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A fast and accurate method for the determination of precious alloys caratage by Laser Induced Plasma Spectroscopy

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Abstract. The purpose of this paper is to present a new and efficient technique for precious alloys caratage based on the Laser Induced Plasma Spectroscopy (LIPS) method. The LIPS analysis can be carried out in few minutes and in an essentially non-destructive way on samples of arbitrary shape. Experimental results showing the feasibility of the method for fast and precise analysis of gold jewellery without the need of calibration are presented. Using a new technique of LIPS spectra analysis, recently developed and patented by the Applied Laser Spectroscopy Laboratory at IFAM, we were able to obtain quantitative information about all the alloy components, including trace elements at concentration down to the order of 1 ppm. Matrix effects do not affect the accuracy of the technique.

PACS. 42.62.Fi Laser spectroscopy – 42.62.-b Laser applications – 82.80.Ch Ultraviolet, visible, infrared, Raman, microwave, and magnetic resonance spectroscopic analysis methods; spectrophotometry; colorimetry

1 Introduction

The problem of determining the composition of precious alloys is particularly important for jewel manufacturers and their suppliers of the raw materials. In fact, the manufacturing process, in compliance with domestic and international regulations, requires a careful quality control and certification of the products that, up to now, can only be achieved by application of the traditional cupellation ("fire assay") method. This kind of analysis, although very accurate (around 0.01% in gold concentration determination) is essentially destructive and requires a number of critical measuring stages – including weighing of the sample up to the fifth decimal digit, acid attack of the sample and successive weighing of the gold residual – and can be performed, therefore, only by highly skilled operators [1].

In recent years the need for fast determination of precious alloys composition stimulated the proposals of different alternative techniques for caratage determination, among which the following are worth mentioning: Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Neutron Activation Analysis (NAA) and X-Ray Fluorescence Spectrometry (XRF) techniques.

Although it's not the purpose of this paper to review the pros and cons of the different techniques, it's common opinion that none of these techniques can be considered, at present time, as a valid alternative to the cupellation method. In particular, the only non-destructive technique (XRF) gives information exclusively about the composition of the sample surfaces (about 2 μm penetration depth) and is therefore very limited in its applications. Moreover, all the above-mentioned techniques require a calibration of the system with a reference sample of similar composition; unfortunately, the composition of precious alloys may greatly vary in function, for example, of the color of the jewels or of its physical and mechanical properties. Paradoxically, one might say that all the traditional spectroscopic techniques require an *a priori* knowledge of the composition itself, in order to determine the alloy composition.

In order to overcome these problems, we developed a new technique for precious alloys analysis, which is based on the Laser Induced Plasma Spectroscopy method [2–7]. Although the LIPS technique was already applied in several previous works for metallic alloys analysis [8–10], the relevant experimental results were often affected by large uncertainties because of the calibration problems related to the matrix effect. It seems clear now that conventional LIPS analysis is not feasible for the precise determination of caratage of precious alloys of unknown composition.

We have developed a completely new procedure of LIPS spectra analysis [11,12], which allows to obtain the precious alloy composition without having recourse to external calibration. The fundamental characteristics of our method are described in the following sections.

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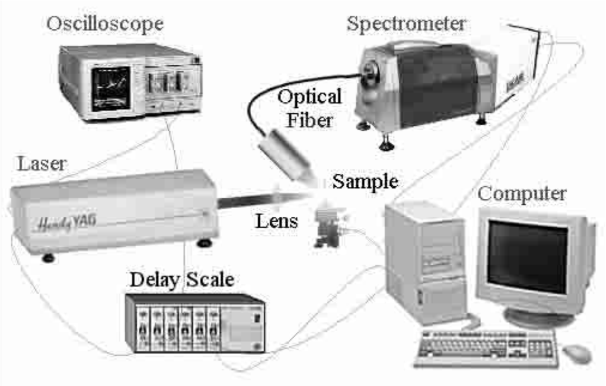

Fig. 1. Schematic view of the LIPS experimental apparatus operating at IFAM-CNR Pisa.

