Aplicación 043

Determinación de elementos presentes en aleaciones de acero con contenidos altos de carbono mediante plasma acoplado inductivamente (ICP-OES)

Introduction

Carbon steels comprise more than 85% of the steel produced in the United States. Classified by the amount of carbon they contain, variations in carbon content (shown in Table I) significantly affect the mechanical properties of the final steel product. Carbon is the most cost-effective alloying material for iron. Higher carbon content leads to increasing hardness and strength, while lower carbon content produces steels that are easier to bend and form. Other alloying elements can also be used to alter the steel's properties including Manganese and Vanadium. Consequently, accurate analysis of the steel for alloying elements is a requisite quality control measure. This application note will demonstrate the Teledyne Leeman Lab's Prodigy7 High-Dispersion ICP's ability to determine alloying elements in high-carbon steel.

Table I Carbon Steel Classification

Type	Carbon Content	Typical Uses
Low	< 0.30%	Auto Body Panels, Wire Products
Medium	0.30 - 0.60%	Axles, Gears, Crankshafts
High	0.60 - 1.00%	Springs, Dies, High-Strength Wires
Ultra-High	1.25 - 2.0%	Metal Cutting Tools, Truck Springs

Instrument

The Prodigy7 is a compact bench-top simultaneous ICP-OES system featuring a 500 mm focal length Echelle optical system coupled with a mega-pixel Large Format CMOS (L-CMOS) detector. At 28 x 28 mm, the active area of the L-CMOS is significantly larger than any other solid-state detector currently used for ICP-OES. This combination allows the Prodigy7 to achieve higher optical resolution than other solid-state detector-based ICP systems. The detector also provides continuous wavelength coverage from 165 to 1100 nm, permitting measurement over the entire ICP spectrum in a single reading without sacrificing wavelength range or resolution. This detector design is inherently anti-blooming and is capable of random access, non-destructive readout that results in a dynamic range of more than 6 orders of magnitude. The Prodigy7 also uses a 40.68 MHz rugged, water-cooled, free-running RF Generator, allowing it to handle the most difficult sample matrices, as well as common organic solvents.

The sample introduction system consists of a four-channel peristaltic pump, HF resistant Ryton Scott spray chamber, demountable quartz torch with an alumina injector and a Hildebrand Grid nebulizer.

Method

Sample Preparation

A high-carbon steel (0.87% C) reference material, SRM 364 (NIST), was used in this study. Approximately 1 gram of the material was placed in a Teflon® beaker, covered with a minimum of deionized water (DIW) and placed on a hot plate. The samples were dissolved using 5 mL of nitric acid (HNO_3) and 1 mL hydrofluoric acid (HF) while gently heating. Once the dissolution was complete, the samples were diluted to 100 mL with DIW.

Calibration Standards

Calibration standards were made from single-element stock solutions (VHG Labs). Standards were matrix-matched to the Fe concentration of the sample by dissolving an electrolytic iron reference material (NIST SRM 365). The final acid concentration in the standards was 5% HNO_3/1% HF. The concentrations of the calibration standards are listed in Table II.

Table II Calibration Standards Concentrations, ppm

Element	STD1 (ppm)	STD2 (ppm)	STD3 (ppm)
Mo	0	50	100
Mn, Cu, Ti	0	15	30
Ni, V, W, Co, Nb, Ta	0	10	20
Si, Cr, As, Zr	0	5	10
Sn, B, Pb, Sb	0	2.5	5

Instrument Operating Conditions

The Prodigy7 operating parameters are listed in Table III.

Table III Instrument Operating Parameters

Instrument	
RF Power	1.20 kW
Coolant Flow	14 L/min
Auxiliary Flow	0.0 L/min
Nebulizer Pressure	1.0 L/min
Uptake Rate	25 rpm
Sample Introduction	
Nebulizer Type	Hildebrand Grid
Spray Chamber	HF Resistant Ryton Scott
Torch	Quartz Demountable
Injector	Alumina, 2.5 mm bore
Uptake Tubing	Aqueous, Black Tab 030
Drain Tubing	Aqueous, Red Tab 045
Sample	
Internal Standard	None
Integration Time	30 seconds

Contact Teledyne Leeman Labs for the appropriate sample introduction component part number.

The analytical viewing zone was set by using a 10 ppm Mn standard. The optimum viewing position is automatically selected by the Prodigy7's Salsa software.

