Analytica Chimica Acta 877 (2015) 33–40

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Analytical potential of a laser ablation–glow discharge–optical emission spectrometry system for the analysis of conducting and insulating materials

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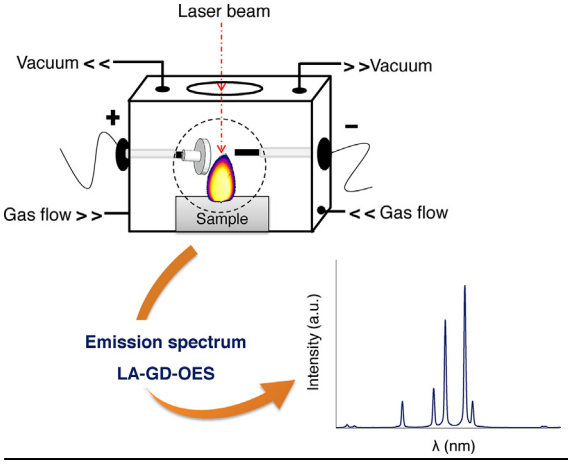
HIGHLIGHTS

- An ablation chamber to generate a GD has been designed for LA–GD–OES analysis.
- The combination of LA–GD showed signal enhancements when compared with LIBS.
- Better linear correlations and lower matrix effects have been found in LA–GD.
- Special advantages of LA–GD–OES have been demonstrated for fluorine analysis.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 January 2015
Received in revised form 8 April 2015
Accepted 16 April 2015
Available online 22 April 2015

Keywords:
Glow discharge
Laser induced breakdown spectroscopy
Optical emission spectrometry
Fluorine analysis

ABSTRACT

The analytical capabilities of a glow discharge (GD) as a secondary source for excitation/ionization of the material provided by laser ablation (LA) have been compared to conventional laser induced breakdown spectroscopy (LIBS). In LA–GD both sources can be independently adjusted to optimize the sampling process and then its subsequent excitation. This could involve a number of analytical performance advantages, such as reduced matrix dependence, greater precision and sensitivity than those encountered in LIBS. For such purpose, an ablation chamber design including two electrodes to generate the GD discharge has been built and assayed. A comparison between LIBS and LA–GD–OES has been carried out, both, under reduced argon and helium atmospheres. Different sets of samples (conducting reference materials, glass and fluorine pellets) have been used to evaluate the novel coupled technique. The LA–GD coupled system has shown to provide lower detection limits. In addition, best linear correlations between intensities and concentrations and lower matrix effects have also been found using the coupled system. Moreover, special advantages of the LA–GD–OES have also been demonstrated for the analysis of fluorine.

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http://dx.doi.org/10.1016/j.aca.2015.04.034
0003-2670/

1. Introduction

Glow discharge (GD) devices are typically used as primary spectrochemical sources for direct solid analysis with favorable analytical features, such as fast sputtering rate (in the order of $\mu m\,min^{-1}$), multi-element capabilities, low matrix effects and depth profile analysis with depth resolution in ranges of nm [1,2]. Nevertheless, the lateral resolution of the chemical information, which is obtained via cathodic sputtering of the solid sample surface, is rather poor, typically limited to the anode diameter (1–4 mm).

On the other hand, laser induced breakdown spectroscopy (LIBS) is widely employed for solid elemental analysis due to its important advantages such as little or no sample preparation and good lateral resolution (~~μm), allowing analysis of small selected areas [3]. LIBS permits the analysis of a wide variety of solid materials such as metal alloys, glasses, geological and environmental samples, or pieces of cultural heritage, as well as gases or liquids [4,5]. Conversely, comparatively poor depth resolution (currently limited to a few hundred nanometers) and severe matrix effects in quantitative analysis are well established drawbacks of LIBS.

Plasma characteristics in LIBS are dependent on the chemical composition of the sample, laser parameters, the specimen surface conditions as well as on thermal and optical properties of the sample. Even though, quantitative analysis without calibration standards (based on the measurement of line intensities, plasma properties and on the assumption of a Boltzmann population of excited levels) have been proposed [6]. However, the full exploitation of such "calibration-free" approaches are still far from real life applications, especially due to the lack of a complete and proper characterization of the effects of experimental constraints.

To minimize matrix effects, different approaches have been developed. For instance, standardization methods using internal standards to avoid unwanted experimental fluctuations [7] or matrix-matched calibration using reference samples with a similar matrix composition have been used [8]. However, in many cases it is impossible to have an internal standard of known concentration, or no standards are available. Thus, analytical procedures based on chemometric algorithms and multivariate statistical techniques have also been proposed [9,10]. These latter methods still required the use of standards, followed by a certain type of correction or data treatment algorithm in order to extract useful quantitative information from LIBS analysis. Furthermore, double-pulse and the coupling of laser ablation (LA) to LIBS have also been suggested as an alternative strategy to reduce the well known sample matrix dependency in quantitative analyses applications [11].

