



Comparison of x-ray fluorescent analysis and cupellation method for determination of gold in gold jewellery alloy

Jotanović, A.^a, Memić, M.^b, Suljagić, Š.^a, Huremović, J.^b

^a Institute of metrology of Bosnia and Herzegovina, Augusta Brauna 2, 71000 Sarajevo, Bosnia and Herzegovina

^b University of Sarajevo, Faculty of Science, Department of Chemistry, Zmaja od Bosne 33-35, 71000 Sarajevo, Bosnia and Herzegovina

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*Corresponding author:

E-mail: m_memic@yahoo.com

Phone: 00-387-33-279-882

Fax: 00-387-33-649-359

Abstract: To make jewellery of gold, gold is alloyed with other metals. It is of great importance to accurately determine the total amount of pure gold in alloys used for making the jewellery and in jewellery made of gold, because it determines its value on the market. Several analytical methods are used for this purpose. This study was based on comparison of results of analysis of gold alloy for 14-carat jewellery obtained by non-destructive fluorescent analysis method and destructive cupellation method. The null hypothesis with 95 % confidence level on equivalence in measurement precision of percent by percent mass of gold in three very similar gold alloy samples in reproducibility conditions (three measurement series) for standard cupellation method and the method compared (validated), XRF method, has been confirmed. F-test did not confirm null hypothesis on precision equivalence for two mentioned analysis methods. There is a significant difference in variance values. However, the t-test was carried out, which verified the null hypothesis on equivalence between mean values of results achieved in two compared values. In order to confirm applicability of two methods, Z_{score} was calculated giving values of less than 2, using statistical data from inter-laboratory program with 62 participating laboratories applying cupellation method, and 60 laboratories applying XRF method for analysis of gold alloy used in production of 14-carat jewellery.

INTRODUCTION

Gold is a chemical element that plays an important role in many industry branches, primarily in industry of valuable jewellery. Over 80 % of all pure gold produced is used in manufacturing of various adornments, jewellery and money. Gold is the type of metal that is too soft for jewellery production, thus is alloyed with other metals, usually with silver, copper, zinc, nickel, palladium, iridium, etc. nickel and palladium are used for white gold alloys. Consequently gold jewellery is never made of gold only. Percentage of gold in jewellery alloys and jewellery itself is usually expressed in carats or degree of fineness (purity). According to these markers pure gold is defined as 24 carat gold. If an alloy is marked as 18-carat gold that means it contains 18 parts of gold and 6 parts of one metal or a number of other metals. The degree of gold fineness

describes the number of gold parts in 1000 parts of alloy. According to this mark, 18-carat gold is 750 fineness, which means that it has 750 parts of gold in 1000 parts of alloy, i.e. there is 75% of gold in alloy. Nowadays, jewellery available in the market is of 375; 585; 750; 915 and 999 fineness. It is very important to accurately determine the total amount of pure gold in alloys used for jewellery production and in jewellery made of gold, because their market worth is determined on that value.

There are several methods in jewellery industry dealing with quantitative determination of gold in alloys for jewellery production, that are based on determination of fineness or caratage of gold. Which method will be used depends on several factors, but most important one is measurement accuracy and precision of the respective method. In addition, the cost of measurement method and

device used for a specific analysis plays an important role in selecting the method of analysis.

