

# Matching standard procedure and method of theoretical coefficients in XRF spectrometry analysis of jewelry gold alloys

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MEMORIE

*Samples of jewelry gold alloys have been analyzed by XRF spectrometry. Two possible approaches were considered: (a) the matching standard procedure, a simple method based on the construction of empirical curves requiring a number of suitable calibrants very close in composition to the samples under analysis, and (b) the method of theoretical coefficients, a method of calibration with mathematical correction of matrix effects for analysis of 8-24 carat gold alloys containing Ag, Cu, Zn, Pd and/or Ni.*

*In this case, the analyses were performed basing on one set of 16 certified reference materials only. Theoretical coefficients were calculated by the method of fundamental parameters with Criss XRF11 and De Jong-ALPHAS programs. Self absorption effects related to gold and silver were corrected by using a coefficients, while enhancement effects were corrected by using  $\beta$  coefficients, both empirically calculated with the Raspberry-Heinrich model. The investigation was performed on different spectrometers equipped with various tubes; instrumental parameters influencing accuracy and precision were carefully evaluated. XRF spectrometry results were compared to cupellation (Au) and ICP spectrometry (other elements) results: the gold fineness is determined with an accuracy of 0.3‰ to 1.2‰, depending on the method, and hence very close to cupellation, while for other alloy constituents the analysis accuracy ranges between 1 and 2‰.*

## 1. INTRODUCTION

The high value of jewelry gold articles requires the choice of an accurate and possibly non-destructive analysis method, particularly focused on gold determination [1-5]. From the standpoint of the attainable quality, cupellation is still unrivalled, since it generally ensures an accuracy better than 1 wt. ‰ and reaches 0.2‰ in pure gold as well as in 750 ‰ ternary Au-Ag-Cu alloys [6]. Nevertheless, in some cases, this method is inconvenient for the following reasons:

1. the analysis is destructive and requires 2 samples of alloy (250mg each) + 1 reference sample;
2. the delicate analytical procedure can not be automated and requires an experienced analyst;
3. the operations of weighting, heating, solutioning, rolling, etc. are time-consuming; moreover, when the gold alloy contains elements such as nickel, palladium, platinum and platinum's group metals or silver over 40%, the procedure becomes particularly sluggish since requires important modifications (partition, inquartation, etc.) [1];
4. the entire composition of a gold alloy can not be certified by cupellation, since the non precious metals can be only determined as a concentration sum;
5. the analytical technique is lead-based and involves the use of strong acids at high temperature with production of toxic fume. Possible effects on the analyst health and environmental pollution must be then carefully avoided.

In spite of that, cupellation was recently standardized by the International Organization for Standardization [7] and it re-

presents, up to now, the unique internationally recognized referee analytical procedure for determining the fineness of gold in gold alloys.

In the last years, the performances of spectrometry techniques have increased so much to satisfy the large majority of the analytical needs of precious alloy producers, as well as custom or assay officers. As a consequence, an increasing number of precious alloy assayers are routinely and successfully using different spectrometry techniques.

The economical, easy-handly and time-saving Energy Dispersive X-Ray Spectrometry (EDXRF) is the best candidate for the replacement of the touchstone test for quick-sorting determination of the fineness of finished gold articles, since objects are non-destructively analyzed in few minutes without sample preparation [2,5,8]. On the other hand, Inductively Coupled Plasma (ICP) and wavelength dispersive X-Ray Fluorescence (XRF) spectrometry, provide methods for accurate and precise analysis of the entire composition of precious alloys, including impurities [2,8]. Both methods allow to determine the gold fineness in a gold alloy with accuracy and precision very close to cupellation, the choice of either ICP or XRF spectrometry mainly depends on the kind of samples to be analyzed. The ICP solution spectrometric method, with use of yttrium or indium as internal standard, assures a rapid analysis on very small samples; a very low quantity of alloy (10-20 mg) is to be dissolved, but sample weighting and solutioning will remain extremely delicate and time-consuming procedures [9-12]. On the contrary, XRF spectrometry supplies a rapid non-destructive technique for surface analysis of massive samples of suitable shape, size and surface finishing.

Though the limitation in the sample dimension makes XRF spectrometry as an unsuitable technique for assaying gold in the large majority of finished gold jewelry articles, it finds a number of important applications in the laboratories of the

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Standard	Au ‰	Ag ‰	Cu ‰	Pd ‰	Zn ‰	Ni ‰
Au-1	333.2 ± 0.4	665.9 ± 0.4	-	-	-	-
Au-2	333.5 ± 0.3	446.5 ± 0.5	219.8 ± 0.5	-	-	-
Au-3	370.7 ± 0.8	105.7 ± 0.4	201.0 ± 0.7	324.6 ± 0.9	-	-
Au-4	370.6 ± 0.6	200.0 ± 0.7	105.3 ± 0.5	-	-	324.3 ± 1.0
Au-5	371.4 ± 0.5	250.9 ± 0.8	238.3 ± 0.7	-	49.2 ± 0.5	89.6 ± 0.6
Au-6	499.9 ± 0.7	125.4 ± 0.5	125.3 ± 0.5	249.6 ± 0.4	-	-
Au-7	578.8 ± 0.4	276.8 ± 0.4	-	144.3 ± 0.6	-	-
Au-8	590.1 ± 0.7	76.4 ± 0.1	119.8 ± 0.5	-	67.4 ± 0.5	145.7 ± 0.7
Au-9	578.1 ± 0.9	-	153.1 ± 0.5	-	97.4 ± 0.6	169.7 ± 0.9
Au-10	748.3 ± 0.6	-	96.4 ± 0.5	-	26.0 ± 0.3	128.9 ± 0.4
Au-11	749.5 ± 0.6	-	-	100.0 ± 0.5	-	150.5 ± 0.5
Au-12	749.8 ± 0.4	-	-	-	-	249.4 ± 0.6
Au-13	916.7 ± 0.6	29.6 ± 0.4	52.9 ± 0.4	-	-	-
Au-14	960.0 ± 0.5	-	40.2 ± 0.3	-	-	-
Au-15	986.0 ± 0.5	-	14.0 ± 0.1	-	-	-
Au-16	999.9 ± 0.2	-	-	-	-	-

