

Challenge

Trace element detection of additives and impurities in high-alloyed steel products featuring complicated emission spectra

Solution

HR ICP-OES with high-resolution optical system in combination with a powerful software routine (CSI), being able to resolve severe spectral interferences originating from iron and refractory additives in typical steel matrices

Analysis of High-alloyed Steel by HR ICP-OES

Introduction

Due to its excellent properties in terms of tensile strength and its high availability at comparatively low cost, steel is a major construction component in many areas such as buildings, machinery, tools, and many more. The main components of steel are iron and carbon, whereas their content defines the properties of the resulting steel grade. One way of further altering steel's material properties such as hardness, corrosion resistance, ductility, and processability is the use of additives (cobalt, nickel, vanadium, molybdenum, and others). For instance, in the production of stainless steel, chromium and nickel are added, whereas tool steels are alloyed with large amounts of tungsten and cobalt. In high-alloyed steel, trace and ultra-trace amounts of additives and impurities have great influence on performance and grade. On the other hand, traces of elements such as phosphorus, sulfur or silicon deteriorate the properties of steel and ought to be minimized in final steel products. Reliable trace detection has thus become the key objective of many laboratories entrusted with product control and quality assurance of steel products. For conventional ICP optical emission spectrometry (ICP-OES), the trace and ultratrace analysis of high-alloyed steel samples poses a complex problem, as more than 3,300

registered iron emission lines give rise to severe spectral interferences. Moreover, significant amounts of refractory additives, such as molybdenum or vanadium, that also contribute numerous emission lines often further complicate the emission spectra. That is, for high-alloyed steel samples, spectral interferences are infamous for impairing the quantification of trace elements such as phosphorus, aluminum, and boron.

Here, the exceptionally high spectral resolution and sensitivity of the PlasmaQuant 9100 Elite offers new analytical potential. It allows for an interference-free analysis of trace elements in a complicated matrix such as steel. Furthermore, the high plasma robustness of the high-frequency generator and the sample introduction system with its centerpiece, the V-Shuttle torch, allow for the analysis of high matrix samples with high accuracy and high precision. For severely complicated spectra, powerful software tools such as the fully automatic baseline fitting ABC and the CSI-tool for mathematical correction of spectral interferences significantly ease data handling and ensure highest data quality.

Materials and Methods

Samples and reagents

A certified high-alloyed steel (EURONORM standard reference material 284-2) was submitted to the analysis of traces and main components on the PlasmaQuant 9100 Elite.

Sample preparation

The material was digested by closed vessel digestion using the TOPwave microwave of Analytik Jena. 0.5 g of sample were weighed in and mixed with 6 mL HCl, 2 mL HNO₃ and 1 mL HF. After digestion at 200 degrees Celsius in the

microwave, the solutions were filled up to 100 mL with deionized water.

Calibration

Al, B, Co, Cr, Cu, Mo, Ni, P and V were analyzed by matrix-matched calibration in 3.5 g/L Iron. Accounting for the different proportions of all elements in the CRM, a custom-made calibration stock standard was used for the preparation of the calibration standards. The concentration levels of the standards are displayed in Table 1.

Table 1: Concentration of calibration standards

Element	Unit	Cal. 0	Cal. 1	Cal. 2
Al	mg/L	0	0.4	1.0
B	mg/L	0	0.4	1.0
Co	mg/L	0	1.0	5.0
Cr	mg/L	0	40	100
Cu	mg/L	0	5.0	10.0
Mo	mg/L	0	5.0	10.0
Ni	mg/L	0	40	100
P	mg/L	0	0.4	1.0
V	mg/L	0	1.0	5.0

Instrumentation

For the analysis, a PlasmaQuant 9100 Elite equipped with HF kit and ASPQ 3300 autosampler was used. The detailed system configuration is given in Table 2. The digestion was performed in the TOPwave microwave system equipped with CX-100 vessels.

