

Measuring Pipeline Chemical Composition Using Laser Induced Breakdown Spectroscopy (LIBS) Technology

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Abstract

Recent PHMSA safety rules governing the operation of gas pipelines require operators to ensure material records are 100% traceable, verifiable, and complete (TVC) within the guidelines for the Pipeline Material Verification process defined under 192.607. Testing for chemical composition is a critical input where records are incomplete and while performing grade estimations for MAOP reconfirmation.

Emerging non-destructive technology using portable handheld laser induced breakdown spectroscopy (LIBS) for in-situ analyses offers one NDE methodology for assessing pipeline steel composition. The LIBS technology will be presented including performance for carbon, carbon equivalency in addition to the concentrations of microalloying elements that may be present in the sample.

LIBS Technology

LIBS is a type of optical emission spectroscopy used to measure elemental concentrations in a material. LIBS operates by using a pulsed, focused laser that is fired at a sample with sufficient pulse energy as to create a plasma around the area struck. Bound atomic electrons are stripped from the atoms comprising the material. As the plasma cools, atoms recombine with electrons and in the process emit light in the UV, optical and IR regimes.

The handheld LIBS, like spark OES, must use argon purge for quantitative chemical analysis. Argon is an inert gas that helps increase signal by increasing the lifetime of the plasma. As the plasma wants to cool down very quickly, argon slows the rate of cooling because it is less conductive than standard atmosphere. A longer plasma life allows the optics to collect light over a longer period allowing for better signal to noise and absolute intensity. **(Figure 1)**

HH LIBS argon purge consists of a replaceable cartridge within the analyzer, typically in the handle or along the chassis. **(Figure 2)** For carbon and low alloy steel analysis, the cartridge supports between 150-200 individual measurements.

- A pulsed laser, typically in the 5-6 mJ/pulse energy range and pulsing 50 times per second (50Hz) is fired at a sample. The 1064nm laser passes through a focusing lens, to focus the laser beam down to approximately a 50um diameter. The pulse duration is 1-2ns (billionths of a second) thus yielding a high enough power density (energy/area/time) to vaporize the material producing a plasma. **(Figure 3)**
- As the plasma cools over a few hundred micro-seconds, the electrons that were stripped from the atoms recombine with the atoms, emitting light in the UV, optical and infra-red spectrum.
- An on-board spectrometer that spans 190nm - 620nm analyzes the emitted light by measuring the wavelength and intensity (amount) of light at specific wavelengths – the optical spectrum. Also installed is a dedicated high-resolution spectrometer at the 193nm range where carbon is measured.

- On-board software compares the spectral lines with known wavelengths to identify what elements are present and uses the intensity of those lines with an on-board calibration, to quantify the concentration of the element.

