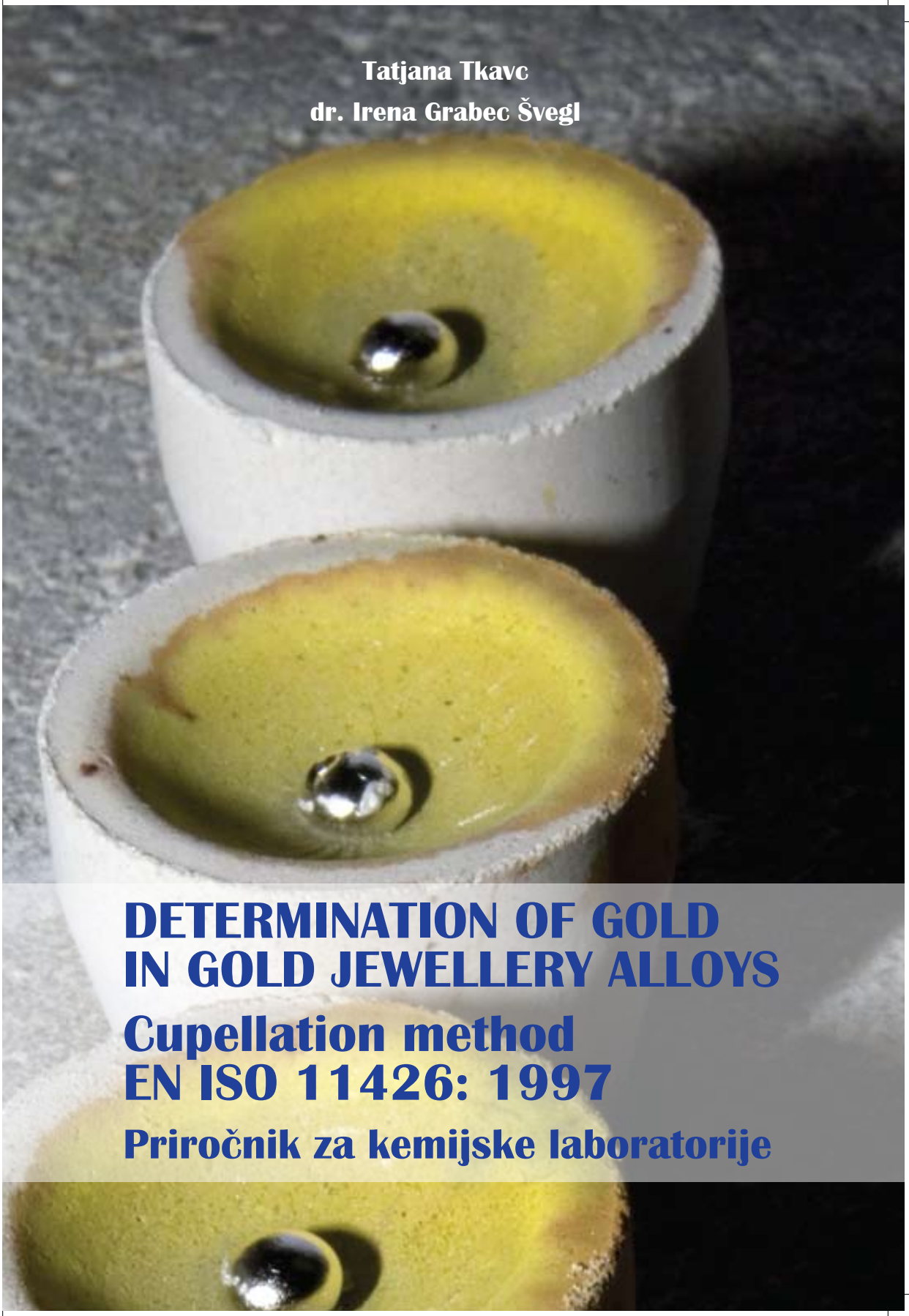
Tatjana Tkavc
dr. Irena Grabec Švegl



DETERMINATION OF GOLD IN GOLD JEWELLERY ALLOYS

Cupellation method EN ISO 11426: 1997

Priročnik za kemijske laboratorije

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Predgovor

Preskušanje in označevanje zlatih in srebrnih predmetov ima več stoletno tradicijo in sodi med ene od najstarejših oblik zaščite in varstva potrošnika pred poneverbo. Značilno je, da ima večina držav vzpostavljen bolj ali manj strog sistem preverjanja masnega deleža zlata v odgovarjajočih izdelkih. Za merjenje masnega deleža zlata v izdelkih iz plemenitih kovin je tako sprejet celo poseben mednarodni standard EN ISO 11 426 (1999): Determination of gold in gold jewellery alloys – Cupellation method (fire assay). Ob uvedbi omenjenega standarda v rutinsko, vsakodnevno delo preskuševalnega laboratorija se izvajalci kemijskih analiz srečajo z nizom praktičnih vprašanj povezanih z izvedbo kupelacije v skladu z zahtevami standarda. Z namenom, da bi bilo to delo čim lažje in enostavnejše, smo na osnovi naših dolgoletnih praktičnih izkušenj z izvedbo kemijskih analiz zlatih zlitin in odgovarjajočo akreditacijo kemijskega laboratorija pripravili ta priročnik. Upamo, da bo vsem, ki ga boste želeli uporabljati, v pomoč in spodbudo pri delu.

