

Quantitative analysis of mercury in silver dental amalgam alloy using laser induced breakdown spectroscopy with a portable Echelle spectrometer

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Abstract

Nowadays it is commonly ascertained that, Laser- induced breakdown spectroscopy (LIBS) was investigated to evaluate the feasibility as a fast, accurate, non contact and simple technique used in both qualitative and quantitative elemental analysis of metals in various environments. The used portable Echelle spectrometer (Mechelle 7500 - Multichannel Instruments, Stockholm, Sweden) permit real simultaneous multi-elemental analysis in rang of 200-900 nm with a high resolution in few minutes. In the present work, the proposed LIBS setup has been applied to perform elemental analysis of mercury in platinum modified non gamma 2 spherical dental amalgam alloy samples. Moreover, the content of the dental amalgam samples was qualitative analyzed.

A detailed study has been performed on optimization of many experimental parameters to avoid experimental fluctuations and to enhance the system sensitivity as possible.

Calibration curve for mercury was achieved with linear regression coefficient of 0.93, detection limit of 2.9 ppm and relative standard deviation (RSD %) of 7.5 % in dental amalgam samples.

The obtained results show the capability of the proposed LIBS setup for in-stiu real time analysis of Hg in dental amalgam with good sensitivity and high precision.

Keywords: LIBS, Echelle spectrometer, mercury, dental amalgam.

Introduction

For centuries dentists have been cleaning out decay and creating dental fillings, using filling material such as stone chips, resin, cork, turpentine, gum, lead and gold leaf. Amalgams were the first true standard filling material. Mercury amalgams were used in dentistry because they were cheap, easy to use, durable, and are regarded as safe. They were made by mixing approximately equal measures of mercury and an alloy of silver, copper, tin and other metals. The first people to use amalgams to fill cavities appear to be the French. In 1816 Auguste Taveau developed first dental amalgam from silver coins and mercury. This early amalgam was low in mercury and had to be heated in order for the silver to dissolve at any appreciable rate. More modern dental amalgams are mixed cold. The wide use of Ag-Sn-Cu amalgams as dental restorative materials makes them important biomaterials. Their physical and mechanical properties, stability, and ease of use and relatively low cost have made amalgams the preferred choice in many clinical situations when compared with other direct restorative materials [1].

Current dental amalgams contain copper to eliminate the gamma-2 phase of the silver-mercury-tin alloy. The gamma 2 phase is weaker than the other phases so a high copper, low gamma-2 dental amalgam has superior strength. It is believed by many and supported by scientific and clinical evidence that they can in rare circumstances be the predominant cause, catalyst or trigger in individual cases several diseases [1-3]. Jones et al. [1] proved that Mercury leaves dental amalgam continuously throughout the lifetime of the filing. Mercury vapor is the main way that mercury comes out of amalgam and is absorbed at a rate of 80% through the lungs into the arterial blood [2, 3].

Recently, Z. Odanovic et al. [4] studied the mechanism of mercury removal from a silver dental amalgam alloy through the analysis of silver dental amalgam decomposition. They used sophisticated laboratory equipments and high temperature treatment for many hours to analyses the amalgam decomposition. The decomposition process was analyzed during thermal treatment in the temperature interval from 400°C to 850°C and for times from 0.5 to 7.5 hours. Moreover, the chemical compositions of the silver dental amalgam alloy and the treated alloy were tested and microstructure analysis using optical and scanning electron microscopy was carried out.

Laser-induced breakdown spectroscopy (LIBS), offers unique capabilities for on-line composition determination. The use of spectroscopy LIBS as an analytical tool has considerably grown over the past 10 years. Spectrochemical analysis using LIBS has proven to be extremely versatile, providing multi-element analysis in real time without sample preparation. LIBS can be regarded as a universal sampling, atomization, excitation and ionization source, since laser induced plasmas can be produced in gases or liquids, as well as from conducting or non-conducting solid samples.

