Concentration Dependent Studies on the Laser-Induced Mid-Infrared Emission from KCl-NaCl Tablets

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Abstract—Laser Induced Breakdown Spectroscopy (LIBS) is a technique for determining the elemental composition of a chemical substance [1]. Pumping with a 1064nm Nd:YAG pulse laser, mid-infrared emissions from LIBS plasma produced from KCl were examined between 2.0μm and 4.5μm, with atomic emission lines observed at 2.72μm, 3.15μm, 3.77μm and 4.05μm for potassium, consistent with NIST atomic spectra database. With further focus on the 2.72μm emission, detection limit studies were carried on different concentration samples of KCl_NaCl mix, to determine the detection limit of potassium (K). A limit of detection of ~0.19wt%/wt was obtained for potassium in the mid-IR region.

Laser-Induced Breakdown Spectroscopy as a technique for investigating trace elements in materials has been widely employed using visible and near infrared emission bands [2]. Very little work, however, has yet been done on longer wavelength IR LIBS [3]. In particular, no report has yet been made in the literature on the limits of detection for LIBS measurements in the mid-IR region. The first attempts on mid-IR LIBS have been undertaken by Yang et al [4], who observed atomic transitions of K and Na within the 2–5μm wavelength region. The details of their result and its agreement with NIST standard data have been reported elsewhere [5].

The observance of the atomic emission lines of potassium indicates the presence of potassium in a given substance but does not necessarily give information on how much potassium is contained therein. Thus it is of interest to determine not only how much potassium is contained in a given substance, but also the sensitivity of the mid-IR LIBS technique in identifying trace elements in a substance. It is therefore useful to know how much potassium must be present in a substance for the mid-IR LIBS technique to identify it. However, the determination of the limit of detection depends on a number of experimental conditions including the wavelength of emission, excitation energy as well as the spectral response of the detector. Radziemski *et al.* [3] studied the detection limits of the near infrared emissions of a number of neutral elements. For potassium monitored at various near-IR wavelengths, they found detection limits ranging from 0.02 to 0.087 wt%/wt. They also obtained detection limits using IR detectors that were twice as much as obtained with the standard intensified charge-coupled device (ICCD) detector [3].

The goal of the concentration dependent studies is to determine the detection limit of potassium in solid samples using the strongest mid-IR peak of potassium located at ~2.72μm, which corresponds to the $5^2P_{3/2} \rightarrow 5^2S_{1/2}$ (2.71 μm) and $5^2P_{1/2} \rightarrow 5^2S_{1/2}$ (2.72 μm) atomic transitions [5].

Using sodium chloride (NaCl) as the matrix, different masses of KCl were mixed with a fixed mass (10g) of NaCl to obtain samples containing different concentrations of potassium. Several units of measuring detection limit have been reported but most commonly used are parts per million (ppm) [6] and weight percent per weight (wt%/wt) [3]. Since materials were mixed in mass ratios, wt%/wt was the preferred unit for measuring detection limit in this work. Five samples of the KCl-NaCl mix were made with different grams (50 – 1000mg) of KCl each added to 10g of NaCl to obtain concentrations of 0.26, 0.39, 0.5, 2.5, and 4.8 wt%/wt of potassium in the sample. For uniform distribution of potassium in the sample, each mixed sample was ball-milled and pressed into pellets of fairly equal sizes using a bench top press. To ensure that the intensity of the laser pulse delivered to each sample is uniform, pellets of equal thickness were made. This was achieved by ensuring that the samples were pressed with the same load pressure and for the same length of time. Typical pellets obtained and the bench top press used are shown in Fig. 1. The experimental setup for the mid-IR LIBS emission study is shown in Fig. 2. The

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sample was excited by a Q-switched Nd:YAG pulsed laser with 5ns pulse width, 10Hz repetition rate, and 1064nm wavelength, delivering 32mJ pulse energy on the sample. The pulsed laser beam was focused onto the sample surface using a plano-convex lens (*f*=20 cm), resulting in a beam size diameter of ~0.5mm. The sample was translated continuously at about 1.5mm/min to ensure that each arriving laser pulse hits a fresh spot.

