

QUANTITATIVE DETERMINATION OF KAOLINITE AND HALLOYSITE BY NH_4Cl RETENTION MEASUREMENT

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ABSTRACT

A chemical method based on specific retention of NH_4Cl on kaolinite and halloysite was developed for quantitative estimation of these minerals in clay mixtures. The procedure involves grinding with KCH_3COO crystals (KCH_3COO -complex formation), subsequent washings with 4 *N* NH_4Cl (NH_4Cl -complex formation), methyl-isopropyl alcohol mixture (1:1)—isopropyl alcohol (removal of excess NH_4Cl) and 2 *N* NaCl (extraction of NH_4Cl retained and exchangeable NH_4^+), and NH_3 determination by Nesslerization. The NH_4Cl retention of the sample is calculated by subtracting the amount of exchangeable NH_4^+ from total NH_4 retention.

The retention values for reference kaolinites and halloysites were 220 ± 20 m mols NH_4Cl per 100 g of clay, while the corresponding figures for 2:1 and 2:2 minerals were negligibly small. Only allophane exhibited some NH_4Cl retention, 20–40 m mols per 100 g of clay. The retention values were shown to be independent of temperature between 13 to 28° C., and to be a linear function of kaolin content in artificial mixtures. These make possible quantitative estimation of kaolinite and halloysite in the overall accuracy of about 10 per cent of the reported value. Parallel x-ray diffraction analysis for NH_4Cl -treated samples permits a check of the presence of kaolinite (10.2 Å) and halloysite (10.4–10.5 Å).

INTRODUCTION

Several methods have been tried for quantitative determination of kaolinite and halloysite in view of wide occurrence of these minerals in sediments and soils. Quantitative determination of kaolinite by x-ray diffraction was recently suggested to be possible when orientation was controlled (Brindley and Kurtossy, 1961, 1962), but this was questioned by van der Marel (1962) because of rather large variations in the reflected intensities of different kaolinites. In differential dissolution analysis, the amount of dissolving component in NaOH solution after dehydroxylation at 500° C. was used as a quantitative measure of kaolin minerals (Hashimoto and Jackson, 1958). Differential thermal and thermogravimetric analyses have also been tried with relatively simple mixtures, including kaolinite or halloysite. None of these methods is entirely adequate, because the methods depend on the crystallinity and crystallite size of the kaolin minerals, and are often lacking in the specificity of the criteria used.

The purpose of the present investigation is to develop a new method for quantitative determination of kaolin minerals based on salt-complex formation. The reaction was first noted between hydrated halloysite and certain K, NH_4 , Rb and Cs salts (Wada, 1958, 1959a, b; Garret and Walker, 1959). Later, grinding with KCH_3COO crystals or immersing in

concentrated KCH_3COO solutions was found to make possible the lattice expansion of metahalloysite and kaolinite (Wada, 1961), and further of dickite (Andrew *et al.*, 1960) as well as hydrated halloysite. The resulting increase in basal spacing was found to be useful for x-ray differentiation of the 7 Å peak of kaolinite and halloysite from that of chlorite, either thermally stable or unstable (Andrew *et al.*, 1960, Jackson, 1962).

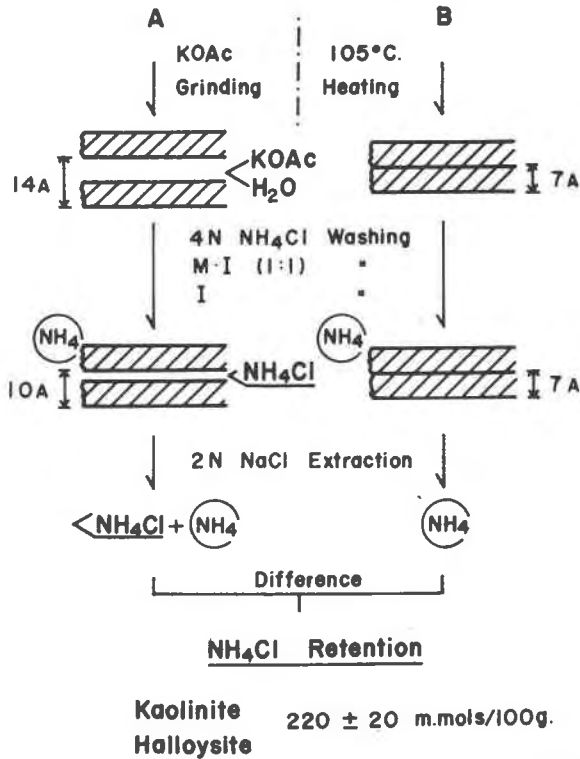
Kaolin minerals (1:1 dioctahedral) have so far been known as the only minerals that form definite interlayer salt complexes. In this type of complex, the salt generally forms "monomolecular layers" between kaolin layers. The facts strongly suggest the possibility of quantitative determination of kaolinite and halloysite based on the surface area of these minerals as derived from measurement of salt retention. The same principle has already been applied for estimation of 2:1 expandable minerals utilizing organic solvation on these minerals (Dyal and Hendricks, 1950).

