Quantitative and sensitive analysis of CN molecules using laser induced low pressure He plasma

by Mangasi Alion Marpaung
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We report the results of experimental study on CN 388.3 nm and C I 247.8 nm emission characteristics using 40 ml laser irradiation with He and N2 ambient gases. The results obtained with N2 ambient gas show undesirable interference effect between the native CN emission and the emission of CN molecules arising from the recombination of native C ablated from the sample with the N dissociated from the ambient gas. This problem is overcome by the use of He ambient gas at low pressure of 2 kPa, which also offers the additional advantage of cleaner and stronger emission lines. The result of applying this favorable experimental condition to emission spectrochemical measurement of milk sample having various protein concentrations is shown to yield a close to linear calibration curve with near zero extrapolated intercept. Additionally, a low detection limit of 5 μg/g is found in this experiment, making it potentially applicable for quantitative and sensitive CN analysis. The visibility of laser induced breakdown spectroscopy with low pressure He gas is also demonstrated by the result of its application to spectrochemical analysis of fossil samples. Furthermore, with the use of CO2 ambient gas at 600 Pa mimicking the Mars atmosphere, this technique also shows promising applications to exploration in Mars. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4915344]

I. INTRODUCTION

Thanks to the continued improvements of laser system and spectroscopic detection techniques, the Laser Induced Breakdown Spectroscopy (LIBS) has quickly emerged as a widely adopted modern technique for practical, versatile, and rapid multi-element analysis. Nowadays, it has found a large variety of applications in the scientific research laboratories and industrial laboratories as well as for in situ, real time, or stand-off measurements.1 In fact, it has found its way into field applications with the development of its portable system. While most of the earlier applications are focused on inorganic materials, its possible extension to organic materials has attracted growing interest of research since around the turn of the century. Reports are available in the literatures on the applications of LIBS to polymer classification or identification,2-6 analysis of pharmaceutical materials,7 organic explosives,8-12 inspection and investigation of environmental contamination13-17 as well as biomedical applications.18-21

Most organic and biological materials are known to contain the four common basic elements of H, C, N, and O. The uses of these atomic lines for polymer analysis have been reported in the literature.22-23 However recent studies have demonstrated the more favorable discriminating power by means of measuring both the atomic and molecular emission lines and their intensity ratios.3-5,24,25 Among the most cited examples are the H/C, O/C, C/N, and O/N intensity ratios, as well as the diatomic molecular bands of C2 and CN, and their

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appropriate intensity ratios which are expected to provide direct molecular information of the related materials. However, the use of molecular emission bands is not without problems. It has been shown for instance, that CN molecules can be formed as a product of recombination between the ablated C in the plasma plume and the dissociated N in the ambient air. Therefore, a clear separation of the two different contributions must be made in order to achieve a reliable analysis for the native molecules of interest. A systematic study by Russo et al. using time resolved emission spectra of CN band under different laser energies demonstrated the importance of proper control of the laser fluence for the exclusive detection of native CN bonds. UV-LIBS with low laser fluence allows the detection of native CN bond without complication from the ambient air.

In most of those studies mentioned above, no serious attempt was made on the quantitative analysis utilizing the CN band emission. This is likely due to the weak intensity of CN emission in the atmospheric pressure regime and in the ambient air. In a previous study dedicated to the H and D analysis in metal samples, combination of low pressure plasma with the use of helium ambient gas was employed, taking advantage of the role of helium metastable excited state for the clean detection of the delayed emission lines. The result shows a greatly improved spectral quality of those fully resolved emission lines. It is the purpose of the current experiment to study the possibility of producing improved spectral quality of CN molecular band without disturbance from the ambient gas by employing the same experimental conditions adopted in those previous works. Having demonstrated the desirable results, the possibility of doing quantitative analysis utilizing CN molecular band emission is investigated by repeating the experiment using milk powder samples containing different protein concentrations. It is shown that the calibration curve close to a linear line is obtained for a reasonable range with extrapolated zero intercept. This result is further shown to offer the potential application of CN analysis to carbon dating of fossils as well as for its applications in Mars.

