Application Note

Metals

# Analysis of Steel and Its Alloys by ICP-OES Following the GB/T 20125-2006 Standard

## Accurate, robust, and stable measurements using the Agilent 5800 VDV ICP-OES and AVS 7 sampling valve

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## Introduction

Elemental impurities in steel or steel alloys can affect the performance of the final product. So, steel manufacturers conduct rigorous quality control (QC) testing for a range of metals and trace elements to ensure the grade and price of their final products. There are various standard methods that relate to the QC of manufactured steel products, including the Standardization Administration of China GB/T 20125-2006 standard. The GB/T standard uses ICP-OES to determine multiple elements in low-alloy steel (*1*).

Different grades of steel have different specifications for elemental content. Most steel and stainless-steel grades are required to have less than 0.05% by weight of sulfur (S) and less than 0.04% by weight of phosphorus (P). In addition to measuring low-level contaminants, such as S and P, labs are also required to provide quantitative results for major components such as nickel (Ni) and iron (Fe).

Nowadays, laboratories demand more from their instrumentation than simply measuring elements in a sample over a wide dynamic range. Many QC laboratories process hundreds of samples per day, so achieving high sample throughput with easy-to-use and reliable instrumentation is critical. High levels of accuracy, stability, and robustness are also needed to reduce the time spent remeasuring samples so that analysts can focus on more productive tasks. Typically, samples are remeasured because of an instrument-related problem or sample-related problem.

To prevent the most common causes of having to remeasure a sample, the Agilent 5800 ICP-OES and Agilent 5900 ICP-OES use a series of tools that provide useful information on samples, methods, and the operational status of the instrument. Features such as IntelliQuant, IntelliQuant Screening, and Early Maintenance Feedback (EMF) (*2–4*) improve data accuracy and reduce unscheduled downtime for maintenance, providing labs with greater confidence in the method and results. If selected, IntelliQuant is run as part of the quantitative method while IntelliQuant Screening is run independently, as a standalone method.

Also, spectral interferences arising from the complex elemental content of stainless-steel sample matrices—especially line-rich Fe—can impact the accuracy of the data for some analyte elements such as S. The 5800 and 5900 ICP-OES include freeform optics to enhance spectral resolution and an advanced detector that lowers detection limits. The higher resolution optics mean that more analyte lines are separated from neighboring lines, enabling the 5800 or 5900 to achieve lower detection limits for elements in complex matrices.

To resolve interferences, Agilent ICP Expert software includes the widest range of background correction techniques for ICP-OES. For an element like Al, which isn't affected by directly overlapping interferences, Fitted Background Correction (FBC) can be used to improve the accuracy of the measurement (*5*). FBC is the simplest correction method, requiring no setup. To resolve interferences arising from more complex background signals, Fast Automated Curve Fitting Technique (FACT) is a powerful technique that ensures accurate results (*6*). When direct overlaps are observed in the spectrum, inter-element correction factors and off-peak background correction can be used.

In this study, an Agilent 5800 Vertical Dual View (VDV) ICP-OES was used to measure 15 elements in three stainless steel certified reference materials (CRMs) in accordance with the GB/T 20125-2006 standard. The CRMs were prepared by microwave acid digestion.

## Experimental

### Instrumentation

All measurements were performed using a 5800 VDV ICP-OES fitted with a SeaSpray concentric nebulizer, double-pass cyclonic spray chamber, and an Agilent Easy-fit demountable VDV torch with a 1.8 mm injector. The instrument was configured with an integrated Advanced Valve System (AVS 7) seven-port switching valve and an Agilent SPS 4 autosampler. The AVS 7 uses a high-speed positive displacement pump to rapidly fill the sample loop, speeding up the analysis and reducing argon consumption (*7*). The valve also reduces maintenance and cleaning requirements of the torch, as less sample passes through the sample introduction system compared to conventional sample introduction.

The Vista Chip III detector of the 5800 provides high-speed continuous wavelength coverage from 167 to 785 nm, ensuring that a suitable, interference-free line can be found for most analytes. There is no time penalty when adding extra wavelengths for an element to the analysis. The wide range of the detector enables both major (e.g., Ni and Fe) and trace elements (e.g., S and P) to be analyzed in the same sample digest, avoiding the need to perform multiple dilutions.

Internal standard correction was used to correct for matrix and easily ionizable element (EIE) interferences. Europium (Eu) and lutetium (Lu) were used as internal standards, each at a concentration of 10 mg/L.