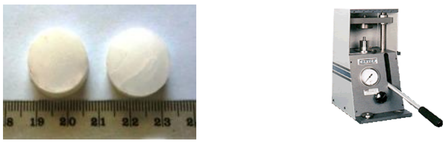

Fig. 1. Picture of the bench top press and some pressed sample pellets.

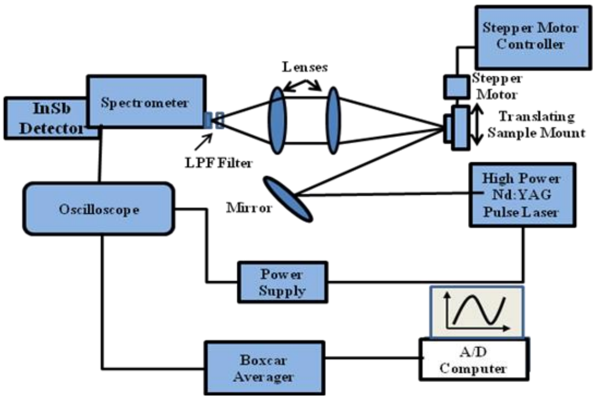

Fig. 2. Schematic diagram of the experimental setup for IR-LIBS emission studies developed at Hampton University.

In order to further improve the signal to noise ratio of the 2.72μm potassium emission, the spectrometer was scanned over a narrower spectral range (2650−2800nm) at a slow scan rate (25nm/min). The resulting emission was collimated into a 0.15m, 4μm grating spectrometer (1.0mm slit width) with plano-convex CaF_2 lenses, through a 2000nm long pass filter. The signal was detected with a liquid nitrogen-cooled InSb detector and recorded using an integrated boxcar averager set at 10μs gate delay and 16μs gate width. Additional details of the setup can be found in references [4] and [5]. Each sample was scanned two to three times and the average spectrum determined. The spectrum of each of the five sample concentrations is shown in Fig. 3, while Fig. 4 shows the spectra plotted on the same intensity scale.

Since the real life use of IR LIBS is the identification of trace elements in substances that are hybrid in nature, similar experiments as above were conducted on a commercially obtained substance – potassium gluconate, a dietary supplement quoted to contain 3% of potassium [7]. Samples of potassium gluconate were prepared by crushing and pressing a few tablets into pellets and scanned under identical experimental conditions as done for the mixed samples of KCl and NaCl. The IR LIBS spectrum of potassium gluconate over the 2.72μm transition is shown in Fig. 5.

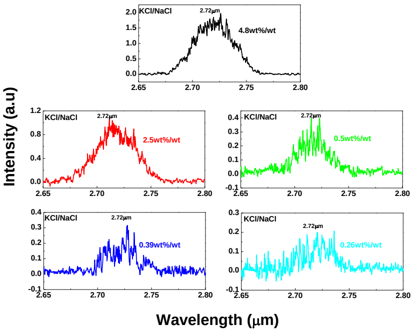

Fig. 3. Separated concentration dependent spectra showing potassium emission at 2.72μm for different concentrations (wt%/wt) of K in KCl/NaCl mix.

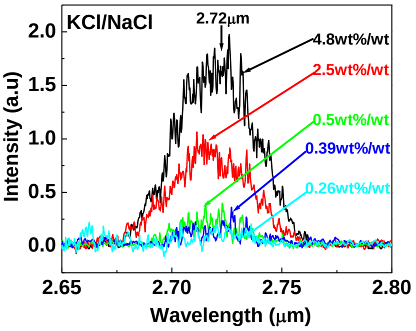

Fig. 4. Concentration dependent spectra showing potassium emission at 2.72μm for different concentrations (wt%/wt) of K in KCl/NaCl mix on the same intensity scale.

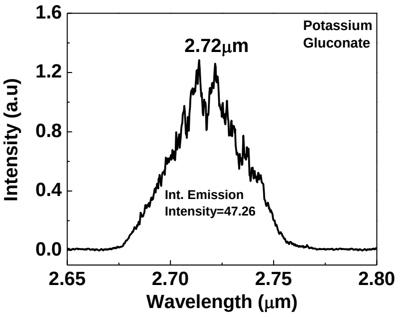

Fig. 5. IR LIBS spectrum of Potassium Gluconate showing the 2.72μm emission band.