Wavelength Parameters

The Prodigy7 typically uses a 27 pixel wide subarray, centered on the wavelength of interest, to collect data for each analyte. However, subarrays can be up to 57 pixels in width if needed. The analytical peaks and background correction points are defined in each subarray with pixel position and width values. In Table IV below, wavelength and background correction position data are listed. Where possible, two wavelengths were used for each element. All data in the subarrays is collected simultaneously. Additionally, all pixel data are saved, permitting recalculation of results at a later time.

Table IV Wavelength Parameters

Element	Wavelength, nm	Left Background Correction		Right Background Correction	
		Position	Width	Position	Width
Mn	257.610	8	2	27	2
	259.372	2	2	27	2
Si	251.611	9	2	26	2
	288.158	2	0	27	2
Cu	324.754	-	-	27	2
	327.396	6	2	-	-
Ni	231.604	2	2	28	2
	221.648	2	2	-	-
Cr	267.716	2	0	28	2
	205.552	-	-	28	2
V	309.311	2	2	27	2
	310.230	2	2	27	2
Mo	202.030	2	2	27	2
W	207.911	2	2	27	2
	224.875	2	2	26	2
Co	228.615	2	2	27	2
	345.351	2	0	27	2
Ti	337.280	2	2	27	2
	334.941	2	2	27	2
As	189.042	-	-	27	2
	197.262	-	-	27	2
Sn	189.991	-	-	28	2
Nb	313.079	2	2	27	2
Ta	263.558	-	-	21	2
	226.230	2	2	27	2
B	182.641	-	-	27	2
Pb	220.353	2	2	27	2
Zr	343.823	2	2	22	2
	339.198	2	2	24	2
Sb	206.833	7	7	27	2

Figure 1 illustrates the element parameters for the W 207.911 nm line as an example. The left and right background regions begin at pixel positions 2 and 27, respectively. The width of both positions is 2 pixels. The analytical region of interest, where the "W" peak is found, begins at pixel position 13 and has a width of 5 pixels.

Figure 1 W 207.911 nm Wavelength Parameter Example

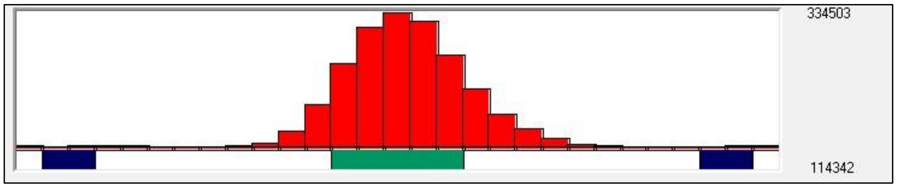
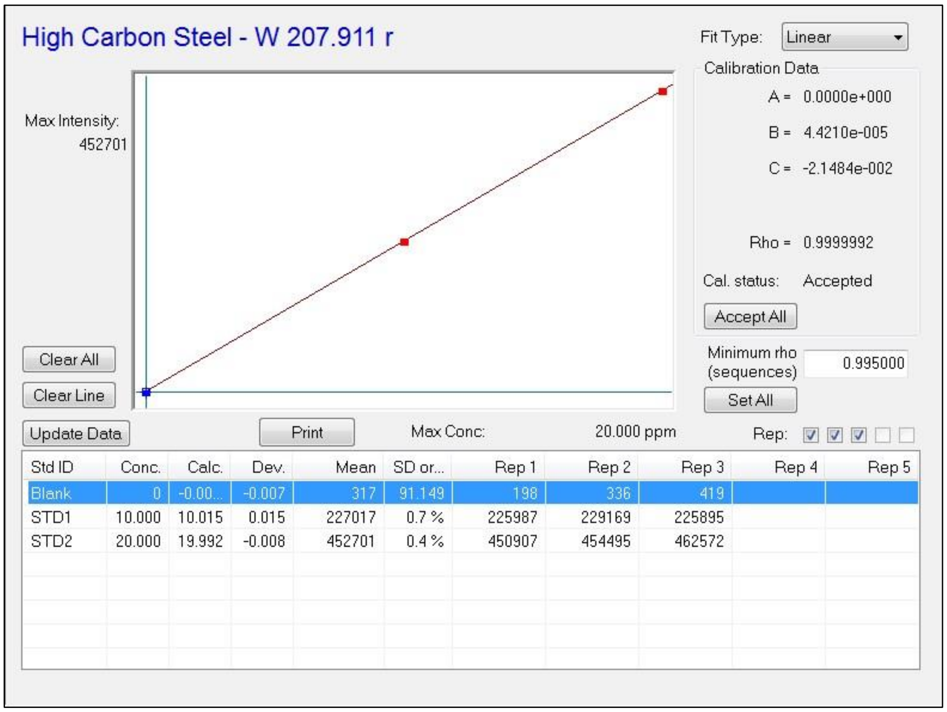


Figure 2 illustrates a calibration curve showing typical precision and linearity for the concentration range used.

