# Quantification of eroded Fe, Cu and Al contamination in plasma activated water using Surface Assisted LIBS

## Introduction

Cold plasma discharges generate reactive oxygen and nitrogen species (RONS), which can be trapped in the liquid phase to form plasma-activated water (PAW), a chemically rich solution with applications in agriculture, biomedicine, and environmental treatment. When transient spark (TS) discharges are coupled with electrospray (ES) microdroplet generation, PAW production efficiency increases significantly due to the enhanced plasma–liquid interaction area. However, this configuration also leads to electrode degradation and the release of metallic ions and nanoparticles, which can alter PAW chemistry through catalytic or Fenton-type reactions [1, 2]. In this work, we employ surface assisted laser induced breakdown spectroscopy (SA LIBS) [3,4] to detect and quantify the eroded metallic species in PAW produced by the TS–ES system [5]. The PAW samples were dried on polished silicon wafers to form a thin film, providing a stable surface for ablation and minimizing splashing and plasma quenching associated with direct liquid analysis.

## Goal

This work involved a preliminary evaluation of the emission lines of the elements in the EUROFER. This preliminary evaluation consisted of determining the optimal emission lines for studying the concentrations of the elements using the LIBS technique. Their selection was based on the following properties:

The lines have to be isolated from other emission lines (interference free) and should not be self-absorbed, which could contribute to an error. The preselection of the good lines of all elements and degree of ionization for future CF-LIBS analysis is crucially important.

## Experimental Setup

A tuneable OPO laser (EKSPLA NT342C, 532 nm) was focused onto the dried films to generate laser-induced plasma, and the resulting emission spectra were recorded using an echelle spectrometer (ME5000, Andor) equipped with an iCCD detector (iStar DH743, temporal resolution 5 ns). The quantification was done using Calibration-Free LIBS at different gate timings under air at atmospheric pressure [6].

## Experimental Setup

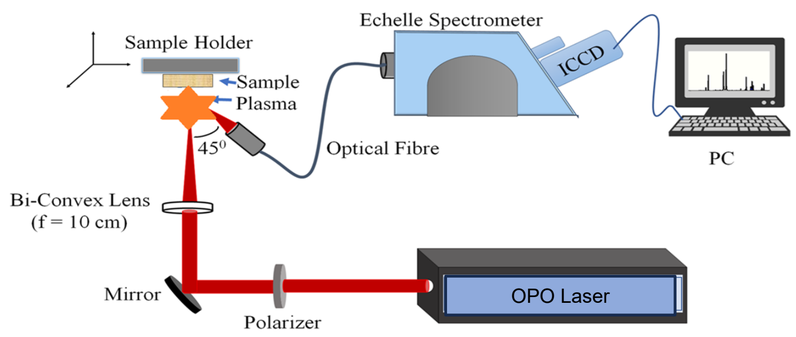


Fig. 1. LIBS experimental setup.

## Results

| Electrode Material | Sample Code | Current (mA) | Voltage Range (kV) | Notes |
|---|---|---|---|---|
| Copper (Cu) | S1 | 0.7 | 10.3 – 11.0 | Low-current discharge |
| | S2 | 1.1 | 10.3 – 11.0 | Medium current |
| | S3 | 1.5 | 11.3 – 11.9 | Highest current, higher voltage |
| Aluminium (Al) | A1 | 0.92 | 10.8 – 11.3 | Low-current discharge |
| | A2 | 1.18 | 11.6 – 12.3 | Medium current |
| | A3 | 1.48 | 12.2 – 12.8 | Highest current, highest voltage among Al |
| Iron (Fe) | P1 | 0.7 | 12.6 | Single voltage value measured |
| | P2 | 1.1 | 12.6 – 13.2 | Medium current |
| | P3 | 1.5 | 13.1 – 13.6 | Highest current; highest voltages overall |

## Results

LIBS analysis showed strong and clear Cu and Al emission lines in the corresponding PAW samples, indicating significant degradation of the copper and aluminium electrodes under the applied discharge conditions. Fe lines were minimal, suggesting much lower iron dissolution.

