agronomie: agriculture and environment

A comparison between three methods for the determination of cation exchange capacity and exchangeable cations in soils

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Summary — The object of this study is to compare the results obtained with three standardized methods of determination of cationic exchange capacity (CEC) and exchangeable cations (Ca, Mg, K) in soils. The three methods are based on different exchange reagents: cobalt hexamine (Cohex) trichloride, barium chloride and ammonium acetate. Exchange procedures are different as well; they are, respectively, single extraction, successive extractions and percolation. Values measured with barium and Cohex as index cations are very comparable and reveal the uniformity of the physicochemical processes at play. Concerning these processes, the two methods can be considered as equivalent. Ammonium acetate, buffering the pH of the extracts, causes significant variations in the proportion of negatively charged sites and particularly those bonded to organic matter. This produces large divergences from CEC values obtained with the two other methods. Nevertheless, it is possible to reduce these differences for a given soil sample, by considering its pH and organic carbon content. Quantities of calcium and potassium extracted may also change due to the dissolution of carbonated species and ammonium ability for exchanging fixed potassium.

soil analysis / cation exchange capacity / exchangeable cation / cobalt hexamine trichloride

Résumé — **Comparaison de trois méthodes de détermination de la capacité d'échange et des cations échangeables des sols.** L'objet de cet article est de comparer les résultats obtenus au moyen de trois méthodes normalisées de détermination de la capacité d'échange cationique des sols (CEC) et des cations échangeables (Ca, Mg, K). Les méthodes examinées utilisent des réactifs d'échange différents : le chlorure de cobaltihexammine, le chlorure de baryum et l'acétate d'ammonium. Les procédures d'échange varient également : ce sont, la simple agitation, les extractions successives et la percolation. Les teneurs mesurées avec le chlorure de baryum et le chlorure de cobaltihexammine sont étroitement corrélées et montrent l'uniformité des processus physicochimiques mis en jeu. De ce point de vue, les deux méthodes peuvent être considérées comme équivalentes. L'acétate d'ammonium, en tamponnant le pH du milieu d'extraction, induit des variations importantes dans les proportions de sites électronégatifs et en particulier, ceux liés à la matière organique. La prise en compte du pH et de la teneur en carbone des échantillons nous a cependant permis de réduire les différences entre méthodes. Les quantités de calcium et de potassium extraites varient également à cause de la dissolution d'espèces carbonatées et l'aptitude particulière de l'ammonium à s'échanger avec le potassium.

analyse de sol / capacité d'échange cationique / cation échangeable / cobaltihexammine

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INTRODUCTION

Numerous methods are proposed to measure the cation exchange capacity (CEC) and exchangeable cations in soils. Some use buffered solutions such as ammonium acetate at pH = 4.8 (McLean et al, 1959) or pH = 7.0 (Thomas, 1982), sodium acetate (Bower et al, 1952) or barium chloride (Bascomb, 1964) at pH = 8.2. With others, the exchange reaction is carried out by means of unbuffered salts, as, for example, ammonium chloride (Shuman and Duncan, 1990) or barium chloride (Gillman, 1979). For a given reagent, CEC values can be obtained either by summing the exchanged cations (Hendershot and Duquette, 1986) or by determining the quantity of a fixed cation (index cation) (Gillman, 1979). The first method implies that the cations extracted were exchangeable. In fact, some elements can be released from non-exchangeable sources, for instance calcium from calcium carbonate or aluminium from (free) aluminium oxides (Espiau and Peyronel, 1976). As iron and aluminium oxides, kaolinitic clays and organic matter have variable charges which depend upon the pH and the ionic strength of the reagent used; the measured CEC values may be highly sensitive to the method used.

For all methods the first stage involves the saturation of the soil sample with an index cation. In a previous work (Ciesielski and Sterckeman, 1997) in which we studied the use of Cohex chloride, we examined three different exchange procedures: single extraction, successive extractions and percolation. The reagent was used at a low concentration (0.01666 mol·L^{-1}) and CEC was determined from the depletion of the initial solution. The comparisons led to close linear regressions with slopes of about one, depending on the yield of the exchange reaction.

The three procedures were therefore considered as equivalent and we chose the single extraction protocol on account of its ease of implementation.

