

# APPLICATION OF AN INTERNAL STANDARD TECHNIQUE BY TRANSMISSION X-RAY DIFFRACTION TO ASSESS LAYER CHARGE OF A MONTMORILLONITE BY USING THE ALKYLAMMONIUM METHOD

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**Abstract**—Transmission X-ray diffraction (XRD) of C<sub>6–16</sub> alkylammonium ion-exchanged montmorillonite SAz-1 with Ag-behenate as an internal standard provided accurate estimates of *d*(001) values of the alkylammonium ion-exchanged montmorillonite. Inspection of *d*(001) values were made to assess the possible formation of gauche conformers (alternate arrangements of the molecules) in the interlayer and to determine the critical carbon chain length, *n<sub>c</sub>*. Using conventional constraints for *n<sub>c</sub>*(I') and *n<sub>c</sub>*(II) equal to 1.36 and 1.77 nm, respectively, provided ambiguous *n<sub>c</sub>*(I') and *n<sub>c</sub>*(II) values. The dependence of full-width at half-maximum values on *n<sub>c</sub>* allowed better estimates of *n<sub>c</sub>*(I') and *n<sub>c</sub>*(II) because “integral” and “non-integral” peak characteristics relating to interstratification could be included in the assessment.

The effect of inaccurate estimates of *n<sub>c</sub>*(I') and *n<sub>c</sub>*(II) values on calculated interlayer cation exchange capacity (*C<sub>i</sub>*) using two conventional concepts of calculation were compared. It was found that a procedure based on the summation of fractions of the layer charge gave relative errors of *C<sub>i</sub>* < 2%, even where the number of carbon atoms corresponding to both *n<sub>c</sub>*(I') and *n<sub>c</sub>*(II) differed by ± 1 *n<sub>c</sub>* from the correct values. This method of calculation of *C<sub>i</sub>* is recommended when reliable values of *C<sub>i</sub>* are needed.

**Key Words**—Alkylammonium Method, Interlayer Cation Exchange Capacity, Layer-Charge Determination, Montmorillonite, Silver Behenate, XRD

## INTRODUCTION

Layer charge is one important characteristic of expandable phyllosilicates, and it has been frequently investigated using the alkylammonium method (AAM) proposed by Lagaly and Weiss (1969, 1971). The method was later extended for characterizing layer-charge heterogeneities by layer-charge population histograms, using the peak-migration curve method (Lagaly and Weiss, 1975) and results from XRD experiments on randomly interstratified layers (MacEwan *et al.*, 1961; Reynolds, 1980). This approach was used to obtain charge attributes for ~200 mica-type layer silicates in an extensive study by Lagaly and Weiss (1975). These authors determined that layer-charge heterogeneities were common features of the natural clay minerals studied.

Charge characteristics obtained with AAM applied to Li<sup>+</sup>-treated smectites (Maes *et al.*, 1979; Malla *et al.*, 1987; Mermut, 1994) or H<sup>+</sup>-exchanged smectites (Janek *et al.*, 1997) as well as many other layered compounds (Beneke and Lagaly, 1982; Lagaly and Beneke, 1991) were reported also. Restrictions due to effects of particle-size distributions or non-ideal adsorption of alkylamines on edges of crystals were recognized and discussed by Lagaly *et al.* (1976), Lagaly (1981, 1994), Laird *et al.* (1987, 1989), Laird (1994), and Mermut (1994).

The advantage of the AAM is that it provides charge-population distributions on the layers, whereas the other methods supply an average value of the property proportional to the layer charge, *e.g.*, cation ex-

change capacity (CEC). Attempts were made to improve the time required to prepare alkylammonium derivatives (Ruehlicke and Kohler, 1981), and to evaluate the effect of layer charge by Lorentz and polarization-corrections and by curve fitting of measured XRD patterns (Stanjek *et al.*, 1992).

