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Optimised gating for detecting chlorine and fluorine in molecular form using microwave-assisted LIBS

M. A. Wakil and Z.T. Alwahabi,
School of Chemical Engineering, The University of Adelaide, S.A. 5005, AUSTRALIA
mdabdul.wakil@adelaide.edu.au

ABSTRACT

Microwave assisted laser-induced breakdown spectroscopy (MW-LIBS) has been applied to detect chlorine and fluorine in solid matrix at ambient conditions. Chlorine and fluorine have been detected using strong molecular emission band at 617.9 nm and 605 nm for CaCl and CaF respectively. The detector's gate-delay has been optimised to achieve the optimum signal to noise (SNR) of CaCl and CaF molecular emission. The results show that using a constant gate-width of 300 μs, the highest SNR of CaCl and CaF can be achieved at gate-delay of 500-1000 and 400 ns respectively. It was found that the MW-LIBS enhances the CaCl and CaF signal up to 4.5 and 8 times respectively compared with LIBS. The SNR improvement was 2.5 times for both bands.

1. INTRODUCTION

The detection of chlorine and fluorine is important for process analysis, environmental and geological exploration. In addition, chlorine acts as an active corrosive agent in concrete structures. Harmful species such as chlorides may penetrate together with water through the capillary pore space, which may trigger different damage processes such as pitting corrosion, concrete corrosion [1]. On the contrary, Chlorine act as an essential element in chemical building blocks, food, water purification, medicines, advanced technological devices, air conditioning refrigerants, paint, energy efficient windows etc [2]. On the other hand, Chlorine and fluorine can play role in the process of stress corrosion cracking of dry cask storage located in marine environments [3] as well as partial melting of the Martian mantle [4]. On the contrary, fluorine is used as a compound in industries for metallic aluminium, ceramic, ionic superconducting material production [5]. However, chlorine and fluorine are difficult to detect using atomic emission or absorption techniques because of absence of transitions with reasonable population at the upper electronic states.[6].

Laser-induced breakdown spectroscopy (LIBS) is considered to be a well-established laser-ablation based analysis technique due to its distinguishing characteristics such as to perform chemical analysis on any solid sample directly. Although LIBS is advantageous due to its unique characteristics such as requiring no sample preparation, real time, easy of handling and its non-destructive nature, it is found to be less sensitive to element (nuclear fuel) having complex structure [7], low excitation efficiency [8] and high ionization energy [9] such as halogens. Detection limits for halogens using their most excited atomic lines are less than satisfactory for demanding applications. Among the possible alternatives such as surrogate measurement, molecular emission rather than atomic emission [3, 10], the sensitivity of LIBS can be improved significantly using molecular emission [11]. C. Haisch et al. [12] has shown in their study that the detection limit of halogens can be significantly enhanced using molecular emission bands. D. Vogt et al. [13] suggested in their study that calcium-free salt is not suitable for detecting Cl via CaCl. M. Gaft et al. [14] detected Cl in the mixture of 0.4% $CaCl_2$ using a CaCl molecular emission band. Forni et al. [4] detected F with 0.6% fluorine content using a CaF molecular emission band. Y. Foucaud et al. [5] used fluorine-containing rock samples for fluorine quantification using CaF molecular emission band.

Microwave-assisted (MW) LIBS is one of the available signal enhancing techniques among others such as Double-pulse LIBS, spark discharge LIBS, Laser-induced fluorescence LIBS, resonant LIBS, due to its underlying benefits such as long plasma lifetime, larger volume, ability to reduced self-absorption, strong emission intensity and stability with time [15-17].

In this work, the measurement of chlorine and fluorine is evaluated with MW-LIBS using molecular emission band such as those of CaCl and CaF. The strong emissions of CaCl and CaF are optimised using optimised time gating of detector at wavelength of 617.9 nm and 605 nm respectively. The experiment includes molecular emission of chlorine and fluorine with LIBS and MW-LIBS, optimised gate-delay and detector gain.

