

# Identification of nitro-compounds with LIBS

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**ABSTRACT** Laser-induced breakdown spectroscopy (LIBS) is applied to characterize the organic compounds 4-nitroaniline and 4-nitrotoluene by measuring the intensity of atomic lines. The hypothesis of local thermodynamic equilibrium (LTE) is verified by comparing the measured value of electron density in the laser-induced plasma with its lower limit, for which LTE holds good. The present study infers that the O/N intensity ratio is a unique parameter to discriminate each nitro-compound from the explosives.

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## 1 Introduction

Most of the energetic compounds are organic in nature and their detection is of scientific and environmental interest because of possible health hazards [1]. Currently, there are many sensitive techniques like ion-mobility spectroscopy and mass spectrometry coupled with gas chromatography, which are being used for qualitative and quantitative analysis of these compounds [2]. The main disadvantage of these methods is that the sample must be first collected and then sent to a laboratory for analysis, unless special expensive analytic equipment is used. Therefore there is a need for a technique, which has real-time, in situ and quick detection capability. LIBS is such a technique to differentiate energetic compounds from innocuous substances by providing spectral signatures that enable the unique identification of different species. The special features of LIBS, to provide remote, rapid and multi-elemental analysis of bulk and trace sample in any phase (solid, liquid and gas) [3–8] without any sample preparation, are very advantageous compared with other analytical approaches [9–13].

A high intensity nanosecond pulsed laser vaporizes the sample, and creates an expanding plasma plume of target material. The laser-created plasma characteristics are strongly dependent upon several parameters like laser intensity, pulse duration, wavelength, and chemical composition of the target material and also on the surrounding atmosphere. LIBS

is basically an optical emission spectroscopy in which we compare the intensities of atomic lines of different species present in the sample under local thermodynamic equilibrium (LTE) [14]. One of the aims of the present work is to characterize the laser-induced plasma plume in order to verify the existence of LTE, by determining parameters like plasma temperature and electron density. If thermodynamic equilibrium exists, the relative populations of atomic energy levels are determined by the equilibrium temperature. When this equilibrium occurs for a small region of plasma plume it leads to the concept of LTE, although it may be somewhat different for different regions. LTE exists after a sufficient number of collisions have occurred to thermalize the plasma, and heavy species (atoms and ions) and light species (electrons) are in equilibrium. In the present work, intensities of the atomic lines corresponding to oxygen (O) and nitrogen (N) from the laser-induced plasma of organic compounds (4-nitroaniline and 4-nitrotoluene) have been measured. This has led to the estimation of the (O/N) ratio in these compounds for comparison with that obtained from their chemical formulas.

## 2 Experimental method

4-Nitroaniline and 4-nitrotoluene in powder form were purchased from the Central Drug House Ltd., India and were used to form pellets (1 mm thick and 12 mm diameter) by applying a pressure of approximately  $2 \times 10^8$  Pa.

Laser pulses from a frequency-doubled Q-switched Nd:YAG laser (Continuum Surelite III-10, 10 Hz, 425 mJ at 532 nm, 3–4 ns pulse width) were focused onto the surface of the pellet by using a 150 mm focal-length lens (quartz) as shown in Fig. 1. The diameter of the focal spot was 0.02 mm and the intensity of the laser light within the focal volume was estimated to be  $1.97 \times 10^{16}$  W/m<sup>2</sup>. One end of a fiber bundle was used to collect the light emitted from the plasma, and its other end was connected to the entrance slit of the broadband spectrometer (Ocean Optics LIBS 2000+ working in Windows 2000 professional mode) equipped with a CCD. The pellet was placed on a rotating stage so that every laser pulse was incident at a fresh location on the sample surface and thus crater formation was avoided. We have recorded four spectra of both the compounds, each of which is an average of ten laser shots. Thus each LIBS spectrum in the present paper represents an average of 40 shots.

