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Jewellery — Determination of palladium in palladium jewellery alloys — ICP-OES method using yttrium as internal standard element

Joaillerie, bijouterie — Dosage du palladium dans les alliages de palladium pour la joaillerie, bijouterie — Méthode par ICP-OES utilisant l'yttrium comme étalon interne

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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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).

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

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 174, *Jewellery*.

This second edition cancels and replaces the first edition (ISO 11495:2008), which has been technically revised with the following changes:

a) change in the scope that this method is the referee method;

b) addition of a warning in Clause 8 that suitable health and safety procedures should be followed;

c) addition of a standard solution in 8.1;

d) addition of an alternative calibration solution in 8.2.2;

e) addition of an alternative sample solution in 8.3.2;

f) addition of an alternative route for calculation in 8.5.4;

g) International Standard editorially revised.

Introduction

The following definitions apply in understanding how to implement an ISO International Standard and other normative ISO deliverables (TS, PAS, IWA):

- "shall" indicates a requirement;
- "should" indicates a recommendation;
- "may" is used to indicate that something is permitted;
- "can" is used to indicate that something is possible, for example, that an organization or individual is able to do something.

ISO/IEC Directives, Part 2 (sixth edition, 2011), 3.3.1 defines a requirement as an "expression in the content of a document conveying criteria to be fulfilled if compliance with the document is to be claimed and from which no deviation is permitted."

ISO/IEC Directives, Part 2 (sixth edition, 2011), 3.3.2 defines a recommendation as an "expression in the content of a document conveying that among several possibilities one is recommended as particularly suitable, without mentioning or excluding others, or that a certain course of action is preferred but not necessarily required, or that (in the negative form) a certain possibility or course of action is deprecated but not prohibited."

Jewellery — Determination of palladium in palladium jewellery alloys — ICP-OES method using yttrium as internal standard element

1 Scope

This International Standard describes a method for the determination of palladium in palladium jewellery alloys, preferably within the range of fineness specified in ISO 9202, by means of inductively coupled plasma optical emission spectrometry (ICP-OES).

The preferred palladium content of the alloys lies between 500 ‰ (parts per thousand) and 950 ‰ palladium.

NOTE This method can be used to analyse other contents of palladium.

This method is intended to be used as the recommended method for the determination of fineness in alloys covered by ISO 9202.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 11596, *Jewellery — Sampling of precious metal alloys for and in jewellery and associated products*

3 Terms and definitions

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

3.1
bracketing
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

4 Short description of method

At least two accurately weighed samples are dissolved in aqua regia and made up to an exactly weighed mass. Exactly weighed portions (aliquots) of these sample solutions are mixed with the internal standard and made up to the standard measuring volume.

Using ICP-OES, the palladium content of the sample solution is measured by comparison of the ratio intensities of the spectral emission of palladium (recommended line is 340,45 nm) and yttrium (at 371,03 nm) or other appropriate lines, with the ratios for solutions containing known masses of palladium and yttrium, using the bracketing method.

Other palladium emission lines may be used, but have to be checked for spectral interferences and the instrumental performance.

5 Reagents

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

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 Pure palladium (Pd).

The palladium content shall be at least 999,9 ‰. If a lower palladium content (999,5 ‰) is used, appropriate corrections could be applied.

5.4 Internal standard.

An yttrium compound like yttrium chloride ($YCl_3 \cdot 6H_2O$) or yttrium oxide (Y_2O_3) in analytical grade.

5.5 Aqua regia.

Mix 3 volumes of hydrochloric acid (5.1) and 1 volume of nitric acid (5.2).

6 Equipment

6.1 Customary laboratory apparatus.

6.2 ICP-OES, capable of simultaneously measuring the palladium emission line and the emission line of the internal standard yttrium 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 shall 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 680 mg $YCl_3 \cdot 6H_2O$ (5.4) in 200 ml water and make up to 1 000 ml with water. Alternatively, dissolve approximately 250 mg Y_2O_3 in a mixture of 25 ml water and 25 ml nitric acid and make up to 1 000 ml with water. Due to the sensitivity of the instrument, the concentration may be changed to achieve optimum performance.

This also applies to the calibration solutions (see 8.2) and the sample solutions (see 8.3).

8.2 Calibration solutions

8.2.1 Weigh approximately 100 mg of palladium accurately to 0,01 mg into a tared 100 ml volumetric flask and add 40 ml of aqua regia (5.5). Heat gently until complete dissolution of the sample. Allow to cool. Make up with water to 100 ml and mix thoroughly. Weigh this palladium stock-solution.

