CEN/TC 223/WG 4 "Analytical methods"
WG Secretariat: **ASI**
Convenor: **Baumgarten Andreas Mr**

1st WD_WI 00223xxx_AR extractable elements

Document type	Related content	Document date	Expected action
Project / Draft		2021-12-02	

Description

Please find enclosed the 1st working draft on WI 00223xxx, Soil improvers and growing media - Determination of aqua regia soluble elements for your information.

As agreed during the meeting of CEN/TC 223/WG 4 on 2021-11-09, the enclosed 1st working draft and the forms for the adoption of the new work item will 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: 2021-11

WI00223xxx:2021

Secretariat : NEN

Soil improvers and growing media - Determination of aqua regia soluble elements

ICS:

Contents

Page

European foreword ... 3
Introduction ... 4
1 Scope ... 5
2 Normative references ... 5
3 Terms and definitions ... 5
4 Principle ... 5
5 Interferences ... 5
5.1 General ... 5
5.2 Spectral interferences ... 5
5.3 Transport interferences ... 6
5.4 Excitation interferences ... 6
5.5 Chemical interferences ... 6
5.6 Memory interferences ... 6
6 Reagents ... 7
6.1 General ... 7
6.2 Nitric acid, substance concentration c(HNO3) ≈ 14,3 mol/l; mass concentration ρ ≈ 1,4 g/ml ... 7
6.3 Hydrochloric acid, c(HCl) ≈ 12 mol/l; ρ ≈ 1,18 g/ml ... 7
6.4 Mixed acid solution, 0,8 mol/l nitric acid and 1,8 mol/l hydrochloric acid ... 7
6.5 Standard stock solutions, concentration of 1 000 mg/l for each element ... 7
6.6 Argon, purity 99,995 % or better. ... 7
7 Apparatus ... 8
7.1 Common laboratory glassware. ... 8
7.2 Inductively coupled plasma atomic emission spectrometer ... 8
8 Procedure ... 8
8.1 Preparation of test and blank solution ... 8
8.2 Preparation of the calibration solutions ... 8
8.3 Measurement ... 9
9 Calculation and expression of the results ... 10
10 Test report ... 11
Bibliography ... 12

European foreword

This European Standard 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 has been prepared under a standardization request given to CEN by the European Commission and the European Free Trade Association.

Introduction

This document is part of a modular approach and concerns the analytical measurement step. “Modular” means that a test standard concerns a specific step in assessing a property and not the whole chain of measurements. Inductively coupled plasma atomic emission spectrometry (ICP-AES) is nowadays widely used and a well established method in many laboratories.

1 Scope

This document specifies a method for the determination of elements in soil improvers or growing media extracts using inductively coupled plasma-atomic emission spectrometry (ICP-AES)

NOTE 1 Alternatively, inductively coupled plasma mass spectrometry (ICP-MS) can be used for the measurement if the user proves that the method gives the same results.

This method is applicable to aqua regia extracts prepared according to EN 13650:— [1].

NOTE 2 The method may be used for the determination of other elements, provided the user has verified the applicability.

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 13650:—: *Soil improvers and growing media – Digestion by aqua regia for subsequent determination of elements*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in CEN/TS 00223137:— [2] apply.

4 Principle

The method is based on the inductively coupled plasma atomic emission spectrometry (ICP-AES) measurement of the concentration of elements in soil improvers and growing media in aqua regia extracts. The elements are determined after an appropriate dilution of the extract, if necessary. The solution is dispersed by a suitable nebulizer of the ICP-AES instrument and the resulting aerosol is transported into the plasma torch. Element specific emission spectra are produced by a radiofrequency inductively coupled argon plasma where atoms or ions are excited at high temperature. The emission spectra are dispersed by a spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Multi-element determinations using sequential or simultaneous optical systems and axial, radial or dual viewing of the plasma may be used.

5 Interferences

5.1 General

Interferences and matrix effects shall be recognized and appropriate measures to minimize them shall be made. There are several types of interferences – see 5.2 to 5.6.

5.2 Spectral interferences

[1] Under preparation. Stage at the time of publication: EN 13650:20**.

[2] Under preparation. Stage at the time of publication: CEN/TS 00223137:—.

