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ERROR DUE TO SEGREGATION IN QUANTITATIVE CLAY MINERAL *X*-RAY DIFFRACTION MOUNTING TECHNIQUES[1]

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ABSTRACT

Experimental study of seven common mounting techniques for quantitative analysis of clays by *x*-ray diffraction showed an acceptable precision, or reproducibility (about $\pm 10\%$) for all techniques. Accuracy, or closeness to "true" value, however, varied as much as 250% in the four techniques involving particle settling in aqueous solutions. Use of these techniques resulted in a surface segregation of montmorillonite due to its smaller size and therefore lower (1/100) settling velocity than kaolinite or illite. This segregation was demonstrated by (1) analysis of samples with the surface layer removed and (2) top and bottom analysis of samples mounted on *x*-ray-transparent plastic membrane. The four techniques not acceptable for clay mineral analysis include: centrifuge-on-glass slide and centrifuge-on-ceramic tile techniques; pipette- or dropper-on-glass slide technique; and beaker-on-glass slide technique. The three mounting techniques acceptable for clay mineral analysis with regard to precision and accuracy are: smear-on-glass slide, suction-on-ceramic tile and powder press techniques.

INTRODUCTION

Clay minerals, which constitute the major portion of most sediments and soils and of many rocks, are studied mainly by *x*-ray techniques using either basal or randomly oriented clay specimens. Use of the basal oriented specimens has become widespread for most general sedimentary or soil clay mineral studies for several reasons: (1) the diagnostic basal reflections are emphasized and non-basal reflections are suppressed, thereby simplifying the overall pattern; (2) the sensitivity is increased many times, allowing detection of small amounts of poorly crystalline materials.

In order to determine which of a number of common mounting techniques should be used for quantitative clay analysis, subsamples of the $<2\mu$ fraction of several sediments were mounted using these techniques. Significant differences observed among the test mountings encouraged a detailed study to determine (1) which mounting technique was most precise (best reproducibility), and (2) which technique was most accurate ("truest" value).

METHODS OF STUDY

Sample preparation. Size fractions of clay minerals separated for analysis vary with the field of interest. English-speaking geologists and oceanog-

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raphers use the $<2\mu$ fraction, while soil scientists subdivide the $<2\mu$ fraction into two or three sub-fractions. Russian geologists, oceanographers and soil scientists use the $<1\mu$ particle size fraction. The $<2\mu$ size fraction was used for all experiments performed in this study. All size fractionations were done in distilled water by decanting, and settling times were determined using Stokes' law.

Completeness of clay removal from, and degree of dispersion of the suspensions were monitored with an ultra-microscope, against a black background, using a strong, narrow light beam directed from the side.

The four samples used in the experiments are identified as:

Sample A: a high montmorillonite clay with lesser amounts of illite, kaolinite, and chlorite (Scripps Institution of Oceanography: RIS-5V, 0–10 cm., 20°19′N, 117°29′W, water depth: 4010 m.);

Sample B: a high kaolinite and mica clay with lesser amounts of montmorillonite and chlorite (Gibbs: Amazon estuary, 0·114B);

Sample C: an intermediate montmorillonite clay with kaolinite and lesser amounts of illite and chlorite (Gibbs: South Atlantic, 0·105B);

Sample D: an artificial mixture of American Petroleum Institute standards consisting of 25% montmorillonite (API 22), 50% illite (API 35), and 25% kaolinite (API 7).

A total of sixty specimens were prepared from these samples using thoroughly mixed suspensions of each. In methods involving settling in aqueous solutions, the concentration of the suspension was varied and both the dispersed and flocculated states were tested.

The seven mounting methods investigated were selected as being the basic methods from which many of the techniques available are actually variations. A general summary of mounting methods is given in Chapter 1 of Brown (1961) and also by Kittrick (1961). Discussion of the mounting methods used in this study follows.

(1) *Smear-on-glass slide.* This technique was improved by using a spatula made of a 12 mm ×30 mm rectangular piece of clear plastic 0.2 to 0.3 mm thick mounted in a plastic holder so that the amount extending could be changed depending on the consistency of the clay and the flexibility of the plastic. The thick clay paste was placed along the edge of a 25 mm wide glass slide and spread across the slide in a thin, even layer with a single stroke with the spatula.

