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Exploring LIBS for simultaneous estimation of Sr, Ba and La in LiCl-KCl salt

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ABSTRACT

In this work, we report the simultaneous estimation of Sr, Ba and La in LiCl-KCl salt using laser induced breakdown spectroscopy (LIBS). The samples are prepared in aqueous medium and the solution is spread over a filter paper. The laser (532 nm) is focussed on the paper to produce plasma in air at atmospheric pressure. Using Yb (369.42 nm) as an internal standard, linear calibration curves are obtained from 50 – 800 ppm for Sr (421.55 nm), 50 – 1000 ppm for Ba (455.40 nm) and 300 – 4000 ppm for La (394.91 nm) with a detection limit of 21, 19 and 68 ppm, respectively in 12.5 % salt matrix. Salt effect on LIBS intensity is studied and found to be negligible over 5–20 % of salt. Low value of correlation uncertainty (5–11 %) illustrates that LIBS technique has a great potential for monitoring the quality of pyro-processing salt.

1. Introduction

Laser induced breakdown spectroscopy (LIBS) has been widely demonstrated as a versatile technique for the elemental analysis and has grown considerably over past 10 years [1–8]. This technique is based on atomic emission where the target sample is irradiated by focusing a high-power pulsed laser, usually ns pulse width, to produce plasma. The emission from the formed plasma is subsequently analysed by a spectrometer with proper time gating. The characteristic atomic and ionic lines are the spectral fingerprints of the elements present in the sample and can be easily used for qualitative multi-elemental analysis. Certain characteristics such as quickness, very low sample consumption, little sample preparation, remote sensing etc. have enabled the wide applications of LIBS in carrying out elemental analysis from conducting to non-conducting samples [9].

In nuclear energy technology, to improve the economics of the nuclear fuel cycle, reprocessing of spent fuel is desired after a specified irradiation in the reactor. In this respect, pyro-chemical reprocessing is being developed worldwide and of considerable interest for the recovery of heavy metals from the high burn up spent metal fuels with minimum waste generation [10–12]. The first step of the pyro-processing involves dissolution of fuel in molten eutectic salt (44 wt% LiCl + 56 wt% KCl) at 773 K which leads to the formation of chloride species of U, Pu and the fission products [13,14]. These species are selectively electro-transported and deposited on appropriate electrodes [15]. The chloride species of some of the fission products such as alkali, alkaline earth and rare earth metals are more stable than those of actinides and therefore does not deposit on to the electrodes and remain in the salt phase during electro-refining [16]. The accumulation of fission products chlorides in salt after few runs significantly modifies its properties and as a result electrochemical reduction reaction slows down [17]. To avoid it the salt is sent for distillation periodically, before it can be reused after few runs. Usually when the content of fission product chloride exceeds 10 % in the salt, techniques of zeolite ion

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exchange, phosphorylation precipitation, melt crystallization are used for purifications of salt [18–20]. Therefore, knowledge of concentration of fission product chloride becomes a very important criterion to check the quality of the salt before its reuse. It is also important from the material accountability and waste generation point of view [21,22].

Usually, the analysis of fission products in salt is carried out via ICP (inductively coupled plasma) based methods [23–25]. As an alternative, laser induced breakdown spectroscopy (LIBS) can be used for the simultaneous estimation of these fission products. In this paper, using LIBS technique, simultaneous estimation of lanthanum (La) and alkaline earth metals (Sr, Ba) in LiCl-KCl salt matrix is explored. There are some previous reports on the in situ analysis of molten salt using LIBS technique. Effenberger has demonstrated the LIBS method to detect CoCl_3 , MnCl_3 and CrCl_3 in molten salt [26]. Williams et al. have reported LIBS technique as a promising method to estimate the composition of molten salt [21]. There are very few reports on the quantitative estimation of U and lanthanides (Eu, Pr, Ce, Gd) in eutectic salt [27–29]. It should be mentioned that the estimation of Sr, Ba using LIBS are scarce in the literature and those are in the field of firearm residue [30], food technology [31] and nuclear materials [32,33]. In case of La, limited reports are available for its estimation in matrix using LIBS. Martin et al. have performed LIBS estimation of La in graphite matrix [34]. Bhatt et al. have reported La estimation in ore/mineral [35]. Recently, feasibility study of La estimation in LiF-KCl matrix by LIBS has been reported from our laboratory [36]. To the best of our knowledge, no LIBS study is available and the present work will demonstrate for the first time the feasibility of LIBS estimation of Sr, Ba and La in LiCl-KCl salt. These elements are chosen here to verify the potential application of LIBS technique for the simultaneous estimation of lanthanides and alkaline earth metals in LiCl-KCl salt.

The direct analysis of salt requires inert atmosphere as LiCl-KCl salt is hygroscopic in nature. With the objective to investigate the feasibility of LIBS in the analysis of Sr, Ba and La in LiCl-KCl salt, experiments are carried out in open atmosphere after dissolving the salt in aqueous medium. It is well known that direct LIBS analysis of liquid samples results lower figure of merits as compared to solid [37]. As conversion of liquid into solid shows advantages [38–40], here aqueous samples are spread over filter paper and then LIBS analysis are carried out. Internal standard method [41] is used for quantification of the elements.

