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Fertilizers - Determination of trace elements - Determination of chromium(VI) by photometry (method A) and by ion chromatography with spectrophotometric detection (method B)

Engrais - Dosage des éléments traces - Dosage du chrome (VI) par spectrophotométrie (méthode A) et chromatographie ionique avec détection spectrophotométrique (méthode B)

Düngemittel - Bestimmung von Elementspuren - Bestimmung von Chrom(VI) mit Photometrie (Verfahren A) und mit Ionenchromatographie mit spektrometrischer Detektion (Verfahren B)

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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Contents		Page
Foreword.....		3
1	Scope	4
2	Normative references	4
3	Terms and definitions	4
4	Sampling and sample preparation	4
5	Method A: Determination by water extraction and spectrophotometric detection	5
6	Method B: Determination by alkaline digestion and ion chromatography with spectrophotometric detection	8
7	Precision	15
8	Test report	15
Bibliography		16

Foreword

This document (FprCEN/TS 16318:2011) 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.

FprCEN/TS 16318:2011 (E)

1 Scope

This document specifies two methods for the determination of the content of soluble chromate in fertilizers.

Method A specifies the determination of chromate after extraction with water by photometry. This method can be used to determine Cr(VI)-mass fractions in solids higher than 1 mg/kg.

Method B specifies the determination of chromate by alkaline digestion and ion chromatography with spectrophotometric detection. This method can be used to determine Cr(VI)-mass fractions in solids higher than 0,1 mg/kg.

NOTE In case of reducing or oxidizing fertilizer matrix, no valid Cr(VI) content can be reported.

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 15192:2006, *Characterisation of waste and soil — Determination of Chromium(VI) in solid material by alkaline digestion and ion chromatography with spectrophotometric detection*

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 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 [2].

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

Reasonable precautions have to be taken to prevent oxidation of chromate present in the sample. Samples shall be taken using appropriate devices and placed in containers that do not contain stainless steel (e.g. plastic, glass).

After digestion, the sample shall be analysed as soon as possible.

5 Method A: Determination by water extraction and spectrophotometric detection

5.1 Principle

Chromate is extracted from the sample with water at room temperature. The chromate concentration in the extract is measured by colorimetry using 1,5-diphenylcarbazide.

When chromate reduces the 1,5-diphenylcarbazide a magenta coloured complex of 1,5-diphenylcarbazone and chromium is formed which can be measured colorimetrically at 540 nm.

5.2 Reagents

Use only reagents of recognized analytical grade and water conforming to 5.2.1.

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

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

5.2.3 Hydrochloric acid, diluted, $c(\text{HCl})$ approximately 6 mol/l.

Mix equal volumes of hydrochloric acid (5.2.2) and water (5.2.1).

5.2.4 Diphenylcarbazide solution.

Dissolve 1,0 g Diphenylcarbazide [$\text{CO}(\text{NHNHC}_6\text{H}_5)_2$] in 100 ml acetone and add one drop of acetic acid. If this solution is stored in a glass bottle in the dark at 4 °C, it may be used for approximately two weeks. This solution shall be clear without colour. If the diphenylcarbazide solution has become coloured it shall be discarded and freshly prepared before use.

5.2.5 Chromate standard stock solution, $\rho(\text{chromate}) = 1\,000 \text{ mg/l}$.

Dissolve 2829 mg potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in 1 000 ml water (5.2.1) using a volumetric flask. This solution may be used for two weeks if stored in the dark at 4 °C.

5.2.6 Chromate standard stock solution, $\rho(\text{chromate}) = 50 \text{ mg/l}$.

Dilute 5 ml chromate stock solution (5.2.5) to 100 ml with water using a volumetric flask. This solution shall be freshly prepared on the day of use.

