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14. ABSTRACT Laser Induced Breakdown Spectroscopy (LIBS) can be used for the chemical characterization of glass to provide evidence of an association between a fragment found at a crime scene to a source of glass of known origin. Two different laser irradiances, 266 nm and 1064 nm, were used to conduct qualitative and quantitative analysis of glass standards. Single-pulse and double-pulse configurations and lens-to-sample-distance (LTSD) settings were optimized to yield the best laser-glass coupling. Laser energy and acquisition timing delays were also optimized to					
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Report Title

Wavelength Dependence on the Forensic Analysis of Glass by Laser Induced Breakdown Spectroscopy

ABSTRACT

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List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

1 paper to be submitted to "Applied Optics" entitled " Wavelength Dependence on the Forensic Analysis of Glass by Laser Induced Breakdown Spectroscopy"

Number of Papers published in peer-reviewed journals: 0.00

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(c) Presentations

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Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Erica Cahoon	0.50
FTE Equivalent:	0.50
Total Number:	1

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Jose Almirall	0.05	No
FTE Equivalent:	0.05	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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This section only applies to graduating undergraduates supported by this agreement in this reporting period

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Names of personnel receiving PhDs

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Total Number:

Names of other research staff

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Wavelength Dependence on the Forensic Analysis of Glass by Laser Induced Breakdown Spectroscopy

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Abstract:

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1. Introduction

Glass is a commonly encountered type of trace evidence found at many crime scenes. Glass fragments can provide forensic investigators valuable information of association to a crime and often link a suspect to the scene of a crime. When someone breaks glass as in the case of a hit-an-run accident, for example, a number of tiny fragments may be transferred to both the victim and the driver. The fragments can be used as evidence associating the individuals to the event. Since much of the glass formulations are very similar in chemical composition a highly discriminating technique is required to distinguish between similar fragments that have originated from different manufacturing sources.

Numerous elemental analysis techniques have been employed for the discrimination and chemical characterization of glass. These techniques include spark source mass spectrometry [1], atomic emission spectroscopy [2,4], atomic absorption spectroscopy (AAS) [3], x-ray fluorescence (XRF) [3,4], neutron activation analysis (NAA) [5], scanning electron microscopy (SEM) coupled to both energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy [6], particle induced x-ray emission (PIXE) [6], inductively coupled plasma atomic emission spectrometry (ICP-AES) [3,4,7], inductively coupled plasma mass spectrometry (ICP-MS) [8], and laser ablation-ICP-MS (LA-ICP-MS) [9].

These mature techniques are known for their advantages but also are subject to certain limitations. The use of laser ablation as a sample introduction system for ICP-MS has simplified the direct analysis of solid samples such as glass and is regarded as the “gold standard” for the discrimination between similar glass samples known to originate from different sources, or to determine if the glass samples are indistinguishable from the source of origin. While excellent analytical performance results from the elemental analysis of glass evidence with LA-ICP-MS, this complex and expensive instrumentation requires a well-trained operator and a pre-determined element menu prior to analysis. LA-ICP-MS is out of reach for many forensic laboratories due to the high cost of acquisition and operation of this instrumentation. There is a need to develop a less expensive alternative to LA-ICP-MS that is also a robust, precise and accurate method to evaluate the chemical characterization of trace evidence materials that can be encountered in the forensic laboratory.

LIBS is an emerging method of atomic emission spectroscopy proving to be a viable alternative for the elemental characterization of forensic glass samples [10,11]. The advantages of LIBS have been clearly established and include the ability for real time analysis, little-to-no sample preparation or destruction, ease of use, low cost, and simultaneous multi-element detection without the need to know the element menu to be analyzed. Many variables such as laser power, laser wavelength, gate delay, integration time, and sample matrix will influence the precision and accuracy of LIBS measurements. LIBS is a comparable method to LA-ICP-MS in that small sample sizes may be analyzed with good precision but there is no, as of yet, agreement on the optimum operation conditions that result in the best quantitative data.

Commercial laser ablation systems are now equipped with shorter wavelengths, i.e. 193nm, 213 nm or 266 nm because it has been shown that these UV LA systems provide better laser-sample coupling resulting in increased mass removal [12] compared to IR ablation, better crater morphology and improved reproducibility of signal, demonstrating that the shorter wavelengths provide a more controlled ablation rate [12,13]. For this reason, our group has been interested in the investigation and comparison between the use of UV (266 nm) and the more widely used (1064 nm) wavelength for LIBS analysis. Several researchers have reported some results from the use of different wavelengths [14] ranging from the plasma characteristics such as temperature and density [14] and plasma formation [15] to fractionation [12], laser-sample coupling [12,16], and quantification of analytical results [14,17]. The coupling of the laser energy to the sample is clearly affected by the irradiation wavelength. Previous studies have shown that the UV wavelength can improve the coupling efficiency when compared to the longer wavelengths, i.e. 532 nm and 1064 nm [14,12].

The focus of this study was to investigate the effects on varying the irradiation wavelength on the analytical results for forensic glass analysis. Quantification of the trace elements Sr, Ba, and K, were determined for both 266 nm and 1064 nm under varying conditions. Although LIBS produces an information-rich spectrum, only a few elements will actually provide the forensic investigator with useful discrimination information for comparison purposes. The variations of the major constituents in glass, i.e. Si, Ca, or Na, do not discriminate between similar formulations [18] but the comparison of the trace element composition, usually arising from impurities from raw materials or due to the slight differences between glass manufacturing plants, do provide excellent discrimination between glass fragments of different manufacturing origin.

2. Experimental

The LIBS instrumentation presented in this work consisted of different single-pulse and double-pulse wavelength configurations. The LIBS system built in our laboratory consists of a Q-switched Nd:YAG NewWave Research Tempest laser (New Wave Research, Fremont, CA) operating at the fourth harmonic (266 nm) and a second Nd:YAG Big Sky laser (Big Sky, MT) operating at the fundamental wavelength of 1064 nm, both having pulse widths of 3-5 ns full width half max. Flashlamps and q-switches were both externally controlled by a Berkeley Nucleonics (San Rafael, Ca) delay generator model 656. Beam expanders were used to enlarge the beams from ~4 mm to nearly 12 mm using a Galilean telescope. The beams were then focused at a normal incidence to the sample through a plano-convex lens with a focal length of 150 mm (see Fig. 1) with a 90° viewing angle to the laser.

