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Organska in organsko-mineralna gnojila - Določevanje anorganskega arzena

Organic and organo-mineral fertilizers - Determination of the inorganic arsenic content

Organische und organisch-mineralische Düngemittel - Bestimmung des Gehalts an anorganischem Arsen

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65.080

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**Organic and organo-mineral fertilizers - Determination of
the inorganic arsenic content**

Organische und organisch-mineralische Düngemittel -
Bestimmung des Gehalts an anorganischem Arsen

This draft Technical Specification is submitted to CEN members for 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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European foreword

This document (FprCEN/TS 17775) 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 Vote on TS.

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

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FprCEN/TS 17775:2021 (E)**Introduction**

This document describes a procedure of extraction and measurement for the determination of inorganic arsenic in organic or organo-mineral fertilizers. The standard is based on a mild acid oxidative extraction of the arsenic species followed by liquid chromatography (HPLC or IC) coupled to the element-specific detector ICP-MS for the determination of the mass fraction of iAs.

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1 Scope

This document specifies a method for extraction, separation, and determination of inorganic arsenic (iAs) in organic or organo-mineral fertilizers using anion-exchange HPLC or IC coupled to ICP-MS.

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

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:

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

4 Principle

This document describes a method for the determination of inorganic arsenic in organic or organo-mineral fertilizers. Inorganic arsenic consists of arsenite As (III) and arsenate, As (V). A representative test portion of the sample is treated with a diluted nitric acid and hydrogen peroxide solution in a heated water bath. By this means the sample is solubilised, arsenic species are extracted into solution and As (III) is oxidised to As (V). The inorganic arsenic is selectively separated from other arsenic compounds using anion exchange HPLC (High Performance Liquid Chromatography) coupled on-line to the element-specific detector ICP-MS (Inductively Coupled Plasma Mass Spectrometer) for the determination of the mass fraction of the inorganic arsenic. External calibration with solvent matrix-matched standards is used for the quantification of the amount of the inorganic arsenic. Alternatively, IC (ion chromatography) coupled to ICP-MS can be used.

A preliminary determination of the total arsenic in aqua regia extracts by ICP-AES (FprCEN/TS 00260233) could reduce the number of the samples where the determination of iAs is necessary because if the content of aqua regia (total) extractable arsenic is lower than the legislative limit for iAs then the determination of iAs is not necessary.

5 Sampling

Sampling should be performed carefully, following principle described in EN 1482 (all parts) with appropriate adaptations required account for specificities of organic and organo-mineral fertilizers.

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6 Reagents

6.1 General

When using a method of high sensitivity like ICP-MS, the control of the blank levels of water, acid and other reagents is very important. The reagents shall be of adequate purity and of recognized analytical grade. The concentration of arsenic species in the reagents and water used shall be negligible and low enough not to affect the results of the determination. Generally, ultra-pure water and nitric acid of minimum p.a. quality is recommended.

6.2 Nitric acid (HNO₃), concentrated, ≥ 65 % (mass fraction), mass concentration of approximately ρ (HNO₃) 1,4 g/ml.

Use only nitric acid available with high purity (minimum p.a. quality) in order to avoid potential contamination.

6.3 Hydrogen peroxide, H₂O₂ not less than 30 % (mass fraction).

High purity is essential to avoid potential contamination. Commercially available hydrogen peroxide for analysis should be tested for contamination of arsenic prior to use. It is necessary to prevent peroxide degradation and ensure the stability of the solution.

6.4 Extraction solution, 0,1 mol/l HNO₃ in 3 % (volume fraction) H₂O₂.

Add 6,5 ml of HNO₃ (6.2) and thereafter 100 ml of hydrogen peroxide (6.3) into 800 ml water in a 1 000 ml volumetric flask. Fill the flask to the mark with water. This solution is prepared on the day of use.

NOTE It is recommended that the total volume needed for the analysis is estimated and only this amount is produced in the day of use.

6.5 Ammonium carbonate, (NH₄)₂CO₃, mass fraction w ≥ 99,999 %, for preparation of the mobile phase solution.

6.6 Aqueous ammonia, (NH₃(aq)), mass fraction w ≥ 25 %, for adjustment of pH in the mobile phase.

6.7 Methanol, (CH₃OH), HPLC grade, for preparation of the mobile phase solution.

6.8 Mobile phase, e.g. 50 mmol/l ammonium carbonate in 3 % methanol at pH 10,3.

Dissolve 4,80 g of ammonium carbonate (6.5) in approximately 800 ml water. Adjust the pH to 10,3 with aqueous ammonia (6.6) and add 30 ml of methanol (6.7) and then fill up to 1 000 ml with water. Prior to use filter the mobile phase solution through a 0,45 μm filter using a filtering device (7.4).

The optimal concentration of ammonium carbonate in the mobile phase depends on the analytical column used (e.g. brand, particle size and dimensions) and should be verified in advance. The appropriate concentration of ammonium carbonate (usually between 10 mmol/l to 50 mmol/l) is highly dependent on the column used and is up to the discretion of the analyst. It should fulfil the criteria for sufficient resolution of the arsenate peak.

Methanol is added to the mobile phase in order to enhance the signal intensity for arsenic. The concentration of methanol to achieve the highest signal to noise ratio depends on the instrument used and should be identified by the analyst.