In LIBS, a small volume of the target is intensely heated by the focused beam of a pulsed laser, and thus brought to a transient plasma state where the sample's components are essentially reduced to individual atoms. In this high-temperature plasma, atoms are ionized, or brought to excited states. Such states decay by emission

of radiation, which is observed in the ultraviolet (UV), visible and near-infrared (NIR) regions of the spectrum. An atomic spectrum is obtained by means of a spectrograph, thereby allowing elemental components of the target to be identified and, using a calibration curve, quantified. LIBS measurements are generally carried out in ambient air at atmospheric pressure. For this reason, and also due to its rapidity, non-contact optical nature, and absence of sample preparation, since the only requirement is the optical access to the samples, LIBS is a useful technique for on-line process analysis. The basic features of this spectroscopic technique and its applications for on-line measurements have been reviewed in several papers [5-8].

O. Samek et al. [9] used LIBS technique for the analysis of teeth and dental materials. They concluded that the technique is easy to apply, and the results obtained indicate a near-100% identification rate for materials of both healthy and carious tooth sections.

In this work, we propose a method based on the LIBS technique, capable of monitoring mercury in silver dental amalgam alloy by monitoring and analyzing the luminescent plasma in vivo and in real time; thus precise monitoring of the amount of Hg leave the amalgam and enter the body can be achieved. The plasma, which is created during the ablation using short laser pulses, can be spectrally analyzed using a one-fiber light collection system.

Materials and Methods

A schematic diagram of LIBS experimental setup used is illustrated in figure (1). The plasma formation was attained with the aid of a Q-switched Nd: YAG laser (surelite I, continuum, USA) operating at 1064 nm (pulse duration of 7 ns) and repetition rate of 0.1 Hz -10 Hz. An energy meter (Nova 978, Ophir Optronics Ltd., USA) was employed to monitor the shot to shot pulse energy. The laser beam with pulse energy of 100 mJ was focused on the amalgam alloy samples by a 10 cm focal length quartz lens to generate the plasma. A one meter length fused-silica optical fiber (600 μm diameter) mounted on a micro xyz-translation stage is used to collect the emission light from the plasma plume and feed it to a portable echelle spectrometer of a 0.17 m focal length (Mechelle 7500, Multichannel instruments, Sweden). The Echelle grating spectrometers designed for operation in high orders and high angles of incidence and diffraction, can provide high resolution in a more compact size and cover a much wider spectral range than conventional grating spectrometers [11]. The Mechelle 7500 provides a constant spectral resolution (CSR) of 7500 corresponding to 4 pixels FWHM over a wavelength range 200 – 1000 nm displayable in a single spectrum. A gateable, intensified CCD camera, (DiCAM-Pro-12 bit, UV enhanced, 43000 channels, PCO Computer Optics, Germany) coupled to the spectrometer was used for detection of the dispersed light. The overall linear dispersion of the spectrometer camera system ranges from 0.006 (at 200 nm) to 0.033 nm/pixel (at 1000 nm). To avoid the electronic interference and jitters, the intensifier high voltage was triggered optically. Echelle spectra display, control, processing and analysis were done using both Mechelle software (Multichannel instruments, Stockholm, Sweden) and

GRAMS/32 version 5.1 Spectroscopic Data Analysis Software (Galactic Industries, Salem, NH, USA).

