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A Study of Wheat Flour Tortillas using Laser Induced Breakdown Spectroscopy (LIBS)

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ABSTRACT

Wheat flour tortillas of different colors and composition were studied with the aid of laser induced breakdown spectroscopy (LIBS). Due to its simplicity, fast response, little or no sample preparation, LIBS is presented as an effective tool for rapid in situ sample analysis of food samples with emphasis on tortillas. Spectroscopic analysis of the plasma generated by Nd:YAG laser irradiation of tortilla was carried out. A careful selection of spectral lines of Ca, Na and K which do not suffer from spectral interference was made. Spectral properties of the above mentioned elements such as peak intensities, intensity ratios, and area under spectral lines were analyzed. Optimization of laser pulse energy, detection gate width and gate delay for well resolved spectra with high signal-to-noise ratio was done and other parameters studied. Among the spectral lines selected for analysis, the Na I 589.00 and 589.60 nm doublet were found to show interesting properties. Tortillas manufactured by Gruma Corporation and Mexamerica, of brown, orange, green and white colors as well as homemade tortillas were studied in this work and the results from both dried and undried samples is presented.

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1. INTRODUCTION

Tortillas are widely used for consumption and also are major sale products for many manufacturing companies. Improving the quality of tortillas will be a boost not just for the companies but for the consumers as well.

Nutritional shortfall presents widespread occurrence affecting not only the less-developed nations but also the richer ones [1, 2]. Cereals are the major components of the human diet, providing 52% of the global caloric intake and a meaningful source of inorganic nutrients [3].

Wheat is an important food source and it is considered as one of the "big three" cereal crops, together with rice and maize [2]. Wheat grains have to be milled into flour prior to consumption. However, this industrial process may result in substantial losses of nutrients from the whole grain [3].

In this context, tortilla analysis is an important strategy to ascertain the quality of dough used and also when the overall diet does not supply the adequate levels of a specific element [3, 4].

In the case of wheat flour, the enrichment in vitamins B1 and B2, niacin, iron and calcium is a standard procedure in several countries. Reliable methods for micronutrient and elemental evaluation are important for establishing good food quality and safety needs, as well as its nutritional impact [3]. The control of minor element concentrations in food is necessary to evaluate sanitary risks. Several studies have shown a correlation between health problems and exposure to specific substances [5].

XRF (X-ray fluorescence) is a well-established technique allowing simultaneous, multi-elemental and non-destructive analysis. This technique has been used for the determination of inorganic nutrients in a variety of cereals such as rice [6-8], pearl millet [6], maize [8, 10], quinoa [11], and wheat [12, 13]. Direct analysis of wheat flour performed using energy dispersive X-ray fluorescence (EDXRF) system based on three-axial geometry was evaluated with secondary targets such as Al, Ti, Ge and Mo. Linear calibration curves were obtained for Na, Mg, Al, P, S, Cl, K, Ca, Mn, Fe, Cu, Zn, Br, Rb, Sr, Mo, and Cd with pellets of biological certified reference materials from National Institute of Standards and Technology (NIST), National Metrology Institute of Japan (NMIJ) and National Institute for Environmental Studies

(NIES). Accurate results were obtained for all above mentioned analytes [14].

LIBS is another attractive method, whose features and applications can be found in a comprehensive review form Hahn and Omenetto [15]. LIBS also enables the simultaneous determination of inorganic nutrients in food samples, and it has been used for evaluating the elemental composition of wheat grain tissues [16], for estimating the wheat grain tissue cohesion according to its ionization effectiveness [17], and for the analysis of rice powder, unpolished-rice flour and starch [18]. The quantitative determination of Ca in pellets of breakfast cereals was also carried out by LIBS In addition, LIBS can be used in association with EDXRF aiming at quality control of staple products such as wheat flours [20]. LIBS is used in this work because of its advantages over other methods which include the fact that it is experimentally simple, it has a very fast response with results being readily available immediately and it requires little or no sample preparation.

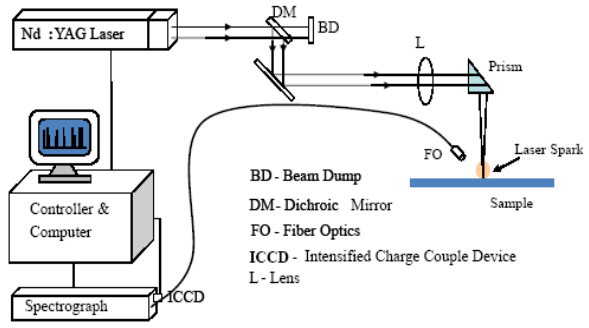
The present contribution is aimed at giving a better understanding of the behavior of three basic elements in tortilla under different experimental conditions, providing a much needed analysis on a food item that not much study has been done on with the use of LIBS and to show-case the fact that LIBS is an effective tool for analysis of food items and their quality.

