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CEC determination with Cu-triethylenetetramine: recommendations for improving reproducibility and accuracy

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ABSTRACT: The strongly coloured Cu-triethylenetetramine complex (Cu-Trien) provides a fast and easy way to measure the cation exchange capacity of clay samples, but the reliability of this method has been questioned in recent publications. This work identifies several reasons for the poor reliability, thus improving both the precision and accuracy of the CEC method. Pure Trien is shown here to intercalate as does the Cu-Trien complex. Hence, the purity of Trien and also the Cu/Trien ratio require special attention. Using cold Cu-Trien solutions produces systematic deviations in CEC determinations caused by errors in the pipetted volumes. The present study demonstrates, for the first time, that the Cu-Trien complex protonates and changes its effective charge beyond 2^+. Based on titration experiments at three different temperatures, a correction function is derived for calculating the total charge of the Cu-Trien complex as a function of pH. Accounting for these pH-corrected charges indicates that Cu-Trien may well be insensitive to edge charges on smectite. Finally, it is shown here that the ratio of sample mass to the initial amount of Cu-Trien is critical because excess adsorption of Cu-Trien in addition to CEC *sensu strictu* was observed.

KEYWORDS: cation exchange capacity, Cu-Trien exchange, protonation, pH titration, reproducibility, accuracy, *PHREEQ*.

The cation exchange capacity (CEC) is one of the most important properties of clay minerals and reflects the ability to adsorb and desorb, reversibly, a certain molar amount of cations per mass of solid. Since its first description in 1852 (Way, 1852, cited by Dohrmann *et al.*, 2012b) numerous methods have been developed to quantify the CEC, either by direct quantification of the exchanged cations or by determining the balance for an index cation calculated from the difference between an amount added initially and the amount remaining in solution following exchange (for further details see Bergaya *et al.*, 2006). The latter approach has been elaborated by Meier & Kahr (1999) and Ammann *et al.* (2005) in the so-called Cu-Trien method, which quantifies the concentration of the strongly coloured Cu^{2+}-Trien complex in solution by photometry. Other coloured complexes such as Cu-ethylenediamine (Bergaya & Vayer, 1997), hexaminecobalt (III) (Remy & Orsini, 1976) methylene blue (Kahr & Madsen, 1995), crystal violet (Yariv *et al.*, 1990) and others (*e.g.* Grauer *et al.*, 1987) are generally less used for a variety of reasons: (1) they lack sufficient affinity for complete exchange with clay mineral phases; (2) their photometrical extinction is not high enough to allow for precise determination (Meier & Kahr, 1999); and (3) they do not adsorb on an equimolar basis due to the formation of dimers and higher species, a problem particularly associated with using methylene blue (Bujdák *et al.*, 1998; Bujdák, 2015).

The technical ease of use of the Cu-Trien method is considered to supersede more conventional approaches

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TABLE 1. Protonation (log K) and complex formation (log β) constants for Cu*p*TrienH*q* Cl*r*.

p	*q*	*r*	log K, β	Reference
0	1	0	9.67	1
0	2	0	18.54	1
0	3	0	24.65	1
0	4	0	27.03	1
0	1	1	9.36	1
0	2	1	19.32	1
0	3	1	26.08	2
0	4	1	28.78	2
1	0	0	20.3	3
1	1	0	23.4	3

(1) De Robertis *et al.* (2001).
(2) De Robertis *et al.* (1993).
(3) Nurchi *et al.* (2013).

to CEC determination, such as the ammonium acetate method (*e.g.* Borden & Giese, 2001), because larger sample sets can be analysed in a shorter time (*e.g.* Grygar *et al.*, 2009; Stanjek *et al.*, 2013). Furthermore, the metal-complex methods do not suffer from problems arising from dissolution reactions in the sample with, for example, gypsum and calcite (Dohrmann *et al.*, 2012b). The precision of the Cu-Trien method has recently been investigated in a round robin (Dohrmann *et al.*, 2012b) and found to be acceptable, when the solid-Cu-Trien ratio and the solution pH were kept constant (Dohrmann *et al.*, 2012b). Earlier work by Grygar *et al.* (2005, 2009) showed consistent deviations between the sum of charges of exchanged cations and the CEC from Cu-Trien, whereas Czímerová *et al.* (2006) found good agreement for source clays and other minerals. One possible source for these systematic discrepancies could be protonation reactions of the NH-groups of the Trien molecule (see Bencini *et al.*, 1999, for a review), a detail, which has not been addressed in the CEC literature. Such an uptake of protons would imply that the Cu-Trien complex bears variable amounts of proton charges in addition to the copper charge of +2. The aim of the present work was therefore to test this hypothesis and to consider implications for the Cu-Trien method. Additionally, a careful examination of other factors that may affect this CEC technique, such as the purity of the Trien, was undertaken: problems associated with pipetting Trien solutions, the influence of sample:Trien ratios and concentration variations. In addition, chloride was tested as an alternative to Cu-Trien preparation.

THEORETICAL BACKGROUND

The oligoamines triethyleneamine (Trien), tetraethyleneamine (Tetren) and pentaethyleneamine (Penten) form stable complexes with Cu^{2+} by chelating the cation with four or five nitrogen atoms of the amine groups (see Cheng, 1962). However, these amines protonate to various extents (Cascio *et al.*, 1999; Bencini *et al.*, 1999; De Robertis *et al.*, 2001) and the Cu-Trien-complexes do this as well (Doyle & Liu, 2003; Nurchi *et al.*, 2013). The complexation of chloride anions render the protonation reactions dependent on ionic strength (De Robertis *et al.*, 1993). The complex formation reactions can be summarized as:

$$\text{Trien} + p\text{Cu}^{2+} + q\text{H}^{+} + r\text{Cl}^{-} \leftrightarrow [\text{Cu}p\text{TrienH}q\ \text{Cl}r]^{2p+q-r} \quad (1)$$

The corresponding K or complex formation constants β (see Table 1) have been added to the database *Wateq4f.dat* of *PHREEQC* (Parkhurst & Appelo, 1999) and used to model the species distributions as a function of pH (Fig. 2).

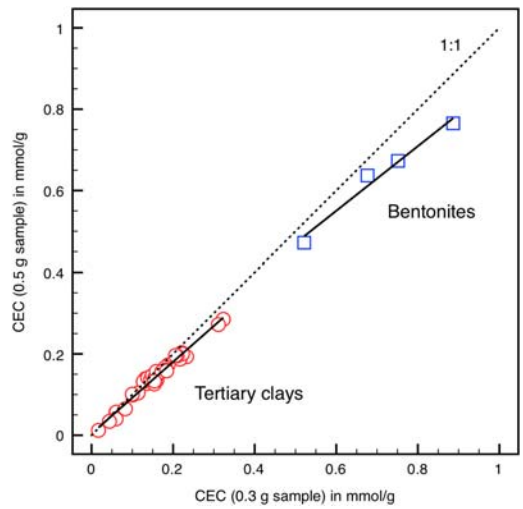


FIG. 1. Cation exchange capacities determined with two sample weights and constant Cu-Trien addition. (○) Samples from Tertiary clays, Hambach, Germany ($y = 0.0039 + 0.883x$, $n = 38$, $r^2 = 0.988$). (□) Mg smectites ($y = 0.074 + 0.794x$, $n = 4$, $r^2 = 0.988$). Cu-Trien_{60} concentration = 0.02 M, solution volume = 51 mL.

