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Laser-induced breakdown spectroscopy measurement for liquids: Experimental configurations and sample preparations

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Laser-induced breakdown spectroscopy (LIBS) is an analytical spectroscopy technique that offers precise quantitative chemical analysis using high energy laser pulse. Although LIBS has been linked as an analytical technique with no sample preparation, this case may be a boundary in preventing it from being a more advanced technique. Regardless of LIBS countless contributions in providing measurements for solid samples, the future applications of LIBS can be explored with the aid of sample preparation methods. This review highlights the previous works of researchers that have proposed and improved various configuration methods specifically targeting to upgrade the LIBS measurements of liquid samples.

Keywords: Laser-induced breakdown spectroscopy; liquid sample; experimental configuration; sample preparation.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) technique is one of the methods of atomic emission spectroscopy (AES) that can provide elemental analysis of samples regardless of its physical forms. This technique uses a laser pulse with energy ranging from tens to hundreds mJ/s to produce plasma of the sample. A spectrometer diffracts a fragment of the plasma light while a detector is used to record the signals of the light emission of excited atomic and ionic species in the plasma. Then, a computer will assist in analyzing and displaying the LIBS results.[1]

The development of laser is one of the keys in leading to the development of LIBS. The first laser was developed by Theodore Harold Maiman, using ruby crystal in 1960.[2] Three years later, Llyod Cross and Fred Brech developed the first LIBS by developing a Q-switched laser that is able to produce a short single pulse (SP) with high focused power densities. This laser is capable of initiating breakdown, generating plasma and thus providing a spectrum from the induced plasma.[3] Runge *et al.*[4]

in 1964 used the pulsed Q-switched ruby laser and discovered the direct sparks excitation on metals enabling them to analyze molten metal.[1]

Nowadays, the focus is more on developing compact LIBS components for building portable LIBS system and at the same time increasing their sensitivity. Until now, LIBS has been involved in huge amount of research due to its simple sample preparation requirement, non or minimal destructive method and ability to do remote analysis.[5] However, fewer LIBS research were done on liquid samples because of some drawbacks such as shockwave formation, strong splashing and higher limit of detection (LOD).[6]

To overcome these drawbacks, either sample preparations or plasma emission signal improvement can be done. The latter is more preferable due to LIBS' credibility as an AES with no sample preparation needed.[7,8] However, enhancing the plasma emission means upgrading components such as the laser itself or the detector to increase LIBS performance, which in turn will increase the expenditure. Hence, sample treatment approach with less operational cost has been reconsidered once again to decrease the LOD. This approach includes mechanical treatment (surface polishing or roughness augmentation) or deeper treatment (physical or chemical changes).[9]

Although some disadvantages might resurface such as a change in sample chemical composition, possible sample contamination and increasing analysis time, this approach has its own alternatives in overcoming these issues. Therefore, in this paper, we will review the procedure, advantages, drawbacks and the ways in overcoming the drawbacks of each sample treatment methods available.

2. Basic Principles

The processes which involve in LIBS technique include laser–sample interaction, sample removal, breakdown process and element-specific emission. First, for LIBS analysis purpose, a pulsed laser beam is focused onto the target sample surface. Once the laser has impinged on the sample, the laser–sample interaction happens when the sample absorbs the energy from pulsed radiation field. The pulse duration is usually in nanoseconds, femtoseconds or picoseconds. The absorbed energy will be converted into heat, causing ablation (vaporization) of the sample once the temperature reaches the sample material's boiling point. Vapor will form above the sample surface due to particulate matter of surface removed.[3,10] The vapor pulse will be illuminated continuously by the laser pulse and will condense into submicrometer droplets. Continuous strong heating will lead to ionization and plasma formation. The plasma plume dynamical evolution could be categorized by fast expansion and cooling. In addition, the element-specific emission could be identified from the spectrum roughly a few microseconds after the laser ablation pulse.[3]

Meanwhile, the term breakdown in LIBS implies the breakdown process of target sample surface due to the very high energy from the focused short pulse laser source. The breakdown and plasma yielding process depend on several factors. The first is

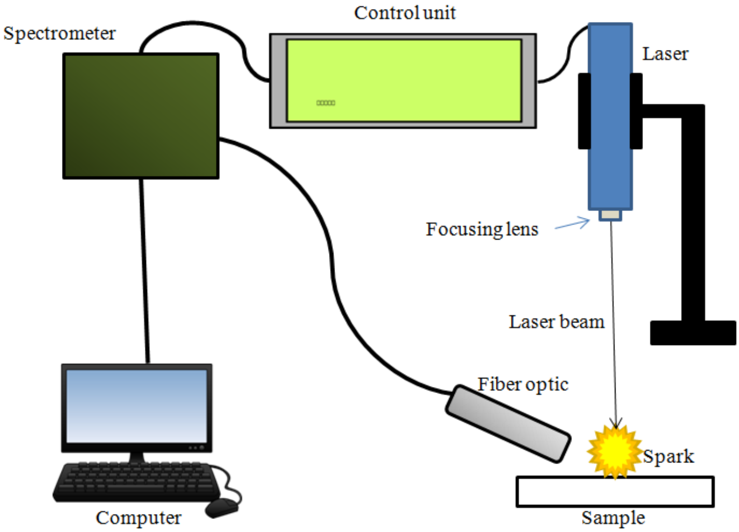

Fig. 1. Example of LIBS technique experimental setup.

the laser itself, which includes its pulse duration, wavelength and irradiance. The second factor is the target sample's physiochemical characteristics and aggregation state.[10] Once the pulse irradiance exceeds certain threshold value, breakdown process will take place. The threshold value depends on material's aggregation state. Precise irradiance value is important in getting high electron density plasma and temperature of target sample. The ablated target sample will then expand at supersonic velocity, orthogonal to the target.[11] Plasma plume will emit radiation during finite lifetime. This radiation is useful in determining qualitative and quantitative analysis of each element in plasma plume. Hence, a time control unit is also necessary in order to avoid strong continuum emission at early plasma stages.[12]

The plasma light spectrum shows both the wavelength and intensity. The wavelength indicates the element identification whereas intensity indicates the amount of the element in sample.[6,10] The experimental setup of an LIBS system is shown in Fig. 1. This system usually consists of several elements such as high power Q-switched laser, spectrometer to diffract the collected light emitted by plasma, control unit to synchronize the spectrometer and to avoid continuum plasma radiation by controlling the gating pulse, fiber optic to guide the light and computer and software to analyze the sample.[3]

3. Strength and Limitation of LIBS on Liquid Sample

Despite LIBS accuracy and experiment repeatability quality that are slightly incomparable with better analytical techniques such as X-ray fluorescence (XRF), inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS), LIBS has its own strengths such as lower instrumentation cost, flexible experiment environment preference, ability to characterize various types of samples, no or less additional sampling procedure, ability to conduct real time and *in situ* measurement and contactless probing performance with distance up to 100 m.[13] Liquid sample analysis using LIBS is important due to the LIBS strengths as mentioned before and LIBS capability in real-time analysis of several elements existed in samples with minimal sampling procedure needed.[14]

Nowadays, more attention is given on applying LIBS on liquid samples and solid samples in liquid surrounding due to their crucial roles in many fields. Some applications are rapid analysis of pharmaceutical liquid formulations,[15] feedback guide in laser surgery performed with liquid coverage,[16] analysis of sample with ultra-low amount of volume for forensics and speciation analysis,[17] sample analysis in deep-ocean environments,[18] analysis of archaeological materials,[19] quality control of red wines[20] and many others. LIBS also contributed in environmental-related analysis such as chromium detection from waste water,[21,22] detection of platinum group metals in nuclear waste,[23] detection of sediments underwater[24] and many more.

However, LIBS analysis of liquid samples is always associated with some constraints. Liquid samples or solid samples in liquid environment tend to have higher density and cooling effect, resulting to stronger quenching of the plasma produced and lower plasma temperature. As the plasma possesses lower temperature, the plasma emission intensity and lifetime will also be lower.[25] The reasons for lower plasma emission in liquid environment include laser and plasma radiation absorption by the medium, the scattering on suspended particles and microbubbles, high density plasma shielding[26] and plasma quenching in denser medium.[6,27]

The laser energy required for ablation of liquid sample in order to generate breakdown inside the sample is usually higher.[6] Most of the laser energy is spent on the vaporization of liquid while only a small remainder of it is present for plasma excitation. Cremers *et al.*[28] mentioned that approximately only 25% of the laser energy was available for the excitation and formation of plasma inside or on liquid. Even though the major mechanical scavenging causes the ablation rate inside liquid medium to increase,[29] the LIBS signal (at similar laser excitation) will still be lower if compared to experiment conducted in gas medium. Inside the liquid, the spectral lines from the plasma also tend to be more broadened with intense continuum emission due to the high electron density.[26,27] This situation leads to the formation of plasma with less efficiency and poor LIBS signal measurements.[28]

