



## Article

# Study of Electronic Bands of Diatomic Molecules for the Evaluation of Toxicity of Green Crackers Using LIBS Coupled with Chemometric Method

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**Abstract:** Laser-induced Breakdown Spectroscopy (LIBS) is primarily an atomic emission spectroscopic method based on analyzing the spectral lines of elements in the laser-induced plasma. However, when the plasma cools down after its ignition, i.e., when one collects the emissions from the plasma after a certain interval of time/gate delay (~1 micro-second), the signature of the electronic bands of diatomic molecules is also observed along with ionic/atomic emission lines. The present manuscript reports the evaluation of toxicity/pollutants in green crackers based on the intensity of the electronic bands of the Aluminum Oxide (AlO), calcium oxide (CaO), and strontium oxide (SrO) molecules observed in the laser-induced plasma of the firecrackers. LIBS spectra of the green crackers show the presence of spectral lines of the heavy/toxic elements such as Al, Ca, Sr, Cr, Cu, and Ba, along with the electronic bands of the AlO, CaO, and SrO. Fourier Transform Infra-Red Spectroscopy (FTIR) has been used to validate the LIBS results and confirm the molecules in these crackers. The concentration of toxic elements in green crackers such as Aluminum (Al), Copper (Cu), and Chromium (Cr) has also been estimated using the Partial Least Square Regression method (PLSR) to evaluate and compare the extent of the toxicity of green crackers.

**Keywords:** green crackers; PLSR; FT-IR; LIBS; electronic bands



**Citation:** Dubey, D.; Kumar, R.; Dwivedi, A.; Rai, A.K. Study of Electronic Bands of Diatomic Molecules for the Evaluation of Toxicity of Green Crackers Using LIBS Coupled with Chemometric Method. *Electron. Mater.* **2023**, *4*, 1–14. <https://doi.org/10.3390/electronicmat4010001>

Academic Editors: Alessandro Dell’Era, Erwin Ciro Zuleta, Enrico Bocci and Carla Lupi

Received: 9 November 2022

Revised: 19 December 2022

Accepted: 20 December 2022

Published: 27 December 2022



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## 1. Introduction

People celebrate their festivals full of joy and thrill. To adorn the festivals, firecrackers are used to emit sound and sparks, which is icing on the cake. Although, this looks good if one does not care about the hazardous effect of crackers on human beings and the environment [1]. In festivals, generally traditional firecrackers are used, which emit a lot of sound and spark [2]. Behind this magic of emitting colors and sparks, many hazardous elements/compounds are used in firecrackers. For producing different colors, the compounds of toxic elements such as Sr, Cu, Cd, Ni, Al, Sb, Ba, As, Li, Na, Ca, K, Mg, Ti, and Pb in the form of SrCO<sub>3</sub>, CuSO<sub>4</sub>, CuCO<sub>3</sub>, BaNO<sub>3</sub>, BaCl<sub>2</sub>, NaNO<sub>3</sub>, NaCl, Na<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub>, CaSO<sub>4</sub>, etc., are used [3]. Different elements emit different colors; for example, a compound of Cu is used to produce a blue color, a compound of Sr for red, Ca for orange, Na for yellow, Ba for green, and a compound of Sr + Cu for purple color [1,2]. The powders of Al, Mg, and Ti are used for a silver/white spark, and the compound of Sb (Sb<sub>2</sub>C<sub>3</sub>) is also used for the same purpose [1]. These compounds present in crackers lead to serious health diseases such as cancer, respiratory irritation, Alzheimer’s disease, Contact dermatitis, lung infections, skin irritation, wart formation, bioaccumulation, etc. Not only are these compounds toxic for human health, but also to the environment, and cause serious problems such as acid rain, polluting water sources and air of the surroundings [4]. These compounds are used for producing colors in crackers but seeing their hazardous effects

of particular elements on human health, which is dreadful, the traditional firecrackers are temporarily banned in India. The drawback of the traditional crackers is overcome by a new cracker developed by the National Environmental Engineering Research Institute (NEERI), Council of Scientific and Industrial Research (CSIR), India, called “green crackers” [5]. Green crackers are supposed to contain less polluting element compounds, up to 30%, compared to normal crackers [5]. The excess amount of Ba present in traditional crackers is replaced by other additive compounds used by CSIR-NEERI [5]. It is assumed that green crackers do not contain the much toxic elements generally used in traditional firecrackers such as aluminum, barium, potassium, nitrate, and carbon, making them eco-friendly [5]. Apart from this, green crackers also have a reduced amount of SO<sub>2</sub> and NO<sub>2</sub> molecules which is supposed to produce less Particulate Matter (PM<sub>10</sub>) and PM<sub>20</sub> levels [2,3,5]. In addition to this, traditional crackers also contain oxidizers and propellants, which help in the burning of crackers. PbNO<sub>3</sub>, PbO, PbCl<sub>2</sub>, KNO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub>, and sulphates are some of the compounds that are mixed in firecrackers as propellants/oxidizers [1,3]. These propellants/oxidizers are very harmful for human health and specially to the environment because the burning of propellants/oxidizers produces SO<sub>2</sub> and NO<sub>2</sub> molecules that pollute the PM<sub>10</sub> and PM<sub>20</sub> levels and are also responsible for acid rain [2]. Green crackers are supposed to be less polluting and emit less sound compared to traditional crackers. To compare the extent of toxicity and harmfulness due to green crackers on human health and the environment, it is necessary to find the concentration of the constituents used in these crackers.

There are several conventional methods for elemental detection and quantification such as X-Ray Fluorescence (XRF), Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), Atomic Absorption Spectroscopy (AAS), Inductive Coupled Plasma-Mass Spectroscopy (ICP-MS). However, these methods are very time-consuming, uneconomical, and require a long sample preparation process [6,7]. Laser-induced Breakdown Spectroscopy (LIBS) is an atomic emission analytical method that is quick, requires minimal sample preparation, and is cost-effective. LIBS has been used for qualitative and quantitative analysis since the 1960s and has proven its importance in several fields, from space to agricultural land [8–10].

LIBS is mainly an atomic emission method used for the analysis of materials using atomic lines of elements. However, electronic bands of diatomic molecules are also observed in LIBS spectra when the spectra are recorded after a certain gate delay [11,12]. The molecular transitions involving a change of vibrational states can exhibit up to several orders of magnitude larger in isotopic shifts than atomic transitions. Thus, the isotopic spectral shift in the vibrational bands of diatomic molecules is large compared to those in atomic spectra. Therefore, molecular bands of diatomic molecules are usually used to measure optical emission in laser-induced plasmas for isotopic analysis, and the name of this technique is Isotope Laser Ablation Molecular Isotope Spectroscopy (LAMIS). LAMIS is preferred for the molecular analysis of materials [13]. The present work is an attempt to correlate the Al, Sr, and Ca toxicity present in green crackers based on the electronic bands of Aluminum Oxide (AlO), Strontium Oxide (SrO), and Calcium Oxide (CaO) molecules observed in their LIBS spectra, respectively. To evaluate the toxicity of green crackers, we have compared the intensity of the electronic bands of AlO, CaO, and SrO with the intensity of the spectral lines of Al, Ca, and Sr. We have also performed a compositional analysis of these green crackers and evaluated their toxicity using the spectral lines of the elements present in the samples [14]. For the identification of the functional group of the compounds present in green crackers, FTIR technique has been used. To validate the result (toxicity of the crackers) obtained by the analysis of the AlO bands, we have also calculated the concentrations of toxic elements such as Al, Cu, and Cr present in green crackers using the Partial Least-Square Regression (PLSR) method. By calculating the concentrations of the toxic elements and intensities of electronic bands of the diatomic molecules presents in the LIBS spectra of green crackers, one can predict the toxicity level of green crackers.

