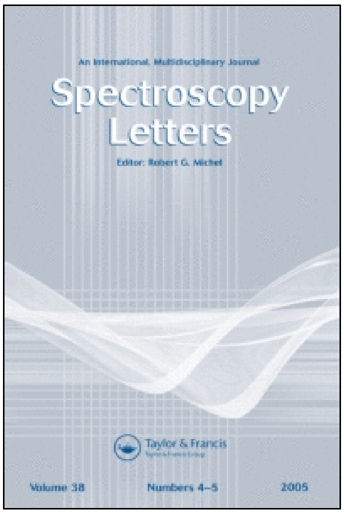

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Determination of Chloride Content in Different Types of Cement Using Laser-Induced Breakdown Spectroscopy

M. A. Gondal[ab]; Z. H. Yamani[ab]; T. Hussain[c]; O. S. B. Al-Amoudi[d]
[a] Laser Research Laboratory, Physics Department, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia [b] Center for Nano Technology, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia [c] Institute of Environmental Science & Engineering, National University of Sciences and Technology (NUST), Rawalpindi, Pakistan [d] Civil Engineering Department, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia

To cite this Article Gondal, M. A. , Yamani, Z. H. , Hussain, T. and Al-Amoudi, O. S. B.(2009) 'Determination of Chloride Content in Different Types of Cement Using Laser-Induced Breakdown Spectroscopy', Spectroscopy Letters, 42: 4, 171 — 177

To link to this Article: DOI: 10.1080/00387010902827668

URL: http://dx.doi.org/10.1080/00387010902827668

Spectroscopy Letters, 42:171–177, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010902827668

Determination of Chloride Content in Different Types of Cement Using Laser-Induced Breakdown Spectroscopy

M. A. Gondal[1,2],
Z. H. Yamani[1,2],
T. Hussain[3],
and O. S. B. Al-Amoudi[4]

[1]Laser Research Laboratory, Physics Department, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia
[2]Center for Nano Technology, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia
[3]Institute of Environmental Science & Engineering, National University of Sciences and Technology (NUST), Rawalpindi, Pakistan
[4]Civil Engineering Department, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia

ABSTRACT The characterization and accurate determination of the chloride content in cement/concrete is very important for the assessment of the durability and safety of a concrete structure. The available analytical techniques are relatively expensive and time consuming. In this study, a laser-induced breakdown spectroscopy (LIBS) system was used for determination of elemental composition in three different types of cement samples. The plasma was generated by focusing a pulsed Nd: YAG laser at 1064 nm on the cement samples. The concentrations of different elements of significance for structural stability in cement samples were determined. The evaluation of the potential and the capabilities of LIBS as a rapid tool for characterization of cement samples is discussed. The optimum LIBS setup and experimental conditions to detect and measure chloride in building materials are reported. The LIBS results were compared with the results obtained using a standard analytical technique such as inductively coupled plasma emission spectroscopy (ICP–ES). The limits of detection were determined, and calibration curves were measured. The results of this investigation indicate the reliability of LIBS to characterize different cement samples and to assess the chloride content in these cements.

KEYWORDS atomic emission plasma spectroscopy, chloride content, environmental impacts of trace metals, laser-induced breakdown spectroscopy, multielemental analysis, nondestructive testing, on-line analysis, reinforced concrete, reinforced corrosion, structural stability

INTRODUCTION

The chloride content is an important criterion to assess the durability of reinforced concrete structures. Cement is a key ingredient in the concrete structure. Comprising roughly 12% of the average residential-grade ready-mixed concrete, cement is the binding agent that holds sand and other aggregates together in a hard, stone-like mass.[1] The choice of cement type for construction purposes involves the correct knowledge of the cement ingredients. Even a small variation in the chemical composition or physical state of cement can cause substantial variations in its performance.[2,3] The

Received 28 May 2008;
accepted 24 December 2008.

