

EVALUATION OF METHODS FOR QUANTITATIVE ANALYSIS OF HALLOYSITE-KAOLINITE CLAYS

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ABSTRACT

A number of methods were tested for their applicability to the problem of determining the content of halloysite in kaolin clays. These analytical methods included the thin-section point-count technique, base-exchange determinations, electron microscope techniques and infra-red absorption spectra differences.

Base-exchange determinations were made on a number of monodisperse fractions of pure halloysites and kaolinites. Consistent values of 12 meq/100 g were obtained for the halloysites and 4 meq/100 g for the kaolinites in the size range 1-0.25 micron.

Electron micrographs were taken of prepared homogenized mixtures and counts made of the two morphologically different varieties. Application of this technique to several natural halloysitic kaolins, of which the proportions were known by DTA methods, gave good correlative results.

The thin section method gave very good results on residual clays where the kaolinite occurs as vermicular aggregates.

Infra-red absorption spectra were run by associates on prepared mixtures and the differences were sufficiently marked to give semi-quantitative results.

These four techniques are evaluated with respect to accuracy and application and are compared with other reported techniques.

INTRODUCTION

Kaolinite, halloysite, and endellite¹ are the members of the kaolinite group found most commonly in soils and related materials. Since endellite dehydrates to halloysite under atmospheric conditions, unless special precautions are taken, the sample usually obtained for analysis in the laboratory is halloysite. Because of the close similarity in chemical composition and properties of halloysite and kaolinite, quantitative mineralogical analysis of these two minerals in the same clay is difficult. With the exception of porcelain-like halloysite, the sample must usually be analyzed in the laboratory to detect the presence of halloysite. The electron microscope probably is the principal tool utilized for this purpose. The petrographic microscope and x-ray diffraction and differential thermal analysis procedures have been used to determine the presence of halloysite.

¹ Nomenclature of Alexander, et al. (1943)

Some attempts to determine quantitatively the percentages of halloysite and kaolinite present in a kaolinitic clay by differential thermal analysis methods have been reported in the literature. The endellite content of a kaolin clay can be determined quantitatively by the method developed by Sand and Bates (1953) using glycol-treated samples.

Bramao, et al. (1952) have utilized the different degrees of slope on the high temperature endothermic peak to differentiate between a halloysitic and a kaolinitic clay. However, since they found that the slope values overlap, the usefulness of this technique as a quantitative tool is limited. Brindley (1951) has pointed out the differences existing in x-ray diffraction patterns. Owing to the difficulty in obtaining reproducible results because of undesirable orientation effects, this method has not been developed quantitatively.

A study was made of the methods which showed the greatest promise for the quantitative analysis of halloysite-kaolinite mixtures, and results of these investigations are presented.

EXPERIMENTAL METHODS AND RESULTS

Thin Section Analysis

The possibilities of the petrographic microscope as a means of quantitatively determining the amounts of halloysite present were first investigated. Thin sections of residual kaolinitic clays developed from granites and pegmatites in the Southern Appalachian region were examined by the point counter method developed by Chayes (1949). In these particular residual clays the kaolinite is derived from the weathering of mica and occurs as coarse, vermicular aggregates pseudomorphous after mica; and the halloysite, which is derived from the feldspar, occurs as extremely fine-grained, almost isotropic masses (Sand, 1952).

Two thin sections of the same subsample (698, Spruce Pine, N. C.) were made at right angles to each other, and the mineral composition as determined by the point counter method is shown in Table 1. This analysis gave the relative percentage by volume of halloysite to kaolinite as 90:10. Differential thermal analysis of the glycol-treated subsample gave a relative percentage by weight of 83:17.

