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Fireworks — Test methods for determination of specific chemical substances —

Part 10:
Nitrogen content in nitrocellulose by iron(II) sulfate titration

Artifices de divertissement — Méthodes d'essai pour la détermination de substances chimiques spécifiques —

Partie 10: Taux d'azote dans la nitrocellulose par titration de l'ion sulfate de fer (II)

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 264, *Fireworks.*

A list of all the parts in the ISO 22863- series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Fireworks — Test methods for determination of specific chemical substances —

Part 10:
Nitrogen content in nitrocellulose by iron(II) sulfate titration

1 Scope

This document specifies the method for determination of the nitrogen content in nitrocellulose within pyrotechnic compositions of fireworks by iron(II) sulphate titration.

2 Normative reference

The following referenced documents are indispensable for the application of this document. For dated reference documents, only dated editions are applicable to be used. For undated references, the latest edition of the referenced document (including any subsequent amendments) applies.

ISO 22863-1, *Fireworks — Test methods for determination of specific chemical substances — Part 1: General*

3 Terms and definitions

No terms and definitions are listed in this document.

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

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

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

4 Principle

In a preliminary step, samples of pyrotechnic compositions containing nitrocellulose are submitted to special treatment to make them suitable to the determination, without error, of the nitrogen content of nitrocellulose. Thereby, the other molecules that possibly contain nitrogen atoms such as nitrates - except nitrocellulose (cellulose nitrate) - shall be removed from the sample before that determination.

The remaining cellulose nitrate in the sample is released by concentrated sulphuric acid, forming nitric acid which is then titrated with iron(II) sulphate ($FeSO_4$) according to the following reaction:

$$4\ FeSO_4 + 2\ HNO_3 + 2\ H_2SO_4 \rightarrow N_2O_3 + 2\ Fe_2(SO_4)3 + 3\ H_2O$$

The reaction is followed by potentiometry. The titration curve obtained exhibits an inflexion point corresponding to the quantitative neutralization of the nitrogen radicals of the sample.

5 Reagents and materials

All reagents shall be of recognized analytical grade. Verify whether the reagents are applicable for this specific purpose and free of interfering compounds.

5.1 Sulphuric acid (H_2SO_4) Chemical purity 94-97 %

5.2 Potassium Nitrate (Pure)

5.3 Iron(II) sulphate ($FeSO_4 \bullet 7H_2O$) Crystals (pure)

5.4 Distilled Water

5.5 Acetone (Pure and anhydrous)

6 Apparatus

6.1 Any (manual or automatic) pH meter capable of measuring pH with a precision better than 0,1

6.2 Platinum Electrode for pH measurement

6.3 Glass, graphite or tungsten Electrode for pH measurement (reference electrode)

6.4 Magnetic Stirrer base with stirring bar

6.5 Blender

6.6 Cooling bath (e.g. ice bath) and/or other mechanical cooling system

6.7 Opaque vessel

6.8 Agate mortar

6.9 150 ml and 200 ml beakers

6.10 Petri dishes

6.11 250 ml Erlenmeyer

6.12 Antistatic plastic bags

6.13 Balance, accurate to 0,0001 gram or 1/10000

6.14 Desiccator with drying agent (with colour indicator)

6.15 Laboratory reflux apparatus

6.16 100 °C drying oven

6.17 40 °C drying oven

6.18 50 °C drying oven

6.19 Timer (seconds)

6.20 Tissue paper or filtration paper

7 Preparation of the sample

7.1 Preliminary precaution

Before preparing the sample, all information on the chemical content of the pyrotechnic composition to be tested (at least chemical name and proportions) shall be given by the manufacturer.

The determination of the nitrogen content of the nitrocellulose requires that all other molecules that contain nitrogen atoms are extracted from the sample before the titration process. In most cases, such molecules are nitrates that can be extracted by dissolution with hot distilled water: depending on the solubility of nitrates in water and their percentage in the composition, such operation may need an iterative process as described in 7.3.

When other nitrogen-containing molecules are present and are not soluble in water, a specific solvent shall be used provided it does not dissolve nitrocellulose.

The extraction of nitrocellulose from the sample is carried out by dissolution in acetone. Such operation is applied to the sample after elimination of all nitrates and nitrogen-containing molecules if any. It shall then be checked whether acetone is also a solvent for the other remaining ingredients of the pyrotechnic composition to be tested. In such case, acetone shall be replaced by another solvent which, among the ingredients of the pyrotechnic composition, only dissolves nitrocellulose.