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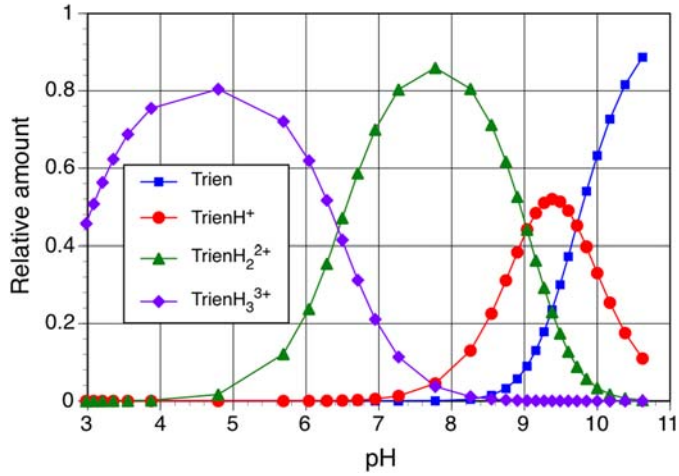


FIG. 2. Distribution of species *vs*. pH of a 4 mM Trien solution and 9 mM NaCl. Constants from De Robertis *et al.* (2001). Species $TrienH_4^{4+}$ was not plotted, and complexes with Cl^- were omitted because of negligible amounts.

MATERIALS

Triethylenetetramine (Sigma-Aldrich, CAS 112-24-3) with a purity of 60% and 97%, denoted as $Trien_{60}$ and $Trien_{97}$, respectively, was used. When not indicated explicitly, $Trien_{97}$ was used.

$CuSO_4 \cdot 5H_2O$ (CAS 7758-99-8) and $CuCl_2 \cdot 2H_2O$ (CAS, 10125-13-0) were obtained from Sigma Aldrich. The Cu-Trien solutions were prepared by dissolving $CuSO_4 \cdot 5H_2O$ in ~0.5 L of H_2O (Micropure). Trien was taken up with a syringe from the bottle. Then, an amount corresponding to the Cu sulfate was dropped into a beaker placed on a four-digit balance. The Trien was combined with the sulfate solution and made up to 1 L volume. The samples tested are described in Table 2. Sample BeW was used by Heuser *et al.* (2014). The clay fractions (<2 μm) were collected by the Atterberg method, where the suspensions containing <2 μm were coagulated with large amounts of $MgCl_2$. After the last collection step, the suspensions were treated three times with 1 M $MgCl_2$, NaCl or $CaCl_2$ to obtain homoionic clays. All clay fractions were dialysed down to an electrical conductivity of <20 μS/cm and then freeze-dried. Additional clay fractions were exchanged fully with Cu-Trien, dialysed and freeze-dried.

METHODS

Cation exchange capacities were measured by adding 1–4 mL of a 0.1 M Cu-Trien solution to a suspension of *x* g of smectite dispersed in either 25 or 50 mL of H_2O, where *x* ranged between 0.1 and 0.5 g. After equilibration for 60 min under shaking, the supernatant was filtered with an inline filter (pore size 0.45 μm) or alternatively centrifuged at 4000 min^{-1}. Filtering did not affect the Cu-Trien concentrations compared to centrifuging. Cu-Trien was quantified photometrically at 584 nm using a Specord 210 Plus (Analytik Jena). In contrast to the procedure of Meier & Kahr (1999) and Ammann *et al.* (2005) the present study relied on a full calibration curve based on six to 10 calibration solutions. Selected reference CECs were measured by exchanging the interlayer cation suite with either Cs^+ or NH^+ ions and quantification of the exchanged cations by ion chromatography (IC). These absolute CEC values are not considered to be very precise, however, due to impurities in the salts used and to unknown amounts of cations dissolving from solids in the samples (see Dohrmann & Kaufhold, 2009, for further detail).

To check whether the Trien itself adsorbs onto smectite, pure Trien solutions (4 mM) were added to 200 mg clay samples. Tests for residual Trien remaining in solution were performed by adding $CuSO_4$ after 1 h to the supernatant solution. Alternatively, 0.8 or 2.0 mL Cu-Trien solution was added to check whether the Cu-Trien exchanges after the intercalation of the pure Trien. In selective experiments, the pH of the suspensions was adjusted either before adding the Trien or Cu-Trien solution or after the adsorption process. Equilibration time was 1 h in each case. The

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TABLE 2. Samples, mineral contents (g/g) and CEC (mmol(+)/g at $m/n = 0.5$, sulfate system, 1 h) of clay samples.

Sample	Smectite	Illite	Kaolinite	Quartz	other phases	CEC
B1 Bavaria	0.80	0.18	0	0.02	0	0.73
BeW (<2 µm)	0.84	0.02	0	0.05	0.09	0.82
Na-Icosorb (<2 µm)	0.77	0.06	0	0.02	0.15	0.79
Reuver Ton	0.14	0.41	0.14	0.25	0.06	0.17

sediments were transferred subsequently to ceramic plates, air dried and X-rayed.

The protonation reactions of Trien and Cu-Trien were measured by potentiometric titration in a thermostated vessel with a background electrolyte of constant ionic strength (Cascio *et al.*, 1999). The temperatures of the solutions were kept constant at ±0.05°C using a Julabo water bath. To obtain stable readings, it was essential to purge the solutions with N_2, which passed a washing bottle to moisten the gas. The solutions were stirred with a small Metrohm stirrer plunging into the solution from the top. The potential E of the pH electrode (A1180 from SI Analytics) relative to a double salt bridge (B2220+ with Pt diaphragma, SI Analytics) was measured using a Keithley 6514 electrometer with an input impedance of $>2 \times 10^{14}$ Ω, a resolution of 10 µV and an accuracy of ±0.025%. The Ag/AgCl electrode of the salt bridge was in contact with a 3 M KCl and the outer compartment filled with the solution of the corresponding pH measurement. The potentials were monitored by an Agilent 34461A multimeter connected to the preamplifier output of the Keithley electrometer. Simultaneously, a second 34461A meter measured the temperature in the solution with a four-wire PT100. The pH electrode was tested for linearity, asymmetry and liquid junction potentials, E_j, using secondary buffers and following the protocols of Westcott (1978), Jarlbring *et al.* (2005) and especially Szekeres & Tombácz (2012) for testing electrode performance at ~pH 7.

The normality of the base solutions was measured by conductometric titration with an acid (Titrisol solutions, Merck), in which the intersection of both regression lines in a Gran plot povides the normality of the base (Gran, 1950, 1952). It is important that the pH electrode was not immersed in these Gran experiments because efflux from the reference electrode into the solution resulted in a parabolic deviation around the neutralizing point. The proton balance was obtained by calculating the difference between the amount of protons added and the amount of protons in solution. The latter was calculated from the pH of the solution.

RESULTS

The motivation for the present study came from previous initial CEC experiments which showed that systematic differences in the measured CEC occur, depending on the solid:Cu-Trien ratio used. These effects are in accordance with those observed by Grygar *et al.* (2009) and occur even in pH-buffered solutions (Fig. 1).

Influence of temperature on pipetting aliquots

During previous CEC studies the first sample within a series of repeat measurements was often observed to have a consistently lower CEC value than subsequent samples, and in some sample series this effect was apparently absent. A scrutiny of all potential causes revealed that the temperature of the Cu-Trien solution used was the cause; this varied between the storage temperature of ~5°C and room temperature. In order to further study this effect, the influence of temperature on the pipetting volumes was measured by weighing the solutions on a balance and ignoring minor changes in density with temperature. A comparison between solutions pipetted with fresh and used tips revealed that cold Cu-Trien resulted in significantly different volumes (Fig. 3). Lochner *et al.* (1996) described the same phenomenon and attributed this to the complex interplay of temperature variations in the pipette tips relative to the temperature of the solution. The amount of liquid sucked into a tip depends on the volume of air displaced by pushing the piston downward. A later change of temperature of this air cushion influences the pipetted volumes, therefore. Pipetting a cold liquid into a warm pipette results in a larger volume because the contraction of the cooling air acts as an additional

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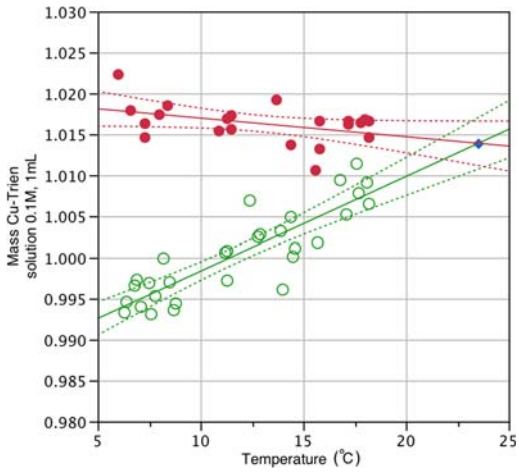


