INTERNATIONAL STANDARD

ISO
15093

Third edition
2020-02

Jewellery and precious metals — Determination of high purity gold, platinum and palladium — Difference method using ICP-OES

Joaillerie, bijouterie et métaux précieux — Dosage de l'or, du platine et du palladium à haute pureté — Méthode par différence utilisant l'ICP-OES

Reference number
ISO 15093:2020(E)

COPYRIGHT PROTECTED DOCUMENT

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

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 15093:2015), which has been technically revised. The main changes compared to the previous edition are as follows:

a) change of title of standard;

b) change of scope for measuring also gold, platinum and palladium with a nominal content above 999 ‰ (parts per thousands);

c) revision of this document in order to comply in structure with ISO 15096.

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 high purity gold, platinum and palladium — Difference method using ICP-OES

1 Scope

This document specifies the analytical procedure for the determination of gold, platinum and palladium with a nominal content of and above 999 ‰ (parts per thousand).

This document specifies a method intended to be used as the recommended method for the determination of gold, platinum and palladium of fineness of and above 999 ‰. For the determination of fineness of and above 999,9 ‰, modifications described in Annex B apply.

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

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 http://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

4 Principle

The sample is weighed and dissolved in aqua regia to prepare a 10 g/l solution (higher concentration is used for fineness of and above 999,9 ‰). The impurities are determined by ICP-OES (see Table A.1 for wavelengths), and the precious metal content is obtained by subtraction of the total content of impurities in the sample from 1 000 ‰. For the determination of fineness of and above 999,9 ‰, modifications described in Annex B shall be applied.

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), 30 % to 37 % HCl (mass fraction).

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

5.3 Aqua regia (should be prepared just before use). Mix three volumes of hydrochloric acid (5.1) and one volume of nitric acid (5.2).

5.4 Stock solution A (shall not contain any chloride), Ag, Al, Cd, Cr, Cu, Fe, Mg, Mn (100 mg/l each) in 3 % to 7 % HNO_3 (5.2) (mass fraction).

NOTE The stock solution "A" is typically prepared by mixing 10 % (of the total volume) of each 1 000 mg/l monoelemental solution with 5 % of nitric acid (5.2) (volume fraction) and making up with water. It can be kept for up to 12 months under proper storage conditions.

5.5 Stock solution B (may contain both chlorides and nitrates), Bi, Co, Ga, In, Se, Sn, Te, Ti, Zn (100 mg/l each) in 3 % to 7 % aqua regia (5.3) (volume fraction).

5.6 Stock solution C (may contain both chlorides and nitrates), As, Ni, Pb, Sb, Si, Tl, W, Zr (100 mg/l each) in 3 % to 7 % aqua regia (5.3) (volume fraction).

5.7 Stock solution D (may contain both chlorides and nitrates), Au, Ir, Pd, Pt, Rh, Ru (100 mg/l each) in 3 % to 7 % aqua regia (5.3) (volume fraction).

NOTE 1 Elements which do not need to be analysed can be omitted. Other elements can be added, provided they are stable and do not generate significant interferences.

NOTE 2 The stock solutions "B" to "D" are typically prepared by mixing 10 % (of the total volume) of each 1 000 mg/l monoelemental solution with 5 % of aqua regia (5.3) (volume fraction) and making up with water. They can be kept for up to 12 months under proper storage conditions.

5.8 Reference materials: gold, platinum or palladium, of 999,9 ‰ minimum purity. The content of each impurity shall be specified and taken into account in the calibration.

6 Apparatus

6.1 Customary laboratory apparatus.

6.2 ICP-OES, with a minimum optical resolution of 0,02 nm, a detection limit of 0,02 mg/l or better, and capability of background correction.

NOTE For preferably used wavelengths, see Annex A.

6.3 Analytical balance, with a reading accuracy of 0,1 mg.

7 Sampling

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

8 Procedure

8.1 General

WARNING — Suitable health and safety procedures should be followed.

All vessels and reagent bottles shall be teflon (e.g. PFA, FEP) or plastic.

8.2 Sample solution

For each sample to be analysed, two sample solutions shall be prepared as follows and analysed.

The sample should be etched, washed and dried before use to remove any surface contamination.

Weigh (500 ± 10) mg of the sample portion to the nearest 0,1 mg, transfer into a 50 ml beaker, and add 20 ml of aqua regia (5.3). Heat at an appropriate temperature until complete dissolution of the sample and continue to heat to expel the nitrogen oxides. Allow to cool, transfer into a 50 ml volumetric flask, make up with water to 50 ml, and mix thoroughly. Dissolution may alternatively be performed directly in chemical and temperature resistant volumetric flasks.

If an insoluble material is observed, dissolution under pressure should be performed.

8.3 Calibration solutions

Weigh three portions of (500 ± 10) mg of the reference material (5.8), and dissolve, cool and transfer into 50 ml volumetric flasks each one as specified in 8.2.

