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Soil quality — Determination of effective cation exchange capacity (CEC) and exchangeable cations using a hexamminecobalt(III)chloride solution

Qualité du sol — Détermination de la capacité d'échange cationique (CEC) effective et des cations échangeables à l'aide d'une solution de trichlorure de cobaltihexammine

Reference number
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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical and physical characterization*.

This second edition cancels and replaces the first edition (ISO 23470:2007), which has been technically revised.

The main changes compared to the previous edition are as follows:

- the scope has been broadened for soils with a pH > 6,5;
- a new Annex C has been added;
- a new Annex D has been added;
- a new Annex E has been added;
- the document has been editorially revised.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The cation exchange capacity (CEC) of soils and clays as well as the exchangeable cation population are essential features of soil fertility. Various attempts have been made in the literature to measure these parameters accurately and efficiently. The completeness of cation exchange on the other hand is not absolute but should be comparable between different methods. Traditional methods used ammonium or barium as exchangeable cations which require repeated treatments to ensure complete cation exchange. The oldest one-step CEC method is based on hexamminecobalt(III)chloride solution which has a much stronger affinity to soil clay minerals than the typical cations of the soil solution (usually Ca, Mg, Na and K). The principle of this method was published by Morel (1958)[11] and has been modified by Ciesielski and Sterckeman (1997)[7]. This method, as described in this document, is very efficient and comparable to the established CEC methods. It determines the effective CEC when used for soils with pH value of <6,5.

All CEC methods including hexamminecobalt(III)chloride have typical limitations such as inflation of exchangeable cations caused by dissolution of carbonates, sulfates or other soluble minerals (compare also ISO 13536). Carbonate dissolution is one of the most frequently occurring source of error (e.g. in the procedure described in ISO 13536), hence, many studies focused on minimization of their dissolution or correction of the dissolved fraction. Reference [13] summarized the discussion and presented solutions for this analytical problem. For calcareous soils or clays, the authors used exchange solutions that were previously equilibrated with calcite. In the course of the extraction, dissolution of carbonates present in the samples was minimized largely and resulting exchangeable Ca values were nearly free of errors. It was a great success compared to methods used in the past (Annex E). This method using calcite-saturated hexamminecobalt(III)chloride exchange solutions was published as VDLUFA-method[6]. The resulting exchangeable cation values agreed well with the total CEC when tested in a round robin (Annex C) which is a good measure for the plausibility of the results. Using different solution/solid ratios, identical exchangeable cation values were measured indicating absence of systematic errors caused by mineral dissolution (compare the model described in Reference [12], for detection of inflated exchangeable Ca values as described in Annex D). This calcite-saturated hexamminecobalt(III)chloride exchange solution should be used for calcareous soils and clays only, practically for soils with pH values of ≥6,5 in which only Ca, Mg, Na and K are present as “exchangeable bases”. Thus, the results are comparable to the determination of potential CEC (for example according to ISO 13563). This method was introduced to avoid erroneous (inflated) Ca values.

Hexamminecobalt(III)chloride is recommended as extractant for non-calcareous soils with a pH value of ≤6,5. As the pH value of a soil suspension in the hexamminecobalt(III)chloride solution is close to the pH value of the suspension in water, this method is considered to give the effective CEC, i.e. the CEC at the soil pH value (e.g. according to ISO 11260).

Soil quality — Determination of effective cation exchange capacity (CEC) and exchangeable cations using a hexamminecobalt(III)chloride solution

WARNING — Persons using this document should be familiar with usual laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices.

IMPORTANT — It is absolutely essential that tests, conducted in accordance with this document, be carried out by suitably qualified staff.

1 Scope

This document specifies a method for the determination of cation exchange capacity (CEC) and the content of exchangeable cations (Al, Ca, Fe, K, Mg Mn, Na) in soils using a hexamminecobalt(III)chloride solution as extractant. For soils containing calcium carbonate a calcite saturated hexamminecobalt(III) chloride solution is specified particularly for determination of exchangeable Ca. This document is applicable to all types of air-dry soil samples which have been prepared according to ISO 11464.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 11464, *Soil quality — Pretreatment of samples for physico-chemical analysis*

ISO 11465, *Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

Cations adsorbed to a soil sample are exchanged with the hexamminecobalt ions of an aqueous solution, with a (60 ± 5) min shaking at a temperature of (20 ± 2) °C. The CEC is obtained by difference between the initial quantity of hexamminecobalt in solution and the quantity remaining in the extract after the exchange reaction. The measurement of hexamminecobalt concentration in the extract can be performed by determination of total ammonium nitrogen (see 7.3.2), direct spectrophotometric measurement (see 7.3.3) or total cobalt concentrations (see 7.3.4).

The quantities of exchanged cations are determined on the same extract using spectrometric methods such as inductively coupled plasma atomic emission spectrometry (ICP-AES). In case the calcite saturated hexamminecobalt(III)chloride solution is used, the initial Ca concentration of the pure exchange solution shall be determined and subtracted from each exchange solution that has been in contact with soil or clay.

NOTE 1 Exchangeable acidity can also be measured in the hexamminecobalt extract.

NOTE 2 When exchangeable cations are held in micropores into which ammonium ions can enter but hexamminecobalt ions cannot, the CEC and exchangeable cations values determined with this method can be smaller than those determined by ammonium acetate method. This has been observed in some soils containing allophane and imogolite, for example soils developed on volcanic rocks.

NOTE 3 When gypsiferous soils or clays are examined, gypsum is dissolved even in calcite saturated hexamminecobalt(III)chloride solution throughout the exchange experiment, which in turn increases measureable Ca concentrations. Dolomite dissolution on the other hand is lowered very much in calcite saturated hexamminecobalt(III)chloride solution and resulting Ca and Mg concentrations are nearly error-free.

NOTE 4 Variation of extraction intensity, particularly time, was proven to be insignificant for bentonites tested in an interlaboratory CEC and exchangeable cation study when varied between 15 min and 120 min using different dispersion techniques such as hand-shaking, vibrating table, rocking platform, sonication, and end-over-end shaking. This was verified for Cu-triethylenetetramine which is similar to cobalthexammine(III) chloride[13].

5 Reagents

Only reagents of recognized analytical quality shall be used.