2. METHODOLOGY

2.1. MW-LIBS SETUP

The experiment was carried using a MW-LIBS setup as shown in Figure 1. A Q-switched Nd:YAG laser of second harmonic with a repetition rate of 10 Hz was used. A half-wave plate with Glan-laser polarizer was used to control the pulse energy. The beam was focussed onto the sample surface using a fused silica lens with f=100 mm. The spot size obtained at the focal point was estimated to be 7.32 μm while the propagation of laser beam was at an angle of 15^{o} to the vertical. The sample was placed on a rotating disk with an angular velocity of 7 revolutions per minute to achieve ablation from a fresh surface at each laser pulse. A second CW laser, with a camera, was used to monitor the exact distance between the sample surface and the fused silica lens. A water-cooled pulsed-microwave system (Seirem) at 2.45 GHz was used as the microwave source. The microwave radiation was directed via a WR340 waveguide to a 3-stub impedance tuner and then to a waveguide-to-coaxial adaptor (WR340RN) through a quartz window. The waveguide-to-coaxial adaptor was connected to a 1m flexible coaxial cable (50 Ω NN cable) with 0.14 dB @ 2.45 GHz. A semi rigid cable (RG402/U) was then connected at the end of the coaxial cable. The other end of semi rigid cable was attached to a near field applicator (NFA). The NFA was located about 1 mm above the sample surface and 0.5 mm horizontally away from the ablation spot. For the spectroscopic detection, an Andor Shamrock 500i spectrometer with a grating of 2400 lines/mm was used. The plasma emission was collected through a plano-convex lens (f=100 mm) and was then focussed by an off-axis parabolic mirror onto an achromatic reflector coupler through a lens (f=20 mm) that was connected using a bifurcated

fibre bundle (Thorlabs, BFY400HS02. The fibre bundle has a core size of 400 µm and a transmission range of 250-1200 nm. The optical line, the sample holder, the NFA and one end of the fibre were placed inside an aluminium box to minimise the residuals microwave radiation. One side of the aluminium box was covered with metal mesh acting as an observation window. The attainable wavelength range for the spectrometer, with a Holographic grating, is 200-705 nm. An intensified CCD camera (Andor, iStar) was utilized to record the spectral signal, which was synchronised with the laser and the microwave generator. For each experiment, 100 single shots were recorded and averaged. The experiment was conducted in atmospheric environment. The experimental uncertainties are calculated as laser energy (10 ± 0.127 mJ), microwave power (600 ± 6 W), microwave coupling efficiency 90%.

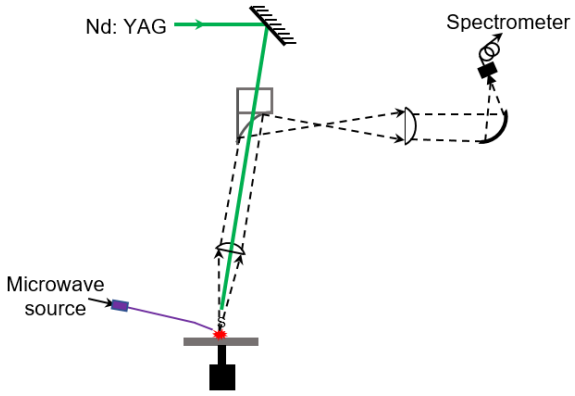

Figure 1. MW-LIBS experimental setup

2.2. MATERIALS

As a source of calcium, Portland cement (~ 40% Ca content) was used as primary matrix. For the source of chlorine and fluorine, KCl and NaF were purchased from Sigma Aldrich. 2.07% Cl in KCl and 1.63% F in NaF were mixed up separately with distilled water to make solution. Each solution was mixed with correct amount of cement (4 g) to make a paste. The paste was placed in a circular disk to make pellet and then dried with a dryer.

