# Fertilizers — Determination of sulfates content using three different methods

ICS 65.080

British Standards

# National foreword

This British Standard is the UK implementation of EN 15749:2009. It supersedes DD CEN/TS 15749:2008 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee CII/37, Fertilisers and related chemicals.

A list of organizations represented on this committee can be obtained on request to its secretary.

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# Fertilizers - Determination of sulfates content using three different methods

Engrais - Dosage des sulfates selon trois méthodes différentes

Düngemittel - Bestimmung von Sulfat mit drei verschiedenen Verfahren

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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of an identical text or by endorsement, at the latest by April 2010, and conflicting national standards shall be withdrawn at the latest by April 2010.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.

# 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 $\rho$(HCl) = 1,18 g/ml with one volume of water.

#### 6.1.2 Barium chloride solution, $\rho(BaCl_2 \cdot 2\ H_2O)$ = 122 g/l.

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

### 6.2 Apparatus

#### 6.2.1 Porcelain crucibles

#### 6.2.2 Hot water bath

#### 6.2.3 Drying oven, set at 105 °C ± 1 °C.

#### 6.2.4 Electric oven, set at 800 °C ± 50 °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 $SO_3$.

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 (± 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 $SO_3$.

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

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

Calculate the $SO_3$ content, $w_{SO3}$, as mass fraction in percent of the fertilizer according to Equation (2):

$$w_{SO_3} = w_S \times 2{,}5 \tag{2}$$

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 ($Na_2SO_4$) 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 ($Na_2SO_4$). 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

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<br>alternatives:<br>180,676<br>182,568 |
| Background correction | Yes |
| Working range mg/l | 1 to 150 |
| Possible internal standard: Molybdenum | 202,030 nm<br>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:

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

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

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:

$$w_S = \frac{(\rho_f - \rho_{bl})}{m} \cdot V_t \tag{9}$$

where

$\rho_f$ is the concentration, in mg/l, of the filtrate of the test portion, as determined using Equation (8);

$\rho_{bl}$ is the concentration, in mg/l, of the blank solution;

$m$ is the mass of sample, in kg, taken for the extraction, and corrected for water content;

$V_t$ is the total volume, in l, of extract (filtrate of the test portion).

Sulfur contents of secondary nutrient fertilizers are to be expressed in the oxide form ($SO_3$) or the elemental form (S). As the results of the determination are expressed as sulfur (S), the following conversion factor shall be used:

$S = 0{,}400\ SO_3$.

## 8 Method C – IC method

### 8.1 Reagents

Use only reagents of recognized analytical grade, and water conforming to grade 2 of EN ISO 3696:1995.

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

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

**8.1.2 Sulfate stock solution**, corresponding to 1 000 mg/l $SO_4$.

Dry to constant weight in an oven at (150 ± 2) °C a sufficient quantity of anhydrous sodium sulfate ($Na_2SO_4$). Allow to cool in a desiccator. Weigh to the nearest 0,1 mg, approximately 1,479 0 g of the dried sodium sulfate ($Na_2SO_4$). Dissolve and make up to the mark with water in a 1 000 ml volumetric flask.

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

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

#### 8.1.3 Standard sulfate solution of 100 mg/l $SO_4$

Prepare a tenfold dilution of the stock standard (8.1.2) with water.

#### 8.1.4 Eluent

Different eluents may be used; follow the column manufacturer's instructions.

For example, with ion chromatography using suppressor technique and electrolytic generator the eluent is a potassium hydroxide solution.

NOTE The use of automatic generation of eluents is also allowed.

## 8.2 Apparatus

### 8.2.1 General

Common laboratory equipment and glassware, in particular equipment according to 8.2.2 to 8.2.4.

Ordinary laboratory glassware.

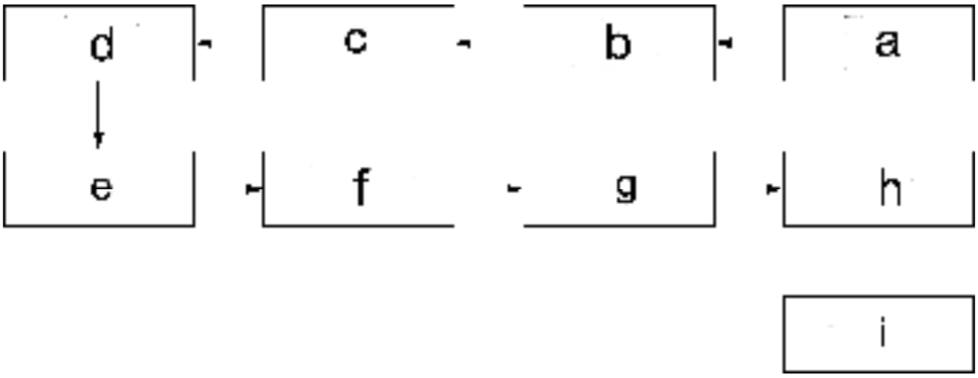
**8.2.2 Analytical balance**, capable of weighing to an accuracy of 0,1 mg.