5.1 Distilled or demineralized water, exempt from the elements under analysis and having a conductivity under 0,5 µS/cm.

5.2 Hexamminecobalt(III)chloride solution, $\beta[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3} = 0{,}016\,6$ mol/l.

Take care that hexamminecobalt(III)chloride is free of adsorbed water before use. Dissolve, to within a milligram, 4,458 g of hexamminecobalt(III)chloride in a volumetric flask containing 700 ml of water (5.1). Make up to the volume and mix.

Supplier: e.g. STREM[1], 93-2708. CAS Number: 10534-89-1. 50 g are needed for about 10 l of exchange solution.

5.3 Anti-bumping granules (e.g. pumice stone in grain form, glass beads).

5.4 Boric acid, $\beta(\mathrm{H_3BO_3}) = 40$ g/l.

5.5 Tashiro indicator.

Dissolve 2,0 g of methyl red and 1,0 g of methylene blue in 1 000 ml of 95 % ethanol.

5.6 Phenolphthalein.

Dissolve 1 g of phenolphthalein in 1 000 ml of 95 % ethanol.

5.7 Sodium hydroxide solution, with a density of 33 %.

5.8 Sulfuric acid, $c(\mathrm{H_2SO_4}) = 0{,}025$ mol/l.

5.9 Ammonium sulfate, for analysis.

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[1] STREM (strem.com) is an example of a product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

5.10 Stock solutions of Al, Ca, Fe, K, Mg, Mn, Na, β(Me) = 1,000 g/l.

These solutions are supplied with a certified composition from a reputable source and are checked on a regular basis.

5.11 Calcite saturated hexamminecobalt (III)chloride solution.

Fill up a 2 l beaker with hexamminecobalt(III)chloride solution (5.2). Add 2 g of fine-ground calcite. This mixture is placed in an ultrasonic bath for 30 min. To minimize temperature effects on the solubility of calcite, the solution is stirred for a further 30 min using a magnetic stirrer. After switching off the stirrer, undissolved calcite is allowed to settle overnight. The 2 l beaker is protected by a plastic foil on top during calcite saturation. The solution may be decanted or filtered, however, addition of un-reacted (settled) calcite to the soil sample should be avoided. Two litres (2 l) of exchange solution can be used for approximately 34 samples (34 × 50 ml) plus 2 blanks (2 × 50 ml).

NOTE Reagents 5.3 to 5.9 are prepared only in the case when determination of CEC is carried out by determination of ammonia nitrogen using distillation. They are not needed when spectrophotometric determination is used.

6 Apparatus

6.1 Analytical balance, the weighing uncertainty range of which will not exceed ±0,1 % of the test portion mass.

6.2 Containers for shaking, tightly stoppered, rigid or non-rigid wall, having a volume between 75 ml and 100 ml.

6.3 50 ml dispenser, set at ±0,25 ml of the delivered volume.

6.4 End-over-end shaker, allowing the permanent suspension of the soil/extraction solution mixture, placed in ambient air at (20 ± 2) °C.

6.5 Centrifuge and relevant centrifuge vials.

Centrifugation time and speed depend on the type of centrifuge and are selected with a view of securing a clear supernatant. 4 000 r/min for 20 min are generally sufficient but special care shall be taken due to the high content of fixed hexamminecobalt ions on colloidal particles.

6.6 Distillation apparatus, the different parts of the apparatus shall be assembled ensuring tightness in order to prevent any loss of ammonia or entrainment of sodium hydroxide.

6.7 Microburette.

6.8 Spectrophotometer, allowing measurements to be performed at wavelengths 380 nm and 475 nm, equipped with a 10 mm path length measuring cell.

6.9 Inductively coupled plasma atomic emission spectrometer.

6.10 Ultrasonic bath.

6.11 Magnetic stirrer and magnetic stir bar.

7 Procedure

7.1 Test portion

Pretreat soil in accordance with ISO 11464.

If Q is the number of centimoles of positive charges provided by a given volume of hexamminecobalt (III)chloride solution, the centimoles of positive charges carried by the test portion shall lie between $Q/10$ and $Q/3$ inclusive.

Table 1 gives examples of suitable test portions for a range of expected CEC values.

Table 1 — Test portions (in 50 ml of solution 5.2)

Measured CEC, in cmol+/kg	<2,5	2,5 to 5	5 to 10	10 to 32	32 to 64
Test portion, g	10	10	5	2,5	1,25

Weigh to within 0,1 % the selected mass of the test portion (see ISO 11464) and transfer to a container for shaking (6.2). Evaluation of plausible CEC and exchangeable cation values may be performed using the diagram type called Carbonate and Sulphate Field Model (CSF model); see Reference [12]. Two different sample masses are used and plausibility is given when both resulting values (any exchangeable cation pair or the CECs) lie on the $y = x$ line as shown in Annex D.

7.2 Exchange reaction

Add 50 ml of the hexamminecobalt(III)chloride solution (5.2) or calcite saturated hexamminecobalt(III) chloride solution (5.11) and shake for (60 ± 5) min by means of the shaker (6.4). Centrifuge by means of 6.5. Collect the clear filtrate or supernatant. Carry out the determinations no later than 24 h after extraction at the latest, otherwise, ascertain that the storage conditions do not influence the test result. Such storage may be done after diluting the samples in acidified solutions.

Produce an extraction “blank” under the same conditions, but without the test portion.

7.3 Determination of CEC

7.3.1 General

The measurement of hexamminecobalt concentration in the extract can be performed by determination of total ammonium nitrogen (according to 7.3.2), direct spectrophotometric measurement (according to 7.3.3) or total cobalt concentrations (according to 7.3.4).

7.3.2 Determination of ammonia nitrogen by distillation

7.3.2.1 Procedure

Pipette 10 ml of the extract (see 7.2) into the distilling apparatus flask. Make up to the volume, to around 200 ml, with water (5.1). Add the anti-bumping granules (5.3).

Add to the distillate recovery container 40 ml of boric acid solution (5.4) and a few drops of Tashiro indicator (5.5). Immerse the end of the cooling apparatus to a depth of at least 1 cm in the recovery liquid. Add a few drops of phenolphthalein (5.6) into the distilling apparatus flask.