FIG. 3. Masses of Cu-Trien$_{97}$ solution pipetted with fresh and with used tips as a function of solution temperature. Filled circles represent fresh tips, open circles denote used tips, which were used twice or more. The intersection point of both regression lines is denoted with the diamond.

suction pressure (Fig. 3). This effect diminishes with increasing fluid temperature, as the temperature differences between the warm tip and colder fluid decrease. However, once the air cushion in the pipette has cooled, a second pipetting step results in correspondingly lower volumes. An additional effect on the pipetting volume is the development of a vapour pressure in the tip, which is reduced at lower temperature. Counteracting this effect is the repeated usage of the same tip, in which the vapour pressure will increase (Lochner *et al.*, 1996). All of these temperature-related effects described can be eliminated easily by storing the Cu-Trien solution at room temperature, which also minimizes the uptake of CO_2 from the air, as discussed below.

Purity of Trien

The purity of the Trien was checked by a complexiometric titration (*e.g.* Rohwer *et al.*, 1995, and references therein). Adding $CuSO_4$ to the Trien$_{97}$ solution increased the absorption linearly ($r^2 = 0.999989$, $n = 19$) up to a molar Cu/Trien ratio of ~1. For ratio values of >1, the absorption at 584 nm remained essentially constant (Fig. 4, right). The intersection of both regression lines resulted in a Cu/Trien ratio of 0.97 in perfect agreement with the stated purity of 0.97. For the Trien$_{60}$ the increase in absorption was much less perfect and resulted in wavy deviations in the residuals (Fig. 4, left). The increase in absorption, however, extended to Cu/Trien ratios of >>1, which indicates that it is not just the 0.6 Trien *sensu strictu* complexed Cu, but the impurities which contribute to the increased absorption.

pH dependence of the extinction coefficient

The pH dependence of the molar extinction coefficient given by Ammann *et al.* (2005) had only

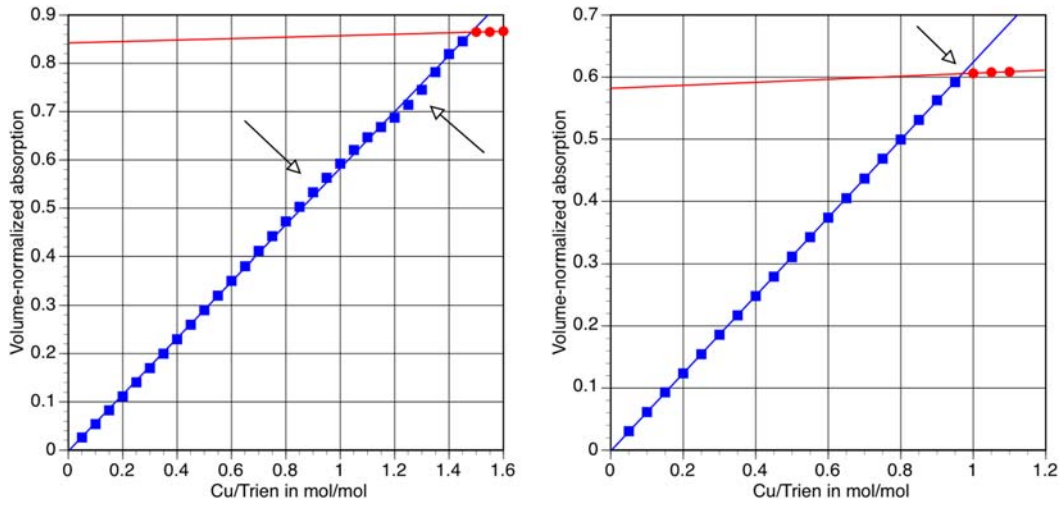


FIG. 4. Absorption values of a 4 mmol/L Trien$_{60}$ (left) and Trien$_{97}$ (right) solution, to which a $CuSO_4$ solution was added. (Left) Note that the intersection is far above the equivalence point; arrows indicate regions with significant deviation from the linear regression. (Right) Arrow indicates equivalence point, where all Cu is complexed.

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one data point between pH 3 and 12, and was therefore improved by Kaufhold & Dohrmann (2013) who placed many more points in this pH region but did not provide a polynomial fit of the measurements. The present measurements (Fig. 5) confirm, essentially, the data of Ammann *et al.* (2005) and of Kaufhold & Dohrmann (2013) except for the fact that the extinctions start to decrease below pH = 6. The measurements were fitted by the polynomials

$$\varepsilon_{pH=7} = -8.57948(\pm 0.4877) + 6.84813(\pm 0.3929) \times pH - 1.84242(\pm 0.1179) \times (pH)^2 + 0.220832(\pm 0.01561) \times (pH)^3 - 0.009939(\pm 0.00077) \times (pH)^4 \quad (2)$$

for $4 < pH < 6$, ($n = 20$, $r^2 = 0.9998$) and

$$\varepsilon_{pH=7} = 0.600886(\pm 0.0877) + 0.211994(\pm 0.0419) \times pH - 0.041589(\pm 0.00743) \times (pH)^2 + 0.0035774(\pm 0.000582) \times (pH)^3 - 0.000114(\pm 0.000017) \times (pH)^4 \quad (3)$$

for $6 \leq pH < 10.6$, ($n = 15$, $r^2 = 0.9968$). All CEC measurements were corrected with these functions, although the corrections are rather minor compared to those caused by protonation.

CO_2 uptake of Cu-Trien

A fresh solution of 96 mL of degassed H_2O mixed with 4 mL of a 0.1 M Cu-Trien$_{97}$ had a pH of ~8.1 (Fig. 6). Stirring this solution in contact with air decreased the pH to 7.6 within 40 min. After starting purging with N_2, the pH increased continuously with time and reached a constant value of pH 8.24 after 1 day.

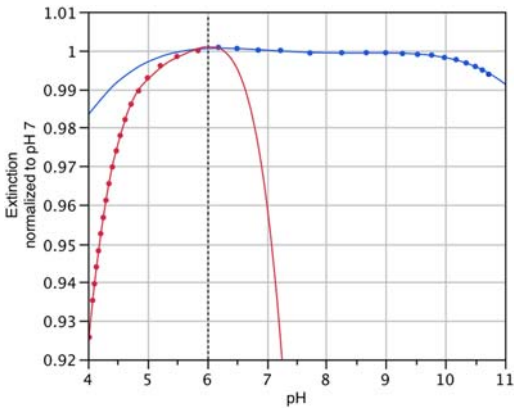


FIG. 5. pH dependence of the extinction of Cu-Trien$_{97}$ at 584 nm normalized to the extinction value at pH 7. The lower and upper lines denote the polynomial fits of the regions below pH 6 and above, respectively.

Protonation of Trien

A mixture of 4 mM Trien with 9 mM NaCl as a background electrolyte had an initial pH of 10.56 which is identical to the modelled value of pH = 10.62 (Fig. 7). Down to ~pH 7, the measured proton uptake agreed well with the model calculations, but in the acidic range the deviations increased.

Protonation of Cu-Trien

Solutions of 4 mM Cu-Trien using 10 mM K_2SO_4 as a background electrolyte were titrated at 288, 298 and 308 K. Cu-Trien was increasingly protonated with decreasing pH and with decreasing temperature (Fig. 8). The data could be fitted well with a polynomial for pH ($4 < pH < 9.5$) and a term correcting for the temperature:

$$\Delta H^+(\text{mol/mol}) = 1.752(\pm 0.096) - 0.622(\pm 0.045) \times pH + 0.07693(\pm 0.00070) \times (pH)^2 - 0.003283 (\pm 0.000035) \times (pH)^3 - 0.364(0.307)(T - 298) \times (pH)^{-3.28(\pm 0.52)} \quad (4)$$

The linear regression of predicted (equation 4) *vs.* measured values resulted in $y = 0.001(\pm 0.001) + 0.989 (\pm 0.011)x$, ($n = 88$, $r^2 = 0.988$).

