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Determination of Trace Metals Using Laser Induced Breakdown Spectroscopy in Insoluble Organic Materials Obtained from Pyrolysis of Plastics Waste

Mohammad N. Siddiqui · Mohammad A. Gondal · Mohammed M. Nasr

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Abstract Laser induced breakdown spectroscopy (LIBS) was applied for the detection of trace elements in non-degradable part of plastics known as insoluble organic material, obtained from thermal and catalytic degradation of plastics. LIBS signal intensity for each metal measured in the test sample was unique and different. The capability of this technique is demonstrated by analyzing various trace metals present inside plastics and also compared with ICP results. The metal concentration (ppm) measured with LIBS and verified by ICP for Ag (901), Al (522), Fe (231), Co (628), V (275), Ni (558), Pb (325), Mn (167) and Cd (378) are higher than permissible safe limits.

Keywords Laser induced breakdown spectroscopy (LIBS) · Trace metal detection · Plastics recycling · Environmental impacts of plastic waste

A dramatical increase in the consumption of plastics and subsequently generating more plastic waste is being witnessed worldwide. It has been estimated that almost 170 million tones of plastics were produced worldwide during the year 2003. Western Europe estimated the annual total consumption of plastic products at 48.8 million tons for 2003 and generating ~15 million tons of waste plastics throughout the Europe (Achilias 2007). In 2006, the US generated about 14 million tons of plastics in the form of municipal solid waste (MSW) as containers and packaging, over 6 million tons as nondurable goods, and almost 9 million tons as durable goods. The total amount of plastics in MSW – almost 30 million tons – represented 11.7% of total MSW generation in 2006 (EPA 2006). Saudi Arabia is one of the major producers of plastic in the world with total production capacity of around 6 million tons per year. The amount of plastic wastes in Saudi Arabia is about 15% wt in the composition of domestic municipality waste (Ali et al. 2004). Plastics are produced from petroleum derivatives and are composed primarily of hydrocarbons but also contain additives such as antioxidants, colorants, heavy metals and other stabilizers which are undesirable from environmental and pollution perspectives (Hamid et al. 1992). Due to these reasons, untreated disposal of plastics and its effects on human health has become a matter of great concern. Plastic waste is harmful as its pigment contains many trace elements that are highly toxic in nature.

Due to the above mentioned facts, recycling and waste management of plastic waste is highly important and has become a major response to the environmental challenges facing the plastic industry (Perugini et al. 2005; Rahman et al. 2006). The first step in plastic recycling process is the sorting of plastics and its classification. This requires a proper instrumentation for rapid identification of plastics and LIBS provide a unique advantage for plastic characterization and successfully applied for fast and non-destructive measurements. For in-depth and comprehensive understanding of the non-degradable hazardous portion of

M. N. Siddiqui
Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

M. A. Gondal (✉)
Laser Research Laboratory, Physics Department and Center of Nanotechnology (CENT), King Fahd University of Petroleum and Minerals, Box 372, Dhahran 31261, Saudi Arabia
e-mail: magondal@kfupm.edu.sa

M. M. Nasr
Department of Natural Sciences, College of Dentistry and Pharmacy, Riyadh 11671, Saudi Arabia

plastic wastes, a rapid, advanced, efficient and on line analytical technique is very essential. For this purpose, LIBS was developed locally and applied for the first time to determine the number and amount of trace metals in the non-degradable portion of plastics called insoluble organic materials (IOM) which are not easily and accurately detectable with other conventional techniques due to different reasons on rapid time scale. In LIBS, a plasma spark is created by focusing the high energy laser beam at the IOM samples and spectrally resolved emissions are recorded with spectrometer having reasonable resolution (0.1 nm) to identify the elements present in IOM samples. This analytical technique enables the determination of elemental compositions of different trace elements present in the IOM of mixed plastic samples (Gondal and Hussain 2007; Gondal et al. 2006, 2007a, b, c). The unique features of LIBS are that no or a little sample preparation requirement, fast and rapid analysis and in-situ detection which are lacking in other conventional analytical techniques such as atomic absorption and inductively coupled plasma (Gondal 1997; Gondal and Hussain 2007; Gondal et al. 2006, 2007a, b, c). The work on LIBS for environmental and other analytical applications is a continuity of laser-based research activities being developed at the Physics Department-KFUPM including LIDAR and photo-acoustic spectroscopy (Gondal 1997; Gondal and Mastromarino 2000, 2001).