It can be seen that the intensity of the 2.72μm potassium emission decreased at smaller concentration as seen in Fig. 3. In order to establish the relation between the intensity of the 2.72μm emission and the potassium concentration, the peak intensity and the integrated intensity over the 2.72μm band were determined for each sample as shown in Table 1.

Table 1. Peak intensity and integrated intensity of potassium emission at 2.72μm for different concentrations of potassium in KCl/NaCl mix.

Mass of KCl (g)	Mass of NaCl (g)	Concentration of Potassium (wt%/wt)	Peak Intensity @ 2.72μm (a.u)	Integrated Intensity (a.u)
0.05	10.0	0.26	0.20673	5.37116
0.075	10.0	0.39	0.31576	8.08960
0.1	10.0	0.5	0.39915	10.35031
0.5	10.0	2.5	1.06470	40.90551
1.0	10.0	4.8	1.97426	75.69830

The integrated intensity was determined by measuring the entire area under the 2.72 μm emission band. The peak intensity and the integrated intensity were separately plotted as a function of concentration as shown in Fig. 6 and Fig. 7.

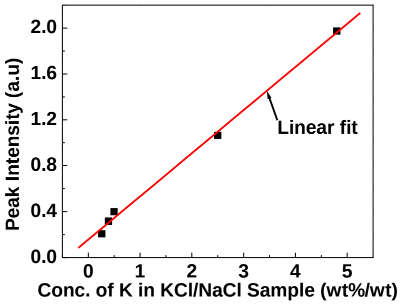

Fig. 6. Concentration dependence of potassium emission at 2.71μm: Peak intensity as a function of concentration.

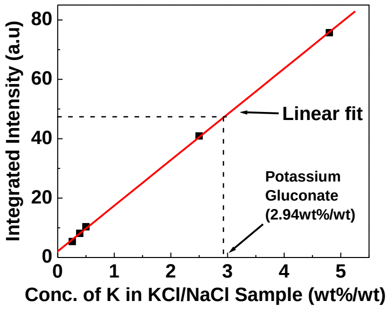

Fig. 7. Concentration dependence of potassium emission at 2.71μm: Integrated intensity as a function of concentration.

By linear regression analysis, the integrated intensity curve, with $R^2=0.9999$ provides a better calibration curve for determining the limit of detection (LOD), than the peak intensity curve which gave $R^2=0.9985$. Using the IUPAC definition [8] for limit of detection ($LOD=3\sigma_B/S$), where σ_B is the standard deviation of the background and S is the slope of the calibration curve, a LOD of ~0.19 wt%/wt. was obtained under the given experimental conditions. The integrated emission intensity at 2.72μm from a commercial potassium gluconate sample was measured and yielded a potassium content of approximately 2.94 ±0.07 wt%/wt (Fig. 7). This compares well with the 3% potassium content quoted by the manufacturers of the dietary supplement.

In conclusions, concentration dependent LIBS studies were performed on the 2.7 μm mid-IR emission from potassium and a limit of detection of 0.19 wt%/wt was obtained. Although this result is not as good as LOD values reported for near-IR LIBS measurements [3], it is significant given that mid-IR emissions are usually weaker than those observed in the UV-VIS region. In its debut appearance, the MIR LIBS technique has proven to be a worthwhile compliment to the established UV-VIS LIBS technique. As MIR LIBS further develops, improvements in experimental conditions would yield higher sensitivity and lower detection limits. For example, an improvement of the sample mount translation technique could result in IR LIBS spectra that exhibit increased reproducibility and reduced noise levels. It would also appear that the NaCl matrix used for sample mixing was not efficient as it introduced much background to the signal, thus reducing the signal to noise ratio, especially at low concentrations. However, real life measurement of detection limits offers limited flexibility in the choice of the mixing matrix as substances containing trace elements would be hybrid in nature,

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