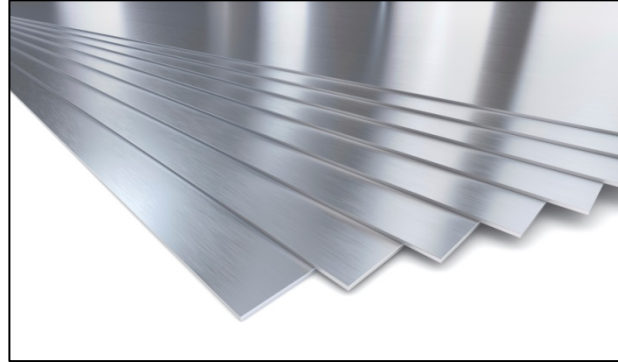


Analysis of Stainless Steel by Dual View Inductively Coupled Plasma Spectrometry

Introduction

Stainless steels are a corrosion resistant family of iron alloys that have a minimum of 10.5% Chromium (Cr). The corrosion resistance is due to the formation of a passive chromium (III) oxide (Cr_2O_3) layer, approximately 1 to 5 nanometers (nm) thick, on the surface of the steel. If this layer is damaged by cutting, scratching or abrasion, it will regenerate, provided sufficient oxygen is available, preventing corrosion. Stainless steels have poor corrosion resistance in low oxygen environments since the oxide layer cannot be repaired quickly enough. Nickel (Ni), molybdenum (Mo) and niobium (Nb) are also alloyed to improve corrosion characteristics.



There are three main types of stainless steels: austenitic, ferritic and martensitic. These three types of steels are identified by their microstructure or predominant crystal phase.

Austenitic steels have austenite (γ -iron) as their primary phase. These are alloys containing chromium and nickel (sometimes manganese and nitrogen), structured around the Type 302 composition of iron, 18% chromium, and 8% nickel. They are normally non-magnetic. Type 304 surgical stainless steel is the most widely used stainless steel and contains 18-20% chromium and 8-10% nickel.

Ferritic steels have ferrite (α -iron) as their main phase. These steels contain iron and chromium, based on the Type 430 composition of 17% chromium. Ferritic steels are magnetic and are less ductile than austenitic steels. Typical uses are in automotive exhaust systems, catalytic converters and chimney liners.

Martensitic steels are low carbon steels built around the Type 410 composition of iron, 12% chromium, and 0.15% carbon. They have great strength and are magnetic. Typical uses include cutlery, springs, screen and strainers.

Table 1 shows acceptable ranges and maximum concentrations for elements in some stainless steels.

Table I Composition of Various Stainless Steels								
AISI Number	Type	C	Mn	Si	Cr	Ni	P	S
		Wt %						
302	Austenitic	0.15	2.00	1.00	17.0 - 19.0	8.0 - 10.0	0.045	0.03
304	Austenitic	0.08	2.00	1.00	18.0 - 20.0	8.0 - 10.5	0.045	0.03
430	Ferritic	0.12	1.00	1.00	16.0 - 18.0	0.75	0.04	0.03
410	Martensitic	0.15	1.00	1.00	11.5 - 13.5	0.75	0.04	0.03

This application note will demonstrate the ability of the Teledyne Leeman Labs Prodigy7 High Dispersion ICP-OES to analyze stainless steels. The dual viewing capability will be used to determine the high concentration elements on the radial view while the axial view will determine the lower concentration, such as phosphorus (P) and sulfur (S).

Instrument

The Prodigy7 is a compact bench-top simultaneous ICP-OES system featuring a 500mm focal length Echelle optical system coupled with a state-of-the-art mega-pixel large format CMOS. At 28 x 28 mm, the active area of the CMOS device is significantly larger than any other solid-state detector currently used for ICP-OES. This combination allows Prodigy7 to achieve higher optical resolution and dispersion 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 8 orders of magnitude allowing both bright and weak emission lines to be measured during a single integration.