The instrument and method parameters for the 5800 VDV ICP-OES are given in Table 1 and the AVS 7 settings are given in Table 2.

**Table 1.** Agilent 5800 VDV ICP-OES instrument and method parameters.

| Parameter | Radial | Axial |
|---|---|---|
| Read Time (s) | 5 | 20 |
| Replicates | 3 | |
| Sample Uptake Delay (s) | 0 | |
| Stabilization Time (s) | 10 | 0 |
| Rinse Time (s) | 0 | |
| Pump Speed (rpm) | 12 | |
| RF Power (kW) | 1.5 | |
| Auxillary Flow (L/min) | 1 | |
| Plasma Flow (L/min) | 12 | |
| Nebulizer Flow (L/min) | 0.8 | |
| Viewing Height (mm) | 8 | NA |
| Sample Pump Tubing | White-white | |
| Internal Standard Pump Tubing | Black-black | |
| Waste Pump Tubing | Blue-blue | |
| Background Correction | FBC/FACT/Off-peak | |

**Table 2.** AVS 7 switching valve system parameters.

| Parameter | Setting |
|---|---|
| Sample Loop Size (mL) | 1.5 |
| Pump Rate - Uptake (mL/min) | 36 |
| Pump Rate - Inject (mL/min) | 5 |
| Valve Uptake Delay (s) | 7 |
| Bubble Inject Time (s) | 2 |
| Pre-emptive Rinse Time (s) | 1 |

## Samples

Three steel CRMs, GH-135 6934 and GSBH 40031-93 (China National Analysis Center for Iron and Steel), and BCS-336 (British Chemical Standards), were used to validate the 5800 VDV ICP-OES method. Pure iron wire (≥99.99% trace metal basis, Sigma Aldrich) was used as a blank sample.

## Sample preparation

The samples were prepared by microwave digestion using a Mars 6 Microwave Digestion System (CEM Corporation, NC, USA). First, 0.25 g of each CRM was digested in 1 mL $H_2O$, 3 mL of $HNO_3$, 1 mL $H_2O_2$, and 9 mL of HCl using the microwave digestion program shown in Table 3. The digests were then made up to a volume of 50 mL with 18 MΩ de-ionized water (DIW) to give a final matrix of 24% aqua regia. A method blank was prepared at the same time as the CRMs, using the same method to digest 6N high purity iron wire. This method blank solution was prepared with a final concentration of 5000 mg/L of Fe.

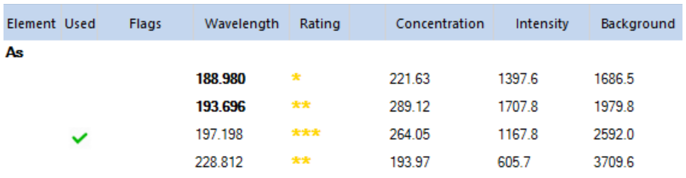
**Table 3.** Microwave digestion parameters.

| Parameter | Value |
|---|---|
| Power (W) | 0–1200 |
| Temperature (°C) | 200 |
| Ramp Time (min) | 25 |
| Hold Time (min) | 20 |

## Wavelength selection using IntelliQuant Screening

IntelliQuant Screening allows analysts to run a quick, semiquantitative screening of unknown samples, and is especially useful for samples with a complex matrix (*3*). In this study, IntelliQuant Screening was used during method development, particularly for wavelength selection, and to determine the approximate concentration of elements in some of the steel CRM digests.

Figure 1 shows the IntelliQuant Screening results for As in the BCS-336 steel CRM. The IntelliQuant algorithm automatically identified 197.198 nm as the best As wavelength to use in the quantitative method, as indicated by the highest star rating and 'green' tick.

