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Qualitative elemental analysis of farm animals' milk adopting laser spectroscopic technique

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ABSTRACT

Information about the elements in milk represents a major tool to identify different milk types and their quality. This is because milk constituents of minerals, proteins and fats differ by different mammals and even for different breeds. In the present work, fresh samples of widely consumed farm animals' milk, namely from buffaloes, camels, sheep and goats were analyzed qualitatively using laser induced breakdown spectroscopy (LIBS) technique. It was focused on calcium, magnesium, iron, sodium, strontium and barium. Molecular bands of CN in the LIBS spectra were used to study the proteins levels in different milk samples. The results revealed that milk samples from different animals could be characterized as completely different combination of the elements constituents were present in magnesium and iron were higher in goat milk compared to the other animals; in addition, the percentage of barium relative to calcium was lower in all milk samples which confirm plant feeding for all studied animals. In general, this work demonstrates the feasibility of using LIBS as a simple, fast and cost effective technique to perform in situ qualitative analysis of milk samples in dairy farms without any need to transport samples to the laboratories.

Key words: Elements, Farm animals, Milk, LIBS, Protein

Milk and dairy products contain many essential nutrients and their regular consumption is recommended, especially for young children. It is of both nutritional and hygienic importance to have detailed and accurate information about the elemental composition of milk. Atomic absorption spectroscopy (AAS) was applied to address these problems. Navarro-Alarcón *et al*. (2011) determined selenium (Se), zinc (Zn), magnesium (Mg) and calcium (Ca) levels in fermented milk from goats and cattle. Rahimi (2013) studied lead (Pb) and cadmium (Cd) concentration in milk of goats, bovines, sheep and buffaloes from different regions of Iran.These methods often require laboratory- scale equipment and sophisticated sample treatment protocols. LIBS has now emerged as a powerful analytical technique for direct spectrochmical analysis of a variety of solids, liquids and gases with no or little sample pretreatment. In the present study, LIBS as a simple and straight forward elemental analysis technique was used for the characterization of the elemental and molecular composition of milk samples from buffalo, sheep, goat and camel.

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MATERIALS AND METHODS

Samples collection: Samples (5) of milk (5ml) from every species namely, Egyptian buffalo *(Bubalus bubalis)*, camel *(Camelus dromedaries),*goat *(Capra aegagrus hircus)* and sheep *(Ovis aries)* were collected from different animals. Samples were directly transported in cold conditions (4 °C) from the farm to the laboratory for analysis.

Milk samples for LIBS analysis: Droplets of milk samples (0.5 mL/droplet) were taken on to ashless filter paper, the samples are left for about 15 min in clean air atmosphere to guarantee that the milk has been homogeneously expanded and absorbed in the filter paper before further LIBS analysis.

LIBS arrangement: A typical LIBS experimental setup (Fig. 1) was used in the present work. The used laser source is a Q-switched Nd:YAG laser, operating at the fundamental wavelength (ë=1064 nm), with a pulse duration of 5 ns. The laser pulse energy was set to 50 mJ and the repetition rate to 1Hz. The laser beam was tightly focused onto the sample surface using a 10 cm focal length planoconvex quartz lens. The target was mounted on an X-Y micrometric translation stage. To optimize the signal-to-noise ratio and guarantee results reproducibility LIBS spectra were collected from three fresh spots of the same seminal plasma sample, spectra of 5 consecutive shots were recorded for

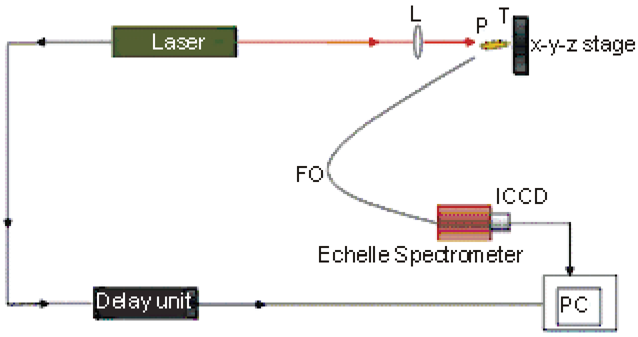

Fig.1. Block diagram of the experimental setup of the LIBS system. L is the focusing lens, T is the target, P is the laser induced plasma plume, and FO is the optical fiber.

each spot. The plasma optical emission was collected by a fused-silica optical fiber with diameter of 600 mm held at a distance of 2 cm above the laser induced plasma at an angle of 30° with respect to the target surface. The collected plasma emission is then fed via the optical fiber to the entrance slit of an echelle spectrometer. Camera coupled to the spectrometer, was used for the detection of the dispersed light. Spectra display, processing and analysis were performed using the commercial 2D- and 3D- Gram/32, software programs.

RESULTS AND DISCUSSION

Data concerning the elemental contents of farm animals' milk is shown in Fig. 2. The presented typical LIBS spectrum extending from 200 nm up to 600 nm where the insets show zoomed segments of Ca, Sr and Ba spectral lines for illustration.

The composition of farm animals' milk has been thoroughly studied in the published literature during the last decade (Khan *et al.* 2006, and Navarro-Alarcón*et al.* 2011).

