

Analysis of steel and its alloys using the GB/T 20125-2006 standard and an Agilent 5100 ICP-OES in dual view mode

Application note

Metals analysis and production

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Introduction

Steel manufacturers conduct quality control testing for a range of metals and trace elements to ensure the grade and performance of their final product. The Standardization Administration of China uses their GB/T 20125-2006 standard “Low-alloy steel – Determination of multi-element contents – Inductively coupled plasma atomic emission spectrometric method” to control the quality of manufactured steel products.

Different grades of steel have different specifications for elemental content, with most steel and stainless steel grades required to have less than 0.05 % by weight of Sulfur and 0.04 % by weight of Phosphorus. With the Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) technique easily able to measure elements at this concentration within a sample, laboratories are looking beyond whether an instrument can ‘do the job’ to whether a specific instrument can improve their sample throughput, lower their costs, simplify sample preparation and instrument operation, and deliver reliable results throughout the analysis of a large batch of samples.



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This application note demonstrates the performance and benefits of Agilent’s 5100 Vertical Dual View (VDV) ICP-OES instrument in the analysis of steel samples, using the GB/T 20125-2006 method. The instrument offers many advantages for this application, which involves the rapid analysis of a large number of challenging steel samples.

Experimental

Instrumentation

Agilent’s 5100 Vertical Dual View (VDV) ICP-OES was used for this analysis and has a range of features that deliver high sample throughput and reproducible, accurate results for challenging steel samples.

The instrument uses the Vista Chip II detector with a 1 MHz processing speed, the fastest of any charge coupled device (CCD) detector used in ICP-OES. This delivers high throughput, high sensitivity, and the largest dynamic range.

The instrument’s Vertical Dual View (VDV) configuration allows measurements to be performed in axial and radial modes. The analyst can achieve sensitivity for elements in low concentrations such as phosphorus and sulfur by measuring them in axial view as well as measuring percent concentrations of nickel and chromium, without having to dilute the sample, by using radial view. Refer to Table 2 to determine which plasma view was used for each element.

Agilent’s 5100 VDV ICP-OES features a vertical torch, capable of handling the toughest matrices. Over the years, a vertical torch has been accepted as a standard configuration for running challenging matrices as it requires less cleaning and fewer replacements [1]. The combination of the vertical torch and a robust solid state radio frequency (SSRF) system operating at 27 MHz, provides a reliable, robust plasma, delivering excellent long term stability for challenging samples. This means accurate results even at the end of a whole day of measuring steel sample digests. The plug-and-play torch loader automatically aligns the vertical torch and connects the gases for fast start up, ensuring reproducible results, even with multiple operators.

For the analysis, the RF power was increased to 1.5 kW and the nebulizer flow rate was set to 0.55 L/min to improve the detection limits for difficult elements such as S and P in the elevated Fe matrix. The plasma flow was left at a low setting of 12 L/min and did not need to be increased to handle the higher RF power and complex matrix. Instrument operating conditions are listed in Table 1.

For this application, the 5100 VDV ICP-OES was fitted with a sample introduction system comprising a OneNeb nebulizer, double-pass glass cyclonic spray chamber and a 5100 Dual View torch (demountable, quartz, 1.8 mm injector). An SPS 4 autosampler was used to deliver sample to the instrument.

Table 1. Instrument operating parameters.

Parameter	Setting
Torch	Demountable Dual View torch (1.8 mm ID injector)
Nebulizer	OneNeb
Spray chamber	Double-pass glass cyclonic
Read time (s)	20 for axial, 5 for radial
Replicates	3
Sample uptake delay (s)	15
Stabilization time (s)	10
Rinse time (s)	50
Fast pump (80 rpm)	Yes
Nebulizer gas flow (L/min)	0.55
RF power (kW)	1.5
Plasma gas flow (L/min)	12.0
Aux gas flow (L/min)	1.0

Sample preparation

Two CRMs, GH-135 6934 and GSBH 40031-93 (China National Analysis Center for Iron and Steel), were analyzed to verify the method, with the certified concentrations of elements in the CRMs shown in Table 3.

The sample was prepared by digesting 0.5 g of the CRM in a combination of nitric, hydrochloric, and perchloric acids on a hot plate, as described in the GB/T 20125-2006 method. The digest was made up in a 100 mL volumetric flask using 18 M Ω de-ionised water, giving a TDS of approximately 0.5 %.

Standard preparation

Multi-element calibration standards were prepared from Agilent single element stock solutions. Blanks and standards were all matrix matched with a 5000 mg/kg Fe sample, which was made using the same digestion method as the samples, using a 6N high purity iron wire.

Correction techniques

Inter Element Correction (IEC) was required for S due to the presence of Mn, Mo and Ti interferences, and for As due to the presence of Cr interference. To simplify the analysis, the calibration standards were used as IEC analyte standards. Single element interferent standards were prepared in the same Fe matrix used in the calibration standards. IEC factors were simply setup using the ICP Expert 7 software and once the factors were determined, they were stored in a template and reused in subsequent analyses. No internal standard correction was required.

