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RESEARCH ARTICLE

Determination of Potassium and Sodium in Commercially Sold Fireworks by Flame Photometry

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Abstract

The alkali and alkaline earth metals such as potassium, sodium, barium and strontium are generally used as oxidizer in fireworks. The arbitrary use of these chemicals in fireworks is an acute issue responsible for higher emissions. Hence, efforts are underway to monitor these chemicals in fireworks. This work reports the precise determination of potassium and sodium in fireworks samples by flame photometry. The average deviation by flame photometry analysis was 7 to 8 % and 3 to 4 % for potassium and sodium, respectively, when the concentration of the respective metal nitrates in fireworks composition was less than 50%. R^2 value 0.9943 and 0.9968 calculated from a better-fit regression model for potassium and sodium, respectively, corroborated the smaller difference between the predicted value and the observed value of flame photometry results. The effect of different components in fireworks mixture, such as nitrate and metal precursor, were also studied to understand their impact on results. A brief study in terms of limit of detection (LOD), limit of quantification (LOQ) and dynamic range was also performed, which showed 0.42 and 3.26 mg/L as LOD and 1.29 and 9.88 mg L^{-1} as LOQ for the analysis of sodium and potassium, respectively. In summary, the study proved the prospective of flame photometry for determining sodium and potassium in fireworks samples.

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1. Introduction

Over the past decades, air pollution has increased dramatically and is therefore recognized as a severe threat to human health, the environment and climate change. Air pollution can be natural (volcanos, forest fires, etc.) or due to anthropogenic activities (industrial pollution, vehicular pollution, bursting of fireworks and firecrackers, microbial decaying process, open garbage burning, construction and demolition, etc.). These activities release particulate matter ($PM_{2.5}$ and PM_{10}) and gaseous emissions (CO_2, CO, SOx, NOx, VOC, HC) in the environment. Studies revealed that exposure to particulate matter leads to short and long-term health effects, viz. headaches, decreased lung function, emphysema, asthma, range of cardiovascular and respiratory diseases[1][2]. Air pollution alone is responsible for around 8 million deaths every year worldwide[3].

In several countries, fireworks and firecrackers are used during festive celebrations and cheering moments mainly due to their entertaining and aesthetic view of light and sound shows. Fireworks and firecrackers are part of various festivals like Diwali in India, Bastille Day in France, Australia Day, Lunar New Year in China and other Asian countries, Guy Fawkes Night in Great Britain and other commonwealth countries, and New Year's Eve celebrations across the world[4]. Although fireworks are famous, the higher emissions post massive celebrations is a serious issue and thus caught the attention of the judiciary and pollution board. The blanket ban is not feasible as fireworks are more globally well-known, and the livelihood of several people, directly and indirectly, depends on this sector. The blanket ban may cause a flow of illegal and unregulated fireworks. Fireworks have also a history dating back to 600 AD, and, in several countries, it is closely attached to their faith and festive celebration. However, the use of excess, adulterated and banned chemicals in fireworks may cause serious health issues[5][6][7]. Therefore, it is important to streamline the process for the monitoring of fireworks components, and in this direction, this work provides a simple and cost-effective partial approach for the monitoring of fireworks components such as sodium and potassium in fireworks.

Fireworks are generally classified into two major categories: individual or family celebration and mass celebration. The latter generates more smoke and pollution than the former one[8]. Fireworks mainly consist of four major components that are (i) fuel - charcoal or sulphur or aluminium, (ii) oxidising agent - metal nitrates, (iii) combustible binder - organic components such as nitrocellulose, shellac, dextrin and resins and (iv) metal-containing colourants - barium, sodium, zinc, iron and aluminium[9][10]. Few metal salts like barium and strontium nitrate have dual oxidizer and color producer properties. Recently, there has been a consistent change in the composition of firecrackers to reduce the environmental consequences[11][12]. The use of barium, chlorate and perchlorates is banned due to toxicity and environmental issues. The conventional firecrackers or fireworks in the market generally consist of potassium nitrate, aluminium and sulphur as significant components, where potassium salt plays the oxidising agent. The feasibility and poor hygroscopic properties of potassium ensure its deployment in fireworks. Also, the spectra of potassium do not interfere much with the desired colour spectra, giving the manufacturer a good scope to get the desired colour with burning[13]. Sodium nitrate salt also possesses similar physical and chemical properties to potassium, except hygroscopicity. It is preferred in fewer fireworks compositions owing to its hygroscopic nature. It is also used as a nitrate precursor in potassium nitrate production. It has higher efficiency of light emissions; hence used in fireworks to produce the desired colour during burning. The black powder or flash powder rich in potassium nitrates may result in a higher concentration of potassium ions in fireworks. The performance of fireworks can also be improved with the appropriate percentage of alkali metal salts. The release of alkali or alkaline metals after a fireworks celebration may ultimately end in emission and enter the human body through inhalation. Although alkali metals like potassium improve soil quality, their higher concentration in the human body may lead to heart palpitations, shortness of breath, chest pain, nausea or vomiting, muscle fatigue, weakness, and paralysis. Similarly, the higher sodium concentration may cause increased thirst and brain dysfunction, coma, swollen feet or hands, headaches and a rise in blood pressure[14][15][16]. Hence, detecting these alkali metals becomes essential to improve fireworks performance and to curb the adverse impacts on human health.

The conventional methods used to determine potassium and sodium are complexometric titration, ion-selective electrode, spectrophotometry, gravimetry, ICP-AES or MS, and flame photometry, etc. The advantages and disadvantages of these techniques based on their applications in particular fields are discussed in Table 1.

