SLOVENSKI STANDARD
kSIST-TS FprCEN/TS 16320:2011

01-november-2011

Gnojila - Določevanje elementov v sledovih - Določevanje živega srebra s tvorbo pare po raztapljanju v zlatotopki

Fertilizers - Determination of trace elements - Determination of mercury by vapour generation (VG) after aqua regia dissolution

Düngemittel und Calcium-/Magnesium-Bodenverbesserungsmittel - Bestimmung von Elementspuren - Bestimmung von Quecksilber mit Verdampfungstechnik (VG) nach Königswasseraufschluss

Engrais - Dosage des éléments traces - Détermination du mercure par génération de vapeur (VG) après digestion à l'eau régale

Ta slovenski standard je istoveten z: FprCEN/TS 16320

ICS:

65.080	Gnojila	Fertilizers

kSIST-TS FprCEN/TS 16320:2011 en,fr,de

TECHNICAL SPECIFICATION
SPÉCIFICATION TECHNIQUE
TECHNISCHE SPEZIFIKATION

FINAL DRAFT
FprCEN/TS 16320

September 2011

ICS 65.080

English Version

Fertilizers - Determination of trace elements - Determination of mercury by vapour generation (VG) after aqua regia dissolution

Engrais - Dosage des éléments traces - Détermination du mercure par génération de vapeur (VG) après digestion à l'eau régale

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

This draft Technical Specification is submitted to CEN members for formal vote. It has been drawn up by the Technical Committee CEN/TC 260.

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Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Ref. No. FprCEN/TS 16320:2011: E

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Foreword

This document (FprCEN/TS 16320:2011) 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 the Formal Vote.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association.

1 Scope

This document specifies a method for the determination of the content of mercury in fertilizers after extraction with aqua regia and 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.

2 Normative references

The following referenced documents are indispensable for the application 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 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*

EN ISO 3696, *Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 12944-1:1999 and EN 12944-2:1999 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 methods specified in this Technical Specification. 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 supplier or after one year if prepared in the laboratory from available salts. Standard solutions shall be renewed monthly as a general rule of thumb.

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

6.2 Hydrochloric acid, c(HCl) = 12 mol/l; 37 % mass/volume; $\rho \approx$ 1,18 g/ml.

6.3 Nitric acid, $c(HNO_3)$ = 16 mol/l; not less than 65 % mass/volume, $\rho \approx$ 1,42 g/ml.

6.4 Mixed 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. ρ = 1 000 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, ρ = 10 mg/l for mercury.

Dilute 1,00 ml 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 µg/l mercury working standard solution.

6.6.2 Working standard solution II, ρ = 200 µg/l for mercury.

Dilute 2,00 ml 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, $\rho(SnCl_2 \cdot 2\,H_2O)$ = 100 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 every day.

6.7.3 Sodium borohydride solution, e.g. ρ = 2 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 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 optimised 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 589/2 or equivalent quality.

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 necessarily available. These two techniques may thus not be practical to use in routine fertilizer laboratories.

It is therefore suggested that calibration 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 synthetically imitated easily. 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 mean 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 with no problems.

8.2.2 Preparation

8.2.2.1 Weigh 3 g ± 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, with mixing, 21 ml ± 0,1 ml of hydrochloric acid (6.2) followed by 7 ml ± 0,1 ml of nitric acid (6.3) drop wise 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 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. Rinse the condenser with further with 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, allowed to settle, or filtered before transferring into a suitable sized volumetric flask. For example, the solution should be allowed to pass through the filter paper and then the insoluble residue washed onto the filter paper with a minimum of water (6.1). The method used has to be reported in the test report. Filter paper may cause contaminations (e.g. lead) and it may be necessary to use ash-free filter paper (7.7).

8.2.2.4 Transfer the digested sample into a 150 ml volumetric flask and dilute to the mark with water (6.1). This yields an acid concentration approximately equal to the mixed acid solution (6.4). This test solution corresponds to a 50 times dilution of the solid sample (action 4).

8.2.2.5 Test solutions are diluted with the mixed acid solution (6.4) using a dilutor (7.6) to obtain a concentration of mercury between 0,2 µg/l and 10 µg/l (action 5).

NOTE 1 It is important that the total dilution of the test solution is equal to the dilution of the spiked test solution (see 8.3 on how to prepare the spiked test solution).

NOTE The concentrations in the solutions in 8.2.2.5, action 5 are chosen such that they are above the typical limits of quantification, and that the concentrations fall within the linear working range of the analytical technique.

8.3 Preparation of the test solution for the correction of matrix effects by spike recovery

For each test solution analysed, a spiked test solution with a known addition of a standard solution is required to correct for matrix effects by correcting for the spike recovery measured under close to identical measurement conditions. The addition of a spike of the standard solution shall increase the analyte concentrations by at least 100 % without changing the matrix of the test solution (from 8.2.2.4, action 4) or the diluted test solution (from 8.2.2.5, action 5). See Example 1 and Example 2 below for suggestions on how to spike a diluted and an undiluted test solution, respectively when determining mercury.

EXAMPLE 1 If the test solution (from 8.2.2.4, action 4 or 8.2.2.5, action 5) contains 2,0-10 µg/l of mercury, spike addition corresponding to 2,0 µg/l of mercury is done while diluting the sample 5 times. Thus, taking 2,00 ml test solution and adding 0,100 ml 200 µg/l mercury working standard solution II (6.6.2) and 7,90 ml mixed acid solution (6.4). The test solution (from 8.2.2.4, action 4 or 8.2.2.5, action 5) shall also be 5 times diluted with the mixed acid solution (6.4) prior to analysis by vapour generation AAS/ICP-AES.