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THE DENSITY SEPARATION OF CLAY MINERALS IN THALLOUS FORMATE SOLUTIONS*

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With the many recent improvements in identification of clay minerals by *x*-ray diffraction, the main problem in clay mineral analysis has become one of quantitative analysis. *X*-ray diffraction as a quantitative method is hindered by such sample variables as crystal perfection, orientation, particle size, and chemical composition. To obtain more reliable quantitative results, additional information, such as cation exchange capacity, sorption of polar liquids, elemental analysis, and differential thermal analysis are often considered. But even use of all of these methods will not necessarily give correct quantitative results, because percentage composition must be determined in terms of a set of of standard minerals with relatively ideal mineral properties. These standard minerals are seldom, if ever, identical to the clay minerals in the sample. On the relatively rare occasions when the *precision* of analyses has been determined, the data are frequently presented as representing *accuracy* when, in reality, the accuracy is almost always unknown in quantitative clay mineral analysis.

At present, the only way in which one could quantitatively analyze a natural mixture of clay minerals without involving tenuous assumptions as to some of their chemical or physical properties, would be to separate the individual mineral components and weigh them. To this end, differential starch precipitation (Beavers and Marshall, 1951) and retention by ion exchange resins (mentioned by Wiklander, 1951) did not show initial promise as clay mineral separation methods. Differential absorption in nitrobenzene-tetrabromethane and continuous flow electrophoresis showed only slight initial promise and were not extensively tested. Efforts were then concentrated on the one method which did show initial promise, the density separation of clay minerals in thallous formate solution.

MATERIALS AND METHODS

Kaolinite H-2, montmorillonites H-11, H-23, H-24, and H-26, and illite H-36 were obtained from Wards Natural Science Establishment;

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similar materials have been extensively studied (API, 1951). Kaolinite 81 (England) and vermiculite 189 (Libby, Montana) were also obtained from Wards and kaolinite 91 (Edgar, Florida) from the Edgar Plastic Kaolin Company.

In order to determine the apparent densities of clay minerals, approximately 0.1 gm. clay samples were added to about 10 ml. of thallous formate solution of suitable density in 15 ml. culture tubes. Interaction between the clay and thallous formate appeared to be complete after about 30 minutes. Centrifuging at about 1000 rpm. for 5 minutes completed clay movement (either up or down). Tl^+ was removed from the exchange sites* by precipitating the Tl^+ as TlCl and then oxidizing the Tl^+ to Tl^{+++} with bromine. $TlCl_3$ is water soluble, and was removed by centrifuge washing. Densities of Tl^+ solutions were determined by weighing a known volume.

Density Separation in Thallous Formate Solution

This method is based on density variations acquired by clay minerals in concentrated thallous formate solutions. Several non-clay minerals are known to increase their densities in Clerici solution (thallium formate-malonate mixture). Hutton (1950) also noted a tendency for the density of montmorillonite to increase. Rodda (1952) made practical use of this to separate a mixture of kaolinite from montmorillonite with Clerici solution of specific gravity 3.55. At this specific gravity, the kaolinite floated as anticipated, but the montmorillonite (normal specific gravity of about 2.6) sank anomalously, presumably owing to adsorption of the thallium.

Kaolinite—Montmorillonite Mixtures

The densities acquired by several layer silicates in thallous formate are shown in Table 1. Illite and vermiculite sank in solutions of specific gravity 3.00 and lower and floated in solutions of specific gravity 3.10 and higher, whereas kaolinite floated and montmorillonite sank over the whole specific gravity range tested. The easiest separation in this group appeared to be that of kaolinite from montmorillonite. To this end, equal amounts of three pairs of pure kaolinite and montmorillonite (kaolinite H-2 and montmorillonite H-23, kaolinite 81 and montmorillonite H-24, kaolinite H-2 and montmorillonite H-11) were mixed *dry*. Approximately 0.1 gm. portions of the mixtures were added to thallous formate solutions of 3.2 specific gravity. The mixtures were allowed to

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* Necessary because it was found that Tl^+ saturation essentially eliminates the diagnostic (001) peak of montmorillonite; the mechanism is to be discussed in another publication.

TABLE 1. DENSITIES ACQUIRED BY LAYER SILICATES IN THALLOUS FORMATE SOLUTION

Mineral	Float (+) or sink (−) in Tl^+ formate of specific gravity:				
	2.6	2.8	3.0	3.2	3.4
Kaolinite 91	+	+	+	+	+
Illite H-36	−	−	−	+	+
Vermiculite 189	−	−	−	+	+
Montmorillonite H-26	−	−	−	−	−

separate with no stirring. All three kaolinite-montmorillonite mixtures split into two roughly equal components, one of which sank and the other floated. Floating material was removed with a suction-tube device and excess thallous formate was removed from both components by centrifuge washing prior to *x*-ray diffraction analysis.

A rather good separation of kaolinite and montmorillonite was achieved as was indicated by the *x*-ray diffraction patterns (not shown). In some cases, small percentages of kaolinite or montmorillonite remained in the wrong fraction, but these presumably could be removed with further separations. Similar results were obtained at specific gravity 3.4 and neither solution pH nor previous ion saturation of the clay appeared to affect the separation.

Effect of Agitation

Agitation of any kind diminished the completeness of separation and a relatively prolonged or violent agitation frequently prevented any separation at all. The mineral particles would no longer move independently; instead the whole mass moved either up or down, depending on the solution density and the dominant mineral component. Apparently, agitation causes the montmorillonite component to create a network (perhaps like that shown by Kittrick, 1957) that completely envelopes the kaolinite component, resulting in the movement of kaolinite and montmorillonite as a unit. The same result was obtained when the montmorillonite and kaolinite were mixed *wet* prior to the separation attempt. No way was found by which this entrapment could be eliminated, so the method as it now stands appears to have no practical value for the separation of clay minerals.

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A FAYALITE-BEARING PEGMATITE, BURNET COUNTY, TEXAS

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Fayalite has been reported from numerous localities throughout the world, and it is associated with quartz in some igneous rocks and in a few pegmatites (Shibata, 1937).

A fayalite-bearing pegmatite is located half a mile N. 78° W. from the north end of Buchanan Dam on the shore of Lake Buchanan, Burnet County, Texas. The pegmatite strikes N. 50° W., dips 50° to 80° NE., averages 4 to 6 feet wide, and is exposed for about 120 feet when the lake surface elevation is less than 1,010 feet above sea level. The country rock is pink Precambrian granite composed mostly of pink microcline, quartz, biotite, and hornblende.

There are two readily discernible zones in the pegmatite, an outer zone of perthitic pink microcline, in which there are microcline crystals up to 8 inches in diameter, and an inner zone or core of smoky quartz. The quartz and microcline are graphically intergrown at several places along the boundary between the two zones.

The fayalite occurs in anhedral masses and rough tabular crystals in the quartz core of the pegmatite. Crystals 6 inches long and weighing in excess of 2 pounds have been found, but the average size is about 2 inches long and the average weight between 3 and 4 ounces. On fresh surfaces the fayalite is lustrous black and on weathered surfaces dark brown.

X-ray diffraction with copper K_α radiation shows the following prominent peaks in decreasing order of intensity: 2.833, 2.502, 2.567, and 5.250 Å.

Properties are as follows:

Biaxial (−)
$r > v$ distinct
$\alpha = 1.819$, $\beta = 1.858$, $\gamma = 1.868$
$\gamma - \alpha = 0.049$
$2V = 53°$
Specific gravity (28° C.) $= 4.22 \pm 0.02$