To ensure representative sampling and to account for any heterogeneity, each glass standard was analyzed 5 times at different locations. Both single-pulse and double-pulse spectra were collected as a result of 100 laser shots with the accumulation of the last 50 shots used to generate the spectra for analysis conducted at atmospheric pressure in air. In order to gain the best reproducible optical emission spectra possible, both the 266 nm and the 1064 nm experiments were optimized for laser power, lens-to-sample surface-distance (LTSD), gate delay, and integration time. Both laser energies for the single-pulse ablation were held at constant values throughout the experiments at 29 mJ and 47 mJ for the 266 nm and the 1064 nm laser, respectively. The laser was focused 1.30 mm into the sample surface during the 266 nm experiment and 0.50 mm into the surface for the 1064 nm experiment.

A Scanning Electron Microscope (SEM) Philips XL 30 with EDX detector (Philips, The Netherlands and EDAX, USA, respectively) was used for the imaging of the craters created by UV and IR ablation. The amount of mass ablated was calculated using the density and volume. Using a glass density of 2.5 g/cm³, the volume was converted to nanograms removed.

The laser beams are focused perpendicular and parallel to the sample to create either single-pulse ablation or double-pulse pre-spark or plasma reheating schemes. The geometric configurations for double-pulse LIBS were optimized as follows; the orthogonal configuration included one beam perpendicular to the surface while the other pulse was parallel to the surface. During pre-spark experiment, the IR beam was focused 0.75 mm above the sample

surface at 160 mJ creating a spark in air followed 7 μs later by the perpendicular UV ablation pulse at 29 mJ. In the plasma reheat configuration, the UV ablation beam was pulsed at an energy of 27 mJ, followed 400 ns later by a 35 mJ IR beam, focused 0.75 mm above the sample to reheat the plasma.

Optical emissions from the plasma were acquired from the side (90°) by a pair of plano-convex lenses ($f = 75$ mm) onto a fiber with a diameter of 50 μm that was coupled to the entrance slit of an Andor Mechelle 5000 spectrometer equipped with an Andor iStar intensified CCD camera using a 1024 X 1024 chip. The optimized gate delays for both the 266 nm and 1064 nm experiments were 1.2 μs , while the optimized integration time was 3.5 μs and 11.0 μs for the 266 nm and the 1064 nm wavelengths, respectively. The broadband detector captured the spectral range between 200-950 nm with a resolution of ~ 5000 . Due to broadband spectral analysis, the repetition rate for the spectrometer was ~ 0.67 Hz.

Analytical glass standards from National Institute of Standard and Technology (NIST) 614, 610, 612, 1831 and Bundeskriminalamt (BKA) glass reference standards FGS 01 and FGS 02 were used for development of the analytical protocols and to determine the precision, accuracy and repeatability of the LIBS analysis.

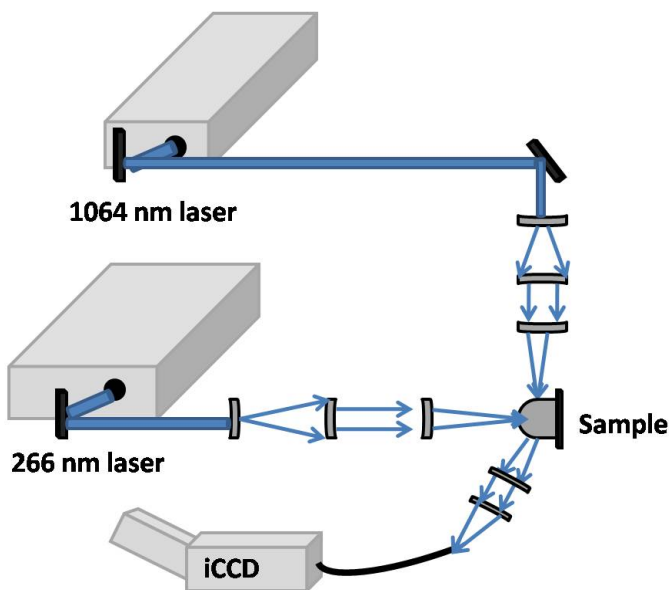


Fig. 1 Simple Single-Pulse and Double-Pulse LIBS schematic

3. Results and Discussion

Quantitative spectral analysis by LIBS involves relating the LIBS signal produced to the concentration of the selected element(s) in the matrix. For optimized performance, the experiments were conducted to study the effects of changing the various parameters.

3.1 Crater Morphology.

LTSD is a critical parameter for LIBS measurements. A change in the depth of focus can affect the LIBS signal and reproducibility. It was found that by defocusing the beam, forcing the laser to focus *into* the surface, the reproducibility and precision of the LIBS emission signals improved. It was then determined a requirement to focus the beam into the surface for the 1064 irradiance, to prevent shattering and cracking of the glass. The optimal LTSD determined for both the 1064 nm and 266 nm wavelengths were 0.50 mm and 1.30 mm focused into the sample, respectively.

LIBS typically removes mass from the sample in the ng- μ g range, classifying it as a surface sampling technique. However, multiple pulses at the same location can be used to progressively ablate the surface, thereby removing more material and permitting depth profiling or bulk analysis of the sample. Researchers have reported that the 266 nm ablation removes more mass than the 532 nm or 1064 nm [14,16,17] ablation experiments, which may be due to the better energy coupling provided by the UV combined with less plasma shielding. The crater diameter has been proven independent of the sample matrix, while the crater depth is dependent on sample matrix [19]. It has been theorized that more mass ablated with minimal sample heating can provide a more stoichiometric sampling [12]. It has been demonstrated that the IR plasma is hotter [20], which will increase the plasma shielding and reduce the amount of the IR energy that can be transferred to the sample surface [13].

Crater morphology produced at these LTSDs resulted in a diameter of 75 μ m and depth of 70 μ m for the 266 nm laser and a diameter of 37 μ m and depth of 26 μ m for the 1064 nm laser. The total mass removed by the 266 nm ablation was found to be ~790 ng, approximately ten times higher than that of the 1064 nm, 81 ng. It was determined that the differences of the mass removed between the single and double-pulse LIBS ablations was negligible, this is in agreement with previous research conducted by Santagata et al [21]. However, this contradicts research reported by Scaffidi et al., where they reported an eight to ten fold increase in mass ablated using the orthogonal double-pulse configuration [22].

The crater morphology can be appreciated at high 1000 times magnification as shown in Fig. 2, demonstrating the differences for 100 shot ablations from the 266 nm ablations (Fig 2a) compared to the 1064 nm

ablations (Fig 2b). Investigation of the crater morphology also reveals a more uniform crater produce by the 266 nm laser, which may translate to better precision in LIBS measurements.