Table 1. Advantages and disadvantages of process or technique used for the determination of sodium and potassium

Technique	Advantages	Disadvantages
Complexometric titration	• Metal ions, including alkali, alkaline earth and transition metals, can be detected simultaneously. • Technique is fast and accurate.	• Interference of multiple metals leading to the variation in endpoint results. • For independent metal analysis, parameters like pH and masking agents are to be taken care of. • The stability of the metal complexing agent should be higher than the metal indicator complex. • Higher cost due to complex chemicals
Ion-selective electrode (ISE)[17]	• Both positive and negative ions in the sample can be determined. • The activity of the ion with time can be measured. • It is relatively easy to operate. • ISE has a wide concentration measurement range.	• It allows the detection of a particular type of ion. • At higher concentration there is slight deviation in the potential as the conc. at the membrane junction is less compared to the bulk of the solution due to the interionic attractions. • Higher fluctuation rate and lower sensitivity are major drawbacks. • Higher electrode cost and lower shelf life
Gravimetric analysis	• Provides accurate and precise results compared to volumetric techniques. • It's a cheaper method. • Overcomes the problem of temperature fluctuations, calibration errors etc.	• It can analyse one element at a time or sometimes a group of elements. • Lengthy and time-consuming process. • A small mis-step can cause formation of another compound • Requires accurate weighing. • It includes the involvement of co-precipitation leading to possible error in detection.
ICP-AES or MS analysis[18]	• Provides the simultaneous multi element analysis. • It has high throughput screening. • High precision and accuracy is possible through ICP. • Metal concentration detection is possible even in lower traceable concentration.	• Requires the usage of non-green solvents for the acid digestion process. • The standards required for the analysis and instrument maintenance is a costly expense. • Instrument handling requires special training and pre-requisite knowledge regarding sample preparation. • Higher investment and operating cost
XRF[19]	• It is a non-destructive analytical technique that can be used for the quantitative and qualitative analysis of the elements from the unknown samples.	• The quantitative detection by XRF, the sample should be homogeneously mixed, otherwise leading to biased results • Requires higher investment and operating cost • Requires skilled manpower for the operation of the instrument. • It is also not sensitive towards sodium
Kjeldahl's Method[20]	• Modified Kjeldahl's method can be used for K/Na nitrate estimation by determining the amount of nitrogen content followed by nitrate calculation and, finally, from the stoichiometry relations, arriving at the amount of potassium nitrate present in the sample mixture.	• In the case of mixed samples containing different nitrate precursors. This ancient method cannot determine the amount of a particular metal nitrate. Hence, this method can be ruled out as it fails to fulfil the requirement.
		In case of multiple nitrates in the mixture, the intensity of the

UV-Visible Spectroscopy[21]	• It can be employed to detect metal nitrate in the sample solution as nitrates generally absorb at a characteristic wavelength of around 200 nm. • Metal can also be traced by forming complexes, as complexes absorb different wavelengths of light useful for concentration detection. • Simple and cost effective in comparison to the other sophisticated techniques.	• In case of multiple nitrates in the mixture, the intensity of the peak corresponding to the nitrates would be higher than the expected value. Hence the determination of particular alkali metal nitrates from this method may lead to added error. • Complex method is not useful for the sample containing multiple metal ions as each metal ions forms respective metal complexes with the added chelating agent. • The method is not reliable for all metals as chelation is not possible in all cases.

Flame photometry has its own advantages and disadvantages. However, it easily jumps across many hurdles of above stated problems[22]. Flame photometry lies in the principle of atomic excitation and emission, where the excitation of an atom is performed in the presence of an ignited flame. Each elemental atom has a characteristic emission that differentiates it from each other and performs accurate detection. The light intensity produced by a specific metal depends on the number of excited atoms, which is directly proportional to the metal cation concentration in the solution sample. For instance, barium produces a green flame; sodium produces a yellow flame; potassium has violet, and calcium produces orange-red. The emitted light at a specific wavelength is measured and correlated to the concentration of the element in the sample. Therefore, metal excitation techniques can also be used for the analysis of firecrackers and pyrotechnics to detect alkali and alkaline earth metals like sodium and potassium[23]. Since the whole sample of fireworks is procured for sample preparation, the issue of homogeneity is removed at the very first instant. It detects metal ions based on their characteristic emission light, and hence the presence of other metal salt doesn't create much more interference[24][25].

To the best of our information, a valid process has yet to be reported for the determination of potassium and sodium in fireworks samples. This work was initiated to provide scientific support to accurately detect alkali and alkaline earth metals in fireworks samples. In particular, this article throws light on the privilege of flame photometry for determining alkali and alkaline metals in fireworks samples, which is discussed in brief, along with feasibility, accuracy, precision, and other relevant factors.

2. Material and Methods

2.1. Materials

Analytical-grade reagents were used throughout the experimentation. The chemicals potassium nitrate, sodium nitrate, barium nitrate and strontium nitrate were procured from Rankem Chemicals, India. The other chemicals, namely sulphur, dextrin, aluminium powder grade 999 and 222, zeolite, gum, magnesium alloy and iron powder used in the preparation of the known composition of firecrackers, were commercial grade and supplied by the local fireworks manufacturer. Milli-Q deionised water of the Millipore system was used in all experiments to avoid the contamination of the common metal ions.

2.2. Instrumentation

The flame photometer, Microprocessor based flame photometer with an inbuilt calcium filter, Make- ESICO, Model-1385, was used to determine the sodium and potassium ions in the firecracker sample. The operating parameters include Flame system – LPG & dry oil-free air, Flame height – 5 to 10 min, Aspiration rate – 2 to 5 ml/min, Detector- Photodiode, Wavelength- 589 (Na) and 766.5 (K), Slit width – 0.1 to 1.0 mm, Gain- Adjust as necessary, Compressor pressure- 0.2 to 0.4 bar. The pre-calibration and calibration steps for sodium and potassium are provided in supporting information. The device was calibrated by permitting it to warm up and then aspirating de-ionized (DI) water to maintain a constant temperature in the burner while producing a reliable "0" ppm reading. The next stage involved selecting the necessary metal elements and inputting the produced standard samples' known concentration to ensure accurate calibration. Following calibration, the necessary elements were analyzed by aspirating samples of unknown crackers in the analysis window. The detectable range of instrument was in between 1-1000 ppm concentration. The samples having concentration >1000 ppm can be analyzed by dilution and back calculation (as per dilution). The instrument consists of the following components: nebulizer, mixing chamber, flame/burner, filter and photodetector. Each of these components has a specific role in metal cation detection. In the actual flame photometry process, the sample cell will be exposed first to the burner via a nebulizer or atomizer. After converting into tiny droplets, the sample matrix will get vaporized along with the atomization of the sample. Further, the flame helps to excite the electrons corresponding to the metal atoms. Each electron emits a characteristic wavelength corresponding to a particular metal upon de-excitation, which is isolated using a monochromatic filter and then detected by a photodetector. The colour intensity emitted during this analysis is proportional to the concentration of the metal ions present in the sample. The reader can refer to Figure 1 for a better understanding of the process[26][27][28].