A combination of Fitted Background Correction (FBC) and off-peak background correction techniques [2] were used to correct for any spectral interferences. The FBC technique simplifies method development and ensures fast, accurate background correction by eliminating the need to determine off-peak background correction points for each element. Table 2 lists which method was used for each element.

Table 2. The background correction method and plasma view used for each element.

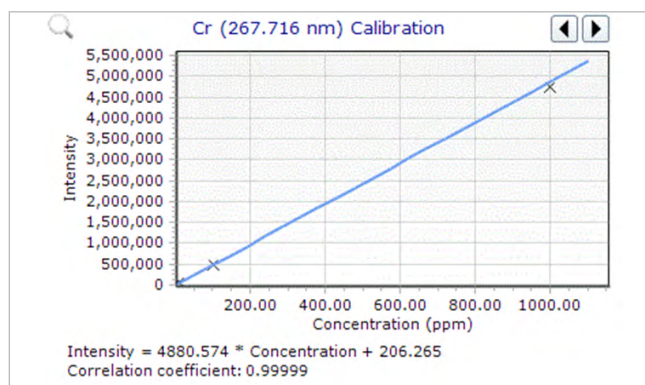
Element & wavelength (nm)	Background correction used	Plasma view
Al 396.152	Fitted	Radial
As 193.696	Off-Peak Right	Axial
Co 228.615	Fitted	Axial
Cr 267.716	Fitted	Radial
Cu 327.395	Fitted	Axial
Mn 257.610	Fitted	Radial
Mo 202.032	Fitted	Radial
Ni 231.604	Fitted	Radial
P 178.222	Off-Peak Left	Axial
S 181.972	Fitted	Axial
Si 251.611	Fitted	Axial
Ti 334.941	Fitted	Radial
V 309.310	Fitted	Axial

Results and discussion

Calibration linearity

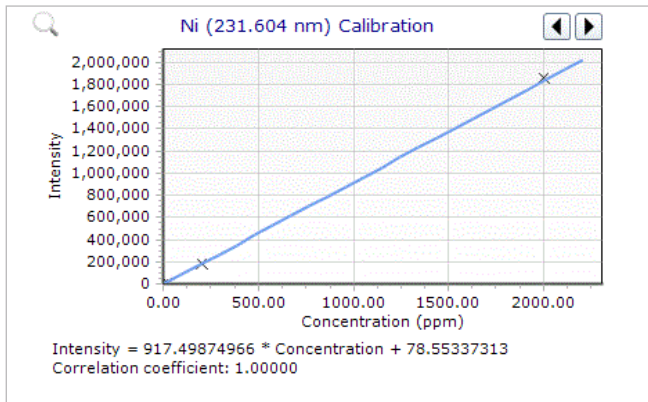
Linear calibrations were obtained with a correlation coefficient greater than 0.99999 for all wavelengths over a wide concentration range. This high degree of linearity means the wide range of concentrations expected in steel samples can be determined without the need to perform additional dilutions. This improves sample throughput and removes potential dilution errors and sample contamination.

Figures 1–3 show typical calibration curves for Cr, Ni and P for this application.



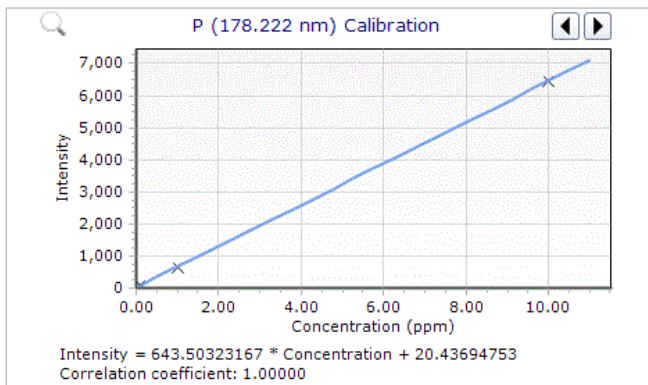
Standards	Conc (ppm)	% Error
Blank	0	N/A
Standard 1	10	0.44
Standard 2	100	0.60
Standard 3	1000	2.82

Figure 1. Calibration curve and standard concentrations – Cr 267.716 nm line.



Standards	Conc (ppm)	% Error
Blank	0	N/A
Standard 1	20	0.08
Standard 2	200	2.32
Standard 3	2000	1.08

Figure 2. Calibration curve and standard concentrations – Ni 231.604 nm line.



Standards	Conc (ppm)	% Error
Blank	0	N/A
Standard 1	0.1	5.06
Standard 2	1.0	0.06
Standard 3	10.0	0.14

Figure 3. Calibration curve and standard concentrations – P 178.222 nm line.

Method Detection Limits and CRM recoveries

For this application, MDLs were determined by analyzing the 5000 mg/kg Fe matrix blank solution 10 times. The MDL was calculated as 3 times the SD of the 10 measurements of the matrix blank. This analysis was performed on 3 independent runs.

The CRMs (GH – 135 6934 and GSBH 40031-93) were analyzed in duplicate, with the results averaged over 3 separate analyzes. The results shown in Table 3 display excellent recoveries within $\pm 10\%$ of the certified value, demonstrating the accuracy of the instrument when analyzing samples with difficult matrices.