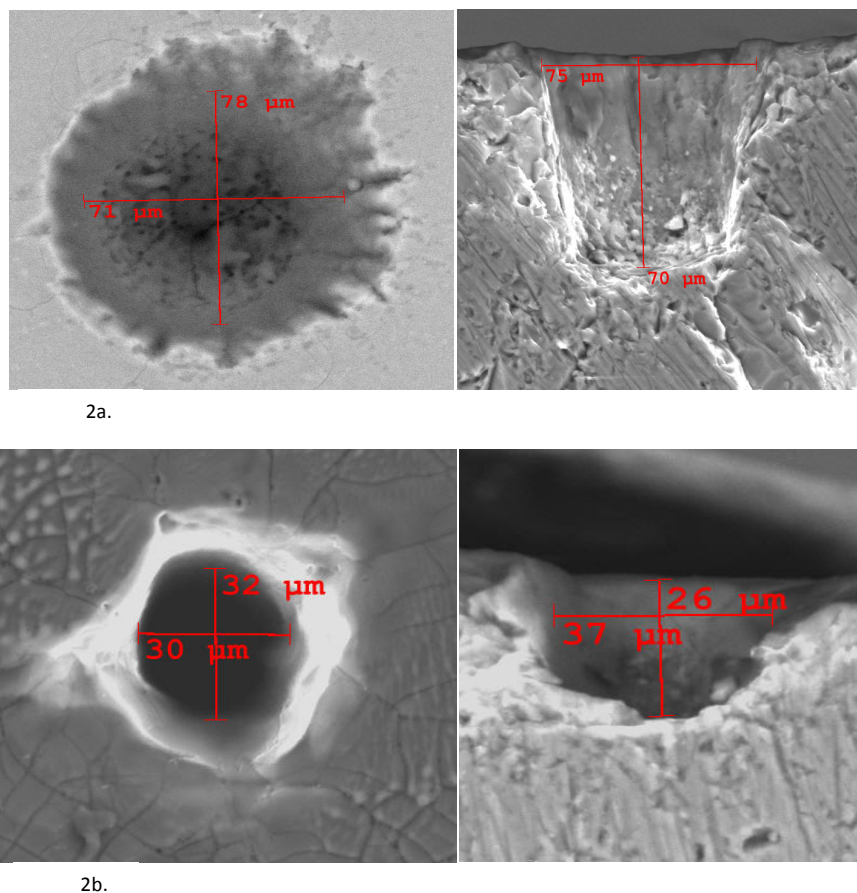


Fig. 2. 2a) Crater formed using a 266 nm laser on NIST glass stanard 1831, 2b) Crater formed using a 1064 nm laser on NIST glass standard 1831

3.2 Calibration Curves

Quantitative analysis by LIBS is still difficult and many quantification methods have been proposed for chemical analyses. One of the key reasons for the proposal of different methods is due to the lack of standard reference materials. However, the availability of glass standard reference materials permits calibration curves for the quantitative chemical analyses and have been proven effective for many years.

Construction of the calibration curves were produced by the line intensities (max counts of intensity minus the background). The calibration curves of the different atomic lines of the same element were very reproducible (see the error bars in figures 3-5) and were utilized for the quantification of trace elements in glass. All chosen spectral

lines have minimal spectral interferences. Each point on the calibration curves represent an average of five replicates, with the second 50 of 100 shots being averaged. The vertical error bars are represented as ± 1 standard deviation calculated from the 5 replicates. The five glass standard reference materials and their corresponding concentrations are listed in Table 1. NIST glass standard 1831 is a float glass formulation and was analyzed twice for this study, with the second set of measurements treated as an “unknown” sample for comparison purposes. Limits of detection (LOD) and limits of quantitation (LOQ) were calculated according to $LOD=3s_B$ and $LOQ=10s_B$, where s_B is the standard deviation of the background, which is taken as close to the emission line as possible without encountering spectral interferences.

Trace elements K I 766.49 nm, Ba II 493.41 nm, Sr II 407.77 nm and Ti II 336.12 nm, were chosen due to previous work by our group, demonstrating the high discriminating power of these elements in the glass matrix [10].

Glass						
SRM	Sr	Ba	Al	K	Mg	Ti
1831	89	32	6381	2738	2116	114
610	497	424	10006	486	465	434
612	76	38	11165	66	77	48
FGS 1	57	40	1500	920	23900	69
FGS 2	253	199	7400	4600	23400	326

Table 1. Certified concentration of glass standards reported in $\mu\text{g/g}$ (ppm)

3.2.1 Single-Pulse LIBS

Single-pulse LIBS spectra were acquired as described by using both by 266 nm and 1064 nm lasers. The experimental conditions that provided the highest precision and accuracy were determined and used throughout the study.

The energy of the 266 nm laser was held constant at 29 mJ, while the 1064 nm laser was held at 47 mJ. It was found that at these energies the reproducibility of the experiments increased and limiting the IR wavelength to 47 mJ prevented cracking and damaging of the glass during ablation, see Fig. 3. A detector delay of 1.20 μs was used, which allowed for the decay of background continuum and production of sharp emission lines.