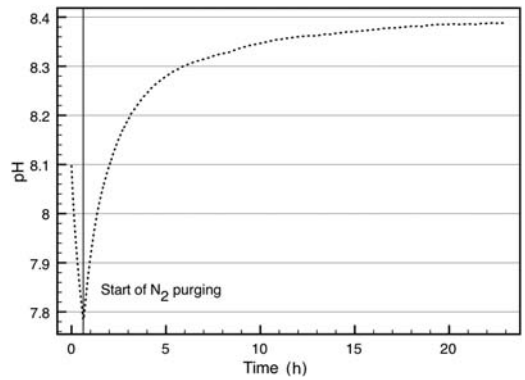


FIG. 6. pH of a stirred 4 mM Cu-Trien$_{97}$ solution, open to air for the first 40 min and then purged with N_2.

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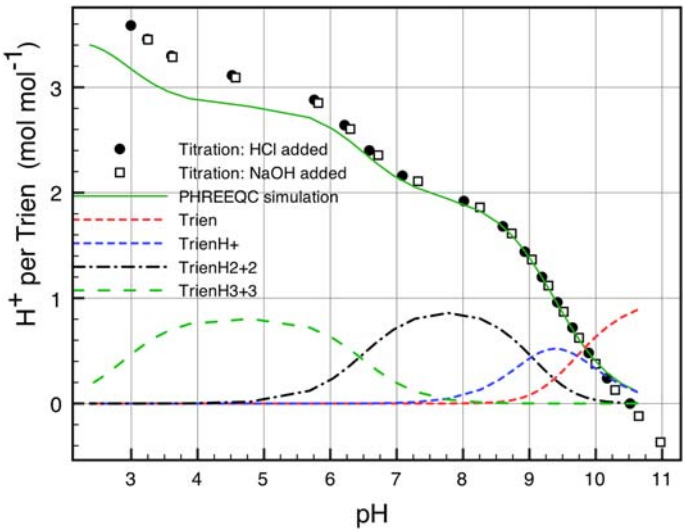


FIG. 7. Proton uptake of $Trien_{97}$ *vs.* pH. The solid line denotes the theoretical values calculated with *PHREEQC* using the values listed in Table 1.

Intercalation of Trien and Cu-Trien

In the untreated, air-dried state the Mg-BeW sample showed a d_{001} value of 14.4 Å typical of Mg-smectites. Kaufhold *et al.* (2011) showed that Cu-Trien leads to a smaller interlayer spacing of smectites with a fairly constant d_{001} value of ~13.1 Å, which was confirmed in the present study (data not shown). Adding pure Trien to Mg-smectite also produced the same intercalation with fairly sharp and symmetric 001 peaks except when using the mixture of 2.0 mL Trien and 2 mL Cu-Trien, which seems to have either contributions from the Mg spacing or had not been fully dried in air (Fig. 9). Adding $CuSO_4$ after the intercalation process did not result in the typical colour of a Cu-Trien solution, nor did the solid turn blue. This indicates that all Trien had intercalated in the smectite and Cu^{2+} did not complex with the Trien within the interlayer space. Addition of a Cu-Trien solution did not result in further exchange. Analyses of the supernatant solutions of the Trien-exchanged samples by IC (data not shown) showed significant concentrations of Mg, but the charge balance was not perfect due to foreign cations not originating from the smectite.

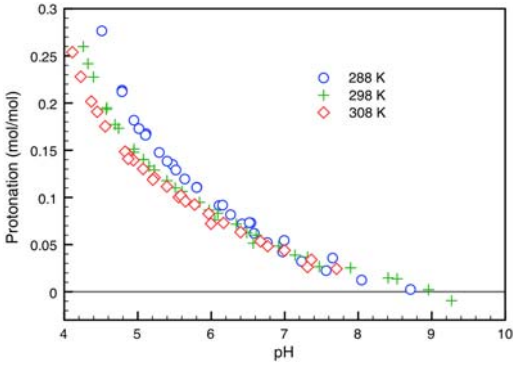


FIG. 8. Protonation of $Cu\text{-}Trien_{97}$ as a function of pH and temperature. The titrations were run from high to low pH, back again, and, for some points, down again.

pH dependence

The pH dependence was checked using the Na-BeW and Mg-BeW samples by either adjusting the suspension pH prior to adding Cu-Trien (Fig. 10, left) or after addition of Cu-Trien (Fig. 10, right). The initial pH values were 8–9. For Na-BeW the regressions (pH adjustment before and after Cu-Trien addition) are significantly different with:

$$y_{\text{before}} = 0.630(\pm 0.013) + 0.0275(\pm 0.0024) \times \text{pH} \quad (5)$$

and

$$y_{\text{after}} = 0.731(\pm 0.021) + 0.0117(\pm 0.0004) \times \text{pH} \quad (6)$$

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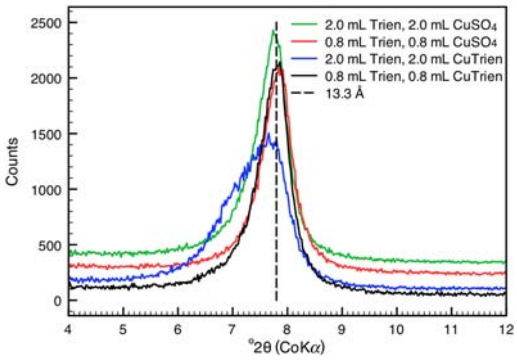


FIG. 9. XRD traces of oriented of Mg-BeW treated first with pure triethylene (200 mg of sample, 4 mM Trien). After 1 h of equilibration time either $CuSO_4$ solution or Cu-Trien solution was added (volumes indicated). The scans are shifted relative to each other.

whereas for Mg-BeW statistically identical regressions were found:

$$y_{\text{before}} = 0.687(\pm 0.011) + 0.0142(\pm 0.0001) \times \text{pH} \quad (7)$$

and

$$y_{\text{after}} = 0.684(\pm 0.003) + 0.0145(\pm 0.0001) \times \text{pH} \quad (8)$$

The CEC values in Fig. 10 were calculated assuming a constant charge of Cu-Trien. Including the protonation of Cu-Trien (equation 4) removed the pH dependence of the CEC values (Fig. 11). The absolute values, however, still differed slightly, possibly due to slightly different water contents.

Sample mass to Cu-Trien ratio

Figure 1 showed that the ratio of sample mass to Cu-Trien (m/n in g mol(+)$^{-1}$) added results in systematically different CEC values. This was investigated in detail using Na- and Mg-smectites by varying the sample mass between 50 and 200 mg and the Cu-Trien addition between 1 and 4 mL (0.1 M). As an additional variation, we also used a Cu-Trien solution made up of $CuCl_2$. For a Na-smectite (Icosorb) the CEC (sulfate system, 25 mL) decreased with increasing m/n (Fig. 12, left) and could be modelled with two regression lines:

$$0 < m/n < 0.5: \quad \text{CEC} = 0.879(\pm 0.008) - 0.172(\pm 0.022) \times m/n; \quad n = 6, r^2 = 0.94 \quad (9)$$

$$m/n > 0.5: \text{CEC} = 0.823(\pm 0.004) - 0.062(\pm 0.006) \times m/n; \quad n = 6, r^2 = 0.96 \quad (10)$$

Extending the equilibration time to 70 h resulted in similar trends but with more scatter in the data (Fig. 12, left). The same experiment repeated with the Cu-Trien (Cl^-) solution (Fig. 12, right) resulted in two significant differences. First, the slope of −0.022

