EURAMET TC Project
Final Report

Project Title

HybriComparison on determination of gold content in white alloy

Coordinator, Institute, Country

Aida Jotanovic (IMBiH)

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Subject Field

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IMBIH

INSTITUTE OF METROLOGY OF BOSNIA AND HERZEGOVINA

EURAMET PILOT STUDY 1455

Comparison on determination of gold content in alloy

Final Report

March, 2025

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COORDINATOR:

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SUMMARY

The need for comparison in methods used to analyze the gold content in gold alloys has been identified among several national metrology institutes, with a focus on establishing traceability of measurements against a reference value. One of the key analytical methods for achieving these objectives is the gravimetric cupellation method, which is widely regarded as the method of choice for quantitative analysis of gold content in alloys. In addition to this gravimetric method, various spectroscopic methods were also employed, and the results were highly comparable, showing no significant differences between gravimetric and spectroscopic techniques.

Four national metrology institutes participated in the EURAMET Pilot Study 1455: Comparison on Determination of Gold Content in Alloy. The participants were tasked with evaluating the mass fraction (mg/g) of gold in a white gold alloy. To calculate the reference value for gold, the median was utilized.

Successful participation in this study demonstrates the measurement capabilities of the institutes in determining gold content in the range of 100 mg/g to 999 mg/g in gold alloys, specifically in white gold.

The study was designed with the specific purpose of comparing different analytical methods for determining gold content in alloys, considering varying measurement uncertainties and traceability.

TABLE OF CONTENTS

1. INTRODUCTION

The Bosnian-Herzegovinian and Slovenian National Metrology Institutes (NMIs) are currently the only institutions with Calibration and Measurement Capabilities (CMCs) for gold alloys, a material predominantly used in jewellery production. As part of the supporting evidence for these CMCs, participation in Interlaboratory Comparisons (ILCs) organized by the International Association of Assay Offices (Hallmarking Convention) was crucial, as well as the use of NIST-SRM 685-R, a highly pure gold standard (99.999%). Despite this, no key or supplementary comparison has been available in this area so far. Ensuring consistency and reliability in gold measurements is of international importance, as gold holds critical value in both financial and jewellery sectors.

This study aims to compare different methods, each with different uncertainty sources and traceability chains, to establish a measurement that supports the core competencies of national metrology institutes. Furthermore, it aids in the development of certified reference materials (CRMs) and proficiency testing schemes.

In 2018, the EURAMET SCIA approved Pilot Study 1455, focusing on the comparison of gold content determination in alloys. A key challenge in this study is establishing a reliable traceability chain for CRM-pure gold, used to prepare proof samples or calibration solutions, depending on the method used. The Canadian National Research Council (NRC) had previously published a CMC for pure gold analysis using the Glow Discharge Mass Spectrometry (GDMS) method, considered primary. Commercially available pure gold was sent to NRC for validation to ensure proper traceability, and participants in the comparison were provided with an Au sample and a gold CRM, both accompanied by a GDMS report.

The gravimetric cupellation method is the most widely applied method in the study. This method is well suited for high-content gold analysis in the range of 100 mg/g to 999 mg/g, with a measurement uncertainty of approximately 0.1% relative. It is especially effective in matrices containing significant alloying metals such as silver, copper, nickel, and palladium. The process involves dissolving non-precious metals in lead oxide, extracting residual silver and/or palladium in nitric acid, and leaving behind high-purity gold, which is determined through differential weighing. This standardized method is widely used by governmental laboratories responsible for jewellery market control.

Additionally, two participants used spectrometric method involving optical emission with plasma (ICP OES), a widely known technique for determining lower limits of the measurand. However, developing a new procedure for analyzing high-concentration and complex matrices using this method posed some challenges.

Despite this, the results from participants, along with their uncertainties, are highly comparable across both gravimetric and spectroscopic methods, showing no significant differences.

TIMELINE

ACTION	DATE
Proposed to EURAMET TCMC IAWG	February 2018
Draft protocol distributed	May 2018
CRM – traceability	December 2022
Distribution of samples	February 2023
Deadline for results submission	November 2023
Presentation of the results at EURAMET TCMC SCIA meeting	February 2024
Draft report distributed to participants	January 2025
Report presented to TCMC IAWG	February 2025

2. MEASURAND

Measurand of this study was the content of gold in white gold alloy expressed as mass fraction. Nominal mass fraction of gold in the sample is 585 mg/g ± 10 mg/g Au, containing other alloying metals: Ni, Zn and Cu.