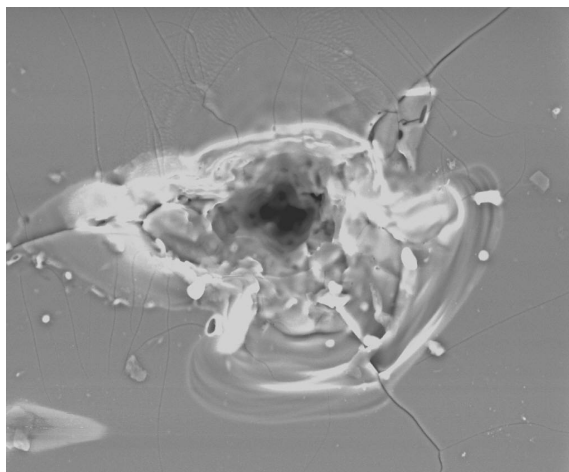
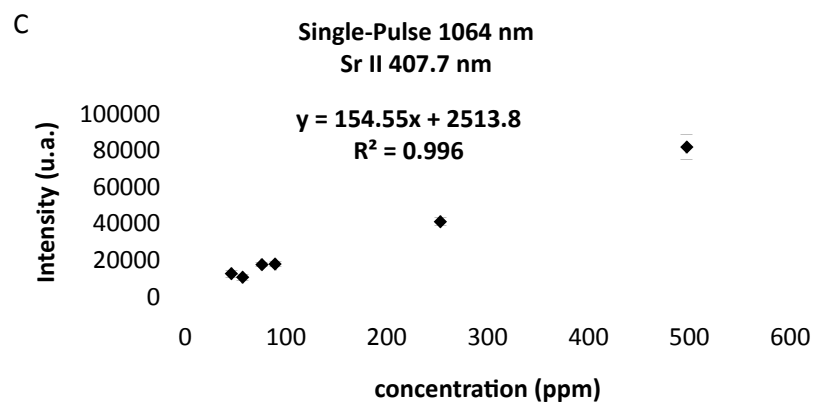
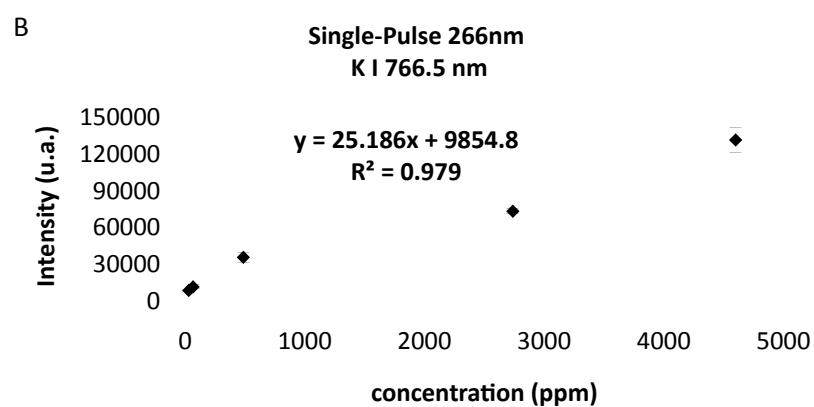
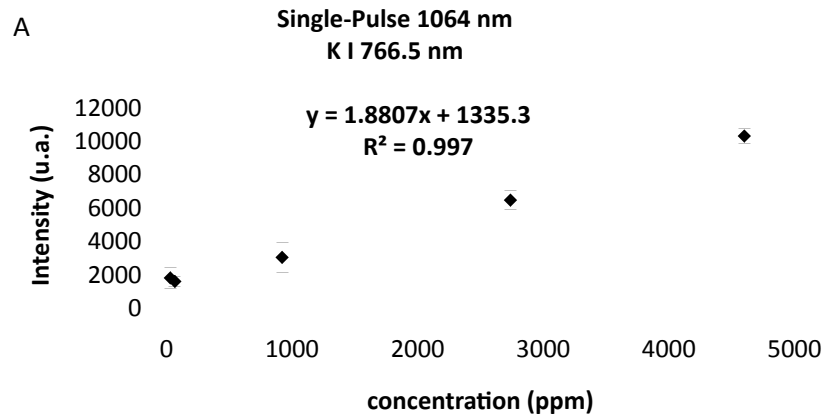


Fig. 3. NIST 1831 glass. The damage of glass by cracking and irregular crater shapes occur by too high of IR laser power

Fig. 3. illustrates calibration curves produced by single-pulse 266 and 1064 nm. Each measurement corresponds to the intensity of the emission line of interest obtained with an accumulation on the detector of the second 50 accumulation of 100 laser shots. Both configurations demonstrate good correlation with most R^2 values being greater than 0.990. It has been demonstrated in previous research that IR irradiances show greater enhancement with ionic emission lines [23], this is witnessed when comparing K I 766.5 nm and Sr II 407.7 nm. However, contrary to this observation, Ba II 493.4 emitted a higher signal when irradiated with the 266 nm laser, than with the 1064 nm.

As mentioned earlier in this paper, NIST 1831 standard was chosen and analyzed twice, the second time being treated as an “unknown” sample. As both methods show good correlation, the UV irradiance demonstrated better precision for the K and Sr lines. The IR irradiance proved to have lower limits of detection, however, in trace elemental analysis of glass, the LOD obtained by UV LIBS ablation would provide sufficient sensitivity for the chemical characterization of glass, see Table 2.



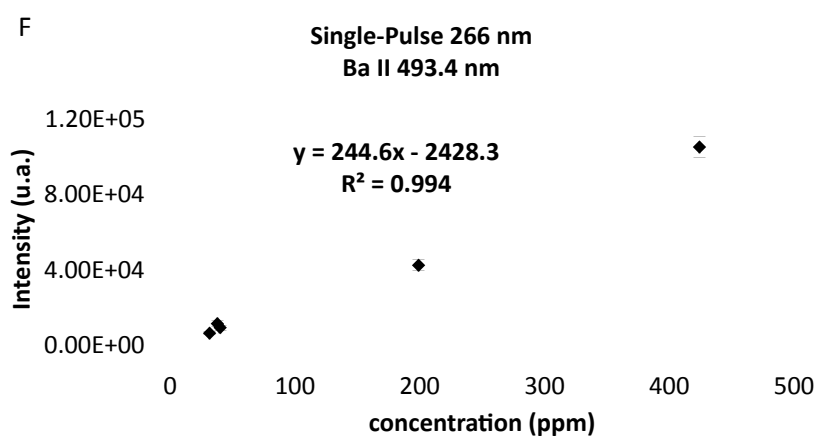
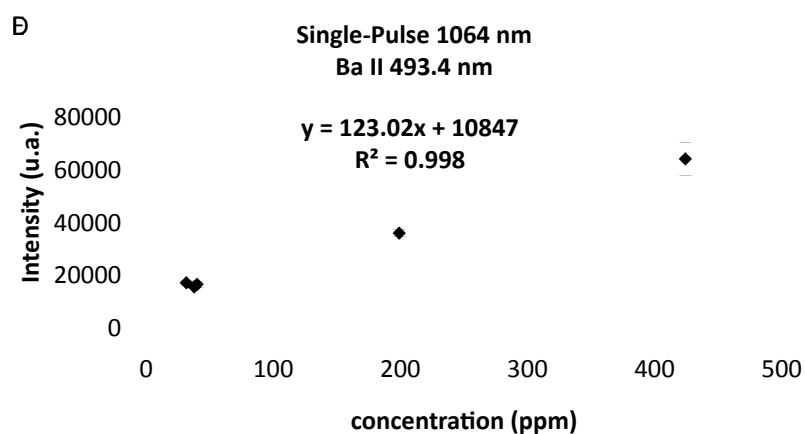
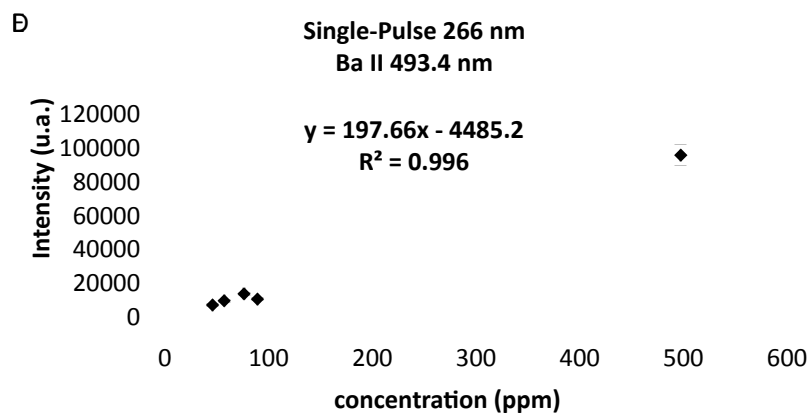


