

Development of an XRF spectrometry analytical method for gold determination in gold jewellery alloys

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Abstract

The chemical compositions of 27 ternary Au-Ag-Cu alloys and quaternary Au-Ag-Cu-Zn or Pd alloys were determined by XRF spectrometry by developing a mathematical method for the correction of the matrix effects for the analysis of Au, Ag, Cu, Zn, Pd and Ni. The analysis performance has been tested by measurements conducted on 16 certified gold reference materials and the results were compared to those obtained by cupellation, ICP spectrometry as well as XRF spectrometry by using empirical curves. The impact of the method on speed of analysis and quality of data produced is discussed in this paper. The experimental results indicated XRF spectrometry, with the use of the mathematical method described in this paper, as an advantageous alternative to the traditional cupellation method to be utilized in selected cases for determining the gold concentration in gold alloys with an accuracy of close to one part per thousand. The versatility of this technique is higher as compared to cupellation, since all alloying elements are determined simultaneously allowing to certify the entire alloy composition.

INTRODUCTION

The analysis of gold in gold jewellery alloys as been performed during the last thirty centuries by the cupellation or fire assay method. Despite its venerable age, this is still considered as the most accurate technique available, since it allows the determination of gold in Au 750‰, 18 ct gold alloys with an accuracy of better than 1‰ in weight and reproducibility of 0.2‰ (1,2). It must be considered that this method is destructive, since 250 mg of alloy are necessary for each analytical sample and that, although the equipment cost is low, the analysis is expensive, since an analyst with considerable experience is required. The procedure is time-consuming, since the determination of the gold concentration requires hours, even days when other precious metals are present in composition. Fire assay is also inadequate to certify the alloy composition since the alloying metals can only be determined as a concentration sum. Finally, cupellation is a lead-based technique involving the use of strong acids with high temperature and production of toxic fume, hence the installation of sophisticated engineering devices is required for protection of analysts and the environment.

Despite the numerous disadvantages mentioned above, the cupellation method was recently

standardized by the International Organization for Standardization and represents today the international referee analytical procedure for determining the fineness of gold to all form of gold-bearing material (3).

Nowadays, the increasing performances of modern spectrometers based on several decades of experience and the existence of sophisticate analytical software packages have lead to such a versatility of instruments and ease of operation, enabling the metallurgical industry to meet a much wider range of analytical needs for the production control. As a consequence, the spectrometry techniques have recently begun to play a crucial role in the analysis of fineness of precious alloys too. Among the different techniques available today, X-Ray Fluorescence (XRF) and Inductively Coupled Plasma (ICP) Spectrometry are the more promising alternative to the traditional cupellation method (4-6).

The wavelength-dispersive XRF spectrometry is a non-destructive analytical technique for the identification and measure of concentrations of the atoms of the same species present in an alloy. The sample excited by X-rays emits a short wavelength radiation (fluorescence) characteristic of each alloying element. A parallel beam of the secondary radiation is directed, by means of a

collimator, onto the analysing crystal, it is separated according to wavelengths and then reflected into a radiation detector mounted on a high precision goniometer. The angular position of crystal and goniometer is a function of the wavelength and allows the identification of the element in the matrix. The XRF analysis is computer-aided with a wide variety of programs and can be fully automated: there exists specimen holders for hundreds of samples, which can be placed in the X ray chamber and then irradiated under appropriate conditions with automatic display of results in few minutes via computer terminal.

This technique is being increasingly and successfully applied by several assayers of precious jewellery alloys, since it provides a very rapid non-destructive method for analysing a large number of massive samples and allows the determination of the fineness of gold in gold alloys with an analytical exactness of 2 to 5 parts per thousand that is sufficient for many purposes (7,8). E.g., the American National Gold and Silver Marking Act requires that gold or any of its alloys imported, exported or transported through interstate commerce, are measured and marked with fineness accurate to 0.3%, without solder, or 0.7%, with solder taken into account (Jewellers Vigilance Committee Inc., 1989).