Spectral interferences are due to incomplete isolation of the radiation emitted by the analyte from other detected radiation sources. Spectral interferences are caused by the background emission from continuous or recombination phenomena, by stray light which causes background increase or overlap of a spectral line from another element, or by the unresolved overlap of molecular band spectra. Background emission and stray light can usually be compensated for by subtracting the background emission measured adjacent to the analyte wavelength peak. To correct a sloping background shift background correction points on each side of the peak are used. The increase of background is more intensive with axial-view instruments. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. A spectral line overlap usually leads to the choice of an alternative line. If this is not possible, mathematical correction procedures (e.g. inter-element correction technique or multi-component spectral fitting) can be used to compensate for the interference. These correction procedures are usually a part of the instrument software.

5.3 Transport interferences

Transport interferences are caused by differences in the properties between the sample solutions and the calibration solutions (viscosity, surface tension, density, dissolved solid content, type and concentration of acids). As a consequence, the supply of solution to the nebuliser, the efficiency of nebulisation and the droplet size distribution of the aerosol is altered, resulting in a change of sensitivity. Errors due to these interferences can be overcome by dilution of the solutions, by matrix matching, by standard addition or by internal standard.

5.4 Excitation interferences

Excitation interferences are attributed to a change in the excitation conditions in the plasma, especially by the presence of easily ionisable elements. The interference depends on the operating conditions of the plasma (e.g. power, sample introduction, gas flowrate or observation height) and differ from element to element. Improvement of the plasma conditions can therefore reduce excitation interferences. Other possibilities are dilution of the solutions, matrix matching or the standard addition technique.

5.5 Chemical interferences

Chemical interferences are not significant with the ICP-AES technique, but if observed, they can be minimized by a careful selection of operating conditions (e.g. radio frequency power, observation position, gas flow rate and so forth).

5.6 Memory interferences

Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. This type of interference may be caused by sample deposits or the accumulation in pump tubing, nebulizer, spray chamber or plasma torch. The possibility of memory interferences should be recognized within an analytical run and suitable rinse steps and rinse times should be used.

6 Reagents

6.1 General

All reagents including water shall be of recognized analytical grade and they shall have negligible concentration of the element to be determined if compared to the lowest concentration of that element in the sample solution.

6.2 Nitric acid, substance concentration c(HNO3) ≈ 14,3 mol/l; mass concentration ρ ≈ 1,4 g/ml.

6.2.1 Diluted nitric acid solution, $c(HNO_3)$ = 5 mol/l.

Add 350 ml of nitric acid (6.2) to 650 ml of water.

6.3 Hydrochloric acid, c(HCl) ≈ 12 mol/l; ρ ≈ 1,18 g/ml.

6.4 Mixed acid solution, 0,8 mol/l nitric acid and 1,8 mol/l hydrochloric acid.

Add 150 ml of hydrochloric acid (6.3) and 56 ml nitric acid (6.2) to 800 ml of water.

6.5 Standard stock solutions, concentration of 1 000 mg/l for each element.

Both single-element stock solutions and multi-element stock solutions with adequate specification, stating the acid used and the preparation technique, are commercially available. Multi-element stock solutions are usually available at the individual mass concentration *equal to* 100 mg/l for each element. These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered. Alternatively, the stock solutions may be prepared by the dissolution of high purity metals.

6.5.1 Standard solution, concentration of 100 mg/l of element.

Use commercially available solution of this concentration for each element or pipette, 10 ml of the appropriate element stock solution (6.5) into a 100 ml volumetric flask. Add 10 ml of diluted nitric acid (6.2.1), fill to the mark with water and mix well. This solution is used to prepare spiked test solutions and calibration solutions.

6.5.2 Standard solution, concentration of 10 mg/l of element.

Pipette 10 ml of standard solution (6.5.1) into a 100 ml volumetric flask. Add 10 ml of diluted nitric acid (6.2.1), fill to the mark with water and mix well. This solution is used to prepare calibration solutions e.g. for cadmium.

6.6 Argon, purity 99,995 % or better.

7 Apparatus

7.1 Common laboratory glassware.

7.2 Inductively coupled plasma atomic emission spectrometer.

WARNING – It is essential that the manufacturer's safety instructions are strictly observed when using this apparatus.

The inductively coupled plasma atomic-emission spectrometer consists of a sample introduction system, the plasma as an excitation source, an optical system, a detector and a computer with suitable software. The sample is transported by the introduction system (rotation tube pump, nebuliser and a spray chamber) to the plasma torch. Around the torch a water-cooled RF coil is placed. A frequency of 27 MHz to 56 MHz with a power of 600 W to 2 000 W is usually used. The emission from the plasma can be observed either from the side (radial) or from the torch central symmetrical axis (axial). Axial viewing gives more signal intensity due to the increased observation path length of the normal analytical zone of the plasma, but an increase of interference is also commonly observed. Spectral lines are measured and registered either in a sequential or a simultaneous manner.