Fig. 3. A) Single-pulse 1064 nm calibration curves for K I 766.5 nm; B) Single-Pulse 266 nm calibration curve for K I 766.5 nm; C) Single-pulse 1064 nm calibration curves for Sr II 407.7; D) Single-Pulse 266 nm calibration curve for Sr II 407.7; E) Single-pulse 1064 nm calibration curves for Ba II 493.3; F) Single-Pulse 266 nm calibration curve for Ba II 493.3 nm

3.2.2 Double-Pulse LIBS

Double-pulse LIBS has gained merit over the recent years. Improvements in the figures of merit by double-laser pulse configurations have contributed to better sensitivity and gain signal for LIBS analyses [24,25]. Several double-pulse geometric configuration approaches have been used consisting of either one laser [26], or two different lasers [27] to encompass a double-pulse LIBS setup.

Orthogonal pre-spark and plasma reheat were the two configurations used during this work. Optimal separation time between the two laser pulses was determined by plotting the LIBS emission intensity versus the delay time. The main objective of this study was not given to the highest intensity enhancement, but rather to increased precision and accuracy. Demonstrated here in figures 3 and 4, an intensity decrease is seen from single-pulse to double-pulse orientation. This event was also reported by Gautier et al. [24], when they observed lower line emissions using UV ablation, from elements with lower excitation energies of approximately 4 eV, in the double-pulse reheating approach when compared to single-pulse. The elements of interest investigated here all have lower excitation energies of 1.6, 3.0, and 2.5 eV for K I 766.5 nm, Sr II 407.7 nm, and Ba II 493.4 nm, respectively, which could account for the witnessed decrease in intensity.

Double-pulse plasma reheat has been attributed to higher plasma temperatures and electron densities due to the larger plasma size after the second plasma reheat beam, which would allow for longer integration times. As can be seen by Fig. 4., all correlation coefficients are above 0.990, demonstrating very good linearity. The precision demonstrated by the plasma reheat scheme is moderately lower than that by single-pulse UV, which has also been reported by Scaffidi et al. [28], and comparable to that of single-pulse IR. As emission enhancement is not seen, however, most LODs have decreased. The LOD for K I 766.5 nm and Sr II 407.7 nm have decreased from the single-pulse value of 5.93 and 4.10 ppm to 4.30 and 3.17 ppm, respectively, showing an increase in the double-pulse plasma reheat sensitivity, see Table 2.

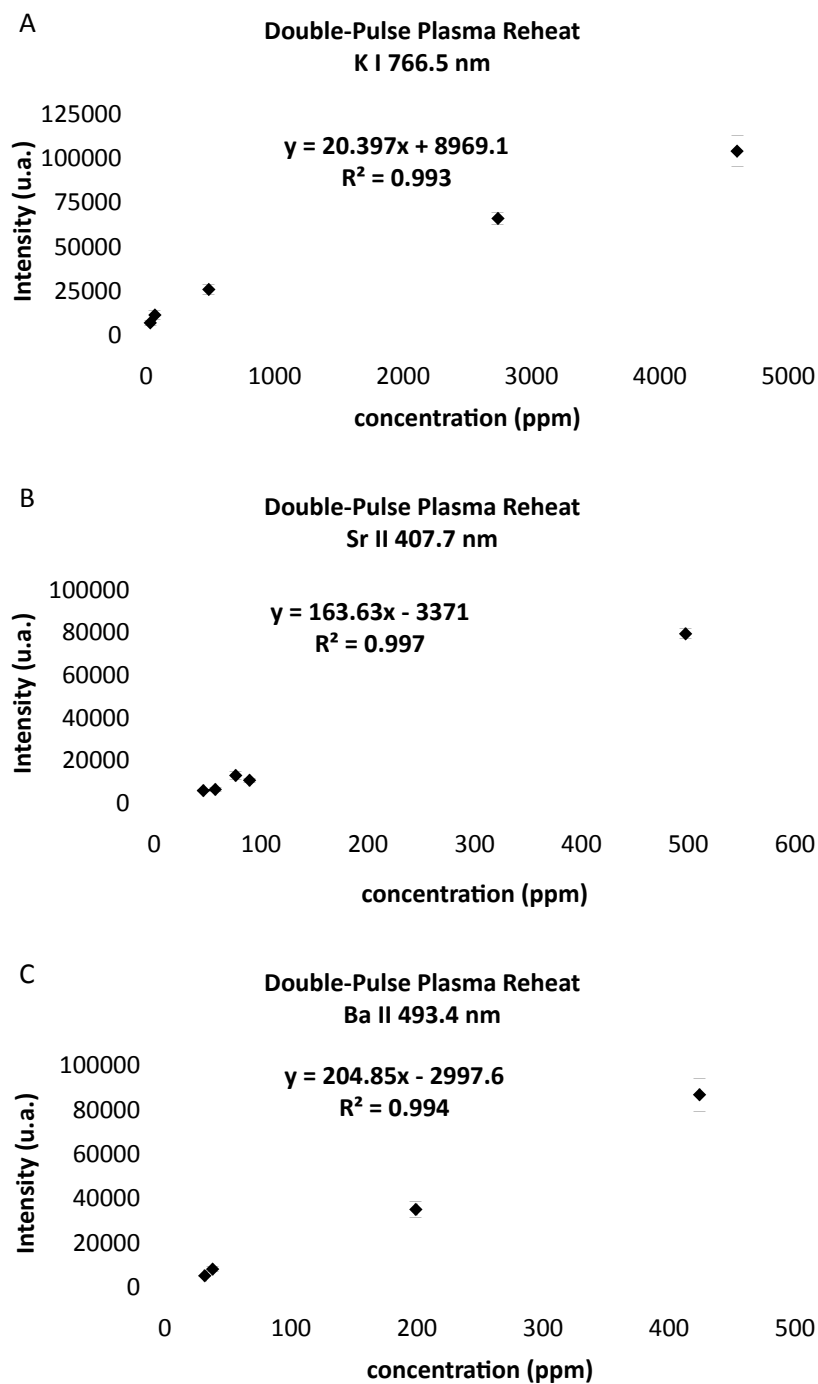
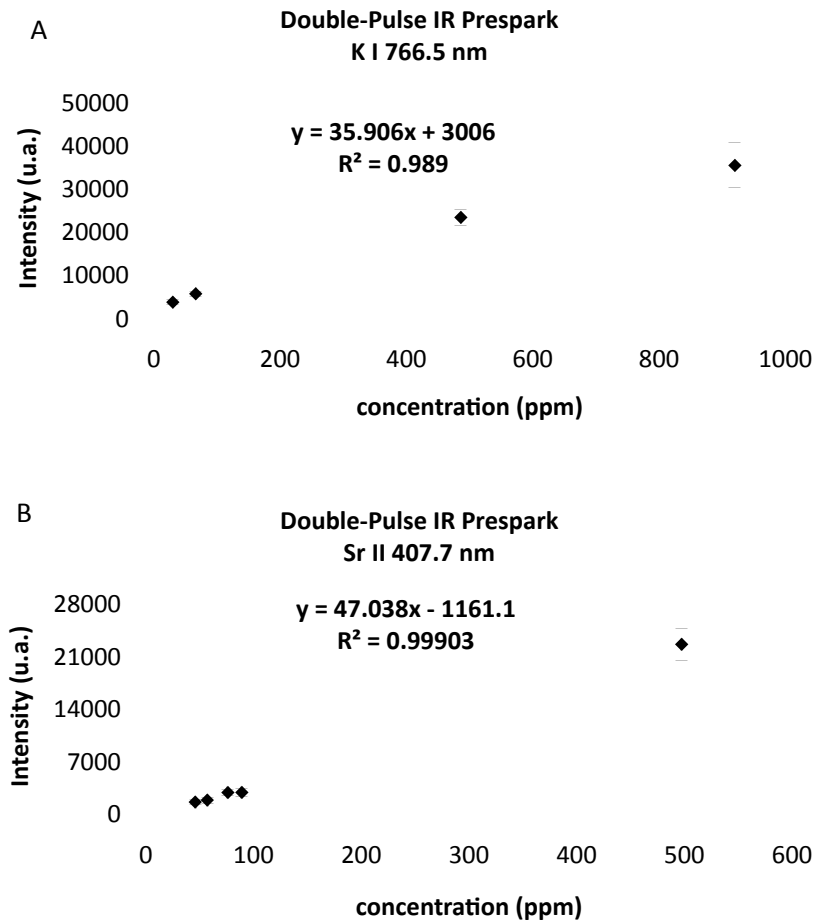


