



SLOVENSKI STANDARD
SIST-TS CEN/TS 17778:2023

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Organska in organsko-mineralna gnojila - Določevanje kroma Cr(VI) s kromatografijo

Organic and organo-mineral fertilizers - Determination of the chromium (VI) content by chromatography

Organische und organisch-mineralische Düngemittel - Bestimmung des Gehalts an Chrom(VI) mittels Chromatographie

Engrais organiques et organo-minéraux - Détermination de la teneur en chrome(VI)

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**Organic and organo-mineral fertilizers - Determination of
the chromium (VI) content by chromatography**

Engrais organiques et organo-minéraux -
Détermination de la teneur en chrome(VI)

Organische und organisch-mineralische Düngemittel -
Bestimmung des Gehalts an Chrom (VI)

This Technical Specification (CEN/TS) was approved by CEN on 13 March 2022 for provisional application.

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CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels

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European foreword

This document (CEN/TS 17778:2022) has been prepared by Technical Committee CEN/TC 260 “Fertilizers and liming materials”, the secretariat of which is held by DIN.

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CEN/TS 17778:2022 (E)

Introduction

Regulation (EU) 2019/1009 [3] lays down the rules on the making available on the market of EU fertilizing products and the specific safety and quality requirements for the defined product function categories (PFCs). Organic and organo-mineral fertilizers have been classified as PFC 1(A) and PFC 1(B).

This document defines test methods for the determination of the chromium (VI) content to be used for organic and organo-mineral fertilizers in order to measure the compliance with the related requirement in the Regulation (EU) 2019/1009 [3].

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1 Scope

This document is applicable to fertilizing products, which are classified as PFC 1(A) and PFC 1(B) or the PFC 1(A) and PFC 1(B) component in PFC 7 of Regulation (EU) 2019/1009 [3]. However, the present method was not validated on blends.

This document specifies a method for the determination of hexavalent chromium (chromium (VI)) in organic and organo-mineral fertilizers.

The method described is suitable to quantify the chromium (VI) content in organic and organo-mineral fertilizers down to 2 mg/kg dry matter.

The results obtained from this method are strictly dependent on the extraction conditions. Results obtained by using other extraction procedures (extraction solution, pH of the extraction solution, extraction time, extraction temperature, etc.) are not comparable with the results produced by the procedure described in this document.

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 ISO 3696:1995, *Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)*

CEN/TS 17773:2022, *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 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

Chromium (VI) content

amount of chromium (VI) in organic and organo-mineral fertilizers determined after extraction with an aqueous salt solution at pH 7,0 to pH 8,0.

Note 1 to entry: The chromium (VI) content is reported as chromium (VI) in milligrams per kilogram (mg/kg), expressed as the dry mass of the sample.

[SOURCE: EN ISO 17075-2:2017, 3.1, modified: “leather” is replaced by “organic and organo-mineral fertilizers” and “pH 7,0 to 8,0” is replaced by “pH 7,0 to pH 8,0”]

4 Principle

Extractable chromium (VI) is leached from the sample in phosphate buffer at pH 7,0 to pH 8,0. An aliquot of the filtered extract is analysed for chromium (VI) using ion-exchange chromatography with UV-VIS detection.

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5 Reagents

All reagents used shall have at least analytical grade.

5.1 Extraction solution

Dissolve 22,8 g dipotassium hydrogen phosphate $K_2HPO_4 \cdot 3H_2O$ in 1 000 ml water (5.7), adjusted to $pH 8,0 \pm pH 0,1$ with phosphoric acid (5.2). Degas this solution with either argon or nitrogen (5.6) or ultrasonic bath.

Standard practice is to make up a fresh solution each day. However, the solution may be kept for up to one week in a refrigerator at $(4 \pm 3) ^\circ C$ but shall be warmed to room temperature and degassed prior to use.

5.2 Phosphoric acid solution

700 ml *o*-phosphoric acid, density $\rho = 1,71$ g/ml, made up to 1 000 ml with water (5.7).

First add approximately 200 ml of deionised water (5.7) to a 1 000 ml volumetric flask, then add the 700 ml of *o*-phosphoric acid and dilute to the mark with deionised water.