PROCEDURE

Preceding studies (Wada, 1958, 1959b) showed that a definite amount of a salt was required for complete formation of a salt complex; the orientation maximum of NH_4Cl , RbCl and CsCl on halloysite corresponded nearly to two molecules per unit cell. It might be expected that direct determination of this amount could serve as the basis for the mineral estimation. However, the same and other studies (Wada, 1958, 1959b; Garret and Walker, 1959) indicated that the complex formation was a physical adsorption in nature and that the saturation of interlayer surface with respect to salt molecules would occur only when the salt-clay mixture was dried up. This would create some analytical difficulties in applying the procedure to routine work. An alternative procedure (Fig. 1) was adopted in which salt retention was measured under a given set of conditions. The details of this procedure are first given below, and then the experimental results on which it is based are presented.

Divide a clay sample into two portions (*A* and *B* in Fig. 1). Mix 0.30 g of clay (*sample A*) with 0.50 g KCH_3COO crystals with a spatula, and dry grind the mixture for 30 minutes in a mechanical agate mortar under an infrared lamp (20 minutes preliminary heating of the agate mortar under the infrared lamp might be necessary at high relative humidity). Transfer the ground material with a spatula to a 5 ml tube with a stopper. Add 1 ml of 8–10 *N* KCH_3COO solution, stopper, shake and allow to stand overnight. Add 4 ml of 4 *N* NH_4Cl solution to the same tube, stopper and shake. Take 1 ml of the NH_4Cl - KCH_3COO -clay suspension into a 10 ml centrifuge tube of known weight (Tw_A) in duplicate. Take about 0.05 g of finely ground clay (*sample B*) into another 10 ml centrifuge tube of known weight (Tw_B) in duplicate, and place it in an oven

at 105° C. overnight. Add 5 ml of 4 *N* NH₄Cl solution to the tube in which *sample A* or *B* is taken, stopper, shake, allow to stand for 1 hour or longer and centrifuge for 5 minutes at 2000 rpm. Repeat the 4 *N* NH₄Cl washing thrice. Wash the clay with 10 ml of methyl-isopropyl alcohol mixture (volume ratio; 1:1) to remove excess NH₄Cl, and repeat



M: Methyl alcohol I: Isopropyl alcohol

FIG. 1. Scheme for NH₄Cl retention measurement.

a 5 ml isopropyl alcohol washing twice. Invert the centrifuge tube on a blotting paper for 15 minutes. Add 10 ml of 2 *N* NaCl solution to the tube, shake and allow to stand for 1 hour or longer. Centrifuge and take 1 ml of a supernatant into a 50 ml volumetric flask for NH₄ determination. Discard the remaining supernatant and wash the residue with 5 ml of methyl alcohol-water mixture (1:1), methyl alcohol and methyl alcohol-acetone mixture (1:1), successively by centrifugation. Place the centrifuge tube into an oven at 105° C. for 2 hours and weigh to give the sample weight,