2 Experimental set-up

The experimental prototype for LIPS analysis, operating since several years at IFAM-CNR Institute in Pisa [13–19], is sketched in Figure 1. The prototype uses a Q-switched Nd:YAG laser (Handy 100 by Quanta system) – delivering about 150 mJ at 354 nm (3rd harmonics of the Nd:YAG emission) in 7 ns pulses, at a maximum repetition rate of 10 Hz – for generating a micro-plasma at the sample surface. The laser beam was focused on the sample by means of a lens of 20 cm focal length. The light emitted by the sample was collected using an optical system and then sent through an optical fibre to an Echelle type Spectrometer (Mechelle 7500 by Multichannel Instruments, Sweden) coupled with an intensified CCD camera (PCO). The use of an Echelle spectrometer allows acquiring a whole spectrum (from 200 to 900 nm) in a single laser shot, thus greatly reducing the time needed for the measurement. The importance of using Echelle spectrometers in LIPS measurements has been discussed in [11]. The resulting spectrum was analysed by computer using specialised software developed at IFAM. Using a suitable delay scale the CCD camera was triggered 10 μs after the laser pulse, in order to reduce the contribute of the continuum *Bremsstrahlung* radiation to the LIPS signal. A gate width of about 5 μs is used, which allowed obtaining a good LIPS signal in a regime where space and time variations of plasma parameters are almost negligible [20]. Under these conditions, the LIPS spectra were obtained by averaging over 60 laser shots (giving a total measurements time of about 15 s per sample, at a 5 Hz laser repetition rate). The sample was placed on a motorised translation stage for changing the measurement point after a few laser shots, in order to avoid the formation of deep craters on the sample surface that might change the laser-sample coupling efficiency. A typical LIPS spectrum from a precious alloy is shown in Figure 2.

3 Analysis of LIPS spectra

The method used for the analysis of LIPS spectra has been described in detail elsewhere [11,12], therefore we will just present here the basic characteristics of our approach. Assuming the plasma in Local Thermal Equilibrium (LTE), the LIPS line integral intensity corresponding to the transition between two levels E_k and E_i can be expressed as:

$$I_\lambda^{ki} = FC_sA_{ki}\frac{g_k\exp(-\frac{E_k}{KT})}{U_s(T)} \tag{1}$$

where λ, C_s, A_{ki}, g_k and F are the wavelength of the transition, the concentration of the emitting atomic specie, the transition probability for the given line, the k level degeneracy and a constant to be determined after normalization of the species concentrations, respectively. $U_s(T)$ is the partition function for the emitting species defined as:

$$U_s(T) = \sum_k g_k \exp\left(-\frac{E_k}{KT}\right). \tag{2}$$

Taking the logarithm of equation (1) and substituting the following definitions:

$$\begin{aligned} y &= \ln\frac{I_\lambda^{ki}}{g_kA_{ki}}, & m &= -\frac{1}{KT} \\ x &= E_k, & q_s &= \ln\frac{C_sF}{U_s(T)} \end{aligned} \tag{3}$$

we obtain a linear relationship between the y and x parameters

$$y = mx + q_s \tag{4}$$

which can be graphically represented as a "Boltzmann plot" (see Fig. 3). According to equation (3), the slope of the plot is related to the species temperature. According to the LTE model, this temperature is the same for all the species. Thus, it is possible measuring the temperature on one or several species (for example AuI, CuI and AgI in Fig. 3) and using the same temperature for the other species (AgII in Fig. 3), for which the slope of the plot is not obtainable with sufficient precision.

The dispersion of the experimental points, is due both to the experimental uncertainties and to the uncertainties existing in the literature on the A_{ki} parameters. The overall error in the Boltzmann plot can be estimated as the standard deviation of the points with respect to the best linear fit.

The q_s parameter in equation (4) is proportional to the logarithm of the species concentration *via* the F constant factor. The F factor can be determined by normalizing the species concentrations as

$$\sum_s C_s = 1.$$

The application of the above described method to precious alloys allows to obtain the concentration of all the components of the alloys, including the trace elements in concentrations down to the detection limit of the technique (typically 1 ppm), without the need of calibration. The minimum error in alloy composition determination is of the order of the concentration of the undetected elements.