(2) *Suction-on-ceramic tile.* A 2 to 3 cm deep clay suspension was placed on an unglazed ceramic tile and the liquid portion was drawn through the tile by a vacuum from below (in less than five minutes), leaving the clays on the tile. Porous stainless steel slides proved unsatisfactory since the finest pore size available (5μ) allowed $<2\mu$ material (flocculated suspensions included) to pass through.

(3) *Pipette-on-glass slide.* The clay suspension was transferred by pipette or dropper to a glass slide and dried at room conditions. This required from forty minutes to four hours.

(4) *Beaker-on-glass slide.* A 2 to 3 cm deep clay suspension was placed over a glass slide at the bottom of a 100 ml beaker and allowed to evaporate to dryness under a bank of infrared heat lamps at such distance that the surface temperature never exceeded 40° C.

(5) *Centrifuge-on-glass slide.* A 5 cm deep clay suspension was placed over a glass slide

at the bottom of a flat-bottomed centrifuge shield and centrifuged at 1600 G for 60 minutes to assure complete sedimentation. The clear water was carefully decanted using a pipette, and the sample was dried at room conditions.

(6) *Centrifuge-on-ceramic tile.* A 2 to 5 cm deep clay suspension was placed on a ceramic tile in a holder that allowed the liquid to pass through the tile into a reservoir below, leaving the clays on the tile when centrifuged at 1500 G for 60 minutes.

(7) *Powder press technique.* Approximately 150 mg of thoroughly mixed sample was loaded into an aluminum holder from the back, with the surface to be exposed to the *x*-ray beam placed face downward. For randomly-oriented specimens, the surface to be exposed was placed on filter paper and the sample was lightly packed with low pressure (10 psi). For partially-oriented specimens, the surface to be exposed was placed on polished metal and the sample was packed with one high-pressure (180 psi) piston stroke in an arbor press.

All slides were glycolated by the vapor method of Brunton (1955) for at least 1.5 hours immediately before analysis.

In order to obtain comparable results from the different techniques, the area exposed to the *x*-ray beam was maintained at 21 mm$\times$10 mm.

X-RADIATION PROCEDURE

The specimens were *x*-rayed on a standard Norelco wide-angle *x*-ray diffractometer with geiger counter using nickel-filtered copper Kα radiation at 35 Kv and 20 Ma. Scanning speed was $\frac{1}{2}°2\theta$ per minute and chart speed was $\frac{1}{2}$ inch per minute, giving $1°2\theta$ per inch for all oriented specimens. This reduced the rerun error to $\pm 6\%$ of the measured mean peak area above the background, computed at a 95% confidence level. For powder mounted specimens, a scanning speed of $\frac{1}{8}°2\theta$ per minute was used. Peak area was measured (using a polar planimeter) since the amount of a mineral present is more closely related to peak area than to peak height, although results varied only slightly when peak height was measured. Measurements were made of 17 Å (montmorillonite), 10 Å (illite) and 7 Å (kaolinite and chlorite) peaks.

RESULTS

The results of quantitative *x*-ray determinations of samples A and B are shown in Figs. 1 and 2. The peak areas were compared by computing ratios of 17 Å/7 Å (montmorillonite relative to kaolinite and chlorite) and 17 Å/10 Å (montmorillonite relative to illite) peaks. These ratios are indicated for each specimen by a white dot in a black bar, with the horizontal line through the bar representing the mean. Percentages calculated to show the magnitude of the difference between each mean and the powder press technique mean are given at each mean line.

Precision. The precision, or reproducibility, of each method is roughly represented by the length of the black bar. All of the basic techniques investigated show a generally adequate precision of about $\pm 10\%$ of each

