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Jewellery — Determination of silver in 999 ‰ silver jewellery alloys — Difference method using inductively coupled plasma optical emission spectroscopy (ICP-OES)

Joaillerie, bijouterie — Dosage de l'argent dans les alliages d'argent 999 ‰ pour la joaillerie, bijouterie — Méthode de la différence utilisant la spectrométrie d'émission à plasma induit par haute fréquence (ICP-OES)

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 15096 was prepared by Technical Committee ISO/TC 174, *Jewellery*.

Jewellery — Determination of silver in 999 ‰ silver jewellery alloys — Difference method using inductively coupled plasma optical emission spectroscopy (ICP-OES)

1 Scope

This International Standard specifies the analytical procedure for the determination of silver in silver jewellery alloys, with a nominal content of 999 ‰ (parts per thousand), by measuring specific elements listed in Table A.1.

2 Normative references

The following referenced documents are indispensable for the application 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 Principle

The samples of the silver alloys are weighed and dissolved in nitric acid to prepare a 10 g/l solution. Hydrochloric acid is added to precipitate the silver. The solutions are filtered to separate the silver chloride. The impurities are determined in the filtrate by inductively coupled plasma optical emission spectroscopy (ICP-OES), and the silver content is obtained by subtraction of the total content of impurities in the sample from 1 000 ‰.

4 Sampling

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

NOTE Equivalent methods can be used, as described in ISO 5725-1.

For coated articles, appropriate precautions that have been agreed upon shall be taken to exclude the coating from the determination.

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); ρ_{20} = 1,16 g/cm^3; 32 % HCl (mass fraction).

5.2 Nitric acid (HNO_3); ρ_{20} = 1,20 g/cm^3; 33 % HNO_3 (mass fraction).

5.3 Mixed stock solutions.

Using appropriate certified reagents, the following mixed stock solutions shall be prepared in order to obtain the indicated concentrations.

5.3.1 Nitric stock solution (chloride free): Bi, Pb (100 mg/l each) in 2 mol/l of HNO_3 (5.2).

5.3.2 Hydrochloric stock solution (nitrate free): Sn, Ti (100 mg/l each) in 2 mol/l of HCl (5.1).

5.3.3 Acid stock solution (may contain both chlorides and nitrates): all remaining relevant elements (100 mg/l each) in 1 mol/l of HCl (5.1) and 1 mol/l of HNO_3 (5.2).

Any desired element may be added in the nitric stock solution (5.3.1) or the hydrochloric stock solution (5.3.2) instead of the acid stock solution (5.3.3), provided that no chlorides are introduced in the nitric stock solution (5.3.1) and no nitrates are introduced in the hydrochloric stock solution (5.3.2).

5.4 Filter paper with a pore diameter < 7 µm, e.g. white ribbon.

6 Apparatus

Customary laboratory apparatus and the following.

6.1 ICP optical emission spectrometer, with:

— fixed and/or scanning channels;

— an optical resolution of 0,02 nm for the relevant elements and a detection limit of 0,05 mg/l or better;

— the capability of background correction.

NOTE Annex A specifies preferably used wavelengths.

6.2 Analytical balance accurate to 0,01 mg.

7 Procedure

7.1 Test solution

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

Weigh (500 ± 2,5) mg of the test portion to the nearest 0,01 mg, transfer into a 50 ml beaker and add 15 ml of HNO_3 (5.2). Heat gently until complete dissolution of the sample and the total disappearance of the nitric oxides. If necessary, add distilled water.

If insolubles are observed, they shall be weighed and their amount shall be added to the impurities.

Add 2 ml of HCl (5.1). Wait 10 min to 15 min to precipitate the silver as silver chloride.

Transfer the liquid over a filter paper (5.4) (e.g. white ribbon) into a 50 ml volumetric flask. Wash the filter with 10 ml of water. Add 15 ml of HCl (5.1), make up with water and mix thoroughly.

7.2 Calibration solutions

Calibration solution 1 (blank solution): transfer 15 ml of HCl (5.1) into a 50 ml volumetric flask, dilute up to 50 ml and mix thoroughly.

Calibration solution 2: transfer 15 ml of HCl (5.1) into a 50 ml volumetric flask, add 5 ml of each mixed stock solution (5.3), dilute the solution up to 50 ml and mix thoroughly.

7.3 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 at least 30 min before use.

Spray the 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 to enough decimal places to provide an accurate indication of concentrations at the detection limits of the relevant elements.

Each solution shall have a preintegration time of at least 30 s, followed by five integrations of at least 5 s each for the determination of the net intensities (i.e. background-corrected).

The intensity of the chosen matrix line (see Table A.1) shall not be included in the calculation described in 8.2.

8 Expression of results

8.1 Calibration curves

Set the concentration in calibration solutions 1 and 2 and calculate the calibration curve for each element, using the net intensities obtained for the calibration solutions 1 and 2.

8.2 Method of calculation

By means of the calibration curves (see 8.1), convert the net intensity values into concentration values and use Equation (1) to calculate the mass ratio of each relevant element, W_i:

$$W_i = \frac{c_i \times V_\mathrm{s}}{m_\mathrm{s}} \tag{1}$$

where

c_i is the concentration of element i in the sample solution or the detection limit of element i, whichever is higher, in milligrams/litre;

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 calibration solution 1.

The silver fineness, W_sp, expressed in parts per thousand, is thus calculated as follows:

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

where $\sum W_i$ is the sum of the mass ratio of each relevant element.

8.3 Repeatability

The results of duplicate determinations shall not deviate by more than 0,2 ‰ of the precious metal. If the variation is greater than this, the assays shall be repeated.

9 Test report

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) the method used by reference to this International Standard;

d) precious metal content of the sample, in parts per thousand, as single values and mean values, with the result reported to one decimal place only;

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

f) any unusual features observed during the determination;

g) date of test;

h) identification of the laboratory carrying out the analysis;

i) signature of the laboratory manager and operator.

Annex A
(normative)

Wavelengths

Other wavelengths than those specified in Table A.1 may be used. In such cases, attention shall be paid to optical interferences.

Table A.1 — Silver

Element	Wavelength	Alternative	Element	Wavelength	Alternative
Au	242,795	—	Pt	306,471	203,646
Bi	223,061	—	Rh	343,489	—
Cd	228,802	226,502	Ru	240,272	—
Co	228,616	238,892	Sb	206,833	217,581
Cu	324,754	—	Sc	361,384	—
Fe	259,94	—	Se	196,090	203,985
Ir	215,278	—	Sn	189,989	—
Mn	257,610	—	Te	214,281	238,578
Ni	352,454	231,604	Ti	334,941	—
Pb	168,220	220,353	Y	371,030	—
Pd	340,458	355,308	Zn	213,856	—