Assemble the apparatus taking care to ensure its tightness.

Add approximately 10 ml of the sodium hydroxide solution (5.7) and progressively heat the flask so as to distil around 150 ml of liquid within 30 min. After this lapse of time, verify the neutrality of the distillate which flows from the end of the cooling apparatus by means of phenolphthalein paper. If the reaction is alkaline, resume the distillation.

Titrate the ammonia by the standard volumetric solution of sulfuric acid (5.8).

Perform a titration blank test with water using the same reagents. The poured acid volume in this case will not exceed 0,1 ml.

Verify periodically the efficiency of the apparatus by distilling a synthetic sample containing 5 mg of nitrogen provided in the form ammonium sulfate (5.9). The poured volume, corrected for the blank, shall be between 6,95 ml and 7,35 ml inclusive (for a theoretical value of 7,15).

Then sample 10 ml of the extraction blank and determine the ammonia in the same manner. In case of adsorption, especially caused by the filter, the solution described in 5.2 is to be used for this test.

7.3.2.2 Calculation of the CEC

The cation exchange capacity (CEC), expressed in centimoles of positive charges per kilogram, is calculated according to Formula (1):

$$\mathrm{CEC} = \frac{(V_1 - V_2) \times 2 \times C \times 50 \times 100}{2 \times v \times m} \cdot \frac{100 + w}{100} \tag{1}$$

where

V_1 is the volume of the sulfuric acid solution used for the test, in millilitres, ml;

V_2 is the volume of the sulfuric acid solution used for the blank test, in millilitres, ml;

C is the concentration of the sulfuric acid solution, in moles per litre, mol/l;

V is the distilled volume of extract and blank test, in millilitres, ml;

M is the mass of the test portion, in grams, g;

w is the percentage of water content by mass on the basis of oven-dried soil, determined in accordance with ISO 11465.

Verify periodically the efficiency of the apparatus by distilling:

— 10 ml of the hexamminecobalt(III)chloride solution (5.2);

— 5 ml of this same solution.

The difference between the two volumes of sulfuric acid (5.8) added in the titration step shall be 9,7 ml and 10,3 ml inclusive (for a theoretical value of 10,0).

7.3.3 Spectrophotometric determination

7.3.3.1 Calibration and measurement

The spectrophotometric determination of the dissolved hexamminecobalt is carried out at a wavelength of 475 nm without any pretreatment of the analysed solution. The calibration function shall be linear especially in the highest range of concentrations. Check it regularly using the following solutions: water, solution 5.2, solution 5.2 diluted with water at ratios 1/5, 2/5, 3/5, 4/5.

In such a case, for each series of measurements, calculate the coefficients of the straight calibration line using two standard solutions: water (5.1) and hexamminecobalt(III)chloride solution (5.2).

Transfer the test solution into the spectrophotometer and record the optical absorption at 475 nm; deduce the quantity of dissolved hexamminecobalt. Subtract this concentration from that contained in solution 5.2 in order to obtain the adsorbed quantity (q) in moles per litre (mol/l). Correction of the influence of the soluble organic matter.

By colouring the extract, the organic matter solubilized during the extraction absorbs light at 475 nm. When the solubilized quantities are high, the measurement of the CEC is affected by this phenomenon. This interference can be corrected by conducting a measurement at 475 nm and another one at 380 nm. The ratio between the optical absorption (DO) of the pure hexamminecobalt (III)chloride solutions, measured at the two previous wavelengths, is R_1 = [DO(475)/DO(380)] = 8,13.

The ratio between the optical absorptions of the solutions containing soluble organic matter, measured at the two previous wavelengths, is R_2 = [DO(475)/DO(380)] = 0,2. This value has been estimated by conducting extractions of soils containing variable organic matter contents in presence of a 0,05 (mol/l) solution of ammonium chloride.

Considering X_1 and X_2 the optical absorptions of the test solution measured respectively at 475 nm and 380 nm, the specific optical density for hexamminecobalt at 475 nm is calculated according to Formula (2):

$$\mathrm{DO} = (\mathrm{X}_1 - \mathrm{R}_2\mathrm{X}_2)\mathrm{R}_1 / (\mathrm{R}_1 - \mathrm{R}_2) \quad (2)$$

where

DO is the optical absorption of the hexamminecobalt(III)chloride solution;

R_1 is the ratio between the optical absorption (DO) of the pure hexamminecobalt(III)chloride solutions, measured at the two wavelengths at 475 nm and at 380 nm;

R_2 is the ratio between the optical absorption (DO) of solutions containing soluble organic matter, measured at the two wavelengths at 475 nm and at 380 nm;

X_1 is the optical absorption of the test solution measured respectively at 475 nm;

X_2 is the optical absorption of the test solution measured respectively at 380 nm.

Once this value is obtained, deduce the real quantity of remaining hexamminecobalt with reference to the coefficient determined by calibration. Subtract this concentration from that contained in solution 5.2 in order to obtain the exchanged quantity (q') in moles per litre (mol/l).

7.3.3.2 Calculation of the CEC

If m is the mass of the test portion in grams, V the volume of hexamminecobalt(III)chloride solution used in ml, one obtains the CEC using Formula (3):

$$\mathrm{CEC} = 300qV / m, \text{in cmol}^+ \cdot \text{kg}^{-1} \cdot \frac{100 + w}{100} \quad (3)$$

where

q is the exchanged quantity, in moles per litre, mol/l;

V is the volume of hexamminecobalt(III)chloride solution used, in millilitres, ml;

m is the mass of the test portion in grams, g;

w is the percentage of water content by mass on the basis of oven-dried soil, determined in accordance with ISO 11465.

If a correction of soluble organic matter is necessary, use Formula (4):

$$\mathrm{CEC} = 300q'V / m, \text{in cmol}^+ \cdot \text{kg}^{-1} \cdot \frac{100 + w}{100} \quad (4)$$

where q' is the exchanged quantity after correction of soluble organic matter, in moles per litre, mol/l.

7.3.4 Spectrometric determination of cobalt

7.3.4.1 General

Cobalt concentrations are assumed to be quantitatively linked to hexamminecobalt concentrations. CEC is given as the difference between hexamminecobalt content of the original extracting solution and hexamminecobalt content remaining in the extract after exchange reaction with soil.