The intensities of some elements of nutritional importance in milk samples, namely magnesium (Mg), iron (Fe), strontium (Sr), calcium (Ca), barium (Ba), and sodium (Na) normalized with respect to that of the corresponding

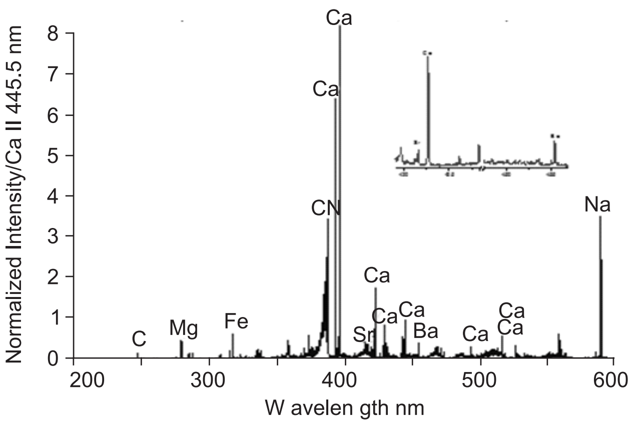

Fig. 2. Typical LIBS spectrum of farm animal's milk. The inset shows zoomed parts of Sr, Ca and Ba spectral lines.

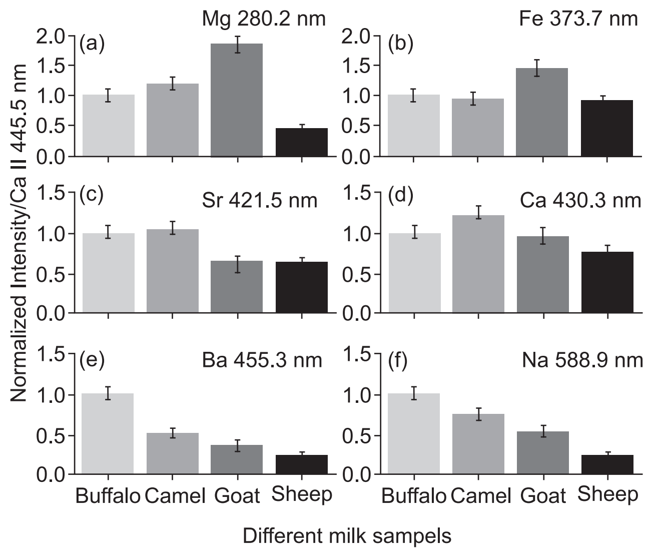

Fig. 3. Mg, Fe, Sr, Ca, Ba and Na spectral emission lines in the LIBS spectra of different farm animals' milk.

spectral lines in buffalo milk are presented in Fig. 3. The intensities of both Mg and Fe spectral lines are higher in goat than that of other animals (Figs 3a and b). The levels of Mg and Fe in goat milk ash were significantly higher ($P < 0.05$) than those in the cow milk ash (Ceballos *et al.* 2009). However, as far as minor and trace elements are concerned, concentrations are highly variable according to studies and sampling (feeding, geographic areas, pollution, etc.) and therefore it is difficult to compare species and breeds. Febio availability is higher in goat milk than in bovine milk due to higher nucleotide content contributing to better absorption in gut (Cullugh 2003).

The spectral lines relative intensities of Ca and Sr elements in milk of camel are higher than that in buffaloes, goats and sheep (Fig. 3c,d). However, Ba and Na spectral lines normalized intensities are the highest in buffalo milk (Fig.3 e and f). In particular, Sr and by analogy Ba are used as indicators for varying diets. Reconstruction of nutrition is based on the process of physiological bio-purification of calcium in food chains by discriminating against strontium and barium. Strontium is just below calcium in the periodic table sharing many of its chemical properties, and therefore it can partially replace calcium in the metabolic processes in plants and animals. In general, plants do not discriminate between calcium and strontium, so the proportion of each of these two elements in plants reflects its proportion in their environment. It is well established that mammals have the ability to discriminate against strontium in favour of calcium.The discrimination against the absorption of barium is even stronger than that against strontium. LIBS measurements of Sr and Ba (Fig. 4) with respect to Ca reflect lower levels of strontium and barium for all farm animals' milk samples. These results are expected since all milk samples are obtained from herbivores.

LIBS is essentially a well-established elemental analysis technique. However, it is possible to make use of LIBS spectra of organic materials to follow up some molecules

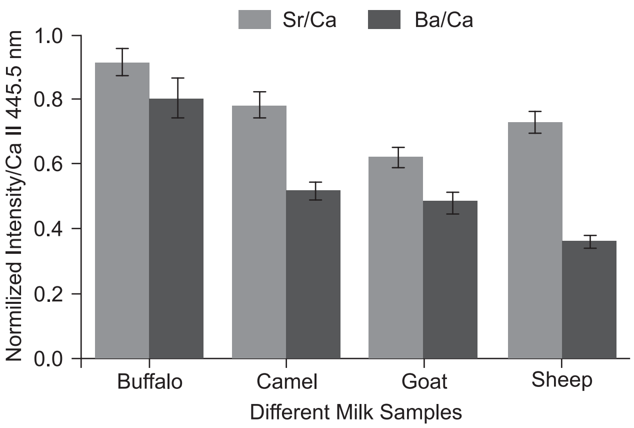

Fig. 4. Barium and strontium spectral line intensities relative to calcium in different milk samples. The error bars represent the standard deviation of the experimental data of each anim.

through the presence of their molecular emission bands such as CN, C_2 and OH (Fortes *et al*. 2010, Elnashartyet *al*. 2011, Kasem *et al*. 2011).

