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

Brian Wilson, SciAps, Inc., United States

Objectives

- PHMSA Mega Rule
- LIBS Technology Overview
- Sample Preparation
- Testing Method
- Testing Results
- Observations
- Q&A



PHMSA Mega Rule

- 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.

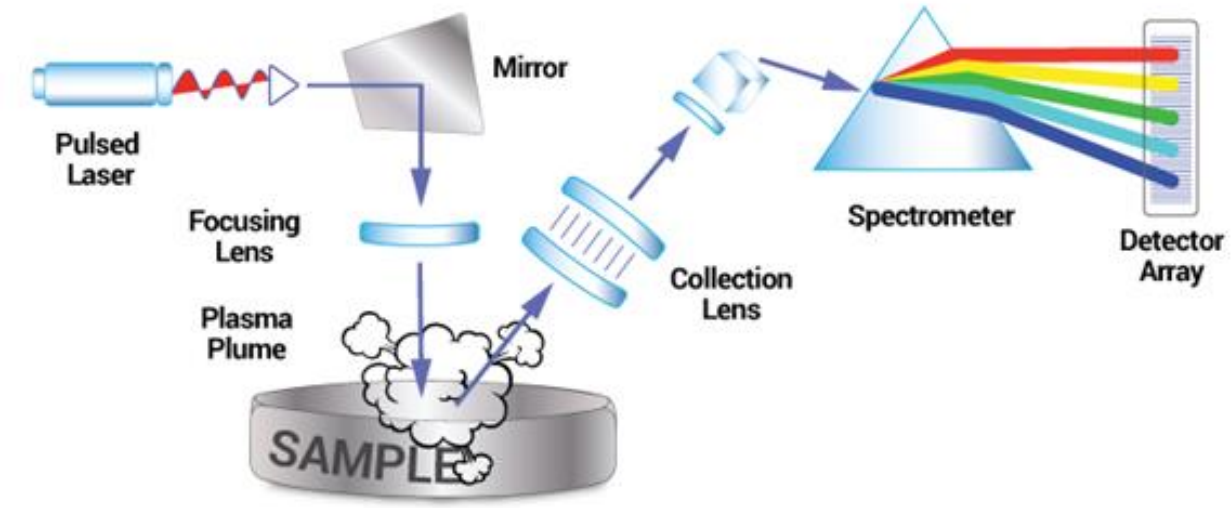
- Testing for chemical composition is a critical input where records are incomplete and while performing grade estimations for MAOP reconfirmation.

- 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.

- We will present the LIBS technology including performance for carbon, carbon equivalency in addition to the concentrations of microalloying elements such as Nb, V, Ti, Al that may be present in the sample.

LIBS (Laser Induced Breakdown Spectroscopy)

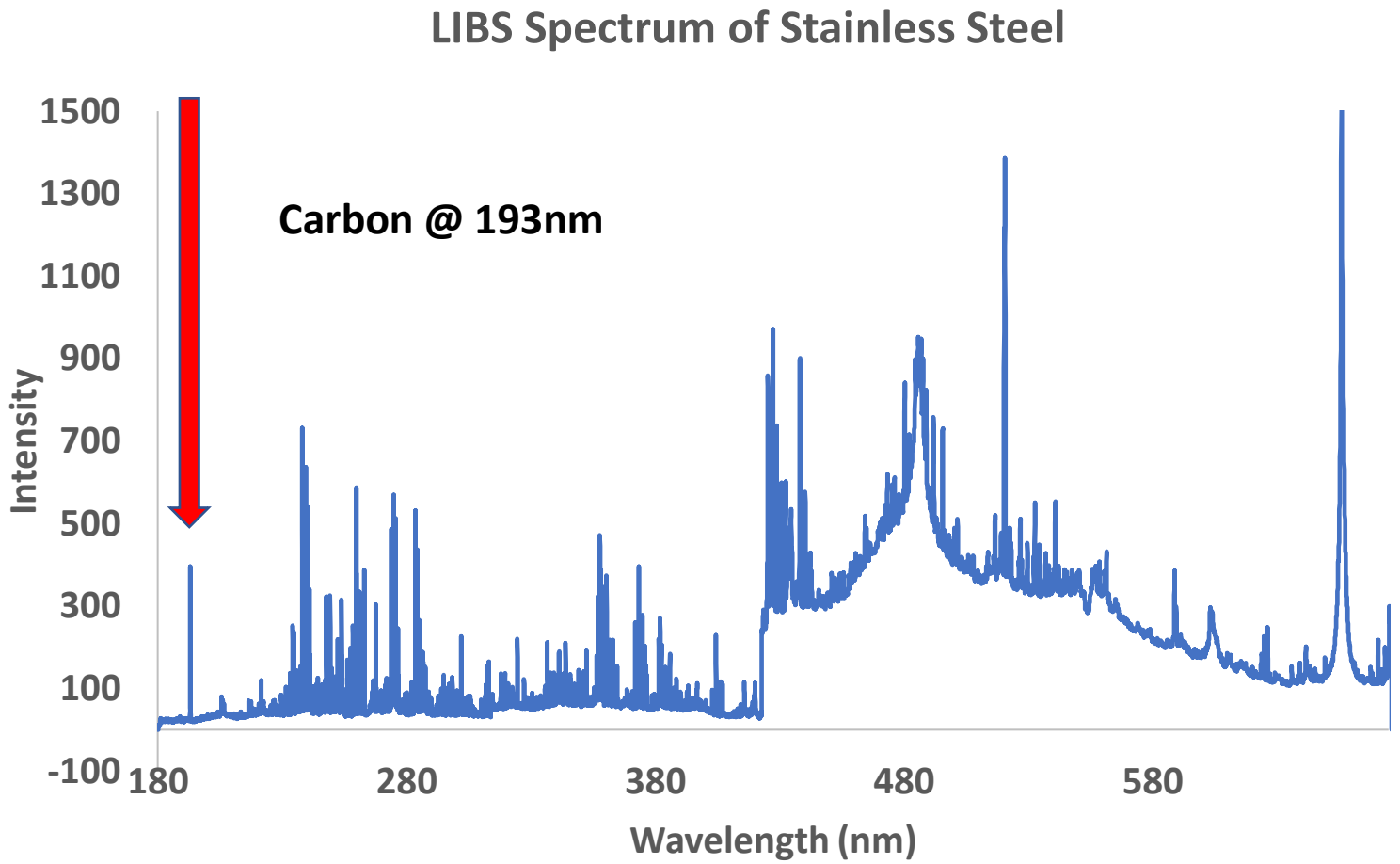
- Optical Atomic Emission Spectroscopy (OES)
- Focused laser ablates surface to create a plasma
- Light from plasma is collected, run through a spectrometer and projected onto the detector creating a spectrum (x – wavelength, y – intensity)



