Analysis of Stainless Steel Using the ProdigyPlus Dual-View ICP-OES

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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 resistance 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 include 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 I 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
		% Weight						
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 Prodigy Plus High-Dispersion ICP to analyze stainless steels. The instrument was equipped with a dual-view option. Radial viewing of the plasma was used to determine high concentration lines, while the axial view was used to determine low concentration phosphorus (P) and sulfur (S).

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Instrument

A Prodigy Plus High Dispersion Inductively Coupled Plasma (ICP) Spectrometer equipped with a twist-lock torch and a Teledyne CETAC ASX-280 120-position autosampler (Teledyne CETAC Technologies, Omaha NE) was used to generate the data for this application note.

The Prodigy Plus is a compact bench-top simultaneous ICP-OES system featuring an 800 mm focal length Echelle optical system coupled with a CMOS (Complementary Metal Oxide Semiconductor) detector. At 28 x 28 mm, the active area of the detector is significantly larger than any other solid-state detector currently used for ICP-OES. This combination allows Prodigy Plus 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 8 orders of magnitude.

The Prodigy Plus uses a 40.68 MHz free-running, water-cooled oscillator, allowing it to handle the most difficult sample matrices. A high-sensitivity sample introduction system ensures that sufficient and steady emission signals are transmitted to the spectrometer. The sample introduction system consists of a four-channel peristaltic pump, Ryton® Scott spray chamber, twist-lock quartz torch and a Hildebrand Grid nebulizer.

Method

Sample Preparation

Four Stainless Steel Certified Reference Materials (CRM) were used in this study: NIST SRMs 121b and 123c (AISI 348), BCS CRM 467/1 and Euronorm ZRM 286-1. Approximately 1 gram of each material was placed in a Teflon® beaker, covered with a minimum of deionized (DI) water and placed on a hot plate. The samples were dissolved using 5 mL of aqua regia (HCl/HNO_3, 3:1) and 1 mL hydrofluoric acid (HF) while gently heating. Once the dissolution was complete, the samples were diluted to 100 mL with DI water.

Calibration Standards

Calibration standards were made from single element ICP standards from VHG Labs. In addition, the standards were matrix-matched to the Fe concentration of the samples by digesting the appropriate amount of NBS SRM365 (Electrolytic Iron). The final acid concentration in the standards was 5% Aqua Regia/1% HF. Calibration standards and concentrations are listed in Table II.

Table II Calibration Concentrations, ppm

	Std1	Std2	Std3
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 Prodigy Plus operating parameters are listed in Table III.

Table III Instrument Operating Parameters

Parameter	Setting
RF	1.2 kW
Coolant Flow	14 L/min
Auxiliary Flow	0.0 L/min
Nebulizer Pressure	38 psi
Torch	Demountable with Alumina Injector
Sample Uptake Rate	25 RPM
Nebulizer	Hildebrand Grid
Spray Chamber	Ryton® Scott
Optical Purge Flow	Low (0.7 L/min)
Axial Integration Time	30 s
Radial Integration Time	15 s

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 Prodigy Plus's Salsa software.

Wavelength Parameters

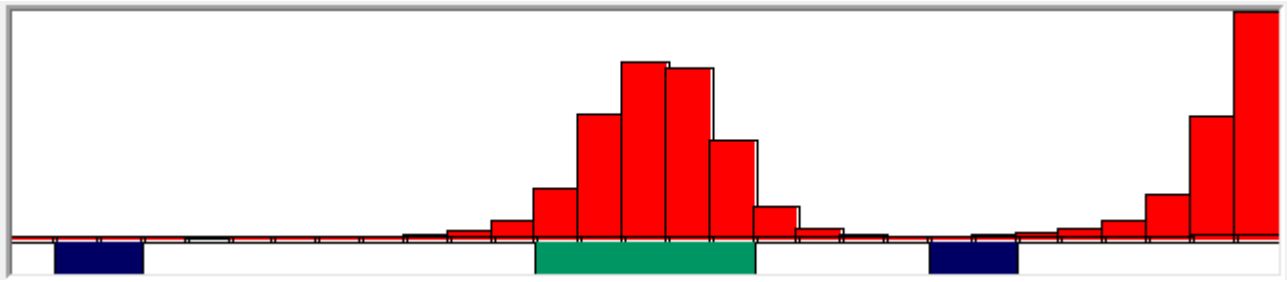
The Prodigy Plus typically uses a 29 pixel-wide sub array, centered on the wavelength of interest, to collect data for each analyte (Figure 1). However, sub arrays can be up to 57 pixels in width if needed, allowing additional background correction point flexibility in complicated matrices. The wavelengths used in this method are listed in Table IV. 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. Additionally, all pixel data is saved, allowing for future data recalculation based on method changes (such as different calibration fit, standard concentrations, and background correction points).

