SUMMARY

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The field of laser spectroscopy has been continuously expanding and developing rapidly over the past few decades, giving rise to many new thought processes and realization of new techniques. The field of Laser-Induced Breakdown Spectroscopy (LIBS) has shown remarkable progress over the past few decades. It is becoming an attractive analytical method for the analysis of wide range of samples related to environment, geology, bio-medicine, pharmacy, industry, etc. [1-6]. The growing applications of LIBS is mainly due to its appealing features like minimal/no sample preparation and the ability to perform remote measurements etc. [7]. Currently, there is no other technique available, which can offer the above-specified features with very high sensitivity. Further, the technique is fast, inexpensive and can provide simultaneous measurement of multiple elements. Yet, there are few challenges like matrix effects and their effect on quantitative measurements impeding LIBS to accept as a standard technique at par with other techniques like ICP-AES, ICP-MS, etc. [1,8]. In practice, conventional univariate methods are popular for the LIBS data analysis, which employ single emission line to estimate the amount of analyte. This approach is well suited for the sample consisting of few elements and interference free emission lines [9]. However, LIBS spectral data is multivariate and consists of many emission lines from same element. Consequently, implementing multivariate methods can minimize the difficulties arise due to the matrix effects and thereby improve the performance of quantitative analysis [10].

The objectives mentioned in the beginning of the thesis have been studied in detail and the results obtained for the respective objectives are described in different chapters. In Chapter 1, a thorough literature survey on LIBS in combination with various chemometric methods are discussed. Initially an introduction on the evolution of chemometrics and the various methods available for the data analysis are given. Later, the importance of LIBS, its basic principle and applications have been described.

The present study focuses mainly on analyzing various types of glass samples using LIBS. These materials are found to be promising due to their special physical and chemical properties. From many years, various types of glasses, such as soda lime, borosilicate, phosphate glasses, etc. have been prepared and being used for specific applications. Samples such as soil, rocks, metals, alloys, etc. have been extensively studied using LIBS, whereas, very few reports are found on elemental analysis of glass materials. Soda lime glasses are
widely used in the making of windows, containers, windshields, etc. Many reports are found on the LIBS analysis of these glasses focusing on forensic applications [11-14]. Further, borosilicate and iron phosphate glasses studied in this work are mainly used as hosts for the storage of high-level nuclear waste. Of late, the LIBS technique has been investigated for the analysis of novel optical materials such as rare earth doped phosphate glasses. Among all the samples studied here, no reports are available till date on LIBS study of phosphate glasses. 

In view of this, the first objective is executed on reference samples like NIST SRM 610, soda lime, borosilicate and phosphate based glass samples using a LIBS system and the results are discussed in Chapter 2. Since, there are many parameters involved in LIBS experiments, it is necessary to identify the optimized conditions to obtain the reliable qualitative and quantitative information. The experimental conditions such as laser energy, number of laser pulses, wavelength, detection window and focusing optics must be optimized to avoid any undesirable signal. Samples like soda lime, NIST SRM, borosilicate and iron-phosphate glasses have been studied and the optimal conditions are reported. In general, the optimum gate width of 5.0 $\mu$s and gate delay from 0.7 $\mu$s to 1.0 $\mu$s is desirable for these studies. The effect of wavelength on the LIBS emission intensity is investigated. The maximum intensity of the LIBS spectrum is observed with second harmonic (532 nm) as compared to the fundamental (1064 nm) and third harmonic wavelength (355 nm) of the Q-switched Nd-YAG laser. Further, the percentage relative standard deviation (%RSD) of emission line intensity decreased with increasing the laser pulse energy and number of laser pulses. In LIBS, proper focusing of the laser beam is important and the Lens-to-Sample-Distance (LTSD) studies showed better intensity near the Rayleigh range.

In Chapter 3, the rare earth elements (Pr and Sm) in phosphate glasses have been studied using absorption, fluorescence and LIBS techniques. The results obtained using these three techniques highlight the usefulness of LIBS as a complementary technique for the analysis of rare earth elements. Further, the rare earth doped phosphate glasses are investigated for the quantitative analysis using LIBS. The emission lines of doped elements such as Sm, Tm and Yb have been identified by comparing the recorded emission spectrum with the National Institute for Standards and Technology (NIST) database. Using P as an internal standard the calibration curves were constructed for all the three elements. Later using the leave-one-out (LOO) method, the concentration of elements in different samples were cross-validated. The correlation uncertainty of the calibration curve obtained varying from 0.6% to 15% for the three rare earth elements. Finally, the limit of detections for Sm, Tm and Yb are calculated...
and they were found to be 0.20, 0.38 and 0.24 wt.% respectively. The work reported here is the outcome of the second objective of the thesis and is discussed in the Chapter 4.