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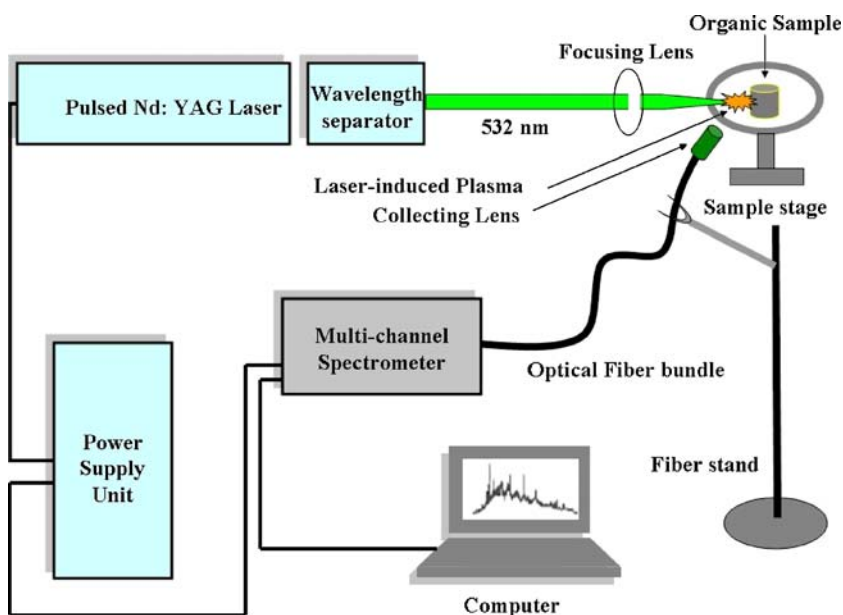


FIGURE 1 Schematic diagram of the experimental setup used to record LIBS spectra of nitro-compounds

### 3 Results and discussion

It is seen from Figs. 2 and 3 that the light emitted from the laser-induced plasma contains atomic lines of atoms and ions of C, H, N, and O as expected for an organic sample. The presence of CN bands in the spectral range from 350 nm to 440 nm and C<sub>2</sub> Swan bands around 450–480 nm region (shown in the inset of Figs. 2 and 3) further confirms the organic molecular nature of the sample. The absence of C<sub>2</sub> Swan bands in the region 510–550 nm is due to the strong scattered laser light at 532 nm, which overlaps these bands. Yinon [15] has shown that the O/N intensity ratio is greater than 4 for explosive compounds and less than that for non-explosive or-

ganic compounds [16]. We have obtained the intensity ratio of O/N by measuring the intensities of the atomic lines of O at 777.1 nm and of N at 744.2 nm after verification of LTE criteria as discussed in the following sections.

#### 3.1 Temperature measurement

In order to verify the Boltzmann distribution, it is essential to make sure that the plasma is not optically thick. In the present case we are concerned with the non-resonant lines of O (*I*) at 777.1 and 844.6 nm, which do not involve the ground state of the atom. The observed intensity ratio of these lines is consistent with the ratio of the products of statistical