8.3.1 Blank solution.

Make up with water to 50 ml and mix thoroughly.

8.3.2 Calibration solution 1.

Add 5 ml of stock solution A (5.4) and 5 ml of stock solution B (5.5), make up with water to 50 ml, and mix thoroughly. This solution is unstable over time and should be prepared just before use, or its stability validated.

8.3.3 Calibration solution 2.

Add 5 ml of stock solution C (5.6) and 5 ml of stock solution D (5.7), make up with water to 50 ml, and mix thoroughly. This solution is unstable over time and should be prepared just before use, or its stability validated.

The volumes of stock solutions shall be lowered to match the concentration of impurities in the sample. It is possible to use a multiple-point calibration by adding calibration solutions with other concentrations.

8.4 Measurement

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.

Spray the blank and calibration solutions 1 (8.3.2) and 2 (8.3.3) in accordance with the defined instrument calibration procedure and then run the analytical procedure for the sample solutions. The result shall be displayed with enough decimal places to provide an accurate indication of concentrations at the detection limits of the relevant elements.

Each solution shall have a stabilization time of at least 30 s, followed by at least three integrations each for the determination of the net intensities (background-corrected).

The rinsing time between each measurement shall be sufficient to allow the signal of each impurity to come back to the baseline.

9 Calculation and expression of the results

9.1 Calibration curves

Set the concentration in the blank solution and the calibration solution, taking into account impurities introduced in the solution by the reference material (5.8) and calculate the calibration curve for each element using the net intensities obtained for the blank solution and the calibration solution.

9.2 Calculation

By means of the calibration curves (see 9.1), convert the net intensity values into concentration values and use Formula (1) to calculate the mass portion of each relevant element (W_i).

$$W_i = \frac{c_i \times V_s}{m_s} \tag{1}$$

where

c_i is the concentration of element, i, in the sample solution, in mg/l;

V_s is the volume of the sample solution, in litres;

m_s is the mass of the metallic sample, in milligrams.

The detection limit is defined as three standard deviations of the concentration of each individual element measured in the blank solution.

The precious metal fineness (W_{sp}), expressed in parts per thousand (‰), is thus calculated using Formula (2):

$$W_{sp} = 1\,000 - (\sum W_i \times 1\,000) \tag{2}$$

where $\sum W_i$ is the sum of the mass portion of each element found above its detection limit.

9.3 Repeatability

Duplicate determinations shall give results differing by less than 10 % for the sum of impurities. If the difference is greater than this, the assay shall be repeated.

10 Test report

The test report shall include at least the following information:

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

b) sampling procedure;

c) method used by reference to this document, i.e. ISO 15093:2020;

d) precious metals content of the sample, in parts per thousand (‰) by mass, as single values and mean values, with the result reported with four significant figures;

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.

Annex A
(informative)

Wavelengths

A.1 General

Other wavelengths than those specified in Tables A.1, A.2 and A.3 can be used. In all cases, attention shall be paid to spectral interferences. Those tables are not exhaustive. If other elements are present, they shall be analysed.

Table A.1 — Wavelenghts for measuring of impurities in gold

Element	Recommended nm	Alternative nm	Alternative nm
Ag	328,068	338,289	—
Al	167,08	396,152	—
As	189,04	193,76	—
Au[a]	389,786	302,920	—
Bi	190,24	223,061	—
Cd	214,438	226,502	228,802
Co	228,616	238,892	—
Cr	205,618	359,349	360,533
Cu	327,396	324,754	—
Fe	238,204	259,941	261,187
Ga	287,424	141,44	417,206
In	303,936	325,609	158,636
Ir	215,268	183,246	—
Mg	279,553	280,270	—
Mn	259,373	294,921	257,611
Ni	352,454	221,648	231,604
Pb	168,22	220,353	283,305
Pd	340,458	360,955	—
Pt	177,71	214,423	203,646
Rh	343,489	233,437	—
Ru	240,272	—	—
Sb	206,833	217,581	—
Se	196,09	204,050	—
Si	251,612	288,158	—
Sn	189,99	147,52	—
Te	214,281	225,902	—
Ti	336,121	334,941	—
Tl	190,86	—	—

[a] Suggested matrix line (only used to ensure sample has been properly prepared and analysed, shall not be included in the calculation as described in 9.2).

Table A.1 *(continued)*

Element	Recommended nm	Alternative nm	Alternative nm
W	239,709	207,911	—
Zn	202,613	206,200	213,856
Zr	339,198	343,823	—

[a] Suggested matrix line (only used to ensure sample has been properly prepared and analysed, shall not be included in the calculation as described in 9.2).

