# Annex D.4

## *Inorganic fertilizers — Determination of the free formaldehyde content in nutrient polymers*

## Draft method

## 1 Scope

This document specifies methods for the determination of the free formaldehyde content in solid nutrient polymers (method A) and in liquid nutrient polymers (method B).

## 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 1482-2, *Fertilizers and liming materials — Sampling and sample preparation — Part 2: General sample preparation provisions*

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

EN 12944-2, *Fertilizers and liming materials— Vocabulary — Part 2: Terms relating to fertilizers*

## 3 Terms and definitions

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

**3.1**
**free formaldehyde**
mass percentage of unreacted formaldehyde in the component material

**3.2**
**nutrient polymers**
component material of EU fertilizing products consisting of polymers exclusively made up of virgin material substances and mixtures, where the purpose of the polymerisation is to control the release of nutrients from one or more of the monomer substances

**3.3**
**virgin material substances and mixtures**
component material of EU fertilizing products consisting of virgin material substances and mixtures

Note 1 to entry: Excluded are the following products: waste and by-products according to [4], materials formerly having constituted in waste or by-products, animal by-products or derived products and polymers.

# 4 Principle

Reaction of the free formaldehyde with sodium sulphite, in the presence of a measured excess of acid, in accordance with the reaction:

$$HCHO + Na_2SO_3 + H_2O \rightarrow CH_2(OH)SO_3Na + NaOH$$

and alkaline titration of the unreacted excess acid.
The acid-sulphite mixture provides an essentially neutral buffered system which prevents hydrolysis of condensed formaldehyde. A reaction temperature close to 0 °C (lower than 4 °C) ensure the absence of side reactions.

# 5 Reagents

**5.1 Hydrochloric acid solution**, aqueous standard volumetric solution, molar concentration $c$ = 0,5 mol/l.

Sulphuric acid solution with a molar concentration of 0,25 mol/l can be used as an alternative.

**5.2 Sodium sulphite solution**, aqueous solution, $c$ = 1,0 mol/l.

**5.3 Hydrochloric acid solution,** aqueous solution in sodium sulphite, $c$ = 0,1 mol/l.

The solution shall be freshly prepared by mixing 80 ml of sodium sulphite solution (5.2) with 20 ml of hydrochloric acid solution (5.1). To be kept in ice and water bath.

**5.4 Sodium hydroxide solution,** aqueous standard volumetric solution, $c$ = 0,1 mol/l.

**5.5 Dimethylsulfoxyde solution,** aqueous solution at a volume fraction of 50 %.

To be kept in ice and water bath.

Another solvent, for example ethylene glycol, can be used. In that case, be sure that this will not produce secondary reactions.

**5.6 Thymolphtalein,** 0,1 % solution in ethanol.

**5.7 Distilled or deionised water**

For all analytical work, the electrical conductivity shall at least be < 0,5 mS/m (at 25 °C)**.**

# 6 Apparatus

The usual laboratory glassware and equipment, in particular, the following shall be used.

**6.1 Magnetic stirrer.**

**6.2 Analytical balance,** capable of weighing to the nearest 0,1 mg.

**6.3 Conical flask,** capacity 250 ml with a glass stopper.

**6.4 Ice and water bath.**

**6.5 Burette,** with a precision of 0,05 ml and a division of 0,1 ml (class A).

**6.6 Stopwatch.**

# 7 Sampling and sample preparation

Sampling is not part of the method specified in this document. Recommended sampling methods are given in EN 1482-1.
Sample preparation shall be carried out in accordance with EN 1482-2.

# 8 Procedure

## 8.1 General

Two analyses shall be performed simultaneously for the determination.

