

*PROCEDURE FOR CLAY MINERAL ANALYSES USED IN THE SEDIMENTARY PETROLOGY LABORATORY OF THE U.S. GEOLOGICAL SURVEY**

By JOHN C. HATHAWAY

U.S. Geological Survey, Beltsville, Md. U.S.A.

[Read 4th November, 1955]

ABSTRACT

The procedure used for fractionation of soils, rocks, and sedimentary materials involves separation of the clay (less than 2 microns) and silt (2 to 62 microns) by centrifugation. Randomly oriented powders and oriented aggregates of these materials are examined using X-ray diffraction as the principal method of analysis.

*Publication authorized by the Director, U.S. Geological Survey.

INTRODUCTION

Part of the work of the sedimentary petrology laboratory of the U.S. Geological Survey requires the identification, and estimation of quantity, of clay minerals in rocks, soils, and other sedimentary materials. The following procedure has been developed for making such analyses.

FRACTIONATION PROCEDURE

A sample collected or received by the laboratory is split and a portion is retained for reference. The remainder of the sample is disaggregated by crushing or by grinding in a disc grinder to pass a 230 mesh screen (0.062 mm openings) if the sample is highly consolidated. About 100 grams of this material, together with a small amount of sodium metaphosphate or sodium tetrphosphate, are placed in a soil dispersion can and stirred from 10 to 15 minutes by a mechanical stirrer. The material is then wet-sieved with about 600 ml of distilled water through a small 230 mesh screen supported by a funnel into a 1000 ml cylinder. The cylinder is placed in an end-over-end shaker and tumbled at about 16 r.p.m. for at least 2 hours. The cylinder is then allowed to stand for the length of time calculated from Stokes' law to be necessary for all particles larger than 2 microns equivalent spherical diameter to settle to the bottom and, if no flocculation has occurred, the suspended material is decanted into a 1000 ml Berzelius beaker. If the sample has flocculated, it is washed by repeated centrifuging until dispersion can be effected. The

suspension is then allowed to stand and is decanted into a beaker as described. Excess water is withdrawn from the suspension by a filter candle under vacuum. This filter is placed in the clay suspension and after a coating of clay has collected around the candle, the vacuum is released and the clay sloughs off or is easily removed with a rubber scraper. Meanwhile, the material that has settled to the bottom of the cylinder is transferred to a 250 ml centrifuge bottle and distilled water is added to fill the bottle. The bottle is shaken by hand, placed in the centrifuge, and spun at 600 r.p.m. for a length of time calculated to remove particles larger than 2 microns equivalent spherical diameter from suspension. The formula from which this time is calculated is derived from Stokes' law.

$$T = \frac{\eta \log_{10} \left(\frac{R_2}{R_1} \right)}{3.81 r^2 N^2 (\rho - \rho_0)} + \frac{2 (t_a + t_d)}{3}$$

T = total time in seconds

t_a = time of acceleration of centrifuge¹

t_d = time of deceleration of centrifuge¹

η = viscosity in poises

R_1 = initial distance of particle from axis of rotation²

R_2 = final distance of particle from axis of rotation³

r = radius of the particle in cm

N = angular velocity in revolutions/sec

ρ = density of the particle in grams/cm³ ⁴

ρ_0 = density of the medium in grams/cm³

1. Acceleration and deceleration are controlled by the centrifuge voltage control and the brake, respectively, and are assumed to be constant. 2. This distance is determined by the level of the liquid in the centrifuge bottle, as the last particle of the given radius r to be removed will start at the surface of the liquid. 3. This distance is determined by the level of accumulated sediment in the centrifuge bottle. The value is adjusted to allow 1 cm of sediment to accumulate. 4. A density of 2.65 is assumed. This would assure the removal of most of the quartz if a 2μ separation is made although larger particles of less dense material would remain in suspension.