Address correspondence to M. A. Gondal, Laser Research Laboratory, Physics Department, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia.
E-mail: magondal@kfupm.edu.sa

chloride present in reinforced concrete can cause severe corrosion to the steel reinforcement. The critical chloride content required to initiate reinforcement corrosion depends on whether the chloride was present at the time of mixing or has been entered during post hardening.[4] Chloride and sulfate ions have a significant effect on the durability of concrete structures,[5,6] and, therefore, quantitative measurements of these deleterious ions (Cl^-, S^-) in the cement are important for condition assessment and quality assurance of the concrete structures.[6]

The measurement of elements like chlorine and sulfur in building materials using optical techniques is a highly challenging task because of the limited number and relatively weak spectral lines of these elements compared with the large number of strong lines of the natural (primary) components of the materials. Another challenge of the optical method is to account for the influence of the matrix and to provide useful calibration. To overcome these limitations of the standard techniques, which are time consuming and need a chemical laboratory for quantitative results, laser-induced breakdown spectroscopy (LIBS) was applied in this work for elemental composition analysis of different cement samples being used in various buildings across Saudi Arabia. It is worth mentioning that Saudi Arabia, as well as many other Arabian Gulf states, are facing alarming durability problems of reinforcement corrosion in concrete structures due to the high content of salt and moisture across the coastal regions of the Red Sea and Arabian Gulf.[7]

LIBS technology provides a rapid elemental analysis of solids, liquids, or slurries and gases[8–19] with little or no sample preparation. On-line systems also provide real-time sample analysis that would be useful for sorting rocks, plastics, and metals. Unique applications of LIBS could be possible for on-site determination of chloride content in concrete and sorting of concrete waste materials for recycling purposes.

In LIBS, a short laser pulse evaporates a small amount of material (typically a few micrograms) creating a plasma plume.[8–10] The light emitted by plasma is spectrally resolved to determine the chemical composition of the targeted material.[11–15] There are many processes that occur when a pulsed laser beam interacts with any solid material resulting in intense plasma generation, thermionic emission, sample heating, phase change, melting, atomization, excitation, and ionization.[16–24]

In this study, LIBS data were measured for three different types of cements that are very often used in Saudi Arabia in the construction of buildings and other structures. In this regard, the optimum setup and the experimental conditions for chloride detection and other elements in cement and calibration curves of pressed pellets of cement samples are presented. Thus, an attempt is made to characterize and analyze the cement samples, and the results obtained are briefly discussed. The concentrations of each element detected with our LIBS setup was counter-verified by the standard inductively coupled plasma (ICP) technique, and the results are compared. The peak wavelengths were identified from data reported by Striganove and Sventitski[25] and also confirmed from NIST atomic spectra database for trace elements present in the cement samples.

MATERIALS AND METHODS

Reagents

Analytical-reagent grade chemicals without further purification were used for the calibration and analysis of cement samples by ICP and LIBS methods. For calibration purposes, the metals used were lead, copper, chromium, calcium, sulfur, magnesium, zinc, titanium, strontium, nickel, iron, aluminum, barium, potassium, and NaCl. All these metals were in powder forms and of high purity (99.99%) and were procured from Fisher Scientific (Pittsburgh, PA, USA). For the construction of the calibration curves, different stoichometric samples comprising these metals were prepared. These metals in powder form were mixed with the matrix material in a ball milling apparatus in order to ensure good mixing and homogeneity. It was thoroughly mixed and ground to make a homogeneous mixture.

Apparatus

The LIBS system used in this study consists of an Ocean Optics LIBS 2000$^+$ spectrometer, a sample chamber, OOILIBS software, and a Nd: YAG Laser (Spectra Physics, Model GCR100) from Ocean Optics (Dunedin, FL, USA) which is described in detail in earlier publications.[21–29] A schematic diagram of the LIBS experimental setup used in the analysis of cement samples is presented in Fig. 1. Nd: YAG laser

