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Organic and organo-mineral fertilizers — Determination of the nitrogen content

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Élément introductif — Élément central — Élément complémentaire

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European foreword

This document (CEN/prEN 17771) has been prepared by Technical Committee CEN/TC 260 “Fertilizers and liming materials”, the secretariat of which is held by DIN.

This is a working document

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This document has been prepared under a Standardization Request given to CEN by the European Commission and the European Free Trade Association.

Introduction

Regulation (EU) 2019/1009 [5] lays down the rules on the making available on the market of EU fertilizing products and the specific safety and quality requirements for the defined product function categories (PFCs). Organic and organo-mineral fertilizers have been classified as PFC 1(A) and PFC 1(B).

This document defines test methods for the determination of the nitrogen content to be used for organic and organo-mineral fertilizers in order to measure the compliance with the related requirement in Regulation (EU) 2019/1009 [5].

1 Scope

This document specifies a method for the determination of the total nitrogen content and the content of ammoniacal, nitric, ureic and organic nitrogen in organic and organo-mineral fertilizers. This method is based on EN 15604:2009 and adapted to be applicable to organic and organo-mineral fertilizers.

This document is applicable to the fertilizing products blends where a blend is a mix of at least two of the following components fertilizers (PFC1), liming materials (PFC2), soil improvers (PFC3), bio-stimulants (PFC6) and where the following category organic fertilizer (PFC1A) or organo-mineral fertiliser (PFC1B) is the highest % in the blend by mass or volume, or in the case of liquid form by dry mass. If PFC1A or PFC1B is not the highest % in the blend, the European Standard for the highest % of the blend applies. In case a fertilizing product blend is composed of components in equal quantity, the user decides which standard to apply”.

Furthermore, the product shall at least contain a total nitrogen content of 1 % by mass. In case of blends, it is unattainable to ascertain the origin of the measured nitrogen with respect to the specific PFC.

Moreover, if the fertilizing product contains chelating or complexing agents or nutrient polymers this may affect the quantification of the different nitrogen forms. If these compounds are present additional care must be given to the verification of results (10).

Be sure of the ~~homogeneity~~homogeneity of the blend or products during the sampling and the preparation.

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 12944-1:1999,¹ *Fertilizers and liming materials — Vocabulary — Part 1: General terms*

EN 12944-2:1999,² *Fertilizers and liming materials — Vocabulary — Part 2: Terms relating to fertilizers*

EN 15604:2009, *Fertilizers — Determination of different forms of nitrogen in the same sample, containing nitrogen as nitric, ammoniacal, urea and cyanamide nitrogen*

[EN 1482 \(all parts\), Fertilizers and liming materials — Sampling and sample preparation](#)

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 12944-1:1999¹ and EN 12944-2:1999² 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>

¹ As impacted by EN 12944-1:1999/AC:2000.

² As impacted by EN 12944-2:1999/AC:2000.

4 Principle

The fertilizer sample shall be analysed according to four different analytical pathways to quantify the different forms of nitrogen in the sample. The nitrogen content determined by the four analytical pathways is representative for:

- 1) total nitrogen content;
- 2) total nitrogen content with exception of nitric nitrogen;
- 3) ammoniacal nitrogen content;
- 4) ammoniacal nitrogen and ureic nitrogen content.

The analysis results that are obtained by the determination of nitrogen according to these four pathways shall be used to calculate the content of ammoniacal, nitric, ureic, and organic nitrogen in the sample (see 9.1).

All four analytical pathways are based on or derived from the Kjeldahl principle. First, the operator shall perform a pretreatment and/or digestion to convert the nitrogen of a certain fraction of nitrogenous compounds to ammonia. Next, the operator shall distil the ammoniacal nitrogen into a known volume and concentration of hydrochloric acid. Finally, the operator shall quantify the ammoniacal nitrogen by titration of excess amount of acid in the receiving flask with sodium hydroxide.

The procedures that shall be performed for the pretreatment, digestion and distillation depend on the analytical pathway, as schematically shown in Figure 1.

