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Discrimination between authentic and false tax stamps from liquor bottles using laser-induced breakdown spectroscopy and chemometrics

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ABSTRACT

This work describes the preliminary application of a compact and low-cost laser-induced breakdown spectroscopy (LIBS) instrument for falsification detection of tax stamps used in alcoholic beverages. The new instrument was based on a diode-pumped passively Q-switched Nd:YLF microchip laser and a mini-spectrometer containing a Czerny–Turner polichromator coupled to a non-intensified, non-gated, and non-cooled 2048 pixel linear sensor array (200 to 850 nm spectral range). Twenty-three tax stamp samples were analyzed by firing laser pulses within two different regions of each sample: a hologram and a blank paper region. For each acquired spectrum, the emitted radiation was integrated for 3000 ms under the continuous application of laser pulses at 100 Hz (integration of 300 plasmas). Principal component analysis (PCA) or hierarchical cluster analysis (HCA) of all emission spectra from the hologram or blank paper region revealed two well-defined groups of authentic and false samples. Moreover, for the hologram data, three subgroups of false samples were found. Additionally, partial least squares discriminant analysis (PLS-DA) was successfully applied for the detection of the false tax stamps using all emission spectra from hologram or blank paper region. The discrimination between the samples was mostly ascribed to different levels of calcium concentration in the samples.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is an analytical technique based on the application of one or more high-power, short-duration laser pulses focused on a region of the sample to be analyzed, thereby promoting its ablation and/or excitation, with the formation of a transient plasma. The emitted radiation is monitored by means of an appropriate detection system (wavelength selector and detector) and is associated with the chemical composition of the sample [1–3]. In addition to the laser source, common LIBS instrumentation also includes an optical system, to drive and focus the laser radiation onto the sample and to collect the radiation emitted by the plasma; a wavelength selector, such as an optical filter [4,5] or a grating polychromator; and a detector, such as a photomultiplier [6,7] or a solid-state sensor array. A typical setup employs an actively Q-switched Nd:YAG laser [8,9] and an echelle polychromator coupled to a bidimensional, intensified, gated and cooled charge-coupled device (ICCD camera) [10,11]. However, due to the large dimensions and high costs of these components, conventional grating polychromators associated with non-intensified linear sensor arrays [12,13] and diode-pumped passively Q-switched solid state lasers (so-called microchip lasers) [3,14,15] have also been employed in LIBS instruments.

One of the interesting fields of LIBS applications is paper analysis, with several publications related to the paper industry, archeology, and forensics, making use of some of the advantages of this analytical technique, such as fast and direct analysis, possibility of distribution analysis or profile analysis, and low sample consumption (it is practically nondestructive). Most publications have reported LIBS applications for the discrimination of paper types and inks [16–18], the identification of pigments and contaminants in historical documents [19–21], and in distribution and depth profile studies (of pigments, organic binders, and coat weight) of paper coatings [22–24]. Other specific publications include optimization studies related to the drying conditions [25] or the manufacturing process [26] of paper. However, there are still few publications reporting the use of LIBS for paper analysis in forensics and practically no publication about falsification of paper-based samples, such as currency bills or tax stamps.

According to the 2013 Tax Stamp Forum, 81 countries make use of tax stamps for tobacco-based products and/or alcoholic beverages [27] so that governments can control, monitor, and combat tax evasion and fraud related to these products. In Brazil, several types of alcoholic beverages (with ethanol content higher than 8% and volume size higher than 180 mL) that are produced nationally or imported must have a tax stamp. These stamps are produced by the National Mint and applied to the bottles by the producer or the importer of the liquors, under control of the Federal Receipt [28]. Despite all this control, the police sometimes seize liquor bottles with false tax stamps during oversight

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operations. In addition, the quality of false tax stamps has increased in the last few years, making it more difficult to combat tax evasion and fraud in the alcoholic beverages market. In this context, LIBS can provide an easy way for fast detection of false tax stamps, with no sample preparation and practically no sample destruction.

Therefore, this work presents some preliminary results obtained in the analysis of several true and false tax stamps from liquor bottles, using a compact and low-cost LIBS instrument. The obtained emission spectra were evaluated for falsification detection using chemometrics [29–31].

