

CEN/TC 260

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**Organic and organo - mineral fertilizers - Digestion by aqua regia for
subsequent determination of elements**

**Bestimmung spezifischer Elemente - Aufschluss durch Königswasser zur
anschliessenden Bestimmung des Elemente**

**Dosage des éléments spécifiques - Digestion à l'eau régale pour le dosage ultérieur
des éléments**

ICS:

CCMC will prepare and attach the official title page.

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European foreword

This document (CEN/prEN 17768) has been prepared by Technical Committee CEN/TC 260 "Fertilizers and liming materials", the secretariat of which is held by DIN.

This document is currently submitted to.

This document will supersede prEN 17768 (N411). In comparison with the previous edition the following main changes have been made:

Introduction revised according to the recommended wording from FprEN 17701-1.

Scope redrafted to include all elements demanded by SR. Analysis of blends added into the Scope

Normative references to the sampling and sample preparation added, reference to dry matter content determination added and deleted from Bibliography.

Terms and definitions added

Principle harmonized with FprEN 17701-1

Chapter concerning Apparatuses (common laboratory glassware) widened to include information about measures avoiding contamination by boron.

Note 4 concerning microwave digestion temporarily deleted. No data available. To be discussed in WG

Editorial changes including N301, and changes demanded for FprEN 17701-1 were included

Bibliography revised

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) / Regulation(s).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN shall not be held responsible for identifying any or all such patent rights.

Introduction

The European Committee for Standardization (CEN) was requested by the European Commission (EC) to draft European standards or European standardization deliverables to support the implementation of Regulation (EU) 2019/1009 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 (“FPR” or “Fertilising Products Regulation”) [1].

The preparation of this document is based on a standardization request to CEN by the European Commission and the European Free Trade Association (Mandate M/564 and relevant amendments) concerning the modernization of methods of analysis of fertilizers within the framework of Regulation (EU) 2019/1009 of the European Parliament and of the Council. This standardization request, presented as M/564, also contributes to the Communication on “Innovating for Sustainable Growth: A Bio economy for Europe”.

Aqua regia is applied to digest different matrices for the subsequent determination of many elements. For example, a multi-matrix standard for aqua regia extraction of soils, sludges and biowaste was prepared by CEN/TC 444 [2, 3]. A similar procedure was applied for determination of aqua regia extractable contents of arsenic, mercury, cadmium, chromium, nickel and lead in fertilizers and liming materials [4, 5, 6], for extraction of micronutrients from mineral fertilizers [7] etc. CEN/TC 223 published a standard for a similar procedure for soil improvers and growing media [1]. CEN/TC 455 published a standard for a similar procedure for plant biostimulants [10]. The interlaboratory study (ILS) for plant biostimulants included also blends of these fertilizer products with some organic and organo-mineral fertilizers. The ILS proved that the method is also suitable for these blends.

Wide use of the aqua regia digestion, availability of the instruments and the possibility to merge the standards for different matrices in future, were the main reasons for also applying this method of digestion for organic and organo-mineral fertilizers. A simple pre-concentration procedure is a part of this document to also cover the digestion of liquid samples with low dry matter content in the case that the measurement method is not sufficiently sensitive. An Annex A describes in detail the calculation of the initial sample mass to be taken for the pre-concentration step to achieve concentrations of the individual elements above the limit of quantification (LOQ).

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

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

1 Scope

This European Standard specifies the procedure for digestion of different organic and organo-mineral fertilizers with aqua regia to enable a subsequent determination of arsenic (As), cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), nickel (Ni), boron (B), cobalt (Co), iron (Fe), manganese (Mn), molybdenum (Mo), zinc (Zn), mercury (Hg), phosphorus (P), potassium (K), magnesium (Mg), calcium (Ca), sulphur (S) and sodium (Na)) and may be also applied for determination of other elements.

This document is applicable to the fertilizing product blends where the EU fertilising product organic and organo-mineral fertilizer contained in the blend represents the highest % by mass in the blend. In case of equal shares, the user may apply either this or the standard(s) applicable to the other component product(s).

The digests are suitable for analysis using prEN 17770¹ [10] and prEN 17769² [11]

NOTE 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.

2 Normative references

prEN 17773³, *Organic and organo-mineral fertilizers - — Determination of the dry matter content*

EN 1482-1 (2007), *Fertilizers and liming materials - Sampling and sample preparation - Part 1: Sampling*

EN 1482-2 (2007), *Fertilizers and liming materials - Sampling and sample preparation - Part 2: Sample preparation*

Commenté [BA1]: Tbd with WG8

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:

- IEC Electropedia: available at <https://www.electropedia.org/>
- ISO Online browsing platform: available at <https://www.iso.org/obp>

3.1

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

3.2

blank test solution

solution prepared in the same way as the test sample solution but omitting the test portion

¹ Under preparation

² Under preparation

³ Under preparation

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4 Principle

The samples are digested by boiling in aqua regia for two hours under reflux conditions.

