

SLOVENSKI STANDARD
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Nadomešča:
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Gnojila in sredstva za apnjenje - Določevanje živega srebra s tehniko hladnih par po raztapljanju v zlatotopki (vključno z dopolnilom A1)

Fertilizers and liming materials - Determination of mercury by vapour generation (VG) after aqua regia dissolution

Düngemittel und Kalkdünger - Bestimmung von Quecksilber mit Verdampfungstechnik (VG) nach Königswasseraufschluss

Engrais et amendements minéraux basiques - Détermination du mercure par génération de vapeur (VG) après digestion à l'eau régale

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ICS:

65.080	Gnojila	Fertilizers
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EUROPEAN STANDARD
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English Version

Fertilizers and liming materials - Determination of mercury by vapour generation (VG) after aqua regia dissolution

Engrais et amendements minéraux basiques -
Détermination du mercure par génération de vapeur
(VG) après digestion à l'eau régale

Düngemittel und Kalkdünger - Bestimmung von
Quecksilber mit Verdampfungstechnik (VG) nach
Königswasseraufschluss

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COMITÉ EUROPÉEN DE NORMALISATION
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European foreword

This document (EN 16320:2013+A1:2017) has been prepared by Technical Committee CEN/TC 260 "Fertilizers and liming materials", the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by August 2017, and conflicting national standards shall be withdrawn at the latest by August 2017.

This document includes Amendment 1 approved by CEN on 11 December 2016.

This document supersedes  EN 16320:2013 .

The start and finish of text introduced or altered by amendment is indicated in the text by tags  .

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EN 16320:2013+A1:2017 (E)

1 Scope

This European Standard specifies a method for the determination of the content of mercury in fertilizers ^{A1} and liming materials ^{A1} after extraction with aqua regia and the detection of mercury by vapour generation (VG) coupled to an atomic absorption spectrometer or an inductively coupled plasma-atomic emission spectrometer. A limit of quantification of 0,01 mg/kg is to be expected.

^{A1} NOTE The term fertilizer is used throughout the body of this European Standard and includes liming materials unless otherwise indicated. ^{A1}

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

EN 12944-1:1999, *Fertilizers and liming materials and soil improvers - Vocabulary - Part 1: General terms*

EN 12944-2:1999, *Fertilizers and liming materials and soil improvers - Vocabulary - Part 2: Terms relating to fertilizers*

^{A1} EN 12944-3:2001, *Fertilizers and liming materials and soil improvers — Vocabulary — Part 3: Terms relating to liming materials* ^{A1}

EN ISO 3696, *Water for analytical laboratory use — Specification and test methods (ISO 3696)*

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3 Terms and definitions

<https://standards.iteh.ai/catalog/standards/sist/ce573365-c0e9-45fb-a1eb-677e8b2d876e/sist-en-16320-2013a1-2017>

For the purposes of this document, the terms and definitions given in EN 12944-1:1999 and EN 12944-2:1999 and ^{A1} EN 12944-3:2001 ^{A1} apply.

4 Principle

Mercury is extracted from the sample with aqua regia and conventional boiling. The concentration of mercury in the extract is measured by (cold) vapour generation (VG) coupled to a suitable detector, such as an atomic absorption spectrometer (AAS) or an inductively coupled plasma-atomic emission spectrometer (ICP-AES).

5 Sampling and sample preparation

Sampling is not part of the method specified in this European Standard. A recommended sampling method is given in EN 1482-1.

Sample preparation shall be carried out in accordance with EN 1482-2.

6 Reagents

Use only reagents of recognized analytical grade.

Commercially available stock solutions shall be replaced according to the specifications from the supplier or after one year if prepared in the laboratory from available salts. Standard solutions shall be renewed monthly as a general rule.

6.1 Water, conforming to grade 2 of EN ISO 3696.

6.2 Hydrochloric acid, $c(\text{HCl}) = 12 \text{ mol/l}$; 37 % volume fraction; ρ approximately 1,18 g/ml.

6.3 Nitric acid, $c(\text{HNO}_3) = 16 \text{ mol/l}$; not less than 65 % volume fraction, ρ approximately 1,42 g/ml.

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

Mix 150 ml of hydrochloric acid (6.2) and 50 ml nitric acid (6.3) to 1,0 l of water (6.1).

6.5 Standard stock solution, mercury standard stock solution, e.g. $\rho = 1\ 000 \text{ mg/l}$.

Use suitable stock solutions. Single-element stock solutions with adequate specification stating the acid used and the preparation technique are commercially available. It is recommended to use commercially available standard stock solutions for mercury.

6.6 Working standard solutions.

Depending on the scope, different working standard solutions may be necessary. In general, the stability of mercury working standard solutions should be checked.

6.6.1 Working standard solution I, $\rho = 10 \text{ mg/l}$ for mercury.

Dilute 1,00 ml of the standard stock solution for mercury (6.5) to 100,0 ml with the mixed acid solution (6.4). This solution is used to prepare 200 $\mu\text{g/l}$ mercury working standard solution.

6.6.2 Working standard solution II, $\rho = 200 \mu\text{g/l}$ for mercury.

Dilute 2,00 ml of the 10 mg/l mercury working standard solution I (6.6.1) to 100,0 ml with the mixed acid solution (6.4). This solution is used to prepare spiked test solutions and calibration solutions.

6.7 Reducing agents.

6.7.1 General.

Tin(II) chloride or sodium borohydride may be used as the reducing agent, but it is not advisable to use the two reagents alternately. Observe the instructions of the manufacturers of the apparatus. The concentration by mass of the reducing agent solutions may be varied to suit the system, and the relevant information provided by the manufacturer of the apparatus shall be observed.