3. STUDY MATERIAL

The raw material (precious metals alloy) was prepared in form of wire with the following nominal composition:

ELEMENT	NOMINAL VALUE (mg/g)
Gold (Au)	**585**
Nickel (Ni)	100
Zinc (Zn)	65
Copper (Cu)	250

The bulk test material (wire) was divided into sub-samples, identified, and labeled prior to conducting preliminary tests. A gravimetric analysis (cupelation method) was performed to determine the level of the element of interest—gold—in order to confirm compliance with the required criteria.

The sub-samples were prepared by cutting the wire into equal pieces, each with an approximate mass of 1.0 gram. These pieces were then packed into small plastic bags. Approximately 40 sub-samples were prepared, with each package containing approximately 1 gram of the sample.

The homogeneity test was conducted under repeatability conditions using an analytical method with known precision performance. Considering that precious metal alloys are not subject to physical or chemical changes, a stability test was deemed unnecessary.

3.1. Homogeneity study

To evaluate the homogeneity of the study material, eleven sub-samples were randomly selected and subjected to analysis. From each sub-sample, two test portions were taken and analyzed using the gravimetric method, ensuring precision and consistency in measurements. The assessment of between-bottle homogeneity was performed using Analysis of Variance (ANOVA) at a 95% confidence level, following the guidelines outlined in ISO Guide 35:2017.

The statistical evaluation confirmed that the study material was sufficiently homogeneous, meeting the necessary criteria for reliable analysis. This ensures that variations between bottles were negligible and did not significantly impact the results.

A summary of the findings is presented in the following Table 1:

MEASURAND	ANOVA		u_c [%] relative standard uncertainty
	F-statistic	F-critical	
Gold (Au)	1.69	2.85	**0.04**

Table 1. *Results of the homogeneity assessment*

The graphical presentation of the homogeneity data for gold are provided at the Figure 1.

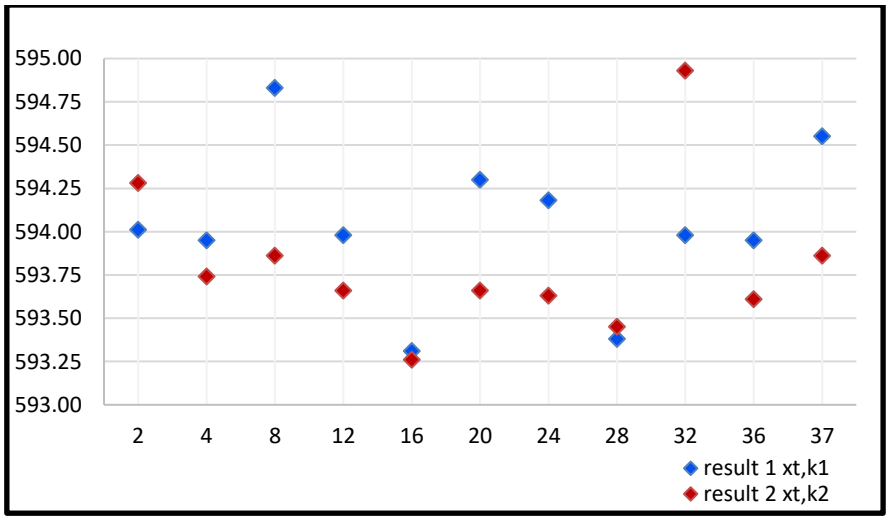

Figure 1. *Between unit homogeneity evaluation*

4. INSTRUCTION TO PARTICIPANTS

A technical protocol was provided to all participants of the EURAMET TCMC 1455 study, detailing the approximate analyte contents, sample handling procedures, and the format for data submission.

Each participant was supplied with at least one piece of wire weighing a minimum of 1 g, accompanied by certified reference material – Au 99.999%. Participants were instructed to analyze at least three subsamples and report results for the measurands as element content mass fractions (mg/g).

To ensure a comprehensive evaluation of the comparison, participants were also required to submit a detailed description of the methods employed. This included information on sample preparation, calibration techniques, metrological traceability, uncertainty assessment, reference materials used, and any other relevant methodological details.

