

Semiquantitative analysis of mercury in landfill leachates using double-pulse laser-induced breakdown spectroscopy

CARLOS R. MENEGATTI,¹ GUSTAVO NICOLODELLI,² GIORGIO S. SENESI,³ OTAVIO A. DA SILVA,¹ HÉLCIO J. I. FILHO,¹ PAULINO R. VILLAS BOAS,² BRUNO S. MARANGONI,⁴ AND DÉBORA M. B. P. MILORI^{2,*}

¹School of Engineering of Lorena, São Paulo University, P.O. Box 116, Lorena, São Paulo 12602-810, Brazil

²Embrapa Instrumentation, São Carlos, SP BR-13560970, Brazil

³CNR, Istituto di Nanotecnologia (NANOTEC), PLasMI Lab, Via Amendola 122/D, 70126 Bari, Italy

⁴Physics Institute, Federal University of Mato Grosso do Sul, P.O. Box 549, Campo Grande, MS 79070-900, Brazil

*Corresponding author: debora.milori@embrapa.br

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Laser-induced breakdown spectroscopy (LIBS) is showing to be a promising, quick, accurate, and practical technique to detect and measure metal contaminants and nutrients in urban wastes and landfill leachates. Although conventional LIBS presents some limitations, such as low sensitivity, when used in the single pulse configuration if compared to other spectroscopic techniques, the use of the double-pulse (DP) configuration represents an adequate alternative. In this work DP LIBS has been applied to the qualitative and quantitative analysis of mercury (Hg) in landfill leachates. The correlation analysis performed between each intensified charge-coupled device pixel and the Hg concentration allowed us to choose the most appropriate Hg emission line to be used for its measure. The normalization process applied to LIBS spectra to correct physical matrix effects and small fluctuations increased from 0.82 to 0.98 the linear correlation of the calibration curve between LIBS and the reference data. The limit of detection for Hg estimated using DP LIBS was 76 mg Kg⁻¹. The cross validation (leave-one-out) analysis yielded an absolute average error of about 21%. These values showed that the calibration models were close to the optimization limit and satisfactory for Hg quantification in landfill leachate. © 2017 Optical Society of America

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1. INTRODUCTION

The issue of urban waste disposal is a major environmental concern faced by modern society. With the intensification of industrial processes combined with population growth and the consequent demand of consumer goods, large quantities of waste are produced, which in most cases are addressed to landfills. In landfills, wastes undergo physical, chemical, and biological decomposition producing gaseous and liquid waste fractions. In particular, the liquid fraction, that is, the leachate [1] resulting from waste decomposition combined with rainfall, is affected by landfill temperature and the composition of the waste deposited. The action of bacteria accelerates the decomposition of waste, while percolating rainwater carries the degradation products to the lower layer of the embankment. The landfill percolate has a variable chemical composition containing large amounts of organic matter and various heavy metals [2,3], thus making it very dangerous for the surrounding environment. The landfill flow may contaminate the underlying soil

and also closer water bodies. Thus, monitoring landfill leachate for the presence and concentration of contaminants is crucial in order to take necessary precautions and apply appropriate treatment measures.

One of the most toxic and hazardous element that may be found in landfill leachate is mercury (Hg), which can be present in three forms: elemental or metallic, inorganic, and organic [4]. The concentration of Hg in municipal waste landfill leachates is evaluated to fall in the range from 0.05 to 160 µg/l [5,6,7]. Currently, the analytical techniques available to determine the concentration of metal contaminants, such as Hg, in landfill leachates include atomic absorption spectroscopy, x-ray fluorescence, inductively coupled plasma atomic emission spectroscopy (ICP-AES), and inductively coupled plasma mass spectrometry [8,9]. Although these techniques are precise and have good limits of detection (LOD) [10], they are relatively time consuming and generate waste. Further, these techniques require a very accurate sample preparation that makes

the whole process very laborious, thus resulting in the impossibility to measure real-time, *in situ* metal contaminants in the leachate.

