

THREE NEW, QUICK CEC METHODS FOR DETERMINING THE AMOUNTS OF EXCHANGEABLE CALCIUM CATIONS IN CALCAREOUS CLAYS

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Abstract—The cation exchange capacity (CEC) is one of the most important properties of clays in terms of their performance in both natural and technical processes. For decades, common methods for determining exchangeable cations have failed when calcareous clays or soils were examined, because calcite is at least partly dissolved throughout the exchange experiment which in turn increases measurable Ca^{2+} concentrations. As a result, exchangeable Ca^{2+} and the sum of exchangeable cations by far exceed the amount of negative charges. In the past, the silver-thiourea method (AgTU) has been modified to overcome this problem (AgTU_{calcite}), but is unsatisfactory as the method is laborious. In the present study three new methods based on two alternative metal complexes, cobalt(III) hexamine (CoHex) and copper(II) triethylenetetramine (Cu-trien), are proposed. The optimum solid/liquid ratios of these methods and the optimum complex concentration of Cu-trien are reported, depending on the mineralogical composition of the samples. The key development is that the exchange solutions are saturated with respect to calcite prior to the experiment. Approximately 70–90% of the dissolution of calcite present as an admixture in a clay sample is suppressed in the subsequent cation exchange experiment, but not all. The Ca^{2+} exchange is not suppressed and there is no evidence for any precipitation of this Ca^{2+} . Three possibilities for how to handle this problem are discussed, one of which is to perform no further correction. The resulting error arises from the remaining calcite solubility of the different solutions after pre-treatment with calcite. This corresponds to errors of 0.2–1.3 (CoHex_{calcite}) and 0.7–8.4 (Cu-trien_{calcite}) meq/100 g Ca^{2+} for samples with small and large CEC values, respectively. As a consequence of the poor performance of Cu-trien_{calcite} for samples with large CEC, a more concentrated Cu-trien_{5 × calcite} solution was developed which performed much better: 0.1–0.8 meq/100 g (Cu-trien_{5 × calcite}). For Cu-trien_{5 × calcite} and CoHex_{calcite} at least, the errors are in the range of the non-systematic scattering for exchangeable Ca^{2+} determination. Therefore, the methods suggested provide ‘operationally correct’ Ca^{2+} values without additional effort. Moreover, owing to the high selectivity of the index cations applied in the present study, only one exchange step is required, providing a significant advantage over the AgTU_{calcite} method.

Key Words—AgTU_{calcite} Method, Bentonites, Calcareous Clays, CEC, CoHex_{calcite} Method, Cu-trien_{5 × calcite} Method, Cu-trien_{calcite} Method, Exchangeable Calcium.

INTRODUCTION

Clays and soils have prominent properties such as low hydraulic permeability and high sorption and retention capacity. Owing to their surface charge these minerals are able to adsorb cations reversibly, a property termed cation exchange capacity (CEC) and this property has been used for decades to characterize soils and clays. Thompson (1850) and Way (1852) identified the property and the reversibility of cation exchange. Cation exchange is incomplete when a common hydrated inorganic cation such as Ba^{2+} is used to replace the natural exchange population in one extraction step (McBride, 1979). Therefore, very laborious methods, with repeated extractions, have been used for >100 y (e.g. Hissink, 1923; Mehlich, 1948). Problems with the CEC analysis of acidic, saline, calcareous, or gypsiferous soils and clays have led to the development of a variety of specialized CEC

methods (summarized by Thomas, 1977). Schoonheydt (1995) stated that CEC results are regarded as ‘operational results,’ though, on the one hand there are differences due to pH conditions (variable charge) which can be classified clearly as operational differences, and, on the other hand, there are real, systematic errors when the exchange solution reacts with parts of the clays studied which may then lead to an increase in or a depletion of the index cation concentration. The same kind of error occurs during the analysis of exchangeable cations if soluble salts (e.g. gypsum, calcite) are present, as these tend to be dissolved – this is relevant because, in several applications, the exchange population is an important parameter. The pore-water composition of possible host rocks for disposal of radioactive waste (e.g. Pearson *et al.*, 2003) is described in terms of the exchange population. In these systems, accompanying minerals occur frequently which are soluble in the exchange solution which is used to determine the CEC. The most commonly occurring and therefore the most relevant of these minerals is calcite. The focus in the present work is on the determination of exchangeable Ca^{2+} calcareous clays

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which do not contain Ca-sulfates or saline or alkaline pore waters.

Why do common CEC methods fail when calcareous clays are studied?

For decades, the common methods used to determine the exchangeable cations failed when calcareous clays or soils were examined, because calcite is at least partly dissolved throughout the exchange experiment, which, in turn, increases the measurable Ca^{2+} concentration. If calcareous soils or clays are analyzed using an exchange solution such as barium chloride, two processes will occur, both of which increase the Ca^{2+} concentration in solution. Firstly, exchangeable Ca^{2+} is desorbed as intended by exchange with Ba^{2+} cations. Secondly, calcite is dissolved by adding additional Ca^{2+} to the same solution. The extent of calcite dissolution depends on the method used and on the sample. As a result, the sum of exchangeable cations by far exceeds the amount of negative charges.

The exchange solutions which are described in the literature differ in terms of chemical composition and ionic strength. Additional, methodologically determined parameters are: reaction time, solution/solid ratio, and the intensity of solution/solid interaction by batch or percolation. Parameters which could increase the CEC by extracting cations from typically non-exchange sites such as K^+ of illite are usually not varied because in CEC methods the goal is comparability of results and not maximum possible exchange capacity. Such parameters could include: temperature, extreme pH values, sonication, or application of crown ethers to extract K^+ from mica (Bracke *et al.*, 1995).

Some salt solutions are relatively aggressive so that much of the calcite present in a calcareous clay sample is dissolved. The differences between several solutions were described by Tucker (1954), who pointed out that ammonium acetate is most aggressive among commonly used CEC solutions. Mechanisms such as the common ion effect are used to explain the dissolution behaviour of calcite (Buhmann and Dreybrodt, 1987). On the other hand, calcite which is present in the sample may be coarse or fine grained, or it may, for example, occur as cement.

A quantitative description of all parameters mentioned above is not feasible so distinguishing between the two sources of Ca^{2+} is not possible; hence, the exchangeable portion of the total Ca^{2+} in solution cannot be calculated by means of correction. The total Ca^{2+} concentration must, therefore, be used to calculate the 'exchangeable Ca^{2+} ', resulting in erroneous 'exchangeable Ca^{2+} ' values.

Can 'operationally correct' exchangeable Ca^{2+} data be obtained using modified CEC methods based on ammonium acetate?

As discussed above, calcite dissolves in exchange solutions. Ammonium acetate dissolves more calcite

than other extracting solutions. Hence, after reaction with calcite, the exchange solution contains significant amounts of Ca^{2+} . The question arises as to what would happen if such a solution were treated so intensively with calcite that it became saturated with it? If this saturated bi-ionic solution were placed in contact with calcite again, would the calcite be stable? If so, perhaps this solution could be used in a CEC experiment to prevent additional calcite dissolution. In any further contact with calcareous clays, only exchangeable Ca^{2+} would be extracted from the sample with none arising through dissolution of calcite. The idea seems feasible, but other complications must also be considered. Such a solution consists of more than one cation, ammonium and calcium in this case, and if the solution is subjected to clay in an exchange experiment, two index cations instead of one are present. In each bi-ionic exchange solution a competition for exchange sites on the clay minerals will occur. This equilibrium can be described for a given sample (Pleysier and Cremers, 1975), but in principle these equilibria will differ from one sample to another. Because of the wide variety of different clay minerals with different exchange sites, static exchange equilibria between both index cations and all exchange sites irrespective of the sample studied, cannot be assumed. To correct for the different clay mineral exchange site equilibria, further parameters would be required: (1) the exchange equilibria for the $\text{NH}_4^+:\text{Ca}^{2+}$ ratio in solution for each clay mineral; and (2) the amount of each clay mineral. Even this is not enough. It is not clear if (3) all montmorillonites, for example, have the same equilibrium with the given $\text{NH}_4^+:\text{Ca}^{2+}$ ratio. Within the group of montmorillonites the crystal chemistry and the layer charge density vary over a wide range. The exchange populations with different ratios of naturally occurring cations (usually Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) would also influence the equilibria.

Corrections of this kind are simply too complicated. For this reason it is impossible to use a 'common' inorganic salt solution such as ammonium acetate saturated with calcite, and obtain unaltered and, therefore, 'operationally correct' exchangeable Ca^{2+} results.

Why can operationally correct exchangeable Ca^{2+} data be obtained using modified CEC methods based on metal complex solutions?