$(T_{w_A} + C_{w_A})$ or $(T_{w_B} + C_{w_B})$. Take 5, 10 and 15 ml of 0.001 N NH_4Cl standard solution into 50 ml volumetric flasks for the standard curve in NH_4 determination. Add about 40 ml water, 1 ml 10 per cent potassium sodium tartrate solution and 2 ml Nessler reagent¹ to the standard and sample solutions. Adjust the volume of the solution to 50 ml with water and mix. After 20–30 minutes, read the percentage transmission at 435 μ . Read the me. of NH_4 per 50 ml sample solutions (NH_{4A} , NH_{4B}) by referring to the standard curve. Calculate the NH_4Cl retention of the sample expressed as m mols per 100 g of oven-dry clay by subtraction of the amount of exchangeable NH_4^+ from total NH_4 retention:

$$\text{NH}_4\text{Cl retention} = \frac{1000 \text{ NH}_{4A}}{(T_{w_A} + C_{w_A}) - T_{w_A}} - \frac{1000 \text{ NH}_{4B}}{(T_{w_B} + C_{w_B}) - T_{w_B}} \quad (1)$$

Calculate the amount of the kaolin mineral in the clay sample:

$$\% \text{ Kaolin mineral} = \frac{100 \text{ NH}_4\text{Cl retention}}{220} \quad (2)$$

in which 220 represents the average value of NH_4Cl retention for kaolin minerals.

RESULTS AND DISCUSSION

FACTORS AFFECTING DETERMINATION OF RETENTION VALUES

Formation of KCH_3COO Complex

1) *Grinding vs. immersing procedure:* Although the dry grinding with KCH_3COO crystals was first shown to be most effective for the lattice expansion of kaolin minerals (Wada, 1961), later studies (Andrew *et al.*, 1960; D. J. Greenland, personal comm.) indicated that it might be replaced by mere immersion in strong KCH_3COO solutions. The effectiveness of the latter process was studied for two size fractions of reference kaolinites from Macon, Georgia, and Mesa Alta, New Mexico. The relative magnitude of the complex formation as a function of immersing time was calculated from the observed reflected intensities according to the following formula:

$$\% \text{ Complex formation} = \frac{100 I(004)_{\text{complex}}}{I(004)_{\text{complex}} + I(002)_{\text{kaolinite}}} \quad (3)$$

In Fig. 2 is given the result only for the Georgia kaolinite. The effective penetration of KCH_3COO into kaolinite depended either on its origin or

¹ NH_4 determination by Nesslerization followed the method given by Yuen and Pollard (1952). Nessler reagent is prepared by dissolving 18.26 g of KI and 22.72 g of HgI_2 in 30 ml of water, pouring this solution into 950 ml of water containing 40 g of NaOH, cooling the mixture, and diluting to 1 liter.

on its size fraction, and practically ceased to progress after 48 hours' standing. Some preliminary treatments in order to improve the complex formation were tried and discarded. Among these were a short time grinding without KCH_3COO which resulted in partial breakdown of kaolinite structure (Wada, 1961), and a treatment with dilute acids (0.1–1 *N*). On the other hand, only 5 minutes grinding with KCH_3COO crystals remarkably increased the rate of complex formation (Fig. 2).

2) *Effect of time of grinding*: From the foregoing result, grinding with KCH_3COO crystals was adopted in the proposed procedure. The grinding

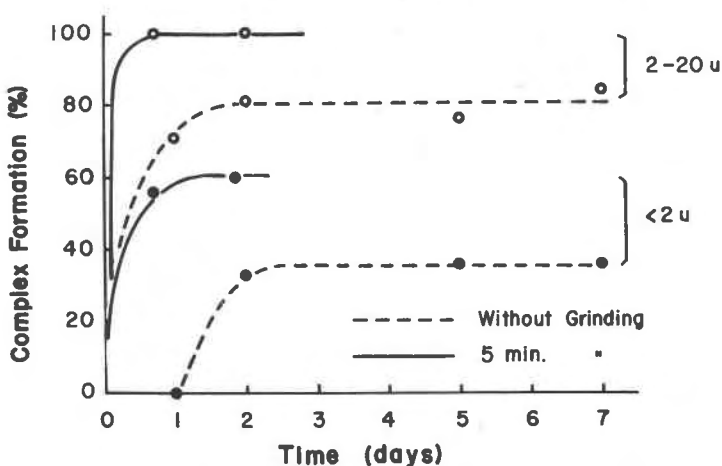


FIG. 2. Effect of time of immersing in saturated KCH_3COO solution on KCH_3COO -kaolinite complex formation.

