Microchemical Journal 137 (2018) 318–323

Contents lists available at ScienceDirect

Microchemical Journal

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

Comparative study of magnesium and calcium in *Codonopsis pilosula* samples detected by CF-LIBS and LCGD-AES

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ARTICLE INFO

Article history:
Received 28 September 2017
Received in revised form 16 November 2017
Accepted 17 November 2017
Available online xxxx

Keywords:
Chinese medicinal materials
Calibration-free laser-induced breakdown spectroscopy
Codonopsis pilosula
Liquid cathode glow discharge-atomic emission spectrometry

ABSTRACT

Emission spectra of *Codonopsis pilosula* samples from nine habitats were measured using calibration-free laser-induced breakdown spectroscopy (CF-LIBS) and liquid cathode glow discharge-atomic emission spectrometry (LCGD-AES). Based on the measured spectra, the elements in the samples and the corresponding compositions were determined, and the results were compared with those from inductively coupled plasma mass spectrometry (ICP-MS) by using the Mg/Ca ratios. In addition, an estimation of the plasma parameters was considered and the stability of the results from both analytical methods was discussed.

1. Introduction

Chinese medicinal materials (CMMs) have been popularly used to cure many kinds of diseases because they are not only rich in organic molecules and clusters but also contain beneficial elements for the human body, and play important roles in pharmacological functions. Recently, many studies have been performed on the elemental concentration levels in traditional CMMs and their therapeutic effects, safety and toxicity [1–3]. Clinical studies show that some CMMs exhibit very high therapeutic effects for trace element deficiencies [4]. If the elemental content of CMMs is beyond the range of being acceptable in the human body, this can also have a negative effect, especially, heavy metals exhibit significant biological toxicity, such as mercury, cadmium, lead, arsenic and chromium [5–7]. Therefore, if the heavy metal content in CMMs exceeds the recommended guidelines, it should be banned from appearing on the market [8]. At present, atomic absorption spectrometry (AAS) [9,10], inductively coupled plasma optical emission spectrometry (ICP-OES) [11] and reflection X-ray fluorescence [12] have been widely used for analyzing, processing, inspecting and sorting the CMMs. However, these methods are time-consuming owing to the complexity of sample pre-treatment, and it is hard to measure all of the elements in the same sample simultaneously. Especially, it is difficult to analyze some refractory elements [13]. It is, therefore, of great importance to determine a fast analytical technique to accurately detect the elemental content in CMMs and their products for quality and safety assessment.

In recent years, calibration-free laser-induced breakdown spectroscopy (CF-LIBS) has become a very attractive elemental analysis technique because of no complicated sample pretreatment, being almost non-destructive for samples, facilitating multi-elements analysis, and enabling fast online analysis [14]. CF-LIBS is already widely used in such fields as industrial and environmental analyses, biomedicine, and space exploration [15–22]. These advantages provide a reliable and facile method to analyze the elements in CMMs. In addition, liquid cathode glow discharge-atomic emission spectrometry (LCGD-AES), developed by our group based on the principle of discharge-atomic emission spectrometry (ELCAD-AES) [23–25], has been used for the determination of multi-metal elements in liquid samples [26,27].

Codonopsis pilosula, also known as *Dangshen*, is a traditional CMM and is widely cultivated. In this work, the *Codonopsis pilosula* samples from nine habitats were chosen, and their solid targets and liquid samples were prepared. LIBS spectra from the solid targets and LCGD-AES spectra from the liquid samples were measured. The corresponding elemental contents were determined and compared with those obtained from ICP-MS. The goal of the present work is to determine a reliable method for sample treatment and element detection of CMMs that will be useful for future classification, identification and fast sorting of CMMs.

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https://doi.org/10.1016/j.microc.2017.11.011
0026-265X/

2. Material and methods

2.1. LIBS setup

The schematic diagram of the LIBS is shown in Fig. 1. Details of the LIBS setup have been reported in our previous work [28–31]. Nd:YAG laser pulses, at a wavelength of 1064 nm with a 10 ns width, were focused on planar sample targets and used to produce plasmas. To freshly make each ablated spot, the target was positioned on a two-dimension translation stage. The space integrated emission from the plasma was collected through a 50 mm focal-length quartz lens onto the entrance slit of a spectrometer (Shamrock SR-500i, Andor Tech.) equipped with an intensified charge-coupled device detector (ICCD, iStar-DH734-18F-03, Andor Tech.). The relative spectral response of the intensity was calibrated by deuterium and tungsten halogen lamps (Avalight-D-CAL1205001). A digital delay generator (DG535, Stanford) was used to synchronize the laser pulse and ICCD detector. To suppress the background signals from the continuum plasma radiation and enhance the spectral stabilities, the optimized experimental conditions were as follows: the detection position was set at 2 mm from the target surface, the delay time and gate time were fixed to 200 ns and 2000 ns, respectively, and the emission from 10 laser shots was averaged in each measurement.