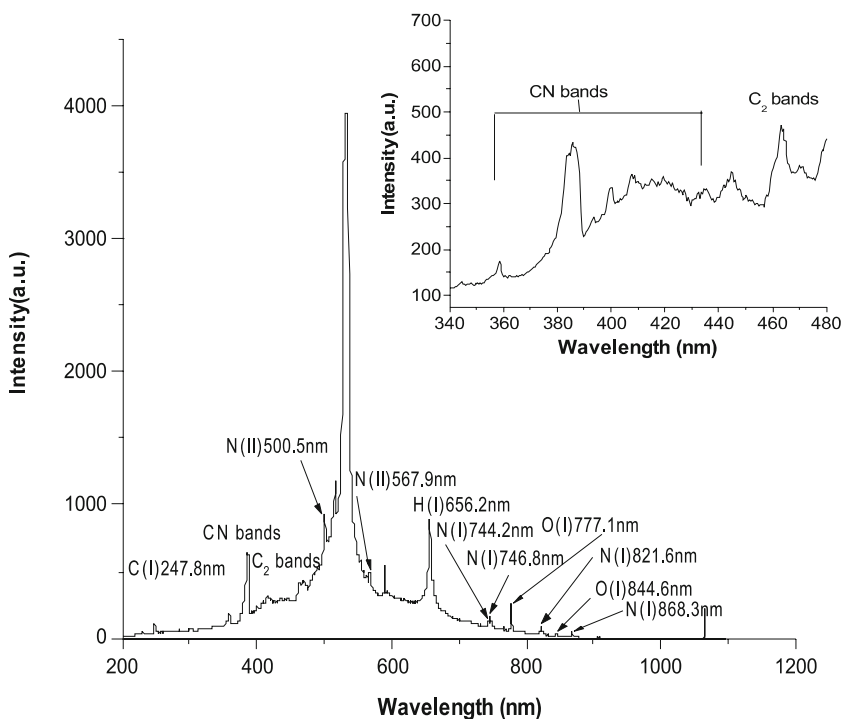
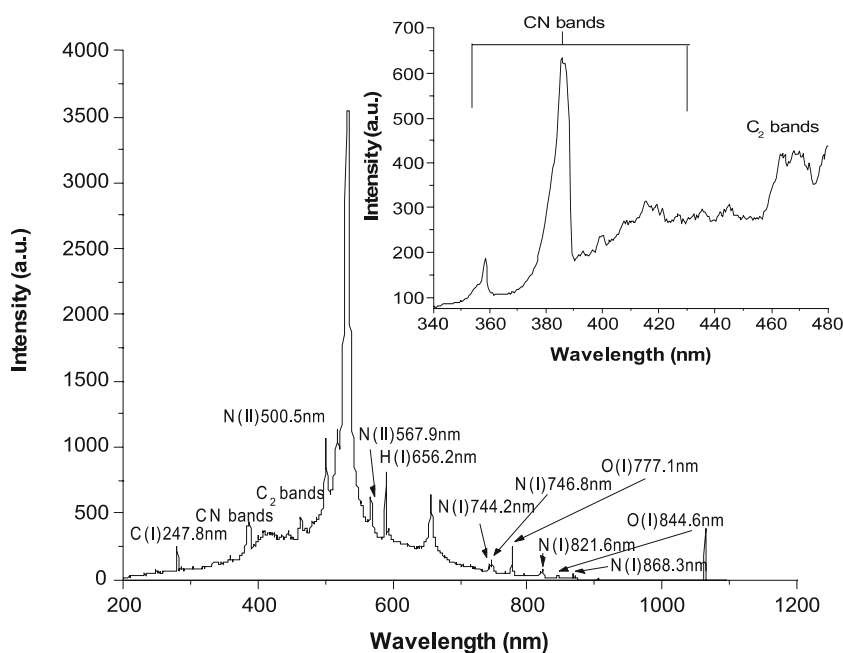
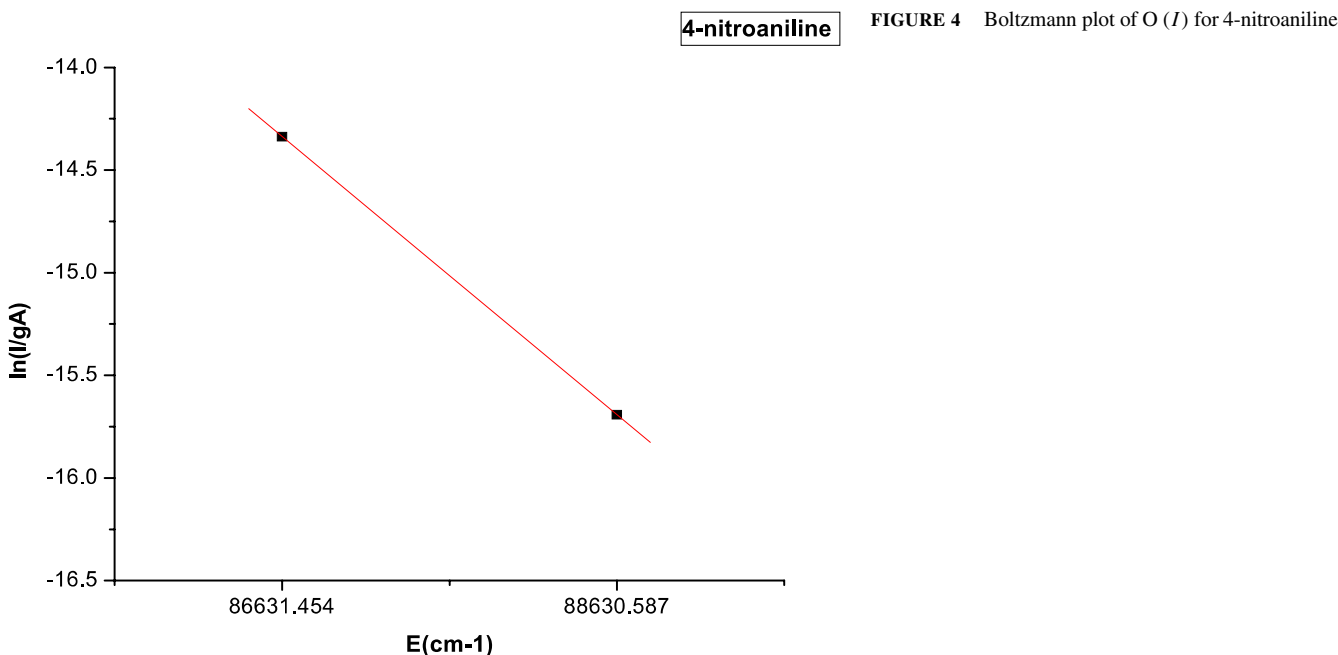