Laser-induced breakdown spectroscopy (LIBS) is a robust, reliable, and simple alternative analytical technique that has been adapted and improved in the years to analyze solid, liquid, aerosol, and gaseous materials in various experimental conditions and is also by, portable instruments, suitable for real-time, on-site analysis [11]. LIBS has been applied in several fields, including the determination of heavy metals in agri-environmental samples like soils and fertilizers [12–16], remote analysis [17], analysis of hazardous materials, and the composition of Mars surface [18].

In particular, in recent years, some improvements have been made for Hg determination by single-pulse (SP) LIBS in solid, liquid, and vapor samples. For example, Srungaram *et al.* [19] used a conventional LIBS apparatus operating at the fundamental wavelength of 1064 nm for Hg analysis in soils with a LOD of 483 mg Kg⁻¹. Sobral *et al.* [20] obtained a LOD of 21.4 and 3.7 mg Kg⁻¹ for Hg in water and ice samples, respectively. Fang and Ahmad [21] obtained a LOD on the order of 85 mg Kg⁻¹ when analyzing the surface of a water sample. Recently, Zheng *et al.* [22] obtained a LOD of 0.36 mg Kg⁻¹ for Hg in aqueous solutions. As a result of these works, it appears that the LOD of Hg obtained by LIBS, especially in solid samples, still needs to be improved. Although LIBS presents some limitations if compared to other spectroscopic techniques [23], such as low sensitivity, the use of double-pulse (DP) LIBS, as an alternative to SP LIBS, has been shown to improve the analytical performance of LIBS [16].

In this work the DP LIBS technique was applied for semi-quantitative analysis in landfill leachate samples doped with HgSO₄, simulating highly contaminated environmental samples. A correlation analysis and a normalization procedure were performed to assist in the choice of an appropriate Hg emission line and to develop a feasible quantification model. The ionic emission line Hg II (194.163 nm) was analyzed as an alternative for the conventional atomic emission line Hg I (253.65 nm) interfered by Fe I (253.56 nm) and Fe II (253.66 nm) emission lines in these samples. To the best of our knowledge, no papers have been published in the scientific literature on the application of DP LIBS to the determination of Hg LOD in landfill leachates.

2. EXPERIMENTAL PART

A. Sample Preparation

The leachate sample was collected in the landfill of Cachoeira Paulista, São Paulo, Brazil, and subjected to a distillation process to obtain a semisolid residue. Generally, the distillation or evaporation process can be used as an alternative technique for the treatment of leachates. The purpose of these techniques is to separate the leachate solution into a nonvolatile solute (concentrate) and a volatile solvent (water vapor and N – NH₃ fractions). Solid compounds and metals are concentrated after distillation. The semisolid residue was then dried in an oven at 120°C. The overall process reduces the mass of residual liquid to approximately 2% of the initial value, thereby increasing by 50 times the concentration of the sample. Once we have

obtained this solid residue, an ICP-AES analysis of Hg was performed, which yielded an Hg concentration lower than the limit of quantification of the equipment, which is approximately 1 × 10⁻⁴ mg kg⁻¹. Thus, the original solid sample was mixed with appropriate amounts of HgSO₄ to obtain 10 samples with an Hg concentration ranging from 50 to 1000 mg Kg⁻¹. After homogenization in a mortar, two pellets were prepared for each sample by pressing the powders at 8 ton for 30 s. The pellets were then heated for 1 h at 60°C to remove excessive moisture and ensure that they were completely dried.

B. DP LIBS Experimental Setup

The LIBS system used was composed by two Nd:YAG lasers operating at wavelengths of either 1064 nm (IR) or 532 nm (VIS). In particular, a Q-switched Nd:YAG laser (Quantel, Ultra) with a pulse duration of 6 ns, a repetition rate of 20 Hz, and a maximum pulse energy of 75 mJ was used to generate the IR pulse (Fig. 1). Another Q-switched Nd:YAG laser (Quantel, Brillant), coupled with a second harmonic generator module, with a pulse duration of 4 ns, a repetition rate of 20 Hz, and a maximum pulse energy of 180 mJ, was used to generate the VIS pulse. A 400-Butterfly Aryelle system was used to detect and select the wavelengths. The spectrometer operated in two spectral bands, 175–330 and 275–750 nm, with a spectral resolution of 13–24 and 29–80 pm, respectively, and was provided with an intensified charge-coupled device camera with 1024 × 1024 pixels.

