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## Fertilizers — Determination of sulfates content using three different methods

*Engrais — Dosage des sulfates selon trois méthodes différentes*

ICS: 65.080

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## Foreword

This document (EN 15749:2009) 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of an identical text or by endorsement, at the latest by April 2010, and conflicting national standards shall be withdrawn at the latest by April 2010.

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## Introduction

This document specifies three different methods for the determination of sulfur. Based on the statistical results of the inter-laboratory tests, obtained with the same samples, the three methods produce equivalent results, and hence can be used all three methods on decision of the user and availability of equipment.

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## 1 Scope

This European Standard specifies three different methods (Methods A, B and C) for the determination of sulfur present in fertilizers extracts in the form of sulfates. Method A specifies the gravimetric method. Method B specifies the method using inductively coupled plasma optical spectrometry (ICP-OES). Method C specifies the method using ion chromatography (IC).

## 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*

CEN/TS 15925, *Fertilizers — Extraction of total sulfur present in various forms*

CEN/TS 15926, *Fertilizers — Extraction of water soluble sulfur where the sulfur is in various forms*

CEN/TS 15960, *Fertilizers — Extraction of total calcium, total magnesium, total sodium and total sulfur in the forms of sulfates*

CEN/TS 15961, *Fertilizers — Extraction of water soluble calcium, magnesium, sodium and sulfur (in the forms of sulfates)*

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 Principle

### 4.1 Method A: Gravimetric method

Sulfur is extracted from the sample according to the methods described in CEN/TS 15925, CEN/TS 15926, CEN/TS 15960 or CEN/TS 15961 and determined based on the gravimetric determination as barium sulfate.

### 4.2 Method B: ICP-OES

Sulfur is extracted from the sample according to the methods described in CEN/TS 15925, CEN/TS 15926, CEN/TS 15960 or CEN/TS 15961 and its concentration in the extract is measured by inductively coupled plasma-optical emission spectrometry (ICP-OES).

### 4.3 Method C: IC

Sulfur is extracted from the fertilizer according to the methods described in CEN/TS 15925, CEN/TS 15926, CEN/TS 15960 or CEN/TS 15961 in the form of sulfate. The sulfate concentration of the extract is measured by ion chromatography (IC) equipped with a suppressor device and a conductivity detector.

## 5 Sampling and sample preparation

Sampling is not part of the methods specified in this European Standard. A recommended sampling method is given in EN 1482-1.

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

## 6 Method A – Gravimetric method

### 6.1 Reagents

Use only reagents of recognized analytical grade and distilled or demineralized water (grade 3 according to EN ISO 3696).

#### 6.1.1 Diluted hydrochloric acid

Mix one volume of  $\rho(\text{HCl}) = 1,18 \text{ g/ml}$  with one volume of water.

#### 6.1.2 Barium chloride solution, $\rho(\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}) = 122 \text{ g/l}$ .

#### 6.1.3 Silver nitrate solution, $\rho = 5 \text{ g/l}$ .

### 6.2 Apparatus

#### 6.2.1 Porcelain crucibles

#### 6.2.2 Hot water bath

#### 6.2.3 Drying oven, set at $105 \text{ }^\circ\text{C} \pm 1 \text{ }^\circ\text{C}$ .

#### 6.2.4 Electric oven, set at $800 \text{ }^\circ\text{C} \pm 50 \text{ }^\circ\text{C}$ .

### 6.3 Procedure

#### 6.3.1 Sampling of the solution

Pipette an aliquot part of one of the extraction solutions containing between 20 mg and 100 mg of sulfur or 50 mg and 250 mg of  $\text{SO}_3$ .

Place this aliquot in a beaker of suitable capacity. Add 20 ml of diluted hydrochloric acid (6.1.1). Make up to about 300 ml with water.

#### 6.3.2 Preparation of the precipitate

Bring the solution to the boil. Add, drop by drop, about 20 ml of the barium chloride solution (6.1.2) while stirring the solution vigorously. Boil for a few minutes.