Tatjana Tkavc
Irena Grabec Švegl

Foreword

Testing and hallmarking of gold and silver articles with its hundred years of tradition represents one of the oldest types of customer protection practice. Different systems for the examination of the mass fraction of gold in precious metal articles can be found in almost all countries, including variations from the compulsory to voluntary approach. For these purposes also a special internationally harmonized technical standard EN ISO 11 426 (1999): Determination of gold in gold jewellery alloys – Cupellation method (fire assay) has been adopted. Various questions, connected to the execution of cupellation, arise when trying to implement the demands of the standard in the routine work of the testing laboratory. Thus in order to facilitate and simplify this task we prepared this handbook, which is based on our long term experience with the performance of chemical analysis of precious metal articles, including also the knowledge obtained in the corresponding accreditation of our chemical laboratory. We wish that the presented handbook will be a helpful and stimulation tool for experimental work for all those who will be using it.

Tatjana Tkavc
Irena Grabec Švegl

CONTENT

Cupellation method

Quantitative chemical method for determination of mass fraction of gold in yellow and white gold alloys. Mass fraction is expressed in parts per thousand (‰).

Range of measurement: mass fraction of Au between 333 ‰ and 999 ‰.

Application of modified cupellation method for:
- determination of Au in Ni and Pd white gold alloys
- determination of Au in gold alloys containing more than 990 ‰ of Au

Yellow gold alloys samples

Weigh gold alloy sample (m_1 = 220 mg) on the analytical scales (± 0,01mg)

Transfer the sample into assay grade Pb foil. Total mass of assay grade Pb should be 6 g.

Possibilities: - sample is wrapped only in Pb foil (6 g)
- sample is placed in Pb foil and some Pb tablets are added (total mass of Pb foil and tablets is 6 g)

Inquartation with pure Ag.

Add pure Ag equivalent to 2,3 to 3 times the mass of fine Au present. Roll and compress the lead foil into a tight ball.

Proof assay sample (yellow gold)

By parallel assaying of standard proof sample ($W_{Au,RM}$), of similar composition as investigated samples, possible systematic errors in the procedure are eliminated.

Standard proof samples for yellow gold alloys are prepared from appropriate metals of high purity and demonstrated traceability:

gold (Au 999,9 ‰)

silver (Ag 999,9 ‰)

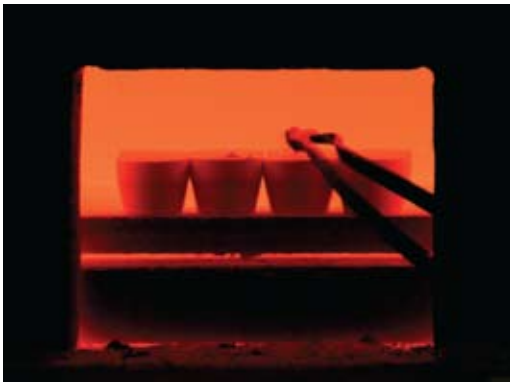
copper (Cu 999,9 ‰)

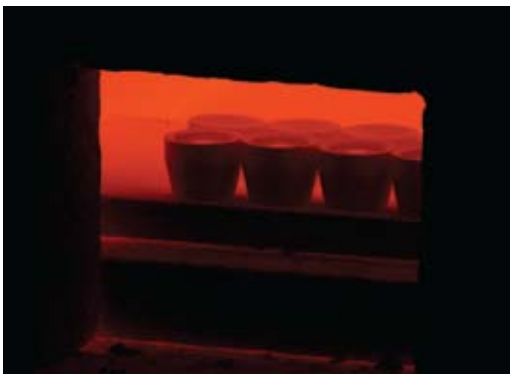

Alfa Aesar
A Johnson Matthey Company

Certificate of Analysis

Fire assay- cupellation

The assay and the proof assay samples tightly wrapped in Pb foil are placed on the magnesium oxide cupels and cupelled at 1050 °C.





Cupellation is completed after 25 min under oxidizing conditions.

