Preparation of dental amalgam and spectral diagnosis of mercury in plasmas-laser in the region of 250 nm - 850 nm

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Abstract. In this paper we presents results of the spectral study of plasmas-laser of dental amalgam by technique Laser-induced Breakdown Spectroscopy (LIBS). Plasmas were generated focusing the beam of a Nd: YAG laser on the matrix of the mixture Ag-Sn-Cu and on amalgams with different proportions of mercury (3:2, 5:2, 6:2). Based on the spectral results and reported atomic parameters, became estimation of electron temperature plasmas- laser and their behavior with the concentration of Hg. The estimated values of the electron temperature for the respective proportions were 20 846 K, 19 139 K and 16 872 K, using the distribution of population of Boltzmann energy levels associated with spectral lines, considering conditions Local Thermodinamic Equilibrium (LTE) of plasmas.

1. Introduction

Technique Laser-Induced Breakdown Spectroscopy (LIBS) is a powerful method in spectroscopic by detection and quantification of chemical species in materials solid, liquid or gaseous phases, which analyzes the spectrum of radiation emitted by the breakdown or plasma generated by laser radiation. These plasmas-laser are a great source of spectral information from which we study different effects and physical processes that occur inside the plasma. In addition, they provide information of your response and behavior under the action of external electric and magnetic fields [1-3]. In this work the technique LIBS was employed for the study of alloys prepared in laboratory similar to mercury-based dental amalgams.

Mercury is a hazardous material for the health and the environment [4-6]. It is a heavy metal that at room temperature is liquid with a high density of 13.55 g/cm³ at 25 °C. These properties of mercury liquid make difficult the obtaining of LIBS Spectra due to splash of liquid in the process of interaction of radiation with material, and other hand, with the increase of the temperature above 40 °C is generated toxic and corrosive vapor of mercury that requires careful handling. Failing that, due to its ease of alloyed with other metals, which melted at room temperature assume a crystalline form with certain properties, manufactured tablets with alloys composed of liquid mercury, Silver, Tin and Copper (amalgam), on which the laser plasmas were generated.

Because to its mechanical and thermal properties, amalgams are still used by dentists for filling and curing of dental caries. The amalgam is a metallic alloy grey composed of mercury liquid (50%) and matrix (50%), which is composed of silver (45%), copper (24%), Tin (31%), and sometimes zinc. The mercury reacts chemically with other metals creating a malleable paste that hardens with certain speed adhering in the dental cavity and facilitating the restoration of the damaged tooth. The mercury in dental amalgams is in its crystalline form that is little toxic. The mercury in dental amalgams is in its
crystalline form is slightly toxic. However, practically the mercury evaporates at room temperature generating mercury vapour highly toxic to human health. Therefore, it is possible that dental amalgams in teeth of people release certain amount of mercury vapor to consume drinks and food hot over 40 °C [7].

The plasmas-laser were formed on the solid matrix composed of Ag-Sn-Cu and on solidified amalgams mercury containing with different proportions or concentrations. The laser plasmas spectra were registered and analyzed in the spectral region of 250 nm to 900 nm. As expected, we identified atomic and ionic lines of the elements belonging to the matrix, whereas the amalgam spectra revealed additionally of mercury lines, without the presence of other impurities. The spectral analysis of the results shows on the one hand an excellent quality of purity of the commercial materials used for preparation of dental amalgam, and a good method of preparation samples. As regards the analysis of spectra, there is evidence of a clear increase in the intensity of characteristic lines of neutral mercury (Hg I) with the increase of the amount of mercury in different proportions employed (3:2, 5:2 and 6:2); we observed also an intensification and a shift in some lines of Sn I in the spectra of the amalgam by effect of the addition of mercury, respect to the same lines in the spectra of the matrix without the presence of mercury. Based on the spectral measurements, and reported atomic parameters from characteristics lines of the elements used, was made estimation of the electron temperature of plasmas in conditions of Local Thermodynamic Equilibrium (LTE) and their behavior with the concentration of mercury [8].

2. Amalgam preparation and experimental description

The preparation of tablets of dental amalgam in the laboratory was an appropriate alloy with materials for dental purposes in healing or filling of dental caries, acquired in the commercial distributors, using a mechanical amalgamator. For the preparation of amalgam we used a powder mixture containing Ag, Sn and Cu which is introduced into the amalgamator together with liquid mercury for one minute. The soft paste (amalgam) is introduced rapidly into a plastic cylindrical tube that to harden takes the form of a small disc of variable diameter and thickness, which depends on the amount of materials used and the diameter of the cylindrical tube. The induced plasmas-laser (LIP) or plasmas-laser were generated on the samples always at the same focal position of the focusing lens of the laser radiation to guarantee the same excitation conditions and the formation of plasmas. Because to their chemical and structural properties liquid mercury is attached only on the surface of the solid, which is desirable as a restorative dental material and for purposes LIBS.