In 5th chapter, the chemometric methods have been used to analyze the borosilicate glass samples. The conventional univariate method has been evaluated along with multivariate chemometric methods such as PCR and PLSR. The accuracy of the quantitative analysis of univariate and multivariate methods is reported through the correlation uncertainty and RMSEP respectively. The univariate calibration curves constructed for the two different intensity ratios have the correlation uncertainty of 10% and 13% respectively. On the other hand, multivariate analysis of region 3 (401.5 nm to 407 nm) has emanated the lowest RMSEP of 0.548 wt.% for PCR and 0.552 wt.% for PLS regression methods. Analysis of LIBS spectra using PCA gave complimentary information to the PCR and PLS regressions. The PCA performed in all regions showed better classification at region 3, where, PCR and PLS regressions have lowest RMSEP, which further envisages the complementary nature of multivariate methods. Thus, LIBS data analysis using PCA, PCR and PLSR carried out for the borosilicate glass samples clearly demonstrated the following:

(i) Significant improvement in the accuracy of the analyte concentrations using multivariate methods as compared to the univariate methods
(ii) The complementary nature of multivariate methods correctly identified the best region of LIBS spectrum for the investigation of sample composition.

Recently, borosilicate and other glass matrices have been investigated extensively using the LIBS system. Since, borosilicate glasses require high melting temperature and have lower waste loading capacity, iron-phosphate glasses have been developed as an alternative host for immobilization of nuclear waste [15]. In view of this, five samples of iron-phosphate glasses have been synthesized with varying concentrations. Three analytes namely, Cr, Sr and Ti were used as doping elements in iron-phosphate host matrix. LIBS spectra have been recorded from all these samples and the results are discussed in Chapter 6. These materials were initially analyzed for the classification using PCA, PLS-DA and support vector classification (SVC). Except the blank glass sample, PCA was not completely successful in separating all the five samples. Further, PLS-DA and SVC performed in the broad region of LIBS spectra of iron phosphate glasses has an overall classification accuracy of 91% and 100% respectively. The classification performed using a linear kernel of SVMs showed promising results. Further, the quantitative analyses of doped elements were carried out using
PLSR and SVR. Calibration curves obtained for the validation sets of Cr, Sr and Ti have similar RMSECV (a measure of accuracy) for both these methods. The accuracy of the calibration curves shows that the advanced statistical methods employed are promising tools to analyze the LIBS data. The work carried out here on iron phosphate glasses is noteworthy due to the following reasons.

(i) The classification of iron phosphate glasses using the LIBS system shows that the method is sensitive enough to identify the samples as a separate class based on the changes in the concentrations of minor (doped) elements.

(ii) LIBS combined with multivariate approach has proven as a robust analytical technique for the routine analysis of the potential elements (Cr, Sr, etc.) which deteriorates the quality of glass matrix.

The time required to analyze the LIBS data is important to employ this method for field applications. Univariate analysis requires identifying the peak height of the emission line or measuring the area under the peak. This procedure is time consuming when one needs to analyze hundreds of spectrum belonging to the large number of samples. On the contrary, the statistical programming language R [16], used here to analyze the borosilicate glass samples took only few minutes to construct the calibration curves. Further, the software Unscrambler X (Version 10.4) is much faster in analyzing hundreds of LIBS spectra which can compute and provide the results in a fractions of seconds. Thus, such robust approaches using LIBS coupled with chemometrics reduce the burden of human efforts in laborious computations using univariate methods and also they have the potential to implement in field applications.
**Future work:** The work carried out in this thesis can be extended in order to broaden its applications in the following topics:

The study of iron phosphate glass samples was carried out using second harmonic wavelength (532 nm) of Q-switched nanosecond pulsed Nd:YAG laser. This work can be repeated using the higher harmonics of the Nd:YAG laser such as 355 nm or 266 nm. The present work demonstrated the routine analysis of iron phosphate glasses using the laboratory based LIBS system. This can be further taken forward to perform remote measurements using Standoff-LIBS (ST-LIBS) system. However, optimization of the LIBS system for the analysis of iron phosphate glasses is essential before employing the ST-LIBS for such applications.

The quantitative analyses of borosilicate and iron phosphate glasses have been studied using PCR, PLSR and SVR. These samples can be further studied using methods such as ANN, Random Forest (RF), etc. ANN is considered to be a method which behaves like ‘black box’ where the analyst has difficulty in explaining the results [17]. Additionally, in certain situations, the results obtained by PLSR may be better than ANN and the prediction of the optimized model is also difficult. Despite these disadvantages, ANN has ability to perform better when data is noisy and non-linear and hence one can implement ANN for the analysis of LIBS data. Like SVMs and ANN, RF method is capable enough to handle the non linearity in the data and have the advantages of being fast, non-parametric and can provide comparable accuracy [18,19]. Thus, RF also can be a potential method for the LIBS analysis of the complex glass matrix.

The field of LIBS has shown a remarkable growth over the past few years. Especially, various applications of LIBS in physics, chemistry, biology and medicine and its significant contributions to the solutions of technical and environmental problems are worth appreciating. Hope it will further strengthen with the advancement of chemometric tools.
References