2. Experimental

2.1. Instrumentation

The plasma was generated in air at atmospheric pressure using a Q-switched Nd:YAG laser (Quantel, Brilliant) operated at 532 nm with repetition rate of 2 Hz. This laser generates pulse width of 8–10 ns. A plano-convex quartz lens of focal length 10 cm was used to focus the laser beam onto the target sample. The focal point was set about 4 mm below the target surface to minimize a breakdown above the surface. The spot size of the beam at the sample surface was about 300 μm . Light emitted from plasma was collected at an angle by an optical fiber of core diameter 600 μm (LTB, Germany), coupled to a collimator with a confocal length of 50 mm. The collected light is then transmitted to the other end of the fibre which is placed to the entrance slit of Aryelle 200 spectrometer (LTB, Germany). The dispersed light was detected by a CCD detector coupled to the spectrometer. Early plasma continuum was cut off by a mechanical chopper placed in front of the entrance slit of the spectrometer. The spectral range covered was 200–770 nm with a resolution of 0.02 nm at 250 nm. ‘Sophi’ software was used to obtain the spectrum. All the measured spectra were corrected for dark spectrum.

2.2. Sample preparation

A stock solution of salt mixture (60 wt% LiCl & 40 wt% KCl) was prepared by dissolving the chloride salts (Loba Chemie, India, 99.9 %) in water. The concentration of salt mixture in this stock was 25 wt% as above this concentration mixture was not fully soluble in water. For better solubility, ratio of wt% of LiCl:KCl was maintained at 60:40 instead of usual ratio of 44:56. High purity (> 99.95 %) rare earth oxides (La, Pr, Nd, Sm, Eu, Gd, Yb) and Y_2O_3 were procured from M/s Indian Rare Earths Ltd. and used for preparing their standard solutions by digesting with supra-pure HNO_3 (Merck make). RbCl, CsCl, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (M/s Sigma Aldrich) were used to prepare stock solutions. De-ionized water (18 M Ω) obtained from a Milli-Q (Millipore) system was used in the preparation of the stock solutions. Suitable dilutions were then made from these stock solutions to prepare experimental solutions. Five calibration standards were prepared by mixing suitable amounts of Sr, Ba and La from the stock solutions with salt mixture. The concentration of Sr, Ba and La in stock solutions was determined by ICP-AES. The concentration of the analytes in the calibration standards was ranged from 10 to 4000 ppm. Four samples containing different amounts of the analytes, salt mixture with different ions were prepared and treated as unknown. Acidity of 1.5 M was maintained in all of the experimental solutions to avoid any precipitation.

2.3. Measurement

12 μL of solution was transferred to a piece of filter paper (Whatman-540) and immediately placed over a tape (double sided) which was mounted on a SS plate holder. The solution spread over the paper and makes an oval shape ($\sim 14 \times 16 \text{ mm}^2$) sample layer on it. The SS plate was then placed over a motorized three-axis translation stage which allowed the acquisition of LIBS at different positions. For each measurement, single laser shots were recorded at 60 different positions and then averaged to improve reproducibility. For each concentration eight such sample loadings and measurements were performed. It is to be noted that the filter paper is not dried before the LIBS analysis like other reports [42,43], hence it is less time consuming and more convenient.