LIBS Technology

- As electrons in plasma settle back to atomic orbitals, they emit characteristic photons
- LIBS uses a diffraction grating, optics and CCD to determine wavelength of the photons to produce a spectrum
- Some elements may only produce 1 or 2 visible peaks, while other elements may have 100's of peaks
- Good spectral resolution is important for finding interference-free peaks
- LIBS uses ultra-high purity Argon purge to increase signal lifetime of the plasma and slow that rate of cooling of the plasma





Handheld LIBS Example



Sample Preparation

- Must be performed to ensure most reliable performance and results
- Rust, pitting, oxidation, residue, greases, oils, paint, primer, dirt, dust, or any contamination will affect results
- Confirming adequate material thickness is a good practice (i.e., in-situ testing)
- Consider disc composition and grit when selecting abrasive media. Ceramic or ZrAlO discs recommended 36-80 grit







Sample Preparation

- Select area ~1”x1” and work the disc near parallel to the surface to avoid dishing or excess material removal
- Remove, replace, discard grinding discs as necessary
- Proper technique will yield shiny surface with faint linear grind marks, not swirls
- Typical removal can be 0.004-0.008”
- Consider pre & post thickness measurements and recording









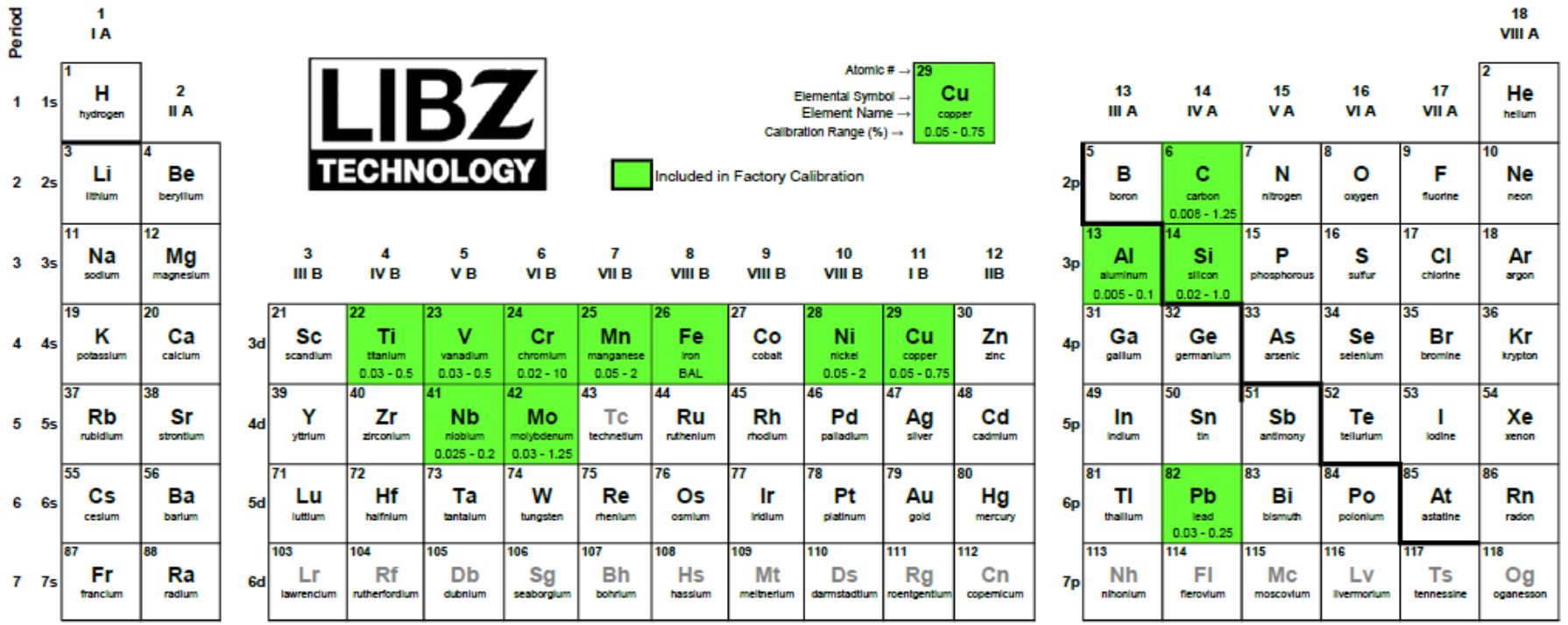
Sample Preparation



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

Test Method

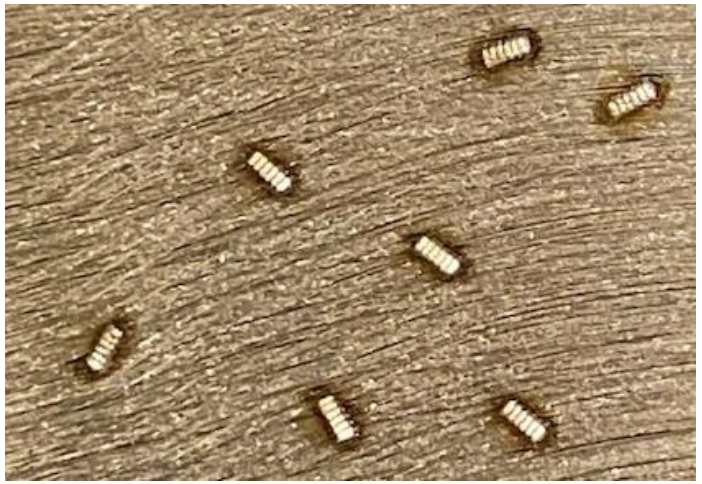
- Carbon is the principal element contributing to hardness and strength
- Addition of micro alloying elements can produce desirable properties
- Nb, V, Ti, Al allow producer to reduce %C and maintain strength
- Carbon equivalency (CE) reduced, increasing weldability, reducing cracking