The only solution for this problem is to use an index cation that is strongly favored by the clay over Ca^{2+} . In this case equilibrium is very wide on the side of the index cation. Consequently the parameters described above are not needed, e.g. for the $\text{NH}_4^+:\text{Ca}^{2+}$ pair. For any given clay, practically all exchange sites will then be covered by the index cation. Metal complexes such as AgTU (Pleysier and Cremers, 1975) fulfil this requirement. The authors report standard free energy changes for the displacement of Na^+ , Ca^{2+} , and Al^{3+} by $[\text{Ag}(\text{TU})_n]^+$ from a Camp Berteau montmorillonite in

the range 19–20.7 kJ equiv⁻¹, indicating that selectivity of AgTU for clay minerals covered with naturally occurring exchangeable cations is very high though this selectivity clearly will not completely prevent specific adsorption. Whether AgTU will be able to cover all the special exchange sites such as frayed edges of illites (see also Środoń and McCarty, 2008) is not clear. Ammonium is similar to K⁺ ions and could block some of these sites. Ca²⁺ is not preferred to AgTU at these sites and this is a question to be answered in this work. Usually the pH buffering capacity of the clay (Kaufhold *et al.*, 2008) influences the final pH of the slurry after addition of the exchange solution and might have an effect on calcite dissolution equilibrium, which may depend also on the solution/solid ratio.

New CEC approaches focusing on the prevention of calcite dissolution in calcareous clays are rare. As described by Dohrmann (2006b), in principle, the well known carbonate dissolution problem may be solved by use of an exchange solution based on a metal complex. The silver-thiourea exchange solution is saturated with calcite prior to the exchange experiment. In fact, AgTU_{calcite} represents a tri-ionic exchange solution which does not affect the selectivity of the metal complex over a wide range. The Ca²⁺ loading of the initial AgTU_{calcite} solution is determined as well as the total Ca²⁺ after the exchange experiment. This total Ca²⁺ represents the desorbed Ca²⁺ from the exchange sites plus the initial loading from calcite saturation. The difference between total and initial Ca²⁺ is used to calculate the exchangeable Ca²⁺. The question arises whether the equilibrium between calcite and the exchange solution is disturbed by the addition of clay, especially because the pH of the suspension after mixing changes due to the pH buffering capacity of the clay. Theoretically this is a problem, though experimental evidence for significant changes in this equilibrium is lacking. Using AgTU_{calcite} exchangeable Ca²⁺ data: (1) agree well for different sample masses; (2) match, together with the other cations (sum of exchangeable cations), the CEC within error; and (3) from non-calcareous clays are recovered even after mixing this sample with calcite in subsequent CEC experiments (Dohrmann, 2006b).

The disadvantage of the AgTU_{calcite} method is that it is laborious because adsorption of excess silver thiourea has to be eliminated by adding two extra exchange steps with deionized water. Here, hydrophobically adsorbed silver thiourea is desorbed, which is then combined with the first filtrate.

The aim of this study is to find new methods which give results which are as useful as the AgTU_{calcite} method, but which save time by minimizing experimental effort. Any of the known metal complexes which are used for CEC determination as one-step procedures could be tested. Two such complexes were examined here: Cu-trien (Meier and Kahr, 1999) and CoHex (Morel, 1958; Ciesielski and Sterckeman, 1997b). The

respective exchange solutions were treated with calcite, as for AgTU_{calcite}, to give Cu-trien_{calcite} and CoHex_{calcite}; the former was also modified by increasing the complex concentration and labeled Cu-trien_{5 × calcite}.

MATERIALS AND METHODS

Samples used for the development of the CEC methods

Pure calcite (Merck), pure dolomite (Algeria), two calcareous clays (a black shale, 'D4', with 40% calcite, and a marl, 'D5', with 38% calcite), and two non-calcareous clays (a Milos bentonite similar to 'B37 = SP-4' with a slightly smaller CEC, and an unconsolidated clay, 'D6 = Reuverton') were used to evaluate the suitability of calcite saturation experiments of the exchange solutions. The samples were described by Dohrmann (2006b).

The CEC data of these samples (Table 1) are known for different exchange solutions (Dohrmann, 1997) and the methods were described by Dohrmann (2006a, AgTU_{mod}), Dohrmann (2006b, AgTU_{calcite}), Dohrmann (2006c, barium chloride, 'BaCl₂'), and Dohrmann (2006d, ammonium acetate, 'AmAc').

Samples used to validate the CEC methods

After development of the new CEC methods, Cu-trien_{5 × calcite} and CoHex_{calcite} were validated using a set of 14 calcareous, gypsum-free bentonites which were described by Ufer *et al.* (2008). Those authors did not consider samples B30 or B35 as they contain mixed-layer minerals. Therefore, sample assignment is different (see Table 5). The bentonite clays were oven-dried at 60°C. In parallel drying analyses the water loss at temperatures of up to 105°C was determined. The difference representing the mass of adsorbed water was used to recalculate the mass in each experiment in a way that all results refer to 105°C dry mass.

CEC methods

In this work, the term CEC is used for a method (CEC method) and as a term for a property (CEC value). A CEC method is a method which gives information about the CEC value and the values of the individual exchangeable cations. If the term CEC is used without further explanation it refers to the property, CEC value.

Five different CEC methods (A–E) were used here to study the optimization of the saturation of exchange solutions with calcite prior to the exchange experiment. The methods are based on Cu-trien and CoHex. Two of the five methods are standard procedures as described in the literature: A and D (without calcite saturation). The results of these methods were used to demonstrate the negative effect of calcite dissolution on exchangeable Ca²⁺ data of calcareous clays. The other three approaches B, C, and E are new variants of calcite-saturated exchange solutions based on the AgTU_{calcite} approach (Dohrmann, 2006b). The pH of the exchange

Table 1. Data from the literature for the clay samples and the calcite standards used (meq/100 g).

Method, mass	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	sum	CEC	sum-CEC
Black shale (40 wt.% calcite)							
AgTU _{calcite} , 1 g	0.2	0.4	1.8	6.2	8.6	5.5	3.1
AgTU _{mod} , 1 g	0.3	0.4	2.0	32.2	34.8	5.2	29.7
AmAc, 2 g	0.4	0.6	5.5	266	272	0.6	271
BaCl ₂ , 2 g	0.3	0.8	3.0	108	112	23.2	88
Marl (38 wt.% calcite)							
AgTU _{calcite} , 1 g	0.1	0.1	0.6	15.3	16.0	17.8	-1.9
AgTU _{mod} , 1 g	0.1	0.2	0.8	39.6	40.6	17.0	23.7
AmAc 2 g	0.1	0.2	1.5	278	280	4.7	275
BaCl ₂ 2 g	0.1	0.6	0.8	61.8	63.2	26.3	37.0
Clay (Reuverton) without carbonates							
AgTU _{calcite} , 1 g	0.2	0.7	5.7	21.4	28.0	33.0	-5.1
AgTU _{mod} , 1 g	0.3	0.8	5.6	21.6	28.3	29.7	-1.4
AmAc, 2 g	0.2	0.8	5.9	23.8	30.7	26.7	-4.0
BaCl ₂ , 2 g	0.3	0.8	5.6	21.6	28.2	29.1	-0.8
Calcite 63–200 µm							
AgTU _{calcite} , 1 g				0.2		0.7	
AgTU _{mod} , 1 g				25.6		1.3	
AmAc, 2 g				309		0.1	
BaCl ₂ , 1 g				58.5		15.2	
Calcite <63 µm							
AgTU _{calcite} , 1 g				3.1		0.6	
AgTU _{mod} , 1 g				28.9		1.3	
AmAc, 2 g				297		0.2	
BaCl ₂ , 2 g				158		21.1	

solutions in the new methods was ~9 (± 0.1). The final pH of the slurries usually differed because of the different buffering capacities of the samples.

Details of the preparation of the exchange solutions and of the exchange experiments are as follows:

Preparation of exchange solutions

(A) *Cu(II) triethylenetetramine (slightly modified after Meier and Kahr, 1999)*. 10.0 mL of Cu-trien solution (0.01 M) + 50.0 mL of deionized water was added to the sample.

(B) *Cu(II) triethylenetetramine with calcite saturation: Cu-trien_{calcite}*. 300 mL of Cu-trien solution (0.01 M) + 1500 mL of deionized water was placed in a 2 L beaker. 2 g of fine-grained calcite was added. This mixture was placed in an ultrasonic bath for 30 min. To minimize temperature effects on the solubility of calcite, the solution was stirred for a further 30 min using a magnetic stirrer. After switching off the stirrer, undissolved calcite was allowed to settle overnight. 50.0 mL of this Cu-trien_{calcite} solution was added to the sample.

(C) *Cu(II) triethylenetetramine (non-diluted) with calcite saturation: Cu-trien_{5 × calcite}*. 2000 mL of Cu-trien solution (0.01 M) was placed in a 2 L beaker without

adding water. The calcite saturation was performed exactly as described in procedure B. 50.0 mL of this Cu-trien_{5 × calcite} solution was added to the sample.

(D) *Co(III) hexamine standard method (Ciesielski and Sterckeman, 1997a)*. 2000 mL of Co(III) hexamine solution (0.0166 M) was prepared by dissolving Cobalt(III) hexamine chloride [Co(NH₃)₆]Cl₃ in water. The concentration of Co³⁺ in this Co(III)Hex solution was 978.3 mg/L. 50.0 mL of this exchange solution were added to the sample.