II. EXPERIMENTAL PROCEDURE

The schematic diagram of the experimental arrangement is similar to our previous works. In this experiment, the 1064-nm Nd:YAG (Quanta Ray, LAB 130-10, 8 ns maximum energy of 450 mJ) is operated in a Q switched mode at a repetition rate of 10 Hz with the laser output energy fixed at 40 mJ yielding a power density of around 25 GW/cm². In the experiment for studying the CN band emission characteristics, a carbon stamp, which is usually used for calligraphy in China and Japan as the source of black ink (98% C and 2% of glue mixture containing 20% animal protein molecules having CN bands) is used as the sample. This sample has a good compositional uniformity and it is also very hard and available in a large size of around 3 cm x 3 cm x 0.5 cm. As such it can be irradiated in both rotated or fixed position. In the experiment performed for exploring and verifying the favorable condition for desirable spectrochemical analysis of CN band emission and its applicability to quantitative analysis, a number of milk powder samples with different protein concentrations are employed. The possibility of measuring total C content in a sample for radio active dating is investigated using samples of buffalo horn fossil of 40 000 years and leaf fossil of 1 000 000 years.

The spectral measurement of the secondary plasma emission is carried out by employing an optical multichannel analyzer (OMA system, Andor iStar intensified CCD 1024 x 256 pixels) of 0.012 nm spectral resolution at 500 nm. This system is attached on one side to a spectrograph (McPherson model 2061 with 1000 mm focal length, ) which is connected to an optical fiber on the other end.

III. RESULTS AND DISCUSSION

A. Emission characteristics of CN band from different origins

Prior to the spectroscopic experiment, a preliminary inspection is conducted on the plasma generated by 40 mJ laser irradiation on the carbon stamp sample in (a) He ambient gas at 2 kPa and (b) N₂ ambient gas at 101 kPa, both in tight focus setup. In the first case, as shown in Fig. 1(a), the plasma is found to exhibit a typical hemispherical shape consisting of a small primary and an extended secondary plasma regions as observed previously. The relatively tiny primary plasma shows a very dense white color, while the much larger secondary plasma extending far beyond the primary plasma displays a bright red and green colour. The radius of the secondary plasma is estimated to be around 15 mm. Meanwhile in the case of LIBS employing atmospheric ambient air as shown in Fig. 1(b), only one observes that the very dense plasma of much smaller size exhibits a bright white colour associated with strong continuum emission of the sample. The related spectra in the two cases are represented in Fig. 2 in which the CN band emission at 388.3 nm appears significantly higher and narrower in the case of 2 kPa He ambient gas compared to that detected in 101 kPa ambient N₂ which approximately corresponds to the condition encountered in LIBS. This unfavorable characteristics of CN emission are probably the reason for the lack of published report on the quantitative CN analysis using the LIBS technique. Nevertheless, it remains to be clarified.

![Figure 1](image_url)

**Fig. 1.** Photograph of the plasma generated by irradiation of Nd:YAG laser of 40 mJ output energy on carbon stamp sample in (a) He ambient gas at 2 kPa and (b) ambient N₂ at 101 kPa.
whether the high gas pressure or the \( \text{N}_2 \) ambient gas itself is responsible for the undesirable emission quality. For this purpose, measurements are performed on the pressure dependent intensity variations of CN band 388.3 nm emission along with C I 247.8 nm emission in He as well as in \( \text{N}_2 \) ambient gases. The results are presented in Fig. 3. It is clear from this figure that the CN emission intensity detected in ambient \( \text{N}_2 \) is consistently higher than that detected in He ambient gas at the same pressure. Meanwhile, the C I 247.8 nm emission intensity detected in \( \text{N}_2 \) ambient gas is perceptibly lower than that measured in He ambient gas. This is indicative of the formation of extra CN molecules and the presence of additional CN emission other than that coming from the ablated native CN molecules. This extra CN molecules are supposedly formed by the reaction between the C atoms ablated from the sample and the N atoms dissociated from the ambient gas. This extra CN emission is on the other not to be expected in the case of using high purity He ambient gas, in which case the CN emission has its sole origin from the ablated native CN molecules. The presence of this extra CN emission is obviously detrimental to the CN analysis of the sample and hence the use of \( \text{N}_2 \) ambient gas or ambient air is not recommended for that purpose.