5. PARTICIPANTS

In total, five participants registered for the EURAMET TCMC 1455 pilot project, demonstrating interest in contributing to this comparative study. Detailed information about the registered participants is summarized in Table 2.

PARTICIPANT	COUNTRY	CONTACT PERSON	MEASURAND
TUBITAK - UME	Turkey	Suleyman Z. Can	Au
PTB	Germany	Olaf Rienitz	Au
MIRS	Slovenia	Irena Grabec	Au
DZM	Croatia	Josipa Aleric	Au
IMBiH	Bosnia and Herzegovina	Gala Kosarac	Au

Table 2. *Participants*

6. METHODS OF MEASUREMENT

Participants were free to use a method of choice for both sample preparation and measurement method. Table 3 summarizes the sample preparation, measurement method (including calibration strategy) and sample mass used.

PARTICIPANT	SAMPLE PREPARATION	MEASUREMENT METHOD	CRM	SAMPLE MASS (g)
TUBITAK - UME	Acid digestion: 3 mL HCl + 1 mL HNO_3 mixture added into the sample. It was kept in a polypropylene tube at room temperature overnight.	ICP-OES; Single point calibration with Sc internal standard (High Performance Method)	NIST SRM 3121	0.04
PTB	Cleaning of the surface, cutting into four pieces, dissolution in HCl + H_2O_2 to yield solution with w(Au) ≈ 650...750 µg/g, dilution + addition of IS (Y) to yield w(Au) ≈ 10 µg/g + w(Y) ≈ 0.18 µg/g	ICP-OES; Two-point-bracketing with internal standard	Sigma Aldrich gold rod 265837-3G Lot # MKCC0849. (*Traceability:* characterized by NRC)	0.30
MIRS	n/a	Gravimetric method – Cupellation	Sigma Aldrich gold rod 265837-3G Lot # MKCC0849. (*Traceability:* characterized by NRC)	0.22
DZM	n/a	Gravimetric method – Cupellation	Sigma Aldrich gold rod 265837-3G Lot # MKCC0849. (*Traceability:* characterized by NRC)	0.30
IMBiH	n/a	Gravimetric method – Cupellation	Sigma-Aldrich gold rod (265837-3G, Lot # MKCC0849, characterized by NRC)	0.25

Table 3. *Participants' Measurement Methods*

7. RESULTS

The participants' results as reported to the coordinating laboratory are shown in Table 4.

PARTICIPANT	x_i	s_r	u_{xi}	k	U_{xi}	MEASUREMENT METHOD
TUBITAK - UME	**594.44**	1.39	0.82	2	1.64	ICP-OES
PTB	**594.49**	0.12	0.36	2	0.72	ICP-OES
MIRS	**594.32**	0.22	0.40	2	0.80	Gravimetric method
DZM	**594.03**	0.42	0.31	2	0.61	Gravimetric method
IMBiH	**594.51**	0.15	0.35	2	0.70	Gravimetric method