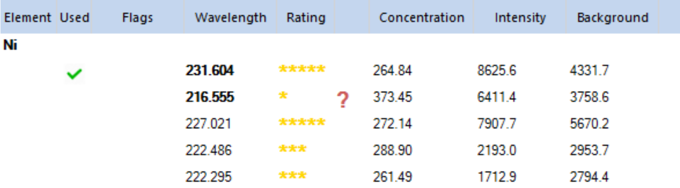


| Element | Used | Flags | Wavelength | Rating | Concentration | Intensity | Background |
|---|---|---|---|---|---|---|---|
| **As** | | | | | | | |
| | | | **188.980** | * | 221.63 | 1397.6 | 1686.5 |
| | | | **193.696** | ** | 289.12 | 1707.8 | 1979.8 |
| | ✓ | | 197.198 | *** | 264.05 | 1167.8 | 2592.0 |
| | | | 228.812 | ** | 193.97 | 605.7 | 3709.6 |

**Figure 1.** Star ranking of As lines in the BCS-336 CRM.

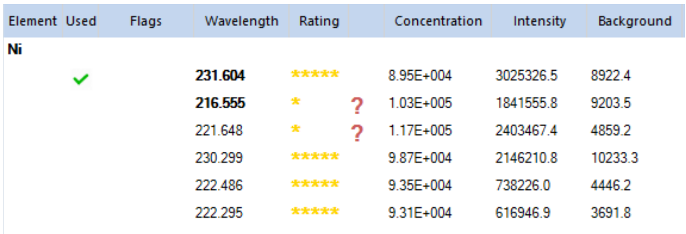
The IntelliQuant Screening wavelength star rankings for Ni in the GSBH 40031-93 and BCS-336 steel CRMs show that Ni 231.604 nm is the preferred line in both matrices (Figures 2 and 3). The IntelliQuant semiquantitative concentration for Ni 231.604 nm of 264.84 mg/kg is in close agreement with the GSBH 40031-93 certified Ni concentration of 260 mg/kg. The BCS 336 CRM contains Ni at a higher concentration than GSBH 40031-93, but the IntelliQuant result for Ni of 89,500 mg/kg compares reasonably well with the certified value of 94,800 mg/kg.

The IntelliQuant Screening results shown in Figures 2 and 3 highlight the linearity of the 5800 VDV ICP-OES, as both measurements selected the same wavelength for Ni at a low and high concentration.



| Element | Used | Flags | Wavelength | Rating |  | Concentration | Intensity | Background |
|---|---|---|---|---|---|---|---|---|
| **Ni** |  |  |  |  |  |  |  |  |
|  | ✓ |  | **231.604** | ★★★★★ |  | 264.84 | 8625.6 | 4331.7 |
|  |  |  | **216.555** | ★ | ? | 373.45 | 6411.4 | 3758.6 |
|  |  |  | 227.021 | ★★★★★ |  | 272.14 | 7907.7 | 5670.2 |
|  |  |  | 222.486 | ★★★ |  | 288.90 | 2193.0 | 2953.7 |
|  |  |  | 222.295 | ★★★ |  | 261.49 | 1712.9 | 2794.4 |

**Figure 2.** IntelliQuant Screening star ranking for Ni in the GSBH 40031-93 CRM.



| Element | Used | Flags | Wavelength | Rating |  | Concentration | Intensity | Background |
|---|---|---|---|---|---|---|---|---|
| **Ni** |  |  |  |  |  |  |  |  |
|  | ✓ |  | **231.604** | ★★★★★ |  | 8.95E+004 | 3025326.5 | 8922.4 |
|  |  |  | **216.555** | ★ | ? | 1.03E+005 | 1841555.8 | 9203.5 |
|  |  |  | 221.648 | ★ | ? | 1.17E+005 | 2403467.4 | 4859.2 |
|  |  |  | 230.299 | ★★★★★ |  | 9.87E+004 | 2146210.8 | 10233.3 |
|  |  |  | 222.486 | ★★★★★ |  | 9.35E+004 | 738226.0 | 4446.2 |
|  |  |  | 222.295 | ★★★★★ |  | 9.31E+004 | 616946.9 | 3691.8 |

**Figure 3.** IntelliQuant Screening star ranking for Ni in the BCS-336 CRM.

## Calibration

Matrix matched calibration standards were prepared from Agilent 10,000 mg/L single element stock solutions in a matrix of 24% aqua regia. The concentration range used for the elements was based on IntelliQuant Screening data and on the expected concentrations to be found in samples from previous studies. Linear calibrations were acquired for all elements, as indicated by the correlation coefficients of greater than 0.999 (Table 4). The calibration blank was made in the same matrix as the calibration standards.

