Organic and organo-mineral fertilizers —

Determination of the total content of specific elements by ICP-AES after digestion by aqua regia

ICS:

prEN 17770 (E)

Contents

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European foreword

This document (CEN/prEN 17770) 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 CEN/TS 17770:2022 (N413). 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 digestion and reference to dry matter content determination added and deleted from Bibliography.
Terms and definitions revised and completed
Chapter concerning reagents widened to include information about measures avoiding contamination by boron.
Chapter 8.1 completely redrafted.
Editorial changes including N394, and changes demanded for FprEN 17701-1 were included
Calculation – editorial changes included, UNI comment applied – the formula changed to be universal for all possible calculations (dry matter, in samples as received, in mg/kg, or in %)
Test report revised
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".

This document concerns the analytical measurement step. Aqua regia digestion followed by inductively coupled plasma atomic emission spectrometry (ICP-AES) is widely used for determination of many elements. For example, a multi-matrix standard for aqua regia extraction of soils, sludges and biowaste [2] and soil [3], water [4]. 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 [5] and for determination of micronutrients in mineral fertilizers [6]. Inductively coupled plasma atomic emission spectrometry (ICP-AES) is nowadays widely used and a well-established method in many laboratories. CEN/TC 455 published a standard for a similar procedure for plant biostimulants [7]. Inductively coupled plasma atomic emission spectrometry (ICP-AES) is nowadays widely used and a well-established method in many laboratories.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is often called also inductively coupled plasma optical emission spectrometry (ICP-OES). Both these terms are synonyms for the same analytical technique.

The inter-laboratory study reflects the final statistical characteristics of the method for the determination of the specific elements in aqua regia digests including both, the digestion and the measurement steps.

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 document specifies a method for the 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), phosphorus (P), potassium (K), magnesium (Mg), calcium (Ca), sulphur (S) and sodium (Na) in aqua regia digests of organic, organo-mineral fertilizers, and their blends using inductively coupled plasma-atomic emission spectrometry (ICP-AES).

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).

This method is applicable to aqua regia digests prepared according to prEN17768[1]. The method can be used for the determination of other elements, provided the user has verified the applicability.

NOTE 1   Alternatively, inductively coupled plasma mass spectrometry (ICP-MS) may be used for the determination of the elements in the aqua regia digests if the user proves that the method gives the same results.

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.

prEN 17768:[2], *Organic and organo-mineral fertilizers – Digestion by aqua regia for subsequent determination of elements*

prEN 17773[3], *Organic and organo- mineral fertilizers - — Determination of the dry matter* content

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

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

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

IEC Electropedia: available at https://www.electropedia.org

3.1
analyte
parameter to be determined

3.2
blank calibration solution
solution prepared in the same way as the calibration solution but leaving out the analytes

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[1] Under preparation

[2] Under preparation

[3] Under preparation

3.3
blank test solution
solution prepared in the same way as the test sample solution but omitting the test portion

3.4
calibration solution
solution used to calibrate the instrument, prepared from stock solutions by adding acids, buffer, reference element and salts as needed

3.5
digest
solution received after mineralization of the organic matter of a sample and dissolution of its mineral part, more or less completely, when reacting with a reagent mixture

3.6
stock solution
solution with accurately known analyte concentration(s), prepared from pure chemicals

3.7
test sample solution
solution prepared after extraction or digestion of the test sample according to appropriate specifications

4   Principle

The method is based on the inductively coupled plasma atomic emission spectrometry (ICP-AES) measurement of the concentration of elements in the digests of organic fertilizers and organo-mineral fertilizers and their blends The elements are determined after an appropriate dilution of the digest, 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

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 can 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

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. All solutions should be stored in clean boron-free vessels to avoid contamination during storage.

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   Nitric acid, $c(HNO_3) \approx 14{,}3$ mol/l, $\rho \approx 1{,}4$ g/ml**.**

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

Add 350 ml of nitric acid (6.2) to 600 ml of water (6.1) and fill up to 1 000 ml with water (6.1).

