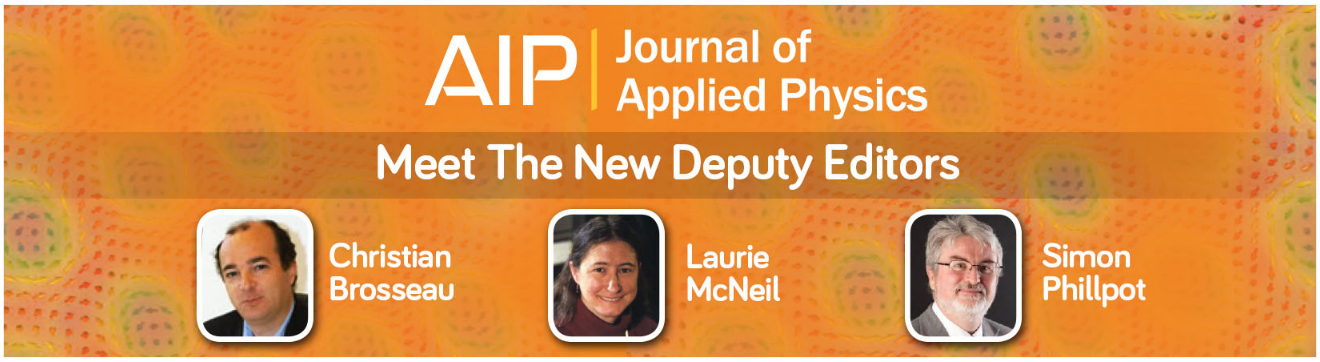
AIP | Journal of Applied Physics

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

Marincan Pardede, Rinda Hedwig, Syahrun Nur Abdulmadjid, Kurnia Lahna, Nasrullah Idris, Eric Jobiliong, Hery Suyanto, Alion Mangasi Marpaung, Maria Margaretha Suliyanti, Muliadi Ramli, May On Tjia, Tjung Jie Lie, Zener Sukra Lie, Davy Putra Kurniawan, Koo Hendrik Kurniawan, and Kiichiro Kagawa

Citation: Journal of Applied Physics **117**, 113302 (2015); doi: 10.1063/1.4915344
View online: http://dx.doi.org/10.1063/1.4915344
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/117/11?ver=pdfcov
Published by the AIP Publishing



JOURNAL OF APPLIED PHYSICS **117**, 113302 (2015)

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

Marincan Pardede,[1] Rinda Hedwig,[2] Syahrun Nur Abdulmadjid,[3] Kurnia Lahna,[3] Nasrullah Idris,[3] Eric Jobiliong,[4] Hery Suyanto,[5] Alion Mangasi Marpaung,[6] Maria Margaretha Suliyanti,[7] Muliadi Ramli,[3] May On Tjia,[8,9] Tjung Jie Lie,[9] Zener Sukra Lie,[9] Davy Putra Kurniawan,[9] Koo Hendrik Kurniawan,[9,a)] and Kiichiro Kagawa[9,10]

[1]*Department of Electrical Engineering, University of Pelita Harapan, 1100 M.H. Thamrin Boulevard, Lippo Village, Tangerang 15811, Indonesia*
[2]*Department of Computer Engineering, Bina Nusantara University, 9 K.H. Syahdan, Jakarta 14810, Indonesia*
[3]*Department of Physics, Faculty of Mathematics and Natural Sciences, Syiah Kuala University, Darussalam, Banda Aceh 23111, NAD, Indonesia*
[4]*Department of Industrial Engineering, University of Pelita Harapan, 1100 M.H. Thamrin Boulevard, Lippo Village, Tangerang 15811, Indonesia*
[5]*Department of Physics, Faculty of Mathematics and Natural Sciences, Udayana University, Kampus Bukit Jimbaran, Denpasar 80361, Bali, Indonesia*
[6]*Department of Physics, Faculty of Mathematics and Natural Sciences, Jakarta State University, 10 Rawamangun, Jakarta 13220, Indonesia*
[7]*Research Center for Physics, Indonesia Institute of Sciences, Kawasan Puspiptek, Serpong, Tangerang Selatan, 15314 Banten, Indonesia*
[8]*Physics of Magnetism and Photonics Group, Faculty of Mathematics and Natural Sciences, Bandung Institute of Technology, 10 Ganesha, Bandung 40132, Indonesia*
[9]*Research Center of Maju Makmur Mandiri Foundation, 40/80 Srengseng Raya, Jakarta 11630, Indonesia*
[10]*Fukui Science Education Academy, Takagi Chuou 2 choume, Fukui 910-0804, Japan*

(Received 2 January 2015; accepted 7 March 2015; published online 19 March 2015)