5 Sampling and sample preparation

Sampling and sample pre-treatment should be performed, following the principles described in EN 1482 (all parts) with appropriate adaptations, required to account for specificities of organic and organo-mineral fertilizers.

6 Reagents

The concentration of the analyte or interfering substances in the reagents and the water should be negligible compared to the lowest concentration to be determined.

6.1 Water with a specific conductivity not higher than 0,2 mS/m at 25 °C, free from the elements to be determined.

6.2 Hydrochloric acid $c(\text{HCl}) \approx 12 \text{ mol/l}$, $\rho \approx 1,18 \text{ g/ml}$.

6.3 Nitric acid $c(\text{HNO}_3) \approx 14,3 \text{ mol/l}$, $\rho \approx 1,4 \text{ g/ml}$.

6.4 Antifoaming agent, e.g., n-dodecane ($\text{C}_{12}\text{H}_{26}$) or octanol (C_8H_{18}) are suitable.

7 Apparatus

7.1 Common laboratory glass and plastic ware

All glassware and plastic ware shall be adequately cleaned and stored to avoid any contamination. If boron content is to be determined, it is necessary to minimize the contact of all solutions with borosilicate glassware. Suitable plastic or silica ware is needed especially for the extraction step. Glass volumetric flasks may be used for making up to volume but not for storage of digests and solutions.

7.2 Apparatus for thermal heating digestion

Temperature controlled with reaction vessel and reflux condenser. The capacity of the reaction vessel should be at least 5 times of the volume of the aqua regia used.

7.3 Filter paper

Ash free paper of recognized and tested quality.

7.4 Analytical balance, capable of weighing to an accuracy of 1 mg or better.

8 Procedure

CAUTION – Suitable precautions shall be taken to avoid any contact of laboratory staff with acid fumes. The digestion procedure shall be carried out in a well-ventilated fume cupboard.

8.1 Sample digestion

This procedure can be used for all samples of organic fertilizers, organo-mineral fertilizers, and their blends if a sufficiently sensitive method for determination is used. For some liquid samples with a low dry matter content, a pre-concentration step (8.2) may be necessary.

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Weigh 2,5 g to 5,0 g of the solid, or liquid sample representing approximately 1,5 g to 3,0 g of dry sample, to the nearest 0,001 g. Transfer the sample quantitatively to the reaction vessel (7.2). Liquid samples are preferably weighed directly into the reaction vessel (7.2). Moisten the solid sample with about 0,5 ml to 1,0 ml of water (6.1) and add, while gently mixing, 21 ml of hydrochloric acid (6.2) followed by 7 ml of nitric acid (6.3) drop wise if necessary. Add one drop of the antifoaming agent (6.4) in the case of excessive foaming. Let the mixture stand at laboratory temperature until any effervescence almost ceases. Transfer to the heating device (7.2) and slowly raise the temperature of the reaction mixture to reflux conditions 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 and rinse the condenser with 10 ml of water (6.1).

Transfer the content of the reaction vessel quantitatively into a 150 ml volumetric flask, dilute to the mark with water (6.1) and mix well.

Test solutions can be filtered or centrifuged if necessary. Use ash-free filter paper of recognized and tested quality (7.3) and discard the first portion of the filtrate (approximately 20 ml).

Carry out the measurement immediately or store the extracts in tightly closed vessels for up to 15 days.

The procedure can be modified for the use of 100 ml or 50 ml volumetric flasks or graduated plastic tubes. In this case the mass of the sample and volumes of the acids should be changed accordingly. For more information, see Annex A.

NOTE 1 Weigh the samples for dry matter determination according to CEN/TS 17773 at the same time and from the same sub-sample to ensure that the dry matter is determined on the samples identical to those used for determination of parameters that relates to dry matter.

NOTE 2 If excessive foaming occurs despite the addition of an anti-foaming reagent, it is possible to leave the samples overnight after the addition of the acids to allow a slow oxidation or to use a digestion block with two independent heating zones.

NOTE 3 The presence of small quantities of organic matter after digestion will not affect determination of the elements by ICP-AES and it is not necessary to apply additional organic matter removal.

NOTE 4 Alternatively, digestion by the use of microwave technique is possible if the user proves that the method gives the same results.

8.2 Sample pre-concentration

This procedure is necessary for liquid samples with low dry matter content in the case that the measurement method is not sufficiently sensitive. See Annex A for calculation of the initial sample mass to be taken for the pre-concentration step to achieve concentrations of the individual elements above the limit of quantification.

Weigh approximately 10 g to 50 g of the liquid sample, representing 1 g to 3 g of dry sample, to the nearest 0,001 g directly into the reaction vessel (7.2) and heat the vessel to approximately 75 °C to evaporate excessive water. After evaporation to approximately 5 ml and cooling, follow procedure 8.1. Adjustment of the pre-concentration step for different final volumes is given in Annex A.

Evaporation of a large volume of sample usually takes several hours. Higher temperature (up to 95 °C) for faster evaporation may be used if the final digest is not intended for the determination of mercury. The fastest evaporation can be achieved by using a 100ml to 250ml beaker or a similar vessel placed on a hot plate for evaporation and consequently also for digestion under a watch glass in the same vessel.

