

Laser Induced Breakdown Spectroscopy signal enhancement of analytes in liquids using microstructured substrates

Alexandre Cherrier^a, Lionel Canioni^a, Bruno Bousquet^a

^a*Institut de chimie de la matière condensée de Bordeaux (ICMCB), UMR CNRS 5026, Univ. Bordeaux, Bordeaux INP, F-33600 Pessac, France*

Laser Induced Breakdown Spectroscopy (LIBS) is an analytical technique that analyses the light emitted by a plasma formed on a sample irradiated by a laser pulse. LIBS has been successfully used in various fields, each with very different sample types: metals, liquids, pellets... Certain sample types can be difficult to analyze with LIBS - for example due to poor laser ablation - hence trace elements present in such samples will be significantly more challenging to detect.

The microstructuring of samples for the purpose of LIBS signal enhancement has been reported through two different approaches: subtractive manufacturing, with the use of a femtosecond laser [2], also shown in Fig.1), and additive manufacturing, with a lithography-based technique [3]. Our work focuses on the optimization of the microstructuring process to maximize the LIBS signal enhancement of a liquid dropped and dried onto a copper substrate with microstructures induced by femtosecond laser ablation. The effect of different fabrication parameters, such as the femtosecond laser power, the microstructure pattern spacing and the translation stage speed has been described in a previous work [4]. It was found that the highest signal enhancement, close to 11, of the Cu I line at 521.8 nm from the bare substrate was achieved for microstructures with a depth of close to 4 μm . The signal enhancement was found to be correlated to a change of the temporal evolution of the plasma parameters, namely the electron density and plasma temperatures. In particular, the initial electron density was shown to be roughly two times higher on a microstructured substrate than on a polished copper substrate.

The LIBS signal enhancement on microstructured copper was found to be transferrable to analytes from solutions dropped and dried onto the substrate, leading to a lower limit of detection of the analyte. Fig.1.b) shows the LIBS spectrum of a Cr droplet dried on top of a microstructured substrate for Cr concentrations between 0.5 and 15 ppm.

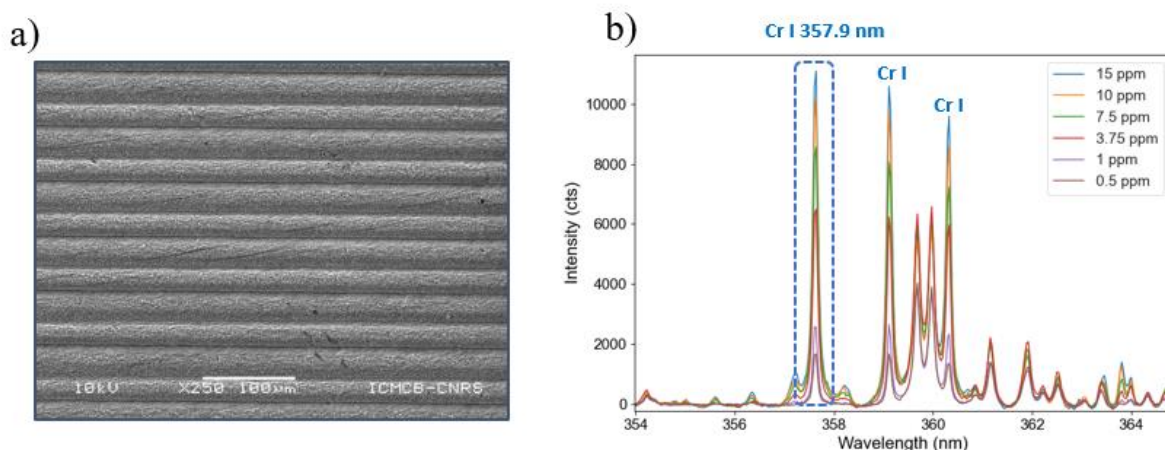


Fig 1. a) SEM image of a femtosecond laser microstructured copper substrate
b) Intensity of the Cr I 357.9 nm line intensity for different Cr concentrations on two different microstructured substrates.

References

- [1] M. Dell'Aglio, R. Alrifai, and A. De Giacomo, "Nanoparticle Enhanced Laser Induced Breakdown Spectroscopy (NELIBS), a first review", *Spectrochim. Acta B*, 2018, doi: 10.1016/j.sab.2018.06.008.
- [2] Q. Wang *et al.*, "Metal micro/nanostructure enhanced laser-induced breakdown spectroscopy", *Anal. Chim. Acta*, 2023, doi: 10.1016/j.aca.2023.340802.
- [3] D. Kaplan, N. Aras, and Ş. Yalçın, "Design, Fabrication, and Application of Micro-Structured Surfaces for Laser-Induced Breakdown Spectroscopic Analysis of Liquids: A Sample-Loading Target Development Studies", *Microchem. J.*, 2024, doi: 10.1016/j.microc.2023.109568.
- [4] A. Cherrier, L. Canioni, and B. Bousquet, "LIBS signal enhancement by laser surface microstructuring of copper," *Spectrochim. Acta B*, 2025, doi: 10.1016/j.sab.2025.107318.