CEN/TC 223/WG 4 "Analytical methods"
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Project / Draft		2021-11-03	**INFO**

Description

Please find enclosed the 1st working draft on WI 00223101, revision of EN 13650, Soil improvers and growing media — Digestion by aqua regia for subsequent determination of elements for your information.

During the last meeting of WG 4 on 2021-10-13, it was agreed that the 1st working draft on WI 00223101 is finalised. The enclosed 1st working draft as well as the forms for the activation of the work item is to be circulated to CEN/TC 223 as soon as the call for tender for the project leaders is completed and the project leaders are known.

CEN/TC 223

Date: 2021-10

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Soil improvers and growing media — Digestion by aqua regia for subsequent determination of elements

Einführendes Element — Haupt-Element — Ergänzendes Element

Élément introductif — Élément central — Élément complémentaire

ICS:

CCMC will prepare and attach the official title page.

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European foreword

This document (prEN 13650:2021) has been prepared by Technical Committee CEN/TC 223 "Soil improvers and growing media", the secretariat of which is held by NEN.

This document is a working document.

This document will supersede EN 13650:2001.

In comparison with the previous edition, the following technical modifications have been made:

- The heating block procedure was added to the reflux digestion procedure
- The scope was expanded including liming materials and preformed materials.

This document has been prepared under a standardization request given to CEN by the European Commission and the European Free Trade Association and supports essential requirements of EU Directive(s).

Introduction

Aqua regia is applied to digest different matrices for the subsequent determination of many elements. For example, a multi-matrix standard for aqua regia digestion of soil, treated biowaste, sludge and waste was prepared by CEN/TC 444. CEN/TC 260 published a standard with a similar procedure for organic and organo-mineral fertilizers.

It is known that the digestion of soil improvers or growing media with aqua regia will not necessarily lead to complete element recoveries, and that the extract from a test sample may not reflect the total concentrations of the target analytes. However, for most applications the result obtained based upon digestion methods specified in this document are considered to be fit for the intended purpose.

WARNING — Persons using this document should be familiar with usual laboratory practice. Some of the reagents used in this document are highly corrosive and very toxic. Safety precautions are absolutely necessary.

All procedures should be performed in a fume hood or in closed force-ventilated equipment. By the use of strong oxidising reagents, the formation of explosive organic intermediates is possible, especially when dealing with samples with a high organic content. Avoid contact with the chemicals and the gaseous reaction products.

IMPORTANT — It is absolutely essential that tests conducted according to this document be carried out by suitably trained staff.

1 Scope

This document specifies a method for the digestion of soil improvers and growing media by the use of an aqua regia digestion.

Materials containing more than about 28 % (m/m) organic matter will require treatment with additional nitric acid. With high solute concentrations in extract solutions, spectral interference's and background enhancement should be expected.

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.

EN 13039:—[1], *Soil improvers and growing media – Determination of organic content and ash*

EN 13040-1:—[2], *Soil improvers and growing media – Sample preparation – Part 1: Sample preparation for chemical and physical tests, determination of dry matter content, moisture content and laboratory bulk density*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in CEN/TS 0223137:—[3] and the following apply:

3.1
aqua regia
digestion solution obtained by mixing 1 volume of nitric acid (mass fraction of 65 % to 70 %) and 3 volumes of hydrochloric acid (mass fraction of 35 % to 37 %)

3.2
digestion
mineralization of the organic matter of a sample and dissolution of its mineral part, more or less completely, when reacting with a reagent mixture

4 Principle

A test portion is digested with aqua regia according to one of the following heating procedures:

- Method A: reflux for 120 min ± 10 min, followed by filtration/centrifugation;
- Method B: heating block at 105 °C ± 5 °C for 120 min ± 10 min, followed by filtration/centrifugation.

[1] Under preparation. Stage at the time of publication: EN 13039:20**.

[2] Under preparation. Stage at the time of publication: EN 13040-1:20**.

[3] Under preparation. Stage at the time of publication: prCEN/TS 00223137:20**.

5 Reagents

5.1 General

Use only acids and reagents of recognized analytical grade to avoid high blank values for subsequent analytical measurements. Use a test blank solution throughout the procedure applying all steps with the same amount of acids, but without a sample.

5.2 Water, having an electrical conductivity not higher than 0,2 mS/cm at 25 °C, free of the elements to be determined.

5.3 Hydrochloric acid, $c(HCl)$ = 12 mol/l; ρ ≈ 1,18 g/ml; 37 % mass/volume.

5.4 Nitric acid, $c(HNO_3)$ = 15 mol/l; ρ ≈ 1,42 g/ml; not less than 65 % mass/volume.

5.5 Nitric acid, $c(HNO_3)$ = 0,5 mol/l. Dilute 35 ml nitric acid (**5.4**) to 1 l with water (5.2).

5.6 Antifoaming agent, e.g. *n*-dodecane ($C_{12}H_{26}$) or *n*-octanol ($C_8H_{18}O$) are suitable.

6 Apparatus

6.1 General

Usual laboratory apparatus. All glassware and plastics ware shall be adequately cleaned and stored in order to avoid any contamination.