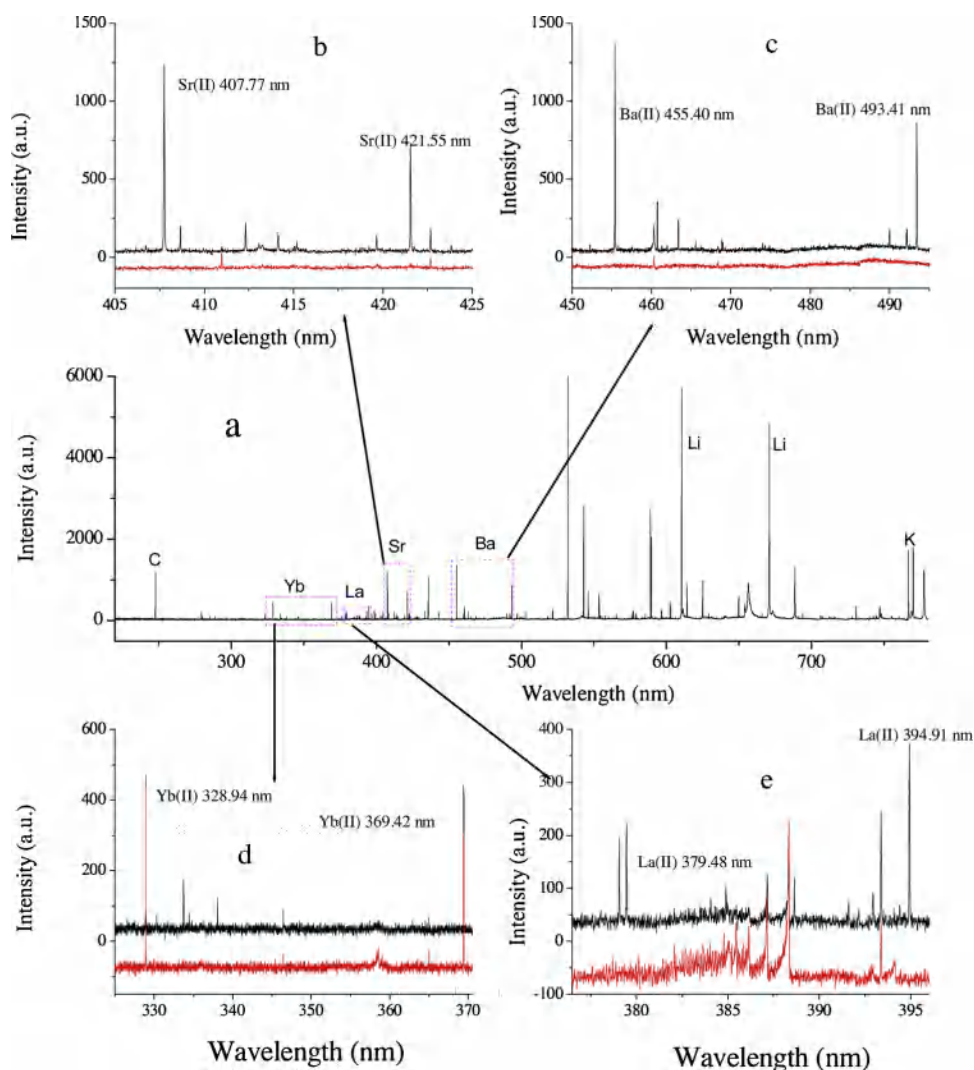


Fig. 1. a LIBS spectrum of Sr, Ba, La and Yb in 12.5 % LiCl-KCl salt. b–e Same spectrum is shown in the expanded window; the emission lines marked are used for calibration. The spectrum shown in red colour is without Sr, Ba and La; for clarity it is offset in Y-scale (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

3. Results and discussions

3.1. Selection of internal standard

It is well known that LIBS signal intensity strongly depends on many factors like laser pulse energy, physical parameter of the sample, efficiency of laser coupling with sample, ablated mass, environmental condition etc. Usually internal standard method is used

Table 1
Characteristics of spectral lines employed for quantitative analysis.

Line	Wavelength (nm)	Transition probability ($\times 10^7 \text{ s}^{-1}$)	Lower level (cm^{-1})	Higher level (cm^{-1})
Sr(II)	407.77	14.72	0.0	24516.65
Sr(II)	421.55	13.43	0.0	23715.19
Ba(II)	455.40	11.89	0.0	21952.42
Ba(II)	493.41	9.69	0.0	20261.56
La(II)	394.91	12.21	3250.35	28565.40
La(II)	398.85	7.20	3250.35	28315.25
Yb(II)	369.42	3.69	0.0	27061.82

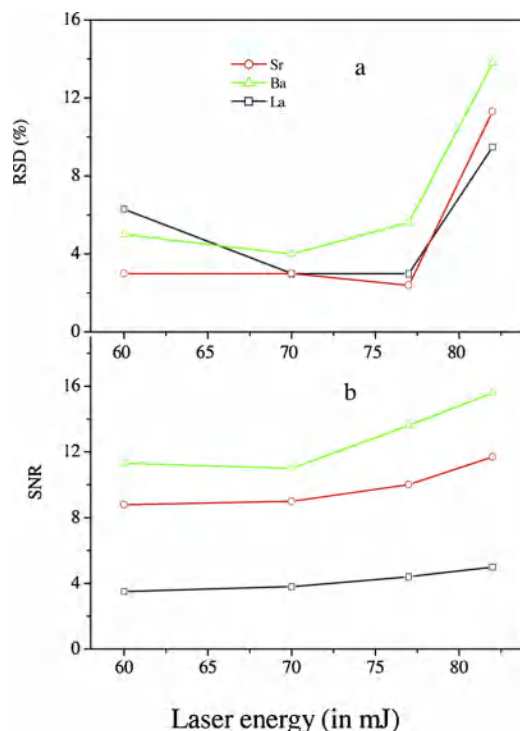


Fig. 2. a Variation of RSD and b SNR with laser energy.

to overcome any unwanted experimental fluctuation to obtain calibration curve [41]. In this method, the ratio of line intensity/area of the analyte of interest to the line intensity/area of the internal standard is plotted as a function of the concentration of the analyte. In our case, Li or K line can be used as internal standard provided their concentration remains nearly same. But in real sample, the presence of other fission products along with the analyte of interest makes the salt concentration to vary and hence the lines of Li/K could not be used as internal standard. Since, filter paper is used as substrate, the intense C line at 247.86 nm can be chosen as an internal standard. Preliminary experiments revealed 16 % RSD, when C line is used as an internal standard, whereas the RSD is less than 10 % when ytterbium (Yb) lines are chosen. Another advantage of choosing Yb as an internal standard is that it is not a fission product and hence for real sample analysis, known amount of it can be added for the purpose of quantitative analysis. Three intense lines of Yb at 328.94, 369.42 and 398.80 nm are observed in LIBS spectra. The first two lines are found to be interference free and can be used for analytical purpose. In the present study, 369.42 nm (YbII) line is chosen as an internal standard and the peak intensity is used for the calculation. The concentration of Yb was 1500 ppm in all our experimental solutions.