We report the results of experimental study on CN 388.3 nm and C I 247.8 nm emission characteristics using 40 mJ laser irradiation with He and N_2 ambient gases. The results obtained with N_2 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 advantages 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 CO_2 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 contamination[13–17] 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, N, and O atomic emission intensities, and the C/H, C/O, C/N, and O/N intensity ratios, as well as the diatomic molecular bands of C_2, CN, and their

---

[a)] Author to whom correspondence should be addressed. Electronic mail: kurnia18@cbn.net.id

0021-8979/2015/117(11)/113302/7/$30.00

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 problem. 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.[2,26–32] 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*.[27,32] 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.[33,34] 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 a 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

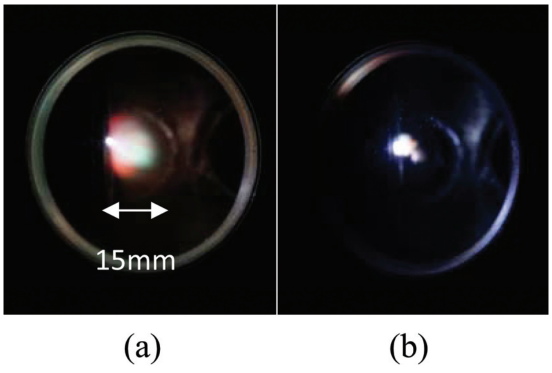
The schematic diagram of the experimental arrangement is similar to our previous works.[34] In this experiment, the ns 1064 nm Nd:YAG (Quanta Ray, LAB 130-10, 8 ns maximum energy of 450 mJ) is operated in a Q switched mode at a repetition rate of 10 Hz with the laser output energy fixed at 40 mJ yielding a power density of around 25 GW/cm^2. 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 sourse 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 × 3 cm × 0.5 cm. As such it can be irradiated in both rotated or fix 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 400 000 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 I*Star intensified CCD 1024 × 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 f/8.6 Czerny Turner configuration) 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) N_2 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.[33,34] 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), one only 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 N_2 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



(a) (b)

FIG. 1. Photograph of the plasmas 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 N_2 at 101 kPa.

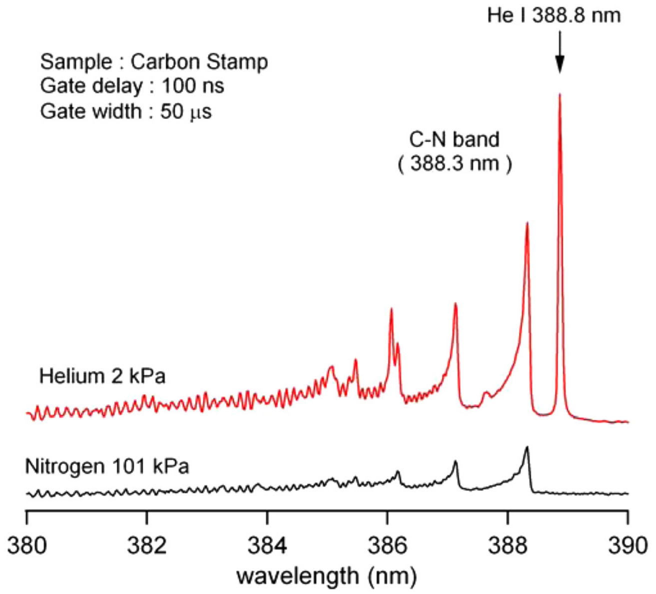


FIG. 2. Emission spectra of CN band at 388.3 nm produced by Nd-YAG laser irradiation of carbon stamp at 40 mJ output energy in (a) He ambient gas at 2 kPa and (b) ambient N_2 at 101 kPa. Gate delay and gate width of the OMA system are set at 100 ns and 50 μs, respectively.

whether the high gas pressure or the 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 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 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 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 the 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 N_2 ambient gas or ambient air is not recommended for that purpose.

In addition to the different effects of He and 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 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. 3. 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 N_2 ambient gas due to the prolonged He assisted excitation process.[34] 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 N_2 ambient gas show markedly different time dependent intensity variations. Apparently the two emission processes are complicated by the C + N → 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