5.2.7 Standard solutions.

Prepare the standard solutions by diluting aliquots of the 50 mg/l chromate standard stock solution (5.2.6) with water in 100 mg/l volumetric flasks. The aliquots and final concentrations of chromate are given in Table 1. Other volumes and concentrations may be used for the preparation of standard solutions if appropriate.

FprCEN/TS 16318:2011 (E)

Table 1 — Aliquots and final concentrations for the preparation of chromate standards from a 50 mg/l chromate standard stock solution in 100-ml volumetric flasks

Aliquot ml	Final concentration of chromate mg/l
0	0 (calibration blank)
0,05	0,025
0,20	0,10
0,50	0,25
1,00	0,50
1,50	0,75

A blank solution shall be prepared in a separate volumetric flask by adding water only.

The standard solutions shall be prepared freshly on the day of use.

5.3 Apparatus

5.3.1 Common laboratory glassware.

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

5.3.3 Membrane filters and vacuum filtration apparatus.

The filters should be made of cellulose nitrate, pore size 5 µm and fit into the vacuum filtration apparatus.

5.3.4 Mechanical shaker.

5.3.5 Pipettes and/or dilutor.

Pipettes with fixed or variable volume and volumetric glassware to perform dilutions. Alternatively a dilutor may be used, which is an instrument used for automated volumetric dilutions. The precision and accuracy of this equipment for volumetric dilutions shall be proved, controlled, and documented regularly.

5.3.6 Spectrophotometer, capable to measure transmitted light at 540 nm and equipped with measuring cells of various dimensions (20 mm, 50 mm).

5.3.7 100 ml bottles, made from PE or PP, equipped with watertight caps.

5.4 Procedure

5.4.1 Preparation of the test solution

Weigh approximately 10 g, to the nearest 0,01 g, of the prepared sample and transfer to a suitable extraction vessel (5.3.7).

Add 40 ml of water (5.2.1). If the sample material (e.g. organic material) absorbs a high amount of water, add additionally water to obtain a fluid suspension. It may be necessary to use larger extraction vessels in such cases. Close the cap tightly and shake vigorously for 15 min on a mechanical shaker (5.3.4). Filter the suspension immediately through membrane filters with 5 µm pore size using the vacuum filtration apparatus (5.3.3).

Pipette 20 ml of the test solution to a 100 ml volumetric flask and continue immediately with the colorimetric measurement. If the test solution shows a yellow colour, the aliquot should be reduced to minimise interferences by the colour of organic substances.

The test solution may not be stored. The chromate content shall be analysed on the day of preparation.

5.4.2 Preparation of the blank test solution

Carry out a blank test at the same time as the extraction, with only the reagents and follow the same procedure as for the samples.

5.4.3 Spectrophotometric measurement

Add approximately 40 ml of water to all volumetric flasks containing the standard solutions (5.2.7), the blank test solution (5.4.2) and the sample test solutions (5.4.1). Then add 2 ml diluted hydrochloric acid (5.2.3). The pH-value of the resulting solution should be between pH 1 and pH 2. Add more diluted hydrochloric acid (5.2.3) if the pH-value is higher until a pH-value between pH 1 and pH 2 is reached.

Add 2 ml diphenylcarbazide solution (5.2.4) to each volumetric flask and fill up to the mark with water. Wait 15 min and measure the extinction of the solutions on a spectrophotometer at 540 nm.

5.5 Calculation and expression of the results

5.5.1 Calibration

In the case of a linear calibration curve, the calibration function can be described as follows.

$$S = c \times b + a \quad (1)$$

where

S is the net signal for Cr(VI) in a solution;

c is the concentration of Cr(VI) in this solution, in milligrams per litre or in micrograms per litre;

b is the slope of the linear calibration function;

a is the intersection of the linear calibration function.

Calculate the analyte concentration c_f in the filtrate of the test portion using the slope b and the intersection a found in Equation (1) as follows.

$$c_f = \frac{S_f - a}{b} \quad (2)$$

where

S_f is the net signal of the test solution.