Table IV Wavelengths Used

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 180.731	Mo 2281.615 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 1 illustrates the elements parameters for the Mo 202.030 nm line. In the figure, the left and right background regions are indicated by a width of 2 pixels. The analytical region of interest, where the Mo peak is found, begins at pixel position 13 and has a width of 5 pixels.

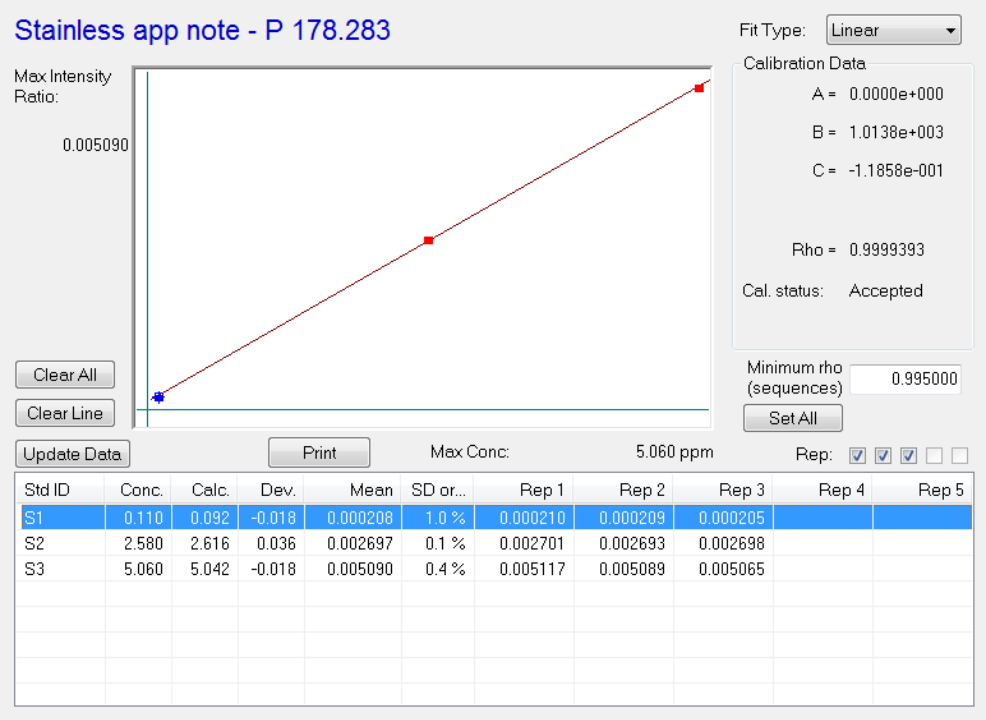
Figure 1 Mo 202.030 nm Element Parameter Example



Results

After igniting the plasma and allowing a 15 minute warm-up period, the Prodigy Plus was calibrated. Figure 2 illustrates a calibration curve showing typical precision and linearity for the concentration range used.

Figure 2 Typical Calibration Curve



Std ID	Conc.	Calc.	Dev.	Mean	SD or...	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5
S1	0.110	0.092	-0.018	0.000208	1.0 %	0.000210	0.000209	0.000205		
S2	2.580	2.616	0.036	0.002697	0.1 %	0.002701	0.002693	0.002698		
S3	5.060	5.042	-0.018	0.005090	0.4 %	0.005117	0.005089	0.005065		

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 samples were analyzed. After the sample analysis, the QC Standard was re-analyzed. The Prodigy Plus's Salsa software combined with the Teledyne Cetac ASX-280 autosampler allowed the entire sequence to be run unattended. In the event that a QC Standard is out of specification, the Prodigy Plus will automatically recalibrate and re-run the QC Standard along with any samples that were analyzed since the last successful QC Standard was run.