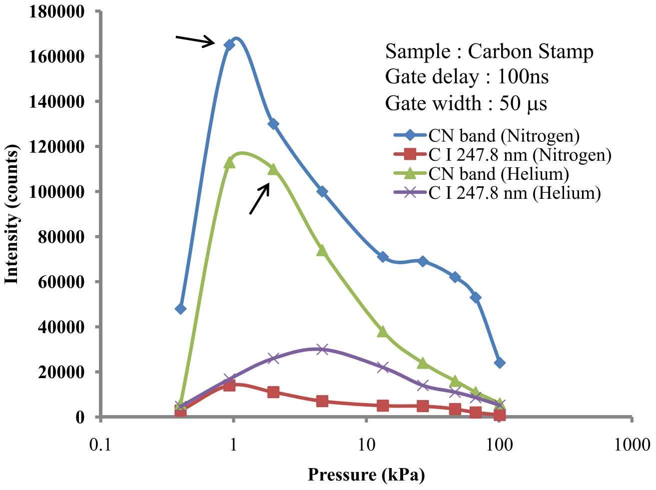


FIG. 3. Variations of CN band at 388.3 nm and C I 247.8 nm emission intensities with respect to increasing gas pressure expressed in logarithmic scale obtained with the same experimental condition cited in Fig. 2. The maximum intensities are indicated by an arrow head.

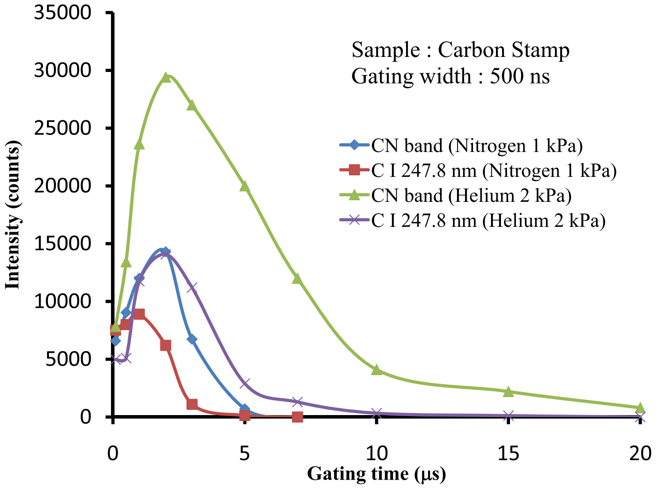


FIG. 4. Time evolution of 388.3 nm CN band and C I 247.8 nm emission intensities in 2 kPa He gas and 1 kPa N_2 gas. The sample is carbon stamp. Nd-YAG laser of 40 mJ energy is used. Gate width of the OMA system is set at 500 ns.

proceed to investigate the feasibility of quantitative analysis of CN band by performing an initial semi quantitative experiment employing milk powder samples containing 20% and 10% of protein. The milk sample is prepared by thoroughly mixing the milk powder with KBr powder and grounded into an average size of less than 50 μm. The resulted fine powder is subsequently pressed under 30 atm for 1 min to form a pellet of 10 mm diameter and 1.5 mm thickness. This pellet is then irradiated with 40 mJ Nd-YAG laser in helium gas of 2 kPa. Fig. 5 shows the resulted spectra for wavelength region around CN band at 388.3 nm. It is seen from the two spectra that the emission intensities of CN band of milk powder containing 20% protein are almost exactly twice that of milk powder containing 10% protein.

Encouraged by those results, we proceed with the following experiment aiming at verifying the possibility to do quantitative analysis using the CN band. For this experiment, a number of liquid samples are prepared with different protein concentrations. This is done by putting the same amount of each milk liquid sample onto the surface of each an alumina plate (15 × 15 mm with thickness of 10 mm). The sample is then heated at 120 °C for 5 min before being mounted on the sample holder inside the chamber for laser irradiation. The resulted CN emission intensities for the corresponding protein concentrations are plotted to give the calibration curve presented in Fig. 6. The calibration curve is quite smooth and nearly linear with extrapolated zero intercept. Each point in the calibration curve is a average result of 10 consecutive measurements. The detection limit is further determined from the spectrum of a sample containing 0.25% protein and the result is shown in Fig. 7. Based on the criterion of three times noise level, the detection limit of CN band at 388.3 nm is estimated around 5 ppm. It should be pointed out that this quantitative result cannot be obtained using LIBS technique at atmospheric ambient air since the large amount of N_2 in air will seriously disturb the native CN emission signal and hence reduce the sensitivity of its detection.