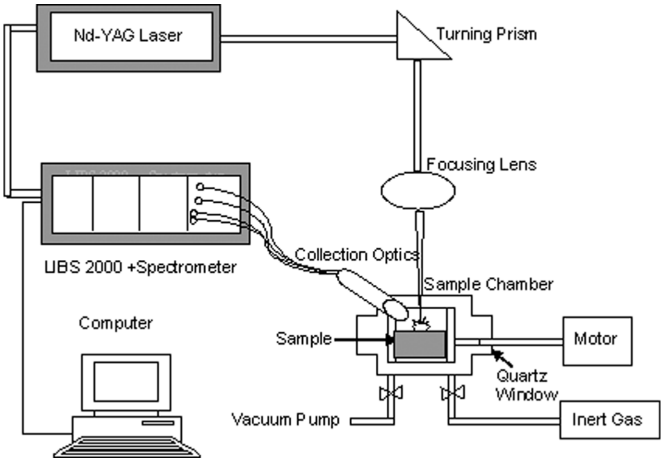

FIGURE 1 Schematic diagram of the experimental setup applied for the analysis of cement samples.

can deliver a maximum pulse energy of 1 J with a laser pulse width of 8 ns and operates at 10 Hz pulse repetition rate, operating in Q-switched mode. In this study, 1064-nm radiation emitted at the fundamental frequency of the Nd: YAG laser was applied for the production of plasma sparks at cement sample surfaces. The laser energy was measured with a calibrated energy meter (Ophir Model 300, Ophir Optics Inc., North Andover, MA, USA) for the study of dependence of LIBS signal on incident laser energy.

The pulse energy used in this experiment was in the range 20–60 mJ. The light from the plasma spark was collected by a collimating lens using a UV-graded fused silica 1 m, multimode sampling fiber with SubMiniature version A (SMA) connectors and was transferred to the LIBS 2000$^+$ Spectrometer (Ocean Optics). Our LIBS 2000$^+$ has four spectrometer modules to provide high resolution full width at half maximum (FWHM 0.1 nm) in the 200-nm to 620-nm wavelength region. The detector has a gated CCD camera, which makes it possible to measure LIBS spectra over a broad spectral range simultaneously with high spectral resolution.

The emission is observed at a 45° angle to the laser pulse, and software built into the spectrometer reads the data from the chip and reconstructs the spectrum. For each LIBS analysis, a cement sample was placed on a stainless steel disk-shaped (20 mm diameter by 10 mm long) platform mounted on a rotary table. The table was positioned such that the focal volume of the laser pulse was centered at the disk holding the sample. Twenty laser pulses were directed into the cup to complete one measurement. The table was rotated using a step motor having 12 revolutions per minute. The concentrations of different elements present in cement samples were also measured with a calibrated ICP spectrometer to verify the results achieved with our LIBS method.

Experimental Procedure for Sample Preparation

For the calibration of our LIBS spectrometer, the following metals were used: copper, chromium, calcium, sulfur, magnesium, zinc, titanium, strontium, nickel, silicon, iron, aluminum, barium, sodium, and potassium. All these metals were procured in powder forms with high purity (99.99%) from Fisher Scientific. For the construction of the calibration curves, different stoichometric samples comprising these metals were prepared. For this purpose, pure metals in powder form were mixed with KBr in a ball milling apparatus in order to ensure good mixing and homogeneity. It is to be noted that the KBr used as a binding material (matrix) was of high purity (99.99%) and was procured from Sigma–Aldrich (Milwaukee, WI, USA). For the analysis of cement samples using ICP technique, the cement samples were digested with acid, diluted with 5% nitric acid, and analyzed for metals using inductively coupled plasma optical emission spectrometry (ICP–ES) calibrated with three levels of mixed standards. For LIBS, the cement samples under investigation were pressed in a pellet form and were placed into the LIBS ablation chamber. In order to test the homogeneity of the cement samples, several LIBS measurements were performed at different locations on the surfaces of cement samples.

RESULTS AND DISCUSSION

The detection limit of any analytical instrument should be enough to detect the trace amounts of individual elements present in the sample. This detection limit varies greatly, according to the transitional strength of the elemental line, delay time (time between the firing of the laser pulse and the opening of the camera shutter), and the gate width (time for which the shutter is open) selected during the measurements, the sample matrix and collection optic geometry and so forth.[15–21] Prior to the applications of our LIBS spectrometer on actual cement samples, these parameters were optimized. Experiments were performed to find optimal conditions of temporal delay and incident laser energy for the

TABLE 1 **Elements Detected in Cement Samples and Comparison of LIBS Technique with ICP**