6.7.2 Tin(II) chloride solution, $\rho(\text{SnCl}_2 \cdot 2\text{H}_2\text{O}) = 100 \text{ g/l}$.

Dissolve 50 g of tin(II) chloride in approximately 100 ml of hydrochloric acid (6.2) in a 500 ml volumetric flask and dilute to the mark. Prepare a fresh solution daily.

EN 16320:2013+A1:2017 (E)**6.7.3 Sodium borohydride solution**, e.g. $\rho = 2 \text{ g/l}$.

Dissolve 2 g of sodium hydroxide pellets in water, add 2 g of sodium borohydride and dilute to 1 000 ml with water (6.1). Prepare a fresh solution daily and, when necessary, filter before use. When the analysis procedure is of a longer time, it is recommended to cool the sodium borohydride solution (i.e. with ice around the flask) during its use in the vapour generation ICP-AES or AAS measurement.

WARNING — It is essential to observe the safety instructions for working with sodium borohydride. Sodium borohydride forms hydrogen with acids and this can result in an explosive air/hydrogen mixture. A permanent extraction system shall be provided at the point where measurements are carried out.

7 Apparatus**7.1 Common laboratory glassware.**

7.2 Analytical balance, capable of weighing to an accuracy of 1 mg.

7.3 Inductively coupled plasma-atomic emission spectrometer, with axial or radial viewing of the plasma and with suitable background correction.

The settings of the working conditions (e.g. gas flows, RF or plasma power, sample uptake rate, integration time, number of replicates) shall be optimized according the manufacturer's instructions. Radial viewing of the plasma may be used if it can be shown that the limit of quantification for mercury is below the required legal limit value.

7.4 Atomic absorption spectrometer, equipped with a heated quartz cuvette or a mercury absorption cell, or optionally with an amalgamation system.

7.5 Vapour generation equipment.

7.5.1 Continuous flow or flow-injection cold-vapour system.

7.5.2 Element-specific lamp for mercury.

7.6 Dilutor.

Instrument used for automated volumetric dilutions or other appropriate equipment (e.g. pipettes and volumetric glassware) to perform dilutions. The precision and accuracy of this type of equipment for volumetric dilutions shall be established, and controlled and documented regularly.

7.7 Ash-free filter paper, i.e. Whatman 589/2¹⁾ or equivalent quality.

¹⁾ Whatman 589/2[®] is an example of a suitable product available commercially. This Information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product. Equivalent products may be used if they can be shown to lead to the same results.

8 Procedure

8.1 General

Calibrations by standard additions with several standards or by matrix matching are very powerful calibration techniques and can be used to accurately correct for matrix effects from easy-ionisable elements (multiplicative matrix effects). Additive matrix effects (i.e. spectral interferences) are not corrected for with standard additions calibration. For matrix matching, additive matrix effects will be corrected for when the added matrix is the cause of the matrix effect. The main drawback of calibration by standard addition with several standards is the requirement for a calibration function for each sample type, which is a time consuming process. For matrix matching, a profound knowledge of the sample matrix is needed, which is not always necessarily available. These two techniques may thus not be practical to use in routine fertilizer laboratories.

It is therefore suggested that calibrations are to be performed by means of external calibration and correction of matrix effects by addition of one known spike of a standard solution (spike recovery). The method of external calibration and correction for spike recovery allows for the analysis of fertilizers with unknown matrix composition or with a matrix that cannot be easily imitated synthetically. This calibration technique may not be as precise as calibration by standard additions with several standards but the increased uncertainty is small compared to the total uncertainty of the method, if the total analyte concentration is in the linear working range after the spike and the added spike corresponds to at least a doubling of the analyte concentration. Many matrix errors can be compensated for by this procedure, if they are not additive (e.g. spectral interferences). Aliquots of the sample solution are analysed by the means of external calibration and then one aliquot is spiked with known concentrations of the analytes without changing the matrix of the sample solution. The calculated spike recovery is then used to correct the concentration calculated from the external calibration function. The concentration of the spikes shall be in the linear working range of the analytical detection technique used.

8.2 Preparation of the test solution

8.2.1 General

The following extraction procedure leads, in most cases for mineral fertilizers, to trace element results which correspond to the total contents of these elements.

Calibration with several standard additions and external calibration after matrix matching may also be used without any problems.

8.2.2 Preparation

8.2.2.1 Weigh ($3 \pm 0,003$) g of the prepared sample and transfer to a suitable reaction vessel (action 1).

8.2.2.2 Moisten the sample with about 0,5 ml to 1,0 ml of water (6.1) and add, whilst mixing, ($21 \pm 0,1$) ml of hydrochloric acid (6.2) followed by ($7 \pm 0,1$) ml of nitric acid (6.3), drop by drop if necessary to reduce foaming. Connect a condenser to the reaction vessel and let the mixture stand at room temperature until any effervescence almost ceases to allow for slow oxidation of any organic mass in the sample (action 2).

8.2.2.3 Transfer to the heating device and raise the temperature of the reaction mixture slowly to reflux conditions. Maintain for 2 h, ensuring that the condensation zone is lower than 1/3 of the height of the condenser, then allow to cool. Rinse the condenser with further 10 ml of water (6.1) (action 3).

If the digested sample contains particulates which can clog nebulisers or interfere with the injection of the sample, the sample should be centrifuged and allowed to settle, or filtered before transferring into a