THE MICROPYCNOMETRIC METHOD FOR THE DETERMINATION OF SPECIFIC GRAVITIES OF MINERALS

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Modern methods for the determination of minerals aim to reduce the quantity of material tested to that minimum which is considered necessary for a positive identification. On the one hand, optically, due to the immersion method, it is possible to determine the indices of refraction of mineral grains, the size of which need not exceed that of a pin head. Microchemical tests also permit the application of a whole series of chemical reactions on an extremely small quantity of material. The use of the blowpipe supplements these various methods of determination. In a number of cases, however, all these methods prove insufficient, and the determinations of hardness and specific gravity are necessary. The first of these is usually measured only approximately; hence the second property frequently plays the decisive role.

The determination of specific gravity of small fragments of a mineral can be accomplished easily by the well known method of mixing two liquids until the specific gravity of the mixture equals that of the mineral. Due to the absence, however, of liquids with a high specific gravity this method is practicable only when the specific gravity is less than that of methylene iodide (3.3), or Thoulet solution (3.2), or Clerici liquid (4.5). In as much as the latter is very expensive, highly poisonous and difficult to obtain, the practical limit is therefore 3.3. Thus the problem of extreme interest is the development of a method for determining the specific gravity of minerals in cases where it exceeds 3.3, using the minimum quantity of material possible. For this purpose a new method, conventionally termed *the micropycnometric method*, has been suggested by the author.

For the determination of the specific gravity of mineral grains a number of methods have been suggested.[1] Some authors use the hydrostatic method, thus increasing the delicacy of weighing over that of the Jolly or the torsion balance. Others make use of the method of immersing the mineral grain in some liquid medium, observing the velocity of its descent in heavy liquids or varying the specific gravity of the liquid within the limits required. From

[1] Rosenbusch, H., Mikroskopische Physiographie, Bd. 1, 1 hälfte, S. 671.

the author's point of view the latter method is more satisfactory with regard to both speed and the accuracy of the determination (± 0.01). It is to be regretted that this method, as mentioned above, has found but limited application.

Although, according the Spencer,[2] minerals with a specific gravity of 2.75 are the most abundant, a whole series of common rock-minerals (hornblende, tourmaline and others), also sulphides, have a specific gravity above the limit indicated. The determination of minerals of friable sedimentary rocks, such as the "heavy" minerals in sands urgently calls for the need of determining specific gravities exceeding the figure three.

Many attempts have been made to extend the application of the immersion method by causing a small fragment of a heavy mineral to adhere to objects having a low specific gravity. In determining the specific gravity of such a system by the ordinary method, the specific gravity of a mineral is comparatively easy to obtain.

A very ingenious method was that described by Retgers,[3] who used glass pincers for picking out mineral grains. Sommerfeld[4] replaced them by an aluminium wire, which is not applicable with liquids of the Thoulet type. This method, called the suspension method, is of special interest to us as it competes with the method described later. We shall, therefore, dwell upon it at some length. Its defect in principle is due to the indirect method of determining the constant. Its drawback in practice is the large surface of the system and the possibility of adhering air bubbles.

Retgers and Rosenbusch have made a study of the errors involved in the method. The accuracy in weighing is of the greatest importance in the determination of the specific gravity of a mineral. The quantity of the material tested also plays an important role, which is well illustrated by the following table 1.

TABLE 1

Volume of the mineral	Specific gravity	Absolute error	Relative error
0.05 cm³	4.4	0.002	0.05%
0.005 "	4.4	0.022	0.50%

[2] *Mineral. Mag.*, vol. **XXI**, pp. 337–365, 1927.
[3] *Zeits. f. phys. Chem.*, vol. **4**, pp. 190–196, 1889.
[4] *Zentrabl. f. Mineral.* p. 482, 1910.

The effect of the size of the float is also noteworthy; it is therefore recommended by the author that a definite correlation be maintained between the quantity of the mineral and the size of the float.

As the result of all these factors, the following limits of error may be established:

TABLE 2

The quantity of mineral weighed	Specific gravity	Accuracy of weighing	Absolute error	Relative error
0.170 gram	4.01	±0.0001	±0.013	0.3%
0.170 gram	4.01	±0.00005	±0.007	0.17%

These figures apply when the specific gravity of a liquid or mixture is determined with an accuracy of from ±0.001 to ±0.0005. According to Rosenbusch this exactness does not present any special difficulty.