In this work, we implement methods of the LIBS technique [9] which can be applied for monitoring almost in real-time of mercury in dental amalgams. Plasmas-laser of the matrix Ag-Sn-Cu and of the amalgams were generated on the surface of samples focusing with a lens of 10 cm focal length the radiation of a pulsed Nd: YAG laser operating at 532 nm, at a maximum energy 80 mJ per pulse, duration of pulses of 3-5 ns and a frequency of 2 Hz. For the registration of spectra, the plasmas-laser radiation was conducted by an optical fiber grade UV-vis to the entrance slit of a optical spectrograph mounting Czerny-Turner of 0.25 m focal distance, equipped with a diffraction grating of 1200 grooves/mm, which produces a spectral resolution of 0.25 nm in the first order, and a CCD linear array of 2048 pixels. The spectra were processed and averaged with Spectral Array software with integration times for taking the spectra of 400 ms and 10 scans. In order to ensure the reproducibility of the plasmas-laser, the pellets were mounted on a positioning system based on stepper motors that allowed zoom out or zoom the sample of the focus point of the lens with a precision of 0.005 mm and/or rotate it with a resolution of 0.6 degrees. As a source calibration of the system was used a spectral lamp Hg/Ar calibration that emits lines of 250 nm to 950 nm. During acquisition of spectra interference filters were used to avoid overlapping of spectra of superior orders and Noch filter at the entrance of the spectrograph to reduce the reflected or scattered laser radiation at 532 nm.
3. Results and discussion

Figure 1 shows a superposition of the spectra of the plasmas-laser of the matrix Ag-Sn-Cu (bottom) and the amalgam based on mercury (upper) in the region centered at 300.009 nm. In this region the spectra show atomic lines of neutral atoms Ag I, Sn I, Cu I, Hg I and the line 335.208 nm of Tin once ionized Sn II. In this sector also observed a shift towards long wavelengths of the Sn I lines in the spectrum of amalgam respect to the same line in the spectrum of the matrix. This fact we attribute to the presence of mercury atoms in the plasma formed, which come to play an important role in the process of interaction between the particles and electric fields.

![Figure 1](image1.png)

**Figure 1.** Spectra of plasmas-laser the matrix Ag-Cu-Sn (lower), and mercury-based dental amalgam (upper) in the spectral region centered at 300,009 nm.

The linear fit of the experimental points in figure 2 show the trend of the increase of the relative intensity of the characteristic lines 364.921 nm and 404.976 nm of Hg I, with increasing the amount of mercury employed in different proportions in the manufacture of amalgams (3:2, 5:2 and 6:2). With previously established calibration curves, the LIBS technique can be applied successfully by professionals in dentistry for the monitoring of the concentration of mercury in the manufacture or commercial dental amalgam [10].

![Figure 2](image2.png)

**Figure 2.** Graph relative intensity of lines 404.976 nm and 364.921 no of Hg I in term of the concentration of mercury in the amalgam.
Figure 3 shows the behavior of the electron temperature of plasmas of amalgams to the different proportions of Hg used (3:2, 5:2, 6:2). Each experimental point on the curve represents the electron temperature calculation using the ratio of relative intensities of the lines 364.921 nm and 404.976 nm of Hg I. The other atomic parameters: coefficients of probability, statistical weights, and energy of the upper levels of the transitions were obtained from the database [11]. The estimated values of the electron temperature for the respective proportions were 20,846 K, 19,139 K, and 16,872 K, using the Boltzmann population distribution of energy levels associated with spectral lines in conditions of Local Thermodynamic Equilibrium (LTE) of plasmas.

![Behavior of the electron temperature of plasmas the amalgams in the proportions of mercury (3:2, 5:2 and 6:2).](image)

4. Conclusions

The analysis of the spectra of the matrix Ag-Sn-Cu and the mercury-based amalgam, reveals that the commercial materials used for dental amalgams are of excellent quality and free from impurities which were not detected with the established LIBS technique. The spectral results show that with the LIBS technique can be able to monitor mercury in almost real time in dental amalgam employed by dentists in curing tooth and restoration of teeth.

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