Table 4. *Participants' reported results*

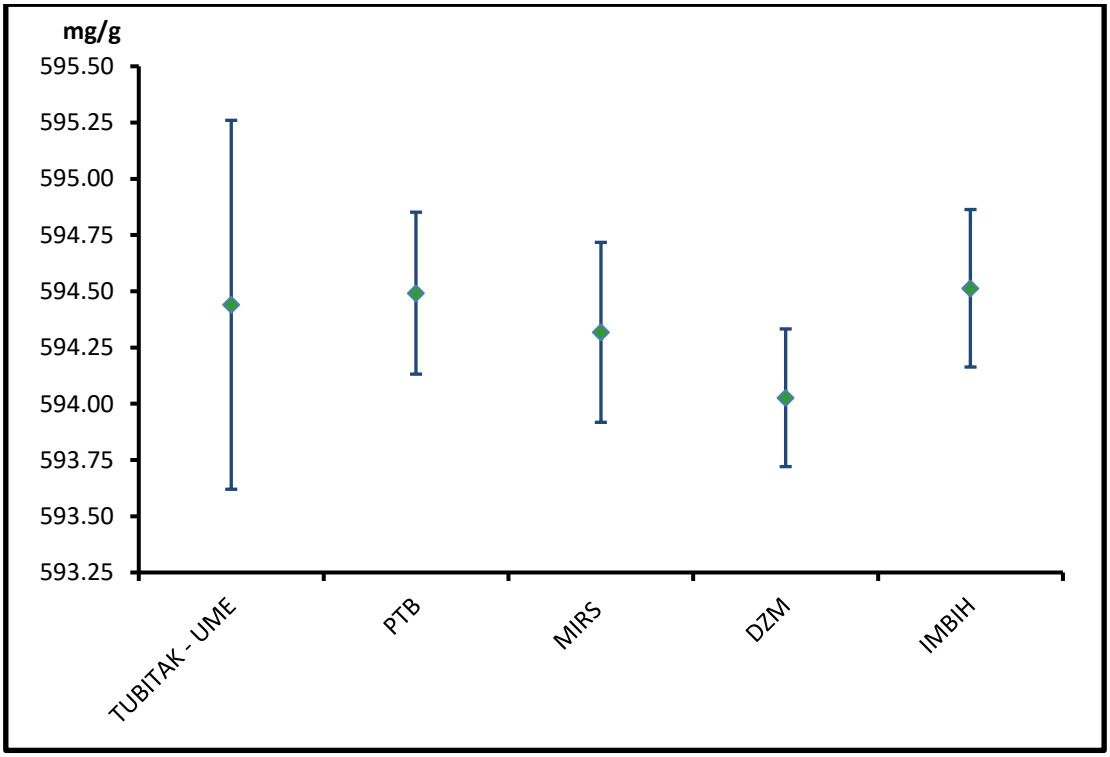

Figure 2: *Au mass fraction reported; error bar is u_c (k=1)*

7.1. Reference Value (RV)

The consensus values and their respective standard uncertainties are calculated and presented in this report, using different location estimators including arithmetic mean and median.

The statistics used for the evaluation of data to determine the RV and RU consist mainly of two approximations: The arithmetic mean and the median of the data set. The formulation used for the calculation of arithmetic mean and the median and their uncertainties are as follows:

Arithmetic mean:

$$x_{A.mean} = \frac{1}{n}\sum_{i=1}^{n} x_i \quad (1)$$

$$s_{A.mean} = \sqrt{\left(\frac{1}{n-1}\sum_{i=1}^{n}(x_i - x_{A.mean})^2\right)} \quad (2)$$

$$u_{A.mean} = \frac{s}{\sqrt{n}} \quad (3)$$

Median:

$$x_{Median} = \begin{cases} \frac{1}{2}(x'_{\frac{m}{2}} + x'_{\frac{m}{2}+1}) & m \text{ is even} \\ x'_{m/2} & m \text{ is odd} \end{cases} \quad (4)$$

$$MAD = median(|x_i - x_M|) \quad (5)$$

$$MAD_E = \hat{\sigma} = MAD * 1.483 \quad (6)$$

$$u_{median} = MAD_E\sqrt{\frac{\pi}{2n}} \quad (7)$$

Value of the RV and respective RU calculated are presented in Table 5; All data are given in mg/g.

n	ARITHMETIC MEAN		**MEDIAN**	
	x_{RV}	u_{xRV}	x_{RV}	u_{xRV}
5	**594.36**	0.09	594.44	0.11

Table 5. *Calculated RV and RU using the arithmetic mean and median approaches*

7.2. Equivalence statements

The degree of equivalence and its uncertainty of a reported result by a participant compared to the RV were calculated using equations (11) and (12) as follows:

$$d_i = x_i - x_{RV} \tag{8}$$

$$U(d_i) = 2\sqrt{u(x_i)^2 + u(x_{RV})^2} \tag{9}$$

where:

d_i is the degree of equivalence (DoE) for participant *i* (*i* = 1,…,n),

x_i is the reported result from the i^{th} participating institute (i = 1,…,n),

x_{RV} is the supplementary comparison reference value,

$U(d_i)$ is the uncertainty of DoE for participant *i* (*i* = 1,…,n).

The equivalence statements for EURAMET PILOT STUDY 1455 are listed in Table 6 and 7 with RV-arithmetic mean and RV-median respectively.