Moreover, the fact that organic or liquid solutions contain hydrogen could lead to rapid thermalization and plasma cooling. Because of an abundance of oxygen atoms in water, different plasma species went through rapid oxidation, thus causing the lower presence of excited analyte atoms and ions.[13] After the plasma is created in the liquid medium, the plume will be confined due to high density and almost incompressible medium.[27] Consequently, intense shockwaves happen due to the plasma formation in liquid, which in turn affects the ablation threshold and the rate of submerged targets. The growth of vapor cavity (lifetime in ms range) also happens after the plasma emission and expansion.[6]

LIBS sampling of liquid sample surface has become more complicated due to the surrounding vapor that is not in equilibrium with the surface of liquid samples. Hence, the net mass flux from the surface of liquid samples to surrounding vapor is higher, causing both of the sample surface's pressure and the boiling temperature to increase.[30] When the normal boiling point is already accomplished, vapor bubble formation will happen due to the presence of higher volumetric energy density compared to the energy density at the saturation temperature. In case the volumetric energy density deposition rate transcends the energy used for vaporization, the liquid sample will attain metastable state (atoms' excited state with longer lifetime) and thus reaching spinoidal temperature.[6]

As the liquid sample reaches spinoidal temperature, the sample will undergo spinoidal decomposition. Spinoidal decomposition happens when a small fluctuation in density (composition) leads to phase separation. In this case, the superheated liquid volume undergoes phase separation (saturated liquid and vapor), hence ejecting them into the atmosphere.[6] All these processes usually happen when LIBS is applied on liquid sample surface. Vogel *et al.*[30] mentioned that half of the deposited energy is used for droplets ejection while the other half transforms into vapor. Meanwhile, the energy used for droplets ejection or the so-called splashing will thus reduce the LIBS signal quality.[30]

Adapting liquid sample specimen for LIBS analysis could provide better potential of LIBS as an analytical tool with excellent sensitivity, precision and accuracy. In the next section, we discuss how liquid sample in bulk along with the other liquid sample treatment methods (laminar flow, liquid droplet, conversion into aerosol and conversion into solid) has been applied for various LIBS applications.

4. Methods on Solving Limitation of LIBS on Liquid Sample

Unlike solid samples, LIBS analysis of liquid samples whether in bulk or on its surface would encounter difficulties such as splashing, surface ripples and shorter plasma duration.[9] To overcome drawbacks, two types of approaches have been suggested. First, by exploring suitable experimental configurations such as using double pulse (DP) laser system to re-excite the plasma, liquid jet pump to promote laminar flows, purpose-built nebulizer sampling unit to produce aerosol sample or liquid in droplet form analysis. The second approach is liquid to solid phase transformation (ice, pellet, substrate or layer) to benefit the advantages of a solid target. Thus, this section will discuss on both of the approaches including the procedures involved, its performance, strengths, limitations and ways in overcoming the limitations. Table 1 shows the summary of all configurations that were reviewed in this paper depicting the sampling method, experimental procedure, sample type, element detected, gate width, delay time and LOD.

Table 1. Examples of the LODs achieved by LIBS under different sampling methods.

Sampling method	Laser specification SP: W, PD, RR, PE DP, Δt: (1) W, PD, RR, PE (2) W, PD, RR, PE	Sample type	Element detected	Gate width (μs), Delay time (μs)	LOD (ppm)	Ref.
Liquid bulk	SP: 1,064 nm, 10 ns, 2 Hz, 115 mJ	$K_2Cr_2O_7$ aqueous solution	Cr	N/A, 1.28	39	21
	SP: 1,064 nm, 5 ns, 1 Hz, 18 mJ	$KCr_2(SO_4)_2\cdot 12H_2O$ aqueous solution	Cr	N/A, 3.5	40	22
	SP: 1,064 nm, 15 ns, 10 Hz, 45 mJ	Aqueous solutions prepared with deionized water	Li	1.0, 0.5	0.006	28
			Na	1.0, 0.5	0.014	
			K	1.0, 0.5	1.2	
			Rb	1.0, 0.5	0.2	
			Cs	1.0, 0.5	1.0	
			Be	0.1, 0.1	10	
			Mg	1.0, 0.5	100	
			Ca	1.0, 0.5	0.8	
			B	0.1, 0.27	1,200	
			Al	1.0, 0.5	20	
	SP: 532 nm, 14 ns, 1 Hz, 60 mJ	Cr in water and oil	Cr	N/A, 500 ns	20/30 (in water/oil)	31
	SP: 1,064 nm, 7 ns, 0.5 Hz, 70 mJ	Conostan® S-21 blended oil standards	Na	1, 1	24	32
			Mg		1.8	
			Al		35	
			Ca		6.2	
			Ti		18.8	
			V		43	
			Mn		20	
			Cu		6.1	
			Zn		11.4	
			Ag		12	
			Cd		22	
			Ba		6.5	
	SP: 1,064 nm, N/A, 1 Hz, 100 mJ	Mg, Cu, Fe, Cd, Cr, Hg and Pb diluted in deionized water	Cd	15, 0.5	7.1	33
			Fe	15, 0.5	10.5	
			Mg	15, 0.5	0.9	
			Cr	15, 0.5	10.5	
			Cu	15, 1	9.6	
			Hg	20, 8	21.4	
			Pb	20, 15	12.5	
	DP, 18 μs: (1) 1,064 nm, 15 ns, 10 Hz, 45 mJ (2) 1,064 nm, 15 ns, 10 Hz, 125 mJ	Aqueous solutions prepared with deionized water	B	0.1, 0.27	80	28
	DP, 30 μs: (1) 1,064 nm, 10 ns, 1.25 Hz, 40 mJ (2) 1,064 nm, 10 ns, 1.25 Hz, 135 mJ	Bacteriostatic sodium chloride (aqueous solution)	Na	N/A, 1	N/A	15
Liquid in laminar flow						
(i) Horizontal	SP: 1,064 nm, 10 ns, 1 Hz, 220 mJ	Table salt (aqueous solution)	Na	N/A, 1	N/A	15

Table 1. (*Continued*)

Sampling method	Laser specification SP: W, PD, RR, PE DP, Δt: (1) W, PD, RR, PE (2) W, PD, RR, PE	Sample type	Element detected	Gate width (μs), Delay time (μs)	LOD (ppm)		Ref.
(ii) Vertical	DP, 3 μs: (1) 532 nm, 6 ns, 20 Hz, 30 mJ (2) 532 nm, 6 ns, 20 Hz, 100 mJ	B in aqueous solution	B	5, 3.25	0.8		39
	DP, 10 μs: (1) 532 nm, 6 ns, 20 Hz, 30 mJ (2) 532 nm, 6 ns, 20 Hz, 100 mJ	Li in aqueous solution	Li	5, 9	0.0008		39
	SP: 532 nm, 3–4 ns, 1 Hz, 120 mJ	ammonium dichromate (aqueous solution)	Cr	N/A	30		36
	SP: 532 nm, 5 ns, 10 Hz, 150 mJ	Aqueous solutions prepared with distilled water	Mg	2, 5	0.1		35
			Cr		0.4		
			Mn		0.7		
			Re		8		
	SP: 1,064 nm, 7 ns, 2 Hz, 150 mJ	Conostan® S-21 blended oil standards	Na	1, 1	8		32
			Mg		0.4		
			Al		15		
			Ca		0.4		
			Ti		9.3		
			V		19		
			Cr		43		
			Mn		6		
			Fe		20		
			Ni		47		
			Cu		2.4		
			Zn		11		
			Mo		31		
			Ag		3.1		
			Cd		10		
			Ba		1.4		
	SP: 1,064 nm, 6–8 ns, N/A, 420 mJ	$CsNO_3$ standard solution in HNO_3	Cs	50, 35	0.0228		38
	SP: 1,064 nm, 6 ns, 10 Hz, 257 mJ	Copper (II) sulfate aqueous solution prepared from 99% purity salts	Cu	60, 2.75	19		37
	DP, 1 μs: (1) 1,064 nm, 6 ns, 10 Hz, 257 mJ (2) 532 nm, 10 ns, 10 Hz, 105 mJ	Copper (II) sulfate and lead (II) acetate aqueous solutions prepared from 99% purity salts	Cu Pb	60, 15	12 13		37
Liquid to aerosol (i) Ultrasonic	SP: 1,064 nm, 8 ns, 10 Hz, 120 mJ	$Pb(NO_3)_2$ aqueous solution	Pb	0.5, 4	2.93		43
					Membrane dryer		
					No	Yes	
(i) Ultrasonic	SP: 532 nm, 10 ns, 10 Hz, 45 mJ	Metal salt in aqueous environment	Na	1,000, 4	1.8	0.45	42
	SP: 532 nm, 10 ns, 10 Hz, 60 mJ	Metal salt in aqueous environment	Ca	1,000, 1	1.4	1.83	42

Table 1. (*Continued*)