FIGURE 2 Laser-induced breakdown spectra of 4-nitroaniline



**FIGURE 3** Laser-induced breakdown spectra of 4-nitrotoluene



**FIGURE 4** Boltzmann plot of O(I) for 4-nitroaniline

weight  $g$  of their upper energy levels and transition probability  $A$ , indicating that the plasma is optically thin. For LTE at temperature  $T$  the emission intensity of a spectral line can be related to the total density  $N(T)$  of neutral atoms or ions by Boltzmann's law [17] as shown in (1)

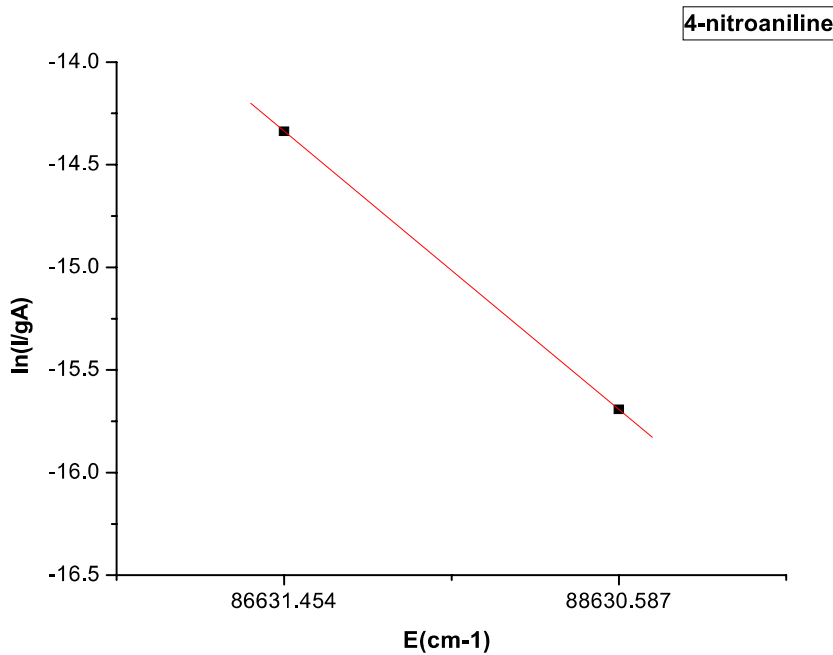
$$\ln \frac{I}{gA} = \ln \frac{hcN(T)}{4\pi U(T)} - \frac{E}{k_B T}, \quad (1)$$

where  $I$  is the intensity of each spectral line,  $g$  and  $A$  are the statistical weight and the spontaneous emission probability, respectively, for the upper energy level  $E$ ,  $k_B$ , and  $h$  are Boltzmann and Planck constants, and  $U(T)$  and  $N(T)$  are partition function and total density of emitting species, respectively. In the present case the multiplet structure is not resolved in the observed atomic lines at 777.1 and 844.6 nm and each of