### 8.2.3 Ionic chromatograph

Use preferably ionic chromatography with suppressor technique and eluent electrolytic generator. It shall be operated according to the manufacturer's instructions.

The essential minimum requirements of the ionic chromatographic system to be applied within the scope of this document are the following:

### 8.2.4 IC apparatus (see Figure 1)



**Key**

| | |
|---|---|
| a | eluent regenerator |
| b | eluent reservoir |
| c | pump having characteristics for HPLC (e.g. high performance ion chromatography) |
| d | sample injection system in a sample loop (preferably 25 µl) |
| e | pre-column (e.g. containing the same resin material as the analytical separator column or packed with a macro porous polymer) |
| f | separating column with a stationary phase of ion-exchange resins bonded to inert polymeric particles, capable of separating sulfate from the other ions present |
| g | anion self-regenerating suppressor (I = 140 mA) |
| h | conductimetric detector |
| i | recorder |

**Figure 1 — IC-apparatus**

### 8.2.5 IC additional apparatus

Membrane filtering apparatus with membrane filters, of pore size 0.45 µm, IC Resolution power.

## 8.3 Sampling and sample preparation

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

## 8.4 Procedure

### 8.4.1 Preparation of the test solution

Dilute the extraction solution prepared according to the methods described in CEN/TS 15925, CEN/TS 15926, CEN/TS 15960 or CEN/TS 15961 with water to obtain a concentration between 10 mg/l and 100 mg/l of $SO_4$.

### 8.4.2 Preparation of the calibration solutions

NOTE An (external) calibration curve method can also be used instead of the standard addition method where the analytical results are demonstrated to be statistically equal.

### 8.4.2.1 Calibration by standard addition

The following is given as an example of standard additions made to an extract with an expected concentration of 40 mg/l $SO_4$.

### 8.4.2.1.1 Addition 1

Pipette 50,00 ml of the test solution (8.4.1) into a 100 ml volumetric flask, add 4,00 ml of the sulfate standard solution (8.1.3), 0,40 ml hydrochloric acid and dilute to the mark with water.

### 8.4.2.1.2 Addition 2

Pipette 50,00 ml of the test solution (8.4.1) into a 100 ml volumetric flask, add 10,00 ml of the sulfate standard solution (8.1.3), 0,40 ml hydrochloric acid (8.1.1) and dilute to the mark with water.

### 8.4.2.1.3 Addition 3

Pipette 50,00 ml of the test solution (8.4.1) into a 100 ml volumetric flask, add 20,00 ml of the sulfate standard solution (8.1.3), 0,40 ml hydrochloric acid (8.1.1) and dilute to the mark with water.

### 8.4.2.2 External calibration

Prepare the series of calibration solutions in 1 000 ml volumetric flasks according to Table 2 and complete to the mark with water.

**Table 2 — Preparation of calibration solutions**

| Number of calibration solution | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Volume of sulfate stock solution (8.1.2), ml | 0 | 10 | 20 | 50 | 100 |
| Volume of hydrochloric acid (8.1.1), ml | 4 | 4 | 4 | 4 | 4 |
| Concentration of sulfur (as $SO_4$), mg/l | 0 | 10 | 20 | 50 | 100 |

### 8.4.3 Determination

#### 8.4.3.1 General

Set up the instrument according to the manufacturer's instructions using appropriate conditions.

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

#### 8.4.3.2 Determination by ion chromatography (IC)

Liquid chromatography separation of ions by means of a separation column. Use of an anion exchanger as the stationary phase, and usually, aqueous solutions of salts of mono basic and dibasic acids as mobile phases (eluent, see 8.1.4). Conductivity detector is combined with suppressor device that decreases the conductivity of the eluent and converts the separated anions into their corresponding acids.

The concentration of the respective anions is determined by a calibration of the overall procedure.

Prior to injection into the analyser, filter the sample through a membrane filter of pore size 0,45 µm (8.2.5) to remove any particulate matter that is present.

#### 8.4.3.3 Procedure

Set up the ion chromatograph according to the instrument manufacturer's instructions. The instrument is ready for operation as soon as the base line is stable and peak repeatability from an injected standard solution is within acceptable limits.