When performing analytical pathway 1, the total nitrogen content shall be determined by a reduction with the aid of reduced iron and stannous chloride to convert nitric nitrogen to ammonia, followed by Kjeldahl digestion of the sample. Subsequently, the ammonia shall be distilled after addition of sodium hydroxide.

NOTE For the determination of the total nitrogen content, the Dumas method can also be applied if it is proven to be as accurate and precise as the Kjeldahl method.

When performing analytical pathway 2, the total nitrogen with the exception of nitric nitrogen shall be determined by a Kjeldahl digestion with ferrous sulfate. Then, the ammonia shall be distilled after addition of sodium hydroxide.

When performing analytical pathway 3, the ammoniacal nitrogen content shall be determined by a mild distillation after addition of magnesium oxide.

Performing pathway 4, the ureic and ammoniacal nitrogen content shall be determined by a pretreatment with urease. Subsequently, the ammonia shall be distilled by a mild distillation after addition of

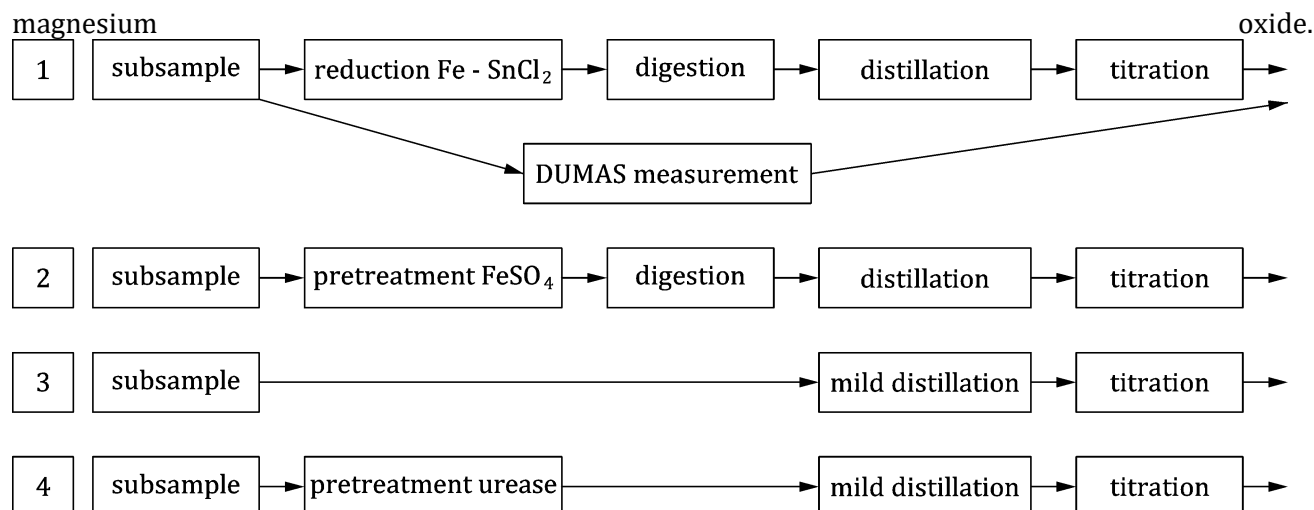


Figure 1 — The four analytical pathways for the determination of the different nitrogen fractions

5 Reagents

Water, with a specific conductivity not higher than 0,2 mS/m at 25 °C, free from the elements to be determined. All reagents should be of recognized analytical grade.

The following reagents shall be used.

5.1 Reduced iron

Iron powder reduced by hydrogen.

5.2 Standard iodine solution (I_2 , substance concentration (c) = 0.05 mol/l), certified.

5.3 Stannous chloride solution ($SnCl_2$, c = 0.532 mol/l)

For the preparation of the stannous chloride solution, the following tasks shall be performed:

- Weigh 120 g of stannous chloride dihydrate and transfer it into a 1 l volumetric flask.
- Add 400 ml concentrated hydrochloric acid (density at 20 ° ($C_{\rho_{20}}$) = 1.18 g/ml) to the flask.
- Bring to volume with water and shake the flask until all stannous chloride is dissolved.

The solution shall be clear and prepared immediately before use.