Depending upon the concentration of the element of interest, particular care should be exercised with respect to the effective cleaning of the vessels.

6.2 Method A — Thermal heating under reflux conditions

6.2.1 Digestion vessel, temperature-resistant and capable of containing the mixture of sample and digest solution, for example a quartz vessel. The digestion vessel shall have a volume of at least 5 times of the volume of the aqua regia used. The inner wall of the vessel shall be inert and shall not release substances to the digest in excess of the purity requirements of the subsequent analysis.

NOTE 1 Silica or borosilicate glass vessels can be used instead of quartz vessels.

NOTE 2 It can be necessary to periodically clean the digestion vessels with a suitable surfactant to remove persistent deposits.

6.2.2 Reflux condenser, adaptable to the digestion vessel (6.2.1).

6.2.3 Absorption vessel, volatile species trap, in an open digestion system capable of trapping one or more volatile measurement species, adaptable to the reflux condenser (6.2.2).

6.2.4 Heating device, for example a heating mantle, thermostatic controlled, or an aluminium block thermostat.

6.3 Method B — Thermal heating with a heating block with containers

6.3.1 Digestion tube, 50 ml plastic tube, temperature-resistant and capable of containing the mixture of sample and digest solution, with a screw cap from e.g. polypropylene.

The part of the tube not being heated and the screw cap function as a condenser, but are not really a reflux system. The material of the tube and screw cap need to be tested in order to be sure that release of elements of interest does not take place. Other materials and vessels with other volumes than mentioned above are allowed to be used if suitability has been proven.

6.3.2 Temperature controlled heating block, heating block able to heat the tube(s) to a temperature of 105 °C ± 5 °C.

6.4 Sample containers, plastics and glass containers are both suitable.

6.5 Filter paper, usually with a pore size of 0,45 µm and resistant to the diluted aqua regia final digestion solution.

6.6 Volumetric flasks, usually of nominal capacity of 50 ml or 100 ml.

6.7 Analytical balance, with an accuracy of 1 mg or better.

6.8 Boiling aids, anti-bumping granules or glass beads, diameter 2 mm to 3 mm, acid washed.

7 Sample pre-treatment

Prepare the sample by reducing the particle size below 0,5 mm in accordance with clause 10 of EN 13040-1:—. The residual moisture in the analysed sample determined in accordance with EN 13040-1:—, clause 11, using 10 g of sample.

8 Procedure

8.1 Blank test

Carry out a reagent blank test digestion in parallel with the determination, using the same procedure and the same quantities of all the reagents as in the determination, but omitting the test portion. The laboratory shall define acceptable limits.

NOTE The measurement of a blank is introduced to determine the contribution of the extracting solution, glassware, digestion tube and filter paper used to the measured value.

8.2 Method A — Thermal heating under reflux conditions

Weigh approximately 1 g to 3 g, to the nearest 0,001 g of the test sample, and transfer to the digestion vessel (6.2.1). In case of dry samples moisten the test portion with about 0,5 ml to 1,0 ml water (5.2). Add while mixing, 21,0 ml ± 0,1 ml of hydrochloric acid (5.3) followed by 7,0 ml ± 0,1 ml of nitric acid (5.4), drop by drop if necessary to reduce foaming. Connect the reflux condenser (6.2.2) to the digestion vessel (6.2.1). Fill the absorption vessel (6.2.3) with approximately 15 ml nitric acid (5.5). Connect the absorption vessel to the reflux condenser and let stand at room temperature until any effervescence almost ceases to allow for slow oxidation of the organic matter in the sample.

The time of standing at room temperature can have an influence on the digestion rate of aqua regia. For consistency, it is recommended to start heating as soon as possible after the first strong reaction has ceased.

NOTE It is common practice to add hydrochloric acid directly to the reaction vessel, followed by the nitric acid, and to assume that the aqua regia forms in the reaction vessel. However, problems have been encountered with materials rich in carbonates, where a substantial portion of the hydrochloric acid has been consumed before the nitric acid can be added. Under such circumstances, the correct formation of aqua regia is doubtful.

The amount of *aqua regia* is sufficient only for oxidation of about 0,85 g of organic matter (corresponding to about 0,5 g of organic carbon). If there is any doubt about the amount of organic matter present, carry out a determination according to EN 13039:—. If there is more than 0,85 g of organic matter in the test sample reduce the quantity of sample analyzed or proceed as follows.

Allow the first reaction with *aqua regia* to subside. Then add an extra 1 ml of nitric acid (5.4) only to every 0,17 g of organic matter above 0,85 g. Do not add more than 10 ml of nitric acid at any time and allow any reaction to subside before proceeding further.

Add a few roughened glass beads (6.8) and connect the digestion vessel (6.2.1) to the heating device (6.2.4). Raise the temperature of the reaction mixture slowly until reflux conditions are reached and maintain for 2 h ensuring that the condensation zone is lower than 1/3 of the height of the condenser, then allow to cool. Add the content of the absorption vessel to the digestion vessel via the reflux condenser, rinsing both the absorption vessel and condenser with further 10 ml of diluted nitric acid (5.5).