Two laser beams with a total power density (laser VIS + laser IR) of approximately 2.0 × 10¹² Wcm⁻² were used for the acquisition of DP LIBS spectra in the collinear geometry configuration. The beams were focused and aligned by dichroic mirrors to hit the target sample in the overlapping mode with a delay between them. To optimize the signal-to-noise ratio, the variations of delay time and interpulse delay (from 300 to 1000 ns) were investigated preliminarily by performing 10 measurements for each configuration at different positions on the surface of each sample. The best performing values obtained from five accumulated pulses were an interpulse delay of 800 ns and a delay time of 1 μs with a width gate of 10 μs. To get an efficient collection of emitted plasma, two silica lenses used at the optical position were placed between the sample and the tip of the fiber. The sample support was placed in a micro-controlled x – y stage for an easy and fast scanning of the laser beam impinging on it. The LIBS spectral background was

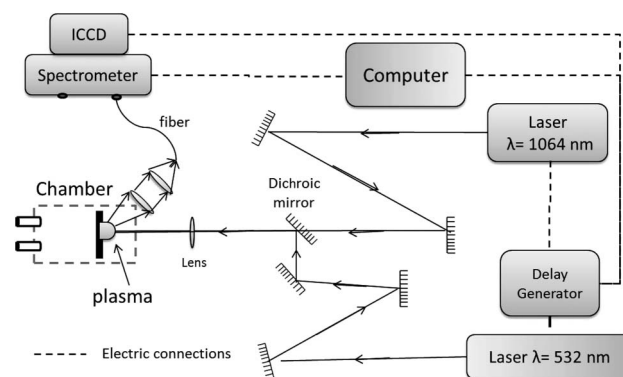


Fig. 1. Schematic diagram of the experimental setup.

corrected by subtracting the average noise region near the element emission line. Results were based on the averaged areas obtained from the Gaussian fit for one peak emission in each spectrum.

C. Spectral Processing

A correlation analysis approach was implemented to identify the emission lines, that is, for each sample a specific pixel was selected in the averaged spectrum, and a Pearson's linear correlation between the pixel intensity and the Hg concentration was determined [13]. Thus, if the pixel intensity increases as the Hg concentration in the sample increases, the correlation number results are positive. The closer to 1 the correlation results, the greater the chances for an Hg electronic emission line to be in that spectral region. By performing the analysis for all pixels in the spectrum, the regions containing the Hg emission line can be identified.

In LIBS, the area below the emission peak of the spectrum is usually correlated with the concentration of a specific element. Using an appropriate model, it is possible to obtain a calibration curve that improves the Pearson's linear correlation coefficient to get values close to 1. The validation model used in this work is based on the leave-one-out cross validation process, which consists in extracting one sample from all samples and using the remaining ones to build the calibration model. The excluded sample (called unknown data) is then used to test the quantification efficiency of the calibration curve obtained by converting the peak area in a predicted Hg concentration. In this way, the peak area and the calibration curve are used to obtain the Hg concentration predicted by the model. This value is then compared to the value of Hg in the leachate measured by the reference technique, which, in turn, generates the prediction error value. The process is then repeated for all samples so that an average prediction error can be recorded. This value can be considered a direct measure of the elemental quantification efficiency of the DP LIBS technique for the determination of Hg in the leachate.

3. RESULTS AND DISCUSSION

Figure 2(a) shows a typical LIBS spectrum of the sample containing 1000 mg Kg^{-1} Hg acquired by the DP LIBS in the region 175–330 nm. According to the literature [22,24,25,26], the most used emission line for Hg analysis by LIBS is the atomic Hg (I) line at 253.65 nm, which is shown in the expansion in Fig. 2(b). This emission line of Hg does not allow us to build an acceptable quantification model because of the poor correlation resulting between this Hg line and the known Hg concentration, which is reasonably caused by interferences of the very close Fe II and Fe I lines. Any attempt to eliminate this interference was unsuccessful because of the high amount of Fe in the samples, of the order of 200 mg Kg^{-1} .

