

# Detection of dissolved chromium in water by laser-induced breakdown spectroscopy assisted with acoustic levitation of single droplets

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## Abstract:

LIBS assisted by acoustic levitation exhibits appealing benefits for liquid analysis, such as signal enhancement and low-volume sampling requirements. This work presents the detection of chromium in water at concentrations of 0.1 to 1 ppm.

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## 1. Introduction

Due to their high toxicity, heavy metals represent one of the most dangerous water pollutants and online water monitoring is important to prevent potential health and environmental problems. However, despite their great sensitivity, conventional analytical techniques are unsuitable for online water monitoring due to specialized facilities and the long time required for the analysis. On the other hand, optical techniques like Laser-induced breakdown spectroscopy (LIBS) represent a suitable alternative for monitoring applications in laboratory and field environments [1]. Although LIBS sensitivity is not appropriate for trace detection when applied directly to liquid samples, preconcentration methods can improve it considerably. Integrating an acoustic levitation system into LIBS represents a simple, fast, and efficient alternative to preconcentrate dissolved impurities in water to enhance their spectroscopic signal. Acoustic levitators keep single droplets in the air in a fixed position, avoiding using sample holders and containers, while water diffuses into the surrounding atmosphere achieving simple preconcentration of dissolved elements. An enhancement of 14 in the Signal-to-noise ratio (SNR) of heavy metals has been achieved when reducing the initial droplet volume of a levitated sample by a factor  $F \sim 30$ , reaching detection limits of concentrations in the order of 1 part-per-million (ppm) level [2].

In this work, we present the detection of dissolved chromium in water at concentrations between 0.1 - 1 ppm by LIBS on acoustically levitated droplets. This detection range is achieved by analyzing single water droplets after their volume reduces from  $V_i \sim 2.0 \mu\text{L}$  to  $V_f \sim 10 \text{ nL}$  providing a preconcentration factor of  $F = V_i/V_f \sim 200$ . For the experiments, a customized acoustic levitator [3], consisting of an axial cavity made of two arrays of 18 ultrasonic transducers placed on spherical caps, was integrated into a LIBS setup to suspend droplets of  $2.0 \mu\text{L}$ . After the droplet evaporation, assisted by a continuous-wave laser heating ( $\lambda = 1550 \text{ nm}$ ), the plasma is induced by a focused laser pulse ( $\lambda = 532 \text{ nm}$ ). For signal analysis, plasma emission is collected with a lens and a fiber optic coupled into a spectrometer (Shamrock 500i, Andor) attached to an ICCD camera (iStar, Andor). Fig. 1(a) shows a schematic representation of the standing wave acoustic levitator with a droplet in its center. A green arrow indicates the laser pulse propagation, fired from left to right, that hits the droplet to produce the plasma emission after dissolved chromium preconcentration, as illustrated in Fig. 1(b).

## 2. Results

The spatial stability of the levitated droplets and their alignment to the focal point of the laser are important to ensure the enhancement and reproducibility of the signal. To study these two parameters, we implemented a visual object tracking (VOT) algorithm to monitor the position and size of the droplet in real time. Our levitator provides a spatial stable levitation during its evaporation process from  $V_i \sim 2.0 \mu\text{L}$  to  $V_f \sim 10 \text{ nL}$  with a standard deviation of  $4.02 \mu\text{m}$  and  $3.57 \mu\text{m}$  in radial and axial directions, respectively. For volumes  $< 10 \text{ nL}$  levitation becomes unstable. Our VOT has a resolution of  $8.5 \mu\text{m}$  per pixel, providing good resolution for droplet alignment in these experiments. Fig. 1(c) and (d) show the VOT frames capturing the moment when the laser pulse hits the droplets

(located inside VOT red rectangles) with a diameter of  $d \sim 250 \mu\text{m}$  ( $V_f \sim 10 \text{ nL}$ ) to produce the plasma. Despite both experiments generate plasma emission, the droplet misalignment of  $40 \mu\text{m}$ , with respect to the laser optical path, produced an asymmetric plasma as shown in Fig. 1(c) and a signal decrement of 70% compared with the signal coming from the droplet aligned to the laser optical path (Fig. 1(d)).

