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# Detection of Toxic Metals in Waste Water from Dairy Products Plant Using Laser Induced Breakdown Spectroscopy

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**Abstract** Laser Induced Breakdown Spectroscopy (LIBS) System was developed locally for determination of toxic metals in liquid samples and the system was tested for analysis of waste water collected from dairy products processing plant. The plasma was generated by focusing a pulsed Nd: YAG laser at 1064 nm on waste water samples. Optimal experimental conditions were evaluated for improving the sensitivity of our LIBS system through parametric dependence investigations. The Laser-Induced Breakdown Spectroscopy (LIBS) results were then compared with the results obtained using standard analytical technique such as Inductively Coupled Plasma Emission Spectroscopy (ICP). The evaluation of the potential and capabilities of LIBS as a rapid tool for liquid sample analysis are discussed in brief.

**Keywords** Laser-induced breakdown spectroscopy (LIBS) · Multi-elemental analysis · Laser diagnostics · Waste water analysis · Atomic emission plasma spectroscopy · Environmental challenges · Environmental impacts of trace metals · Trace metals detection · LIBS applications

In the dairy product industry, there is a need for an analytical technique to be able for on line measurements of heavy metals and other trace elements in waste water coming from different processes involved. The amount of waste water generated by dairy industrial plant is of huge amount and it can have hazardous effects on environment. Most of the dairy plants produce pasteurized milk, cream, buttermilk, chocolate milk, ice cream mix, and fruit juice drinks. During the manufacturing process of dairy products, raw milk processing is one of the important process. Here raw milk is pumped to centrifuge clarifier where undesirable solids in the milk are removed and the waste from the clarifier is collected and can be reused as fertilizer. In pasteurized milk processing, waste water is disposed of to the municipal sewerage system. During the washing process, milk remaining in the presses could be contaminated with the chemicals used for the processing and detergents used for cleaning. This contaminated milk is also disposed of in the municipal sewerage system. Similarly, the skim milk from storage tank is pumped to a processing tank. In the processing tank, the milk is steam-heated to 186°F for 30 min and steam condensate is disposed of also in the municipal sewerage system. Due the above mentioned dairy products processing, numerous heavy metals are released which become the part of the sewerage system. This has resulted contamination of soil, ground water and surface water (US EPA 1992). The dairy product waste water has caused serious health and environmental problems. In addition, dairy plant can be a significant source of phosphorus released to waste water, although phosphorus is a nutrient for plant growth, but excess phosphorus can speed up the aging process of lakes and streams by stimulating algae growth. This creates high biochemical oxygen demand (BOD) as algae decomposes and eat up available oxygen supplies, and is also a threat to the survival of fish and other aquatic organisms. Due to these environmental problems, the characterization of dairy

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products waste water for rapid detection of these hazardous metals is highly significant.

We tested our LIBS spectrometer for the analysis of waste water from dairy product plant. The waste water samples tested in this study were collected from local plant in the city of Dammam in Saudi Arabia. In Laser Induced Breakdown Spectroscopy (LIBS), a plasma spark is created by focusing the high energy laser beam at the surface of the water and spectrally resolved (Winefordner et al. 2000; Radziemski et al. 1989; Evans et al. 2004) emissions are recorded with spectrometer having reasonable resolution (0.1 nm) to identify the elements present in waste water sample. This analytical technique enables the determination of elemental compositions of different trace elements present in the test sample. LIBS can be used in hostile environments using remote sensing methods, such as for nuclear applications and LIBS is also an interesting technique for in situ field applications, such as for geological and environmental issues (Fichet et al. 2003; Stratis et al. 2000).

It is worth mentioning that the LIBS technique is superior to conventional methods like inductively coupled plasma (ICP) and atomic absorption spectrometry currently applied for the analysis of liquid samples. The unique features of LIBS are that no or little sample preparation requirement, fast and rapid analysis and in situe detection which are lacking in the conventional analytical technique (Colao et al. 2004; Wainner et al. 2001). The LIBS technique has proven capable of detecting many metals of environmental concern in solid, liquid and gas samples. Because off-site analysis is possible, the measurement complexity is greatly reduced and there is no chance for sample loss or cross-contamination during transport or complicated preparations for laboratory analysis using conventional techniques. As for as the initial cost of the LIBS system is concerned, it is comparable or even less by 10–20% compared to price of ICP and atomic absorption systems. In addition, the running cost in terms of manpower and time for analysis of contaminated liquid samples at large scale using LIBS is much less as no sample preparation and chemical reagents are required. The work on LIBS for environmental and other analytical applications is a continuity of environment laser-based research activities being developed at the Energy Research Center – KFUPM including LIDAR and photo-acoustic spectroscopy (Gondal 1997; Gondal et al. 2002; Gondal and Mastromarino 2000; Gondal and Hussain 2006; Gondal et al. 2006).