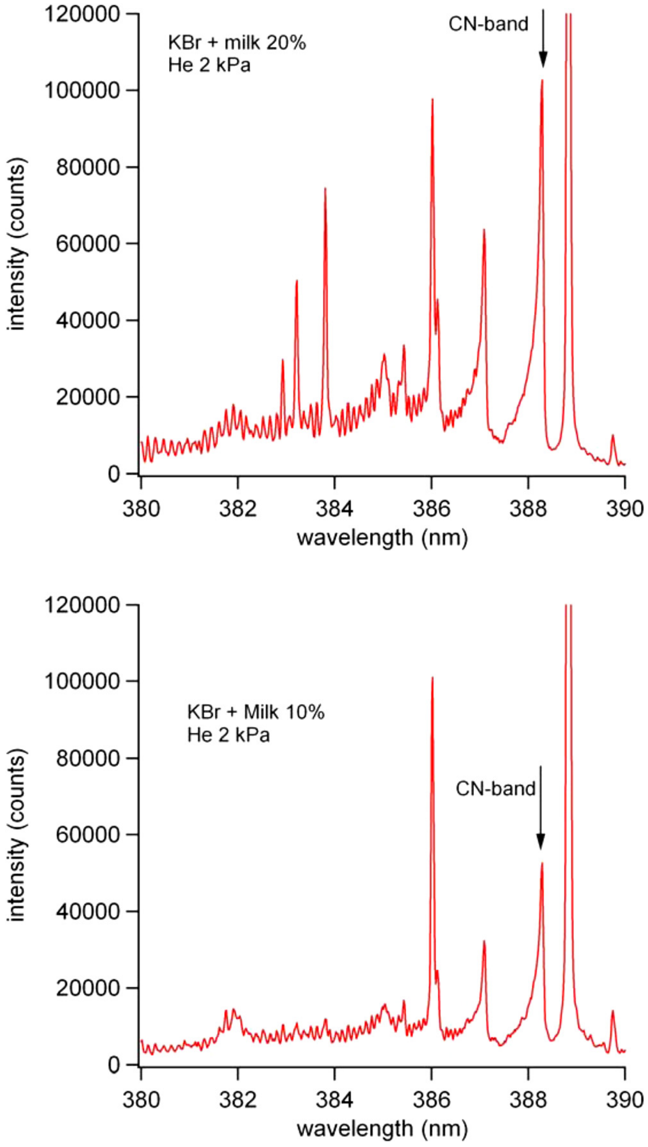


FIG. 5. Emission spectra of milk powder samples containing 10% and 20% protein presented in the 388.3 nm CN band wavelength region which is obtained with He ambient gas at 2 kPa, Nd-YAG laser of 40 mJ energy, gate delay, and gate width of the OMA system set at 100 ns and 50 μs, respectively.

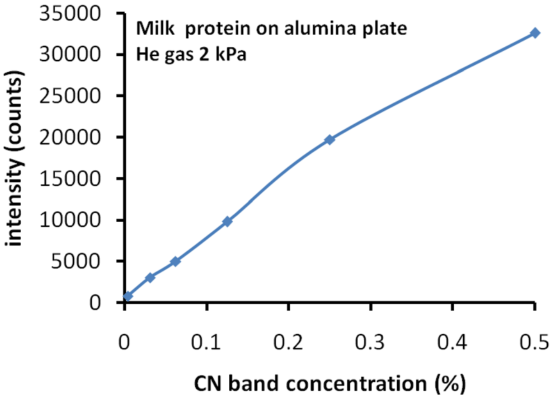


FIG. 6. The 388.3 nm CN band emission intensity plotted as a function of protein concentration in liquid milk. He gas at 2 kPa is used as the ambient gas.

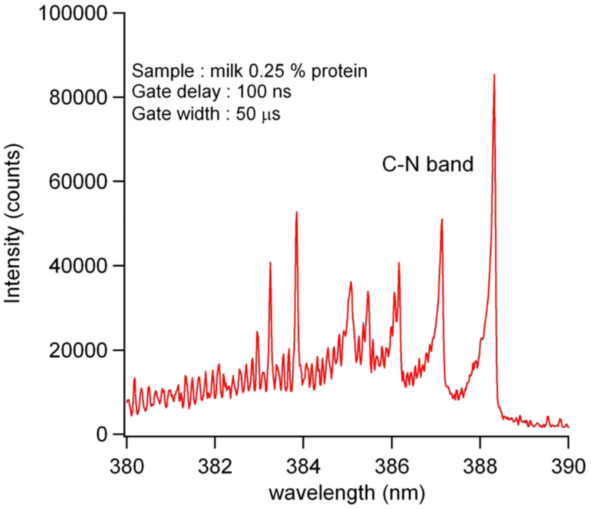


FIG. 7. Emission spectra from liquid milk containing 0.25% protein deposited on an alumina plate detected in He ambient gas at 2 kPa. The curve represents an averaging result of 10 consecutive measurements.

