# AN ACCURATE METHOD FOR THE DETERMINATION OF THE COMPONENTS OF A HETEROGENEOUS PARTICULATE MINERAL SYSTEM

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In the course of the development of a precise technique for the use of the petrographic microscope in rock analysis, attempts have been made to determine the mineral constituents quantitatively. Such determinations have had their greatest success when applied to thin sections of rock samples. However, there are numerous occasions when analyses have to be made of powdered material or loose crystals, and the investigator cannot have recourse to such sections. An attempt has been made, therefore, to develop a method which would be generally applicable to this type of material.

## LIMITATIONS OF THE THIN-SECTION TECHNIQUE

The Rosiwal[1] method of determining the quantitative ratio of mineral constituents in mixed rock samples is ideally adapted to thin or what may be considered two-dimensional sections. Although extensive claims have been made for it, the method is not applicable to mixed particulate substances where it is necessary to measure the intercepts of projections. In fact, even with thin sections, doubt has been expressed as to its accuracy by Julien[2] and later by Williams.[3] Julien pointed out the necessity of considering the shape factor in connection with the use of an average diameter in estimating percentage composition of rocks in general, while Williams showed from careful analyses of Westerly, Rhode Island granite that the results obtained by the Rosiwal method were not in agreement with results obtained by several other generally accepted methods. On the other hand, Johannsen and Stephenson[4] claim remarkable correlations between determinations made by the Rosiwal method and results calculated from chemical analysis, and the method of separation by means of heavy solutions. This result might be expected if Johannsen and Stephenson utilized sections for other analyses similar to those used for the Rosiwal determinations. While this fact is not specifically stated, it is implied. In passing, it is well to point out that Rosiwal in a footnote to the thin-section technique of Delesse states ". . . This thin rock section . . . would have a weight of 1300 mg., and . . . provide sufficient material

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for an ultimate chemical analysis." As might be expected, if thin sections are used for chemical analysis, excellent correlations should be expected between such determinations and those made by the Rosiwal method.

The assumption that average diameters as determined from an examination of the projections of a particulate array can be utilized for estimating the percentage composition of an aggregate is erroneous.This fact follows from a consideration of the shapes of the particles themselves. *Unless the volume shape factors of the components under observation are exactly the same, only approximate values of the composition of a given mineral can be obtained.* It will be shown later that the volume shape factors of minerals vary widely. For irregularly shaped particles the volume shape factor can be shown to be always less than $\pi/6$ (the value for a sphere). The lack of attention to this fact has undoubtedly led to numerous discrepancies which might have been otherwise explained.

## THEORY OF METHOD PROPOSED

### *Statistical Description of an Aggregate*

It is evident from the foregoing that the method of linear intercepts as developed by Rosiwal is applicable only to a two-dimensional distribution. In order to apply such a method to a heterogeneous assembly of particles, the particles must first be imbedded in a suitable medium and sectioned. This process is not only involved and time consuming, but is often impossible to accomplish successfully, especially when the particles are small. However, it is possible to obtain an accurate estimate of the mass of an aggregate without recourse to either the Rosiwal or Delesse methods elsewhere described. This new approach depends upon certain parameters which define the properties of an aggregate. Thus, it is known that the mass of a particle varies as the cube of a dimension:

$$W = \nu\rho d^3 \tag{1}$$

where $W$ defines the weight of a particle of diameter $d$ and density is $\rho$. The term $\nu$ may be called a shape factor which has a specific value for each particulate aggregate. The value of $\nu$ need not be constant for a given mineral and must be determined. Hence, for a sphere $\nu$ is equal to 0.5286. For irregularly shaped bodies, it may be shown that $\nu$ has a value less than that of a sphere.

Hatch and Choate[5] have pointed out that for a heterogeneous aggregate, an average value of $D$ is obtained by measuring the intercepts of particles along a fixed direction. If the particles are uniformly distributed and all particles along a given fixed direction are measured, then the distribution may be assumed to follow the curve:

$$N=\frac{\Sigma n}{\log \sigma_g \sqrt{2\pi}} e^{-(\log d-\log M_g)^2/2 \log^2 \sigma_g} . \qquad (2)$$

where $N$ is the number of particles of a size $d$, $\sigma_g$ is the geometric standard deviation and $M_g$ is the median value of the distribution. Both $\sigma_g$ and $M_g$ are constants that determine the position and shape of the distribution.† They are given by the algebraic equations

$$\log M_g=\frac{\Sigma(n \log d)}{\Sigma n}$$

and

$$\log \sigma_g=\sqrt{\frac{\Sigma\left[n(\log d-\log M_g)^2\right]}{\Sigma n}} .$$