Nowadays, analytical methods used for quantitative gold analyses are the following: stone probe (Walchi and Vuilleumier, 1991; Eluere, 1986; Oddy, 1983) which is practically a non-destructive method used for determination of gold parts with 1-2 % deviation; cupellation method (ISO/ 11426: 1997), which is a destructive method, also used for determination of gold parts but with a deviation under 0,02 %, spectrometric methods, primarily inductively coupled plasma (Wu *et al.*, 2004; Juvonen *et al.*, 2002; Brill and Wiedemann, 1992) which is also a destructive method with deviation of 0,1 % but gives complete alloy analysis. Other, less accurate and less sensitive destructive spectroscopic methods – such as UV-VIS spectrophotometry (Balcerzak *et al.*, 2006; Chen *et al.*, 2006; Hu *et al.*, 2006; Zhao *et al.*, 2006; Gao *et al.*, 2005; Gangadharappa *et al.*, 2004; Melwanki *et al.*, 2002; Fujita *et al.*, 1999; Pal 1999; El-Zawawy *et al.*, 1995) atomic absorption spectrometry – flame and graphite furnace technique (Pyrzynska, 2005; Medved *et al.*, 2004; Petrović *et al.*, 2001) and, finally X-ray fluorescent analysis method (Jurado-Lopez *et al.*, 2006; Linke and Schreiner, 2000; Stankiewicz, 1998; Marucco and Stankiewicz, 1998) which is a non-destructive method with a deviation of 0,1 - 0,5 %, which is used for complete gold alloy analysis. Institute of Metrology B&H, in their precious metals quality control laboratory, determines fineness of gold in golden jewellery that is available on market in Bosnia and Herzegovina. The test method that is commonly used for such purposes is cupellation method or, so called, fire assay. By this method, the sample is melted at high temperature and dissolved in nitric acid, that destructs the sample. Consequently this method is not considered practical, since jewellery pieces are expensive. That is why an introduction of a new method was necessary; x-ray fluorescent analysis, which does not destroy samples and is precise enough to determine fineness of gold.

The aim of this study was to compare results of measurements of percent by mass of gold in golden alloys, used in jewellery production, measured by x-ray fluorescent analysis and cupellation method. Based on the results, we estimated the accuracy and precision of instruments for x-ray fluorescent analysis, excluding systematic error. For this purpose, two samples of 14-carat yellow gold were analyzed and in addition one sample, that was part of an inter-laboratory comparison, in which Institute of Metrology B&H participated, was analyzed.

EXPERIMENTAL

EXPERIMENTAL

Test equipment

To determine the percent by mass of gold present in golden jewellery alloy by X-ray fluorescent analysis, Oxford Instruments *CFI 900* spectrometer was used, with collimator 0,3 and “Multichannel proportionate counter filled with Xe” detector. The x-ray source was 50W (50kV and 1.0 mA); Tungsten anode tube. The instrument has a digital multichannel analyzer with automatic signal processing, including automatic correction parameters. Instrument is equipped with SmartLink Fundamental Parameters software and Statistic and Report Generator software.

Mass measurement was carried out on the analytical electronic balance, Sartorius AG, *LE224S*±0.1 mg. Laboratory furnace Nabertherm, *L 5/13 / B 170* with temperature range 30⁰C – 1300⁰C was used for scorification of samples. In addition, during the application of the cupellation method for determination of percent by mass of gold in samples the following equipment was used: cupels, plate rolling machine, sand bath, Kjeldahls flasks, and crucibles for assays.

Chemicals and reagents:

Silver of 99,998 % purity (*Alfa Aesar*, USA), was used for quartering gold alloys and everything was melted with lead of 99,9 % purity (*Sigma Aldrich*, Germany). Melted material was dissolved in a solution prepared from 65 % HNO₃, (*Fluka*, Germany). To prepare the blank, Austria gold of 99,998 % purity (*Ogussa*), was used. Redistilled water of 0.06 µS/cm conductivity was used in preparation of all solutions.

Analytical Quality Control

Quality assurance (QA) was achieved by: adequate apparatuses with the required measurement precision, chemicals and metals (Ag and Pb) of high degree of purity and series of certified reference materials (CRMs) by competent American manufacturer *X-calibur XRF service* listed in Table 1.