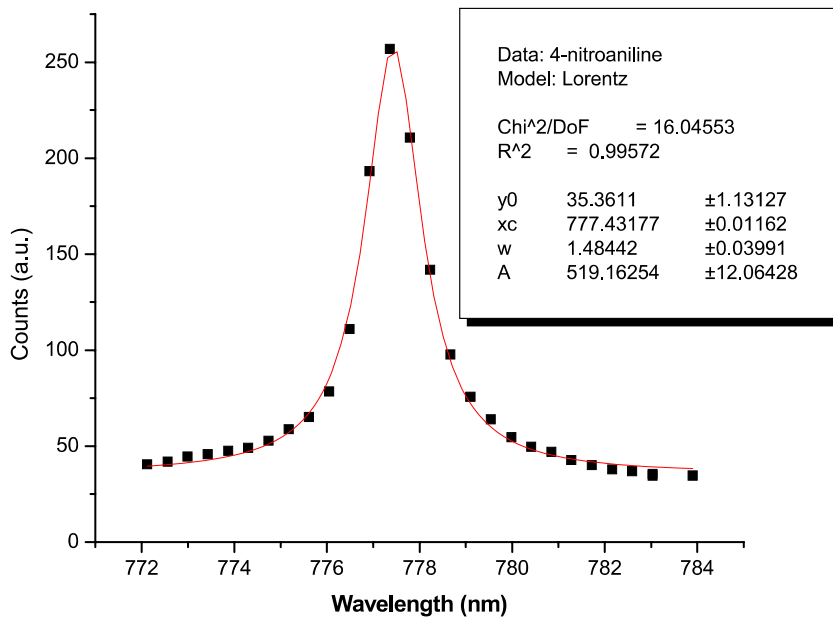
them is composed of three overlapped components. In order to obtain the separate intensity ( $I$ ) of each component we have distributed the observed intensity into three different parts according to the relative intensities of the components as given in the NIST table (see Table 1) [18]. The graph  $\ln I/(gA)$  vs.  $E$  is then plotted for the strongest components at 777.1 nm and 844.6 nm (as shown in Figs. 4 and 5) and the equilibrium plasma temperatures are found to be 2120 and 3050 K for 4-nitroaniline and 4-nitrotoluene, respectively.

### 3.2 Electron density measurement

To verify the existence of LTE, the knowledge of the electron density in the laser-induced plasma is also essential, which may be obtained by measuring the broaden-



**FIGURE 5** Boltzmann plot of O (*I*) for 4-nitrotoluene



**FIGURE 6** Lorentzian profile of O (*I*) of 4-nitroaniline at 777 nm

ing of the spectral lines. In a plasma source the line-width is due to Stark broadening, which results from collisions of charged species [19], whereas pressure and Doppler broadenings are quite small [20]. Lorentzian line shape functions, fitted to the experimental data points of the emission intensities for 777.1 nm lines, are shown in Figs. 5 and 6 for 4-nitroaniline and 4-nitrotoluene, respectively. The observed line-widths, FWHM ( $\Delta\lambda_{\text{observed}}$ ), have been corrected by subtracting the instrumental width ( $\Delta\lambda_{\text{instrument}}$ ) whose value is 0.05 nm for our spectrometer. The corrected values of  $\Delta\lambda$  for 777.1 nm line are 1.434 and 1.330 nm for 4-nitroaniline and 4-nitrotoluene, respectively. The electron densities were calculated by using the relation