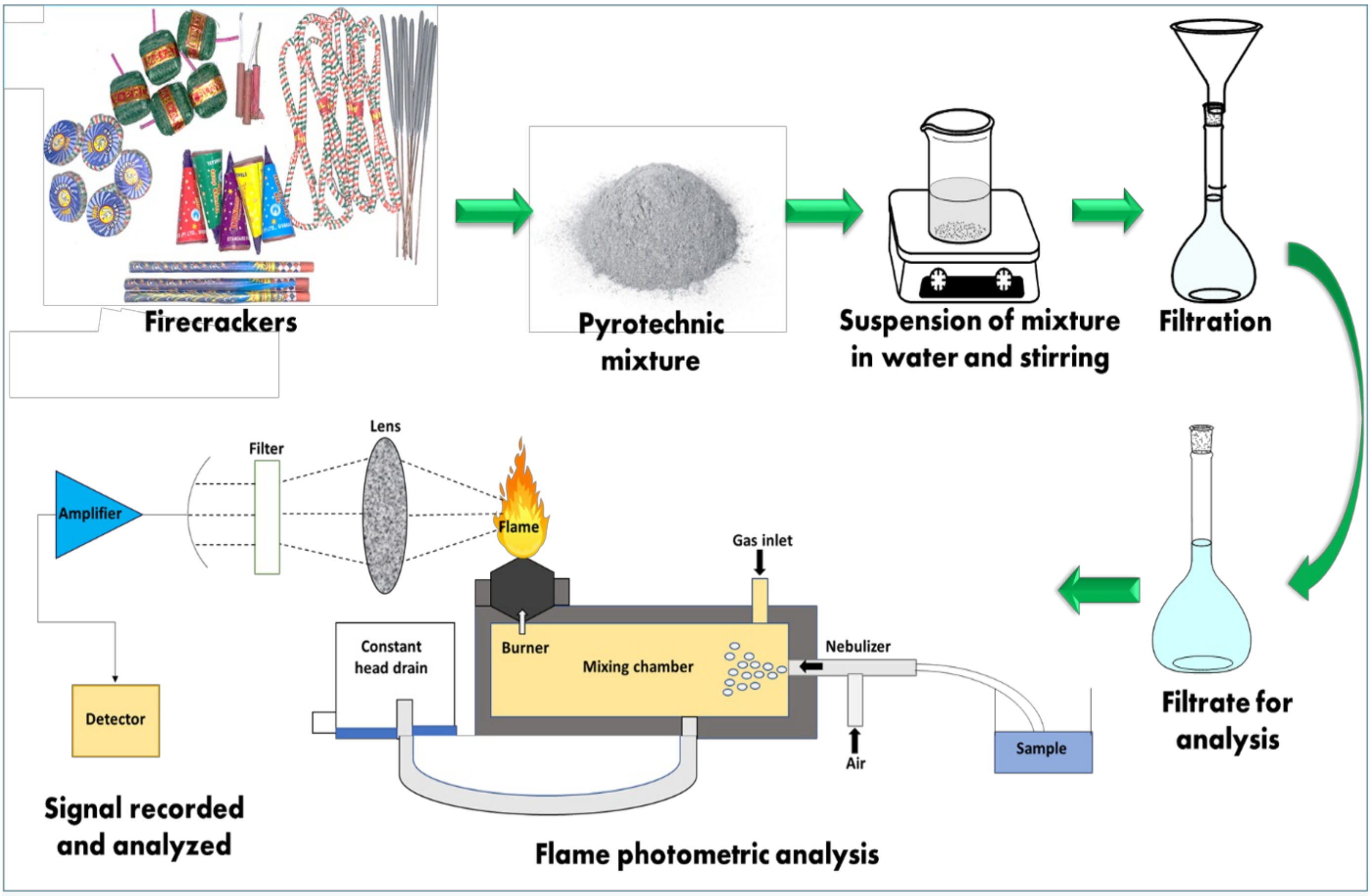

Figure 1. A Schematic view of flame photometer used for the determination of metal ion in firecracker sample

2.3. Methods for the determination of sodium and potassium in firecracker samples

2.3.1. *Preparation of standard sodium and potassium samples and their analysis*

A stock solution of potassium and sodium (1000 ppm) were prepared in a 500 mL volumetric flask by dissolving 1.292 g and 1.848 g of potassium and sodium nitrate, respectively. Once dissolved, the volumetric flask was diluted up to the mark. A set of standards ranging from 100, 80, 60, 40 and 20 ppm were subsequently prepared by serial dilution methods and subjected to flame photometry analysis. The graph was plotted as actual concentration (prepared) against recorded concentration (instrument reading) along with the statistical data of LOD and LOQ and provided in Figure 2. This information in tabular format is also provided in supporting information Table ST 1 and ST2.

2.3.2. *Preparation of known concentrations of sodium and potassium samples and their analysis*

To cross-check the system's compatibility, the cracker samples were initially prepared with the known concentration of sodium and potassium. The details of the prepared compositions are provided in Tables 2, 3, 4 and 5. The whole sample (2 g) was then transferred to the conical flask containing 100 mL water and incubated for 2 h. This followed by filtration and washing thrice with DI water. The collected filtrate was then diluted to 250 mL DI water in the volumetric flask. The samples were diluted again in the case of exceeding the calibration range 0-100 ppm. Finally, the obtained results were compared with the known concentration of sodium and potassium.

2.3.3. *Preparation of firecracker sample and their analysis*

Fireworks are a mixture of powdered solid components, so uniform distribution is not exactly as in liquid samples. Hence, using one part doesn't provide an exact idea about the mixture. By considering this fact, the whole sample (2 g) was dissolved in water, filtered and diluted further to provide accurate analysis data. In the actual process, the firecracker samples with unknown sodium and potassium concentrations were weighed and taken in a 250 ml conical flask containing approximately 100 mL DI water, followed by 2 h incubation/stirring at room temperature and filtration using ordinary filter paper. The collected filtrate was then diluted up to the 250 mL volume, washed thrice and subjected to flame photometry analysis. The sample can be further diluted if the concentration exceeds the detection limit and back-calculation (as per dilution) to ascertain the exact value.

