INSTITUT ZA MJERITELJSTVO BOSNE I HERCEGOVINE ★ ИНСТИТУТ ЗА МЕТРОЛОГИЈУ БОСНЕ И ХЕРЦЕГОВИНЕ ★ INSTITUTE OF METROLOGY OF BOSNIA AND HERZEGOVINA

EMPIR EURAMET
The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

EnvCRM

Validation of methods for determination of specific elements in environmental samples using Microwave Plasma Atomic Emission Spectrometry (MP-AES)

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17-21 September 2017, Heraklion, Greece

Contents:

1. Introduction to the topic

- EMPIR project: 14RPT03 - Matrix reference materials for environmental analysis (ENVCRM)
- Candidate reference material for river water sample: As, Cd, Hg, Ni and Pb, as mandatory elements, and Se, as optional elements
- Candidate reference material for soil sample: As, Cd, Co, Cr Cu, Fe, Mn, Ni, Pb, Sb, V and Zn

ELEMENTS	SOIL RM Target(mg/kg)	RIVER RM Target(ug/kg)
As	15	15
Cd	1.3	0.5
Co	40	/
Cr	70	/
Cu	60	/
Fe	No target	/
Mn	No target	/
Ni	50	15
Pb	60	5
Sb	Sb	/
V	40	/
Zn	140	/
Hg	1.4	0.1

1. Introduction to the topic

- Inter-comparison studies between the partners will be organized in order to produce and characterise the candidate reference material for river water sample and soil sample

- The Agilent 4200 MP-AES (*Microwave Plasma – Atomic Emission Spectrometer*) is one of analytical techniques that will be used for characterisation of RM

- This work presents development and validation of methods for chemical analysis of analytes of interest

- The work to be presented is implemented under the **EMPIR 14RPT03 - Matrix reference materials for environmental analysis**

2. Optimization of instrumental parameters

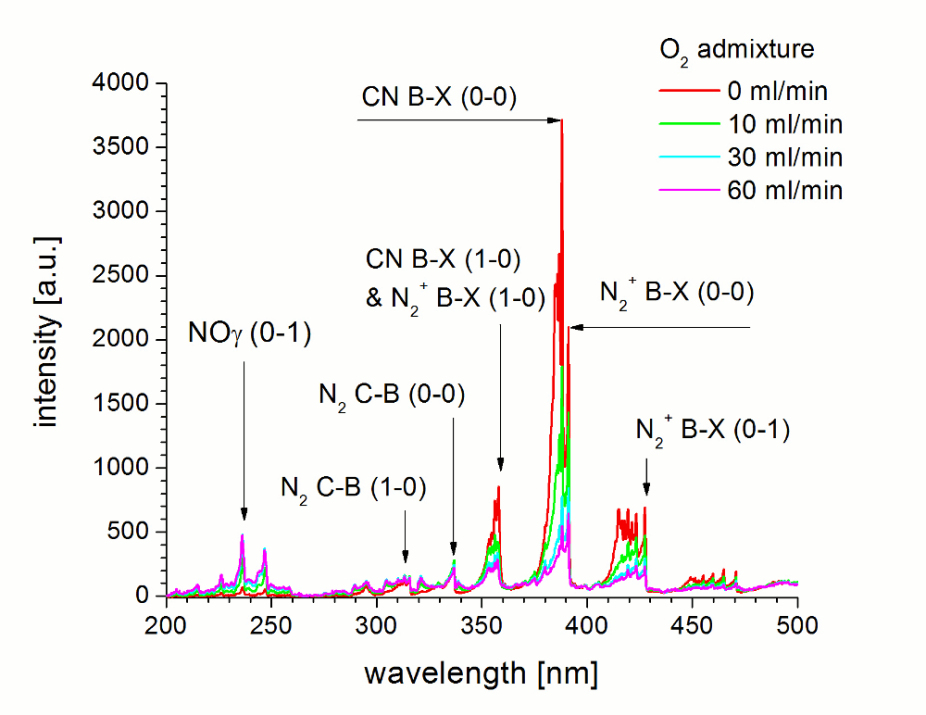
- **Description of the instrumental technique:**

- MWP-AES (Microwave plasma – atomic emission spectrometer)

