

NOTE

DETERMINATION OF THE CATION EXCHANGE CAPACITY (CEC) OF CLAY MINERALS USING THE COMPLEXES OF COPPER(II) ION WITH TRIETHYLENETETRAMINE AND TETRAETHYLENEPENTAMINE

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INTRODUCTION

The ion-exchange capability of clay minerals, in particular, smectites, influences their unique physical properties, such as the cation retention and diffusion processes of charged and uncharged molecules. These processes influence cation and molecule migration through clay-rich barriers in nature. The numerical value of this property is described by the cation exchange capacity (CEC). Methods for determining CEC involve the complete exchange of the naturally-occurring cations by a cationic species, such as ammonium, K, Na, methylene blue, Co(III) hexamine complex (Rémy and Orsini, 1976), Ba, Ag thiourea complex, and Cu(II) ethylenediamine complex. Exchange with organic cations, such as alkylammonium, provides an indirect method for the determination of CEC. This procedure involves determination of the expansion of the layers and calculations involve charge density (Olis *et al.*, 1990; Lagaly, 1981). Depending on the method utilized, the excess of the exchanged cations is removed in a subsequent step and the amount retained on the clay is determined. However, the determined CEC values are dependent on the method used. Although time consuming, the exchange with ammonium acetate is the standard method for CEC determination (Mackenzie, 1951).

To obtain complete ion exchange and to obtain reliable values of CEC, either a high surplus of an exchanging cation or a cation with a high affinity for the clay mineral must be employed. In the former, because of the excess of cations, (usually in 1 M salt solutions) clay suspensions must be washed until salt free. A determination of concentration before and after the cation exchange to assess differences at such high con-

centrations is not appropriate, due to the small relative differences at these high concentrations.

Methylene blue can be used in a rapid qualitative procedure, but results are not reliable in comparison to other methods (Kahr and Madsen, 1995; Yariv *et al.*, 1990). Recent investigations of CEC methods use an Ag thiourea complex (Dohrmann and Echle, 1994; Chabra *et al.*, 1975), Co(III) hexamine complex (Rémy and Orsini, 1976), and Cu(II) ethylenediamine complex (Bergaya and Vayer, 1997). Clay minerals have a high affinity for these ions. This affinity allows CEC determination directly, via the ion concentration decrease in the exchanging solution.

The Cu in the blue Cu(II) ethylenediamine complex has a high affinity for clay minerals. Thus, atomic absorption spectroscopy (Bergaya and Vayer, 1997) would allow for an easy photometrical determination. However, the photometrical extinction in these solutions is too low.

The Cu(II) ion forms stable complexes with the oligamines triethylenetetramine (trien), tetraethylenediamine (tetren), and pentaethylenehexamine (penten), which are bound over four and five N atoms to Cu. They form violet-blue complexes. The stability constants are 20.4 for Cu(II)-trien, 22.8 for Cu(II)-tetren, and 22.4 for Cu(II)-penten, respectively (Gmelin, 1966). The maximum light extinction for these complexes varies slightly in the pH range of 5–10. The maximum absorption is not affected by other cations or anions at low salt concentration (Cheng, 1962). Compared to other methods the Cu(II) complexes with triethylenetetramine and tetraethylenepentamine allow an easy and rapid CEC determination by photometric analysis.

Table 1. Characteristic values of the investigated materials.

Sample	Origin	Clay content %	Interlayer cations exchange
Bentonite SAz-1 ("Cheto")	Arizona (USA)	90	Ca ²⁺
Bentonite Volclay	Wyoming (USA)	89	Na ⁺
Bentonite MX-80	Wyoming (USA)	75	Na ⁺
Bentonite Montigel	Bayern (Germany)	62	Ca ²⁺
K-Bentonite B39	Kinneulle (Sweden)	76	Ca ²⁺
K-Bentonite B31/32	Kinneulle (Sweden)	87	Ca ²⁺
K-Bentonite M40	Montana (USA)	39	Ca ²⁺ /Mg ²⁺
Illite MC	Massif Central (France)	88	Ca ²⁺
Illite S	Sarospatak (Hungary)	86	Ca ²⁺
China Clay (Kaolinite)	St. Austell (UK)	99	Ca ²⁺
Clinoptilolite	Slowakia	160	Ca ²⁺

MATERIALS AND METHODS

Several clay minerals and a zeolite (Table 1) of known CEC were used. Table 2 shows each CEC as determined by the ammonium acetate method and the respective methylene-blue value (not corrected with the CEC of a reference clay) measured with Na hexa metaphosphate as a dispersion agent (Kahr and Madсен, 1995).

Cu(II) sulfate (purum, free of water), triethylenetetramine (purum), tetraethylenepentamine (techn.), and pentaethylenhexamine (techn.) were obtained from FLUKA AG, CH-9471 Buchs. Cu(II)-trien complex was used for the determination because of its high purity. Exchange with the Cu(II)-penten complex solution showed no significant difference to the tetren complex and thus, was not investigated further.