3. RESULTS AND DISCUSSION

To obtain the lowest detection limit, optimization in gating is important in order to achieve the highest signal-to-noise (SNR). To find the efficiency of detector gain, SNR of CaF molecular emission at 605 nm was investigated. Figure 2 shows the effect of detector gain on SNR. As shown in Figure 2, the SNR increases with the amplification of detector gain but after a factor of 100 gain, the noise increment becomes high significantly. The high noise leads to a higher standard deviation of background noise that will worsen the limit of detection according to the equation 1. For the next experiment, 100-detector gain was considered.

$LoD = \frac{3\sigma}{S} \ldots\ldots (1)$, where σ is the standard deviation of background, S is the slope.

The temporal evolution of molecular emission intensity was investigated for MW-LIBS by maintaining a constant gate width of 300 µs and varying the gate-delay from 0 ns to 2 µs. The temporal evolution of MW-LIBS is shown in Figure 3 and Figure 4. It was observed, that the CaCl signal had an interference with CaO signal at around of CaCl signal (617.9 nm) [5]. It was observed that the formation of two radicals such as CaCl and CaO differ in time. CaO signal was high initially and decreased with time until 1000 ns and increased again. Because of the constant amount of Ca presence, the signal of CaO was dominant initially and then CaCl signal became stronger. Figure 3 shows that the SNR of CaCl. It is clearly shown in Figure 3 that the gate-delay at around 500-1000 ns gives the highest SNR of CaCl molecular signal. Figure 4 shows the SNR of CaF at 605 nm. It is shown from Figure 4 that the highest SNR of CaF molecular emission was observed at 400 ns gate-delay.

Typical spectra of molecular CaCl (2.07% of Cl) and CaF (1.63% F) recorded in LIBS with and without microwave radiation are presented in Figure 5 and Figure 6. It was found experimentally that at 10 mJ laser energy, the signal of CaCl improved by 4.5-fold where CaF signal improved by 8-fold by using MW-LIBS compared with LIBS. This is due to the signal enhancing ability of microwave system. The external energy supplied, using the microwave radiation, sustains the free electrons present within the laser-induced plasma. These reenergized free electrons act as an excitation source, via collisional processes, leading to the lifetime extension which finally leading to the signal enhancement. The SNR improvement calculated for both CaCl and CaF was achieved 2.5- fold. It is expecting that the SNR improvement by 2.5- fold will lead to an improvement of ~3-fold detection limit of chlorine and fluorine.

4. FIGURES AND TABLES

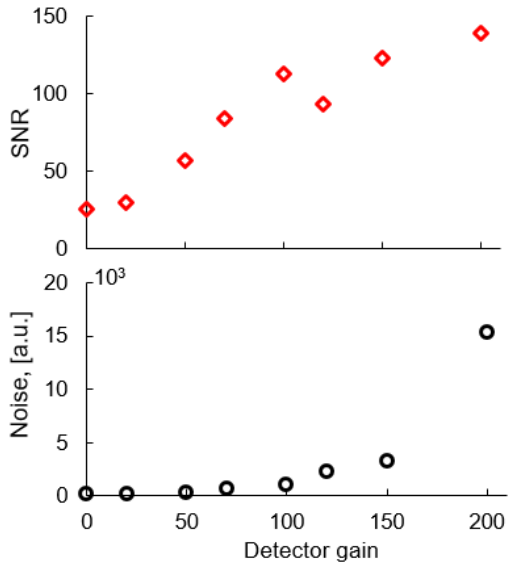

Figure 2. Effect of detector gain on signal to noise ratio using CaF molecular emission at 10 mJ laser energy, 600 W microwave power, 400 ns gate-delay, 300 µs gate-width with 100 accumulation.