C. Application of CN emission for fossils analysis

Given the encouraging result described above, an exploration is conducted on its possible application to carbon dating of fossils. The detection of C along with CN emission intensities can provide information of the total C content of the sample by means of relatively simple and rapid method of LIBS. The following dating process can then be determined on the basis of standardized emission intensity of radioactive ^{14}C in the sample. The highly sensitive and rapid elemental analysis of fossils using the LIBS technique naturally lends itself to the rapid determination of the associated fossilization process *in situ*. While the techniques of radiocarbon dating developed by Krueger[35] and others during the 1960s have laid the groundwork for subsequent development on stable carbon, nitrogen, oxygen, and strontium isotope analysis, so far no report is available on its application for *in-situ* analyses.[36] Meanwhile, portable X-ray fluorescence equipment which has become a popular technique for elemental analysis in many fields cannot be applied to H and C analysis because of their light atomic weights.[33,34]

In this experiment, we perform the spectrochemical analysis of C and CN of fossil samples using the low pressure He plasma. The samples (buffalo horn fossil dated 400 000 years and leaf fossil dated 2.4 million years) are collected from the Sangiran region of Central Java, which is one of only a few hominid sites in the world.

Fig. 8 shows the emission spectra of buffalo horn fossil covering the CN band and C I 247.8 nm emission wavelength region measured separately in He ambient gas at 2 kPa and at atmospheric pressure. It is seen that the emission intensities detected at the lower pressure are generally much higher. Interestingly, the spectrum also shows strong Si emission lines indicating that some exchange process may have taken place between C from the horn and Si from the soil. For a comparison, leaf fossil is also used as an sample and the

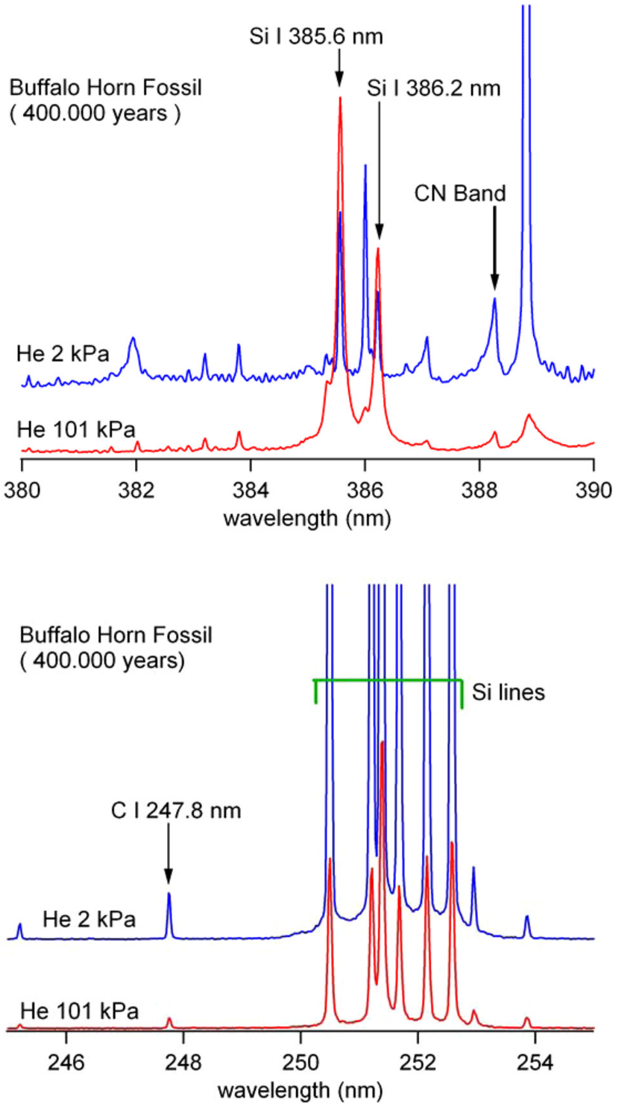
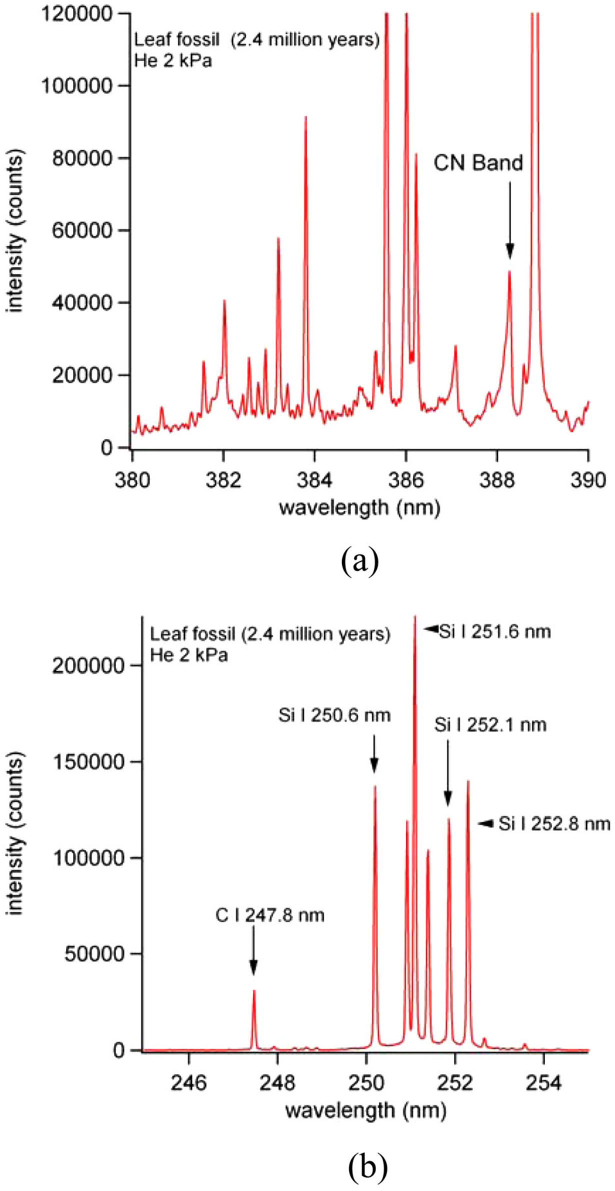