Fig. 4. Calibration curves for double-pulse plasma reheat with 266 nm ablation and 1064 nm plasma reheat for A) K I 766.5 nm B) Sr II 407.7 nm and C) Ba II 493.4 nm

Pre-spark LIBS is theorized to cause ambient gas breakdown before the ablation pulse is produced, creating different effects that could lead to an increased emission by the analyte. It was hypothesized that the reduction in ambient gas causes the plasma to expand faster, thereby reaching a larger size, while producing less plasma

shielding for the ablation pulse [29,30]. Higher sensitivity was also evident in the double pulse pre-spark configuration, than when compared to all other experimental data, due to the resolution of emission line Ti II 336.12 nm. This line was pronounced and a linear correlation achieved, see Fig.5D, while in the other configurations the Ti II line was not resolved well enough for calibration. As seen in the plasma reheat configuration the linearity between concentration and intensity proves well, achieving correlation coefficients most greater than 0.990. However, the pre-spark shows less precision than that demonstrated by either the UV/IR single-pulse or the plasma reheat, see Table 2.



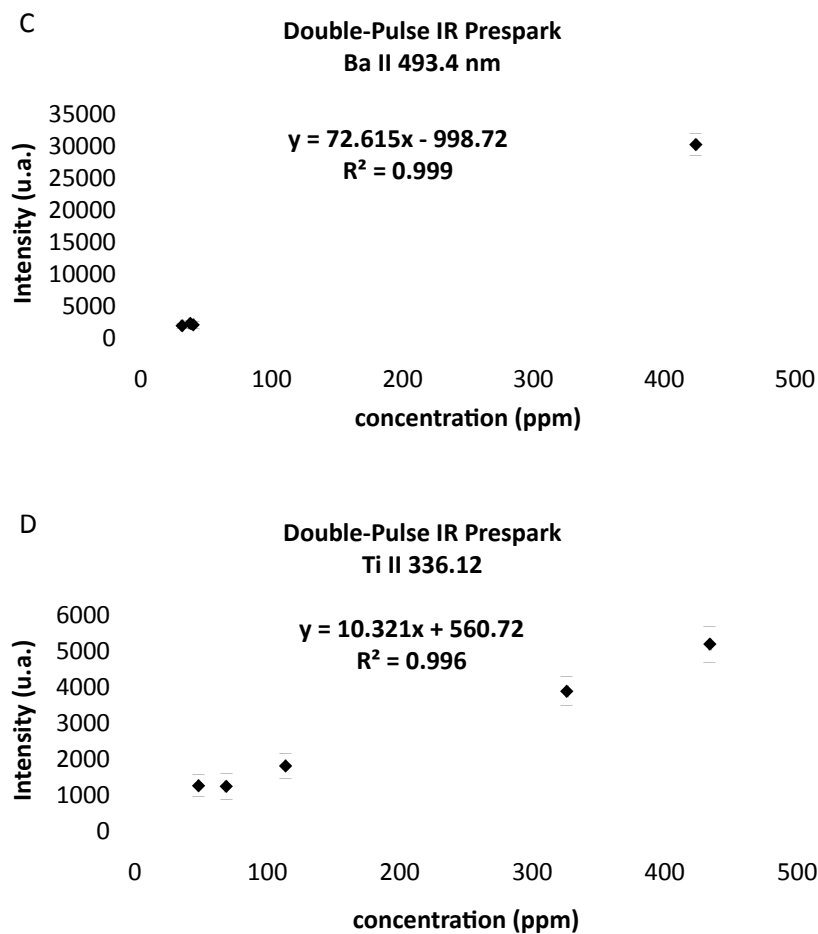


Fig. 5. Calibration curves for double-pulse IR pre-spark with 266 nm ablation for A) K I 766.5 nm, B) Sr II 407.7 nm C) Ba II 493.4 nm and D) Ti II 336.12