**Table 4.** Concentration of calibration standards and calibration correlation coefficients.

| Element | Std 1 | Std 2 | Std 3 | Std 4 | Std 5 | Std 6 | Std 7 | Std 8 | Std 9 | Std 10 | Correlation Coefficient |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  | mg/L |  |  |  |  |  |  |  |  |  |  |
| Al | 2 | 20 | 200 |  |  |  |  |  |  |  | 1.00000 |
| As |  |  |  |  |  |  | 0.1 | 1 | 10 |  | 1.00000 |
| B |  |  |  | 0.5 | 5 | 50 |  |  |  |  | 1.00000 |
| Co |  |  |  | 0.5 | 5 | 50 |  |  |  |  | 0.99981 |
| Cr | 10 | 100 | 1000 |  |  |  |  |  |  |  | 0.99993 |
| Cu | 0.5 | 5 | 50 |  |  |  |  |  |  |  | 1.00000 |
| Fe |  |  |  |  |  |  |  |  |  | 5000 | 1.00000 |
| Mn |  |  |  |  |  |  | 1 | 10 | 100 |  | 1.00000 |
| Mo |  |  |  | 2 | 20 | 200 |  |  |  |  | 0.99999 |
| Ni |  |  |  |  |  |  | 20 | 200 | 2000 |  | 0.99994 |
| P | 0.1 | 1 | 10 |  |  |  |  |  |  |  | 1.00000 |
| S | 0.1 | 1 | 10 |  |  |  |  |  |  |  | 0.99999 |
| Si |  |  |  | 1 | 10 | 100 |  |  |  |  | 0.99999 |
| Ti |  |  |  |  |  |  | 2 | 20 | 200 |  | 1.00000 |
| V |  |  |  | 0.5 | 5 | 50 |  |  |  |  | 1.00000 |

### Quality control

A midrange calibration standard was used as the continuing calibration verification (CCV) sample to check the long-term stability of the instrument.

### Background correction and interference correction

To reduce the impact of spectral interferences arising from the sample matrices, different background correction methods were used. For elements where there were no direct overlaps, FBC was used. An example of FBC for Al 396.152 nm is shown in Figure 4.

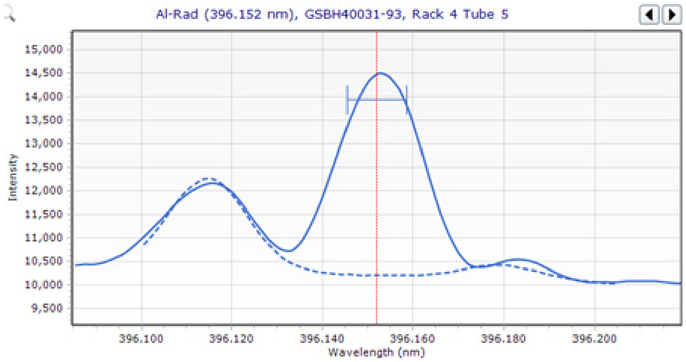


**Figure 4.** Fitted background correction for Al 396.152 nm.

For elements that were affected by more complex background signals, FACT was used. In these instances, a 5000 mg/L Fe solution was used as a matrix in the FACT models. Figure 5 shows a FACT model for Co 230.786 nm with corrections for Cr 230.752 nm, Ni 230.778 nm, Mo 230.798 nm, and Ni 230.817 nm. FACT has accurately modeled the interfering peaks and resolved the analyte signal, providing accurate results for Co.

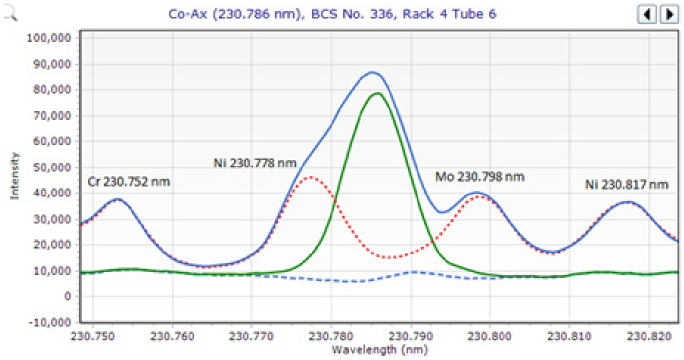


**Figure 5.** FACT model for Co 230.786 nm.

Due to the complexity of steel samples, many direct spectral overlaps can be present. To correct for a direct spectral overlap, a mathematical approach, rather than a graphical approach is required. The contribution to the total signal at the analyte wavelength that is determined to be from the interfering signal is subtracted from the total signal. This approach relies on having a fixed background so that the calculations are consistent. Off-peak background correction was used for S 181.972 and an inter-element correction (IEC) calculation was applied.