2.4.4. *Calculation for the determination of sodium and potassium in firecracker samples*

The amount of potassium (x) in the firecracker sample in 250 ml solution was calculated by using the following equation -

$$x(\text{ in } g) = \frac{(y)ppm \times \left(1 \times 10^{-3}\right)g}{(4)ppm} \qquad (1)$$

Where, 4 ppm is the value supposed by considering the dissolution of 1 mg of metal in 250 mL solution, y is the value obtained by the flame photometry analysis in 250 mL unknown sample, 10^{-3} is multiplied for the unit conversion of mg to g.

From the stoichiometry relationship the amount of potassium nitrate (z) was calculated using the following relations and equations -

$$z(\text{ in } g) = \frac{(x)g \times (101.1032)g}{(39.0983)g} \qquad (2)$$

Where, 39.0983 is the molecular wt. of K, 101.1032 is the molecular wt. of KNO_3, x is the value of potassium obtained from equation (1).

Finally, percentage of potassium nitrate in the given firecracker sample was calculated by the equation as -

$$\%KNO_3 \text{ in firecracker } = \frac{z(\text{ in grams })}{\text{Amt.of Firecracker Sample taken(in gms)}} \times 100 \qquad (3)$$

Where, z is obtained from equation 2.

Similarly, the sodium ion concentration in the sample was calculated by following the same process except the molecular weight of potassium in equation (2), which is taken as 22.98 and 84.99 for Na and $NaNO_3$, respectively.

3. Results and Discussion

3.1. Determination of LOD, LOQ and Dynamic range

LOD is the lowest amount of analyte detected by the instrument, whilst LOQ is the lowest amount that can be quantitated with acceptable accuracy and precision under the stated experimental conditions[29]. The detection of LOD, LOQ and Dynamic range for both potassium and sodium were calculated by preparing two different standard sets, one set corresponding to lower ppm values [0.1,0.125,0.25,0.5,1,5 and 10 ppm] and the other set related to higher ppm values [1000,500,200,100 and 50 ppm]. These samples were tested on flame photometry, and results are plotted as actual concentration value Vs. flame photometry value and is provided in Figure 2 (a and b). The actual concentration values (prepared) against recorded concentration (instrument reading) are also provided in supporting information in Table ST 1.

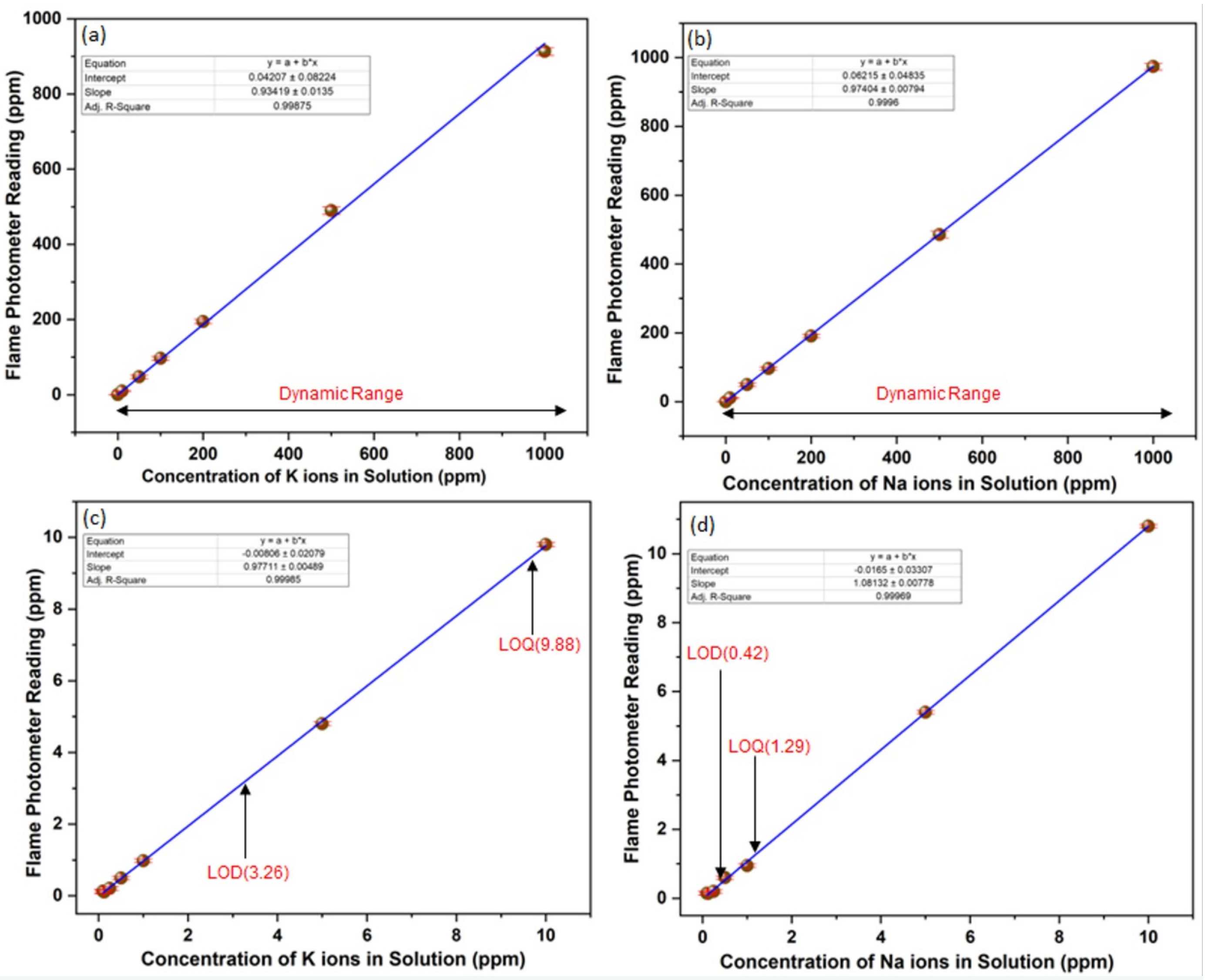

Figure 2. Different curves (a) correspond to the dynamic range to detect potassium ion, (b) dynamic range to detect sodium ion (c) enlarged image of the curve a; LOD and LOQ of the instrument for the detection of potassium, (d) enlarged image of the curve b; LOD and LOQ of the instrument for the detection of sodium.