Test Method

- Specific elements selected to be measured that represent API 5L PSL 1&2 chemistry
- C, Mn, Cu, Si, Ni, Cr, Mo, Nb, Ti, Al, V, CE-IIW
- Six certified reference standards tested (NIST)
- Five measurements captured per sample
- Each measurement features 5 individual tests for average
- The 8 elements included in CE-IIW equation measured and calculated by LIBS software
- Measured vs. certified values graphed and coefficient of determination R2 calculated





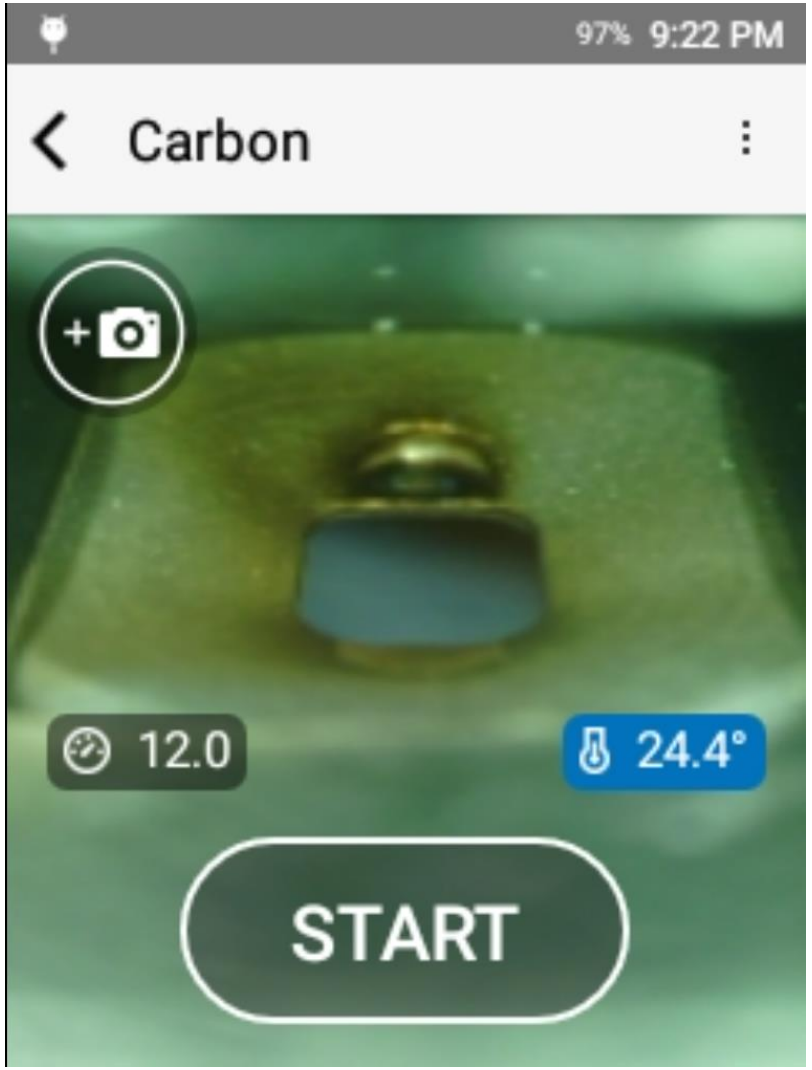
Deardon O'neill (adopted by Int'l Inst. Welding)

$$CE = \%C + \frac{\%Mn}{6} + \left(\frac{\%Cr + \%Mo + \%V}{5}\right) + \left(\frac{\%Cu + \%Ni}{15}\right)$$

American Welding Society Formula (AWS)

$$CE = \%C + \left(\frac{\%Mn + \%Si}{6}\right) + \left(\frac{\%Cr + \%Mo + \%V}{5}\right) + \left(\frac{\%Cu + \%Ni}{15}\right)$$