Table 1. Certified Reference Materials, *X-calibur XRF service*

CRM No	Content						
	Au (%)	Ag (%)	Cu (%)	Zn (%)	Ni (%)	In (%)	Pd (%)
14KY 84	58.43	7.63	29.23	4.71	-	-	-
14KY 820	58.34	4.91	30.33	6.42	-	-	-
14KY 270	58.36	7.26	28.64	5.74	-	-	-
14KY 290	58.39	12.82	24.50	4.29	-	-	-
14KY UA1	58.43	9.51	28.20	3.65	-	0.21	-
14KY VHF3	58.47	4.85	29.98	6.70	-	-	-
14KG 570	58.34	35.03	6.43	0.20	-	-	-

Samples

Two series of samples of analyzed: (a) two different samples of 14-carat yellow gold in form of metal plates; (b) a sample of 14-carat yellow gold that was a part of international inter-laboratory comparison program.

Analysis of Samples by Cupellation Method

Determination of percent by mass of gold in gold alloys by cupellation method was performed by standardized ISO 11426:1997 method. Despite the fact that cupellation is one of the oldest methods of gold fineness determination, it provides very accurate results, which makes it the most used method, provided that sample destruction is not a problem.

To determine percent by mass of gold in alloy by cupellation method, two different samples of gold alloy were used (585 fineness) and for each sample, a series of 10 analyses was performed under conditions assuring repeatability. For that purpose, samples of 0.22 – 0.23 g were weighed on an analytical balance with accuracy ± 0.1 mg. Samples were wrapped into lead foils, weighing

approximately 6 grams each. Pure silver (approximately 0,3 g) was added to each sample. The mass of silver was 2,5-3 times higher than mass of gold in alloy, depending on gold fineness. In the process of adding silver, attention was given to amount of gold already present in the alloy. The samples were compressed into tight balls and placed into preheated furnace cupels. The temperature in the furnace was maintained at $1065 \pm 1^\circ\text{C}$ for approximately 25 minutes under oxidizing conditions. Cupel surface absorbs alloying metals, whereas precious metals remain on the cupel surface in form of metal beads. After cooling to room temperature, beads were rolled with rolling machine into 0.12-0.15 mm thick strips, rolled again into cornets.

Separating gold from silver

As analyzed samples contained no other precious metals, the next step was separation of silver from gold. For this purpose, strips were dissolved in nitric acid, whereby the silver was dissolved, while the gold remained undissolved.

Cornet samples were immersed in 20 mL nitric acid (33 %) preheated in 100 mL Kjehldals flasks at a temperature below the boiling point (at least 5°C below), and brought to the boil. The solution was left to boil around 15 minutes, i.e. until the evolution of nitrous fumes had ceased. The solution was then decanted, cornets washed with redistilled water and 20 mL of nitric acid (49 %) was added. Gentle boiling was continued for 15 minutes. The procedure of dissolution with 49 % acid was repeated twice. The solution was decanted; pure gold cornets were washed in warm redistilled water (60°C - 70°C) and finally transferred into crucibles. They were annealed at 750°C around 5 minutes, cooled and weighed. Results showing percent by mass of gold in alloy are presented in promilles (‰) for two different samples in series of 10 repeated analysis each obtained by cupellation method are presented in Table 2.

Analysis of Samples by X-ray Fluorescent Analysis

To determine percent by mass of gold in alloys using x-ray fluorescent analysis method, the same samples of gold alloy, fineness 585, which were analyzed by cupellation method, were used here. Analyses were repeated ten times. It is a known fact that fluorescence intensity is proportional to mass part of all components present in the sample. Relying on that fact, the concentration of elements in samples was determined by comparing results of sample analysis with results obtained by previous analysis of compatible certified reference materials with known quantitative composition of metals. In this case, relevant *calibration files* were stored into the software of the instrument, which were obtained by measuring the fluorescence intensity for each metal in CRM and in these files a relation was established between the received signal (number of impulses per second) of analyzed sample and CRM signal.

Results showing percent by mass of gold in alloy were presented in promilles (‰) for two different samples and 10 repetitions using x-ray fluorescent analysis method are presented in Table 2.