Table 2: Configuration of the PlasmaQuant 9100 Elite equipped with HF kit

Parameter	Settings	Parameter	Settings
Power	1,200 W	Outer tube/Inner tube	SiAlON/alumina
Plasma gas flow	12 L/min	Pump tubing	PVC
Auxiliary gas flow	0.5 L/min	Sample pump rate	1.0 mL/min
Nebulizer gas flow	0.5 L/min	Rinse/Read delay	45 s
Nebulizer	Parallel path nebulizer, PFA, 1.0 mL/min	Integration time	3 s (3 replicates)
Spray chamber	PTFE cyclonic spray chamber, 50 mL	Plasma view	Axial
Room temperature	20 °C	Baseline fit	Automatic Baseline Correction (ABC), except for Al (static)
Injector	Alumina, inner diameter 2 mm		

Evaluation parameters

Table 3: Overview of method-specific evaluation parameters

Element	Line [nm]	Plasma view	Integration mode	Read time [s]	Evaluation			
					No. of pixel	Baseline fit	Polynomial degree	Correction
Al	394.401	axial	peak	3	3	static	0	Y ¹ , CSI ²
B	182.581	axial	peak	3	3	ABC ³	auto	Y
Co	228.615	axial	peak	3	3	ABC	auto	Y
Cr	267.716	axial	peak	3	3	ABC	auto	Y
Cu	327.396	axial	peak	3	3	ABC	auto	Y
Mo	202.030	axial	peak	3	3	ABC	auto	Y
Ni	341.476	axial	peak	3	3	ABC	auto	Y
P	178.224	axial	peak	3	3	ABC	auto	Y
V	290.881	axial	peak	3	3	ABC	auto	Y

1 ... Yttrium used as internal standard

2 ... CSI software tool used to correct for matrix interference

3 ... Automatic baseline correction (ABC)

Results and Discussion

Excellent method robustness for the analysis of high-alloyed steel was found for the major elements chromium, nickel, molybdenum and copper with recovery rates for the certified reference material in the range from 95% to 103% (Table 4). Within the same measurement, good agreement with the reported value was also achieved for the trace (Co, V, P) and ultra-trace elements (Al, B).

Table 4: Overview of results for ECRM 284-2

Element	ECRM No. 284-2			DL ¹ [mg/kg]
	Certified value [mg/kg]	Measured value [mg/kg]	Recovery [%]	
Al	27.0	28.5	105	0.64
B	26.0	24.8	95.4	0.64
Co	530	498	94	0.76
P	258	248	96.1	9.78
V	425	400	94.1	0.20
Cu	1.83	1.87	102	0.24
Cr	168	173	103	0.14
Mo	21.1	21.0	99.4	0.52
Ni	107	102	95.5	0.22

1 ... Matrix-specific detection limit obtained from 3 σ of SD for QC matrix blank (3.5 g/L Fe)

The impact of the high resolution on the analysis of high-alloyed steel is illustrated exemplarily in Figure 1, which contains the HR ICP optical emission spectrum of the B 182.581 nm line. The latter appears as a well-separated individual line embedded within a complex spectral pattern of emission lines (in the range from 182.50 to 182.67 nm), most of which originating from iron and molybdenum. While the B 182.581 nm line is not the most sensitive of the boron lines, it certainly is interference-free and offers excellent sensitivity given a detection limit of 0.64 mg/kg.