In this study, we developed a LIBS set up for the analysis of the waste water collected from local dairy product plant. It is worth noting that the majority of applications of LIBS technique have been applied for analysis of solid samples. However, much less attention has been paid to the LIBS analysis of liquid samples which is due to the fact that a considerable number of alternative analytical techniques with superior sensitivity as compared to LIBS are available for liquid sample analysis. Furthermore, plasma generation in liquids presents several problems, for example the strong splashing and sloshing of the liquid produced by the shock waves generated by powerful laser pulses. In addition to that, the spectral emissions are self quenched by the water vapour present in the path of incoming laser beam due to splashing of liquid. We tried our best to overcome the problems of splashing of water on the optical components like focusing lens, fiber optics etc by designing of special cell. The LIBS spectrum of the waste water sample was recorded and the finger print wavelengths of the specific elements were employed for the identification of those elements using reference (Striganove and Sventitski 1968) and also NIST atomic spectra data base. The LIBS system developed at our laboratory was tested for analysis of many real waste samples in liquid phase collected from various industrial plants such as plastic syringes, paint manufacturing plants and even for the liquid waste generated at oil exploration sites.

## Materials and Methods

The plasma generation in liquids is not a trivial problem and one has to face many difficulties due to strong splashing and sloshing of the liquid produced by the shock waves generated by powerful laser pulses. In addition, the luminous phase of the plasma is rather short and the spectral lines originating from transitions between high-energy states are severely reduced. Keeping in view of these problems, we designed special cell to overcome the problem of splashing of water. Further more, the spectral emissions are self quenched by the water vapour present in the path of incoming laser beam due to splashing of liquid. An attempt was made in these experiments for the detection of contaminants in dairy products waste water by designing a special cell for testing the waste water. The main precaution in the designing of the cell was to avoid any splashing of liquid on the optical components. In this regards, cell of different geometries were tried and final design shown in Fig. 1 was employed for the analysis of waste water collected from dairy plant and reported in this paper. The experimental arrangement applied for the analysis of waste water sample from dairy products manufacturing plant is shown in Fig. 1. As clear from Fig. 1 a special glass cell having LIBS system used in this study consists of Ocean Optics LIBS 2000+ spectrometer; a special liquid cell was developed locally, OOILIBS software, Nd. YAG Laser (Spectra Physics, Model GCR100). The laser energy was measured with a calibrated energy meter (Ophir Model 300) for the study of dependence of

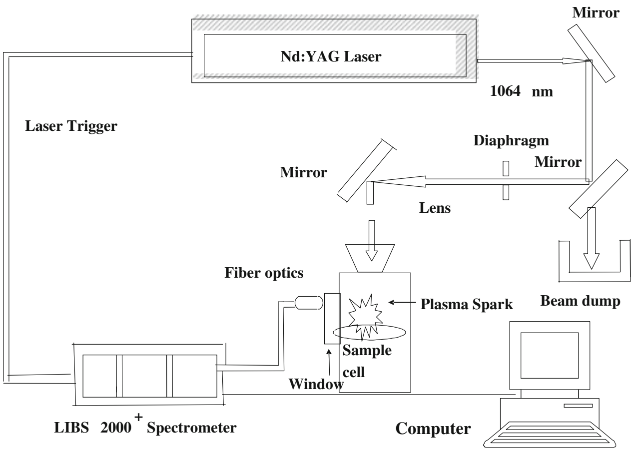

**Fig. 1** Schematic diagram of the experimental setup applied for the analysis of waste water samples collected from dairy product manufacturing plant

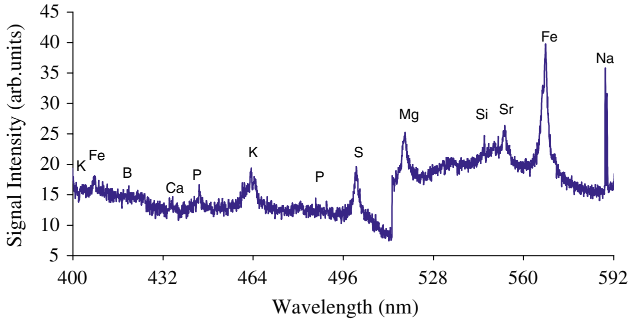

**Fig. 2** Typical LIBS Spectra of dairy products waste water sample in the region of 400 to 592 nm recorded at delay time of 5.00 µs and laser pulse energy of 100 mJ