Thin section analysis of Sample S-6 (Alexander deposit, Buncombe Company, N. C.) gave a relative percentage of halloysite and kaolinite of 81:19 whereas differential thermal analysis gave the ratio 83:17. Good

TABLE 1. — SAMPLE 698 (SPRUCE PINE, N. C.), BULK MINERAL COMPOSITION AS DETERMINED BY POINT COUNTER METHOD

	698A	698B
Halloysite	85.6%	84.9%
Kaolinite	8.8	8.8
Mica	3.8	6.3
Quartz	1.8	—

checks were also obtained on Sample S-11 from the same deposit; these values were 92:8 by thin section analysis and 90:10 by differential thermal analysis (glycol method).

Electron Microscope Studies

One of the largest differences existing between halloysite and kaolinite is in their morphologies. For this reason a study was made of electron micrographs of artificial and natural mixtures. In order to obtain representative samples, all the materials selected were homogenized in a Manton-Gaulin unit. Langley kaolinite and Dragon halloysite were chosen for the study and mixtures in the ratios 25-75, 50-50, and 75-25 were prepared. Two natural mixtures also were evaluated by this technique. The electron microscopist, Mr. H. W. Stetson, prepared the screens in the same manner for all the samples and took pictures of five fields at random for each preparation. Point counts were made of these five frames by projecting the frames onto an arithmetic grid and identifying the presence of halloysite or kaolinite at the intersections on the basis of morphology. These results are presented in Table 2.

TABLE 2.—ELECTRON MICROGRAPH COUNTS ON PREPARED NATURAL AND ARTIFICIAL MIXTURES OF DRAGON HALLOYSITE AND LANGLEY KAOLINITE

Mixture No.	<i>Artificial Mixtures</i>					
	1		2		3	
Composition:—	25 percent Halloysite		50 percent Halloysite		75 percent Halloysite	
Frame No.	H	K	H	K	H	K
1	101	280	304	304	193	92
2	189	589	302	411	603	220
3	107	876	220	154	330	131
4	124	438	192	154	534	240
5	137	653	173	156	398	232
TOTALS	658	2836	1191	1179	2058	915
Percent Halloysite	18.85		50.44		69.1	
Mixture No.	<i>Natural Mixtures</i>					
	S-34		S-698			
Frame No.	H	K	H	K		
1	371	670	751	289		
2	495	533	574	188		
3	571	626	595	110		
4	704	343	503	178		
5	358	447	654	10		
TOTALS	2499	2619	3077	775		
Percent Halloysite	48.8		79.9			

Base-Exchange Capacity Determinations

The use of base-exchange capacity determinations as a possible tool for a quantitative mineralogical analysis of these mixtures was investigated. Values in the literature are reported as high as 70 meq/100 g (Kerr, et al., 1950) for halloysite whereas kaolinite is reported as having a much lower base-exchange capacity. In order to minimize variations in the base-exchange values arising from variable procedures the current studies were made using 1) a single method of determination, 2) fractionated samples, and 3) samples analyzed as free from mineral impurities. The manganese saturation method was chosen because it is rapid and can be used on relatively small samples. The manganese was determined by the classical method of Willard and Greathouse (1917) as adapted to photoelectric colorimetry by Mehlig (1939). The samples were saturated with manganese and the excess salts removed by the usual centrifuge washing procedures. The exchange equivalence of divalent manganese to other cations, particularly calcium, was shown by Bower and Truog (1940). The precision of this method on kaolinitic clays was determined by running pure kaolinite, pure halloysite and mixtures of these two varieties in triplicate. The results are tabulated in Table 3 and shown graphically in Figure 1.

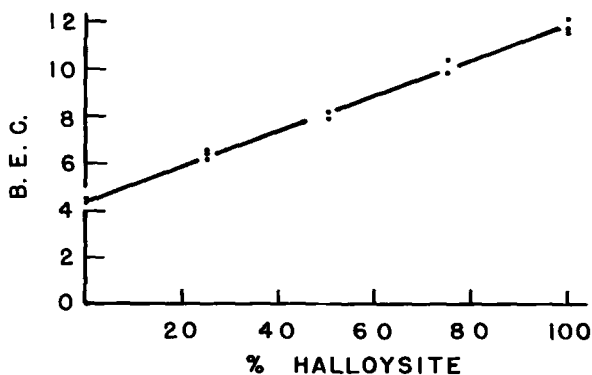


FIGURE 1. — Results of precision experiment on fractionated (1-0.25 micron) Langley kaolinite — Dragon halloysite. Base-exchange capacity in meq Mn²⁺/100 g.