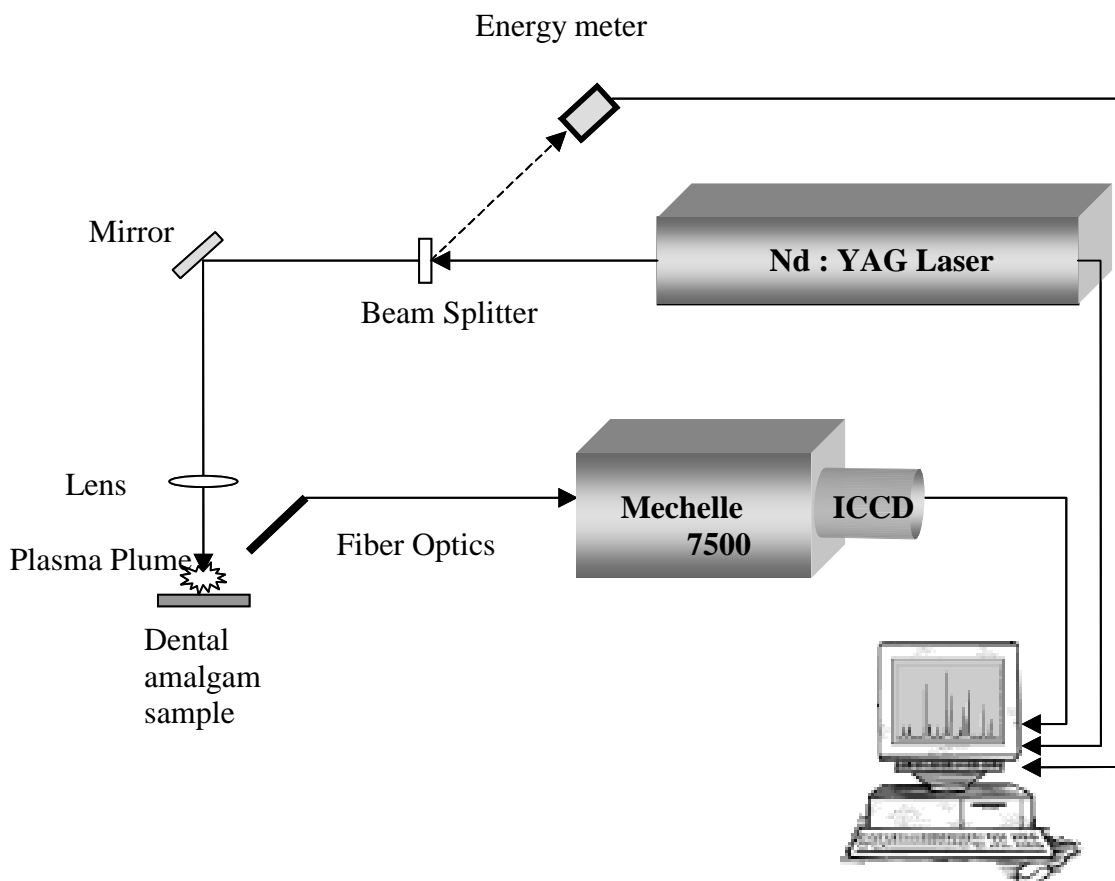


Figure 1: Schematic diagram of LIBS setup.

The analyzed samples are platinum modified non gamma 2 spherical amalgam alloy (46%Ag, 29%Sn, 24%Cu, 0.95% In , 0.05Pt) and mercury (Southern Dental Industries, SDI, LTD. Austria). For construction of the calibration curves the mercury was added with concentrations ratio from 0.1 to 1 (W/W). Then the mixtures were mixed using Ultramat 2 amalgamator (Southern Dental Industries, SDI, LTD. Austria) for 16 seconds. Ultramat 2, has a high precision microprocessor controlled timer provides consistent and accurate trituration, with a mixing frequency of 4600 oscillations per minute, ensuring the optimal handling and clinical characteristics of mixed materials.

Many optimization procedures were performed to enhance the signal intensities of the elements in dental amalgam samples. Here below, we optimized many experimental parameters to improve our LIBS resolution and sensitivity and to minimize the measurements fluctuations and problems due to the sample heterogeneity.

To improve data reproducibility, and to avoid electronic jittering problem, the laser was set to single shot mode. Then, the Nd:YAG laser beam was focused onto the sample surface at 90° angle. This was done using a 25 mm diameter dichroic mirror that reflects 99% of high energy 1064 nm wavelength. This mirror placed just before the laser-focusing lens as shown in figure (1). The focal point was set 5 mm below the surface of the sample in order to generate plasma of 800 µm spot diameter. This also minimize breakdown above the surface of any particles and aerosols generally present above the sample. On the other hand, the use of a micro *xyz*-translation stage as a holder for fused-silica optical fiber facilities maximum intensity of the observed emission light from the plasma plume.

For each new sample, before spectral collection, 20 laser pulses were performed to clean the sample surface and removes surface oxides and contamination to ensure that the observed spectrum is representative of the sample composition.