In this article we compare methods using three different electrolytes: Cohex chloride, barium chloride and ammonium acetate. For the last two reagents, we follow standardized protocols, which implement, respectively, successive extractions (NF ISO 11260) and percolation (AFNOR NFX 31-130). We try to point out the main factors influencing exchange reaction, in order to facilitate the comparison of results issued from different methods as well as the choice of a reagent and protocol.

MATERIALS AND METHODS

Soil samples

Forty-eight soil samples collected in various regions of France (loamy soils from the North, granitic ones from Brittany, volcanic soils from the Massif Central, alluvials from the Rhineland, calcareous soils from Champagne) are studied. The samples were air-dried and passed through a 2 mm sieve before being analyzed. Their main characteristics are listed in table I.

Methods

The cobalt hexamine chloride method

The operating protocol which forms our basic reference has been described in a previous study (Ciesielski and Sterckeman, 1997). The exchange is carried out by simply shaking the test portion in the reagent. For a given volume of reagent (100 mL), the quantity of sample weighed (5, 10 or 2.5 g) is such that a sufficient concentration of Cohex ions remains

Table I. Main characteristics of the soils used in the experiments.

Clay (g·kg^{-1})		Carbon (g·kg^{-1})		pH in water	
Class	Frequency	Class	Frequency	Class	Frequency
0–100	7	0–10	17	4–5	3
100–200	20	10–20	13	5–6	9
200–300	11	20–30	8	6–7	10
300–400	6	30–50	5	7–8	15
400–600	4	50–200	5	8–8.3	11

Distribution according to clay content, organic carbon content and pH determinated according to AFNOR standards X 31-107, X 31-109, X 31-103.

in solution. This concentration is determined by spectrocolorimetry without chemical pretreatment of the solution. The loss of Cohex from solution gives the CEC of the sample. Exchangeable cation contents are measured either by flame atomic emission spectrometry for K or by flame atomic absorption spectrometry for Ca and Mg.

The barium chloride method

A first version of this method was proposed by Gillman (1979) and subsequently modified (Gillman and Sumpter, 1986). After several adaptations had been tested, it was standardized in 1994 under the reference ISO 11260 described later.

A test portion of 2.5 g is shaken for 1 h with 30 mL of 0.1 mol·L^{-1} BaCl$_2$ solution. The solid and liquid phases are separated by centrifugation. This operation is repeated twice and the three supernatants are collected for the determination of exchanged cations. After equilibrating the soil with 30 mL of 0.0025 mol·L^{-1} BaCl$_2$, the solid phase is shaken once again, but this time with 30 mL of 0.02 mol·L^{-1} magnesium sulphate (MgSO$_4$) solution (in a first version the shaking time was 2 h; in the final version, overnight). The adsorbed barium exchanges with magnesium and precipitates in the form of BaSO$_4$. The residual content of this latter is measured by flame atomic absorption spectometry and substracted from the initial content. The difference gives the CEC value.

The ammonium acetate method

Widely used throughout the world, the ammonium acetate method was proposed by Metson in 1956. It has undergone many adaptations, such as those suggested in France by Lefevre (1961). In this study we follow the procedure described in the French standard AFNOR NFX 31-130.

The saturation of the exchange sites by ammonium is carried out by percolating a 1 mol·L^{-1} ammonium acetate solution (~75 mL) through a test portion of 2.5 g of soil. The excess reagent is eliminated with several rinsings with ethanol (~75 mL). After drying in air, the solid phase is agitated in 50 mL of a 1 mol·L^{-1} solution of sodium chloride. The exchanged ammonium is measured by spectrocolorimetry, which permits the measurement of CEC.

For practical reasons, the cations are currently measured after a single extraction of 2.5 g of sample in 50 mL of a molar solution of ammonium acetate. This procedure is described in the AFNOR NFX 31-108 standard and is the one followed in this work.

Comparison between methods

A comparison between methods can reveal particular behaviour among the samples tested which show that the reactions induced by the extractants may vary according to soil characteristics.

On the contrary, when close linear correlations are observed the compared methods are considered as equivalent. We make a distinction between two kinds of equivalence: a metrological equivalence (which we call interchangeability), relative to the measured quantities, and a physicochemical equivalence (which we simply call equivalence), relative to the use made of the results obtained. Requirements to meet each kind of equivalence have been discussed previously by Ciesielski and Sterckeman (1997) and identical conditions are adopted in the present work.

RESULTS AND DISCUSSION

Comparison of the barium and cobalt hexamine chloride methods

Table II shows the relations obtained for the different parameters under examination. Figure 1 shows the one obtained for CEC.