TABLE 3. — BASE-EXCHANGE CAPACITIES (meq/100 g) FOR FRACTIONATED (1-0.25 MICRON) KAOLINITE - HALLOYSITE MIXTURES

Mixture No.	1	2	3	4	5
Composition percent	100 K	75 K	50 K	25 K	0 K
Base-Exchange Capacity	4.4	6.2	7.9	9.9	12.1
	4.3	6.5	8.1	10.4	11.6
	4.3	6.4	7.9	9.9	11.8
Average	4.3	6.4	8.0	10.1	11.8

Base-exchange capacity determinations which were made on a selection of pure, fractionated (1-0.25 micron) kaolinites and halloysites are listed in Table 4. From this tabulation it is seen that the base-exchange capacities group around 4 meq/100 g for kaolinites and around 12 meq/100 g for halloysites.

TABLE 4. — BASE-EXCHANGE CAPACITIES OF HALLOYSITES AND KAOLINITES (1-0.25 Micron Fraction)

	B.E.C. (meq/100 g)	Literature Values (Range) meq/100 g
<i>Halloysites</i>		6-70
Wendover, Utah	13.5	
New Park, Utah	10.8	
Bedford, Indiana	11.6	
Eureka, Utah*	11.8	
Georgia**	16.9	
<i>Kaolinites</i>		1-16
Macon, Georgia	3.9	
Langley, South Carolina	4.1	Generally less than 5

* Dragon Endellite (-1 micron): 13.7 meq

** Contaminated with Pyrolusite

Base-exchange capacity determinations were also made on a series of bulk mixtures. Results of these tests are shown in Table 5 and Figure 2.

TABLE 5. — BASE-EXCHANGE CAPACITIES (meq/100 g) FOR BULK LANGLEY KAOLINITE-DRAGON HALLOYSITE MIXTURES

Mixture No.	1	2	3	4	5
Composition percent	100 K	75 K	50 K	25 K	0 K
Base-Exchange Capacity	3.9	7.1	7.4	10.0	8.7
	4.4	5.2	7.2	8.2	—
	4.2	5.3	7.2	8.7	9.9
Average	4.2	5.9	7.3	9.0	9.3

The base-exchange capacity of the Langley kaolinite bulk sample was the same as that of the size fraction (1-0.25 micron) studied. The size distribution determined for this sample showed the modal size to be 0.8 microns, so that the bulk sample was essentially within the size range of the fractionated sample.

Infra-red Spectroscopy

Launer (1952) has shown the differences in infra-red absorption spectra between halloysite and kaolinite, and Dr. R. Roy suggested the possibility of using them in arriving at the proportions of these mixtures. Mixtures prepared in the same manner as those used in the base-exchange determinations were submitted to Dr. Roy's group for infra-red analysis. On the basis of these patterns they claimed that the relative proportions of halloy-

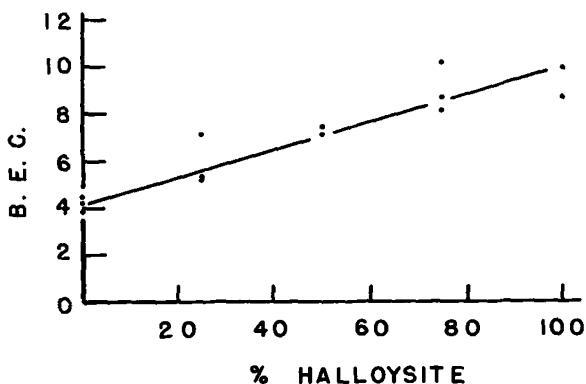


FIGURE 2.—Results of precision experiment on bulk Langley kaolinite—Dragon halloysite. Base-exchange capacity in meq $Mn^{2+}/100$ g.

site and kaolinite could be determined with an accuracy of around ± 15 percent (personal communication, R. Roy).