It is essential to check the reducing power of stannous chloride dihydrate. In order to check the reducing power, the following steps shall be performed:

- Weigh 0.5 g of stannous chloride dihydrate and transfer it into a 50 ml volumetric flask.
- Add 2 ml concentrated hydrochloric acid (ρ_{20} = 1.18 g/ml) to the flask.
- Bring to volume with water and shake the flask until all stannous chloride is dissolved.
- Transfer the content of the volumetric flask into a glass beaker.
- Weigh 5 g of Rochelle salt (potassium sodium tartrate) and transfer into the glass beaker.

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— Add sufficient quantity of sodium bicarbonate for the solution to be alkaline to litmus paper.

Titrate this solution with an iodine solution (I₂) (5.2) in the presence of a starch solution as an indicator. 1 ml of the iodine solution corresponds to 0.011 28 g of stannous chloride dihydrate. At least 80 % of the total tin present in the solution thus prepared shall be in bivalent form.

Therefore, at least 35 ml of the iodine solution should be required for the titration.

5.4 Defoaming agent

Octyl alcohol shall be used as defoaming agent, or any other non-nitrogen containing agent.

5.5 Ferrous sulfate

Crystalline ferrous sulfate heptahydrate (FeSO₄·7H₂O).

5.6 Sulfuric acid ($c = 18 \text{ mol/l}$)

Concentrated sulfuric acid (H₂SO₄), $\rho_{20} = 1.84 \text{ g/ml}$.

5.7 Hydrochloric acid solution ($c = 6 \text{ mol/l}$)

For the preparation of this hydrochloric acid solution gradually add one volume of concentrated hydrochloric acid ($\rho_{20} = 1.18 \text{ g/ml}$) to one volume of water.

5.8 Hydrochloric acid solution ($c = 0.1 \text{ mol/l}$)

For the preparation of this hydrochloric acid solution, the following tasks shall be performed:

- Fill a 1 l volumetric flask about three-quarters with water.
- Add 8.5 ml of concentrated hydrochloric acid ($\rho_{20} = 1.18 \text{ g/ml}$).
- Bring to a volume of 1 l.

5.9 Sodium hydroxide solution ($c = 7.5 \text{ mol/l}$)

For the preparation of the sodium hydroxide solution of about 30 % (mass concentration), the following tasks shall be performed:

- Fill a 1 l flask about three-quarters with water.
- Weigh 300 g sodium hydroxide and gradually add it to the flask.
- Stir the solution until all sodium hydroxide is dissolved.
- Bring to a volume of 1 l.

5.10 Sodium hydroxide solution ($c = 0.1 \text{ mol/l}$)

Certified standard solution of sodium hydroxide 0.1 mol/l.

5.11 Phosphate buffer ($c = 0.15 \text{ mol/l}$, pH 6.8)

- Weigh 12.60 g NaH_2PO_4 and transfer into a 1L volumetric flask,
- Weigh 6.38 g $\text{Na}_2\text{HPO}_4 \cdot 2 \text{H}_2\text{O}$ and transfer into the 1 l volumetric flask,
- Bring to volume with water and shake until all sodium phosphate is dissolved.
- Adjust the pH to 6,8 by adding hydrochloric acid solution (5.8) or sodium hydroxide (5.10)

5.12 Urease solution

For the preparation of the urease solution the following tasks shall be performed:

- Suspend 5 g of active urease, with an activity of at least 5 U/mg in 1 l of phosphate buffer pH 6.8 (5.11).
- Adjust the pH to 6.8 by adding hydrochloric acid (5.8) or sodium hydroxide solution (5.10).

5.13 Catalyst

A mixture of: (a) 10 g of potassium sulfate (K_2SO_4) and 0.3 g of copper oxide (CuO) or (b) 10 g of potassium sulfate and 1 g of copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) shall be used as catalyst for the digestion, possibly in the form of tablets containing similar amount of the chemicals mentioned.

5.14 Boiling chips**5.15 Indicator solutions**

The following tasks shall be performed to prepare the indicator solutions:

5.15.1 Indicator solution I

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- Weigh 1 g of methyl red and transfer it into a 1 l volumetric flask.
- Add 0.5 ml of sodium hydroxide solution 7.5 mol/l (5.9).
- Bring to volume with water and shake the flask until all methyl red is dissolved.