usually suffers from a partial breakdown of clay mineral structure. This would affect NH_4Cl retention measured through a decrease of the inter-layer surface of kaolin minerals, and an increase of exchangeable NH_4^+ due to newly created broken bonds. Total NH_4 retention was measured by varying the grinding time in the proposed procedure (Fig. 3). From the result, a 30 minute grinding period was adopted. During that time, NH_4Cl retention for kaolin minerals approached a definite value, while no appreciable increase of NH_4 retention occurred for montmorillonite (Clay Spur, Wyoming) and illite (Matsushiro, Shimane). The protective action of KCH_3COO on the breakdown of clay mineral structure was fortuitously fit for the present purpose, because the same would not be expected for other ordinary salts. For example, a 15 minutes grinding with $\text{Ca}(\text{CH}_3\text{COO})_2$ resulted in 28 per cent increase of NH_4 retention for the same montmorillonite, and marked blurring of x-ray diffraction pattern.

3) *Effect of clay-salt ratio:* The complex formation appearing on the x-ray diffraction pattern was practically not affected by the clay-salt ratio ranging from 1:1 to 1:3 (weight ratio). There were some indications that a partial breakdown of clay mineral structure and incomplete complex formation would occur above and below this range, respectively. In the proposed procedure, the clay-salt ratio, 1:1.66 was adopted.

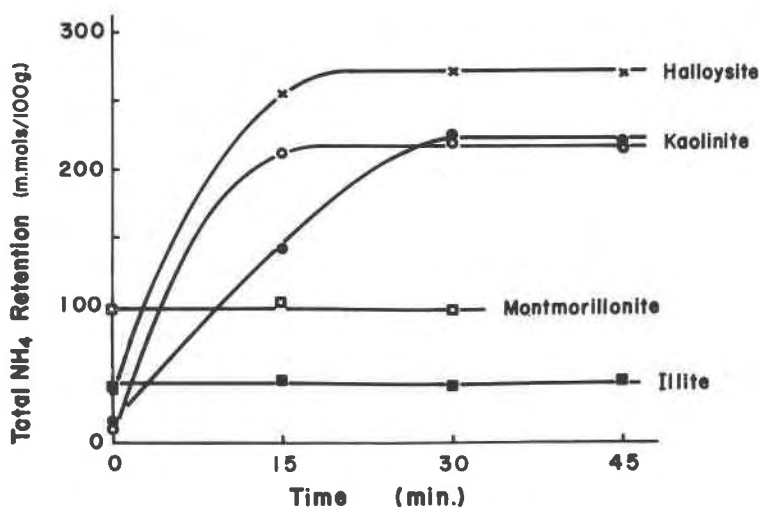


FIG. 3. Effect of time of grinding with KCH_3COO on total NH_4 retention. Halloysite; Yoake, Oita, -10μ , heated at $200^\circ C.$; Kaolinite; Dry Branch, Georgia, -10μ (○); Macon, Georgia, -2μ (●); Montmorillonite; Clay Spur, Wyoming, -2μ ; Illite; Matsushiro, Shimane, -2μ .

Measurement of NH_4Cl Retention

1) *Kind of salt used for retention measurement:* No extensive search was made for the salt most adequate for retention measurement. Previous studies (Andrew *et al.*, 1960; Wada, 1961) suggested that either NH_4Cl or NH_4NO_3 could be used for this purpose. In this study, NH_4Cl was chosen simply because it formed the complex in less concentrated solutions and stood more stably against washings for removal of excess salt than did NH_4NO_3 . On the other hand, the use of KCH_3COO alone would make impossible the estimation of exchangeable cation and/or external retention of the salt (*measurement B* in Fig. 1). In the case of NH_4Cl , interlayer penetration practically did not occur for kaolinite and even for halloysite which was heated once at $105^\circ C.$ without the preceding KCH_3COO treatment.