Materials and Methods

Plastics used in this study for pyrolysis were procured from Saudi Basic Industries Corporation (SABIC), Riyadh, Saudi Arabia. These model polymers were polystyrene (PS), low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polyethylene terephthalate (PET) and poly-vinyl chloride (PVC) in the granular and powder forms. Waste plastics were collected as used plastics cups (WCup), water bottles (WP) and water bottle caps (WCap). Recycling reaction of plastics were carried out in a 25 cm^3 stainless steel tubular micro autoclave reactor with a programmable temperature controller obtained from the Parr Scientific, USA as described in our previous work (Ali et al. 2004; Ali and Siddiqui 2005). The recycling reaction products were separated into gaseous, liquid and solid fractions. The liquid product was dissolved in three different solvents successively in hexane, toluene and tetrahydrofuran and the remaining insoluble portion is called insoluble organic material (IOM) as shown in Fig. 1. This IOM fraction is characterized by LIBS and ICP for toxic metal contents.

All IOM samples were prepared in the pellets form to carry out the LIBS analysis. Care was taken to avoid any contamination due to mixing of other species during the pellet formation process. The samples were accurately weighed, according to standard procedures. The samples were first dried and grinded in Spectro Mill Ball Pestle impact Grinder (Model 1100-11, Chemplex Industries, Inc., USA) to suitable mesh size for the preparation of pellets. The pellets were made in a dye of cylindrical form having diameter 20 mm and thickness 2 mm using a hydraulic press (Carver Laboratory Press Model, C Sterling USA). The applied pressure was 12,500 psi for 15 min. The samples were stored in air-tight desiccators to avoid any moisture and humidity effects.

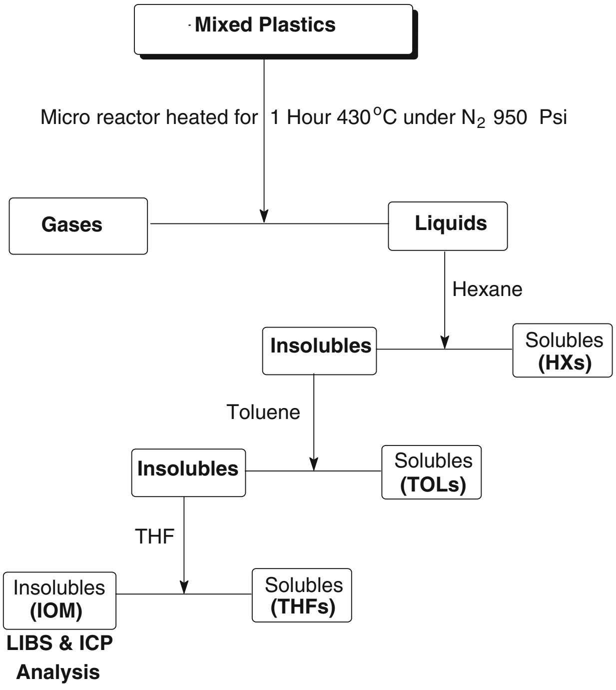

Fig. 1 Schematic separation procedure for insoluble organic materials (IOM) from mixed plastics on pyrolysis