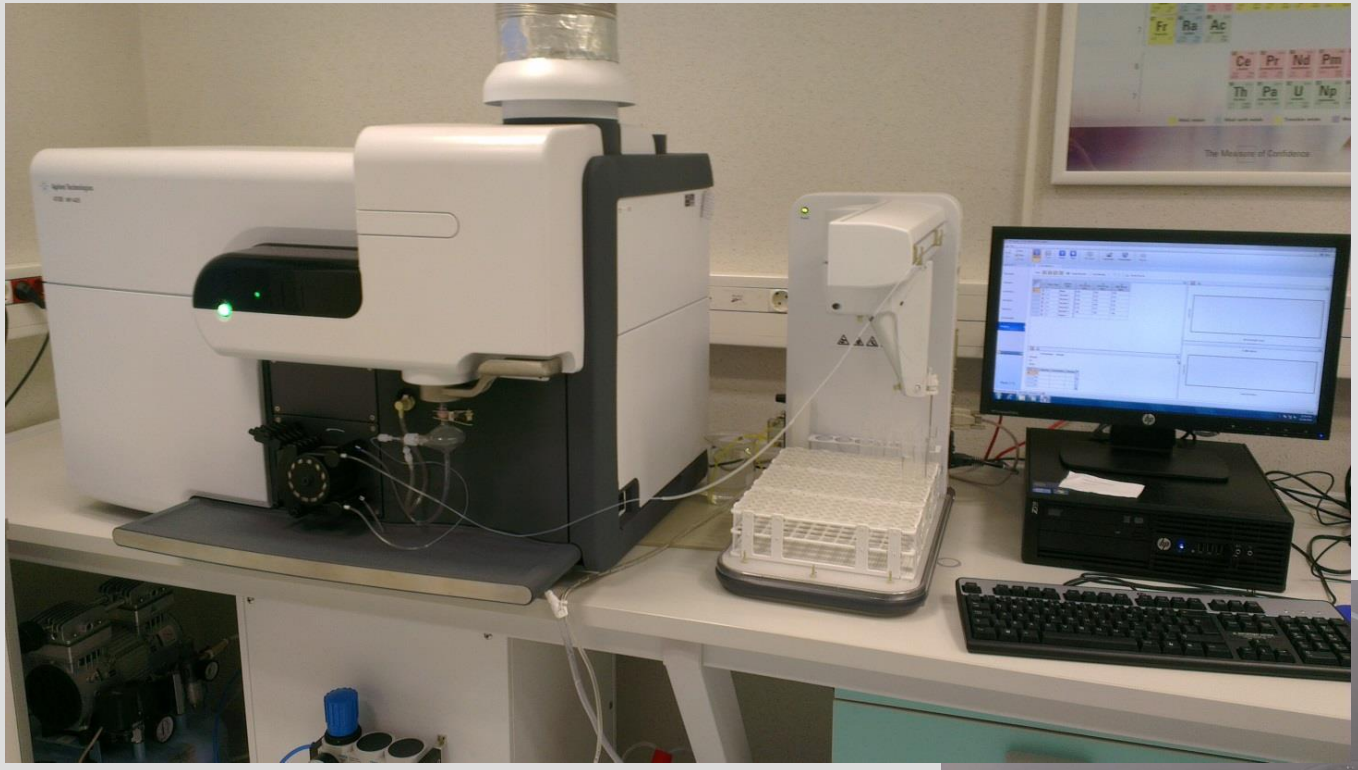
- Nitrogen plasma ignited indirectly by means of temporary formed Ar plasma

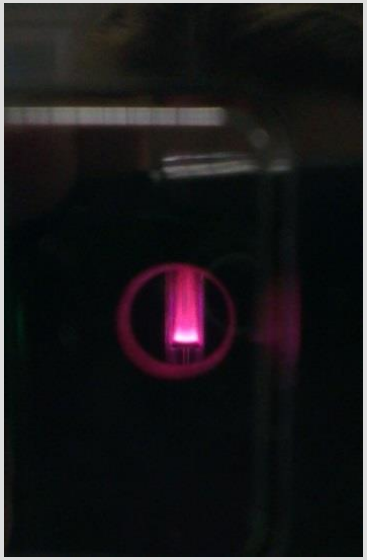
- The stability and composition of N_2 plasma is a function of amount of oxygen present

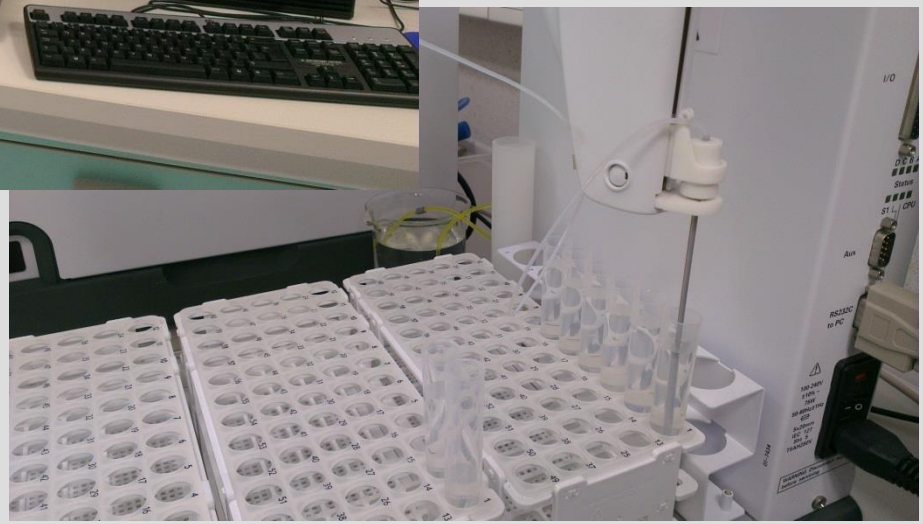
- Plasma temperature is around 6000°C and it emits high levels of microwave radiation