2. Materials and Methods

2.1. Experimental setup

Fig.1 shows the experimental setup. A frequency doubled second harmonic Q-switched Nd:YAG laser (Quantel CFR400 20Hz, 7ns pulse width, 6mm diameter, 235mJ maximum) was used as excitation source. A portion of tortilla is cut in the form of glass slide and the sample is placed on a rotating platform to ensure that the laser hits on fresh spot. Laser is focused onto the sample surface through a 30cm focal length quartz lens and a right angle prism. Spectra were collected with an Andor (Mechelle ME5000) broadband spectrometer (200–975 nm spectral range) through a 100 µm diameter optical fiber equipped with a pickup lens (Ocean Optics Inc. (OOI) Part No.74-UV). The latter was placed 5cm away from sample and 45^0 with respect to the beam axis. Andor Solis software was used for acquisition setup. The spectrograph was connected to a personal computer for data acquisition. The acquisition gate width was set to 5µs and gate delay optimized to 2µs while the pulse energy was set to 68mJ.

Fig1. LIBS experimental set up



2.2. Sample preparation

The tortilla is cut in pieces similar to size of slide length, width and thickness.

Initially, tortilla of various composition is bought from the shop. The tortilla are placed in different categories in accordance with their colors.

Homemade tortillas were made using great value tortilla mix. Half cup of warm water is mixed with two cups of great value tortilla mix. We preheat griddle to 400-425°F. Warm water is added to tortilla mix in a large bowl and mixed well. We knead for about five minutes until dough is smooth and elastic. If dough appears sticky, we add more mix. Dough is covered with a damp cloth and let to rest for fifteen minutes. Dough is divided into eight portions and rolled out on a lightly floured surface to 1/8 inch thickness. It is cooked for one and the half minutes on each side until lightly browned. Homemade tortillas nutrients are shown in table 2.

Table1 Tortilla manufactured by Gruma Corporation/Mexamerica, of different colors. Nutrients as indicated on the product package for different types of Tortilla.

Type	Nutrients	Calories/g	%Daily Value
Brown	Total Fat	< 80	3
	Saturated fat	< 25	3
	Cholesterol	< 0.30	0
	Sodium	< 2.4	13
	Calcium	< 2.5	15
	Total	375	8
	Carbohydrate		
	Dietary Fiber	30	16
White	Total Fat	< 80	5
	Saturated fat	< 25	3
	Cholesterol	< 0.30	0
	Sodium	< 2.4	18
	Calcium	< 2.5	8
	Total	375	8
	Carbohydrate		
	Dietary Fiber	30	4
Green	Total Fat	< 80	5
	Saturated fat	< 25	3
	Cholesterol	< 0.30	0
	Sodium	< 2.4	18
	Calcium	< 2.5	2
	Total Carbohydrate	375	9
	Dietary Fiber	30	4
Orange	Total Fat	< 80	5
	Saturated fat	< 25	3
	Cholesterol	< 0.30	0
	Sodium	< 2.4	18
	Calcium	< 2.5	2
	Total Carbohydrate	375	9
	Dietary Fiber	30	4

Table2 Great Value Flour Tortilla mix used to make homemade tortillas. Nutrients as indicated on the product package distributed by Wal-Mart Stores, Inc., Bentonville, AR 72716©2001.

Nutrients	Calories/g	% Daily Value
Total Fat	< 65	12
Saturated fat	< 20	19
Cholesterol	< 0.30	0
Sodium	< 2.4	20
Potassium	3.5	1
Total Carbohydrate	300	10
Dietary Fiber	25	0

3. Theoretical Background

LIBS is based on atomic emission. When a high power laser pulse is focused onto a material target (solid, liquid, gas and aerosols), the intensity in the focal spot produces rapid local heating and intense evaporation followed by plasma formation. The interaction between a laser beam and a solid is dependent on many characteristics of both the laser and the solid material. Various factors affect ablation of material, which includes the laser pulse width, its spatial and temporal fluctuations as well as its power fluctuations. The plasma expands normal to the target surface at a supersonic speed in vacuum or in the ambient gas. The hot expanding plasma interacts with the surrounding gas by two mechanisms (i) the expansion of high pressure plasma compresses the surrounding gas and drives a shock wave, (ii) during this expansion, energy is transferred to ambient gas by the combination of thermal conduction, radiative transfer and heating by shock wave. Light emitted as a result of gaseous discharge is examined by a spectrometer and found to form a spectrum of discrete lines, bands and sometimes an overlying continuum. Discrete lines (and sometimes accompanying continuum) are characteristic features of emission from neutral atoms and ions in the discharge source. The spectral lines are characterized by three properties: wavelength, intensity and shape. These properties are dependent on the structure as well as the environment of the emitting atoms [21].