3.2. Selected analytical line

Fig. 1a shows a typical LIBS spectrum of a sample containing Sr, Ba and La in 12.5 % salt matrix along with Yb. The figure shows a couple of emission lines from Yb, Sr, Ba and La over 240–770 nm along with lines due to K and Li coming from the matrix. For quantitative estimation, two interference free lines for each element have been identified. These lines are marked in Fig. 1b–e and the corresponding spectroscopic data are given in the Table 1 [44]. It can be noticed that except La lines, Sr and Ba lines are resonant lines. To reduce the self-absorption effect, resonant lines are not a better choice but in our experimental conditions those lines have been chosen because their intensities can be measured with better accuracy even at low concentration.

3.3. Selected experimental condition

At the outset, in order to obtain optimum signal to noise ratio (SNR) and minimum relative standard deviation (RSD), experimental conditions like laser energy, laser repetition rate, number of laser pulses, time delay and gate width were varied. In our LIBS spectrometer, gate width was decided by the laser repetition rate. To ablate fresh sample point by each laser shot, 2 Hz was found to be optimum. Time delay was varied from 1.5 to 2.2 μ s and the best signal was obtained for 1.8 μ s delay. Laser energy controlled by the LIBS spectrometer was varied from 60 to 82 mJ and the spectra were recorded for a sample containing Sr, Ba and La with Yb as internal standard. Though the SNR was better for higher energy, but the RSD values for all the elements were found to be more. The variation of RSD values for the intensity ratios of emission lines of La(II) 394.91 nm, Sr(II) 421.55 nm and Ba(II) 455.40 nm with respect to Yb(II) 369.42 nm line are shown in Fig. 2a whereas variation of SNR are shown in Fig. 2b. For all the elements, RSD value was found to be least at 70 mJ and hence this laser energy was used in our following experiments.

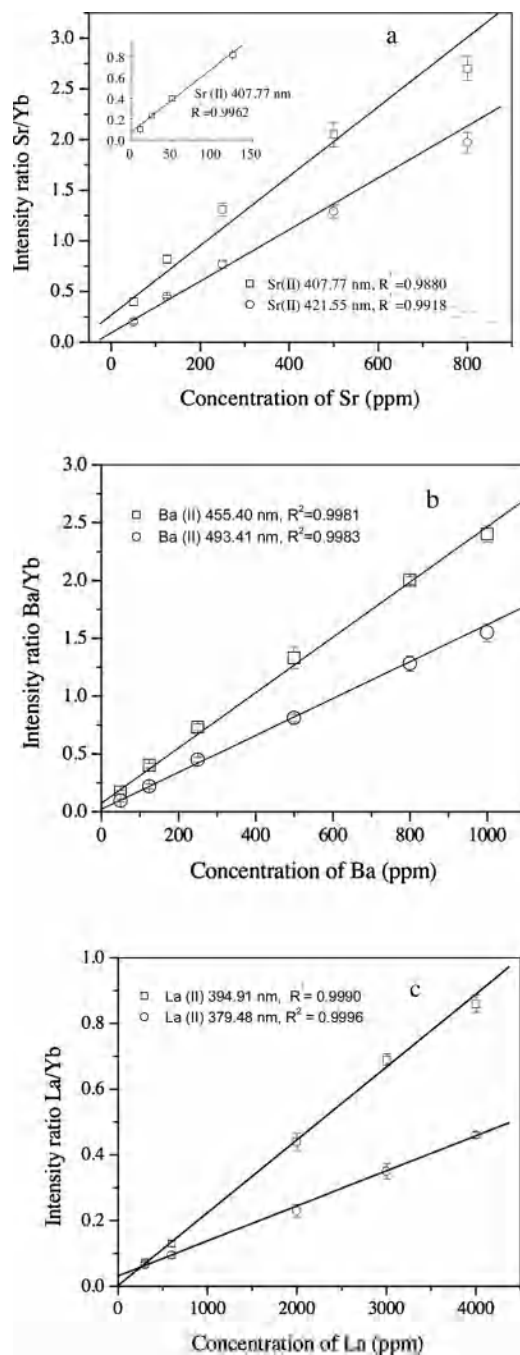


Fig. 3. Normalised elemental emissions of Sr (a), Ba (b) and La (c) as a function of concentration.

3.4. Calibration curves and detection limits

The feasibility of LIBS for quantitative analysis of Sr, Ba and La in LiCl-KCl matrix is evaluated by getting calibration curves. The normalized intensity of the selected emission lines as a function of the elemental concentration is plotted to obtain the calibration curve for each element. The normalized intensity as mentioned earlier is obtained by taking ratio of the intensity of the analyte line of interest with that of 396.42 nm line of Yb II. The calibration plots over which linearity has been observed are shown in Fig. 3a-c for Sr, Ba and La respectively. The concentration range shown here is 50–800 ppm for Sr, 50–1000 ppm for Ba and 300–4000 ppm for La respectively. The salt concentration used in all the experiments is 12.5 %. Each point in these plots corresponds to an average of eight measurements of eight different sampling. It can be seen from the plots that regression coefficient (R^2) values are nearly one (average value of 0.99) for both the emission lines chosen for each of the elements. It clearly tells that out of two emission lines any

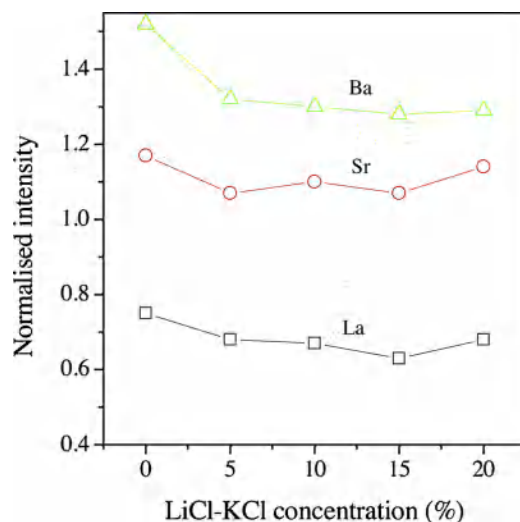


Fig. 4. Variation of normalized intensity of Ba, Sr and La with LiCl-KCl concentration.