7.3.4.2 Experimental conditions

See details given in 7.4.

7.3.4.3 Calculation of the CEC

In a first step, concentrations, *c*, of cobalt have to be converted in terms of moles per litre (mol/l) of hexamminecobalt (*c*’), for example, if *c* is given in mg/l: *c*’ = *c*/58 933.

If c'_0 is the concentration of hexamminecobalt in mol/l in the original extracting solution, the exchange quantity is given by Formula (5):

$$q = \left(c'_0 - c'\right) \tag{5}$$

where

c'_0 concentration of hexamminecobalt in the original extracting solution, in mols per litre, mol/l;

c’ concentration of hexamminecobalt of the test solution, in moles per litre, mol/l.

If *m* is the mass of the test portion in grams and *V* is the volume of hexamminecobalt(III)chloride solution used in ml, then CEC is calculated according to Formula (6):

$$\mathrm{CEC} = 300qV/m, \text{in } \mathrm{cmol}^{+} \cdot \mathrm{kg}^{-1} \cdot \frac{100+w}{100} \tag{6}$$

where

q is the exchanged quantity in moles per litre (mol/l);

V is the volume of hexamminecobalt(III)chloride solution used in ml;

m is the mass of the test portion in grams;

w is the percentage of water content by mass on the basis of oven-dried soil, determined according to ISO 11465.

7.4 Determination of cobalt and exchangeable cations

7.4.1 General

The following conditions for the determination of Al, Ca, Co, Fe, K, Mg, Mn and Na by inductively coupled plasma atomic emission spectrometry (ICP-AES) in hexamminecobalt extracts are given as an example.

Due to the large variety of available instruments, the sensitivity of measurement signals to operating conditions, each adaptation of this example shall take into account the instructions provided by the manufacturer, the range of linearity, the possibility of spectral and non-spectral interferences. CEC values calculated based on VIS spectroscopy analysis was found to be in good agreement with CEC values calculated from ICP OES analysis of Co in the same solutions. This indicates that careful adoption of measurements may give comparable results as those listed in this norm. A standard material which is used in every measurement cycle is recommended for quality control.

7.4.2 Standard solutions for exchangeable cations

Solution 5.2 is the blank solution (standard 0) for the determination of exchangeable cations. Note that for the determination of CEC through the measurement of cobalt content, this solution constitutes the highest calibration point (see 7.4.3).

For each element, transfer the volumes of the stock solution (5.10) given in Table 2 into a 500 ml volumetric flask. Add and dissolve 2,229 g of hexamminecobalt(III)chloride, adjust the volume to the mark with water (5.1) and homogenize. This solution constitutes the highest calibration point for the determination of exchangeable cations (standard 3, see Table 2).

Table 2 — Standard solutions for exchangeable cations (standard 3)

Element	Volume of stock solution (5.10) ml	Final concentration mg/l	Final concentration cmol+/kg
Al^{3+}	20	40	8,895
Ca^{2+}	200	400	39,94
Fe^{2+}	10	20	1,432
K^{+}	20	40	2,046
Mg^{2+}	10	20	3,292
Mn^{2+}	10	20	1,456
Na^{+}	20	40	3,480

NOTE 1 Final concentrations in cmol+/kg are calculated for a ratio extractant/soil (V/m) of 20.

NOTE 2 High range of concentrations for calcium is useful when both acid and calcareous soils are analysed. When only acid soils are envisaged, the highest level of concentration can be reduced.

Transfer 50 ml of standard 3 in a 100 ml volumetric flask, adjust to the mark with standard 0, homogenize to obtain standard 2.

Transfer 25 ml of standard 3 in a 100 ml volumetric flask, adjust to the mark with standard 0, homogenize to obtain standard 1.

7.4.3 Standard solutions for cobalt

Determination of CEC is based on the difference of cobalt concentrations between standard 0 and test sample solution. The concentration range of interest can be reduced to the only highest half part of the full range.

Dissolve the quantities given in Table 3 in 1 000 ml volumetric flasks in water (5.1).

Table 3 — Standard solutions for cobalt

Standard	Hexamminecobalt(III)chloride g	Final concentration cmol+/kg
0	4,458	100,00
1	3,789	85,00
2	2,898	65,00
3	2,229	50,00

NOTE Final concentrations in cmol+/kg are expressed here in terms of CEC for the theoretical case of a total adsorption by soil considering a ratio of 20 (2,5 g of soil in 50 ml of extractant).

7.4.4 Spectrometric determination of exchangeable cations

Calibration standards (standards 0 to 3), extraction blank and test sample extracts can be injected after or without a former dilution step. Dilution reduces the risk of nonlinearity and disturbing effects due to non-spectral interferences but increases detection and quantification limits, this last effect may be of some importance for the determination of Fe, K, Mn and Na. Whatever the envisaged option, linearity, absences of spectral and non-spectral interferences shall be checked and background corrections shall be set up when necessary.

Table 4 gives the wavelengths of some suitable spectral lines.

Table 4 — Spectrometric determination of exchangeable cations

Element	Wavelength nm
Al	396,152
Ca	184,006 or 422,673
Fe	259,940
K	766,490
Mg	285,213
Mn	259,373
Na	588,995

After setting up the instrument according to the instructions of the manufacturer and allowing the operating conditions to reach stability, run the calibration step, inject standard solutions 0 to 3.

Inject blank of extraction and test sample extracts. Instrumental drift is checked and if necessary corrected by means of calibration standard or quality control sample injected at regular intervals.

7.4.5 Spectrometric determination of cobalt

In the present case, unlike classical determinations, the reference point is not a blank solution but the most concentrated one. As the differences between concentrations may be low, taking some precautions turns out to be necessary.

- The working range can be reduced to the second half of the full range of concentrations (standard 0 to 3), as a consequence, linearity is primarily checked in the upper part of the range.
- Instrumental drift, effects of possible spectral and non-spectral interferences induced by the exchange reaction shall be carefully controlled or corrected.

