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Foreword

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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 11426 was prepared by Technical Committee ISO/TC 174, *Jewellery*.

This second edition cancels and replaces the first edition (ISO 11426:1997), which has been technically revised.

Jewellery — Determination of gold in gold jewellery alloys — Cupellation method (fire assay)

1 Scope

This International Standard specifies a cupellation method (fire assay) for the determination of gold in gold jewellery alloys. The gold content of the alloys should preferably lie between 333 and 999 parts per thousand (‰).

The procedure is applicable specifically to gold alloys incorporating silver, copper and zinc. Some modifications are indicated where nickel and/or palladium are present in the so-called white gold alloys, as well as for alloys containing 990 or more parts per thousand (‰) of gold.

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

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, *Sampling of the precious metal alloys in jewellery and associated products*

3 Principle

The gold alloys are inquarted with silver, compounded with lead and cupelled in a cupellation furnace until a precious metal button is obtained. After flattening and rolling, the silver is extracted (parted) in nitric acid and the gold weighed. Possible systematic errors in the procedure are eliminated by assaying standard proof samples in parallel.

4 Reagents

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

4.1 Nitric acid (HNO_3); ρ_{20} = 1,20 g/cm^3, 33 % HNO_3 (mass fraction), with sufficiently low content of halides (check with silver nitrate test).

4.2 Nitric acid (HNO_3); ρ_{20} = 1,30 g/cm^3, 49 % HNO_3 (mass fraction), with sufficiently low content of halides (check with silver nitrate test).

4.3 Lead, assay grade, free of precious metals and bismuth, as foil, beads or tablets.

4.4 Silver, for inquartation, minimum purity 999 parts per thousand (‰) by mass, free of gold and platinum group metals.

4.5 Pure gold, for proof samples

- for determination of gold between 333 and 990 parts per thousand (‰) by mass, minimum purity 999,9 parts per thousand (‰) by mass;
- for determination of gold more than 990 parts per thousand (‰) by mass, minimum purity 999,99 parts per thousand (‰) by mass.

4.6 Palladium, for proof samples, minimum purity 999 parts per thousand (‰) by mass, free of gold and other platinum group metals.

4.7 Nickel, for proof samples, minimum purity 999 parts per thousand (‰) by mass, free of gold and platinum group metals.

4.8 Copper, for proof samples, foil or wire, minimum purity 999 parts per thousand (‰) by mass, free of gold, and platinum group metals.

4.9 Sodiumtetraborate ($Na_2B_4O_7$), anhydrous.

5 Apparatus

Ordinary laboratory apparatus and the following.

5.1 Cupellation furnace, in which an oxidizing atmosphere can be maintained.

CAUTION —A standard muffle furnace is not satisfactory for this purpose.

5.2 Magnesium oxide cupels, usually of diameter 22 mm to absorb 6 g lead, or of diameter 26 mm to absorb 10 g lead, or blocks of cupels of similar absorption.

5.3 Parting flasks or **nitric acid resistant basket** with thimbles**.**

5.4 Annealing crucibles, made of refractory materials.

5.5 Cupellation tongs.

5.6 Assay pliers.

5.7 Polished anvil, which may be replaced by a press, polished and reserved for this purpose.

5.8 Polished hammer, of minimum mass 400 g, which may be replaced by a press, polished and reserved for this purpose.

5.9 Scorification dishes, usually of diameter 50 mm.

5.10 Jewellers' rolls.

5.11 Scorification tongs.

5.12 Assay cleaning brush, of stiff bristle or nylon but not brass.

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

6 Sampling

The sampling procedure for jewellery gold alloys shall be performed in accordance with ISO 11596.

7 Procedure

When the composition of the samples is unknown, use a preliminary assay for the estimation of the fineness of gold, e.g. XRF analysis or touch stone test. For the distinction between palladium and nickel white gold, the touch stone test can also be used.

7.1 Yellow gold alloys, free of nickel and free of palladium white gold alloys

7.1.1 Assay sample

Transfer at least two samples of the alloy, preferably between 125 mg and 250 mg, weighed to the nearest ± 0,01 mg, into assay-grade lead foil (4.3). The mass of the foil (or foil and beads) should be at least 4 g for yellow gold samples up to 200 mg, and 6 g for samples from 201 mg to 300 mg (250 mg). Add pure silver (4.4) equivalent to 2,3 to 3 times the mass of fine gold present. Roll and compress the lead foil into a tight ball.

