Bull Environ Contam Toxicol (2007) 78:270–274
DOI 10.1007/s00128-007-9141-7

Determination of Toxic Metals in Petroleum, Cultivated Land and Ore Samples Using Laser-Induced Breakdown Spectroscopy

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The growth of the petroleum industry worldwide and the marketing of petroleum products have resulted in the pollution of the environment with heavy metals due to oil spills and leakage from oil tanks and waste oil dumps. The effects of such pollution on the environment, humans, livestock, wildlife, aquatic life, crops, and soil have been enormous. The hazardous waste generated from the petroleum industry poses great dangers to human and animal health, especially since some of the waste is non degradable. For example, it could stay in the soil for many years and pollute precious water resources.

The determination of nutrients and trace metal in soil samples is important due to the following reasons: i) soil contaminated with high concentrations of trace metals could pollute underground water resources, ii) within a single farming field, an agricultural producer may encounter non uniform distribution of nutrients (NUDN). Due to NUDN, the field may result in an over or under stress of nutrients (Lal, 1999). This can affect the overall crop yield. Precision farming, where uniform nutrient distribution is managed, is of growing interest among agriculturists and crop producers. In precision farming, management of nutrients allows growers to optimize inputs of nutrients like calcium, phosphorus, nitrogen, sulfur, iron and potassium, on a site-specific basis. By identifying sites where there is deficiency of nutrients in a field, farmers can create management zones and treat these areas with nutrients to enhance the crop yield. Hence the soil analysis is essential for guiding farmers to better identify fertilizer needs within a field. Many researchers are presently investigating optimum soil testing methods for precision agriculture. Efficient testing methods for measuring the concentration of nutrients are required for better estimates of crop yield.

The interest in the analysis of ore samples is due to two main factors: i) runoff from mineral processing, and ii) open pit mines dumping tons of toxic waste into nearby water reservoirs, which can directly affect human life, vegetation and livestock in the region. Another significance of ore sample analysis is the determination of ore content quality and the identification of the constituents present in the ore sample. Thus the identification of analytical techniques for detecting elemental composition of ore samples is very important and needs rapid attention.

Due to the above-mentioned reasons, a laser induced breakdown spectroscopy (LIBS) spectrometer was tested for the determination of heavy and toxic metals in crude oil residue sample obtained from a local oil producing company. The LIBS system was also tested for analysis of the soil samples collected from tomato cultivated green house soil. LIBS was also used for the chemical elemental analysis of ore samples.

In addition to pollution control, information regarding the chemical composition of a substance is also of fundamental importance for numerous tasks during process control and quality assurance in industrial production units.

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Conventional methods for chemical analysis like atomic absorption and inductively coupled plasma (ICP) involve the following major steps: (a) taking a sample of the substance to be inspected or taking of a product from the industrial processing line (b) transporting the sample to an inspection device or to a laboratory (c) preparation of sample for the chemical analysis (d) separation of impurities and (e) finally determination of the composition. In step (c), the sample is transformed into a physical–chemical state, which is necessary for the respective analyzing methods. Step (d) is a separation process, e.g., a stepwise dissolution in acid or solvent–acid mixtures, to obtain the insoluble fraction.

However, on-site, rapid analysis requires simplifying the analysis. Laser-based methods are among the best for rapid chemical analysis, and they do not require the complicated steps a–d, above. Moreover, the special properties of laser radiation enable a variety of spectroscopic methods for the chemical analysis of a substance or for the determination of the physical state. The tunability of the laser wavelength to specific atomic or molecular transitions offers high selectivity. The high spectral intensity of laser radiation increases the sensitivity; hence even small trace element concentrations (ppb) can be determined (Demtroeder, 1999). Highly sensitive laser spectroscopic methods include: laser-induced fluorescence (LIF), laser absorption spectroscopy, cavity ring down spectroscopy, and photoacoustic spectroscopy (Gondal and Mastermarino, 2001). For practical applications, laser spectroscopic methods are important, as they are able to determine several species simultaneously with minimum equipment; laser induced breakdown spectroscopy (LIBS) is one of these methods (Chechter, 1997; Lal, 1999; Vadillo and Laserna, 1996; Rusak et al., 1997; Bolger, 2000).