LIBS system applied in this study consists of Ocean Optics LIBS 2000 + spectrometer; a special home built chamber, OOILIBS software, Nd. YAG Laser (Spectra Physics, Model GCR100). The Nd: YAG laser can deliver maximum pulse energy of one joule with a pulse width of 8 ns and operate at a 10 Hz pulse repetition rate, operating in Q-switched mode. Here 1,064 nm radiations emitted at fundamental frequency from Nd: YAG laser were applied for production of plasma spark at the IOM test sample. The laser energy was measured with a calibrated energy meter (Ophir Model 300) for the study of dependence of LIBS signal on incident laser energy. The pulse energy utilized in this experiment was in the range of 50–120 mJ. The light from the plasma spark is collected by a collimating lens using UV grade fused silica 1 m, 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 200–620 nm wavelength region. The detector has a gated CCD camera having 14,336 pixels. This makes it possible to measure a LIBS spectrum over broad spectral range (200–620 nm) simultaneously with spectral resolution (0.1 nm). The plasma emission was recorded at a 90° angle to the laser pulse. Software built in the spectrometer read the data from the chip and reconstructed the spectrum. The concentrations of different trace metals present in IOM samples were also measured with a calibrated ICP spectrometer to verify the results achieved with our calibrated LIBS method. For each LIBS analysis, fresh IOM test sample was kept in the LIBS chamber. In order to test the homogeneity of our test samples, several LIBS measurements were performed at the surface of IOM test samples. For calibration purposes, the metals used were Ca, S, Mg, Zn, Si, Fe, P, Na and K. All these metals in powder forms were of high purity (99.99%) and procured from Fisher Scientific USA. For the construction of the calibration curves, pure metals in powder form were thoroughly mixed using a special grinder with IOM samples in known concentrations.

Results and Discussion

Prior to measurements on IOM samples, the optimal experimental conditions were investigated to enhance the sensitivity of the LIBS system which can improve the limit of detection (LOD). For this purpose, various experimental parameters such as laser energy, delay time, focusing lens for incident laser radiation, and collecting lens for laser produced plasma emission were optimized before testing the IOM samples. The reproducibility for each data point was calculated with a confidence level of 95%.

Typical emission spectra of IOM samples in the spectral region of 200–592 nm are presented in Figs. 2 and 3. Here the laser pulse energy was 50 mJ. The optical fiber and the plasma had a distance of 10 mm in between. The most sensitive lines in LIBS for each element under investigation were recorded for the above mentioned spectral region. The major elements detected in the IOM samples are Co, Fe, V, Ni, Pb, P, Mo, Mg, Ag, Ca, S, Si, Al, Ti, Mn, B, Cd and Cu. The signature spectral lines of all elements were clearly identified and labeled. The 292.4 nm emission line for V signature, 279.8 nm emission line for Mg signature, the 324.7 nm emission line for Cu signature, the 220.3 nm emission line for Pb signature, the 422.6 nm emission line for Ca signature, 425.5 nm emission line for Al signature, 228.8 nm emission line for Co signature, 338.3 nm emission line for Ag signature, 202.1 nm emission line for Mo signature, 253.6 nm emission line for P signature, 257.6 nm emission line for Mn signature and 588.9 nm emission line for Na signature have been selected for quantitative analysis. The selected emission lines have minimal interference from other emission lines, these emission lines are strongly intense and do not involve the ground state so that self-absorption is almost absent. Due to these reasons, these lines are useful for quantitative analysis. The spectral lines for all trace elements present in IOM recorded with our LIBS setup were identified using the NIST atomic spectral data base and also using the reference (Striganove and Sventitski 1968).

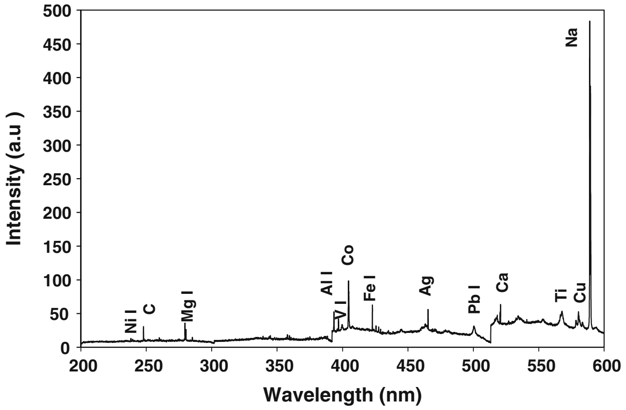

Fig. 2 LIBS spectra of IOM derived from wp/wcup plastics showing line intensity of various elements

