SLOVENSKI STANDARD
SIST EN 17246:2019

01-november-2019

Gnojila - Določevanje perkloratov v mineralnih gnojilih z ionsko kromatografijo in detekcijo na osnovi prevodnosti (IC-CD)

Fertilizers - Determination of perchlorate in mineral fertilizers by ion chromatography and conductivity detection (IC-CD)

Düngemittel - Bestimmung von Perchlorat in mineralischen Düngemitteln mit Ionenchromatographie und Leitfähigkeitdetektion (IC-CD)

Engrais - Détermination du perchlorate dans les engrais minéraux par chromatographie ionique et détection conductimétrique (IC-CD)

Ta slovenski standard je istoveten z: **EN 17246:2019**

ICS:

65.080	Gnojila	Fertilizers

SIST EN 17246:2019 **en,fr,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 17246

August 2019

ICS 65.080

English Version

Fertilizers - Determination of perchlorate in mineral fertilizers by ion chromatography and conductivity detection (IC-CD)

Engrais - Détermination du perchlorate dans les engrais minéraux par chromatographie ionique et détection conductimétrique (IC-CD)

Düngemittel - Bestimmung von Perchlorat in mineralischen Düngemitteln mit Ionenchromatographie und Leitfähigkeitsnachweis (IC-CD)

This European Standard was approved by CEN on 7 July 2019.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN-CENELEC Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Republic of North Macedonia, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.

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

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

Ref. No. EN 17246:2019 E

Contents

Page

European foreword

This document (EN 17246:2019) 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 February 2020, and conflicting national standards shall be withdrawn at the latest by February 2020.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN shall not be held responsible for identifying any or all such patent rights.

According to the CEN-CENELEC Internal Regulations, the national standards organisations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Republic of North Macedonia, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

1 Scope

This document specifies a method for the determination of traces of perchlorate in mineral fertilizers by ion chromatography and conductivity detection (IC-CD).

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

EN 12944-2, *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)*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 12944-1 and EN 12944-2 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 http://www.iso.org/obp

4 Principle

The perchlorate content of the fertilizer sample is determined by ion chromatography with conductivity detection after extraction in water. The ion chromatograph comprises a sample injection part, a separation part and detection part. For lower noise and background level of detection, a suppressed conductivity detector may be used. Anion exchange resin is used as stationary phase and aqueous solutions of monobasic and dibasic salts are used as mobile phase.

5 Reagents

All reagents shall be of recognized analytical grade and shall have negligible concentration of the element to be determined if compared to the lowest concentration of that element in the sample solution.

5.1 Water, grade 1 according to EN ISO 3696.

5.2 Perchlorate standard solutions, with a mass concentration of $\rho(ClO_4^-)$ = 0,05 mg/l, 0,1 mg/l, 0,3 mg/l, 0,5 mg/l, 0,7 mg/l and 1 mg/l, prepared from a stock solution with verified concentration of perchlorate, e.g. with $\rho(ClO_4^-)$ = 1 000 mg/l.

The 0,5 mg/l calibration standard is used for a regular calibration testing.

5.3 Quality control sample, with a mass concentration of $\rho(ClO_4^-)$ = 0,5 mg/l prepared from a solution (e.g. $\rho(ClO_4^-)$ = 1 000 mg/l of perchlorate standard).

5.4 Eluent for IC-CD, as advised by the manufacturer to be used for determining perchlorate.

The eluent advised by the manufacturer of the instrument depends on the instrument used, hence different eluents may be used.

6 Apparatus and equipment

Usual laboratory equipment, glassware, and the following:

6.1 Ion chromatograph, with IC-CD technique.

For lower noise and background level of detection, a suppressed conductivity detector is preferred. For column selection, instrumental conditions and additional information on how to operate follow the instructions of the manufacturer. Examples of instrument parameters are given in Table 1.

Table 1 — Examples of instrument parameters[1]

Column specification	Eluent
Dionex IonPac AS-16	40 mM KOH
Dionex IonPac AS-16 and Dionex IonPac AG-16	45 mM NaOH
Dionex IonPac AS-19	KOH/H_2O gradient eluent
Dionex IonPac AS-19 and Dionex IonPac AG-19	10–58 mM KOH
Metrosep A Supp 5 and Metrosep A Supp 4/5 S-Guard	3,2 mM Na_2CO_3 + 1,0 mM $NaHCO_3$
Metrosep A Supp 5	15 mM Na_2CO_3 + 10 % acetone
Metrosep A Supp 7	10 mM Na_2CO_3 + 35 % acetonitrile
Phenomenex starion A300 size: 100x4.6mm	5 mM Na_2CO_3 in 12 % acetone

6.2 Volumetric flasks, capacity 250 ml, 100 ml and 50 ml.

6.3 Analytical balance, with an accuracy of ± 0,1 mg.

6.4 Graduated pipettes, capacity 5 ml and 10 ml.

6.5 Filtration membrane and syringe, with a filter membrane of 25 mm diameter and 0,22 µm pore size.

7 Sampling and sample preparation

Sampling is not part of the method specified in this document. A recommended sampling method is given in EN 1482-1 [1].