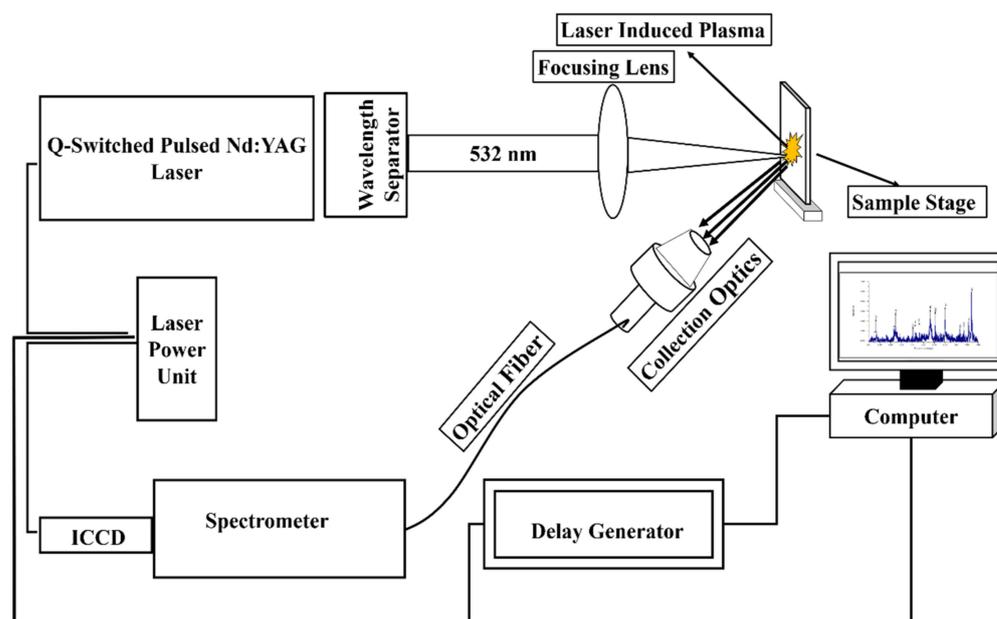
## 2. Materials and Methods

Three types of green crackers are procured from the local market of Delhi, India. Out of three crackers, two are flower pots, and the third is a sparkler. The powder of these samples is extracted and crushed gently to produce a homogeneous powder. After sieving it, pellets are made using 0.60 g of powder sample with the help of a hydraulic press machine (K-Br Press MODEL M-15). The details of the samples are given in Table 1.

**Table 1.** List of the green crackers used for the analysis.

Name	Type	Amount (g)
S1	Sparkler	0.600
S2	Flower Pot	0.600
S3	Flower Pot	0.600

For recording the LIBS spectra, a Q-Switched pulsed, Nd-YAG laser (Continuum Surelite III-10) having pulse width FWHM = 4 ns at 532 nm, variable repetition rate 1–10 Hz, and gate width and gate delay of 1  $\mu$ s for both has been used. A plano-convex lens (the focal length of the lens is 15 cm) is used for focusing the laser light beam on the sample's surface. Radiated emission from plasma is collected by collection optics (CC 52, Andor) containing a spectrometer (Andor, Mechelle 5000), ICCD (Andor, iSTAR DH334), and using an optical fiber having a diameter of 600  $\mu$ m. The schematic diagram of the LIBS setup is shown in Figure 1.



**Figure 1.** Schematic diagram of Laser set-up.

The Fourier Transform Infra-Red Spectroscopy (FT-IR) of the same pellet is used to identify the functional group. For recording the FT-IR spectra, PerkinElmer FT-IR/FIR frontier spectrometer is used in the spectral range of 400–4000  $\text{cm}^{-1}$ .

Sample preparation for AAS method:

A duplicate sample of all the studied samples was weighed in a digestion tube. Then, it was treated with 5 mL of concentrated nitric acid ( $\text{HNO}_3$ ). A blank was prepared by treating it with 5 mL of nitric acid in a digestion flask. After this, the flask/plate was heated up to 450  $^\circ\text{C}$  in a digester, to obtain a clean solution. A few drops of HCl were added after digestion. After heating the solution, the residue was again subjected to digestion, and the filtrate was obtained. After cooling it, it was filtered with Whatman paper. The filtrate was taken in a 100 mL of volumetric flask and made up the volume by adding distilled deionized water. The standard solution of Cu, Cr, and Al was prepared from the

stock standard solutions containing 500 ppm of the element in a normal concentration of nitric acid. Measurement of the sample was performed using the atomic absorption spectrophotometer (model: A-Analyst 700, Perkin Elmer, Waltham, MA, USA).

### 3. Results and Discussion

#### 3.1. Qualitative Analysis

Before using the spectral lines of the elements for the qualitative and quantitative analysis of the samples, the laser-induced plasma should satisfy the following conditions:

- (i). Stoichiometric Ablation
- (ii). Optically thin Plasma.
- (iii). Local thermal equilibrium (LTE).

The above three conditions are discussed in the following section.

- (i). Stoichiometric Ablation.

If the composition of the laser-induced plasma is the true representative of the sample's composition, the ablation is stoichiometric. To satisfy this condition, the laser irradiance at the focal spot on the sample surface should be greater than  $10^9 \text{ W cm}^{-2}$  [15]. In the present experiment, the calculated laser irradiance is equal to  $3.14 \times 10^{12} \text{ W/cm}^2$ , which is greater than  $10^9 \text{ W cm}^{-2}$  [14]. Hence, in the present case, laser-induced plasma is stoichiometric in nature.

- (ii). Optically thin plasma:

The plasma is optically thin if the measured/experimental intensity ratio of two interference-free emission lines of the same element having nearly the same upper energy state is equal to the theoretical intensity ratio ( $A_{ki}g_k\lambda'/A'_{ki}g'_{k}\lambda$ , where  $\lambda$  and  $\lambda'$  are the wavelengths of upper energy levels of the ionic and atomic species of the element having transition probabilities  $A_{ki}$  &  $A'_{ki}$  and statistical weights  $g_{ki}$  &  $g'_{ki}$ ) of these lines. The values of calculated and theoretical intensities are given for the spectral lines of Al. The theoretical value of the intensity ratio is 0.84 [14]. The calculated/experimental value of the intensity ratio is 0.78 [14], which is very close to each other. Hence, in the present case, plasma is optically thin.