Figure 2 Typical Calibration Curve



Results

After igniting the plasma and allowing a 15 minute warm-up period, the Prodigy7 was calibrated using the Teledyne CETAC ASX-520 autosampler. Once the calibration was complete, a 1 ppm QC Standard was analyzed with an acceptance criteria of ±10%. Upon successful completion of the QC Standard analysis, the reference sample was analyzed. After the sample analysis, the QC Standard was reanalyzed. The Prodigy7's Salsa software allows the entire sequence to be run unattended.

If a QC Standard result is out of specification, the Prodigy7 will automatically recalibrate and rerun the QC Standard and any samples that were analyzed since the last successful QC Standard was analyzed.

Results from the analysis are shown in Table III. All concentrations are shown in percentages. The values measured by the Prodigy7 are contained in the column labeled "Found %" while the certified values are in the column labeled "Certified %". The certified value listed is not expected to deviate from the true value by more than ±1 in the last significant figure reported. For a subscript figure, the deviation is not expected to be more than ±5. The agreement between the measured and certified values is quite good.

Table V NIST 364 Analysis Results, %

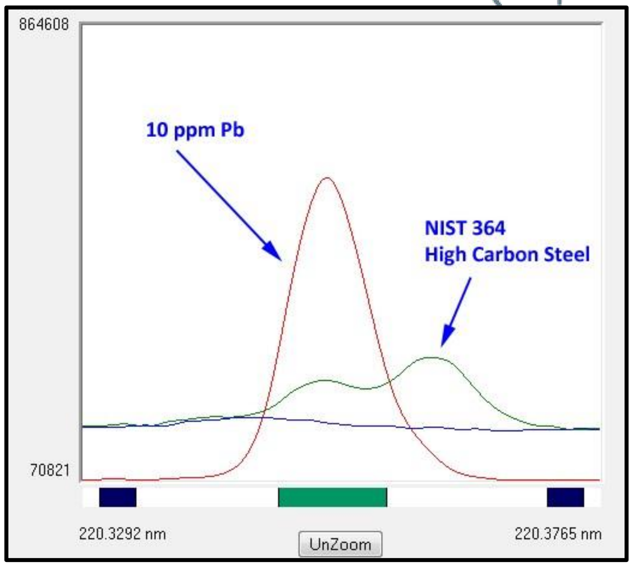
		Found %		Certified %
Mn 257.610 r		0.25		0.25
Mn 259.372 r		0.25		
Si 251.611 r		0.05		0.06_5
Si 288.158 r		0.05		
Cu 324.754 r		0.24		0.24_9
Cu 327.396 r		0.24		
Ni 231.604 r		0.14		0.14_4
Ni 221.648 r		0.13		
Cr 267.716 r		0.06		0.06_3
Cr 205.552 r		0.06		
V 309.311 r		0.11		0.10_5
V 310.230 r		0.11		
Mo 202.030 r		0.50		0.49
W 207.911 r		0.09		0.1
W 224.875 r		0.10		
Co 228.615 r		0.15		0.15
Co 345.351 r		0.15		
Ti 337.280 r		0.25		0.24
Ti 334.941 r		0.25		
As 189.042 r		0.04		0.05_2
As 197.262 r		0.05		
Sn 189.991 r		0.008		0.008
Nb 313.079 r		0.15		0.15_7
Ta 263.558 r		0.10		0.11
Ta 226.230 r		0.10		
B 182.641 r		0.011		0.0106
Pb 220.353 r		0.024		0.023
Zr 343.823 r		0.069		0.068
Zr 339.198 r		0.065		
Sb 206.833 r		0.033		0.034

Discussion

The determination of the alloying elements in the 364 high-carbon steel reference material was straightforward. Of all the elements determined, the most challenging was Lead (Pb).