LAB	x_i	u_{xi}	k	U_{xi}	method	ARITHMETIC MEAN		MEDIAN	
						d_i	U_{di}	d_i	U_{di}
TUBITAK - UME	594.44	0.82	2	1.64	ICP-OES	**0.08**	**1.65**	**0.00**	**1.64**
PTB	594.49	0.36	2	0.72	ICP-OES	**0.13**	**0.74**	**0.05**	**0.73**
MIRS	594.32	0.40	2	0.80	gravimetric method	**-0.04**	**0.82**	**-0.12**	**0.81**
DZM	594.03	0.31	2	0.61	gravimetric method	**-0.33**	**0.64**	**-0.41**	**0.62**
IMBIH	594.51	0.35	2	0.70	gravimetric method	**0.16**	**0.72**	**0.07**	**0.71**

Table 5. *Calculated DoE and U_{DoE} the arithmetic mean and median approaches*

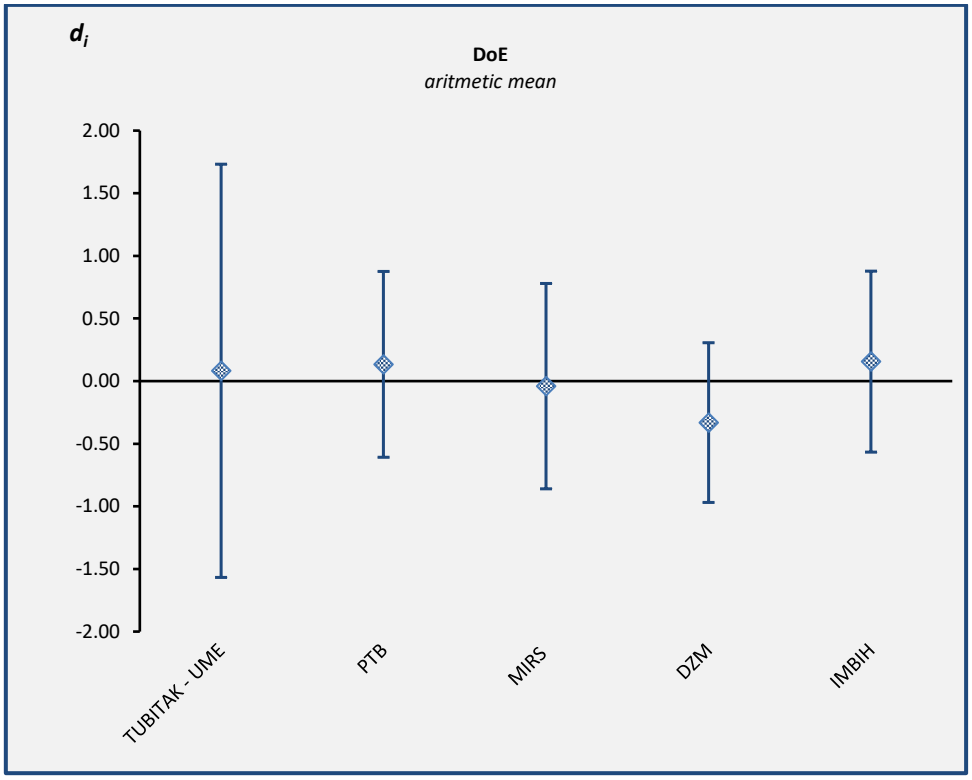

Figure 3: *DoE – mean approach; error bar is U_{DoEc} (k=2)*

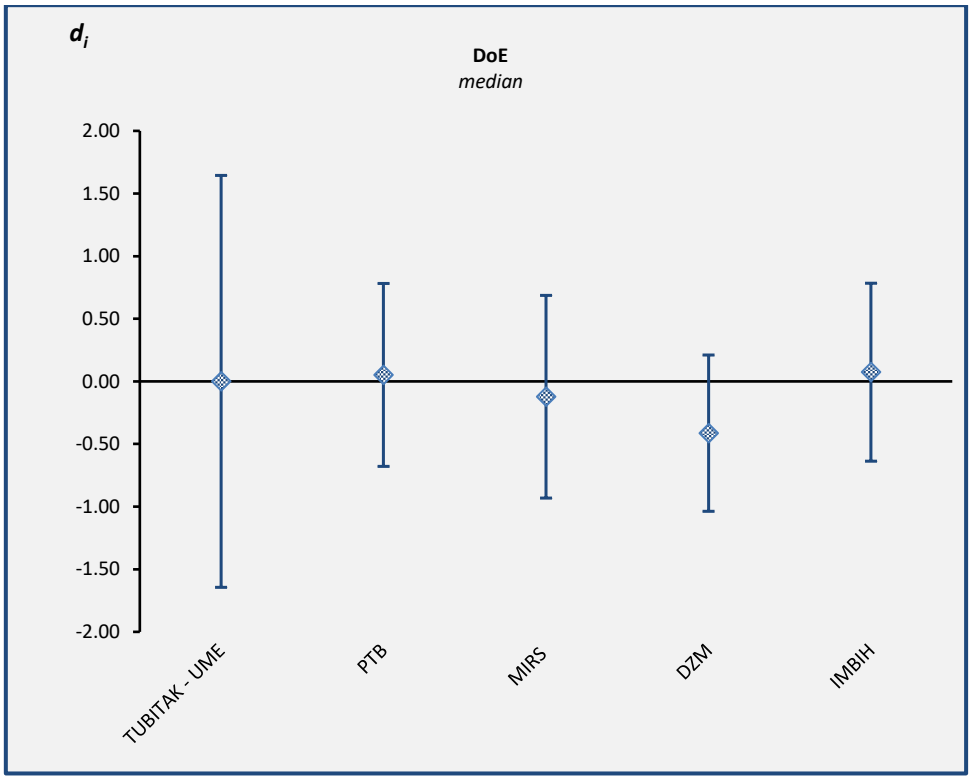

Figure 4: *DoE – median approach; error bar is U_{DoEc} (k=2)*

8. CONCLUSION

This study was proposed as the EURAMET Pilot Study, with the specific purpose of comparing different analytical methods for determining the gold content in alloys, considering varying measurement uncertainties and traceability approaches. The study was conducted in collaboration with EURAMET TC-MC to evaluate the participants' capabilities in measuring gold concentrations in mg/g in metal alloys.

Initially, the study aimed to propose a gold alloy comparison (either as a key or supplementary comparison) with the goal of expanding the Calibration and Measurement Capability (CMC) scope to include different matrices. However, this proposal was withdrawn by the CCQM IAWG, primarily due to the absence of a traceable gold Reference Material which is essential for establishing a reliable traceability chain.

The Canadian National Metrology Institute (NRC), at the request of the Institute for Metrology of Bosnia and Herzegovina (IMBiH), utilized its previously published CMC for pure gold analysis using the Glow Discharge Mass Spectrometry (GDMS) method, considered a primary method, to validate commercially available pure gold for proper traceability, after which participants in the comparison were provided with a gold sample and an Au CRM accompanied by a GDMS report.

