INTERNATIONAL STANDARD

ISO 22863-12

First edition
2022-09

Fireworks — Test methods for determination of specific chemical substances —

Part 12: Picrates and picric acid by high performance liquid chromatography

Reference number
ISO 22863-12:2022(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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 12: Picrates and picric acid by high performance liquid chromatography

1 Scope

This document specifies the test method for the determination of picrates and picric acid in firework compositions by high performance liquid chromatography.

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.

ISO 22863-1:2020, *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 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/

4 Principle

Picric acid (C_6H_2–OH) and picrates (C_6H_2–OR, R being a metal or organic cation) in pyrotechnic compositions are extracted by dissolution in hot water which let free the picrate anion (C_6H_2–O^{-1}) in the sample solution and determined by high performance liquid chromatography (HPLC) under acidic conditions.

Qualitative analysis can then be carried out by setting the chromatograph to an appropriate detection wavelength and detect the possible emergence of a peak at the characteristic “retention time” of picric anions (characteristic time spent by such anions in the chromatograph column after the sample solution is injected).

Quantitative analysis is carried out by comparing the area under the peak, corresponding to picric anions in the chromatographic response of the sample solution, to that of external standards (ESTD) of known concentrations of picric acid.

5 Reagents

All reagents are of analytical purity, except for special provisions.

5.1 Standard picric acid, of purity 99 %.

5.2 Hydrochloric acid, (ρ = 1,19 g/ml).

5.3 Glacial acetic acid, with an amount of water less than 1 %.

5.4 Methanol, chromatographically pure (≥99,9 %).

5.5 Standard reserve solution of picric acid

Weigh an appropriate amount of standard picric acid by using the analytical balance (6.2) and prepare a 100 µg/ml reserve solution with methanol (5.4). Keep the solution at low temperature (4 °C).

5.6 0,1 % glacial acetic solution

Pour 1 ml of glacial acetic acid (5.3) in 1 000 ml of deionized water and keep the solution at ambient temperature.

Laboratory operations should comply with appropriate safety requirements for flammable and explosive materials and samples as well as strong acids and toxic materials. Operators should wear appropriate protection equipment and follow appropriate safety rules. Special measures should be taken for contingencies or uncontrollable reactions.

6 Apparatus

6.1 High performance liquid chromatograph, with diode array detector or equivalent.

6.2 Analytical balance, accuracy 0,1 mg.

6.3 Centrifuge, greater than or equal to 3 000 r/min.

6.4 Ultrasonic mixer

6.5 Graduated centrifuge tube, 10 ml.

6.6 Micropipette

6.7 Organic millipore filtration device, 0,45 µm.

6.8 10 ml graduated pipette

6.9 Volumetric flask, 25 ml.

7 Preparations

Preparation of sample shall be performed according to ISO 22863-1:2020, 5.2 and 5.3.

8 Procedure

8.1 Sample size

Take one 0,5 g sample, using the analytical balance (6.2).

8.2 Extraction process

Weigh a 0,5 g sample in a 10 ml centrifuge tube (6.5) by using the analytical balance (6.2). Add 5 ml of hot distilled or deionized water. Place the solution in an ultrasonic mixer (6.4) for 40 minutes. Take it out, then centrifuge it for 2 min at 3 000 r/min (6.3).

Drain the supernatant in a 10 ml graduated pipette (6.8). The operation shall be repeated three times, then the three extractions of supernatant shall be combined into the 25 ml volumetric flask (6.9), the volume shall be adjusted to 25 ml and the resulting solution shall be shaken well.

Finally, filter the supernatant using the organic millipore filtration device (6.7).

8.3 HPLC settings

As shown below:

a) Hydrophilic column (HILIC): C18 column (4,6 × 250 mm, 5 µm) or equivalent

b) Heating program: constant temperature or programmed heating mode

c) Mobile phase: methanol (5.4) - 0,1 % glacial acetic acid solution (5.6) (55:45, volume ratio)

d) Velocity of flow: 0,8 ml/min

e) Sample size: 10 µl

f) Detection wavelength: 350 nm

8.4 Qualitative analysis

Take 10 µl of the sample solution (8.2) by using a micropipette (6.6) and insert it in the column of the high-performance liquid chromatograph (6.1).

According to the method of qualitative identification based on the consistency of retention times, record the response created by the analytes exiting the column of the chromatograph (6.1) at the detection wavelength [8.3 f)] — the so-called "chromatogram" — and detect whether a peak appears at the characteristic retention time of picric anions by comparison to the retention time of standard samples (see Figure A.1).

The emergence of such peak at the right retention time proves the presence of picric anions in the sample solution and then the presence of picric acid or picrates in the sampled pyrotechnic composition.

If necessary, use other methods to further qualitative confirmation.

8.5 Quantitative determination

8.5.1 Standard response curve

Prepare five diluted solutions of the standard reserve solution of picric acid (5.5) by diluting it with methanol (5.4) to appropriate concentrations as required. Concentration values shall be taken in an interval that ranges from 0 % to 50 % or more than the expected concentration of the sample.

Record chromatograms of those diluted standard solutions of picric acid by using the high-performance liquid chromatograph (6.1). Calculate the area under the peaks corresponding to picrate anions.

Plot the points corresponding to the diluted standard solutions of picric acid in a diagram with the standard solution concentrations of picric acid in abscissas and the peak areas in ordinates.

Draw the standard curve that links all those points. The response value of picric acid in the diluted standard solutions should be linear in the detection range of the chromatograph, showing the direct

proportionality of the areas to the concentrations. The line should go through the origin of the peak response vs concentration graph.

8.5.2 Sample solution chromatogram

Having detected the presence of a peak at the characteristic retention time of picric anions in the chromatogram (8.4), calculate the area under the peak. The response value of picric acid in the sample solution should lie in the linear part of the standard response curve.

8.6 Blank test

A blank test shall be carried out in parallel with the sample determination by using the same analytical procedure and a blank solution made of the same amounts of all reagents, without any extraction from any sample.

8.7 Parallel test

A second sample shall be processed according to (8.2) and measured according to (8.5).

9 Results calculation

The amount of picric acid in the sample shall be calculated by using a chromatographic data processor or according to Formula (1):

$$X = \frac{A c_s V}{A_S m} \tag{1}$$

where

X is the amount of picric acid in the sample in milligrams per kilogram (mg/kg) or micrograms per gram (µg/g);

A is the peak area corresponding to picrate anions in the sample solution;

V is the volume of sample solution, in millilitres (ml);

c_S is the concentration of picric acid of a diluted standard solution corresponding to a point of the standard response curve, in micrograms per millilitre (µg/ml);

A_S is the peak area corresponding to picric acid in the same diluted standard solution as selected above for the value of c_S (note that the ratio c_S / A_S can be replaced by the slope of the standard response curve in the above equation);

m is the amount of sample in the final sample solution (8.2) in grams (g).

Blank test result X_0 (see 8.6) if not zero shall be deducted from the calculation result.

10 Precision

When the concentration is in the range (0,5 mg/kg, 20 mg/kg), the recovery rate lies between 89,4 % and 96,4 %, and the relative standard deviation, C_V, is less than 10 %.

Under the condition of repeatability, the absolute difference of two independent measurement results should not exceed 10 % of the arithmetic mean value.

11 Test report

The test report shall include at least the following information:

— name and address of the testing laboratory;

— date of issue;

— reference to this document, i.e. ISO 22863-12;

— necessary description of the sample and how it was obtained according to ISO 22863-1;

— the identification of qualitative analysis and quantitative analysis;

— results of the analysis;

— any anomaly that occurred while performing the tests.