- (iii). Local Thermal Equilibrium (LTE):

The laser-induced plasma is in LTE if, the electron density (calculated using FWHM of the spectral lines of the elements) must be greater/equal to McWhirter criteria (Sufficient condition) i.e.,  $N_e (\text{cm}^{-3}) > 1.6 \times 10^{12} T^{1/2} (\Delta E)^3$  where  $N_e$  is an experimentally measured electron density,  $T$  plasma temperature and  $\Delta E$  is maximum energy difference of a spectral line. Experimentally, electron density is calculated using an equation  $N_e \approx 10^{16} \frac{\Delta\lambda}{2w}$ . Here,  $w$  is the electron impact parameter,  $\Delta\lambda$  is the difference between  $\Delta\lambda_{\text{observed}}$  and  $\Delta\lambda_{\text{spectrometer}}$ . The McWhirter limit [ $1.6 \times 10^{12} T^{1/2} (\Delta E)^3$ ] is equal to  $2.39 \times 10^{15} \text{ cm}^{-3}$  [14] and the calculated/experimental value of electron density is  $1.6 \times 10^{17} \text{ cm}^{-3}$  [14], which is greater than McWhirter criteria. Hence sufficient condition for LTE is satisfied. Further, to ensure the LTE, the excitation temperature calculated using the Boltzmann plot and the ionization temperature calculated using the Saha-Boltzmann plot should be similar. (Sufficient condition). For the present laser-induced plasma, the calculated value of ionization temperature using the Saha-Eggert equation is  $16,200 \pm 400 \text{ K}$  [14] which is close to the excitation temperature  $17,300 \pm 800 \text{ K}$  [14], with a difference of almost 11%. Thus, the sufficient condition is satisfied. Hence, we can say that LTE holds [14].

#### 3.2. Plasma Parameters Using AIO Molecular Bands

In the laser-induced plasma of the sample, the molecule formation occurs at low plasma temperature, and at high plasma temperature, the elemental compositions break and produce the ionized charge of the elements. Now at low temperatures, when this ionized atom is combined with some reactive elements present in samples such as O and N,

it forms the molecule. Here in the present manuscript, vibrational/plasma temperature is calculated at which we observed the molecular bands. The above temperature is calculated by measuring the area under the curve of the molecular bands. The Boltzmann equation is given in Equation (1). In this manuscript, the Boltzmann plot is drawn using the intensity of the molecular bands instead of the spectral lines of the elements. So, for the molecular bands, the plasma temperature is calculated in the same way as it is calculated using the spectral lines of the elements [14]. In the present manuscript, our aim is to correlate the toxicity of Al and Ca with the intensity of the electronic bands of AlO and CaO molecules. Therefore, we have compared the vibrational temperature calculated using the intensity of the molecular band with the plasma temperature calculated using the spectral line of constituents/elements Al and Ba [14].

The intensity of molecular bands is given by following equation no Equation (1)

$$\ln \sum_{v''} (\lambda^4 I_{v''}) = C - G(v'') \frac{\hbar c}{kT_{\text{vib}}} \quad (1)$$

The above equation can be used to calculate the vibrational temperature using molecular bands. A graph is plotted between  $G(v)$  and  $\ln(\lambda^4 I)$ , as shown in Figure 2. The slope of the above graph will correspond to vibrational temperature. The slope of these graphs is 1.86 and 1.84 for CaO and AlO, using Tables 2 and 3, respectively. Thus, the vibrational temperature using AlO and CaO molecular bands are equal to 0.67 and 0.66 eV, respectively. Similar to the result reported by Vera-Londoño et al., the value 0.67 eV is with high correlation value of  $0.76 \approx 1$  [16].

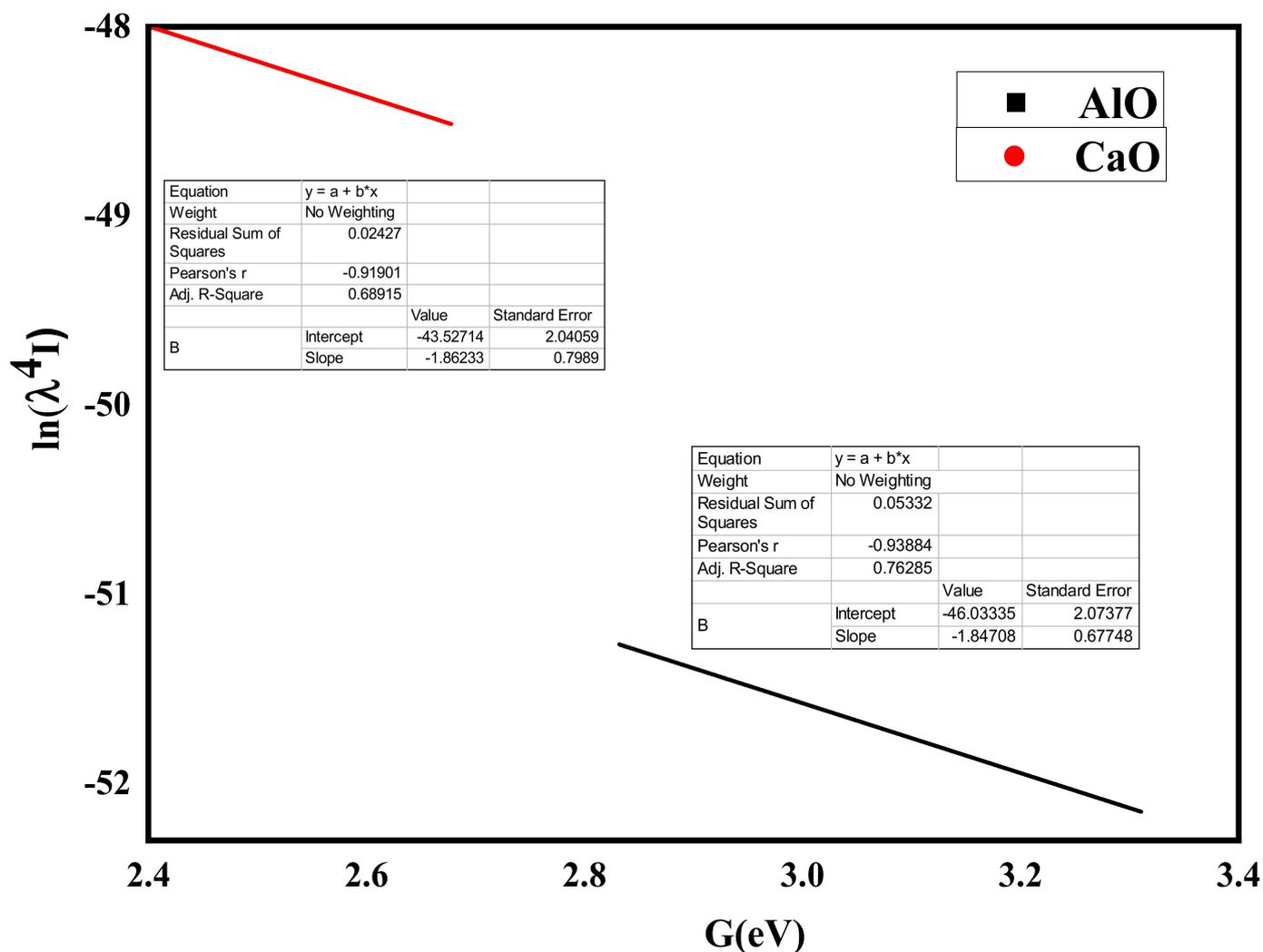
Here, the terms  $\lambda$  stand for wavelength corresponding emission band head,  $I$  is their corresponding intensity, and  $c$  is the constant.  $G(v')$  is an expression for vibrational energy level at the upper electronic state. Term  $\hbar$  is the plank constant,  $c$  is the velocity of light,  $k$  is the Boltzmann constant, and  $T_{\text{vib}}$  is the vibrational temperature.