The second batch analysis was conducted on a sample that was the testing sample of inter-laboratory comparison, i.e. inter-laboratory program of testing precious metals alloy. The program was organized by IAAO (*International Association of Assay Offices*) and HMC (Hallmarking Convention). Laboratory for Precious Metals of B&H Institute of Metrology took part in this program. The

program was identified as *Round Robin No. 22* and included analysis of two samples of 14-carat yellow gold (sample ID: RR-22) by methods of x-ray fluorescent analysis and cupellation. Analyses were repeated four times, in line with participation protocol of inter-laboratory comparison.

Analyses results, expressed as percent by mass of gold in alloy, presented in promilles (‰) are shown in Table 2.

RESULTS AND DISCUSSION

Analyzed results presenting percent by mass of gold in alloys used to make 14-carat jewellery by cupellation method and x-ray fluorescent analysis are shown in Table 2. We can conclude that there is little variation in results obtained by cupellation method for all three samples. The difference is shown on the first decimal place for results expressed in promilles. Results obtained by XRF method for all three samples vary to a part of promille.

Table 2. Results of percent by mass of gold in gold alloys for production of 14-carat jewellery obtained by cupellation method and x-ray fluorescent analysis method for 10 and 4 repetitions respectively, expressed in promilles (‰).

	IRM ¹ -1		IRM-2		ILC ²	
	KUP ³	XRF ⁴	KUP	XRF	KUP	XRF
	588.5	588.0	583.9	582.5	588.2	589.0
	588.8	585.3	583.0	584.2	587.6	582.4
	588.4	588.9	583.9	588.4	588.2	588.2
	588.6	587.1	583.5	585.1	587.7	589.9
<i>Au</i> (‰)	588.4	588.8	583.3	583.9		
	588.3	586.8	583.5	585.6		
	588.8	587.8	583.7	582.0		
	588.7	586.4	583.5	587.0		
	588.9	588.5	583.4	586.7		
	588.4	585.6	583.3	582.1		

¹Internal Reference Material; ²International Inter-laboratory comparisons; ³Cupellation Method; ⁴X-ray Fluorescent Analysis Method

For comparison of two analysis methods F- test and Student t-test were performed. To perform this tests the following condition were met: (a) Possession of the reference test method (cupellation method); (b) Multiple testing of at least one sample by the new method and reference method in terms of repeatability.

To calculate the F-test and t-test, the following parameters were previously calculated: mean value of series of measurement (\bar{X}) for each individual sample, standard deviation for a series of repeated measurements (s), pooled standard deviation (S_c). They are shown in Table 5.

Verification of the null hypothesis on absence of significant differences in methods precision

Statistical data, relevant for verification of the null hypothesis on equivalence in precision of measurement by the same method in three very similar test samples in comparable conditions (different analyses time) are presented in tables 3 and 4. All comparisons were performed with 95 % confidence level.

Table 3. Statistical parameters for reproducibility of cupellation method

	KUP1	KUP2	KUP3
No. of measurements	10	10	4
Standard deviation (S)	0.210	0.279	0.320
F1 ex (2/1)		1.76	
F2 ex (3/2)		1.32	
F3 ex (3/1)		2.32	
F _{tab} (95 %)	F1(9 ; 9) 3.18	F2(3 ; 9) 3.86	F3(3 ; 9) 3.86

Table 4. Statistical parameters for reproducibility of XRF method

	XRF1	XRF2	XRF3
No. of measurements	10	10	4
Standard deviation (S)	1.290	2.221	3.389
F1 ex (2/1)		2.96	
F2 ex (3/2)		2.32	
F3 ex (3/1)		6.90	
F _{tab} (95 %)	F1(9 ; 9) 3.18	F2(3 ; 9) 3.86	F3(3 ; 9) 3.86

The null hypothesis on equivalence in measurement precision with 95 % confidence level was tested in following cases: (a) Contents of gold, using one method (CUP) for three selected samples (three measurement series); (b) Contents of gold, using one method (XRF) for three selected samples (three measurement series).