In April 1997 the World Gold Council published "The Assaying and Refining of Gold - A guide for the Gold Jewellery Producer", indicating XRF as a possible analytical technique for the analysis of gold alloys in all cases of limitations of the fire assay technique, e.g. in alloys containing either nickel, or palladium, or platinum group metals (PGM'S) such as rhodium, iridium, ruthenium and osmium or over 40% silver as alloying elements.

The important limitations of the XRF spectrometry are to be taken into consideration, since this technique can only guarantee the surface analysis (during exposure X-rays only penetrate a few microns layer, depending on the alloy composition) of a relatively large (>10 mm diameter), perfectly flat and accurately polished sample. The restrictions on sample size and preparation make such a method for assaying gold unsuitable for a large amount of finished jewellery objects, but it has a number of other important applications, since it can be applied almost directly on samples from ingots, cast products, semi-finished articles and also finished objects in the shape of coins or medals. Furthermore, monitoring the work-in-progress composition during precious metal refining is possible by this technique.

XRF spectrometry appears particularly advantageous, as compared to the traditional fire assay, for the following reasons: (a) the method is non-destructive, and hence it would provide a correct assay without destroying expensive materials or irrevocably damaging precious objects; (b) all alloying elements are simultaneously determined, either non-precious metals, whose concentrations cannot be determined by cupellation, or precious metals, today analysed by a second cupellation through very complicate and time-consuming procedures handled by knowledgeable assayers; (c) the analysis procedure is fully computer-aided requiring incomparably shorter time with significant reduction of the analysis cost.

Other disadvantages of this method, with possible solutions, are also to be mentioned here: (a) the analysis is matrix-dependent and hence the method cannot be used

when the matrix is unknown, nevertheless, the XRF spectrometry allows a previous rapid semi-quantitative scan of the sample, giving the analyst a breakdown of the alloying elements present and their approximate concentrations; (b) all samples need the same size and surface preparation as the calibration standards, since they are essential requisites for the reproducibility of the results, but it must be considered that an infinite variety of secondary calibration standards can be prepared according to any particular requirement; and (c) if the homogeneity of the alloy is doubtful, sampling must include surface and transversal sections of the sample, since the analysis guarantees the composition of a thin surface layer only.

EXPERIMENTAL DETAILS

The fineness of gold in five series of experimental ternary and quaternary gold jewellery alloys with selected compositions was determined by XRF spectrometry. The measurements were conducted on certified gold reference materials and the results of gold analysis were compared to those obtained by cupellation. Other alloying elements, such as silver, copper, zinc and palladium were also simultaneously analysed and the results were compared to those obtained by ICP spectrometry with use of an internal standard as well as XRF spectrometry by using empirical curves and no mathematical corrections (9).

Gold reference materials

A series of certified gold reference materials, intended for use as analytical standards in XRF Spectrometry (both, energy- and wavelength-dispersive) as well as Neutron Activation Analysis, were recently produced jointly by the Polish State Mint (Warsaw) and the Polish Institute of Non-Ferrous Metals (Gliwice) (10-14). The range of standards comprises 16 gold alloys (333.2 - 999.9 Au wt.%) alloyed with silver, copper, palladium, zinc and/or nickel, covering the composition range of conventional coloured and white carat gold jewellery alloys, dental alloys, coinage and electronic materials.

Each certified reference material is in the form of thin gold alloy foil, 100-200 microns thick, mounted on a special aluminium holder. The thickness of gold alloy foils in each case is greater than the so-called "critical thickness" of the layer and hence is "infinite" for primary and secondary X-ray beams.

The certified values of the compositions of each alloy have been obtained by comprehensive analysis (cupellation, titration, gravimetric, potentiometric, electrolytic, flame atomic absorption and ICP spectrometry) in co-operation with 8 independent and internationally recognized analytical laboratories in South Africa, Canada and USA (11). The chemical compositions of standards are reported in Table 1.

