

**Application Example –  
PlasmaQuant® PQ 9000 Elite**

# Analysis of Heavy Metals in Iron-based Fertilizers by HR ICP-OES

## Abstract

The analysis of Iron-rich samples by ICP-OES is often very demanding since prominent Iron-based spectral interferences affect many of the most sensitive commonly used emission lines of heavy metals. That is, for the analysis of fertilizers for example Iron interferences are often a source for false quantification, high RSD values and relatively high limits of detection. When using High-Resolution Array ICP-OES many of these shortcomings can be avoided.

Here, the unique potential of the PlasmaQuant® PQ 9000 Elite equipped with Salt Kit was tested in the analysis of Cr, Cu, Mn, Ni, Pb and Zn contents in a commercial Iron (II) sulfate provided by a manufacturer of fertilizers. A nitric acid digest with a nominal  $\text{FeSO}_4$  content of 50 g/L was analyzed using an aqueous standard calibration without matrix-matching and internal standards. However, 5 g/L of high-purity Iron was dissolved in nitric acid and used for the identification and correction of Iron interferences. Results for multiple emission lines per element, QC standards as well as matrix-specific detection limits were obtained to evaluate the quality of the analytical routine. Excellent agreement between results for multiple lines per element was achieved for all elements. Further, the elemental contents for Cr, Mn and Zn met the specified values of the commercial fertilizer material ( $\text{FeSO}_4$ ). Yet, lower specification limits for Cu, Ni and Pb can be realized on PlasmaQuant® PQ 9000 Elite thanks to its exceptional resolving power that deals with Iron-based interferences.

Please note that RSD values were  $< 1.4\%$  except for Lead, which is particularly good since no internal standard has been used here. Thus, heavy metal analysis in Iron-rich agricultural samples benefits from the excellent precision of the PlasmaQuant® PQ 9000 Elite.



## Challenge

Reduction of specification limits for heavy metals

## Matrix

5 % iron matrix

## Purpose

Method development for an agricultural lab

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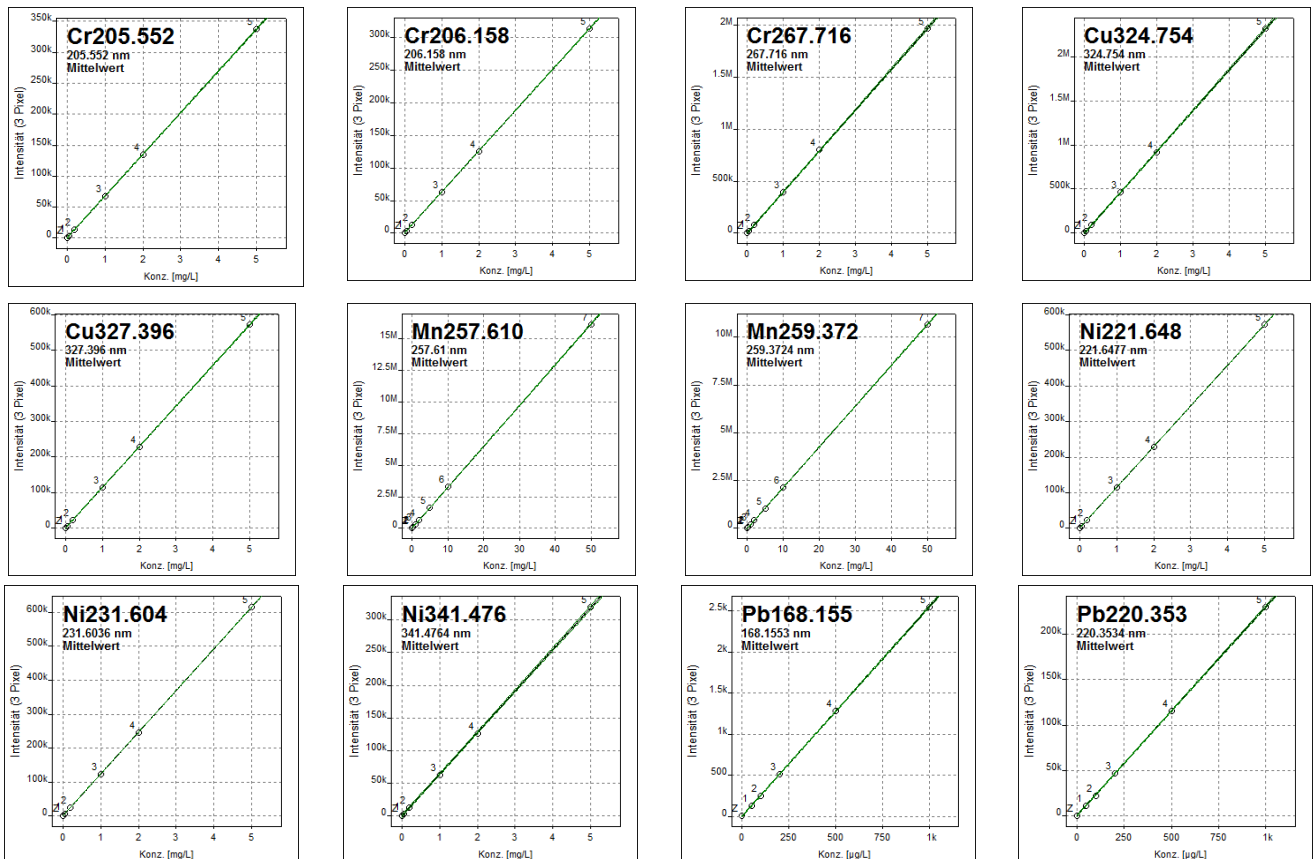
### Materials and Methods