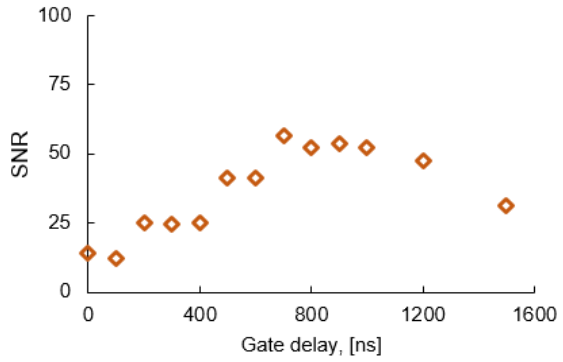

Figure 3. Signal to noise ratio of CaCl molecular emission at 10 mJ laser energy, 750 W microwave power, 300 µs gate-width with 100 accumulation.

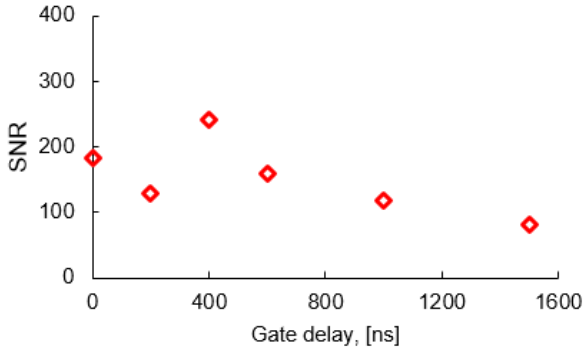

Figure 4. Signal to noise ratio of CaF molecular emission at 10 mJ laser energy, 600 W microwave power, 300 µs gate-width with 100 accumulation.

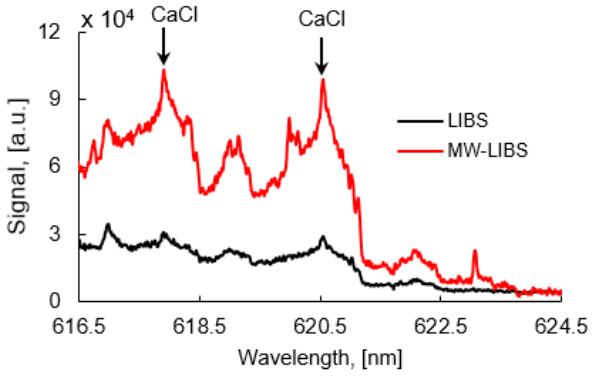

Figure 5. Typical spectra of CaCl molecular emission at 10 mJ laser energy, 750 W microwave power, 500 ns gate-delay, 300 µs gate-width with 100 accumulation.

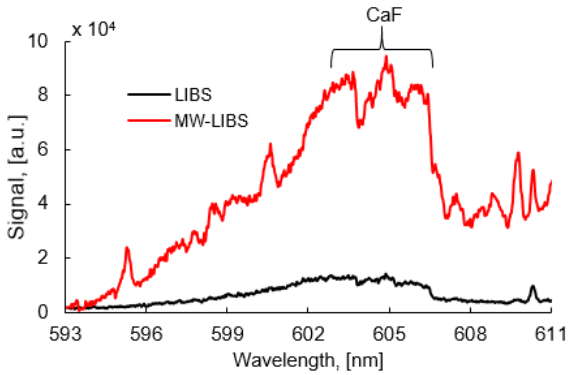

Figure 6. Typical spectra of CaF molecular emission at 10 mJ laser energy, 600 W microwave power, 400 ns gate-delay, 300 µs gate-width with 100 accumulation.

5. CONCLUSIONS

The main goal of this work was to demonstrate the possibility of an accurate detection of chlorine and fluorine at ambient condition. Microwave-assisted laser-induced breakdown spectroscopy has been investigated to evaluate the optimum signal enhancement for CaCl and CaF following ablation of sold matrix.. The detection of chlorine and fluorine is demonstrated by using molecular emission of CaCl and CaF at 10 mJ laser energy. It is found that highest signal to noise ratio can be achieved for CaCl and CaF at 500-1000 and 400 ns gate-delay respectively with a gate-width of 300 µs. SNR improvement for both bands is reported to be 2.5-fold by using MW-LIBS than LIBS. It is observed that the amplification of detector's gain more than 100 is not suitable because of high increasing order of noise.

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