5.15.2 Indicator solution II

- Weigh 1 g of methylene blue and transfer into a 1 l volumetric flask.
- Bring to volume with water and shake the flask until all methylene blue is dissolved.

5.15.3 Combined indicator solution

- Mix one volume of indicator solution I (5.15.1) with two volumes of indicator solution II (5.15.2).

The combined pH indicator (5.15.3) changes colour from violet to green between pH 4.4 and pH 6.2 and is grey at the equivalence point (pH 5.2). A quantity of 0.5 ml (10 drops) of this indicator solution should be used.

5.15.4 Methyl red indicator solution

- Weigh 1 g of methyl red and transfer it into a 1 l volumetric flask.
- Add 0.5 l of ethanol.
- Bring to volume with water and shake the flask until all methyl red is dissolved.
- Filter the solution if necessary.

This pH indicator changes colour from red to yellow between pH 4.4 and pH 6.2 and may be used instead of that described in 5.15.3. A quantity of four or five drops of this indicator solution should be used.

5.15.5 Phenolphthalein solution

- Weigh 1 g phenolphthalein and transfer it into a 100 ml volumetric flask.
- Add 50 ml of ethanol.
- Bring to volume with water and shake the flask until all phenolphthalein is dissolved.

This pH indicator changes from colourless to pink between pH 8.3 and pH 10.0.

5.16 Magnesium oxide

5.17 Indicator paper

Litmus, bromothymol blue or other papers sensitive from pH 6 to pH 8.

5.18 Potassium thiocyanate

5.19 Potassium nitrate

5.20 Ammonium sulfate

5.21 Urea

5.22 Bovine serum albumin

Lyophilized, crystalized bovine serum albumin.

6 Apparatus

In order to facilitate automatization, commercially available automated apparatuses can be used if equal reaction conditions (e.g. reagents, temperature) are attained. Furthermore, the operations shall comply with the necessary safety precautions, including the precautions that are required for the avoidance of ammonia loss. If automated equipment is used then it must be proven to be as accurate and precise as the here described method. A pH electrode may be used for potentiometric determination of the pH, instead of the prescribed indicator solutions. In that case the pH electrode shall be used according to the corresponding user manual.

7 Sampling and sample preparation

Sampling and sample preparation should be performed following the principles described in EN 1482 (all parts) with appropriate adaptations, required to account for specificities of organic and organo-mineral fertilizers.

Nitrogen might be lost due to ammonia volatilization throughout the procedure, depending mainly on pH and temperature. When needed appropriate precautions shall be taken.

8 Procedure

8.1 General

The fertilizer sample shall be analysed according to four different analytical pathways to quantify the different forms of nitrogen that are present in the sample. Table 1 shows the standard unit operations that shall be carried out to obtain the results for the four analytical pathways.

Table 1 — Unit operations

Pathway	Pretreatment	Digestion	Distillation	Titration
1	8.2.1	8.2.5	8.2.6 (A: Distillation)	8.2.7
2	8.2.2	8.2.5	8.2.6 (A: Distillation)	8.2.7
3	8.2.3		8.2.6 (B: Mild distillation)	8.2.7
4	8.2.4		8.2.6 (B: Mild distillation)	8.2.7

NOTE The standard unit operations that shall be carried out to obtain the results for the four analytical pathways, of which the results shall be used to determine total nitrogen content and the contribution of the individual nitrogen fractions.

Be sure to take into account the safety of the fertilising product to avoid harm due to explosions, caking, foaming, bumping, toxic gases, toxic compounds for peoples.

8.2 Standard unit operations

The following tasks shall be performed by the operator.

8.2.1 Pretreatment for the determination of total nitrogen by reduction of nitric nitrogen to ammoniacal nitrogen

- Weigh to the nearest 0.001 g an amount of the sample not exceeding 40 mg of nitrogen or a maximum of 650 mg organic matter.
- Transfer the sample into a Kjeldahl tube e.g. 250 ml.
- Add 0.5 g of reduced iron (5.1) and 40 ml of stannous chloride solution (5.3).
- Shake the flask and leave it to stand for 0.5 h. During this half hour, stir a few times. If necessary, add a few drops of defoaming agent (5.4).
- Proceed with the digestion described in 8.2.5.