Test Method

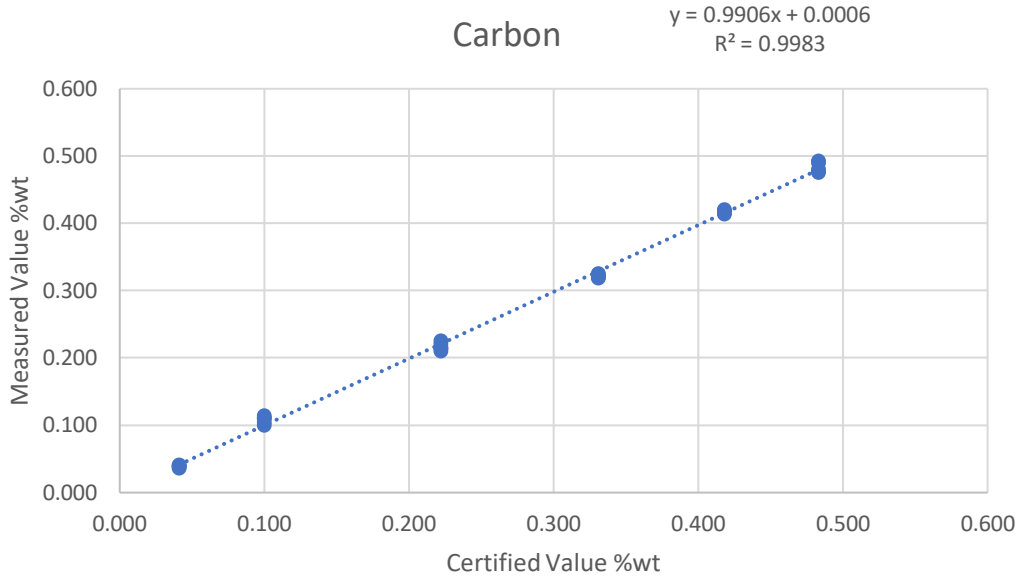


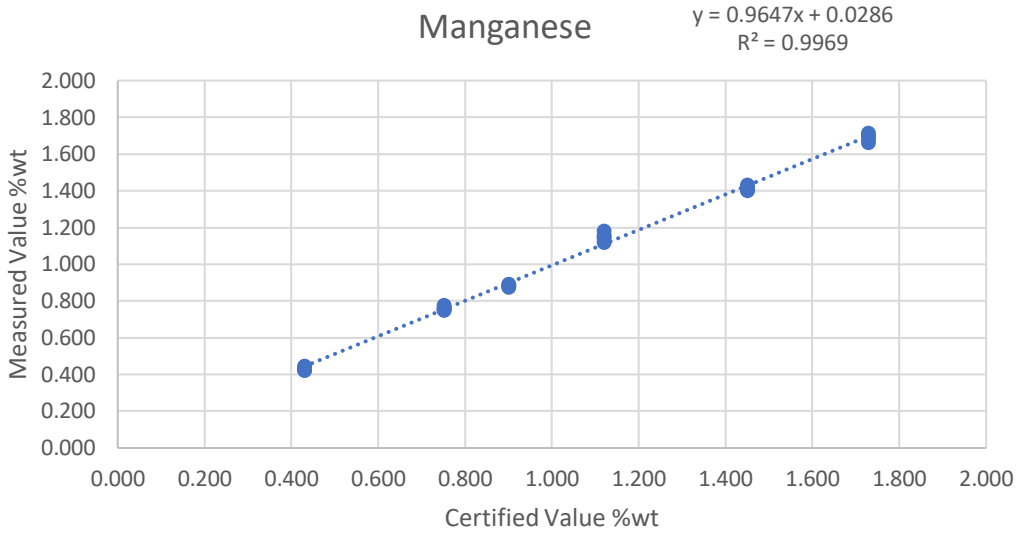
Carbon SAVE

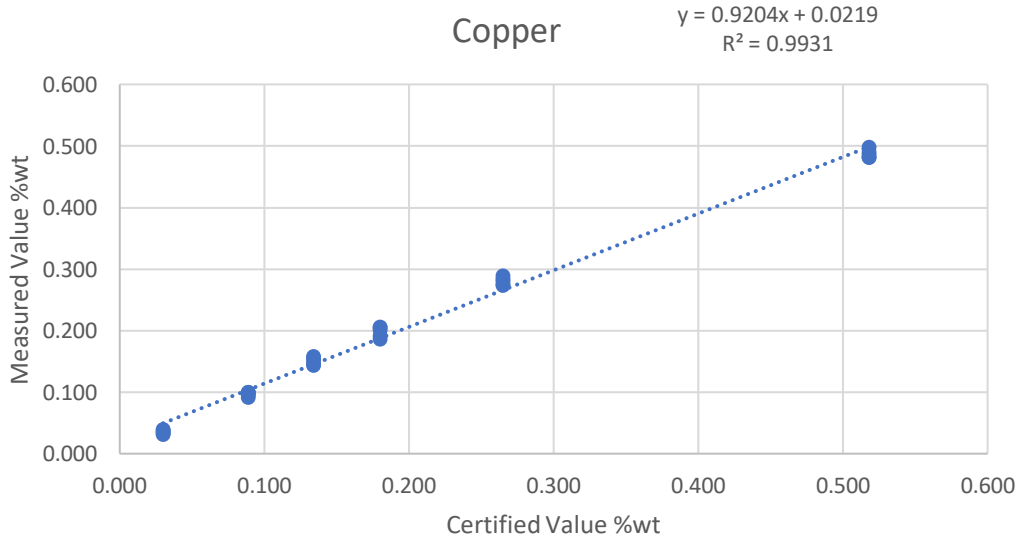
	AVG	3	2	1
IIW	0.3156	0.3166	0.3195	0.3106
C	0.2150	0.2146	0.2169	0.2134
Mn	0.4112	0.3970	0.4173	0.4192
Cu	0.0351	0.0360	0.0372	0.0321
Si	0.2329	0.2328	0.2394	0.2265
Ni	0.0566	0.0522	0.0520	0.0655
Cr	0.0183	0.0251	0.0212	0.0086
Mo	0.0718	0.0847	0.0727	0.0580
Nb	0.0032	0.0102	0.0035	-0.0039
Ti	0.0070	0.0065	0.0073	0.0073
Al	0.0502	0.0334	0.0477	0.0696
V	0.0399	0.0404	0.0419	0.0374
Fe	98.8419	98.8507	98.8266	98.8485