In order to find a better Hg emission line to be used in the quantification model, the “peak finding” algorithm was applied to the spectra by which each pixel was compared with the actual Hg concentration in the samples. The correlation graph obtained (Fig. 3) indicated that the highest correlation value ($R = 0.65$) was featured by the 194.163 nm pixel [Fig. 1(c)], which corresponds to the ionic Hg emission line (Hg II,

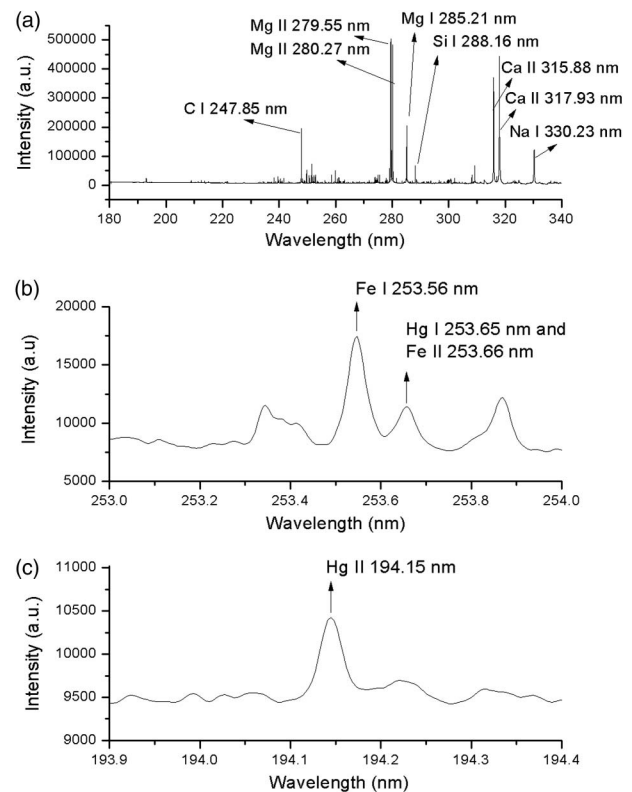


Fig. 2. (a) LIBS spectrum of the sample containing 1000 mg Kg^{-1} Hg acquired by DP LIBS in the region 175–330 nm; (b) expansion of the spectrum in the region 253–254 nm showing the Fe I (253.56 nm), Hg I (253.65 nm), and Fe II (253.66 nm) emission lines; (c) expansion of the region 193.9–194.4 nm showing the Hg II (194.163 nm) emission line.

$5d^{10}6s(2S_{1/2}) \rightarrow 5d^{10}6p(2P_{1/2})$, $A = 7.5 \times 10^8 \text{ s}^{-1}$) according to the NIST database [27]. It is important to note that when using SP LIBS measurements it was not possible to observe the Hg II emission line at 194.163 nm in all samples, and at 253.65 nm no signal was observed below an Hg concentration of 500 mg Kg^{-1} . The inset graphic in Fig. 3 shows the poor correlation resulting between the atomic Hg(I) line at 253.65 nm and the known Hg concentration.

The correlation of the Hg II 194.163 nm emission line was surrounded by a background noise region (Fig. 3) that can be due to a combination of factors, which include the low number of samples analyzed (10 in total), the fluctuation of the DP-LIBS system, and the low intensity of the Hg II emission line. Thus, a Gaussian function was fitted to the emission line (Fig. 4) in order to extract the information from it by applying a baseline correction to eliminate the non-negligible background fluctuation and improve the correlation between the LIBS signal and Hg concentration in the matrix. The LIBS signal area was corrected on the basis of the average of a background region selected nearby the emission line using the following equation:

$$A = A_L - \alpha * A_B, \quad (1)$$

where A_L is the area extracted from the fitted Gaussian curve in Fig. 3, A_B is the averaged background and α is an optimization