The Prodigy7 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

Four Stainless Steel reference materials NIST SRMs 121b and 123c (AISI 348), BCS CRM 467/1 and Euronorm ZRM 286-1 were used in this study. Approximately 1 gram of each 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 10mL of aqua regia (HCl/HNO₃, 3:1) and 1mL hydrofluoric acid (HF) while gently heating. Once the dissolution was complete, the samples were diluted to 100mL with DIW

Calibration Standards

Calibration standards were made from single element stock solutions (VHG Labs Standards). Standards were matrix-matched to the Fe concentration of the samples by using electrolytic iron standard. Standard concentrations ranged from 0 – 2000 ppm. Table II

Table II Calibration Standards Concentrations, ppm			
Element	STD1 (ppm)	STD2 (ppm)	STD3 (ppm)
Ni, Cr	0	1000	2000
Mn	0	150	300
Si, Nb	0	100	200
Mo, Ti	0	25	50
S	0	15	30
Cu, Co	0	10	20
V	0	5	10
P	0	2.5	5

Instrument Operating Conditions

The Prodigy7 operating parameters for this application are listed in Table III.

Table III Instrument Operating Parameters	
Instrument	
RF Power	1.20 kW
Coolant Flow	16 L/min
Auxiliary Flow	0.0 L/min
Nebulizer Flow	1.0 L/min
Sample Uptake Rate	25 rpm
Sample Introduction	
Nebulizer Type	Hildebrand Grid
Spray Chamber	HF Resistant Ryton™ Scott
Torch	Demountable with Alumina Injector
Sample	
Internal Standard	Yes
Integration Time	Axial = 30 seconds Radial = 30 seconds

The analytical viewing zone for both the axial and radial views was set by using a 10 ppm Mn standard. The optimum viewing position is automatically selected by the Prodigy7's software.

Yttrium was used as an internal standard and was added to standards and samples using the Glass Expansion Triton Mixing Kit for HF solutions.

Wavelength Parameters

The Prodigy7 typically uses a 27 pixel wide sub array, centered on the wavelength of interest, to collect data for each analyte (Figure 1). However, sub arrays can be up to 57 pixels in width if needed. The wavelengths used in this method are outlined in Table 2. The letter "r" indicates the wavelength was measured using radial mode. Where possible, multiple wavelengths were used for each element. For each analyte of interest, background correction was performed simultaneously with the peak measurement. Background correction points were chosen by evaluating wavelength scans of samples and standards (Figure 2). In addition, all pixel data are saved which allows for future data recalculation based on method changes such as different calibration fit, standard concentrations and background correction points.

Figure 1 Typical Sub Array Data

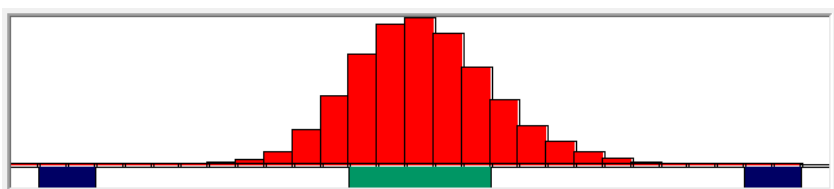
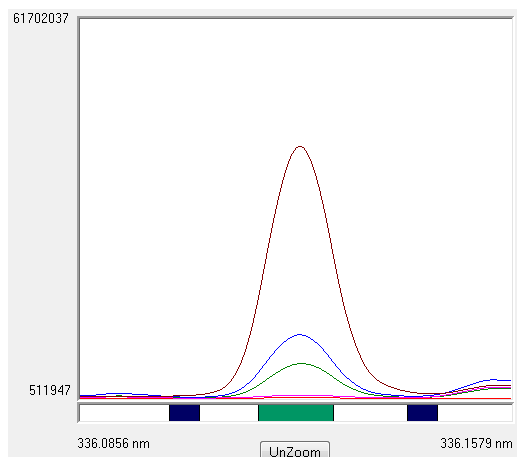


Table IV Method Wavelengths, nm	
Mn 257.610 r	Ni 341.476 r
Mn 259.372 r	Ni 221.648 r
P 178.283	Cr 267.716 r
P 177.495	Cr 283.563 r
S 182.624	Mo 202.030 r
S 182.034	Mo 281.615 r
Si 251.611 r	Nb 316.340 r
Si 288.158 r	Nb 309.418 r
Si 250.690 r	Co 228.615 r
Cu 324.754 r	V 310.230 r
Cu 327.396 r	Ti 334.941 r
Ni 231.604 r	Ti 336.122 r