Calibration standards (standards 0 to 3), extraction “blank” and test sample extracts can be injected after or without a former dilution step. Dilution reduces the risk of nonlinearity and disturbing effects due to non-spectral interferences. Whatever the envisaged option, linearity, absences of spectral and non-spectral interferences shall be checked and background corrections shall be set up when necessary. The cobalt spectral line at 241,765 nm can be used.

7.4.6 Calculation of exchangeable cations

Calculate the exchangeable sodium, potassium, calcium and magnesium contents in the soil samples using Formulae (7) to (10):

$$\mathrm{c}(\mathrm{Na,exch}) = 2{,}174\,9\left(\rho_3 - \rho_{\mathrm{b}1}\right)/m \cdot \frac{100+w}{100} \tag{7}$$

$$\mathrm{c}(\mathrm{K,exch}) = 1{,}278\,8\left(\rho_3 - \rho_{b1}\right)/m \cdot \frac{100+w}{100} \tag{8}$$

$$c(\mathrm{Ca,exch}) = 4{,}990\ 3(\rho_3 - \rho_{b1}) / m \cdot \frac{100 + w}{100} \tag{9}$$

$$c(\mathrm{Mg,exch}) = 8{,}228\ 8(\rho_3 - \rho_{b1}) / m \cdot \frac{100 + w}{100} \tag{10}$$

where

c(Na,exch)	is the content of exchangeable sodium in the soil, in centimoles positive charge per kilogram, cmol⁺/kg;
c(K,exch)	is the content of exchangeable potassium in the soil, in centimoles positive charge per kilogram, cmol⁺/kg;
c(Ca,exch)	is the content of exchangeable calcium in the soil, in centimoles positive charge per kilogram, cmol⁺/kg;
c(Mg,exch)	is the content of exchangeable magnesium in the soil, in centimoles positive charge per kilogram, cmol⁺/kg;
ρ_3	is the concentration of sodium, potassium, calcium or magnesium in the diluted extracts, in milligrams per litre, mg/l;
ρ_{b1}	is the concentration of sodium, potassium, calcium or magnesium in the diluted blank, in milligrams per litre, mg/l;
m	is the mass of air-dried soil, in grams, g.

8 Test report

The test report shall include the following information:

a) a reference to this document, i.e. ISO 23470:2018;

b) the complete identification of the sample;

c) whether hexamminecobalt(III)chloride solution or calcite saturated hexamminecobalt(III)chloride solution was used as an extractant;

d) the results of the determination;

e) any details not specified in this document, or which are optional, as well as any factor which may have affected the results.

9 Validation

See Annex B and Annex C.

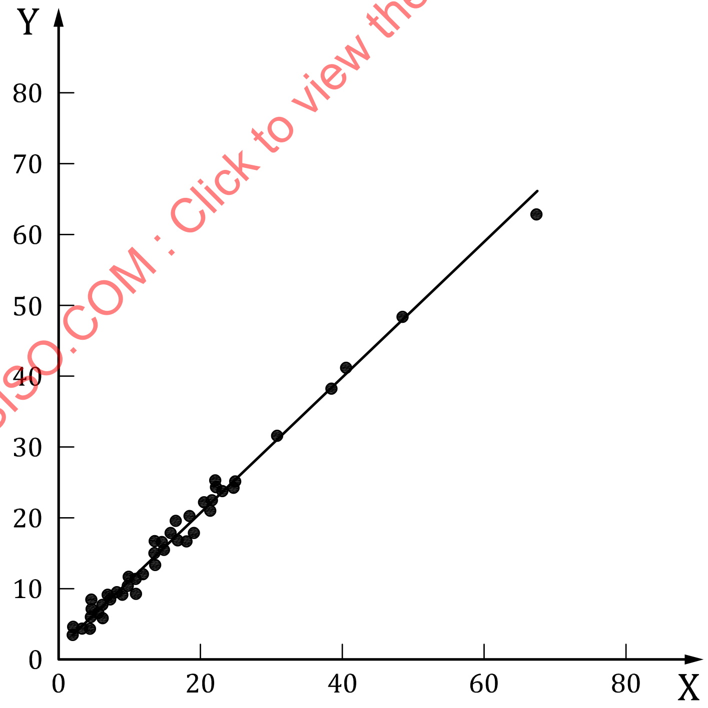
Annex A
(informative)

Comparison of different methods for the determination of effective CEC

Results on the comparison of different methods for the determination of effective cation exchange capacity (CEC) and exchangeable cations can be found in Reference [7].

Reference [7] shows that the method using hexamminecobalt(III)chloride (ISO 23470) gives results very close to those obtained with barium chloride (according to ISO 11260) for effective CEC (see Figure A.1) and exchangeable cations. For soils containing some non-crystalline and microporous aluminium silicates like allophane and imogolite, the hexamminecobalt(III)chloride method may give smaller values (see Table A.1 and Figure A.4). This may be because the bulky hexamminecobalt ion cannot replace exchangeable cations held at sites in micropores of the minerals due to steric hindrance. Note that for both methods, the sum of exchanged cations is less than the CEC, suggesting an incomplete exchange of the cations on this type of soil and, simultaneously, a fixation of ammonium and hexamminecobalt.

CEC obtained with ammonium acetate according to NF X31-130 can be converted into effective CEC using soil pH in water and organic carbon content (Figure A.2 and Figure A.3).



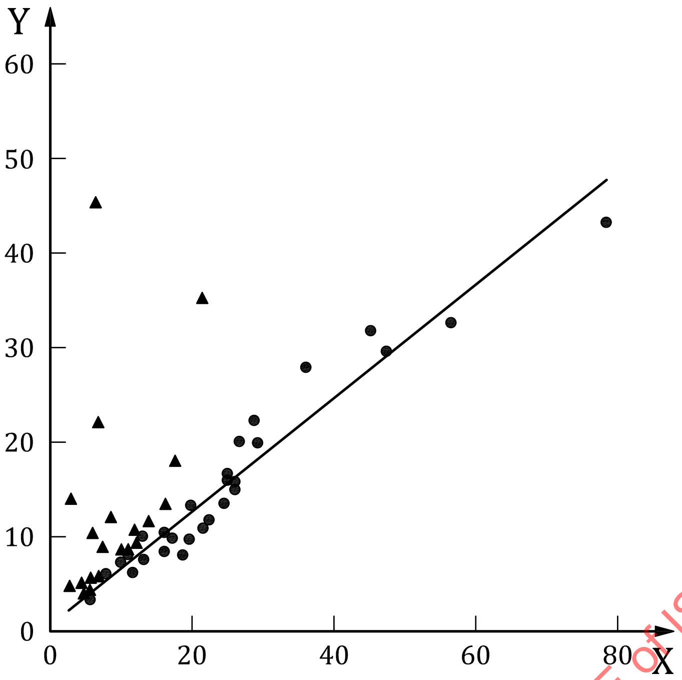
Key

X CEC using hexamminecobalt(III)chloride (ISO 23470), in cmol+/kg

Y CEC using bariumchloride (ISO 11260), in cmol+/kg

NOTE $y = 0{,}977x$; $r^2 = 0{,}989$.