6.3   Hydrochloric acid, $c(HCl) \approx 12$ mol/l, $\rho \approx 1{,}18$ 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) consecutively to 600 ml of water (6.1) and fill up to 1 000 ml with water (6.1).

6.5   Single element standard stock solutions, ρ = 10 000 mg/l of Ca, K , P and S

Single-element stock solutions with adequate specification, stating the acid used and the preparation technique, are commercially available. 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 elements or their suitable compounds.

6.6   Single element standard stock solutions, ρ = 1 000 mg/l

For Ca, K, and P pipette 10 ml each of the single 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.

For the other elements single-element stock solutions and multi-element stock solutions with adequate specification, stating the acid used and the preparation technique, are commercially available. 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 elements or their suitable compounds.

6.6.1   Multielement standard stock solution A, ρ = 100 mg/l of As, Co, Mo and Ni

Use commercially available solution of this concentration for each element or pipette 10 ml of the appropriate element stock solution (6.6) 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.

6.6.2   Multielement standard stock solution B, ρ = 100 mg/l of B, Cr, Cu, Fe, Mn, Pb and Zn.

Use commercially available solution of this concentration for each element or pipette 10 ml of the appropriate element stock solution (6.6) 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.

6.6.3   Standard solution for Cd, ρ = 10 mg/l

Pipette 1 ml of standard solution (6.6.) 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.

6.7   Argon, purity 99,995 % or better.

7   Apparatus

7.1   Common laboratory glass and plastic ware.

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 shall be used. Glass volumetric flasks may be used for making up to volume but not for storage of digests, reagents, and solutions.

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 digests 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 solution is prepared for the measurement following the same procedure as for test sample solutions.

If dilution is necessary, dilute an aliquot portion of the aqua regia digest 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 test solution by pipetting a blank test solution and dilute in the same way as the test sample solution.

8.2 Preparation of the calibration solutions

For aqua regia digests three sets of calibration solutions are recommended. The first containing arsenic, cadmium, copper, chromium, lead, nickel, zinc, boron, cobalt, iron, manganese and molybdenum. The second containing phosphorus, potassium, magnesium, calcium and sodium, and the third only for sulphur. The concentrations of the suggested calibration solutions are given in Table 1.

Set 1: Pipette volumes of 0 ml, 0,5 ml, 1 ml, 2 ml, and 5 ml of the multielement standard stock solution A (6.6.1) into the five 100ml volumetric flasks. Add 0 ml, 1 ml, 2 ml, 5 ml, and 10 ml of the multielement standard stock solution B (6.6.2) into the same five 100ml volumetric flasks. Finally add to the same volumetric flasks 0 ml, 0,5 ml, 1 ml, 2 ml, and 5 ml of the standard solution for cadmium (6.6.3). Fill the volumetric flasks to the mark with the mixed acid solution (6.4) and mix well.

Set 2: Prepare five 100ml volumetric flasks for this calibration set. Pipette 0 ml, 2 ml, 5 ml of the single element stock solutions (6.6) for calcium, potassium, and phosphorus into the three volumetric flasks. Pipette 1 ml, and 2,5 ml of the single element stock solutions (6.5) for calcium, potassium, and phosphorus into the remaining two100ml volumetric flasks. Pipette into the five volumetric flasks 0 ml, 1 ml, 2 ml, 5 ml, and 10 ml of the single element stock solution (6.6) of magnesium and finally add to the same volumetric flasks 0 ml, 0,5 ml, 1 ml, 2 ml, and 5 ml single element stock solution (6.6) of sodium. Fill the volumetric flasks to the mark with the mixed acid solution (6.4) and mix well.

Set 3: Pipette 0 ml, 2 ml, 5 ml, 10 ml, and 25 ml single element stock solution (6.5) of sulphur into the five 100ml volumetric flasks. Fill the volumetric flasks to the mark with the mixed acid solution (6.4) and mix well.

Different mixed calibration solutions or individual sets of calibration solutions for each element may be used. If necessary, calibration solutions of higher or lower concentrations than given in Table 1 may be prepared.

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

NOTE 2   It is possible to calibrate the instrument for higher concentrations of the elements than given in Table 1 if the calibration curve is linear.