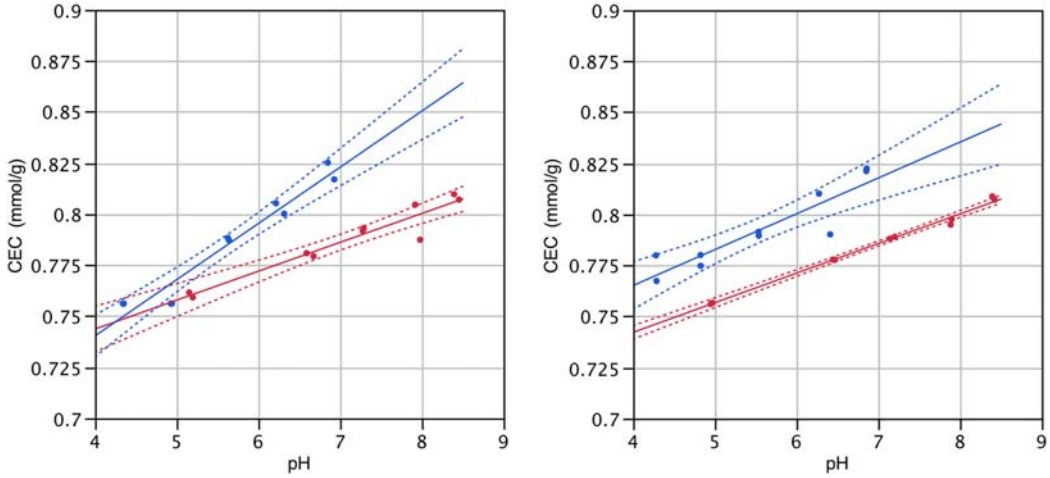


FIG. 10. pH dependence of CEC. (Left) pH adjusted prior to addition of Cu-Trien. (Right) pH adjusted after addition of Cu-Trien. Upper curve (solid line): Na-BeW, lower curve (solid line): Mg-BeW. (Dotted traces = confidence curves.)

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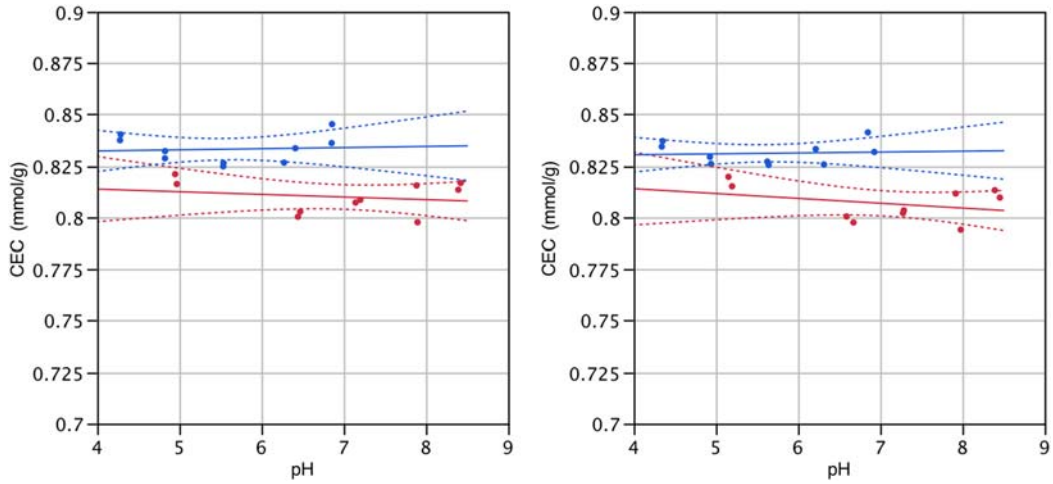


FIG. 11. Series of Fig. 10 repeated and corrected for effective charge of Cu-Trien. (Left) pH adjusted prior to addition of Cu-Trien. (Right) pH adjusted after addition of Cu-Trien. Upper curve (solid line) BeW-Na; lower curve (solid line): BeW-Mg. (Dotted traces = confidence curves.)

(±0.006) is significantly smaller than the −0.062(±0.006) value of the sulfate system, but is still different from zero ($t = 0.0017$). Second, all samples can be modelled with a single regression line. After an equilibration time of 70 h the slope increased to −0.11(±0.02).

Measurements of the Mg-B1 (Bayern) sample exemplify the trends observed for other Mg-smectites. Using water volumes of 25 or 50 mL and Cu-Trien-sulfate or Cu-Trien-chloride resulted in different CEC values and trends of m/n (Fig. 13). For the 25 mL measurements, two trends occurred now only in the chloride system in contrast to the sulfate system (Fig. 13b,d). Furthermore, the slopes and the absolute values differed. The CEC values of the chloride system are, at 0.775 mmol/g at $m/n = 0.5$, significantly above the values of the sulfate system (Fig. 13c,d). The sulfate system, however, resulted in significantly lower slopes but identical intercepts (Table 3).

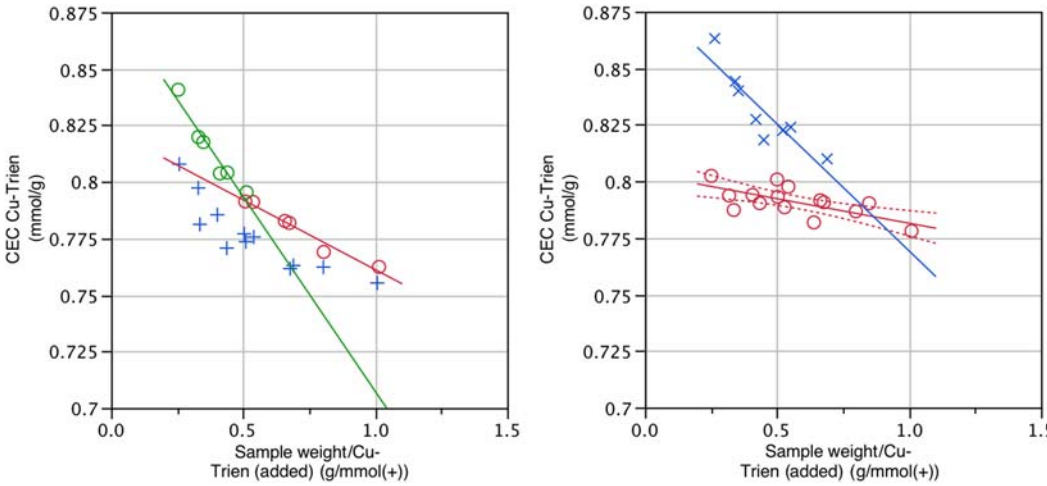


FIG. 12. CEC of Na-Icosorb measured with Cu-Trien-sulfate (left) and Cu-Trien-chloride (right) as a function of sample: Cu-Trien ratio (25 mL of H_2O). The circles denote samples with equilibration times of 1–2 h, the crosses those of 70 h.

