SLOVENSKI STANDARD
SIST EN 13466-1:2002

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Gnojila - Dolo̧ evanje koli̧ ine vode (Karl Fischerjeve metode) - 1. del: Ekstrakcija z metanolom

Fertilizers - Determination of water content (Karl Fischer methods) - Part 1: Methanol as extracting medium

Düngemittel - Bestimmung des Wassergehaltes (Karl-Fischer-Verfahren) - Teil 1: Methanol als Extraktionsmittel

Engrais - Détermination de la teneur en eau (Méthodes Karl Fischer) - Partie 1: Le méthanol comme milieu d'extraction

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Fertilizers - Determination of water content - (Karl Fischer methods) - Part 1: Methanol as extracting medium

Engrais - Détermination de la teneur en eau (Méthodes Karl Fischer) - Partie 1: Le méthanol comme milieu d'extraction

Düngemittel - Bestimmung des Wassergehaltes (Karl-Fischer-Verfahren) - Teil 1: Methanol als Extraktionsmittel

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Foreword

This European Standard 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of an identical text or by endorsement, at the latest by April 2002, and conflicting national standards shall be withdrawn at the latest by April 2002.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

Introduction

The water content of fertilizers has a significant effect on their quality and, especially, their storage and handling properties.

Water can be present in a number of forms such as free water, bound water and water of crystallization. It is often important to be able to distinguish between these forms of water. The gravimetric methods for determination of water standardized in EN 12048 and EN 12049 have only limited applicability.

The Karl Fischer method is applicable to a wide range of fertilizers. However, there are several variations to the basic technique, different formulations of the Karl Fischer reagents are commercially available and a number of different solvents can be used. In this standard, methanol and 2-propanol are used as extracting media to distinguish between the different forms of water present in fertilizers.

EN 13466 "Fertilizers – Determination of water content (Karl Fischer methods)" consists of two parts:

— *Part 1 : Methanol as extracting medium*

— *Part 2 : 2-propanol as extracting medium*

As examples of the difference between methanol and 2-propanol as extracting media methanol gives a result which is a combination of free water and extracted water of crystallization from the following components of fertilizers: calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$); calcium hydrogen phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$); calcium sulfate dihydrate (gypsum, $CaSO_4 \cdot 2H_2O$) calcium sulfate hemihydrate ($CaSO_4 \cdot 0{,}5H_2O$); magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$); potassium chloride magnesium sulfate water (1/1/2,75, Kainite, $KCl \cdot MgSO_4 \cdot 2{,}75H_2O$); potassium magnesium sulfate hexahydrate (Schoenite, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$); potassium magnesium sulfate tetrahydrate (Leonite, $K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$); potassium sulfate calcium sulfate monohydrate (Syngenite, $K_2SO_4 \cdot CaSO_4 \cdot H_2O$); potassium chloride magnesium chloride hexahydrate (Carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$); magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$).

Extraction with 2-propanol gives a result which is a combination of free water and extracted water of crystallization from the following components of fertilizers: calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$); magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$); potassium chloride magnesium chloride hexahydrate (Carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$); magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$).

1 Scope

This European Standard specifies a Karl Fischer titrimetric method for the determination of the water content of fertilizers based on the use of methanol as extracting medium.

The method is applicable to all solid mineral fertilizers. The result (KFM water) includes "free" water and extracted water of crystallization from the following components of fertilizers: calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$); calcium hydrogen phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$); calcium sulfate dihydrate (gypsum, $CaSO_4 \cdot 2H_2O$), calcium sulfate hemihydrate ($CaSO_4 \cdot 0{,}5H_2O$); magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$) ; potassium chloride magnesium sulfate water (1/1/2,75, Kainite, $KCl \cdot MgSO_4 \cdot 2{,}75H_2O$); potassium magnesium sulfate hexahydrate (Schoenite, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$); potassium magnesium sulfate tetrahydrate (Leonite, $K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$); potassium sulfate calcium sulfate monohydrate (Syngenite, $K_2SO_4 \cdot CaSO_4 \cdot H_2O$); potassium chloride magnesium chloride hexahydrate (Carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$); magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$).

Metal oxides and hydroxides soluble in methanol and pyridine will have an effect which can be corrected for, if their content is known.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text, and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN 1482, *Sampling of solid fertilizers and liming materials.*

3 Principle

Extraction of water from the fertilizer into methanol and titration of the water with a Karl Fischer reagent, previously standardized by titration with a known mass of water.

4 Reagents

4.1 General

All reagents shall be of recognized analytical grade.

