INTERNATIONAL STANDARD

ISO 15096

Third edition
2020-02

Jewellery and precious metals — Determination of high purity silver — Difference method using ICP-OES

Joaillerie et métaux précieux — Dosage de l'argent à haute pureté — Méthode par différence utilisant l'ICP-OES

Reference number
ISO 15096:2020(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 15096:2014), 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 silver with a nominal content above 999 ‰ (parts per thousands);

c) revision of this document in order to comply in structure with ISO 15093;

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 silver — Difference method using ICP-OES

1 Scope

This document specifies the analytical procedure for the determination of silver 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 silver 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 nitric acid to prepare a 10 g/l solution (higher concentration is used for fineness of and above 999,9 ‰). The suspension, which can be present in that solution, is isolated by centrifugation or microfiltration and dissolved in aqua regia. Both nitric and aqua regia solutions are analysed separately by ICP-OES and the total content of each impurity (see Table A.1 for wavelengths) in the sample is obtained by adding together the results of the two analyses. The silver 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), Al, Cd, Cr, Cu, Fe, Mg, Mn (100 mg/l each) in 3 % to 7 % HNO_3 (5.2) (mass fraction).

5.5 Stock solution B (shall not contain any chloride), Ni, Sb, Se, Te, Ti (100 mg/l each) in 3 % to 7 % HNO_3 (5.2) (mass fraction).

5.6 Stock solution C (shall not contain any chloride), As, Bi, Co, Pb, Pt, Si, Sn, Zn (100 mg/l each) in 3 % to 7 % HNO_3 (5.2) (mass fraction).

5.7 Stock solution D (shall not contain any chloride), Ga, Ge, Hg, In, Pd, Tl (100 mg/l each) in 3 % to 7 % HNO_3 (5.2) (mass 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 Stock solutions “A” to "D" are 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. They can be kept for up to 12 months under proper storage conditions.

5.8 Stock solution E (may contain both chlorides and nitrates), Al, Au, Cr, Fe, Mg, Ni, Pt, Sn (100 mg/l each) in 3 % to 7 % aqua regia (5.3) (volume fraction).

NOTE Stock solution “E” is 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. It can be kept for up to 12 months under proper storage conditions.

5.9 Reference materials: silver 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.

6.4 Centrifuge, suitable for 10 ml to 50 ml tubes and rotating at least at 3 000 r/min (revolution per minute), or

6.5 Microfiltration system, with cellulose membrane filter (approximately 0,45 µm pore size) and a vacuum system.

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 7,5 ml of H_2O and 7,5 ml of HNO_3 (5.2). Heat gently until complete dissolution of the sample and continue to heat to expel the nitrogen oxides. Add 10 ml of water. After cooling to room temperature, transfer the solution from the 50 ml beaker to the centrifuge tube. Centrifuge the mixture at 3 000 r/min for 5 min and transfer the liquid phase into a 50 ml volumetric flask. Add 5 ml of water to the residue, centrifuge the mixture again at 3 000 r/min for 5 min more, and add the newly formed liquid phase to the 50 ml volumetric flask. This operation is repeated two extra times. Make up the volume of the volumetric flask water to 50 ml, and mix thoroughly.

Alternatively, after cooling to room temperature, filter the solution through a microfiltration system (6.5), add the filtrate to a 50 ml volumetric flask and make up the volume of the solution with water to 50 ml, and mix thoroughly. Analyse this solution without delay using the calibration solutions specified in 8.3.

Add 2 ml of freshly prepared aqua regia (5.3) to the residue after centrifugation or microfiltration (if microfiltration is used, the filter shall be dissolved, too). Heat until complete dissolution and continue to heat to expel the nitrogen oxides. Cool to room temperature, transfer to a 5 ml volumetric flask, rinse with water, and make up with water to 5 ml. Analyse this solution using the aqua regia calibration solutions specified in 8.4.

8.3 Silver matrix calibration solutions (10 g/l)

Weigh three portions of (500 ± 10) mg of the silver (5.9), and dissolve, cool and transfer into 50 ml volumetric flasks each one as specified in 8.2.

8.3.1 Blank solution 1.

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 Aqua regia matrix calibration solutions

8.4.1 Blank solution 2.

Transfer 20 ml of aqua regia (5.3) into a 50 ml volumetric flask. Make up to 50 ml with water and mix thoroughly.