Cabalin and Laserna investigated the effect of laser wavelength on the plasma initiation threshold on metal samples using infrared (1064 nm), visible (532 nm), and ultraviolet (266 nm) regions. It was found that laser wavelength plays an important role in the plasma initiation threshold, and a shorter laser wavelength improved the mass ablation process of metals [22].

Magnetic et al. investigated the effect of laser pulse duration using 6 ns and 170 fs laser pulses on brass samples in argon shield gas. It was found that more reproducible data was obtained with the fs-laser pulse than with the ns-laser pulse [23]. Gondal et al. investigated the effect of laser pulse energy on signal intensity. It was found that signal intensity linearly increased when laser pulse energy increased from 10 mJ to 30 mJ [24].

The LIBS emission spectra consists of both continuum and line radiation. Due to the presence of continuum radiation at the very beginning, the detection of emission lines from the laser-induced plasma is far from the satisfactory. The technological advancements of charge-coupled device (CCD) and intensified charge-coupled device (ICCD) detectors make time-resolved LIBS measurements. Gate delay (td) means time delay between plasma formation and the start of the observation of the plasma light. Gate width (tw) means time period over which the plasma light is recorded [25]. The td and tw are controlled by using a time-resolved detection system in such a way that the continuum emission from the plasma can be gated off and enhancement of signal can be achieved drastically. Wisbrun et al. investigated the effect of td, tw and repetition rate on signal intensity and sample-to-noise ratio (SNR) using soil and sand samples. The results concluded that the td and tw were element-dependent; however a common condition could be found [26]. They also found that the optimum repetition rate for soils was 1 Hz, and td was more significant than tw in controlling the LIBS signal intensity and stability. Eppler et al. investigated the effect of tw on signal intensity. It was found that tw longer than 50μs was unnecessary because most of the analytical emission lines had completely decayed [27].

4. Results and discussion

Brown, Orange, Green and White Tortillas are cut in sizes comparable to that of a slide (25x75x1.0mm) using a pen knife and a pair of scissors. Laser is focused on the tiny slices as it would have been the case of powder samples on the double sided tape of a glass slide. The spectra that result are then analyzed.

First of all, we identified the elements of interest in our tortillas (i.e. Calcium, Sodium and Potassium) with the help of NIST (National Institute of Standards and Technology) spectroscopic data base. Peaks resulting from the spectra showed strong lines of Calcium at 393.37nm, 396.85nm and 854.21nm (CaII(1), CaII(2) and CaII(3) respectively). Strong lines of Sodium were found at 589.00nm, 589.60nm, and 819.7nm (NaI(1), NaI(2) and NaI(3) respectively). Potassium strong lines at 766.49nm and 769.90nm were also found.

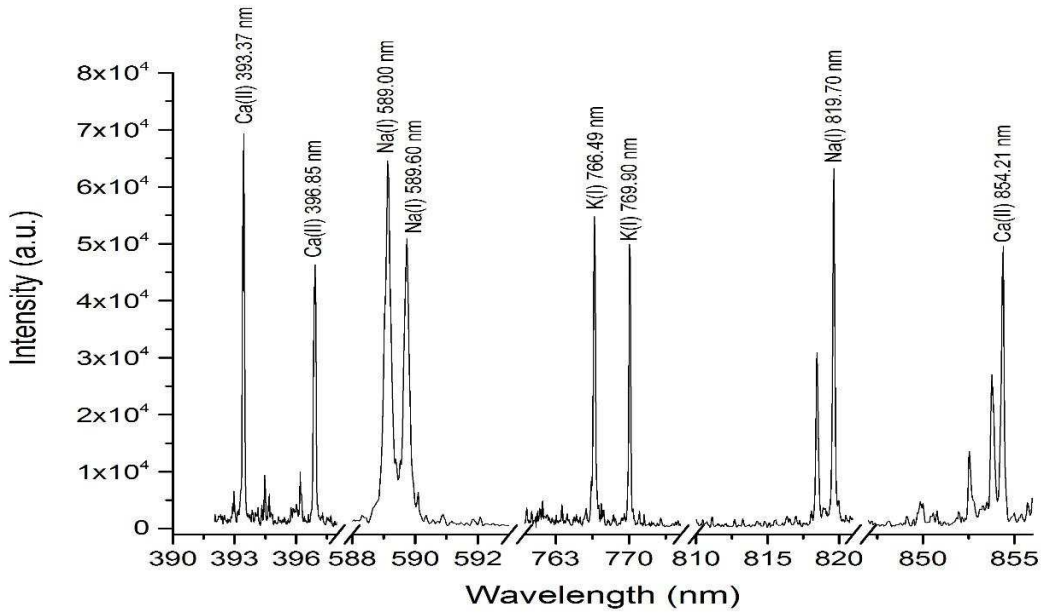


Fig.2.0 Spectra showing strong lines of Interest for Ca, Na and K.