4.2 Methanol, containing no more than a mass concentration of 500 mg/l water.

4.3 Karl Fischer reagent, equivalence from 1 mg to 5 mg water/ml reagent (see Tables 1 and 2).

4.4 Sodium tartrate dihydrate $Na_2C_4H_4O_6 \cdot 2H_2O$ (15,66 % mass fraction of water).

Sodium tartrate dihydrate $Na_2C_4H_4O_6 \cdot 2H_2O$ can be stored over 60 % H_2SO_4 in a desiccator. Check the water content by drying at about 150 °C.

5 Apparatus

Ordinary laboratory apparatus and glassware and in particular the following:

5.1 Balance, capable of weighing to the nearest 0,0001 g.

5.2 **Mortar** and **pestle**.

5.3 **Centrifuge** capable of operating at a rate of 3 500 min^{-1}.

5.4 **Centrifuge tubes**, diameter 4,5 cm, height 10 cm fitted with rubber stoppers.

5.5 **Dispersing apparatus** : turbine type, minimum rotational frequency 9 500 min^{-1}, suitable for introduction into centrifuge tubes (5.4), for instance Ultra Turrax®[1]

5.6 **Karl Fischer titrator**

NOTE There are several titrators on the market for the Karl Fischer method.

6 Installation and test of the Karl Fischer titrator

Follow the instruction manual for the particular titrator used.

7 Sampling

Carry out sampling in accordance with EN 1482.

8 Procedure

8.1 Calibration of the Karl Fischer reagent

Titrate a known amount of water or sodium tartrate dihydrate (4.4) accurately weighed to the nearest 0,0001 g following the instruction manual for the titrator.

NOTE Calibration frequency should be adapted to the frequency of analysis.

8.2 Drift

Control the diffusion of water from the air into the titration vessel during the determination following the Instruction Manual for the titrator. Take account of any recorded drift (m_d) when expressing results.

8.3 Determination

8.3.1 General

If the fertilizer is dispersible in methanol (4.2), the extraction and titration can be carried out in the titration vessel (see 8.3.2). If not, a separate extraction step will be needed (see 8.3.3).

Urea, ammonium nitrate and CAN (= calcium ammonium nitrate) are usually dispersible in methanol.

8.3.2 Fertilizers dispersible or soluble in methanol

8.3.2.1 Preparation of test portion

Rapidly crush the test sample prepared in accordance with clause 7 and immediately weigh a test portion (see Table 1) to the nearest 0,0001g.

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[1] Ultra Turrax S25® equipped with dispersing turbine S25KR - 18G is an example of equipment commercially available. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of these products.

NOTE Products such as urea and ammonium nitrate which are fully soluble in methanol should not be crushed.

Table 1 — Mass of test portion for fertilizers dispersible or soluble in methanol

Expected water content [mass fraction in %]	Mass of test portion	
	titre of KF-Reagent 5 mg/ml	titre of KF-Reagent 2 mg/ml
< 5	1 g	1 g
5 to 20	0,5 g	0,2 g
>20 to 50	0,2 g	---

8.3.2.2 Titration

Introduce 20 ml of methanol (4.2) into the reaction vessel of the titrator (5.6).

Introduce the weighed test portion (8.3.2.1) directly into the reaction vessel of the titrator (5.6). Start stirring and ensure, that the grains of the fertilizer are fully dispersed. Titrate with the Karl Fischer reagent (4.3) until the equivalence point is reached following the instruction manual for the titrator. Record the mass m_s, in milligrams of water, indicated by the titrator. Adapt the dead-time of the titrator to the grain size of the dispersed fertilizer in accordance with the instruction manual of the titrator used.

8.3.3 Fertilizers not dispersible in methanol

8.3.3.1 Test portion

Weigh a test portion of the test sample, in accordance with clause 7 and Table 2 to the nearest 0,0001 g directly into the previously dried and tared centrifuge tube (5.4).

Table 2 — Mass of test portion for fertilizers not dispersible in methanol

Expected water content [mass fraction in %]	Mass of test portion	
	titre of KF-Reagent 5 mg/ml	titre of KF-Reagent 2 mg/ml
< 5	5 g	5 g
5 to 20	1 g	1 g
>20 to 50	---	1 g

8.3.3.2 Extraction

Add 25 ml of methanol (4.2) with a calibrated pipette to the test portion in the centrifuge tube. Insert the dispersing apparatus (5.5) ensuring that the distance from any part of the dispersing tool to the inner surface of the centrifuge tube is greater than the grain size of the fertilizer.

Place the dispersing tool near to the surface of the fertilizer layer. Disperse for 60 s at room temperature at 9 500 min^{-1} at least.

Make sure that the temperature during the dispersion-extraction does not exceed 40 °C or, in case of fertilizer containing magnesium sulfate, 25 °C.

Repeat the dispersion for a further 60 s if the fertilizer has not been completely dispersed in the first operation. Repeat the extraction if the dispersion is still not complete.

NOTE The dispersion can be controlled acoustically; the turbine pitch changes once the dispersion is complete.