The results of the comparison demonstrated that most participating NMIs/DIs successfully showcased their measurement capabilities for gold within acceptable uncertainty limits.

Data from the participants, including uncertainties, showed strong agreement across gravimetric and spectroscopic methods, with no significant differences observed between the methods.

IMBIH

INSTITUTE OF METROLOGY OF BOSNIA AND HERZEGOVINA

CHEMISTRY DEPARTMENT

EURAMET PILOT STUDY: 1455

COMPARISON ON DETERMINATION OF GOLD CONTENT IN WHITE ALLOY

Draft protocol

I. Introduction

The need for comparisons with the application of the methods for analyzing the content of gold in gold alloys is expressed among several national metrology institutes with the main focus on establishing traceability of their measurements in relation to the reference value. One of the analytical methods for achieving the stated goals implies the application of gravimetric method - cupellation method as a method of choice for the quantitative analysis of gold content in gold alloys. This method is suitable for the analysis of high content of gold in the range of 333 to 999 mg/g with the measurement uncertainty of approximately 0.1% rel. in the matrix containing significant values alloying metals such as silver, copper, nickel, palladium, etc. Cupellation method involves the use of the natural phenomenon of dissolution of non-precious metals in lead oxide, and the extraction of residual silver and/or palladium in nitric acid, leaving behind high-purity gold. The content itself is determined in the process of differential weighing.