The relations for the parameters collectively are extremely close, as shown by the determination coefficients r^2. Barium chloride extracts larger quantities of cations (A > 1) owing to the use of a larger volume of reagent. Paradoxically, these deviations are not compensated for by those recorded for the CEC (A = 0.977), with the result that saturation rates are also higher. This observation may be explained if the exchange reaction between adsorbed barium and magnesium is not quantitative. A similar remark has already been made by Gillman (1979), who finally chose a reaction time of 16 h instead of 2 h to attain equilibrium. Unfortunately, it was not the case for a first version of ISO 11260 on which this work is based.

Table II also shows results obtained in a previous study by Ciesielski and Sterckeman (1997). The Cohex chloride method is applied to the same samples by means of a single extraction as described here (M1) and successive extractions (M2) according to the barium chloride procedure. For all the parameters, the comparison of the determination coefficients (r^2 and r'^2) do not point out any additional variability induced by the change of reagent for all the paramaters, and the amounts of cations extracted are then lower for barium chloride as compared with Cohex chloride (A1 > A). This shows that the yield of exchange reaction is more influenced by the quantities of reagents used than by the reagents themselves.

Table II. Comparison of cation exchange capacity (CEC) and exchangeable cations obtained with different extraction procedures using a linear regression passing through the origin.

Units	CEC $cmol+\cdot kg^{-1}$	Calcium (all soils) $cmol+\cdot kg^{-1}$	% CEC	Magnesium $cmol+\cdot kg^{-1}$	% CEC	Potassium $cmol+\cdot kg^{-1}$	% CEC
Y = A × M1	A = 0.977 r^2 = 0.989	A = 1.142 r^2 = 0.977	A = 1.165 r^2 = 0.935	A = 1.074 r^2 = 0.995	A = 1.123 r^2 = 0.976	A = 1.192 r^2 = 0.982	A = 1.201 r^2 = 0.979
M2 = A1 × M1	A1 = 1.121 r'^2 = 0.991	A1 = 1.221 r'^2 = 0.966	A1 = 1.112 r'^2 = 0.912	A1 = 1.156 r'^2 = 0.990	A1 = 1.001 r'^2 = 0.952	A1 = 1.334 r'^2 = 0.987	A1 = 1.169 r'^2 = 0.958

Y: $BaCl_2$, M1: Cohex single extraction; M2: Cohex successive extractions; $cmol+\cdot kg^{-1}$: values related to soil; % CEC: values related to CEC; A and A1: regression coefficients, r^2; and r'^2: determination coefficients.
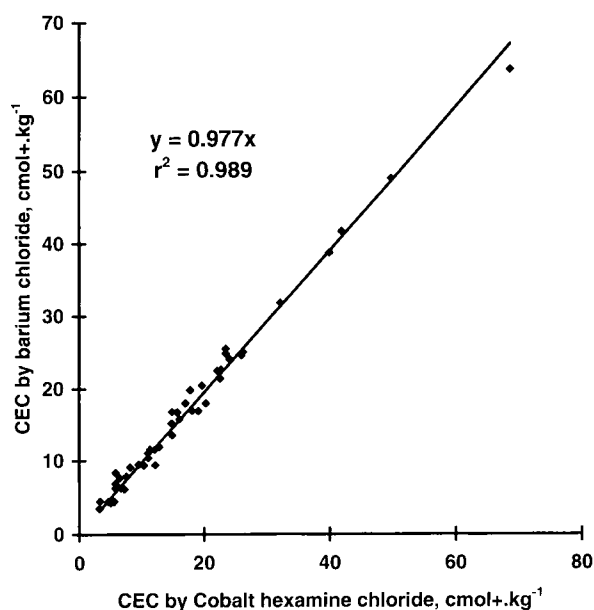
Fig 1. Relationship between cation exchange capacity (CEC) values obtained with Cohex chloride and barium chloride.

Despite those remarks, the barium chloride method and the single extraction Cohex method can be considered as equivalent except for calcium saturation rates (r^2 = 0.935), and metrological interchangeability can even be envisaged for magnesium (r^2 = 0.995).