At the end of step three (7.4), the last solid residue should then only be nitrocellulose.

7.2 Step One

Take 10 grams of the composition containing nitrocellulose, accurately weighed to 1/10000 (6.13). Split it in three equal quantities and place each one in three antistatic plastic bags (6.12). Close the bags tightly.

Place the quantity of one first bag in a Petri dish (6.10) and then place the whole in an oven at 40 °C (6.17) for 12 h.

Grind the dried composition in an agate mortar (6.8) to obtain a fine powder of grain size less than 500 µm. Warning: compositions that are known to be sensitive to impact and friction shall be grinded cautiously with appropriate personal protective equipment or by use a specific grinding apparatus.

Keep the grinded dry composition in a desiccator for less than 3 h. If the sample is out of the oven for more than 3 h, re-dry it in an oven at 100 °C (6.16) for 1 h.

Weigh 3 grams of the dry grinded composition to 0,0001 gram (6.13).

If the pyrotechnic composition does not contain nitrates, except nitrocellulose, go to step three.

7.3 Step Two

Place the weighed 3 grams in a 250 ml Erlenmeyer (6.11), add 100 ml of distilled water (5.4) and heat the whole in a laboratory reflux apparatus (6.15) at 100 °C for 3 h. Take care that water does not evaporate quickly and totally during the reflux process.

Separate the solid residue by filtration on an appropriate tissue paper or filtration paper (6.20).

Rinse carefully with 30 ml of warm (> 80 °C) distilled water. Repeat the operation 3 times.

Check for the remaining presence of nitrates by means of infrared spectrometry: the characteristic peaks of the nitrates contained initially in the pyrotechnic composition (except those that characterize nitrocellulose) shall not appear in the infrared spectrum of the solid residue.

If such peaks are still observed, add 100 ml of distilled water (5.4) to the solid residue and heat the whole in a laboratory reflux apparatus (6.15) at 100 °C for 3 h. Separate the solid residue by filtration on an appropriate tissue paper or filtration paper (6.20).

Rinse carefully with 30 ml of hot (> 80 °C) distilled water. Repeat the operation 3 times.

Check again for the remaining presence of nitrates by means of infrared spectrometry. If such peaks are still observed, repeat the reflux process until there is no trace of nitrates (except nitrocellulose).

7.4 Step Three

Place the sample or the solid residue of step two in a 200 ml beaker (6.9) and add 100 ml of acetone (5.5). Stir the whole for 2 h at ambient temperature, using a magnetic stirrer (6.4).

Separate the liquid phase from the possible solid residue that lay at the bottom of the beaker and let it evaporate in an oven at 50 °C (6.18) for 48 h to obtain a last solid residue that contains nitrocellulose to be tested for its nitrogen content.

Check the absence of other molecules than nitrocellulose in the solid residue by infrared spectrometry.

If the weight of that last solid residue is smaller than the weight of the specimen to be used in the next titration phase, repeat the whole process with one or the two other thirds of the initial sample.

8 Preparation and calibration of the iron(II) sulphate solution

8.1 Preparation

Dissolve 90 grams of iron(II) sulphate (5.3) in 160 cm^3 of hot distilled water (5.4) using a blender (6.5) or equivalent equipment to crush the iron(II) sulphate crystals and help their complete and homogeneous dissolution.

Cool the iron(II) sulphate solution to room temperature using a cooling bath or other mechanical cooling system (6.6).

Add 800 cm^3 of a solution of 60 % concentrated sulphuric acid (5.1) in distilled water (5.4) to the iron(II) sulphate solution while cooling the whole solution during the process.

Complete to 1 l with distilled water (5.4).

Keep the resulting iron(II) sulphate solution in an opaque vessel (6.7).

8.2 Calibration

Weigh precisely a mass m around (0,275 ± 0,025) g of dry potassium nitrate (5.2) to 0,0001 g (6.13) and place it in a 150 ml beaker (6.9).