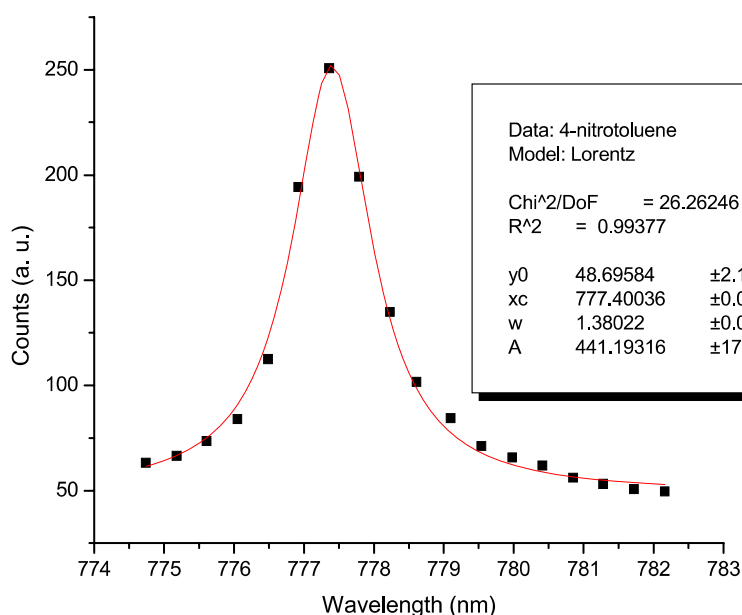
$$N_e = \frac{\Delta\lambda \times 10^{16}}{2w} [\text{cm}^{-3}], \quad (2)$$

where  $\Delta\lambda$  is FWHM and  $w$  is the electron impact parameter. The impact parameter of O at 777.1 nm line for the plasma temperature range 2000–5000 K has been obtained from the work presented in [17] as  $1.99 \times 10^{-3}$  and  $2.48 \times 10^{-3}$  nm for 4-nitroaniline and 4-nitrotoluene, respectively, and the values of  $N_e$  for the two samples are found to be  $3.60 \times 10^{18}$  and  $2.68 \times 10^{18} \text{ cm}^{-3}$ , respectively. We have also calculated the lower limit for the electron density for a plasma exhibiting LTE by using the McWhirter criterion [21]

$$N_e [\text{cm}^{-3}] \geq 1.6 \times 10^{12} (T [\text{K}])^{1/2} (\Delta E [\text{eV}])^3, \quad (3)$$

where  $T$  is the plasma temperature and  $\Delta E$  is the largest energy transition.

By substituting the value of  $T = 2120$  and  $3050$  K (computed from Boltzmann plots) and  $\Delta E = 1.59$  eV from the



**FIGURE 7** Lorentzian profile of O (*I*) of 4-nitrotoluene at 777 nm

NIST data table [18] in the above equation, the values of electron densities come out to be  $2.98 \times 10^{14}$  and  $3.58 \times 10^{14} \text{ cm}^{-3}$  for 4-nitroaniline and 4-nitrotoluene, respectively. Thus it is found that the electron densities obtained from (2) are greater than their respective lower limits given by equation (3) and the condition for LTE is fulfilled for the laser-induced plasma in our experiments.

### 3.3 O/N intensity ratio

The use of LIBS as an experimental tool for identification of compounds on an operational level needs extensive developments in two directions. The first is the determination of stoichiometry of the compound by using intensity ratios of spectral lines of one or more pairs of elements and the second is matching of the unknown spectrum with the predetermined and assembled spectral library of reference materials of interest. In the present case we have attempted to determine the stoichiometry of the compound from the ratio O/N of spectral lines, which has been found to yield good results [22–25] for distinction between different organic compounds. The measured intensities of O at 777.1 nm and N at 744.2 nm determined

from the area under line profile give (O/N) ratios of 13.97 and 10.28 for 4-nitroaniline and 4-nitrotoluene, respectively. The ratio of O/N obtained from the chemical formula of 4-nitroaniline ( $\text{C}_6\text{H}_6\text{N}_2\text{O}_2$ ) is 1 and that of 4-nitrotoluene ( $\text{C}_7\text{H}_7\text{NO}_2$ ) is 2.

The mismatch between the O/N ratio obtained from the spectrum and that from the chemical formula may arise due to two factors. The first reason is the superimposition of three components of the atomic line of O (*I*) (777.19, 777.41, and 777.53 nm), not resolved due to lack of resolution (0.75 nm) in our spectra (see Figs. 2 and 3). The second reason is the specific values of transition probability and statistical weight for upper levels of each of the observed lines. To account for these shortcomings we distribute the observed intensity (*I*) into three distinct intensities by fractional ratio for each of the three overlapped components on the basis of their counts reported in NIST data table [18] and then take (*I*/*gA*) for each of them. This ratio (*I*/*gA*) for each component line of O relative to that of the 744.2 nm line of N for each of the four spectra of 4-nitroaniline and 4-nitrotoluene are shown in Tables 2 and 3, respectively. A perusal of Tables 2 and 3 shows that the O/N ratios obtained from 777.1 nm of O with respect to 744.2 nm of N are in better agreement with their