Figure A.1 — Comparison of the determinations of effective CEC using hexamminecobalt(III) chloride (ISO 23470) and barium chloride (ISO 11260) on 48 cultivated soil samples from France



Key

X CEC using hexamminecobalt(III)chloride (ISO 23470), in cmol⁺/kg

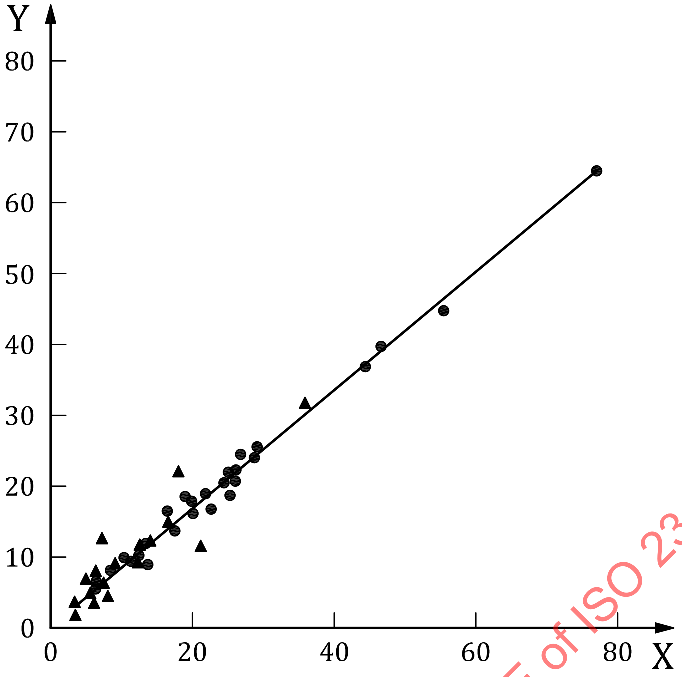
Y CEC using ammonium acetate (NF X31–130), in cmol⁺/kg

▲ pH-value < 7

● pH-value > 7

NOTE $y = 0{,}763x$; $r^2 = 0{,}396$.

Figure A.2 — Comparison of the determinations of effective CEC using hexamminecobalt(III) chloride (ISO 23470) and ammonium acetate (NF X31-130) on 48 cultivated soil samples from France



Key

X CEC using hexamminecobalt(III)chloride (ISO 23470), in cmol+/kg

Y CEC using ammonium acetate (NF X31–130), in cmol+/kg

▲ pH-value < 7

● pH-value > 7

NOTE $y = 0{,}989x$; $r^2 = 0{,}989$.

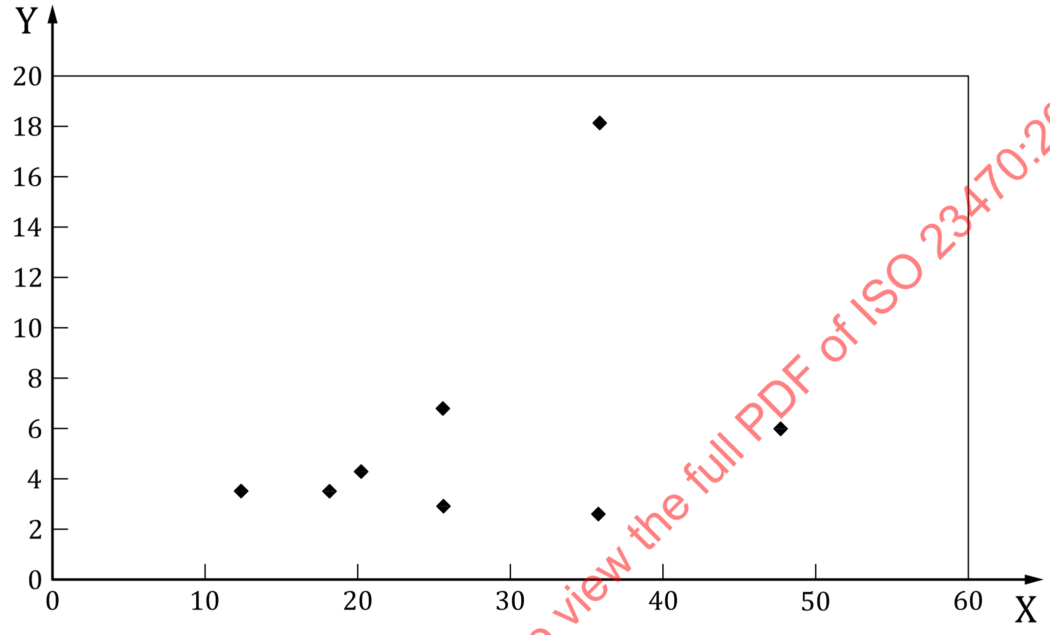
Figure A.3 — Comparison of the determinations of effective CEC using hexamminecobalt(III) chloride (ISO 23470) and CEC calculated from measurement of CEC using ammonium acetate (NF X31-130), pH value in water (ISO 10390), and carbon content (ISO 14235), on 48 cultivated soil samples from France

Table A.1 — Comparison of hexamminecobalt(III)chloride method (Cohex) according to this document with ammonium acetate method (AmAc) for the determination of CEC and exchangeable cations of some volcanic soils from Japan