Now, we aim to produce LIBS spectra with high precision. Precision is the measure of the degree of reproducibility of a measurement. It is generally measured as the RSD of a set of repeated measurements precision. Typical LIBS precision is 5-20 % [12]. Laser shot-to-shot variation causes differences in the plasma properties, therefore affects the magnitude of the element signal, and hence degrades the LIBS precision. To improve LIBS precision, spectra from several laser shots have to be averaged in order to reduce statistical error due to laser shot-to-shot fluctuation. Moreover, we found that enhancement of the data reproducibility can be achieved by accumulation of consecutive measured spectra for exposures of duration 10000 ns, each delayed 2500 ns from the laser pulse. These values of delay time and exposure window time (gate time) for the ICCD camera produced spectra with minimal background and signals from major lines that did not saturate the detector. Twenty shots were fired at each sample surface and saved in separated files and the average was computed and saved to serve as the library spectrum. Moreover, for each spectrum recorded, the peak intensity, the full at width half maximum FWHM, and the center wavelength of each line, as well as the background emission continuum are determined. Data treatment preprocessing of the averaged spectra data was performed in the Windows environment on a Pentium III PC using GRAMS/32 version 5.2 (Thermo Galactic, USA.) and Excel (Microsoft office Excel 2003). The averages of peak tables (lists of wavelengths and intensities) of the averaged spectra were roll generated in GRAMS/32 and exported for data evaluation.

Results and Discussion

Qualitative analysis

One of the most promising approaches to atomic emission spectroscopy (AES) and particularly for the LIBS experiment involves the use of a portable Echelle spectrometer [10, 11]. Hence, for medical applications, it is necessary to be able to analyze several elements at once; therefore, the use of an Echelle spectrometer that covers the emission spectra from the UV to visible with sufficient resolution is desirable.

Twenty laser shots were accumulated on the ICCD of the system to analyze each sample. The spectrum can be investigated simultaneously with an Echelle spectrometer (typically 200-700 nm); the wavelengths of interest (with minimum around 254 nm for Hg and maximum around 578 nm for Cu) in one spectral window are presented.

Figure (2) shows a typical LIBS spectrum for platinum modified non gamma 2 spherical amalgam alloy. This spectrum is the average of 20 single shot spectra recorded at 2.5 μ s delay time and 10 μ s gate width. The panoramic Echelle spectra in the spectral range 200 – 600 nm show the UV-visible emission lines of dental amalgam as a major element and the emission lines of silver, tin, copper, indium, platinum, and mercury elements in the dental amalgam alloy sample. The recorded wavelengths of the spectral lines throughout the analysis of the dental amalgam elemental composition were Sn at 224.67 nm, Hg at 253.652 nm, 312.56 nm, 313.18 nm, 365.01 nm, 404.65 nm, 435.83 nm, 546.07 nm and 576.9 nm, Pt at 265.94 nm, In at 304 nm, Cu at 324.7 nm, 327.4 nm and 578.21 nm, and Ag at 520 nm.