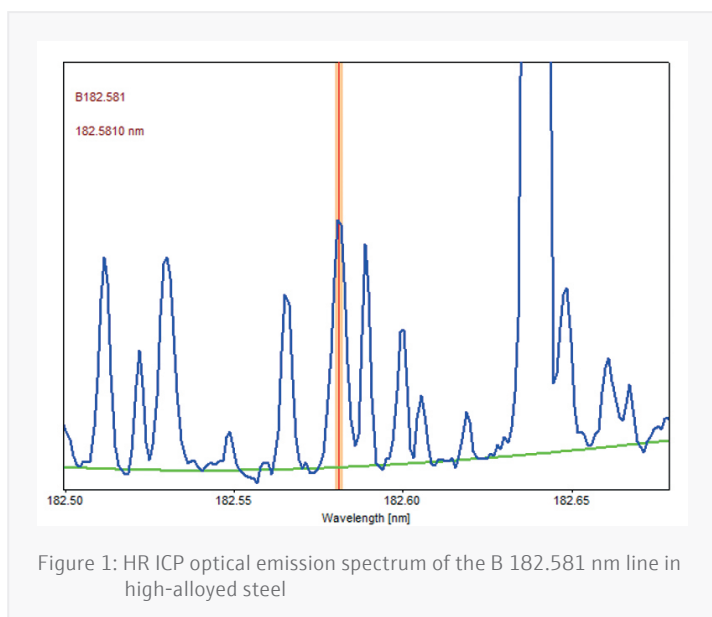


Figure 1: HR ICP optical emission spectrum of the B 182.581 nm line in high-alloyed steel

The green baseline fit in Figure 1 is the result of the automatic baseline correction (ABC). Here a global baseline is automatically fitted over the entire spectrum, which improves data handling, precision and productivity for the analysis of complex sample matrices. The superiority of this patented baseline fitting protocol over manual setting of baseline points for static fits is evident from this spectrum. The total analysis time per sample including rinse and read delays was less than 150 seconds.

Summary

Ensuring the quality of high-alloyed steel products by the analysis of intentionally added components (i.e., Cr, Ni, Co, V, or Mo) and unwanted components (i.e., P or S) is a key objective of quality control labs in the steel and metal industry. The wealth of emission lines originating from iron matrix, but also from additives such as Mo or V, results in highly complex spectra with the inherent risk of interferences.

The PlasmaQuant 9100 Elite exhibits two powerful features to overcome such spectral interferences: the high resolution of the optical system and the CSI software tool. The former makes it possible to spectrally resolve even severe interferences without further mathematical correction schemes, and the latter is able to correct for most difficult interferences by applying a mathematical algorithm to provide an interference-free result. The method described here provides detection limits in the $\mu\text{g}/\text{kg}$ range in high-alloyed steel products with the ability to quantify major contents as well as traces of additives or unwanted contaminations in a single run.

With the ABC tool for automatic baseline fitting on PlasmaQuant 9100 Elite, tedious static baseline fits become a relic of the past, which is a clear advantage for the operator as well as for the integration of this system in the routine analysis of high-alloyed steels.

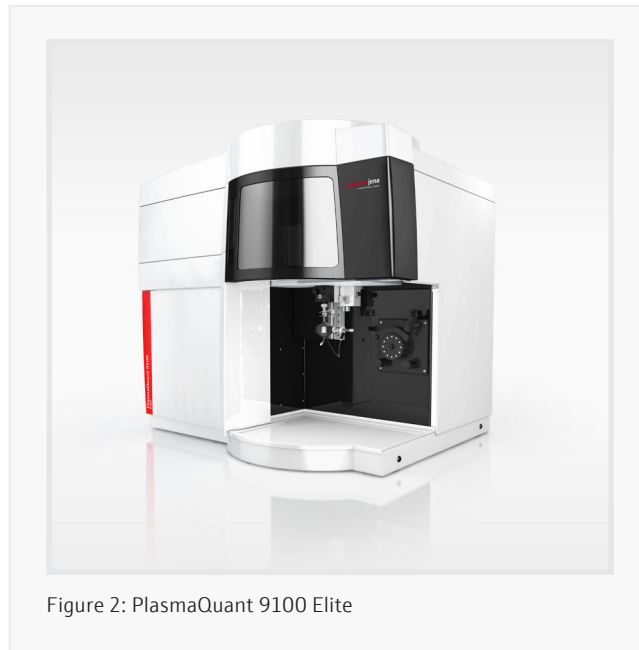


Figure 2: PlasmaQuant 9100 Elite

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