8.2.2 Pretreatment for the determination of total nitrogen with exception of nitric nitrogen

- Weigh to the nearest 0.001 g an amount of the sample not exceeding 40 mg of nitrogen or a maximum of 650 mg organic matter.
- Mix the sample in a Kjeldahl tube e.g. 250 ml with 50 ml water.
- Add 5 g of ferrous sulfate (5.5) and 5 ml of sulfuric acid (5.6).
- Proceed with the digestion described in 8.2.5.

8.2.3 Pretreatment for the determination of ammoniacal nitrogen content

- Weigh to the nearest 0.001 g an amount of the sample containing a maximum of 40 mg of ammoniacal nitrogen.
- Mix the sample in a distillation flask with water.
- Directly after proceed with the mild version of the distillation described in 8.2.6.

If the distillation cannot be carried out immediately afterwards, add 5 ml of hydrochloric acid solution (5.7).

8.2.4 Pretreatment using the urease method

- Weigh to the nearest 0.001 g an amount of the sample containing a maximum of 40 mg of ammoniacal and ureic nitrogen.
- Suspend the sample with 80 ml of phosphate buffer pH 6.8 (5.11).
- Add 20 ml of urease solution (5.12), mix and leave it to stand for 1 h at 20 °C to 25 °C.
- Transfer the sample into a distillation flask and proceed with the mild version of the distillation described in 8.2.6.

8.2.5 Digestion

- Add the catalyst (5.13) to the Kjeldahl tube.
- Add 20 ml of sulfuric acid (5.6) and mix thoroughly, add boiling chips (5.14) if necessary.
- Heat gently until foam is no longer formed.
- Increase the heat slowly: first the liquid darkens and then it clears with the formation of a yellow-green suspension.
- Continue heating for 1 h after obtaining a clear solution, maintaining it at simmering point.
- Allow the flask to cool.
- Transfer the contents of the Kjeldahl tube into a distillation flask quantitatively or proceed with the Kjeldahl tube as distillation flask for the distillation described in 8.2.6.

8.2.6 Distillation

- Transfer to the nearest 0.5 ml a volume of 50 ml of hydrochloric acid solution (5.8) into the receiving flask of the distillation.
- Add the indicator solution (5.15.3 or 5.15.4) to the receiving flask.
- Ensure that the tip of the condenser is at least 1 cm below the level of the solution in the receiver.
- Add demineralized water to the distillation flask with the pretreated sample to obtain sufficient volume for the distillation, then connect the distillation flask to the distillation setup.
- Dependent on the pathway, proceed with either step A (distillation) or B (mild distillation).

A: Distillation

Taking the necessary precautions to avoid any loss of ammonia, carefully add to the distillation flask enough sodium hydroxide solution (5.9) to make the liquid strongly alkaline (150 ml sodium hydroxide solution is generally sufficient). This should be checked by adding a few drops of phenolphthalein solution (5.15.5) or by the pH electrode (pH > 10).

B: Mild distillation

Taking the necessary precautions to avoid any loss of ammonia, carefully add 3 g of magnesium oxide (5.16) to the distillation flask with a funnel. Rinse the funnel with about 30 ml of demineralized water and immediately place the tube on the round bottom flask or immediately connect the flask to the distillation setup in order to avoid any loss of ammonia.

- Adjust the heating of the flask to distil approximately 150 ml, with a maximum speed of 50 ml per minute. When using fast and vigorous distillation, extra care shall be taken to ensure no droplets/splashes from the distillation flask pass into the receiving flask.
- Check with indicator paper (5.17) or by the pH electrode that the distillation has been completed. The distillation is finished if the freshly collected distillate has a neutral pH. If not, distil another 50 ml and repeat the test until the supplementary distillate has a neutral pH. Then, lower the receiver and distil a few millilitres more and rinse the tip of the condenser.

8.2.7 Titration

Titrate the excess of acid in the receiving flask with a standard solution of sodium hydroxide (5.10). The end point of the titration is indicated by the indicator changing colour or by potentiometric determination at pH 5.2. The result is noted as V_i (see 9.1).