The superimposed laser induced breakdown spectra (Fig. 5a) depicted the CN molecular bands in UV spectral region of milk samples from different animals. Such molecular bonds are representative of the organic material, including proteins and fats in the milk. The high intensity of CN band in camel's milk indicated its high proteins content, mainly caseins, compared to all other types of the studied farm animals' milk (Fig. 5a). Milk proteins, particularly caseins, have an appropriate amino acid composition of high nutritional importance. The caseins comprise the major protein component of milk of most mammals and represent family of phosphoproteins synthesized in the mammary gland in response to lactogenic hormones and other stimuli and secreted as large colloidal aggregates termed micelles, which are responsible for many of the unique physical properties of milk (Abdel Salam *et al*. 2013). Therefore, it is possible to evaluate proteins in milk samples qualitatively through CN band intensity in the relevant LIBS spectra. Casein which is the major milk protein is bound to calcium, this relation between calcium and casein is shown in Fig. 5 b which demonstrates the proportionality between the CN intensity and that of calcium at 387.07 nm and 430.36 nm respectively.

The camel milk showed both higher contents of both calcium and proteins (represented by CN bands) relative to other milk samples of the other investigated farm animals. However, camel milk is an important source of proteins for the people living in the arid lands of the world as mentioned before. Also, camel milk is known for its medicinal properties, which are widely exploited for human health, as in several countries (Kenzhebulatet *al*. 2000, Mal *et al*. 2006). Camel milk is considered to have anti-cancer (Magjeed 2005), hypo-allergic (Shabo *et al*. 2005) and anti-diabetic properties (Agrawal *et al*. 2003). A high content in unsaturated fatty acids contributes to its overall dietary quality (Karray *et al*. 2005, Konuspayeva *et al*. 2008).

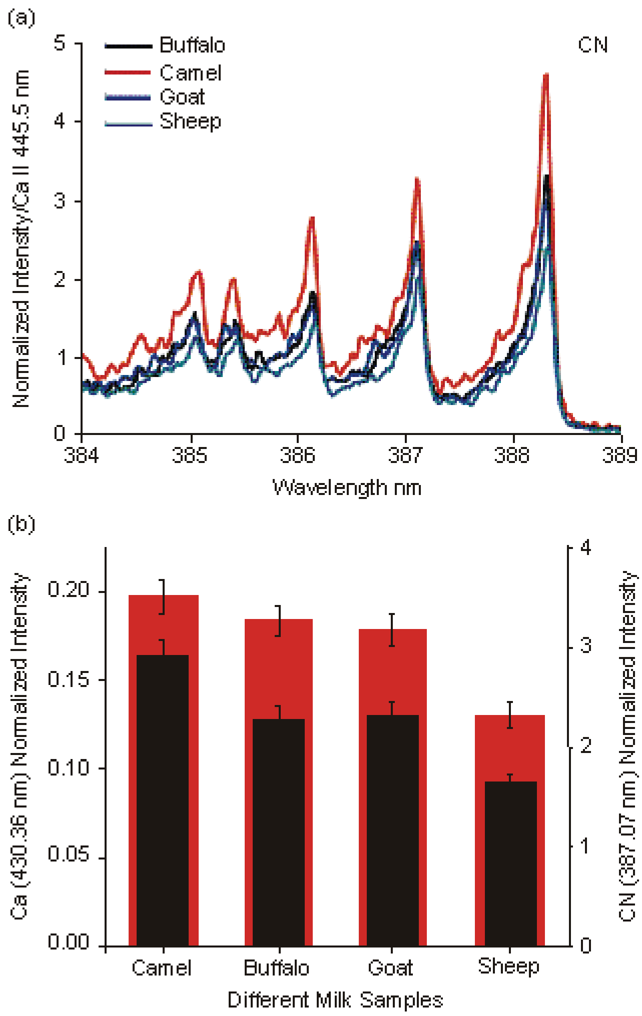

Fig. 5 b. Trends of summation of the normalized intensities for CN and Ca spectral lines for different samples of farm animals' milk. The error bars represent the standard deviation of the experimental data of each grop.

In conclusion, compared with other previously published works in the same field, the present study adopted LIBS as a non-invasive, quasi-nondestructive, fast and possibly *in situ* elemental analysis technique to estimate magnesium, iron, strontium, barium, calcium and sodium of milk from selected farm animals. The discrepancy between the relative concentrations of different elements in the studied milk samples is mainly due to the species itself.This study demonstrated the feasibility of using LIBS in farms directly to evaluate the milk qualitatively instead of performing that via the conventional complicated laboratory techniques.

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