FIG. 8. Emission spectra of buffalo horn fossil (400 000 years) covering separately CN band of 388.3 nm and C I 247.8 nm wavelength regions. He at 2 kPa and 101 kPa are separately used as an ambient gas. The same laser energy, gate delay, and gate width of the OMA system are used.



(a)

(b)

FIG. 9. Emission spectra of leaf fossil (2 400 000 years) covering separately the 388.3 nm CN band and C I 247.8 nm wavelength regions measured with He ambient gas at 2 kPa and the same laser energy as well as the same gate delay and gate width of the OMA system, as cited for Fig. 3.

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 N_2 at 1 kPa covering separately the wavelength regions of CN band at 388.3 nm and C I 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 CO_2 ambient gas of 600 Pa mimicking the Mars atmospheres and using the carbon stamp as an 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 dissociated from the CO_2 ambient gas. This result has thus shown the promising application of LIBS for CN band detection in Mars.

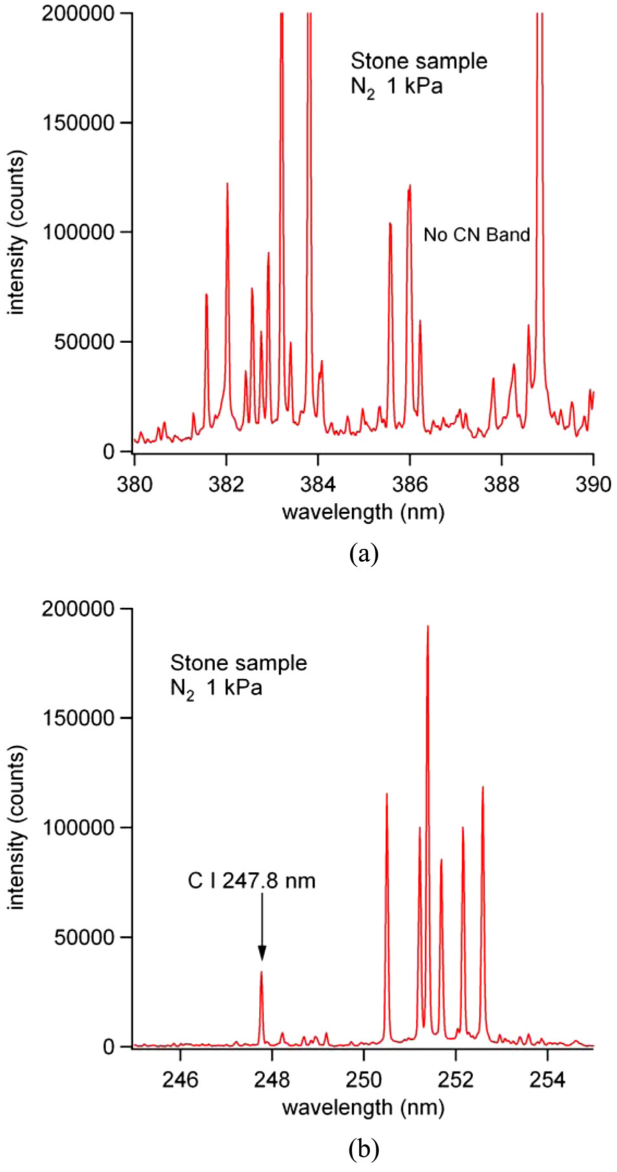


FIG. 10. Emission spectra of volcano stone covering the 388.3 nm CN band and C I 247.8 nm wavelength regions. N_2 at 1 kPa is used as an ambient gas. The same laser energy as well as the same gate delay and gate width of the OMA system employed.