Vaia *et al.* (1994) reported a wide range of molecular environments of alkyl chains varying from “solid-like” to “liquid-like” in a series of intercalated alkylammonium silicates investigated by Fourier transform infrared (FTIR) spectroscopy, XRD, and thermal gravimetric analysis (TGA). Such molecular environments were believed to exist due to changes in alkyl chain length of the alkylammonium cations used, which resulted in a formation of gauche conformers (*i.e.*, alternative arrangements of the molecules). The existence of carbon-chain conformers in the interlayer space of layered silicates was reported also by Lagaly (1994). He suggested that chain conformers and/or chain kinks would increase the *d*(001)-value of alkylammonium cation-exchanged clays by ~0.1 nm.

No suitable XRD internal standard for the low-angle region has been used in previous AAM studies. Therefore, the accuracy of the determined *d*-values is questionable. Recently, Blanton *et al.* (1995) suggested Ag-behenate as a standard, which covers the low-angle region. This region is not adequately covered by the standards offered by the National Institute of Standards and Technology (NIST). The round-robin study of the lattice parameters of Ag-behenate (Blanton *et al.*, 1995) determined *d*(001) = 5.8361(6) nm. This value produces diffraction peaks near and within the

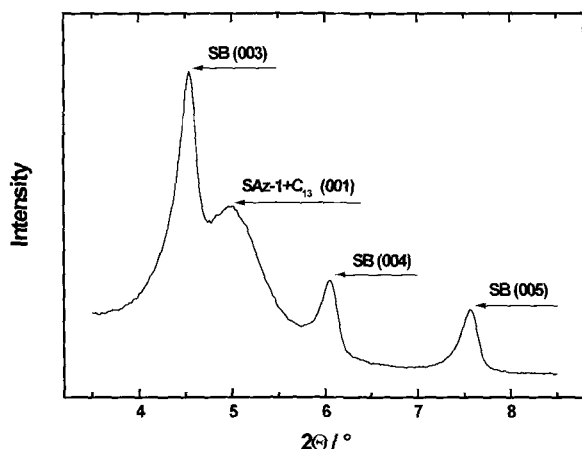


Figure 1. Transmission XRD pattern of the mixture of SAZ-1 sample exchanged with  $C_{13}$  alkylammonium cations and Ag-behenate (SB) used as an internal standard (intensity in arbitrary units).

regions of 003 and 005 peaks common in 2:1 phyllosilicates and their alkylammonium derivatives.

The objective of this study is to test the reliability of  $n_c(I')$  and  $n_c(II)$  estimates as derived from accurate  $d(001)$ -values obtained by an internal standard method using Ag-behenate. We examine also the effect of incorrect  $n_c(I')$  and  $n_c(II)$  values on derived potential interlayer cation exchange capacity values.

## MATERIAL AND METHODS

### Sample preparation

Montmorillonite SAZ-1 obtained from the Source Clays Repository of the Clay Minerals Society was used in this study. The  $<2 \mu\text{m}$ -size clay-fraction was saturated with  $\text{Ca}^{2+}$ , washed free of excess ions, dried at  $60^\circ\text{C}$  and ground to pass a 0.2 mm sieve. The structural formula was recalculated from the total chemical analysis (Kelley, 1955; Čížel and Komadel, 1994) and yielded  $\{\text{Ca}_{0.28}\}\{\text{Si}_{4.00}\}[\text{Al}_{1.34}\text{Fe}^{3+}_{0.07}\text{Mg}_{0.60}]\text{O}_{10}(\text{OH})_2$ . Before the preparation of alkylammonium derivatives, the sample was  $\text{Na}^+$  saturated by using 1 M NaCl solution, washed free of excess ions using water and ethanol, air dried at  $60^\circ\text{C}$ , and ground to pass a 0.2 mm sieve. Subsequent treatments to remove readily soluble oxo-hydroxo-phases from Na-saturated SAZ-1 were described elsewhere (Janek *et al.*, 1997).

The solid phase was re-suspended in distilled water to prepare a near 1% dispersion. Two-milliliter portions of this dispersion were exchanged with the alkylammonium cations of increasing chain length from  $C_6$ – $C_{16}$ , washed with water and ethanol, air dried at  $65^\circ\text{C}$ , ground, and vacuum-dried for 24 h (Lagaly, 1994). Prior to transmission XRD measurements, the alkylammonium derivatives were mixed with Ag-behenate in nearly a 1:1 mass ratio.