2.2. LCGD-AES setup

The schematic diagram of LCGD-AES is shown in Fig. 2 and the detailed LCGD-AES setup has been reported previously [26,27], and only a brief description is presented here. The sample solution was introduced through a quartz capillary with the aid of a peristaltic pump and flowed over the top of the capillary into the grooves on the graphite rod, which acted as the liquid cathode. Tip–gas discharge plasma was produced at the 2 mm region between the capillary and the 0.5 mm diameter platinum wire. A stable discharge was maintained using a high-voltage DC power supply (DH 1722-6, Beijing). The emission from the plasmas was focused by a 50 mm focal-length quartz lens onto the entrance slit of the monochromator (Omni-λ500, Zolix) with a 1800 grooves/mm grating. A photomultiplier (PMTH-S1-CR131) detector was operated at −1000 V. The spectral resolution of the monochromator was 0.05 nm, and the integration time was 2 ms at 0.1 nm intervals for each measurement.

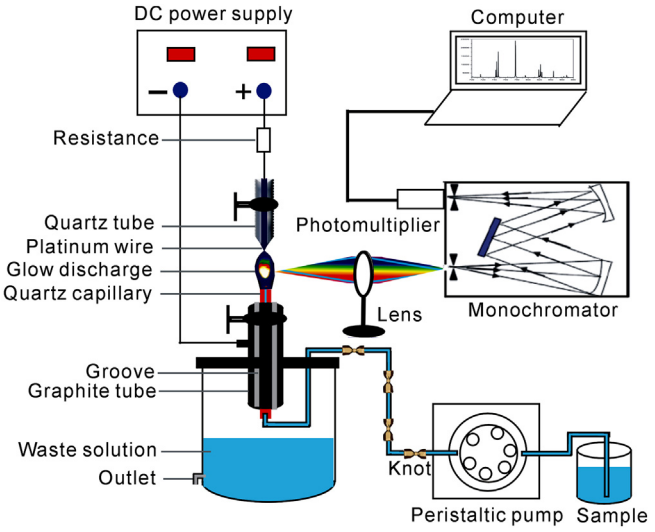

Fig. 2. Schematic diagram of the LCGD-AES experiment setup.

2.3. Sample pretreatment

In this work, nine kinds of *Codonopsis pilosula* samples, which were collected from eight provinces and nine habitats in China, were prepared. The detailed serial numbers and distributions are shown in Fig. 3. These samples were crushed into powder and filtered by using a 300 mesh sieve. Powder samples (1.0 g) were weighed and then were pressed to pellets with a diameter of 20 mm and thickness of 2.5 mm. These pellets were prepared for the LIBS measurement.

In addition, for the LCGD-AES measurement of each *Codonopsis pilosula* sample, powder samples (0.5 g), and concentrated nitric acid (5 mL, 65%) and concentrated hydrochloric acid (10 mL, 35%) were placed into a teflon digestion jar to implement the pre-digestion for 30 min at 25 °C. The temperature of the digestion instrument was gradually raised to 240 °C over 4 h, and then the acid was evaporated until the solution was near to dryness. After cooling to room temperature, the samples were transferred to a volumetric flask and made up to 50 mL with pH = 1 nitric acid solution.

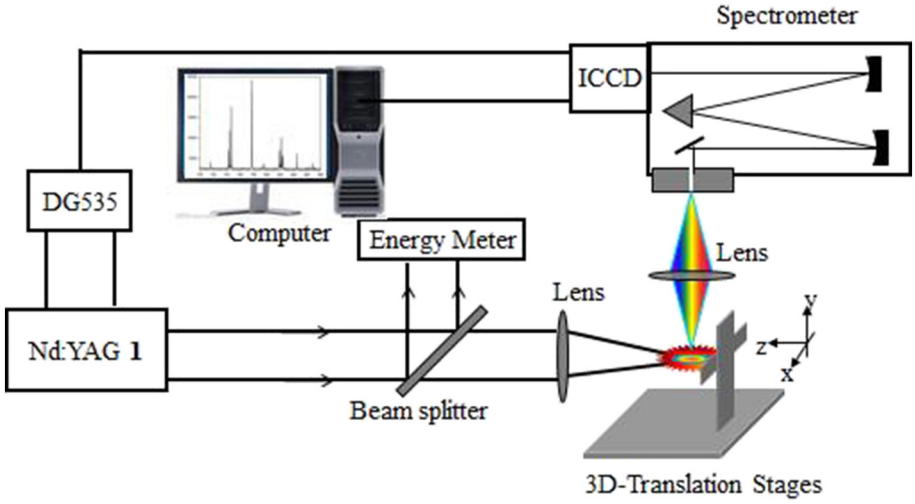

Fig. 1. Schematic diagram of the LIBS experiment setup.