Table 1. Chemical composition of certified gold reference materials (‰)

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±0.02	-	-	-	-	-

Materials and sample preparation

A series of 5 ternary 22 ct gold alloys named T22A-E, a series of 7 ternary 18 ct gold alloys named T18A-G, a series of 5 quaternary 18 ct white gold alloys containing Pd named B18A-E, a series of 5 quaternary 18 ct gold alloys containing Zn named Q18A-E and a series of 5 quaternary 14 ct gold alloys named Q14A-E were produced by PAMP S.A., Castel S. Pietro, Switzerland. The fineness of gold in each alloy was firstly determined by cupellation at PAMP S.A. laboratories. Cupellation analysis were then repeated at CCIAA-Istituto Metalli Preziosi, Vicenza, and at CCIAA- Laboratorio SAGOR, Arezzo (Italy), confirming the analytical results previously obtained (9). The concentrations of Ag, Cu, Pd and Zn were determined by ICP spectrometry, with use of an internal standard, at PERKIN ELMER laboratories, Monza (Italy) as well as by XRF spectrometry by using an empirical curve for each series of alloys and no matrix corrections (also known as *matching standards* procedure) at SGS Alfalab, Cagliari (Italy) and SIEMENS, Karlsruhe (Germany) laboratories. Details are described elsewhere (9). The chemical compositions of gold alloys, determined by different techniques and/or laboratories, are reported in Table 2.

Table 2. Chemical compositions of gold alloys (‰)

Alloy	Au (cupellation)	Ag (ICP, XRF)	Cu (ICP, XRF)	Pd (ICP, XRF)	Zn (ICP, XRF)
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		
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		
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

The quantity of metal impurities in the alloy composition was also evaluated by ICP spectrometry at PAMP S.A. laboratories and results are as follows:

Pb<0.05; Si<0.05; Ni<0.05; Sn<0.05;
Fe<0.05 and Al<0.05 ppm.

It must be pointed out that X-ray fluorescence is a surface or spot analysis, thus the sample surface being analyzed must be representative of the entire sample; in other words, the matrix must be homogeneous, since non-homogeneity would produce insufficient reproducibility of measurements. The homogeneity of the reference materials as well as the samples was then controlled by scanning electron microscopy techniques.

Finally, to avoid possible surface effects, the sample surface must also be perfectly flat, clean and free of impurities of surface coatings; the surfaces of both reference materials

Table 3. Analytical conditions

Element line	Angle 2θ, degrees	Tube power kV	mA	Detector	Counting time, seconds
Au (Lα)	37.010	50	40	F+S	30
Ag (Kα)	16.045	55	50	S	20
Pd (Kα)	16.780	60	50	S	20
Cu (Kα)	45.085	50	45	F+S	20
Zn (Kα)	60.670	60	50	F	20
Ni (Kα)	48.735	50	40	F	20

and samples (in the shape of 35cm diameter discs), were carefully polished on felt saturated with diamond compound.

flow proportional counter (F) and/or a scintillation counter (S). The experimental conditions are summarised in Table 3.

Equipment and analytical conditions

Measurements were carried out on a Philips PW 1480 automatic spectrometer, equipped with a 3.0 kW rhodium tube. The analyzing crystal was LiF200, with exception of the ZnKα for which LiF220 crystal has been applied, and the detector was a

Table 6. XRF analytical results without and with matrix effect corrections (‰)

Alloy	Au		Ag		Cu		Pd		Zn	
	<i>without</i>	<i>with</i>	<i>without</i>	<i>with</i>	<i>without</i>	<i>with</i>	<i>without</i>	<i>with</i>	<i>without</i>	<i>with</i>
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				
T18A	745.9	740.4	111.0	130.1	122.7	129.7				
T18B	752.7	747.1	106.6	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				
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 datum is attributed to the effect of a not perfectly flat sample surface.

RESULTS AND DISCUSSION

Calibration Method

See Appendix 1.

Analytical Results

The analytical results of XRF measurements, without and with the matrix effect corrections calculated as described in the Appendix, are reported in Table 6. The data with the matrix effect corrections reported in this table are in excellent agreement with analytical results reported in Table 2.

Figures 1 to 5 show the calibration lines for each alloying element of precious alloys with approx. 300-1000‰ Au, 0-700‰ Ag, 0-330‰ Cu, 0-330‰ Pd and 0-100‰ Zn concentrations. Each graph also contains the intensity of radiation with and without the matrix effect corrections described above as well as the values of slope (E), intercept (D) and root mean square (RMS) for the corrected values. It is very important that the presence of Ni in the composition of several standards used for calibration does not affect the analysis results of Ni-free gold alloys.