8 Procedure

8.1 Preparation of test and blank solution

Aqua regia extracts are usually measured using ICP-AES directly with calibration solutions of the same final concentration of aqua regia. The aqua regia extracts may also be used for the determination of other elements.

A blank test is prepared for the measurement following the same procedure as for samples.

If dilution is necessary, dilute an aliquot portion of the extract in one or more steps so that the final concentration of the element to be determined is approximately in the middle of the given calibration range (8.2). In the final diluting step fill to the mark with the mixed acid solution (6.4) and mix well. Prepare a diluted blank solution by pipetting a blank solution and dilute in the same way as the test solution.

8.2 Preparation of the calibration solutions

Individual calibration series for each element or mixed series may be used. For cadmium calibration standards, pipette volumes of 0 ml; 0,5 ml; 1 ml; 2 ml and 5 ml of the standard solution (6.5.2) into five 100 ml volumetric flasks respectively. For arsenic, copper, chromium, lead, nickel and zinc calibration standards pipette volumes of 0 ml; 1 ml; 2 ml; 5 ml and 10 ml of the standard solution (6.5.1) into the same five 100 ml volumetric flasks respectively.

Fill the volumetric flasks to the mark with the mixed acid solution (6.4).

The mass concentrations of cadmium in the calibration solutions are: 0 mg/l; 0,05 mg/l; 0,1 mg/l; 0,2 mg/l and 0,5 mg/l. The mass concentrations of arsenic, copper, chromium, lead, nickel and zinc in the calibration solutions are: 0 mg/l; 1 mg/l; 2 mg/l; 5 mg/l and 10 mg/l respectively.

Individual sets of calibration solutions for each element can be used instead of the mixed calibration solutions for all elements. If necessary, calibration solutions of higher or lower concentrations can be prepared in the same way.

NOTE 1 Small differences in acid concentration between sample extracts and calibration solutions do not affect the measurement.

NOTE 2 It is possible to calibrate the instrument for higher concentrations of the elements if the calibration curve is linear.

8.3 Measurement

8.3.1 Instrument conditions

Due to differences between various kinds of instruments, no detailed instructions can be given to operate the specific instrument. The instruction provided by the manufacturer for waiting time, instrument stability, gas flows, plasma conditions, nebuliser conditions, sample uptake rate, etc. should be followed.

Examples of conditions for two types of instruments are given in Table 1.

The software of the instrument is used to calculate concentrations of the elements in the individual test solutions. All test solutions, blanks and calibration solutions are measured under the same optimized conditions using background correction and other suitable steps to eliminate or minimize interferences.

8.3.2 Optimization of the instrument conditions

The aim is to find the best sensitivity and precision and to minimize interferences for the set of lines to be used. Emission efficiency is related, amongst other parameters, to the plasma temperature, which is a function of RF power, argon gas flows and observation height (for radially viewed plasmas). Also, the type of nebuliser and sample uptake rate will have an impact on the signal and the background.

8.3.3 Interferences

Background shall be measured adjacent to analyte lines on sample during analysis. The position selected for the background intensity measurement, on one or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analytical line. When working with an unknown matrix it is necessary to check the signal of every element to be measured for possible interferences by studying the region of the line. If spectral interferences (partial line overlap, line coincidence) occur, the measurement shall be carried out at another wavelength. If this is not possible, correction of the interference by mathematical correction procedures shall be carried out. High plasma power can minimize the matrix influence. Examples of suitable instrument conditions are given in Table 1.

Spectral lines which are free of interference by other elements shall be selected. As the spectral interferences depend on the instrument resolution, they shall be identified for each type of instrument in practical trials using mixtures of standard solutions containing the elements typically contained in organic fertilizers and organo-mineral fertilizer samples of varying concentrations.

8.3.4 Matrix effects

The calibration blank and calibration solutions, calibration verification solution (one of the calibration standard solutions used to check calibration of the instrument), blank test, sample solutions and quality control solutions are measured after the stabilisation of the instrument and verification of stable conditions. Read the emission intensity of the solution at least twice and average the values. Run a calibration blank and a calibration check solution every 20 samples or less and at the end of the measurement.

Whenever an unknown matrix is encountered, check the following:

— matrix effects by running the spike sample;

— matrix effects by running a fivefold diluted sample;

— matrix effects by analysing at a different wavelength.