Method	Sample	Peak (nm)	Precision (%)	Bias (%)	LOD (ppm)	LOQ (ppm)
SP UV	1831	K I 766.5	8.23	12.15	5.93	19.77
SP UV	1831	Sr II 407.7	5.80	16.82	4.10	13.68
SP UV	1831	Ba II 493.4	10.83	9.48	2.25	7.51
DP Reheat	1831	K I 766.5	3.61	14.82	4.30	14.34
DP Reheat	1831	Sr II 407.7	8.43	5.89	3.17	10.56
DP Reheat	1831	Ba II 493.4	12.38	19.95	1.72	5.73
DP PS	1831	K I 766.5	10.45	19.06	3.77	12.58
DP PS	1831	Sr II 407.7	30.38	47.74	3.02	10.07

DP PS	1831	Ti II 336.1	31.67	42.13	11.03	36.77
SP IR	1831	K I 766.5	9.13	16.50	4.07	13.56
SP IR	1831	Sr II 407.7	8.26	8.98	3.28	10.92
SP IR	1831	Ba II 493.4	4.51	39.68	1.98	6.59

Table 2. Figures of merit for the single-pulse 266 nm (SP UV), double-pulse plasma reheat (DP Reheat), double-pulse 1064 nm pre-spark (DP PS), and single-pulse 1064 nm (SP IR)

The reproducibility of each point in the calibration curve was 10-15%. The accuracy of the analysis was evaluated to be ~10%. The determined limits of detection for metal ions in this work were certainly comparable, if not lower with those reported in other publications. Kurniawan et al. performed quantitative analysis on glass samples and reported the LODs for Ba, K, and Ti were 190 ppm, 190 ppm, and 410 ppm, respectively [31]. Ismail et al. reported the LOD of Ti to be 100 ppm for single-pulse and 10 ppm for double-pulse, Yamamoto et al. detected Ba and Sr in toxic soil and produced a LOD of 265 ppm and 42 ppm, respectively, and Cremers et al. detected Ba in soil to have an LOD of 26 ppm [32-34]. This exhibits the evolution LIBS is making as a choice analytical technique in the forensic science community.

4. Conclusions

The LIBS technique has increasingly gained merit as a competitive analytical tool for surface analysis, depth profiling and bulk analysis of solid. In the case of forensic glass analysis, LIBS was determined to provide the same power of discrimination between different glass sources as either μ XRF or LA-ICP-MS [10]. In the current work, correlation coefficients of > 0.990 were achieved for calibration curves for the trace elements analyzed in the range between 32 and 4600 ppm. Precision and accuracy for the quantitative analysis of standards ranged from as good as 4.5% RSD for the precision of 1831 NIST glass at 32 ppm for the measurement of Ba and an accuracy of 5.9% bias but more typically resulting in 9-10 %RSD precision and 10 % bias for most elements of interest in these glasses both the UV and IR experiments and the single and double-pulse experiments. The IR ablations resulted in typically less emission intensities an indication that less mass was ablated when IR was used. This was corroborated with mass removal calculations.

The plasma shielding was demonstrated to be less with UV irradiance and the laser-sample energy coupling

was more efficient with the UV, resulting in better precision and accuracy in most, but not all experimental configurations. The UV irradiation produced a more uniform crater, translating to better precision from better signal reproducibility. The craters formed resulting from IR irradiance, even when higher power than UV was used, resulted in less mass ablated and severe cracking and damage to the sample surface, in comparison to the UV.

The LODs for the elements of interest in forensic glass analysis were adequate for the proper characterization and comparison of glass using any of the UV and IR configurations used in this study. The same emission lines were used in the comparisons for all configurations and, under these comparison conditions, it was concluded that the use of 266 nm irradiation was recommended for the forensic analysis and comparison of glass with single-pulse experiments providing very good analytical data and minimal sample damage.

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References and Links

1. B. German, Deborah Morgans, A. Butterworth, A. Scaplehorn "A Survey of British Container Glass Using Spark Source Mass Spectrometry with Electrical Detection," J. Forensic Sci. **18**, 113-121 (1978).
2. E.C. Blacklock, A. Rogers, C. Wall, B.B. Wheels, Forensic Sci. **7**, 121 (1976).
3. J. Buscaglia, "Elemental analysis of small glass fragments in forensic science," Anal Chim Acta **288**, 17-24 (1994).
4. R.D. Koons, C.A. Peters, P.S. Rebbert, "Comparison of refractive index, energy dispersive X-ray fluorescence and inductively coupled plasma atomic emission spectrometry for forensic characterization of sheet glass fragments," J. Anal. At. Spectrom. **6**, 451-456 (1991).
5. R.F. Coleman, G.C. Goode, "Comparison of glass fragments by neutron activation analysis," J. Radioanal. Chem. **15**, 367-388 (1973).
6. P. Kuisma-Kursula, "Accuracy, precision and detection limits of SEM-WDS, SEM-EDS and PIXE in the multi-elemental analysis of medieval glass," X-Ray Spectrom. **29**, 111-118 (2000).
7. K.L. Wolnik, C.M. Gaston, F.L. Fricke, "Analysis of glass in product tampering investigations by inductively coupled plasma atomic emission spectrometry with a hydrofluoric acid resistant torch," J. Anal. At. Spectrom. **4**, 27-31 (1989).
8. A. Zurhaar, M. Mullings, "Characterization of forensic glass samples using inductively coupled plasma mass spectrometry," J. Anal. At. Spec. **5**, 611-617 (1990).
9. C. Latkoczy, S. Becker, M. Dücking, D. Günther, J.A. Hoogewerff, J.R. Almirall, J. Buscaglia, A. Dobney, R.D. Koons, S. Montero, G.J. van der Peijl, W.R. Stoecklein, T. Trejos, J.R. Watling, and V.S. Zdanowicz "Development and evaluation of a standard method for the quantitative determination of elements in float glass samples by LA-ICP-MS," J. Forensic Sci. **50**, 1327-1341 (2005).
10. B. E. Naes, A. Umpierrez, S. Ryland, C. Barnett, J.R. Almirall, "A comparison of laser ablation inductively coupled plasma mass spectrometry, micro X-ray fluorescence spectroscopy, and laser induced breakdown spectroscopy for the discrimination of automotive glass," Spectrochim. Acta Part B **63B**, 1145-1150 (2008).