Element	Wave-length (nm)	Cement type I		Cement type V		Cement type SF		LOD (ppm)	Delay (μS)
		LIBS (ppm)	ICP (ppm)	LIBS (ppm)	ICP (ppm)	LIBS (ppm)	ICP (ppm)		
Al	394.4	34,500	34,100	24,350	24,200	521.4	474	8.0	4.5
Ba	493.4	6,280	6,080	6,731	6,620	nd	Nd	5.0	5.0
Ca	396.1	433,500	433,000	443,480	443,000	2,090	2,043	6.0	5.0
Cr	427.3	96.58	87.8	Nd*	Nd*	Nd*	Nd*	4.0	5.5
Fe	526.9	20,230	193,00	21,980	21,200	396	366	7.0	3.5
Mg	518.2	8017	7,470	13,905	13,400	2,801	2,700	2.0	4.5
Mn	403.4	226.6	206	306.9	279	510.1	475	4.0	4.5
Na	588.9	3211	3,010	3,977	3,680	2,852	2,760	3.0	3.5
P	438.51	Nd*	Nd*	Nd*	Nd*	825.3	783	7.0	4.5
S	373.81	11,320	11,000	8,480	8,080	304.7	277	10.0	4.0
Si	390.5	92,020	88,200	81,600	81,200	351,590	349,000	11.0	4.5
Cl	585.7	1,825	1,720	1,590	1,520	6,690.7	6,595	12	5.0

Source for wavelengths: Ref. 25 and NIST database; Nd, not detected.
LOD, Limit of Detection

analysis of different cement samples under investigation. From these parametric dependence studies, it was confirmed experimentally that incident laser pulse energy of 40 mJ at time delay of 5.0 μs was optimum for detection of different metals present in the cement samples under investigation. Hence LIBS spectra of different samples were recorded over a 200-to-650 nm wavelength range for qualitative and quantitative analysis at 40 mJ and time delay of 5.0 μs.

Calibration Curves for Cement Samples

Different stoichiometric samples of each metal were prepared for the construction of the calibration curves. This task was essential for accurate measurement of concentration of trace metals present in different cement samples. The concentration of the prepared samples was also verified by a calibrated ICP spectrometer.

In this experimental work, known concentrations 100,000 ppm, 10,000 ppm, 1000 ppm, and 100 ppm of Mg, Ca, Zn, Fe, Cu, Cr, Mn, Al, S, and other metals under investigation were prepared in the KBr matrix. Utmost care was taken to avoid any impurity during the preparation of standard samples for calibration purposes. 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. Average spectra were recorded for each data point. Further, to confirm results, the initial calibration was performed on cement samples with well-defined sodium-chloride additions.

The detection limits for LIBS analysis of pellet samples under investigation were calculated by using the standard equation.[8] The results achieved from cement samples were comparable with the results obtained by ICP analysis. The limits of detection for the elements under investigation are given in Table 1.

LIBS Analysis of Cement Samples

Figures 2–4 depict the emission spectra of type I, type V, and type SF cement samples recorded with our setup at the time delay of 5.0 μs in the spectral region of 200 to 650 nm. The laser pulse energy

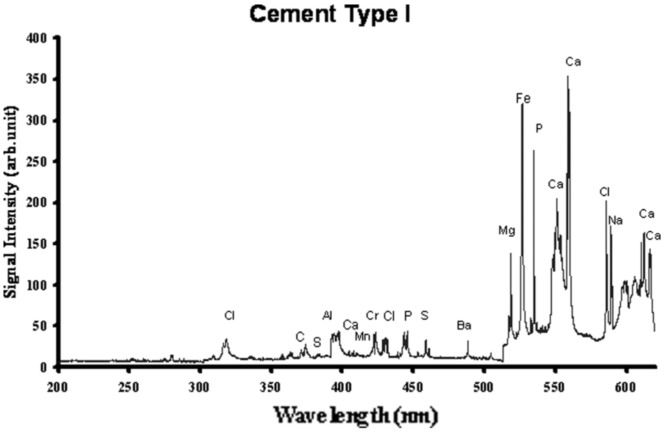

FIGURE 2 **Typical LIBS spectra of type I cement sample in the region 200–650 nm recorded at delay time of 5.0 μs and laser pulse energy of 40 mJ.**