Summing up what has been said we can state that the suspension method of determining the specific gravity of a mineral when the weight is about 0.2 gram is about one tenth of a per cent, provided the weighing be precise.

Considering the method from the standpoint of actual practice it is necessary first of all to point out the fact that the use of a float is impossible in cases where the mineral is in the form of small grains, and such is frequently the case. Further, such precision in weighing and determining the specific gravity of a liquid is rather time consuming. In the author's opinion such exactness in determining the specific gravity of a mixture of liquids cannot be attained, due to changes of temperature with consequent changes in composition as the light component undergoes slight volatilization. Therefore, the actual accuracy of the suspension method is lower than that indicated by its authors. Finally, mention should be made of the fact that an increase in the specific gravity of a mineral still further reduces the accuracy.

It is well known that the pycnometric method of determining specific gravity is the most precise of all existing methods. Consequently, it was natural to attempt to apply it to the case of small quantities of weighed material. A study of the errors of the pycno-

metric method[5] brings us to the conclusion that it is necessary to bring the volume of the quantity weighed as near as possible to that of the pycnometer.

The ideal case for the mineralogist and the petrographer would be to measure the specific gravity of one small grain of the mineral, i.e., with a volume of about 1 cubic mm. In practice, however, it is nearly always possible, with few exceptions, to have about ten such grains, or a single fragment with an equivalent volume. That is why we have assumed a volume of 10 cubic mm. = 0.01 cc. as most suitable.

Further, the question arose as to the size and shape of the pycnometer. We have proposed the use of a simple glass tube with one end closed, while on the other end a line was drawn at the beginning of the test in order to establish the meniscus. The volume of the liquid was about 0.07 cc.

The first tests with garnet showed the general adaptability of the method. With the quantity of material equal to 0.04 gram and with the specific gravity of about 4, this gives the required volume of 0.01 cc., and the error of a particular determination will not exceed ± 0.01. With especially careful work the accuracy of ± 0.01 was attained. The weak point was found in the difficulty of establishing the level in the same place. Here considerable liberty was left to the personal equation of the observer. We have eliminated this defect by applying a polished glass plate to the edges of the tube (see fig. 1). After the pycnometer had been filled with the liquid, the cover was applied, the excess of liquid was removed, and the pycnometer was weighed by the extrapolation method. Proceeding thus in determining the volume of the pycnometer a precision of a few units in the fifth decimal place was attained, while formerly the variations had been of the order of ± 0.01 cc. Moreover, this method afforded the possibility of reducing the time required for the determination. We have called this procedure the "micropycnometric" method. Further improvements will, no doubt, fully justify this name.

The sequence of the method is briefly as follows:

(1) The determination of the volume of the micropycnometer. After being washed with alcohol, dried and weighed on a delicate balance, the pycnometer is filled with a liquid. We have used bro-

[5] В. Карандеев и А. Ферсман, О погрешностях при определении уд.веса твердых тел пикнометром. 1914г. стр. 5.

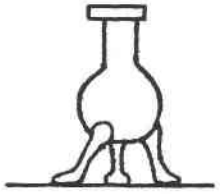

FIG. 1.

moform, the high specific gravity of which permits of a more accurate measurement of the volume. The most convenient way of filling is by means of a capillary tube. Keeping the pycnometer in a vacuum for 20–30 minutes frees the liquid from air bubbles. Then the cover is applied in such a way as to remove any excess of liquid.

As soon as the excess of liquid has been removed by means of a filter paper, the stopwatch is started, and the micropycnometer is weighed by the extrapolation method.

Our observations have shown a velocity for the fall of a weight of 0.0001 gram to be 75 seconds. To obtain the constant it is necessary to make this determination several times.

(2) A quantity of the weighed mineral is placed in a clean, dry micropycnometer. The filling of the pycnometer with bromoform[6] comes next, which is followed by freeing the pycnometer from air bubbles in a vacuum. The whole process does not take more than 2 hours.