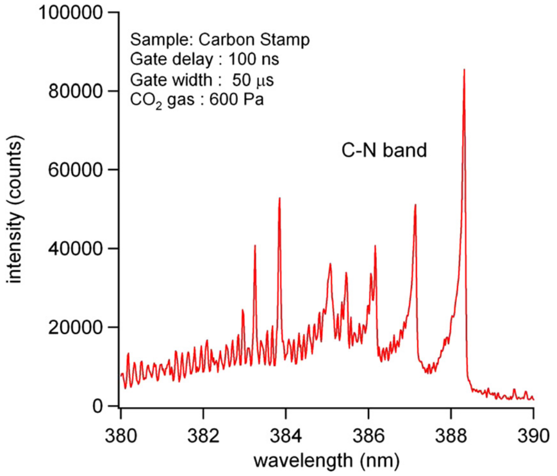


FIG. 11. Emission spectra from carbon stamp sample in CN band of 388.3 nm wavelength region. CO_2 ambient gas at 600 Pa is used as an ambient gas. Nd-YAG laser of 40 mJ energy is used. Gate delay and gate width of the OMA system are set at 100 ns and 50 μs, respectively.

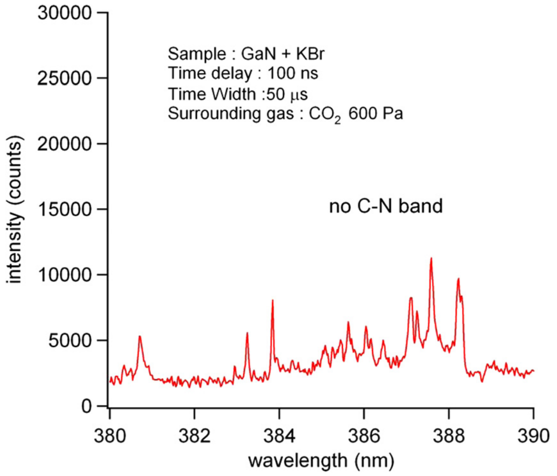


FIG. 12. Emission spectra from a pellet of 50% GaN and 50% KBr powder mixture obtained with CO_2 ambient gas at 600 Pa and the same Nd-YAG laser energy of 40 mJ, gate delay, and gate width of 100 ns and 50 μs, respectively.

IV. CONCLUSION

We have shown in this experimental study the CN emission characteristics in N_2 ambient gas or equivalently N_2 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 (2 kPa). 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 I 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 CO_2 ambient gas at very low pressure simulating the Mars atmosphere also succeeds to produce the expected CN emission lines of excellent spectral quality.

ACKNOWLEDGMENTS

The authors wish to express his sincerest thanks to Mr. Sutanto from Sangiran, Central Java Prefecture, for providing small fraction of buffalo horn fossil used in this work.

[1] A. W. Miziolek, V. Palleschi, and I. Schechter, *Laser-Induced Breakdown Spectroscopy (LIBS) Fundamentals and Applications* (Cambridge University Press, Cambridge, 2006).

[2] L. St-Onge, R. Sing, S. Bechard, and M. Sabsabi, Appl. Phys. A **69**, S913–S916 (1999).

[3] R. Sattmann, I. Monch, H. Krause, R. Hall, S. Couris, S. Hatziapostolou, A. Mauromanolakis, C. Fotakis, E. Larrauri, and R. Miguel, Appl. Spectrosc. **52**, 456–462 (1998).

[4] J. Anzano, R. J. Lasheras, B. Bonilla, and J. Casas, Polym. Test **27**, 705–710 (2008).

[5] S. Gregoire, M. Boudinet, F. Pelascini, F. Surma, V. Detalle, and Y. Holl, Anal. Bioanal. Chem. **400**, 3331–3340 (2011).

[6] Y. Yu, L. B. Guo, Z. Q. Hao, X. Y. Li, M. Shen, Q. D. Zeng, K. H. Li, X. Y. Zeng, Y. F. Lu, and Z. Ren, Opt. Express **22**, 3895–3901 (2014).

[7] L. St-Onge, E. Kwong, M. Sabsabi, and E. B. Vadas, Spectrochim. Acta B **57**, 1131–1140 (2002).

[8] J. L. Gottfried, F. C. De Lucia, Jr., C. A. Munson, and A. W. Miziolek, J. Anal. At. Spectrom. **23**, 205–216 (2008).

[9] J. D. Hybl, G. A. Lithgow, and S. G. Buckley, Appl. Spectrosc. **57**, 1207–1215 (2003).