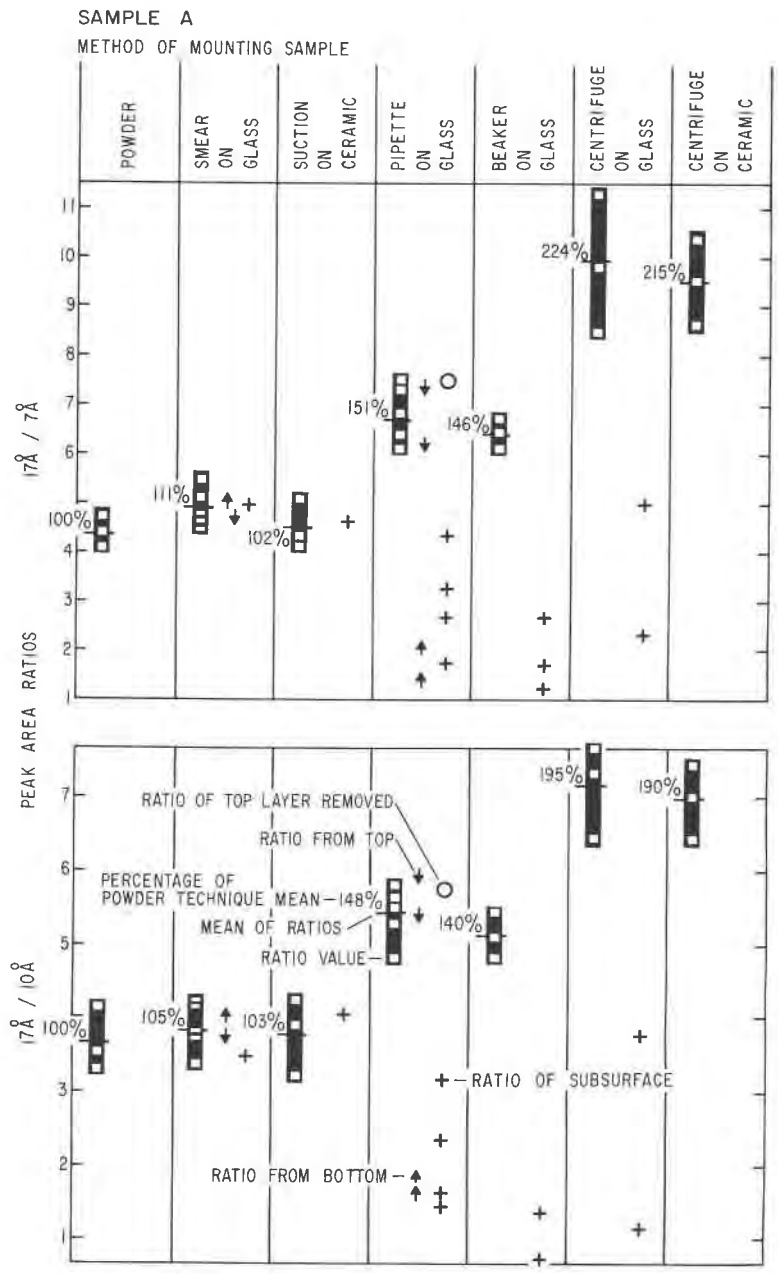

FIG. 1. Peak area ratios of Sample A, mounted by various methods. Symbol explanation is included in the figure.