The combination of techniques is a common practice in analytical chemistry, in order to obtain the maximum information of a given sample. To overcome matrix effects and some of the other mentioned drawbacks in LIBS, it could be possible to decouple the excitation/ionization processes from the desorption/atomization by resorting to a secondary source. A possible approach is the combination of LA with GD, where the laser vaporizes the solid samples and once in the gas phase they are efficiently excited by the GD. This arrangement allows analysis with high lateral resolution as well, overcoming one of the disadvantages suffered by traditional GDs. In this line, Tarik and Günther have explored the combination LA–GD coupled to mass spectrometry (MS), showing its efficiency as a molecular analytical technique by analyzing organic compounds [12]. In combination to optical emission spectroscopy (OES) several studies have demonstrated the capabilities of the GD to excite the ablated material. Naeem et al. proposed a LA-hollow cathode GD in helium atmosphere for the determination of minor elements (Cr, Mn and Ni) in low-alloyed steel samples using Fe as internal standard [13]. Some papers have also been published reporting the use of argon pulsed-GD. For example, the studies done by Tereszchuk et al. provided a positive indication that the coupled system can effectively be utilized to improve depth profile resolution in the depth profiling analysis of multi-layered materials [14]. More recently, the spatial and temporal distribution of plasma species produced in the LA–GD have been investigated as well [15].

In the light of such previous knowledge, the aim of the present study was to perform a detailed assessment of the analytical capabilities of a GD as secondary excitation/ionization source for the material previously ablated by a ns pulsed Nd:YAG laser in terms of detection limits (DL), calibration graphs and matrix interferences for different set of samples (conducting materials, glass and fluorine pellets). Significant analytical performance advantages could be brought about by the coupling since sampling and excitation steps are spatially and temporally separated (so they can be independently optimized). Finally, a comparison between LIBS and actual LA–GD–OES potential has been carried out, both, under reduced argon and helium atmospheres by measuring conducting and insulating materials.

2. Experimental

2.1. Instrumentation

A Nd:YAG laser (EKSPLA, NL301HT) operating at 1064 nm, with a pulse duration of 4.5 ns, was used as primary source. The laser pulse energy was set at 50 mJ/pulse using an attenuator (LOTIS-TII) and the laser repetition rate was fixed at 2 Hz. The laser beam was guided to the surface of the sample with a mirror (Newport, 10QM20HM.15) placed at 90° and a focusing lens (Newport, KPX094AR.18) with a focal length of 10 cm. The sample was located within the discharge chamber, where the processes of ablation and plasma formation occurred.

A cross-section of the discharge chamber is depicted in Fig. 1. It consists on a copper cube whose inputs/outputs are arranged symmetrically with three quartz windows (one for the incident laser and two laterals) with two gas inlets and outlets to a rotary pump. The pressure of the ambient gas (helium and argon 99.999% purity, Air Liquide) was measured with a Baratron gauge (MKS, Instruments France S.A.). Cathode and anode (made of copper) are located on two of the sides, facing on the same axis. These are coated by a high resistance insulating ceramic to prevent electrical arcing inside the chamber. One of them has a small copper disc at its end to provide a major available surface for the discharge. The

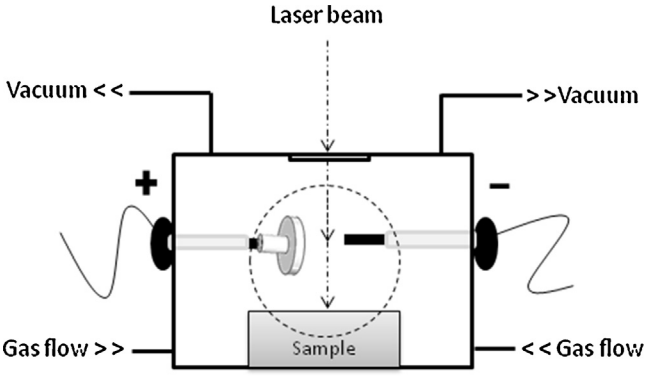

Fig. 1. Schematic cross-sectional view of the LA–GD chamber. The chamber has three quartz windows: one at the top for laser beam entrance, another (depicted as a dashed circle) to obtain plasma images with a Photron CMOS camera, and a third one at the opposite side for spectrometric detection with a Czerny–Turner system and an ICCD.