

A Quick Method to Determine the Impurity Content in Gold Ornaments by LIBS Technique

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Abstract: Laser induced breakdown spectroscopy (LIBS) and low energy dispersive X-ray fluorescence (ED-XRF) spectrometer, were used to determine the line intensity and concentration ratios of the major impurities (Cu and Ag) with respect to Au in gold ornaments with different caratage. Calibration curves were drawn with the data sets, obtained from LIBS and XRF, and from these calibration curves the unknown caratage of gold ornaments were obtained by using the line intensity of elements determined by LIBS. We have demonstrated the accuracy of this method by comparing the result with the carat value obtained by typical XRF method. This is yet another novel application of LIBS as a versatile analytic technique.

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1 INTRODUCTION

Fast, reliable and accurate determination of the elemental composition of gold alloys along with its carat value has become an important task not only for its use in worldwide jewelry manufacturing but also in fields like nano-medicine (Ali et al., 2011) and microelectronic industries (Goodman, 2002). Traditional cupellation method or ‘Fire Assay’ (Bugbee, 1950) is one of the most trusted procedures till date for measuring the caratage of gold and hallmarking them. However, cupellation method is destructive, time consuming, operator dependent and involves the usage of lead and nitric acid which also produces toxic fume at high temperature. Because of these complications, X-ray fluorescence spectrometry (Beckhoff et al., 2006) (wavelength dispersive, WD-XRF and energy dispersive, ED-XRF) has been adopted as a convenient and reliable technique in gold market for testing gold purity as they offer fast and sample preparation free (unlike atomic absorption spectroscopy) nondestructive analysis. In practice, high energy dispersive XRF can provide fairly accurate result although it is quite expensive and requires expert analysts; so they are not commercially feasible for detecting caratage of gold ornaments. But there exists low energy dispersive XRF spectrometer specifically designed and pre-calibrated by international standards for simultaneous analysis of alloy constituents. Low energy dispersive XRF offers accuracy of 2-5 %.

However, its accuracy deteriorates if the sample is small, curved or ball-shaped. Furthermore, with XRF only about 1-2 μm of surface depth can be examined. So XRF technique is less precise in detecting forgery like a copper or silver bar electroplated with a thick layer of pure gold. The topic of gold jewelry analysis by XRF has been reviewed by Marucco (Marucco, 2006). Also Gamma ray transmission technique, proposed in (Suzuki et al. 2006) provides analysis of gold samples which are about 1-5 mm thick with 99% accuracy. But because of radiation hazard due to strong gamma ray and lack of portability, this method is also not commercially feasible in analyzing gold purity. Laser Induced Breakdown Spectroscopy (LIBS) (for details, see (Mizolek et al, 2006, Singh et al. 2007), on the other hand has no extra trouble of special sample preparation and hence posses simplicity along with detection limit of few ppm and unlike XRF, has larger information depth of 10 μm or more depending on laser pulse power which makes it an ideal choice for testing gold purity within a very short period of time. Using LIBS, all the elements in the periodic table can be measured in a single setup of the spectrometer.

Despite all these advantages, LIBS has never been adopted as an ideal method for impurity detection in gold. Typically, the signal intensity for an element present in the plasma depends on laser parameters: laser energy, irradiance, laser focusing and pulse duration. Fluctuations in any of these

parameters and also sample inhomogeneity and matrix effects may lead to nonlinearity in the calibration curves, affecting the analytical precision and consequently lowering the accuracy of measurement by LIBS technique.

In general, sample inhomogeneity can be categorized into two classes: bulk non-uniformity and non-representative surface composition. The first can be dealt with by averaging results of multiple measurements taken over different parts of the sample. Samples whose outer layers don't represent bulk composition can be probed by making crater with depth ranging from few μm to 10-20 μm depending on the laser parameters. This will usually solve the problem of non representative surface composition. Low ED-XRF, as mentioned before, can't probe such depth.

Matrix effect corresponds to the change in the signal intensity of a specific element with variation in the concentration of one or more elements forming the matrix even though the overall elemental concentration remains constant in the sample. One approach to correct such effects is to use internal standard principle i.e. to consider the ratio of the intensity of analytical spectral line to that of another component of the sample which has fixed or known concentration because even if the measured values change significantly, their ratio alter a little (Haider et al. 2014). As LIBS offers immense possibilities for spectroscopic analysis, significant efforts are given to develop new calibration methods (for a review, see (Zorov et al. 2010)) to correct LIBS measurements and increase its ability of quantitative analyses.