Soil sample	PA	VA	576	510	w-222	w-211	w-136	Goshi
Carbon, g/kg	1,38	1,92	13,06	29,39	120,48	60,61	188,64	64,67
pH value (water)	6,7	6,8	5,9	5,7	4,8	4,8	5	6,3
CEC Ammonium acetate, cmol+/kg	25,6	12,3	18,1	20,2	35,8	25,6	47,8	36,1
Exchangeable Ca (AmAc), cmol+/kg	3,7	2,65	0,2	1,4	0,45	4,65	1	14,15
Exchangeable Na (AmAc), cmol+/kg	0,24	0,35	0,31	0,09	0,09	0,16	0,23	0,05
Exchangeable Mg (AmAc), cmol+/kg	2,4	0,96	0,06	0,38	0,38	0,41	0,71	3,22
Exghangeable K (AmAc), cmol+/kg	0,32	0,14	0,26	0,6	0,49	0,85	0,54	0,9
Sum (Ca+Na+Mg+K), cmol+/kg	6,66	4,1	0,83	2,47	1,41	6,07	2,48	18,32
R = Sum/CEC (AmAc)	0,26	0,33	0,05	0,12	0,04	0,24	0,05	0,51
CEC hexamminecobalt, cmol+/kg	6,8	3,5	3,5	4,3	2,6	2,9	6	18,1
Exchangeable Ca (Cohex), cmol+/kg	2,36	1,63	0,12	0,88	0,36	2,29	0,92	12,89
Exchangeable Mg (Cohex), cmol+/kg	1,74	0,64	0,03	0,24	0,29	0,26	0,63	2,89
Exchangeable K (Cohex), cmol+/kg	0,21	0,08	0,15	0,46	0,27	0,45	0,37	0,55

Table A.1 *(continued)*

Soil sample	PA	VA	576	510	w-222	w-211	w-136	Goshi
Exchangeable Na (Cohex), cmol$^+$/kg	0,25	0,32	0,28	0,09	0,08	0,14	0,22	0,05
Exchangeable Al (Cohex), cmol$^+$/kg	0,14	0,12	0,41	0,11	1,63	0,58	3,37	0,07
Exchangeable H (Cohex), cmol$^+$/kg	<0,05	<0,05	<0,05	<0,05	0,36	0,24	0,2	<0,05
Sum (Ca+Na$^+$Mg+K$^+$Al+H), cmol$^+$/kg	4,7	2,79	0,99	1,67	2,99	3,96	5,71	16,45
R = Sum/CEC (Cohex)	0,69	0,80	0,28	0,39	1,15	1,37	0,95	0,91



Key

X CEC AmAC, cmol$^+$/kg

Y CEC Cohex, cmol$^+$/kg Cohex

Figure A.4 — Comparison of the hexamminecobalt(III)chloride method (Cohex) with the ammonium acetate method (AmAc) for the determination of CEC of some volcanic soils from Japan

Annex B
(informative)

Results of the interlaboratory comparison for extraction with hexamminecobalt(III)chloride

An interlaboratory trial was organized to test the procedures specified in this document.

For this interlaboratory trial, the determination of the CEC and exchangeable K, Na, Ca and Mg of four soils was carried out by 13 laboratories from Austria, Czech Republic, Germany, France, Korea, Netherlands, Poland, Spain, Sweden and United Kingdom.

The summary of the results of the interlaboratory trial is presented in Tables B.1 to B.5.

Sample 1 came from Czech Republic, from a cultivated sandy-clay loam soil (Cambisol). Samples 2, 3 and 4 came from France. Sample 2 was taken in the ploughed horizon of a vertic Cambisol (about 540 g/kg clay), while sample 3 was taken from the topsoil of a stagnic Luvisol developed in clayey loam, under forest. Sample 4 was taken from the ploughed horizon of a Cambisol developed in loess loam.

The repeatability limit, *r*, and the reproducibility limit, *R*, listed in these tables were calculated according to ISO 5725-2.

Table B.1 — Results of the interlaboratory trial for the determination of the CEC

Sample No.	**1**	**2**	**3**	**4**
Number of laboratories retained after eliminating outliers	13	13	13	13
Number of outliers (laboratories)	0	0	0	0
Number of accepted results	26	26	26	26
Mean value, cmol$^+$/kg	9,824	23,594	7,119	16,627
Repeatability limit ($r = 2{,}8\ s_r$), cmol$^+$/kg	0,476	0,305	0,285	0,492
Coefficient of variation of repeatability ($r = 2{,}8\ s_r$), %	4,85	1,29	4,01	2,96
Reproducibility limit ($R = 2{,}8\ s_R$), cmol$^+$/kg	0,856	1,977	0,969	1,687
Coefficient of variation of reproducibility ($R = 2{,}8\ s_R$), %	8,72	8,38	13,62	10,14

Table B.2 — Results of the interlaboratory trial for the determination of the exchangeable calcium

Sample No.	**1**	**2**	**3**	**4**
Number of laboratories retained after eliminating outliers	10	11	12	11
Number of outliers (laboratories)	2	1	0	1
Number of accepted results	20	22	24	22
Mean value, cmol$^+$/kg	8,562	22,495	4,235	16,701
Repeatability limit ($r = 2{,}8\ s_r$), cmol$^+$/kg	0,160	0,499	0,086	0,259
Coefficient of variation of repeatability ($r = 2{,}8\ s_r$), %	1,87	2,22	2,02	1,55
Reproducibility limit ($R = 2{,}8\ s_R$), cmol$^+$/kg	0,267	1,838	0,343	1,421
Coefficient of variation of reproducibility ($R = 2{,}8\ s_R$), %	3,11	8,17	8,09	8,51

Table B.3 — Results of the interlaboratory trial for the determination of the exchangeable magnesium

Sample No.	1	2	3	4
Number of laboratories retained after eliminating outliers	12	11	11	11
Number of outliers (laboratories)	0	1	1	1
Number of accepted results	24	22	22	22
Mean value, cmol+/kg	1,110	1,492	1,244	0,464
Repeatability limit (r = 2,8 s_r), cmol+/kg	0,025	0,022	0,019	0,004
Coefficient of variation of repeatability (r = 2,8 s_r), %	2,23	1,50	1,55	0,78
Reproducibility limit (R = 2,8 s_R), cmol+/kg	0,082	0,074	0,058	0,044
Coefficient of variation of reproducibility (R = 2,8 s_R), %	7,39	4,95	4,63	9,43