## Results and discussion

### Method detection limits

Method detection limits (MDLs) were determined by analyzing a 5000 mg/L iron blank solution 10 times on three days. The MDL was calculated as three sigma of the blank concentration determined for each element (apart from iron) multiplied by the dilution factor. The MDLs in Table 5 are reported on an in-sample basis.

**Table 5.** Method detection limits for all elements in a 5000 mg/L iron blank solution.

| Element | Background Correction Method | Wavelength (nm) | MDL (mg/kg) |
|---|---|---|---|
| Al | FBC | 396.152 | 2.04 |
| As | FACT | 197.198 | 2.19 |
| B | FBC | 182.577 | 0.988 |
| Co | FACT | 230.786 | 0.284 |
| Cr | FBC | 267.716 | 0.475 |
| Cu | FACT | 327.395 | 0.163 |
| Mn | FBC | 257.61 | 0.689 |
| Mo | FBC | 202.032 | 0.721 |
| Ni | FBC | 231.604 | 1.49 |
| P | Off-peak | 178.222 | 1.24 |
| S | Off-peak | 181.972 | 2.26 |
| Si | FBC | 251.611 | 1.51 |
| Ti | FBC | 337.28 | 0.545 |
| V | FACT | 311.837 | 0.217 |

### Accuracy of the method

To validate the sample preparation procedure and the accuracy of the 5800 VDV ICP-OES method, the three CRMs were analyzed in triplicate and the average of the results was calculated. The results in Table 6 show excellent recoveries within ±10% of the certified value, demonstrating the accuracy of the method for the analysis of samples with complex matrices. The results also show the robustness and analytical range of the 5800 ICP-OES to measure high concentration elements such as Ni, Fe, and Cr in the same run as trace elements such as As, B, Co, P, and S.

### Long-term stability

The long-term stability (LTS) of this application was tested by analyzing 217 CRM samples over six hours by 5800 VDV ICP-OES. A QC solution was measured after every 10 samples and the recoveries are shown in Figure 6. All measurements were within ±10% of the expected concentrations, demonstrating the excellent robustness and stability of the 5800 ICP-OES for the analysis of high matrix steel sample digests over six hours.

**Table 6.** Recoveries for elements in three steel CRMs. Blank cells indicate no certified or reference value.

| Element, Wavelength (nm) | GH 135 | | | GSBH40031-93 | | | BCS No. 336 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Measured (mg/kg) | Certified (mg/kg) | Recovery (%) | Measured (mg/kg) | Certified (mg/kg) | Recovery (%) | Measured (mg/kg) | Certified (mg/kg) | Recovery (%) |
| Al 396.152 | 30390 | 31500 | 96 | 170.4 | 170 | 100 | 1058 | | |
| As 197.198 | 54.99 | | | 65.76 | 66 | 100 | 232 | | |
| B 182.577 | 83.19 | 87 | 96 | 1.471 | | | 3.248 | | |
| Co 230.786 | 35.21 | | | 57.56 | 58 | 99 | 593.7 | 630 | 94 |
| Cr 267.716 | 132200 | 139400 | 95 | 363.4 | 350 | 104 | 163300 | 176000 | 93 |
| Cu 327.395 | 228.1 | | | 314.4 | 340 | 92 | 1120 | 1100 | 102 |
| Fe 273.358 | 405100 | | | 962700 | | | 674400 | | |
| Mn 257.61 | 4146 | 4500 | 92 | 5167 | 5500 | 94 | 7719 | 8100 | 95 |
| Mo 202.032 | 16840 | 18400 | 92 | 54.23 | 59 | 92 | 23120 | 24300 | 95 |
| Ni 231.604 | 337700 | 358500 | 94 | 283.6 | 260 | 109 | 95910 | 94800 | 101 |
| P 178.222 | 36.52 | 40 | 91 | 171.8 | 170 | 101 | 211.3 | 200 | 106 |
| S 181.972 | 38.65 | 37 | 104 | 159.6 | 170 | 94 | 244.6 | 230 | 106 |
| Si 251.611 | 4793 | 4520 | 106 | 2281 | 2280 | 100 | 5359 | 5100 | 105 |
| Ti 337.28 | 22080 | 24490 | 90 | 12.65 | | | 57.73 | | |
| V 311.837 | 1202 | | | 6.838 | | | 300.9 | 300 | 100 |