The vibrational temperature calculated by the intensity of the electronic bands of the diatomic molecules is almost equal to the plasma temperature in the laser-induced plasma [17,18].

Using the slope value 1.86 for CaO and 1.84 for AlO, the value of vibrational temperature is calculated and is equal to 0.67 and 0.66 eV, respectively. The value 0.67 eV is with a high correlation value that is  $R^2$  of  $0.76 \approx 1$ . Thus, in the present case, the vibrational temperature (which implies plasma temperature) is found to be 12,000 K, almost close to the plasma temperature calculated using spectral lines of the elements [16].

LIBS spectra of S1 are shown in Figure 3a,b. As the LIBS spectra of samples S2 and S3 have almost identical spectral signatures, therefore in the present manuscript, LIBS spectra of only sample S2 are presented. The LIBS spectra of S1 contain the atomic emission lines along with the electronic bands of CaO around 356.5 nm at  $\Delta v = -1$  at (0,1), 412.5 nm at (1,2), 440.1 nm, and 376.5 nm corresponding to  $\Delta v = -2$  at (0,2) [19–21]. In addition to this, molecular bands of SrO are also observed at 600 nm to 627 nm, which overlaps with molecular bands of the CaO molecules. Due to this, it is difficult to separate these bands in the spectral range of 600–627 nm [19,21].

LIBS spectra of S2 shown in Figure 4 shows the presence of the electronic bands of the AlO molecules corresponding to the  $\Delta v = 0$  sequence at 484.2 nm (0,0), 486.1 nm (1,1), and 488.8 nm (2,2),  $\Delta v = +1$  sequence at 464.8 nm (1,0), 467.2 nm (2,1), 469.4 nm (3,2), and  $\Delta v = -1$  sequence at 507.9 nm (0,1), 510.2 nm (1,2), and 512.3 nm (2,3) [19,21,22].



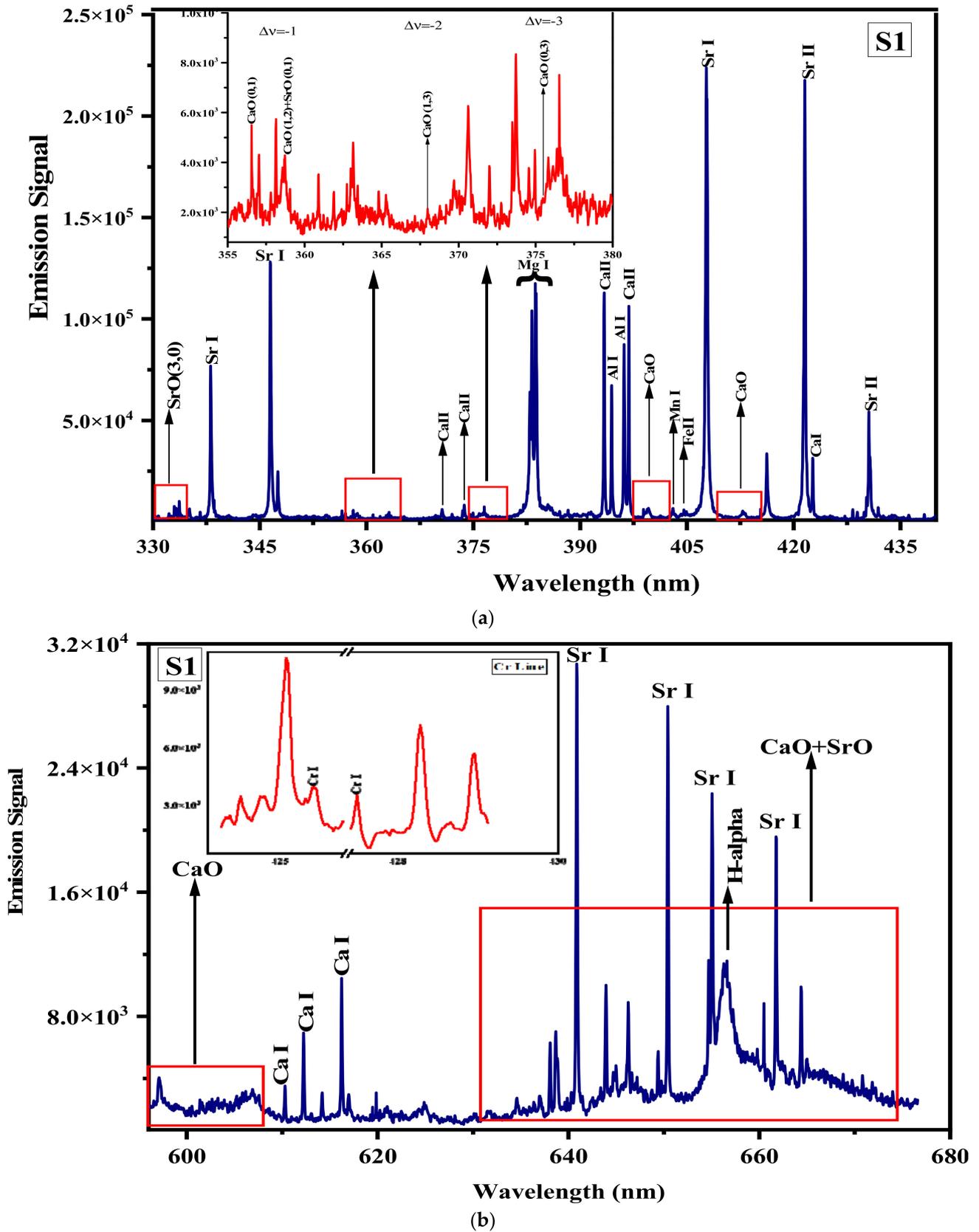
**Figure 2.** Boltzmann plot to calculate vibration temperature using electronic bands of AlO molecule and CaO molecule.

**Table 2.** The intensity of the electronic bands of the AlO molecule to calculate the vibrational temperature (plasma temperature).

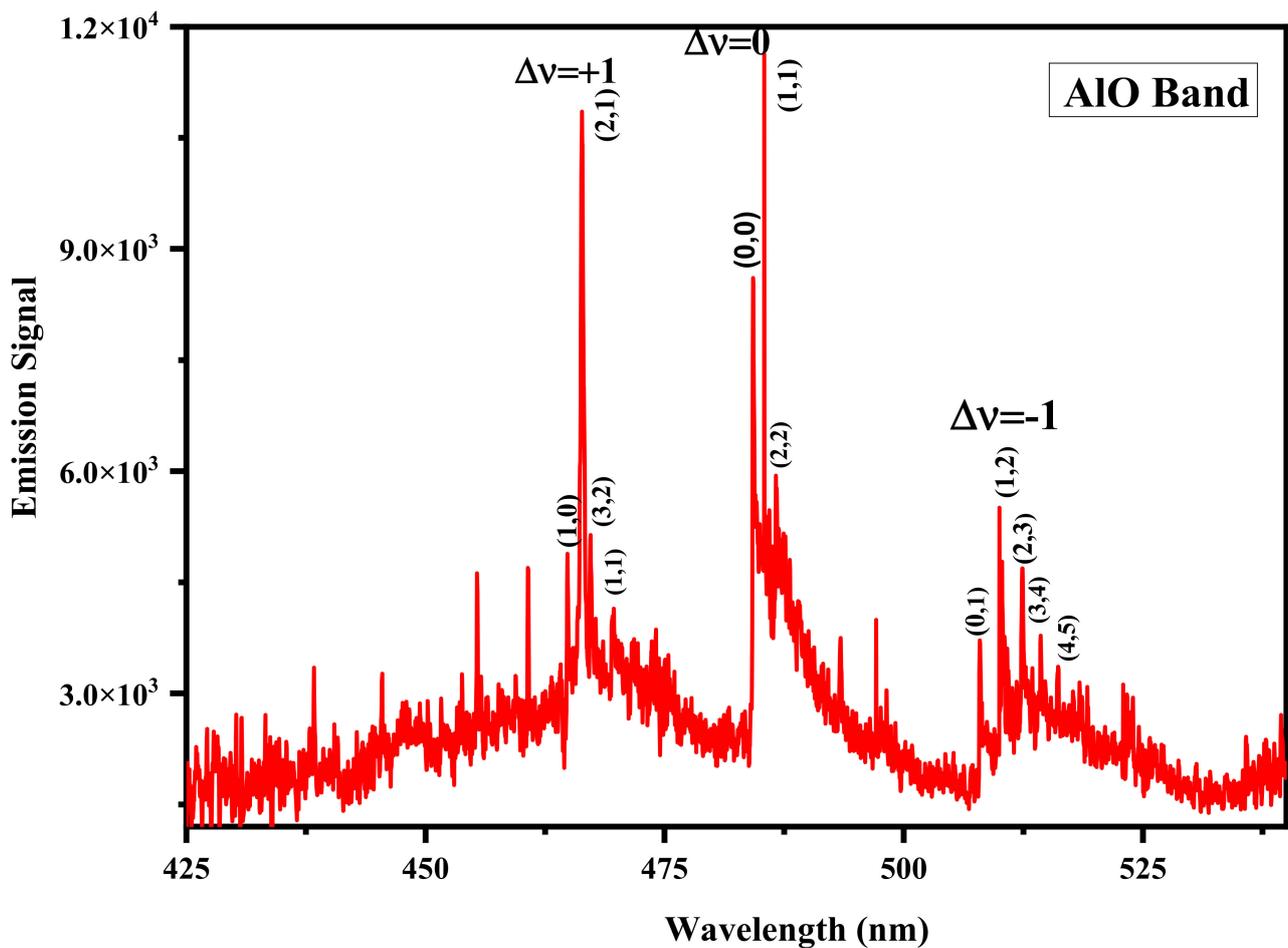
Wavelength $\lambda$ (nm)	Intensity Observed	$\ln(\lambda^4 I_{\nu, \nu'})$	$G(\nu)$ (eV)
484.4	1040.0	-52.2	3.31
465.4	1598.4	-51.4	3.02
518.1	1296.3	-51.38	2.83

**Table 3.** The intensity of the electronic bands of the CaO molecule to calculate the vibrational temperature (plasma temperature).

Wavelength $\lambda$ (nm)	Intensity Observed	$\ln(\lambda^4 I_{\nu, \nu'})$	$G(\nu)$ (eV)
376.5	21,336.6	-48.1	2.57
412.5	18,711.8	-48.0	2.40
440.1	16,796.6	-48.5	2.68



**Figure 3.** Emission spectra of S1 crackers containing electronic bands of CaO molecule (a) in the spectral range of 330–435 nm (b) 600–680 nm and elements such as Ca, Mg, Sr, Al, Cr, and Fe.



**Figure 4.** LIBS spectra of S2 crackers in the spectral range of 425–525 nm show the presence of electronic bands of AlO.

The electronic bands of diatomic molecules (CaO, SrO, AlO) in the LIBS spectra of samples S1 and S2 reveals that these bands are formed in the laser-induced plasma when the amount of the corresponding elements is significantly high in the sample. Sample S1 contains the electronic bands of SrO and CaO, reflecting that the concentration of Sr and Ca are higher in S1. The Sr and Ca are ionized at high plasma temperatures, and these ionized forms of elements react with oxygen present in that particular sample and form the oxide of these elements. Similarly, in sample S2, the same phenomenon happened with Al elements and formed the oxide of AlO. So, we can say that the concentration of Sr and Ca is higher in S1, and Al concentration is higher in S2.

Generally, transition elements are added to green crackers to produce colors after burning [1–3]. That is why elements such as Al, Cu, Cr, and Sr are present in green crackers. The intensity of the spectral lines of an element is directly proportional to its concentration in the sample. Therefore, we have calculated the intensity of the spectral lines of Al, Cu, and Cr by measuring the area under the corresponding peak/spectral line. The integrated intensity bar plot of the spectral lines of toxic elements Al, Cu, and Cr are shown in Figure 5b. Figure 5b shows that the concentration of Cu is higher in sample S1 compared to samples S2 and S3. In contrast, the concentration of Al and Cr is higher in samples S2 and S3 compared to sample S1. This is because sample S1 is a sparkler, and samples S2 and S3 are flower pots. That is why sample S1 shows different behavior than samples S2, and S3, and samples S2 and S3 show similar behavior.

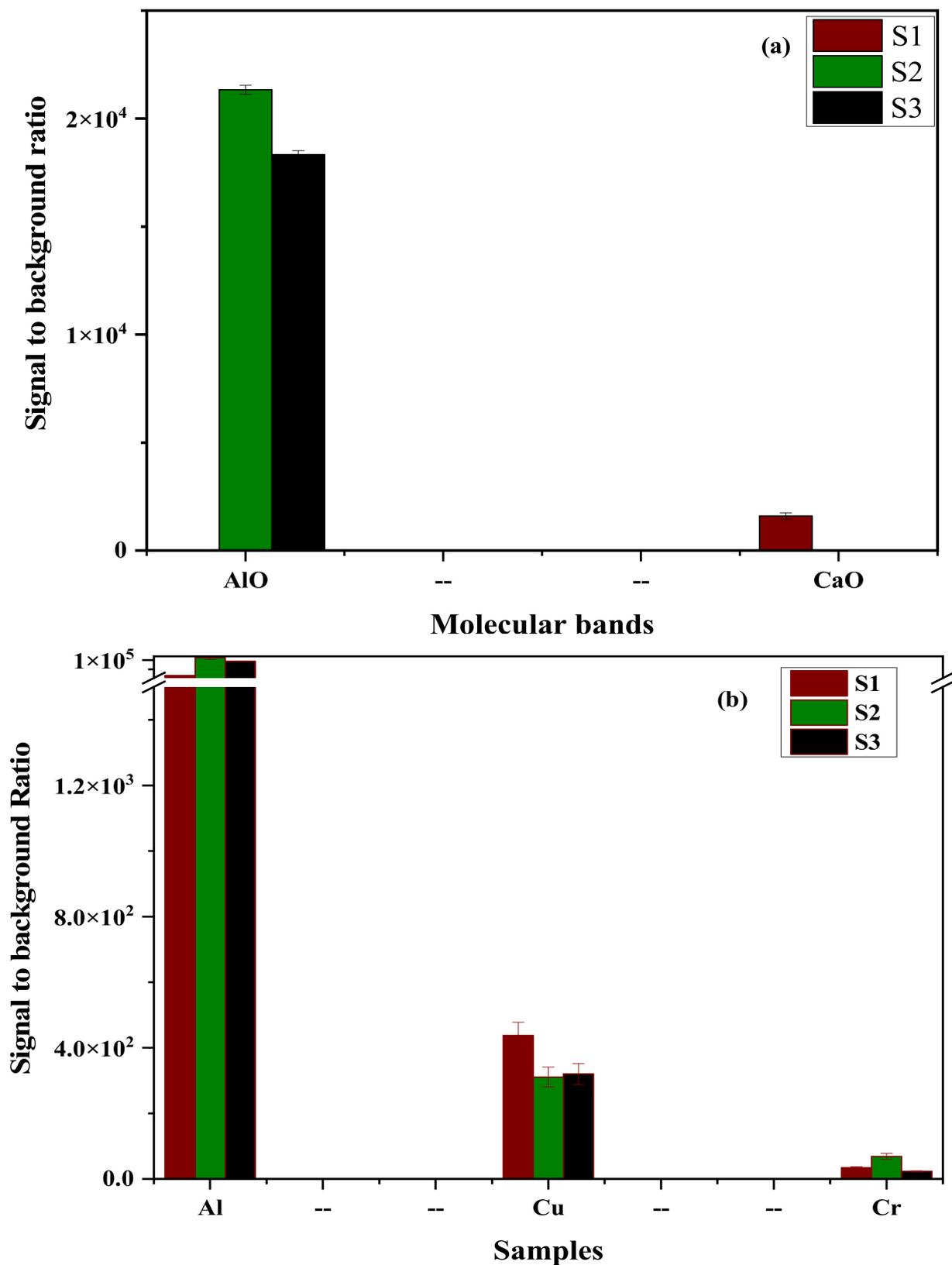


Figure 5. (a): Intensity bar plot of Molecular bands of AlO and CaO in different samples. (b): Intensity bar plot of elements Al, Cu, and Cr in different samples.

The presence of the electronic bands CaO and SrO in the LIBS spectra of sample S1 shows that the concentration of Sr and Ca is higher in sample S1 than in S2 and S3. Similarly, the presence of molecular bands of AlO molecule in LIBS spectra of samples S2 and S3 reflects that the concentration of Al is higher in samples S2 and S3 compared to S1. AlO is absent in S1 while CaO is absent in S2 and S3. The above observation/results can be explained using the intensity of the electronic bands of the AlO and CaO molecules and the intensity of the spectral lines of Al and Ca shown in Table 4 and Figure 5a.

**Table 4.** The intensity of the electronic bands of AlO and CaO molecules and the intensity of the spectral lines Al and Ca.

Sample	AlO	Al (I)	CaO	Ca (I)
S1	0	15,409.3	1598.4 (0,1)	5045.5
S2	21,336.4 (0,0)	113,468.8	0	1051.8
S3	18,711.3 (0,0)	92,950.8	0	1634.5

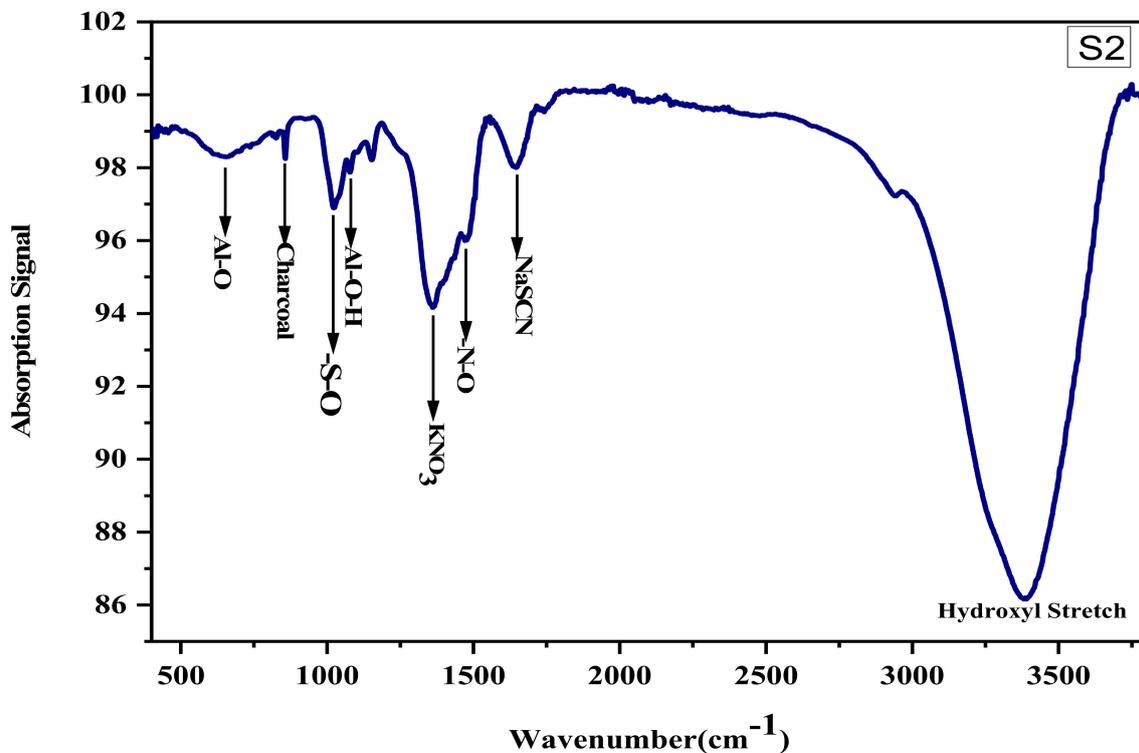
### 3.3. Fourier Transform Infrared Analysis (FTIR) Analysis

The Fourier Transform Infrared (FTIR) technique is used to identify the functional group of the compounds present in green cracker samples; FTIR spectra of S2 and S3 are almost similar, therefore, FTIR spectra of only sample S2 are shown in Figure 6a. The FTIR spectra of sample S2 contain the vibrational stretching of the Al-O molecule at  $650\text{ cm}^{-1}$ , charcoal at  $855\text{ cm}^{-1}$ , the functional group of S-O at  $1020\text{ cm}^{-1}$ , Al-O-H at  $1086\text{ cm}^{-1}$ , the functional group of nitrates at  $1366\text{ cm}^{-1}$ , C-N group at  $1650\text{ cm}^{-1}$  functional group of N-O at  $1471\text{ cm}^{-1}$ , and the hydroxyl group at  $3372\text{ cm}^{-1}$ . Stretching Al-O is observed in S2 because it contains the compound of Al in the form of oxides/sulphate/nitrate and other salts used as propellants/oxidizers in crackers. Similarly the FTIR spectra of Sample S1 shown in Figure 6b contain the functional group of Cl-O at  $619\text{ cm}^{-1}$ ,  $\text{NO}_3^-$  at  $735\text{ cm}^{-1}$  and  $812\text{ cm}^{-1}$ ,  $-\text{CO}_3^-$  at  $855\text{ cm}^{-1}$ ,  $1081\text{ cm}^{-1}$  and  $1431\text{ cm}^{-1}$ , C-N at  $1641\text{ cm}^{-1}$ , S-S at  $1154\text{ cm}^{-1}$ , S-O at  $1631\text{ cm}^{-1}$ , and Hydroxyl group at  $3367\text{ cm}^{-1}$  [23,24]. Functional group  $\text{CO}_3^-$  is found because the carbonates of the different elements are used in crackers for producing different exciting colors.  $\text{NO}_3^-$ ,  $\text{SO}_4^-$ , and chlorate of  $\text{NH}_4^-$  and K are used as propellants/oxidizers. Sample S1 contains the more intense vibrational peak of  $\text{CO}_3^-$  because it is a sparkler that produces more colors after burning.

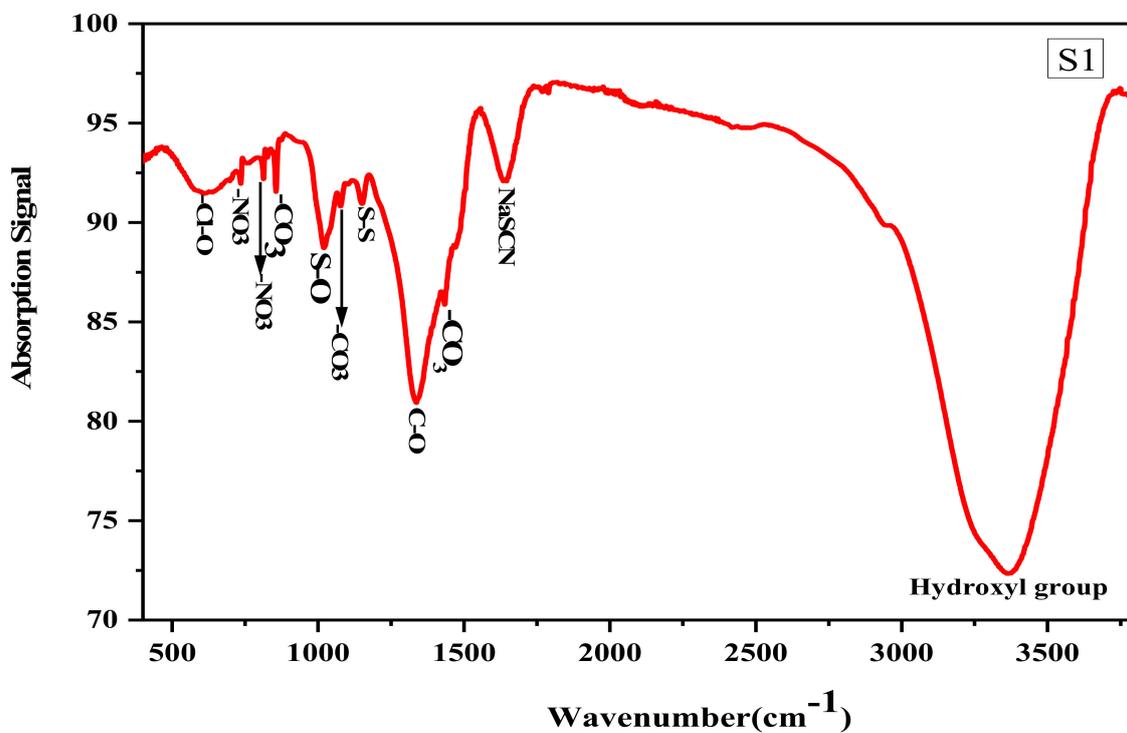
### 3.4. Partial Least Square Regression Method (PLSR)

PLSR is one way to perform a multivariate regression. Multivariate regression is for correlating the information in another matrix ( $X \rightarrow Y$ ). Partial Least Square Regression (PLSR) constructs a model from one matrix (known matrix) to another one (unknown matrix) so that, in the future, we only need the X (known) matrix and can predict Y (unknown) matrix. PLSR is the multivariate technique that gives the relation between dependent and independent variables. These methods are used to build the calibration curve, which helps to predict the concentration of unknown samples. This technique works on the principle of Partial Least Square (PLS). To know the concentration of toxic elements such as Al, Cu, and Cr, a statistical approach Partial Least Square Method (PLSR), is used. The PLSR model is preferred in place of traditional calibration curve methods because, in the PLSR model, independent variables and dependent variables have a good correlation at element characteristics spectral lines, but the calibration curve method does not. For applying the PLSR method, the concentration of elements Al, Cu, and Cr are known in samples S1 and S2, which is referred to as the "known sample". The concentrations of elements Al, Cu, and Cr are evaluated with the Atomic Absorption Spectroscopic (AAS) method. The samples S3 in which the concentrations of elements to be evaluated are known as "unknown samples". The PLSR method is applied to the LIBS dataset using 15 (total number of 45) spectra of each sample taken. The PLSR method is applied using Unscrambler X (Camo Ltd., Tokyo, Japan) software.

The predicted vs. reference plot of the PLSR model is drawn in Figure 7 for the Cu element. An assessment of the model can be conducted based on  $R^2$  and Root Mean Square Error (RMSE). For a good PLSR model, the value of RMSE should be low while  $R^2$  should be high.

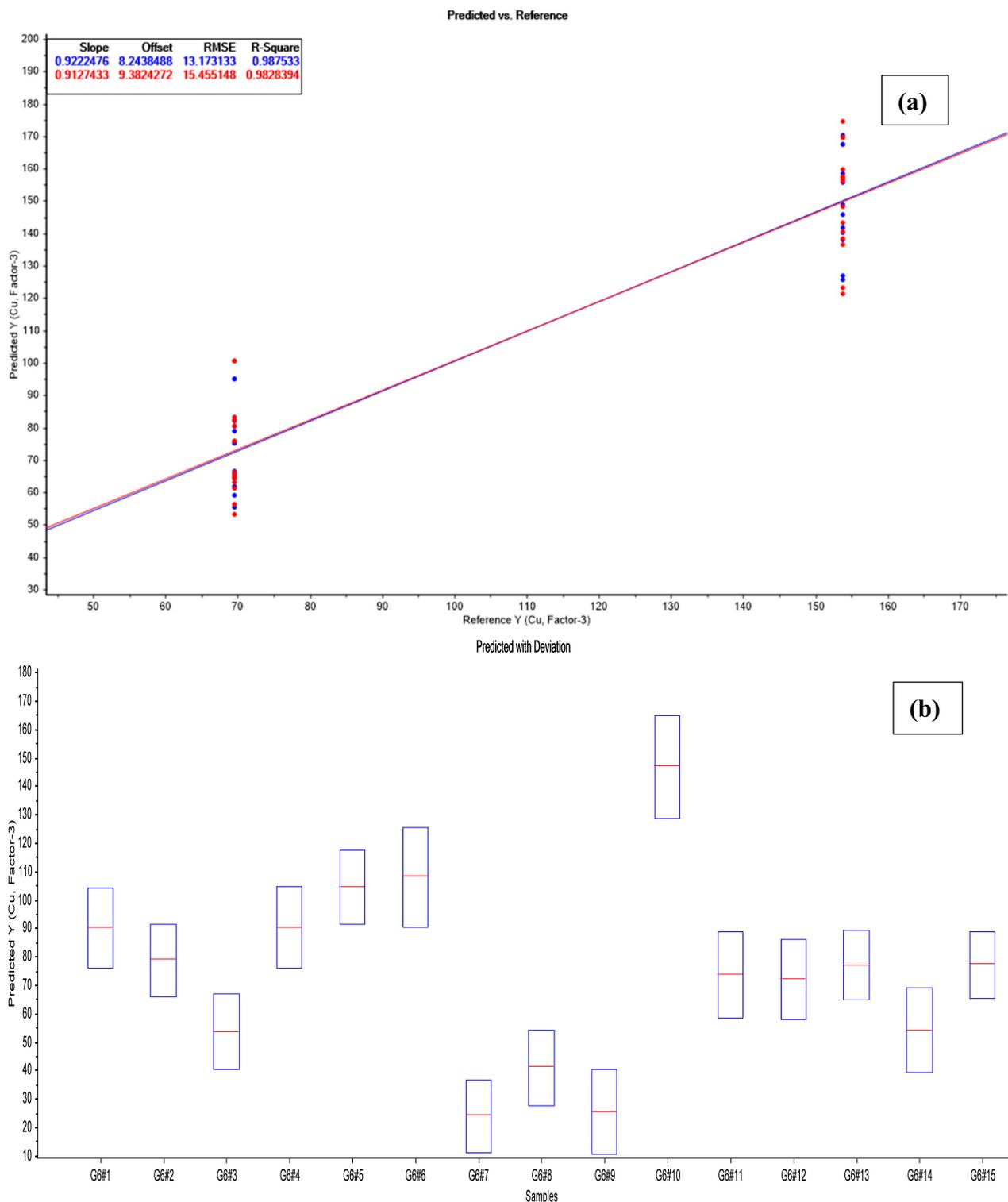


(a)



(b)

Figure 6. (a). Fourier Transform Infrared spectra of S2 in spectral range 500 to 3500  $\text{cm}^{-1}$ . (b). Fourier Transform Infrared spectra of S1 in spectral range 500 to 3500  $\text{cm}^{-1}$ .



**Figure 7.** (a) Predicted vs. Reference plot of Partial Least Square Regression model (b) Prediction of concentration using PLSR model.

The PLSR model is good because, in the predicted vs. reference plot, the assessment of calibration (blue) and prediction can be performed when the value of  $R^2$  is high 0.989, and the value of RMSE is 13. The predicted and deviated values of constituents (Al, Cu, Cr) are listed in Table 5. The maximum deviation in concentration with actual concentrations in elements is 21% in Al, 7% in Cu, and 12% in Cr, respectively. For the prediction of concentrations of the toxic elements, the concentrations calculated by AAS for S1 and S2

were used as reference samples. The concentrations of constituents estimated by AAS are listed in Table 6.

**Table 5.** Predicted and deviated values of concentrations in unknown samples.

Element	Predicted Value S1	Deviated Value (%)	Predicted Value S2	Deviated Value (%)	Predicted Value S3	Deviated Value (%)
Al	13,710.2	21.0	102,448.8	9.7	92,448.8	6.5
Cu	149.6	7.2	73.6	18.8	99.1	18.1
Cr	77.1	12.6	99.1	10.0	249.1	10.0

**Table 6.** Concentration of toxic constituents (Cr, Cu, and Al) obtained from AAS in (mg/kg).

Elements	S1	S2	S3
Al	12,377.7	118,161.0	94,369.8
Cu	153.7	69.6	143.2
Cr	71.9	333.9	204.7

#### 4. Conclusions

LIBS is a suitable technique for investigating toxic elements (toxicity of the materials) using the intensity of the electronic bands of their oxides in addition to measuring the intensity of the spectral lines of the elements. In this paper, the LIBS technique is used to correlate the intensity of the electronic bands of CaO, AlO, and SrO with the intensities of the corresponding elements (Ca, Al, and Sr). The presence of electronic bands of AlO in the LIBS spectra of the samples S2 and S3 implies that these crackers contain Al in a higher concentration than S1. This statement is supported by the fact that the concentration of Al (12,377.72 ppm) is less in sample S1 compared to S2 (118,161 ppm) and S3. The electronic bands of the CaO and SrO molecules again show that the Ca and Sr are higher in the green crackers. In addition, the concentration of Cu is higher in S1 in comparison to S2 and S3, whereas the concentration of Cr is higher in S2 (Al 118,161 ppm, 69.60 ppm, 333.98 ppm) and S3 (Al 94,369.802 ppm, Cu 143.234 ppm, Cr 204.734 ppm) in comparison to S1 (Al 12,377.72 ppm, Cu 153.76 ppm, Cr 71.97). The FTIR spectra of sample S2 contain the vibrational stretching of the Al-O molecule, which supports the presence of the electronic bands of AlO in the LIBS spectra. Thus, the results of the LIBS spectra are supported by FTIR spectroscopy. We have used the PLSR method to predict the concentrations of Al, Cr, and Cu in unknown samples, which shows that the PLSR model is an alternative method to the conventional calibration curve method to find the concentration of the elements in the sample. The results of the present study demonstrate that green crackers are also toxic to humans and the ecosystem.

**Author Contributions:** Conceptualization, D.D. and R.K.; methodology, D.D. and R.K.; methodology-FTIR, A.D.; formal analysis, D.D.; writing—original draft, D.D.; writing—review and editing, R.K., A.D. and A.K.R.; supervision, A.K.R. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Data used to produce the figure/table in the manuscript are “available on request”.

**Acknowledgments:** One of the authors, Darpan, is grateful for the DST-INSPIRE Fellowship, New Delhi, India.

**Conflicts of Interest:** There is no conflict of interest among the authors.

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