The work entailed in the calculation of $M_g$ and $\sigma_g$ may be considerably reduced if, following the method proposed by Hatch and his coworkers, a special log-probability grid is used. As a rule, skew frequency data plot as a straight line on this type of grid. The median value $M_g$ may be directly obtained by observing the value for which 50 per cent of the particles are less than the stated size. The value of $\sigma_g$ may be determined from the grid by calculation of the following ratio:

$$\sigma_g=\frac{84.13 \text{ per cent size}}{50 \text{ per cent size}}=\frac{50 \text{ per cent size}}{15.87 \text{ per cent size}} .$$

The above follows from the probability integral.

In the problem on hand we are concerned with a comparison between known weights of an aggregate of particles and a calculated weight based upon the statistical parameters $M_g$ and $\sigma_g$. This requires a relation between these parameters and the volumetric properties of the system under consideration. Thus, if $D$ defines the diameter of a particle in the aggregate having an average volume, we have

$$D=\sqrt[3]{\frac{\Sigma(nd^3)}{\Sigma n}}$$

or, from equation 2

$$\frac{\Sigma(nd^3)}{\Sigma n}=\frac{\Sigma n}{\log \sigma_g \sqrt{2\pi}}\int_0^\infty d^3 e^{-(\log d-\log M_g)^2/2 \log^2 \sigma_g}\, d \log d$$

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† The size frequency equation above is for a skew distribution. It assumes, of course, asymptoticity of values at both extremes, a condition which is rarely true with particulate substances, but for practical purposes, as will be shown, is sufficiently accurate.

from which it may be shown

$$\frac{\Sigma(nd^3)}{\Sigma n} = e^{3 \log M_g + 4.5 \log^2 \sigma_g}$$

or reduced to the base 10

$$\log D^3 = \log M_g{}^3 + 10.3617 \log^2 \sigma_g. \tag{3}$$

*Determination of Components*

From equation 3, $D$ may be readily calculated. Hence for a two component system $\alpha$, $\beta$, the determination of the statistical parameters $M_g$ and $\sigma_g$ leads directly to an estimation of the mass of all the particles counted and measured in a given field. (That is, in any field all particles must be counted and measured with due regard to their identity. In a two-component system this implies the identification, count, and measurement of all $\alpha$ particles in a series of fields and all $\beta$ particles in other fields, assuming, of course, that the fields are representative of the sample under examination.) Thus, we may write

$$\frac{\text{Weight of } \alpha-\text{particles, } W_\alpha}{\text{Weight of } \beta-\text{particles, } W_\beta} = \frac{\nu_\alpha \rho_\alpha N_\alpha D_\alpha{}^3}{\nu_\beta \rho_\beta N_\beta D_\beta{}^3} \tag{4}$$

and if $\nu_\alpha$, $\nu_\beta$, $\rho_\alpha$, $\rho_\beta$ are known and $N_\alpha$, $N_\beta$, $D_\alpha$, and $D_\beta$ are determined the percentage composition of the two-component system is readily determined

$1/\left(\frac{W_\alpha}{W_\beta}+1\right) \times 100 =$ percentage of $\beta$ component, and $100 - 100\ W_\beta = 100\ W_\alpha$.

The extension to an $n$-component system is equally simple, although tedious, since it requires the determination of the shape factor $\nu$ and density $\rho$ for all components together less the component under determination. This procedure, however, is not always possible.

Let the components of the $n$-component system be $\alpha_1, \alpha_2, \alpha_3 \cdots \alpha_n$; we may then write symbolically for determining the $\alpha_1$ component, assuming all the $\alpha$-components taken together to be $\Sigma\alpha$.
Hence

$$\frac{\text{Weight of } \alpha_1 \text{ particles, } W_{\alpha_1}}{\text{Weight of } {}_{\Sigma\alpha} \text{ particles, } W_{\Sigma\alpha}} = \frac{\nu_{\alpha_1} \rho_{\alpha_1} N_{\alpha_1} D_{\alpha_1}{}^3}{\nu_{\Sigma\alpha} \rho_{\Sigma\alpha} N_{\Sigma\alpha} D_{\Sigma\alpha}{}^3} \tag{5}$$

Successive applications of this procedure may in certain cases be used to determine several components of a system.