#### 8.4.3.4 Calibration

Identify peaks for sulfate. In calculations concentrations, use the fact that the area of the peak is proportional to the concentration of sulfate.

a) Prepare calibration solutions as described in 8.4.2.1 or 8.4.2.2 depending on whether a standard addition or an external calibration technique is being used;

b) analyse the calibration solutions chromatographically;

c) use the data obtained to calculate the regression line (reject it if not linear);

d) calculate the slope (b) and the ordinate intercept (a) of the calibration function.

#### 8.4.3.5 Measurement

Inject the sample into the chromatograph and measure the sulfate peak.

Check if the sample to be analysed is in the calibration range. If not, change the dilution and retry.

#### 8.4.3.6 Validity check of the calibration function

After each sample series at least, but in any case after twenty measurements, measure a minimum of two calibration solutions of different concentrations in lower and upper parts of the working range, in order to check the continuing validity of the calibration function.

## 8.5 Expression of the results

### 8.5.1 Calculation of results using standard addition technique

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 sulfate concentration of the test solution. Generally, this model can be written as:

$$y_\mathrm{i} = a + b \times x_\mathrm{i} \tag{10}$$

In this particular case of three standard additions:

$$y_\mathrm{i} = S_\mathrm{i} \text{ (for } i \text{ = 0, 1, 2, 3)} \tag{11}$$

$$x_\mathrm{i} = \rho_\mathrm{s} \times V_\mathrm{i} \text{ (for } i \text{ = 0, 1, 2, 3)} \tag{12}$$

where

$\rho_\mathrm{s}$ is the concentration, in mg/l, of the standard solution;

$V_\mathrm{i}$ are the various volumes, in l, of the standard solution added;

$S_\mathrm{i}$ are the net signals after the various additions.

The values of $b$ and $a$ can then be calculated as follows:

$$b = \frac{n \times \sum x_\mathrm{i} y_\mathrm{i} - \sum x_\mathrm{i} \sum y_\mathrm{i}}{n \times \sum x_\mathrm{i}^2 - \left(\sum x_\mathrm{i}\right)^2} \tag{13}$$

$$a = \frac{\sum y_\mathrm{i} - b \times \sum x_\mathrm{i}}{n} \tag{14}$$

where

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

Calculate the mass concentration of sulfate, $\rho_\mathrm{f}$, in mg/l, of the filtrate of the test portion using the following equation:

$$\rho_\mathrm{f} = \frac{a/b}{V_\mathrm{f}} \tag{15}$$

where

$V_\mathrm{f}$ is the volume, in l, of the filtrate of the test portion used to prepare the test solution.

Calculate the sulfate content in the sample as a mass fraction of sulphate, $w_\mathrm{SO4}$, in mg of sulfate per kg of fertilizer using the following equation:

$$w_\mathrm{SO4} = \frac{\left(\rho_\mathrm{f} - \rho_\mathrm{bl}\right)}{m} \times V_\mathrm{t} \tag{16}$$

where

$\rho_f$ is the mass concentration, in mg/l, of the filtrate of the test portion, as determined using Equation (15);

$\rho_{bl}$ is the mass concentration, in mg/l, of the blank solution;

$m$ is the mass of the sample, in kg, taken for the extraction, and corrected for water content;

$V_t$ is the total volume, in l, of extract (filtrate of the test portion).

### 8.5.2 Calculation of results using external calibration

Estimate the mass concentration, $\rho$, in mg/l, of the anion in the solution using the peak area and the rearranged calibration equation as follows:

$$\rho = \frac{(y-a)}{b} \tag{17}$$

where

$y$ is the sulfate peak area of the sample to be analysed;

$a$ is the ordinate intercept of the calibration function (see Equation (14));

$b$ is the slope of the calibration function (see Equation (13)).

Take into account all dilution steps.

Calculate the sulfate content in the sample as a mass fraction of sulphate, $w_{SO4}$, expressed in mg of sulfate per kg of fertilizer using the following equation:

$$w_{SO_4} = \frac{V_0 / 1000 \times \rho \times D \times 100}{M_0} \tag{18}$$

where

$M_0$ is the amount of the weighted test portion, in g (before extraction);

$V_0$ is the volume of extraction solution in ml;

$\rho$ is the mass concentration in mg/l, measured by IC as calculated using Equation (17);

$D$ is the dilution of extract solution injected in chromatogram taking into account any dilutions made in the sample extraction stage (CEN/TS 15925, CEN/TS 15926, CEN/TS 15960 or CEN/TS 15961).