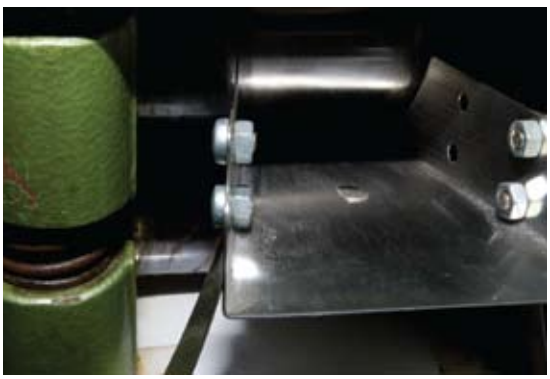
Treatment of precious metal buttons

Allow the precious metal buttons to cool down before lifting them from the cupels with the assay pliers.

Squeeze the buttons and brush their undersides carefully with a brush to remove any adhering cupel material.

Flatten the beads on the polished anvil with a polished hammer, roll them into 0,12 to 0,15 mm (aproximative) thick strips and anneal by heating just to red heat (cup. furnace: 905 °C for 5 minutes).

Roll the strips into cornets without contamination or loss of gold.



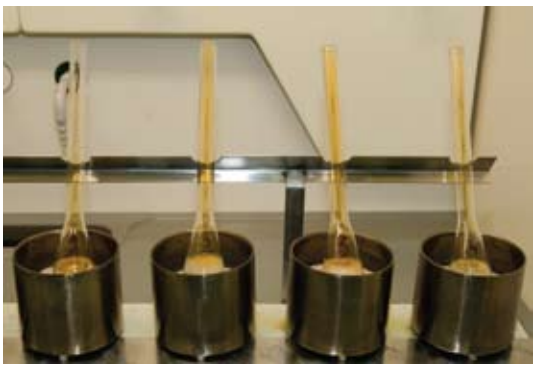
Parting of the silver/gold samples

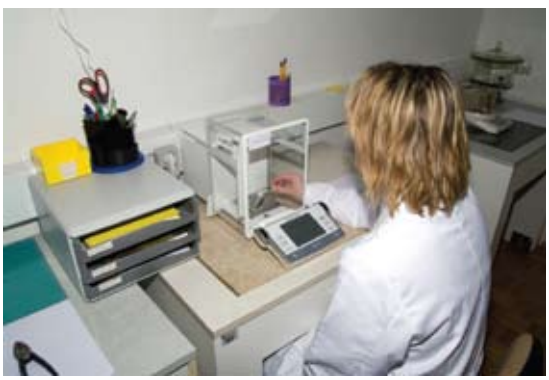
The precious metal cornets are placed in parting flasks and silver is extracted in nitric acid:

First immerse the cornet in 20 ml of 33 % HNO_3 at a temperature at least 5 °C below boiling temperature and bring to the boil Continue heating until evolution of nitrous fumes has ceased.

Decant and immerse the cornet in 20 ml of 49 % HNO_3, boil gently for 15 minutes and decant.

Immerse the cornet in 20 ml of 49 % HNO_3 and boil for 10 min.





Decant and wash the undissolved remaining gold with warm water until it is free of silver nitrate.

Transfer the gold cornets to small parting cups, dry, anneal at a temp. of 750 °C for about 5 min, cool and weigh the gold cornet.

White gold alloys containing nickel

Cupellation with additional lead

Effective cupellation requires an additional 4 g of lead because it is difficult to extract all the Ni in the alloy into the cupel by using the standard quantity of lead.

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

White gold alloys containing palladium

Recupellation

Traces of palladium may remain in the cornet after a single cupellation and parting.
With these alloys, the cornets from the sample and the proof assay should be recupelled with 4 g of Pb, Ag equal to 2,5 times the weight of Au and a small piece (about 50 mg) of Cu.
The parting process is repeated and the final cornets are weighed.

The proof assay should contain approximately the same proportion of palladium as the sample.

Method of calculation

Mass fraction of Au in the sample is calculated as:

W_{Au}	mass fraction of Au in the sample (‰)
m_1	mass of the sample (mg)
m_2	mass of pure Au obtained from the sample after a cupellation (mg)
$W_{Au,REF}$	certified mass fraction of Au in pure Au used for preparation of proof sample (‰)
$m_{1,REF}$	mass of pure Au used for the preparation of proof sample (mg)
$m_{2,REF}$	mass of pure Au obtained from the proof sample (mg)