#### Calibration

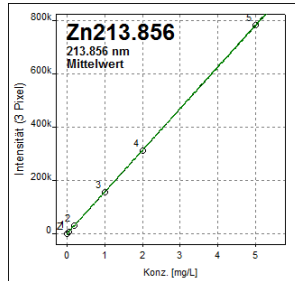
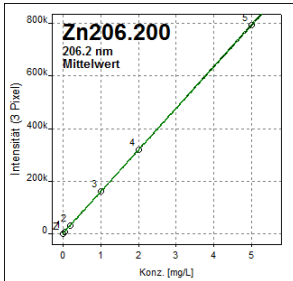
Table 1: Concentration of calibration standards

Element	Unit	Cal.0	Cal.1	Cal.2	Cal.3	Cal.4	Cal.5	Cal.6	Cal.7
Cr	mg/L	0	0.05	0.2	1.0	2.0	5.0	-	-
Cu	mg/L	0	0.05	0.2	1.0	2.0	5.0	-	-
Mn	mg/L	0	0.05	0.2	1.0	2.0	5.0	10	50
Ni	mg/L	0	0.05	0.2	1.0	2.0	5.0	-	-
Pb	mg/L	0	0.05	0.1	0.3	0.5	1.0	-	-
Zn	mg/L	0	0.05	0.2	1.0	2.0	5.0	-	-

#### Calibration curves



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### Method Parameters

Table 2: Plasma configurations and set-up of the sample introduction system

Parameter	Specification
Power	1300 W
Plasma Gas Flow	15 L/min
Auxiliary Gas Flow	1.0 L/min
Nebulizer Gas Flow	0.5 L/min
Nebulizer	concentric nebulizer with self-washing tip <sup>1</sup> , 1.0 mL/min
Spray Chamber	cyclonic spray chamber with dip tube <sup>1</sup> , 50 mL, borosilicate
Injector	Alumina <sup>1</sup> , inner diameter 2 mm
Outer Tube / Inner Tube	Syalon <sup>1</sup> / alumina1
Pump Tubing	PVC
Sample Pump Flow	1.0 mL/min
Rinse / Read Delay	45 s
Auto Sampler	Yes

1 ... the Salt Kit was used

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### 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
Cr	205.552	axial	peak	3	3	ABC <sup>1</sup>	auto	-
Cr	206.158	axial	peak	3	3	ABC	auto	-
Cr	267.716	axial	peak	3	3	ABC	auto	-
Cu	324.754	axial	peak	3	3	ABC	auto	-
Cu	327.396	axial	peak	3	3	ABC	auto	-
Mn	257.610	radial	peak	3	3	ABC	auto	-
Mn	259.372	radial	peak	3	3	ABC	auto	CSI <sup>2</sup>
Ni	221.648	axial	peak	3	3	ABC	auto	CSI
Ni	231.604	axial	peak	3	3	ABC	auto	CSI
Ni	341.476	axial	peak	3	3	ABC	auto	-
Pb	168.155	axial	peak	3	3	static	2	CSI
Pb	220.353	axial	peak	3	3	static	2	CSI
Zn	206.200	axial	peak	3	3	ABC	auto	-
Zn	213.856	axial	peak	3	3	ABC	auto	-