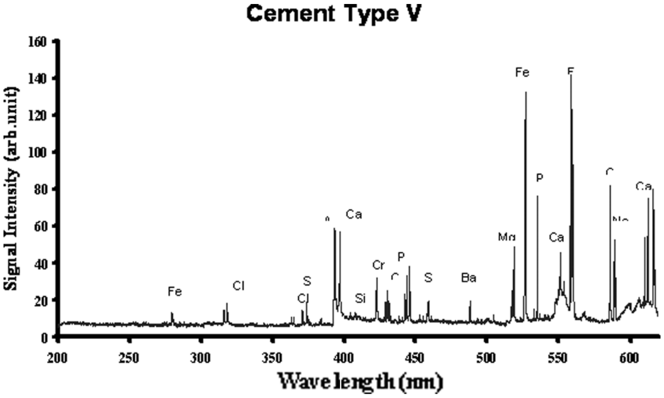

FIGURE 3 Typical LIBS spectra of type V cement in the region 200–650 nm recorded at delay time of 5.0 μs and laser pulse energy of 40 mJ.

was fixed at 40 mJ for recording of these spectra. The distance between the optical fiber and the plasma emission was kept at 10 mm. The average spectra due to 20 laser shots were recorded for each data point. It is to be noted that averaging the 20 laser shots spectra tended to reduce the background noise to a great extent when compared with the single laser shot spectrum of the sample.

The elements present in the above-mentioned cement samples were identified and marked in the figures. The major elements detected in the samples are calcium, aluminum, silicon, iron, chromium, magnesium, sodium, chlorine, sulfur, phosphourus, and manganese. All the spectral lines for the above-mentioned elements recorded with our LIBS setup were identified using the NIST atomic spectral database and also using the data in Ref. 25. The elements detected and the corresponding concentrations are listed in Table 1. The concentration for each element, as summarized in Table 1, was confirmed by the analysis using ICP. Comparison of the values obtained with our LIBS setup with the ICP results indicates a good agreement between the two techniques.

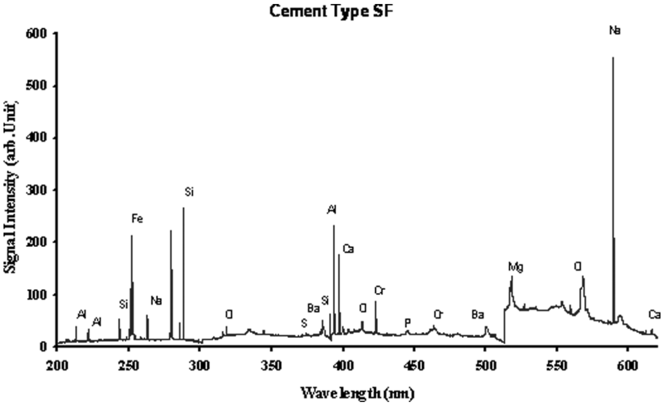

FIGURE 4 Typical LIBS spectra of type SF cement in the region 200–650 nm recorded at delay time of 5.0 μs and laser pulse energy of 40 mJ.

Precision and Accuracy of Cement Results

The precision of any analytical instrument is defined as the repeatability of the analyte measurement and is usually estimated in LIBS with the relative standard deviation (RSD) as follow:[21–24]

$$\mathrm{RSD} = \frac{\text{standard deviation}}{\text{mean}}$$

For cement samples, the precision of LIBS measurements depends on the complexity and homogeneity of the sample and the reproducibility of the laser shots. Typical values for LIBS are in the range 1–7%.[8–10] For precision of our results for the three cement samples, the same method was adopted as applied for the analysis of samples like paint and ore,[21–24] and the precision was found to be 2–4%.

The accuracy of an analytical method is defined as the measured experimental values that are true or close to the accepted "actual" values. Generally speaking, the accuracy of any measurement or analytical technique is defined as the percentage difference between the experimental values measured with LIBS and the actual values measured with a standard method like ICP. The details about the method applied for determination of the accuracy of our results regarding concentration of contaminants like Cl and S and other trace metals is discussed in depth in our earlier publications concerning crude oil, different binding materials, and plastic samples.[19,21–24] For the three cement samples studied in this work, the values obtained by two methods (ICP and LIBS as presented in Table 1) are in good agreement within the 2% error limit.