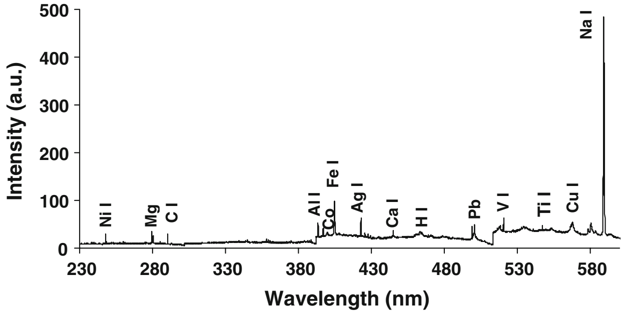

Fig. 3 LIBS spectra of IOM derived from wp/ps plastics showing line intensity of various elements

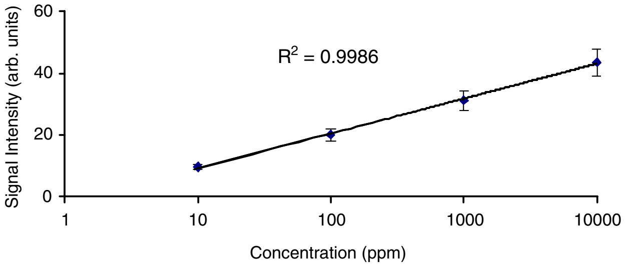

Fig. 4 Calibration curve for LIBS measurements of trace metal (Cu). The curve was plotted by recording the LIBS signal intensity of the Cu (521.82 nm) emission line at time delay = 5 µs and the laser pulse energy = 100 mJ

Table 1 Trace elements detected in IOM by LIBS and ICP techniques

		WP/WCap		WP/PS/Cat		WP/PS		PP/PS/PET	
Metals	Wave-length (nm)	LIBS (ppm)	ICP (ppm)	LIBS (ppm)	ICP (ppm)	LIBS (ppm)	ICP (ppm)	LIBS (ppm)	ICP (ppm)
Ag	430.02	901.5	883.8	102.6	100.62	107.9	105.76	348.6	341.74
Al	396.15	522.1	516.95	50.7	50.16	109.1	108.06	27.9	27.66
Ca	551.3	474.6	435.45	101.8	93.4	587.8	581.98	630.3	578.3
Cd	260.85	133.5	139.08	215.3	224.32	20.2	21.08	378.3	394.11
Co	344.1	353.3	346.41	621.8	609.68	ND	ND	110.8	108.65
Cu	570.02	123.2	110.03	97.2	86.79	91.9	82.13	90.6	80.94
Fe	404.58	174.9	173.21	202	200	231.4	229.13	115.7	114.56
Mg	285.21	222.2	215.7	218.9	212.53	89.4	86.82	357.6	347.25
Mn	322.79	8.7	8.08	56.8	52.6	167.6	155.25	7.8	7.2
Mo	423.26	256.7	270.55	677.6	705.87	166.3	173.21	902.4	940.22
Na	588.9	340.1	327	375.4	361	504.4	485	969.3	932
Ni	553.4	286.5	136.47	57.8	27.52	558.4	265.96	22.5	10.73
P	404.4	134.8	130.93	141.4	137.27	310	301.02	75.5	73.32
Pb	338.28	95.4	90.88	133.5	127.17	341.1	324.82	275.7	262.6
S	373.6	194.3	183.29	184.9	174.48	27.6	26.06	226.1	215.4
Si	517.37	169.2	156.66	129.8	120.19	307.3	284.52	141.4	130.93
Ti	498.17	24	22.85	85.8	81.79	18.4	17.56	654.6	623.48
V	519.53	60.4	58.8	275.2	271.44	47.2	46.74	39.1	37.5

WP waste water bottle; *WCap* waste bottle cap; *Cat* catalyst

Table 2 Trace elements and their spectral assignment along with the finger print wavelength detected in IOM samples

