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

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Abstract *Plasma-activated water (PAW) containing reactive oxygen and nitrogen species (RONS) has important applications in agriculture, biomedicine, and environmental treatment. In this work, PAW was generated using a transient spark (TS) discharge coupled with electrospray (ES) microdroplet generation under different plasma conditions. Surface-assisted laser-induced breakdown spectroscopy (SA-LIBS) was employed to investigate metallic contamination caused by electrode erosion during plasma operation. PAW samples were dried on polished silicon substrates and analyzed using an OPO laser-based LIBS system combined with an echelle spectrometer and an iCCD detector. Different electrode materials and discharge conditions were studied to evaluate their influence on metal release into PAW. Strong Cu and Al emission lines were observed, while Fe emission remained comparatively weak. Additionally, PAW samples produced using an unknown electrode material under three plasma conditions were analyzed to identify the electrode composition. The results demonstrate the potential of SA-LIBS for monitoring electrode degradation and metallic contamination in plasma–liquid systems.*

Keywords Plasma-activated water (PAW), Surface-assisted LIBS (SA-LIBS), Reactive oxygen and nitrogen species (RONS)

Introduction

Cold plasma discharges are widely used for the generation of reactive oxygen and nitrogen species (RONS), which can dissolve into liquids to form plasma-activated water (PAW). PAW has attracted considerable interest due to its potential applications in agriculture, environmental remediation, sterilization, and biomedicine. In transient spark (TS) discharge systems coupled with electrospray (ES) microdroplet generation, the plasma–liquid interaction area is significantly enhanced, leading to improved production efficiency of reactive species. However, the use of metallic electrodes in these systems also results in gradual electrode erosion and the release of metallic contaminants into the liquid phase. These metallic ions and nanoparticles may modify the chemistry of PAW through catalytic and Fenton-type reactions, thereby influencing its stability and chemical activity [1,2].

To investigate this contamination, surface-assisted laser-induced breakdown spectroscopy (SA-LIBS) was employed for the detection and quantification of metallic species released into PAW during TS–ES discharge operation. In comparison with direct liquid LIBS, SA-LIBS provides improved signal stability and reproducibility by depositing the liquid sample onto a solid substrate prior to analysis. In this work, PAW samples were dried on polished silicon wafers to form thin

films suitable for laser ablation. The study focused on the detection of Fe, Cu, and Al originating from electrode degradation under different discharge conditions [3, 4].

Experimental Setup

PAW samples generated using the transient spark–electrospray system were deposited onto polished silicon wafers and allowed to dry, forming thin films for surface-assisted LIBS analysis. This approach minimized splashing effects and reduced plasma quenching typically observed during direct liquid analysis, resulting in more stable plasma generation and improved spectral reproducibility.

The LIBS measurements were performed using a tuneable optical parametric oscillator (OPO) laser system (EKSPLA NT342C) operating at 532 nm. The laser beam was focused onto the dried PAW films to generate laser-induced plasma on the sample surface. The emitted plasma radiation was collected and analyzed using an echelle spectrometer (ME5000, Andor) coupled with an intensified CCD detector (iStar DH743) with a temporal resolution of 5 ns. Measurements were carried out in ambient air at atmospheric pressure, and spectra were recorded at different gate delays and gate widths for Calibration-Free LIBS (CF-LIBS) analysis.

Different discharge conditions were investigated using copper, aluminium, and iron electrodes at varying discharge currents and voltages in order to study the relationship between plasma operating conditions and electrode erosion. Strong Cu and Al emission lines were observed in the corresponding PAW samples, while Fe emission remained comparatively weak, indicating lower iron dissolution under the investigated conditions.