2. Experimental

2.1. Instrumentation

A compact and low-cost LIBS analyzer was employed in this work. It was developed using a Standa STA-01-8 microchip laser, a Quantum Composers Sapphire 9212 digital pulse generator, a Thorlabs LMH-10X-1064 microscope objective lens, a fused silica collimating lens, a 100 μm core diameter optical fiber cable, a B&W Tek Exemplar LS mini-spectrometer, and a sample holder coupled to a Standa 8MT30-50 translation stage. The laser was a diode-pumped passively Q-switched Nd:YLF one with a 1053 nm wavelength, 600 μJ pulse energy, 470 ps pulse duration, and 100 Hz pulse repetition rate. The laser pulses were driven and focused onto the sample surface using the microscope objective lens, which was placed about 15 mm above the sample surface. The laser spot on the sample surface had about 80 μm diameter, giving a power density of about 2.5×10^{14} W m^{-2}. The emitted plasma radiation was collected by means of the collimating lens coupled to the optical fiber cable, which was connected to the entrance of the spectrometer. The spectrometer has a classical Czerny–Turner polychromator (25 μm entrance slit) coupled to a 2048 pixel non-gated, non-intensified, and non-cooled CCD sensor array, covering the spectral range from about 200 to 850 nm (1.2 nm resolution). The translation stage was employed for changing the sample surface region exposed to the laser pulses. The digital pulse generator was used to trigger the spectrometer at the first laser pulse of a series of laser pulses applied for the acquisition of each spectrum (discussed later). A microcomputer was used to control the laser source, the digital pulse generator and the translation stage and for the acquisition of the emission spectra. A schematic representation of the instrument is shown in Fig. 1. The instrument had a total cost of about USD$ 20,000 (in comparison with hundreds of thousands of dollars for higher resolution/sensitivity instruments) and its components can be placed within a volume as small as a backpack volume (in comparison with tenths to few cubic meters for higher resolution/sensitivity LIBS instruments).

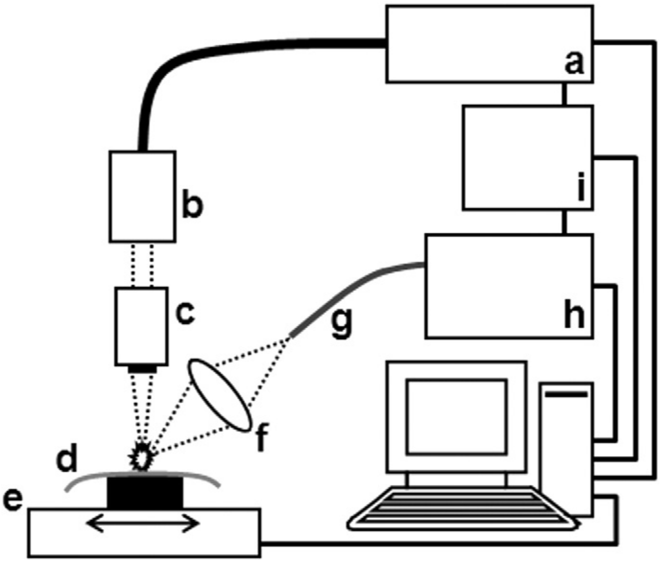

Fig. 1. Schematic representation of the LIBS instrument: (a) laser control unit, (b) laser head, (c) objective lens, (d) sample, (e) translation stage, (f) fused silica collimating lens, (g) optical fiber cable, (h) spectrometer, and (i) digital pulse generator.

2.2. Samples

Twenty-three tax stamp samples (15 authentic samples and 8 false samples) from liquor bottles were analyzed using the developed LIBS instrument. The authentic samples were collected by purchasing different types of liquor bottles randomly in local supermarkets and removing the stamps. The false samples were collected from liquor bottles seized by the Civil Police of São Paulo State during oversight operations. The authenticity of the samples (authentic or false) was previously checked by optical microscopy in comparison with admittedly authentic standards. However, this was a time-consuming analysis that required a well-trained expert. Fig. 2 shows photographs of part of one authentic (A) and two false samples (B and C). As can be seen, although there are differences between the samples, it is not easy to tell which samples are authentic or false based only on visual inspection by naked eye. The regions where the laser pulses where fired in order to acquire the emission spectra (discussed below) are also shown in the figure.

2.3. Experimental procedure

Two different regions from each sample were analyzed: a region containing a hologram (Fig. 2a) and a region of blank paper (Fig. 2b or 2c). Printed regions (containing ink) were not analyzed because different samples could have inks with different colors and the ink colors were not related to the authenticity of the samples (see Fig. 2). Each region was analyzed in five replicates by firing laser pulses on five different locations within the region. For each replicate, a single spectrum was obtained by integrating the emitted radiation for 3000 ms, under application of laser pulses at 100 Hz (integration of about 300 plasmas), continuously displacing the translation stage at 125 μm s^{-1} (100 steps of 1.25 μm per second and total displacement of 375 μm per replicate) in order to avoid the sample perforation. The five spectra of replicates

Fig. 2. Photographs of part of one authentic (A) and two false (B and C) tax stamp samples showing the sample regions used in the analysis: (a) hologram, (b) or (c) blank paper.