NOTE Different mobile phase can be also used according to the instructions of the manufacturer of the column but it is necessary to verify optimal separation conditions.

For example, Agilent column G3154-65001 with a guard column G3154-65002¹ and a recommended mobile phase for this column (dihydrogen potassium carbonate 2 mmol, EDTA 0,2 mmol, pH 6,0 adjusted with sodium hydroxide solution 1 mol) were successfully used for the analysis.

6.9 Arsenic (V) standard stock solution, with an arsenic (V) mass concentration of 1 000 mg/l.

The use of commercial standards of arsenic As (V), with a mass concentration of 1 000 mg/l is recommended.

6.10 Arsenic (V) standard solution I, with an arsenic (V) mass concentration of 10 mg/l in 2 % (volume fraction) HNO₃.

Pipette 1 ml of arsenic standard stock solution (6.9) into a 100 ml volumetric flask. Add 2 ml of nitric acid (6.2), fill to the mark with water and mix well. This solution is stable in a refrigerator at least one week.

6.11 Arsenic (V) standard solution II, with an arsenic (V) mass concentration of 1 mg/l.

Pipette 10 ml of arsenic standard solution I (6.10) into a 100 ml volumetric flask, fill to the mark with water and mix well. This solution should be prepared on the same day of use.

6.12 Solution for checking chromatographic separation, containing organic arsenic compounds (e.g. 10 µg/l) monomethylarsenous acid (MMA), dimethylarsinic acid (DMA) and arsenobetaine (AB), as well as arsenate (e.g. 10 µg/l) and chloride (e.g. 100 mg/l).

7 Apparatus

7.1 Common laboratory glass (plastic) ware.

Plastic volumetric flasks are recommended for the preparation of the mobile phase and calibration solutions. All glassware and plastic ware shall be adequately cleaned and stored to avoid any contamination, including Arsenic V contamination

7.2 Laboratory grinder, capable of grinding to a particle size less than 0,5 mm.

7.3 Analytical balance, capable of weighing to the nearest mg or better.

7.4 Filtering device, for filtration of mobile phase with a filter, pore size 0,45 µm.

7.5 Heated water bath, capable of maintaining 90 °C.

7.6 Centrifuge, for minimum 4 000 min⁻¹ (approx. 2 000 g).

7.7 Single use syringe filters (0,45 µm) or HPLC vials with filters, compatible with acidic solutions for filtering of test solutions prior to analysis.

7.8 High Pressure Liquid Chromatograph (HPLC).

7.9 Anion exchange column, suitable for the selective separation of arsenate from other arsenic compounds present in the sample extracts.

It is highly recommended to use a guard column to prolong the life-time of the analytical column.

¹ Agilent column G3154-65001 with a guard column G3154-65002 is an example of a suitable instruments available commercially. This information is given only as an example and does not constitute an endorsement by CEN of these products.

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Use of a different column and a different mobile phase is possible. The other columns may be used in combination with the suitable type of mobile phase depending on the recommendations of the manufacturer (see 6.8), e.g. IonPac® AS7, ICSep Ion120® and Hamilton PRP X-100®²

7.10 Inductively coupled plasma mass spectrometer (ICP-MS).

7.11 Argon gas, purity $\geq 99,99\%$.

8 Procedure**8.1 Sample preparation**

Solid samples are milled using a laboratory grinder (7.2) according to EN 1482-2:2007 and homogenized. Excessive heating during the sample pre-treatment should be avoided. Liquid samples are homogenized by thorough mixing before weighing the test portion.

8.2 Water bath extraction

Weigh a test portion of approximately 0,2 g to 0,6 g solid sample or an equivalent of liquid sample to the nearest milligram into an extraction tube and add to 10 ml of the extraction solution (6.4). The tubes shall be securely closed with a tight lid. Shake the tubes thoroughly in order to ensure that the sample is wetted sufficiently in the extraction solution (6.4) prior to placing it in the water bath in order to ensure a satisfactory extraction of the analyte.

The solutions are then placed into a heated shaking water bath (7.5) at $90\text{ °C} \pm 2\text{ °C}$ and extracted for $60\text{ min} \pm 5\text{ min}$.

Include also a reagent blank sample. A blank solution is prepared following the same procedure as for samples.

After extraction and cooling to room temperature the tubes are centrifuged for 10 min at $4\ 000\text{ min}^{-1}$ (approx. 2 000 g). The supernatant is transferred to clean plastic (PE or PP) tubes. Sample extracts should be filtered by a syringe filter (7.7) to clean HPLC vials prior to analysis. The sample extracts can be stored in a refrigerator (at approximately 4 °C) for a maximum of one week.

8.3 Preparation of the calibration solutions

The external calibration is used for quantification. Prepare a blank calibration solution and at least three calibration standard solutions in the linear range of calibration for inorganic arsenic (As V) by diluting the arsenic standard solution II of As (V) concentration 1 mg/l (6.11) with extraction solution (6.4). Concentrations of calibration standards 0, 25, 50 and 100 $\mu\text{g/l}$ are recommended. Transfer an aliquot of the calibration solutions to HPLC vials prior to analysis.

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

8.4 Measurement**8.4.1 General instrumental conditions**

The analytical procedure requires an adequate amount of experience in operating and optimizing the apparatus.

² IonPac® AS7, ICSep Ion120® and Hamilton PRP X-100® 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.