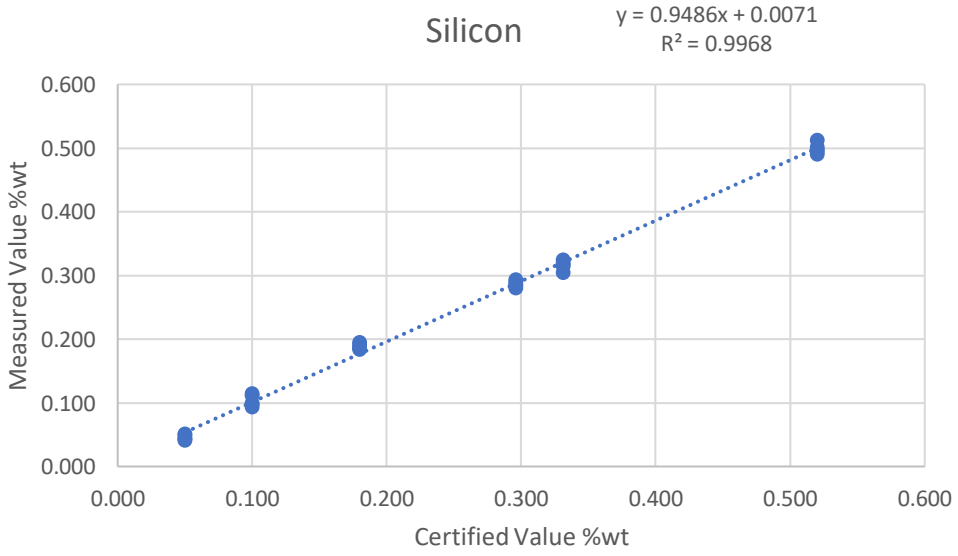
Test Method

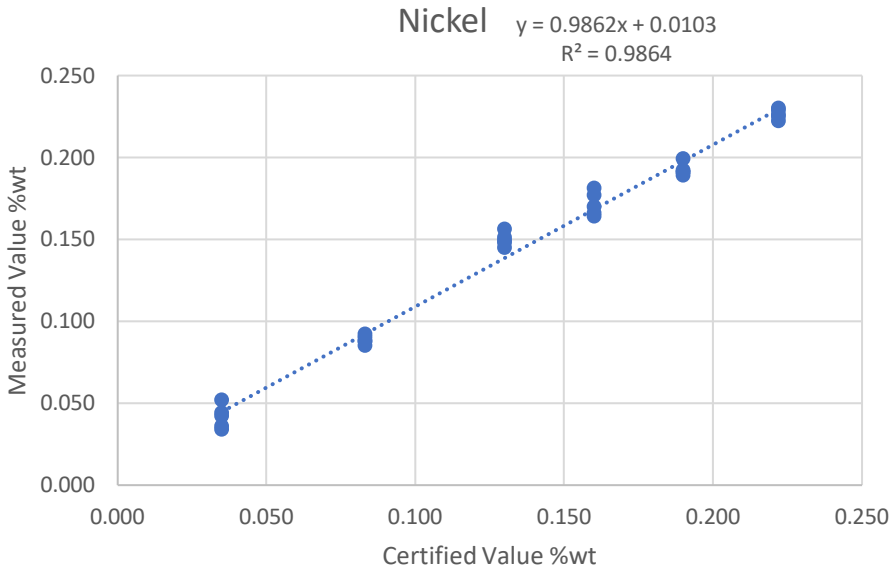
Sample	CE-IIW	CE-AWS	C	Mn	Cu	Si	Ni	Cr	Mo	V	Ti	Al
X65	0.287	0.335	0.049	1.061	0.118	0.286	0.117	0.090	0.056	0.081	0.005	0.038
X65	0.306	0.352	0.042	1.209	0.118	0.279	0.095	0.087	0.064	0.087	0.005	0.024
X65	0.291	0.338	0.040	1.134	0.125	0.277	0.105	0.091	0.061	0.085	0.005	0.030
X65	0.290	0.338	0.042	1.116	0.118	0.284	0.112	0.096	0.065	0.077	0.005	0.031
X65	0.300	0.346	0.039	1.196	0.116	0.276	0.094	0.080	0.068	0.088	0.005	0.028
X65	0.294	0.341	0.034	1.171	0.113	0.280	0.102	0.092	0.078	0.083	0.005	0.030
X65	0.278	0.326	0.039	1.091	0.124	0.289	0.106	0.090	0.049	0.069	0.006	0.032
X65	0.295	0.340	0.046	1.127	0.116	0.273	0.109	0.087	0.063	0.081	0.005	0.034
X65	0.282	0.333	0.041	1.078	0.117	0.310	0.107	0.095	0.059	0.075	0.004	0.038
X65	0.280	0.325	0.036	1.115	0.110	0.275	0.098	0.089	0.053	0.079	0.005	0.034
AVG	**0.290**	**0.337**	**0.041**	**1.130**	**0.118**	**0.283**	**0.105**	**0.090**	**0.062**	**0.080**	**0.005**	**0.032**
STDEV	**0.009**	**0.008**	**0.004**	**0.049**	**0.004**	**0.011**	**0.007**	**0.005**	**0.008**	**0.006**	**0.000**	**0.004**
RSD	**3.1%**	**2.4%**	**10.7%**	**4.3%**	**3.8%**	**3.8%**	**7.1%**	**5.1%**	**13.3%**	**7.2%**	**9.1%**	**13.7%**

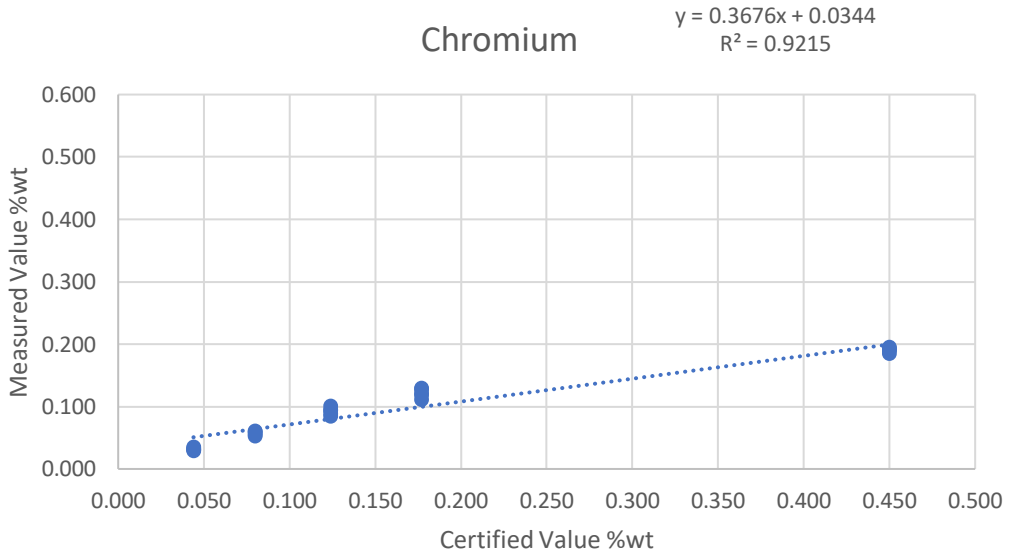

Carbon
y = 0.9906x + 0.0006
R² = 0.9983
Measured Value %wt
Certified Value %wt
0.000
0.100
0.200
0.300
0.400
0.500
0.600