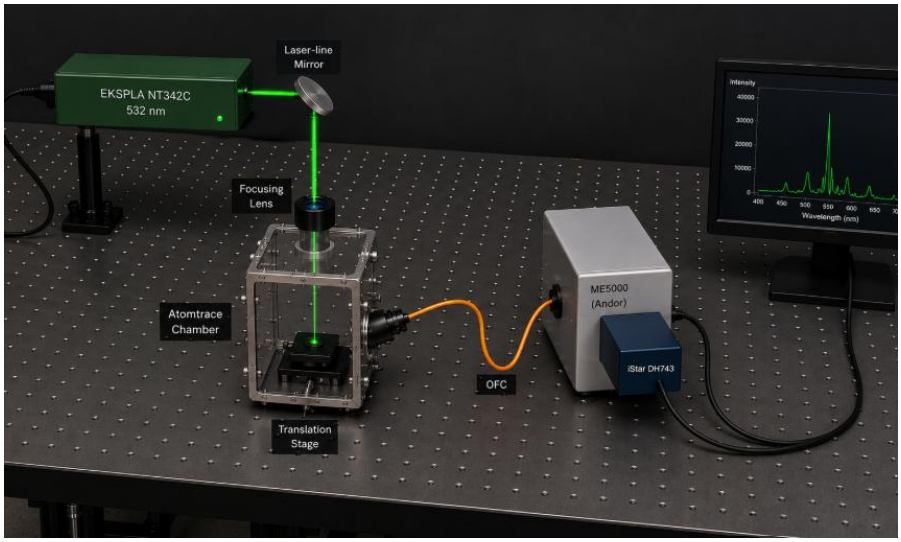

Figure 1: Schematic experimental setup for SA-LIBS

Sample Description

PAW samples were prepared using copper (Cu) and iron (Fe) electrodes under three different plasma conditions corresponding to low, medium, and high discharge currents. The discharge current and voltage ranges for each sample are summarized in Table 1. These varying plasma conditions were used to study the influence of discharge parameters on electrode erosion and metallic contamination in PAW.

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, highest voltage
Iron (Fe)	P1	0.7	12.6	Low-current discharge
	P2	1.1	12.6 – 13.2	Medium current
	P3	1.5	13.1 – 13.6	Highest current; highest voltages overall

Table 1: Description of the samples

In addition to the known Cu and Fe electrode samples, another set of PAW samples produced using an unknown electrode material was also prepared under three different plasma conditions. LIBS analysis is performed to identify the elemental composition of the unknown electrode and evaluate its erosion behavior under different discharge regimes.

Results:

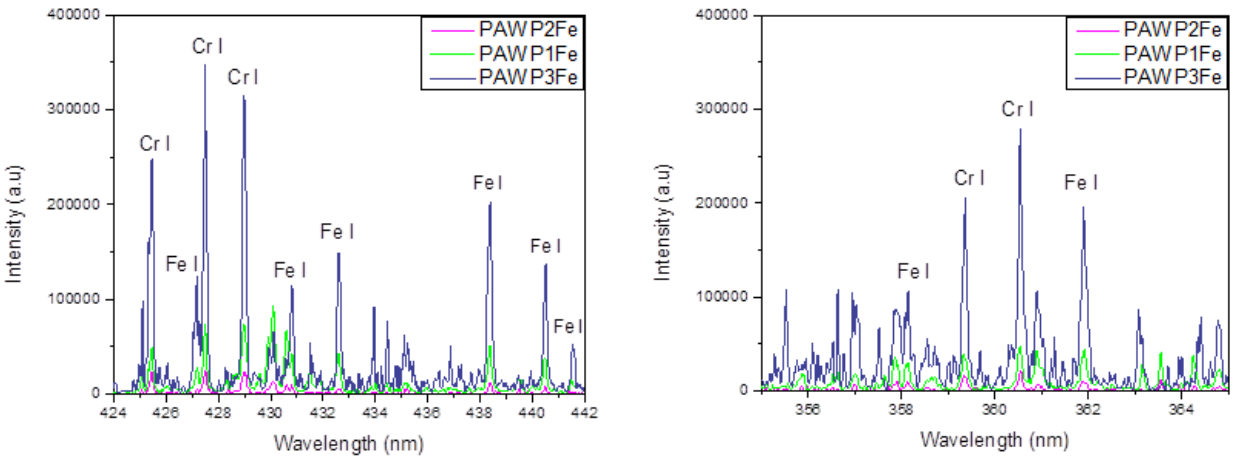

Figure 2: Spectra showing the presence of Fe and Cr in the PAW

For simplicity, only the Fe electrode samples are presented in this work. The SA-LIBS spectra of PAW P1Fe, P2Fe, and P3Fe show several identifiable Fe emission lines in the investigated wavelength regions, confirming the presence of iron in the plasma-activated water. The Fe signal is most pronounced for the P3Fe sample, which was generated under the highest discharge current and voltage conditions. This suggests that stronger plasma conditions lead to increased erosion of the iron electrode and higher release of Fe-containing species into the liquid.

Although levitation-assisted LIBS is useful for liquid analysis and avoids substrate-related effects, SA-LIBS provides an advantage for detecting weak or trace elements because drying the liquid on a solid substrate preconcentrates the residue and improves signal stability [4]. Therefore, this approach is also more suitable for detecting elements such as Cr, which may be difficult to observe clearly in levitated droplet LIBS measurements. For this presentation, Fe is shown as the representative electrode-eroded element to keep the discussion simple and focused.

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