8.3 Blank test solution

Prepare a blank test solution following the same procedure as for samples. The measurement of a blank test solution is necessary to determine the contribution of the digesting solution, glassware and filter paper used.

9 Test report

The test report shall contain at least the following information:

- a) all information necessary for the complete identification of the sample;
- b) the Standard used (including its year of publication)
- c) test method used with reference to this document;
- d) date of sampling and sampling procedure (if known);
- e) date of the test;
- f) all operating details not specified in this document, or regarded as optional, together with details of any incidents that occurred when performing the method, which might have influenced the test result(s).

Annex A (informative)

Adjustment to different digestion procedures and measurement apparatuses

A.1 Adjustment of the procedure to different final volumes

Volumetric flasks or graduated plastic tubes for 150 ml, 100 ml, or 50 ml may be used for the final volume adjustment. In Table A.1 there are given recalculated parameters for the different final volumes.

Table A.1 – Recalculated parameters for different final volumes

V_F ml	V_{HNO_3} ml	V_{HCl} ml	m_{DM} g	V_{max} ml
150	7	21	1,5 to 3	6
100	4,7	14	1 to 2	4
50	2,3	7	0,5 to 1	2
V_F – final volume of a volumetric flask or a graduated plastic tube m_{DM} – mass of the sample recalculated to dry matter V_{max} – maximum volume after pre-concentration step (approximately)				

A.2 Calculation of the sample mass

A.2.1 General

According to the given legislative limits and the limits of quantification for the individual elements and the measurement apparatus, the mass of the sample should be adjusted to ensure that the concentration of the element in the final digest is above the limit of quantification). In practice the calculation of the mass of the sample is necessary only for cadmium. The lowest legislative limit for this element is 1,5 mg/kg. Recalculated limit for the digest (1 g sample (dry matter), final volume 50 ml) is 30 µg/l. A typical LOQ for an ICP-AES instrument is 7,5 µg/l.

A.2.2 Calculation of the mass of the sample (dry matter)

Calculation of the mass of the sample (dry matter) is given in Formula (1):

$$m_{DM} = LOQ \times V_F / L$$

(1)

where

- m_{DM} is the mass of the sample expressed as dry matter in g;
- LOQ is the limit of quantification for the given element, matrix and instrument expressed as a mass concentration in µg/l;
- V_F is the final volume of a volumetric flask or a graduated plastic tube in l;
- L is the legislative limit expressed as a mass fraction in mg/kg.

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A.2.3 Calculation of the mass of the sample for analysis

Calculation of the mass of the sample for analysis is given in Formula (2):

$$m_S = m_{DM} \times 100/w$$

(2)

where

m_S is the real sample mass in g;

w is the dry matter of the sample expressed as a mass fraction in %.

Example

Sample of organic fertilizer, $w = 8\%$.

The legislative limit for Cd is $1,5 \mu\text{g/g}$ and the LOQ for the individual apparatus and laboratory was $7,5 \mu\text{g/l}$. The final volume of the volumetric flask was 150 ml (0,15 l).

$$m_{DM} = 7,5 \times 0,15/1,5 = 0,75 \text{ g}$$

$$m_S = 0,75 \times 100/8 = 9,35 \text{ g}$$

The result: 9,35 g should be taken for the analysis of this sample. In practice, about 10 g of the sample will be taken for the analysis. After pre-concentration to approximately 5 ml to 6 ml and cooling, the sample will be digested and measured.

Bibliography

- [1] Regulation (EU) 2019/1009 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
- [2] EN 16174, *Sludge, treated biowaste and soil — Digestion of aqua regia soluble fractions of elements*
- [3] EN ISO 54321, *Soil, treated biowaste, sludge and waste — Digestion of aqua regia soluble fractions of elements (ISO 54321)*
- [4] EN 16317, *Fertilizers and liming materials — Determination of arsenic by inductively coupled plasma-atomic emission spectrometry (ICP-AES) after aqua regia dissolution*
- [5] EN 16319, *Fertilizers and liming materials — Determination of cadmium, chromium, lead and nickel by inductively coupled plasma-atomic emission spectrometry (ICP-AES) after aqua regia dissolution*
- [6] EN 16320, *Fertilizers and liming materials — Determination of mercury by vapour generation (VG) after aqua regia dissolution*
- [7] EN 16964, *Fertilizers — Extraction of total micro-nutrients in fertilizers using aqua regia*
- [8] EN 13650, *Soil improvers and growing media — Extraction of aqua regia soluble elements*
- [9] FprEN 17701-1, *Plant biostimulants – Determination of specific elements – Part 1: Digestion by aqua regia for subsequent determination of elements*
- [10] CEN/TS 17769, *Organic and organo-mineral fertilizers — Determination of the mercury content*
- [11] CEN/TS 17770, *Organic and organo-mineral fertilizers — Determination of the total content of specific elements by ICP-AES after digestion by aqua regia*