(E) *Co(III) hexamine with calcite saturation: CoHex_{calcite}*. 2000 mL of Co(III) hexamine solution (0.0166 M) was placed in a 2 L beaker. The calcite saturation was performed exactly as described in procedure B. 50.0 mL of this CoHex_{calcite} solution was added to the sample.

Selection of suitable solution/solid ratios

The selection of suitable solution/solids ratios was important to optimize the precision of the CEC results. In each of the five methods described, suitable solution/solid ratios were used which were designed to achieve reasonable results with small errors. If, for example, an unsuitably large solution/solid ratio was chosen, very

small amounts of exchangeable cations were extracted during the CEC experiment. The precision of the subsequent inductively coupled plasma (ICP) analysis could be much less if this concentration was close to the detection limit of elemental analysis. If, on the other hand, an unsuitably small solution/solid ratio was chosen, the selectivity of the index cations would be too small to desorb all the cations during the exchange experiment. If the same volume of solution was used in all instances, then the sample mass would be the determining factor for optimum precision of the CEC and exchangeable cations. When dealing with soils and clays that have a very wide range of CEC values, further optimization of the solution/solid ratios is worthwhile.

In most modern CEC studies, batch procedures are described. Percolation is often unsuitable, especially when sealing clays are studied, because the solution will not percolate through the sample within a reasonable time (hours). In batch procedures, centrifuge tubes are used which can be filled with sample powder and exchange solution leaving some free volume on top for mixing the slurry when subjected to shaking. A good choice is a tube with a 70–100 mL capacity. In the present study, 50 or 60 mL of exchange solution was used in all cases so that the only parameter which varied was the sample mass.

The range of sample masses depends on the CEC of the clay and on the concentration of the index cation. The upper limit for sample mass is caused by exchange competition as described above. The exchange competition limit usually ranges from 50 to 75% of the initial complex concentration. If more than a critical amount of index cation is adsorbed then the CEC value is systematically reduced. On the other hand, a minimum of index cation adsorption in the range of 5% or more is necessary. If less is adsorbed, the uncertainty of elemental or complex analysis (ICP or VIS spectroscopy, both $\sim\pm 1\%$) increases the scattering. Consequently, for results outside of these ranges, the experiment has to be repeated with a suitable sample mass. For seven different methods these masses are given for typical bentonites with a CEC of ~ 100 meq/100 g and clays with a CEC of ~ 20 – 30 meq/100 g (Table 2).

Ciesielski and Sterckeman (1997a) recommend repeating CoHex experiments if $>35\%$ and $<5\%$ of the initial complex concentration is adsorbed. In the present experiments, a range of 5 to 50% was deemed acceptable.

Exchange experiments and determination of cation concentrations

Exchange experiments and elemental analysis were performed in a thermo-constant laboratory (23°C) as follows. First, the samples were weighed in centrifuge tubes and the exchange solutions were then added to the samples. The resulting slurries were shaken end-over-end for 2 h followed by centrifugation. 2 mL of the clear

supernatant was diluted (1:10) using HNO₃ solution, followed by ICP analysis of exchangeable cations and index cations. Two blanks (whole experiment but with no sample) were added to each series of experiments to control the index-cation concentration.

The quality of dilution was controlled using a 100.0 mg/L Cu standard in duplicate. The ICP results were corrected according to the blanks if the deviation exceeded 1.5%. A special correction was necessary for those methods with prior calcite saturation. To calculate exchangeable Ca²⁺, the Ca²⁺ concentration of the blank (~ 10 – 20 mg/L Ca²⁺, precision ± 0.1 mg/L) was subtracted. Control of the Ca²⁺ concentrations of the blank solutions with each new measurement series and use of these values for the correction procedure was recommended.

RESULTS

Development of the new methods

The best way to evaluate new CEC methods is to compare the experimental results of standard materials with those of known methods (A and D in this case). Pure calcite and dolomite were selected for this evaluation. The CEC and exchangeable Ca²⁺ values of these minerals are close to zero. Results which differ systematically from zero prove that the methods produce erroneous results as described for barium chloride and other methods.

CEC. The results of these comparison tests emphasize that the CEC values (average values of n repetitions) of the new methods with calcite saturation show some unsystematic scattering for calcite and dolomite but no significant systematic deviation from zero:

CoHex _{calcite} (E):	CEC = 0.7 ± 1.8 meq/100 g, $n = 14$
Cu-trien _{calcite} (B):	CEC = 0.5 ± 0.3 meq/100 g, $n = 4$
Cu-trien _{5 × calcite} (C):	CEC = 0.0 ± 0.3 meq/100 g, $n = 6$

CEC methods without calcite saturation give similar results. Cu-trien (A) has the smallest deviation:

Cu-trien (A):	CEC = 0.0 ± 0.1 meq/100 g, $n = 6$
CoHex (D):	CEC ≈ 0 meq/100 g, $n = 2$

The CEC of calcite using CoHex (D) is close to zero, though statistical assessment of the two data points is inappropriate.

The CEC range of calcite determined using all these methods (representing unsystematic scattering) is similar to the methods based on AgTU (Table 1).

'Exchangeable Ca²⁺'. The amount of calcite dissolved in the saturation procedure differs significantly between different exchange solutions. This obviously depends on the chemical characteristics of the index cation solutions (cationic complexes).

Cu-trien (A):

9.9 mg/L of Ca^{2+} (1.48 mg of calcite/60.0 mL of solution)

CoHex (D):

20.0 mg/L of Ca^{2+} (2.50 mg of calcite/50.0 mL of solution)

Following saturation with calcite, these solutions were expected to be unable to dissolve any more calcite which could be added as pure calcite or as a calcareous sample. Unfortunately, however, an unexplained capacity to dissolve calcite remained. The remaining capacity to dissolve calcite in experiments with pure calcite depends on the type of exchange solution, as follows:

Cu-trien_{calcite} (B):

2.7 mg/L of Ca^{2+} , dissolution reduction of 73%

Cu-trien_{5 × calcite} (C):

1.3 mg/L of Ca^{2+} , dissolution reduction of 89% compared to (A)

CoHex_{calcite} (E):

4.2 mg/L of Ca^{2+} , dissolution reduction of 79%

As expected, Ca^{2+} concentrations were greatest in the cases of A and D (not calcite saturated). The reduction of calcite dissolution accounts for ~70–90% using the new methods (B, C, and E). In absolute concentrations, these are 1.3–4.2 mg/L. This is close to the remaining Ca^{2+} concentrations of 2.7 ± 2.2 mg/L Ca^{2+} ($n = 5$, after reaction with ‘fresh’ calcite) of the AgTU_{calcite} solution which was developed previously (Dohrmann, 2006b). Owing to the relatively large calcite solubility of ~100 mg/L of Ca^{2+} in the AgTU_{mod} exchange solution, this is a reduction of ~97%, deemed a great success compared to traditional methods such as that using barium chloride. The difference between 97 and 100% was regarded as a minor effect as it was in the range of the laboratory error for exchangeable Ca^{2+} (0.6–2.2 meq/100 g depending on the type of clay used) and not discussed by Dohrmann (2006b). Because of the importance of this effect for the solution of the well known problem with exchangeable Ca^{2+} , it was decided to investigate this effect in detail in the present study.

Calculation of the falsification of ‘exchangeable Ca^{2+} ’ values of calcareous clays

Three solutions were identified as possibly being suitable to handle the ‘remaining-solubility-problem’:

(1) Further improvement of the conditions for calcite saturation (more energy, repetition of saturation procedure, ...).

(2) Additional correction of the Ca^{2+} concentration (second calcite blank correction).

(3) Acceptance of the result without correction.

Option 1 would probably minimize the problem, but additional preparation steps would be necessary. As the aim of this study was to identify methods which are easy to handle and to control, this option was dismissed.

Option 2 is an efficient alternative and can be applied in all three new methods. It can be performed so that parallel to samples with unknown exchangeable Ca^{2+} values, pure calcite is used as a ‘blank correction sample’. The Ca^{2+} concentration of this experiment with calcite (second calcite blank correction) is used to correct the measured Ca^{2+} concentrations of all calcareous samples instead of the Ca^{2+} concentration of the calcite-saturated solution (regular blank correction) which is usually less. This second calcite blank correction procedure was performed successfully for a series of clays from the Bure site in France (unpublished BGR report). The exchangeable Ca^{2+} was corrected using the Ca^{2+} concentration of calcite in the AgTU_{calcite} solution. In the first calculation, exchangeable Ca^{2+} values ranged from 4.5 to 13.4 meq/100 g (average 9.1 meq/100 g). After subtraction of the additional Ca^{2+} from the parallel calcite experiment, the range was reduced to 3.5–10.2 meq/100 g (average 6.9 meq/100 g). This type of correction can only be successful if the sample contains calcite. If not, the resulting exchangeable Ca^{2+} value will be too small because the second calcite blank correction procedure then cuts off part of the exchangeable Ca^{2+} . This means that the user of the method has to be sure that calcite is present (*e.g.* by XRD) which is an additional step in the procedure. In some CEC applications users have no such data (*e.g.* in soil-science mapping projects). On one hand the second calcite blank correction increases the degree of complication. On the other, this is an efficient means by which to further improve the exchangeable Ca^{2+} data of calcareous clays and soils.