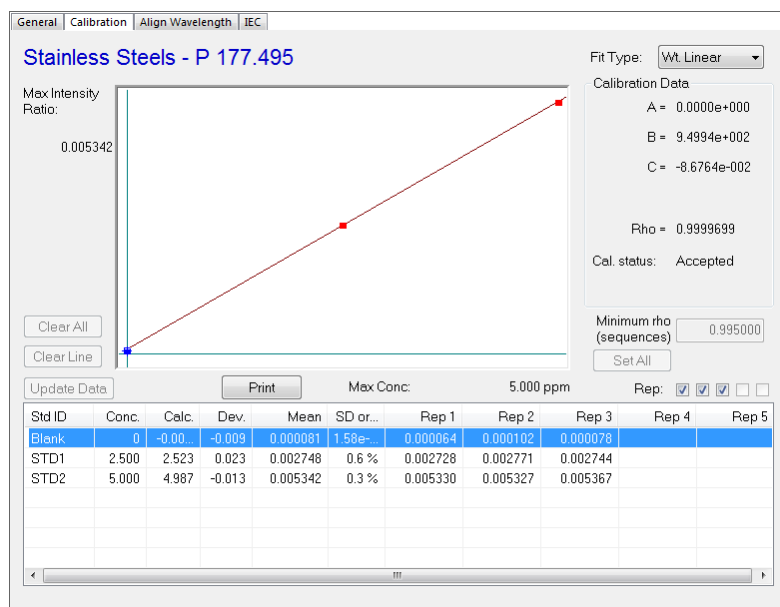
Figure 2 Wavelength Scan for 336.122 nm Ti line



Results

After igniting the plasma and allowing a 15 minute warm-up period, the Prodigy7 was calibrated using the Teledyne CETAC ASX260 autosampler. (Figure 3 illustrates a calibration curve showing typical precision and linearity for the concentration range used.) Once the calibration was complete, a 1 ppm QC Standard was analyzed with an acceptance criteria of $\pm 10\%$. Upon successful completion of the QC Standard analysis, the reference samples were analyzed. After the sample analysis, the QC Standard was re-analyzed. (The Prodigy7's software allows the entire sequence to be run unattended. Should a QC Standard be 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 run.)

Figure 3 Typical Calibration Curve



The analysis results are shown in Table V through Table VIII. All concentrations are in “%”. 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. The Prodigy software is also capable of calculating the average concentration for an element when multiple analysis lines are used. The column labeled “Average %” displays the results from the multiple lines used.

Table V NIST 121b Results			
Element	Found, %	Average, %	Certified, %
Mn 257.610 r	1.47	1.50	1.50
Mn 259.372 r	1.52		
P 178.283	0.026	0.026	0.026
P 177.495	0.026		
S 182.624	0.006	0.007	0.007
S 182.034	0.008		
Si 251.611 r	0.587	0.588	0.596
Si 288.158 r	0.564		
Si 250.690 r	0.612		
Cu 324.754 r	0.109	0.114	0.125
Cu 327.396 r	0.120		
Ni 231.604 r	11.28	11.12	11.16
Ni 341.476 r	10.82		
Ni 221.648 r	11.27		
Cr 267.716 r	17.56	17.59	17.69
Cr 283.563 r	17.63		
Mo 202.030 r	0.075	0.075	0.073
Mo 281.615 r	0.075		
Nb 316.340 r	-	-	-
Nb 309.418 r	-	-	-
Co 228.615 r	-	-	-
V 310.230 r	0.041	-	0.041
Ti 334.941 r	0.404	0.405	0.414
Ti 336.122 r	0.406		