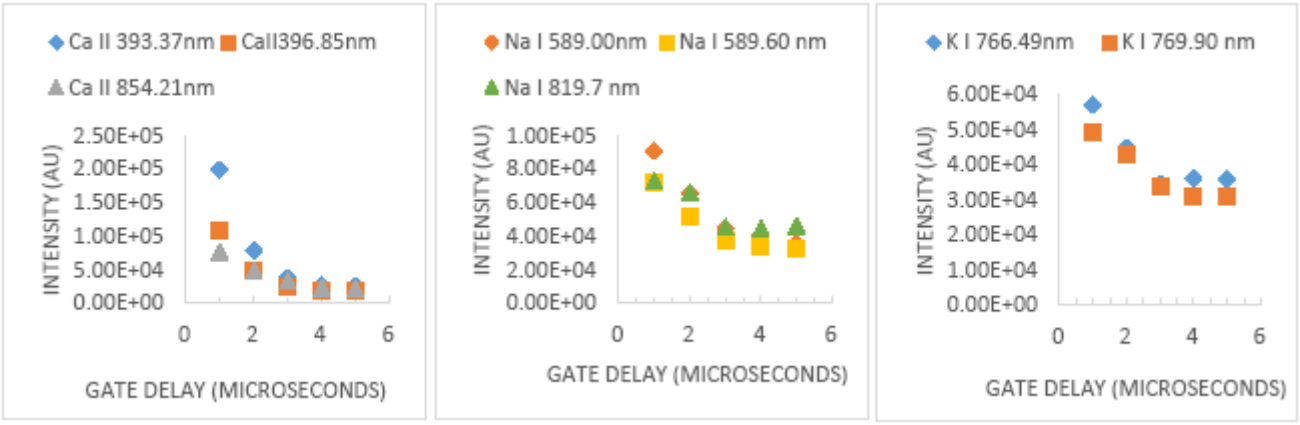


Fig.2.1 Variation of peak intensity versus gate delay for brown tortilla

The variation of peak intensity with gate delay for brown tortilla is presented and showed a similar pattern for all the elements of interest i.e. decreasing peak intensity values with increasing gate delays. It is worth noting, that the same result is obtained for the orange, green and white tortillas as shown in Figure.2.1

We know that the laser keeps giving continuous pulses once we turn it on, but the detector takes a time called the gate delay time before it starts collecting the signals and it lasts for a period called the gate width.

These results indicate better intensity at smaller gate delay. Nevertheless, the optimized value is obtained by selecting the gate delay with the highest signal-to-noise ratio.

A qualitative comparison was then made of the variation of peak intensity with gate delay and the variation of area under curves with gate delay, to see the trend between the above mentioned four types of tortilla. The following was obtained for two of the strong lines of calcium. It is also worth noting the same pattern is observed when a plot is made for sodium and potassium lines.