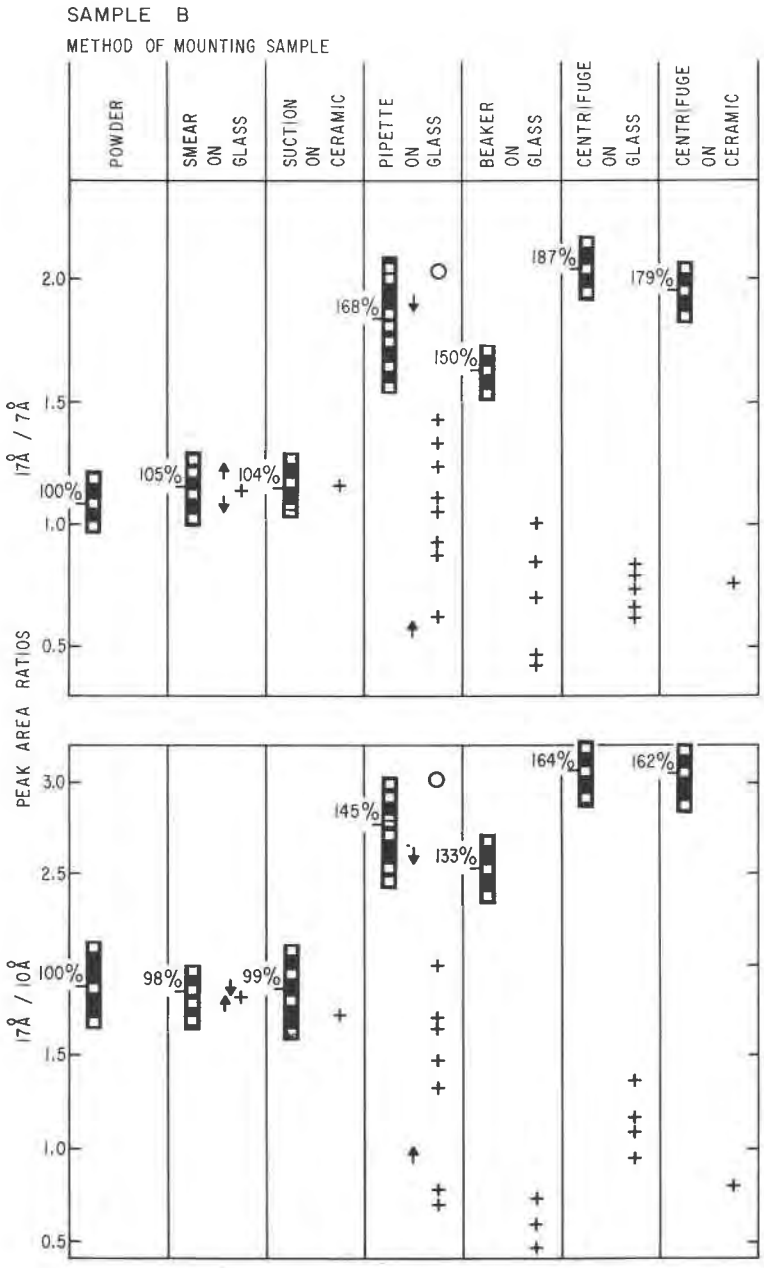

FIG. 2. Peak area ratios of Sample B, mounted by various methods. Symbols are the same as those in Fig. 1.

mean. It is possible to improve this precision by perfecting the control of the physical processes involved during mounting: settling and drying times, amount of pressure, centrifuge speed, etc.

Accuracy. The accuracy, or closeness to "true" value, of the various methods differs consistently, however, to a degree warranting consideration of the use of some of the methods. To demonstrate the magnitude of the discrepancies in results obtained by the various techniques, the powder technique was chosen as the reference to which the other techniques were compared. The smear-on-glass and suction-on-ceramic tile techniques produce peak area ratios not significantly different from one another, nor from those of the powder press technique, for both samples A and B (Figs. 1, 2). The pipette and beaker technique peak area ratios cluster at a higher montmorillonite content, approximately 133% to 168% of the powder technique value. The peak area ratios obtained using the two centrifuge techniques group at a still higher level, approximately 162% to 224% of the powder technique value. Similar plots (not shown) of the 10 Å/7 Å peak area ratios for both samples A and B indicated a higher concentration (about 125% of the powder technique ratio) of illite relative to the 7 Å minerals for the pipette, beaker and centrifuge techniques compared to the powder, smear, and suction techniques.

In order to determine if the high montmorillonite trend in some techniques is as consistent as that observed in samples A and B, the $<2\mu$ size fractions of additional samples, C and D, were studied by smear-on-glass and pipette-on-glass techniques. The results are shown in Table 1.

The trend of montmorillonite ratios relative to 10 Å and 7 Å minerals is therefore observed to be consistently higher (120% to 247%) for the pipette technique than for the smear technique in samples C and D. Lesser, but significant differences occur in the 10 Å/7 Å peak area ratios, with the pipette specimen again higher than the smear specimen.

The results of a systematic comparison of seven common mounting techniques on four samples of widely differing nature showed higher amounts of montmorillonite relative to 10 Å and 7 Å minerals in those techniques which depend upon settling through an aqueous solution. It is proposed that this large error is due to surface segregation of the smallest clay particles (mainly montmorillonite) caused by the different settling velocities of the various minerals in those mounting techniques involving settling in aqueous solutions.

Varying the concentrations of suspensions influenced the surface segregation only slightly in supplementary tests. With very thick suspensions, flocculation generally occurs, which, with the accompanying settling interference and quicker drying, reduces, but does not eliminate the segregation.