Table I - Chemical compositions of International Gold Alloy Standards

Tab. I - Composizioni chimiche degli Standard Internazionali di leghe d'oro per gioielleria

Alloy	Au ‰	Ag ‰	Cu ‰	Pd ‰	Zn ‰
T18A	740.1	129.8	129.6	-	-
T18B	748.3	125.9	125.8	-	-
T18C	749.2	126.2	125.2	-	-
T18D	750.2	124.9	124.8	-	-
T18E	751.3	124.4	124.3	-	-
T18F	752.4	124.0	124.0	-	-
T18G	760.4	120.0	120.3	-	-
T22A	915.1	32.5	51.7	-	-
T22B	915.8	32.0	51.5	-	-
T22C	917.2	31.9	50.6	-	-
T22D	918.1	31.9	51.0	-	-
T22E	919.2	30.7	50.5	-	-
B18A	745.0	31.9	98.0	125.0	-
B18B	749.0	30.0	96.0	124.9	-
B18C	749.9	29.7	95.0	125.0	-
B18D	751.2	29.7	94.1	124.5	-
B18E	755.1	28.0	91.9	124.1	-
Q18A	748.4	50.1	190.4	-	10.9
Q18B	750.2	49.9	189.4	-	10.3
Q18C	750.5	49.6	189.2	-	9.7
Q18D	751.3	49.7	189.9	-	9.0
Q18E	751.8	49.8	189.4	-	9.3
Q14A	581.1	40.3	316.2	-	62.3
Q14B	584.6	40.2	310.9	-	64.2
Q14C	585.2	39.8	309.8	-	65.1
Q14D	587.0	39.0	309.5	-	64.5
Q14E	587.6	39.4	307.8	-	64.3

Table II - Reference chemical compositions of PRO-Art certified gold alloys

Tab. II - Composizioni chimiche di riferimento delle leghe d'oro certificate PRO Art

precious alloys industry, in particular to monitor the work-in-progress composition during precious metal refining and to analyze samples from ingots, cast products, semi-finished articles or some specifically shaped object such as coins, medals, buttons and labels.

In the last decade, a simple method based on the construction of empirical curves, also known as matching standard procedure, has been rather frequently applied by precious alloys analysts utilizing their own calibrants, but there is very little information in the literature [2,13]. A new systematical approach to the analysis of gold alloys by XRF spectrometry was made possible by the recent availability of a set of Internationally Certified Gold Reference Materials produced in Poland [14] and a number of reference materials produced in Italy in the frame of the C.N.R. PRO Art Project [15].

A number of gold alloys were analyzed on different XRF spectrometers, equipped with various tubes, taking into consideration a mathematical approach based on the development of a calibration method for the correction of the matrix effects with use of theoretical coefficients. The analysis were carried out on the PRO Art certified gold alloys in combination to secondary standards produced by UNO AERRE,

Arezzo, Italy and VALCAMBI, Balerna, Switzerland. The results of analysis performed on different spectrometers by using different analytical methods will be compared and discussed in the following paragraphs.

## 2. MATERIALS

### 2.1. Jewelry gold alloys

For centuries, pure gold was commonly alloyed with other metals in order to improve the mechanical properties of its manufactured goods. The large majority of precious alloys used for jewelry fabrication are colored gold alloys based on the ternary Au-Ag-Cu system. The colors range from gold-yellow to silver-white to copper-red, depending on the ratio of silver to copper. Small additions of zinc can be made to de-oxidize, lighten the color, reduce hardness or lower the melting point of the alloy. In addition to such elements white gold alloys (developed as a substitute of expensive platinum alloys) contain nickel or palladium as decolorizers. The composition varies in order to satisfy the requirements of the jewelry producers and users. The proportion of precious

metals in gold alloys is expressed in parts per thousands in weight of alloy, although the ancient carat system for gold is still widely used. One carat represents 1/24 of the total metal, so that 18 Ct is equivalent to 750‰; 22 Ct to 917‰; 14 Ct to 585‰; 9 Ct to 375‰ (fineness levels recommended by ISO9202). Very rarely jewelry gold alloys contain elements out of the system Au-Ag-Cu-Pd-Zn-Ni.

**2.2. Internationally Certified Gold Reference Materials**

A set of 16 certified gold reference materials intended for use as analytical standards in XRF spectrometry, were recently produced by Polish State Mint (Warsaw) and Institute of Non-Ferrous Metals (Gliwice) [14]. This set of standards consists of 16 gold alloys (333.2-999.9 Au‰) alloyed with Ag, Cu, Zn, Pd and/or Ni, in order to cover the composition range of the conventional colored and white jewelry gold alloys. The composition of each alloy was certified by comprehensive analysis (cupellation, titration, gravimetric, potentiometric, electrolytic, flame atomic absorption and ICP spectrometry) carried out by eight internationally recognized laboratories in U.S.A., Canada and South Africa. The chemical compositions of the gold alloy standards are reported in Table I.

**2.3. PRO-Art Certified Reference Materials**

Five alloys frequently utilized for jewelry production were considered, with the following nominal compositions: 750Au-125Ag-125Cu; 917Au-32Ag-51Cu; 750Au-30Ag-95Cu-125Pd; 585Au-40Ag-10Cu-65Zn and 750Au-50Ag-190Cu-10Zn. For each material, 5 to 7 alloys of similar compositions were prepared as calibrants. In particular, 2 series of ternary Au-Ag-Cu alloys (18 and 22Ct), 1 series of quaternary 18Ct white gold alloys containing Pd and 2 series of quaternary gold alloys containing Zn (18 and 14Ct) were produced and certified by PAMP S.A. (Castel S.Pietro, Switzerland) [16]. The presence of metal impurities, evaluated by ICP spectrometry, were insignificant (Pb<0.05; Si<0.05; Ni<0.05; Sn<0.05; Fe<0.05 and Al<0.05 ppm) [16]. Moreover, at the end of the working procedure, the alloy homogeneity of the samples was controlled by scanning

electron microscopy [16]. The gold concentrations of the PRO Art certified gold alloys, were determined by cupellation in PAMP S.A. laboratories and then repeated in Laboratorio Metalli Preziosi-CCIAA (Vicenza, Italy) and SAGOR (Arezzo, Italy). The comparison of data shows excellent agreement, since in all cases the accuracy is better than 1‰ in weight [16]. The concentrations of Ag, Cu, Pd and Zn were determined by ICP spectrometry, with use of yttrium or indium as internal standard, at Perkin Elmer laboratory (Monza, Italy) on Optima 3000 DV spectrometer. The experiments are thoroughly detailed elsewhere [12]. The reference chemical compositions of the PRO-Art certified gold alloys are reported in Table II.