The LOD and LOQ were calculated by using following formula as shown in equation (4) and (5) -

$$\text{LOD} = 3.3\text{SD} \times \text{S}, \qquad (4)$$

and

$$\text{LOQ} = 10\text{SD} \times \text{S}, \qquad (5)$$

Where SD = standard deviation of intercept, S = slope of the calibration curve and values 3.3 and 10 are used as multiplication factors to account for the uncertainty and variability in the measurement [30]. The limit of detection (LOD) and limit of quantification (LOQ) for potassium was found to be 3.26 and 9.88 mg/L, respectively, and for sodium, their value was calculated to be 0.42 and 1.29 mg/L, respectively (Figure 2). The statistical validation (R^2, LOD and LOQ) of sodium and potassium by flame photometry is also provided in supporting information in Table ST 2. The concentration of sodium and potassium ions in the samples of different brands after the first dilution was observed to be in the range of 0-100 ppm.

3.2. Determination of potassium in firecracker samples

Firecracker samples are mainly composed of single or multiple oxidizers such as potassium nitrate, barium nitrate and strontium nitrate. Therefore, the experimentations were conducted over a different known set of a mixture, including (i) potassium nitrate in the presence of different nitrate precursors, e.g. potassium nitrate, sodium nitrate, barium nitrate, strontium nitrate, (ii) potassium nitrate in the presence of different potassium salts e.g., potassium nitrate, potassium sulphate, potassium chloride with objective to comprehend the effect of different nitrate and metal species on determination of potassium in firecracker samples.

3.2.1. *Effect of different metal nitrate precursors in the determination of potassium in firecrackers*

The sample mixture contained potassium nitrate with different known nitrate precursors, i.e., potassium nitrate, sodium nitrate, barium nitrate and strontium nitrate, along with firecrackers component aluminium and sulphur were prepared and tested for the determination of potassium on a flame photometer. In total five samples were prepared and named as Sample 1, 2, 3,4, and 5. The percentage composition of these samples as in Table 2, was finalized to comprehend the effect of different nitrate precursors and potassium precursors on the analysis of potassium, to apprise the effect of broad range (lower and higher potassium concentrations) on the flame photometry and to test the suitability of flame photometry for varied fireworks compositions.

The compositions of each sample is provided in Table 2.

Table 2. Composition used to comprehend the effect of different nitrate precursors on determination of potassium

Sample Name	KNO_3	$Ba(NO_3)_2$	$Sr(NO_3)_2$	Al 999	S
Sample 1	5%	35%	30%	20%	10%
Sample 2	30%	20%	20%	20%	10%
Sample 3	50%	10%	10%	20%	10%
Sample 4	70%	5%	5%	10%	10%
Sample 5	90%	0%	0%	5%	5%

The graph was plotted as a known potassium concentration in solution versus flame photometer reading and is provided in Figure 3(a). Similarly, these values in tabular format are provided in supporting information in Table ST3. The intercept, slope and R^2 value calculated from this plot are also provided in the inset of Figure 3(a). R^2 value 0.9943 calculated from a better-fit regression model corroborated the smaller difference between the predicted value and the observed value of flame photometry results. The error graph Figure 3(b) corresponding to this plot illustrates the higher deviation of about 15% when the potassium percentage was in higher concentrations of about 70 and 90%. This may be attributed to the increased ionic interactions. The error goes down to 8% with a reduced potassium concentration of less than 50%. Therefore, it is substantiated that flame photometry provides better results when the percentage of potassium is less than 50% in the sample.

3.2.2. *Effect of different potassium metal salts precursors on the determination of potassium in firecracker samples*

As discussed above in section 3.2.1, in a similar way, experiments were performed to understand the effect of different salt precursors on the determination of potassium. The firecracker samples contain common metals with varying salt precursors, e.g., potassium nitrate, potassium sulphate and potassium chloride were used and tested. The corresponding samples were prepared and analysed on a flame photometer. The composition of each of the sample is provided in Table 3.

Table 3. Composition used to comprehend the effect of different potassium precursors on determination of potassium

Sample Name	K_2SO_4	KCl	K_2CO_3	KNO_3	Al	S
Sample 1	-	-	-	25%	25%	50%
Sample 2	50%	-	-	-	25%	25%
Sample 3	-	40%	-	-	30%	30%
Sample 4	-	-	100%	-	-	-
Sample 5	25%	25%	25%	25%	-	-
Sample 6	-	30%	50%	-	10%	10%

The graph plotted and provided in Figure 3(c) corresponds to the concentration of potassium ions in the presence of other potassium salts showing the better-fit regression model (R^2 value 0.9911). The percentage error was a maximum of 7-8%

and can be seen in Figure 3(d). These values in tabular format are also provided in supporting information in Table ST4.