X-Ray Diffraction

Because of large variations in particle orientation as a result of sample (slide, fiber, etc.) preparation, the x-ray method was not investigated as a quantitative analytical tool for studying these halloysite-kaolinite mixtures. If these orientation effects could be overcome, then the x-ray method might be used as a quantitative tool.

Differential Thermal Analysis

It is felt that the work of Bramao, et al. (1952) covers the possibilities in this type of analysis for halloysite, and no further research was done on this technique in order to evaluate its quantitative possibilities.

DISCUSSION AND CONCLUSIONS

On the basis of these studies it is believed that sufficient tools exist for the quantitative determination of halloysite in a kaolinitic clay. Each method, of course, has its limitations and these must be taken into account in making an analysis. As can be seen in Table 6 from the analyses on natural mixtures of residual halloysite and kaolinite from Spruce Pine, N. C., good checks can be obtained between some of the methods but wide discrepancies exist between others. Where the sample can be kept in the hydrated condition, the differential thermal analysis method of Sand and Bates (1953), which determines the endellite-kaolinite content, is probably the best to be employed. When dehydration has occurred and halloysite is the variety present, it is believed that a combination of several of the techniques evaluated will give a quantitative mineralogical analysis of

the clay. Where kaolinite occurs as coarse, vermicular aggregates, the thin-section point-counter method can be utilized. This method also has the advantage of determining the content of other minerals in the clay. If both kaolinite and halloysite are fine grained, this method cannot be used and combinations of the electron microscope, base-exchange, and infra-red absorption techniques should be employed. These methods require supplemental techniques in order to determine the amount of impurities.

TABLE 6. — SUMMARY OF RESULTS OBTAINED ON NATURAL MIXTURES BY DIFFERENT METHODS (HALLOYSITE:KAOLINITE)

Method	S-698	S-34
Differential		
Thermal Anal.	83:17	72:28
Thin Section	90:10	—
Electron Microscope	80:20	49:51
Base-Exchange	43:57	33:67

Note: Differential thermal and thin section analyses were made on the same subsample by the senior author as part of a thesis (in 1951); base-exchange determinations and electron microscope studies were made on different subsamples by both authors (in 1952).

Electron microscope studies, contrary to expectations, gave surprisingly good results on the artificial mixtures (± 6 percent accuracy). Good correlation with other methods was obtained on one natural sample but not on the other. It would appear that the method has good possibilities as an analytical tool but further basic studies should be made.

The base-exchange capacity determinations on mixtures of fractionated clays indicate that this method, if applied with discretion, may be a useful tool in studying halloysitic kaolins. While the difference between the capacities of halloysite and kaolinite was not as large as one would expect from some of the literature values, no overlapping of values was obtained. The precision of the method (± 3 percent) is good considering the fact that the absolute capacity values of these materials are comparatively small. The importance of fractionating samples is emphasized by the lack of precision and overlapping of values when determinations were made on bulk samples. The percentages of halloysite in samples S-34 and S-698 (Table 6) are based on the base-exchange capacities of bulk samples of these materials. These determinations illustrate the large errors that can be made using this method without the proper controls. Large particle sizes and most mineral impurities effect a lower base-exchange capacity; White (1953) has recently suggested that the common association of halloysite and allophane may be a reason for some high base-exchange capacities reported for the former mineral. It is necessary, therefore, to work in a close particle size range to eliminate these variables. If this cannot be done, the base-exchange method should not be used unless further basic information is obtained.

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