Option 3 is, of course, the easiest method by which to handle the problem. Acceptance of the result without correction is described and discussed in more detail here. The question is how large the errors will be for the different methods and what consequence will they have for the different clay materials studied. The experimentally determined specific Ca^{2+} concentrations of the exchange solutions after contact with (fresh) calcite are given above. Based on these data, the remaining exchangeable Ca^{2+} errors are calculated for typical calcareous bentonites and for calcareous clays with CECs of ~100 meq/100 g or 20–30 meq/100 g, respectively (Table 2). Acceptable errors which are in the range of precision of the method (for precision see Table 6) are marked in bold.

To compare the effect of the solubility of calcite on the calculated amount of ‘exchangeable’ Ca^{2+} for different exchange solutions, the remaining Ca^{2+} error is plotted against the sample masses (Figure 1a). For each method, the calcite dissolution abilities of experiments with pure calcite were used (see the ‘Exchangeable Ca^{2+} ’ section).

As expected, the largest errors occur when solutions without calcite pre-treatment are used, *e.g.* as in the AgTU_{mod} method (Table 2, Figure 1a). If the AgTU_{mod} method is used instead of AgTU_{calcite} for exchangeable

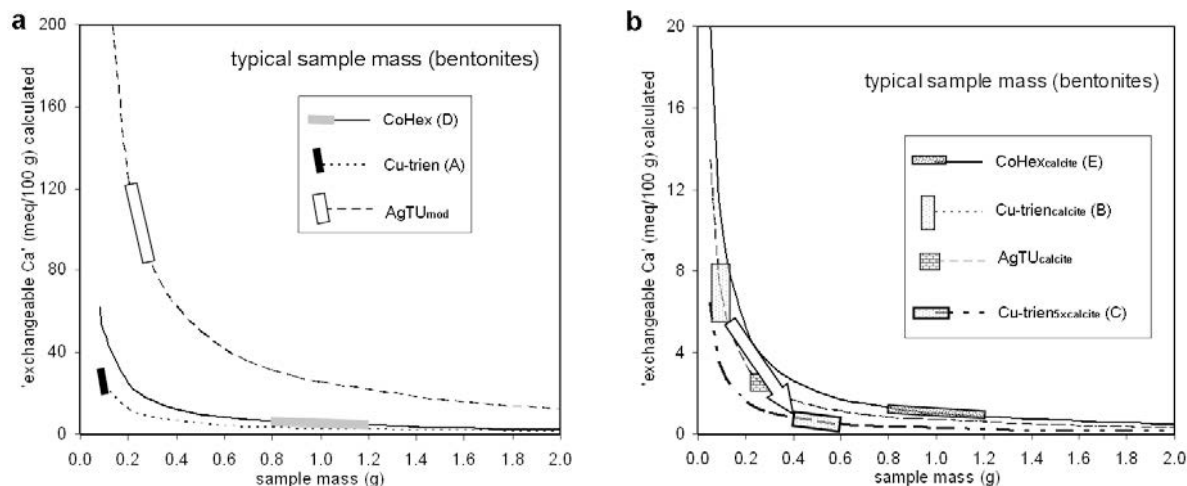


Figure 1. Theoretical error for 'exchangeable calcium' of calcareous samples calculated for exchange solutions with metal organic complexes. The shaded areas represent the expected errors when these methods are applied for bentonites. (a) No pre-saturation with calcite; (b) Pre-saturation with calcite. The curves of $\text{Cu-trien}_{\text{calcite}}$ and $\text{AgTU}_{\text{calcite}}$ are superimposed.

Ca^{2+} measurements of calcareous clays, at calcite concentrations of >8–12 wt.% (bentonites) or >2–5 wt.% (clays), respectively, ~100 mg/L of Ca^{2+} will be extracted in addition to the exchangeable Ca^{2+} . These 100 mg/L are multiplied with a factor that depends on the reciprocal sample mass. When large sample masses of ~5 g are used (e.g. for kaolin), the resulting error is relatively small, in the range 2–5 meq/100 g. One of the problems with this method, however, is that, for high-CEC clays such as bentonites, only ~200–300 mg can be used. This can easily inflate the exchangeable Ca^{2+} error to >100 meq/100 g. For common clays and soils, between 0.5 and 1 g is used. The resulting error is 25–50 meq/100 g. These values are in the range of up to two times or more the CEC of the samples. In principle, the same kind of falsification occurs for Cu-trien and CoHex but the resulting errors

are smaller. At first glance one would expect a smaller error for Cu-trien because in this solution ~50% less calcite is dissolved. But this advantage is compensated by the fact that CoHex is more concentrated and Co^{3+} is trivalent. Hence, typical sample masses are larger in CoHex experiments.

Calculated errors for exchangeable Ca^{2+} using methods with pre-treatment of calcite are less (Table 2, Figure 1b) than without calcite saturation. The largest errors remain for $\text{Cu-trien}_{\text{calcite}}$ (B). This is followed by $\text{AgTU}_{\text{calcite}}$ (Dohrmann, 2006b) and $\text{CoHex}_{\text{calcite}}$ (E). As a consequence of the poor performance of $\text{Cu-trien}_{\text{calcite}}$ (B) for samples with a large CEC, a more concentrated $\text{Cu-trien}_{5 \times \text{calcite}}$ (C) solution was developed. This exchange solution contains the same complex but five times more concentrated: i.e. 50 mL instead of 10 mL, and no addition of water. Using this $\text{Cu-trien}_{5 \times \text{calcite}}$ (C) more sample mass can be used which in

Table 2. Suitable solution/solid ratios expressed by different sample masses of the different methods and calculation of the corresponding 'exchangeable Ca^{2+} ' errors assuming that the samples are calcareous. Acceptable errors which are in the range of precision of the method (for precision see Table 6) are marked in bold.

Method, code	Clays		Bentonites	
	Sample mass (g)	Ca^{2+} error (meq/100 g)	Sample mass (g)	Ca^{2+} error (meq/100 g)
Methods without calcite saturation				
Cu-trien (A)	0.3–1.0	2.5–8.3	0.08–0.12	20.6–30.9
CoHex (D)	2.0–3.0	1.7–2.5	0.8–1.2	4.2–6.2
AgTU_{mod}	0.5–1.0	25–50	0.2–0.3	83–125
Methods with calcite saturation				
$\text{Cu-trien}_{\text{calcite}}$ (B)	0.3–1.0	0.7–2.2	0.08–0.12	5.6–8.4
$\text{Cu-trien}_{5 \times \text{calcite}}$ (C)	2.0–3.0	0.1–0.2	0.4–0.6	0.6–0.8
$\text{CoHex}_{\text{calcite}}$ (E)	2.0–3.0	0.2–0.5	0.8–1.2	0.5–1.3
$\text{AgTU}_{\text{calcite}}$	0.5–1.0	0.7–1.3	0.2–0.3	2.2–3.4

turn minimizes the remaining Ca^{2+} error. Errors of 0.6–0.8 meq/100 g (bentonites) and 0.1–0.2 meq/100 g (clays) have to be accepted if no correction is performed. This is <1% of the typical CEC.

Selection of the most suitable method

Selection of the most suitable method depends on the type of material and the amount of available sample mass. For soils which are sieved to a size of <2 mm or for clays from a clay deposit, enough material usually is available. In such cases, a method with a high concentration of index cation such as $\text{Cu-trien}_{5 \times \text{calcite}}$ (C) or $\text{CoHex}_{\text{calcite}}$ (E) is preferred. Scattering due to possible sample inhomogeneities is avoided and the precision of the CEC data increases (Figure 1, Table 2). If only small masses of material are available, e.g. of special reaction products, then a less concentrated exchange solution such as $\text{Cu-trien}_{\text{calcite}}$ is preferable.

Test application of the new methods using standard clays

After testing the new methods with pure calcite, calcareous and non-calcareous clays were used to evaluate whether the methods can be applied to natural samples.

Non-calcareous clays. The results of exchangeable cations of non-calcareous clays are more or less identical, within a small range, for all methods applied (Table 3). Exchangeable Na^+ , K^+ , Mg^{2+} , and Ca^{2+} data scatter between 0.0–0.2 (outlier 0.6), 0.5–0.9, 4.8–6.2, and 20.3–23.8 meq/100 g (Reuverton). As reported by Dohrmann (2006b), exchangeable Ca^{2+} of a non-calcareous clay can be desorbed and measured in solution in the same quantity regardless if the exchange solution is pre-treated with calcite or not. Assuming desorbed Ca^{2+} would react with exchange solutions of $\text{Cu-trien}_{\text{calcite}}$ (B), $\text{Cu-trien}_{5 \times \text{calcite}}$ (C), or $\text{CoHex}_{\text{calcite}}$ (E) in a way that precipitates are formed would result in a depletion of Ca^{2+} and the resulting exchangeable Ca^{2+} values would be significantly smaller compared to

Table 3. Comparison of the results of the different CEC methods used for the non-calcareous clays, Reuverton and Milos-Bentonite (meq/100 g).