Table 2

Composition of the major elements ('other ions') present in 12.5 % salt matrix.

Element	Concentration found in 12.5 % salt (ppm) ^a	Concentration used in synthetic samples (ppm)
RbCl	262	300
YCl ₃	550	800
CsCl	1912	2000
PrCl ₃	888	1400
NdCl ₃	3038	5800
SmCl ₃	575	1100
EuCl ₃	38	760
UCl ₃	7450	2380
Total	14,713	14,540

^a [51].

Table 3

Comparison of the actual and measured concentration of La, Sr and Ba in salt mixture.

Sample ID	Salt (%)	'Other ions' (ppm)	Concentration as prepared (ppm)	Concentration as measured (ppm)		
				LIBS	ICP-AES	
S1	10	0	Sr	300	285 (-5.0 %)	-
			Ba	300	332 (+10.7 %)	-
			La	400	443 (+10.8 %)	-
S2	10	0	Sr	80	73 (-8.8 %)	-
			Ba	165	179 (+8.5 %)	-
			La	2000	1890 (-5.5 %)	-
Syn1	12.5	14540 ^a	Sr	180	200 (+11.1 %)	194 (+7.8 %)
			Ba	180	201 (+11.7 %)	198 (+10.0 %)
			La	620	562 (-9.4 %)	690 (+11.3 %)
Syn2	12.5	14540 ^a	Sr	360	330 (-8.3 %)	380 (+5.6 %)
			Ba	360	348 (-3.3 %)	390 (+8.3 %)
			La	1240	1115(-10.0 %)	1270 (+2.4 %)

^a according to Table 2.

one can be used for analysis. The more sensitive line of Sr i.e. 407.77 nm can be used to cover the concentration range below 50 ppm and it is shown in the inset of Fig. 3a. Using this line, linear calibration plot is observed over 10 – 125 ppm of Sr with R² value of 0.9962.

To use these calibration plots for analysis purpose, one needs to check the effect of salt concentration on the plots, as in real sample salt concentration may vary depending on the presence of other fission products along with the elements of interest. Fig. 4 shows the variation of normalised intensity of La (3000 ppm), Sr (400 ppm) and Ba (800 ppm) over salt concentration varied from 0 % to 20 %. It can be seen from the figure that the maximum value was obtained when no salt was present. As salt concentration is

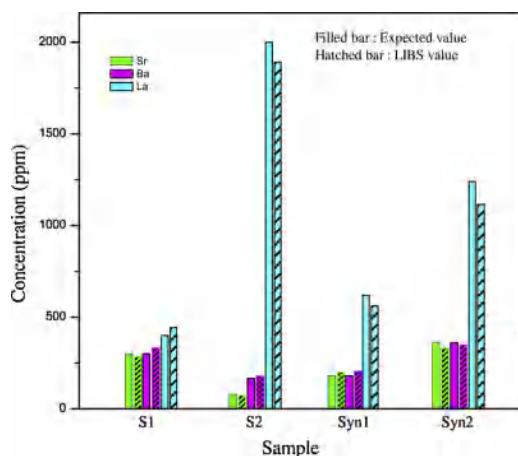


Fig. 5. Comparison of the expected values (filled bars) and LIBS values (hatched bars) of samples.

raised to 5 %, the normalised intensity is decreased by nearly 13 % and there is a slight variation in intensities over the range 5–20% of salt. It clearly tells that the calibration plots shown in Fig. 3a-c can be used for quantitative analysis of samples in LiCl-KCl matrix over a wide range of salt concentration (5–20 %) with adequate accuracy.

The detection limits (LOD) of the elements were calculated using $3\sigma/s$ criteria where σ is the standard deviation of eight experimentally measured normalised intensity of the element at the lowest concentration and s is the slope of the calibration curve. The LODs for Sr, Ba and La using the calibration plots constructed with 421.55 (for Sr), 455.40 (for Ba) and 394.91 nm (for La) lines are 21, 19 and 68 ppm respectively at 12.5 % salt matrix. In case of Sr, 4 ppm LOD can be achieved by using 407.77 nm line. The LODs measured in our experiments are very much comparable to reported values. Using multivariate analysis percentage level quantification of La were reported in graphite matrix and geological samples [34,35]. A few ppm of detection limits for Ba and Sr were reported in ice/10 % soil mixture in a controlled atmosphere of CO₂ [45,46]. The LOD for Ba in sand and soil matrix was reported to be 76 and 42 ppm respectively [47]. About 10 ppm LOD for Sr and Ba was reported in glass window by Deftar et al. [48]. Picogram (pg) level quantification of Sr and Ba in micro-drops which corresponds to LOD of nearly 10 ppm was reported by Cahoon et al. [49].