The analysis results are shown in Table V and Table VI. All concentrations are in % weight. The values measured by the Prodigy Plus are listed in the "Measured %" column, while the certified values are shown beneath "Certified %". A review of the results indicates that the agreement between the measured and certified values is quite good. The Salsa software is also capable of calculating the average concentration for an element when multiple analysis lines are used as shown beneath the column labeled "Average %".

Table V NIST 123c and NIST 121b Results

	NIST 123c				NIST 121b		
	Measured %	**Average %**	**Certified %**		**Measured %**	**Average %**	**Certified %**
Mn 257.610 r	1.77	1.77	1.75		1.50	1.51	1.50
Mn 259.372 r	1.78				1.53		
P 178.283	0.025	0.025	0.024		0.027	0.027	0.026
P 177.495	0.024				0.028		
S 182.624	0.011	0.014	0.014		0.008	0.008	0.007
S 182.034	0.017				0.009		
Si 251.611 r	0.57	0.58	0.59		0.586	0.601	0.596
Si 288.158 r	0.58				0.614		
Si 250.690 r	0.58				0.604		
Cu 324.754 r	0.106	0.100	0.103		0.126	0.118	0.125
Cu 327.396 r	0.095				0.100		
Ni 231.604 r	11.12	11.24	11.34		11.27	11.28	11.16
Ni 341.476 r	11.29				11.23		
Ni 221.648 r	11.30				11.33		
Cr 267.716 r	17.23	17.44	17.40		17.72	17.87	17.69
Cr 283.563 r	17.64				18.01		
Mo 202.030 r	0.23	0.23	0.22		0.074	0.074	0.073
Mo 281.615r	0.23				0.075		
Nb 316.340 r	0.66	0.66	0.65		-	-	-
Nb 309.418 r	0.66						
Co 228.615 r	0.12	0.12	0.12		-	-	-
V 310.230 r	-	-	-		0.040	0.040	0.041
Ti 334.941 r	-	-	-		0.402	0.400	0.414
Ti 336.122 r		-	-		0.397		

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Table VI Euronorm ZRM 286-1 and BCS CRM 467/1 Results							
	Euronorm ZRM 286-1				BCS CRM 467/1		
	Measured %	**Average %**	**Certified %**		**Measured %**	**Average %**	**Certified %**
Mn 257.610 r	1.88	1.90	1.92 ± 0.03		0.785	0.780	0.788
Mn 259.372 r	1.92				0.774		
P 178.283	0.025	0.025	0.026 ± 0.002		0.021	0.021	0.018
P 177.495	0.025				0.020		
S 182.624	0.275	0.275	0.280 ± 0.014		0.018	0.020	0.019
S 182.034	0.274				0.021		
Si 251.611 r	-	-	-		0.51	0.52	0.52
Si 288.158 r	-				0.52		
Si 250.690 r	-				0.52		
Cu 324.754 r	-	-	-		-	-	-
Cu 327.396 r	-				-		
Ni 231.604 r	8.41	8.49	8.54 ± 0.04		9.16	9.20	9.21
Ni 341.476 r	8.61				9.24		
Ni 221.648 r	8.46				-		
Cr 267.716 r	18.20	18.26	18.13 ± 0.08		17.98	17.99	18.09
Cr 283.563 r	18.31				18.00		
Mo 202.030 r	0.327	0.329	0.329 ± 0.009		-	-	-
Mo 281.615r	0.331				-		
Nb 316.340 r	-	-	-		1.03	1.03	0.99
Nb 309.418 r	-				1.02		
Co 228.615 r	0.147	0.147	0.150±0.008		-	-	-
V 310.230 r	-	-	-		-	-	-
Ti 334.941 r	-	-	-		-	-	-
Ti 336.122 r	-	-	-		-	-	-

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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 and Table VI. The agreement between the measured and certified values is very good.

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 using ICP-OES or other atomic spectroscopy techniques.

Conclusion

The determination of alloying elements in stainless steels was carried out for 12 elements using a Teledyne Leeman Labs Prodigy Plus High Dispersion ICP with dual-view option. 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.

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