LIBS is based on the focusing of a high-power pulsed laser beam onto a sample surface leading to the creation of a plasma composed of excited species, which emit light. Collection of the plasma light, followed by spectral dispersion and detection, permits identification of the elements present in the sample using their characteristic spectral lines and allows quantitative analysis. This technique has been applied to many samples for simultaneous multi-element analysis such as solids, liquids, gases (Song et al., 1997; Fisher et al., 2001; Castle et al., 1998; Sneddon et al., 1999), environmental and geological samples (Radziemski and Cremers, 1989; Lee et al., 1997). The main advantages of LIBS technique include: stand-off analysis capability, little or no sample preparation requirements, rapid analysis, and simultaneous multi-elemental detection (major, minor and trace elements) ability, and the competence to measure the composition of weathered layers and the underlying bulk rock composition through depth profiling (repeated ablation) (Aguilerra and Aragon, 2004).

LIBS analysis capabilities must be investigated, and instrument development is required to take into account constraints such as instrument size, weight, power and environmental atmosphere (pressure and ambient gas). The LIBS spectrometer was tested and calibrated for the determination of trace metals (e.g., Cr, Li, Mg, Mn, Ni, Si, Sr) present in green house soil, Arabian oil waste residue samples, and samples collected from a local iron ore. Some of the results are presented in this paper. The concentrations of these elements were determined with this setup and were verified by an inductively coupled plasma (ICP). The LIBS results agreed well with the results obtained from ICP.

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 and Mastromarino, 2000, Gondal et al., 2002).

Materials and Methods

Three different kinds of samples (oil residue waste, cultivated soil and ore waste samples) were analyzed using the LIBS spectrometer. The details about each sample collection and its preparation are described:

For analysis of crude oil waste, the crude oil in liquid phase was obtained from Saudi Aramco, one of the major oil producing company in the Middle East. The initial phase of the residue was obtained by true boiling point (TBP) distillation process at 350°C under atmospheric pressure. The samples were further distilled under vacuum at 550°C over a longer period of time in order to get a solid paste of the residue. To prepare the pellets for LIBS analysis, the solid sample was first heated in an electric furnace up to 150°C. Then the melting material was poured into a stainless steel mold designed to obtain cylindrical discs approximately 20 mm diameter and 10 mm thick.

For the analysis of cultivated soil samples, soil samples were collected from soil at depths of 10–20 cm, and from different locations of a local green house farm located at Kateef, Saudi-Arabia. These samples were first sieved, then dried and grinded in Spectro Mill Ball Pestle Impact Grinder (Chemplex Industries, New York, USA) to obtain a mesh size suitable for preparation of pellets. The pellets were made into a cylindrical form, diameter 20 mm and thickness 10 mm, by hydraulic press (Carver model C, Sterling, USA). The applied load was 12,500 psi for 15 min. The ore samples tested in this study were collected from one of the open pits of the Al- Khnaiguiyah Zn - Cu deposits, located at GPS: N, 24° 16′ 10.2″ E, 45° 05′ 24.5″

and an altitude of 850 m, near the small town of Gorahia, west of Riyadh, Saudi Arabia.

The open pits at this location are a part of the operations of the Saudi Arabian Mining Company, ''Ma'aden''; they were used in ancient times to mine for Cu and Zn. The mine outcrops still have staining of malachite and azurite. There are many minerals exhibiting the presence of Fe, Mn, Zn and Cu around this area. The mine outcrops exhibit surficial staining of malachite and azurite. The slag surrounding this area also shows the signs of green cupriferous staining. The ore samples were machined in dimensions of 4 cm × 6 cm with a thickness of 2 cm. The samples were then filed and polished to achieve a smooth surface, necessary for generation of uniform plasma sparks for LIBS analysis.

A Nd: YAG laser (Spectra-Physics Lasers, Model GCR 100) at a wavelength of 1064 nm (30 mJ per pulse of 8 ns pulse width) was focused with a lens of 30 mm focal length on each test sample. The light from the plasma spark was collected by a collimating lens using UV graded fused silica 1 m multimode sampling fiber with SMA connector and was transferred to a LIB2000+ spectrometer (Ocean Optics) . The 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 14,336 pixel CCD camera. This makes it possible to measure a wide wavelength range (200–620 nm) simultaneously with high spectral resolution (0.1 nm). The emission was observed at a 45° angle to the laser pulse. For each LIBS analysis, a sample was placed on a rotary table in a stain less steel sample holder 20 mm in diameter and 10 mm in length. It was positioned such that the focal volume of the laser pulse was centered in the sample holder holding the sample. Three different locations on the sample surface were measured. Twenty laser pulses were directed into the sample holder for each measurement. The concentrations of different trace metals present in the test samples were also measured by ICP and then used to verify the calibrated LIBS method against different samples. By this standard technique, the results achieved with the LIBS setup were verified.