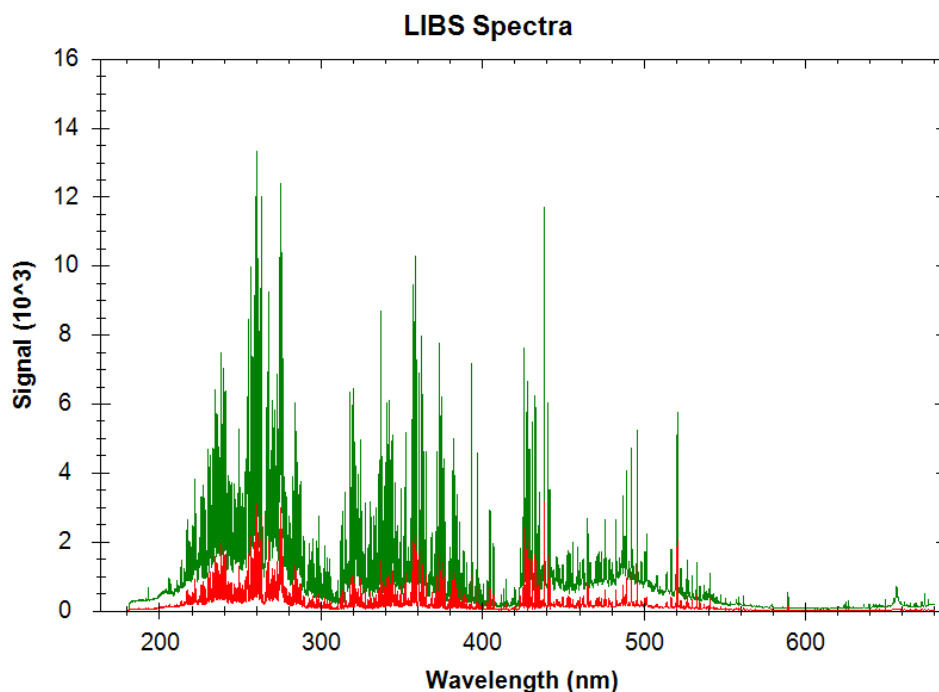


Figure 1. LIBS spectra using argon gas



Figure 2. LIBS analyzer and argon canister location

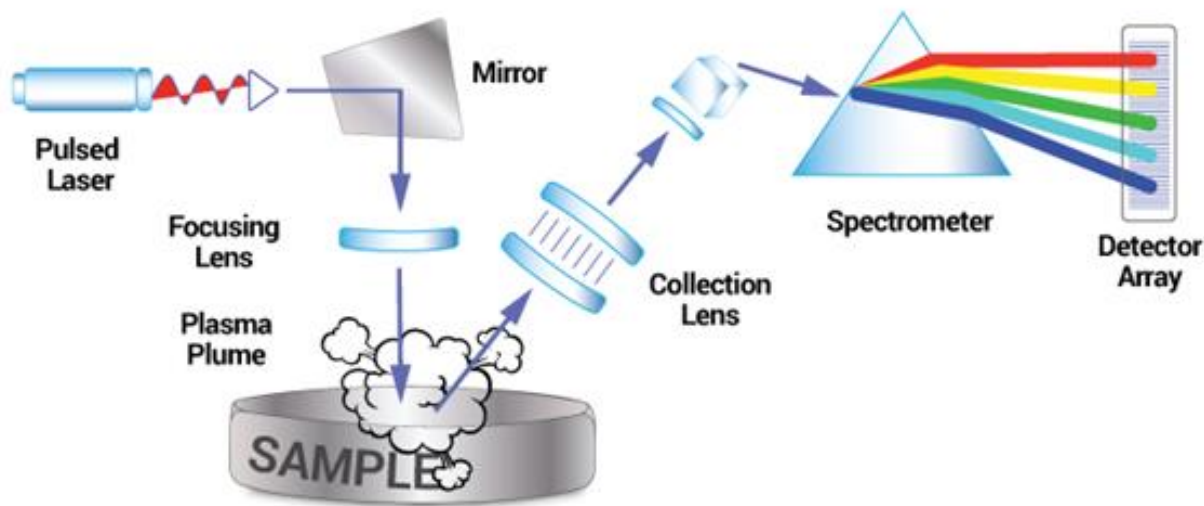


Figure 3. Overview of the LIBS process

Alloy Sample Preparation

Sample preparation must be performed before any measurement process to ensure the most reliable performance and results. LIBS is a surface analysis technique; results are heavily dependent on sample condition. The LIBS process makes use of laser sample cleaning, and this helps to remove material from the surface such as dust, dirt, oxide, corrosion, or other contamination that could affect elemental results. **(Figure 4)**

Start by choosing an acceptable test location and avoid areas of heavy pitting or grinding on critical dimensions such as flange faces, shaft journals or over markings such as heat or lot numbers. Confirming adequate material thickness is a good practice prior to preparation of in-situ pressure containing components such as process piping. Consider material composition and grit when selecting abrasive grinding media. 60-80 grit ceramic or zirconium aluminum oxide is recommended for typical carbon and low alloy steels. **(Figure 5)**

Work the disc near parallel to the surface evenly to produce an ~1"x1" area for easy positioning. Avoid using excessive pressure while maintain positive control to avoid dishing or removing excessive material. Remove, replace and discard used discs often, be aware of spark/debris discharge direction and wear personal protective equipment (PPE) as appropriate. **(Figure 6)**

Proper grinding technique will result in a shiny surface with faint linear grind marks, not swirls. Typical sample preparation may remove between 0.004"-0.008" material depending on surface condition. A good, recommended practice is to perform pre and post grinding wall thickness measurements.



Test	Sample	C
1	20" X52	0.256
2	20" X52	0.337
3	20" X52	0.184
4	20" X52	0.409
5	20" X52	0.314
6	20" X52	0.551
7	20" X52	0.198
8	20" X52	0.602
9	20" X52	0.585
10	20" X52	0.247
AVG		0.3683
STDEV		0.16015
RSD		43%