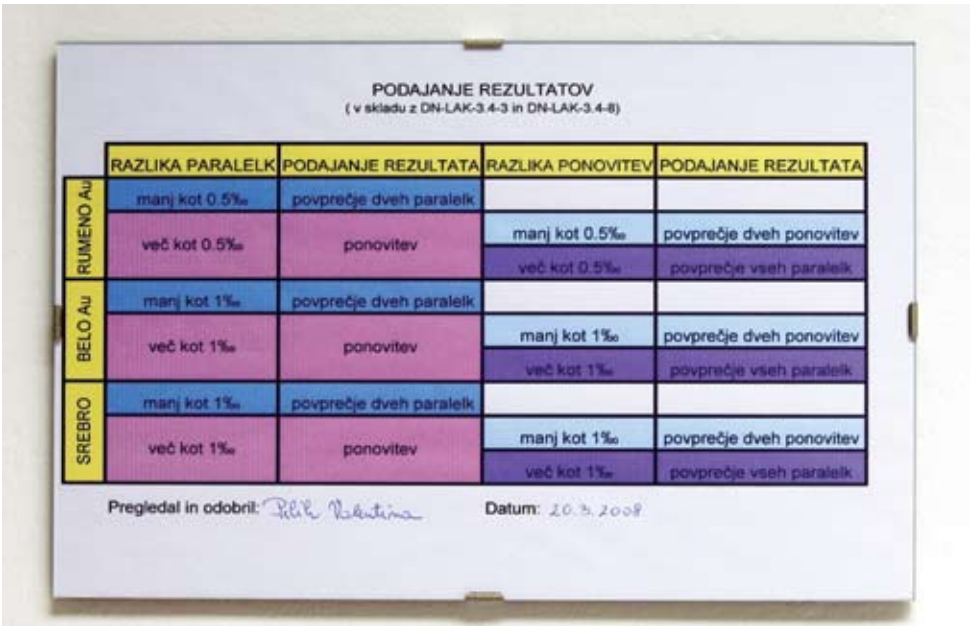
$$W_{Au} = \frac{m_2}{m_1} \frac{W_{Au,REF} \times m_{1,REF}}{m_{2,REF}}$$

Repeatability

Duplicate determinations shall give results differing by:

For yellow and red gold alloys: less than 0,5 ‰
For white gold alloys: less than 1,0 ‰

If the difference is greater than this, the assay shall be repeated



PODAJANJE REZULTATOV
(v skladu z DN-LAK-3.4-3 in DN-LAK-3.4-8)

	RAZLIKA PARALELK	PODAJANJE REZULTATA	RAZLIKA PONOVITEV	PODAJANJE REZULTATA
RUMENO Au	manj kot 0.5‰	povprečje dveh paralelk		
	več kot 0.5‰	ponovitev	manj kot 0.5‰	povprečje dveh ponovitev
			več kot 0.5‰	povprečje vseh paralelk
BELO Au	manj kot 1‰	povprečje dveh paralelk		
	več kot 1‰	ponovitev	manj kot 1‰	povprečje dveh ponovitev
			več kot 1‰	povprečje vseh paralelk
SREBRO	manj kot 1‰	povprečje dveh paralelk		
	več kot 1‰	ponovitev	manj kot 1‰	povprečje dveh ponovitev
			več kot 1‰	povprečje vseh paralelk

Pregledal in odobril: Datum: 20.3.2008

Test report

The test report shall include the folowing information:

- identification of the sample including source, date of receipt, form of the sample
- sampling procedure
- the method used by reference to this International Standard
- gold content of the sample, in parts by mass per thousand (‰) as single and mean values
- any unusual features observed during the determination
- date of test
- identification of the laboratory carrying out the analysis
- signature of the laboratory manager and operator

REPUBLIKA SLOVENIJA
MINISTRSTVO ZA VISOKO ŠOLSTVO, ZNANOST IN TEHNOLOGIJO
Urad RS za meroslovje
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3000 Celje, Tkalska 15

POROČILO O PRESKUSU S KVANTITATIVNO KEMIJSKO METODO

SLOVENSKA AKREDITACIJA
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Št. zadeve: 6431-33/2009 (Št. vzorca 2)
Ime in naslov stranke: Omerzo Marija s.p. Koprivnica 10 8282 Koprivnica
Datum sprejema: 19.02.2009
Datum preskusa: 24.02.2009
Vzorec: Verižica 1 kos m= 8.5 g (belo)
Preskusna metoda: SIST EN ISO 11426
Rezultati paralelnih meritev: 588.88/1000; 588.60/1000;

Knjiga analiz - zap. št.: 56/2009
Vzorčenje: DN-LAK-3.7-1
Opombe: belo

Material:	Povprečni rezultat:	Merilna negotovost:
Zlato (Au)	**588.7/1000**	**U = ± 0,5/1000**

Preskus opravil: Pooblaščena oseba:

*Podana je razširjena merilna negotovost (U), ki jo dobimo ko standardno merilno negotovost pomnožimo s faktorjem pokritja k=2, ki pri normalni porazdelitvi ustreza verjetnosti 95%.

Rezultati se nanašajo izključno na preskušani vzorec!
Poročila o preskusu brez pisnega dovoljenja laboratorija ni dovoljeno reproducirati, razen v celoti! **Stran 1/1**

OB-LAK - 2.4-2/9 Verzija:5 Odobreno 22.02.2007

Aurum “light beam”

Notes