**2.4. Secondary standards of jewelry gold alloys**

A series of 13 gold alloys samples were produced by UNO AERRE (Arezzo, Italy) and a series of 5 gold alloy samples were produced by VALCAMBI (Balerna, Switzerland). Both series of samples were previously analyzed by the respective producers with extreme accuracy and precision by means of classical chemical methods [17]. Owing to the full compatibility with the standards described in Par. 2.1 and Par. 2.2., such materials were considered as secondary standards for the calibration of spectrometers.

**3. EXPERIMENTAL RESULTS AND DISCUSSION**

**3.1. Matching standard procedure**

Although the traditional cupellation represents today the unique referee analytical procedure for determining the fineness of gold to all form of gold-bearing material, the XRF spectrometry is being increasingly and successfully applied by a number of precious alloy assayers, since it provides a very fast non-destructive method for determining the chemical composition of massive, plane and well polished samples [2,13,16,17]. In these cases, the composition of a gold alloy is generally determined by utilizing empirical curves, designed on the base of an appropriate set of secondary standards, without any matrix corrections. This simple analytical

Table III - Cupellation and XRF spectrometry (matching standard procedure) Au analysis results

Tab. III - Concentrazioni di Au nelle leghe d'oro certificate PRO Art, ottenute per coppellazione e spettrometria XRF (metodo empirico)

Alloy	% (Cupellation)			Au ‰ (XRF Spectrometry)		
	PAMP S.A.	CCIAA	SAGOR	SIEMENS	SGS Alfalab	VALCAMBI
T18A	740.2	740.1	740.1	740.2	740.0	741.0
T18B	748.4	748.2	748.2	747.9	748.2	748.7
T18C	749.3	749.2	749.2	749.2	749.2	749.9
T18D	750.2	750.2	750.2	750.3	749.8	750.4
T18E	751.2	751.2	751.2	751.2	751.0	751.9
T18F	752.3	752.4	752.5	752.7	752.0	752.8
T18G	760.4	760.3	760.5	760.3	760.2	760.2
T22A	914.8	915.2	915.3	915.0	915.3	-
T22B	915.8	915.7	915.9	915.7	916.6	-
T22C	917.2	917.2	917.2	917.7	916.4	-
T22D	918.1	918.2	918.0	917.5	918.0	-
T22E	919.2	919.2	919.1	919.3	919.0	-
B18A	745.0	745.5	745.6	745.0	-	-
B18B	749.0	749.3	749.3	749.2	-	-
B18C	749.9	750.3	750.5	749.6	-	-
B18D	751.2	751.4	751.5	750.3	-	-
B18E	755.1	755.6	755.5	755.0	-	-
Q18A	748.5	748.4	748.2	748.6	748.6	748.5
Q18B	750.3	749.9	749.3	750.2	750.2	751.5
Q18C	750.5	750.4	750.4	751.1	750.1	751.3
Q18D	751.4	751.4	751.1	750.4	751.2	750.8
Q18E	751.9	751.9	752.2	751.7	751.7	751.4
Q14A	581.1	581.0	580.7	579.7	-	-
Q14B	584.6	584.5	584.5	584.3	-	-
Q14C	585.3	585.4	585.2	585.9	-	-
Q14D	587.0	586.6	586.6	587.2	-	-
Q14E	587.6	587.4	586.9	587.0	-	-

method, also known as matching standard procedure, enables the gold alloy analysts to meet a wide range of needs for the production control and to satisfy the precision and accuracy requirements. On the other hand, this procedure requires the preparation and the storage of an adequate number of secondary standards for each type of alloy under analysis, the quality of results being obviously proportional to the number of the available standards.

In order to quantify the best achievable analytical quality, the PRO Art certified alloys were firstly analyzed by XRF spectrometry by designing an empirical curve for each element in each series of alloys. The analysis were repeated in three different laboratories: SIEMENS (Karlsruhe, Germany), SGS Alfalab (Assemini, Italy) and VALCAMBI (Balerna, Switzerland), by means of different instruments: SIEMENS 3000, RIGAKU 3000 and PHILIPS PW2400 XRF spectrometers, respectively.

The results of gold analysis obtained by cupellation and XRF spectrometry with use of empirical curves are reported in Table III. The comparison of data shows excellent agreement, since the differences are of the same order of magnitude and always below 1%. The results of the full analysis are reported in Table IV and also show very good agreement.

**3.2. Method of theoretical coefficients for matrix effects correction**

It is well known that the correlation between the intensities of spectral lines and the concentrations of the elements in a sample under XRF analysis is rarely linear. Matrix effects, both absorption and enhancement effects, result in a non-linear relation of the measured intensities with the concentrations of the elements. This especially occurs when the sample contains neighboring elements or elements with widely different atomic numbers, as in the case of jewelry gold alloys containing silver, palladium, zinc, copper and/or nickel. It has been thus considered that the large majority of jewelry gold alloys are susceptible to be analyzed by developing a suitable mathematical method for the correction of the matrix effects in the 6-element system Au-Ag-Cu-Pd-Zn-Ni with use of theoretical coefficients. Mathematics details are thoroughly described elsewhere [20,21].

In general, the correction coefficients are empirically determined by the least square method basing on common analytical curves for each alloy constituent. In this case, they are strongly dependent on the analyte and matrix concentration ranges. Moreover, the empirically derived coefficients not only describe the matrix effects but also conceal other effects such as poor chemical data, poor sample preparation, measurement errors, etc. These effects have the tendency to fluctuate from day to day and from operator to operator; as a consequence the use of such calibration lines might result in sensible fluctuations of the analysis results. Finally, when the sample under analysis does not belong to the set of calibrants utilized, the use of such calibration lines might produce large errors. The statistical method thus requires a series of reference materials containing all information necessary for the determination of coefficients. Owing to the matrix effects, the complex alloys require to calculate several coefficients; in particular, the number of calibration standards, N, is  $N=2n+1$ , where n is the number of coefficients. From the other hand, the correction coefficients may be determined one at a time with the aid of binary and ternary standards.