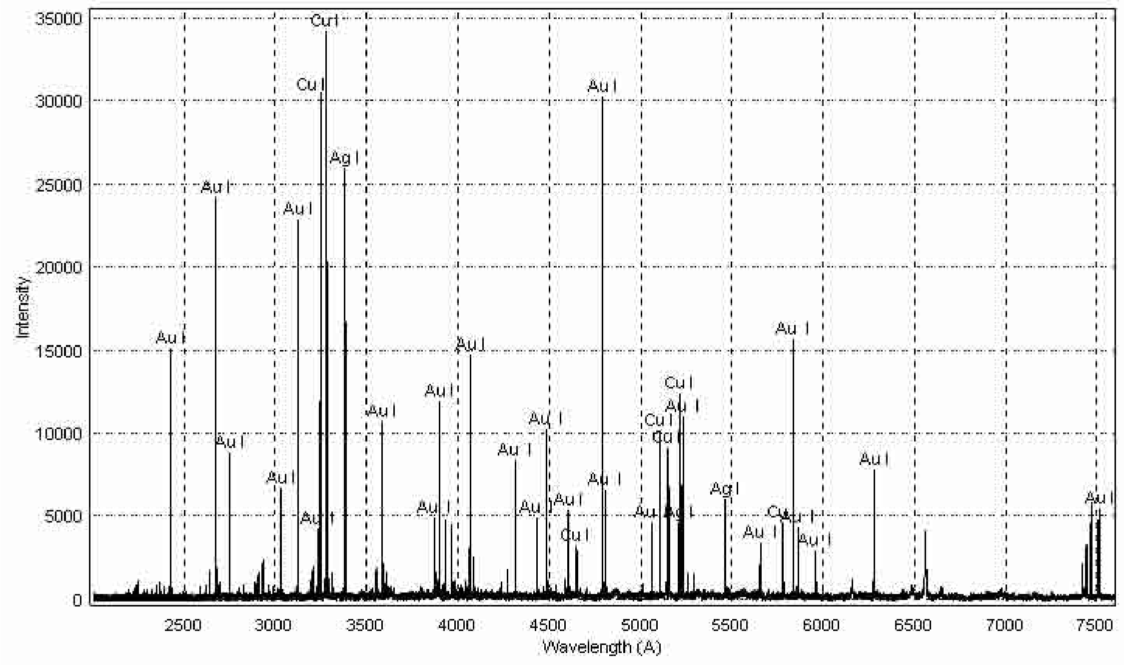

Fig. 2. LIPS spectral signal collected during the analysis of the Au 917/1000 alloy (sample D). Specific lines emitted by Au, Ag and Cu atoms are marked.

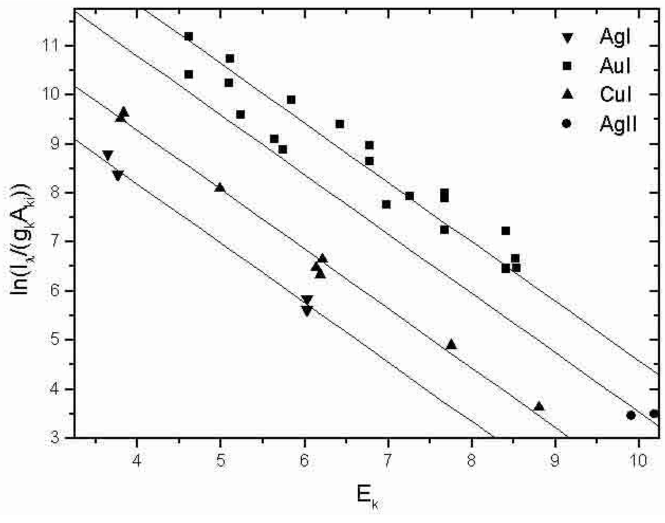

Fig. 3. Boltzmann plot for the Au 917/1000 alloy (sample D) analysed in this paper. Continuous lines represent the result of a linear best fit. Note that the best fit lines corresponding to different species are practically parallel, *i.e.* the temperature of all the species in the sample is the same (within the experimental errors), according to the predictions of LTE assumption.

4 Experimental results

In order to test the accuracy of the LIPS prototype and the reliability of the above described method, we performed a LIPS analysis on five precious alloy samples, in the form of irregular foils of about 10 mm × 10 mm × 0.5 mm, corresponding to gold concentrations ranging from 200/1000 up to 1000/1000 in weight. Four of them were ternary alloys (Au, Ag and Cu) and one was a quaternary alloy (Au, Ag and Cu with addition of palladium). A typical LIPS analysis of these samples is compared in Table 1 with the nominal elemental concentrations. The error on the LIPS concentration, due to the dispersion of the experimental data and the consequent uncertainty in the measured temperature, is below 1%.

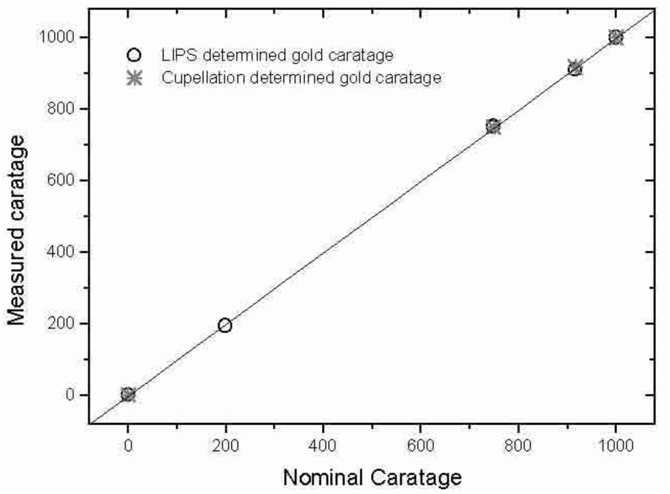

Fig. 4. LIPS-determined gold caratage for the set of precious alloys studied and the corresponding results of cupellation technique analysis *vs.* the gold nominal concentration (the errors on the LIPS and cupellation measurements are of the order of the point dimensions in the plot).