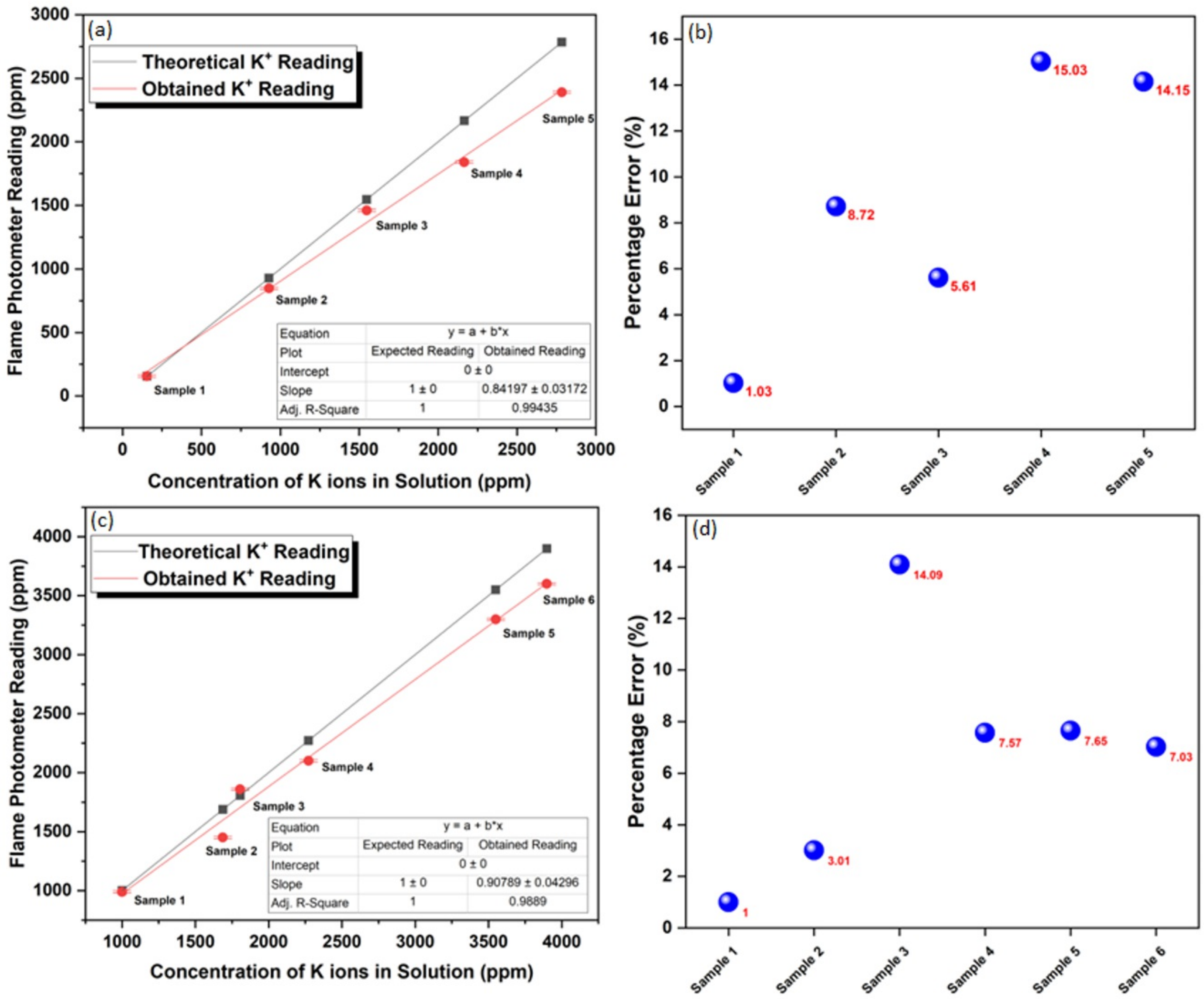

Figure 3. The curves depict the (a) potassium in presence of different metal nitrate precursor (b) error percentage of potassium in presence of different metal nitrate precursors (c) potassium nitrate in presence of mixture of different potassium precursor salts (d) error percentage of potassium ions in presence of mixture of different potassium salts.

Further, the results in ppm obtained from the flame photometer were used to calculate the percentage amount of potassium nitrate present in the prepared firecracker sample with the help of equations (1), (2) and (3) as discussed in section 2.4. The data regarding the same is tabulated and provided in supporting information Table ST 3 and 4.

3.3. Determination of sodium in firecracker samples

The concentration of sodium in different firecracker samples was detected by flame photometers, as discussed in section 3.2. Firecracker samples are mainly composed of single or multiple oxidizers. Therefore, the experimentations were conducted over a different known set of mixture, including (i) sodium nitrate in the presence of different nitrate precursors, e.g., sodium nitrate, potassium nitrate, barium nitrate, strontium nitrate, (ii) sodium nitrate in the presence of different sodium salts, e.g., sodium nitrate, sodium carbonate, sodium chloride with the objective to understand the effect of different nitrate and metal species on the determination of sodium in firecracker samples.

3.3.1. *Effect of different metal nitrate precursors in the determination of sodium in Firecrackers*

Sodium was determined in the samples containing the nitrate precursor, i.e., potassium nitrate, barium nitrate, strontium nitrates, in the presence of iron powder, dextrin, gum, Mg alloy, zeolite, and aluminium. The following table consists of known concentrations of sodium nitrate in the presence of other metal nitrates. (These compositions were made similar to those of the cracker composition)

Table 4. Composition used to comprehend the effect of different nitrate precursors on determination of sodium

Sample Number	Na NO$_3$	K NO$_3$	Na$_2$ CO$_3$	Na Cl	Ba NO$_3$	Sr NO$_3$	Fe powder	Dex-trin	Al 222	Al 999	Zeo-lite	Gum	Mg Alloy
Sample 1	20%	25%	-	-	-	-	30%	10.5%	6%	3%	4%	1.5%	-
Sample 2	30%	20%	-	-	20%	30%	-	-	-	-	-	-	-
Sample 3	40%	-	-	-	-	-	27.5%	10%	6%	3%	4%	1.5%	8%
Sample 4	45%	-	-	-	-	-	30%	10.5%	6%	3%	4%	1.5%	-
Sample 5	50%	-			-	-	30%	10%	10%	-	-	-	-

The corresponding data were recorded and plotted as flame photometer readings versus the concentration of sodium ions in the solution and is provided in Figure 4(a). Similarly, these values in tabular format are provided in supporting information in Table ST5. The R^2 value obtained from the regression model 0.9968 confirmed a smaller difference between the predicted values and obtained values from the flame photometer. Also, the error graph corresponding to this showed a deviation of about 4% when the percentage of sodium was less than 50%. However, the error reached a 10 % deviation when the amount of sodium crossed the 50% limit. Therefore, it is confirmed that better results with smaller variation can be obtained when the sample mixture containing sodium concentration is less than 50%.