TABLE 1. PEAK AREA RATIOS FOR SAMPLES C AND D

	Peak Area Ratios	Mounting Techniques		Dropper / Smear ×100
		Smear	Dropper	
Sample C (0105B)	17 Å/7 Å	3.60	3.82	
		3.35	4.55	
		av. 3.48	av. 4.18	120%
	17 Å/10 Å	8.9	12.75	
		7.9	10.20	
		av. 8.4	av. 11.65	139%
	7 Å/10 Å	2.20	3.20	
		2.60	3.52	
		av. 2.40	av. 3.36	139%
Sample D (API)	17 Å/7 Å	1.36	3.25	
		1.40	2.81	
		av. 1.35	av. 3.03	220%
	17 Å/10 Å	3.62	8.50	
		3.19	7.51	
		3.64		
		av. 3.58	av. 8.00	247%
	7 Å/10 Å	2.67	2.90	
		2.49		
		2.64	2.81	
		av. 2.60	av. 2.86	110%

All flocculation experiments run using pipette and beaker-on-glass techniques produced unfavorable results because the liquid evaporates and leaves a salt deposit of the flocculant ($AlCl_3$ or $MgCl_2$). The centrifuge methods, in which the supernatant solution could be decanted off, resulted in a wide scattering of peak area ratios. Controlling the degree and rate of flocculation is difficult, since both vary from sample to sample due to different exchange cations, amounts of organic material, oxide coatings, etc.

Supporting Evidence. Additional support for the proposed explanation of the discrepancies observed due to mineral segregation by settling in the suspension comes from a consideration of the following.

(1) *Mineral settling velocities.* The size distribution of the clay minerals produces segregation in the mounted specimens according to their settling velocities in aqueous solutions. The $<4\mu$ fraction showed a greater degree of segregation than the $<2\mu$ fraction. The $<1\mu$ fraction showed a slightly lesser degree of segregation than the $<2\mu$ fraction. The settling times at 25° C. for particles in the $<2\mu$ fraction, calculated by Stokes'

law, are as follows:

Diameter in μ	2	1	0.5	0.2	0.1
min/cm	41	162	650	4040	16000

The diameters of clay particles as determined by electron microscope studies (Grim, 1953) are, for kaolinite: average, 1μ; range, 0.3 to 4μ; for illite: average, not given; range, 0.1 to 0.3μ; and for montmorillonite: average, 0.1μ; range, 0.02 to 0.2μ. Since the "average" montmorillonite particle would take 100 times longer to settle a given distance than an "average" kaolinite particle, the settling time difference for these two minerals could be sufficient to cause segregation in the settling techniques. This would result in a graded specimen with a predominance of the coarser kaolinite and illite on the bottom grading upward into the top layer with a predominance of the finer montmorillonite.

(2) *Depth of x-ray penetration.* The depth of x-ray penetration varies at different gonimeter angles and should therefore be considered in comparing the different methods. Moreover, if montmorillonite is enriched in the surface layer by settling, this segregation would be accentuated relative to 10 Å and 7 Å minerals according to the depth of x-ray beam penetration. A linear absorption coefficient for equal parts of montmorillonite, kaolinite, and illite was used in the equations in Cullity (1948, p. 270–271) to calculate the penetration values in Table 2.

At the lower 2θ angle for montmorillonite, the major portion of the diffraction pattern represents the upper surface and this surface bias decreases at the higher angles of 10 Å and 7 Å (Table 2).

The thickness of the clay on a glass slide, assuming an average density of 2.6 g/cm^3 and neglecting pore space which has negligible attenuation effect on the x-ray beam, was calculated for the different concentrations as follows:

Concentration	10 mg/cm^2	15 mg/cm^2	20 mg/cm^2
Thickness	38.5μ	57.7μ	77.0μ

At the angle for montmorillonite, 50% of the recorded pattern comes from the upper 2.4% of a sample and 90% from the upper 8.3% of a sample of 15 mg/cm^2 (*i.e.* an "average" specimen with a thickness of

TABLE 2. DEPTH FROM WHICH X% OF DIFFRACTION PATTERN ORIGINATES

Mineral	2θ	x=50%	x=75%	x=90%
Montmorillonite	5.2°	1.4μ	2.9μ	4.8μ
Illite	8.2°	2.6	5.2	8.6
Kaolinite	12.4°	3.6	7.4	11.9

57.7μ). For quantitative determinations, the upper surface should therefore be representative of the total sample since the x-ray beam penetrates only a minor fraction of the sample.

(3) *Surface and subsurface compositions.* Duplicate slides were prepared from samples A and B and, before they were completely dry, each was held at an angle to wash off the surface layer with water. For the pipette technique, a series of slides was made with increasing amounts of the top layer removed. Peak area ratios for the surface material indicated very high montmorillonite contents (Figs. 1, 2). The results of these tests are plotted with those of the original undisturbed specimens in Fig. 1 and 2, and are indicated by black crosses (+). For the smear-on-glass and suction-on-ceramic techniques, no differences were observed between the washed and the original unwashed specimens, whereas, for all the methods depending on settling, significantly less montmorillonite was observed in the lower layers than in the surface.