Spike recovery shall be between 90 % and 110 %. The difference between the results for the original sample and the fivefold-diluted sample shall be less than 10 %. If the spike recovery or difference for the diluted sample exceeds the given limit, a standard addition method shall be used.

8.3.5 Spiking

Add a known amount of a standard solution of the analyte and an equal amount of a blank solution to two separate but equal portions of the sample solution (or its dilution). The spike shall be between 0,4 and 2 times the expected sample mass concentration. Measure both solutions as sample solutions. Determine the 'measured spike concentration' as the difference in mass concentration between the two spiked sample portions.

EXAMPLE Spiking procedure: pipette 10 ml of an soil improver or growing medium extract or diluted extractinto two test tubes, add 0,1 ml of a standard solution (6.5.1) into the first test tube and 0,1 ml of blank into the second test tube. Mix well and measure. To achieve a higher concentration of an element by spiking, stock solutions of higher concentration can be used.

NOTE If the analytical results according to the standard addition method and the standard calibration method are equal, the calibration curve method may be applied.

The standard addition method, spike recovery and dilution are recommended to check the efficiency of interference reduction especially in complicated matrices and for unknown samples.

Table 1 – Example of instrument parameters[3]

Instrument	Spectro Arcos	Agilent 5100
Plasma view	**Radial**	**Radial**
Coolant flow	14,30 l·min^{-1}	12,00 l·min^{-1}
Auxiliary flow	1,20 l·min^{-1}	1,00 l·min^{-1}
Nebulizer flow	1,10 l·min^{-1}	0,70 l·min^{-1}
Peristaltic pump	30 r·min^{-1}	12 r·min^{-1}

Examples of adequate wavelength are to be found in EN ISO 11885 (alternative wavelengths can be used according to the instrument and recommendations of the producer) as well as potentially interfering elements.

9 Calculation and expression of the results

Calculate the content of an element in the fertilizer, w_X, as a mass fraction in mg/kg according to Formula (1).

$$m_X = \frac{V_{\text{dig}} \times (X_S - X_b) \times D \times 100}{M \times DM} \quad (1)$$

where

3) Spectro Arcos and Agilent 5100 are examples of suitable instruments available commercially. This information is given only as an example and does not constitute an endorsement by CEN of these products.

m_X is a mass fraction of the individual element, in mg/kg; expressed on dry matter basis

V_{dig} is the final volume after extraction, in ml;

X_s is the concentration of the test solution, in mg/l;

X_b is the concentration of the blank solution, in mg/l;

m is the mass of the test sample, in g;

DM is the dry matter content of the test sample in percent;

D is the dilution factor calculated according to Formula (2).

$$D = \frac{V_1}{V_{p1}} \times \frac{V_2}{V_{p2}} \times \ldots \frac{V_n}{V_{pn}} \quad (2)$$

where

$V_{1,2\ldots n}$ are the volumes of the volumetric flasks, in ml;

$V_{p1,2\ldots n}$ are the volumes of the pipetted solutions used for an individual diluting step, in ml.

10 Test report

The test report shall contain at least the following information:

a) identification of the sample;

b) the test method used with reference to this document (EN 00223xxx:2021);

c) the method used for preparation of the extraction solution;

d) the test results obtained;

e) date of sampling and sampling procedure (if known);

f) date when the analysis was finished;

g) whether the requirement of the repeatability limit has been fulfilled; - optional

h) all operating details not specified in this document, or regarded as optional, together with details of any incidents occurred when performing the method, which might have influenced the test result(s).

Bibliography

[1] Regulation (EC) No 1009/2019 of the European Parliament and of the Council of 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003. Official Journal of the EU, L 170.

[2] EN 16963, *Fertilizers — Determination of boron, cobalt, copper, iron, manganese, molybdenum and zinc using ICP-AES*

[3] EN 16170, *Sludge, treated biowaste and soil — Determination of elements using inductively coupled plasma-optical emission spectrometry (ICP-OES)*

[4] ISO 22036, *Soil quality — Determination of trace elements in extracts of soil by inductively coupled plasma — atomic emission spectrometry (ICP - AES)*

[5] EN 16319:2013, *Fertilizers — Determination of trace elements — Determination of cadmium, chromium, lead and nickel by inductively coupled plasma-atomic emission spectrometry (ICP-AES) after aqua regia dissolution*

[6] EN 16317, *Fertilizers — Determination of trace elements — Determination of arsenic by inductively coupled plasma-atomic emission spectrometry (ICP-AES) after aqua regia dissolution*

[7] EN ISO 11885, *Water quality — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)*

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