Method, code, mass	Na^+	K^+	Mg^{2+}	Ca^{2+}	sum	CEC	sum-CEC
Clay (Reuverton) without carbonates							
Methods without 'calcite saturation'							
AgTU _{mod} , 0.5, 0.25 g	0.1	0.7	4.8	21.4	27.0	30.0	–3.0
AgTU _{mod} , 1 g	0.2	0.8	5.7	22.6	29.3	30.5	–1.2
AmAc, 0.5 g	0.6	0.8	6.2	23.7	31.3	26.1	5.1
AmAc, 2 g	0.2	0.8	5.9	23.8	30.7	26.7	4.0
BaCl ₂ , 0.5 g	0.0	0.5	5.5	21.6	27.6	30.2	–2.6
BaCl ₂ , 2 g	0.3	0.8	5.6	21.6	28.3	29.1	–0.8
Cu-trien (A) 0.3 g	0.1	0.7	5.8	22.2	28.8	27.0	1.8
Cu-trien (A) 0.5 g	0.1	0.7	5.6	21.5	27.9	26.6	1.3
CoHex (D) 2 g	0.2	0.9	6.1	22.0	29.2	29.0	0.2
CoHex (D) 3 g	0.2	0.9	6.0	22.0	29.1	29.0	0.1
Methods with 'calcite saturation'							
AgTU _{calcite} , 0.5, 0.25 g	0.0	0.7	5.9	23.2	29.8	37.0	–7.3
AgTU _{calcite} , 1 g	0.2	0.7	5.7	21.4	28.0	33.0	–5.1
Cu-trien _{calcite} (B) 0.3 g	0.2	0.5	5.7	21.9	28.3	29.7	–1.4
Cu-trien _{calcite} (B) 0.5 g	0.1	0.5	5.6	20.5	26.7	27.5	–0.8
Cu-trien _{5 × calcite} (C) 2 g	0.2	0.7	5.6	21.6	28.2	28.2	–0.1
Cu-trien _{5 × calcite} (C) 3 g	0.2	0.6	5.4	20.3	26.5	26.8	–0.3
CoHex _{calcite} (E) 2 g	0.1	0.8	6.1	23.5	30.5	33.2	–2.7
CoHex _{calcite} (E) 3 g	0.2	0.8	6.1	23.7	30.8	31.9	–1.1
Bentonite (Greece, Milos) without carbonates							
Methods without 'calcite saturation'							
Cu-trien (A) 0.08 g	22.4	1.5	44.1	34.7	102.7	95.0	7.7
Cu-trien (A) 0.12 g	22.5	1.7	44.3	34.8	103.3	97.0	6.3
Methods with 'calcite saturation'							
Cu-trien _{calcite} (B) 0.08 g	23.3	0.3	46.9	34.4	104.9	103.8	1.1
Cu-trien _{calcite} (B) 0.12 g	23.1	0.7	46.2	34.4	104.4	103.5	0.9
Cu-trien _{5 × calcite} (C) 0.4 g	24.2	1.4	46.2	37.2	109.2	108.5	0.7
Cu-trien _{5 × calcite} (C) 0.6 g	24.6	1.5	46.1	37.1	109.4	106.0	3.4
CoHex _{calcite} (E) 0.6 g	21.9	1.4	44.6	36.4	104.3	105.1	–0.8
CoHex _{calcite} (E) 0.8 g	22.4	1.5	45.1	36.3	105.3	105.8	–0.5

Cu-trien (A) or CoHex (D). No such difference occurred (Table 3); the exchangeable Ca^{2+} values of all methods are comparable. This indicates the absence of any systematic falsification processes for any of these methods.

Compared to methods without calcite pre-treatment, the CEC values of non-calcareous clays typically can be significantly greater for 'calcite-saturated' exchange solutions. This CEC overstep can be explained mainly by the greater pH value of the exchange solutions which can cause an increase in the amount of variable charges as described by Dohrmann (2006b). For the Reuverton, the differences are in the range of up to +10%: The CEC of this clay using conventional techniques ranges from 26.1 to 30.5 meq/100 g whereas it ranges from 26.8 to 33.2 meq/100 g using methods with prior calcite saturation. The largest CEC values among the proposed new methods were obtained using CoHex_{calcite} (E): 31.9–33.2 meq/100 g. Cu-trien_{calcite} (B) and Cu-trien_{5 × calcite} (C) yielded CEC values of 26.8–29.7 meq/100 g which was more or less identical to methods without pre-treatment with calcite. The pH of the starting exchange solutions was identical in the new methods, but the CEC overstep is not observed in all methods. Accordingly, pH cannot be regarded as the only controlling parameter for the observed increase in CEC; the mechanism is not yet understood.

One result was clearly out of scope (37 meq/100 g, AgTU_{calcite}, 0.25 g) showing that the method (the sample contains no calcite) and the sample mass (too small) were unsuitable. An important result for this study is that there is no indication of excess adsorption on swellable clay minerals if CoHex_{calcite} (E) is used. This kind of error is well known for other metal complexes and was discussed by Dohrmann (2006a). At fixed amount of solution, the CEC results for the Milos bentonite do not vary if a sample mass of 0.6, 0.8, or 1.2 g is used (each in duplicate). The resulting CEC is 104.7, 105.8, and 103.1 meq/100 g. This holds true also for Cu-trien_{calcite} (B) (0.08 and 0.12 g) and Cu-trien_{5 × calcite} (C) (0.4 and 0.6 g).

Calcareous clays. Firstly, exchangeable Ca^{2+} values provided by the standard methods (without calcite saturation) were considered in order to identify the actual errors of these methods. The amount of exchangeable Ca^{2+} of the black shale was strongly affected by dissolution of calcite, ranging from 11 up to ~500 meq/100 g (Table 4). As expected, the sample mass was particularly important. The most unrealistic results were obtained using ammonium acetate, barium chloride, and the AgTU_{mod} method with small sample masses. More reasonable but still incorrect data were obtained using Cu-trien and the AgTU_{mod} method with large sample masses, ranging from 10 to ~30 meq/100 g Ca^{2+} . The same was observed in case of the marl (error: 17–762 meq/100 g Ca^{2+}).

There are some indications that the calcareous clays could contain traces of dolomite which could not be detected by XRD. In accordance with the study using AgTU_{calcite}, dolomite dissolution was minimized by calcite saturation of exchange solutions as well. Exchangeable Mg^{2+} was reduced to 1.8–2.1 meq/100 g for the black shale and to 0.3–0.6 meq/100 g for the marl using calcite-saturated exchange solutions. Using conventional techniques the range was greater: 2.0–8.9 meq/100 g (black shale) and 0.3–3.6 meq/100 g (marl), respectively.

Evaluation of the improved methods (with calcite saturation) proves a significant reduction of the exchangeable Ca^{2+} errors, e.g. in the case of the black shale (marl) down to realistic exchangeable Ca^{2+} values of 6.2–8.4 (13.5–21.3) meq/100 g. In the scope of this study these results are defined as 'operationally correct.'

The CEC of the black shale (marl) using conventional techniques ranges from 0 to 70 (5–65) meq/100 g. This range reflects the difficulties with the methods used and can be explained by the types of calcite reactions during the exchange experiments. As described by Dohrmann (2006c), witherite (BaCO_3) forms if calcite reacts with barium chloride. Witherite is dissolved again if magnesium chloride is used for the re-exchange leading to super-elevated CEC values. Another type of error can occur if ammonium acetate is used (Dohrmann, 2006d). Here a partial or complete Ca^{2+} saturation (instead of NH_4^+) of the exchange positions can reduce the CEC which is determined by quantification of NH_4^+ (Kjeldahl distillation). The process that causes this error is as follows. If the clays contain a lot of calcite (e.g. 15 wt.%) then this mineral is dissolved only partially during the saturation processes with the index cation solutions (ammonium acetate). The undissolved calcite can then be dissolved during the washing steps that are performed to remove excess salt prior to Kjeldahl distillation. The other conventional techniques (without calcite saturation) don't show these systematic CEC errors, and the resulting CEC values vary within a narrow and realistic range of 4.9–7.5 meq/100 g for the black shale and 14.1–17.0 meq/100 g for the marl. This is slightly smaller, but, in principle, in the same range as found using the calcite-saturated procedures: 5.5–9.1 meq/100 g for the black shale and 14.6–19.1 meq/100 g for the marl.