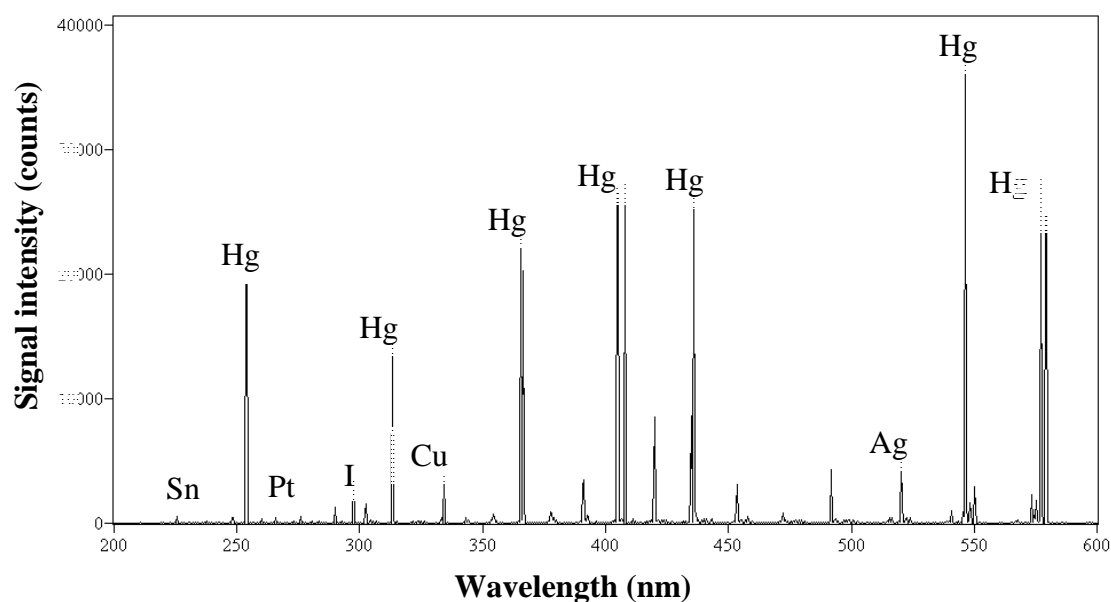


Figure 2: Typical LIBS spectrum for platinum modified non gamma 2 spherical dental amalgam alloy. The Nd:YAG laser energy was 100 mJ at wavelength 1064 nm, plasma emissions are accumulated with delay 2.5 μ s, and gate width 10 μ s.

Figure (3) show zoomed window in the UV range 220 to 313 nm for tin at 224.67 nm with resolution of 0.04 nm ($\lambda/\Delta\lambda = 5617$) and signal to noise ratio SNR = 9.8 in the dental amalgam sample.

Our observed spectra reflect the wide spectral range and the high resolution of the used spectroscopic system. These improve both the reliability and reproducibility of

the used LIBS technique that needed for the quantitative analysis of the dental amalgam alloy samples.

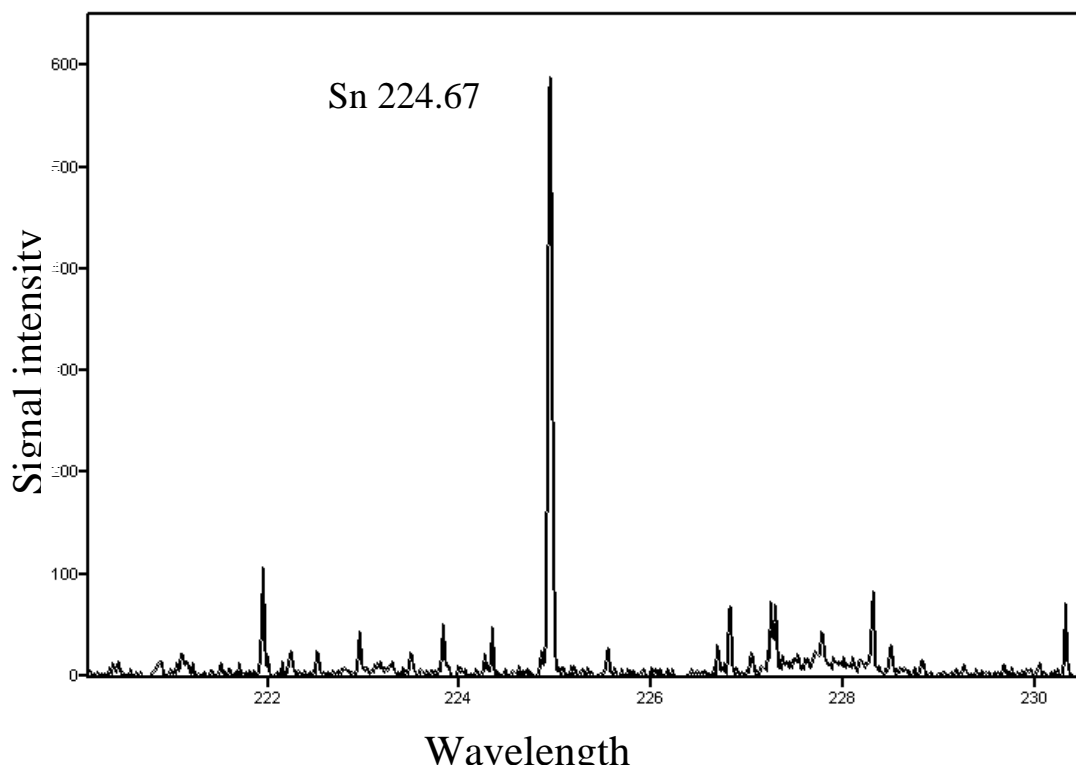


Figure 3: Zoomed window in the UV range 220 to 313 nm for tin at 224.67 nm with resolution of 0.04 nm ($\lambda/\Delta\lambda = 5617$) and signal to noise ratio SNR = 9.8 in the dental amalgam sample.