Table A.2 — Wavelenghts for measuring of impurities in platinum

Element	Recommended nm	Alternative nm	Alternative nm
Ag	328,068	338,289	—
Al	167,08	396,152	—
As	189,04	197,26	—
Au	267,595	—	—
Bi	223,061	—	—
Cd	226,502	—	—
Co	228,616	238,892	—
Cr	205,618	283,563	—
Cu	327,396	324,754	—
Fe	259,941	261,187	—
Ga	294,364	417,206	—
In	230,606	158,636	—
Ir	212,681	215,268	183,246
Mg	279,553	280,270	—
Mn	257,611	260,569	—
Mo	202,095	203,909	281,615
Ni	231,604	221,648	—
P	168,60	169,40	—
Pb	168,22	220,353	—
Pd	324,270	340,458	—
Pt[a]	212,861	330,186	273,396
Rh	343,489	233,437	369,236
Ru	240,272	273,425	—
Sb	206,833	217,581	—
Se	196,09	—	—
Si	251,612	288,158	—
Sn	189,99	147,52	140,05
Ta	240,063	268,517	—
Te	214,281	225,902	—
Ti	336,121	334,941	—
Tl	190,86	132,17	—

[a] Suggested matrix line (only used to ensure sample has been properly prepared and analysed, shall not be included in the calculation as described in 9.2).

Table A.2 *(continued)*

Element	Recommended nm	Alternative nm	Alternative nm
W	239,709	207,911	209,475
Zn	202,613	213,856	—
Zr	349,621	343,823	339,198

[a] Suggested matrix line (only used to ensure sample has been properly prepared and analysed, shall not be included in the calculation as described in 9.2).

Table A.3 — Wavelenghts for measuring of impurities in palladium

Element	Recommended nm	Alternative nm	Alternative nm
Ag	328,068	338,289	—
Al	167,08	396,152	—
As	200,334	—	—
Au	242,795	267,595	—
Bi	222,825	—	—
Cd	226,502	228,802	—
Co	228,616	238,892	—
Cr	267,716	283,563	357,869
Cu	213,598	324,754	—
Fe	259,941	261,187	—
Ga	294,364	287,424	417,206
Ge	209,426	259,253	—
Ir	205,222	224,268	183,246
Mn	257,611	260,569	—
Mo	202,095	203,909	—
Ni	231,604	222,486	352,454
Pb	220,353	283,305	405,078
Pd[a]	300,978	416,984	257,710
Pt	273,396	203,711	306,471
Rh	343,489	233,437	369,236
Ru	240,272	273,425	—
Sb	206,833	217,581	—
Si	251,612	288,158	—
Sn	189,99	147,52	—
Te	214,281	225,902	—
Ti	336,121	334,941	—
Tl	190,86	—	—
W	239,709	207,911	209,475
Zn	202,613	213,856	—
Zr	349,621	343,823	—

[a] Suggested matrix line (only used to ensure sample has been properly prepared and analysed, shall not be included in the calculation as described in 9.2).

Annex B
(normative)

Determination of fineness of and above 999,9 ‰

B.1 General

If this document is applied for the determination of fineness of and above 999,9 ‰, the following changes in procedure shall be applied in order to adjust the calibration and take into account the sensitivity of the ICP-OES spectrometer.

The easiest way to increase the sensitivity of the ICP-OES spectrometer is to increase the concentration of the matrix in the standards and test samples. For gold, palladium and platinum, the matrix concentration shall be increased between 20 g/l and 50 g/l. The following procedure is for a concentration of 40 g/l.

B.2 Reagents

B.2.1 Reference materials.

B.2.1.1 Gold, of 999,99 ‰ minimum purity.

B.2.1.2 Platinum and palladium, of 999,95 ‰ minimum purity.

The content of each impurity shall be specified and taken into account in the calibration.

B.3 Procedure

B.3.1 General

WARNING — Suitable health and safety procedures should be followed.

All vessels and reagent bottles shall be teflone (e.g. PFA, FEP) or plastic.

B.3.2 Sample solution

For each sample to be analysed, two sample solutions shall be prepared as follows and analysed.

The sample should be etched, washed and dried before use to remove any surface contamination.

Weigh (2 000 ± 10) mg of the sample portion to the nearest 0,1 mg, transfer into a 50 ml beaker, and add 20 ml of aqua regia (5.3). Heat at an appropriate temperature until complete dissolution of the sample and continue to heat to expel the nitrogen oxides. Allow to cool, transfer into a 50 ml volumetric flask, make up with water to 50 ml, and mix thoroughly. Dissolution may alternatively be performed directly in chemical and temperature resistant volumetric flasks.

If insoluble material is observed, dissolution under pressure should be performed.

B.3.3 Calibration solutions

Weigh three portions of (2 000 ± 10) mg of the reference material (B.2.1), and dissolve, cool and transfer into 50 ml volumetric flasks each one as specified in B.3.2. The number of calibration solutions can be increased if necessary.