Sampling method	Laser specification SP: W, PD, RR, PE DP, Δt: (1) W, PD, RR, PE (2) W, PD, RR, PE	Sample type	Element detected	Gate width (μs), Delay time (μs)	LOD (ppm)		Ref.
	SP: 532 nm, 10 ns, 10 Hz, 80 mJ	Metal salt in aqueous environment	Mg	1,000, 0.6	1.0	1.85	42
	SP: 532 nm, 10 ns, 10 Hz, 120 mJ	Metal salt in aqueous environment	K	500, 3	7.7	6.01	42
	SP: 532 nm, 10 ns, 10 Hz, 130 mJ	Metal salt in aqueous environment	Al	75, 10	2.7	6.47	42
			Cr	75, 0.7	5.4	6.49	
			Cd	1,000, 0.5	82.3	43.99	
	SP: 532 nm, 10 ns, 10 Hz, 140 mJ	Metal salt in aqueous environment	Cu	500, 9	1.7	1.99	42
	SP: 532 nm, 10 ns, 10 Hz, 150 mJ	Metal salt in aqueous environment	Zn	750, 8	54.3	41.64	42
			Pb	100, 0.5	50.2	13.6	
(ii) Collison	SP: 532 nm, N/A, 2 Hz, 55 mJ	Deionized water with additives of $CeCl_3$, $GdCl_3$ and $NdCl_3$	Ce	20, 6	209.7		44
			Gd		216.4		
(iii) Meinhard	SP: 532 nm, 8 ns, 10 Hz, 170 mJ	Metal solutions in water with 2% HNO_3	Mg	10, 6	0.17		41
			Mn		0.6		
			Cr		0.16		
(iv) Micro	SP: 532 nm, 3–5 ns, 0.66 Hz, 65 mJ	Multi-element solutions prepared with varied final concentrations (ppm)	Sr	6.75, 1.75	3.3		45
			Mg		2.6		
	DP, 50 ns: (1) 532 nm, 3–5 ns, 0.66 Hz, 65 mJ (2) 532 nm, 3–5 ns, 0.66 Hz, 65 mJ	Multi-element solutions prepared with varied final concentrations (ppm)	Sr	8.75, 1.75	1.0		45
			Mg		0.3		
			Ba		0.7		
			Ca		0.6		
Liquid droplet	SP: 1064 nm, 5 ns, 5 Hz, 315 mJ	Ca and Au standard solutions	Ca	20, 30	0.05		17
			Au	20, 20	29		
	DP, 50 ns: (1) 532 nm, 3–5 ns, 0.66 Hz, 35 mJ (2) 532 nm, 3–5 ns, 0.66 Hz, 35 mJ	Elemental solutions prepared to final concentrations (ppm) and giving absolute mass (pg per drop)	Sr	8.75, 1.75	1 pg		45
			Mg		1 pg		
			Ba		1 pg		
			Al		3 pg		
	SP: 1,064 nm, 10 ns, 10 Hz, 180 mJ	Manganese solution $MnCl_2{\cdot}2H_2O$	Mn	2000/1.3	N/A		61
	SP: 532 nm, 10 ns, 20 Hz, 200 μJ	NaCl aqueous solution	Na	1, 0.1	6		47
	SP: 266 nm, 10 ns, 10 Hz, 25 mJ	Solution with constant analyte concentration	Na	N/A	2		48
	SP: 1,064 nm, 10 ns, 10 Hz, 60 mJ	Solution with constant analyte concentration	Na	N/A	0.75		48
	SP: 1,064 nm, 10 ns, 10 Hz, 140 mJ	Sample diluted from 100 ppm Ca stock solution stabilized with 5% nitric acid	Ca	50, 1.5	0.02		48
Liquid to solid pellet	SP: 1,064 nm, 4 ns, 1 Hz, 42 mJ	Red wines with added collagen gel	Mg	1,000, 2	N/A		20
			Ca		Sensitivity: 99.2%		
			K		Generalization ability: 98.6%		
			Na				
	SP: 1,064 nm, 7 ns, 2 Hz, 160 mJ	Cr, Pb, Cd and Zn aqueous solution mixed with 6 mg Aldrich Powder (CaO)	Cr	2, 7	1.2		54
			Pb		20		
			Cd		129		
			Zn		21		

Table 1. (*Continued*)

Sampling method	Laser specification SP: W, PD, RR, PE DP, Δt: (1) W, PD, RR, PE (2) W, PD, RR, PE	Sample type	Element detected	Gate width (μs), Delay time (μs)	LOD (ppm)	Ref.
	SP: 1,064 nm, 8 ns, 10 Hz, 40 mJ	Crude oil obtained by true boiling point (TBP) distillation process	Ca	N/A, 5	14	55
			Fe		9	
			Mg		6	
			Cu		3.5	
			Zn		5	
			Na		10	
			Ni		11	
			Mo		2	
	SP: 532 nm, 10 ns, N/A, 70 m J	Vacuum residues of crude oils heated at 60°C to get molten samples	Ni	15, 1	N/A	53
			V		REP 7%	
					N/A	
					REP 5%	
Liquid to solid (ice)	SP: 9–11 μm, 100 ns, 10 Hz, N/A (CO_2 laser)	Na in ice	Na	5, 4	2	56
	SP: 532 nm, N/A, 10 Hz, 20 mJ	Al in ice	Al	5, 4	1	56
	SP: 1,064 nm, N/A, 1 Hz, 100 mJ	Mg, Cu, Fe, Cd, Cr, Hg and Pb diluted in deionized water and then immersed in liquid nitrogen	Cd	15, 0.5	1.4	33
			Fe	15, 0.5	1.3	
			Mg	15, 0.5	0.3	
			Cr	15, 0.5	1.4	
			Cu	15, 1	2.3	
			Hg	20, 8	3.7	
			Pb	20, 15	1.3	
Liquid to solid (substrate)						
(i) nonpermeable substrate	**Graphite**					
	SP: 1,064 nm, 7 ns, 10 Hz, 200 mJ	Boric acid dissolved in deionized water	B	10, 1.5	0.01	60
	Metal plate					
	SP: 1,064 nm, 10 ns, 10 Hz, 180 mJ	Manganese solution $MnCl_2 \cdot 2H_2O$	Mn	2000/1.3	6	61
	SP: 1,064 nm, 8 ns, N/A, 160 mJ	Cs standard solution: CsCl dissolved in double deionized water Biological samples: Lyophilized human standard materials	Cs	N/A, 2	6/27 (in urine/blood)	62
	SP: 532 nm, 5 ns, N/A, 60 mJ	La, Ce, Pr and Nd aqueous solution	La	2, 2	0.85	64
			Ce		4.07	
			Pr		2.97	
			Nd		10.98	
	SP: 532 nm, 5 ns, N/A, 60 mJ	Unitary solutions prepared by dissolving $CrCl_3$, $CdCl_2$, $CuCl_2$ and $Pb(NO_3)_2$ in distilled water	Cu	1, 1	0.257	63
			Pb		0.136	
			Cd		0.386	
			C		0.016	

Table 1. (*Continued*)

Sampling method	Laser specification SP: W, PD, RR, PE DP, Δt: (1) W, PD, RR, PE (2) W, PD, RR, PE	Sample type	Element detected	Gate width (μs), Delay time (μs)	LOD (ppm)		Ref.
(ii) permeable substrate	**Filter paper**						
	SP: 532 nm, 6 ns, 10 Hz, 200 mJ	Mono-disperse colloids generated by homogeneous nucleation	Fe	N/A, 0.75	32 ng		66
			Al		137 ng		
			Cd		670 ng		
			Mn		562 ng		
			Co		44 ng		
			Zn		98 ng		
			Ni		841 ng		
			Si		183 ng		
	SP: 1,064 nm, 7 ns, 1 Hz, 170 mJ	Conostan® S-21 blended oil standards	Ag	1, 1	2		72
			Al		7		
			Cd		7		
			Cr		29		
			Cu		4		
			Fe		4		
			Mn		4		
			Mo		7		
			Ni		20		
			Ti		5		
			V		5		
			Zn		5		
			Si		19		
			Pb		18		
	DP, 1 μs: (1) 1,064 nm, 7 ns, 1 Hz, 170 mJ (2) 2,1064 nm, 7 ns, N/A, 95 mJ	Conostan® S-21 blended oil standards	Ag	1, 1	1		72
			Al		4		
			Cd		4		
			Cr		12		
			Cu		1		
			Fe		3		
			Mn		3		
			Mo		5		
			Ni		7		
			Ti		2		
			V		2		
			Zn		2		
			Si		11		
			Pb		3		
	SP: 1,064 nm, 7 ns, 10 Hz, 60 mJ	Standard solutions of individual lanthanides (Sm, Eu and Gd)	Sm	10, 3.2	1.3 ppmw		65
			Eu		1.9 ppmw		
			Gd		2.3 ppmw		
	SP: 532 nm, 16 ns, 1–10 Hz, 300 mJ	High purity reagent $CaCl_2$ and $MgCl_2 \cdot 6H_2O$ dissolved in deionized water	Ca	1, 0.5	1.9		68
			Mg		3.2		
					Preconcentration		
					Yes	No	
	SP: 532 nm, 8 ns, 10 Hz, 10 mJ	Heavy metals ions dissolved in water	Pb	1, 5	0.075	2.7	67
			Cr		0.018	0.36	

Table 1. (*Continued*)