3.5. Quantitative analysis

Four unknown samples containing all the three elements with varied concentration were prepared. Two of these solutions contain ‘other ions’ which constitute major elements present in salt phase along with the analytes of interest [50]. The concentrations of ions are provided in Table 2 and they are based on a salt composition in the electro-refining bath of an experimental breeder reactor (EBR II) that is processed from nuclear fuel [51]. The concentration of ‘other ions’, given in this Table, corresponds to 12.5 % salt mixture. All these synthetic solutions were subjected to LIBS analysis under the same experimental conditions of those of standards. The calibration curves having more slope value were used for obtaining the concentration of La and Ba. For Sr, calibration curve with slope having less value was used as the R² value of the corresponding fit was better. The measured values are given in Table 3. It can be seen from this table that the LIBS values are in good agreement with the expected values. The estimated values are also shown graphically in Fig. 5. The concentrations of the analytes in samples (Syn1 and Syn2) containing ‘other ions’ were also measured by ICP-AES after dilution by 100 times. The values obtained are also provided in the same table. It can be seen from the table that the values obtained from ICP-AES analysis are higher than the expected one for all cases. This could be due to the presence of high content of LiCl-KCl mixture and ‘other ions’ (total ~ 1400 ppm) which probably enhances the emission line intensities of the analytes. It is to be noted here that the results obtained by LIBS does not show any such systematic error.

4. Conclusion

In the present work, the feasibility of LIBS as an analytical method for the measurement of Sr, Ba and La contents in LiCl-KCl matrix using Yb as an internal standard has been demonstrated. An accuracy of 5–11 % has been achieved in the estimated values for synthetic samples using LIBS technique. Further, a comparison of the estimates with ICP-AES analysis verifies LIBS versatility in the simultaneous quantification of these elements for pyro-processing. The LIBS measurement is advantageous over ICP based method as sample dilution by nearly two orders is required in later to avoid the matrix effect. Calibration curve does not change significantly even up to 20 % of salt mixture and hence the present method can be easily applied for pyro-processing. This is certainly an encouraging for LIBS technique in nuclear industry for its robustness in quantitative multi elemental analysis.