*Availability of Data on $\nu$ and $\rho$*

Values of the volume shape factor $\nu$ for various minerals are generally not available from the literature. Hatch, by the procedure outlined above for determining the statistical parameters $M_g$ and $\sigma_g$ and $D$, and by substitution in the equation

$$W=\nu\rho D^3$$

obtained the following values of $\nu$.

| | |
|---|---|
| For quartz | 0.14 |
| For granite | 0.14 |
| For calcite | 0.135 |

These values are much less than the value for a sphere ($\pi/6=0.5286$). Thus, the assumption that particles are spheres may, as Hatch and Choate point out, leads to considerable errors. In the present investigations, a hypothetical value of unity was assigned as the shape factor of one component (quartz), and from an *a priori* knowledge of the densities of the components and all other factors, the relative shape factors for other components could be determined. Thus, from equation 4, assuming $\nu_\alpha=1$,

$$\nu_\beta=\frac{W_\beta\rho_\alpha N_\alpha D_\alpha{}^3}{W_\alpha\rho_\beta N_\beta D_\beta{}^3}\cdot$$

This procedure unfortunately does not yield absolute values of $\nu$ which are frequently desired as a matter of interest. In a later paper, the authors will show how the shape factor varies with size distribution ($D$ and $\sigma_g$) for various minerals.

Values for the density of a given mineral can generally be secured from petrographical handbooks. Where some question exists, however, as to the value of a given mineral or mineral aggregate, pycnometer determinations can be readily made.

## PROCEDURE USED IN PRESENT INVESTIGATION

For the purpose of this investigation, mineral powders were selected of a size range and properties so that microscopic identification was fairly simple. The minerals were all crushed and then sieved. The portion passing through a 200-mesh sieve and retained on a 325-mesh sieve was used as a stock sample. Its specific gravity was determined and it was also given a preliminary petrographic examination. Determinations were then made as follows:

A mixture of two minerals was made up by weighing out a definite quantity of each on the analytical balance so that the total weight of the sample was about one gram. The sample was then thoroughly mixed by shaking it in a small glass weighing bottle.

A slide of the sample was next prepared. A pinch of the material was transferred to the slide by means of a small knife blade. A drop of the immersion media was added and after mixing as well as possible it was covered with a 13 mm. cover glass, taking care that air bubbles had been excluded.

The slide was then examined with the petrographic microscope using a 16 mm. objective (10×). The microscope was also equipped with a filar micrometer. All the particles in a field were identified, measured, and counted. The diameter of the particle read off was its maximum projection on a given straight line which was used as a base line for all measurements. With the aid of a person to take down the readings on the filar micrometer, it took about three hours for the microscopic examination. This is very short, indeed, when we consider the time required for a chemical analysis.

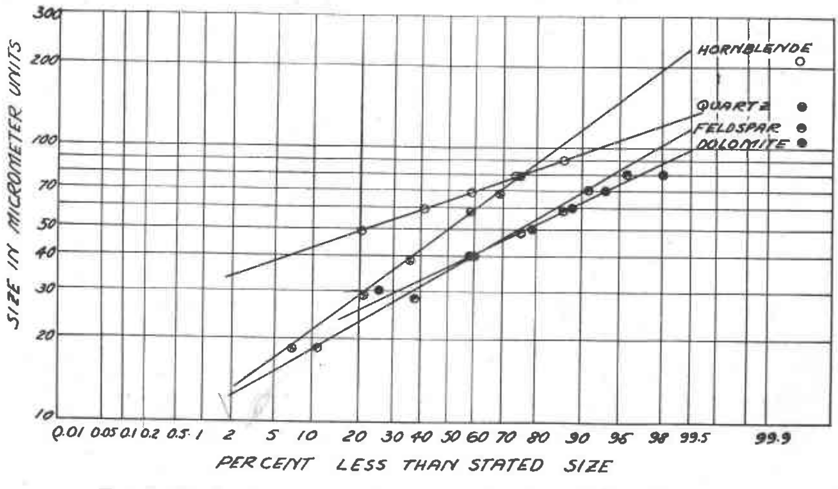

FIG. 1. Size frequency summation curves for determining $M_g$ and $\sigma_g$

## DATA AND RESULTS

Table 1 gives the necessary data for the four minerals studied in order to determine their percentage composition when mixed with one another. $M_g$ and $\sigma_g$ are read off from the curve in Fig. 1. The average diameter $D$ is then calculated from equation 3. $\nu$ is obtained from equation 4 by starting with a mineral system $\alpha_\beta$ whose percentage composition and $\nu_\alpha$ are known.