One of the following hypotheses was to be confirmed: H_0 ; there is no significant difference in precision if $F_{tab} > F_{exp}$; H_1 ; there is significant difference in precision if $F_{tab} < F_{exp}$.

Experiments confirmed null hypothesis on equivalence in precision of measuring mass of gold in three very similar samples of gold alloy in conditions of reproducibility (three measurement series) by standard cupellation method. The null hypothesis on equivalence in precision of determining parts of gold in conditions of reproducibility, using comparison (validation) method of X-ray fluorescent analysis (XRF) was also confirmed. In one of the three measurement series there was $F_{tab} < F_{exp}$ (by comparison of the third and the first measurement batch variances), which can be attributed to the random error effect.

Verification of the null hypothesis on absence of significant difference in results means value for two methods

The results of analyses of percent by mass of gold in alloys obtained by utilizing two analysis methods, CUP and XRF, for three measurement series in repeatability conditions were compared.

F-test did not confirm the null hypothesis on precision equivalence for two mentioned analysis methods. There is significant difference in variance values. Increased variance values are obvious for XRF methods (for all measurement series), which indicates reduced precision in results obtained through application of this method.

Although the null hypothesis on equivalence for two compared methods was not confirmed, t-test was taken for verification of the null hypothesis on equivalence between mean values of results for two measurement series (of two analysis methods) in repeatability conditions.

Table 5. Values of relevant statistical parameters for comparison of two methods

N	IRM-1		IRM-2		ILC	
	10	10	10	10	4	4
\bar{X} (%)	588.6	587.3	583.5	584.6	587.9	587.4
S	0.210	1.290	0.279	2.221	0.320	3.389
Sc	0.92		1.58		2.40	
F _{exp} (95 %)	37.7		63.4		112.2	
F _{tab} (95 %)	3.18		3.18		9.28	
t _{exp} (95 %)	3.16		1.56		0.29	
t _{tab} (95 %)	2.10		2.10		2.45	

One of the following hypotheses was to be confirmed: H_0 ; there is no significant difference in mean values if $t_{tab} > t_{exp}$; H_1 ; there is significant difference in mean values if $t_{tab} < t_{exp}$.

The null hypothesis on equivalence between mean values of results achieved by two compared methods – cupellation method and XRF – has been confirmed.

In one of three measurement series there was $t_{tab} < t_{exp}$ (by comparison of the third and the first measurement batch values), which can be attributed to the random error effect.

By comparing t-values (t_{ex}) for all three samples with critical value (t_{tab}), obtained from table data for the Student's t distribution for n_1+n_2-2 degrees of freedom and 95 % confidence level, we can conclude that XRF method results in adequate precision. The method has been confirmed only for the alloy type used in making 14-carat yellow gold. For all other types of alloy, the same or similar procedure should be repeated in order to confirm that the method does not cause systematic error in relation to the relevant reference method.

ILC Results Analysis

Statistic interpretation of data from inter-laboratory program was performed by the organizer laboratory (*Swiss Assay Office*) in accordance with ISO 5725-5:1998. The following statistic parameters were calculated: Mean value (\bar{X}) of results for each laboratory individually and all participating laboratories, standard deviation (s) of results for each laboratory individually and all participating laboratories, population mean (μ) of the mean value of all results of participating laboratories, standard deviation of reproducibility (σ_{Repro}) of all participating laboratories results (*note: only laboratories whose results were within the interval of $\mu \pm 10 \cdot \sigma_{Repro}$ were considered*). Z-values for each participating laboratory were calculated from obtained statistical data shown in Table 6, according to ISO Guide 43-1- Proficiency testing by inter-laboratory comparisons, excluding all results which were outside acceptable interval.

$$Z_{SCORE} = \frac{\bar{X}_{LAB} - \mu}{\delta_{REPRO}}$$

The mentioned parameters were determined for x-ray fluorescent analysis method and cupellation method separately. Results of statistical analysis of data collected via *Round Robin No 22 program* were presented in Table 6. All presented data indicate that calculated Z_{score} values are

less than 2, meaning that laboratory results for both methods applied are satisfactory.