The correction coefficients can be calculated by using the fundamental parameter method, based on an equation describing the physical relationship involving primary wavelength distribution, absorption coefficients, fluorescent yields and spectrometer geometry. This method can be used in two variants: (a) as a standardless method or (b) as a method for calculation of the theoretical matrix effect correction coefficients, which are then considered as the constants in the empirical type equations, such as the Rasberry and Heinrich equation [22].

The  $\alpha$  and  $\beta$  coefficients, calculated by W.Stankiewicz et al. [20], are more resistant for eventual change of the concentration ranges of analyte and matrix elements.

One set of internationally certified reference materials (Table I) was demonstrated to be enough to develop a good calibration method for the mathematical correction of matrix effects for the PRO Art certified reference materials (Table II). The chemical compositions of those experimental alloys, were determined by measurements conducted on a Philips

Alloy	Au ‰	Ag ‰	Cu ‰	Zn ‰	Ni ‰	Pd ‰
T18A	740.2	129.9	129.6			
T18B	747.9	125.8	125.8			
T18C	749.2	125.5	125.6			
T18D	750.3	124.9	124.8			
T18E	751.2	124.4	124.4			
T18F	752.7	124.0	124.1			
T18G	760.3	120.0	120.3			
T22A	915.0	32.4	51.6			
T22B	915.7	32.0	51.7			
T22C	917.7	32.0	50.6			
T22D	917.5	32.0	51.1			
T22E	919.3	31.6	50.5			
B18A	745.0	31.9	97.8	125.0		
B18B	749.2	30.0	96.2	124.9		
B18C	749.6	30.0	95.0	125.2		
B18D	750.3	30.0	94.1	124.5		
B18E	755.0	28.0	91.9	123.7		
Q18A	748.6	50.4	190.3		10.7	
Q18B	750.2	50.3	190.0		10.2	
Q18C	751.1	50.1	189.7		9.5	
Q18D	750.4	50.2	190.0		9.1	
Q18E	751.7	50.5	189.9		9.2	
Q14A	579.7	39.9	315.5		60.3	
Q14B	584.3	39.3	311.0		63.0	
Q14C	585.9	39.5	309.3		63.6	
Q14D	587.2	38.9	308.9		63.2	
Q14E	587.0	39.3	307.6		63.0	

Table IV- XRF spectrometry-matching standard procedure analysis results (SIEMENS 3000)

Tab. IV - Composizioni chimiche delle leghe d'oro certificate PRO Art ottenuti con spettrometro XRF SIEMENS 3000 (metodo empirico)

Alloy	Au ‰		Ag ‰		Cu ‰		Pd ‰		Zn ‰	
	without	with	without	with	without	with	without	with	without	with
T18A	745.9	740.4	111.0	130.1	122.7	129.7				
T18B	752.7	747.1	106.0	125.6	118.9	125.9				
T18C	752.5	748.8	106.1	125.2	118.5	125.2				
T18D	756.1	750.5	105.9	124.9	117.6	124.5				
T18E	756.9	751.3	105.3	124.3	117.1	124.0				
T18F	757.6	752.1	104.5	123.5	116.8	123.8				
T18G	766.3	760.8	100.9	119.7	113.0	119.8				
T22A	921.5	915.3	25.5	32.9	46.3	52.2				
T22B	924.2	916.6	25.0	32.2	47.0	51.5				
T22C	925.5	917.3	24.7	31.9	46.5	50.6				
T22D	922.1	* 915.5	24.7	31.9	47.4	51.0				
T22E	926.4	920.5	23.8	30.8	46.3	50.5				
B18A	770.0	745.1	28.1	32.4	92.1	98.2	106.6	124.6		
B18B	774.9	749.8	26.3	30.3	90.7	96.7	106.5	124.8		
B18C	776.2	750.1	26.4	30.5	89.5	95.5	106.5	125.0		
B18D	777.3	751.7	26.4	30.5	88.6	94.6	106.1	124.6		
B18E	781.5	755.6	24.6	28.4	86.7	92.6	105.4	124.1		
Q18A	717.0	748.4	42.9	49.8	186.7	190.3			11.0	10.5
Q18B	719.7	751.1	43.1	50.1	185.9	189.5			10.2	9.7
Q18C	719.4	750.6	42.7	49.9	184.6	189.6			9.5	9.1
Q18D	721.2	751.9	42.9	49.6	185.8	188.2			9.9	9.5
Q18E	720.6	751.8	42.7	49.8	185.8	189.6			9.2	8.8
Q14A	525.0	580.6	39.4	40.3	335.4	315.6			67.1	60.2
Q14B	528.3	584.4	38.3	39.3	329.9	310.8			69.6	62.6
Q14C	509.0	584.9	38.7	39.8	328.4	309.6			70.0	62.9
Q14D	530.0	586.3	37.4	38.5	328.7	308.9			69.8	62.8
Q14E	530.6	586.2	38.3	39.4	326.4	307.9			69.5	62.5

\* The less accurate result is attributed to the effect of a not perfectly flat surface of this sample

Table V - Chemical compositions of PRO Art certified materials by XRF-spectrometry, without/with mathematical correction of matrix effects (PHILIPS PW1480).

Tab. V - Composizioni chimiche delle leghe d'oro certificate PRO Art ottenuti con spettrometro XRF Philips PW1480 senza/con correzione degli effetti matrice.

PW 1480 spectrometer equipped with a 3.0 kW rhodium tube at the Institute of Non-Ferrous Metals (Gliwice, Poland). The experimental details are thoroughly described elsewhere [21]. The analysis results, with and without mathematical correction of the matrix effects, are reported in Table V.

It can be observed that the accuracy of gold analysis in the full composition range of the PRO Art alloys (580-920‰ Au) is ±1.2‰ and hence somewhat lower than the accuracy of the analysis performed by cupellation or XRF spectrometry by using different empirical curves for each specific compositions. The accuracy of the analysis of other alloy constituents is fully comparable with the accuracy of the more commonly applied chemical methods, i.e.: ±0.5‰ Ag, ±1.3‰ Pd, ±0.6‰ Cu, ±0.8‰ Zn and ±0.6‰ Ni.