Weigh approximately 4,5 g, 5,5 g, 6,5 g, 7,5 g, 8,5 g, 9,5 g, and 9,8 g of the palladium stock solution accurately to at least 0,001 g, each into a 100 ml volumetric flask. Add 10 g of the internal standard solution (8.1) accurate to at least 0,001 g. Add 10 ml HCl (5.1) and make up to 100 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 50 ml. The acid concentration of calibration solutions and sample solutions shall be consistent.

8.2.2 Alternatively weigh 45 mg, 55 mg, 65 mg, 75 mg, 85 mg, 95 mg, and 98 mg palladium accurately to 0,01 mg each into a 1 l flask and dissolve in 100 ml HCl (5.1) plus 30 ml HNO3 (5.2). Add 100 g accurately to 0,01 g of the internal standard solution (8.1). Add 100 ml HCl (5.2) and make up to 1 l 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.

NOTE Depending on the range of the palladium contents in the samples, not all the standards are necessary.

8.3 Sample solutions

8.3.1 Weigh approximately 100 mg of the sample to the nearest 0,01 mg, dissolve and treat the sample as described in 8.2.1. Weigh approximately 10 g of this sample stock solution accurately to 0,001 g into a 100 ml volumetric flask and add 10 g of the internal standard solution (8.1) accurately to 0,001 g. Add 10 ml HCl (5.1) and make up to 100 ml. 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 50 ml. The acid concentration of calibration solutions and sample solutions shall be consistent.

8.3.2 Alternatively weigh 100 mg sample accurately to 0,01 mg into a 1 l flask and dissolve and treat the sample as described in 8.2.2.

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.

NOTE Attention is drawn to the possibility that smaller samples will also be more affected by any variation on homogeneity in the material sampled.

8.4 Measurements

The data processing unit of the ICP-OES is used to establish a measuring program in which the intensities of the emission lines of Pd 340,45 nm and of the internal standard element yttrium (at 371,03 nm) 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.

Each standard and sample solution shall have a minimum stabilization time of 30 s, followed by the integration times and the number of integrations required to obtain a maximum relative standard deviation (RSD) of 0,2 % [see 8.5.2, Formula (1)]. The accurate mass of palladium of the sample solution is derived from the measurement of the two calibration solutions bracketing the rough value of the sample solution [see 8.5.3, Formula (4) or 8.5.4, Formula (9), depending on the way of calibration and sample solution preparation].

8.5 Calculation and expression of results

8.5.1 If the solution has been prepared in accordance with 8.2.1 and 8.3.1, use 8.5.3 for calculation or if the solution is prepared according to the alternative route (8.2.2 and 8.3.2), use 8.5.4 for calculation.

8.5.2 The method of internal standardization is based on the linear relation between the intensity ratios $I_{\text{Pd}}/I_{\text{Y}}$ and the concentration ratios $C_{\text{Pd}}/C_{\text{Y}}$ or, better, mass ratios $m_{\text{Pd}}/m_{\text{Y}}$. 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 100 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_{Pd} instead of $m_{\text{Pd}}/m_{\text{Y}}$, nominal.

In general, the data processing unit provides the quotients from the simultaneously registered single measurements of the palladium 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):

$$\overline{Q}=\frac{1}{5}\left(\sum_{n=1}^{5}\frac{I_{\text{Pd}}}{I_{\text{Y}}}\right) \qquad (1)$$

then this mean value shall have an RSD from Q not larger than 0,2 %.

8.5.3 In view of deviations from the nominal mass, m_{IS}, in grams, of the internal standard solution (m_{IS} = 10,000 g), each intensity quotient belonging to a measuring solution shall be corrected by the corresponding real mass of internal standard solution $W_{\text{IS,n}}$, in grams, used to prepare this measuring solution. The corrected quotient, Q_{C}, is calculated using Formula (2):

$$Q_C=Q\cdot\frac{W_{\text{IS,n}}}{m_{\text{IS}}} \qquad (2)$$

To determine the palladium content of the sample using the corrected intensity quotient, the exact masses of palladium in the calibration solutions $m_{\text{Pd,Cs,n}}$, in milligrams, are required. These masses shall be calculated individually for each calibration solution or calibration point using Formula (3):

$$m_{\text{Pd,Cs,n}}=\frac{W_{\text{Pd,SS}}}{m_{\text{SS,Pd}}}\cdot W_{\text{SS,Pd,n}} \qquad (3)$$

where

$W_{\text{Pd, SS}}$ is the mass of palladium used to prepare the palladium-stock solution, in milligrams;

$m_{\text{SS, Pd}}$ is the mass of the prepared palladium-stock solution, in grams;

$W_{\text{SS, Pd, n}}$ is the mass of palladium stock solution used to prepare the calibration solution, n, in grams.