Trace metals	Measured wavelength (nm)	LIBS signal intensity	Spectral assignment of observed transitions upper state → lower state
Na I	589.59	2,848.3	${}^2P_{1/2} \rightarrow {}^2S_{1/2}$
Ti I	517.37	273.2	${}^3F_2 \rightarrow {}^3F_2$
Ni I	215.19	13.9	${}^1F_3 \rightarrow {}^3F_2$
Fe I	445.63	434.7	${}^3H_5 \rightarrow {}^1G_4$
Fe II	318.01	283.1	${}^2F_{5/2} \rightarrow {}^2D_{3/2}$
Mg I	285.21	22.2	${}^1P_1 \rightarrow {}^1S_0$
Mg II	279.55	859.6	${}^2P_{3/2} \rightarrow {}^2S_{1/2}$
Ca II	315.89	168.3	${}^2D_{3/2} \rightarrow {}^2P_{1/2}$
C II	525.36	133.8	${}^4D_{5/2} \rightarrow {}^4F_{5/2}$
Al I	396.15	596.8	${}^2S_{1/2} \rightarrow {}^2P_{3/2}$
Si I	251.43	165.2	${}^3P_1 \rightarrow {}^3P_0$
Mn II	293.31	19.4	${}^5P_1 \rightarrow {}^5S_2$
Cr I	478.93	67.5	${}^5G_6 \rightarrow {}^5F_5$
Co II	236.38	26.9	${}^5D_4 \rightarrow {}^5F_4$
Hg I	224.76	15.7	${}^3S_1 \rightarrow {}^3S_0$

In order to detect the concentration of each trace elements present in the IOM samples, the LIBS system was calibrated. For the calibration of trace elements under study in the IOM sample, LIBS spectra of these elements were recorded in 200–620 nm regions. 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 IOM in a ball milling apparatus in order to ensure good mixing and homogeneity and were pressed in a 10 bar pellet 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 concentration of the prepared samples was also verified by a calibrated inductively coupled plasma (ICP) spectrometer.

In this work, known concentration of 100,000, 10,000, 1,000, and 100 ppm of Mg, Ca, Zn, Fe, Cu, V, Mn, Al and other metals under investigation were prepared in the matrix of IOM and LIBS spectra were recorded for these four concentrations of each element. All these spectra were recorded with an average of 20 laser shots, at three different locations on the sample surface. A typical calibration curve for LIBS measurements of Cu metal is shown in Fig. 4. The curve was plotted by recording the LIBS signal intensity of the Cu 521.82 nm emission line at above mentioned concentrations. Average spectra were recorded for each data point which reduced the back ground noise to a great extent when compared to the single shot spectrum of the sample.

The IOM used in this study were isolated from the degradation reactions of mixed plastics carried out as bottle/waste bottle cap, waste bottle/ps with catalyst, waste bottle/ps and pet/pp/ps. Table 1 shows the trace elements present in different IOM samples detected by our LIBS system and counter verified by ICP technique. The metals detected in the IOM samples are very toxic and hazardous in nature so pose great environmental threat. Table 2 summarizes the transitions used for the identification of various elements. The table shows the average values obtained by this procedure. A standard deviation of 2%–3% in the concentration values was found for different elements.

Conclusion

Trace metals present in IOM were detected using laser induced breakdown spectroscopy. The concentrations of 18 trace metals (Co, Fe, V, Ni, Pb, P, Mo, Mg, Ag, Ca, S, Si, Al, Ti, Mn, B, Cd and Cu) present in IOM were estimated and results achieved are in good agreement with the conventional techniques such as ICP spectrometry. The maximum concentration measured with our setup and verified by ICP method for Ag (901 ppm), Al (522 ppm), Fe (231 ppm), Co (628 ppm), V (275 ppm), Ni (558 ppm), Pb (325 ppm), Mn (167 ppm) and Cd (378 ppm) are higher than the permissible safe limits. The parametric dependence of signal intensity for improvement of the sensitivity of LIBS spectrometer was carried out. This work demonstrates that LIBS technique could be applied for rapid on line analysis of plastics waste samples.

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