Comparison between the ammonium acetate and cobalt hexamine chloride methods

Cation exchange capacity

In the previous comparison, the exchange reagents are different but the acid-base equilibria

are not fundamentally changed. This leads to close relationships between the parameters under observation. The buffering capacity of neutral ammonium acetate makes a comparison more difficult on account of its influence on the pH of the suspensions and consequently on variable charges of soils. Figure 2 shows how this parameter changes when the same soils are suspended in ammonium acetate and Cohex chloride in identical proportions (m/v = 1/20); values obtained in water (according to standard NFX 31-103) are also reported.

Table III and figure 3 show that the CEC values are not well related (r^2 = 0.396). The two methods are not equivalent with reference to the soils studied because of the large range of their pH values. To obtain a good agreement between the two procedures, only neutral soils or soils with little pH dependent charges should be considered.

Assuming that for the studied soils the bulk of variable charges is furnished by organic matter, in comparison to Cohex chloride, ammonium acetate provokes: i) a higher pH in acid soil suspensions, leading to an increase in the negatively charged sites of organic matter; ii) an acidification of basic suspensions translating as a decrease of these negatively charged sites.

According to these remarks, we tried to improve the relation. To do so, we introduced for each sample two readily available factors: organic carbon content expressed in $g \cdot kg^{-1}$ (C), and the water pH (pH), respectively determined by means of AFNOR standards NFX 31-109 and NFX 31-103. To calculate the CEC according to Cohex chloride (Y′) from the CEC given by ammonium acetate (Y), we used the following expressions:
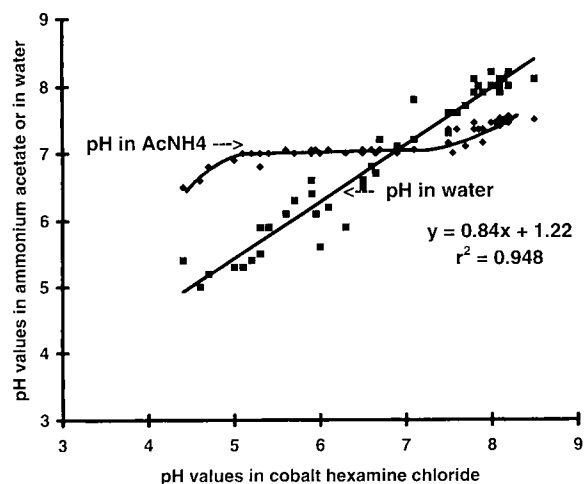
Fig 2. Comparison of the pH values of soil extracts obtained with Cohex chloride and ammonium acetate.

Fig 3. Relationship between cation exchange capacity (CEC) values determined by the Cohex chloride method and by ammonium acetate method.

For soils whose $6.0 < pH \leq 8.2$,

$$Y' = Y + 0.15 \times (pH - 5.5) \times C$$

and $Y' = Y + 0.15 \times (8.2 - 5.5) \times C$

for soil $pH > 8.2$

For soils whose $4.5 < pH \leq 6.0$,

$$Y' = Y - 0.15 \times (6.5 - pH) \times C$$

and $Y' = Y - 0.15 \times (6.5 - 4.5) \times C$

for soil $pH < 4.5$

These relations are valid for soils with organic carbon content (C) lower than 30 $g \cdot kg^{-1}$. On the contrary, these formulae must be slightly modified, the terms in parentheses becoming, respectively, $(pH - 6.0)$ and $(7.0 - pH)$.

It must be noted that such a correction is not a purely empirical calculation. It takes into account a simplified form of a neutralization curve of organic matter in soils.

Under these conditions, the relation $Y' = A' \times X$ gives us $A' = 0.989$, with $r^2 = 0.989$, as illustrated in figure 4. This example shows that
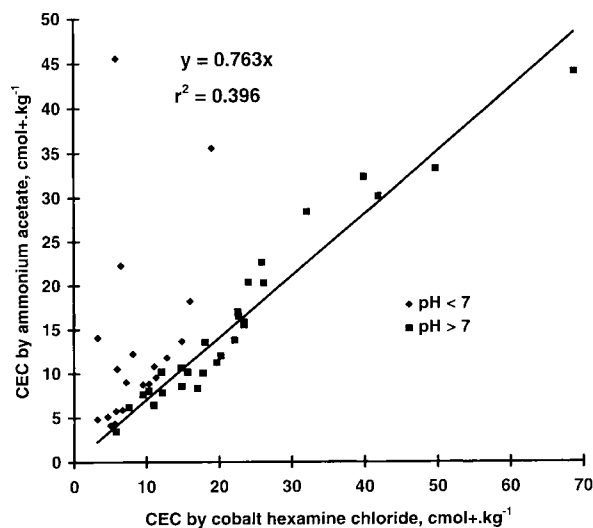
one can make a relatively accurate estimate of the results of one method by using the other.