LIBS signal on incident laser energy. The pulse energy utilized in this experiment was in the range of 80–100 mJ. The light from the plasma spark is collected by a collimating lens using UV grade fused silica 1 meter, multimode sampling fiber with SMA connector and is transferred to LIB2000 + Spectrometer (Ocean Optics). Our LIBS 2000$^{+}$ has four spectrometer modules to provide high resolution (FWHM 0.1 nm) in the 200 nm to 620 nm wavelength region. The detector has a gated CCD camera having 14,336 pixels. The concentrations of different trace metals present in waste water samples were also measured with a calibrated ICP spectrometer to verify the results achieved with our calibrated LIBS method. For each LIBS analysis, fresh waste water sample was kept in a liquid cell. In order to test the homogeneity of our samples, several LIBS measurements were performed at the surface of waste water samples.

## Results and Discussion

In order to enhance the sensitivity of the LIBS system, for analysis of waste water samples, the optimal experimental conditions, which can affect the limit of detection (LOD) in LIBS, were investigated. Prior to the analysis of dairy product waste samples, different parameters such as laser energy, delay time, focusing lens for incident laser radiation, collecting lens for laser produced plasma emission were optimized. Figure 2 depicts the emission spectra of the dairy waste water sample for spectral region of 400 nm to 592 nm. The laser pulse energy was 100 mJ. The distance between the optical fiber and the plasma was 10 mm.

Average spectra due to 20 laser shots were recorded for each data point. All the spectral lines for above mentioned elements recorded with our LIBS setup were identified using the NIST atomic spectral data base and also using the reference (Striganove and Sventitski 1968). The trace metals present in waste water sample were identified and are marked in the Fig. 2. The major elements detected in the waste water sample are Calcium, Magnesium, Phosphorus, Silicone, Iron, Sodium and Potassium and the concentration determined for each element measured with our LIBS set up, is listed in Table 1 and has been confirmed by the analysis using conventional analytical technique such as ICP.

The values obtained with our LIBS setup are in well agreement with the ICP results.

In LIBS analysis of liquid samples, one requires high pulse energy of the incident laser beam to generate plasma and to excite the sample species into ionic and neutral atomic transitions. In order to study the effect of the laser energy on the line emission intensity, we recorded the plasma emission spectra of waste water sample at different laser energies. To investigate, the effect of laser energy on the plasma emission intensity, the intensity of the standard Mg 518.29 nm line from waste water was recorded in the 400–592 nm region at laser energies of 40, 20, 60, 80 and 100 mJ. A time delay of 5.0 µs was used where maximum signal intensity of LIBS signal for Mg was achieved. Figure 3 shows a typical trend of dependence of laser produced plasma on incident laser energy for Mg element present in the test sample. Here the line intensity of Mg versus incident laser energy is plotted. It is clear from the Fig. 3 that the line intensity increases with rise in incident laser energy from 40 to 100 mJ. The line intensity (for Mg) shows linear dependence on the incident laser energy which is clear from the least square fit, $R^2 = 0.9974$. It is worth mentioning that incident laser pulse energy of 100 mJ was enough for detection of contaminant metals present in dairy product waste water samples.

A common method in all spectrometric techniques for quantitative measurement of unknown sample is the establishment of a calibration curve. For the construction of the calibrations curves during this study, different stoichiometric

**Table 1** Trace elements detected in waste water collected from dairy products manufacturing plant and comparison of LIBS with ICP

| Elements detected in waste water | Wave length (nm)* | Comparison of LIBS & ICP and relative accuracy (RA) | | | Standard deviation (LIBS) | Maximum permissible safe limit (mg kg$^{-1}$)** |
|---|---|---|---|---|---|---|
| | | LIBS ppm | ICP ppm | RA | | |
| Ca | 435.5 | 152 | 144 | 0.058 | 0.122 | – |
| Fe | 567.8 | 1.4 | 0.96 | 0.463 | 0.129 | 25 |
| Mg | 518.2 | 100 | 93.6 | 0.078 | 0.091 | – |
| K | 464.2 | 580 | 572 | 0.014 | 0.132 | – |
| Na | 588.9 | 1050 | 1040 | 0.010 | 0.115 | 1000 |
| P | 486.2 | 13 | 11.4 | 0.147 | 0.095 | 50 |
| S | 501.2 | 381 | 375 | 0.017 | 0.119 | 800 for sulphate |
| Si | 546.07 | 44 | 41.7 | 0.060 | 0.125 | – |
| Sr | 460.7 | 4 | 3.33 | 0.232 | 0.132 | – |