In addition to the different effects of He and \( \text{N}_2 \) ambient gas described above, it is also useful to take a look at the dynamical behaviors of the CN band and C I 247.8 nm emission lines in the two ambient gases. To that end, the time profiles of CN and C emission intensities are measured separately in He ambient gas of 2 kPa and \( \text{N}_2 \) ambient gas of 1 kPa. These gas pressures are chosen for the near maximum CN and C emission intensities as shown in Fig. 2. Fig. 4 shows the time evolution of the two emission intensities in each of those two ambient gases. It is clear that the CN and C emission lines generated in He plasma exhibit higher intensities and last longer than their corresponding emission lines generated in \( \text{N}_2 \) ambient gas due to the prolonged He assisted excitation process. In the mean time while the CN and C emission lines display qualitatively similar intensity time profiles, the former has significantly higher intensity and sustains a longer decaying process, which is probably related to the lower excitation energy of CN band. It should be further noted from Fig. 4 that CN and C emission lines in the \( \text{N}_2 \) ambient gas show markedly different time dependent intensity variations. Apparently the two emission processes are complicated by the \( \text{C} + \text{N} \rightarrow \text{CN} \) recombination reaction which results in higher CN emission intensity as well as its longer lifetime.

**B. Quantitative analysis of milk powder using CN band at 388.3 nm**

Having demonstrated the superior result of low pressure He ambient gas for the detection of native CN emission, we...
C. Application of CN emission for fossil and modern samples

Figure 4 shows the emission spectra of modern fossil and
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resulted emission spectra are presented in Fig. 9 for the case of using He ambient gas at 2 kPa. Strong CN band emission at 388.3 nm and C emission at 247.8 nm as well as Si emission are fully exhibited.

It is important to remember that CN emission is not always in the emission spectrum of organic sample. This is verified by an experiment on volcano stone which is free from N content. Fig. 10 shows the measured emission spectra obtained with ambient N₂ at 1 kPa covering separately the wavelength regions of CN band at 388.3 nm and C 1 247.8 nm. It is obvious that no CN band is visible whereas a sharp C emission line appears very clearly.

D. Potential application in Mars

Finally, preliminary work exploring the possibility for tracing possible sign of life in Mars is conducted by the detection of CN band with low pressure CO₂ ambient gas of 600 Pa mimicking the Mars atmosphere and using the carbon stamp as a sample. The resulted spectrum is presented in Fig. 11. A strong CN band clearly appears in the spectrum. In order to clarify the origin of this emission band, the measurement is repeated on a sample of pelletized GaN and KBr powder mixture. The resulted spectrum given in Fig. 12 does not turn up the CN band. This implies that no CN molecule is produced as a result of reaction between N ablated from the sample and C dissociate from the CO₂ ambient gas. This result has thus shown the promising application of LIBS for CN band detection in Mars.

IV. CONCLUSION

We have shown in this experimental study the CN emission characteristics in N₂ ambient gas or equivalently N₂ rich ambient air which are complicated by the formation of extra...
CN molecules and making it undesirable for CN analysis. On the other hand, our experimental results demonstrate a clean emission and other favorable emission characteristics observed with He ambient gas at low pressure (23 Pa).

The results further show its potential application to quantitative and sensitive CN analysis as supported by a near linear calibration curve with extrapolated near zero intercept. The applications to fossil samples yield very clean C 1 247.8 nm and CN 388.3 nm emission signals which provides the information of total C content in the sample and may be useful for in situ radiocarbon dating. Finally, the use of CO2 ambient gas at very low pressure simulating the Mars atmosphere also succeeds to produce the expected CN emission lines of excellent spectral quality.

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