Test application of the new methods using calcareous bentonites

Ufer *et al.* (2008) reported on quantification of bentonites. Of these samples, the calcareous bentonites which are free of gypsum were used to test the applicability of the new methods. Sample 12 was excluded as well because it also contains a trace of gypsum (0.2–0.3 wt.%). No AgTU_{calcite} data are available for these samples. Kaufhold and Dohrmann (2008) published CEC and exchangeable cation population data, though the exchangeable Ca^{2+} values of the calcareous

Table 4. Comparison of the results of the different CEC methods used for the calcareous clays, black shale, and marl (meq/100 g).

Method	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	'sum'	CEC	'sum'-CEC
Black shale (40 wt.% calcite)							
Methods without 'calcite saturation'							
AgTU _{mod} , 0.5 g/0.25 g	0.3	0.5	3.1	109	113	7.5	105
AgTU _{mod} , 1 g	0.3	0.4	2.0	32.2	34.9	5.2	29.7
AmAc, 0.5 g	0.2	0.4	8.9	496	506	0.0	506
AmAc, 2 g	0.4	0.6	5.5	266	273	0.6	272
BaCl ₂ , 0.5 g	0.0	0.5	3.9	183	187	70.3	117
BaCl ₂ , 2 g	0.3	0.8	3.0	108	112	23.2	89
Cu-trien (A) 0.5 g	0.2	0.4	1.8	12.8	15.2	4.9	10.3
Cu-trien (A) 0.8 g	0.2	0.4	1.8	11.1	13.5	5.4	8.1
Methods with 'calcite saturation'							
AgTU _{calcite} , 0.5 g/0.25 g	0.1	0.3	2.1	8.4	10.9	6.4	4.5
AgTU _{calcite} , 1 g	0.2	0.4	1.8	6.2	8.6	5.5	3.1
Cu-trien _{calcite} (B) 0.5 g	0.3	0.3	1.9	8.0	10.5	5.8	4.7
Cu-trien _{calcite} (B) 0.8 g	0.2	0.3	1.9	8.2	10.6	5.7	4.9
CoHex _{calcite} (E) 2 g	0.2	0.5	2.0	8.0	10.7	9.1	1.6
CoHex _{calcite} (E) 3 g	0.2	0.5	2.0	8.4	11.1	7.8	3.3
Marl (38 wt.% calcite, traces of dolomite)							
Methods without 'calcite saturation'							
AgTU _{mod} , 0.5 g/0.25 g	0.3	0.2	0.9	118	119	16.1	103
AgTU _{mod} , 1 g	0.1	0.2	0.8	39.6	40.7	17.0	23.7
AmAc, 0.5 g	0.1	0.2	3.6	762	766	6.7	759
AmAc, 2 g	0.1	0.2	1.5	278	280	4.7	275
BaCl ₂ , 0.5 g	0.1	0.7	1.2	168	170	65.2	104
BaCl ₂ , 2 g	0.1	0.6	0.8	61.8	63.3	26.3	37.0
Cu-trien (A) 0.3 g	0.0	0.3	0.3	20.3	20.9	14.1	6.8
Cu-trien (A) 0.5 g	0.1	0.2	0.3	17.4	18.0	14.2	3.8
Methods with 'calcite saturation'							
AgTU _{calcite} , 0.5 g/0.25 g	0.1	0.1	0.6	21.3	22.1	17.6	4.5
AgTU _{calcite} , 1 g	0.1	0.1	0.6	15.3	16.1	17.8	-1.9
Cu-trien _{calcite} (B) 0.3 g	0.0	(-0.1)	0.3	14.0	14.2	15.1	-0.9
Cu-trien _{calcite} (B) 0.5 g	0.0	0.0	0.3	13.5	13.8	14.6	-0.8
CoHex _{calcite} (E) 2 g	0.1	0.3	0.4	17.3	18.1	18.6	-0.5
CoHex _{calcite} (E) 3 g	0.1	0.3	0.4	17.1	17.9	19.1	-1.2

samples are incorrect owing to the problems discussed in the present study.

The exchangeable Ca²⁺, sum of exchangeable cations, and CEC values obtained by the different methods applied in the present study (Table 5) were compared and clearly proved the improvement.

DISCUSSION

Methods based on Cu-trien

All exchangeable Ca²⁺ values of the calcareous bentonites determined by Cu-trien (A) were systematically erroneous (Figure 2a). This is particularly evident in the case of most of the bentonites containing >1.2 wt.% calcite (solid squares in Figure 2a). As expected and as explained above, Ca²⁺ values were greater for smaller sample masses (average of these samples: 51.7 meq/100 g) than for larger masses (average of these samples: 44.4 meq/100 g) which was caused

by different degrees of calcite dissolution. According to the maximum calcite dissolution capacity of method A, the calcite portion of a given sample was dissolved entirely if the calcite content was <1.2 wt.% (for a 120 mg sample mass). This corresponds to 1.48 mg of dissolved calcite/60.0 mL of Cu-trien A solution. Consequently, the Ca²⁺ values of the bentonites (with <1.2 wt.% calcite, open squares) should be on the $y = x$ line (within typical scattering). In general the differences between different sample masses should be negligible for all these samples with <1.2 wt.% calcite. In fact, the average difference is only 1.9 instead of 7.3 meq/100 g as for the more calcareous bentonites. Only one (IB07) of the five bentonites containing >1.2 wt.% calcite was close to the $y = x$ line. The reason is that it contains 1.3 wt.% calcite, which is 0.1% above the calculated saturation concentration. This is clearly within the range of unsystematic error of the XRD quantification which explains the deviation.

Table 5. Results of the different CEC methods used for the 14 calcareous bentonites.

Sample assignment This study <i>Ufer et al.</i> (2008)	Wt.% calcite	Cu-trien (A)		Cu-triens × calcite (C)		CoHex (D)		CoHex _{calcite} (E)							
		120 mg 80 mg	average diff.	600 mg 400 mg	average diff.	1200 mg 800 mg	average diff.	1200 mg 800 mg	average diff.						
B01	0.9	46.3	49.5	34.2	34.1	34.2	-0.1	37.7	39.2	38.5	-1.5	35.8	36.7	36.3	-0.9
B07	1.3	29.5	31.4	21.8	21.7	21.8	-0.1	24.4	26.0	25.2	-1.6	22.7	23.3	23.0	-0.6
B10	0.6	47.6	49.6	42.0	42.2	42.1	0.2	44.8	46.5	45.7	-1.7	43.5	44.7	44.1	-1.2
B11	0.8	30.9	32.0	31.5	31.5	21.9	0.4	26.7	28.7	27.7	-2.0	24.8	25.7	25.3	-0.9
B13	2.9	54.0	64.3	59.2	37.0	36.9	0.2	42.1	44.3	43.2	-2.2	40.3	40.4	40.4	-0.1
B14	0.5	45.2	47.6	46.4	37.7	37.8	0.2	42.8	44.5	43.7	-1.7	40.4	42.0	41.2	-1.6
B15	15.7	51.3	59.4	55.4	34.6	34.6	0.0	39.9	41.9	40.9	-2.0	37.0	38.5	37.8	-1.5
B17	0.5	34.5	37.4	36.0	23.9	24.5	1.2	27.0	28.9	28.0	-1.9	24.9	25.8	25.4	-0.9
B18	0.8	41.5	42.4	42.0	34.4	34.4	0.0	37.5	39.1	38.3	-1.6	35.9	36.5	36.2	-0.6
B19	2.2	42.4	49.2	45.8	27.9	28.0	0.2	31.4	33.4	32.4	-2.0	29.3	30.5	29.9	-1.2
B22	0.3	26.0	26.2	26.1	25.5	25.6	-0.2	25.5	25.7	25.6	-0.2	26.6	26.6	26.6	0.0
B26	0.5	48.0	49.8	48.9	42.2	42.4	0.2	43.4	45.3	44.4	-1.9	42.1	43.7	42.9	-1.6
B31	0.9	31.4	33.9	32.7	19.4	19.6	-0.3	23.6	25.4	24.5	-1.8	21.9	22.8	22.4	-0.9
B38	7.4	44.9	54.3	49.6	28.8	28.7	-0.3	30.6	32.8	31.7	-2.2	30.1	30.6	30.4	-0.5
Average		41.0	44.8	42.9	30.9	30.9	0.1	34.1	35.8	35.0	-1.7	32.5	33.4	33.0	-0.9
Std. dev.							0.4				0.5				0.5