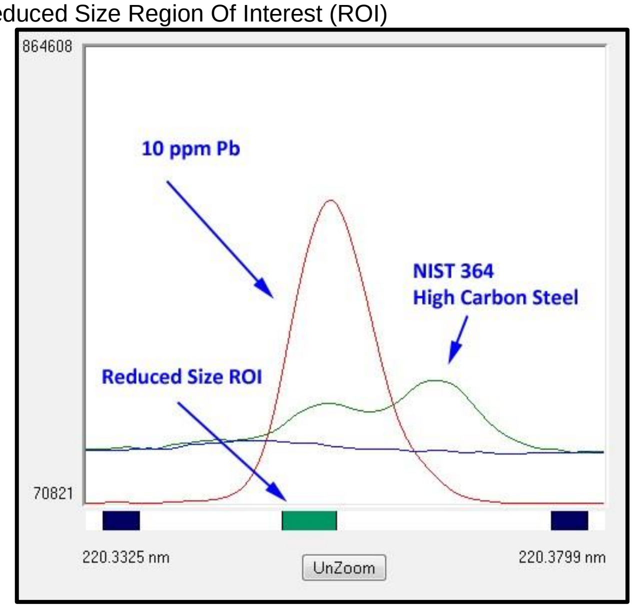
During line selection, a number of Pb lines were examined. All were found to have significant interferences. The most promising line was the primary Pb line at 220.353 nm. A scan of a 10 ppm Pb standard (not matrix matched) and the 364 reference sample is displayed in Figure 3, where the interference is clearly seen.

Figure 3 Interference on Pb 220.353 nm Line



The Prodigy7 software has sufficient flexibility to provide solutions to deal with this type of interference. First, the analytical Region Of Interest (ROI) can be reduced in size thereby avoiding the contribution from the interfering peak. The advantage in this method is that the identity of the interfering peak does not necessary need to be determined. An example of this technique is shown in Figure 4. Without reducing the ROI interval, the Pb concentration was reported as 0.348%. The reduced size ROI reported the accurate value of 0.024%, as shown in Figure 4.

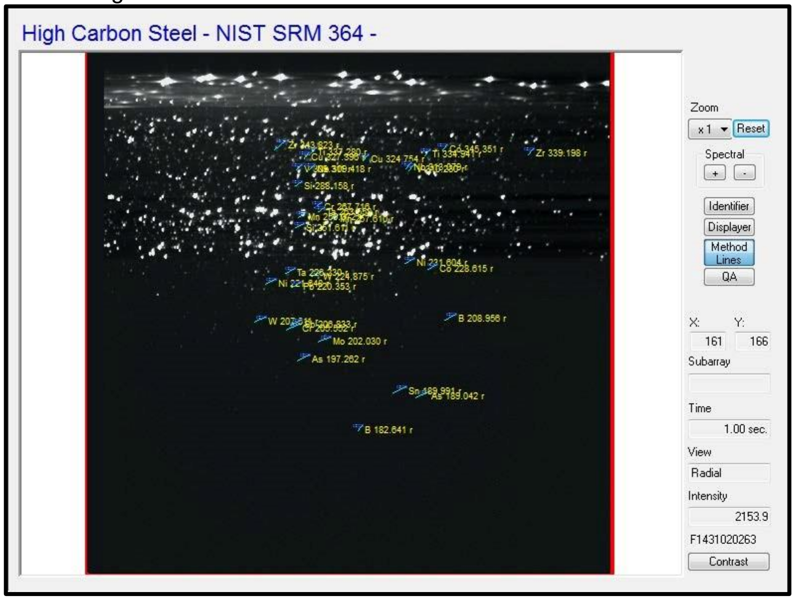
Figure 4 Example of Reduced Size Region Of Interest (ROI)



The second method is to perform an Interfering Element Correction (IEC). In order to perform this correction, the element responsible for the interfering peak must be determined. The Prodigy7 software also provides tools to easily identify unknown peaks.

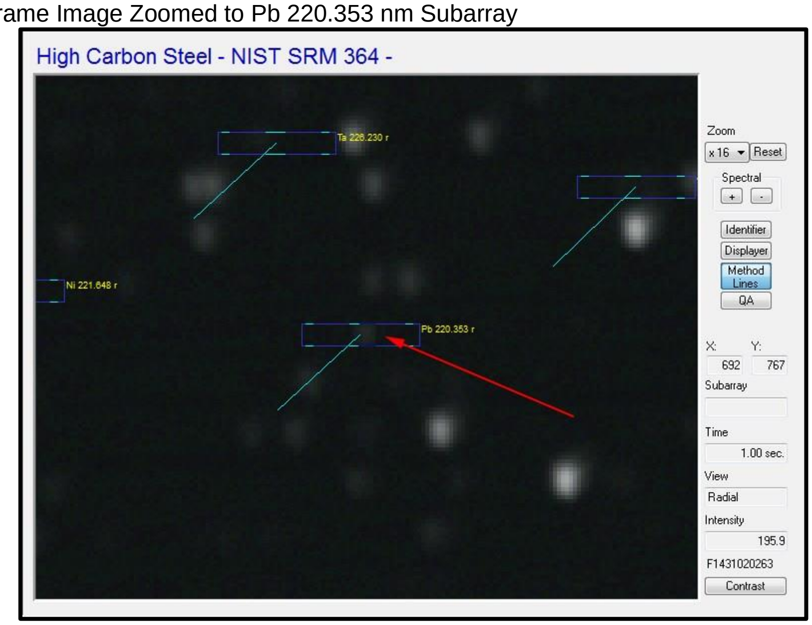
The first step in identifying an unknown peak is to take a Full Frame Image of the sample. The Full Frame image takes a complete spectrum from 165 to 1100 nm without any gaps in a single exposure. A Full Frame Image of the 364 reference sample, with analytical wavelengths superimposed is shown in Figure 5.