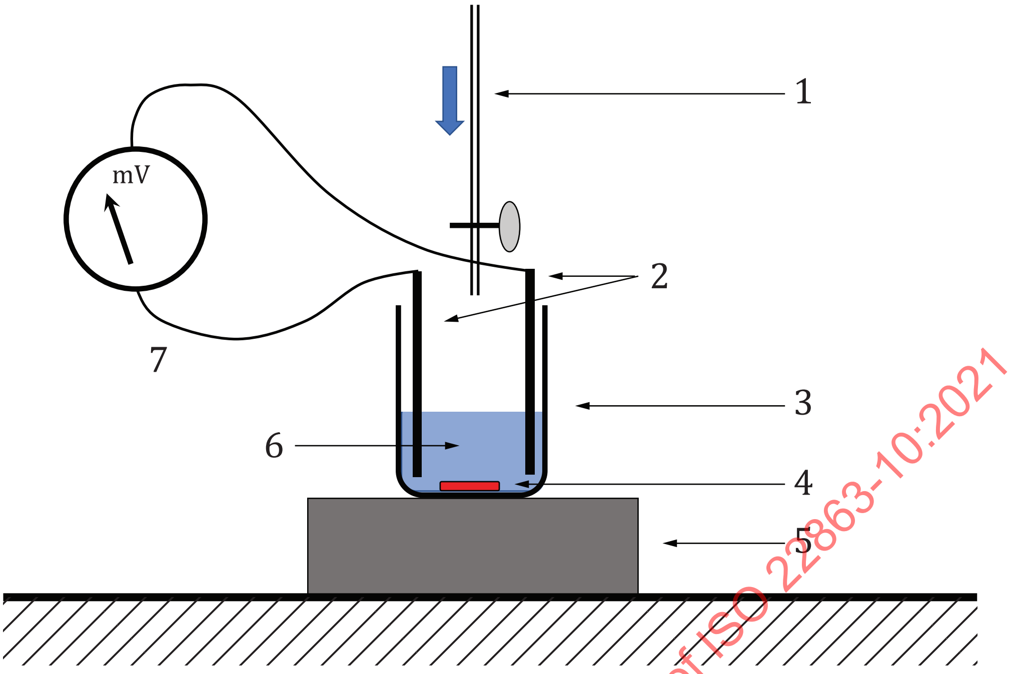
Add 100 cm^3 of sulphuric acid (5.1) and mix without heating with a magnetic stirrer (6.4) until potassium nitrate is fully dissolved.

Cool the solution by placing the beaker in an ice bath (6.6).

Lower the electrodes of the pH-meter (6.1) into the solution.

The electrodes should have a minimum of 4 h conditioning time in clean sulphuric acid before using.

After 8 min (6.19), start titrating by adding successively small quantities of the calibrated iron(II) sulphate solution (see Figure 1). Do not titrate so fast that heat builds up in the sample and causes localized oxidation of the sample. Overall titration time should be approximately 6 to 8 min (6.19).