Sample assignment This study <i>al.</i> (2008)	Wt.% calcite	Cu-trien (A)		Cu-triens × calcite (C)		CoHex (D)		CoHex _{calcite} (E)							
		CEC	sum	CEC	diff.	CEC	diff.	CEC	diff.						
IB01	0.9	91.8	109.7	92.7	93.3	92.7	0.6	96.3	97.4	97.4	1.1	94.3	96.6	96.6	2.3
IB07	1.3	88.3	101.1	89.3	90.6	89.3	1.3	90.5	91.6	91.6	1.1	92.2	91.8	91.8	-0.4
IB10	0.6	87.8	98.4	90.6	90.9	90.6	0.3	88.2	93.1	93.1	4.9	93.2	92.5	92.5	-0.7
IB11	0.8	89.4	109.6	91.4	98.0	91.4	6.7	90.3	100.6	100.6	10.3	94.4	100.3	100.3	5.9
IB13	2.9	78.1	100.1	77.2	75.7	77.2	-1.5	85.1	83.8	83.8	-1.3	85.5	81.8	81.8	-3.7
IB14	0.5	81.5	92.2	82.2	80.5	82.2	-1.7	90.6	87.9	87.9	-2.6	90.0	85.8	85.8	-4.2
IB15	15.7	73.0	95.3	75.6	72.3	75.6	-3.3	82.5	80.1	80.1	-2.4	81.7	77.0	77.0	-4.7
IB17	0.5	95.6	113.5	96.7	98.5	96.7	1.8	100.0	97.6	97.6	-2.4	96.6	97.9	97.9	1.3
IB18	0.8	98.6	110.2	100.1	99.5	100.1	-0.5	104.7	102.9	102.9	-1.8	100.8	101.6	101.6	0.8
IB19	2.2	82.3	101.7	82.6	82.5	82.6	-0.1	86.5	86.3	86.3	-0.2	84.2	84.3	84.3	0.1
IB22	0.3	88.8	94.1	86.9	90.1	86.9	3.2	88.3	86.2	86.2	-2.1	90.0	89.7	89.7	-0.3
IB26	0.5	85.3	90.7	82.8	82.7	82.8	-0.1	81.4	83.2	83.2	1.9	86.8	82.2	82.2	-4.6
IB31	0.9	84.6	101.8	82.2	86.6	82.2	4.4	82.6	87.6	87.6	5.0	84.3	86.3	86.3	2.0
IB38	7.4	64.7	86.9	63.4	65.1	63.4	1.7	65.7	68.2	68.2	2.6	65.1	66.7	66.7	1.6
Average		85.0	100.4	85.2	86.1	85.2	0.9	88.0	89.0	89.0	1.0	88.5	88.2	88.2	-0.3
Std. dev.							2.5				3.6				3.0

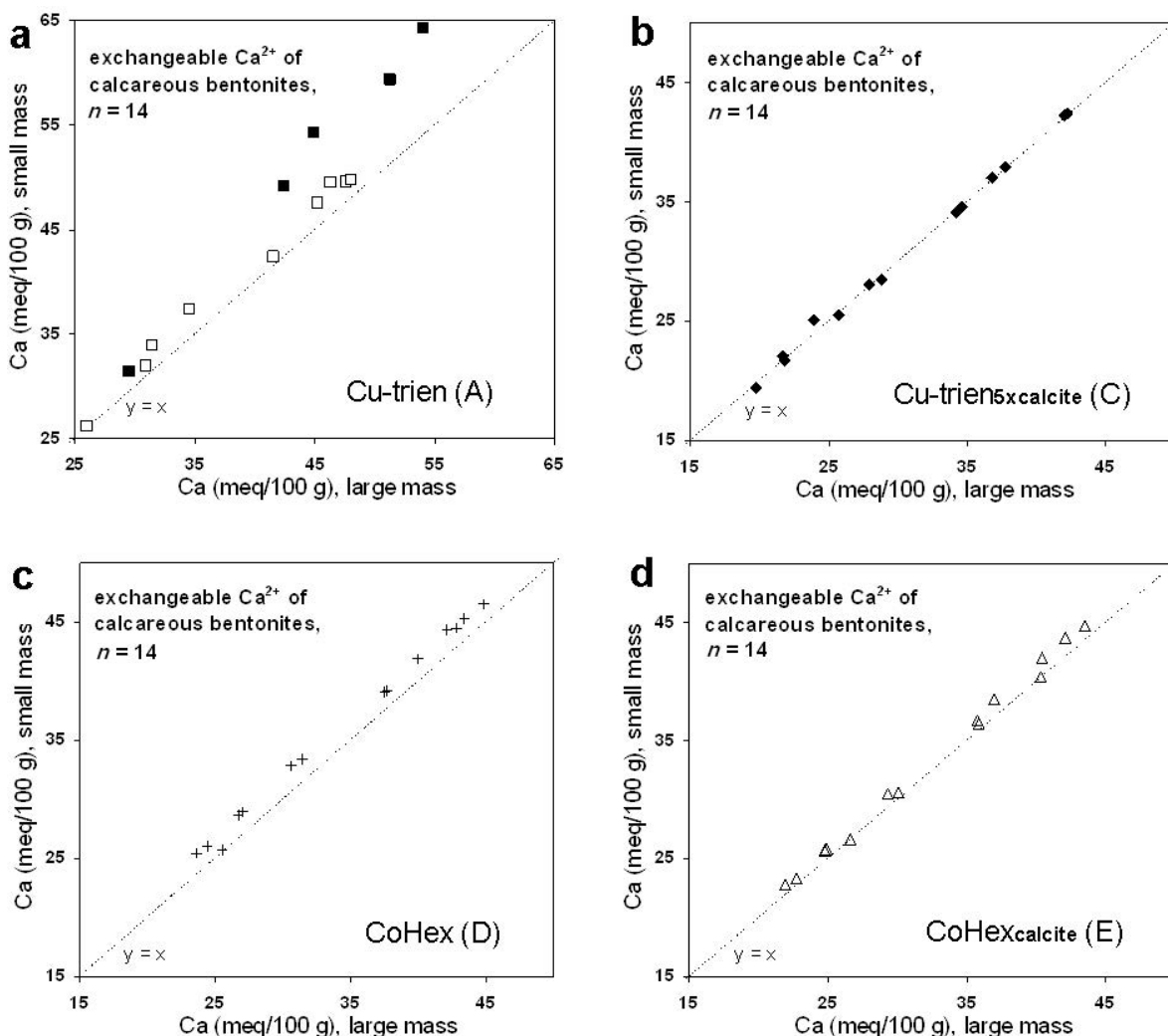


Figure 2. Exchangeable Ca^{2+} data (using two different sample masses) of 14 calcareous bentonites (free of gypsum). The results are compared for common methods based on Cu-trien (A) (a) and CoHex (D) (c) on the one hand and for the proposed new metal-organic complex methods with pre-saturation of calcite on the other hand: diamonds: Cu-trien₅ × calcite (C) (b), triangles: CoHex₅ × calcite (E) (d) (averages of two different sample masses).

To evaluate if the data are erroneous, the difference between the sum of exchangeable cations and the CEC must be considered as well. This difference can be seen in Figure 3a clearly showing that the sum of exchangeable cations exceeds the CEC (all samples). Therefore, all the Cu-trien (A) Ca^{2+} data are erroneous regardless of the pseudo-agreement of some bentonites with <1.3 wt.% calcite in Figure 2a.

Using the new Cu-trien₅ × calcite (C) method (Figure 2b), the systematic errors for exchangeable Ca^{2+} data of bentonites were 0.6 and 0.8 meq/100 g (600 mg and 400 mg sample mass, Table 2) which equals the size of the diamond symbols in the diagram. According to this comparably low error a good correlation of the values obtained with different sample masses is observed (average values for smaller and larger samples, respec-

tively, are 31.2 and 31.0 meq/100 g). This in turn results in significantly smaller differences in the sum of exchangeable cations and the CEC. Therefore, the results are closer to the $y = x$ line (Figure 3b). Compared with exchangeable Ca^{2+} data, however, the precision is poorer for the difference between the sum of exchangeable cations and the CEC. One reason is that the errors in four independent measurements performed as duplicates are totalled (Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) and compared with the CEC which is also the average of experiments performed as duplicates. An additional source for the scattering may be the presence of soluble components other than calcite (excess electrolytes in the pore water, conceivably NaCl). Kaufhold and Dohrmann (2008) reported on very different anion concentrations of the bentonites in their experiments noting that these are only relative differences;