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

$$m_{\mathrm{Pd}} = a + \frac{(b-a)\cdot(Q_{Cs}-Q_{Ca})}{(Q_{Cb}-Q_{Ca})} \qquad (4)$$

where

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

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

Q_{Ca} is the corrected intensity ratio $I_{\mathrm{Pd}}/I_{\mathrm{Y}}$ of the "low-standard";

Q_{Cb} is the corrected intensity ratio $I_{\mathrm{Pd}}/I_{\mathrm{Y}}$ of the "high-standard";

Q_{Cs} is the corrected intensity ratio $I_{\mathrm{Pd}}/I_{\mathrm{Y}}$ of the sample measuring solution.

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

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

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

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

$$X_{\mathrm{Pd}} = \frac{\overline{m}_{\mathrm{Pd}} \cdot m_{\mathrm{SS,Sa}}}{W_{\mathrm{Sa}} \cdot W_{\mathrm{SS,Sa}}} \cdot 1000 \qquad (6)$$

where

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

$m_{\mathrm{SS,Sa}}$ is the mass of the prepared sample stock solution, in grams;

$W_{\mathrm{SS,\,Sa}}$ is the mass of sample stock solution used to prepare the sample measuring solution, in grams.

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

8.5.4 Alternatively, in view of deviations from the nominal mass, m_{IS}, 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, $W_{\mathrm{IS,n}}$, in grams, used to prepare this measuring solution. The corrected quotient, Q_{C}, is calculated using Formula (7):

$$Q_C = Q \cdot \frac{W_{\mathrm{IS,n}}}{m_{\mathrm{IS}}} \qquad (7)$$

To determine the palladium content of the sample using the corrected intensity quotient, the exact masses of palladium in the calibration solutions $m_{\mathrm{Pd,Cs,n}}$, in milligrams, are required, using Formula (8):

$$m_{\mathrm{Pd,Cs,n}} = W_{\mathrm{Pd,Cs,n}} \qquad (8)$$

where

$W_{\mathrm{Pd,\ Cs,n}}$ is the mass of palladium used to prepare the palladium calibration solution, in milligrams.

The two calibration points nearest to the expected palladium sample content, corresponding to the low mass, a, and to the high mass, b, are used to determine the palladium mass in the sample solution using Formula (9):

$$m_{\mathrm{Pd}} = a + \frac{(b-a)\cdot(Q_{\mathrm{Cs}} - Q_{\mathrm{Ca}})}{(Q_{\mathrm{Cb}} - Q_{\mathrm{Ca}})} \qquad (9)$$

where

a is the mass of palladium in the calibration solution used as “low-standard”, according to Formula (8), in milligrams;

b is the mass of palladium in the calibration solution used as “high-standard”, according to Formula (8), in milligrams;

Q_{Ca} is the corrected intensity ratio $I_{\mathrm{Pd}}/I_{\mathrm{Y}}$ of the “low-standard”;

Q_{Cb} is the corrected intensity ratio $I_{\mathrm{Pd}}/I_{\mathrm{Y}}$ of the “high-standard”;

Q_{Cs} is the corrected intensity ratio $I_{\mathrm{Pd}}/I_{\mathrm{Y}}$ of the sample measuring solution.

The final mass of palladium of the sample solution corresponds to the mean value of five measuring cycles and evaluations of this type, $\overline{m}_{\mathrm{Pd}}$, and is calculated using Formula (10):

$$\overline{m}_{\mathrm{Pd,fin}} = \frac{1}{5}\left(\sum_{n=1}^{5} m_{\mathrm{Pd}}\right) \qquad (10)$$

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

Once $\overline{m}_{\mathrm{Pd}}$ has been determined from the five single determinations of the sample solution, the palladium content of the sample, X_{Pd}, expressed in parts per thousand, is calculated using Formula (11):

$$X_{\mathrm{Pd}} = \frac{\overline{m}_{\mathrm{Pd}}}{W_{\mathrm{Sa}}} \cdot 1000 \qquad (11)$$

where

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

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