INTERNATIONAL STANDARD

ISO 11494

Third edition
2019-07

Jewellery and precious metals — Determination of platinum in platinum alloys — ICP-OES method using an internal standard element

Joaillerie et métaux précieux — Dosage du platine dans les alliages de platine — Méthode par ICP-OES utilisant un étalon interne

Reference number
ISO 11494:2019(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
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 174, *Jewellery and precious metals*.

This third edition cancels and replaces the second edition (ISO 11494:2014), which has been technically revised.

The main changes compared to the previous edition are as follows:

a) the definition of bracketing in Clause 3 has been removed;

b) the recommended lines in Clause 4 have been removed;

c) reagents in Clause 5 have been changed and removed, and the requirements about yttrium in 5.4 have been changed;

d) the preparation of the internal standard solution in 8.1 has been changed;

e) the list of standards to be prepared and precisions about qualification of them by linearity as well as way to choose the low and high standards in 8.2 have been changed;

f) the way of preparation by aliquots for both standard and sample solutions in 8.2 and 8.3 has been removed;

g) the preparation of both standard and sample solutions in 8.2 and 8.3 has been changed;

h) precisions about quantity of acids to be used in case of dissolution under pressure in 8.4 have been added;

i) the definition of bracketing and recommended lines in 8.5 have been added;

j) the formulae in 9.1 after having removed the way of preparation by aliquots have been adapted;

k) the emission line as an information to be mentioned in the test report in Clause 10 has been removed;

l) the document has been editorially revised.

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.

Jewellery and precious metals — Determination of platinum in platinum alloys — ICP-OES method using an internal standard element

1 Scope

This document describes an analytical procedure for the determination of platinum in platinum alloys with a nominal content up to 990 ‰ (parts per thousand), including alloys according to ISO 9202.

2 Normative references

There are no normative references in this document.

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

At least two accurately weighed samples are dissolved in aqua regia and made up to an exactly weighed mass. These sample solutions are mixed with the internal standard and made up to the standard measuring volume.

Using ICP-OES, the platinum content of the sample solution is measured by comparison of the ratio intensities of the spectral emission of platinum and appropriate internal standard (e. g. yttrium) line(s) with the ratios for solutions containing known masses of platinum and internal standard (e. g. yttrium) using the bracketing method.

Minor modifications are required when the alloy contains ruthenium, rhodium, iridium, or tungsten.

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

5.1 Hydrochloric acid (HCl), approximately 30 % to 37 % HCl (mass fraction).

5.2 Nitric acid (HNO_3), approximately 65 % to 70 % HNO_3 (mass fraction).

5.3 Platinum (Pt) of 999,9 ‰ minimum purity; if a lower platinum content (e.g. 999,5 ‰) is used, appropriate corrections shall be applied.

5.4 Yttrium compound, like yttrium chloride ($YCl_3 \cdot 6H_2O$ or Y_2O_6), of analytical grade.

5.5 Copper of 999,9 ‰ minimum purity, and platinum free.

5.6 Orthophosphoric acid (H_3PO_4), 85 % (mass fraction).

6 Equipment

6.1 Customary laboratory apparatus.

6.2 ICP-OES, capable of simultaneously measuring the platinum and the internal standard emission lines with a minimum optical resolution of 0,02 nm.

6.3 Analytical balance, with a reading accuracy of 0,01 mg.

7 Sampling

The sampling procedure should be performed in accordance with ISO 11596.

8 Procedure

WARNING — Suitable health and safety procedures should be followed.

8.1 Internal standard solution

Dissolve approximately 20 mg $YCl_3 \cdot 6H_2O$ (5.4) in 200 ml water and make up to 1 000 ml with water. Alternatively, prepare a solution in order to obtain a concentration of approximately 6 mg/l of yttrium. Due to the sensitivity of the instrument, the concentration may be changed to achieve optimum performance.

8.2 Calibration solutions

The sequence by bracketing needs the use of only two standards that shall correspond to the nearest points (low standard and high standard as used in 8.5) to the expected platinum sample content. It is recommended to prepare a set of at least three standards and to check their linearity.

Weigh approximately 45 mg, 55 mg, 65 mg, 75 mg, 82,5 mg, 87,5 mg, 92,5 mg, 97,5 mg and 100 mg platinum accurately to 0,01 mg each into a glass beaker. Heat gently the sample in the glass beaker covered with a watch glass in a mixture of 100 ml HCl (5.1) and 30 ml HNO_3 (5.2) until complete dissolution and continue to heat to expel the nitrogen oxides. Transfer the solution in a 1 000 ml flask. Add 100 g accurately to 0,01 g of the internal standard solution (8.1). Add 100 ml HCl (5.1) and make up to 1 000 ml with water. Mix thoroughly.

In the presence of certain other elements (e.g. silver), it can be necessary to increase the HCl concentration to a maximum of 500 ml. The acid concentration of calibration solutions and sample solutions shall be consistent.

8.3 Sample solutions

Weigh 100 mg sample accurately to 0,01 mg into a glass beaker and dissolve and treat the sample as described in 8.2.

The acid concentration of calibration solutions and sample solutions shall be consistent.

8.4 Preparation of the platinum alloy solution containing ruthenium, iridium, or tungsten

Platinum alloys containing more than 5 % of the cited elements can require a pressure dissolution (quantity of acids to be adapted according to the vessels used and to the manufacturer's recommendation) or involve a preliminary alloying stage with a quantity of 10 times of platinum-free copper (5.5).

In the presence of tungsten, 200 µl of orthophosphoric acid (5.6) shall be added.

Calibration solutions and sample solutions shall be matrix matched.