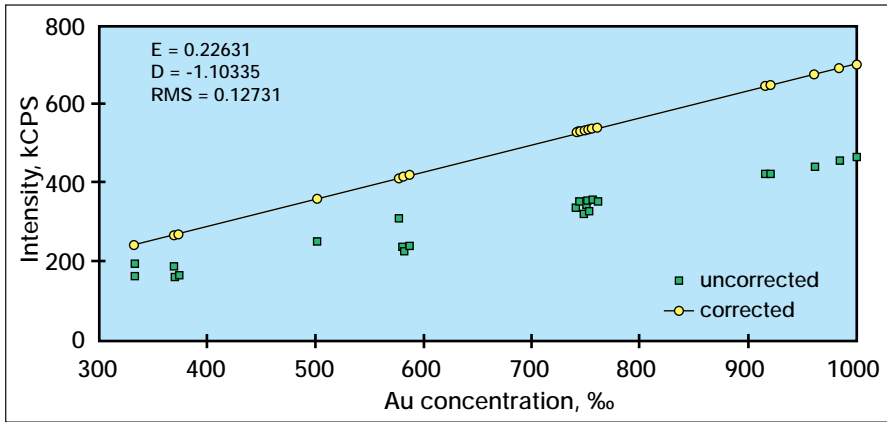


Figure 1 - Calibration line for XRF analysis of gold (approx. 300-1000‰ Au concentration).

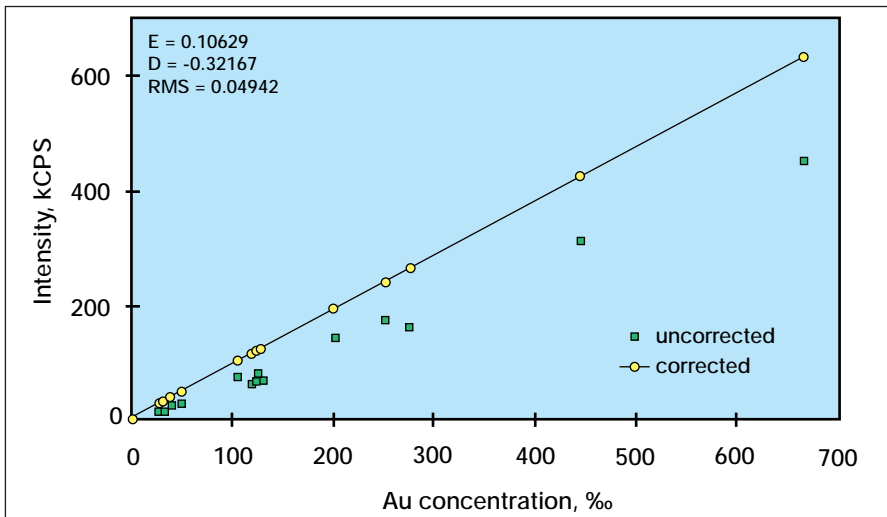


Figure 2 - Calibration line for XRF analysis of silver (approx. 0-700‰ Ag concentration).

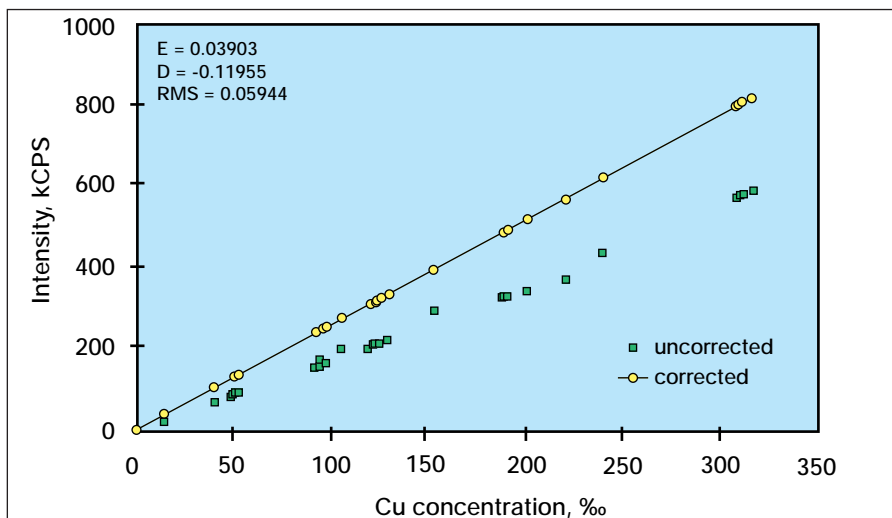


Figure 3 - Calibration line for XRF analysis of copper (approx. 0-330‰ Cu concentration).