---

1 The columns with instrument parameters specified in Table 1 are examples of suitable instruments available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of these products. Equivalent products may be used if they can be shown to lead to the same results.

8 Procedure

8.1 Verification of the quantification limit of the method (LOQ method)

8.1.1 Run 10 blank samples by injecting water (5.1). Integrate the area of the blank samples using a time interval for perchlorate.

8.1.2 Prepare the samples for the calibration curve and run the samples.

8.1.3 Calculate the instrumental quantification limit ($LOQ_{\text{instrumental}}$ in mg/l) according to Formula (1).

$$LOQ_{instrumental} = \frac{10 \times SD}{a} \quad (1)$$

where

SD is the standard deviation for the 10 blank samples, in milligrams per litre;

a is the slope of the calibration curve.

8.1.4 Calculate the quantification limit of the method (LOQ_{method} in mg/kg) according to Formula (2).

$$LOQ_{method} = \frac{LOQ_{instrumental} \times D \times V \times 1000}{m} \quad (2)$$

where

D is the final dilution factor;

V is the volume of the sample, in litres;

m is the mass of the test portion, in grams.

8.2 Preparation of the test solutions and sample analysis

With the analytical balance (6.3), weigh (25 ± 0,1) g of ground sample.

Transfer the test portion to a 250 ml volumetric flask and add 150 ml of water (5.1) to dissolve the sample. Add additional water (5.1) until the indicated volume is reached. Stir manually to homogenize (= solution 1).

Take an aliquot of 5 ml of solution 1 and transfer quantitatively to a 50 ml volumetric flask. Add water (5.1) to the mark and stir manually to homogenize (= solution 2). Keep the remainder of solution 1.

Take an aliquot of 10 ml of solution 2 and transfer quantitatively to a 50 ml volumetric flask. Add water (5.1) to the mark and stir manually to homogenize (= solution 3). Keep the remainder of solution 2.

Filter 10 ml of solution 3 using a filtration membrane (6.5). Discard the first filtrate collected. Filter another 10 ml and collect in a 10 ml vial.

Proceed according to the operation instructions for the given instrument.

If the perchlorate concentration is below the lowest calibration point (0,05 mg/l), take solution 2 for the analysis. If the concentration exceeds the calibration range, dilute accordingly.

NOTE If the concentration of the sample injected falls outside the calibration range, an extra dilution step can be taken.

9 Calculation and expression of the results

For solid fertilizers, the result shall be expressed as a mass fraction (mg/kg). In the case that a liquid fertilizer sample is analysed, the result may be expressed as a mass concentration (mg/l). All calculations are performed using the appropriate IC software, according to Formula (3).

$$w\left(ClO_4^-\right) = \frac{\rho \times D \times V \times 1\,000}{m} \quad (3)$$

where

$w(ClO_4^-)$	is the mass fraction of ClO_4^- in the fertilizer, in milligrams per kilogram;
ρ	is the mass concentration of the reading of the sample from the calibration curve, in milligrams per litre;
D	is the dilution used;
V	is the volume of the sample solution, in litres;
m	is the mass of the test portion, in grams.

10 Precision

10.1 Quality assurance

Blank, quality control sample (5.3) and internal reference material (if available) should be analysed in each series of samples. LOQ has to be checked regularly and a quality control sample should be measured after every five samples.

10.2 Inter-laboratory test

An inter-laboratory test was carried out in 2016 with ten participating laboratories analysing four different samples. Repeatability and reproducibility were calculated according to ISO 5725-2 [2]. Each laboratory carried out three determinations on each sample. The statistical results are explained in Table A.1. The values derived from the inter-laboratory test might not be applicable to concentration ranges and matrices other than those given in Annex A.

10.3 Repeatability

The absolute difference between two independent test results obtained with the same method on identical test material, in the same laboratory, by the same operator, using the same equipment within a short interval of time, will in no more than 5 % of the cases exceed the values of r given in Table 2.

10.4 Reproducibility

The absolute difference between two single test results obtained with the same method on identical test material, in different laboratories, by different operators, using different equipment, will in no more than 5 % of the cases exceed the values of R given in Table 2.