Quantitative analysis and Calibration curves

Based on our qualitative investigation of the dental amalgam alloy samples by LIBS, we are now in a position to determine the most suitable conditions for the quantitative analysis of mercury in dental amalgam alloys. Here below, we tried to avoid the experimental fluctuations and all types of interferences to observe calibration curves for the trace elements with good linearity and lower detection limits.

The wavelength of the spectral line used throughout the analysis of mercury was 253.65 nm. Figure (4) show the calibration curve of mercury obtained by drawing the Hg emission intensities against their relative concentrations. Each data point represents the mean value of typically five individual measurements. The given error bars show the calculated standard deviation for the measured LIBS intensities for each trace content of the dental amalgam alloy sample. They represent the variation in our measurements.

Calibration curve of mercury in the dental amalgam matrix pass nearly through the origin and have well linear fitting ($R^2 = 0.9346$) within the experimental uncertainty.

The obtained linear equation ($y = 305079x - 15321$) and the correlation coefficient R^2 indicate that the proposed LIBS technique has a capability for a good linearity of the calibration curve attaining a wide range of Hg concentrations in dental amalgam.

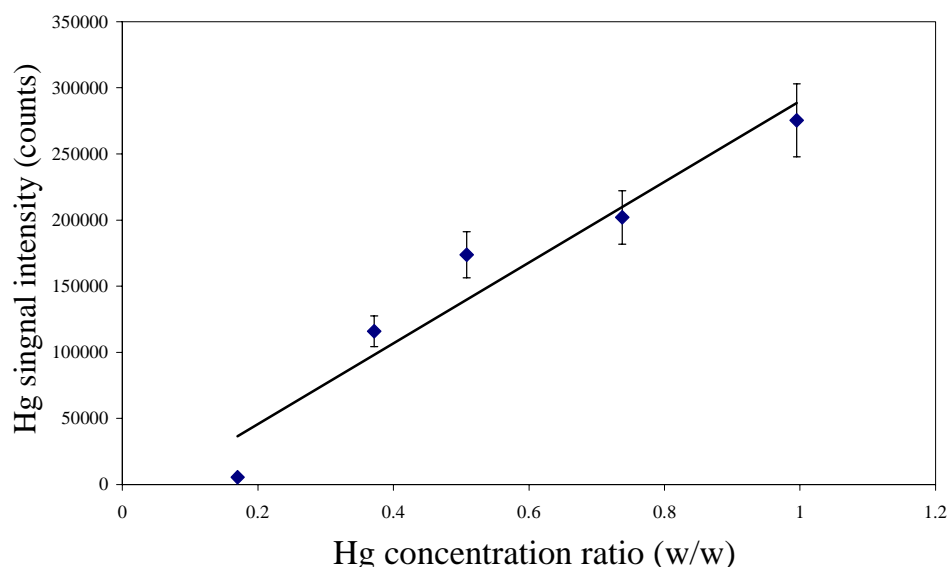


Figure 4: calibration curve of mercury obtained by drawing the Hg emission intensities against their relative concentrations in dental amalgam alloy. Each data point represents the mean value of typically five individual measurements. The given error bars show the calculated standard deviation for the measured LIBS intensities for each trace content of the dental amalgam alloy sample.

The limit of detection was calculated from the formula [13]

$$\text{LOD} = 3 \sigma / s$$

Where σ is the standard deviation of the background and s is the calibration slope. The obtained LOD value and the relative standard deviation (RSD %) for Hg in dental amalgam alloy are 2.9 ppm and 7.5 % respectively.

These obtained results show the capability of the proposed LIBS setup for in-stiu real time analysis of Hg in dental amalgam with good sensitivity and high precision.

Conclusion

In summary, we have carried out an accurate LIBS setup using portable commercial Echelle spectrometer equipped with ICCD detector for qualitative analysis of platinum modified non gamma 2 spherical dental amalgam alloy samples. Mercury is quantitatively analyzed with good sensitivity and high precision.

Moreover, the proposed LIBS setup represents no-contact technique capable of remotely analyzed the dental amalgam samples contents in few minutes using one

meter length fused-silica optical fiber. All of these, facilitate it to be used for in-situ real time medical applications monitoring and follow up mercury content in dental amalgam alloy.

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