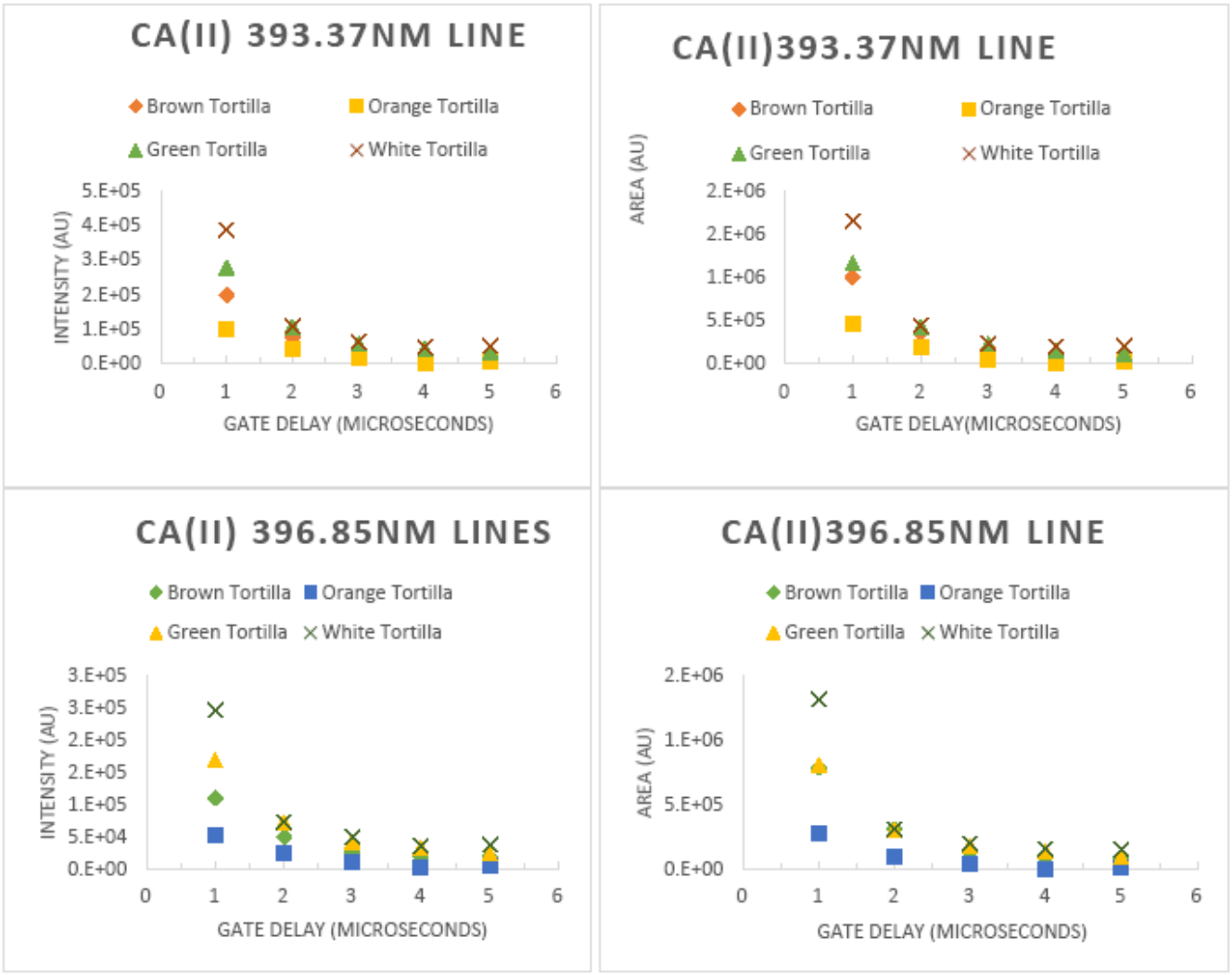


Fig.3 Variation of intensity and area under curve with gate delay for Calcium lines

Figure 3 reveals that the peak intensity and area under curve follow the same pattern and in all cases, the orange tortilla always has lower intensities compared with the other tortillas. This could be attributed to the contents of this tortilla and its nutritional composition indicated in table1. This, suggests that the concentration of the above mentioned elements were smaller in the orange tortilla than all the other tortillas.

The same comparison was made for sodium and potassium lines with the same results obtained.