8.4.2 Calibration solution 3.

Transfer 20 ml of aqua regia (5.3) into a 50 ml volumetric flask, add 2,5 ml of the stock solution E (5.8), make up to 50 ml with water, and mix thoroughly.

The volume of stock solution E (5.8) shall be lowered to match the concentration of impurities in the sample.

8.5 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 and 2 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.

Each analysis (silver 10 g/l and aqua regia) shall be carried out separately with the calibration solutions specified in 8.3 and 8.4.

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 silver (5.9) 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 for both analyses in silver 10 g/l matrix and aqua regia matrix using Formula (1) to calculate the mass ratio of each relevant element (W_i).

$$W_i = \frac{c_{i,\mathrm{Ag}} \times V_{\mathrm{s,Ag}}}{m_\mathrm{s}} + \frac{c_{i,\mathrm{ar}} \times V_{\mathrm{s,ar}}}{m_\mathrm{s}} \qquad (1)$$

where

$c_{i,\mathrm{Ag}}$ is the concentration of element, *i*, in the silver (10 g/l) matrix sample solution, in mg/l;

$V_{\mathrm{s,Ag}}$ is the volume of the silver (10 g/l) matrix sample solution, in litres (0,05 l as defined in 8.2);

$c_{i,\mathrm{ar}}$ is the concentration of element, *i*, in the aqua regia matrix sample solution, in mg/l;

$V_{\mathrm{s,ar}}$ is the volume of the aqua regia matrix sample solution, in litres (0,005 l as defined in 8.2);

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 for the corresponding matrix.

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

$$W_{\mathrm{sp}} = 1\,000 - \left(\sum W_i \times 1\,000\right) \quad (2)$$

where ΣW_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 15096:2020;

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 Table A.1 can be used. In all cases, attention shall be paid to spectral interferences. This table is not exhaustive. If other elements are present, they shall be analysed.

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

Element	Recommended nm	Alternative nm	Alternative nm
Ag[a]	276,754	351,338	224,641
Al	167,08	396,152	
As	189,042	193,76	
Au	242,795	267,595	
Bi	190,24	223,061	
Cd	214,438	226,502	228,802
Co	228,616	238,892	
Cr	267,716	205,618	283,563
Cu	219,226	324,754	
Fe	238,204	259,941	261,187
Ga	287,424	141,44	294,364
Ge	265,118	164,92	
Hg	184,95	194,23	
In	303,936	325,609	203,606
Mn	259,373	294,921	260,569
Ni	174,83	221,648	231,604
Pb	168,22	172,68	283,305
Pd	340,458	360,955	
Pt	177,71	191,17	203,711
Sb	187,12	206,833	217,581
Se	196,09	204,05	
Si	251,612	288,158	
Sn	189,99	140,05	
Te	214,281	225,902	
Ti	336,121	334,187	
Tl	190,86		
Zr	339,198	257,139	

[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 silver matrix in the standards and test samples. The silver 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 Silver, of 999,99 ‰ 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 7,5 ml of H_2O and 7,5 ml of HNO_3 (5.2). Heat gently until complete dissolution of the sample and continue to heat to expel the nitrogen oxides. Add 10 ml of water. After cooling to room temperature, transfer the solution from the 50 ml beaker to the centrifuge tube. Centrifuge the mixture at 3 000 r/min for 5 min and transfer the liquid phase into a 50 ml volumetric flask. Add 5 ml of water to the residue, centrifuge the mixture again at 3 000 r/min for 5 more minutes, and add the newly formed liquid phase to the 50 ml volumetric flask. This operation is repeated two extra times. Make up the volume of the volumetric flask water to 50 ml, and mix thoroughly.

Alternatively, after cooling to room temperature, filter the solution through a microfiltration system (6.5), add the filtrate to a 50 ml volumetric flask and make up the volume of the solution with water to 50 ml, and mix thoroughly. Analyse this solution without delay using the calibration solutions specified in B.3.3.

Add 2 ml of freshly prepared aqua regia (5.3) to the residue after centrifugation or microfiltration (if microfiltration is used, the filter shall be dissolved, too). Heat until complete dissolution and continue to heat to expel the nitrogen oxides. Cool to room temperature, transfer to a 5 ml volumetric flask, rinse