### XRD measurements and data evaluation

A Stoe Stadi-P transmission X-ray powder diffractometer with a curved Ge(111) primary beam monochromator and Cu radiation were used. X-ray data were collected with a linear-position detector. In preliminary scans, we found the  $d(001)$ -value of Ag-behenate to be 5.8362(12) nm, which is in excellent agreement with the value reported by Blanton *et al.* (1995). All subsequent patterns were scanned in the  $2\theta$  range of  $3.5$ – $8.5^\circ$  and the step-time was chosen differently for each sample to obtain a minimum of 10,000 counts at the  $d(001)$  maximum. The positions of three 00 $l$  peaks of the standard and one peak of SAZ-1 were obtained by pattern decomposition using a split Pearson VII profile function. The split Pearson VII function uses left and right side full-width at half-maximum (FWHM) parameters and two shape factors (Hall *et al.*, 1977).

## RESULTS AND DISCUSSION

A typical XRD profile obtained from the mixture of an alkylammonium derivative and Ag-behenate (SB) is shown in Figure 1. Peaks from SB are labeled 003, 004, and 005 at  $4.54$ ,  $6.05$ , and  $7.58$   $2\theta$ , and correspond to 1.946, 1.460, and 1.165 nm respectively. The broad peak labeled  $C_{13}$  is the 001 peak of SAZ-1 exchanged with alkylammonium cations of  $C_{13}$  chain length. Figure 1 shows that low-angle diffraction of alkylammonium-exchanged clay is associated with the 00 $l$  SB peaks. This suggests the suitability of SB as an internal standard.

Systematic errors in peak positions from SAZ-1 were corrected by linear interpolation between either  $\Delta_{003}-\Delta_{004}$  or  $\Delta_{004}-\Delta_{005}$ , where these values were calculated as the differences between the observed and calculated positions of 003, 004, and 005 peaks of SB. Since the nonlinear *least-squares* procedure used for parameter estimation provided corresponding variances but no covariance elements, it was not possible to estimate correctly the variances of peak positions after correction. Therefore, instead of assigning estimated standard deviations, 95% confidence intervals were constructed for the corrected interplanar distances using the critical values of  $t_\alpha$  distribution and observed standard deviations of fitted peak positions (error bars on Figure 2). We believe that these intervals are good estimates for the errors of the corrected positions.

Dependence of corrected  $d(001)$ -values on the number of the carbon atoms of the alkylammonium molecule is shown in Figure 2. We observed a decrease of  $d(001)$ -values for the alkylammonium derivatives with a critical carbon chain length,  $n_c$ , equal to 13 and 14 compared to  $n_c = 12$ . A similar trend was found by Laird (1994) for alkylammonium derivatives of Wyoming bentonite with  $n_c = 16$ –18. This behavior was noted by Lagaly (1994) and Vaia *et al.* (1994) and

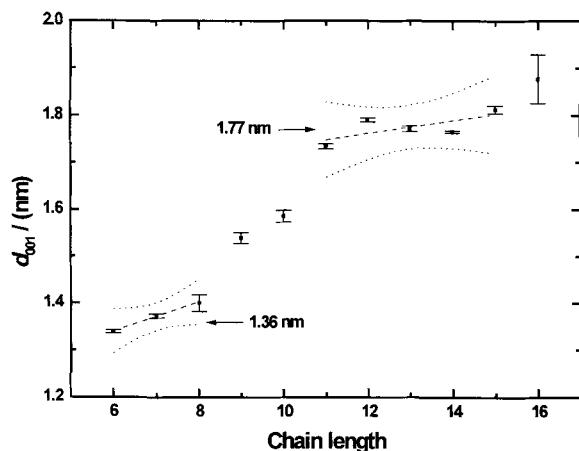


Figure 2. Dependence of the basal spacing of alkylammonium derivatives of SAz-1 on the chain length of alkylammonium ions. The error bars represent 95% confidence intervals of corrected  $d(001)$  values. Dotted lines show 95% confidence bands of linear dependence  $d(001)$  vs.  $n_c$  for  $n_c \in \{6, 8\}$  and  $n_c \in \{11, 15\}$ .

is believed to be direct evidence for the formation of gauche conformers. Prolongation of carbon chains is restricted by geometrical constraints and the pseudo-trimolecular (Lagaly, 1994) layer arrangement of alkyl chains that start to form in the interlayer. A remarkably large confidence interval for the  $n_c = 16$  case (Figure 2) was due to considerable overlap of the SAz-1 and SB peaks.