5.3 Potassium dichromate ($K_2Cr_2O_7$), dried for (16 ± 2) h at $(105 \pm 2) ^\circ C$.

5.4 Chromium(VI) stock solution

Dissolve 2,829 g potassium dichromate ($K_2Cr_2O_7$) (5.3) in water (5.7) in a volumetric flask and make up to 1 000 ml with water (5.7). 1 ml of this solution contains 1 mg of chromium.

A stock solution at this concentration level of hexavalent chromium is an alternative available commercially.

5.5 Chromium(VI) standard solution

Pipette 1 ml of solution (5.4) into a 1 000 ml volumetric flask and make up to the mark with extraction solution (5.1). 1 ml of this solution contains 1 μg of chromium.

The solution may be kept for up to one week in a refrigerator at $(4 \pm 3) ^\circ C$ but shall be warmed to room temperature prior to use.

A stock solution of hexavalent chromium at this concentration level is an alternative available commercially.

5.6 Argon or nitrogen, oxygen-free

Preference should be given to argon as an inert gas instead of nitrogen because argon has a higher specific mass than air.

5.7 Distilled or deionised water, Grade 3 quality as specified in EN ISO 3696:1995.

6 Apparatus

Usual laboratory equipment and, in particular, the following.

6.1 Suitable mechanical orbital shaker, $(100 \pm 10) \text{ min}^{-1}$.

6.2 Conical flask, of capacity 250 ml, with stopper.

6.3 Aeration tube and flow meter, suitable for a flow rate of $(50 \pm 10) \text{ ml/min}$.

6.4 pH meter, with glass electrode.

6.5 Membrane filter, 0,45 µm pore size [polytetrafluoroethylene (PTFE) or polyamide 66].

6.6 Common laboratory glassware and pipettes.

6.7 Vacuum device, suitable for filtration of extraction solution, mobile phase, and sample extracts.

6.8 Ion-exchange chromatograph, with UV detector or high-performance liquid chromatography (HPLC) with anion-exchange column and UV detector. A photo diode array detector (DAD) is recommended.

6.9 Analytical balance, capable of weighing to 0,1 mg.

6.10 Syringe membrane filters of nylon, 0,45 µm pore size, for filtration of standards.

6.11 Suitable vials for HPLC.

7 Procedure

7.1 Sampling and sample preparation

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

Details about the sampling and sample preparation shall be given in the test report.

7.2 Preparation of analytical solution

7.2.1 Solid samples

The operator shall weigh (6.9) approximately ($2 \pm 0,1$) g of sample of organic or organo-mineral fertilizer to the nearest 0,001 g.

Following tasks shall be performed:

- Pipette 100 ml (V_0) of degassed solution (5.1) into a 250 ml conical flask (6.2). Displace oxygen by passing oxygen-free argon (or nitrogen) (5.6) into the flask for 5 min with a volume flow of (50 ± 10) ml/min. Remove the aeration tube (6.3), add the sample and close the flask with a stopper.
- Shake the conical flask with the sample for (180 ± 5) min on a mechanical orbital shaker at (100 ± 10) min^{-1} (6.1) at room temperature to extract the chromium (VI).
- Shake the suspension in a smooth circular movement to keep the sample from adhering to the wall of the flask and avoid shaking faster than specified.
- Immediately after completing the 3 h of extraction, filter the contents of the conical flask through a membrane filter into a glass or plastic vessel with lid. Check the pH of the solution. The pH of the solution shall be between 7,0 and 8,0. If the pH of the solution is not within this range, start the complete procedure again. Consider using a smaller sample mass, if the pH is not between 7,0 and 8,0.
- Transfer an aliquot of the filtered extract into a vial (6.11). Instrumental determination of chromium (VI) should be performed as soon as possible and no later than 60 min after the extraction phase to avoid risks of reduction.

CEN/TS 17778:2022 (E)**7.2.2 Liquid samples**

The operator shall weigh (6.9) approximately $(10 \pm 0,1)$ g of sample of organic or organo-mineral fertilizer to the nearest 0,001 g.