Transfer quantitatively the solution content of the digestion vessel into a suitable sized volumetric flask and add water (5.2) to the volume mark.

Alternatively, another procedure can be applied, such that the adjustment to volume with the solid residue still present shall be carried out immediately after digestion.

If the measurement solution contains particles due to precipitation which may clog nebulizers or interfere with an injection of the sample into the instrument, the sample may be centrifuged, allowed to settle, or filtered (6.5).

The extracts are suitable for analysis using WI 00223xxx, Soil improvers and growing media - Determination of aqua regia soluble elements (2020-02.27) and 00223123, Soil improvers and growing media - Determination of mercury in aqua regia extracts.

8.3 Method B — Thermal heating with a heating block with containers

Weigh an amount of not more than 2 g of the test portion (typically 0,5 g to 1 g of dry sample), to the nearest 0,001 g, and transfer to the digestion vessel (6.3.1). In case of dry samples moisten the test portion with a few drops of water (5.2). Add 12,0 ml ± 0,1 ml hydrochloric acid (5.3) followed by 4,0 ml ± 0,1 ml nitric acid (5.4). Let stand at room temperature until any effervescence almost ceases to allow for slow oxidation of the organic matter in the sample.

The amount of *aqua regia* is sufficient only for oxidation of about 0,50 g of organic matter (corresponding to about 0,3 g of organic carbon). If there is any doubt about the amount of organic matter present, carry out a determination according to EN 13039:—. If there is more than 0,50 g of organic matter in the test sample reduce the quantity of sample analyzed or proceed as follows.

Allow the first reaction with *aqua regia* to subside. Then add an extra 1 ml of nitric acid (5.4) only to every 0,17 g of organic matter above 0,50 g. Do not add more than 10 ml of nitric acid at any time, and allow any reaction to subside before proceeding further.

NOTE For some elements, e.g. chromium, the additional volume of HNO_3 is essential in order to have a sufficient recovery upon digestion.

The time of standing at room temperature can have an influence on the digestion rate of aqua regia. For consistency, it is recommended to start heating as soon as possible after the first strong reaction has ceased.

Loosely screw on the tube cap (not very tight!) and place the digestion vessel on the heating block (6.3.2) and slowly increase the temperature to the boiling point. Keep the temperature on the boiling point during 120 min ± 10 min.

Let the vessel cool down to room temperature and fill up with water (5.2) to the volume mark.

If a non-graduated digestion tube is used, transfer quantitatively the solution into a suitable sized volumetric flask and add water (5.2) to the volume mark.

Alternatively, another procedure can be applied, such that the adjustment to volume with the solid residue still present shall be carried out immediately after digestion.

If the measurement solution contains particles due to precipitation which may clog nebulizers or interfere with an injection of the sample into the instrument, the sample may be centrifuged or filtered (6.5).

The extracts are suitable for analysis using WI 00223xxx, Soil improvers and growing media - Determination of aqua regia soluble elements (2020-02.27) and 00223123, Soil improvers and growing media - Determination of mercury in aqua regia extracts.

9 Precision

The repeatability and reproducibility of the aqua regia soluble element content in separately prepared samples should be in accordance with Tables A.1 to A.6.

A summary of the results of an interlaboratory trial to determine the precision of the method, in accordance with ISO 5725 [2], is given in annex A.

NOTE The values derived from this interlaboratory trial may not be applicable to concentrations and matrices other than those tested.

Kommentiert [VC1]: To be adapted according to the new interlaboratory validation trial.

10 Test Report

The test report can be prepared separately or in conjunction with the test report of the subsequent analytical method.

The test report shall include the following information:

a) the digestion method used, together with a reference to this document;

b) a complete identification of the sample;

c) all the analytical methods used;

d) the results of the determination expressed as mass/mass on dry matter basis;

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

Annex A
(informative)

Results of an interlaboratory trial to determine aqua regia soluble elements.

An interlaboratory trial was organized in 1997 under the auspices of the European Committee for Standardization, to test the procedures specified in this European Standard.

In this trial the number of laboratories given in Tables A.1 to A.6 determined the aqua regia soluble elements in six sample types.

All results are reported on a dry matter basis.

A summary of the results of the interlaboratory trial for the determination of *aqua regia* soluble elements is given in Tables A.1 to A.6.

To be amended.

Bibliography

[1] EN ISO 54321, *Soil, treated biowaste, sludge and waste – Digestion of aqua regia soluble fractions of elements (ISO 54321:2020)*

[2] ISO 5725, *Accuracy (trueness and precision) of measurement methods and results*

[3] CEN/TS 00223137:—, *Soil improvers and growing media — Terminology*

[4] WI 00223xxx:—, *Soil improvers and growing media – Determination of aqua regia soluble elements*

[5] WI 00223123:—, *Soil improvers and growing media – Determination of mercury in aqua regia extracts*