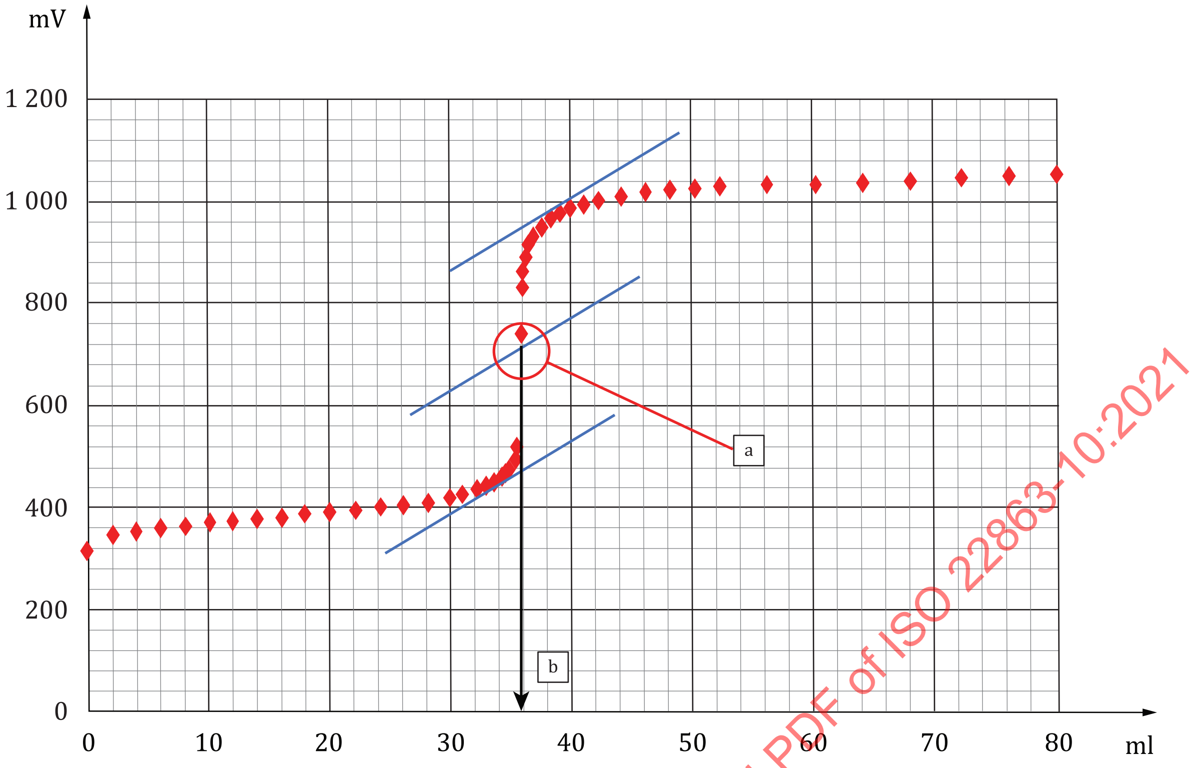
Key

1	pipet containing $FeSO_4$
2	electrodes of the pH-meter
3	150 ml beaker
4	stirring bar
5	magnetic stirrer
6	pH-meter
7	solution to be titrated

Figure 1 — Iron(II) sulphate titration apparatus

As the inflexion point of the voltage curve is neared (see Figure 2), slow the titration to the lowest volume increment possible and allow time for each increment to completely disperse before adding the next one.

Continue the addition of the iron(II) sulphate solution after the inflexion point. Stop the titration when the voltage curve allows an accurate determination of the volume of iron(II) sulphate solution corresponding to the inflexion point.



Key

[a] inflexion point.

[b] inflexion Volume *Vi.*

Figure 2 — Voltage curve

Raise the electrodes.

Rinse the electrodes with a beaker of clean sulphuric acid and allow excessive sulphuric acid to drain into the beaker while preparing for the next sample.

Calculate the nitrogen content of the potassium nitrate solution using Formula (1):

$$T = 0{,}1386 \cdot \frac{m}{Vi} \qquad (1)$$

where

m is the mass (in grams) of the sample of potassium nitrate as weighted in 8.2

Vi is the volume of iron(II) sulphate solution (in ml) corresponding to the inflexion point of the voltage curve

9 Titration of the last solid residue

Weigh a quantity of m_1 gram of the last solid residue obtained at the end of step three (7.4) to 0,0001 g (6.13) and place it in a 150 ml beaker (6.9).

The specimen should preferably consist of a 0,5000 ± 0,0500 g of sample.

Add 100 cm^3 of sulphuric acid (5.1) and mix without heating with a magnetic stirrer (6.4) until the solid residue is fully dissolved.

Cool the solution by placing the beaker in an ice bath (6.6).

Lower the electrodes of the pH-meter (6.1) into the solution and proceed in the same manner as for the calibration of the iron(II) sulphate solution. Stop the titration when the voltage curve allows an accurate determination of the volume of iron(II) sulphate solution corresponding to the inflexion point.

Raise the electrodes.

Rinse the electrodes with a beaker of clean sulphuric acid and allow excessive sulphuric acid to drain into the beaker while preparing for the next sample.

Calculate the nitrogen content of the solution as given in Formula (2):

$$N\% = \frac{T \cdot Vi_1 \cdot 100}{m_1} \qquad (2)$$

where

T is the nitrogen content of the potassium nitrate solution (7.2)

m_1 is the mass (in grams) of the sample of last solid residue

Vi_1 is the volume of iron(II) sulphate solution (in ml) corresponding to the inflexion point of the voltage curve

NOTE When the electrodes are not in use, they will be kept submerged in a beaker of clean sulphuric acid but not the pipet that is used to add the iron(II) sulphate solution. The end of the pipet will be capped to prevent evaporation of the solution. This evaporation would cause recrystallization of the iron(II) sulphate and clog the pipet tip.

10 Test report

The test report shall include at least the following information:

a) Name and address of the testing laboratory;

b) Date of issue;

c) Reference to this document, i.e. ISO 22863-10:2021;

d) Necessary description of the sample and how it was obtained according to ISO 22863-1;

e) Results of analysis;

f) Any anomaly that occurred while performing the tests.