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Second edition
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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

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Contents

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).

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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).

INTERNATIONAL STANDARD **ISO 23470:2018(E)**

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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, $\beta[Co(NH_3)_6]Cl_3$ = 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, $\beta(H_3BO_3)$ = 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, $c(H_2SO_4)$ = 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.