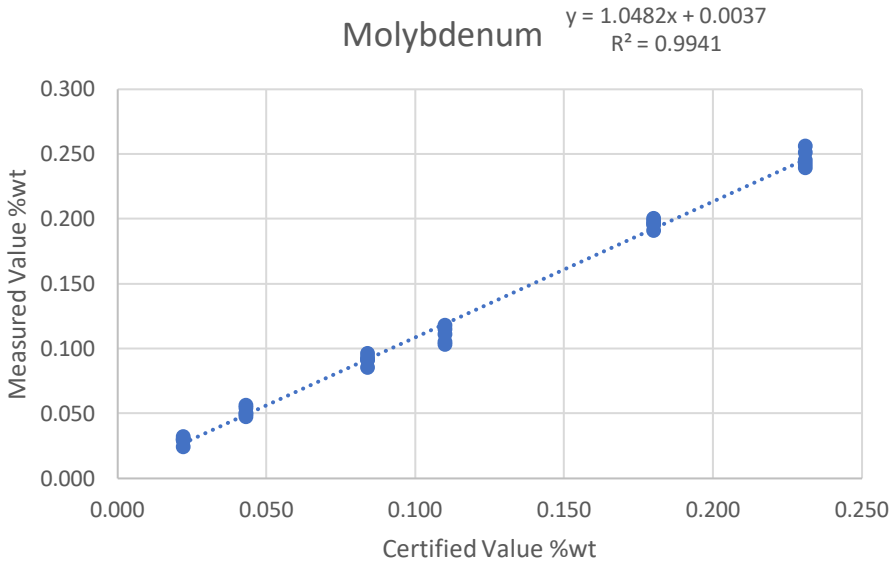

Manganese
y = 0.9647x + 0.0286
R² = 0.9969
Measured Value %wt
Certified Value %wt
0.000
0.200
0.400
0.600
0.800
1.000
1.200
1.400
1.600
1.800
2.000

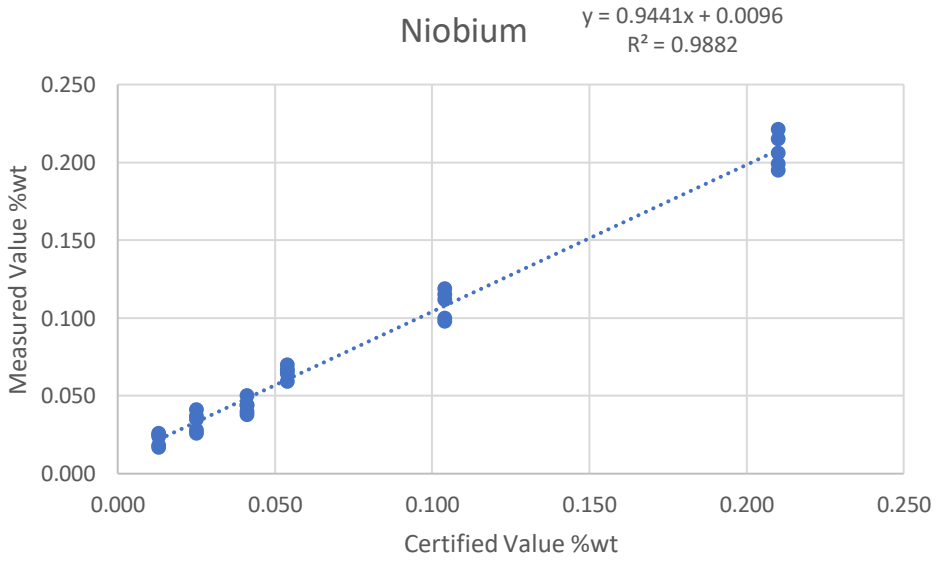

Copper
y = 0.9204x + 0.0219
R² = 0.9931
Measured Value %wt
Certified Value %wt
0.000
0.100
0.200
0.300
0.400
0.500
0.600

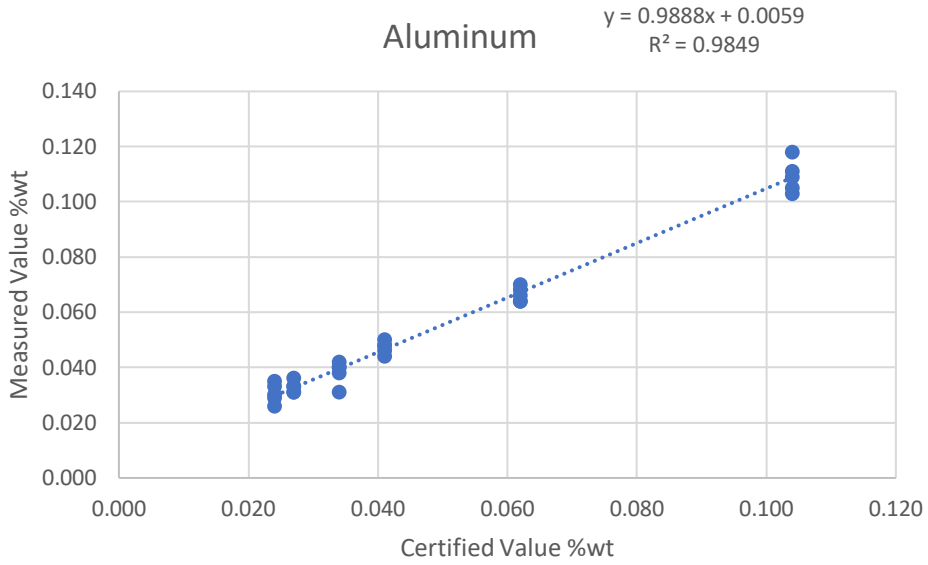

Silicon
y = 0.9486x + 0.0071
R² = 0.9968
Measured Value %wt
Certified Value %wt
0.000
0.100
0.200
0.300
0.400
0.500
0.600

