Annex D.6

Inorganic fertilizers - Determination of the organic carbon content in ammonium nitrate fertilizers of high nitrogen content

Draft method

1 Scope

This document specifies a method for the determination of total organic carbon (TOC) by elemental analysis using dry combustion. The method is applicable for ammonium nitrate (AN) with high N-content (N higher 31,5 %). In Regulation (EU) 2019/1009 [1] the mass of combustible material in PFC 1(C)(I)(a)(i-ii)(A) type products must not exceed 0.4 % if N content is between 27,8 % and 31,5 %, and 0,2 % if N content is 31,5 % or higher.

2 Normative references

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

EN 1482-2 *Fertilizers and liming materials — Sampling and sample preparation — Part 2: Sample preparation*

3 Terms and definitions

For the purpose of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1 Total organic carbon (TOC)

Quantity of carbon that originates from organic molecules and is converted into carbon dioxide by combustion and which is not liberated as carbon dioxide by acid treatment.

3.2 Total inorganic carbon (TIC/IC)

Quantity of carbon that is liberated as carbon dioxide by acid treatment. Typically, TIC represents the carbonates in a sample.

4 Principle

The samples are crushed into a powder, weighed into the measuring vessel. In the vessel a constant amount of acid will be added to react with the crushed sample. The sample will react with the acid causing it to release CO_2 because of the dissociation of the inorganic carbons (carbonates) leaving behind the organic carbon. The sample which is dissolved in the acid solution is then dried at 80 °C and when it has recrystallised and is completely dry again the sample can be measured on the carbon analysing apparatus. The organic carbon will be released as CO_2 in the apparatus and measured by means of CO_2 detector (e.g. Non dispersive infrared detector (NDIR) or infrared detector (IR)).

5 Applicability

The method is applicable to ammonium nitrate with high-N (> 31.5% N) on solid material.

The determination is not selective, because combustion occurs for both organic and inorganic carbon, so a pretreatment with acid is necessary.

6 Interferences

Follow instructions from manufacturer on how to use chemicals, and other set ups in instrument to remove interferences.

Acidic molecules/ halogen atoms (Cl^-) will be present in the sample. If the apparatus is not resistant to this it could harm the apparatus and thus interfere with a correct measurement.

If the sample is measured with a ramping temperature profile, there could be an interference caused by ammonium nitrate. The exothermic decomposition and the oxidative nature of ammonium nitrate could cause inorganic carbons to combust at lower temperatures causing inconsistencies in the organic carbon measurement.

7 Reagents

All reagents should be of recognized analytical grade.

7.1 Calibration standards (that suits measuring range)

7.2 Demin-water

Water with a specific conductivity not higher than 0.2 mS/m at 25 °C, free from elements to be determined.

7.3 Hydrochloric acid 37% (12 M), CAS 7647-01-0, e.g. EMSURE ® ACS, ISO, Reag. Ph Eur from Merck, or equivalent[1].

7.4 Hydrochloric acid solution (2.4 M)

Hydrochloric acid solution (2.4 M) is made by diluting hydrochloric acid 37% (7.2) in a 1:4 ratio (e.g. 10 ml acid + 40 ml demin-water (7.2)).

[1] EMSURE ® ACS, ISO, Reag. Ph Eur from Merck is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of this product.

7.5 Carrier gas, e.g. oxygen of purity according to manufacturer's instructions. Free of carbon dioxide and organic impurities.

8 Apparatus

8.1 Precision balance, capable of measuring to nearest 0.5 % of test portion mass

8.2 Instrument for determination of carbon in solids, with accessories and reagents (as described by instrument manufacturer)

8.3 Crucibles, capsules or boats, made of acid resistant material (e.g. quartz-glass or ceramic)

8.4 Drying system (e.g. heating plate)

The drying system is used to evaporate the acid after it has been added to the sample.

8.5 Pipette (suitable to dispense droplets)

The pipette is used to add the acid as droplets to the sample.

9 Procedure

WARNING High temperatures will be present during the measurement.

Ammonium nitrate that is combusted at a high temperature (starting at 200-250 °C) will release NO_x-gasses.

9.1 General

In this procedure, the TIC present in the sample is previously removed by treating the sample with acid. The carbon dioxide released by the following combustion step is measured by one of the techniques mentioned in 4 and indicates the TOC directly.

9.2 Carbon analyser

The carbon analyser used to measure the TOC after the acid treatment needs to fulfil certain specifications to protect the apparatus and the user also for a consistent use of the method.

It is important that the combustion tube of the apparatus can be stable at a high temperature (900-1500°C), based on the material (e.g. ceramic/ quartz glass) used for the combustion tube. The apparatus will need to stay at high temperature or can be cooled down in standby mode.

The equipment needs to be resistant to the acidic gas molecules that will travel through the tubing. If there are no countermeasures for this, the apparatus tubing could react with the molecules and deteriorate. Countermeasures can be an equipment which has components that are resistant to these kinds of molecules or a halogen trap to catch the chlorine that is present.

The apparatus needs to be able to use pure oxygen gas to make an oxidizing atmosphere within the equipment.

The carbon analyser makes use of a detector which is capable of measuring CO_2 emissions from the combusted sample (e.g. IR or NDIR sensor with a specific wavelength to measure CO_2).

Different instruments utilize different combustion procedures, the main difference being an isothermal versus ramping-temperature combustion. For determination of TOC in AN, ramping temperature analysis is not suited for this sample matrix.