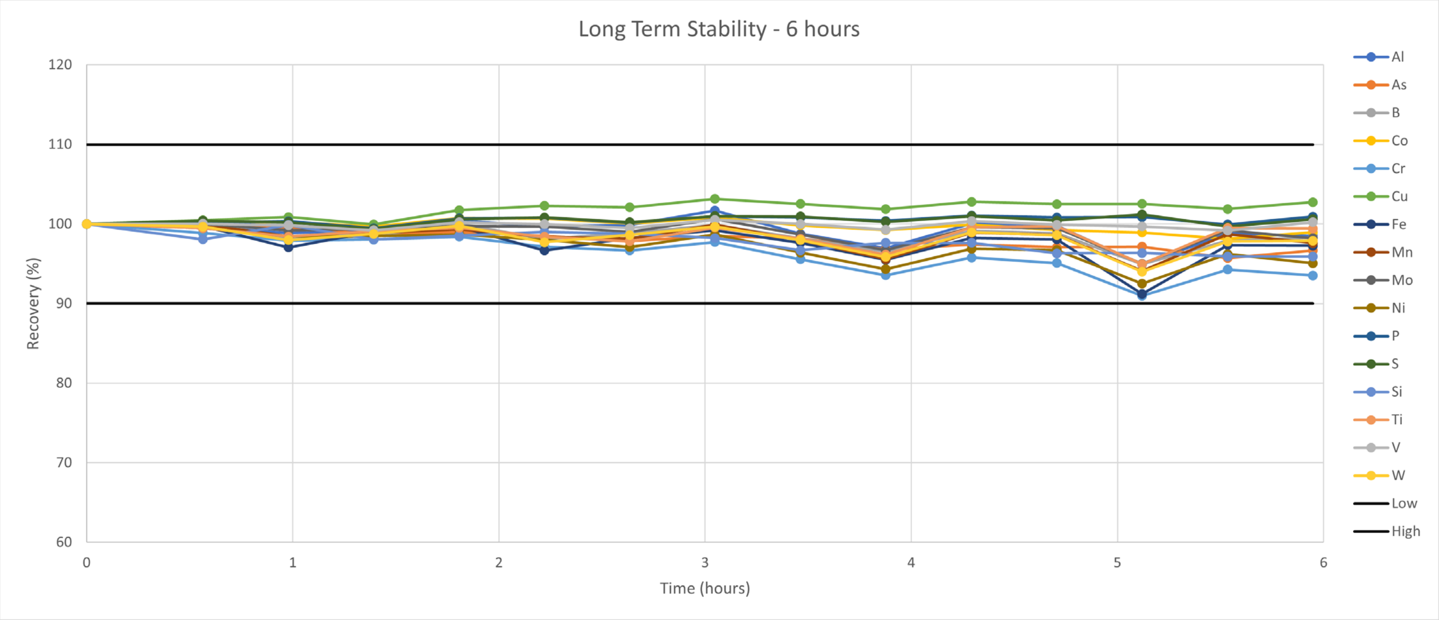


**Figure 6.** Stability of trace elements in a QC sample analyzed after each block of 10 steel digest samples over six hours.

## Conclusion

The Agilent 5800 VDV ICP-OES with high-resolution optics and continuous wavelength range detector was used to analyze multiple elements in three steel CRMs, prepared using microwave acid digestion. The method was based on the GB/T 20125-2006 standard for the elemental determination of low-alloy steel.

The Fe content of steel digests can be problematic due to the high number of Fe lines in the ICP-OES spectra that interfere with analytes such as sulfur. To help with method development, IntelliQuant Screening semiquantitative data was used to select or confirm the best wavelengths for some elements. The IntelliQuant Screening data was also used to help with selecting the best background correction technique for the analytes in this application.

The method showed good accuracy and dynamic range as all major (percent-level) components and trace (ppm in the solid) elements in the three CRMs recovered within ±10% of the certified values. The matrix tolerance and robustness of the 5800 was shown by the excellent recoveries of trace elements measured throughout the analysis of high matrix steel sample digests over six hours.

The study has demonstrated that the 5800 VDV ICP-OES fitted with an AVS 7 sampling valve is suitable for the routine analysis of steel digest samples, in accordance with industry standard methods.

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