[10] R. Gonzalez, P. Lucerna, L. M. Tobaria, and J. J. Laserna, J. Anal. At. Spectrom. **24**, 1123–1126 (2009).

[11] J. L. Gottfried, F. C. De Lucia, Jr., and A. W. Miziolek, J. Anal. At. Spectrom. **24**, 288–296 (2009).

[12] J. L. Gottfried and F. C. De Lucia, Jr., Anal. Bioanal Chem. **395**, 283–300 (2009).

[13] R. E. Neuhauser, U. Panne, R. Niessner, G. A. Petrucci, P. Cavalli, and N. Omenetto, Anal. Chim. Acta **346**, 37–48 (1997).

[14] O. Samek, D. C. S. Beddows, J. Kaiser, S. Kukhlevsky, L. Miroslav, H. H. Telle, and J. A. Whitehouse, Opt. Eng. **39**, 2248–2262 (2000).

[15] Y. Ito, O. Ueki, and S. Nakamura, Anal. Chim. Acta **299**, 401–405 (1995).

[16] H. A. Archontaki and S. R. Crouch, Appl. Spectrosc. **42**, 741–746 (1988).

[17] F. Y. Yueh, R. C. Sharma, J. P. Singh, and H. J. Zhang, Air Waste Manage. Assoc. **52**, 1307–1315 (2002).

[18] M. O. Al-Jeffery and H. H. Telle, Proc. SPIE **4613**, 152–161 (2002).

[19] T. Prohaska, C. Stadlbauer, R. Wimmer, G. Stingeder, L. Latkaczy, E. Hoffmann, and E. Stephanowitz, Sci. Total Environ. **219**, 29–39 (1998).

[20] M. H. Niemz, Appl. Phys. B **58**, 273–281 (1994).

[21] I. G. Pallikaris, H S. Ginis, G. A. Kounis, D. Anglos, T. G. Papazoglou, and L. P. Naomidis, J. Refractive Surg. **14**, 655–660 (1998).

[22] J. M. Anzano, I. B. Gornushkin, B. W. Smith, and J. D. Winefordner, Polym. Eng. Sci. **40**, 2423–2429 (2000).

[23] J. Jasik, J. Heits, J. D. Pedamig, and P. Veis, Spectrochim. Acta B **64**, 1128–1134 (2009).

[24] M. Tran, Q. Sun, B. W. Smith, and J. D. Winefordner, J. Anal. At. Spectrom. **16**, 628–632 (2001).

[25] M. Dong, J. Lu, S. Yao, Z. Zhong, J. Li, J. Li, and W. Lu, Opt. Express **19**, 17021–17029 (2011).

[26] C. Vivien, J. Hermann, A. Perrone, C. Boulmer-Leborgne, and A. J. Luches, Phys. D: Appl. Phys. **31**, 1263–1269 (1998).

[27] M. Baudelet, M. Boueri, J. Yu, S. S. Mao, V. Piscitelli, X. L. Mao, and R. E. Russo, Spectrochim. Acta B **62**, 1329–1334 (2007).

[28] S. S. Harilal, R. C. Issac, C. V. Bindhu, G. K. Varier, V. P. N. Nampoori, and C. P. G. Vallabhan, Pramana J. Phys. **46**, 145–151 (1996).

[29] P. Lucerna, A. Dona, L. M. Tobaria, and J. J. Laserna, Spectrochim. Acta B **66**, 12–20 (2011).

[30] M. Baudelet, L. Guyon, J. Yu, J. P. Wolf, T. Amodeo, E. Frejafon, and P. Laloi, Appl. Phys. Lett. **88**, 063901–063909 (2006).

[31] G. Dinescu, E. Aldea, M. I. De Giorgi, A. Luches, A. Peronne, and A. Zocco, Appl. Surf. Sci. **127–129**, 697–702 (1998).

[32] M. Boueri, M. Baudelet, J. Yu, X. L. Mao, S. S. Mao, and R. E. Russo, Appl. Surf. Sci. **255**, 9566–9571 (2009).

[33] K. H. Kurniawan and K. Kagawa, Appl. Spectrosc. Rev. **41**, 99–130 (2006).

[34] K. H. Kurniawan, M. O. Tjia, and K. Kagawa, Appl. Spectrosc. Rev. **49**, 323–434 (2014).

[35] H. W. Krueger, in *Proceeding of the 6th International Conference on Radiocarbon and Tritium Dating*, edited by R. M. Chatters and E. A. Olson (Pullman, WA; Clearinghouse for Federal Science and Technology Information, National Bureau of Standards, Washington, DC, 1965), pp. 332–337.

[36] T. E. Cerling and Z. D. Sharp, Palaeogeogr., Palaeoclimatol., Paleoecol. **126**, 173–186 (1996).