Although LIBS is a standalone analytical method, over the years, it has been combined with other analytical methods to enhance performance for selected applications. One such example is LIBS-LIF (Laser Induced Fluorescence) where free atoms in the plasma formed by LIBS laser are excited with second laser beam tuned at specific frequency to induce some transition in atoms and this method, though not have multi-elemental detection capability, has higher sensitivity to detect single specific element in the sample. This has been reflected in spectro-chemical analysis of metals in soil (Hilbk-Kortenbruck et al., 2001).

In this paper, we report a method for determining the carat values of gold in general, and in particular of gold ornaments, by combining LIBS with low energy dispersive XRF. This technique was also adopted by Pouzar et al., 2011, for quantitative LIBS analysis of vanadium in samples of hexagonal mesoporous silica catalysts. One can thus bypass

the limitations, which both the systems suffer individually, and enhance the detection ability of impurity content in gold ornaments using calibration curves obtained by correlating LIBS and XRF data. It has been shown that improved accuracy of determination of caratage of gold ornaments of any size and shape are possible by using these calibration curves and comparatively more reliable results can be obtained from the LIBS technique.

2 EXPERIMENTAL

Suisse gold bar (24 carat) obtained from Singapore Bullion market and gold ornaments: 3 finger rings with known carat values, as determined by ED-XRF technique, of 22.024K, 20.912K and 18.507K, a round solid earring (20.495K), a round flat pendant (18.807K), a curved ear-top (18.649K) and a stone studded ring (8.040K) were used as samples. The thickness of the targets was different for different samples depending upon the type of ornaments. Later an ornament of unknown carat value was used for verification of the proposed method. It was evident from XRF analysis that goldsmiths mostly use copper and silver, as impurity to gold alloys for obtaining desired color, shine and solidity of the ornaments. The percentage content of impurity elements (Cu and Ag) in the samples were ascertained by low energy dispersive XRF. Other elements which were present in trace amount were Ni, Cd and Zn. That's why in our work we have mainly focused on establishing two separate calibration curves; one for copper and another for silver as the inclusion of other base metals were negligible. These calibration curves were used to estimate the impurity content of the gold ornament of unknown caratage to verify the applicability of this technique. The concentrations of constituent elements in the gold samples were obtained by desktop energy dispersive XRF spectrometer (EDX 3600B) which is equipped with Tungsten anode X-ray tube operated at 40 KeV and 80 μA and electro-cooling UHRD detector which leads to good energy linearity, energy resolution, spectral property and high peak-background ratio (<http://www.skyrayxrf.com/ edx3600b>). The LIBS spectrometer used in the present work is shown figure 1 (Haider et al., 2014). It has a pulsed Q-switched Nd:YAG laser operating at 1064 nm with pulse duration of 8ns and repetition rate of 10 Hz. But we have used harmonic generator that has a nonlinear Potassium Dihydrophosphate (KDP) crystal to obtain the 2nd harmonic at 532 nm with