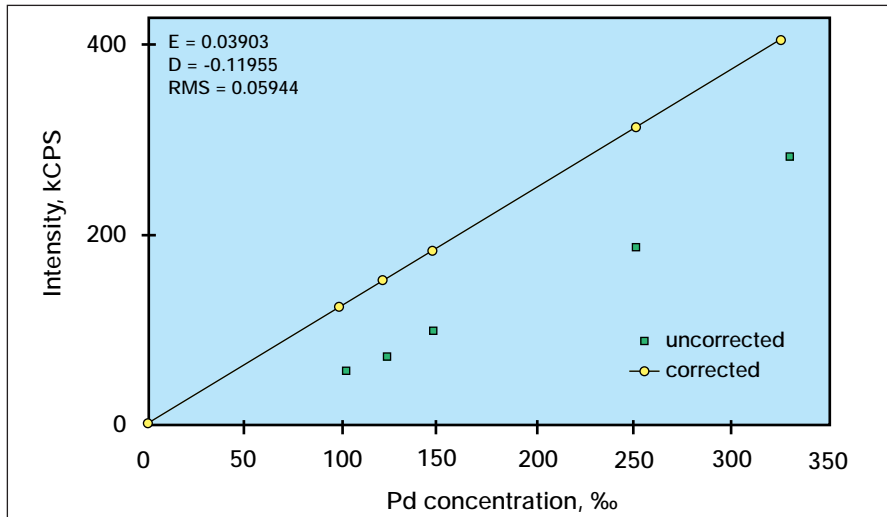


Figure 4 - Calibration line for XRF analysis of palladium (approx. 0-330‰ Pd concentration).

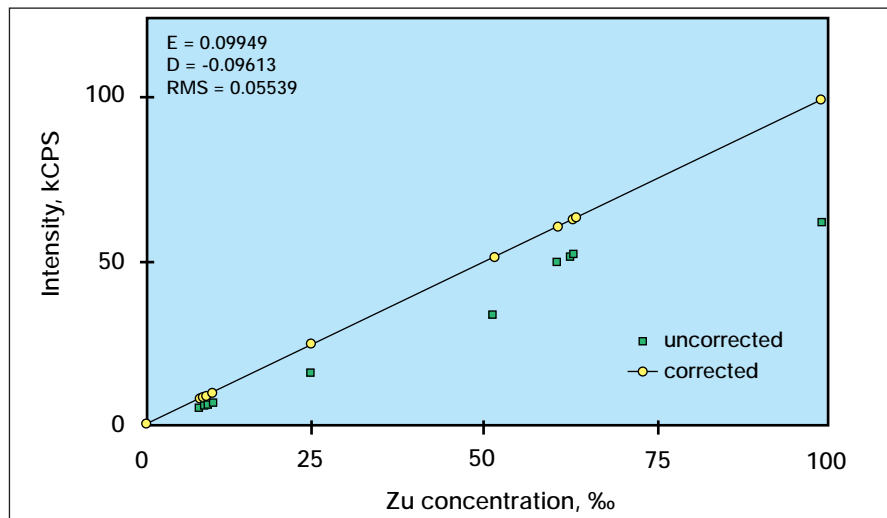


Figure 5 - Calibration line for XRF analysis of zinc (approx. 0-100‰ Zn concentration).