For the construction of the calibrations curves, different stoichiometric samples of each metal were prepared. Pure metals in powder form, purchased from Alfa Aesar, were mixed with the matrix material KBr in a ball milling apparatus in order to ensure good mixing and homogeneity. Then, they were pressed in a 10 bar pellet hydraulic press. In order to test the homogeneity of the samples, several LIBS measurements were performed at different locations at the surface of the pellets. The concentrations of the prepared samples were also verified by a calibrated ICP spectrometer. For calibration purposes, four samples of known concentrations, 100,000, 10,000, 1000, and 100 ppm, of Mg were prepared in KBr matrix. LIBS spectra were recorded for these four concentrations of each element. All spectra were recorded with an average of 20 laser shots.

The detection limit is a very important parameter for any spectrometer and for analysis of samples under investigation. Detection limit here means the lowest concentration that can be detected with LIBS. The limit of detection (LOD) was estimated using the equation (Radziemski and Cremers, 1989):

$$LOD = \frac{2\sigma_B}{S}$$

Where σ_B is the standard deviation of the background measurements, and S is the sensitivity which is given by the ratio of the intensity to the concentration.

Results and Discussion

A typical calibration curve for Mg (emission line at 518.4 nm) is presented in Fig. 1. The log-log plot displays the relation between the detected LIBS signal intensity and the Mg sample concentration. That the R^2 value is close to 1.000 shows the relation between concentration and signal intensity is linear. The curve was plotted by recording the LIBS signal intensity of the Mg 518.4 nm emission line at various known concentrations in standard samples of magnesium.

A typical LIBS spectrum of an oil residue sample is presented in Fig. 2. The trace metals present in the residue crude oil waste sample were identified and are marked in Fig. 2.

The major elements detected in the sample were Ca, Fe, Mg, Cu, Zn, Na, S, Ni, K and Mo. The concentrations determined with the LIBS set up, as listed in Table 1, have been confirmed by analysis using conventional ICP, and the results of the two analytical methods are in good agreement. A typical LIBS spectrum of an agricultural soil

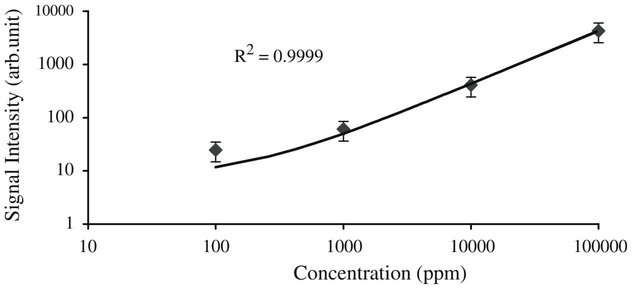

Fig. 1 Calibration curve for LIBS measurements of trace metal (magnesium)

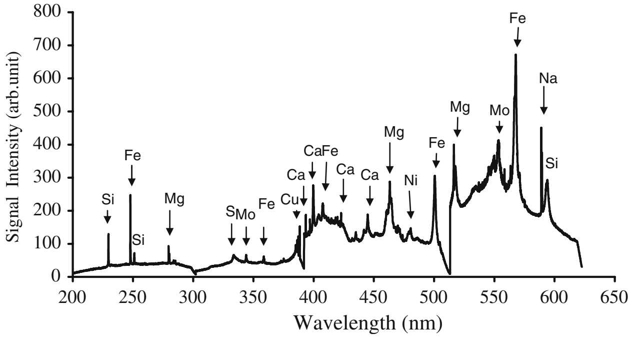

Fig. 2 Typical LIBS spectrum of an oil residue sample recorded in the 398 – 620 nm region

sample is depicted in Fig. 3. The different metals and non-metal peaks in the region 200–650 nm are displayed. The peak wavelengths were identified from Striganov and Sventitski (1968) and also confirmed from the NIST atomic spectra database. Table 1 displays the concentrations of these different elements. A typical LIBS spectrum of the ore sample is presented in Fig. 4. The elements present in the ore sample are indicated in the figure, and the concentrations of each element detected with the LIBS setup and with standard ICP technique are listed in Table 1. The peak wavelength were identified from Striganov and Sventitski (1968) and also confirmed from the NIST atomic spectra database.

The limits of detection for some elements under investigation ares given in Table –1. For these elements, the LOD was only a few parts per million. For all the soil and ore samples, LIBS concentration agrees within 10% to that determined by ICP. With the oil residue samples, however, some metal concentrations were close to the limit of detection, and there was some discrepancy in the results between the two methods. In the present study, laser induced breakdown spectroscopy was successfully applied for the detection of trace metals in soil, ore samples and oil residues.