The specific gravity is determined with the aid of the well known simple formula:

$$\lambda = \frac{W_2 - d}{W_1 + W_2 - W_3}$$

where

W_1 is the weight of bromoform in the micropycnometer.

W_2 is the weight of the mineral.

W_3 is the weight of bromoform + the mineral.

d is the specific gravity of the bromoform.

An analysis of this formula shows the following:

The error of determination will be equal to:[7]

$$(1) \qquad d\lambda = \Delta w \cdot \frac{\lambda}{d} \cdot \frac{W_2 - W_3}{w_2^2} + \Delta d \cdot \frac{\lambda}{d},$$

where

$$d\lambda,\ \Delta w \text{ and } \Delta d$$

are the corresponding errors of the measurements λ, w and d. Under the conditions of our test λ has twice, and rarely three times,

[6] Another liquid may be used.

[7] This expression is obtained in the usual way according to the formula: $d\lambda = \Delta w\ \partial\lambda/\partial w + \Delta d\ \partial\lambda/\partial d$; the deduction is omitted.

the value of d. Therefore, the second member of the formula must play an insignificant part, for Δd usually does not exceed ± 0.001. The error of weighing is ± 0.0001. With the use of a microchemical balance it can be still further reduced. Its coefficient, however, may be rather large. The quantity of the mineral weighed under our conditions is always a small fraction, consequently the raising to the second power will considerably increase the magnitude of the error. In the numerator we have the difference $W_2 - W_3$, which is also a fraction. The smaller it is, the less will be the influence of the quantity of the mineral weighed and the smaller the error of the measurement.

As an example let us calculate the error of the determination of the specific gravity in the following instance:

$$\lambda = 6.0,\ d = 3.0,\ W_1 = 0.20,\ W_2 = 0.06,\ W_3 = 0.23.$$

Let us take into consideration only the first member of the formula (1).

Then we shall have:

$$d\lambda = \pm 0.0001 \cdot \frac{6}{3} \cdot \frac{0.17}{(0.06)^2} = \pm 0.009.$$

These figures show that: (1) the absolute error is near ± 0.01; (2) the increase in the specific gravity of the mineral reduces the error of its measurement.

Experience has shown that the actual errors are very close to the calculated values (see table 3).

TABLE 3

Mineral	Quantity of mineral weighed	Specific gravity	Average	Probable error of an individual determination	Calculated error
Garnet	0.0380	4.157	—	—	—
"	0.0383	4.150	4.144	±0.014	±0.014
"	0.0445	4.125	—	—	—
Lead	0.1058	11.275	—	—	—
"	0.1007	11.266	11.271	±0.006	±0.005

Hence the practical accuracy of the determination by the micropycnometric method may be assumed to be: $d = \pm 0.01$.

This is the absolute error. Accordingly, the relative error will be easily found to be equal to

$$\frac{d\lambda}{\lambda} = 0.3\%$$

or less.

Let us compare the results obtained with those of the suspension method. Previously we have seen that with 0.1700 gram of a mineral the specific gravity can be determined with a relative error also of 0.3% (with on accuracy of weighing $= \pm 0.0001$). So large a sample does not speak favorably for the suspension method. Indeed, if we took such a quantity using the micropycnometric method, we should obtain a relative error of only 0.02%, that is, more than ten times as accurate. By increasing the exactness of weighing, both methods can be made correspondingly more accurate.

As to the length of time consumed, the two methods hardly differ in any essential respect.

Summarizing we may draw the following conclusion: the micropycnometric method is a step forward both as regards accuracy and the reduction of the quantity of material tested.

Further improvements are possible in the direction of reducing the size of the micropycnometer, with regard to its shape, the accuracy of weighing and the corrections for temperature, for the error of determining the specific gravity of the liquid, etc. Every development may permit either more accurate results, or a decrease in the quantity of the material used. But even what we have obtained at present will facilitate considerably the indentification of minerals.

The development of this method was perfected in the physical and chemical departments of the Petrochemical Laboratory of the Institute of Economic Mineralogy. The determinations of specific gravities by the micropycnometric method was performed by T.J. Shashkina, a laboratory assistant in the department.