### 3.3 Theoretical influence coefficient method

Second important aim of this work was the evaluation of the effectiveness of the theoretical coefficients for correction of matrix effects in XRF analysis of a number of industrial gold alloy samples.

In 1966 Lachance and Traill [23] have proposed the following definition of the absorption influence coefficient for monochromatic incident source of wavelength  $\lambda_k$ :

$$\alpha_{ij}(\lambda_k) = \frac{\mu_j(\lambda_k)\sin\Psi + \mu_j(\lambda_i)\sin\Phi}{\mu_i(\lambda_k)\sin\Psi + \mu_i(\lambda_i)\sin\Phi} - 1$$

Where  $\mu$  denotes the mass absorption coefficients of the i- and j-elements, measured for primary or secondary photons of wavelength  $\lambda_k$  and  $\lambda_i$ , respectively, corrected for the angle of incidence  $\Psi$  or the take off angle  $\Phi$ .

The  $\alpha_{ij}$  coefficients correct for the absorption effect of the j-element of the matrix on the i-analyte, when the incident X-ray source is monochromatic. Monochromatic excitation

considerably simplifies the quantitative treatment of spectral data, but this case is only randomly met in wavelength dispersive XRF. The commonly used excitation source is the X-ray tube, which delivers a spectrum of characteristic lines superimposed on a white spectrum. In 1984, Rousseau [24] has generalized this definition for a polychromatic incidence source:

$$\alpha_{ij} = \frac{\sum_k W_i(\lambda_k)\alpha_{ij}\lambda_k}{\sum_k W_i(\lambda_k)}$$

Where:

$$W_i(\lambda_k) = \frac{\mu_i(\lambda_k)}{\mu_i(\lambda_k)\sin\Psi + \mu_i(\lambda_i)\sin\Phi} \times \frac{I_0(\lambda_k)\Delta\lambda_k}{1 + \sum_j C_j\alpha_{ij}(\lambda_k)}$$

Where:

$I_0(\lambda_k)$  is the intensity of excitation source for a given  $\lambda_k$ ;

$C_j$  is the concentration of the j-element;

$W_i(\lambda_k)$  is the weighting factor of each wavelength  $\lambda_k$  of the incident polychromatic X-ray spectrum;

The  $\alpha_{ij}$  coefficient is the weighted mean of all absorption effects caused by the j-element of the matrix on the i-analyte in a given sample, when it is hit by a polychromatic incident spectrum.

The coefficient  $\alpha_{ij}\lambda_k$  is a binary coefficient depending on i- and j-element only, while the coefficient  $\alpha_{ij}$  is a multi-element coefficient depending on the matrix composition, including the j-element.

If there is no enhancement, the concentration of the analyte  $C_i$  is calculated by the following algorithm:

$$C_i = R_i \left( 1 + \sum_j \alpha_{ij} C_j \right)$$

where  $R_i$  is the relative X-ray intensity of the  $i$ -element. This algorithm has the same form of the Lachance-Traill algorithm.

If both matrix effects, absorption and enhancement, are present, the above algorithm becomes:

$$C_i = R_i \frac{1 + \sum_j \alpha_{ij} C_j}{1 + \sum_j \epsilon_{ij} C_j}$$

Which is the fundamental algorithm [25] (exactly the same as the original fundamental equation proposed in 1955 by Sherman [26], where  $\epsilon_{ij}$  is the weighted mean of all the enhancement effects caused by the  $j$ -element of the matrix on the  $i$ -analyte, when it is hit by a polychromatic incident spectrum.

The values of  $\alpha_{ij}$  and  $\epsilon_{ij}$  coefficients are unique and fundamental for a given set of experimental conditions and for a given sample.

The theoretically determined influence coefficients allow the error sources (chemical composition, measurement and quality of sample surface) to be detected, isolated and estimated, thereby giving greater confidence in reliability and applicability of the calibration data. The use of theoretical  $\alpha_{ij}$  coefficients reduces the number of required calibration standards. The  $\alpha_{ij}$  coefficients can be calculated by using the XRF-11 Criss [27] software and ALPHAS elaborated by de Jongh [28]. Both software programs are commercially available.

### 3.4. Analysis of different jewelry gold alloys

In addition to the benefits of the theoretical coefficient method previously enumerated, it must be considered that from many points of view the gold alloys are ideal samples for XRF analysis of all elements (except the impurities at few ppm levels). Moreover, the sample preparation is easy and relatively rapid, since a surface polishing on fine diamond abrasive and then cleaning in ethanol (or acetone) is sufficient. Different dimensions of samples and standards are simply accommodated by a suitable mask on the specimen holder, so that areas under irradiation become identical. It was then decided to validate the method, by analyzing other alloys on other instruments.

The UNOERRE secondary standards were analyzed at UNOERRE laboratories on a Philips PW1404 spectrometer equipped with Cr-tube, while the VALCAMBI secondary

standards were analyzed at VALCAMBI laboratories on a Philips PW2400 spectrometer equipped with Rh-tube. Both instruments were supplied with appropriate PC software for analysis driving, data processing and storage of measurement conditions and results; the software-reprocessing feature was an essential requisite for the analytical method development. The instrumental analytical conditions are summarized in Table VI.

In both cases, the spectrometers were calibrated by using the same set of internationally certified gold reference materials. Matrix effects were compensated by means of the  $\alpha$  coefficients, theoretically calculated by using the XRF11 Criss software for Philips PW1404 and ALPHAS-on line for Philips PW2400. These coefficients were introduced as the constants to the Rasberry-Heinrich equation.

In some case enhancement effects as well as self-absorption effects have been considered. They were corrected by empirical coefficients calculated by using the least square method.