TABLE 1. NH_4Cl RETENTION BY REFERENCE CLAY MINERAL SAMPLES (OVEN-DRY BASIS)

Minerals	Total NH_4 retention	Exchangeable NH_4	NH_4Cl retention
	<i>m mols/100g</i>	<i>m mols/100g</i>	<i>m mols/100g</i>
<i>Kaolinite</i>			
Macon, Georgia, 2-20 μ	245	14	231
Dry Branch, Georgia, -10 μ	213	10	203
Mesa Alta, New Mexico, -2 μ	228	10	218
<i>Halloysite</i>			
Isshochi, Kumamoto, -10 μ	242	33	209
Yoake, Oita -10 μ	270	35	235
Bedford, Indiana -10 μ	266	29	237
Bedford, Indiana -2 μ	254	33	221
<i>Allophane</i>			
Choyo, Kumamoto, WVA ¹ , -2 μ	126	102	24
Choyo, Kumamoto, WP ² , -2 μ	164	125	39
<i>Montmorillonite</i>			
Clay Spur, Wyoming, -2 μ	97	98	-1
Polkville, Mississippi, -2 μ	139	137	2
<i>Illite</i>			
Matsushiro, Shimane, -2 μ	42	40	2
<i>Chlorite</i>			
Kuroshiroishi, Fukushima, 2-20 μ	19	18	1
Okushi, Nagasaki, -10 μ	23	25	-2

¹ WVA: weathered volcanic ash.

² WP: weathered pumice.

The proposed concentration of NH_4Cl solution was chosen based on an adsorption isotherm of NH_4Cl on halloysite (Wada, 1958). At that concentration, NH_4Cl retention measured for kaolin minerals was high enough to differentiate them from other minerals (Table 1), and the solution could be handled without any difficulty which might be encountered for more concentrated solutions.

2) *Removal of excess NH_4Cl* : The removal of excess salt presented a problem in measurement of salt retention, since the adsorption forces were chiefly weak non-Coulombic forces. Total NH_4 retention measured for kaolinities and halloysite decreased remarkably by washing with water or methyl alcohol (Fig. 4), indicating that NH_4Cl retained, as well as excess NH_4Cl , was extracted by these solvents. The effectiveness of various solvents on the removal of excess salts in cation-exchange capacity de-

terminations was recently investigated by Rich (1962). In consideration of his result, several solvents were tried, and finally a methyl-isopropyl alcohol mixture (1:1) was found to be most adequate (Fig. 4). One wash with this mixture, followed by two washes with isopropyl alcohol, completely removed excess NH_4Cl , as shown in the cases for montmorillonite and illite, whereas NH_4Cl remained in the kaolin complex and was recovered quantitatively by a succeeding 2 *N* NaCl extraction.

3) *Effect of temperature*: In view of physical nature of adsorption, it was considered that a temperature effect might affect the retention meas-

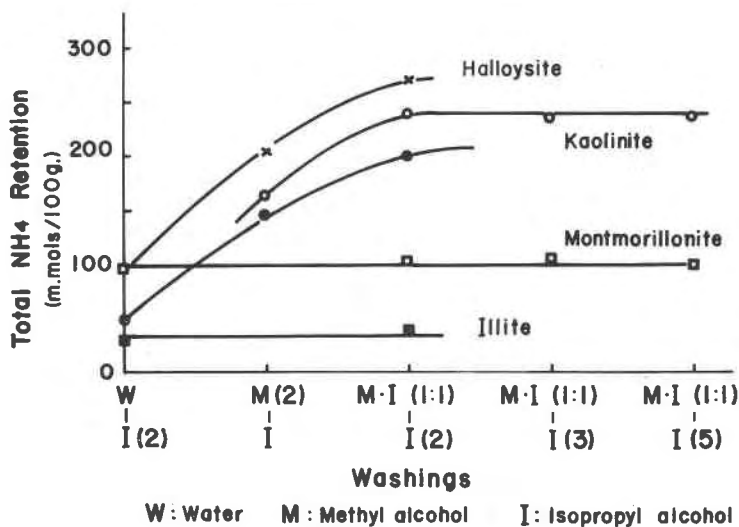


FIG. 4. Effect of washings with various solvents on total NH_4 retention. Figures in parentheses, such as 2, 3 and 5 indicates number of washings. Halloysite; Yoake, Oita, -10μ ; Kaolinite; Macon, Georgia, -10μ (○); Mesa Alta, New Mexico, -10μ (●); Montmorillonite; Clay Spur, Wyoming, -2μ ; Illite; Matsushiro, Shimane, -2μ .

urement. This possibility was tested for kaolinite (Mesa Alta, New Mexico) and halloysite (Yoake, Oita) using rooms in which the temperature was adjusted to 15, 21 and 28° C. The total NH_4 retention values obtained for the kaolinite were 224, and 224 and 222, and those for the halloysite, 262, 257 and 259, respectively. Therefore, no special caution for temperature during the measurement is needed at room temperature.