The parametric dependence of LIBS signals and the elemental concentrations were investigated. This work demonstrates that the LIBS technique is applicable for elemental chemical analysis of such samples. The results show excellent agreement with the results obtained from ICP and the calibration curves were effective in quantifying the trace metal concentrations.

The main advantages of LIBS system over the ICP method are the following:

1. Little to no sample preparation is needed for LIBS analysis.
2. Solid, liquid and/ or gaseous samples can be analyzed.

Table 1 Elements detected in soil, ore and oil residue samples, and comparison of elemental concentrations measured using LIBS and ICP techniques

Element	Wave length (nm)	Greenhouse soil samples		Ore samples		Oil residues samples		LOD (ppm)
		LIBS (ppm)	ICP (ppm)	LIBS (ppm)	ICP (ppm)	LIBS (ppm)	ICP (ppm)	
Al	461.0	1630	1575	10205	10100	Nd*	Nd*	12
Ba	553.5	19	17.5	Nd*	Nd*	Nd*	Nd*	14
Ca	616.2	3830	3573	1215	1110	74.9	67.5	14
Cd	361.3	Nd*	Nd*	Nd*	Nd*	Nd*	Nd*	16
Cr	429.0	12	11	73	60	Nd*	Nd*	7
Cu	521.8	8	7.5	805	716	5	2.1	3.5
Fe	527.0	2670	2428	597000	591000	177	170	12
Mg	518.3	6694	6177	3478	3380	20	14	6
Mn	294.0	74	68	16463	1150	Nd*	Nd*	6
Mo	553.5	Nd*	Nd*	Nd*	Nd*	3.2	2.5	2
Na	589.0	740	681	Nd*	Nd*	21	16	10
Ni	313.4	11	10	Nd*	Nd*	51.6	46.5	11
P	438.5	1010	919	Nd*	Nd*	Nd*	Nd*	4
S	373.8	1311	1249	Nd*	Nd*	Nd*	Nd*	7
Si	250.7	1081	996	81150	80600	Nd*	Nd*	10
Sr	487.2	377	343	Nd*	Nd*	Nd*	Nd*	7
Ti	488.1	82	76	Nd*	Nd*	Nd*	Nd*	10
V	413.2	10	9	Nd*	Nd*	Nd*	Nd*	5
Zn	280.2	40	37	Nd*	Nd*	6	4.3	5
K	404.7	2670	2428	Nd*	Nd*	7.7	5.8	4

Nd*, not detected

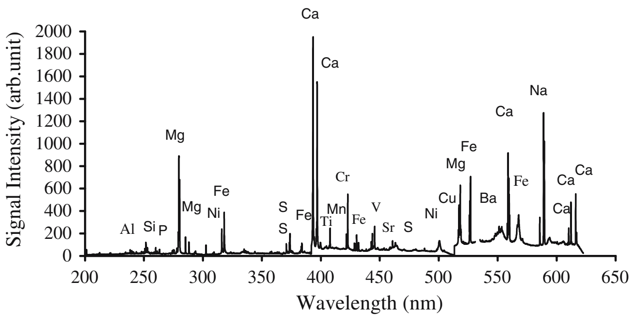

Fig. 3 LIBS spectrum of greenhouse soil sample recorded in the 200–620 nm region

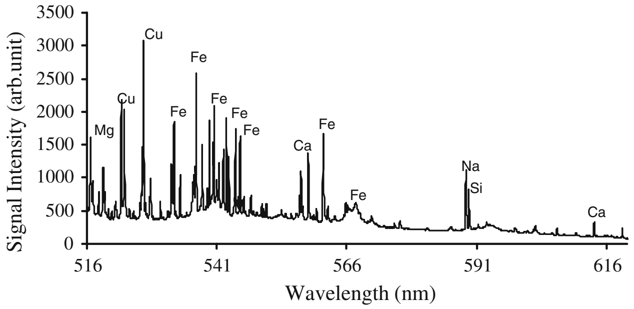

Fig. 4 Typical spectrum recorded in the 516–620 nm region with the LIBS spectrometer of the ore sample

3. Samples may be conductive or nonconductive.
4. A small amount (micrograms) of sample is vaporized (Lee et al. 2000)
5. Capability of remote analysis, in harsh environments (Bolger et al., 2000)
6. Capable of simultaneous multi-element analysis

Acknowledgments The support by the KFUPM Physics Department is gratefully acknowledged. One of the authors (T.H.) is thankful to National University of Sciences and Technology and the government of Pakistan for financial support for his Ph.D. work. He is also thankful to KFUPM for its hospitality and permission to work at its research facilties.

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