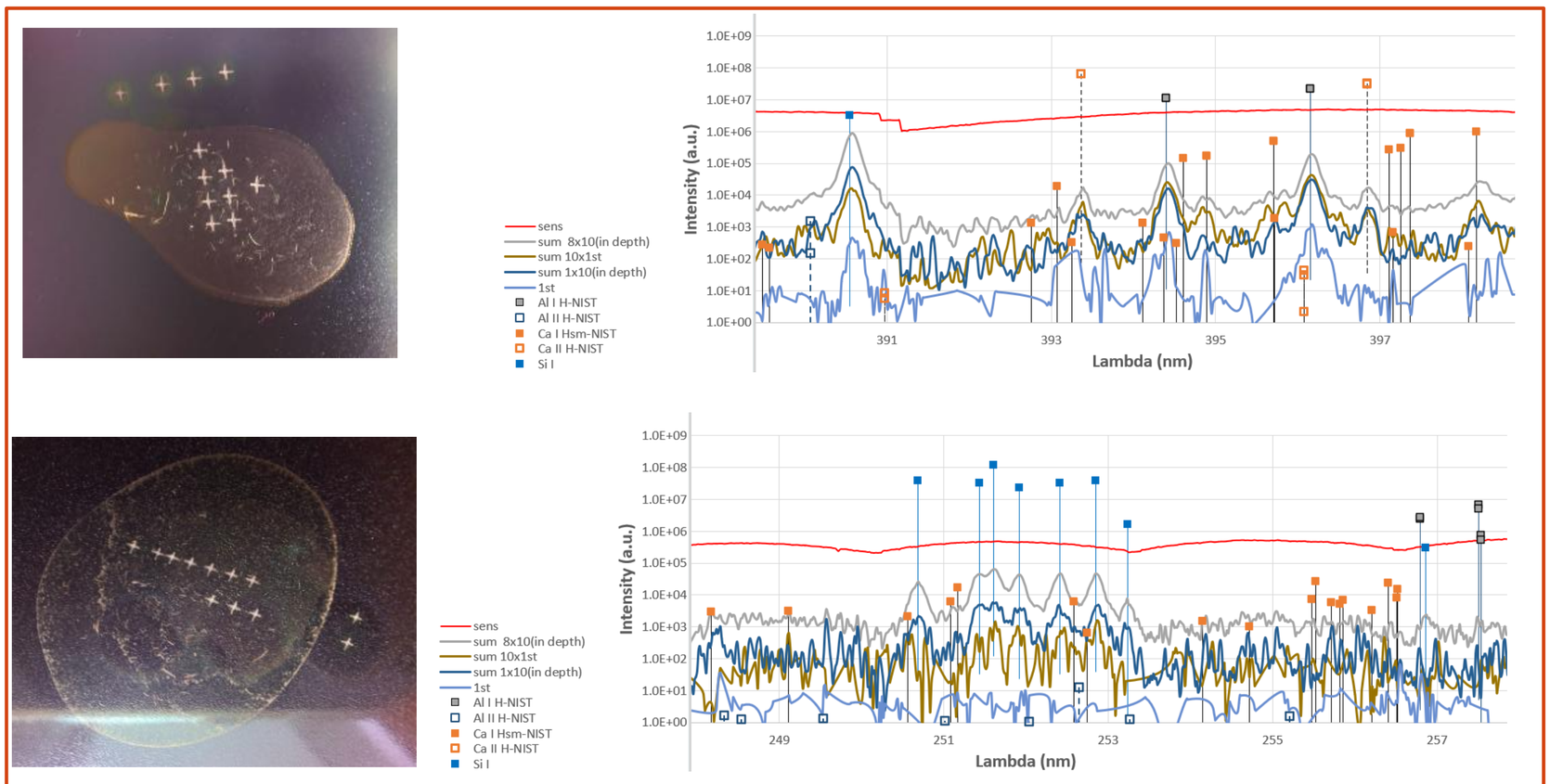


Fig. 2. LIBS Spectra obtained experimentally

## Conclusion and Future work

LIBS analysis of the PAW samples showed strong and distinct Cu and Al emission lines, confirming significant degradation of the copper and aluminium electrodes, while Fe signals remained weak. In future work, the extent of this metal release will be compared directly with the experimental discharge parameters used during PAW generation to evaluate how current and voltage conditions influence electrode erosion. This correlation will help identify operating settings that minimise degradation and improve the stability of the PAW system. Additionally, CF-LIBS will be applied to obtain a more quantitative estimation of metal concentrations in the PAW. This correlation will support the identification of operating conditions that minimise electrode degradation and improve PAW stability.

## Reference


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