\ gr.}{dT} = -0.0012 \text{ g./cc./degree C.}$$

Both these figures are constant for this concentration only, and will decrease with increased water-dilution.

Specific Gravity Determination of Mineral Grains

Because most rocks crushed to 80 to 200 mesh yield particles essentially monomineralic, the following method of gravity determination was developed particularly for use with such grains. It follows that a method applicable to individual grains so small (0.15 to 0.32 mm. in diameter) has the additional advantage of requiring minute amounts of material for positive results. In dealing with individual grains, more-

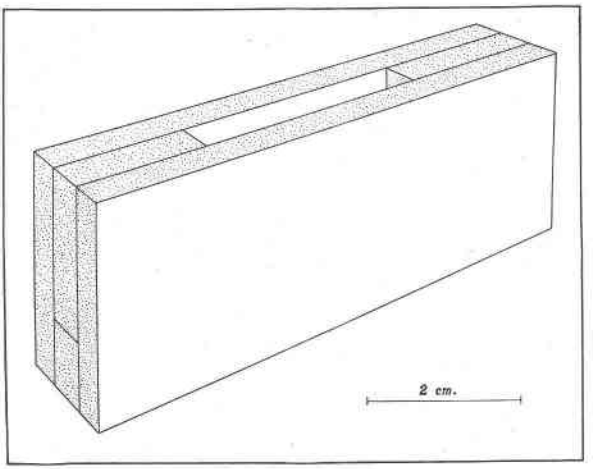

Fig. 3. Small glass settling tank used for the suspension of mineral grains in Clerici solution.

over, a preliminary inspection under the microscope is possible, in which pure grains of the desired identity and of optimum shape and size can be selected.

A small settling tank of about 0.5 cc. capacity must be constructed from glass plates, as shown in Fig. 3. Two ordinary glass microscope slides are held apart by strips of a third, thicker slide in the manner indicated; the pieces are cemented with a syrupy celluloid-acetone mixture. Celluloid strips may be substituted for the glass if desired. The tank is placed on the microscope stage, where it can be cemented lightly or held by the mechanical stage. The barrel and stage are tilted until the

microscope axis is horizontal; in this position the tank is correctly oriented for receiving the Clerici solution.

Into the liquid-filled tank is introduced the mineral grain to be tested. It may be handled with a camel-hair brush, with the helpful device designed by Howard (4), or by any of the methods suggested by Partridge (9). Once the grain is "wetted" and freed from air bubbles by agitation with a thin wire, its behavior in the liquid is easily noted through the low-power objective. When it floats in the concentrated solution, water is added drop by drop from a length of music wire until the grain remains suspended or nearly so. Thorough stirring is essential to obtain a homogeneous liquid.

Care must be taken, too, to prevent the microscope lamp from heating the solution in the tank to a point above standard temperature (about 21°C.). A flask filled with 0.5 *N* copper sulfate solution placed between the microscope and the lamp obviates this difficulty.

When the specific gravity of the liquid has been brought into correspondence with that of the grain, several drops are placed on the Abbe refractometer and their index quickly determined. This is converted into specific gravity by means of the curve in Fig. 1. Several tests have shown that this simple and rapid method gives results reliable to the nearest 0.01 in specific gravity. Additional refinements in the procedure would undoubtedly decrease this figure.

The Clerici solution should be checked from time to time with the Westphal balance or with standard mineral grains (7). Should there be a slight departure from the norm in specific gravity at any given concentration (due to fractional crystallization of thallium malonate or any other cause), the corresponding refractive index may be determined and a new point plotted on the grid of Fig. 1. Through this point a new curve may be drawn parallel to the standard curve, taking over the function of the latter in ensuing determinations. For very accurate work, a correction factor is necessary if the obtaining temperature is other than 21°C. A correction in gravity of +.001 per degree above 21° and −.001 per degree below 21° should be made.

Earlier investigators have constructed refractive index-specific gravity tables for Thoulet solution (potassium-mercuric iodide) (3) and for Rohrbach's solution (barium-mercuric iodide) (6). Because it is difficult to prepare and maintain in a standard condition, the former is not well suited for determinative work. Rohrbach's solution is more satisfactory, but requires a complex technique in handling. Further, it has a maximum density little greater than 3.55, and its refractive indices corresponding to gravities above 3.1 fall outside the range of the Abbe refractometer, which is the most convenient tool for index determination.

Conclusions

Clerici solution is considered one of the most desirable liquids for immersion methods of specific gravity determination because:

(*a*) It combines great mobility, even at high concentrations, with a specific gravity greater than that of most other heavy liquids.
(*b*) It is odorless and has no objectionable color.
(*c*) It can be used at room temperature, and at such is inert and stable.
(*d*) Its specific gravity is lowered by addition of water and raised by evaporation of the water. The latter feature makes for easy and efficient recovery of concentrated solution and somewhat offsets its high initial cost.
(*e*) The relation between its specific gravity and its refractive index is a simple and constant one.

The method of specific gravity determination of individual grains in the manner outlined has certain outstanding advantages:

(*a*) Individual grains, of very small size if necessary, can be selected and microscopically inspected before their gravity is obtained. This is particularly helpful where there is little material available.
(*b*) The accuracy of this method compares favorably with that of the more laborious pycnometric method.
(*c*) The time required for a determination is much less than that needed for similar material in other methods.

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