The results of XRF spectrometry analysis performed at UNOERRE and VALCAMBI laboratories are compared to the respective reference values in Table VII and Table VIII. The data show very good agreement with cupellation and ICP results and, in particular, it can be observed that:

1. in gold determination the average difference is 0.65%, differences exceed 1% (1 to 1.4%) in five samples only, while a larger difference (2.2%) was measured in a sample with high Ni concentration. The best accuracy was obtained by applying the same theoretical and empirical  $\alpha$  and  $\beta$  coefficients, by using either XRF11 or ALPHAS software.
2. the average difference for silver determination is 0.95%. With XRF11 software, all theoretical  $\alpha$  coefficients plus empirical  $\alpha_{Ag}$  coefficient were applied for compensation of self-absorption effects; on the contrary, with ALPHA software, comparable accuracy was obtained without the application of theoretical  $\alpha_{Zn}$  and empirical  $\alpha_{Ag}$  coefficients.
3. the average difference for copper determination is 1.01%. With XRF11 software, empirical  $\alpha_{Cu}$  coefficients were applied for compensation of the self-absorption effects. It is very interesting to note that the concentrations of copper in six samples (ranging from 251 to 541 %) has been accurately determined though in the standards the copper concentration is lower (0 to 238 %). In other words, the

XRF Spectrometer	Emission Line	Crystal	KV/mA	Collimator	Detector	Lower level	Upper level	Measuring time
PHILIPS PW1404	AgK $\alpha$	LiF 200	60/40	Fine	FS	26	80	40
	AuL $\alpha$	LiF 200	60/40	Fine	FS	18	85	60
	CuK $\alpha$	LiF 200	40/20	Fine	SC	21	75	20
	NiK $\alpha$	LiF 200	60/40	Fine	FL	20	70	20
	PdK $\alpha$	LiF 200	60/40	Fine	SC	25	75	40
	ZnK $\alpha$	LiF 220	60/40	Fine	FS	20	70	20
PHILIPS PW2400	AgK $\alpha$	LiF 200	60/40	0.15*	SC	25	75	20
	AuL $\alpha$	LiF 200	60/40	0.15	SC	25	75	100
	CuK $\alpha$	LiF 200	60/20	0.15	DU	35	65	20
	NiK $\alpha$	LiF 200	60/40	0.15	DU	35	65	20
	PdK $\alpha$	LiF 200	60/40	0.15	SC	25	75	20
	ZnK $\alpha$	LiF 220	60/40	0.15	SC	25	75	20

Table VI - Experimental conditions for different spectrometers

Tab. VI - Condizioni di lavoro dei differenti spettrometri XRF

\*plus Cu 0.3 mm filter

FS = Flow proportional + Scintillation detector

SC = Scintillation detector

FL = Flow proportional

DU = Flow proportional + Sealed detector

Sample	Au ‰		Ag ‰		Cu ‰		Zn ‰		Ni ‰		Pd ‰	
	Ref.	XRF	Ref.	XRF	Ref.	XRF	Ref.	XRF	Ref.	XRF	Ref.	XRF
3 cr	374.8	373.4	64.5	62.1	479.5	482.3	80.5	79.9	0.0	0.1	0.0	0.1
7 cr	375.2	375.1	40.0	40.4	540.7	541.3	29.7	29.9	14.0	13.6	0.0	0.1
2 cr	376.0	376.5	135.0	137.2	420.0	418.2	70.0	71.2	0.0	-	0.0	-
8 br	585.8	586.6	25.7	24.6	340.0	337.0	14.0	13.6	35.0	33.7	0.0	0.1
5 br	585.9	585.6	62.5	62.5	309.0	309.0	43.0	42.7	0.0	0.1	0.0	0.2
2 br	586.0	586.2	314.5	313.9	100.0	100.0	0.0	0.1	0.0	-	0.0	-
3 br	586.3	585.8	135.2	135.4	251.5	251.5	26.5	23.8	0.0	-	0.0	0.2
14 br	588.8	587.6	219.0	217.0	45.5	45.8	0.0	0.2	70.0	72.0	80.8	79.4
12 ar	750.0	752.2	0.0	2.6	130.5	128.9	34.0	33.1	85.0	83.2	0.0	0.1
5 ar	750.2	750.5	140.1	139.0	110.0	110.2	0.0	-	0.0	0.1	0.0	-
14 ar	750.3	749.9	122.8	122.6	13.7	15.5	0.0	0.1	33.0	32.3	80.0	79.8
1 ar	750.7	751.9	79.1	80.4	164.5	163.1	5.1	4.8	0.0	-	0.0	0.1
4 ar	751.1	750.7	134.3	133.8	112.5	113.2	0.0	0.1	0.0	0.1	0.0	0.1

for AuL $\alpha$ : theoretical  $\alpha$  coefficients for Ag, Pd, Cu, Zn, Ni;  
 empirical  $\alpha$  coefficients for Au;  
 empirical  $\beta$  coefficients for Ag and Pd.  
 for AgL $\alpha$ : theoretical  $\alpha$  coefficients for Au, Pd, Cu, Zn, Ni;  
 empirical  $\alpha$  coefficients for Ag.  
 for CuL $\alpha$ : theoretical  $\alpha$  coefficients for Au, Ag, Pd, Zn, Ni;  
 empirical  $\alpha$  coefficients for Cu.  
 for PdK $\alpha$ : theoretical  $\alpha$  coefficients for Au, Ag, Cu, Zn, Ni.

Table VII - Chemical compositions of UNOAERRE gold alloy standards

Tab. VII - Composizioni chimiche degli standard secondari UNOAERRE per leghe d'oro

Sample	Au ‰		Ag ‰		Cu ‰		Zn ‰		Ni ‰		Pd ‰	
N.1	730.0	731.0	220.0	219.1	40.0	40.2	10.0	10.1	0.0	-	0.0	0.1
N.2	740.0	740.0	180.0	179.0	80.0	80.4	0.0	-	0.0	0.1	0.0	-
N.3	750.0	749.9	125.0	124.3	125.0	125.4	0.0	-	0.0	0.1	0.0	0.2
N.4	760.0	759.6	78.0	77.6	160.0	160.5	2.0	2.1	0.0	-	0.0	-
N.5	770.0	769.9	25.0	24.7	200.0	199.7	5.0	5.1	0.0	-	0.0	0.1

for AuL $\alpha$ : theoretical  $\alpha$  coefficients for Ag, Pd, Cu, Zn, Ni;  
 empirical  $\alpha$  coefficients for Au;  
 empirical  $\beta$  coefficients for Ag and Pd.  
 for AgK $\alpha$ : theoretical  $\alpha$  coefficients for Au, Pd, Cu, Ni;  
 for CuL $\alpha$ : theoretical  $\alpha$  coefficients for Au, Ag, Pd, Zn, Ni;  
 for ZnK $\alpha$ : theoretical  $\alpha$  coefficients for Au, Ag, Pd, Cu, Ni.  
 for NiK $\alpha$ : theoretical  $\alpha$  coefficients for Au, Ag, Pd, Cu, Zn;  
 empirical  $\alpha$  coefficients for Ni.  
 for PdK $\alpha$ : theoretical  $\alpha$  coefficients for Au, Ag, Cu, Zn, Ni;  
 empirical-line overlapping coefficients for AgK $\alpha$ .