Sulfur contents of secondary nutrient fertilizers are to be expressed in the oxide form ($SO_3$) or the elemental form (S). As the results of the determination are expressed as sulphate ($SO_4$), the following conversion factors shall be used:

$S = 0{,}333 \times SO_{4;}$

$SO_3 = 0{,}833 \times SO_{4.}$

## 9 Precision of methods A, B and C

### 9.1 Inter-laboratory tests

Details of inter-laboratory tests on the precision of the methods are summarized in Annex A. The values derived from those tests may not be applicable to concentration ranges and matrices other than those given.

### 9.2 Repeatability

The absolute difference between two independent single test results, obtained using 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 not more than 5 % of the cases be greater than the repeatability limits $r$ given in Table 3 (method A), Table 4 (method B) and Table 5 (method C).

### 9.3 Reproducibility

The absolute difference between two single test results, obtained using the same method on identical test material in different laboratories with different operators using different equipment, will in not more than 5 % of the cases be greater than the reproducibility limits $R$ given in Table 3 (method A), Table 4 (method B) and Table 5 (method C).

**Table 3 — Precision data method A**

| **Samples** | **Extraction method** | $\bar{x}$ **(mg/kg)** | $r$ **(mg/kg)** | $R$ **(mg/kg)** |
|---|---|---|---|---|
| NPK (16-16-8+4S) | CEN/TS 15960 | 10,22 | 0,39 | 0,84 |
| NS (AN based) | CEN/TS 15960 | 15,66 | 0,31 | 0,78 |
| NPK (16-16-8+4S) (repetition) | CEN/TS 15960 | 10,25 | 0,36 | 0,45 |
| Urea+S | CEN/TS 15925 | 13,85 | 0,42 | 1,13 |
| Urea+S (repetition) | CEN/TS 15925 | 14,08 | 0,32 | 1,74 |
| NPK (16-16-8+4S) | CEN/TS 15961 | 9,83 | 0,37 | 1,01 |
| NS (AN based) | CEN/TS 15961 | 14,32 | 0,5 | 3,69 |
| NS (AN based) (repetition) | CEN/TS 15961 | 14,1 | 0,7 | 4,4 |
| UAN+S | CEN/TS 15926 | 16,35 | 0,52 | 4,63 |
| UAN+S (repetition) | CEN/TS 15926 | 17,43 | 0,24 | 0,27 |

**Table 4 — Precision data method B**

| Samples | $\bar{x}$ (mg/kg) | $r$ (mg/kg) | $R$ (mg/kg) |
|---|---|---|---|
| NPK (16-16-8+4S) | 10,09 | 0,34 | 1,63 |
| NS (AN based) | 15,05 | 0,71 | 3,17 |
| UAN+S | 13,55 | 0,42 | 2,56 |

**Table 5 — Precision data method C**

| Samples | $\bar{x}$ (mg/kg) | $r$ (mg/kg) | $R$ (mg/kg) |
|---|---|---|---|
| NPK (16-16-8+4S) | 10,25 | 0,18 | 1,13 |
| NS (AN based) | 14,8 | 0,8 | 3,5 |
| UAN+S | 13,95 | 0,6 | 5,3 |

## 10 Test report

The test report shall contain at least the following information:

a) all information necessary for the complete identification of the sample;

b) test method (A, B or C) used with reference to this document;

c) test results obtained expressed as percentage mass fraction of sulfur in the fertilizer;

d) date of sampling and sampling procedure (if known);

e) date when the analysis was finished;

f) whether the requirement of the repeatability limit has been fulfilled;

g) all operating details not specified in this document, or regarded as optional, together with details of any incidents occurred when performing the method which might have influenced the test result(s).

# Annex A
(informative)

## Statistical results of the inter-laboratory tests

The precision of the method was established in 2005 and 2006 by Working Group 7 “Chemical analysis” of CEN/TC 260 “Fertilizers and liming materials” in inter-laboratory tests evaluated in accordance with ISO 5725-1. The statistical results are given in Table A.1 (method A), Table A.2 (method B) and Table A.3 (method C).

NOTE Based on the statistical results described in Annex A it can be concluded that the methods for the determination of sulfur give poor results, in particular under reproducibility conditions. Two alternative instrumental methods, using ICP-OES (method B) and IC (method C) have been ring tested and perform equally.

Considering the statistical data of both the alternative methods, the definition of the reproducibility limit, as well as the tolerances mentioned in Annex II of Regulation (EC) 2003/2003, it can be concluded that in most cases difficulties occur. The value of *R* already exceeds the allowed tolerance of maximum 0,9 %, whereas this tolerance meant to cover variations in manufacturing, sampling and analysis.