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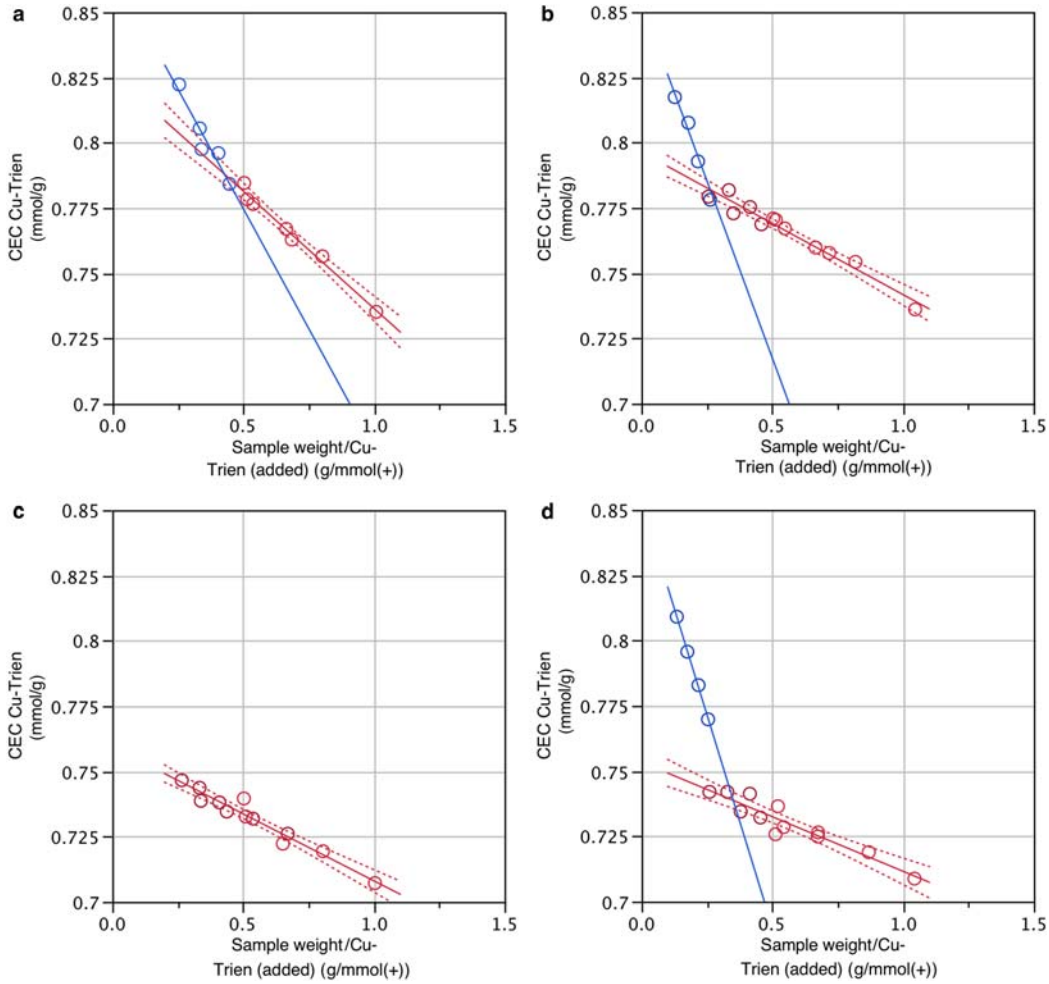


FIG. 13. CEC of Mg-B1 measured with Cu-Trien-chloride (upper figures: a, b) and Cu-Trien-sulfate (lower figures: c, d) added to 25 mL of H_2O (left: a, c) and 50 mL of H_2O (right: b, d). The regression parameters are listed in Table 3. The darker and lighter coloured lines and symbols (blue and red, respectively, in colour) represent different regressions.

The CEC values of the *Reuver Ton* did not depend on the sample/Cu-Trien ratio for $m/n > 0.5$ (Fig. 14). Below this threshold value, the CEC values increased significantly. The Cu-Trien-chloride values were slightly higher than the sulfate values.

DISCUSSION

In the present study the potential sources of error of the Cu-Trien method have been identified and reproducibility of values has been improved to a level where subtle details in our observations will help to answer two crucial questions. To what extent does adsorption contribute to the Cu-Trien method and which of the measured CEC values match with those of other CEC methods?

The intercalation of pure Trien in smectite (Fig. 9) confirms that Trien molecules are adsorbed like to many other organic molecules such as methylene blue or glycerol. Possible complexation of Trien with interlayer Mg might have contributed in our experiments, but we consider it less important because the complexation constants for Mg-Trien and Ca-Trien are similarly small at log K = 1.4 (De Stefano *et al.*, 1999). Nevertheless, this adsorption is the basis for the high selectivity of Cu-Trien and related complexes such as

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TABLE 3. Regression parameters for the samples Na-Icosorb (Fig. 12, $t_{equ.}$ = 1 h), Mg-B1 (Fig. 13) and Reuver Ton (Fig. 14).

Sample	Anion	H_2O (mL)	Regression	r^2	n
Na-Icosorb	SO_4^{2-}	25	$y = 0.823(\pm0.004) - 0.0616\ (\pm0.0059)x$	0.964	6[a]
Na-Icosorb	Cl^-	25	$y = 0.803(\pm0.003) - 0.0217\ (\pm0.0056)x$	0.518	16
Mg-B1	SO_4^{2-}	25	$y = 0.759(\pm0.002) - 0.0513(\pm0.0038)x$	0.948	12
Mg-B1	SO_4^{2-}	50	$y = 0.753(\pm0.003) - 0.0418\ (\pm0.0046)x$	0.892	12
Reuver Ton	SO_4^{2-}	25	$y = 0.175(\pm0.004) - 0.0075\ (\pm0.0061)x$	0.23	7[a]
Reuver Ton	Cl^-	25	$y = 0.181(\pm0.003) - 0.0077\ (\pm0.0041)x$	0.41	7[a]

[a]Samples with $m/n > 0.5$.

Cu-ethylenediamine (Bergaya & Vayer, 1997; Bujdák, 2015). The addition of a twofold charge (Cu^{2+}) to the complex will shift the positioning from non-specific adsorption sites towards charged sites on the surface, but this transition from adsorption to cation exchange may be gradual. In the following these aspects are discussed in more detail.

Accuracy of the Cu-Trien method

Meier & Kahr (1999) reported satisfactory agreement between Cu-Trien and ammonium acetate values, but mentioned that the former values were slightly higher. The general agreement between various CEC methods was also shown by Dohrmann *et al.* (2012b), provided that optimum solid/liquid ratios were used. In spite of possible variations in layer charge, the CEC values of our samples fit perfectly with the regression of Boom Clay samples described by Zeelmaekers *et al.* (2015) (Fig. 15). Therefore, in the present work, CEC values determined at sample mass to Cu-Trien ratios ≥0.5 are deemed to be the 'correct' values (Fig. 15).

Protonation of Trien and Cu-Trien

As amines typically used for CEC study are variously protonated in aqueous solution at different pH values (see Cascio *et al.*, 2000, for a review) and co-sorb Cl^- on protonated sites (De Robertis *et al.*, 2001), this behaviour is not considered to be specific to the Trien method. For example, diamines (*A*) undergo protonation reactions similar to Trien (Cascio *et al.*,

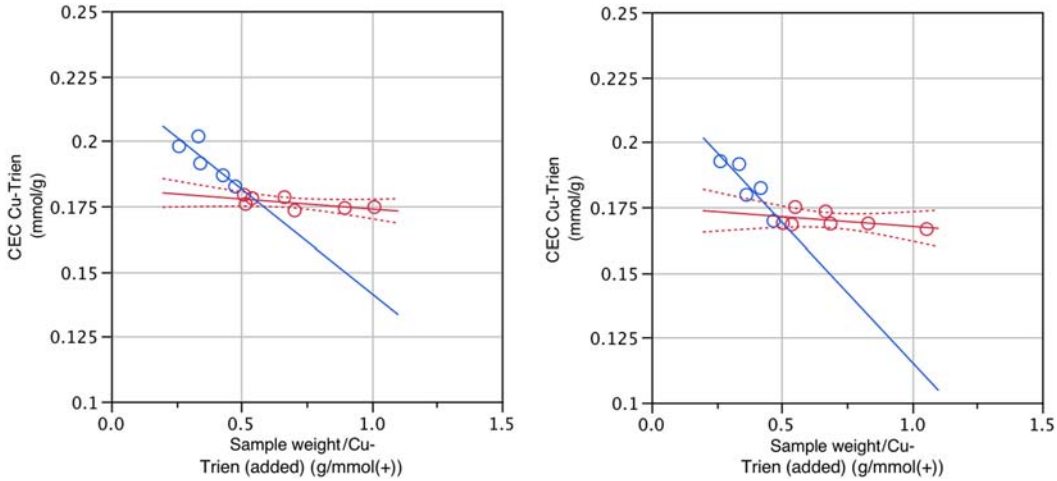


FIG. 14. CEC of Reuver Ton measured with Cu-Trien-chloride (left) and Cu-Trien-sulfate (right) and 25 mL of H_2O. The slopes for the red-circled values ($m/n > 0.5$) are with −0.0077(±0.0041) and −0.0075(±0.0061) identical to zero.