The correlation between LIPS determined gold caratage and the nominal caratage is shown in Figure 4. It should be noted that the standard deviation of the LIPS

Table 1. Comparison between LIPS determined alloy composition and nominal composition for the five samples analysed in this study. The cupellation determined gold concentration, when available, is also reported.

Sample A

Element	LIPS concentration (in weight)	Nominal concentration (in weight)	Cupellation concentration (in weight)
Au	194/1000	200/1000	-
Ag	404/1000	400/1000	-
Cu	402/1000	400/1000	-

Sample B

Element	LIPS concentration (in weight)	Nominal concentration (in weight)	Cupellation concentration (in weight)
Au	753/1000	750/1000	749.7/1000
Ag	120/1000	125/1000	-
Cu	126/1000	125/1000	-

Sample C

Element	LIPS concentration (in weight)	Nominal concentration (in weight)	Cupellation concentration (in weight)
Au	751/1000	750/1000	750.7/1000
Ag	38/1000	30/1000	-
Cu	96/1000	95/1000	-
Pd	115/1000	125/1000	-

Sample D

Element	LIPS concentration (in weight)	Nominal concentration (in weight)	Cupellation concentration (in weight)
Au	911/1000	917/1000	917/1000
Ag	34/1000	32/1000	-
Cu	55/1000	51/1000	-

Sample E

Element	LIPS concentration (in weight)	Nominal concentration (in weight)	Cupellation concentration (in weight)
Au	1000/1000	1000/1000	999.9/1000
Ag	-	-	-
Cu	-	-	-

determined caratage from the "perfect correlation" line is about 0.1%; the accuracy of the LIPS measurements thus lies in the same range as that of the cupellation technique. Moreover, the LIPS analysis gives almost identical results for the ternary and quaternary alloy (both samples corresponding to the same gold concentration of 750/1000 in weight); the matrix effect does not affect, thus, the accuracy of LIPS measurements performed by our calibration-free procedure.

It's interesting to compare the accuracy of the CF-LIPS results with those that could be obtained from exactly the same experimental data by using conventional calibration techniques. In this case one should build one calibration curve by plotting the intensity of one (or more) Au lines *versus* the nominal Au concentration. Four hypothetical calibration curves are shown in Figure 5 for the Au lines at 2675 Å, 2748 Å, 3122 Å and 6278 Å. It is clear from Figure 5 that, due to the unavoidable fluctuations in laser energy and laser-sample coupling, the scattering of the experimental data with respect to a hypothetical calibration line is very high. This error would greatly affect the precision of LIPS measurements based on the standard calibration techniques. Moreover, because of the matrix effect, the data corresponding to the same gold caratage for ternary and quaternary alloys do not coincide at all. One should thus build different calibration curves for the different possible compositions of the precious alloy to be analysed. These results reinforce our considerations on the difficulty of obtaining precise determination of gold caratage with conventional analysis techniques on unknown samples.

5 Conclusions

In this paper, we have shown the results of application of LIPS technique to determine the caratage of precious alloys. A careful reduction of the effects affecting the reproducibility of the experimental results and the application

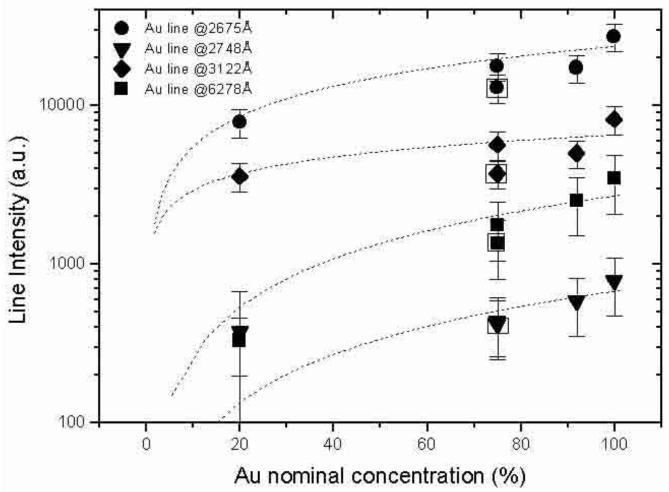

Fig. 5. Line intensity (arbitrary units) of the four most intense Au lines *versus* gold nominal concentration, for the same set of samples as in Figure 4. Dashed lines are guides for the eye drawn through the experimental points. The points surrounded with the square correspond to the quaternary Au 750/1000 alloy (Au, Ag, Cu, Pd – sample C).

of a new method for the quantitative analysis of the LIPS spectra allowed us to obtain precise results not affected by matrix effects.

We thus conclude that the LIPS technique can be considered as a promising method for precious alloys caratage, alternative to the standard and complex cupellation technique. Work is in progress for the realization of a compact LIPS prototype for fast *in situ* analysis of manufactured gold jewels.

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