(4) *Top and bottom compositions.* Additional proof of segregation was obtained by mounting samples A and B by pipette and smear techniques on plastic membranes which are transparent to x-ray radiation (Gude and Hathaway, 1961) and then covering the specimen with the same plastic material. The samples were x-rayed from the top and from the bottom. The results showed that, using the pipette-on-glass method, the top layer contained relatively more montmorillonite than the bottom layer, whereas, using the smear-on-plastic method, the top and bottom layers contained the same amount of montmorillonite. In Figs. 1 and 2 the downward pointing arrows ($\downarrow$) represent top composition; the upward pointing arrows ($\uparrow$) represent bottom composition. A comparison of patterns is shown in Fig. 3. Note the difference in amount of mineral detected, as illustrated by the difference between the area of each peak in the pattern from the top, and the area of the same peak in the pattern from the bottom. Note particularly the difference in detection of chlorite in the two patterns. This experiment conclusively demonstrated that montmorillonite was concentrated at the surface of clay mounts when the suspensions were allowed to settle.

Intensity. The intensity of a basal reflection above the background influences sensitivity and precision of the analysis. Therefore, consideration of the intensity obtained using the techniques which have been shown to give most accurate results (powder, smear, and suction) should be the final point to consider in selection of method to be used.

Table 3 shows that the intensity obtained using the smear technique is 9% more than that obtained using the suction technique, which is 10% more than that obtained using the partially-oriented powder press

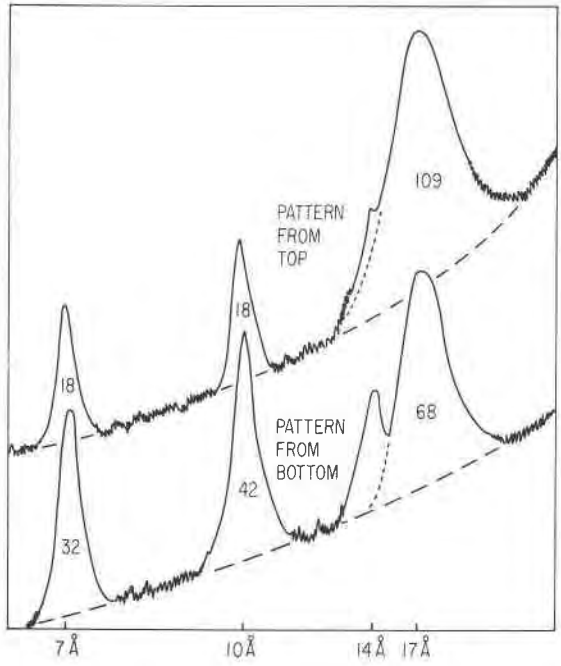

FIG. 3. *X*-ray diffractometer patterns from top and bottom of Sample B, mounted by pipette technique on plastic membrane. Peak area is indicated by the number within each peak.

technique. The order of preference among the techniques, considering precision, accuracy, and intensity (although the differences in intensity are not large) is (1) smear, (2) suction, and (3) partially-oriented powder press technique.

TABLE 3. RELATIVE PEAK AREA OBTAINED USING VARIOUS TECHNIQUES

Technique	Relative Peak Area
1. Powder press	
randomly-oriented	2
partially-oriented	5
2. Suction-on-ceramic	5.5
3. Smear-on-glass	6
4. Pipette-on-glass	7
5. Beaker-on-glass	7
6. Centrifuge-on-glass	10
7. Centrifuge-on-ceramic	10

Conclusion

The results of quantitative *x*-ray analysis of clay samples, and additional data on settling velocities of individual minerals, demonstrate that mounting techniques using settling in aqueous solutions cause mineral segregation. The precision of all techniques investigated was comparable and acceptable. However, the accuracies deviated widely. In those techniques utilizing settling, the ratios obtained differed by as much as 250% of the reference value. This is considered sufficient to warrant a reappraisal of the techniques involving settling in quantitative clay mineral analysis. However, three of the seven common techniques do fulfill the requirements of precision and accuracy, namely, the powder press, smear, and suction techniques.

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