**Table A.1 — Statistical results of the inter-laboratory test method A**

| Sample | Extraction method | Number of labs | Number of labs after elimination of outliers | Mean $\bar{x}$ | Repeatability standard deviation $s_r$, % | Relative repeatability standard deviation $RSD_r$ | Repeatability limit $r$, % | Reproducibility standard deviation $s_R$, % | Relative reproducebility standard deviation $RSD_R$ | Reproducibility limit $R$, % |
|---|---|---|---|---|---|---|---|---|---|---|
| NPK 16-16-8+4S | 8.1 | 19 | 19 | 10,22 | 0,14 | 1,4 | 0,39 | 0,3 | 2,9 | 0,84 |
| NS (AN based) | 8.1 | 18 | 17 | 15,66 | 0,11 | 0,7 | 0,31 | 0,28 | 1,8 | 0,78 |
| NPK 16-16-8+4S (repetition) | 8.1 | 10 | 10 | 10,25 | 0,13 | 1,3 | 0,36 | 0,16 | 1,6 | 0,45 |
| Urea+S | 8.2 | 13 | 11 | 13,85 | 0,15 | 1,1 | 0,42 | 0,4 | 2,9 | 1,13 |
| Urea+S (repetition) | 8.2 | 7 | 7 | 14,08 | 0,11 | 0,8 | 0,32 | 0,62 | 4,4 | 1,74 |
| NPK (16-16-8+4S) | 8.3 | 19 | 19 | 9,83 | 0,13 | 1,3 | 0,37 | 0,36 | 3,7 | 1,01 |
| NS (AN based) | 8.3 | 18 | 18 | 14,32 | 0,18 | 1,3 | 0,5 | 1,32 | 9,2 | 3,69 |
| NS (AN based) (repetition) | 8.3 | 10 | 10 | 14,1 | 0,2 | 1,7 | 0,7 | 1,6 | 11,11 | 4,4 |
| UAN+S | 8.4 | 15 | 14 | 16,35 | 0,19 | 1,1 | 0,52 | 1,65 | 10,1 | 4,63 |
| UAN+S (repetition) | 8.4 | 8 | 6 | 17,43 | 0,09 | 0,5 | 0,24 | 0,09 | 0,5 | 0,27 |

**Table A.2 — Statistical results of the inter-laboratory test method B**

| Sample | Number of labs | Number of labs after elimination of outliers | Mean $\overline{x}$ | Repeatability standard deviation $s_r$, % | Relative repeatability standard deviation $RSD_r$ | Repeata-bility limit $r$, % | Reproduci-bility standard deviation $s_R$, % | Relative reproduce-bility standard deviation $RSD_R$ | Reproduci-bility limit $R$, % |
|---|---|---|---|---|---|---|---|---|---|
| NPK (16-16-8+4S) | 16 | 16 | 10,09 | 0,12 | 1,2 | 0,34 | 0,58 | 5,8 | 1,63 |
| NS (AN based) | 16 | 16 | 15,05 | 0,25 | 1,7 | 0,71 | 1,13 | 7,5 | 3,17 |
| UAN+S | 12 | 10 | 13,55 | 0,15 | 1,1 | 0,42 | 0,91 | 6,7 | 2,56 |

**Table A.3 — Statistical results of the inter-laboratory test method C**

| Sample | Number of labs | Number of labs after elimination of outliers | Mean $\overline{x}$ | Repeatability standard deviation $s_r$, % | Relative repeatability standard deviation $RSD_r$ | Repeata-bility limit $r$, % | Reproduci-bility standard deviation $s_R$, % | Relative reproduce-bility standard deviation $RSD_R$ | Reproduci-bility limit $R$, % |
|---|---|---|---|---|---|---|---|---|---|
| NPK (16-16-8+4S) | 8 | 6 | 10,25 | 0,06 | 0,6 | 0,18 | 0,4 | 3,9 | 1,13 |
| NS (AN based) | 8 | 8 | 14,8 | 0,3 | 1,9 | 0,8 | 1,2 | 8,3 | 3,5 |
| UAN+S | 7 | 6 | 13,9 | 0,2 | 1,4 | 0,6 | 1,9 | 13,6 | 5,3 |

# Bibliography

[1] EN 1482-1, *Fertilizers and liming materials - Sampling and sample preparation - Part 1: Sampling*

[2] ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results - Part 1: General principles and definitions*

[3] *Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13 October 2003 relating to fertilisers,* Official Journal L 304, 21/11/2003 P. 0001-0194, Annex IV, method 8.9, Annex II.

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