The supernatant liquid is decanted into the Berzelius beaker mentioned above, the centrifuge bottle is refilled with distilled water, shaken up, and centrifuged again. This process is repeated until the supernatant liquid is reasonably clear. After the filter candle has removed all but 200 ml of water from the suspension, the sample is stirred with a motor-driven brush to disperse lumps of clay which form around the filter candle. A portion of the suspension is then passed through a calcium ion-exchange resin column in order to saturate the cation exchange positions with Ca^{2+} . Better orientation of the clay particles usually results when oriented aggregates are prepared

from such suspensions and the clay films show less tendency to curl on drying or when heated. The oriented aggregates are prepared from this portion by placing 2 to 4 ml of the suspension on each of three glass slides, 25×45 mm, with an automatic pipette. Surface tension at the edges of the slides effectively holds the suspension on the slide while the water evaporates. No attempt is made to standardize the amount of solid placed on each slide because optimum thickness of clay from the standpoint of degree of orientation, tendency of the clay film to curl, and evenness of distribution of clay on the slide, vary from sample to sample. A 16-ml portion of the Ca^{2+} treated clay suspension is preserved in a specimen vial so that additional slides may be prepared if the original slide should curl on drying or heating or be lost through accident. Meanwhile the water is removed from the remaining suspension by the filter candle, and the clay allowed to dry at room temperature. The clay is then crushed and placed in 8 ml specimen vials. The silt fraction (2 to 62 microns) is also allowed to dry and is placed in a sample envelope or vial.

EXAMINATION PROCEDURE

X-ray analysis. At least six X-ray diffractometer patterns are made for each sample, as follows:

- | | | |
|---------------|---|---|
| Clay fraction | { | 1. Untreated oriented aggregate |
| | | 2. Oriented aggregate treated with ethylene glycol |
| | | 3. Oriented aggregate heated to 400°C |
| | | 4. Oriented aggregate heated to 500°C |
| Silt fraction | { | 5. Randomly oriented powder |
| | | 6. Randomly oriented powder |

After pattern No. 1 in the above list is made, the slide is treated with ethylene glycol either by spraying the surface with the liquid or by a vapor pressure method (Brunton, 1955) in which the slide is allowed to stand in a desiccator containing ethylene glycol at about 60°C for at least 2 hours. The same chart on which pattern No. 1 was made is used to record pattern No. 2 but with a different colour pen placed in the recorder, (Jeffries, 1949) and with the zero point in terms of counts per second advanced slightly to avoid confusion of the patterns.

An additional slide is placed in a muffle furnace, heated to the appropriate temperature for at least half an hour, air quenched, and a diffractometer pattern made immediately on the same chart as Nos.

1 and 2, again with a different colour pen and with the zero point shifted. If any delay occurs between the removal of the slide from the furnace and the making of the diffractometer pattern, the slide is placed in a desiccator at 0 per cent relative humidity to prevent rehydration of the clay.

The randomly oriented powders (patterns 5 and 6) are recorded on a separate chart from the other four patterns. These powders are mounted in an aluminum slide 2 mm thick with a rectangular opening, 10×41 mm, that passes completely through the slide. The method is similar to that described by McCreery (1949). The face of the slide is covered by a glass slide fastened to the aluminium with cellophane tape and the opening is filled from the back by brushing the powder through a 200-mesh sieve (74-micron openings) into the opening. A second glass slide is then taped to the back of the mount, the slide is turned over and the glass covering the face is removed. Preferred orientation is greatly lessened because the clay fraction consists of small pieces that are roughly equidimensional and therefore tend to assume a random orientation even though the flake-shaped clay mineral grains in a given piece may show a preferred orientation. If the silt contains minerals with irregularly shaped particles, such as quartz, preferred orientation can be lessened for that fraction because the irregular shapes tend to disrupt a regular arrangement of the flake-shaped particles.

Additional patterns are made for a sample if, in the above patterns, ambiguities occur that can be resolved by further treatments. These treatments may include further heating at temperatures other than 400° or 500°C , or treatment with HCl to determine if any of the minerals are soluble in this acid.

Some clay fractions in which there may be a large range of particle sizes may exhibit a stratification of the various sizes in the oriented aggregate, as the larger particles tend to settle on the slide first (Schultz, 1955). If the clay film is relatively thick this layer of larger particles may be obscured by the layer of fine particles overlying it and the diffraction intensity for the larger particles may then be seriously reduced. For this reason it is advisable to invert the clay film of many of the thick oriented aggregates and make a separate diffractometer pattern of the back of the aggregate. The inverting of the clay film is accomplished by the use of cellophane tape with adhesive on both sides of the tape. As this tape has paper backing on one side, the unbacked side may be pressed down on the surface of the aggregate and the clay film stripped from the glass

slide. The paper backing is then removed from the tape and the exposed adhesive is pressed against the slide. The layer of clay that was formerly adjacent to the glass is now exposed and if care has been taken to prevent wrinkles from developing in the tape when it is pressed on the slide, little intensity is lost in the X-ray pattern from lack of flatness of the specimen surface.

In the sedimentary petrology laboratory the X-ray diffractometer is used primarily in the examination of clays and the X-ray powder cameras are used principally in the examination of nonclay minerals. However, the sample preparation procedures outlined above can be used with either type of instrument. Oriented aggregates may be used in the powder camera as slivers cut from the clay film on the glass slide. One of the advantages of the powder-camera technique is that it requires a much smaller sample than the X-ray diffractometer.

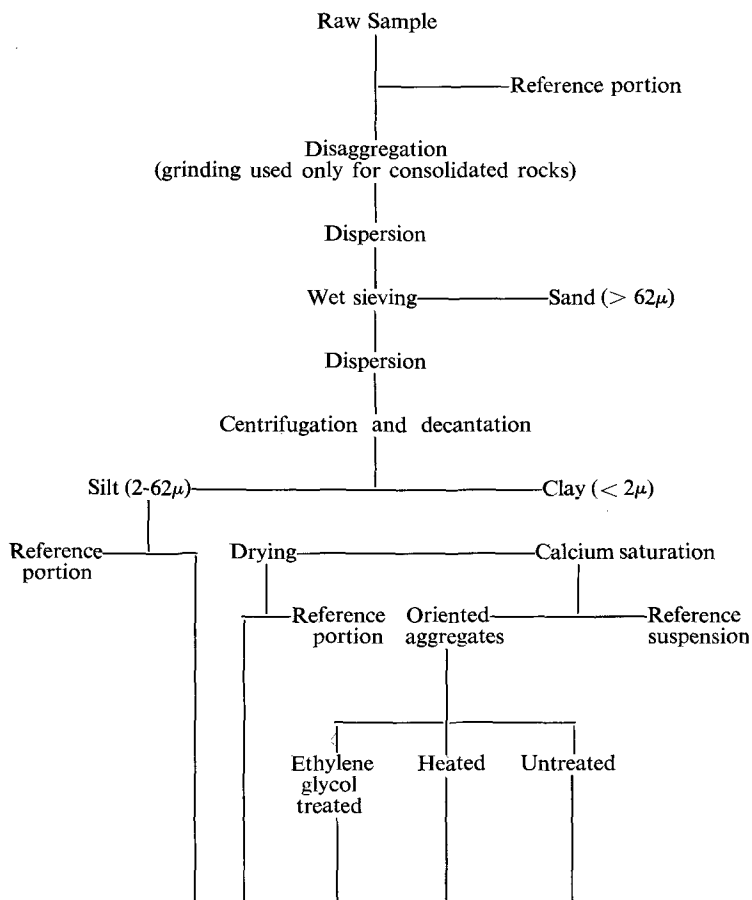
Differential thermal analysis. Differential thermal analyses are not made for all clay samples examined in the laboratory. Portable field d.t.a. units (Parker et al., 1956) are usually used where such analyses are made, but curves from standard laboratory units can be obtained for a sample if needed.

Other methods of examination. The laboratory is equipped for examination of samples with the petrographic microscope, visual arc spectroscope, by staining techniques, and by partial chemical analysis, including ion-exchange capacity determinations. Other methods, for which the laboratory is not equipped but which are available to it, include complete chemical analysis, spectrographic analysis, electron microscopy and diffraction, and infrared absorption spectrography.

SUMMARY

The steps in the preparation and examination of materials for determination of their clay mineral composition are summarized in diagrammatic form in Table 1. The products of the basic fractionation procedure can be used in any of numerous methods of examination, but primary reliance is placed on X-ray powder diffraction for routine clay mineral analyses.

TABLE 1



Material available for X-ray or other methods of examination.

REFERENCES

- Brunton, George 1955. *Amer. Min.*, **40**, 124-126.
 Jeffries, C. D. 1950. *Proc Soil Sci. Soc. Amer.*, **14**, 378-379.
 McCreery, George, L. 1949. *J. Amer. Ceram. Soc.*, **32**, 141-146.
 Parker, C. J., Hathaway, J. C. and Blackmon, P. D. 1956. *Bull. U.S. geol. Survey*, 1021-G.
 Schultz, Leonard, G. 1955. *J. Sediment Petrol*, **25**, 124-125.