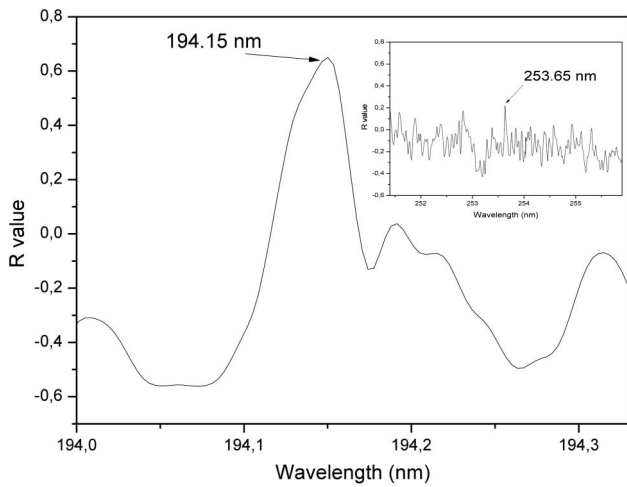


Fig. 3. Correlation graph for Hg. Each pixel was linearly correlated with the Hg content in the samples.

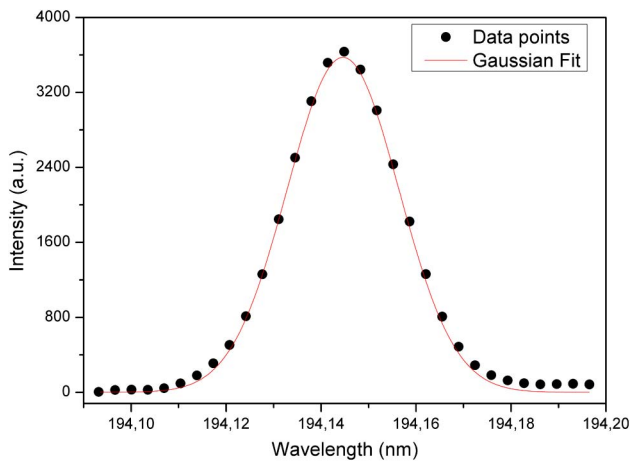


Fig. 4. Gaussian function fitting data of the Hg II peak emission line in the sample containing 1000 mg Kg⁻¹ Hg.

factor. The α parameter was optimized by performing a linear fitting for the best Person's coefficient in the calibration model. To evaluate this model the value of A was linearly correlated with the Hg concentration in the landfill leachate matrix. The model details can be found in a previous paper [13]. Figures 5(a) and 5(b) show that a much better correlation ($R = 0.98$) could be obtained when the normalization process using Eq. (1) was applied to LIBS spectra to correct physical matrix effects and small fluctuations, with respect to the correlation obtained when no correction was applied ($R = 0.82$).

The LOD is a measure of the lowest concentration of the element that can be detected by a technique and is calculated according to the following equation [28]:

$$\text{LOD} = 3.3 \frac{\sigma}{b}, \quad (2)$$

where σ is the standard deviation of the background for the lowest concentrate sample and b is the slope of the calibration

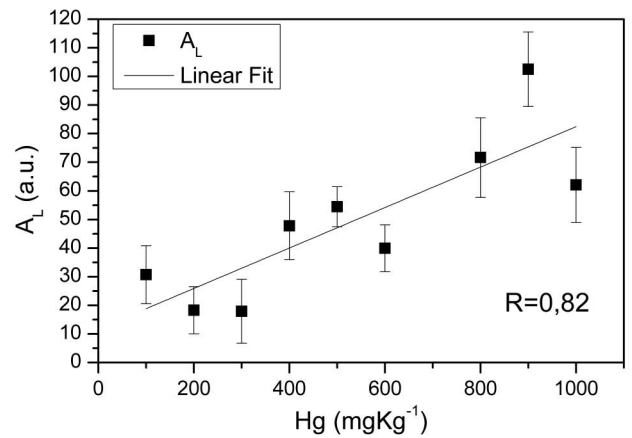
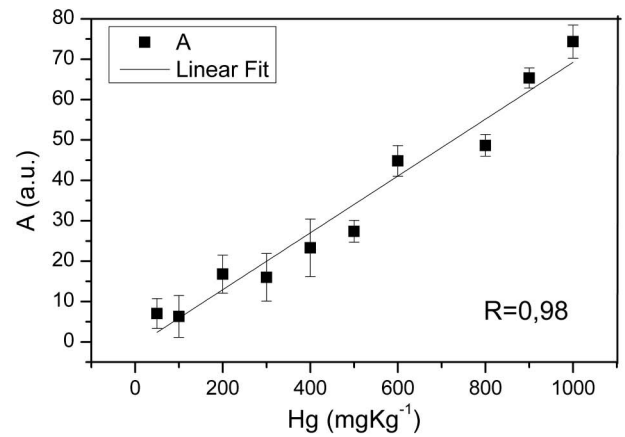