3.3.2. *Effect of common metal salts in the determination of sodium in firecracker samples*

The firecracker samples containing common metal salt precursors (e.g. sodium nitrate, sodium carbonate, sodium chloride) were analysed to understand the impact of different metal salts precursor on the determination of sodium by flame photometer.

Table 5. Composition used to comprehend the effect of different sodium precursors on determination of sodium

Sample	NaCl	Na_2CO_3	$NaNO_3$	Al	S
Sample 1	25%	-	25%	25%	25%
Sample 2	-	25%	25%	25%	25%
Sample 3	25%	25%	-	25%	25%
Sample 4	25%	25%	25%	15%	10%
Sample 5	-	100%	-	-	-

As discussed in section 3.2, in a similar way, Figure 4(c) corresponds to the samples of potassium ions in the presence of other potassium salts showing the R^2 value 0.9990. The percentage error in this case was found to be around 3-4% (better than potassium analysis) and can be seen in Figure 4(d). Moreover, it also doesn't show much more deviation at higher sodium concentrations. These values in tabular format are provided in supporting information in Table ST6.

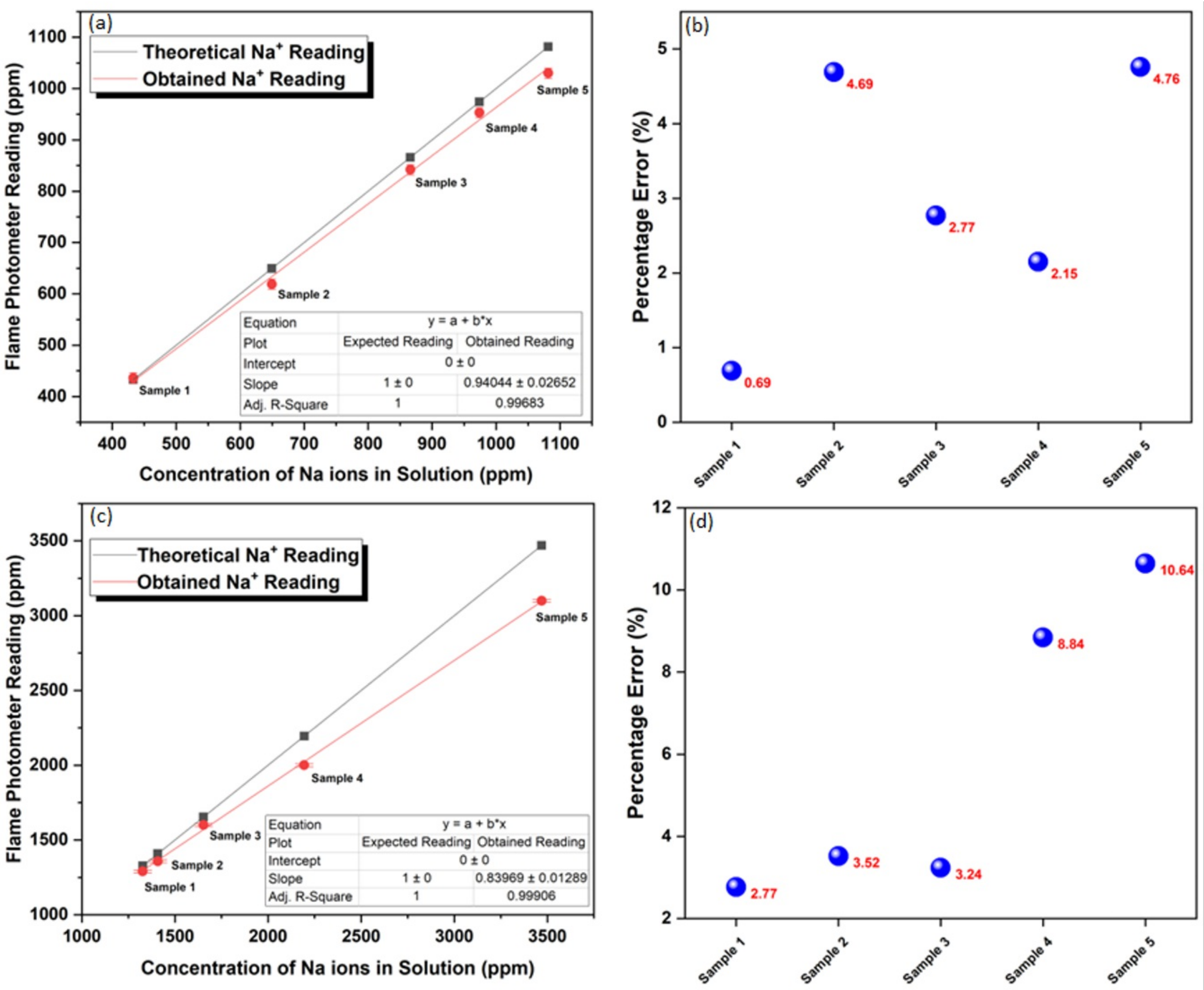

Figure 4. The curves depict the readings corresponding to (a) sodium ions in presence of other functional groups (b) error percentage of sodium ions in presence of other functional groups (c) sodium nitrate in presence of mixture of different sodium precursor salts (d) error percentage of sodium ions in presence of mixture of different sodium salts.

A study reported by Jesus et al.[30] using atomic absorption spectroscopy (AAS) mentioed precision ranges of 1.5 to 4 % for sodium and potassium. Another study by[31] employing inductively coupled plasma mass spectrometry (ICP-MS) achieved precision ranges of 12% and 8%, for sodium and potassium. By considering these reports, the precision of 3-4% for sodium and 7-8 % for potassium by flame photometry provides a better position comparable to the results of AAS and ICP-MS, especially by considering the fact of low-cost investment and ease of operation.

3.4. *Determination of potassium and sodium in the commercially sold firecrackers*

After validation of the process as discussed in sections 3.1 to 3.3., the analysis work was undertaken to determine the concentration of potassium and sodium in firecracker samples. Four different types of fireworks samples (approx. 1 g each) containing different compositions such as flower pots (sample 1), mini bullet (sample 2), ground chakkar (sample 3) and rocket bombs (sample 4) were collected from the local market of Nagpur, India. These samples have different potassium nitrate concentrations. The samples were analysed on flame photometry, and obtained results are provided in Figure 5(a). The data relating to these unknown firecracker samples containing potassium and sodium are also presented in supporting information in Table ST 7 (a & b) and ST8 (a & b), respectively.