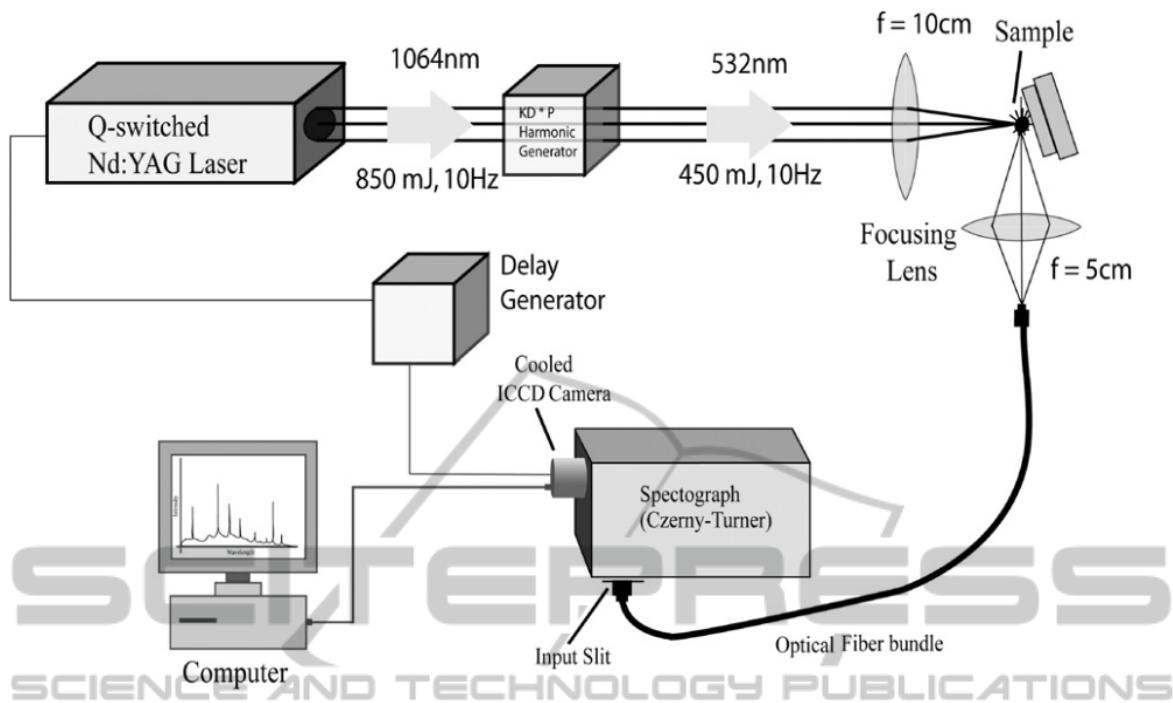


Figure 1 A Schematic diagram of LIBS set-up.

ablation energy varying from 40 mJ to 150 mJ for our analysis. The spectrometer, SpectraPro 2758 (<http://www.princetoninstruments.com/products/spec/actonseries>), used is a Czerny Turner spectrograph with focal length of 750 mm and a triple grating turret. With the focusing geometry used in the experiment [see figure 1] the beam waist at the focus of the lens is 10 micro-meters. The spectrograph is equipped with three ruled gratings in the turret, viz., 300 grooves/ mm blazed at 300 nm , 600 grooves/mm blazed at 500 nm, and 2400 grooves/mm blazed at 240 nm, which are interchangeable under computer control. The selection of the gratings determines the resolution of the instrument. If the 600 grooves/mm grating is used, as was the case in the present experiment, a spectrum of about 38 nm of spectral width can be captured without moving the grating. The output end of the spectrograph is coupled with an intensified and gated CCD camera (Princeton PI-MAX with Unigen II coating and programmable delay generator). The ICCD camera has 1024 x 1024 pixels and was cooled to -20°C by a Peltier cooler to reduce noise (<http://www.princetoninstruments.com/products/imcam/pixis>). The camera was electrically triggered by the Nd: YAG Q-switch pulses after a software-controlled, adjustable time delay. With a suitable time delay, the intense background initially created by the high-temperature plasma can be largely eliminated, and the atomic

emission lines of the elements were more clearly observed. In most of our experiments, a time delay of about 1.0 micro-second was selected. Usually, spectra from a number of laser shots (about 40-80) were acquired and averaged to increase the signal-to-noise ratio. The ICCD was interfaced with the spectrometer and data acquisition and spectral analysis were carried out by the integrated software WinSpec/32, provided by the manufacturer.

The LIBS spectrum, taken in ambient air, was analyzed by using the 600 grooves/mm grating. The resolution of the spectrometer for the 600 grooves/mm grating is about 0.02 nm (Haider et al., 2014) and the repeatability and accuracy of the computer-controlled system is ± 0.05 nm and ± 0.1 nm respectively (manufacturer supplied data).

The plasma was checked for optical transparency (optical thinness) following the method described in one of our earlier paper (Haider et al., 2014).

3 RESULT AND DISCUSSION

The LIBS spectra of samples with different carat values are shown in figure 2. The spectral lines were identified using the online NIST (US National Institute of Standards and Technology) Atomic Spectra Database and the presence of Au and two other alloying elements (Cu and Ag) was confirmed