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References

- [1] R. Noll, C.F. Begemann, S. Connemann, C. Meinhardt, V. Sturm, LIBS analyses for industrial applications – an overview of developments from 2014 to 2018, *J. Anal. At. Spectrom.* 33 (2018) 945–956.
- [2] A.P.M. Michel, Review: Applications of single-shot laser-induced breakdown spectroscopy, *Spectrochim. Acta B* 65 (2010) 185–191.
- [3] D.W. Hahn, N. Omenetto, Laser-induced breakdown spectroscopy (LIBS), part II: review of instrumental and methodological approaches to material analysis and applications to different fields, *Appl. Spectrosc.* 66 (2012) 347–419.
- [4] F. Colao, S. Almaguilla, L. Caneve, G. Maddaluno, T. Fornal, P. Gasior, M. Kubkowska, M. Rosinski, LIBS experiments for quantitative detection of retained fuel, *Nucl. Mat. Energy* 12 (2017) 133–138.
- [5] V.C. Costa, J.P. Castro, D.F. Andrade, D.V. Babos, J.A. Garcia, M.A. Speranca, T.A. Catelani, E.R.P. Filho, Laser-induced breakdown spectroscopy (LIBS) applications in the chemical analysis of waste electrical and electronic equipment (WEEE), *TrAC Trends in Anal. Chem.* 108 (2018) 65–73.
- [6] I. Rehan, M.A. Gondal, K. Rehan, S. Sultana, M.A. Dastageer, F.F. Al-Adel, LIBS for the detection of lead in ready to use henna paste and nutrients in fresh henna leaves and cultivated soils, *Talanta* 199 (2019) 203–211.
- [7] G. Bilge, B. Sezer, K.E. Eseller, H. Berberoglu, H. Koksel, I.H. Boyaci, Ash analysis of flour sample by using laser-induced breakdown spectroscopy, *Spectrochim. Acta B* 124 (2016) 74–78.
- [8] S. Moncayo, S. Manzoor, J.D. Rosales, J. Anzano, J.O. Caceres, Qualitative and quantitative analysis of milk for the detection of adulteration by laser induced breakdown spectroscopy (LIBS), *Food Chem.* 232 (2017) 322–328.
- [9] M. Khater, Trace detection of light elements by laser-induced breakdown spectroscopy (LIBS): applications to non-conducting materials, *Opt. Spectrosc.* 115 (2013) 574–590.
- [10] E.-Y. Choi, S.M. Jeong, Electrochemical processing of spent nuclear fuels: an overview of oxide reduction in pyroprocessing technology, *Prog. Nat. Sci. : Mat. Int.* 25 (2015) 572–582.
- [11] T. Koyama, Y. Sakamura, M. Iizuka, T. Kato, T. Murakami, J.-P. Glatz, Development of pyro-processing fuel cycle technology for closing actinide cycle, *Proc. Chem.* 7 (2012) 772–778.
- [12] D. Rodrigues, G.D. Klie, S. Delpech, Pyrochemical reprocessing of molten salt fast reactor fuel: focus on the reductive extraction step, *Nukleonika* 60 (2015) 907–914.
- [13] J.L. Willit, W.E. Miller, J.E. Battles, Electrorefining of uranium and plutonium – a literature review, *J. Nucl. Mater.* 195 (1992) 229–249.
- [14] K. Nagarajan, B.P. Reddy, S. Ghosh, G. Ravisankar, K.S. Mohandas, U.K. Mudali, K.V.G. Kutty, K.V.K. Viswanathan, C.A. Babu, P. Kalyanasundaram, P.R.V. Rao, B. Raj, Development of pyrochemical reprocessing for spent metal fuels, *Energy Proc.* 7 (2011) 431–436.
- [15] D. Vaden, S.X. Li, B.R. Westphal, K.B. Davies, T.A. Johnson, D.M. Pace, Engineering- scale liquid cadmium cathode experiments, *Nucl. Tech.* 162 (2008) 124–128.
- [16] K.C. Pithaiah, K. Sujatha, J. Deepitha, S. Ghosh, N. Sivaraman, Recovery of uranium and plutonium from pyrochemical salt matrix using super critical fluid extraction, *The J. Super. Fluids* 147 (2019) 194–204.
- [17] Y.-Z. Cho, T.-K. Lee, H.-C. Eun, J.-H. Choi, In-T. Kim, G.-Il Park, Purification of used eutectic (LiCl–KCl) salt electrolyte from pyroprocessing, *J. Nucl. Mater.* 437 (2013) 47–54.
- [18] M.T. Harrison, H.E. Simms, A. Jackson, R.G. Lewin, Salt waste treatment from a LiCl–KCl based pyrochemical spent fuel treatment process, *Radiochim. Acta* 96 (2008) 295–301.
- [19] H.C. Eun, J.H. Choi, N.Y. Kim, T.K. Lee, S.Y. Han, K.R. Lee, H.S. Park, D.H. Ahn, A reactive distillation process for the treatment of LiCl–KCl eutectic waste salt containing rare earth chlorides, *J. Nucl. Mater.* 480 (2016) 69–74.
- [20] A. Williams, S. Phongikaroon, M. Simpson, Separation of CsCl from a ternary CsCl–LiCl–KCl salt via a melt crystallization technique for pyroprocessing waste minimization, *Chem. Eng. Sci.* 89 (2013) 258–263.
- [21] A.N. Williams, S. Phongikaroon, Laser-induced breakdown spectroscopy (LIBS) in a novel molten salt aerosol system, *Appl. Spectrosc.* 71 (2017) 744–749.
- [22] J.-H. Choi, H.-C. Eun, H.-S. Park, D.-H. Ahn, A study on the separation and solidification of group II nuclides from LiCl waste salt generated from a pyrochemical process, *J. Nucl. Fuel Cycle Waste Tech.* 13 (S) (2015) 77–84.
- [23] H.-C. Eun, H.-C. Yang, Y.-J. Cho, H.-S. Park, E.-H. Kim, I.-T. Kim, Separation of pure LiCl–KCl eutectic salt from a mixture of LiCl–KCl eutectic salt and rare-earth precipitates by vacuum distillation, *J. Nucl. Sci. Tech.* 44 (10) (2007) 1295–1300.
- [24] Y. Liu, K. Liu, L. Luo, L. Yuan, Z. Chai, W. Shi, Direct separation of uranium from lanthanides (La, Nd, Ce, Sm) in oxide mixture in LiCl–KCl eutectic melt, *Electrochim. Acta* 275 (2018) 100–109.
- [25] Y.-D. Yan, Y.-L. Xu, M.-L. Zhang, Y. Xue, W. Han, Y. Huang, Q. Chen, Z.-J. Zhang, Electrochemical extraction of neodymium by co-reduction with aluminum in LiCl–KCl molten salt, *J. Nucl. Mater.* 433 (2013) 152–159.
- [26] A.J. Effenberger, Methods for Measurement of Heterogeneous Materials With Laser Induced Breakdown Spectroscopy (LIBS), Ph.D. Dissertation, University of California, San Diego, 2009.
- [27] A. Weisberg, R.E. Lakis, M.F. Simpson, L. Horowitz, J. Craparo, Measuring lanthanide concentrations in molten salt using laser-induced breakdown spectroscopy (LIBS), *Appl. Spectrosc.* 68 (2014) 937–948.
- [28] A. Williams, S. Phongikaroon, Laser-induced breakdown spectroscopy (LIBS) measurement of uranium in molten salt, *Appl. Spectrosc.* 72 (2018) 1029–1039.
- [29] A. Williams, K. Bryce, S. Phongikaroon, Measurement of cerium and gadolinium in solid lithium chloride–potassium chloride salt using laser-induced breakdown spectroscopy (LIBS), *Appl. Spectrosc.* 71 (2017) 2302–2312.
- [30] T. Trejos, C.V. Pyl, K.M. Hoggatt, A.L. Alvarado, L.E. Arroyo, Fast identification of inorganic and organic gunshot residues by LIBS and electrochemical methods, *Forensic Chem.* 8 (2018) 146–156.
- [31] S. Zivkovic, J. Savovic, M. Kuzmanovic, J. Petrovic, M. Momcilovic, Alternative analytical method for direct determination of Mn and Ba in peppermint tea based on laser induced breakdown spectroscopy, *Micro. J.* 137 (2018) 410–417.
- [32] A. Lang, D. Engelber, N.T. Smith, D. Trivedi, O. Horsfall, A. Banford, P.A. Martin, P. Coffey, W.R. Bower, C. Walther, M. Weiß, H. Bosco, A. Jenkins, G.T.W. Law, Analysis of contaminated nuclear plant steel by laser-induced breakdown spectroscopy, *J. Haz. Mat.* 345 (2018) 114–122.
- [33] M.Z. Martin, S. Allman, D.J. Brice, R.C. Martin, N.O. Andre, Exploring laser-induced breakdown spectroscopy for nuclear materials analysis and in-situ applications, *Spectrochim. Acta B* 74–75 (2012) 177–183.
- [34] M. Martin, R.C. Martin, S. Allman, D. Brice, A. Wymore, N. Andre, Quantification of rare earth elements using laser-induced breakdown spectroscopy, *Spectrochim. Acta B* 114 (2015) 65–73.
- [35] C.R. Bhatt, J.C. Jain, C.L. Gouguel, D.L. McIntyre, J.P. Singh, Determination of rare earth elements in geological samples using laser-induced breakdown spectroscopy (LIBS), *Appl. Spectrosc.* 72 (2018) 114–121.
- [36] S. Maji, S. Kumar, K. Sundararajan, K. Sankaran, Feasibility study for quantification of lanthanides in LiF–KCl salt by laser induced breakdown spectroscopy, *J. Radioanal. Nucl. Chem.* 314 (2017) 1279–1285.
- [37] V. Lazic, F. Colao, R. Fantoni, V. Spizzichino, S. Jovicevic, Underwater sediment analyses by laser induced breakdown spectroscopy and calibration procedure for fluctuating plasma parameters, *Spectrochim. Acta B* 62 (2007) 30–39.
- [38] D.M.D. Pace, C.A. D'Angelo, D. Bertuccelli, G. Bertuccelli, Analysis of heavy metals in liquids using laser induced breakdown spectroscopy by liquid-to-solid matrix conversion, *Spectrochim. Acta B* 61 (2006) 929–933.
- [39] M.A. Aguirre, E.J. Selva, M. Hidalgo, A. Canals, Dispersive liquid-liquid microextraction for metals enrichment: a useful strategy for improving sensitivity of laser-induced breakdown spectroscopy in liquid samples analysis, *Talanta* 131 (2015) 348–353.