Table VI NIST 123c Results			
Element	Found, %	Average, %	Certified, %
Mn 257.610 r	1.74	1.71	1.7 ₅
Mn 259.372 r	1.67		
P 178.283	0.026	0.026	0.024
P 177.495	0.027		
S 182.624	0.013	0.012	0.014
S 182.034	0.012		
Si 251.611 r	0.585	0.591	0.590
Si 288.158 r	0.591		
Si 250.690 r	0.596		
Cu 324.754 r	0.107	0.104	0.103
Cu 327.396 r	0.101		
Ni 231.604 r	11.4	11.3	11.3 ₄
Ni 341.476 r	11.2		
Ni 221.648 r	11.4		
Cr 267.716 r	17.3	17.3	17.4 ₀
Cr 283.563 r	17.3		
Mo 202.030 r	0.228	0.227	0.220
Mo 281.615 r	0.226		
Nb 316.340 r	0.682	0.653	0.650
Nb 309.418 r	0.624		
Co 228.615 r	0.12	-	0.12
V 310.230 r	-	-	-
Ti 334.941 r	-	-	-
Ti 336.122 r	-	-	-

Table VII Euronorm ZRM 286-1			
Element	Found, %	Average, %	Certified, %
Mn 257.610 r	1.87	1.89	1.92 ± 0.03
Mn 259.372 r	1.91		
P 178.283	0.025	0.025	0.026 ± 0.002
P 177.495	0.025		
S 182.624	0.236	0.242	0.280 ± 0.014
S 182.034	0.247		
Si 251.611 r	-	-	-
Si 288.158 r	-		
Si 250.690 r	-		
Cu 324.754 r	-	-	-
Cu 327.396 r	-		
Ni 231.604 r	8.61	8.54	8.54 ± 0.04

Ni 341.476 r	8.36		
Ni 221.648 r	8.66		
Cr 267.716 r	17.84	17.84	18.13 ± 0.08
Cr 283.563 r	17.83		
Mo 202.030 r	0.326	0.330	0.329 ± 0.009
Mo 281.615 r	0.334		
Nb 316.340 r	-	-	-
Nb 309.418 r	-		
Co 228.615 r	0.150	-	0.150 ± 0.008
V 310.230 r	-	-	-
Ti 334.941 r	-	-	-
Ti 336.122 r	-		

Table VIII BCS CRM 467/1

Element	Found, %	Average, %	Certified, %
Mn 257.610 r	0.80	0.80	0.79
Mn 259.372 r	0.80		
P 178.283	0.021	0.022	0.018
P 177.495	0.022		
S 182.624	0.019	0.017	0.019
S 182.034	0.015		
Si 251.611 r	0.535	0.528	0.520
Si 288.158 r	0.527		
Si 250.690 r	0.524		
Cu 324.754 r	-	-	-
Cu 327.396 r	-		
Ni 231.604 r	9.25	9.28	9.21
Ni 341.476 r	9.32		
Ni 221.648 r	9.26		
Cr 267.716 r	17.35	17.79	18.09
Cr 283.563 r	18.23		
Mo 202.030 r	-	-	-
Mo 281.615 r	-		
Nb 316.340 r	0.976	0.991	0.990
Nb 309.418 r	1.006		
Co 228.615 r	-	-	-
V 310.230 r	-	-	-
Ti 334.941 r	-	-	-
Ti 336.122 r	-		

Discussion

A comparison of the measured and certified values of the elements determined in the four stainless steel reference samples is shown in Table V - Table VIII. The agreement between the measured and certified value is very good, except for the S in the ZRM 286-1, which is low.

The ZRM reference material was re-prepped and reanalyzed two additional times with any significant change in the measured S value. Spike recoveries on both of these preps yielded recoveries of close to 100%. Determination of sulfur in steels by ICP-OES can be challenging due to the potential loss of S during the digestion. The form of sulfur in the sample is important. Examination of the COA for the ZRM material indicates the sulfur determination was not performed by using ICP-OES or other atomic spectroscopy technique.

Conclusion

The determination of alloying elements in stainless steels has been carried out for 12 elements using a dual view Teledyne Leeman Labs Prodigy7 High Dispersion ICP. Accurate results were obtained by carefully matrix matching the base iron concentration of the samples to the calibration standards.

The flexibility of the dual view configuration permits the analysis to be carried out with a single dilution of the sample. High concentration analytes are measured using the radial view, while the lower level elements are determined using the sensitive axial view. With this configuration, samples need only be analyzed a single time, maximizing throughput and reducing the cost of analysis.

The HF sample introduction system (Hildebrand Grid Nebulizer and Ryton™ spray chamber) performed without any clogging of the torch or nebulizer and did not require the use of an argon humidifier.

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