## 8.2 Method A – Solid nutrient polymers

In a 250 ml conical flask (6.3) put a magnetic stirrer (6.1), 1 ml of thymolphtalein (5.6) and 50 ml of dimethylsulfoxyde solution (5.5) previously cooled and kept in the ice and water bath (6.4). Weigh, to the nearest 0,1 mg, around 20 g of the sample and put it into the conical flask. Close the flask, shake it slightly by hand and put it immediately in the ice and water bath to keep the internal temperature close to 0 °C. Let it stand for 20 min, stirring at 10 min intervals during standing. Neutralize with sodium hydroxide solution (5.4) to the blue colour change of the thymolphtalein (5.6) and put the flask back into the ice and water bath for 20 min, stirring at 10 min intervals during standing.
The neutralization to the blue colour change of the thymolphtalein before adding the sulphite eliminates the possible interference of an acid/neutral buffered pH of the solid samples.
Add with the burette (6.5), within max 10 seconds and whilst stirring, 20 ml of hydrochloric acid solution (5.3) previously cooled and kept in the ice and water bath. Close the flask, shake it slightly by hand and put it immediately in the ice and water bath. Wait 5 min to ensure complete reaction of the formaldehyde with sulphite. Titrate immediately under stirring (in less than 1 min) the excess of acid with the sodium hydroxide solution (5.4) to the blue colour change. Record the volume, $V_1$, of the sodium hydroxide solution used, in millilitres.
Carry out a blank test under the same conditions, but omitting the test portion, and note the volume $V_2$, in ml, of the sodium hydroxide solution used.

## 8.3 Method B – Liquid nutrient polymers

In a 250 ml conical flask (6.3) put a magnetic stirrer (6.1), 1 ml of thymolphtalein (5.6) and 50 ml of dimethylsulfoxyde solution (5.5) previously cooled and kept in the ice and water bath (6.4). Weigh, to the nearest 0,1 mg, around 20 g of the sample and put it into the conical flask. Close the flask, shake it slightly by hand and put it immediately in the ice and water bath to keep the internal temperature close to 0 °C. Let it stand for 20 min, stirring at 10 min intervals during standing.
Add with the burette (6.5), within max 10 seconds and whilst stirring, 20 ml of hydrochloric acid solution (5.3) previously cooled and kept in the ice and water bath. Close the flask, shake it slightly by hand and put it immediately in the ice and water bath. Wait 5 min to ensure complete reaction of the formaldehyde with sulphite. Titrate immediately under stirring (in less than 1 min) the excess of acid with the sodium hydroxide solution (5.4) to the blue colour change. Record the volume, $V_1$, of the sodium hydroxide solution used, in ml.
Carry out a blank test under the same conditions, but omitting the test portion, and note the volume $V_2$, in ml, of the sodium hydroxide solution used.

# 9 Calculation and expression of results

The free formaldehyde content, $w$, expressed in mg/kg, is given by Formula (1):

$$w = (V_2 - V_1) \times M \times 30{,}02 \times 1\,000/m \qquad (1)$$

where

$V_1$ is the volume of sodium hydroxide solution used for the determination, in ml;

$V_2$ is the volume of sodium hydroxide solution used for the blank test, in ml;

$M$ is the molarity of sodium hydroxide solution, in mol/l;

$m$ is the mass of the test portion, in g.

When the difference ($V_2$ - $V_1$) is slightly negative, the result is assumed to be 0 mg/kg.

# 10 Precision

## 10.1 Inter-laboratory tests

<to be added>
Inter-laboratory tests have been carried out in 20**. The number of participating laboratories and different fertilizer samples are mentioned in Annex A. Repeatability and reproducibility were calculated according to ISO 5725-2.

It is possible that the values derived from these inter-laboratory tests are not applicable to concentration ranges and matrices other than those given in Annex A.

## 10.2 Repeatability

The absolute difference between two independent single 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 not more than 5 % of the cases exceed the values of *r* given in Table 1 (method A) and Table 2 (method B).

## 10.3 Repeatability and 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 not more than 5 % of the cases exceed values of *R* given in Table 1 (method A) and Table 2 (method B).

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**Table 1 — Mean values, repeatability and reproducibility limits – Method A**

| **Sample** | $\bar{x}$ % | $r$ % | $R$ % |
|---|---|---|---|
| <to be added> | | | |
| | | | |
| | | | |

**Table 2 — Mean values, repeatability and reproducibility limits – Method B**

| **Sample** | $\bar{x}$ % | $r$ % | $R$ % |
|---|---|---|---|
| <to be added> | | | |
| | | | |
| | | | |

## 11 Test report

The test report shall contain at least the following information:

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

b) the test method used with reference to this document, including its year of publication;

c) the test results obtained;

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

e) date when the analysis was finished;

f) 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

<to be added>

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# Bibliography


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

[2] EN 1243:2011, *Adhesives — Determination of free formaldehyde in amino and amidoformaldehyde condensates*

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

[4] Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003