This indirectly confirmed the validation procedure applied for 14-carat yellow gold alloys.

Table 6. Analysis of ILC results

Parameters		KUP	XRF
No. of participating laboratories	p	62	60
Set value (%) ± standard deviation of reproducibility	$\mu \pm \sigma_{\text{Repro}}$	588.02±0.27	587.93±2.80
Mean value of precious metals laboratory (%)	\bar{X}	587.93	587.38
Z value of precious metals laboratory	Z_{score}	-0.35	-0.23

CONCLUSIONS

Analysis of gold alloy for 14-carat jewellery was performed via two distinct analysis methods, destructive standardized cupellation method and non-destructive XRF method.

The null hypothesis with 95% confidence level on equivalence in measurement precision of percent by mass of gold in three very similar gold alloy samples in reproducibility conditions (three measurement series) has been confirmed, for standard cupellation method and the method compared (validated), XRF method.

F-test did not confirm the null hypothesis on precision equivalence for two mentioned analysis methods. There is significant difference in variance values. Although the null hypothesis on equivalence for two compared methods was not verified, t-test was taken, verifying the null hypothesis on equivalence between mean values of results achieved in two compared values.

Satisfactory results of both methods in terms of the mentioned analysis were confirmed by calculating the Z_{score} , the value that was significantly below two (2), for statistical data from inter-laboratory program with 62 participating laboratories, applying cupellation method and 60 laboratories applying XRF method of analysis of gold alloy used in production of 14-carat jewellery.

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Summary/Sažetak

Preko 80 % od cjelokupne količine dobivenog čistog zlata koristi se za proizvodnju raznih ukrasa, nakita i novca. Zlato je metal koji je previše mekan da bi se kao takav koristio za izradu nakita, zbog čega se legira sa drugim metalima. Od velike je važnosti tačno odrediti ukupnu količinu čistog zlata u legurama za izradu nakita i u nakitu jer to određuje njihovu vrijednost na tržištu.

Poznato je više analitičkih metoda kako destruktivnih tako i nedestruktivnih za kvantitativnu analize zlata. U ovom radu poređeni su rezultati analize legura zlata za 14-karatni nakit dobiveni nedestruktivnom metodom rendgenske fluorescentne analize i destruktivnom metodom kupelacije.

Potvrđena je nulta hipoteza uz 95 % nivoa povjerenja o jednakosti u preciznosti mjerenja masenog udjela zlata iz tri vrlo slična uzorka legure zlata u uslovima obnovljivosti (tri serije mjerenja), kako za standardnu metodu kupelacije, tako i za metodu koja se komparira (validira), metodi rendgenske fluorescentne analize.

F-testom nije potvrđena nulta hipoteza o jednakosti u preciznosti za dvije navedene metode analize. Postoji signifikantna razlika u vrijednostima varijansi. Iako nije potvrđena nulta hipoteza o jednakosti preciznosti za dvije metode koje se kompariraju, proveden je t-test kojim je potvrđena nulta hipoteza o jednakosti srednjih vrijednosti rezultata dobijenih po dvije komparirane metode.

Za potvrđivanje primjenjivosti dvije metode izračunata je vrijednost Z_{score} koja je bila znatno manja od dva (2), za statističke podatke iz interlaboratorijskog programa u kome su učestvovala 62 laboratorije sa primjenom metode kupelacije i 60 laboratorija primjenjujući XRF metodu analize legura zlata za izradu 14-karatnog nakita.