NOTE 3   Many samples may have relatively high concentration of iron. In this case calibration solutions for iron may be added to the calibration set 2 in the same concentrations as calcium, potassium and phosphorus.

Table 1 — Suggested calibration standards. Concentrations in mg/l.

Calibration solutions	SET 1			SET 2			SET 3
	Cd	Ni, As, Co, Mo	B, Pb, Cr, Cu, Zn, Mn, Fe	Ca, K, P	Mg	Na	S
1	0	0	0	0	0	0	0
2	0,05	0,5	1,0	20	10	5	20
3	0,1	1,0	2,0	50	20	10	50
4	0,2	2,0	5,0	100	50	20	100
5	0,5	5,0	10,0	250	100	50	250

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.

Higher RF power (>1300 W) is preferable because it can very effectively remove some interferences.

The software of the instrument is used to calculate concentrations of the elements in the individual test solutions. All test sample solutions, blank test solutions 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 robustness, 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. Higher plasma power can minimize the matrix influence.

Spectral lines which are free of interference by other elements shall be selected. Recommended wavelengths are given in Table 2. 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, organo-mineral fertilizers, and their blends of varying concentrations.

8.3.4   Measurement

The calibration blank and calibration solutions, calibration check solution (one of the calibration standard solutions used to check stability of the calibration during the measurement), blank test solution, test sample solutions and quality control solutions are measured after stabilization of the instrument and verification of the stable conditions. The instrument is calibrated using all three sets of the calibration solutions (8.2). All elements are determined first in the undiluted sample digests followed by the determination of the elements in the diluted sample digests. The dilution should ensure that the concentrations of the elements exceeding the calibration range in the undiluted digests will be in the calibration range after dilution. 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.

NOTE 4   For most samples 10 times dilution is sufficient. Number 3 calibration solutions (see Table 1) from all three sets of calibration solutions are suitable as check calibration solutions.

8.3.5   Matrix effects

Whenever an unknown matrix is encountered, check the following:

— matrix effects by running the spiked test sample solution;

— matrix effects by running a fivefold diluted test sample solution;

— matrix effects by analysing at a different wavelength.

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

8.3.6 Spiking

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

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.

EXAMPLE   Spiking procedure: pipette 10 ml of a test sample solution or diluted digest into two test tubes, add 0,1 ml of multielement standard stock solutions A (6.6.1) or B (6.6.2) or from the standard solution (6.6.3) into the first test tube and 0,1 ml of blank test solution into the second test tube. Mix well and measure. To achieve a higher concentration of an element by spiking, stock solutions of higher concentration may be used.

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 2 — Recommended wavelengths

Element	Wavelength [nm]	Interfering elements
As	193,696	Fe, Al, Mo
	189,042	Al, La
B	249,773	Fe
	208,959	Al, Mo
	249,678	
Ca	422,673	
	183,801	
Cd	214,438	Fe
	228,802	As, Fe, Co, Cs
Co	228,616	Ti
Cu	324,754	Ti, Fe
	327,396	Co
Cr	267,716	Mn, V
	205,552	Fe, Mo
	357,869	V, As
Fe	259,941	Co
	238,204	
K	766,491	
Mg	285,213	
	279,553	
Mo	202,030	Al, Fe
	202,095	
Mn	259,373	Fe
	257,610	Fe, Mo, Cr

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	293,306	Al, Fe
Na	589,592	
Ni	221,648	Fe, Co, Si
	231,604	Co, Fe
	216,560	Fe, Mn
P	177,495	Cu
	178,287	
	214,914	
Pb	168,215	C
	220,353	Al, Co, Ti
	283,306	Fe
S	182,034	
	180,731	Ca
Zn	213,856	Cu, Ni, Fe
	206,191	Cr

NOTE   Alternative wavelengths may be used.