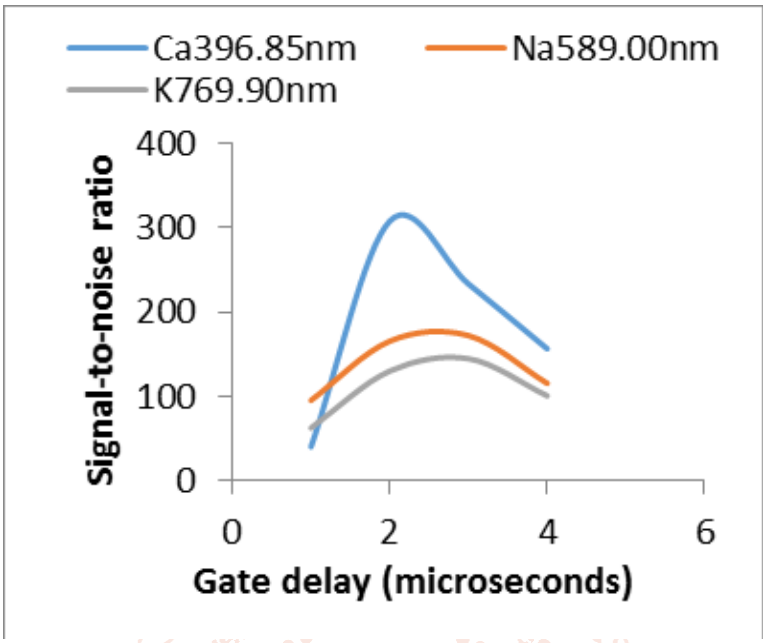


Fig.4 Signal-to-noise ratio for three lines of Na, Ca and K

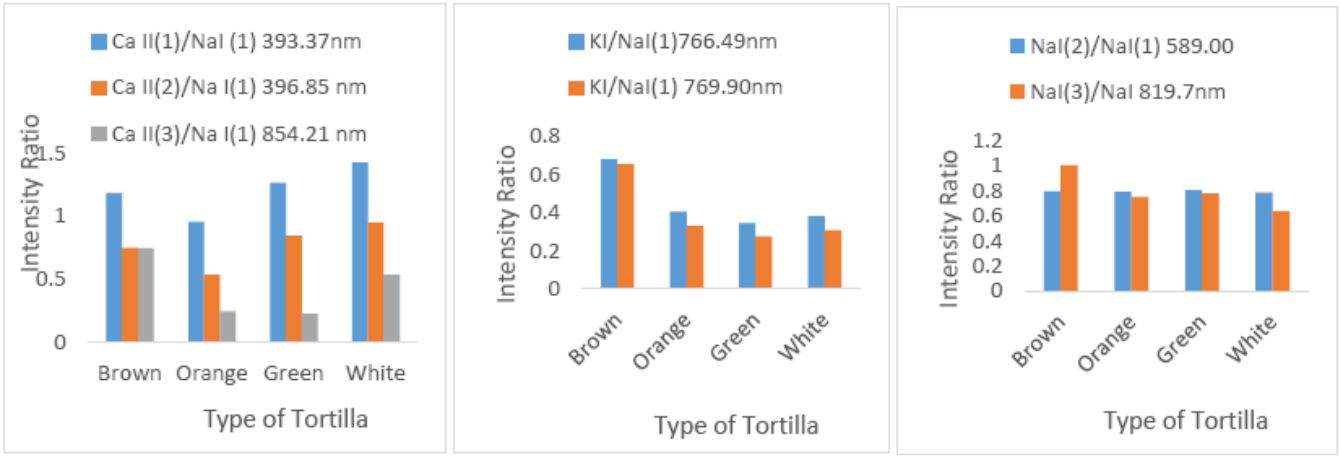


Fig. 5.1 Intensity ratios with respect to Na (I) 589.00nm line (NaI (1)).

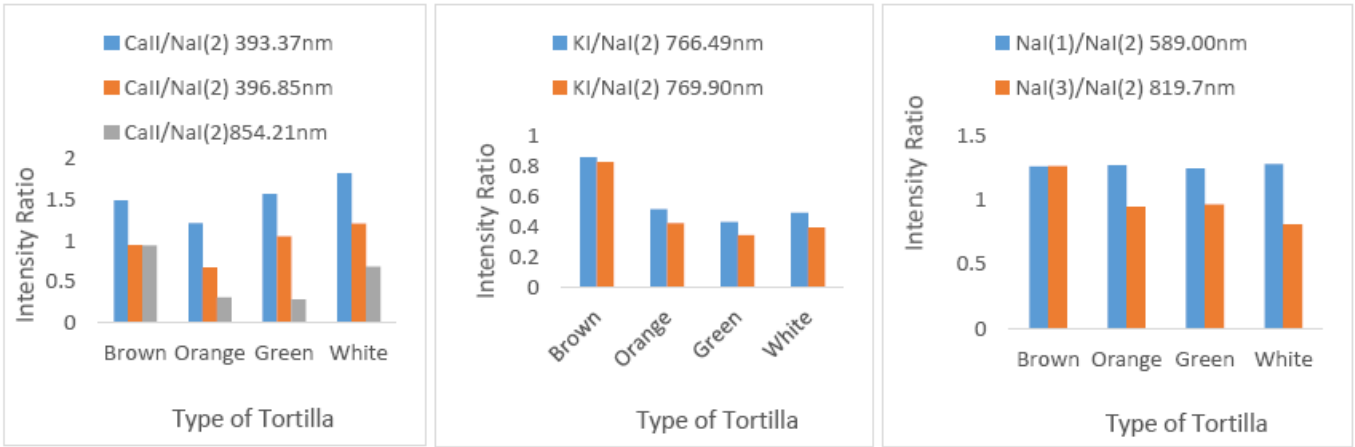


Fig. 5.2 Intensity ratios with respect to Na (I) 589.60nm (NaI (2))

The three lines used in figure 4 are among our lines of interest for the three different elements studied and confirm that a gate delay of 2μs would be suitable for measurements. After optimizing the gate delay to 2μs and doing all other measurements at this gate delay, gate width of 5μs, accumulation of 10 spectra and energy of 68 mJ, the following intensity ratios were obtained.

However, we proceed to do intensity ratio analysis, which is more reliable and not subject to change if good analyte lines are used, to confirm or double check before making conclusions about concentration levels between the various types of tortilla. Therefore, different combinations of ratios among these intensity values were evaluated in order to find those which could be used for comparison purposes. Using 8 peaks, 22 different ratio combinations were evaluated as shown in figures 5.1, 5.2 and 5.3. Figure 5.1 reveals easier detection of Ca(II) 393.37 nm lines, followed by Ca(II)396.85 nm lines and Ca(II)854.21 nm having the lowest ratio for all tortillas. Detection of K(I) 766.49 nm lines would also be higher than for K(I) 769.90 nm line. The Na(I)589.60 nm line had same intensity ratio for all tortillas when Na(I)589.00nm line was used as its divisor. Na(I)589.00nm line also had the same intensity ratio for all four types of tortilla when Na(I)589.60nm line was used as its divisor. This result (see Fig.5.1 and 5.2), confirms that sodium doublet lines are in the same plasma condition as we would expect. Na(I) 819.7 nm line divided by both sodium doublet lines showed several variations in its ratios as shown in Fig.5.1 and 5.2 indicating that it is not a good analyte line for intensity ratio analysis. It shows slightly higher intensity ratios for brown tortilla and slightly lower intensities for white tortilla meanwhile they should be at the same plasma conditions when considering all Na lines present. Na(I) 819.7nm is therefore discarded . Figure 5.2 is very much like a snapshot of Fig.5.1. This reveals that the doublet lines are good analyte lines, whose ratios confirm the same results for calcium and potassium lines, as explained above.