Place the beaker, covered with a watch glass, in a boiling hot water bath (6.2.2) for 1 h. Then leave standing hot ( $\pm 60$  °C) until the supernatant liquor is clear. Decant the clear solution through a slow filtration ash-free filter. Wash the precipitate several times with hot water. Continue to wash the precipitate on the filter until the filtrate is chloride free. This can be checked by using a silver nitrate solution (6.1.3).

### 6.3.3 Incineration and weighing of the precipitate

Place the filter paper and precipitate in a porcelain crucible (6.2.1) previously weighed to the nearest 0,1 mg. Dry in the oven (6.2.3) and ash at approximately 800 °C for half an hour (6.2.4). Allow to cool in a desiccator and weigh to 0,1 mg.

## 6.4 Calculation and expression of the result

1 mg of barium sulfate corresponds to 0,137 mg of sulfur or to 0,343 mg of SO<sub>3</sub>.

Calculate the sulfates content,  $w_S$ , as mass fraction in percent of the fertilizer according to Equation (1):

$$w_S = m_1 \times 0,0137 \times \frac{v_1}{v_2 \times m_2} \quad (1)$$

Calculate the SO<sub>3</sub> content,  $w_{SO_3}$ , as mass fraction in percent of the fertilizer according to Equation (2):

$$w_{SO_3} = w_S \times 2,5 \quad (2)$$

where

- $m_1$  is the mass of the barium sulfate precipitate, in mg;
- $m_2$  is the mass of the test portion, in g;
- $v_1$  is the volume of the extraction solution, in ml;
- $v_2$  is the aliquot volume, in ml.

## 7 Method B – ICP-OES method

### 7.1 Reagents

Use only reagents of recognized analytical grade, and water conforming to grade 2 of EN ISO 3696.

Stock solutions shall be replaced after a maximum of one year, but the standard solution shall be freshly prepared monthly as a minimum.

**7.1.1 Hydrochloric acid**,  $\rho$  approximately 1,18 g/ml;

**7.1.2 Diluted hydrochloric acid**, mix 40 ml of hydrochloric acid (7.1.1) in 1 l of water;

**7.1.3 Sulfur stock solution**, corresponding to 1 000 mg/l sulfur.

Dry in a pre-treatment step some grams of sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) at 105 °C for 1 h. Let cool in a desiccator. Weigh to the nearest 0,1 mg, approximately 4,437 5 g of sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>). Dissolve the weighted



mass in a small quantity of water in volumetric flasks of nominal capacity of 1 000 ml, fill to the mark with water.

The solution is stable for several months if stored at 4 °C to 6 °C.

NOTE Sulfur stock solution of 1 000 mg/l is also readily available commercially, and may be used instead.

## 7.2 Apparatus

Common laboratory equipment and glassware, in particular equipment according to 7.2.1 to 7.2.2.

**7.2.1 Analytical balance**, capable of weighing to an accuracy of 0,1 mg.

### 7.2.2 Inductively coupled plasma – Optical emission spectrometer

Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) with radial viewing of the plasma and simultaneous measurement of emission signals.

For measuring sulfur at wavelengths below 190 nm the optical system shall be evacuated or be filled or continuously flushed with an inert gas as recommended by the instrument manufacturer to obtain high and stable signal intensities.

The instrument shall be equipped with radial plasma as a minimum requirement; axial plasma is equally acceptable, as long as it can be shown that the results are statistically equal to the results obtained with radial plasma. Background correction shall also be performed. Settings of the working conditions (e.g. viewing height, gas flows, RF or plasma power, sample uptake rate, integration time, number of replicates) shall be optimized according the manufacturer's instructions.

## 7.3 Preparation of the extract

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The sulfur is extracted from the sample according to one of the methods described in CEN/TS 15925, CEN/TS 15926, CEN/TS 15960 or CEN/TS 15961.

## 7.4 Procedure

### 7.4.1 General

Calibration shall be performed by means of the standard addition technique. This method allows the analysis of fertilizers with unknown matrix composition or with a matrix that cannot be synthetically imitated easily.