NH_4Cl RETENTION BY REFERENCE CLAY MINERAL SAMPLES

The NH_4Cl retention values of reference clay mineral samples are shown in Table 1, together with the results both for KCH_3COO grinding ("total NH_4 retention," *A* in Fig. 1) and for drying at 105° C. without KCH_3COO treatment ("exchangeable NH_4^+ " and possibly some "external NH_4Cl retention," *B* in Fig. 1). No impurity was detected in the

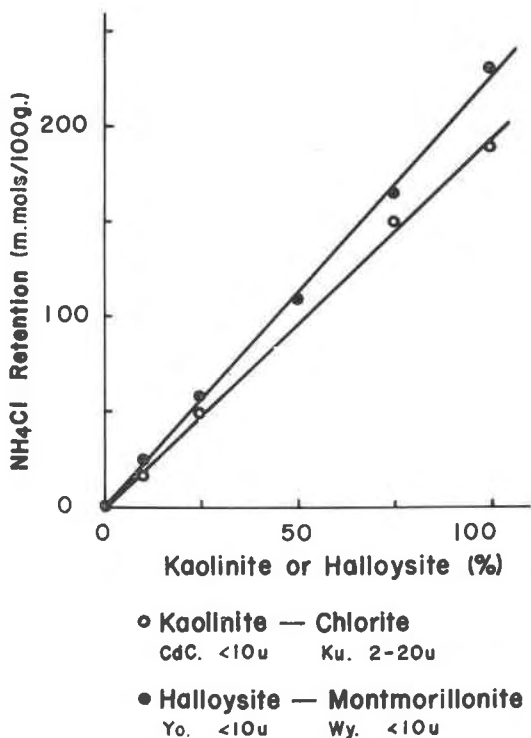
kaolin mineral samples by *x*-ray diffraction, and no traces of kaolinite and halloysite were detected in the other mineral samples. Despite rather large variations in crystallinity and particle size, the NH_4Cl retention values for the kaolinites and halloysites were fairly constant and ranged from 200 to 240 m mols per 100 g of clay, whereas the corresponding values for the 2:1 and 2:2 clay minerals were negligibly small. Either "total NH_4 retention" or "exchangeable NH_4^+ " gives a measure of CEC values for the latter type of minerals except for vermiculite which will fix NH_4^+ to some extent under the conditions. Allophane adsorbed a considerable amount of NH_4Cl , as expected from previous studies (Birrell and Gradwell, 1956; Wada and Ataka, 1958; Birrell, 1961), but its retention values—the difference in NH_4Cl retention between KCH_3COO -ground and unground materials—were much lower as compared to those for kaolinite or halloysite.

The difference in NH_4Cl retention among the kaolin samples might possibly be the result either of dilution by impurities which were not detected or of differences in crystallite size and crystallinity. Since NH_4Cl was retained only on basal but not on edge surfaces, a simple calculation showed that a decrease in crystallite thickness from 20 unit cells (about 200 Å) to 10 unit cells, would result in about 10 per cent decrease in NH_4Cl retention measured. The crystallite thickness estimated from half-maximum angular breadth ($B_{1/2}$) of (001) reflections for the respective NH_4Cl -complex¹ was about 170–200 Å ($B_{1/2}=0.35\text{--}0.45^\circ$) for the kaolinites and 80–95 Å ($B_{1/2}=0.85\text{--}1.00^\circ$) for the halloysites. The apparent constancy of retention values found for the kaolinites and halloysites, however, was not concordant with those predicted from the above calculation. This suggested that another factor—the difference in crystallinity—might affect retention in the opposite way as did the crystallite size, possibly through an adsorption equilibrium. Some qualitative confirmation of this trend was also obtained with the NH_4NO_3 -complex; the halloysite complex stood stably against washing with methyl-isopropyl alcohol mixture (1:1), whereas the kaolinite complex collapsed readily. It might be expected that the range in the retention values found here would hold without serious error for most kaolinites and halloysites unless well-crystallized kaolinite appears in exceptionally small crystallites as compared with those of poorly-crystallized halloysite and *vice versa*.

NH_4Cl RETENTION OF ARTIFICIAL MIXTURES OF KAOLIN AND OTHER MINERALS

The use of NH_4Cl retention in estimating the amount of kaolin minerals in a given clay mixture would require that the retention value be

¹ The corresponding $B_{1/2}$ values for the original minerals were $0.25\text{--}0.35^\circ$ for the kaolinites and $0.65\text{--}0.85^\circ$ for the halloysites which was heated at 200°C .

FIG. 5. NH_4Cl retention of artificial mixtures.

proportional to the percentage of the kaolin minerals in the clay. The retention values were determined for two series of mixtures containing various proportions of kaolinite and halloysite. The results (Fig. 5) verified that retention is proportional to contents of kaolinite and halloysite. The kaolinite, montmorillonite and chlorite samples used here were not pure materials, but no trace of kaolin minerals was detected in the latter two by x -ray diffraction.

ACCURACY OF THE PROPOSED METHOD

The accuracy of the proposed method for quantitative estimation of kaolin minerals, depends on the following factors;

1) inherent differences among kaolin minerals, possibly such as those in the particle thickness and crystallinity of the minerals, 2) elimination of amorphous aluminosilicates—allophane, and 3) analytical error.

The amount of NH_4Cl retained on kaolinite and halloysite spread by about 10 per cent of its value as a limit, that is, 220 ± 20 m mols per

TABLE 2. BASAL SPACINGS (Å) OF CLAY MINERALS AFTER SALT TREATMENT¹

Mineral	Salt			
	NH ₄ Cl		NH ₄ NO ₃	KCH ₃ COO
	Air-dry	Heated to 250° C.	Air-dry	Air-dry
Kaolinite	10.2	7.2	11.6	14.2
Halloysite	10.4-10.5	7.25	11.6	14.2
Montmorillonite	12.1-12.8 ³	10	12.1-12.8 ³	11.9-12.3 ⁴
Vermiculite	11.1-11.2 ⁵	9.3 ^{2,5}	11.1-11.2 ⁵	10.3-10.4 ⁵
Illite	10	10	10	10
Chlorite	14	14	14	14

¹ Salt treatment indicates washings of KCH₃COO-ground clay sample with 4 *N* NH₄Cl, 8 *N* NH₄NO₃ and 5 *N* KCH₃COO respectively, followed by three washings with isopropyl alcohol as shown in the Proposed Procedure. A portion of the drained clay residue is smeared on a glass slide and *x*-rayed. Washing the remaining portion of the clay with water and drying at R.H. 70 per cent also serve for differentiating kaolinite (7 Å) and halloysite (10 Å) (Wada, 1961).

² Heated to 750° C.

³ Values included those for NH₄-montmorillonites obtained by Barshad (1950).

⁴ Values obtained by Barshad (1948) for K-montmorillonites.

⁵ Values obtained by Barshad (1948) for NH₄- and K-vermiculites respectively.

100 g of clay. In view of some compensative effects of the first two factors on retention as already discussed, the value 220 could be used as an empirical index for calculation of the percentage of kaolin minerals, allowing for uncertainty of 10 per cent in its value. Preliminary removal of allophane or correction for allophane present (2-4 m mols NH₄Cl for each 10 per cent of allophane) would improve the accuracy for a clay low in kaolinite or halloysite, but would not be necessary for a clay high in these minerals (more than about 50 per cent). The analytical error in quantitative work including grinding procedure was well within the uncertainties mentioned above, and therefore, the overall accuracy, ±10 per cent of the reported value would be achieved in the proposed procedure. The result is not highly accurate in the sense of quantitative analysis, but will meet the purpose of use for most quantitative estimation of kaolin minerals in clays separated from soils and sediments. On the other hand, the specificity of the reaction used as a criterion (Table 1) would greatly improve the accuracy of quantitative mineralogical analysis in general for the clay mixtures of complex mineral composition.

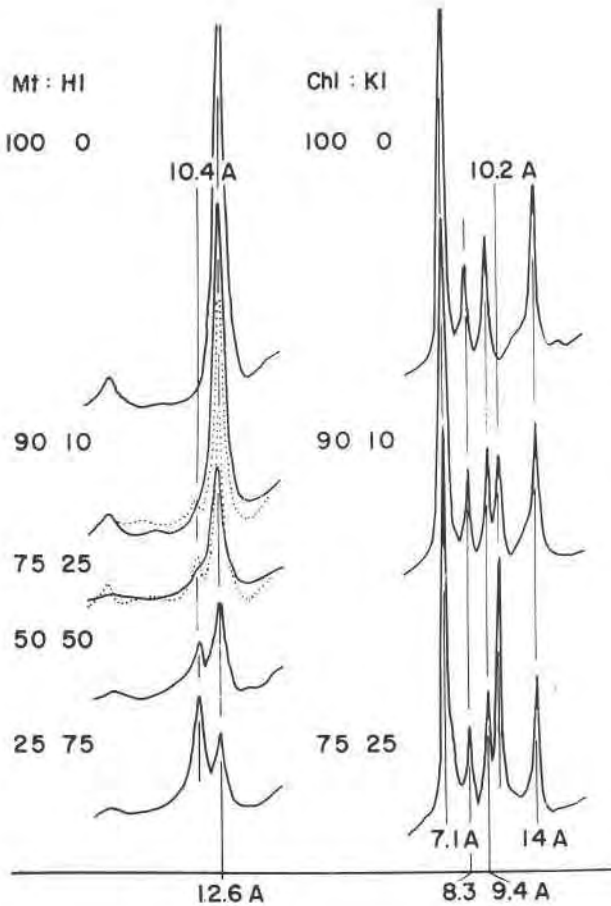


FIG. 6. X-ray diffraction patterns of $\text{KCH}_3\text{COO-NH}_4\text{Cl}$ treated artificial mixtures. Talc (9.4 \AA) and amphibole (8.3 \AA) were present as impurities in the chlorite sample.

USE OF SALT COMPLEX IN IDENTIFICATION OF KAOLIN MINERALS

As pointed out in the Introduction, the resulting increase in basal spacing of kaolin minerals makes the salt complexes ideal for identification of these minerals by x -ray diffraction. Table 2 gives a guide to appropriate salt treatments which depend on the mineral composition of the given clay mixture. Complete or nearly complete removal of excess salts¹ in the present procedure results in enhancement of x -ray diffrac-

¹ The diffraction lines of NH_4Cl and NH_4NO_3 , if any, do not appear in the regions of basal reflections of clay minerals described in Table 2. The diffraction lines of KCH_3COO appear at 13.0 , 10.35 and 8.95 \AA only under relatively low humid conditions, because of its high deliquescent nature.

tion of clay minerals as compared with the former procedure (Andrew *et al.*, 1960; Wada, 1961). The basal spacing of NH_4Cl -kaolinite complex was slightly but consistently smaller than that of halloysite complex (Table 2), suggesting some difference in the packing of NH_4^+ and Cl^- between both the minerals. No similar difference was observed for NH_4NO_3 - and KCH_3COO -complexes.

As an illustration, x -ray diffraction patterns of $\text{KCH}_3\text{COO-NH}_4\text{Cl}$ -treated samples of the artificial mixtures are shown in Fig. 6. Ten per cent of kaolinite was evidently detected in the kaolinite-chlorite mixture, where the 10.2 Å of NH_4Cl -kaolinite complex was of great diagnostic value. In the case of halloysite-montmorillonite mixture, the result was less satisfactory due to poor x -ray diffraction of halloysite. The result obtained by replacing KCH_3COO -grinding with immersing was more favorable to the detection of halloysite in a small amount (Fig. 6, dotted lines), and this could be applied to halloysite hydrated or not completely dehydrated. Combination with organic solvation in x -ray diffraction analysis would provide more adequate means for the purpose, yet was not examined thoroughly.

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