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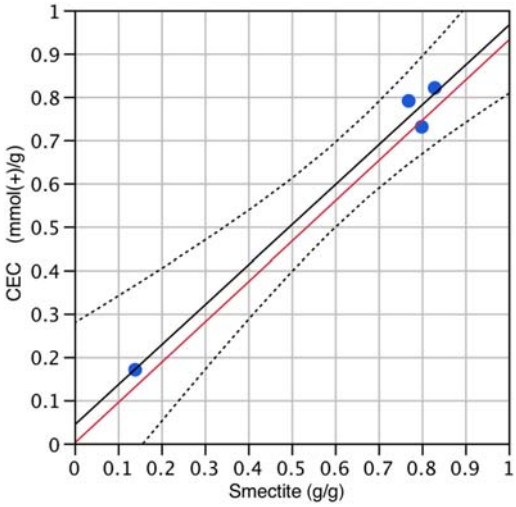


FIG. 15. CEC values determined at $m/n = 0.5$, 1 h of equilibration time and sulfate system *vs.* smectite contents. The second line from the right is the regression given by Zeelmaekers *et al.* (2015) for Boom Clay samples. The dotted lines denote the confidence limits for the present samples.

1999), whereby at an ionic strength $I = 0.5$ mol L^{-1} NaCl the dominant species below pH 10 are AH_2Cl^+ and AH_2^{2+}.

Protonation explains why pure Trien is able to exchange interlayer cations (Fig. 9) because, depending on the pH, it carries up to three charges per molecule (Fig. 7). It is therefore essential to check the purity of the Trien by titration with $CuSO_4$ solution for avoiding excess non-complexed Trien. The latter would exchange like Cu-Trien, but would escape spectrometric quantification. To avoid systematic error in the CEC determination, adding surplus Trien as suggested by Ammann *et al.* (2005) and Grygar *et al.* (2009) is not recommended here.

A new observation in the present study is that the Cu-Trien molecule was also observed to protonate, although to a much lesser extent than pure Trien (Fig. 8). The degree of protonation also depends slightly on temperature, especially at lower pH values. In combination with the tendency to take up CO_2, the starting pH of Cu-Trien solutions changes with time, which can introduce systematic shifts in CEC determinations. Because it is not easy to prevent CO_2 contamination during the analytical procedure, measurement of the pH value of the suspension (measured in the clear supernatant) and application of the charge correction given in equation 4 is recommdended here. As a byproduct, the extinction values of the Cu-Trien solutions can be corrected with equation 2 for higher-precision measurements. Co-sorption of Cl^- on protonated sites reduces the formal charge of the Cu-Trien complex, which explains why the CEC is apparently greater than when using Cu-Trien-sulfate (Fig. 13).

Variation of CEC with pH

The relationship between decreasing CEC values and decreasing pH (Fig.10) has been observed frequently for many smectites (*e.g.* Tournassat *et al.*, 2004; Kaufhold & Dohrmann, 2013; Delavernhe *et al.*, 2015). The slopes of ΔCEC/ΔpH for BeW are within the range reported by Kaufhold & Dohrmann (2013). Kaufhold *et al.* (2011) observed similar trends for Ca/Mg-smectites and interpreted this to reflect edge adsorption of Cu-Trien. After correcting the CEC with the effective charge of Cu-Trien, the CEC values became independent of pH (Fig. 11) and the reported difference when the interlayer cations Na and Mg were present was also no longer evident.

The non-dependence of corrected CEC values on pH might be explained by the negligible variable charge of montmorillonites, as reported in the literature (Tombácz *et al.*, 1990; Keren & Sparks, 1995; Mohan & Fogler, 1997). For example, Eren & Afsin (2008) observed that the adsorption of crystal violet on various cation-exchanged smectites was, within error, constant between pH 2.5 and 8.5. However, researchers using surface complexation models (*e.g.* Bradbury & Baeyens, 2005; Nagy & Kónya, 2006; Bourg *et al.*, 2007) would generally disagree with this viewpoint as, depending on the chemical composition of the smectite, the edge–face site densities of OH groups vary between 0.11 and 4.8 sites per nm^2. Under such conditions the exchange behaviour on *hk*0 faces will be dominated by the AlAl-OH site (2.38 sites/nm^2, $pK_a = 5.1$) and the SiAl-OH site (2.23 sites/nm^2, $pK_a = 7.7$) (Bourg *et al.*, 2007). In the pH range between 5 and 7, both groups will be partially deprotonated and provide roughly one charge per 50 $Å^2$. However, the cross-sectional area of the Cu-Trien complex is 83 $Å^2$ (Ammann *et al.*, 2005). It might be considered that the apparent steric hindrance be partially surmised by co-adsorption of an anion, which would enable the adsorption of one divalent Cu-Trien molecule on a singly charged hydroxyl group. The presence of chloride enhances the sorption of Ca^{2+} in the form of $CaCl^+$ complexes, which may represent ~60% of the interlayer composition of a Ca-

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saturated montmorillonite (Sposito *et al.* 1983; Tertre *et al.*, 2011). The observation that the CEC values obtained with the chloride system are greater than those of the sulfate system (*cf.* Fig. 13, upper and lower) might indicate a similar mechanism. De Robertis *et al.* (1993) showed that Trien forms complexes with Cl^-. Data for Cu-Trien-sulfate are not available yet. A second reason behind the non-dependence of corrected CEC values may relate to the participation of protons in the exchange process at permanently charged sites (*e.g.* Fletcher & Sposito, 1989). However, model calculations predict such absorption will only be significant at low ionic strength (as in our experiments) and low pH conditions ($I = 1 \times 10^{-3}$ mol L^{-1}, pH < 5, Bourg *et al.* (2007)). When considering the pronounced selectivity of Cu-Trien complexes for mono- and divalent cations, it becomes more apparent that proton exchange reactions on structural charge sites are in fact negligible.

Regardless of whether edge sites contribute to CEC or not, we propose that steric effects hinder Cu-Trien exchange at these sites and render the CEC determinations as being largely independent of edge charges. Such a case would provide a much faster experimental approach for determining the permanent layer charge of smectites, which is usually obtained by the very time-consuming n-alkylammonium method (Lagaly & Weiss, 1970; Häusler & Stanjek, 1988). The relevance of obtaining the permanent structural charge is discussed by Emmerich *et al.* (2009).

Exchange beyond the CEC?

Weiss (1958) was the first to observe a transition from cation-equivalent to equimolar exchange for low-charged ion exchangers. The co-sorption of anions to divalent cations yields CEC values that are generally too high. However, in our study we used medium-charged smectites (Fig. 15), where co-sorption should not be of any significance, and therefore these effects are not considered further.

Bergmann & O'Konski (1963) described the adsorption isotherm of methylene blue (MB) on Na-smectite as being influenced by two factors: ion exchange and physical adsorption. Nir (1986) and Margulies *et al.* (1988) combined the ion-exchange reactions with a Boltzmann correction to account for specific binding effects. Hang & Brindley (1970) observed for kaolinites an increase in the apparent CEC with increasing MB concentrations, and for smectites they noted that full exchange of all interlayer cations was only achieved in the case of Na-smectite, but not for divalent-cation exchanged smectites. MB adsorption has been documented to exceed levels beyond the cation exchange capacity (De *et al.*, 1974; Narine & Guy, 1981; Bujdak *et al.*, 2009) and can even lead to a charge reversal (Margulies *et al.*, 1988). The use of MB is known to form various aggregates (H-, J- and twisted dimers; *e.g.* Kowalak *et al.*, 2015) which affect adsorption behaviour (Bujdák, 2015); equivalent mechanisms have not been documented for Cu-Trien, however. Nevertheless, excess adsorption of Cu-Trien molecules could explain a number of features observed in our experiments, described below.

The CEC values of samples Na-Icsorb (Figs 12a, 16), Mg-B1 (Fig. 13) and of many other samples analysed (data not shown) show a different linear gradient below (segment 1) and above (segment 2) a threshold value of *m/n*. The steeper gradients in segment 1 are attributed to the summing effect of cation exchange and excess adsorption, respectively, whereas segment 2 represents solely cation exchange. The intersection point of both segments fitted with regression lines is close to $m/n = 0.5$ for measurements with 25 mL of H_2O and 2 mL 0.1 M Cu-Trien, which is the case even for samples with a low absolute CEC such as the Reuver Ton (Fig. 14). The intercept shifts to $m/n \approx 0.25$ for measurements with 50 mL of H_2O and 4 mL of Cu-Trien (Fig. 13b,d). Note that a $m/n = 0.5$ g/mmol(+) corresponds roughly to a ratio of 1 g of pure smectite with a CEC of 1 mmol/g to 1 mmol of Cu-Trien (or 2 mmol(+)). This novel pattern of two well defined segments of the CEC curve contrasts with that observed when using Cu-ethylenediamine, where only one linear segment occurs depending on the amount added initially and the excess concentration in solution (Bergaya & Vayer, 1997).

The occurrence of two distinct segments in the CEC curve when using Cu-Trien may have several causes. The assumed homoionicity of our samples might not be the case. The exchange of Na-BeW clay sample with ammonium resulted in substantial fractions of Mg^{2+} and minor Ca^{2+}, which confirms the work of Steudel *et al.* (2009), who emphasized that three washings with an index cation is not sufficient to prepare fully homoionic smectites. Hence, to remove residual divalent cations from a smectite, excess Cu-Trien (*i.e.* low *m/n* ratios) would be necessary. Rytwo *et al.* (1991) reported that MB and crystal violet required larger amounts than the CEC of SWy-1 montmorillonite to replace all the inorganic cations. Their isotherms for MB, however, were different from those in the present study and showed either a plateau

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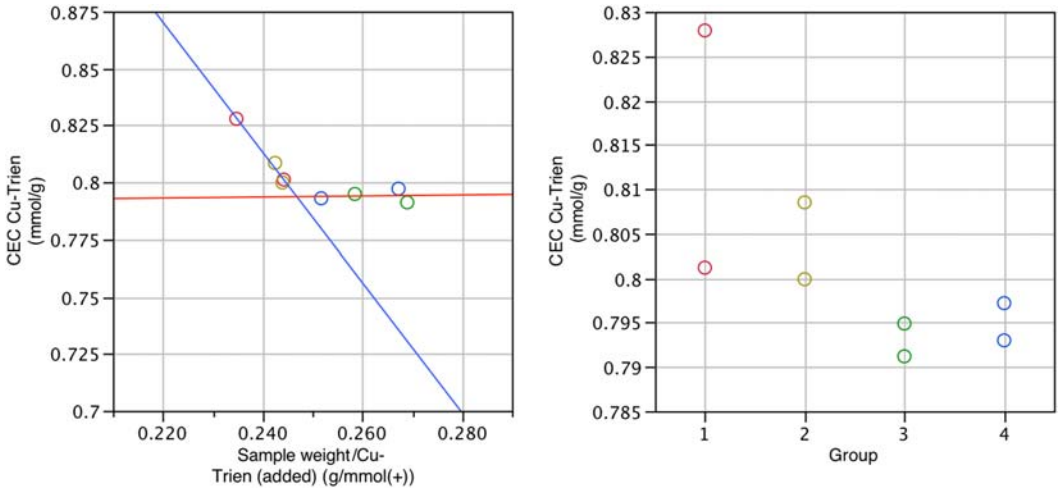


FIG. 16. CEC of Na-Icosorb measured with Cu-Trien-sulfate at an almost constant sample:Cu-Trien ratio, but variations in adding H_2O and Cu-Trien (cf. Table 4 for details of the groups). Final H_2O volume was 20 mL.

after a certain amount was added in the case of Ca-montmorillonite or were linear except when the highest concentrations of MB were added to Na-smectite samples. Two features in the present results, however, do not support this interpretation. Firstly, when treated with Cu-Trien-sulfate, the Na-Icosorb sample developed a two-segment CEC (Fig. 12a, Fig. 16, left), but with Cu-Trien-chloride a shallower segment type-2 curve was observed (Fig. 12b). Second, for any given water volume the intersection points were quite constant regardless of sample mineralogy. Here, the intersection point could be expected to vary with differences in the relative amounts of mono- and divalent cations in the interlayer space.

Note that the horizontal axis in Figs 12–16 in the present study denotes the ratio of the sample mass relative to the initial amount of Cu-Trien added. Regardless of the H_2O volume, doubling both the sample mass and Cu-Trien results in identical CEC values within experimental errors for segment 2 of the curve. After the exchange process, the concentrations of Cu-Trien in solution vary substantially depending on the ratio of CEC:Cu-Trien added, but these final Cu-Trien concentrations have little effect on the occurrence of an intersection point. This is well illustrated by the four samples of Na-Icosorb, for which the addition of 2 mL Cu-Trien to 20 mL H_2O was done either at the beginning of the experiment (group 1) or split into 1 mL at the start and 1 mL after 30 min (group 2, *cf.* Table 4 and Fig. 16). Both groups show a linear dependence with the sample:Cu-Trien ratio. Adding 2 mL of Cu-Trien to 10 mL of H_2O and diluting the suspension after 30 min with 10 mL of H_2O (group 3) resulted in the same CEC values as the fourth variant, in which twice 10 + 1 mL of H_2O + Cu-Trien were mixed after 30 min (group 4).

TABLE 4. CEC values of Na-Icosorb measured with a sample mass of 0.094–0.108 g. Part of the H_2O (mL) and part of the Cu-Trien (mL) was added after an equilibration time of 30 min.

	Initial addition		Addition after 30 min		CEC
Group	H_2O	Cu-Trien	H_2O	Cu-Trien	mmol/g
1	20	2	–	–	0.8145 (±0.0189)
2	20	1	–	1	0.8042 (±0.0061)
3	10	2	10	–	0.7931 (±0.0026)
4	10	1	10	1	0.7951 (±0.0030)

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Although impossible to demonstrate, we consider that above a certain threshold concentration of Cu-Trien relative to the sample, some Cu-Trien is adsorbed onto the sample surface (possibly in the smectitic fraction) without participating in the cation exchange process itself. Because this threshold value shifts from ~0.5 g/mmol(+) for 25 mL of H_2O to about half this value for 50 mL H_2O, normalization yields a minimum value of $\sim 2 \times 10^{-2}$ g mL/mmol(+) to avoid excess adsorption in segment 1 of the CEC curve. Note that the intersection in Fig. 16 should not be included in this interpretation because the samples have been prepared in different ways.

CONCLUSIONS

The reproducibility and accuracy of the Cu-Trien method can be improved by taking care with the following aspects:

(1) The Cu^{2+}:Trien ratio should be adjusted by titration to avoid excess Trien.

(2) The Cu-Trien solution should be kept at room temperature to avoid unwanted volume changes in the pipette tips.

(3) The Cu-Trien complex protonates with decreasing pH. The increase in charge above +2 can be calculated with a function relating the measured pH in the supernatant solution to the protonation.

(4) Excess adsorption of Cu-Trien can be avoided by not exceeding an *m/n* value of 0.02 g mL/mmol(+).

(5) Equilibration times of >1 h cause deterioration in the precision of the method due to undesired side reactions.

(6) Using Cu chloride instead of Cu sulfate is not recommended because of possible co-adsorption of Cl^-. Samples high in soluble chloride phases may be affected by such co-adsorption.

The reason for excess adsorption of Cu-Trien above a certain *m/n* value remains elusive and requires further clarification. This effect may be of importance in measuring the CEC values of shales and other rocks, where *m/n* may be exceeded unintentionally. Future work is also required to test the tacit assumption in this work that intercalated Cu-Trien has the same protonation state as the solution species. An answer to this question might lead to the possible ability to assess the variable charge of clay minerals.

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