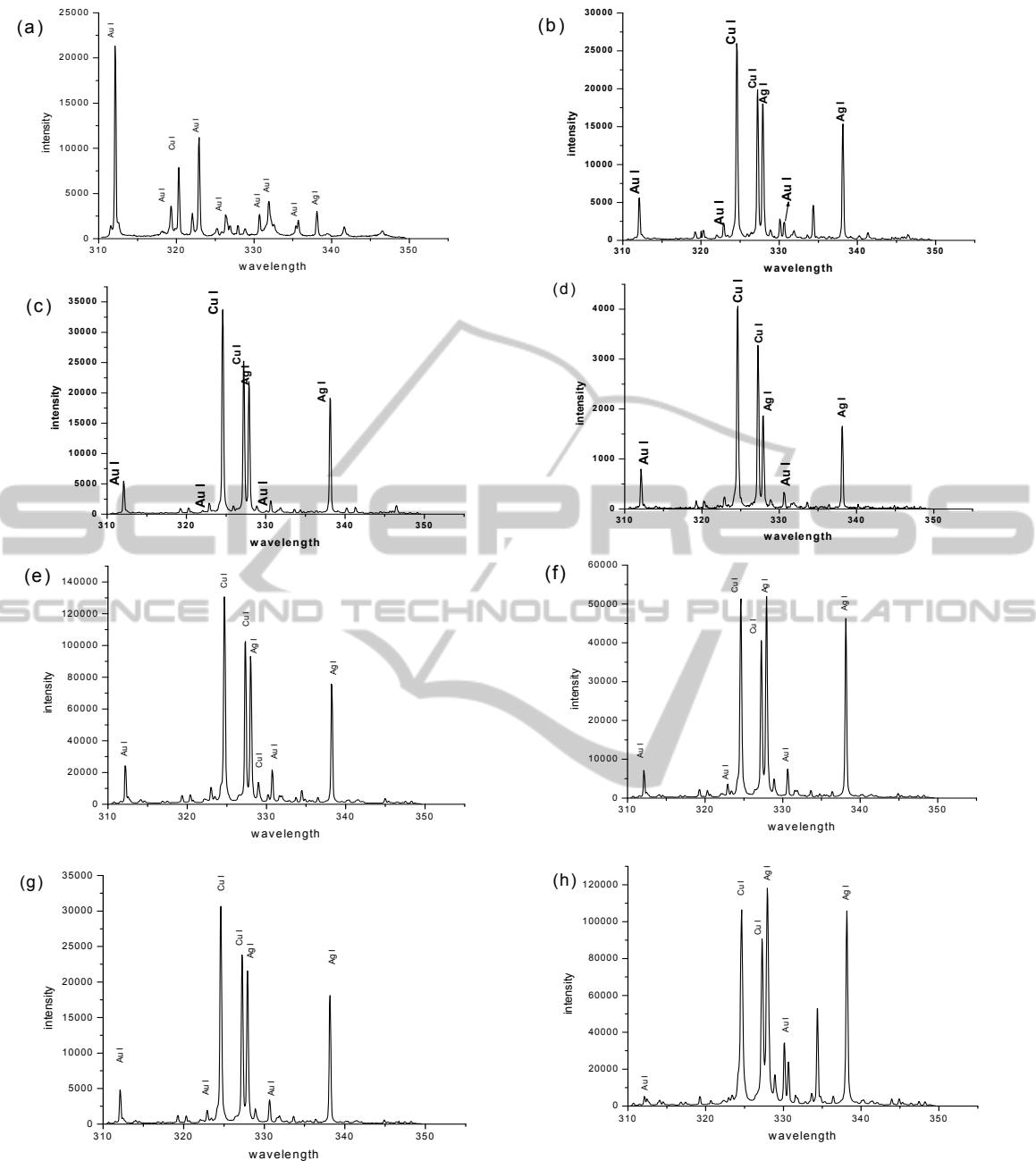


Figure 2: Typical LIBS spectra with identified lines for samples with different carat value (a) 99.99%, (b) 91.76%, (c) 87.13%, (d) 85.390%, (e) 78.36%, (f) 77.7%, (g) 77.10%, (h) 33.5%.

other alloying elements (Cu and Ag) was confirmed in the samples. The intensity of the emission line was measured by multiplying the peak intensity with FWHM of the line. The line intensity ratio of impurity to gold ($I_{\text{Cu}} / I_{\text{Au}}$ and $I_{\text{Ag}} / I_{\text{Au}}$) by LIBS and the ratio of concentration of impurity to gold (Cu / Au and Ag / Au) as determined by XRF were recorded for different samples.

The intensity ratios obtained from LIBS measurement, as well as the ratios of concentration of Cu and Ag, to Au, determined from XRF analysis represent an estimate of how much impurities (mainly Cu and Ag) are present in samples. The LIBS spectral emission lines for Au, Cu and Ag used in the intensity ratio calculations were at 312.278 ± 0.15 nm, 324.754 ± 0.15 nm and 338.207 ± 0.15 nm respectively.

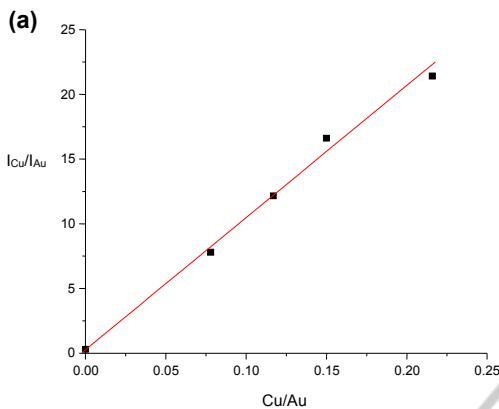


Figure 3: (a) Calibration curves for estimation of Cu impurities in gold ornament.