Table VIII - Chemical compositions of VALCAMBI gold alloy standards

Tab. VIII - Composizioni chimiche degli standard secondari VALCAMBI per leghe d'oro

same theoretical coefficients calculated for an average sample composition with ~150‰ Cu concentration can be used for average sample composition with ~420‰ Cu concentration. As a consequence, it can be concluded that the theoretical  $\alpha$  coefficients are resistant for enlarging the matrix element concentration. Data were reprocessed and theoretical calculations were repeated on Philips PW2400 spectrometer at the Polish Geological Institute (Warsaw) and on Philips PW1480 spectrometer at the Institute of Non-Ferrous Metals. It was observed that the values extrapolated for samples containing more copper than the maximum copper concentration of standards are in good agreement with the true analytical results. It was then concluded that, if the same excitation parameters, analytical lines and spectrometer geometry conditions are fulfilled, the theoretical  $\alpha$  coefficients are constant and independent of the element concentration in the matrix.

4. the average difference for zinc determination is 0.37‰. The same theoretical  $\alpha$  coefficients were used with either XRF11 or ALPHAS software.
5. The differences for nickel and palladium determination

are <1.8‰ and <0.6‰, respectively. It must be observed that the majority of samples analyzed do not contain those elements in the matrix, whereas the standards may contain up to ~325‰ of both elements. In particular, only five UNOAERRE samples contain nickel and two UNOAERRE samples contain palladium in appreciable amounts, while all VALCAMBI samples are Ni- and Pd-free. But, owing to the application of the mathematical method for the correction of matrix effects, often the results of analysis slightly differs from zero (errors of the order of 0.1-0.2‰). With ALPHAS software, better results are obtained by applying empirical coefficients in order to eliminate partial overlapping of PdK $\alpha$  and AgK $\alpha$  lines.

#### 4. CONCLUSIONS

XRF spectrometry analysis was performed on the PRO Art certified gold alloys and other reference materials produced for private use (a) by running simple matching standard procedure or (b) by applying a mathematical method of theoret-

tical coefficients, developed for the matrix effects correction in the Au-Ag-Cu-Pd-Zn-Ni system, and by utilizing a unique appropriate set of international standards.

In the first case the experimental results demonstrated that the attainable analytical quality is very high; in particular, the accuracy of gold analysis (0.3‰) is absolutely comparable to cupellation (0.2‰ to 1‰, depending on the alloy composition). Nevertheless, some difficulties might derive from the need of production and storage of a considerable number of precious standards. In the second case, it has been demonstrated that one series of 16 primary standards was enough to develop a valid calibration method for the correction of matrix effects, with a significant economical benefit. It can be thus concluded that, apart from the unavoidable restrictions in sample shape and size, XRF spectrometry provides an excellent alternative to cupellation in order either to determine the entire composition of a jewelry gold alloy either to verify the gold fineness with only a minor loss of accuracy (1.2‰) with respect to cupellation or the matching standard procedure.

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**A B S T R A C T**

**METODO DI CALIBRAZIONE EMPIRICO  
E METODO DEI COEFFICIENTI TEORICI  
NELL'ANALISI SPETTROMETRICA XRF  
DELLE LEGHE D'ORO PER GIOIELLERIA**

L'analisi delle leghe d'oro per gioielleria ha due scopi:  
(a) determinare con la massima precisione e accuratezza il titolo in oro e (b) determinare l'intera composizione della

lega. Le esigenze però cambiano notevolmente quando si devono analizzare i materiali di partenza, le leghe durante il processo di preparazione, i semilavorati o i prodotti finiti e secondo la qualità analitica desiderata. Si richiede quindi non solo un uso accorto dei metodi classici, come la coppellazione e il metodo della tocca, ma si può prevedere anche l'introduzione di moderni metodi spettrometrici come la spettrometria di emissione al plasma (ICP) e la spettrome-

tria di fluorescenza a raggi X a dispersione in lunghezza d'onda (XRF) o in a dispersione in energia (EDXRF).

La coppellazione, secondo la norma standard ISO11426, è l'unica procedura analitica attualmente riconosciuta su scala internazionale, poiché consente di determinare il titolo in oro con un'accuratezza migliore dell'1‰ in peso. Tuttavia questo metodo analitico presenta notevoli svantaggi in quanto è distruttivo, estremamente lento, richiede molta esperienza da parte dell'analista, comporta l'uso di sostanze tossiche come Pb ed acidi, non consente di determinare la concentrazione dei metalli vili se non come somma di concentrazioni e quella di Ni, Ag, Pd, Pt e platinici solo mediante l'impiego di metodi aggiuntivi (scorificazione, inquartazione, ecc.) che prolungano ulteriormente la durata dell'analisi. Il rapido ma rudimentale metodo della tocca è ancora oggi molto usato, soprattutto per il suo basso costo, per l'identificazione non distruttiva degli oggetti finiti, ma la precisione ottenibile, che dipende esclusivamente dall'esperienza dell'analista, non supera i 20 %.

Anche se i dati in letteratura sono scarsi, è noto ormai che nei laboratori d'analisi per leghe preziose vengono utilizzate sempre più frequentemente alcune tecniche spettrometriche, se non in alternativa alla coppellazione, almeno come tecniche complementari per l'analisi degli elementi accessori.

La produzione di una serie di standard internazionali di leghe auree per gioielleria da parte dell'Istituto per i Metalli Non Ferrosi messi in commercio nel 1996 dalla Zecca di Stato Polacca e la produzione in Italia di un consistente numero di leghe a composizione certificata nell'ambito del Progetto PRO Art del CNR (1996-1999) ha reso possibile un approccio sistematico al problema.