7.1.2 Proof assay samples

Weigh, as in 7.1.1, at least two proof assay samples of proof gold (4.5) and pure silver (4.4) in masses which correspond to the expected gold and silver contents (including the inquartation addition) of the assay sample. The total content of base metals in the assay samples is taken into consideration by the addition of a corresponding quantity of copper.

Treat the proof assay samples and the assay samples in 7.1.3 and 7.1.4 in the same manner.

7.1.3 Cupellation and treatment of precious metal buttons

Place the assay and the proof assay samples (7.1.2), tightly wrapped in lead foil, on magnesium oxide cupels (5.2) which have been preheated to at least 1 000 °C in the cupellation furnace (5.1).

Place the cupels with the proof assay samples as close as possible to the corresponding assay samples in the cupellation furnace maintained at 1 050 °C to 1 150 °C. Continue heating (about 25 min) under oxidizing conditions until the cupellation process is completed. Remove the cupels from the furnace. Allow the precious metal buttons to cool down before lifting them from the cupels with the assay pliers (5.6). Squeeze the buttons and brush their undersides carefully with a brush (5.12) to remove any adhering cupel material. Flatten the beads on the polished anvil (5.7) with a polished hammer (5.8) and anneal by heating just to red heat.

Roll them into 0,12 mm to 0,15 mm thick strips and anneal again. Roll the strips into cornets without contamination or loss of gold.

The cupel should be examined carefully to ensure that the precious metal bead contains all gold of the sample. Small droplet residues indicate the need for a repeat determination in a smaller cupel.

7.1.4 Parting of the silver/gold samples

CAUTION — For the parting operations with nitric acid, a fume hood should be kept clean and used exclusively for this determination.

7.1.4.1 Parting in individual flasks

Place the precious metal cornets in parting flasks (5.3). Immerse the cornet in 20 ml of nitric acid (33 %, see 4.1) and bring to the boil.

Continue heating for 15 min or until the evolution of nitrous fumes has ceased, whichever is longer. Decant, wash with warm water.

Repeat the treatment using 20 ml of nitric acid (49 %, see 4.2). Transfer the gold cornets to annealing crucibles (5.4). Dry them and anneal at 500 °C to 850 °C for about 5 min. Allow to cool and weigh.

7.1.4.2 Parting in a basket

When assaying a series of samples of similar composition, a nitric acid resistant basket equipped with a number of thimbles with perforated bottoms (5.3) can be used for parting the precious metal cornets.

Place the cornets in the thimbles and immerse the basket into the nitric acid (33 %, see 4.1) at about 90 °C. Bring the acid to the boil and allow to boil gently for about 15 min or until the evolution of nitrous fumes has ceased. Remove the basket from the acid and wash with warm water.

Repeat the treatment in a second bath of nitric acid (49 %, see 4.2). Allow to dry.

Finally, place the basket containing the gold cornets in a muffle furnace at 500 °C to 850 °C for about 5 min. Allow to cool and weigh the gold cornets.

7.2 White gold alloys containing nickel

If nickel is present, two equivalent variations on the method specified in this International Standard are acceptable. These involve either the use of additional lead or scorification.

7.2.1 Cupellation with additional lead

It is difficult to extract all the nickel in the alloy into the cupel by using the standard quantity of lead. Effective cupellation requires an additional 4 g of lead (4.3) and the use of larger cupels. This extra lead may be incorporated at the start of the test, if the cupel is large enough to contain the increased volume of melt. Alternatively (preferably) a button of lead is added to the hot precious metal bead in the cupel after the lead oxide fumes from the initial operation have ceased. Care is needed if the cupellation furnace (5.1) is not adapted for this addition.

The proof assays should contain approximately the same proportion of nickel as the sample.