8.2.8 Blank test

A blank test shall be performed for each individual pathway by omitting the sample and following the same procedure. The result is noted as V_0 (see 9.1).

9 Calculation of the results

9.1 Calculation of the nitrogen fractions

The amount of nitrogen, specified as mass fraction w_N , obtained by each pathway is expressed as nitrogen % (mass/mass) of the product according to Formula (2) in g of nitrogen per kg product according to Formula (1):

$$w_N (\%N \text{ by mass}) = \frac{(V_0 - V_i) \times c_{NaOH} \times M_N}{m_{sample} \times 1000} * 100 \quad (1)$$

or

$$w_N (gN/kg) = \frac{(V_0 - V_i) \times c_{NaOH} \times M_N}{m_{sample}} \quad (2)$$

Where

- V_0 is the volume of standard solution of sodium hydroxide (5.10) used for the titration of the blank in ml;
- V_i is the volume of standard solution of sodium hydroxide (5.10) used for the titration of the sample in ml;
- c_{NaOH} is the exact concentration of standard solution of sodium hydroxide solution (5.10) in mol/l;
- M_N is the molar mass of nitrogen (14.007 g/mol);
- m_{sample} is the amount of the sample in g.

Then the different nitrogen fractions shall be calculated using the analysis results obtained from the different pathways and the formulae listed below.

Nitrogen fraction	Formula (results of individual pathways in g/kg that shall be subtracted)	
N-total	= 1	(2)
N-nitric (NO ₃ -N)	= 1 - 2	(3)
N-ammoniacal (NH ₃ -N)	= 3	(4)
N-ureic	= 4 - 3	(5)
N-organic	= N-total - N-mineral = 1 - ((1-2) + 3 + (4 -3)) = 2 - 4	(6)

9.2 Calculation of the maximum ammonium nitrate content

The theoretical maximum for the ammonium nitrate content shall be calculated based on the ammoniacal or nitric nitrogen content. The fraction which is present in minority shall be used to calculate the maximum ammonium nitrate content using the following Formula (7):

$$w_{\text{MAX}_{\text{NH}_4\text{NO}_3}} = \text{MIN}(w_{\text{N}_{\text{NO}_3}}; w_{\text{N}_{\text{NH}_4}}) / M_{\text{N}} \times M_{\text{NH}_4\text{NO}_3} \quad (7)$$

where

- $w_{\text{MAX}_{\text{NH}_4\text{NO}_3}}$ is the maximum ammonium nitrate content in g/kg;
- $w_{\text{N}_{\text{NO}_3}}$ is the nitrate nitrogen content in the sample in g/kg;
- $w_{\text{N}_{\text{NH}_4}}$ is the ammoniacal nitrogen content in the sample in g/kg;
- MIN is the minimum of the values between brackets;
- M_{N} is the molar mass of nitrogen (14.007 g/mol);
- $M_{\text{NH}_4\text{NO}_3}$ is the molar mass of ammonium nitrate (80.043 g/mol).

10 Verification of the result

Check on a regular basis if the apparatus is working properly, with a standard solution including various forms of nitrogen in proportions similar to those of the sample. These standard solutions are prepared from standard solutions of potassium thiocyanate (5.18), potassium nitrate (5.19), ammonium sulfate (5.20), urea (5.21), bovine serum albumin (5.22).

Moreover, in case the fertiliser product contains complexing agents, chelating agents or nutrient polymers, additional checks should be performed to verify if all forms of nitrogen are quantified correctly.

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 with reference to this document (CEN/TS 17771:2022);
- c) test results of the determination, expressed in g N/kg sample in the fertilizer;
- 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 that occurred when performing the method which might have influenced the test result(s).

Bibliography

- [1] EN 1482 (all parts), *Fertilizers and liming materials — Sampling and sample preparation*
- [2] EN 15475, *Fertilizers — Determination of ammoniacal nitrogen*
- [3] EN 16168:2012, *Sludge, treated biowaste and soil — Determination of total nitrogen using dry combustion method*
- [4] EN ISO 3696:1995, *Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)*
- [5] 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