Sampling method	Laser specification SP: W, PD, RR, PE DP, Δt: (1) W, PD, RR, PE (2) W, PD, RR, PE	Sample type	Element detected	Gate width (μs), Delay time (μs)	LOD (ppm)		Ref.
	Wood slice						
	SP:1,064 nm, 12 ns, 5 Hz, 100 mJ	Aqueous solutions of $CrCl_3 \cdot 6H_2O$, $MnCl_2 \cdot 2H_2O$, $CuCl_2 \cdot 2H_2O$, $CdCl_2 \cdot 2½H_2O$ and $PbCl_2$ with deionized water as solvent	Cr	5, 15	0.034		70
			Mn	5, 15	0.036		
			Cu	5, 15	0.029		
			Cd	2.5, 10	0.59		
			Pb	5, 15	0.074		
	SP: 1,064 nm, 6 ns, 10 Hz, 180 mJ	Aqueous solutions of $MnCl_2 \cdot 2H_2O_2$ with deionized distilled water as solvent	Mn	10, 2.5	0.623		71
					No. of shots		
					100	1,000	
	SP: 1,064 nm, 10 ns, 10 Hz, 4 mJ	Lead nitrate dissolved in deionized water	Pb	3, 0.5	0.131	0.043	69
	SP: 532 nm, 10 ns, 10 Hz, 3.5 mJ	Lead nitrate dissolved in deionized water	Pb	3, 0.5	0.113	0.036	69
	SP: 266 nm, 10 ns, 10 Hz, 1.8 mJ	Lead nitrate dissolved in deionized water	Pb	3, 0.5	0.147	0.039	69
Liquid to solid (layer)	SP: 1,064 nm, 10 ns, 10 Hz, 85 mJ	Oil sample prepared with 1:1 cooking oil and surfactant dissolving a saturated concentration of NaCl ratio	Sample: Na Ca H C Cl Target: Al Fe Si Ambient gas: Ar	N/A, 1	N/A		73
	SP: 1,064 nm, 5 ns, 10 Hz, 85 mJ	Oil sample prepared with 1:1 cooking oil (colza oil) and surfactant (dishwasher liquid) dissolving a saturated concentration of NaCl ratio	Sample: Na Ca H Cl Target: Al Fe Si Ambient gas: Ar	1, 1	N/A		74

Table 1. (*Continued*)

Sampling method	Laser specification SP: W, PD, RR, PE DP, Δt: (1) W, PD, RR, PE (2) W, PD, RR, PE	Sample type	Element detected	Gate width (μs), Delay time (μs)	LOD (ppm)		Ref.
	SP: 1,064 nm, 5 ns, 10 Hz, 90 mJ	75cSt blank mineral oil, eight virgin lubricating oils, five used oils and cooking oil Reference standard: Certified blank oil and four virgin lubricating oils spiked with metallo-organic standards	Fe	1.5–3.5, 1	3.0		76
			Cr		1.5		
			Ni		7.0		
	SP: 1,064 nm, 5 ns, 10 Hz, 90 mJ	Sunscreen Reference and validation sample: TiO_2 nano powder and blank cream	Ti	2, 1.5	N/A		77
					Spectrometer		
					Echelle	CT	
	SP: 1,064 nm, 5 ns, 10 Hz, 90 mJ	Samples containing metallic elements (Ag, Al, Cr, Cu, Fe, Mg, Na, Ni, Pb, Si, Sn and Ti) prepared by dilution with a 75 cSt hydro-carbon base oil	Fe	2, 2	3.73	2.05	75
			Mg		0.29	0.24	
			Sn		11.59	8.87	
			Si		9.71	6.71	
			Cu		2.87	0.78	
			Ag		1.50	0.95	
			Ti		3.20	1.41	
			Ni		10.73	7.28	
			Cr		10.59	8.11	
			Pb		> 100	12.51	
			base oil				

W: laser wavelength (m); PD: pulse duration/width (s); RR: repetition rate (Hz); PE: pulse energy (J); Δt: interpulse delay/interval, separation time between spark(s); REP: relative error of prediction; *LOD of emission line with lower detection limit.

4.1. *Standard configuration: Liquid sample in bulk*

LIBS applied on bulk liquids is aimed to provide impurities detection and rapid analysis due to lack of sample preparation method.[13] Without the sample treatment procedure, this method is capable in providing low-cost, real-time and *in situ* LIBS analysis. From Table 1, the samples commonly used for this procedure usually involve various types of oil[31,32] or aqueous solutions.[15,21,22,28,33] LIBS measurements of bulk liquids deal with a few challenges such as the possibility of bubble formation due to energy conversion from laser pulse when it is supposed to induce plasma inside the liquid bulk.[34] Another challenge that accompanies the plasma formation is the shockwave that could also cause splashing, affecting the analysis performance and reproducibility.[15,33] Some previous works also claimed that plasma local thermal equilibrium (LTE) might not accommodate their experiments and unable to derive plasma parameters for delay times more than 1.5 μs.[22,28]

To avoid or reduce splashing and bubbles formation, the laser repetition rate must be fixed at a certain value. Bubbles formation caused by high repetition rate could also lead to poorer average signal and larger signal variability due to the inability to focus the laser beams.[15,33] From previous works, St-Onge *et al.*[15] set a fix of 1.25 Hz repetition rate whereas Sobral *et al.*[33] suggested the laser frequency to be 1 Hz or less and averaging over a large number of laser shots. Meanwhile, Cremers *et al.*[28] reported that plasma is less reproducible and more elongated if the laser is focused further from the window of their cell. This statement is supported by St-Onge *et al.*[15] where the laser was always focused and positioned closer to the bottle inner wall. On the other hand, St-Onge *et al.*[15] found that the laser must be focused 1 cm from the bottom of the 5 cm high bottles to avoid instability of the surface due to perturbation caused by the shock wave.

Both SP and DP LIBS techniques were carried out in bulk liquid analysis. Cremers *et al.*[28] reported the first LIBS analysis of bulk liquids using single and DP laser sources. For the SP LIBS approach, Cremers *et al.*[28] used a laser excitation at 1,064 nm with pulse duration, repetition rate and pulse energy of 15 ns, 10 Hz and 45 mJ, respectively, to observe the B element in the sample. By using gate width and delay time of 0.1 and 0.27 μs, the obtained LOD was 1,200 mg/L. Although this approach successfully demonstrates the use of LIBS to directly detect atomic species in water, the LOD is still quite high.[21,22]

The usage of double or multi-laser pulse to re-excite the plasma induced by the first pulse[33] could also enhance the detect-ability of certain species and discriminate interfering spectra.[28] To provide rapid analysis of Na in bacteriostatic sodium chloride aqueous solution, St-Onge *et al.*[15] used a high power Nd:YAG laser so that the Q-switched laser could be triggered twice. The first laser pulse helps in generating gas bubbles in the water, whereas the proceeding pulse interacts with the gas inside the bubble. Cremers *et al.*[28] also demonstrated that the LOD of DP LIBS analysis (interpulse delay 18 μs) for element B in aqueous solution was 15 times than that of SP analysis.

However, for DP LIBS analysis, self-reversed emission lines and inter-element effects for some high concentration's species may cause complex calibration procedure. This method also requires a more complicated experimental setup and is limited only to observe species with moderate to high concentrations. The LIBS analysis accuracies and repeatability were also unstable.[28]

4.2. *Experimental configurations modification*

4.2.1. *Liquid sample with laminar flow*

LIBS analysis of laminar flow liquids was demonstrated in order to improve the sensitivity, detection limits and data reproducibility of the LIBS system.[6,32] The continuous flow of liquid jet ensures that the analysis of samples is uninterrupted by bubbles formed by the spark before it.[35] The purposes of employing liquid jet stream are to reduce the sample inhomogeneities issue and splashing issues. Resolving these

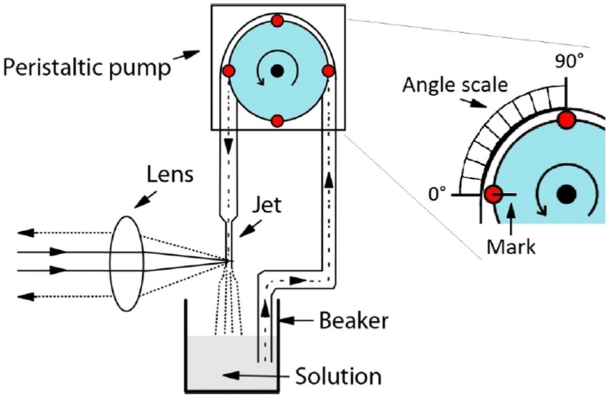

Fig. 2. Peristaltic pump with an angle scale for liquid flow generation.[37]

issues would lower the detection limits. Calibration could be performed without disturbing the optical alignment and thus leads to an improvement over the bulk liquid LIBS method.[6,35] Table 1 shows analyses of several types of aqueous solutions, standard solutions and standard oil. The configurations demonstrated in the previous works are horizontal closed-loop liquid flow[15] and vertical liquid jet system with SP[32,35–38] and DP[37,39] LIBS techniques.

St-Onge *et al.*[15] demonstrated a horizontal closed-loop system with the cell design that could rapidly annihilate the waves caused by the laser-induced shock wave, and thus providing a stable surface for analysis. The working principle of a vertical liquid jet system can be referred from a previous work of Skočovská *et al.*[37] As shown in Fig. 2, a peristaltic pump synchronized with the laser source is responsible in generating liquid flow. The synchronization was done to ablate the same liquid volume for each laser pulse, striking same angle of the jet surface and reducing the emission signal fluctuations due to the experimental apparatus. The liquid jet also has a nozzle with attached needle along with stainless steel cannula and reed (see Fig. 3), specifically developed to reduce splashing. Some other features are pulse generator to control the pump rotor frequency and angle scale to measure relative phase shift of jet and laser pulses. The average liquid flow rate demonstrated is in the range of 3.33 mL/s.[37] The optimal flow rate of the jet is related to a few characteristics such as laser excitation, nozzle construction, sheath gas and the liquid type.[40]

Several recommendations from the previous works also explained on how to improve the LIBS analysis performance. Since splashing is sometimes unavoidable, Yaroshchyk *et al.*[32] suggested to use focusing lens with longer focal length (152 mm) and moved the imaging optics further from the liquid to reduce splashing. Air jet and exhaust are also useful to deflect the droplets and aerosols produced by the interaction between laser and liquid from the optical path, as these issues are also correlated to secondary breakdown in the air space above the sample.[15] The DP laser could also provide an enhanced LIBS signal by optimizing the gate delay time, gate delay width, laser energy, focusing lens and sample distance, reducing laser ray angle

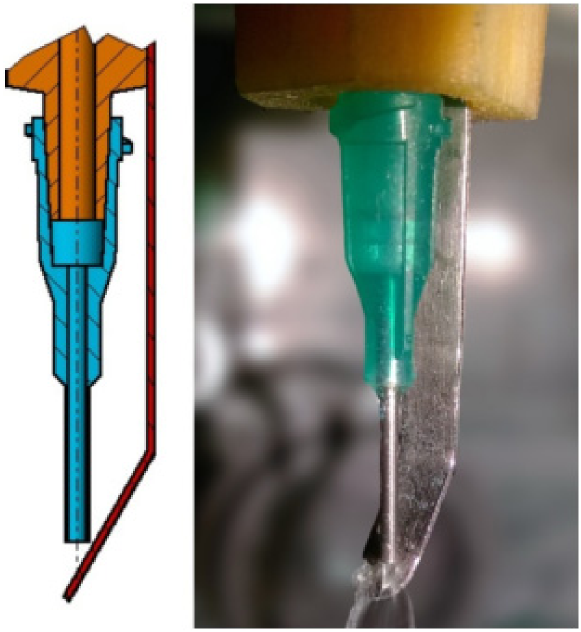

Fig. 3. The nozzle with stainless needle and reed.[37]

incident on jet surface and synchronization of peristaltic pump and the LIBS flash lamp.[37] Skočovská *et al.*[37] demonstrated the analysis of Cu in copper (II) sulfate aqueous solution using DP LIBS system (interpulse delay 1 μs) in collinear configuration with solid state Nd:YAG pulsed laser (wavelength 1,064 nm, pulse length 6 ns, repetition rate 10 Hz and pulse energy 257 mJ) as the first laser and another solid state Nd:YAG pulsed laser (wavelength 532 nm, pulse length 10 ns, repetition rate 10 Hz and pulse energy 105 mJ) as the second laser. The results showed improved LOD of Cu, proving the LIBS-enhanced sensitivity.

When the SP LIBS analysis results of liquid bulk and liquid in laminar flow configurations were compared, the latter shows better LIBS measurements. This is demonstrated by Yaroshchyk *et al.*[32] that studied the quantitative analysis of several elements in engine oil by comparing the results between liquid jets and static liquids. In this study, the liquid jet configuration used a solid state Nd:YAG pulsed laser (wavelength 1,064 nm, pulse length 7 ns, repetition rate 2 Hz and pulse energy 150 mJ) whereas the liquid bulk used a similar laser excitation but with slightly different parameter (repetition rate 0.5 Hz and pulse energy 70 mJ). By using gate width and delay time of 1 μs for each configuration, the LOD of all elements in engine oils is proven to be lower for liquid jet LIBS analysis.[32]

Although many alternatives and recommendations have been proposed, liquid jet configuration still faced a few problems such as material clogging, complex experimental setup restraining *in situ* analysis and unsuitable for limited amount of sample. Therefore, future improvement especially regarding the liquid jet design is important to make sure that this configuration could adapt with all the problems.

4.2.2. *Liquid to aerosol conversion*

The introduction of liquid to aerosol conversion method with the aid of nebulizer has been proposed in the hope to provide better stability, repeatability, LOD and LIBS signal.[25,41] Most of the applications gained from this configuration are focusing on monitoring pollutants such as analyzing environmental pollutants in aqueous systems[41–43] or specifically in nuclear industry.[44] Liquid to aerosol conversion can be done by using several type of nebulizers such as ultrasonic (with[42] or without[43] dryer unit), Collison,[44] Meinhard,[41] micronebulizer[45] or others. Some other benefits of transforming liquid into aerosol are smaller volume requirement, effectively reducing the splashing usually encountered in liquid sample, unlimited shot-to-shot frequency and better use of laser energy to ionize the sample instead of vaporizing it.[41,44]

In collison nebulizer aerosol configuration, the aerosol droplets were produced by mixing the liquid samples and gas stream, thus focusing the laser into a stream of aerosol in order to create plasma.[44] Meinhard nebulizer used by Kumar *et al.*[41] was originally designed for ICP applications. However, it can be applied for LIBS analysis by changing the liquid and gas flow rate to 3.5 mL/min and 200 mL/min, respectively.[41] For ultrasonic nebulizer system, it consists of a buffer chamber (BC) and a sample cell (SC) (see Fig. 4). The oscillating plate (OP) mounted below SC is able to vibrate at an ultrasonic frequency of 1.7 MHz. Vibration of OP could lead to liquid to aerosol transformation with Fan 1 which helped in the flow of aerosol into the BC by

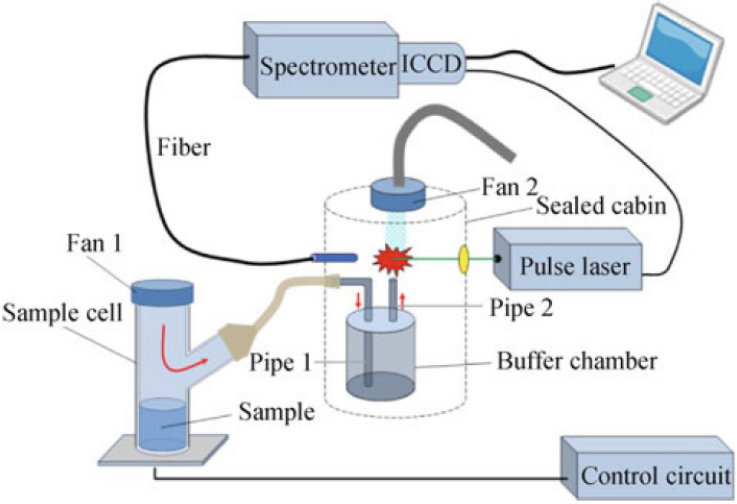

Fig. 4. Liquid to aerosol configuration using ultrasonic nebulizer.[43]

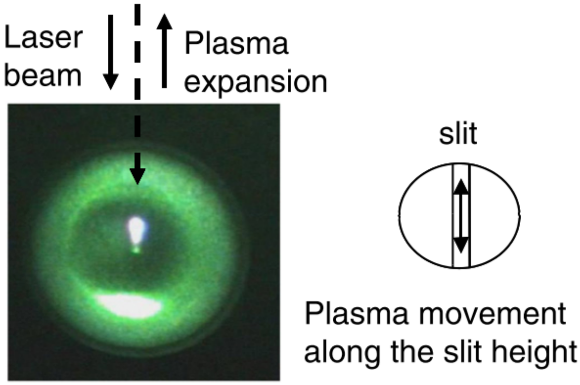

Fig. 5. Laser plasma and its movement direction along the slit height.[42]

passing through pipe 1. Finally, the aerosol would flow out of the BC through pipe 2 and ready for LIBS analysis.[43] The diameter of the aerosol droplets using ultrasonic nebulizer will depend on several criteria such as atmospheric pressure, frequency of the vibration, liquid samples' surface tension and temperature.[46] The criteria of the droplets are important as it could affect the laser energy absorbed under low concentration range whereas its size and location could influence the LIBS response.[44]

Previous works had shown numerous suggestions on upgrading the development of this configuration. For instance, Aras *et al.*[42] had suggested the usage of telescopic system (consists of three highly reflective mirrors) that guides the laser beam perpendicular to the sample flow, thus allowing plasma movement from one laser shot to another along the slit height (Fig. 5). The use of membrane dryer after the desolvation unit was also proposed to produce improved LIBS signal intensity. The dryer is capable of generating drying gas with counter current flow to dry the metal aerosol. In such condition, the LOD of Cd(I) and Pb(I) was reduced two to three times with respect to the LIBS measurements without membrane dryer.[42] Meanwhile, Zhong *et al.*[43] demonstrated the efficient quantitative analysis in their study due to the improved calibration curves by normalizing the LIBS spectral intensity by background. On the other hand, Williams *et al.*[44] proposed the conditional analysis and averaging large shot amounts to eliminate lower experiment repeatability due to the presence of variation of droplets hit per shot and laser light interference caused by the droplets.

To increase LIBS sensitivity, DP LIBS technique approach along with the conventional SP LIBS was applied on liquid to aerosol conversion using micronebulizer. For this type of configuration, the carrier gas (argon, constant flow 700 mL/min) is used to transport the solution that was converted to a fine aerosol (flow rate 40 μL/min). An injector tube was also attached to the flow chamber to produce a fine aerosol mist.[45] Cahoon *et al.*[45] demonstrated the analysis of multi-element (Sr and Mg) solutions prepared with varied final concentrations using DP LIBS system (interpulse delay 50 ns) in collinear configuration with Solo Nd:YAG particle image velocimetry (PIV) dual head laser (wavelength 532 nm, pulse length 3–5 ns, repetition rate 0.66 Hz and pulse energy 65 mJ). The results showed improved LOD of Sr and Mg with respect to the DP LIBS measurements, proving the LIBS-enhanced sensitivity.

Regardless, some drawbacks which are quite similar to liquid jet configuration are frequent system cleaning to avoid clogging, limited for hazardous liquid samples (unsuitable for toxic samples) and impractical for real time on site measurements (involving fragile device).[25] Although the usage of Collison nebulizer is claimed as an anti-clogging method, it still requires rinsing of the system with deionized water and dried with argon gas by purging the system after each use.[44] To upgrade the performance of this method, more efforts should be given on developing a system with less energy consumption and more compact in order to build an instrument that is compatible for on-site LIBS analysis.

4.2.3. *Liquid droplet sample*

Occasionally, bio-analytical chemistry, clinical chemistry, biology experiments, forensics, radioactive analyte experiments, toxicology and speciation analysis are always limited to small amount of sample volume. Providing that, it is quite common if the sample collection available for analysis is only in the range of 10 nL to 50 nL. Although dilution process is possible in raising the limited sample volume, this process could cause another problem related to the sensitivity and LOD.[17] Hence, LIBS-based technique with microdroplet was proposed in order to accommodate simple and inexpensive analysis method especially for sample with small sampling volume.[17,45,47,48] This technique was also claimed as highly compatible in being a portable analysis platform such as performing *in situ* quality control on water sources.[47] Direct LIBS analysis of microdroplet sample is also possible without the presence of carrier gas. Typical drawbacks usually affecting liquid samples (splashing and bubble formation) were also eliminated.[45]

In this method, the microdroplet dispenser is controlling the volume of each microdroplet before the LIBS measurements.[17,45,47] For instance, Groh *et al.*[17] demonstrated a subnanoliter sample introduction system in LIBS using monodisperse piezoelectric microdroplets (MDMD) dispenser system (MD-K-150, Microdrop Technologies) that generated droplets in the size range of 40–50 μm. This system used a piezoelectric nozzle to produce single isolated droplets. Droplet size also depends on several criteria such as nozzle diameter (optimum value 30 μm), viscosity of liquid and parameters control (applied voltage level and pulse width). Similar droplet generator type and droplet introduction method in LIBS were also used by Janzen *et al.*[48] This method also proved the applicability and moderate LIBS measurements result (Ca and Au LODs are 0.05 ppm and 29 ppm, respectively).[17] The example of the experimental setup is shown in Fig. 6.

The breakdown method of single droplet behaves quite differently compared to previous configurations. The droplet acts like a lens (refractive index higher than ambient gas medium), causing an increment of laser energy density on the laser beam

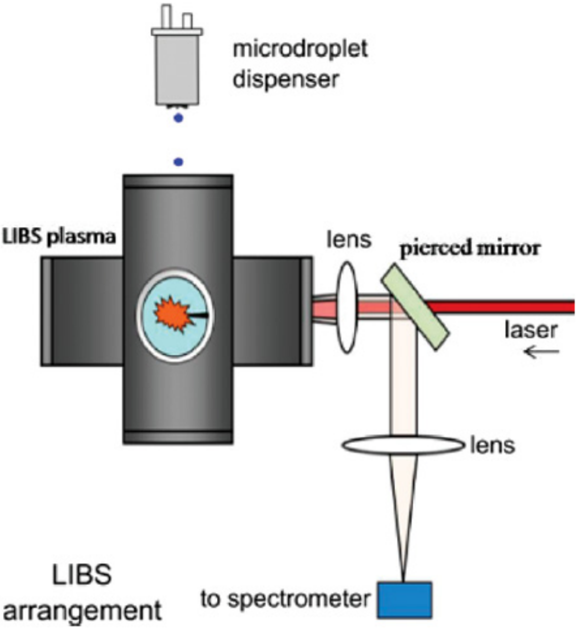

Fig. 6. LIBS experimental setups for liquid droplet LIBS experiments.[17]

propagation direction. Commonly, the breakdown originates on the rear side of the droplet, disperses toward the laser and finally vaporizing the droplet.[6,17] Compared to liquid aerosol sample, the sample introduction in subnanoliter range to the plasma is a better method as the plasma cooling is limited to localized regions. This is because heavy mass loading when using nebulizer can cause plasma cooling and thus disturbing the LIBS signal.[17]

Collinear DP LIBS is often associated with the mass ablation increment and the plasma reheating caused by the second pulse, leading to longer plasma lifetime compared to SP, thereby increasing the LIBS signal.[45,49] This has led Cahoon *et al.*[45] to apply DP LIBS (interpulse delay 50 ns) with Solo Nd:YAG PIV dual head laser (wavelength 532 nm, pulse length 3–5 ns, repetition rate 0.66 Hz and pulse energy 35 mJ) in the quantitative analysis of multi-element (Sr, Mg and Ba) calibration solutions. By comparing the DP LIBS demonstration using microdroplet and aerosol sample done by Cahoon *et al.*, both show good results. However, aerosol LIBS has better average precision, accuracy and LOD ($\sim 3.8\%$ relative standard deviation (RSD), 3.1% bias, 30–170 fg LOD) compared to micro-droplet LIBS ($\sim 14\%$ RSD, 6% bias, 1 pg LOD), proving the microdroplet LIBS less sensitivity.[45]

From the previous research, the authors had come with several suggestions on developing better liquid microdroplet sample LIBS analysis. Since some commercial droplet generator surmounted large amount of still water, Groh *et al.*[17] suggested the application of advanced microfluidic technologies such as MDMD system to decrease the minimum liquid volume requirement for analysis. The authors also suggested keeping the control parameters (applied voltage level and pulse width) within optimum value in order to achieve high droplet reproducibility. Next, for microdroplets generated by printhead device, it is also better to wait until the microdroplet generation is stabilized before starting LIBS analysis. This is because the first few droplets tend to be inconsistent,[50,51] due to the aspects such as surrounding environment, different mass, velocity and trajectory caused by wet printhead ejection orifice and fluctuation of signal.[45] Long-term stable alignment is also important in ensuring temporal and spatial stability. Triggering laser to precise droplet detection with diode could provide temporal stability, while immaculate droplet generators and using particle-free liquid samples can lead to spatial stability.[48]

As mentioned previously, the disadvantage of using this configuration is the variation of signal to noise ratio (SNR) due to droplets nonuniformity. This is because that the varied particle size limit could cause the LIBS signal to change.[45] Although the LIBS analysis result is good, this configuration is still less sensitive if compared with aerosol LIBS system.

4.3. *Sample preparations: Liquid to solid conversion*

4.3.1. *Liquid to solid conversion (pellet)*

Physical state transformation of liquid sample into solid pellet method was introduced to overcome its poor laser to liquid surface coupling that leads to low sensitivity LIBS system. This transformation could also overcome common difficulties of working with liquid in bulk samples (splashing and shockwave), providing an improved sensitivity, surface uniformity, experimental result repeatability, and thereby increasing LIBS analytical performance.[20,52] Despite the existence of many other analytical tools, LIBS-based technique was often chosen due to its simplicity, low cost, less sample amount requirement, *in situ* analysis and sample choice flexibility.[20,53] Some of this method's applications on LIBS analysis as shown by previous works are environmental monitoring (heavy metals analysis),[54] classification procedure of red wine quality,[20] elemental analysis of crude oil residue samples[53,55] and many others.

Different preparation methods on transforming liquid into solid pellet before LIBS analysis have been reported in the literature. Pace *et al.*[54] listed several criteria for determining suitable substrate material to fabricate the pellets. They were cost, simplicity level, fewer chemical composition lines to help reduce spectral interference and possible chemical reaction with liquid sample. To detect Cr, Pb, Cd and Zn in aqueous solution sample, Pace *et al.* added 6 mg of calcium oxide (Aldrich powder 98%) to 6 mL of the liquid samples, and the resulting $Ca(OH)_2$ precipitate was then air dried and pressed into solid pellets (3 cm diameter, 1 cm thick). Moncayo *et al.*[20] proposed a different sample preparation method for red wine samples classification where 1 g of commercial collagen gel was added into the 50 mL of wine sample and later 2.4 mL of the solution was dried in forced ventilation oven at $35 \pm 2°C$, producing a dry solid with a thickness of ~ 0.35 mm.

Another protocol was also developed to convert liquid crude oil into a solid tablet. Tarazona *et al.*[53] demonstrated that Colombian crude oil vacuum residues collected via distillation at low pressure of 0.53 kPa were heated up to 60°C to melt and then poured into metallic cylindrical sample holder (1 cm diameter, 5 mm thick) to form a tablet. Similarly, Gondal *et al.*[55] also obtained crude oil residue in solid paste from double distillation process conducted at 350°C and 550°C. The solid paste was heated again in electric furnace (150°C) and poured into stainless steel sample holder, producing 2 cm diameter and 1 cm thick tablet.[55] The LIBS technique applied following the preparation methods is mostly done by SP LIBS.[20,53–55]

In order to optimize the LIBS quantitative analysis, it is important to acquire optimum time delay between laser pulse and the plasma formation to avoid continuum emission.[55] The delay time selection is also closely related to signal-to-noise ratio and line intensities. The criteria that should be taken into account are type of sample, laser pulse energy and environmental condition.[54] Gondal *et al.*[55] and Pace *et al.*[54] both acquired a delay time of 5 μs and 7 μs, respectively. Gondal *et al.* also recommended that sample preparation and analysis to be done immediately to avoid sample degradation and oxidation. It is also advisable to place the resulting solid sample on a rotatable sample holder to avoid formation of crust and ensuring that every laser–sample interaction only happened on the fresh spot of the sample.[20,53–55]

Both Moncayo *et al.*[20] and Tarazona *et al.*[53] used Artificial Neural Networks (ANNs) statistical model to tolerate function fitting (depending on variables) of nonlinear information results. The ANN method provides a fast and robust classification for elements detection in samples. When LIBS and ANN are combined, a sensitive screening tool with high speed and throughput can be generated. The ANN model performance can be verified by three validation approaches (internal validation, generalization ability and independent external validation).[20] Although the LIBS and ANN combination could provide feasible quantitative analysis, the pre-existing trace elements of the substrate chosen for elemental analysis could affect some element signals.[20,53] To overcome this situation, it is important to ensure that the selected emission lines of the elements within certain wavelength intervals were not overlapped with the one observed in the substrate.[20]

Some disclaimers that should be taken into account before applying this sample's physical state transformation are the possibility of inhomogeneities and contamination during the sample preparation procedure.[52] For future studies, the use of a compact spectrometer in LIBS analysis increases the possibility of building portable LIBS, reducing the experimental setup dimension and an *in situ* classification result. However, since minimum sample preparation is needed in producing solid pellets, this method is less suitable for *in situ* analysis applications.[54]

4.3.2. *Liquid to solid conversion (frozen)*

Liquid to solid conversion by freezing is one of the simplest sample preparation methods in reducing splashing that usually linked to liquid sample. Once splashing is eliminated, the laser repetition rate will increase, resulting in emission enhancement and improved LIBS measurement.[33,56] The liquid sample placed in a holder (cup) is immersed in liquid nitrogen for about 20 s to 30 s.[33,56] Caceres *et al.*[56] also suggested re-freezing the sample before each ablation. Since the solidified sample maintained the inherent homogeneity of the initial liquid sample, it is easier to handle the sample for further analysis.[56] Some other advantages of this method are lack of drastic reduction in plasma emission intensity, negligible solution pre-enrichment requirement, unnecessary liquid optical transparency and less complicated fiber-coupling procedure arrangement.[56]

A comparison between trace elements found in liquid sample and the solidified similar liquid sample has been reported in the literature.[33] The authors conducted the same experimental procedure for both samples using SP laser excitation at 1,064 nm with pulse energy of 100 mJ, and repetition rate of 1 Hz to avoid splashing. The results showed that solidified sample provided better SNR because of the improved coupling between the laser pulse and the components of the sample. The average LOD for solidified sample was found to be six times lower than that of liquid sample. This proved that LIBS is a suitable analytical tool for detection and quantification of trace elements in solidified liquid samples.

The most important precaution when dealing with ice sample is controlling the sample temperature to ensure accurate LIBS measurement. This is because that the sample temperature could also affect the ablation rate and plasma intensity.[24] However, since most of the LIBS experiment involving liquid to solid conversion by freezing usually use liquid nitrogen, the sample temperature is quite difficult to control.[33,56–58] Some other factors that should be looked at are the pre-melting during the warming phase and impurities or elements in the sample that could alter the sample's temperature and properties.[24,59]

It is also possible to apply this sample preparation technique on liquid sample with different viscosity level. A different method in controlling the temperature of the sample is equally important to provide better understanding of the relation between the samples' temperature and the LIBS measurements. In conclusion, research on solidified liquid samples for LIBS analysis could be further enhanced.

4.3.3. *Liquid to solid (substrate)*

Another method for solidifying for LIBS analysis involves the use of absorbent substrate. The substrates can be nonpermeable (graphite[60] and metal plate[61–64]) and permeable (filter paper[32,65–68] and wood slice[69–71]). The sample preparation procedure for both types of substrate involved either dipping the substrate into the sample or drop wise transfer of aqueous sample on the substrate. The substrate is dried before LIBS analysis can be performed.[61,69]

The selection of substrate is important because substrate could produce its own strong emissions leading to several issues in element calibrations.[69] For filter paper substrate, these difficulties could be overcome by washing the papers with acid or using wood substrate with less background line contamination.[72] The leading strength of this method is the lack of experimental apparatus modifications, thereby avoiding set up complexity.[72] According to Haisch *et al.*,[66] some other advantages of using this configuration are reduced sample preparation time because smaller substrate area is taken into account in the study and minimized sample contamination due to possible on-site LIBS analysis on sample.

LIBS analysis of solid substrate presents some improvements over the other liquid sample configurations such as in emission enhancement,[61] better LOD, splashing elimination and sample handling simplicity.[32] Yaroshchyk *et al.*[32] demonstrated the analysis on used engine oil using three different sample configurations such as liquid in bulk, liquid laminar jet and liquid to solid matrix. A Q-switched Nd:YAG laser with a 7 ns pulse duration and different optimum laser energy and repetition rate (see Table 1) was used. Although jets are a better method for liquid LIBS applications compared to liquid bulk, sample splashing is still unavoidable. SP LIBS analyses on the filter paper substrates with added oil samples have an average of two times better LOD than as previously demonstrated by liquid jets. The reason is because of eliminated surface splashing that allowed the imaging lens to be closer to the ablation spot, and thereby generating a stable signal. Yaroshchyk *et al.*[72] also conducted a comparison between SP and DP LIBS for the quantitative elemental analysis of filter paper substrates with added oil samples. The findings showed that DP LIBS exhibits four times LOD improvement than obtained by liquid jets whereas as previously stated, SP LIBS showed two times better LOD. However, SP LIBS is still a better choice because adding laser source to comprehend insignificant improvement of DP LIBS would increase the system's cost and complexity.[72]

The microextraction technique was then developed to overcome limitations encountered by conventional liquid–liquid extraction such as high solvent amount needed, procedure complexity and time-consuming. The liquid–liquid microextraction techniques applied on analyte concentration produced extractant in microvolume quantity. The microextraction technique coupled with LIBS analysis is capable of capturing the trace elements in the samples. Aguirre *et al.*[61] have performed two LIBS analysis on manganese in microdroplets which are direct analysis on microdroplets and analysis of microdroplets dried on metallic substrates. The latter used an approach called surface-enhanced LIBS (SENLIBS) technique where static liquid–liquid microextraction for microdroplets analysis is prepared by drying it on a metallic substrate. Both approaches used the same solid state Nd:YAG pulsed laser (wavelength 1,064 nm, pulse length 10 ns, repetition rate 10 Hz and pulse energy 180 mJ). The SENLIBS approach depicts the hot and dense plasma generated on the metallic substrate which envelops the droplet and thereby causing LIBS signal enhancement. The trace elements' atoms in the droplet reach thermal equilibrium with the plasma. However, in direct microdroplet analysis, direct laser and droplet interaction is unable to produce high temperature and high electron densities, thus lowering the LIBS signal. SENLIBS method thus provided better precision and sensitivity. It also enabled replicated measurements to be carried out in a single

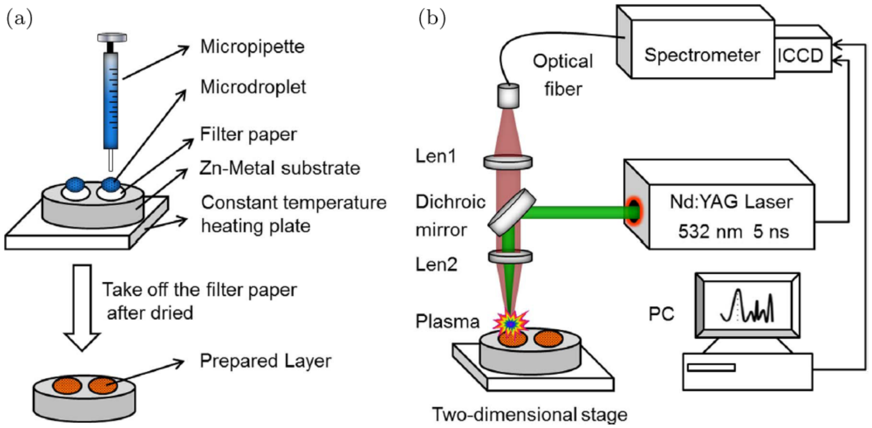

Fig. 7. Microextraction process and LIBS experimental setups for substrate sample LIBS experiments.[64]

microdroplet with the resulting Mn LOD of 6 μg/g. Similar SENLIBS arrangement with different types of metallic substrates are also reported in other works.[63,64] Figure 7 shows the microextraction process and the experimental setup previously done by Yang *et al.*[64]

Lee *et al.*[67] proposed another alternative which involved pre-concentrating the dissolved aqueous sample. The authors used this method in detecting heavy metals (Pb and Cr) in water using LIBS. The pre-concentration approach involved evaporating the 40 g of the sample solution on a filter paper using oven for approximately 1 h. Similar SP Nd:YAG laser excitation at 532 nm (repetition rate 10 Hz, pulse duration 8 ns) with a 10 mJ pulse energy is used in these approaches. By using the gate width of 1 μs and delay time of 5 μs with respect to the laser pulse, the resulting LODs of 75 ppb and 18 ppb were obtained for Pb and Cr. In contrast, when the filter paper is conventionally soaked in the aqueous sample, the LODs obtained were only in the sub-ppm range. The authors also suggested adding higher sample solution amount and argon gas flow on sample surface to provide lower LOD of the pre-concentration approach. Since the signal intensity shot-to-shot variation is quite obvious, it is recommended to acquire large amount of single shot spectra. Although the signal intensity is lower for single shot spectra, the precision is constant for each measurement. This step is done to avoid the shot-to-shot variation caused by sample inhomogeneity where the signal is stronger when the laser beam focuses in the fiber body and weaker if the laser pulse hits in-between the microfibers.

The method of using wood sample substrate has also been reported in the literature for the analysis of toxic heavy metals in aqueous solution.[69–71] Chen *et al.*[69] compared different laser parameters (laser wavelength and energy) and number of shots to investigate the performance of this method. For quantification of Pb element in lead nitrate aqueous solution, the laser excitation at 1,064, 532 and 266 nm with pulse energy of 4.0, 3.5 and 1.8 mJ, respectively, are used. The laser pulse duration and repetition rate are fixed at 10 ns and 10 Hz, respectively. By using the gate width of 3 μs and delay time of 0.5 μs with respect to the laser pulse, lower LOD can be achieved while using lower energy pulse with 1,000 shot accumulation. Laser excitation with shorter wavelength has higher photon energy and lower breakdown threshold. Hundred shot accumulations could give the finest LOD only if laser excitation at 532 nm with pulse energy of 3.6 mJ is used. The performance of LIBS at 266 nm laser pulse could be improved if similar amount of pulse energy of 3.6 mJ is employed.

Aguirre *et al.*[61] suggested more studies initiated on determining most suitable substrate and droplet deposition procedure to avoid inhomogeneity, accuracy analysis of SENLIBS results, sample matrix influence on LIBS signal, and alternative DP LIBS for SNR improvement.

4.3.4. *Liquid to solid matrix (layer)*

This method is proposed for liquid with thick consistency such as gel-textured material, cooking oil,[73,74] lubricating oil,[75,76] sunscreen[77] and others. The sample preparation procedure is done by smearing a thin layer of the sample in mL range uniformly (thickness $\sim \mu$m) on a clean metallic substrate surface.[73–77] Before laser ablation, the prepared sample is left for some time to stabilize the layer formed on the target surface. There was also a proposal about adding surfactant in the sample to lower the surface tension.[73]

Several benefits in LIBS analysis protocol such as flexible application on a variety of soft or gel-like liquids, considerably small sample requirement and simple sample procedure relevant for *in situ* analysis have been demonstrated.[74,75] LIBS elemental analysis of viscous liquid is a competent analytical tool in presenting a sample's quality and performance. For instance, trace metals' LIBS analysis in hydrocarbon base (lubricating) oil could analyze petroleum spill and leakage pollutants,[75,76,78] sunscreen elemental analysis could provide products' formulation and safety status,[77] cooking oil screening could differentiate the hogwash oil[76,79] and others.

Since direct laser ablation of pure and viscous liquid samples has been associated with low efficiency and moderate plasma temperature, indirect breakdown mechanisms have been approached.[77] Similar mechanism had been reported in other works.[73–76] The indirect breakdown of viscous liquid sample on metallic substrate induced plasma on the target surface, with the plasma consisting of substances from the layer, the target and the ambient gas. Consider a thin film of viscous liquid coated on aluminum substrate. Upon breakdown, the Al emission from the substrate expends away from the target surface to ablate the sample and ambient gas.[73–77] A bifurcating circulation of aluminum vapor is formed against a spherical confinement wall (at the front of the plasma plume), thereby causing high plasma temperature to remain in the range of 2 mm above the target surface in order to excite Cl the viscous sample. The emission of Cl from the viscous sample indicated plasma's high temperature ($\sim$ 15,000 K). Cl is usually hard to detect using LIBS due to its high excitation energy. It was suggested that the observation of strong elemental emission happens after an optimum detection delay of 1 μs at approximately 2 mm above the target.[73–76] This is important for positioning the detection systems in order to reduce the self-absorption affecting the selected spectral lines.[75] This breakdown mechanism had successfully shown insignificant matrix effect in lubricating oil samples and lower LOD in sub-ppm range.[76]

To improve the performance of this sample preparation method, some recommendations have been reported in the literature. For instance, Xiu *et al.*[75] reported LOD improvement of metallic elements in lubricating oil with the use of different types of spectrometer. The authors used two types of spectrometer which are Echelle (Mechelle 5000, Andor Technology) and Czerny–Turner (CT) (Shamrock 303, Andor Technology). Even though Echelle spectrometer could provide higher spectral resolution ($\lambda/\Delta\lambda = 5{,}000$) and wider spectral range (220–850 nm), its throughput is smaller due to small entrance numerical aperture. Hence, CT spectrometer equipped with higher throughput is used for improved detection sensitivity. The results showed that the use of CT spectrometer had reduced the average LOD to 4.04 μg/g (for 10 elements) while the average LOD with an Echelle spectrometer is 6.02 μg/g (for 9 elements). However, the use of CT spectrometer failed to improve the LOD of Pb. This is due to the interference of strong nitrogen lines (N I 409.994 nm and N I 410.995 nm) from the base oil and atmospheric air that increased the fluctuation of the background. The authors suggested choosing another ambient gas although it is still possible for the gas to cause interference to other elements.

Compared to liquid conversion procedures as mentioned in Secs. 4.3.1 and 4.3.3, this method faced similar challenges due to the unavoidable presence of substrate in the sample preparation and the sample preparation method itself. For example, Xiu *et al.*[75] were unable to quantify the element Al in the hydrocarbon base oil sample due to the existence of Al in the aluminum substrate used. The authors also removed the element Na from quantitative LIBS analysis due to high contamination probability amid the sample preparation process. Therefore, it is crucial to make sure that the selected emission lines are free from any interference or self-absorption. For instance, Xiu *et al.* selected the less intense Cr I 360.53 nm line due to overlapping of CN molecular band with two more intense lines. In another study, Zheng *et al.*[76] chose the lines Fe II 259.9 nm, Cr II 284.3 nm and Ni I 341.5 nm to represent the concentration of the virgin lubricating oil. The Ni I line was still chosen even if the SNR is lower as it is still observable for 50 ppm concentration. For determination of Ti concentration in sunscreen samples, the authors had identified four classes of titanium lines, namely Ti I resonant (R), Ti I nonresonant (NR), Ti II (R) and Ti II (NR). The Ti II (NR) at 390.054 nm line was selected where the determined Ti concentrations correspond to the actual concentration of Ti in the sample.[77]

As a conclusion, this method has its own strength and limitations. In order to provide a flexible sample preparation method, more assessment of the reported method should be done on different types of viscous liquid samples. Moreover, future research focusing on upgrading the performance of the viscous liquids LIBS configuration is also important for various applications and research fields.

5. Conclusion

Although claimed as an analysis technique that could work with a huge variety of samples regardless of its physical states, work done on liquid samples for LIBS analysis is quite limited due to strong splashing and shockwave formation. In this paper, the strengths and limitations involved in liquid LIBS sample preparation and analyses are discussed. The available methods mentioned are liquid analysis in bulk, laminar flow, liquid to aerosol conversion, liquid in droplet form and liquid into solid transformation.

Despite the status of the LIBS sample preparation as being "out of the ordinary", previous works showed the involvement of sample preparation to provide improved LIBS measurements. The time has come to start reconsidering LIBS sample preparation procedure because even the better version of analytical techniques such as ICP-MS, ICP-OES and XRF also require these procedures. In fact, more sample treatment configurations should be developed to provide various improvements and alternatives for future studies.

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