Here relative accuracy between two methods (LIBS &ICP) is also presented

* A. Striganov, and N. Sventitski, Table of Spectral Lines of Neutral and Ionized Atoms (Plenum New York) 1968 and NIST Data Base

** Environmental Regulation Standards for Saudi Industries set by Royal Commission, Saudi-Arabia

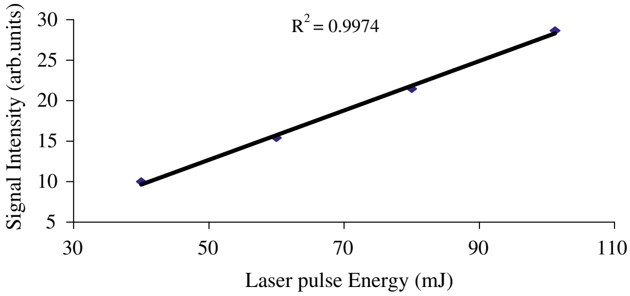

**Fig. 3** Plot of dependence of the intensity of the Mg 518.29 nm emission line on laser energy showing a linear trend

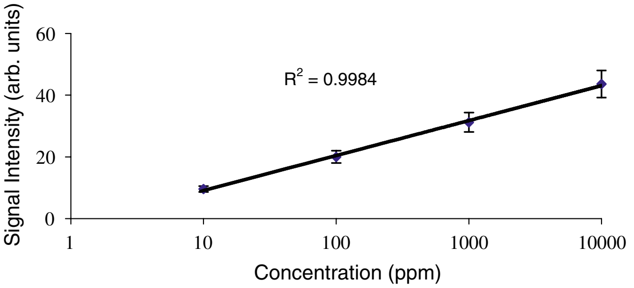

**Fig. 4** Calibration curve for LIBS measurements of trace metal (Si). The curve was plotted by recording the LIBS signal intensity of the Si (546.07 nm) emission line at time delay = 5 µS and the laser pulse energy = 100 mJ

samples of each metal were prepared in distilled water. Pure metals in powder form, purchased from Alfa Aesar, were mixed in distilled water having different known concentrations 100,000 ppm, 10,000 ppm, 1000 ppm, and 100 ppm of Mg, Ca, Fe, Si, and other metals under investigation were prepared and LIBS spectra were recorded for these four concentrations of each element. Calibration curve for LIBS measurements of trace metal (Si) is shown in Fig. 4.

The calibration curve was plotted by recording the LIBS signal intensity of the Si (546.07 nm emission line) at above mentioned concentrations. All these spectra were recorded with an average of 20 incident laser shots. This averaging of the spectra reduces the back ground noise to a great extent when compared to the single shot LIBS spectrum of the sample.

For waste water samples, the precision of LIBS measurements depend on the, homogeneity of the samples, and the reproducibility of the laser shots which is measured by the relative standard deviation (RSD) (Salle et al. 2005). Typical values of RSD for LIBS are in the range 1–10%. In our case for waste water samples, the precision was 2%. The accuracy of an analytical method is defined as how close the measured experimental values to accepted values measured with standard technique like ICP. For LIBS measurement, there are a number of methods to find accuracy of determining an element in a sample provided by the calibrated technique.

The accuracy for the waste water samples under investigation obtained from two detection systems (LIBS and ICP) are compared in Table 1. The relative accuracy (RA) is calculated as follows (Salle et al. 2005)

$$\frac{|d| + SD \times \frac{t_{0.975}}{\sqrt{n}}}{M}$$

where d is the difference between the LIBS measurement and the ICP (standard method). SD is the standard deviation of LIBS measurement, M is the measured value from standard method, n is the number of measurements and $t_{0.975}$ is the t value at 2.5% error confidence. As clear form Table 1, the relative accuracy is in the range of 0.01–0.4 which is quite acceptable for any good instrument.

The experience gained through this work can be useful for the development of a portable system for on line analysis of waste water from dairy products manufacturing plants.

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