Figure 5 NIST SRM 364 High-Carbon Steel Full Frame Image



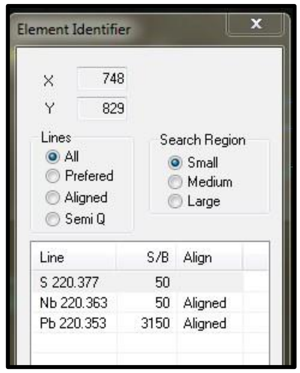
The next step is to zoom into the wavelength in question and use the "Identifier Button" (Figure 6).

Figure 6 Full Frame Image Zoomed to Pb 220.353 nm Subarray



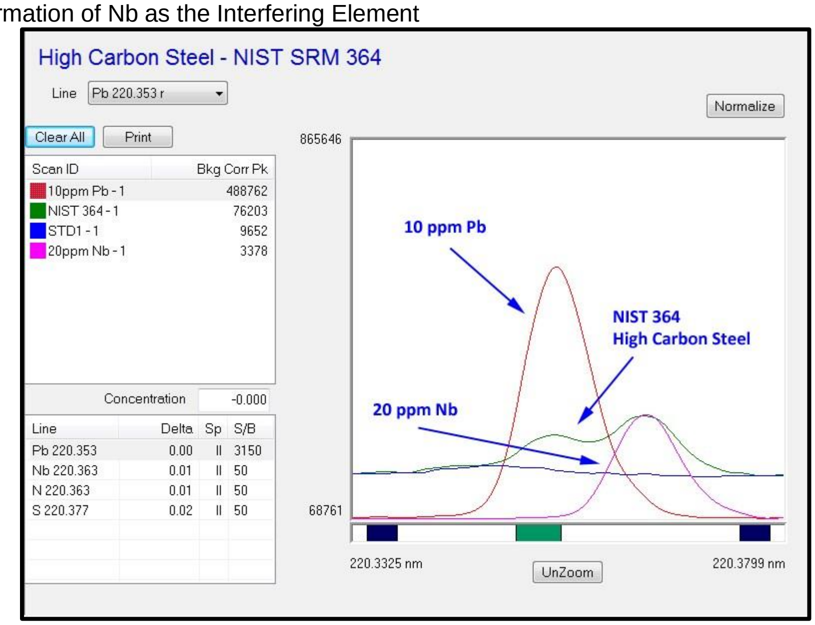
By clicking on the "Identifier Button" and then inside the Pb subarray (as indicated by the red arrow in Figure 6), the wavelength line library will be searched for possible elements. The result of the search is displayed in Figure 7.

Figure 7 Search Results



The search results suggest the interfering peak is due to Niobium (Nb). A scan of an aqueous Nb standard added to the scans in Figure 4 confirms the identification (see Figure 8). Once the interfering element has been identified, the IEC factor can be easily determined by analyzing the Nb standard to obtain the correction ratio.

Figure 8 Confirmation of Nb as the Interfering Element



Conclusion

The analysis of alloying elements in high-carbon steel has been carried out for 18 elements using a radially viewed Teledyne Leeman Lab's, Prodigy7 High-Dispersion ICP. Accurate results were obtained by carefully matrix matching the base iron concentration of the samples to the calibration standards.

The HF sample introduction system performed without any clogging of the torch or nebulizer and did not require the use of an argon humidifier. The Hildebrand Grid nebulizer with its platinum screens is an ideal nebulizer for use with HF containing samples, as well as samples containing high levels of dissolved solids.

The image stabilized plasma and the simultaneous data collection of both peak and background data combine to provide exceptionally precise and stable results.