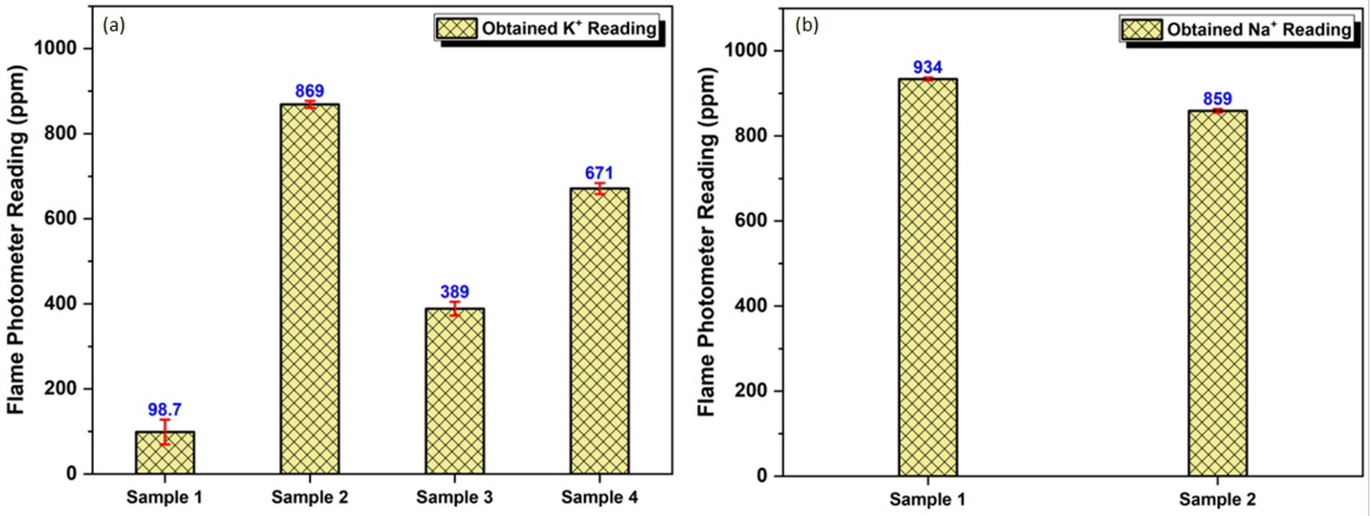

Figure 5. The bar graph depicts the unknown concentration of (a) potassium (b) sodium in a firecracker sample

The concentration of potassium and sodium obtained through flame photometry analysis was in ppm and same converted into percentages by employing the formula listed under section 2.4. The obtained concentration of potassium nitration was found to be 6.38, 52.39, 25.14 and 43.37 for fireworks like supreme giant flowerpot, Mini bullet, Ground Chakkar and Rocket bomb, respectively. The data pertaining to the expected and actual concentration of potassium ion and potassium nitrate is also provided in supporting information in Table ST7(b). According to Figure 5(a), the calculated concentration of potassium nitrate was found to be higher in mini bullets (sample 2) and least in flower pots (sample 1). Similarly, two samples namely classic electric (sample 1) and classic crackling sparklers (sample 2) were analysed for tracing the amount of sodium nitrate percentage, which showed slightly varied concentrations of 43.17% and 39.70% respectively. The data pertaining to the probable and obtained concentration of sodium ion and sodium nitrate is also provided in supporting information ST8(b).

3.5. Limitations of the Flame photometry

Although flame photometry is suitable for detecting alkali and alkaline earth metals, it has also limitations of limited sensitivity and provides higher variation results at higher concentrations. It detects one element at a time; the simultaneous detection of multiple elements is not possible with this technique. Further, one-time training is also required for the chemist to monitor the instrument and prepare fireworks samples.

3.6. Precautions for handling of fireworks samples

The explosive nature of fireworks may cause serious hazards to users. In this view the following precautions are recommended during handling and storage of fireworks - (i) use protective gear such as respiratory protection, fire-resistant clothing, safety goggles, and gloves, (ii) arrange fire hydrants and fire extinguisher near the site (iv) arrange evacuation map for emergency exist (iv) provide proper training for handling and storage of fireworks (v) store fireworks in a dry and cool environment (vi) use non-sparking tools and containers, (vii) don't place any flammable materials, chemicals and other hazardous substances (viii) electrical power supply equipment and connections should be removed other than light fittings and fire detection equipment's near fireworks.

4. Conclusion

The use of excess or adulterated or banned chemicals in fireworks is a major grave issue responsible for higher and more hazardous emissions in the environment. In this context, accurately determining their chemical component is essential to control the higher emission issues. The work was initiated to provide a valid method for the determination of alkali and alkaline earth metals in fireworks samples. This is achieved by deploying a simple and cost-effective flame photometry instrument. It uses a whole part of the sample, thus avoiding the homogeneity issue common in several other techniques in the first instant and delivering results with higher precision and accuracy. The instrument showed an average deviation of around 7-8% and 3-4% for potassium and sodium, respectively, when the concentration of the respective metal nitrates was less than 50%. In fireworks, the percentage contribution of these metal nitrates is generally less than 50%; hence, it can be easily deployed for the estimation of potassium and sodium salt in fireworks samples. Due to rising environmental and health concerns, fireworks industries are struggling with the judiciary and regulatory agencies across the world. The use of excess, adulterated or banned substances in fireworks is a major concern. In this direction, this work provides a simple and cost-effective approach to monitor the sodium and potassium ingredients in fireworks. Further work for the determination of other alkali and alkaline earth metals like Ba and Li in fireworks samples using flame photometry is in progress in our laboratory.

Statements and Declarations

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Conflicts of Interest

All authors declare that, they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethical Approval

All authors agreed with the content and gave explicit consent to submit the manuscript. The consent of our institute was obtained before the submitting manuscript to this journal (Reference No. KRC No.: CSIR-NEERI/KRC/2023/AUG/EMD/2).

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