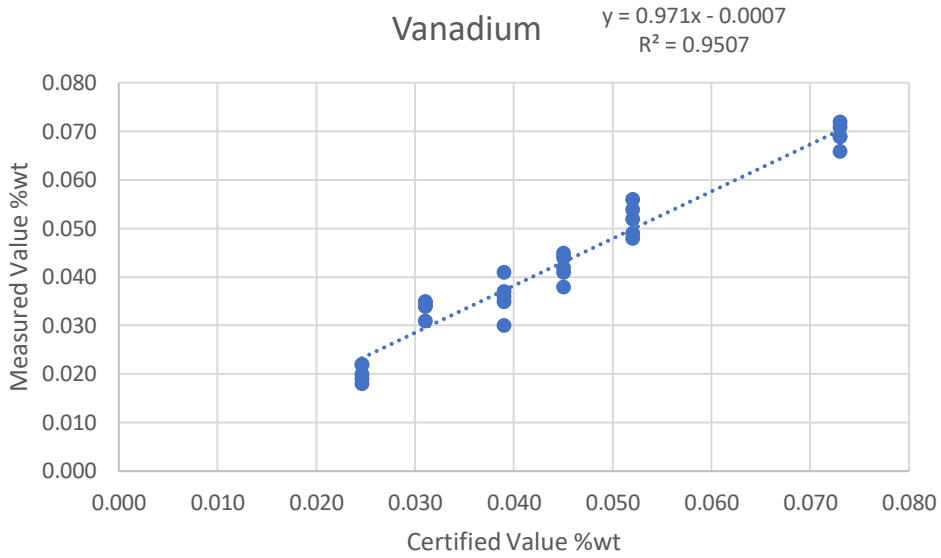

Nickel
y = 0.9862x + 0.0103
R² = 0.9864
Measured Value %wt
Certified Value %wt
0.000
0.050
0.100
0.150
0.200
0.250

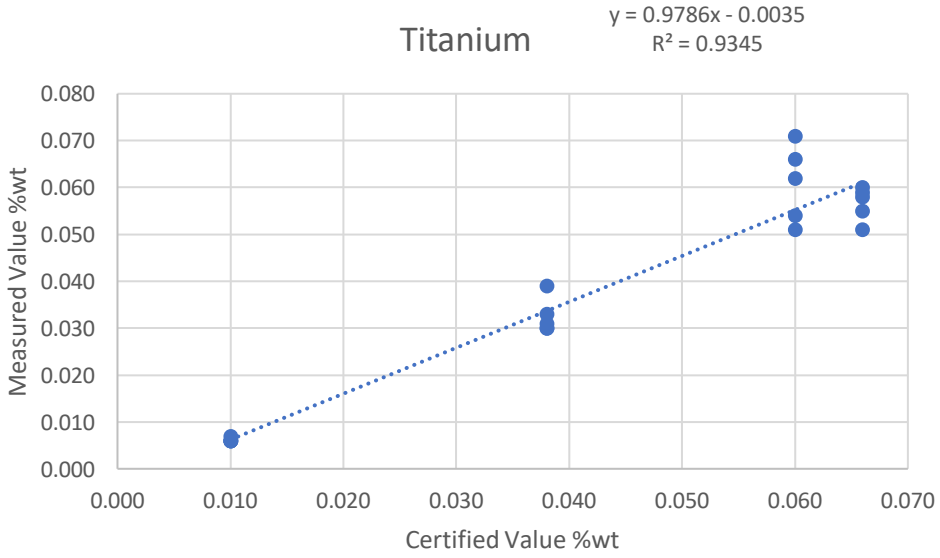

Chromium
y = 0.3676x + 0.0344
R² = 0.9215
Measured Value %wt
Certified Value %wt
0.000
0.100
0.200
0.300
0.400
0.500
0.600
0.050
0.150
0.250
0.350
0.450

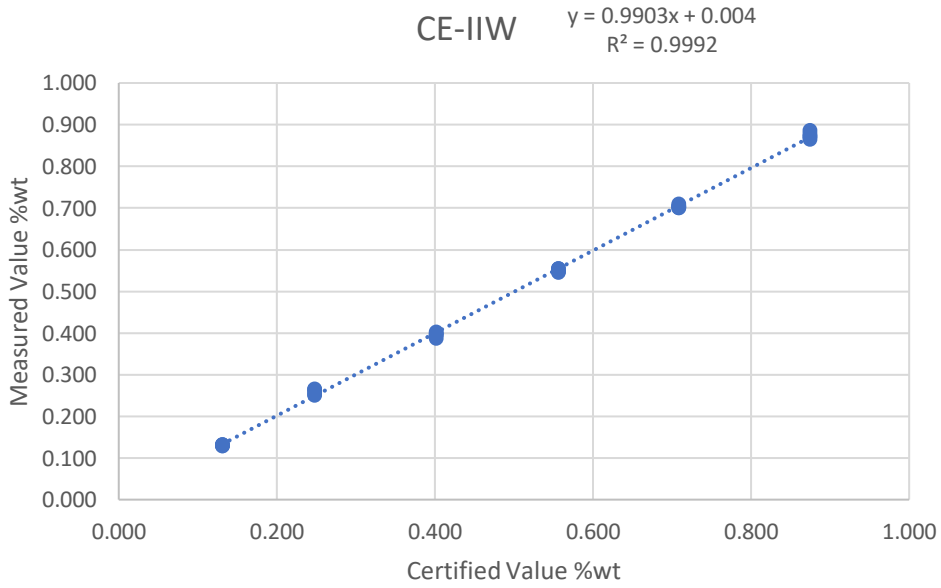

Molybdenum
y = 1.0482x + 0.0037
R² = 0.9941
Measured Value %wt
Certified Value %wt
0.000
0.050
0.100
0.150
0.200
0.250
0.300


Niobium
y = 0.9441x + 0.0096
R² = 0.9882
Measured Value %wt
Certified Value %wt
0.000
0.050
0.100
0.150
0.200
0.250


Aluminum
y = 0.9888x + 0.0059
R² = 0.9849
Measured Value %wt
Certified Value %wt
0.000
0.020
0.040
0.060
0.080
0.100
0.120
0.140


Vanadium
y = 0.971x - 0.0007
R² = 0.9507
Measured Value %wt
Certified Value %wt
0.000
0.010
0.020
0.030
0.040
0.050
0.060
0.070
0.080