Table B.4 — Results of the interlaboratory trial for the determination of the exchangeable potassium

Sample No.	1	2	3	4
Number of laboratories retained after eliminating outliers	11	12	12	11
Number of outliers (laboratories)	1	0	0	1
Number of accepted results	22	24	24	22
Mean value, cmol+/kg	0,333	1,105	0,609	1,940
Repeatability limit (r = 2,8 s_r), cmol+/kg	0,006	0,042	0,018	0,015
Coefficient of variation of repeatability, %	1,79	3,85	2,95	0,76
Reproducibility limit (R = 2,8 s_R), cmol+/kg	0,060	0,177	0,093	0,276
Coefficient of variation of reproducibility, %	17,96	16,00	15,26	14,21

Table B.5 — Results of the interlaboratory trial for the determination of the exchangeable sodium

Sample No.	1	2	3	4
Number of laboratories retained after eliminating outliers	12	11	11	11
Number of outliers (laboratories)	0	1	1	1
Number of accepted results	24	22	22	22
Mean value, cmol+/kg	0,032	0,106	0,059	0,112
Repeatability limit (r = 2,8 s_r), cmol+/kg	0,002	0,004	0,002	0,002
Coefficient of variation of repeatability, %	7,47	3,83	2,65	1,72
Reproducibility limit (R = 2,8 s^R), cmol+/kg	0,011	0,015	0,016	0,017
Coefficient of variation of reproducibility, %	34,60	14,52	27,02	15,60

Annex C
(informative)

Results of the interlaboratory comparison for extraction with calcite saturated hexamminecobalt(III)chloride solution

The test procedure using calcite saturated hexamminecobalt(III)chloride solution (5.11) was tested with two soils containing carbonates in a ringtest of the VDLUFA-working group “Soil Testing” in 2010. Soil 1 is a silty loam, pH value 7,5, Soil 2 is a clay loam, pH value 7,3. Results were evaluated as described in DIN 38402-45 with the ring test evaluation program “ProLab”.

Table C.1 — Results of interlaboratory comparison trials for method 2

	l	n	n_0	$\bar{\bar{x}}$	s_R	s_r	$C_{V,R}$	$C_{V,r}$
				cmol⁺/kg			%	
Soil 1								
*b*Ca	9	27	1	7,810	0,593	0,115	7,6	1,5
*b*Mg	9	27	0	0,543	0,050	0,010	9,1	1,9
*b*K	9	27	1	0,495	0,042	0,013	8,6	2,6
SB	9	27	0	8,860	0,644	0,115	7,6	1,3
CEC	9	27	1	9,930	1,701	0,308	17,1	3,1
Soil 2								
*b*Ca	9	27	1	18,521	0,791	0,206	4,3	1,1
*b*Mg	9	27	0	1,189	0,062	0,016	5,2	1,3
*b*K	9	27	0	0,558	0,051	0,013	9,2	2,3
SB	9	27	1	20,295	0,756	0,201	3,7	1,0
CEC	9	27	0	21,512	1,875	0,281	8,7	1,3

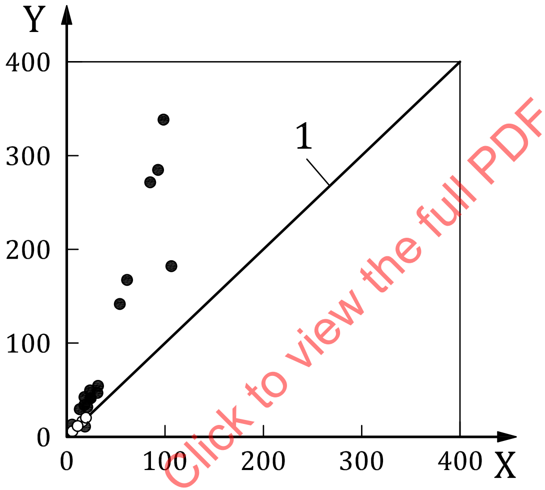
l = number of laboratories participating in the ringtest
n = number of results reported
n_0 = number of results exceeding tolerance limits
$\bar{\bar{x}}$ = Mean value, cmol⁺/kg
s_R = Reproducibility standard deviation cmol⁺/kg
s_r = Repeatability standard deviation, cmol⁺/kg
$C_{V,R}$ = Coefficient of variation of reproducibility, %
$C_{V,r}$ = Coefficient of variation of repeatability, %
SB = Sum of basic exchangeable cations

Results for exchangeable sodium (*b*Na) are not presented because several participating laboratories reported values below the limit of determination which however varied by far between in between 0,2 cmol⁺/kg and 0,01 cmol⁺/kg. Mean values for the remaining results reported for *b*Na were 0,013 cmol⁺/kg and 0,035 cmol⁺/kg for soil 1 and soil 2 respectively. The true values in both soils therefore are considered to be certainly far below 0,1 cmol⁺/kg, and the contribution of Na to cation exchange capacity is negligible in both soils.

Annex D
(informative)

Carbonate and sulfate field model

Evaluation of plausible CEC and exchangeable cation values may be performed using the diagram type called Carbonate and Sulphate Field Model (CSF model), see Reference [12]. Two different sample masses are used and plausibility is given when both resulting values (any exchangeable cation pair or the CECs) lie on the $y = x$ line as shown in Figure D.1 and Figure D.2 which used barium chloride exchange solution for these examples, however the model is also valid for any other index cation. Values were reported in the old nomenclature meq/100 g which equals cmol$^+$/kg. Values cannot be realized in the area below the $y = x$ line. The area above the $y = x$ line indicates erroneous values. This area was called Carbonate and Suphate Field.



Key

X	Ca [meq/100 g], 2 g mass
Y	Ca [meq/100 g], 0,5 g mass
1	$y = x$
●	calcareous samples
○	non-calcareous samples

Figure D.1 — Application of the carbonate and sulfate graph for a series of natural samples

Evaluation of the incorrectness of exchangeable calcium data of calcareous clays is possible by a visible control: Data points that are located within the carbonate and sulfate field are incorrect. Those of non-calcareous clays are placed on the line and are correct.