Assessment of the number of carbon atoms of the longest chains which can be packed in monolayers,  $n_c(I')$ , and bilayers,  $n_c(II)$ , from which the mean layer-charge value is estimated, may be complicated for cases where limited  $d(001)$  data scatter around 1.36 nm and 1.77 nm respectively, since the tolerances of those two critical values are unknown (Figure 2). Reliability of the  $n_c(I')$  and/or  $n_c(II)$  values thus may be significantly influenced by the possible formation of gauche conformers reported by Lagaly (1994) and Vaia *et al.* (1994). These values are also important for the evaluation of the data by means of layer-charge distribution, or for the calculation of the mean layer-charge value.

For another assessment of  $n_c(I')$  and  $n_c(II)$  values, it was assumed that the number of kinks and gauche conformers is directly proportional to the length of the alkyl chain. To estimate possible errors for  $d(001) = 1.36$  and  $d(001) = 1.77$  nm critical values, 95% confidence bands for the linear dependence of  $d(001)$  on  $n_c$  were constructed for the  $n_c$  intervals between 6–8 and 11–15, respectively (Figure 2).

For cases where conventionally accepted estimates for monolayer (1.36 nm) and bilayer (1.77 nm) arrangements are to be used, the values  $n_c(I') = 6$  and  $n_c(II) = 12$  are required. However, a statistical approach to calculate confidence bands indicated that

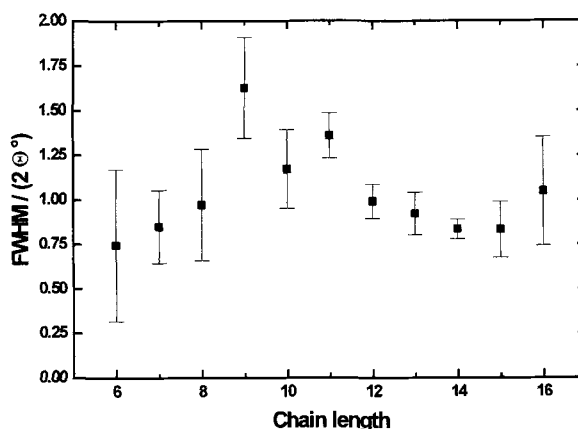


Figure 3. Full width at half maximum of  $d(001)$  peaks as the function of alkylammonium cation chain length. Error bars represent standard deviation of FWHM values.

$d(001)$ -values corresponding to  $n_c = 8$  and 11 can be found within calculated confidence bands (dotted lines in Figure 2). Thus, those values must be considered also as the estimates of the true values of  $n_c(I')$  and  $n_c(II)$ , respectively.

This approach shows that the error intervals of experimental and critical monolayer to bilayer and only bilayer transition values are framed within the confidence bands. This overlap provides different values of  $n_c(I')$  and  $n_c(II)$  in comparison to values obtained by conventionally accepted estimates. To solve this ambiguity, analyses of FWHM of XRD peaks were performed. The FWHM estimates are based on the “integral” and “non-integral” character of XRD for periodic layer sequences or randomly interstratified layers, respectively. The  $d(001)$  “non-integral” diffraction is characterized by broadening of the peak in the XRD pattern (Lagaly, 1994).

In Figure 3, observed FWHM values with standard deviations are shown. Significant deviation from the trends for alkylammonium-exchanged samples are observed for  $n_c = 9$  and  $n_c = 11$ . Hence, for  $n_c(I')$  and  $n_c(II)$ ,  $n_c = 8$  and 12 must be considered, respectively. The decrease of FWHM value for the sample with  $n_c = 10$  is not understood since the “non-integral” character of peaks in the pattern should be observed for samples exchanged with alkylamines in the range from 9–11.

Further, we examined the effect of accuracy of  $n_c(I')$  and  $n_c(II)$  values on the value of the resulting mean layer charge ( $\xi$ ). We also considered the effect of  $\xi$  on the potential interlayer cation exchange capacity ( $C_i$ ). To evaluate the errors on the calculated  $C_i$  values, we used the method as outlined below.