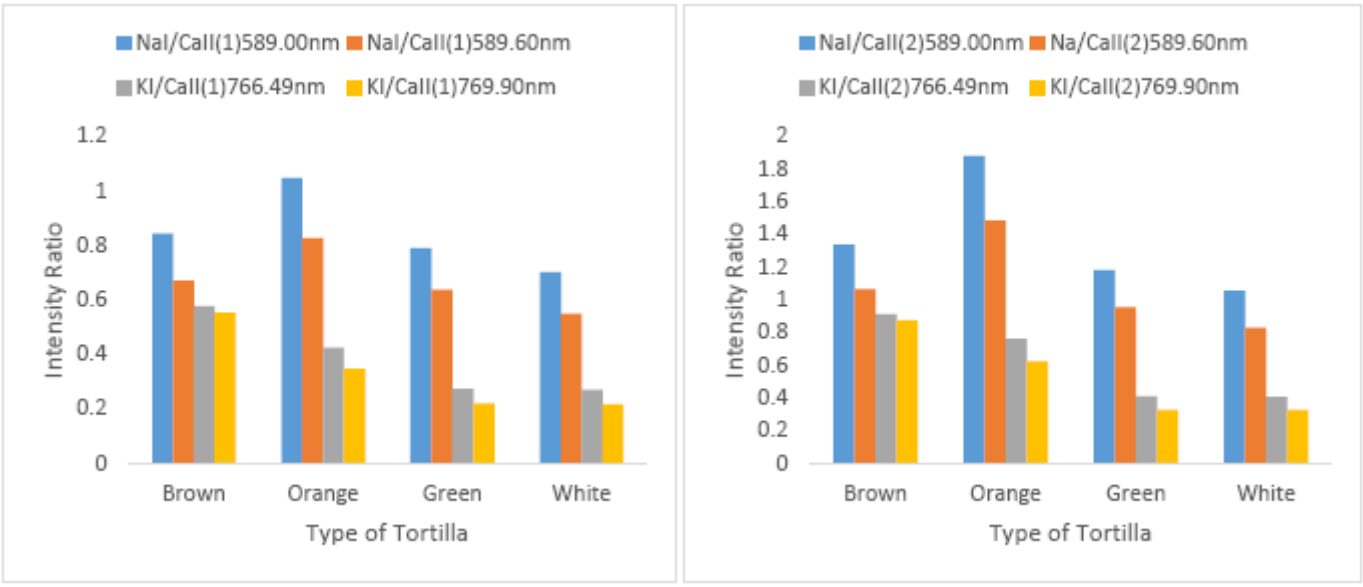


Fig 5.3 Intensity ratios of Na and K with respect to CaII 393.37nm (CaII(1)) and CaII396.85nm (CaII(2)) lines respectively.

Figure 5.3 reveals that CaII393.37nm and CaII396.85nm lines gave the same results when used as divisors for Na and K Intensity lines respectively. They are also good analyte lines for Intensity ratio measurements. In figure 5.2, the intensity ratio for Na(I)589.00nm:Na(I)589.60nm pair was greater than Na(I)589.60nm: Na(I)589.00nm pair. In figure 5.3, the intensity ratio for Na(I)589.00nm with respect to calcium lines is also greater than that for Na(I)589.60nm, this indicates that Na(I)589.00nm line is easier to detect and has higher intensity than Na(I)589.60nm line. This result can be confirmed from the spectra in figure 2.

Figure 5.3 also reveals that intensity ratio of Na:Ca pairs are greater than that of K:Ca pairs for all tortillas. The high presence of Na can be attributed to the use of many salt rich ingredients in making of tortillas which has relatively high percentage daily value as shown in table 1. Percent daily values in table1 are based on a 2500 calorie diet while those of table 2 are based on a 2000 calorie diet as indicated on the package labels. Our result is of great importance for testing of food samples whose package labels need verification and the LIBS method having so many advantages including quicker results will be a suitable method to apply when results are needed immediately and without much sample preparation. This result can also be used to differentiate the various types of tortillas not just by their color but according to the concentration levels of the different elements of interest. However, further attempts to improve reproducibility of spectra collected from tortillas and subsequently intensity ratios evaluated are essential. Hence, an attempt to reduce this error may provide better and more robust ratio analysis results. Several factors could be responsible for poor reproducibility of LIB signals observed in tortilla. These factors may include laser parameters and target sample properties [21]. Temporal and spatial energy fluctuations of pulses may affect the process. Additionally, sample surface topology and density can affect plasma formation, which in turn affects the LIBS signals [21].