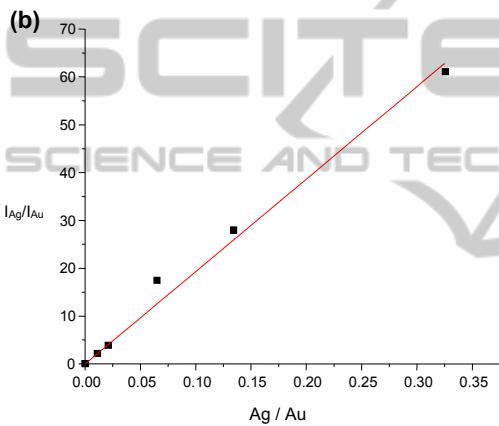


Figure 3: (b) Calibration curves for estimation of Ag impurities in gold ornament.

Therefore, by plotting the intensity ratio (from LIBS) against the elemental concentration ratios

(from XRF), one can draw calibration curves for Cu and Ag impurities as shown in Figures 3(a) and 3(b). From these calibration curves, by knowing the line intensity ratio by LIBS for an unknown sample, one can immediately obtain the elemental concentration ratio in that sample.

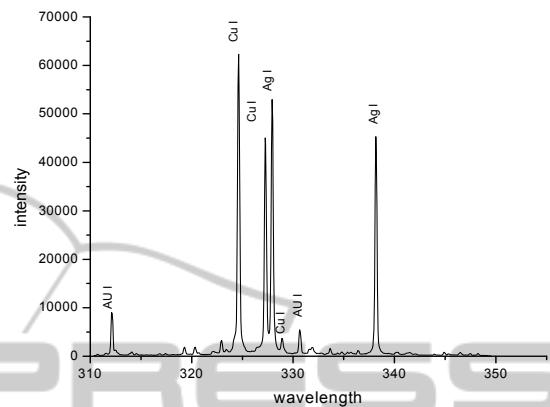


Figure 4: LIBS spectrum for the sample of unknown caratage.

For the verification of this method, LIBS spectra (Fig 4) for an unknown sample was taken and from the recorded spectra, line intensity ratios of impurity (Cu and Ag) to gold i.e. I_{Cu} / I_{Au} and I_{Ag} / I_{Au} were determined. Then the elemental concentration ratios of impurities to gold (Cu/Au and Ag/Au) were measured for the corresponding line intensity ratios from the calibration curves (Fig 3). Now, one can easily calculate the % of impurity content in the unknown sample using the $Cu: Au: Ag$ ratio as shown in Table 1. We have also analyzed the same unknown sample by XRF technique. Table 2 shows a comparison between the results obtained by XRF method and the LIBS technique.

Table 1: Determination of ratio of impurity to gold from calibration curves (figures 3(a) and (b)) for gold sample of unknown carat value.

Sample	By LIBS		From calibration curve		
	Line intensity ratio of impurity to gold		Ratio of impurity to gold		
	I_{Cu}/I_{Au}	I_{Ag}/I_{Au}	Cu/Au	Ag/Au	$Cu: Au: Ag$
	17.702	12.190	0.173	0.065	17.3:100: 6.5

Table 2: Comparison of results obtained by XRF and that of LIBS technique in the present study for gold sample of unknown carat value.

Sample	By LIBS technique in the present study				By XRF			
	% of Au	% of Cu	% of Ag	Carat value	% of Au	% of Cu	% of Ag	Carat value
Unknown	80.78	13.97	5.25	19.39	78.610	14.829	6.252	18.87

4 CONCLUSIONS

We have shown that the LIBS technique can be used as an effective and quick method for the determination of carat value of gold ornaments. The present method using LIBS enjoys a number of advantages over other methods e.g. the XRF method as discussed in the introduction. It only requires the accumulation of the LIBS spectra in a single spectral window (310nm to 348nm), if one uses the 600 grooves/mm grating and takes time of less than 1 second. One can also use the same LIBS set up for detection of trace elements which aren't detected by XRF. The method of determining the caratage of gold ornament by LIBS technique is particularly preferable over the conventional ED-XRF technique where forgery, by simple gold electroplating of ornaments made of other metal, e.g. copper, silver or bronze, is expected.

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