Figure 4. Measurements effects of poor sample preparation



Figure 5. Prepared pipe sample with surface pitting removed using ceramic disc

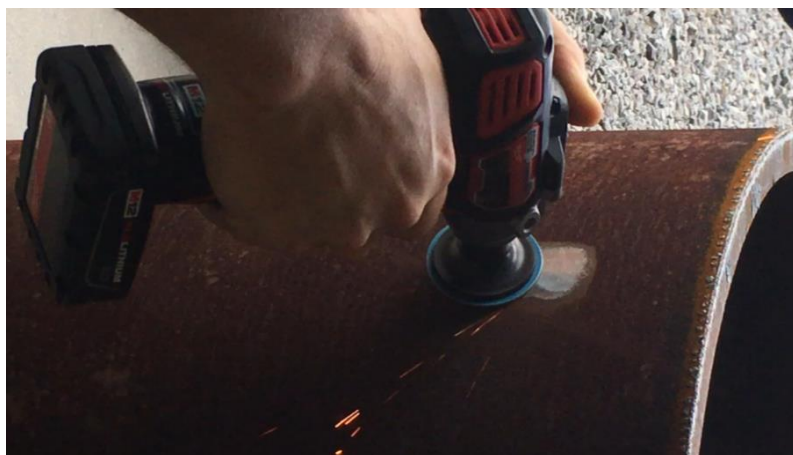


Figure 6. Sample preparation using Milwaukee M12 Sander

Test Method

Carbon is the principal element contributing to a steel's hardness and strength and adjusting the content is simplest practice to change its mechanical properties. Addition of alloying elements can produce favorable characteristics not achievable in typical C-Mn steels and have a strong influence on effects of heat-treating. Microalloying elements such as aluminum, niobium, vanadium and titanium allow the producer to reduce carbon content to achieve strength while reducing susceptibility to cracking with lower carbon equivalency. Therefore, it is important for mills, producers, and fabricators to be able to measure carbon, carbon equivalency and amounts alloying elements in accordance with API Recommended Practice 578.

For this evaluation of LIBS technology for the inspection of API 5L piping material composition, specific elements were selected to be measured. The ranges chosen, in general, cover the range of acceptance criteria per API Specification 5L, 46th edition for PSL 1 and PSL 2 seamless and welded pipe configurations. These elements include carbon (C), manganese (Mn), silicon (Si), copper (Cu), nickel (Ni), chromium (Cr), molybdenum (Mo), niobium (Nb), aluminum (Al), vanadium (V) and titanium (Ti). **(Figure 7)**

An array of certified reference materials (CRM's) was researched and selected to best represent the typical elemental concentration ranges found in both legacy and modern high strength micro alloyed piping. Testing criteria was developed using 6 samples measuring 11 elements 5 times each for average for a total of 30 measurements per element. **(Figure 8)**

Carbon Equivalency (CE) can also be measured and displayed on the HH LIBS screen at the same time its constituent elements are collected. **(Figure 9)** For this study, all supporting elements were graphed and evaluated for accuracy and precision including CE-IIW. Additionally, a removed section of API X65 line pipe was analyzed with LIBS and the results of 10 consecutive measurements were calculated by the analyzer using both Deardon & O'Neill and AWS carbon equivalency formulas. **(Figure 10)**

Results show 7 of the 10 elements measured yielding single digit relative standard deviation (RSD) over the sample size with CE-IIW and CE-AWS in low single digit range with 3.1% and 2.4% respectively.

Period	1	2																18
	I A	II A																VIII A
1	1s																	2
	H	He																
	hydrogen	helium																
2	2s																	
	Li	Be																
	lithium	beryllium																
3	3s																	
	Na	Mg																
	sodium	magnesium																
4	4s																	
	K	Ca																
	potassium	calcium																
5	5s																	
	Rb	Sr																
	rubidium	strontium																
6	6s																	
	Cs	Ba																
	cesium	barium																
7	7s																	
	Fr	Ra																
	francium	radium																

3	4	5	6	7	8	9	10	11	12
III B	IV B	V B	VI B	VII B	VIII B	VIII B	VIII B	IB	IIB
21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
scandium	titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper	zinc
	0.03 - 0.5	0.03 - 0.5	0.02 - 10	0.05 - 2	BAL		0.05 - 2	0.05 - 0.75	
39	40	41	42	43	44	45	46	47	48
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
yttrium	zirconium	niobium	molybdenum	technetium	ruthenium	rhodium	palladium	silver	cadmium
		0.025 - 0.2	0.03 - 1.25						
71	72	73	74	75	76	77	78	79	80
Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
lutetium	hafnium	tantalum	tungsten	rhenium	osmium	iridium	platinum	gold	mercury
103	104	105	106	107	108	109	110	111	112
Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
lawrencium	rutherfordium	dubnium	seaborgium	bohrium	hassium	meitnerium	darmstadtium	roentgenium	copernicium

Figure 7. Key elements in carbon and low alloy steel



Figure 8. Certified Reference Materials and rastered laser beam distribution