Long term stability test

The long term stability and precision of the method was tested by continuously analyzing a steel sample for 8 hours. The results (Figure 4 and Table 4) show the measurement precision for all elements over 8 hours was $< 1.5\%$ RSD. This demonstrates that the 5100 will reliably deliver accurate measurements over many hours of measuring challenging samples like the steel digests.

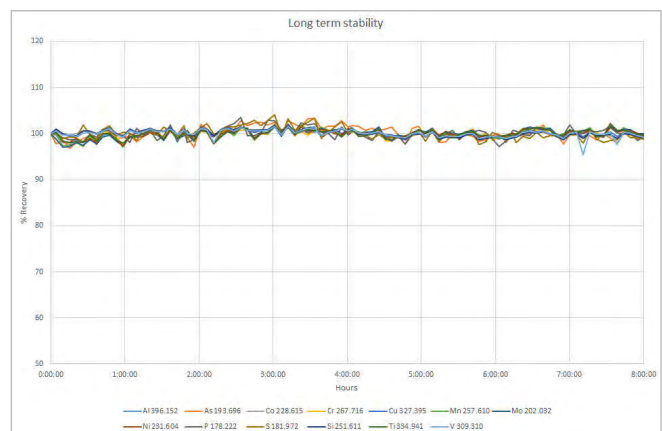


Figure 4. Long term stability plot of a steel sample, analyzed continuously over 8 hours.

Table 3. MDLs in the solid sample and recoveries for 13 elements in two CRMs. MDLs were determined in a 5000 mg/kg Fe matrix.

	MDL (mg/kg)	CRM GH – 135 6934				CRM GSBH 40031-93			
		Measured (mg/kg)	SD (mg/kg)	Certified conc. (mg/kg)	Recovery (%)	Measured (mg/kg)	SD (mg/kg)	Certified conc. (mg/kg)	Recovery (%)
Al 396.152	3.8	30761	465	31500	97.7	183.5	1.7	170	107.9
As 193.696	2.0	38.9	1.7	NA		66.7	1.5	66	101.0
Co 228.615	1.4	71.1	0.9	NA		57.0	0.5	58	98.4
Cr 267.716	1.7	143030	1955	139400	102.6	370.1	3.1	350	105.7
Cu 327.395	0.23	216.3	3.7	NA		328.6	2.8	340	96.7
Mn 257.610	0.43	4719	65	4500	104.9	5940	46	5500	108.0
Mo 202.032	2.2	18526	232	18400	100.7	57.7	2.4	59	97.8
Ni 231.604	5.2	366424	4984	358500	102.2	270.0	2.7	260	103.9
P 178.222	2.6	40.6	1.6	40	101.5	167.6	2.1	170	98.6
S 181.972	3.4	39.7	10.9	37	107.3	170.3	2.8	170	100.2
Si 251.611	1.6	4391	36	4520	97.1	2342	15	2280	102.7
Ti 334.941	0.60	25809	310	24490	105.4	2.3	0.2	NA	
V 309.310	0.81	1007.4	7.9	NA		4.4	0.2	NA	

Table 4. Long term stability data (%RSD) of a steel sample.

Elements	Al 396.152	As 193.696	Co 228.615	Cr 267.716	Cu 327.395	Mn 257.610	Mo 202.032	Ni 231.604	P 178.222	S 181.972	Si 251.611	Ti 334.941	V 309.310
%RSD	0.88	1.47	0.76	0.93	0.71	1.04	1.05	0.88	1.24	1.35	0.79	0.92	0.88

Conclusion

Agilent’s 5100 VDV ICP-OES with a vertical torch operating in dual view mode was used to measure two steel certified reference materials, using the GB/T 20125-2006 standard “Low-alloy steel – Determination of multi-element contents – Inductively coupled plasma atomic emission spectrometric method”.

Despite the difficult samples, the dual viewing capability of the instrument, combined with the GB/T method, delivered accurate results, with recoveries within $\pm 10\%$ of the certified value.

The vertical torch and robust SSRF system of the instrument delivered long term measurement stability, with the measured %RSD for all elements over 8 hours being less than 1.5%.

The wide linear dynamic range of the instrument makes it ideal for the routine analysis of steel samples in a busy laboratory as it reduces the need for sample dilutions, which add to sample preparation time and introduce the risk of errors.

The software supplied with the instrument includes a selection of background correction techniques. This allowed accurate results to be achieved by correcting for any spectral interferences present in the difficult sample matrix.

The Agilent 5100 VDV ICP-OES was able to quickly, accurately and reliably measure the steel digest samples, despite the challenging matrix and wide range of analyte concentrations.

References

1. Benefits of a vertically oriented torch— fast, accurate results, even for your toughest samples, Agilent publication, (2014), 5991-4854EN
2. Fitted Background Correction (FBC) – fast, accurate and fully automated background correction, Agilent publication (2014), 5991-4836EN

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Published November 27, 2015

Publication number: 5991-6157EN



Agilent Technologies