Table 7. Repeatability test for the Au 10 reference standard (‰)

	Au	Cu	Ni	Zn
Run 1	748.3	96.4	128.9	26.0
Run 2	748.0	96.5	129.0	25.9
Run 3	748.1	96.4	129.0	26.0
Run 4	748.3	96.4	129.0	25.9
Run 5	747.9	96.3	128.9	26.0
Run 6	748.1	96.3	129.0	26.0
Run 7	748.0	96.2	128.8	25.9
Run 8	748.1	96.3	128.8	26.0
Run 9	748.1	96.2	128.8	25.8
Run 10	748.1	96.2	128.8	25.9
Average	748.1	96.3	128.9	25.9
Standard Deviation	0.012	0.011	0.009	0.030

Finally, the typical performance of the analytical method for various grades of jewellery gold alloys has been tested. Calibration curves were obtained under optimum analytical conditions. In order to assess the precision of the analysis, a repeatability test (10 runs) has been performed, using counting times of 30 s for gold and 20 s for other elements. Results of the analysis, e.g., of the Au 10 reference sample are reported in Table 7.

Analytical accuracy of $\pm 1.2\%$ for Au in the range 330-1000‰ is somewhat lower than that of cupellation method, while analytical accuracies of $\pm 0.5\%$ for Ag (0-670‰), $\pm 1.3\%$ for Pd (0-320‰), $\pm 0.6\%$ for Cu (0-320‰), $\pm 0.8\%$ for Zn (0-100‰) and $\pm 0.6\%$ for Ni (0-320‰) are fully comparable with the accuracies of the chemical methods more commonly applied. It is noteworthy that these accuracy values are achieved within an analysis time of about 2 minutes (using a sequential spectrometer) and hence the total duration of the XRF analysis results uncomparably shorter than time of cupellation or other chemical analysis needing dissolution of sample.

CONCLUSIONS

The chemical compositions of a wide variety of selected jewellery gold alloys were determined by XRF spectroscopy technique by utilizing a method developed with mathematical corrections of the matrix effects based on common analytical curves for each alloying element, in particular Au, Ag, Cu, Pd, Zn and Ni. The quality of the experimental results indicated this method as a possible advantageous alternative to cupellation for determining the gold concentration in gold alloys, since it allowed to determine the Au concentration with values of accuracy, precision and reproducibility slightly lower than the traditional method. Moreover, the Ag, Cu, Pd and Zn and Ni concentrations were determined in a couple of minutes, with accuracy and precision comparable with those of the chemical methods more commonly applied.

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APPENDIX 1 CALIBRATION METHOD

The measurements were conducted on the certified reference materials described above. Both reference materials and samples were exposed to the primary radiation of the X-ray tube and the resulting fluorescent radiation, characteristic of the

constituents of samples, was measured. The spectrometer was calibrated for the alloying elements, by using the sixteen mentioned standards. The XRF spectral intensity data for standards and samples were processed and least-square regression analysis and statistical evaluation were carried out for each element. The resulting regression equations of form:

$$C_i = D_i + E_i R_i$$

where: R_i is the radiation intensity of the i -element (given in kCPS, kilocounts per second), E_i is the slope, D_i is the intercept and C_i is the concentration of the i -element, could not have meaning of the calibration curves (see average estimation errors given in Table 4), because of strong matrix effects. This occurs since the different alloying elements of a gold alloys can affect each other's X-ray transmission to varying degrees. These matrix effects can be translated into either enhancement or absorption (attenuation) of the radiation of a given element by the presence of one or more elements of the matrix. To overcome these effects the Rasberry-Heinrich equation (15) is used, in the form of:

$$C_i = (D_i + E_i R_i) [1 + \sum_{j=1-n} \alpha_{ij} C_j + \sum_{j=1-n} \beta_{ij} C_j / (1 + C_i)], j \neq i.$$

where: i and j are analyte and matrix element, respectively; α_{ij} are the absorption coefficients, used when the effect of j on i -element is significant; β_{ij} are the enhancement coefficients, used when the effect of j on i -element is *true enhancement*, i.e. when the j -lines excite the i -line.