Wavelength [nm]	Transition probability $A [10^8 \text{ s}^{-1}]$	Statistical weight [g]	Transitions	Energy of the upper level $E [\text{cm}^{-1}]$
777.19 O	0.369	7	$2p^33p(^5P_3) \rightarrow 2p^33s(^5S_2)$	86631.45
777.41 O	0.369	5	$2p^33p(^5P_2) \rightarrow 2p^33s(^5S_2)$	86627.77
777.53 O	0.369	3	$2p^33p(^5P_1) \rightarrow 2p^33s(^5S_2)$	86625.75
844.62 O	0.322	1	$2p^33p(^3P_0) \rightarrow 2p^33s(^3S_1)$	88631.30
844.63 O	0.322	5	$2p^33p(^3P_2) \rightarrow 2p^33s(^3S_1)$	88631.14
844.67 O	0.322	3	$2p^33p(^3P_1) \rightarrow 2p^33s(^3S_1)$	88630.58
744.22 N	0.124	4	$2p^23p(^4S_{3/2}) \rightarrow 2p^23s(^4P_{3/2})$	96750.84

**TABLE 1** Spectroscopic data *g*, *A*, and *E* for upper energy levels of O (*I*) and N (*I*) (from NIST data table [14])



Spectrum number	O (777.1)/ N (744.2)	O (777.4)/ N (744.2)	O (777.5)/ N (744.2)
1	0.9218	1.0755	1.7924
2	0.8985	1.0483	1.7472
3	1.0239	1.1946	1.9911
4	1.4266	1.6644	2.7740
Mean	1.0677	1.2457	2.0762
S.D.	0.183	0.248	0.413
% RSD	17.1	19.9	19.9

**TABLE 2** LIBS intensity ratios of three components of O (*I*) at 777 nm with respect to N (*I*) at 744.2 nm for 4-nitroaniline and their calculated statistical parameters

Spectrum number	O (777.1)/ N (744.2)	O (777.4)/ N (744.2)	O (777.5)/ N (744.2)
1	1.7345	0.8569	1.0711
2	1.6684	0.7798	0.9747
3	1.8723	1.0178	1.2722
4	1.7543	0.8800	1.1000
Mean	1.7596	0.8836	1.1045
S.D.	0.075	0.085	0.149
% RSD	4.3	9.8	13.5

**TABLE 3** LIBS intensity ratios of three components of O (*I*) at 777 nm with respect to N (*I*) at 744.2 nm for 4-nitrotoluene and their calculated statistical parameters

**TABLE 4** The average measured intensity ratio of O (*I*) at 777.1 nm with respect to N (*I*) at 744.2 nm for 4-nitroaniline and 4-nitrotoluene

Nitro compounds	Mw [g mol <sup>-1</sup> ]	Stoichiometry (O/N) ratio	Measured (O/N) ratio	Structure
(1) 4-Nitroaniline C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>	138.12	1/1	1.07	
(2) 4-Nitrotoluene C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>	137.13	2/1	1.76	

stoichiometry from the chemical formula and these are given in Table 4.

#### 4 Conclusion

The present study demonstrates that LIBS is capable of characterizing organic compounds and also has the potential to discriminate one from the other on the basis of the intensity ratio of their characteristic spectral lines. However, to improve the level of reliability, statistical techniques of linear correlation and principal component analysis (PCA) for the identification of compounds have to be used. These attributive features of LIBS would make it a rapid and reliable technique for the identification of different toxic compounds present in any environment including soil. Work is in progress to characterize more organic compounds by mixing them in different matrixes.

#### Abbreviations

C	Carbon
CCD	Charge coupled device
DRDO	Defence Research and Development Organization
FWHM	Full width at half maximum
H	Hydrogen
LIBS	Laser-induced breakdown spectroscopy
LTE	Local thermodynamic equilibrium
Nd:YAG	Neodymium doped:yttrium aluminum garnet
N	Nitrogen
NIST	National Institute of Standards and Technology
O	Oxygen

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