8.5 Measurements

The data processing unit of the ICP-OES is used to establish a measuring program in which the intensities of the platinum emission lines and of the internal standard element yttrium can be measured simultaneously. Set up the instrument in accordance with the manufacturer's instructions and choose appropriate background correction positions. A clean torch, spray chamber, and sample uptake tubes shall be used and the plasma shall be stabilized before use, following the recommendations of the instruments manufacturer.

The bracketing consists in a running of standards and samples in the following sequence: low standard – sample – high standard – sample – low standard – sample – high standard – sample – low standard – sample – high standard.

Each solution shall have a minimum stabilization time of 30 s followed by minimum integration times of 10 s and minimum of 3 integrations. The relative standard deviation (RSD) shall not be larger than 0,3 % after final calculation [see Formula (1)]. The accurate mass of platinum of the sample solution is derived from the measurement of the two calibration solutions bracketing the value of the sample solution [see Formula (4)].

The recommended lines for platinum are 265,945 nm, 214,424 nm, 299,796 nm or 306,471 nm. Only lines without interference effects shall be chosen for calculation. The analytical results obtained with the measured emission lines shall be compared. The recommended lines for yttrium are 371,029 nm 377,433 nm or 321,669 nm.

NOTE The platinum emission at 265,945 nm can be interfered by ruthenium, rhodium, and chromium and the platinum emission at 299,796 nm and 306,471 nm can be interfered by iridium and chromium.

9 Calculation and expression of results

9.1 Calculation

The method of internal standardization is based on the linear relation between the intensity ratios (I_{Pt}/I_Y) and the concentration ratios (C_{Pt}/C_Y) or, better, mass ratios (m_{Pt}/m_Y). Using the same mass of yttrium (internal standard solution) to prepare all solutions, it is not necessary to have an exact volume of the measuring solutions. The accuracy of the 1 000 ml volumetric flask is satisfactory. The other important advantage of always referring to the same mass of the internal standard is that all calculations can be done with m_{Pt} instead of m_{Pt}/m_Y, nominal.

In general, the data processing unit provides the quotients from the simultaneously registered single measurements of the platinum and the yttrium intensities.

If the mean value, $\overline{Q}$, of the five intensity quotients (Q_1, Q_2, Q_3, Q_4, Q_5) belonging to each solution is calculated using Formula (1):

$$\overline{Q} = \frac{1}{5}\left(\sum_{n=1}^{5} \frac{I_{Pt}}{I_Y}\right) \tag{1}$$

then this mean value shall have an RSD from Q not larger than 0,3 %.

In view of deviations from the nominal mass, m_{IS}, expressed in grams, of the internal standard solution (m_{IS} = 100,00 g), each intensity quotient belonging to a measuring solution shall be corrected by the corresponding real mass of internal standard solution, $W_{IS,n}$, expressed in grams, used to prepare this measuring solution. The corrected quotient, Q_C, is calculated using Formula (2):

$$Q_C = Q \cdot \frac{W_{IS,n}}{m_{IS}} \tag{2}$$

To determine the platinum content of the sample using the corrected intensity quotient, the exact masses of platinum in the calibration solutions $m_{Pt,Cs,n}$, expressed in milligrams, are required, using Formula (3):

$$m_{Pt,Cs,n} = W_{Pt,Cs,n} \tag{3}$$

where $W_{Pt,\,Cs,\,n}$ is the mass of platinum used to prepare the platinum calibration solution, in milligrams.

The two calibration points nearest to the expected platinum sample content, corresponding to the low mass, a, and to the high mass, b, are used to determine the platinum mass in the sample solution using Formula (4):

$$m_{Pt} = a + \frac{(b-a)\cdot(Q_{Cs} - Q_{Ca})}{(Q_{Cb} - Q_{Ca})} \tag{4}$$

where

a is the mass of platinum in the calibration solution used as “low-standard”, according to Formula (3), in milligrams;

b is the mass of platinum in the calibration solution used as “high-standard”, according to Formula (3), in milligrams;

Q_{Ca} is the corrected intensity ratio I_{Pt}/I_Y of the “low-standard”;

Q_{Cb} is the corrected intensity ratio I_{Pt}/I_Y of the “high-standard”;

Q_{Cs} is the corrected intensity ratio I_{Pt}/I_Y of the sample measuring solution.

The final mass of platinum of the sample solution corresponds to the mean value of five measuring cycles and evaluations of this type, $\overline{m}_{Pt}$, and is calculated using Formula (5):

$$\overline{m}_{Pt,fin} = \frac{1}{5}\left(\sum_{n=1}^{5} m_{Pt}\right) \tag{5}$$

The RSD of m_{Pt} shall not exceed 0,30 %.

Once $\overline{m}_{Pt}$ has been determined from the five single determinations of the sample solution, the platinum content of the sample, X_{Pt}, expressed in parts per thousand, is calculated using Formula (6)

$$X_{Pt} = \frac{\overline{m}_{Pt}}{W_{Sa}} \cdot 1000 \tag{6}$$

where W_{Sa} is the mass of sample used to prepare the sample stock solution, in milligrams.

CAUTION — In order to comply with this document, other algorithms used shall be validated.

9.2 Repeatability

Duplicate determinations shall give results differing by less than 3 ‰ for platinum. If the difference is greater than this, the assay shall be repeated.

10 Test report

With reference to this method, the test report shall contain at least the following information:

a) identification of the sample including source, date of receipt, form of sample;

b) sampling procedure;

c) method used by reference to this document, i.e. ISO 11494:2019;

d) platinum content of the sample, in parts per thousand (‰) by mass, as single values and mean values;

e) if relevant, any deviations from the method specified in this document;

f) any unusual features observed during the determination;

g) date of test;

h) identification of the laboratory carrying out the test;

i) signature of the laboratory manager and operator.