Fig. 5. Calibration curve for Hg concentration in landfill leachate using (a) the signal area corrected by Eq. (1), A and (b) the non corrected signal area A_L .

curve. In this experiment, σ was calculated using the averaged background intensity of the pixels close to the chosen emission line peak and b was extracted from the slope of the calibration model using all samples. The LOD of Hg II at 194.15 nm was calculated to be 76 mg Kg⁻¹, which is about six times lower than that obtained in previous studies on solid samples such

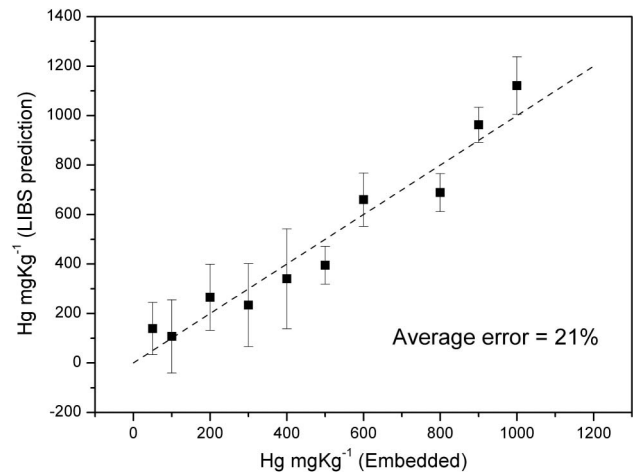


Fig. 6. Leave-one-out cross validation graph.

as soils [19]. The improvement of the detection sensitivity can be ascribed mainly to the use of the DP LIBS, which also allowed us to use the 194.163 nm Hg emission line. However, even if this line is relatively weak compared to the Hg emission line commonly used in other works, the advantage is that this line does not suffer from interference by other elements, allowing the use of a simplified correction model.

Figure 6 shows the result of the leave-one-out cross validation process described in Section 2.C. The average mean error calculated was 21%, which is a value adequate for Hg quantification in landfill leachates.

4. CONCLUSIONS

This work reports for the first time the performance of DP LIBS in the analysis of the toxic metal Hg in landfill leachates. The DP LIBS technique allowed us to detect and use the 194.163 nm Hg II emission line to build a quantification model for Hg. The use of this emission line appears to be a good alternative to eliminate interference by other elements, that is, the Fe I 253.56 nm and Fe II 253.66 nm peaks that have an emission line very close to Hg I (253.65 nm). Because of this interference, it was not possible to construct a reasonable correlation model using Hg I at 253.65 nm. Differently, the emission line of Hg II at 194.163 nm under optimized experimental conditions allowed us to build a model that improved from $R = 0.82$ to $R = 0.98$ the linear correlation between LIBS data and the actual Hg concentrations, with a consequent reduction of the mean error to 21% with a LOD of 76 mg Kg⁻¹.

In conclusion, LIBS is confirmed to represent a promising alternative to the traditional analytical techniques that require sample preparation and the use of chemical reagents for the measurement of trace Hg in landfill leachates. Further, it can be reasonably expected that LIBS instrumentation implementations, such as the resonant excitation and the discharge excitation, would improve further the limits of detection and quantification offered by LIBS.

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