TABLE 1.—STATISTICAL CONSTANTS FOR VARIOUS PARTICULATE MINERALS STUDIED

| Mineral | Density ($\rho$) | Geom. med. ($M_g$) | Geom. S. D. ($\sigma_g$) | Average diameter* ($D$) | Relative volume shape factor $\nu$ quartz=1 |
|---|---|---|---|---|---|
| Quartz | 2.65 | 63.0 | 1.4 | 74.6 | 1.000 |
| Hornblende | 3.22 | 49.0 | 1.9 | 90.9 | 0.157 |
| Feldspar (orthoclase) | 2.57 | 35.0 | 1.6 | 51.0 | 1.86 |
| Dolomite | 2.85 | 35.0 | 1.6 | 47.6 | 1.36 |

* In micrometer units. One micrometer unit = 1.1 microns.

It is to be noted that although all of these minerals have been crushed and sieved in the same way, their diameters show large differences. The average diameter of hornblende is 90.9 while for dolomite it is only 47.6. Hornblende gave a standard deviation of 1.9 while for quartz it is 1.4. It may therefore readily be seen how assumptions concerning uniformity of size and shape[6,7] will lead to erroneous results in estimations of volume—or weight—percentages of the components of a particulate system.

TABLE 2.—RESULTS OF DETERMINATIONS OF VARIOUS PARTICULATE SYSTEMS STUDIED

| Sample No. | Mineral system $\alpha$ - $\beta$ | No particles $\alpha$ | No particles $\beta$ | Value of $\alpha$ determined (Per cent) | Actual value of $\alpha$ (Per cent) | Remarks |
|---|---|---|---|---|---|---|
| H-1 | Quartz-Hornblende | 375 | 132 | 89.0 | 89.6 | |
| H-2 | Quartz-Hornblende | 103 | 100 | 75.8 | 73.1 | |
| H-3 | Quartz-Hornblende | 254 | 274 | 72.5 | 73.1 | Check on H-2 |
| H-4 | Quartz-Hornblende | 255 | 246 | 74.6 | 73.1 | Check on H-2 |
| H-5 | Quartz-Hornblende | 200 | 228 | 71.3 | 73.1 | Check on H-2 |
| H-6 | Quartz-Hornblende | 200 | 519 | 52.3 | 49.5 | |
| H-7 | Quartz-Hornblende | 100 | 2651 | 9.2 | 10.0 | |
| F-1 | Quartz-Feldspar | 92 | 190 | 56.2 | 50.3 | |
| F-2 | Quartz-Feldspar | 193 | 203 | 71.6 | 69.3 | |
| F-3 | Quartz-Feldspar | 595 | 200 | 9.9 | 10.0 | |
| F-4 | Quartz-Feldspar | 330 | 106 | 9.9 | 10.0 | Check on F-3 |
| D-1 | Quartz-Dolomite | 50 | 197 | 50.6 | 50.6 | |
| D-2 | Quartz-Dolomite | 198 | 211 | 79.1 | 79.0 | |
| D-3 | Quartz-Dolomite | 450 | 200 | 90.1 | 90.1 | |
| D-4 | Quartz-Dolomite | 65 | 361 | 42.1 | 40.7 | |
| DF-1 | Dolomite-Feldspar | 217 | 211 | 40.4 | 48.9 | |
| DF-2 | Dolomite-Feldspar | 362 | 200 | 54.4 | 54.3 | |
| DF-3 | Dolomite-Feldspar | 368 | 201 | 54.7 | 54.3 | Check on DF-2 |

Table 2 shows the various combinations of minerals which were determined. Each one of these samples was in turn used to calculate the shape factor $\nu_\alpha$ so that the value of $\alpha$ determined is based on the average value of $\nu_\alpha$.

A further check on the method is given by the dolomite-feldspar samples since the value of $\nu$ is obtained from quartz-dolomite and quartz-feldspar instead of from an additional dolomite-feldspar sample.

It is necessary to count enough particles of a component so that its size distribution curve (Fig. 1) does not change. Two hundred particles are usually sufficient. Once this curve has been determined for each component of a given system, it is only necessary to count enough particles so that the ratio of $N_\alpha$ to $N_\beta$ is constant. For example, in sample *D*-1, only fifty quartz particles and 197 dolomite particles were counted.

## SUMMARY

The results obtained in this study show, first, how the shape factor for a mineral may be obtained; second, how the size distribution curve can be plotted; and finally, how with this data the percentage by weight of any constituent may be determined by making a count of the number of particles present. The method is applicable to all powders and rock dusts provided that they have a uniform distribution and that they are large enough to be counted and identified.

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