It is worth mentioning that the concentration of trace elements in all three cement samples is different, which could be due to the raw materials being used for production of cement at different locations inside the Kingdom of Saudi Arabia. As different locations have different rock compositions, so the elemental composition in different types of cement will not be constant. In addition, the concentration of each element seems to be high in ppm units but in % terms it is not high and it is within the limits as reported in open literature.[27] It is well known that all kinds of cements are manufactured by burning primarily two raw materials; namely, calcareons and agrillaceons in nature.[26] The calcareous materials (i.e., limestone, chalk, etc.) constitute about 70% to provide lime, and the latter materials (i.e., clays, shale, etc.) form 30% to produce silica, alumina, and ferric oxides in addition to the presence of impurities as a result of variability of the raw materials. According to the American Society for Testing and Materials (ASTMC150) C 150 Standard Specification for Portland Cement, there are five basic catagories of cements based on their chemical and mineralogical compositions and their uses by the construction industry.[27] The chemical composition (elements present in raw material) as reported in Ref. 27 varies for different types of cements, which is exactly the findings of our work.

CONCLUSIONS

The concentrations of various elements present in cement samples were measured accurately using the LIBS system. The accuracy of our system in terms of qualitative as well as quantitative analysis is obvious from the comparison of LIBS results with those obtained by ICP. The contaminants and concentrations detected with our setup are shown in Table 1. It is also shown that the LIBS measurements are a suitable tool for the determination of chloride contents in cement. Compared with standard chemical methods, LIBS can provide more rapid information and can be used on-site. In addition, the sensitive lines for many elements were identified. The elemental analysis and the calibration curves were effective in quantifying the trace metal concentration in cement samples. The experience gained through this work can be useful for the development of a portable system for on-line analysis of cement and building materials.

ACKNOWLEDGMENTS

Support from the Physics Departments and King Fahd University of Petroleum & Minerals through project grant IN 080410 is gratefully acknowledged. One of the authors (T.H.) is thankful to the National University of Science and Technology and Government of Pakistan for finacial support for his Ph.D. work. He is also thankful to KFUPM for its hospitality and permission to work at its research facilties. The authors are thankful to Dr. Chandana Senaratne for ICP analysis.