### 7.4.2 Preparation of the test solution

Dilute the extraction solution with the diluted hydrochloric acid (7.1.1) to obtain a concentration between 10 mg/l and 150 mg/l of sulfur.

### 7.4.3 Preparation of the blank test solution

Carry out a blank test at the same time as the extraction, with only the reagents.

### 7.4.4 Preparation of the calibration solutions

The additions to the test solution, prior to the dilution step, should be about 20 %, 50 % and 100 % of the expected sulfur content. After the additions, dilute each of the samples with the diluted hydrochloric acid (7.1.1).

A (external) calibration curve method can also be used instead of the standard addition method where the analytical results are demonstrated to be statistically equal. Appropriate matrix matching of the calibration solutions shall be performed if an (external) calibration method is used.

## 7.5 Determination

### 7.5.1 General

Set up the instrument according to the manufacturer's instructions using appropriate conditions, and with the suitable background correction system in operation.

For each instrument used, selectivity, limits of detection and quantification, precision, linear working area, and interference shall be established separately.

### 7.5.2 Determination by ICP-OES

Aspirate the blank test solution (7.4.3), the test solution (7.4.2) and the various additions (7.4.4) in ascending order separately into the plasma, and measure the emission of sulfur. Perform at least two replicates and average the values if the values fall within an accepted range. After each measurement, aspirate water or diluted hydrochloric acid (7.1.2).

The following special procedures can be used to obtain high precision and accuracy necessary to analyse high sulfur contents in fertilizers:

- a) optimised instrument settings,
- b) simultaneous measurement of the signals of analyte and an appropriate internal standard element;
- c) adjustment of the matrix of calibration solutions to the sample matrix;
- d) consistent identical treatment of samples and calibration solutions during preparation and measurement, or use gravimetric dilution instead of volumetric dilution;
- e) correction of instrumental drift and background (if required).

**Table 1 — General analytical conditions for sulfur determination by ICP-OES**

Wavelength, nm	181,978 alternatives: 180,676 182,568
Background correction	Yes
Working range mg/l	1 to 150
Possible internal standard: Molybdenum	202,030 nm 281,615 nm

## 7.6 Calculation and expression of the results

**NOTE** Net signal is defined as the number of counts per time unit at the selected wavelength, corrected for background contributions.

**7.6.1 Calculation**

In case of several additions, regression techniques on the linear model of variable  $y$  as a function of variable  $x$ , have to be used to determine the sulfur concentration of the test solution. Generally, this model can be written as:

$$y_i = a + b \cdot x_i \tag{3}$$

In this particular case of three standard additions:

$$y_i = S_i \quad (i = 0, 1, 2, 3) \tag{4}$$

$$x_i = \rho_s \cdot V_i \quad (i = 0, 1, 2, 3) \tag{5}$$

where

$\rho_s$  is the concentration, in mg/l, of the standard solution;

$V_i$  are the various volumes, in l, of the standard solution added;

$S_i$  are the net signals after the various additions.

Calculate the values of  $a$  and  $b$  as follows:

$$b = \frac{n \cdot \sum x_i y_i - \sum x_i \sum y_i}{n \cdot \sum x_i^2 - (\sum x_i)^2} \tag{6}$$

$$a = \frac{\sum y_i - b \cdot \sum x_i}{n} \tag{7}$$

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where

$n$  is the number of solutions measured ( $n = 4$  in case of three additions).

Calculate the sulfur concentration  $\rho_f$ , in mg/l, of the filtrate of the test portion using the following equation:

$$\rho_f = \frac{a/b}{V_f} \tag{8}$$

where

$V_f$  is the volume, in l, of the filtrate of the test portion used to prepare the test solution.

**7.6.2 Expression of the sulfur content in the sample**

The sulfur content in the sample or mass fraction of sulfur,  $w_s$ , expressed in mg of sulfur per kg of fertilizer, is determined using the following equation: