

## Investigation of Hazardous Materials in Firecrackers using LIBS Coupled with a Chemometric Method and FTIR Spectroscopy

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### ABSTRACT

This article reports the detection and quantification of toxic constituents in firecrackers using LIBS coupled with PCA and FTIR. Spectral signatures of lethal elements along with other elements and electronic bands of Cyanide, AlO, BaO, and CaO are seen in their LIBS spectra which confirms the presence of inorganic and organic compound in the fireworks. The concentration of each constituent/element is determined using the CF-LIBS method and results are compared with ICP-OES results. The concentration of Al is in adequate amount except S<sub>4</sub>(b). Li and Ba are present in all samples with maximum amount in S<sub>4</sub>(b) and S<sub>3</sub> respectively. Molecular stretching of SO<sub>4</sub><sup>2-</sup>, C<sub>4</sub>H<sub>8</sub>, CuCl, CO<sub>3</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup> are observed in the FTIR spectra of the samples. The combined results of LIBS and FTIR recommends the presence of BaNO<sub>3</sub>, LiCO<sub>3</sub>, SrCO<sub>3</sub>, Al-chip, and charcoal in the firecrackers. To discriminate various firecrackers, PCA of the LIBS data is performed. The results show that S<sub>3</sub> and S<sub>4</sub>(b) are more harmful as they contain higher concentration the compounds of Al, Ba, Li, Sr i.e BaNO<sub>3</sub>, LiCO<sub>3</sub>, SrCO<sub>3</sub>, (Cu<sub>3</sub>As<sub>2</sub>O<sub>3</sub>Cu(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)).

**Keywords:** FTIR; CF-LIBS; Carcinogenic; Firecrackers; Multivariate analysis

### 1. INTRODUCTION

The use of firecrackers during the celebration of festivals (like Diwali, Dussehra, opening/closing ceremony of reality shows), national days (like Independence Day, Republic Day etc.) and ceremonies etc. to express their joy and thrill is widespread. In the last few years, the use of fireworks has been rapidly increasing<sup>1,2</sup>. Firecrackers contain a small amount of explosive materials which are mainly used to emit a large amount of noise, sparks, and a massive amount of smog<sup>1,3</sup>. The toxic elements in gases can cause severe injuries like permanent hearing loss, sleep disturbance, asthma, pneumonia, allergic rhinitis, restlessness and high blood pressure and breathing issues<sup>1,4</sup>.

The presence of toxic/heavy metals such as Cadmium (Cd), Barium (Ba), Cobalt (Co), Copper (Cu), Vanadium (V), Aluminium (Al), Antimony (Sb), Manganese (Mn), Strontium (Sr) and some lighter elements like Lithium (Li), Hydrogen (H) contributes in producing different colour in firecrackers after bursting<sup>1,3</sup>. The elements like, Chlorine (Cl), Nitrogen (N), Magnesium (Mg), and Oxygen (O) play the role of oxidizers, which help a firecracker in bursting<sup>1</sup>. Role of the elements in firecrackers and their harmful effects on human health and environment are summarized in Table 1.

After seeing all these hazardous effects (Table 1) on human health as well as on the environment due to firecrackers the Hon'ble Supreme Court of India banned the use of firecrackers,

by deciding on the petition of Arjun Gopal and others versus the Union of India and others under the right of writ Petition (civil) no. 728 of 2015, writ Petition (civil) no. 891 of 2016, writ Petition (civil) no. 895 of 2016, writ Petition (civil) no. 899 of 2016 and writ Petition (civil) no. 213 of 2017<sup>5</sup>. The Hon'ble Court also gave directions for burning the firecrackers, which would be from 8 pm to 10 pm on Diwali or any other festival like Gurupurab *etc.* and it would be from 11:55 pm to 12:30 am only on New Year evening and on Christmas day.

To minimize the pollutants that arise from these normal/traditional crackers, the CSIR-NEERI introduced a new type of crackers called "Green Crackers" (<https://www.neeri.res.in>). These crackers contain the chemical compositions of STN nitrate, Metal Alloy, Chol, Poly Vinyl Chloride, B. Bondex, KNO<sub>3</sub>, Al, Al-Chip and additives. The Green crackers contain a reduced quantity of KNO<sub>3</sub>, Aluminium powder, fewer oxidizers, reduced chemical uses for colours, and substitution of BaNO<sub>3</sub> with KNO<sub>3</sub>, SrNO<sub>3</sub>. Apart from this, green crackers also contain a lesser amount of chemicals and aluminium powder that produce the colour.

Several works have been reported on elemental analysis of firecrackers using different spectroscopy techniques like X-ray Diffraction (XRD) and Raman effect<sup>6</sup>, Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)<sup>7</sup>, Particle-Induced X-Ray Emission (PIXE), Atomic Absorption Spectroscopy (AAS) and Instrumental Neutron Activation Analysis (INAA)<sup>8-9</sup>. Molecular compositions like sodium nitrate, potassium nitrate and barium nitrate were also identified using Raman spectroscopy<sup>6</sup>. Energy Dispersive X-Ray Spectrometry (EDS) and Scanning

**Table 1. Element used in firecrackers and their role with their adverse effect**

Element	Purpose	Adverse effect
Al	Used for silver color	Skin irritation, accumulation within the body, Alzheimer's disease <sup>4</sup>
Ba	Used for green color	Respiratory irritation, gastrointestinal problems, and muscular weakness <sup>1,4</sup>
Li	Used for Red color	Affects respiratory system
Sr	Used for Red color	Can replace the Calcium in our body, which is toxic <sup>1</sup>
Mg	Very bright white color	growth retardation, fever, sexual impotence and eye blindness <sup>4</sup> .
Sb	Glitter effect	Blurred image, dizziness, constipation and stomach upset
Cu	Used For blue	Stomach aches and irritation of the nose, mouth and eyes <sup>4</sup>
Co	Used for blue	Asthma, hair loss, weight loss, heart issues, vision problems and thyroid damage
Ti	Smoke effect	Bone loss, urticaria, swelling painerythema

Electron Microscope (SEM) also have been performed for the identification of toxic elements like Al, Cl, K, Mg, S and Cl<sup>7</sup>. Further, a study of the emission of undesirable toxic elements to the environment has been performed by Alenfelt *et al.* using ICP and Atomic Fluorescence Spectroscopy<sup>7</sup>. However, these conventional methods are time-consuming, unable to detect lighter elements, required sample preparation which produced undesirable waste in the environment and also the actual chemical composition of the sample may be hindered or lost<sup>10</sup>. Therefore to check the composition of firecrackers we need a technique that is quick, cost-effective and useful for in-situ analysis at the manufacturing place/factory.

LIBS is an eco-friendly and robust optical analytical method used for the simultaneous analysis of lighter, heavy, trace and major elements present in any sample. For the quantification of constituents of the sample, CF-LIBS is a well-established method<sup>11</sup>.

LIBS spectra have extensive data in terms of wavelength and corresponding intensity. Therefore, for classification, detection, regression, and prediction; we have also used multivariate technique<sup>3,12</sup>. There are numerous multivariate tools for statistical analysis like classification, prediction in experiments and data description<sup>3</sup>. Chemometric methods, along with LIBS, are used for qualitative and quantitative analysis<sup>4,13</sup>.

In the present paper, different types of firecrackers have been investigated using LIBS. For the quantification of the constituents of the crackers CF-LIBS method has been used. In addition, FTIR is performed to detect functional groups in the firecracker samples. With the help of FTIR, one can predict the functional groups, bonding type, which finally helps in knowing the molecules present in the materials.

## 2. MATERIALS AND METHOD

For the present study, four brands of firecrackers of different types were purchased from the local market of Allahabad, India. The details about the samples are given in Table 2.

To record the LIBS spectra, a high energy Q switched laser (Nd: YAG laser, INNOLAS Split light 1200) pulse is focused with help of a convex lens on the pelletized firecrackers. The laser pulse energy (15 mJ per pulse) is sufficient to ablate the small amount (~nanogram) of the sample which forms the plasma on the sample surface. Radiation emitted from the

plasma was collected by a collection optics assembly (Andor, ME-OPT-500), which was aligned at a 45-degree angle to the incident laser beam. Further, the emission light was directed towards the spectrometer (Andor, Mechelle 5000) through an optical fibre of a core diameter of 600  $\mu\text{m}$  equipped with an ICCD camera (Andor, iSTAR DH734) connected with a delay generator (SRS-DG-645). The detail about the experimental setup of LIBS are discussed in the article by Junjuri, *et al.*<sup>14</sup>.

**Table 2. Firework sample's detail**

Sample	Sample Type	Amount of sample (gram)
S <sub>1</sub>	Ground cracker	1.00
S <sub>2</sub>	Ground cracker	1.00
S <sub>3</sub>	Sky cracker	1.00
S <sub>4</sub> (a)	Sky cracker (upper part)	1.00
S <sub>4</sub> (b)	Sky cracker (lower part)	1.00

FTIR spectra were recorded with the help of the PerkinElmer FT-IR/FIR frontier spectrometer in the spectral range of 400  $\text{cm}^{-1}$ - 4000  $\text{cm}^{-1}$ .

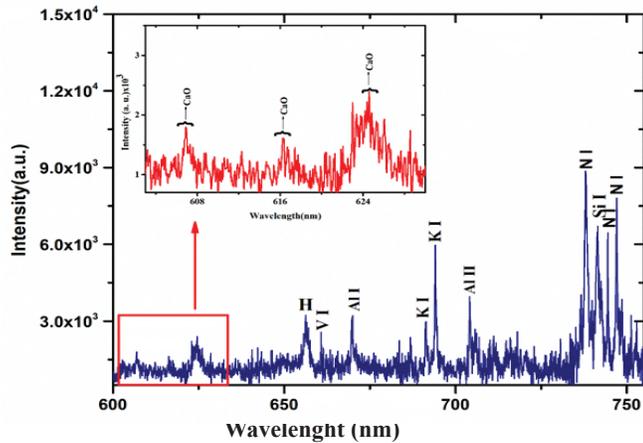
The concentration of the constituents is determined using the CF-LIBS method. CF-LIBS is a mathematical method to determine the concentration based on their spectral line intensities. This is preferred over the traditional calibration curve method as it does not require any reference standard having a similar matrix of the sample. The detailed CF-LIBS methodology has been discussed by Kumar, *et al.*<sup>15</sup>

To validate the results obtained from CF-LIBS, the concentration was also determined using ICP-OES. For this, 0.1 gm of powdered firecracker samples were digested in an acidic mixture of 5 ml  $\text{HNO}_3$  and 2 ml HCl for pre-digestion and then digested in Paar Multiwave Pro. The solution was then filtered sample aliquot, and makeup 25 ml solution and the analysis were performed using ICP-OES (Perkin, Elmer Optima 5300V) method.

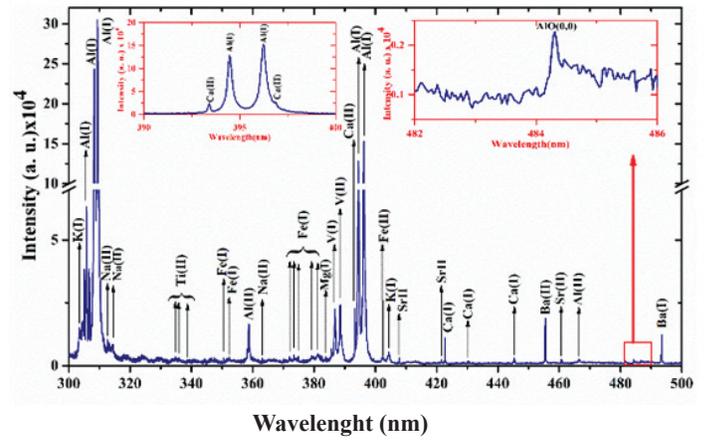
## 3. RESULTS AND DISCUSSION

### 3.1 Qualitative Analysis

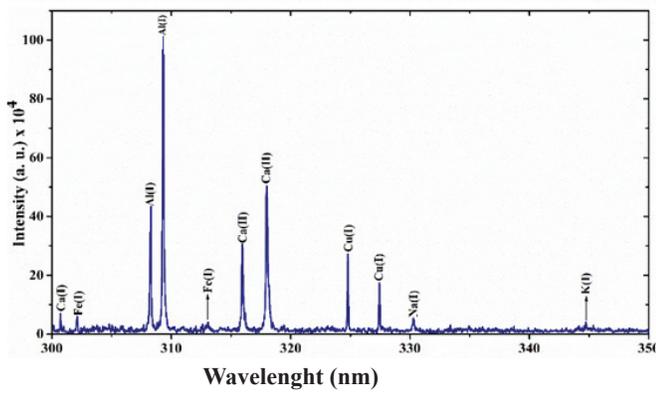
Figures 1(a-b) show a typical LIBS spectra of sample S<sub>2</sub>, S<sub>4</sub>(a) respectively. Figures 1(c-d) show LIBS spectra of S<sub>4</sub>(b) in



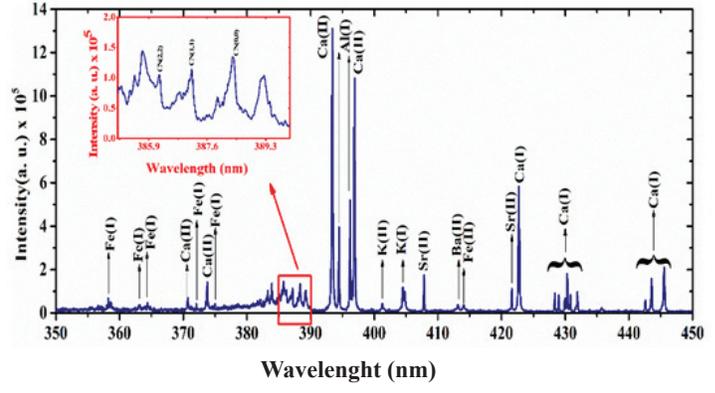
(a)



(b)



(c)



(d)

Figure 1. LIBS spectrum of (a)  $S_2$  in the spectral range of 600 nm to 750 nm, (b)  $S_4(a)$  in the spectral range on 300 nm to 500 nm, (c)  $S_4(b)$  in the spectral range on 300 nm to 350 nm, and (d)  $S_4(b)$  in the spectral range on 350 nm to 450 nm.

the spectral range of 300-350 nm and 350-450 nm respectively. Spectral signature of various elements and molecular bands observed in LIBS spectra of firecrackers are listed in Table 3.

It has been observed that LIBS spectra of samples  $S_1$ ,  $S_2$  and  $S_3(a)$  have almost similar spectral lines of elements like Al, Ba, Ca, Fe, K, Mg, Sr, Ti, and Sr. Similarly the LIBS spectra of  $S_3$  and  $S_4(b)$  have almost similar spectral lines of the elements Al, Ba, C, Cu and Si.

Table 3. List of the elements/Molecules observed in all the samples (using NIST atomic spectroscopic database)<sup>16</sup> and Chemical Spectroscopy by Brode<sup>17</sup> and Gydon<sup>18</sup>

Sample	Elements	Molecular Bands
$S_1$	Ba, Al, Cu, Sr, Ca, Na, Ti, Li, C, O, N, H, Mg, Mn, K	CaO, AlO[19, 20]
$S_2$	Ba, Al, Cu, Sr, Ca, Na, Ti, Li, C, O, N, H, Mg, Mn, K	CaO, AlO
$S_3$	Al, Sr, Cu, Ba, Li, O, Ti, N, Na, V, K, Mg,	BaO[19]
$S_4(a)$	Ti, Na, Sr, Ca, Ba, K	CaO[21], AlO
$S_4(b)$	Al, Sr, Cu, Ba, Li, O, Ti, N, Na, V, K, Mg, C	CN, CaO

### 3.2 Quantitative Analysis

For the quantitative analysis, the intensities of the spectral lines of the elements in the LIBS spectra are used to evaluate their concentration in the samples. But before using the intensity of the spectral lines for the above purpose the laser-induced plasma has to fulfil the following conditions; i) stoichiometric ablation ii) optically thin plasma iii) local thermal equilibrium, which have been verified and described in the following section.

#### 3.2.1 Stoichiometric Ablation

In our experiment, the focal spot at the sample surface is equal to 12.70  $\mu\text{m}$ , the fluence and irradiance of the Laser at the focal spot are calculated to be  $3.94 \times 10^4 \text{ J/cm}^2$  and  $5.64 \times 10^{12} \text{ W/cm}^2$  respectively. Thus, it is clear that Laser-induced plasma satisfies the stoichiometric ablation as the Laser irradiance is higher than  $10^9 \text{ W/cm}^2$ .

#### 3.2.2 Optically Thin Plasma

The laser-induced plasma is supposed to be optically thin, when the spectral intensity ratio of two emission lines (free from interference) of an element that has approximately the same upper energy level is equal to the ratio of the multiplication of the transition probability ( $A_{ki}$ ), statistical weight ( $g_k$ ) and inverse of the wavelength of these spectral lines<sup>23</sup>. In the

present experiment, the intensity ratio for Al lines (308.2 nm and 309.2 nm) has been calculated and tabulated in Table 4. The theoretical and experimental intensity ratio is nearly the same thus the plasma is optically thin.

**Table 4. Calculated intensity of ratio of two atomic lines for Aluminum, 308.2/309.2 nanometer in the LIBS spectra of the different samples**

Samples	$A_{ki}g_k\lambda'/A_{ki}g_k\lambda$	Intensity Ratio, $I/I'$
S <sub>1</sub>	0.84	0.78
S <sub>2</sub>	0.84	0.86
S <sub>3</sub>	0.84	0.92
S <sub>4</sub> (a)	0.84	0.76
S <sub>4</sub> (b)	0.84	0.72

### 3.2.3 Local Thermal Equilibrium

The method used for the verification of the LTE is described in the article<sup>23</sup>. In the present case, the evaluated value of ionization temperature using the Saha-Eggert equation is  $18181 \pm 431$  K, close to the excitation temperature of  $20449 \pm 817$  K, with a difference of almost 11 %. Thus, the necessary,

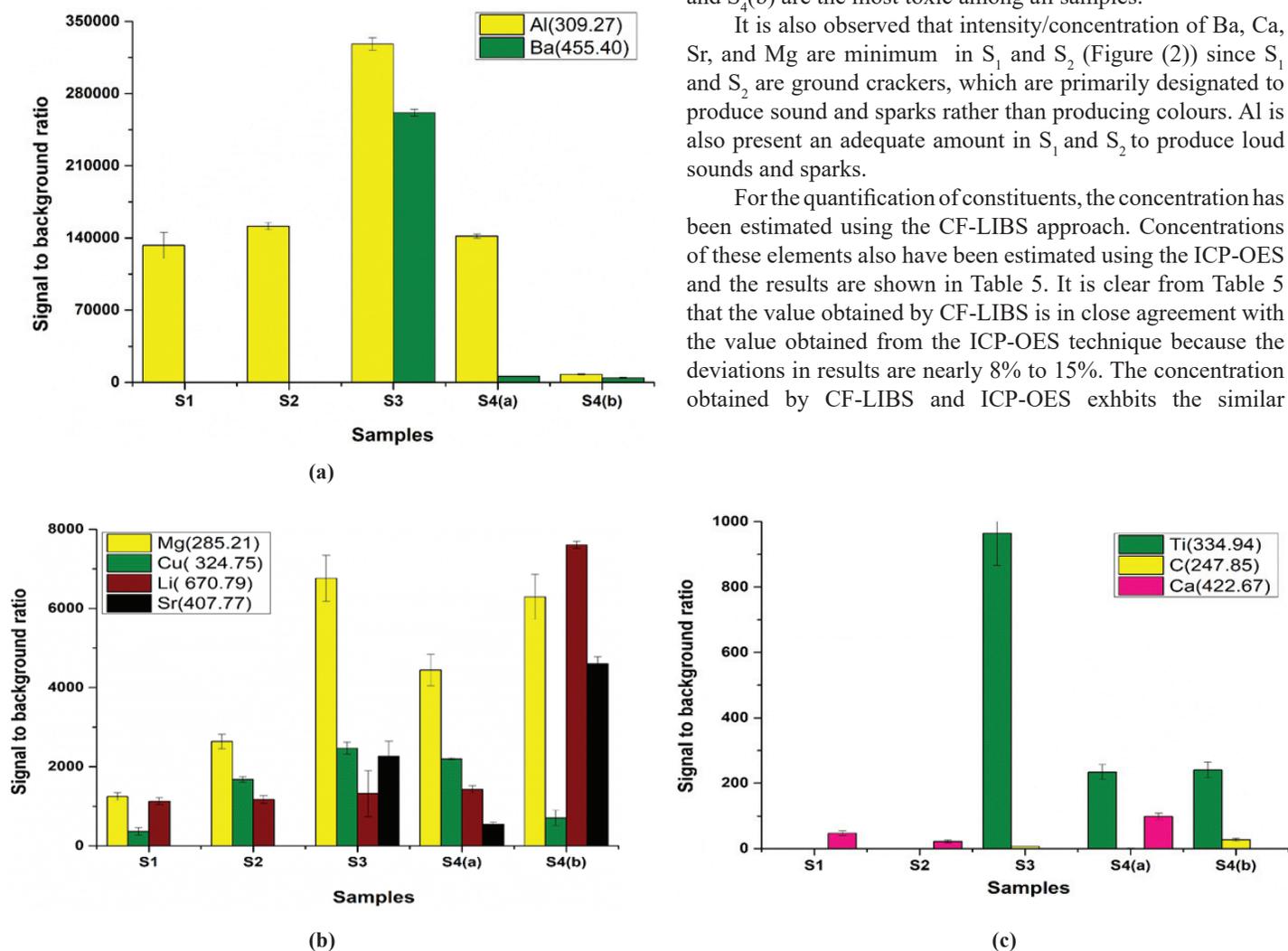
and sufficient conditions, are satisfied and thus LTE holds in the present experiment

Since all the conditions are verified in the present experiment, spectral lines intensities of elements can be used to estimate their concentration in the target materials/samples. The spectral line intensities of the elements are proportional to their concentrations in the sample; therefore, the intensities of the spectral lines are measured to compare their concentrations in the firecrackers. Figure 2 shows the signal to background intensity plot of the spectral lines of Al, Ba, and Mg, Li, Sr, Ti, Cu, Ca and C, in the different firecrackers.

Intensities (concentrations) of Ba, Al, Cu, Mg, and Ti in sample S<sub>3</sub> are higher than the other samples (Figures 2 (a-c)), because S<sub>3</sub> is a areal (rocket) cracker and these elements have been added to produce more sparkle and colour. Concentration of Sr, Li and C are higher in sample S<sub>4</sub>(b) than others because this is also an areal cracker and these elements are added to produce colours after bursting into the sky. For more sparkling, Al is mixed up in aerial crackers; thus, S<sub>3</sub> contains a large amount of Al. S<sub>3</sub> also contains enough Sr, Ca, Cu, Mg, and Mn for producing different colours. Thus, one may conclude that S<sub>3</sub> and S<sub>4</sub>(b) are the most toxic among all samples.

It is also observed that intensity/concentration of Ba, Ca, Sr, and Mg are minimum in S<sub>1</sub> and S<sub>2</sub> (Figure (2)) since S<sub>1</sub> and S<sub>2</sub> are ground crackers, which are primarily designated to produce sound and sparks rather than producing colours. Al is also present an adequate amount in S<sub>1</sub> and S<sub>2</sub> to produce loud sounds and sparks.

For the quantification of constituents, the concentration has been estimated using the CF-LIBS approach. Concentrations of these elements also have been estimated using the ICP-OES and the results are shown in Table 5. It is clear from Table 5 that the value obtained by CF-LIBS is in close agreement with the value obtained from the ICP-OES technique because the deviations in results are nearly 8% to 15%. The concentration obtained by CF-LIBS and ICP-OES exhibits the similar



**Figure 2. (a) Bar diagram/variation of intensities of the spectral lines of Al and Ba in different firecracker samples, (b) Bar diagram/variation in the intensity of the spectral intensities of toxic constituents in the different firecracker samples, and (c) Bar diagram/variation in intensities of Ti, Ca and C in different firecrackers.**

results as shown in Fig. (2). Thus the relative intensities of the spectral lines of the elements can also be used to predict their concentration in the samples.

but in sample  $S_3$ , it is not observed. The reason may be as sample  $S_4(b)$  contains a higher amount of organic compounds having Carbon which is also supported by the fact that  $S_4(b)$  contain a

**Table 5. Concentration (ppm) of constituents obtained from CF-LIBS and ICP-OES.**

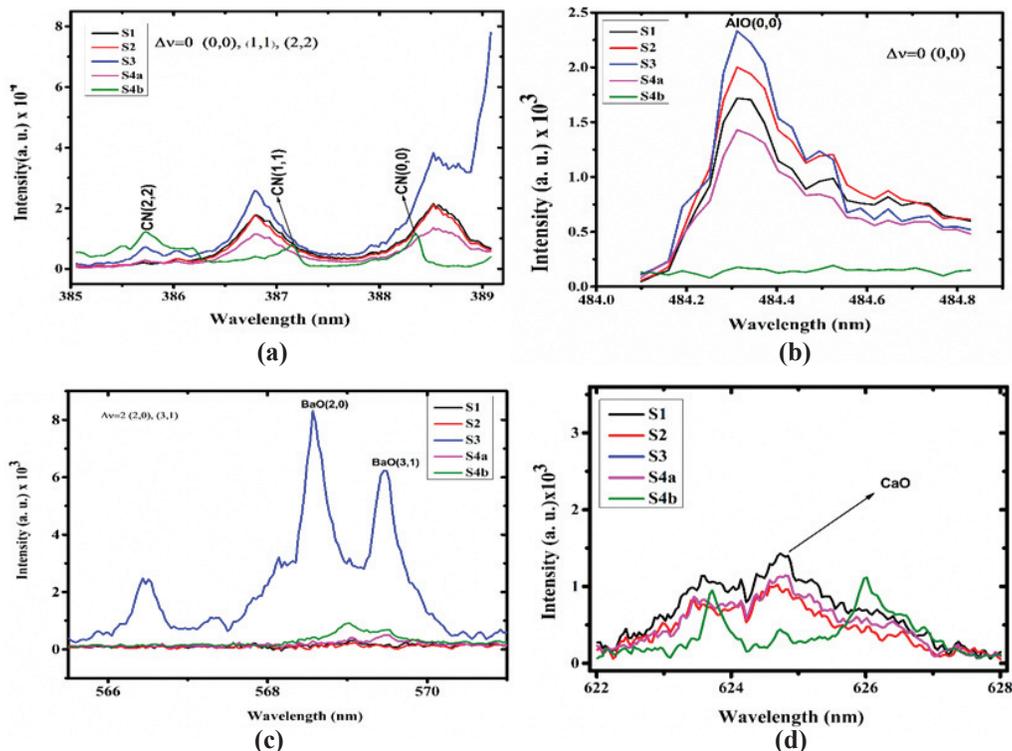
Elements	S1		S2		S3		S4a		S4b	
	ICP-OES	CF-LIBS	ICP-OES	CF-LIBS	ICP-OES	CF-LIBS	ICP-OES	CF-LIBS	ICP-OES	CF-LIBS
Ba	26.91±2.8	24.10±3.2	18.91±2.1	--	1569.90±182.2	994.00±90.0	128.41±13.2	105.40±10.1	152.95±15.5	111.30±17.1
Cu	2.21±.02	1.70±.09	22.17±.25	15.40±1.5	160.17±14.3	116.20±13.4	35.24±.3.5	24.80±1.6	5.23±.05	5.23±.07
Li	--	19.30±2.2	12.80±131.5	--	91.93±1110.0	80.80±8.8	157.12±15.7	148.00±27.2	249.49±36.8	236.00±45.3
Sr	--	--	--	21.70±2.7	41.04±4.1	31.20±2.7	21.92±2.1	15.20±1.8	74.37±10.3	25.80±2.7
Ti	--	--	--	--	--	964.75±100.3	--	234.21±26.0	--	240.67±21.6
Al	7974.96±711.2	8785.00±878.5	5599.97±710.3	3882.00±430.5	14024.90±1402.4	8782.50±911.1	10649.0±1064.9	8610.00±770.2	574.60±181.2	345.00±41.3

### 3.3 Analysis of Molecular Bands in LIBS Spectra of Firecrackers

Figure 1(d) shows the presence of the band heads of (0,0), (1,1) and (2,2) bands corresponding to  $\Delta v = 0$  of CN molecule which indicates that a significant amount of organic compounds (charcoal) having C and N is present in  $S_4(b)$  because charcoal is used as propellant.

The relative intensity of CN bands is shown in Fig. 3(a). It is clear that sample  $S_4(b)$  has a signature of CN molecular band,

higher amount of C (Fig. 2(c)). Band head corresponding  $\Delta v = 0$  sequence of AIO molecule is observed in samples  $S_1$ ,  $S_2$ ,  $S_3$  and  $S_4(a)$  (Fig. 3(b)). The intensity variation of the AIO band (Fig. 3(b)) is almost similar to the intensity variation of the spectral lines of Al (Fig. 2(a)). Thus the presence of Al-Chip in the firecrackers may be estimated by calculating the intensity of the electronic bands of AIO molecules as well as the intensity of the spectral lines of Al atom present in the LIBS spectra of the firecracker.



**Figure 3. Molecular emission of (a) CN at (0,0), (1,1), and (2,2), (b) AIO band (0,0), (c) BaO (2,0), (3,1) band, and (d) CaO band.**

The electronic bands of BaO molecule are observed in the LIBS spectra only when the amount of Ba is high in the sample. Samples  $S_3$  contain the band head of (2,0), (3,1) bands of corresponding  $\Delta v = +2$  sequence of BaO molecule (Figure 3(c)), which is in close agreement that Ba is higher in sample  $S_3$  (Figure 2(a)). Thus sample  $S_3$  contain a high amount of BaNO<sub>3</sub> in comparison to other samples.

LIBS spectra of the samples  $S_1$ ,  $S_2$ , and  $S_4(a)$  show the presence of electronic bands of CaO molecule at 625.6, 605.6, and 606.5 nm (Figure 3)). But these bands are not observed in samples  $S_3$  and  $S_4(b)$  (Figure 3(d)). It is because, in comparison to samples  $S_2$ ,  $S_1$ , and  $S_4(a)$ , the Ca is absent in the  $S_3$  and  $S_4(b)$  (Figure 2(c)).

### 3.4 Fourier Transform Infrared Spectroscopy (FTIR)

For the identification of organic, polymer, and inorganic compounds in the sample Fourier Transform Infra-Red Spectroscopy (FTIR) has been applied. The FTIR spectra (Fig. 4(a) and(b)) contains the absorption bands of NO<sub>3</sub><sup>-</sup> at 1354 cm<sup>-1</sup>, 820 cm<sup>-1</sup> and 1768 cm<sup>-1</sup> in samples  $S_1$ ,  $S_3$ ,  $S_4(a)$  and  $S_4(b)$ <sup>24</sup>. The spectra of this functional group are observed due to the presence of the BaNO<sub>3</sub> molecules in these samples which is supported by the fact that the Ba is present in the samples  $S_3$ ,  $S_4(a)$  and  $S_4(b)$  (Fig. 2(a)). Sample  $S_2$  does not show the absorption band of NO<sub>3</sub><sup>-</sup> because it do not contain BaNO<sub>3</sub> it is also clear from Fig. 2(a) that sample  $S_2$  doesn't contain Ba. Absorption bands of SO<sub>4</sub><sup>-</sup> at 598 cm<sup>-1</sup> and 583 cm<sup>-1</sup> in samples  $S_1$ ,  $S_2$ , and  $S_4(b)$  are present because these three crackers are primarily designed to produce sound and sparks<sup>25</sup>. Sulphur is the best ingredient suitable for producing both light and sound, that is why it is not found in areal crackers  $S_3$  and  $S_4(a)$ . Sometimes SO<sub>4</sub><sup>-</sup> is also used as an oxidizing agent, so sulphur is used to mix firecrackers in the form of sulphate<sup>1</sup>. Similarly, the C-O stretching at 928 cm<sup>-1</sup>, C-H stretching at 1017 cm<sup>-1</sup>, C<sub>8</sub>H<sub>4</sub>O<sup>-</sup> at 1578 cm<sup>-1</sup>, CuCl at 1148.6 cm<sup>-1</sup> and CO<sub>3</sub><sup>-</sup>

at 872 cm<sup>-1</sup> are observed in sample  $S_4(b)$ . It is because sample  $S_4(b)$  contains carbon, as shown in Fig. 2(c). Thus it may be assumed that  $S_4(b)$  contains the compositions in the form of hydro-carbon<sup>26</sup>. Thus the presence of C (Fig. 2(c)) in sample  $S_4(b)$  is justified since all NaCO<sub>3</sub>, CaCO<sub>3</sub>, NaNO<sub>3</sub>, BaCl<sub>2</sub>, CuCl<sub>2</sub>, Carbon black, KNO<sub>3</sub>, Li<sub>2</sub>CO<sub>3</sub>, SrCO<sub>3</sub>, KClO<sub>3</sub>, KClO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub> functional groups were mixed in crackers with a different elemental composition like NaCO<sub>3</sub>, CaCO<sub>3</sub>, NaNO<sub>3</sub>, BaCl<sub>2</sub>, CuCl<sub>2</sub>, Carbon black, KNO<sub>3</sub>, Li<sub>2</sub>CO<sub>3</sub>, SrCO<sub>3</sub>, KClO<sub>3</sub>, KClO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub><sup>1</sup>. These compositions are mixed in crackers to provide an exciting colour and glitter effect. The spectral signature of conjugate elements of the absorption band found in FTIR spectra is also present in LIBS spectra as the spectral signature of Na, Ba, Cu, K, Sr and Ca, are present in the LIBS spectra of these firecracker samples.

### 3.5. Prediction/Investigation of Organic/Inorganic Compounds in Firecrackers

The presence of the spectral lines Ba and electronic bands of BaO in the LIBS spectra, as well as the functional group NO<sub>3</sub><sup>-</sup> in the FTIR spectra, confirm the presence of BaNO<sub>3</sub> in the firecrackers. The concentration Ba is highest in  $S_3$  (Table 5) suggesting that  $S_3$  contains the highest amount of BaNO<sub>3</sub>. This is due to  $S_3$  is areal crackers and these crackers primarily designated to produce different colors in sky. BaNO<sub>3</sub> is responsible for green color and lead to poisonous, fumes can irritate respiratory tract<sup>1</sup>. LiCO<sub>3</sub> is present in all samples as the spectral lines of Li is present in the LIBS spectra of all samples as well as functional group CO<sub>3</sub><sup>-</sup> is present in the FTIR spectra of the firecrackers. LiCO<sub>3</sub> is toxic and irritating fumes when burned<sup>1</sup>. Similarly, Sr is present in a sufficient amount in the samples  $S_3$ ,  $S_4(a)$  and  $S_4(b)$  and functional group CO<sub>3</sub><sup>-</sup> is present in the FTIR spectra which suggests that SrCO<sub>3</sub> is present in these samples in enough amount and SrCO<sub>3</sub> can replace calcium in body. Thus SrCO<sub>3</sub> is highly toxic<sup>1</sup>. Al is present in all samples with highest in  $S_3$  and we may

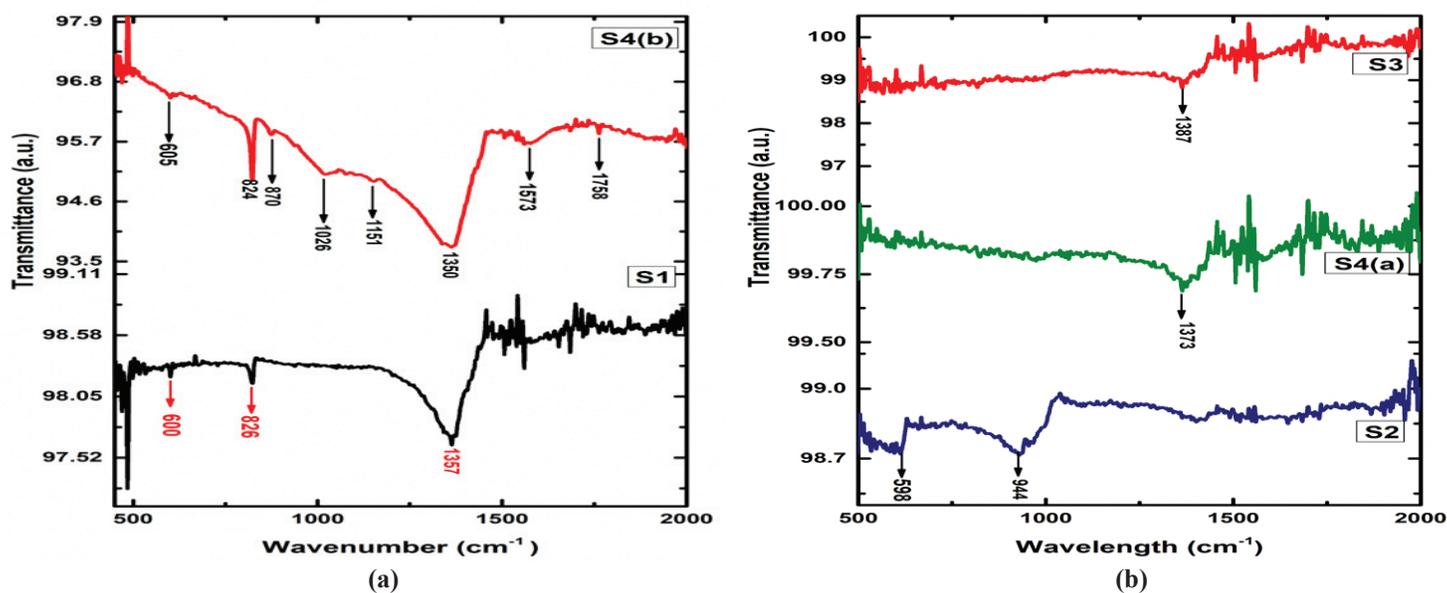


Figure 4. (a) FTIR spectra of sample  $S_1$  and  $S_4(b)$  containing different stretching, and (b) FTIR spectra of samples  $S_2$ ,  $S_3$  and  $S_4(a)$  containing different groups.

conclude that Al-chip is present in all samples and highest in S3. All the crackers contain an adequate amount of Cu (Figure 2(b)), as well as the absorption bands of CuCl, is present in the FTIR spectra of the firecrackers suggesting the presence of  $\text{Cu}_3\text{As}_2\text{O}_3\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$  compounds in these crackers. Cu Compound are polychlorinated dioxins and dibenzofurans can bioaccumalte and invites cancer disease [1]. The presenrnce of atomic lines of carbon and electronic bands of CN molecules in LIBS spectra of C-N stretching is also observed in FTIR spectra which suggests the presence of charcoal in sufficient amount in this sample.

### 3.6. Principal Component Analysis

PCA has been performed on LIBS data to classify the firecrackers using unscrambler software (Camo Ltd). To apply

major constituent (574.60-14024.90 ppm) of these firecrackers. The concentration of Sr (15.20-74.37 ppm), Cu ( 2.21-160.17 ppm), Li (19.30-249.49 ppm), Ba (26.91-1569.90 ppm) and Ti (234.21-964.75 ppm) is also determined. Thus, CF-LIBS can be used to determine the concentration of constituents of firecrackers without any tedious sample preparation. FTIR spectra of firecrackers samples contain the functional group of  $\text{SO}_4^-$ ,  $\text{C}_8\text{H}_4\text{O}$ , CuCl,  $\text{CO}_3^-$ ,  $\text{NO}_3^-$ , C-O, and charcoal. The combined results of LIBS and FTIR reveal the presence of  $\text{BaNO}_3$ ,  $\text{LiCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{Cu}_3\text{As}_2\text{O}_3\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ , and charcoal in firecrackers. Therefore, burning of these crackers is harmful not only to the environment but also harmful for the humans living in that locality. PCA, applied on LIBS data, is a reliable tool for the differentiation/discrimination of various firecrackers based on the constituents present in these samples.

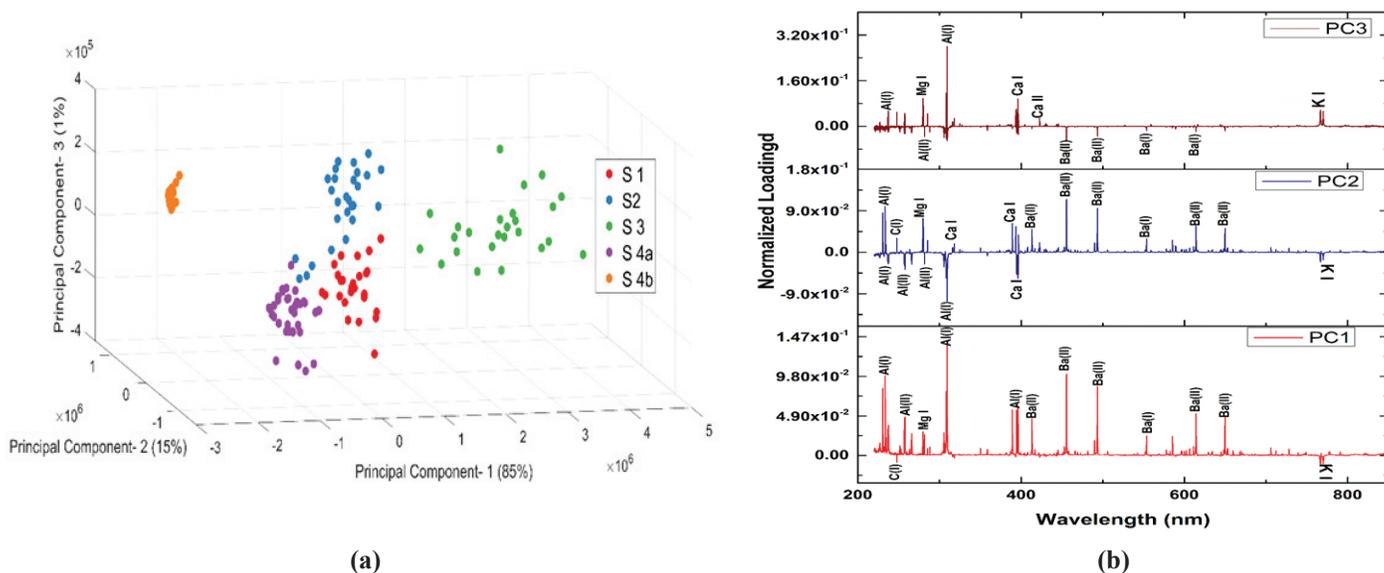


Figure 5. (a) Three-dimensional score plot of principal component analysis, and (b) Loading plot of principal component analysis.

PCA, a data set (140 x 22491), where 140 is the number of spectra (multiple spectra were taken for all samples), and 22491 is the number of features, having an intensity corresponding to each pixel has been used. In the score plot (Fig. 5(a)) five different clusters are formed corresponding to four samples. Data points corresponding to  $S_1$ ,  $S_2$  and  $S_4$  (a) form a cluster,  $S_3$  and  $S_4$ (b) forms another cluster on negative and positive side of the PC-1 respectively. Loading plots (Fig. 5(b)) can explain these clusters

### 4. CONCLUSIONS

The presence of lethal elements like Al, Ba, Ca, Cu, Li, Sr, and Ti are detected/identified in the crackers. Electronic bands of CN, CaO, BaO, and AlO molecules are observed in the LIBS spectra of firecrackers. The electronic bands of diatomic molecules can also be used to predict the concentration of the toxic elements. The presence of the Al-Chip in the firecrackers can be monitored by the presence of the spectral lines of Al and electronic bands of AlO molecule. The concentration of each element in firecrackers are determined using CF-LIBS and compared with ICP-OES. It has been found that Al is the

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