From the  $d(001)$  data of alkylammonium derivatives of the SAz-1 sample, “accurate” values with an acceptable uncertainty interval of  $\pm 1 n_c$  equal to  $n_c(I') = 7$  and  $n_c(II) = 12$  were selected. The  $n_c$  values of

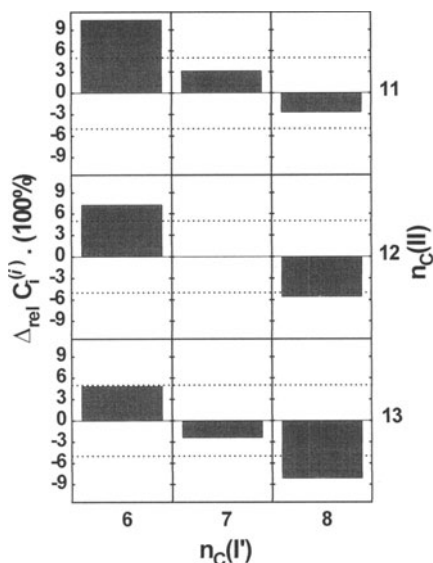


Figure 4. Relative errors of  $C_i$  calculated by the procedure *i*. Dotted lines represent the relative error of 5%.

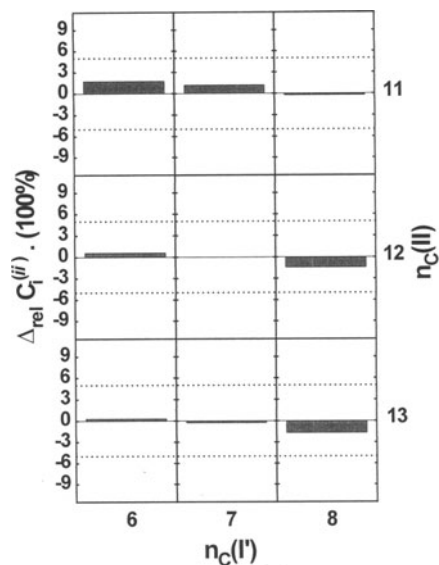


Figure 5. Relative errors of  $C_i$  calculated by the procedure *ii*. Dotted lines represent the relative error of 5%.

lower accuracy were within a tested uncertainty interval from the above selected values. In this case a combination scheme of  $3^2$  values of  $\xi$  and of each  $\xi$  based  $C_i$  was obtained. The “accurate” value of  $C_i$  was thus situated in the center of the uncertainty range.

Lagaly (1994) proposed two approaches to calculate  $\xi$  which we used for every element of the combination scheme. The first calculation procedure (*i*) represents the simplest estimate of  $\xi$  from the charge densities  $\xi_j$  corresponding to  $n_{C(I')}$  and  $n_{C(II)}$  values by arithmetic mean:

$$\xi^{(i)} = \frac{1}{2}(\xi_{n_{C(I')}} + \xi_{n_{C(II)}}) \quad (1)$$

where  $\xi_{n_{C(I')}}$  and  $\xi_{n_{C(II)}}$  are charge densities corresponding to the closest-packed monolayer in an interlayer of the half-unit cell of smectite, with the chain length of alkylammonium cations equal to  $n_{C(I')}$  and  $n_{C(II)}$ . The second procedure (*ii*) was based on the equation:

$$\xi^{(ii)} = \sum_j \xi_j \Delta\chi_j \quad (2)$$

where  $\Delta\chi_j$  is the fraction of layers of average charge density  $\xi_j$ . Mean layer-charge densities  $\xi$  are used to obtain  $C_i$  applying the formula:

$$C_i^{(k)} = 10^3 \xi / M \quad (3)$$

where  $M$  (361.0 g.mol<sup>-1</sup>) is the molar weight of the silicate framework per [O<sub>10</sub>(OH)<sub>2</sub>] unit without exchangeable cations, as obtained from the structural formula (see above), and  $k$  indicates the calculation procedure used (*i* or *ii*). Finally, from the  $C_i$  values obtained by both approaches, relative errors ( $\Delta_{\text{rel}} C_i$ ) are found:

$$\Delta_{\text{rel}} C_i^{(k)} = \frac{\text{acc} C_i^{(k)} - C_i^{(k)}}{\text{acc} C_i^{(k)}} 100\% \quad (4)$$

where  $\text{acc} C_i^{(k)}$  is the “accurate” value of interlayer cation exchange capacity based on the median of the error estimates from the combination scheme,  $C_i^{(k)}$  is the interlayer cation exchange capacity achieved for the corresponding  $\pm 1$  boundaries of  $n_{C(I')} = 7$ ,  $n_{C(II)} = 12$  using calculation procedure  $k$ . The  $d(001)$ -value for  $n_C = 12$  in procedure *ii* was artificially lowered to 1.76 nm to obtain meaningful results of the combination scheme for arrangements with  $n_{C(II)} = 13$ , which was necessary when the peak migration curve data were used (Lagaly, 1994).

Relative errors of  $C_i$  values from *i* and *ii* are shown in Figures 4 and 5, respectively. Although both figures show similar trends, the absolute values of the relative errors obtained from *ii* are significantly lower. An incorrect assessment of  $n_{C(I')} = 7$  to a lower value ( $n_{C(I')} - 1$ ) caused a positive deviation, *i.e.*, an overestimation of the  $C_i$  value occurred, whereas  $n_{C(I')}$  increasing towards a higher value ( $n_{C(I')} + 1$ ) caused a negative deviation, *i.e.*, underestimation of the  $C_i$  value. Similar variations occur for  $n_{C(II)} = 12$  and corresponding ( $n_{C(II)} - 1$ ) and ( $n_{C(II)} + 1$ ) values.

If we accept an upper limit of 5% relative error (dotted lines in Figures 4 and 5), as a reproducible precision of any method currently used to determine, for example, cation exchange capacity, then an incorrect assessment of  $n_{C(I')}$  results in a higher relative error in  $C_i$  than an incorrect assessment of a  $n_{C(II)}$  value (Figure 4). Acceptable relative errors (<5%) of the calculation procedure *i* were found only in the case where the  $n_{C(I')}$  value was assessed correctly and

$n_c(\text{II})$  deviates from the accurate value in the  $\pm 1$  range. Further, in the case where the errors have opposite signs, they compensate for the combinations of  $n_c(\text{I}') + 1$  with  $n_c(\text{II}) - 1$  and  $n_c(\text{I}') - 1$  with  $n_c(\text{II}) + 1$ , respectively (Figure 4).

Alternatively, all relative errors of  $C_i$  calculated by procedure *ii* (Figure 5) are below 2%. This is due to the nature of the calculation procedure used (*ii*) which may be understood as a simple integration procedure following an oblong path. The results obtained in this case are much less sensitive to small errors introduced by the evaluation of the S-shaped dependence curve of  $d(001)$  on  $n_c$ , which intersect at acute angles at limiting 1.36 nm and 1.77 nm values. Because this dependence curve is very common at alkylammonium derivatives of smectites (Lagaly and Weiss, 1975), this procedure is strongly recommended when reliable values of  $\xi$  and/or  $C_i$  are needed.

### CONCLUSIONS

This study showed that Ag-behenate can be used as an internal standard for the low angle region in XRD patterns in the investigation of alkylammonium derivatives of montmorillonites. The main advantage is that this internal standard method allows correction of interplanar distances at high  $d$ -values by interpolation. A statistical approach in the critical evaluation of the dependence of  $d(001)$  on carbon chain length ( $n_c$ ) in the assessment of  $n_c(\text{I}')$  and  $n_c(\text{II})$  values provided ambiguous results in comparison to conventionally accepted constraints. The FWHM values used here to assess carbon chain length ( $n_c$ ) were helpful in the accurate assessment of  $n_c(\text{I}')$  and  $n_c(\text{II})$ .

The estimates of possible errors in the determination of mean layer charge ( $\xi$ ) and potential interlayer cation exchange capacity ( $C_i$ ) were given. The results showed that the procedure based on the summation of fractions of the layer charge gave relative errors of  $C_i < 2\%$ , whereas the values obtained by a simple arithmetic-mean procedure were in error by 3–10%.

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