1 ... automatic baseline correction (baseline fitting protocol)

2 ... CSI software tool for the mathematical correction of interferences originating from Iron (II) sulfate matrix

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**Results and Discussion**

Table 4: Overview of results for metal analysis (for samples A, B, C) and method robustness test (spike recovery)

Element	Line [nm]	Content in µg/L		RSD <sup>1</sup> [%]	Iron-Interference	QC Cal.3 recovery rate	DL <sup>2</sup> in [mg/kg]
		Measured	Specified				
Cr	205.552	31.7±0.23	35	1.20	-	100	0.007
	206.158	31.4±0.15	35	1.39	-	102	0.013
	267.716	30.9±0.47	35	0.78	-	100	0.003
Cu <sup>3</sup>	324.754	2.41±0.52	< 3	0.32	yes	99	0.006
	327.396	0.19±0.21	< 3	1.40	-	100	0.010
Mn	257.610	704±2.25	700	0.70	-	99	0.003
	259.372	729±2.13	700	0.15	yes	103	0.007
Ni <sup>4</sup>	221.648	14.5±0.03	30	0.38	yes	102	0.011
	231.604	18.2±0.02	30	1.01	yes	102	0.007
	341.476	16.8±0.65	30	0.63	yes	100	0.047
Pb	168.155	(0.15) <sup>5</sup> ±0.07	< 1	20.0 <sup>6</sup>	-	120	0.3
	220.353	0.08±0.09	< 1	2.77	yes	102	0.01
Zn	206.200	2.80±0.34	4	0.37	-	102	0.007
	213.856	5.08±0.22	4	0.25	yes	102	0.007

1 ... RSD values obtained from 3 replicate measurements per sample

2 ... matrix-specific detection limits with respect to the solid Iron (II) sulfate from 3σ of SD on QC Blank

3 ... the value for Cu 324.754 nm matches the specified value. Yet, the value for Cu 327.396 nm is significantly lower and since it is free from Iron-interference it ought to be correct.

4 ... value for all Nickel lines is consistently lower than specified value. Hence, lower specification limits can be achieved on PlasmaQuant® PQ 9000.

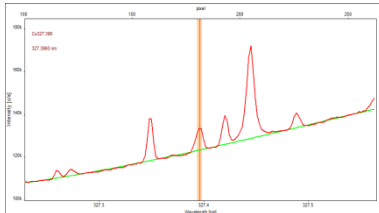
5 ... value below the detection limit

6 ... RSD value is elevated as the Lead signal is smaller than DL, i.e. RSD values originate from noise

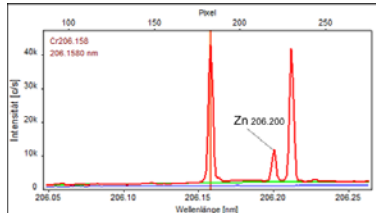
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### Application Advantages

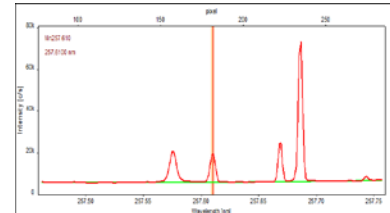
Collection of High-Resolution spectral data



Cu 327.396



Cr 206.158



Mn 257.610

Table 5: High-Resolution spectral data and applicability of the CSI Software Tool

Element	HR-Spectrum	CSI-corrected spectrum <sup>1</sup>
<p>Pb 220.353 nm</p> <p>red ... fertilizer sample</p> <p>blue ... Cal.1</p> <p>brown ... Iron matrix</p> <p>green ... ABC (automatic baseline fit)</p>		
	<p>Close inspection of the spectra of the <i>fertilizer sample</i> and the <i>Iron matrix</i> show that the Lead signal (orange line) is severely overlapped by Iron emission lines.</p>	<p>Using the Software Tool overlapping Iron emission lines are successfully subtracted from the <i>fertilizer sample</i> spectrum and a well-resolved Lead signal (orange line) is obtained.</p>

1 ... mathematical correction of spectral interferences using the CSI software tool

Reference: ICP\_OES\_33\_15\_en.docx

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