11. E.M. Rodriguez-Celis, I.B. Gornushkin, U.M. Heitmann, J.R. Almirall, B.W. Smith, J.D. Winefordner, N. Omenetto, "Laser induced breakdown spectroscopy as a tool for discrimination of glass for forensic applications," *Anal. Bioanal. Chem.* 391, 1961-1968 (2008).
12. R.E. Russo, X.L. Mao, O.V. Borisov, H. Liu, "Influence of wavelength on fractionation in laser ablation ICP-MS," *J. Anal. At. Spectrom.* 15, 1115-1120 (2000).
13. C. Geertsen, A. Briand, F. Chartier, J. Lacour, P. Mauchien, S. Sjö, J. Mermet, "Comparison Between Infrared and Ultraviolet Laser Ablation at Atmospheric Pressure-Implications for Solid Sampling Inductively Coupled Plasma Spectrometry," *J. Anal. At. Spectrom.* 9, 17-22 (1994).
14. C. Barnett, E. Cahoon, J.R. Almirall, "Wavelength dependence on the elemental analysis of glass by Laser Induced Breakdown Spectroscopy," *Spectrochim. Acta Part B* 63, 1016-1023 (2008).
15. L.M. Cabalin, J.J. Laserna, "Experimental determination of laser induced breakdown thresholds of metals under nanosecond Q-switched laser operation," *Spectrochim. Acta Part B* 63B, 723-730 (1998).
16. X.L. Mao, A.C. Ciocan, O.V. Borisov, R.E. Russo, "Laser ablation processes investigated using inductively coupled plasma-atomic emission spectroscopy (ICP-AES)," *Appl. Surf. Sci.*, 127-129, 262-268 (1998).
17. L.M. Berman, P.J. Wolf, "Laser-induced spectroscopy of liquids: aqueous solutions of nickel and chlorinated hydrocarbons," *Appl. Spectrosc.* 52, 438-443 (1998).
18. J.R. Almirall, T. Trejos, "Advances in the Forensic Analysis of Glass Fragments with a Focus on Refractive Index and Elemental Analysis," *Forensic Science Review* 18(2), 73-96 (2006).
19. T. Ishizuka, "Laser Emission Spectrography of Rare Earth Elements," *Anal. Chem.* 45, 538-541 (1973).
20. C. Girault, Ph.D. Thesis, Université de Limoges, France (1990).
21. A. Santagata, A. De Bonis, P. Villani, R. Teghil, G.P. Parisi, "Fs/ns-dual-pulse orthogonal geometry plasma plume reheating for copper-based-alloys analysis," *Appl. Surf. Sci.*, 252, 4685-4690 (2005).
22. J. Scaffidi, W. Pearman, J.C. Carter, B.W. Colston Jr., S.M. Angel, "Temporal dependence of the enhancement of material removal in femtosecond-nanosecond dual-pulse laser-induced breakdown spectroscopy," *Appl. Opt.* 43, 6492-6499 (2004).
23. L. Fornarini, V. Spizzichino, F. Colao, R. Fantoni, V. Lazicm, "Influence of laser wavelength on LIBS diagnostics applied to the analysis of ancient bronzes," *Anal. Bioanal. Chem.* 385, 272-280 (2006).

24. C. Gautier, P. Fichet, D. Menut, J. Lacour, D. L'Hermite, J. Dubessy, "Study of the double pulse setup with an orthogonal beam geometry for laser induced breakdown spectroscopy," *Spectrochim. Acta Part B* 59, 975-986 (2004).
25. L. St-Onge, M. Sabsabi, P. Cielo, "Analysis of solids using laser-induced plasma spectroscopy in double-pulse mode," *Spectrochim. Acta, Part B* 53, 407-415 (1998).
26. F.C. De Lucia Jr, J.L. Gottfried, D.A. Munson, A.W. Miziolek, "Double-pulse laser-induced breakdown spectroscopy of explosives: Initial study towards improved discrimination," *Spectrochim. Acta Part B* 62, 1399-1404 (2007).
27. D. N. Stratis, K. L. Eland, and S. M. Angel, "Enhancement of aluminum, titanium, and iron in glass using pre-ablation spark dual-pulse LIBS," *Appl. Spectrosc.* **54**, 1719–1726 (2000).
28. J. Scaffidi, J. Pender, W. Pearman, S.R. Goode, B.W. Colston, Jr., J. C. Carter, S.M. Ange, "Dual-pulse laser-induced breakdown spectroscopy with combinations of femtosecond and nanosecond laser pulses," *Appl. Opt.* 42, 6099-6106 (2003).
29. G. Cristoforetti, S. Legnaioli, V. Palleschi, A. Salvetti, E. Tognoni, "Influence of ambient gas pressure on laser-induced breakdown spectroscopy technique in the parallel double-pulse configuration," *Spectrochim. Acta Part B* 59, 1907-1917 (2004).
30. V. Burakov, N. Tarasenko, M. Nedelko, S. Isakov, "Time resolved spectroscopy and imaging diagnostics of single pulse and collinear double pulse laser induced break plasma from a glass sample," *Spectrochim. Acta Part B* 63, 19-26 (2008).
31. H. Kurniawan, S. Nakajima, J.E. Batubara, M. Marpaung, M. Okamoto, K. Kagawa, "Laser-Induced Shock Wave Plasma in Glass and Its application to Elemental Analysis," *Appl. Spectro.* 49, 1067-1072 (1995).
32. M.A. Ismail, G. Cristoforetti, S. Legnaioli, L. Pardini, V. Palleschi, A. Salvetti, E. Tognoni, M. Harith, "Comparison of detection limits, for two metallic matrices, of laser-induced breakdown spectroscopy in the single and double-pulse configurations," *Anal. Bioanal. Chem.* 385, 316-325 (2006)
33. K. Y. Yamamoto, D. A. Cremers, M. J. Ferris, and L. E. Foster, "Detection of metals in the environment using a portable laserinduced breakdown spectroscopy instrument," *Appl. Spectrosc.* 50, 222–233 (1996).
34. D.A. Cremers, J.E. Barefield II, A.C. Koskelo, "Remote Elemental Analysis by Laser-Induced Breakdown Spectroscopy Using a Fiber-Optic Cable," *Appl. Spectrosc.* 49, 857-860 (1995).