Exchangeable calcium

Acidification of calcareous soils by ammonium acetate solubilizes calcium. The extracted quantities of this element may depend more on the content of carbonated materials and their solubility products than on the amount present on the exchange complex. In our study, when both acid and basic soils are considered, the slope of the regression line is 1.374 with $r^2 = 0.743$ (table III). The two methods are not equivalent. To preserve the specificity of the exchange reaction, a reagent that does not modify the initial pH value of soils is more appropriate.

When only acid soils are observed, the comparison leads to a close relation (A = 1.014, $r^2 + 0.986$) (table III; fig 5). In such conditions the two methods can be considered as equivalent.

Table III. Y = AX relationship between values obtained with ammonium acetate (Y) and values obtained with Cohex chloride (X).

	CEC	Calcium		Magnesium		Potassium	
	All soils	Acid soils	All soils	Acid soils	All soils	Acid soils	All soils
A	0.763	1.014	1.374	1.052	1.084	1.184	1.175
r^2	0.396	0.986	0.743	0.996	0.984	0.915	0.917

A: regression coefficients; r^2: determination coefficients.

Exchangeable magnesium

Calcium carbonate can contain some magnesium. They will be solubilized together, resulting in higher average quantities of extracted magnesium for ammonium acetate than for Cohex chloride (A = 1.084; table III). As with calcium, but to a much smaller extent, this excess is not a real exchangeable fraction. Nevertheless, the two methods are equivalent (r^2 = 0.984).

Exchangeable potassium

A comparison of the reagents gives a slope coefficient of 1.175 (table III and fig 6). Although ammonium acetate is shown to be the more efficient of the two in the extraction of potassium (A > 1), this trend can be reversed with a simple modification of experimental protocols. When the two reagents are compared using both percolation methods as described in Ciesielski and Sterckeman (1997), we obtain A = 0.978. Nevertheless, whatever the exchange protocol used, we can observe that in soils with a high clay content (clay > 400 g·kg^{-1}), or those rich in organic carbon (C > 30 g·kg^{-1}), ammonium extracts more potassium than the Cohex ion (fig 6). This explains the lower determination coefficient (r^2 = 0.917).

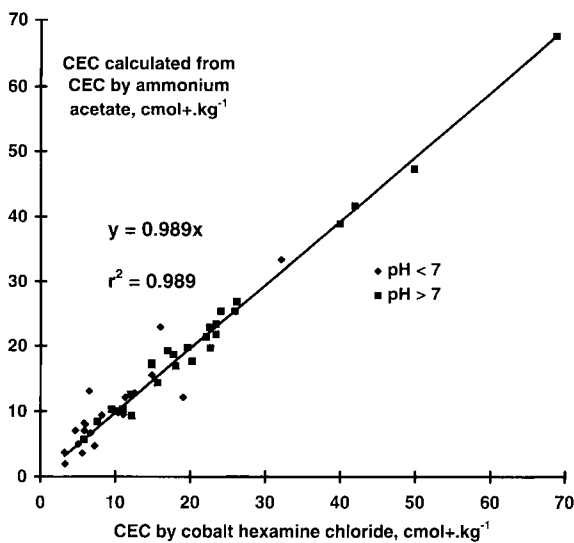As shown in table III, taking the soil pH into account in the comparisons does not change the

Fig 5. Relationship between the amounts of calcium (Ca) extracted with Cohex chloride and with ammonium acetate.

Fig 6. Relationship between the amounts of potassium (K) extracted with Cohex chloride and with ammonium acetate.