REFERENCES

1. Taylor, H. F. W. *Cement Chemistry,* 2nd ed. Thomas Telford Publishing: London, England, 1997.
2. Bogue, R. H. *The Chemistry of Portland Cement,* 2nd ed. Reinhold Publishing Corp: New York, 1955.
3. Whiting, D. *Permeability of Concrete*. ACI: New York; 1988; 195–222.
4. Wiggenhauser, H.; Wilsch, G.; Schaurich, D. LIBS for non destructive testing of element distribution on surfaces. *NDT & E Intern.* **1998**, *31*, 307–313.
5. Al-Amoudi, O. S. B.; Rasheeduzzafar, M. M.; Abduljawwad, S. N. Influence of chloride ions on sulphate attack in plain and blended cements. *Magazine of Concrete Research* **1994**, *46*(167), 113–123.
6. Al-Amoudi, O. S. B.; Rasheeduzzafar, M. M.; Abduljawwad, S. N. Influence of sulfate ions on chloride-induced reinforcement corrosion in plain and blended cements. *J. Cement Concrete Aggregates* **1994**, *16*(1), 3–11.
7. Al-Amoudi, O. S. B. Protection of reinforced concrete structures in sulfate-chloride exposures. NACE Corrosion 2007 Conference and EXPO, 2007, Paper 07279, p. 16.
8. Miziolek, A. W.; Palleschi, V.; Schechter, I. *Laser, Induced Breakdown Spectroscopy*; Cambridge University Press: Cambridge, 2006.
9. Fantoni, R.; Canevá, L.; Colao, F.; Fornarini, L.; Lazic, V.; Spizzichino, V. Methodologies for laboratory laser induced breakdown spectroscopy semi-quantitative and quantitative analysis—A review. *Spectrochim. Acta B* **2008**, *63*, 1097–1108.
10. Salle, B.; Mauchien, P.; Maurice, S. Laser-induced breakdown spectroscopy in open-path configuration for the analysis of distant objects. A reveiw. *Spectrochim. Acta B* **2007**, *62*, 739–768.
11. Aragon, C.; Aguilera, J. A. Characterization of laser induced plasmas by optical emission spectroscopy: A review of experiments and methods. *Spectrochim. Acta B* **2008**, *63*, 893–916.
12. Harmon, R. S.; De Lucia, F. C.; Miziolek, A. W.; McNesby, K. L.; Walters, R. A.; French, P. D. Laser-induced breakdown spectroscopy (LIBS)–An emerging field-portable sensor technology for real-time, in-situ geochemical and environmental analysis. *Geochem. Explor. Environ. Anal.* **2005**, *5*, 21–28.
13. Rusak, D. A.; Castle, B. C.; Smith, B. W.; Winefordner, J. D. Fundamentals and applications of laser-induced breakdown spectroscopy. *Crit. Rev. Anal. Chem.* **1997**, *27*, 257–290.
14. Radziemski, L. J. Review of selected analytical applications of laser plasmas and laser ablation. *Microchem. J.* **1994**, *50*, 218–234.
15. Panne, U.; Haisch, C.; Clara, M.; Neissner, R. Analysis of glass and melts during the vitrification process of fly and bottom ashes by laser-induced plasma spectroscopy. Part I: Normalization and plasma diagnostics. *Spectrochim. Acta B* **1998**, *53*, 1957–1968.
16. Song, K. Y. I. L.; Sneddon, J. Applications of laser induced breakdown spectroscopy. *Appl. Spectrosc. Rev.* **1997**, *32*, 183–235.
17. Adrian, R. S.; Watson, J. Laser microspectral analysis: A review of principles and applications. *J. Phys. D Appl. Phys.* **1984**, *17*, 1915–1940.
18. Bauer, H. E.; Leis, F.; Niemax, K. Laser induced breakdown spectrometry with an echelle spectrometer and intensified charge coupled device detection. *Spectrochim. Acta B* **1998**, *53*, 1815–1825.

19. Gondal, M. A.; Hussain, T.; Yamani, Z. H.; Baig, M. A. Detection of heavy metals in arabian crude oil residue using laser induced breakdown spectroscopy. *Talanta* **2006**, *69*, 1072–1078.
20. Loebe, K.; Uhl, A.; Lucht, H. Microanalysis of tool steel and glass with laser-induced breakdown spectroscopy. *Appl. Opt.* **2003**, *42*, 6166–6173.
21. Gondal, M. A.; Hussain, T. Determination of poisonous metals in waste water collected from paint manufacturing plant using laser-induced breakdown spectroscopy. *Talanta* **2007**, *71*, 73–80.
22. Gondal, M. A.; Hussain, T.; Yamani, Z. H.; Baig, M. A. The role of various binding materials for trace elemental analysis of powder samples using laser induced breakdown spectroscopy. *Talanta* **2007**, *72*, 642–649.
23. Gondal, M. A.; Hussain, T.; Ahmad, Z.; Bakry, A. Detection of contaminants in ore samples using laser induced break down spectroscopy. *J. Environ. Sci. Health A* **2007**, *42*, 879–887.
24. Gondal, M. A.; Siddiqui, M. N. Identification of different kinds of plastics using laser induced breakdown spectroscopy for waste management. *J. Environ. Sci. Health A* **2007**, *42*, 1989–1997.
25. Striganove, A.; Sventitski, N. *Table of Spectral Lines of Neutral and Ionized Atoms*; Plenum: New York, 1985.
26. Lee, F. M. *The Chemistry of Cement and Concrete.* 3rd ed.; Chemical Publishing Co. Inc: New York, 1971.
27. Ksomatka, S. H.; Kerkhoff, B.; Panarese, W. C. *Design and Control of Concrete Mixtures,* 14th ed.; Portland Cement Association: Skokie, Illinois, 2002.