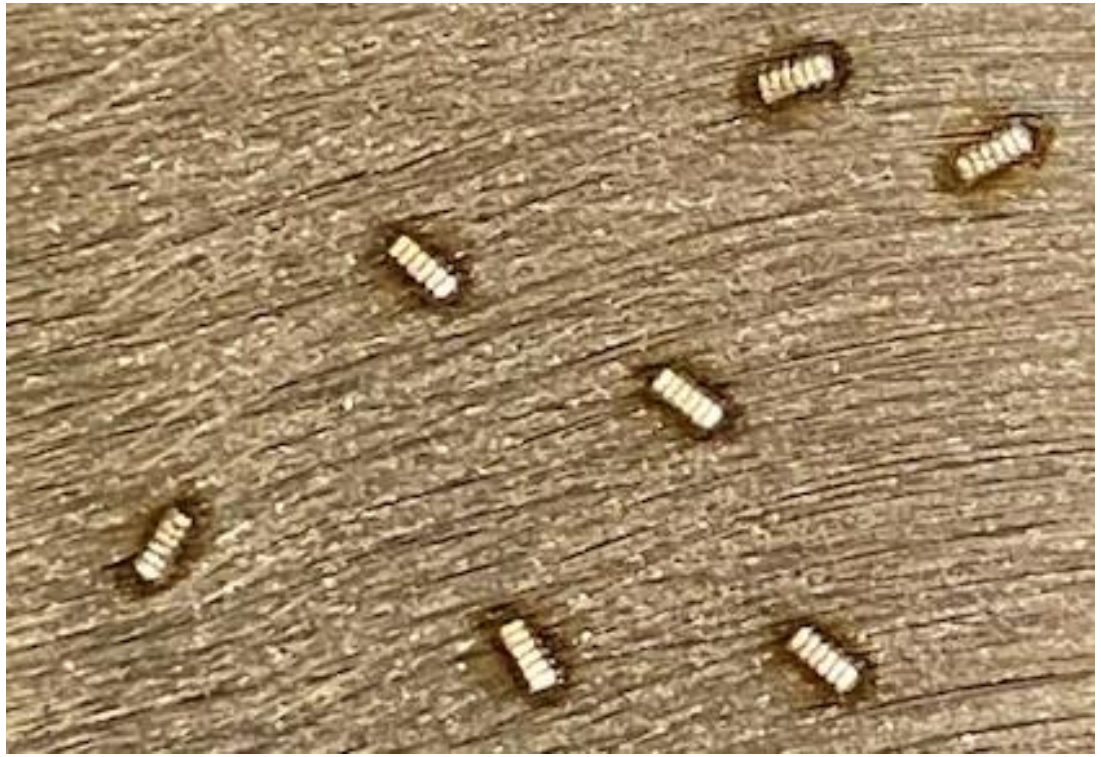

Titanium
y = 0.9786x - 0.0035
R² = 0.9345
Measured Value %wt
Certified Value %wt
0.000
0.010
0.020
0.030
0.040
0.050
0.060
0.070
0.080


CE-IIW
y = 0.9903x + 0.004
R² = 0.9992
Measured Value %wt
Certified Value %wt
0.000
0.100
0.200
0.300
0.400
0.500
0.600
0.700
0.800
0.900
1.000

Element	Low	High	Range	R2
➢ Carbon	0.041	0.483	0.442	0.9983
➢ Manganese	0.430	1.730	1.300	0.9969
➢ Copper	0.030	0.518	0.488	0.9931
➢ Silicon	0.050	0.520	0.470	0.9968
➢ Nickel	0.035	0.222	0.187	0.9864
➢ Chromium	0.022	0.450	0.428	0.9215
➢ Molybdenum	0.022	0.231	0.209	0.9941
➢ Niobium	0.013	0.210	0.197	0.9882
➢ Titanium	0.010	0.066	0.056	0.9345
➢ Aluminum	0.024	0.104	0.080	0.9849
➢ Vanadium	0.025	0.073	0.048	0.9507

Observations

- Results show 7 of the 10 elements measured yielding single digit relative standard deviation (RSD) with CE-IIW and CE-AWS in low single digit range with 3.1% and 2.4% respectively.
- Very few outliers observed or removed during the process
- Drift correction or type standardization features allow user to fine tune the empirical calibration
- Seal-less metal-to-metal interface
- Certain LIBS models interface well with small parts such as weld wire, bolting, valves and round bar.
- Lightweight (~4lbs) offers user all day comfort and excellent circulation area while working safely in excavation or at heights in the pipe racks
- Each argon cartridge would yield approximately 180 carbon measurements between changes
- Missing elements such as phosphorous, sulfur, boron

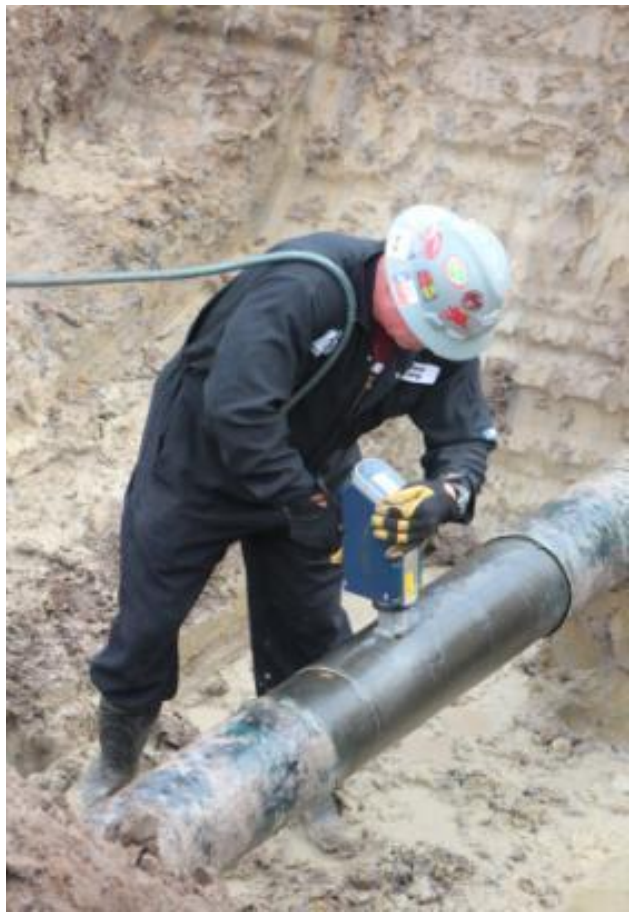


LIBS Portability





Test Conditions







Weld Analysis



AVG: 10 304L 100

C	0.023%	0.002%	0.00
Mn	1.810%	0.082%	0.00
Ni	8.375%	0.311%	8.00
Cr	19.511%	0.277%	18.0
Mo	0.301%	0.016%	0.00
V	0.078%	0.004%	0.00

Questions & Answers?