9   Calculation and expression of the results

Calculate the content of an element in the sample w_X, as a mass fraction in mg/kg or % (mass/mass) according to Formula (1). The results can be expressed in the sample as received or recalculated on dry matter basis.

$$w_X = \frac{V_{\text{dig}} \times (X_S - X_b)}{m \times F} \times D \times T \tag{1}$$

where

w_X is a mass fraction of the individual element, in mg/kg or % (mass/mass); expressed on dry matter basis or in sample as received;

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

X_S is the mass concentration of the test sample solution, in mg/l;

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

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

D is the dilution factor calculated according to Formula (2), if no dilution is applied, $D = 1$;

T is the factor for recalculation on dry matter basis calculated according to Formula (3), if the results are expressed in sample as received, $T=1$;

F is the factor for recalculation of the results. $F = 1$, the results are expressed in mg/kg, F = 10 000, the results are expressed in % (mass/mass);

$$D = \frac{V_1}{V_{p1}} \times \frac{V_2}{V_{p2}} \times \cdots \frac{V_n}{V_{pn}}$$ (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.

$$T = \frac{100}{w}$$ (3)

where

w is the dry matter content of the test sample expressed as a mass fraction in percent determined according to EN 17773[4];

10 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 method used for preparation of the digest;

c)   the Standard used (including its year of publication)

d)   the test method used with reference to this document;

e)   the test results obtained;

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

g)   date when the analysis was finished;

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).

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[4] Under preparation

Annex A
(informative)

Results of the inter-laboratory study

To be included

A.1 Inter-laboratory tests

The precision of the method has been determined in an inter-laboratory study (ILS) with xx participating laboratories from xx EU countries using eight different samples.

The samples were chosen to represent all typical organic and organo-mineral fertilizers available on the market. The concentrations of the elements in the samples were very low (usually below LOQ). Therefore, spiking was necessary to achieve measurable concentrations of the elements.

xx different sample materials (x solid and x liquid, x of them blends) were included in the ILS. A detailed description of the materials is given in Table A1.

Table A.1 – Samples selected for the interlaboratory study

Sample ID	Sample type

A.2 Statistical results for the determination of elements

Statistical evaluation was carried out using a validated software for ILS (ÚKZÚZ) based on the mathematical algorithms prescribed by ISO 5725-2 "Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method"[8]. The ILS reflects the final statistical characteristics of the method for the determination of the specific elements in aqua regia digests including both, the digestion and the measurement steps. The results are summarized in Table A.2 to Table A.8.

Based on the statistical evaluation of the results from the collaborative trial, it is concluded that the proposed method is suitable for the 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), phosphorus (P), potassium (K), magnesium (Mg), calcium (Ca), sulphur (S) and sodium (Na) in aqua regia digests by ICP-AES after digestion of the samples by hot aqua regia in organic and organo-mineral fertilizers and their blends.

Table A.2– Determination of arsenic

Sample	AR-S-1	AR-S-2	AR-S-3	AR-S-4	AR-S-5	AR-S-6	AR-S-7	AR-S-8
L								
L_A								
N								
N_A								
O								
$\bar{\bar{x}}$								
s_R								
s_r								
RSD_R								
RSD_r								
R								
r								
$HorRat$								

L	Number of participating laboratories
L_A	Number of laboratories after elimination of outliers
N	Number of all analytical values
N_A	Number of analytical values after rejection of outliers
O	Percentage of outliers (%)
$\bar{\bar{x}}$	Total mean of results (without outliers) (mg/kg)
s_R	Reproducibility standard deviation (mg/kg)
s_r	Repeatability standard deviation (mg/kg)
RSD_R	Relative reproducibility standard deviation (%)
RSD_r	Relative repeatability standard deviation (%)
R	Reproducibility limit (2,77 s_R) (mg/kg)
r	Repeatability limit (2,77 s_r) (mg/kg)
$HorRat$	HorRat index

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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 16170, *Sludge, treated biowaste and soil – Determination of elements using inductively coupled plasma optical emission spectrometry (ICP-OES)*

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

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

[5]   EN 16319:2013+A1, *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 16963, *Fertilizers – Determination of boron, cobalt, copper, iron, manganese, molybdenum and zinc using ICP-AES*

[7]   FprEN 17701-2, *Plant biostimulants – Determination of specific elements – Part 2: Determination of total content od Cd, Pb, Ni, As, Cr, Cu and Zn*

[8]   ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*