- [40] J. Xiu, S. Zhong, H. Hou, Y. Lu, R. Zheng, Quantitative determination of manganese in aqueous solutions and seawater by laser-induced breakdown spectroscopy (LIBS) using paper substrates, *Appl. Spectrosc.* 68 (2014) 1039–1045.
- [41] W.T.Y. Mohamed, Improved LIBS limit of detection of Be, Mg, Si, Mn, Fe and Cu in aluminum alloy samples using a portable Echelle spectrometer with ICCD camera, *Opt. Laser Tech.* 40 (2008) 30–38.
- [42] D. Alamelu, A. Sarkar, S.K. Aggarwal, Laser-induced breakdown spectroscopy for simultaneous determination of Sm, Eu and Gd in aqueous solution, *Talanta* 77 (2008) 256–261.
- [43] D. Bae, S.H. Nam, S.H. Han, J. Yoo, Y. Lee, Spreading a water droplet on the laser- patterned silicon wafer substrate for surface-enhanced laser-induced breakdown spectroscopy, *Spectrochim. Acta B* 113 (2015) 70–78.
- [44] www.pmp.uni-hannover.de/cgi-bin/ssi/test/kurucz/sekur.html.
- [45] Z.A. Arp, D.A. Cremers, R.C. Wiens, D.M. Wayne, B. Salle, S. Maurice, Analysis of water ice and water ice/soil mixtures using laser-induced breakdown spectroscopy: application to Mars polar exploration, *Appl. Spectrosc.* 58 (2004) 897–909.
- [46] A.K. Knight, N.L. Scherbarth, D.A. Cremers, M.J. Ferris, Characterization of laser- induced breakdown spectroscopy (LIBS) for application to space exploration, *Appl. Spectrosc.* 54 (2000) 331–340.
- [47] A.S. Eppler, D.A. Cremers, D.D. Hickmott, M.J. Ferris, A.C. Koskelo, Matrix effects in the detection of Pb and Ba in soils using laser-induced breakdown spectroscopy, *Appl. Spectrosc.* 50 (1996) 1175–1181.
- [48] M.M.E. Deftar, N. Speers, S. Eggins, S. Foster, J. Robertson, C. Lennard, Assessment and forensic application of laser-induced breakdown spectroscopy (LIBS) for the discrimination of Australian window glass, *For. Sci. Int.* 241 (2014) 46–54.
- [49] E.M. Cahoon, J.R. Almirall, Quantitative analysis of liquids from aerosols and microdrops using laser induced breakdown spectroscopy, *Anal. Chem.* 84 (2012) 2239–2244.
- [50] D. Hundry, I.B. Giboire, A. Rakhmatullin, C. Bessada, F. Bart, S. Jobic, P. Deniard, Synthesis of rare earth phosphates in molten LiCl–KCl eutectic: application to preliminary treatment of chlorinated waste streams containing fission products, *J. Nucl. Mater.* 381 (2008) 284–289.
- [51] S. Priebe, K. Bateman, The ceramic waste form process at Idaho National Laboratory, *Nucl. Tech.* 162 (2008) 199–207.