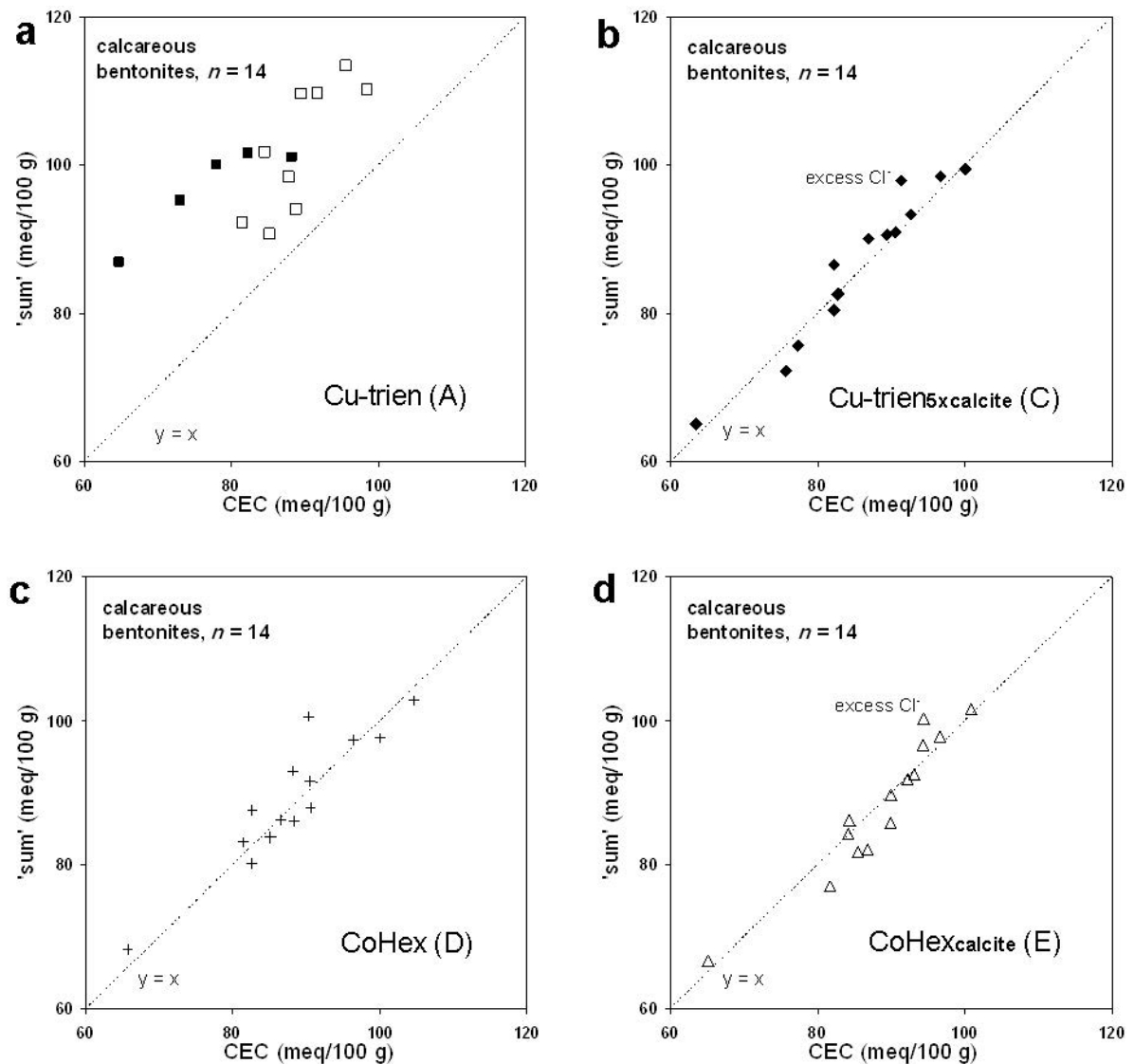


Figure 3. Sum of exchangeable cations ('sum') vs. CEC data of 14 calcareous bentonites (free of gypsum). The results are compared for common methods based on Cu-trien (A) (a) and CoHex (D) (c) on the one hand and for the proposed new metal-organic complex methods with pre-saturation of calcite on the other hand: diamonds: Cu-trien_{5x}calcite (C) (b), triangles: CoHex_{calcite} (E) (d) (averages of two different sample masses).

calculating the anion concentrations in meq/100 g is impossible. The largest Cl^- concentrations of the supernatants after ultracentrifugation of the calcareous bentonites (no gypsiferous bentonites were chosen here), however, are those of sample B11 which is marked in Figure 3b and d as 'excess Cl^- '. This correlates very well with the observed overstepping of the CEC by exchangeable cations.

Methods based on CoHex

All exchangeable Ca^{2+} values determined by CoHex (D) were systematically erroneous as observed in case of method A (Figure 2c). In contrast to method A, the point

of calcite saturation of method D was attained at 0.2 wt.% calcite with a sample mass accounting for 1200 mg. Ufer *et al.* (2008) only identified one bentonite (of those considered in the present study) containing <0.3 wt.% calcite (IB22), the only one with a difference of <1 meq/100 g between experiments with different sample masses: 0.2 meq/100 g leading to a position of the data point directly on the $y = x$ line, all the others are slightly above the line. This confirms the discussion about the limits of the 'Carbonate and Sulphate Field Model' (Dohrmann, 2006c) and indicates that exchangeable Ca^{2+} values obtained by CoHex (D) are affected by partial calcite dissolution. This influence is relatively

Table 6. Precision of CEC and exchangeable cation values (meq/100 g).

	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	CEC
min	0.0	0.0	0.0	0.0	40
max	70	6.0	45	70	105
Method	Within a single series (14 bentonites, $n = 14$) $\pm 3\sigma$				
CoHex _{calcite} (E)	1.3	0.3	0.8	2.2	4.6
Cu-trien _{5 × calcite} (C)	1.9	0.3	0.8	0.8	3.1
Method	Repetition of a complete series (14 bentonites, $n = 28$) $\pm 3\sigma$				
CoHex _{calcite} (E)	2.2	0.3	0.9	1.8	7.2
Cu-trien _{5 × calcite} (C)	1.2	0.2	0.8	2.3	3.8
Method	Comparison of different CEC methods (two series, 14 bentonites each, $n = 28$) $\pm 3\sigma$				
CoHex _{calcite} (E)	2.8	0.6	3.8	6.5	12.9
Cu-trien _{5 × calcite} (C)					

small but it can be evaluated by comparison with Ca²⁺ data of the corresponding new CoHex_{calcite} (E) method. The average exchangeable Ca²⁺ results are ~2 meq/100 g smaller (33.0 instead of 35.0 meq/100 g) compared to CoHex (D). Although this is a systematic effect, the differences are close to the unsystematic scattering of this method.

Precision of CEC and exchangeable cation values

From the analytical data the statistical variation can be calculated (Table 6). The precision of CEC and exchangeable cation values depends on several factors.

Firstly, the error ($\pm 3\sigma$) is different for different cations and the CEC. The scattering is least for K⁺, followed by Mg²⁺, Ca²⁺, Na⁺, and the CEC. If a large range is considered, e.g. for Na (0–70 meq/100 g), it is important to note that the absolute error is smaller for the narrower concentration ranges. As an example, $\pm 3\sigma$ is calculated for CoHex_{calcite} (E) vs. Cu-trien_{5 × calcite} (C). From 0 to 10/10 to 25/25 to 70 meq/100 g of Na⁺, the error is $\pm 0.2/1.3/3.9$ meq/100 g respectively, whereas the overall error for the whole range (Table 6) is ± 2.8 meq/100 g.

Secondly, precision depends on whether the exchange data for the samples compared were measured in one experimental run (*i.e.* on the same day), or between different experimental runs. The scattering is least if data within a single series are compared. Scattering increases after repetition of such a complete series. It increases even more if data from the same samples but from two different methods are compared.

The typical precision of CEC data in a laboratory over a long period of time was quantified using a laboratory standard clay, Reuverton, which has an average CEC of 27.9 ± 1.8 meq/100 g ($n = 34$ independent experiments performed as duplicates over a period of ~4 y). This is a relative error of ~6%.

The average CEC (Table 5) of all bentonites studied was 88.4 meq/100 g for CoHex_{calcite} (E) and 85.7 meq/100 g for Cu-trien_{5 × calcite} (C). This is a systematic difference of ~3%

and one of the major reasons for the relatively large CEC error of ± 12.9 meq/100 g observed when both methods are compared statistically. The same decrease in precision between both methods is observed for Mg²⁺/Ca²⁺/Na⁺/K⁺ cations ($\pm 3.8/\pm 6.5/\pm 2.8/\pm 0.6$ meq/100 g) where average values are 23.6/33.0/29.7/2.4 meq/100 g for CoHex_{calcite} (E) and 22.1/30.9/30.6/2.2 meq/100 g for Cu-trien_{5 × calcite} (C). The reason for the systematic differences in Mg and the CEC are not yet understood.

Finally, worth mentioning is that systematic errors in the CoHex method have been reported. Koppelman and Dillard (1978) showed that, in acidic conditions, Co(III) in the CoHex complex is reduced to Co(II) when adsorbed onto chlorite. The proposed mechanism includes a drastic pH increase from 3 to 8.7. No such complications were detected in the present study where no acidic conditions and mainly smectitic samples were used. Despite these problems, an interlaboratory comparison was performed recently in order to validate the ISO/DIS 23470 “Soil Quality. Determination of effective cation exchange capacity (CEC) and exchangeable cations using a cobaltihexamine trichloride solution” (Sterckeman, 2006).

CONCLUSIONS

The results of the study indicate that all three new methods can be used to determine the exchangeable Ca²⁺ of calcareous clays. The proposed new CoHex_{calcite} (E) and Cu-trien_{5 × calcite} (C) methods are more efficient than the AgTU_{calcite} method. Using these new methods, the exchangeable Ca²⁺ data of calcareous clays can be regarded as ‘operationally correct.’ The results of the other exchangeable cations studied and the CEC are comparable to existing standard methods. Cu-trien_{calcite} (B) was found to be helpful if only very small sample masses are available.

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