Homemade tortillas were made from the Great Value Flour Tortilla mix as indicated in the sample preparation and allowed to dry for several days.

Tortilla allowed to dry for five days and data collected for each day consecutively showed that when tortilla is less moist, it is easier for the laser pulses to form plasma which results in higher intensity for higher days of drying as shown in fig.6. Any discrepancies would be attributed to matrix effect as a result of homemade tortillas not as smooth on the surface and exact in thickness as that manufactured by Gruma Corporation and Mexamerica.

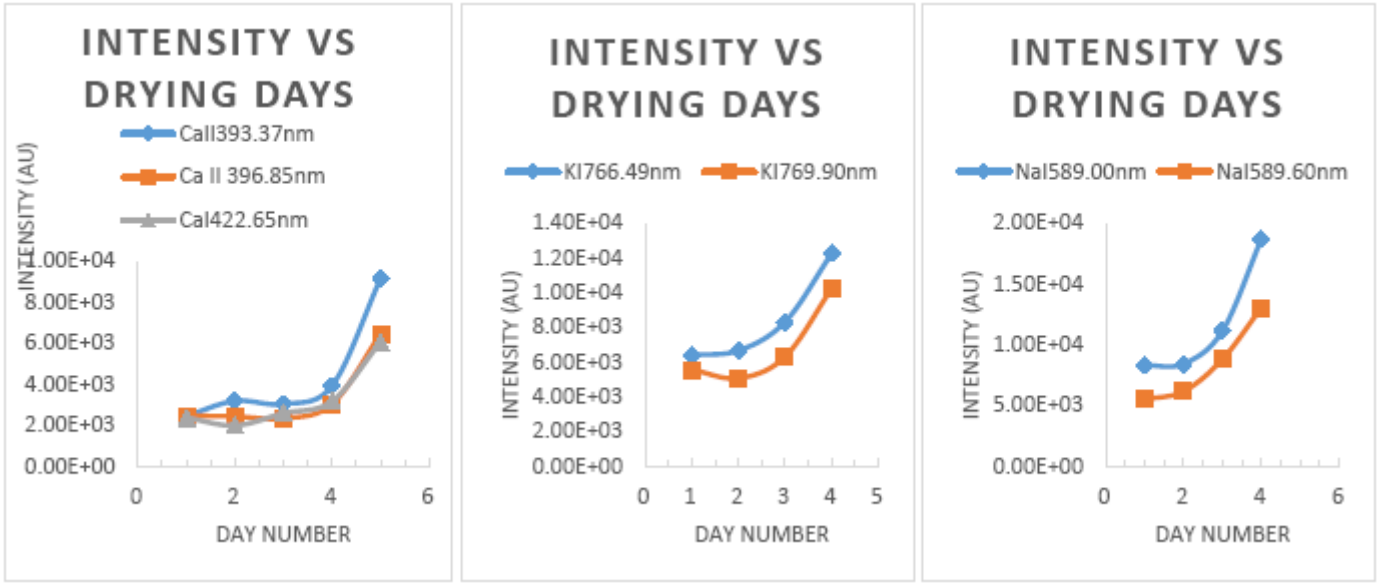


Figure6 Peak Intensity variation with respect to days of drying of homemade tortillas

5. Conclusions

Ca, Na and K were found in all the tortillas. The peak intensities and area under curves variation with gate delay showed a decreasing pattern with increasing gate delay as would be expected. The intensity ratios showed similar patterns for plasmas in similar conditions. There was an increase in peak intensities with increasing days of drying homemade tortillas. Matrix effect played a minute role due to homemade tortillas not having evenly smoothened surface as tortillas from Gruma Corporation and Mexamerica. The choice of analyte lines is also of great importance as shown in the intensity ratio analysis. The analyte lines used were, the sodium doublet lines (Na (I) 589.00 nm and Na (I) 589.60 nm lines), Ca 343.37 nm and Ca (II) 396.85nmlines. The results of ratio analysis of the intensity of atomic emissions provide a sizable range of ratio values for differentiating the various types of tortillas. Due to a growing interest LIBS is receiving for its potential in biomedical, environmental, industrial and space applications, the results obtained buttress the fact that LIBS is an effective tool for in situ analysis and quality control of food samples with little or no sample preparation. However, further studies need to be performed to study its applicability on larger amounts of other food samples, apart from tortilla. Also, by doping the tortilla intentionally with heavy toxic elements we can verify the fact that there are no toxic elements in the tortilla samples by comparing the spectra of doped samples with that of the undoped samples with the intent of identifying peaks which differ and with the help of the NIST data base, we can confirm that there are no toxic elements. We believe, this is a fertile area to develop from this work, not just for tortillas but for other food samples as well.

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