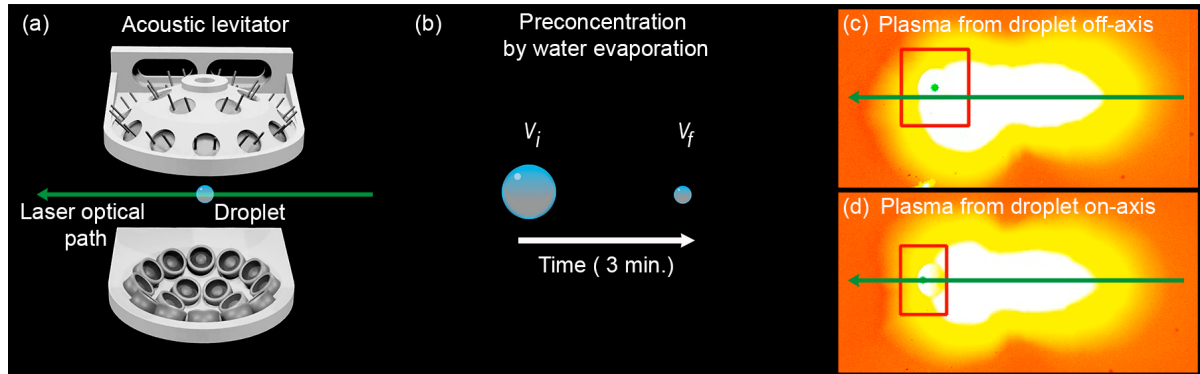


Fig. 1. (a) Schematic representation of a water droplet levitated at the center of an acoustic cavity where the laser optical path of the laser (green arrow) is aligned. (b) Plasma emission from a droplet vertically aligned to the laser optical path. (c) Plasma emission from a droplet that is  $40 \mu\text{m}$  vertically misaligned from the laser optical path.

Fig. 2(a) shows the single-shot LIBS spectrum from an acoustically levitated droplet containing Cr dissolved in water at the initial concentration of 0.5 ppm. A synthetic spectrum of Cr obtained from the NIST Atomic Spectra Database is plotted as a reference. Three Cr peaks are available in the analyzed spectral range. We avoid the most intense line in this analysis because it occasionally saturated the ICCD for 1 ppm samples. Fig. 2(b) shows LIBS spectra from acoustically levitated droplets of five solutions containing different concentrations of Cr. To improve the signal-to-background ratio (SBR), 10 single-shot LIBS spectra were averaged. In Fig. 2(c), the SBR vs the sample concentration of Cr dissolved in water is plotted from 0.1 to 1 ppm. The detection range can be improved by increasing  $F$  by increasing  $V_i$  and/or decreasing  $V_f$  as we'll demonstrate in follow-up research.

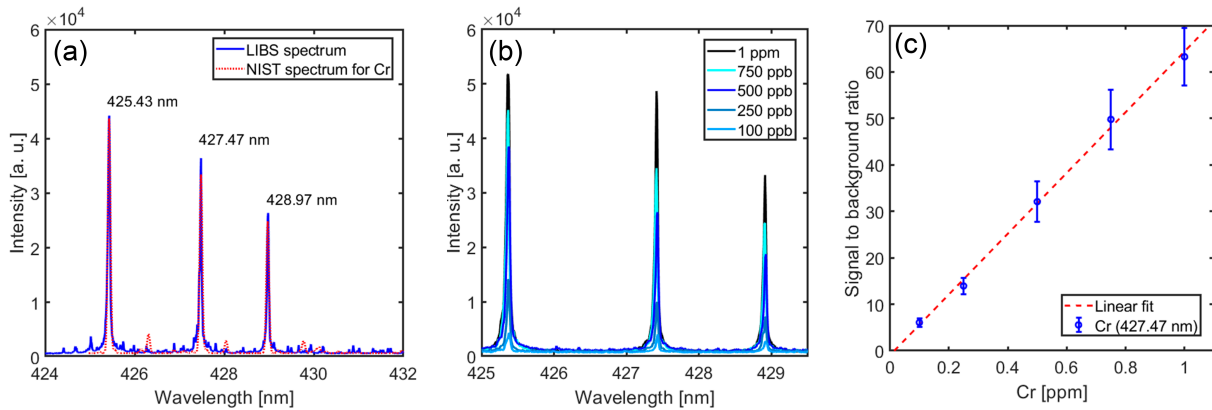


Fig. 2. (a) Experimental (blue) and synthetic (red) spectra obtained from a levitated droplet containing Cr at 500 ppb and from the NIST database. (b) Average of 10 spectra at 5 different chromium concentrations. (c) Calibration curve for chromium in the range 0.1 - 1 ppm.

## References

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