Fig 4. Relationship between cation exchange capacity (CEC) values determined with Cohex chloride method and those calculated from CEC values determined with ammonium acetate, organic carbon content and water pH of the sample.
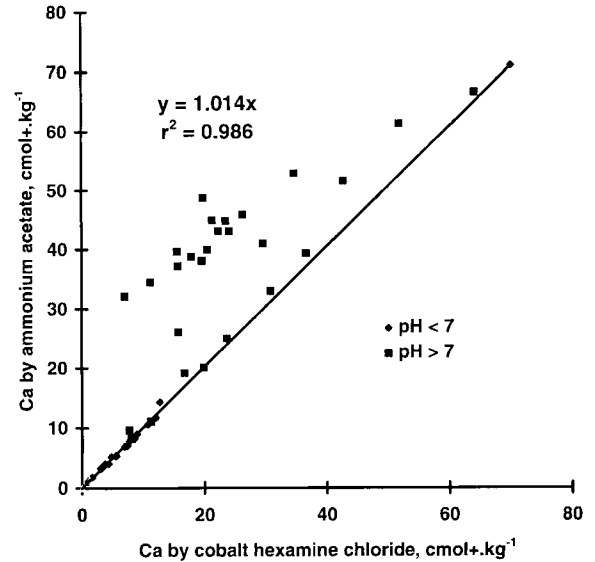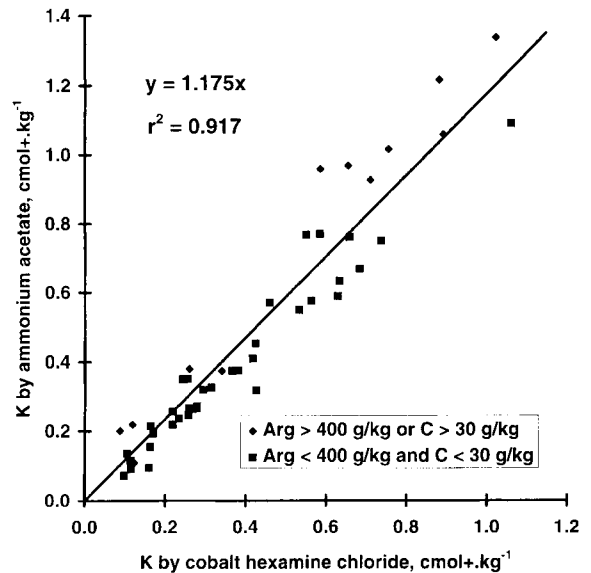
agreement between the methods. This observation is confirmed when we compare ammonium acetate and ammonium chloride under the same conditions. The latter reagent lacks the buffering capacity of the former, but even so the quantities of potassium extracted by the two methods remain perfectly comparable and closely correlated (for our 48 soils:

A = 1.045 and r^2 = 0.996). The greater ability of ammonium acetate for extracting potassium is due to the ammonium ion and not to its effect on the pH of the suspensions. Identical remarks have been made by Gillman (1979) and Quemener and Bosc (1988). The effectiveness of K extraction by ammonium ions is well known. In some clays like illite, potassium can occupy surface adsorption sites and edge-interlattice positions for which ammonium is highly competitive, unlike other replacing cations (Bolt et al, 1963).

Without particular consideration with respect to organic matter and clay contents, Cohex chloride and ammonium acetate methods are not equivalent. Likewise, CEC additional information is necessary to improve relations.

CONCLUSION

CEC values and quantities of cations extracted depend on the soil studied and the precise experimental conditions. The nature and the quantity of index cation used will first have an influence on reaction yields.

The most important divergence between methods is caused by the pH at which extractions are carried out. The nature of exchange sites may cause the measured CEC value to be pH dependent. However, our study shows to a large extent that parameters such as carbon content and soil pH in water can be used to correct data, at least for soils in which the bulk of variable charges is due to organic matter.

From a practical aspect, repeating the exchange procedure (successive extractions, percolation) increase: the yield but sometimes accentuates undesirable secondary reactions such as the dissolution of $CaCO_3$. The resulting increase in the cost of determinations is not always justified. In this case, procedures may be modified with a variable relevance and then the simplicity of a protocol is its best guarantee for a routine use.

For these reasons and with reference to our results, we think that Cohex chloride used as reagent with a single extraction can favourably replace the barium chloride method. As shown in this work, the specificities of the ammonium acetate method make it less easy to choose an alternative procedure. However, most of these specificities are due to a buffered pH value which can be called into question in many cases (eg, for acid soils). The use of an unbuffered extractant as Cohex chloride is then also more appropriate.

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Norme AFNOR NFX 31-103 (1988) Détermination du pH dans l'eau.

Norme AFNOR X 31-107 (1983) Analyse granulométrique par sédimentation.

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Norme NF ISO 11260 (1994) Détermination de la capacité d'échange cationique effective et du taux de saturation en bases échangeables à l'aide d'une solution de chlorure de baryum.