9.3 Pre-treatment

If the sample contains noticeable amounts of IC, it is necessary to perform a pre-treatment step before direct analysis of TOC. The pre-treatment or acid treatment is done with diluted hydrochloric acid (7.3). As a standard weight 300,0 mg of the crushed/mixed sample is weighed evenly in the measuring boat, whereafter 6 droplets of the diluted hydrochloric acid are added evenly across the boat by means of a pipette. It is important the sample is made homogeneous by crushing/mixing the sample to avoid any deviations of a normal measurement.

After the addition of the acid to the sample, the boat/crucible is placed on/in a drying system (80 °C) to evaporate the acid and dry the sample.

The use of a different acid, such as phosphoric acid may be relevant for some samples or combustion equipment not able to handle halogens. In samples where IC is not present, the method presented in this report can be used without pre-treatment.

9.4 Combustion

After the pre-treatment the samples can be analysed. This will be done on a carbon analyser that fulfils the specifications described in 9.2 with a furnace method that is stable at a high temperature. This temperature is chosen and optimized to the capabilities of the used equipment, e.g. 1200 °C.

The boat/ crucible will be combusted fully, releasing the carbon dioxide coming from the remaining TOC in the sample. The carbon dioxide will be measured in the carbon dioxide detector and the signal will be calculated into a value for the TOC amount in the sample based on the calibration curve present in the sample.

9.5 Method validation

9.5.1 Limit of detection (LOD) and limit of quantification (LOQ)

The LOD is the lowest possible measurement where it can be stated with a statistical certainty that the examined analyte is present [3].

The LOD can be determined in 2 ways:

<u>Signal-noise approximation:</u>

Analyse 20 blank samples and determine the standard deviation of the values for the signal to noise ratios. The LOD would be determined by formula (2).

$$\mathrm{LOD} = \bar{x}_{\mathrm{bl}} + 3 \cdot s_{\mathrm{bl}} \qquad (2)$$

where

$\bar{x}_{\mathrm{bl}}$ is the average of all the blank measurements;

s_{bl} is the standard deviation on the blank measurements.

[3]

<u>Calibration line approximation:</u>

A calibration line is plotted, from which the slope (G) and residual standard deviation (s_{yx}) can be determined. The LOD can be calculated by formula (3).

$$\text{LOD} = 3 \cdot s_{yx}/G \tag{3}$$

where

s_{yx} is residual standard deviation of calibration line

G slope of calibration line

[3]

The LOQ is the lowest possible measurement to determine an analyte quantitatively with a certain statistical certainty [4]. The LOQ can be calculated by Formula (4) or Formula (5).

$$\text{LOQ} = \text{LOD} \cdot 2 \tag{4}$$

$$\text{LOD} = 6 \cdot s_{yx}/G \tag{5}$$

[3]

The limit of detection (LOD) and the limit of quantification (LOQ) are both determined on the carbon analyser, as presented. The calibration line, and the standard deviations are used to calculate these values. The values of TOC in relevant samples are expected to be significantly higher than 100 ppm (parts per million).

9.5.2 Repeatability and reproducibility

Repeatability is determined by analysing the same sample under the same conditions, including sample preparation, in quick succession of each other [3]. The sample gets measured 10 to 20 times and the standard deviation, s_r, is calculated. The repeatability r can be calculated by Formula (6).

$r = 2{,}8 \cdot s_r$ [3]

$$\text{RSD}_r = \frac{r}{\text{average measurement}} \cdot 100\ \% \tag{6}$$

where

r is repeatability

s_r standard deviation of measurements

$RSDr$ relative standard deviation of repeatability

The repeatability is determined by measuring sample in question multiple times on different days, by the same operator, with the method mentioned in this paragraph.

The inter-laboratory reproducibility can be determined by executing the analysis with different individuals, that all work in the same lab. All the analyses must be done on the same sample and on the

same equipment at different moments in time, and the standard deviation, s_L, is calculated. The reproducibility R_L can be calculated by Formula (7).

$$R_L = 2{,}8 \cdot s_L \text{ [3]}$$

$$\mathrm{RSD}_{R_L} = \frac{R_L}{\text{average measurement}} \cdot 100\ \% \tag{7}$$

where

R_L is reproducibility

s_L is standard deviation of measurements

RSD_{RL} relative standard deviation of reproducibility

9.6 Safety

The combustion of ammonium nitrate at high temperatures will cause NO_x vapours to be released. To combat the release of the NO_x vapours a proper ventilation system needs to be used (either the equipment or an external ventilation hood).

The boat/ crucible will be handled at high temperatures so a proper way to handle these should be used. This can be done with tweezers and a place to put the vessel on that can handle high temperatures (like a stone plate).

10 Calculation and expression of results

TOC mass contents are calculated from calibration function and sample mass, results are reported in mg/kg (ppm) or percent (%).

Results shall be reported to a maximum of two significant figures for percentages and a whole number for mg/kg values.

EXAMPLE

TOC 1600 mg/kg

TOC 0.16 %

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) a 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) 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)

results from ILS

Bibliography

[1] 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

[2] prEN 15936, *Sludge, treated biowaste, soil and waste — Determination of total organic carbon (TOC) by dry combustion*

[3] Van Assche, Caroline. *Kwaliteitszorg.* Van Assche, C. (2019). *Kwaliteitszorg.* Ghent: Odisee. Ghent : Odisee, 2019