Preparation of the 0.01 M copper(II)-trien sulfate solution

1.463 g of triethylenetetramine were dissolved in 100 ml of distilled water. Another solution was prepared by mixing 1.596 g of dry Cu(II) sulfate with distilled water to give 1 l of solution. These solutions were then mixed together. A series of dilute Cu(II) complex solutions was prepared and the extinction was

determined at 620 nm by a Lange LP 1W Filterphotometer. The extinction maxima was 580 nm for Cu(II)-tren and 630 nm for Cu(II)-tetren and Cu(II)-penten using a Dr. Lange CADAS 100 photometer. Linearity in the absorption was observed in the range of 10⁻⁴ and 10⁻² M in the Cu complexes.

The pH of the Cu complex solution was ~7 and the solution was not buffered for the exchange reactions. However, measurements in phosphate buffers at pH of 7 gave similar results.

Experimental procedure for the photometric measurement with the Copper(II)-tren complex

200 mg (± 0.5 mg) of clay sample with a CEC of <100 mMol/100 g were added to 35 ml of distilled water and dispersed by ultrasonic treatment (20 kHz, 400 W, 5 min). Any remaining sample was washed off the ultrasonic rod. The suspension was diluted in a 50 ml volumetric flask to 50 ml, then completely transferred into a 100 ml beaker. While stirring the suspension, 10 ml of the solution of the Cu complex was added. After 3 min reaction time, the suspension was centrifuged with a microcentrifuge at 13,000 rpm (a force of 11,000 'g') for 3 min. The supernatant solution was carefully removed and the extinction was

Table 2. Measured CEC with the ammonium acetate method and with the copper(II) complexes and the methylene blue value (not corrected with the CEC of a reference clay).

Material	CEC NH ₄ OAc pH 7 (mmol/100 g)	Methylene blue value (mmol/100 g)	CEC Cu-trien (mmol/100 g)	CEC Cu-tetren (mmol/100 g)
Bentonite SAz-1	120	145	122.0	122.0
Bentonite Volclay	81.9	106	84.5	83.7
Bentonite MX-80	71.5	92	75.5	78.9
Bentonite Montigel	62	78	63.9	65.2
K-Bentonite B39	53	75	60.1	59.9
K-Bentonite B31/32	42	63	46.1	48.7
K-Bentonite M40	29	40	31.4	32.6
Illite MC	19	29	20.0	21.9
Illite S	16	25	19.0	20.0
China Clay (Kaolinite)	3.8	12	6.4	4.0
Clinoptilolite	160	10	5.0	4.0

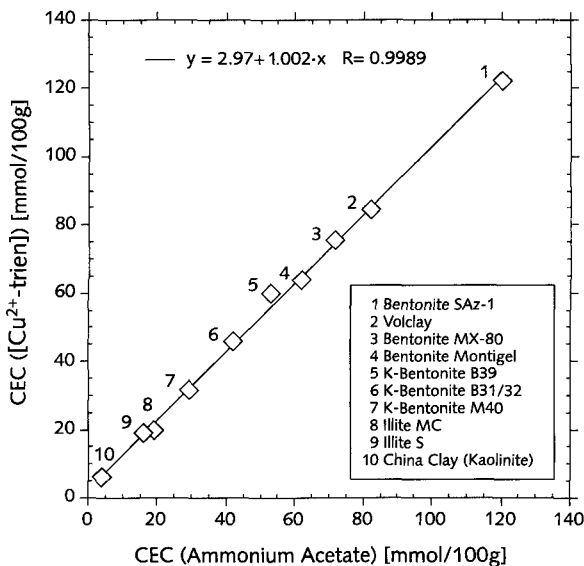


Figure 1. Comparison of CEC measurement methods using ammonium acetate method and Cu(II)trien method.

measured at 620 nm in a 10 mm cuvette against water as a blank. The CEC was then calculated with reference to the dry clay weight:

$$\text{CEC (mmol/100 g)} = (\text{Eb} - \text{Em}) \times 100/\text{Eb}$$

where Eb = Extinction without sample (blank value) and Em = Extinction of the supernatant solution. The water content of the samples was determined from the weight obtained after drying at 105°C overnight.

RESULTS AND CONCLUSIONS

The CEC results obtained from the photometric measurement with the copper complexes are reported in Table 2. Note that the CEC values are slightly higher than the ones obtained with the ammonium acetate method. For the comparison, these values are shown in Figure 1. Clearly, Table 2 shows that the zeolite (clinoptilolite) varies greatly in CEC values with the two methods and is not included in Figure 1. For this case, structural holes in clinoptilolite are accessible to the small ammonium ion but not for the larger Cu complex, which exchanges with only surface-site cations.

Note that Cu determination by atomic absorption spectroscopy (Bergaya and Vayer, 1997) is not sufficiently reliable to determine the CEC. Unavoidable errors are introduced during the dilution procedure. In

summary, the CEC measurement using the Cu complexes of trien, tetren, and penten is a rapid and reliable method. The CEC results using this method are in good agreement with the standard ammonium acetate method. However, this method should not replace the ammonium acetate method for certain materials, such as zeolites. Nonetheless, the method gives reliable values of CEC quickly and without the use of expensive equipment. Values of the CEC are much closer to those obtained using ammonium acetate compared to those obtained using the methylene-blue method (Kahr and Madsen, 1995). In addition, the CEC determination using the Cu(II)-trien complex is suitable for Na and Ca-rich clay.

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