7.2.2 Scorification

For white gold alloys containing nickel, pretreatment of the sample by scorification involves wrapping it in 2 g of lead foil (4.3). The sample consists of 125 mg to 250 mg of gold, and is inquarted with silver equivalent to 2,3 to 3 times the mass of fine gold present. Place this capsule in a scorification dish (5.9), together with 15 g of lead and 1,5 g to 2 g of Sodiumtetraborate (4.9) and heat to 1000 °C in the furnace. An increased air supply may be needed to oxidise the large quantity of lead. After 20 min to 30 min, when a liquid slag covers the surface of the dish, raise the temperature briefly to 1100 °C (for about 2 min). Remove the dish with the tongs, cool, and separate the lead button from the slag. This button, which contains the original gold and silver, is cupelled as described in 7.1.3.

Proof gold samples made with the appropriate amount of added nickel are treated in a similar way.

7.3 White gold alloys containing palladium (nickel absent)

For white gold alloys containing palladium, traces of this metal can remain in the cornet after a single cupellation and parting. With these alloys, the cornets from the sample and the proof assays should be recupelled with 4 g of lead, silver equal to 2,5 times the mass of gold and a small piece (about 50 mg) of copper (4.8). Repeat the parting process and weigh the final cornets.

The proof assays should contain approximately the same amount of palladium as the sample.

7.4 Gold alloys incorporating more than 40 % silver

These alloys shall be treated as yellow gold alloys, with proper allowance being made for the higher silver content when determining the inquartation addition.

7.5 Alloys containing 999 ‰ gold

When analysing samples containing approximately 999 ‰. gold, still increased accuracy in operation and parameter control is needed.

In order to achieve the best results, proceed as stated in 7.1, introducing the following modifications.

a) Weigh at least 250 mg of alloy; add (20 ± 5) mg of copper (4.8) to the sample and an amount of inquartation silver as stated in 7.1.1.

b) For the proof assay samples, proceed exactly in the same way as for the assay samples; use gold of a purity of 999,99 ‰ (4.5) and take care that the mass of the added inquartation silver lies in the same range (± 10 mg) as for the assay samples. Always run in parallel at least two proof assay samples.

c) Carry out the cupellation with a total amount of at least 2 g of lead (4.3).

d) After cupellation, flatten all beads so that they have approximately the same shape and thickness; anneal the flattened beads in a muffle to red heat to obtain the same conditions of recrystallization.

e) Proceed to the parting of the sampling as stated in 7.1.4. Take care that the quantity of acid and the parting time are the same for all samples of the same series. Finally dry and anneal in parallel all fine gold cornets. The use of a basket (5.3) for the parting will be advantageous for this purpose.

NOTE For these alloys a third parting step is recommended.

8 Method of calculation and expression of results

8.1.1 Proof assay sample factor

The proof assay sample factor (F) is calculated using Equation (1)

$$F = \frac{m_1}{m_2} \tag{1}$$

where

m_1 is the mass, in milligrams, of the proof assay sample;

m_2 is the mass, in milligrams, of the proof assay sample cornet.

8.1.2 Calculation of gold content

The gold content, W_{Au}, in parts per thousand (‰) by mass of the alloy is calculated using Equation (2):

$$W_{\mathrm{Au}} = \frac{m_4 \cdot F}{m_3} \cdot 10^3 \qquad (2)$$

where

m_3 is the mass, in milligrams, of the sample,

m_4 is the mass, in milligrams, of the sample cornet,

F is the value of the proof assay sample factors (8.1).

8.2 Repeatability

Duplicate determinations shall give results differing by less than 0,5 parts per thousand (‰) by mass for yellow and red gold alloys, less than 1,0 part per thousand (‰) by mass for white gold alloys and less than 0,2 parts per thousand (‰) by mass for gold alloys containing 990 ‰ or more of gold. If the difference is greater than this, the assay shall be repeated.

When analysing alloys with a fine gold content of 990 ‰ or more, the values for F of the proof assay samples (see 7.1.5) run in parallel shall not differ by more than 0,16 ‰. If the difference is greater than this, the assay shall be repeated.

9 Test report

The test report shall include 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) gold content of the sample, in parts per thousand (‰) by mass, as single and mean values;

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 laboratory manager and operator.

Bibliography

[1] ISO 9202, *Jewellery — Fineness of precious metal alloys*