The following tasks shall be performed:

- Pipette 100 ml of degassed solution (5.1) into a 250 ml conical flask (6.2). Displace oxygen by passing oxygen-free argon (or nitrogen) (5.6) into the flask for 5 min with a volume flow of (50 ± 10) ml/min. Remove the aeration tube (6.3), add the sample and close the flask with a stopper. Record the extract volume as V_0 (100 ml + sample volume in ml).
- Shake the conical flask with the sample for (10 ± 1) min on a mechanical orbital shaker at (100 ± 10) min⁻¹ (6.1) at room temperature to extract the chromium (VI).
- Shake the suspension in a smooth circular movement to keep the sample from adhering to the wall of the flask and avoid shaking faster than specified.
- Immediately after completing the 10 min of extraction, filter the contents of the conical flask through a membrane filter into a glass or plastic vessel with lid. Check the pH of the solution. The pH of the solution shall be between 7,0 and 8,0. If the pH of the solution is not within this range, start the complete procedure again. Consider using a smaller sample mass, if the pH is not between 7,0 and 8,0.
- Transfer an aliquot of the filtered extract into a vial (6.11). Instrumental determination of chromium (VI) should be performed as soon as possible and no later than 60 min after the extraction phase to avoid risks of reduction.

7.3 Chromatographic conditions

Determination of chromium (VI) is performed using the ion chromatographic technique. As the instrumental equipment of the laboratories can vary, no specific applicable instructions can be provided for analysis. However, the operating parameters and examples of the ion chromatographic analysis for chromium (VI) listed in Annex A and Annex B have been successfully tested and used. Annex A determines chromium (VI) by direct detection of chromate peak at 372 nm. Annex B determines chromium (VI) after a post-column reaction with 1,5-diphenylcarbazide by measuring the absorption peak at 540 nm.

The method used should be verified using the recovery rate determination (7.5).

Record the injection volume as V_M and record the area of the chromate peak as A .

7.4 Calibration

The content of chromium (VI) in the sample of organic or organo-mineral fertilizer is determined with an external standard calibration.

The operator shall prepare calibration solutions from the standard solution (5.5). The chromium (VI) concentration in these solutions should cover the expected range of measurement.

The following tasks shall be performed:

- Plot a suitable calibration curve by using at least five standards, within the range 1 ml to 25 ml of standard solution (5.5). Pipette the given volumes of standard solution (5.5) into 25 ml volumetric flasks. Make up to volume with the extraction solution (5.1), mix well, filter (6.10) and transfer a suitable aliquot volume into a vial (6.11).
- Prepare calibration levels as specified in Table 1.

Table 1 — Calibration levels preparation

Volume of the standard solution (5.5) (ml)	0,50 to 1,25	1,00 to 2,50	2,00 to 5,00	3,00 to 12,50	5,00 to 25,00
Final volume (ml)	10 to 25 in volumetric flask				
Concentration of chromium (VI) ($\mu\text{g/l}$)	50	100	200	300 to 500	500 to 1 000

- Transfer an aliquot to a suitable vial (6.11) corresponding for the chromatographic system (6.8).
- Inject the standards in the chromatographic system (6.8). Introduce the same volume for each standard. It is recommended to inject equal volume for samples. Record the volume injected as V_c in μl .
- Plot the chromium (VI) concentrations in micrograms of chromium per milliliter ($\mu\text{g/ml}$) against the measured areas of the peaks of chromate. Plot the chromium (VI) concentration on the x-axis and the area on the y-axis.

7.5 Determination of the recovery rate

The determination of the recovery rate is important to provide information about possible matrix effects which can influence the results.

The operator shall spike an aliquot of the solution obtained in 7.2 with a suitable volume of chromium (VI) solution to increase the chromium (VI) concentration by 10 mg/kg.

The following tasks shall be performed:

- Inject the same volume of this solution as the volume injected in the calibration (recording the area as A_s).
- Spike an aliquot of the extraction solution (the same volume as that taken before of the solution obtained in 7.2) with a suitable volume of chromium (VI) solution to increase the chromium (VI) concentration by 10 mg/kg, so that the final volume of this solution is the same as that of the above spiked solution with chromium (VI) solution. Inject the same volume of this solution as the volume injected in the calibration (recording the area as A_{st}).

The area of the chromate peak of these solutions shall be within the range of the calibration curve, otherwise repeat the procedure using a smaller aliquot. The recovery rate shall be between 80 % and 120 %.

If the added chromium (VI) is not detected or significantly lower than the expected values, this is an indication that the organic or organo-mineral fertilizer contains reducing agents. This leads to the conclusion that this organic or organo-mineral fertilizer has no chromium (VI) content (below detection limit).