Un adeguato numero di campioni di leghe d'oro a composizione certificata è stato analizzato mediante spettrometria ICP, XRF ed EDXRF, utilizzando vari strumenti e adottando diversi metodi analitici. I risultati ottenuti sono stati confrontati tra loro e le conclusioni tratte possono essere sintetizzate come segue:

Spettrometria ICP:

(a) consente la determinazione simultanea della concentrazione di tutti gli elementi in lega con una affidabilità analitica simile alla coppellazione, a patto che i campioni siano pesati e portati in soluzione con estrema cura e che si utilizzi un elemento, ittrio o indio, come standard interno; (b) l'analisi è molto meno distruttiva della coppellazione (è sufficiente il prelievo di 3 campioni da 10-20 mg contro 2 campioni da 250 mg) ed arreca un danno minimo all'oggetto prezioso, risultando così particolarmente indicata alla determinazione del titolo in oggetti finiti; (c) le operazioni di pesata e soluzione dei campioni sono estremamente delicate; (d) il costo della strumentazione è molto alto ma la spesa è giustificata da un numero di analisi elevato, perché l'analisi delle soluzioni è veloce ed automatizzata.

Spettrometria XRF a dispersione in lunghezza d'onda:

(a) consente l'analisi superficiale simultanea di tutti gli elementi in lega con un grado di precisione ed accuratezza simile alla coppellazione, a patto di disporre di campioni di forma opportuna e dei relativi standard di riferimento; (b) l'analisi è non distruttiva, veloce e totalmente automatizzata; (c) l'alto costo della strumentazione ed i limiti di utilizzo di questa tecnica, che consente solo l'analisi superficiale (qualche decina di micron) di campioni relativamente grandi ( $\varnothing$  10-30 mm), piani e ben lucidati, la rendono adatta a soddisfare le esigenze della industria orafa, sia per il controllo della composizione durante il processo di produzione delle leghe che per la certificazione della composizione di barre, lingotti, semilavorati, oggetti finiti di forma particolare.

Spettrometria XRF a dispersione in energia:

(a) consente di determinare il titolo in oro di una lega e di analizzarne simultaneamente gli elementi accessori escluse

le tracce; (c) la tecnica è non distruttiva, estremamente semplice, veloce e permette di analizzare campioni di ogni forma e superficie; (f) basso costo, facilità di impiego e buona affidabilità analitica fanno di questa tecnica un eccellente candidato alla sostituzione del metodo della tocca, ma non un'alternativa alla coppellazione.

In questo lavoro si è effettuata una scrupolosa valutazione della spettrometria XRF come tecnica analitica per le leghe auree per gioielleria. Sono stati messi a confronto due diversi metodi analitici: (a) un semplice metodo di calibrazione basato sulla costruzione di curve empiriche (matching standard procedure), che richiede l'uso di un adeguato numero di standard di calibrazione di composizione opportuna e (b) un metodo basato su coefficienti teorici per la correzione matematica degli effetti matrice, sviluppato per l'analisi di leghe auree 8-24 carati contenenti Ag, Cu, Pd, Zn e/o Ni come elementi complementari. In questo caso ci si è serviti di un unico set di 16 standard internazionali certificati per costruire la retta di calibrazione. I coefficienti teorici a sono stati calcolati in base al metodo dei parametri fondamentali utilizzando i programmi Criss XRF11 e De Jong-ALPHAS. Gli effetti di auto-assorbimento relativi ad Au e Ag sono stati quindi corretti mediante i coefficienti  $\alpha$ , mentre gli effetti di rafforzamento sono stati corretti mediante i coefficienti  $\beta$ , calcolati empiricamente secondo il modello di Raspberry-Heinrich. Le analisi sono state ripetute più volte con diversi spettrometri dotati di tubi a raggi X differenti, dopo una valutazione molto attenta dei parametri strumentali che condizionano l'accuratezza e la precisione dei risultati. Sono state analizzate sia le leghe certificate PRO Art che un certo numero di campioni di leghe di riferimento di produzione industriale.

Le leghe certificate PRO Art sono state analizzate sia con il metodo di calibrazione empirico che applicando il metodo matematico dei coefficienti teorici. Nel primo caso i risultati sperimentali hanno dimostrato che la qualità analitica raggiungibile è molto alta, in particolare l'accuratezza nella determinazione del contenuto di Au (0.3 ‰) è assolutamente confrontabile a quella della coppellazione (0.2-1.0 ‰, secondo la composizione della lega). Tuttavia bisogna considerare le difficoltà legate alla necessità di produzione e conservazione in deposito di un numero non indifferente di standard secondari di materiale prezioso. Nel secondo caso si è dimostrato che una e una sola serie di 16 standard primari è sufficiente a sviluppare un metodo di calibrazione valido per la correzione degli effetti matrice in un sistema di elementi e un range di composizioni che comprende la maggior parte delle leghe d'oro per gioielleria. L'accuratezza analitica ottenuta è di poco inferiore alla coppellazione (1.2 ‰), ma il beneficio economico non è trascurabile.

L'efficacia del metodo dei coefficienti teorici è stata verificata infine sugli standard secondari prodotti per uso privato dalle industrie orafe UNOAERRE e VALCAMBI, con risultati più che soddisfacenti, soprattutto considerando che la storia metallurgica dei campioni e la preparazione delle loro superfici non erano perfettamente identiche. Inoltre, in certe leghe le concentrazioni di alcuni elementi erano molto superiori i valori limite delle rette di calibrazione ottenute con gli standard internazionali.

I risultati raggiunti portano a concludere che, a parte le inevitabili restrizioni sulle dimensioni, la forma e il grado di finitura superficiale dei campioni, la spettrometria XRF offre una eccellente alternativa al metodo analitico tradizionale, perché non solo consente di verificare il titolo dell'oro con accuratezza molto simile alla coppellazione, ma consente anche di determinare l'intera composizione della lega. Il metodo dei coefficienti teorici, nonostante una leggera perdita in accuratezza, offre vantaggi non indifferenti rispetto al metodo empirico per quanto riguarda la rapidità e la semplicità dell'analisi.

MEMORIA

6/2000