The submitters of this proposal, IMBiH – Institute of Metrology of Bosnia and Herzegovina and MIRS – National metrology institute of Slovenia are well experienced in the application of this procedure and have many years of experience in preparing materials - alloys for the implementation of comparison studies, as well as in processing data in accordance with BIPM/CIPM rules. Also, both institutes already have CMCs for reference measurement of gold content in yellow gold alloys.

The study is open for all NMIs/DIs wishing to apply suitable analytical method for the analysis of gold content in gold alloys. Since participants will apply different analytical methods equivalence of the applied methods will be compared when evaluating the results.

This study is proposed as **EURAMET Pilot study** with specific purpose of comparing different analytical methods for determination of content of gold in alloy with different measurement uncertainty as well as different traceability demonstration.

II. Test material

The test material is the gold alloy of the following nominal composition: Au 585 mg/g; Cu 250 mg/g; Ni 100 mg/g and Zn 65 mg/g. It is prepared in a form of wire with diameter of 0.5 mm. Bulk alloy in the form of wire has been screened by means of XFR energy dispersive spectrometer in order to (semi-quantitatively) determine the mass fraction of all metals present in the alloy.

The homogeneity of the test material was performed by selecting number of subsamples by applying random stratified sampling approach. The measurements were conducted with the gravimetric method and the data were evaluated with ANOVA according to ISO Guide 35. Between sample homogeneity value is u_{bb}=0.04%.

Due to high durability and stability of precious metals alloys, stability testing was excluded from the preliminary procedure.

III. Coordinating laboratory

IMBIH, as a pilot laboratory is responsible for the preparation of comparison material, conducting of homogeneity test and sample preparation and distribution. IMBIH will be responsible for informing potential participants, setting the time schedule of the comparison and the evaluation of results and issuance of final report.

IV. Measurand and method

Measurand of this study is the content of gold in white gold alloy expressed as mass fraction. Nominal mass fraction of gold in the sample is 585 ± 10 mg/g Au, containing other alloying metals: Ni, Zn and Cu.

Gravimetric method – cupellation is composed of several analytical steps involving natural phenomenon of separating gold and silver from other alloying metals by means dissolution in molten PbO_2. Further steps include separation of gold and silver by means of nitric acid. Weighing the sample prior and after the cupellation process gives input for the calculation of gold content in mg/g. Other quantitative methods for the analysis of gold content in white gold alloys include, but not limited to optical and mass spectrometry of dissolved sample.

Participants are required to measure the gold content and report mass fraction of gold in the stated units.

V. Reporting and submission of results

Upon distribution of samples, all eligible registered participants will be provided with the reporting form. Using the information provided on the form, each participant shall provide individual results, details about their uncertainty budget, the analytical method applied and CRMs used. Minimum 3 results for stated measurand will be expected from each participant.

VI. Time table of the comparison

Distribution of samples	February 2023
Deadline for results submission	November 2023
Reporting to the participants	January 2024
Presentation of the results at EURAMET TCMC SCIA meeting	February 2024

VII. Participants

Participation in this EURAMET pilot study is open to all interested EURAMET NMIs/DIs.

For enquire participants may contact the coordinating laboratory as follows:

Aida Jotanović, MSc
Institute of metrology of B&H
Branilaca Sarajeva 25, 71000 Sarajevo; B&H

aida.jotanovic@met.gov.ba
+387 (0) 33 568 925

COMPARISON ON DETERMINATION OF GOLD CONTENT IN WHITE ALLOY
EURAMET Project Registration No: 1455

Please, fill out and return the form to Aida Jotanovic (aida.jotanovic@met.gov.ba) by November 30, 2023.

PARTICIPANT'S INFORMATION

Institute	
Contact person	
Analyst(s)	
Date	

RESULTS

SAMPLE	MASS FRACTIONS (mg/g)					
MA/Au.04 - 1455	**Result1**	**Result2**	**Result3**	**Result4**	**Mean**	**Standard Deviation**
					#DIV/0!	#DIV/0!
Standard uncertainty *(u_c)*						
Coverage Factor *(k)*						
Expanded uncertainty *(U)*						

TECHNICAL DETAILS

Sample amount used for analysis	
Sample pre-treatment *(if applicable)*	
Analytical instrumentation used	
Calibration type / details *(if applicable)*	
Calibration standards *(if applicable)*	
Measurement equation and uncertainty budget	
Additional Comments or Observations	