The absorption coefficients, α_{ij} , can be calculated using the fundamental parameter method. It is based on the theoretical expression of the XRF intensity as a function of the sample composition and relies on the photoelectric cross-section, Coster-Kronig transitions and up-to-date mass absorption coefficients. The production of secondary fluorescence, depending on the wavelength difference between various fluorescence lines, and absorption edge wavelength can be significant in some cases, and therefore, has to be taken into account. Qualitative information about the elemental composition can be obtained from the measured fluorescence spectrum and this is used as the starting point for an iterative method leading to quantitative information. This method can be used in two variants: (a) as a standardless method or (b) as the method for calculation of the matrix effect correction coefficients, which can be then used as the constants in the empirical type equations, such as the Rasberry and Heinrich equation. In this paper the XRF11 Criss fundamental parameter program was used (16).

Table 4. Average estimation errors without and with corection of the matrix effects

<i>i</i> -analyte (concentration range, ‰)	Average estimation errors, ‰	
	without correction	With correction (number of calculated coefficients)
Au (333.2-999.9)	38.6	1.3 (5)
Ag (0-665.9)	17.4	0.8 (3)
Pd (0-314.6)	10.1	0.8 (2)
Cu (0-315.6)	8.6	0.6 (3)
Zn (0-99.2)	3.9	0.5 (2)
Ni (0-324.3)	4.1	0.6 (2)

Table 5. Numerical values of the α_{ij} and β_{ij} correction coefficients for each *j*-matrix element

<i>i</i> -analyte	α_{ij} coefficients for						β_{ij} coefficients for	
	Au	Ag	Pd	Cu	Zn	Ni	Ag	Pd
Au	- 0.043*	- 0.301	- 0.356	0.366	0.528	0.320	0.024*	0.028*
Ag	1.095	0.050*	- 0.058	- 0.110	-	-	-	-
Pd	1.280	- 0.301	-	- 0.023	0.098	- 0.074	-	-
Cu	0.620	0.749	0.664	- 0.038*	0.033	0.003	-	-
Zn	0.401	0.824	0.693	- 0.126	-	2.307	-	-
Ni	0.277	0.011	1.032	0.615	- 1.893	-	-	-

(*) empirically calculated values.

The values of E_i , D_i and of the enhancement coefficient, β_{ij} , (only if true enhancement effects could be predicted) were calculated using least-square regression analysis method.

The average estimation errors (RMS) for each corrected calibration curve were calculated from the following formula:

$$\text{RMS} = \sqrt{\sum (c_i^{\text{chem}} - c_i^{\text{calc}})^2 / (n-p-2)}$$

where: n is the total number of standards taken into calculation, p is the number of the matrix effect correction coefficients and 2 is the number of coefficients of the calibration curve (slope and intercept). The average estimation errors without and with correction of matrix effects are reported in Table 4.

The numerical values of α_{ij} and β_{ij} correction coefficients are reported in Table 5. These values demonstrate that the *true enhancement* effects only affect gold determination. These coefficients, as well as the *self-absorption* coefficients (effect observed in gold, silver and copper determination), have been calculated using the least-square regression.

For better comprehension, this table can be commented also in another way. Normally, to correct the absorption effect, the part of the

i -element line intensity, which is absorbed by the j -element, is to be added. Nevertheless, numerous α_{ij} coefficients (responsible for correction of absorption effect) calculated by using fundamental parameters have a negative sign, suggesting that rather enhancement than absorption is being corrected. For example, the sign of the α_{AgCu} coefficient is negative since:

- a) the mass absorption coefficient of the analyte (Ag) μ_i is 13.8;
- b) the mass absorption coefficient of the matrix element (Cu) μ_j is 24.9;
- c) the mass absorption coefficient of an ideal sample of average composition (Au 704.0‰, Ag 88.3‰, Cu 12.1‰, Pd 32.8‰, Zn 15.6 ‰ and Ni 31.9‰) without the j -matrix element $\mu_{m,j}$ is 52.0;

Thus $\mu_{m,j} > \mu_{j,j} > \mu_i$ leading to reversal of absorption effect in heavy matrix.

The expected reduction in the analyte intensity owing to the presence of a specific j -matrix element with high absorption coefficient for the analyte line may actually become an apparent enhancement effect upon change in the overall matrix composition. In this case, when the concentration of j -matrix element increases, it replaces a matrix with a higher absorption coefficient. This effect is known in the literature as *secondary absorption* effect (16).

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