2. Optimization of instrumental parameters







Instrument, autosampler and N_2 plasma

2. Optimization of instrumental parameters

- Identification and quantification of the elements in plasma is done by optical detection of either atomic or ionic emission spectral lines at selected wavelengths

- Detection covers near UV and visible part of the EM spectra enabling extensive elemental analysis

- Liquid sample is introduced in plasma using peristaltic pump & nebulizer. It is preferred that the sample is acidified with nitric acid (pH<2) with TDS up to 3%

2. Optimization of instrumental parameters

- Analytes of interest for soil reference material are selected:
- Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn
- As and Sb is ongoing with aplication of Hydride Generation technique
- Hg will be the last step for development of the method

ELEMENTS	SOIL RM Target(mg/kg)
As	15
Cd	1.3
Co ⇦	40
Cr ⇦	70
Cu ⇦	60
Fe ⇦	No target
Mn ⇦	No target
Ni ⇦	50
Pb ⇦	60
Sb	Sb
V ⇦	40
Zn ⇦	140
Hg	1.4

2. Optimization of instrumental parameters

- Method settings:

a) Emission lines selected for analytes of interest

b) Viewing position for each line and nebulizer pressure optimized prior to analysis using sample solutions (matrix effect included)

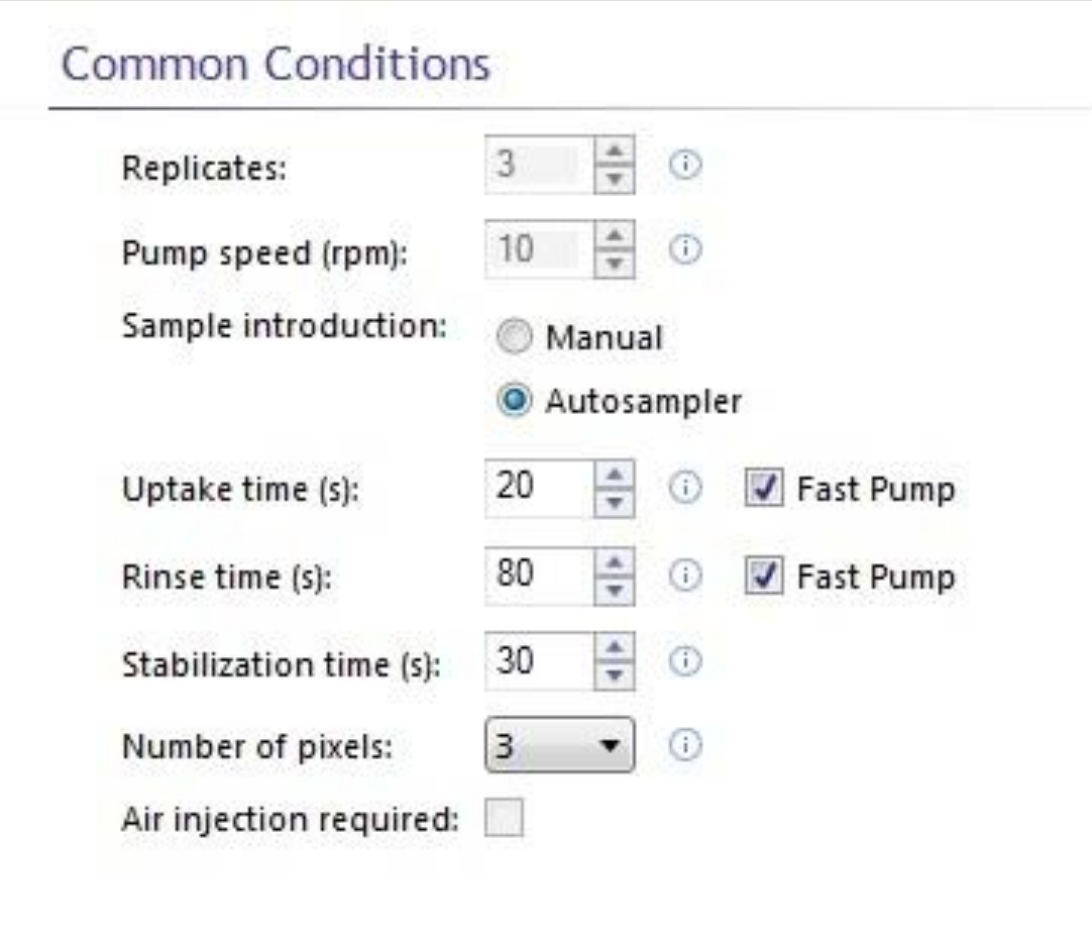
c) Calibration fit: linear / rational with blank subtraction

d) Concentration intervals for analytes of interest

one by one element ...

2. Optimization of instrumental parameters

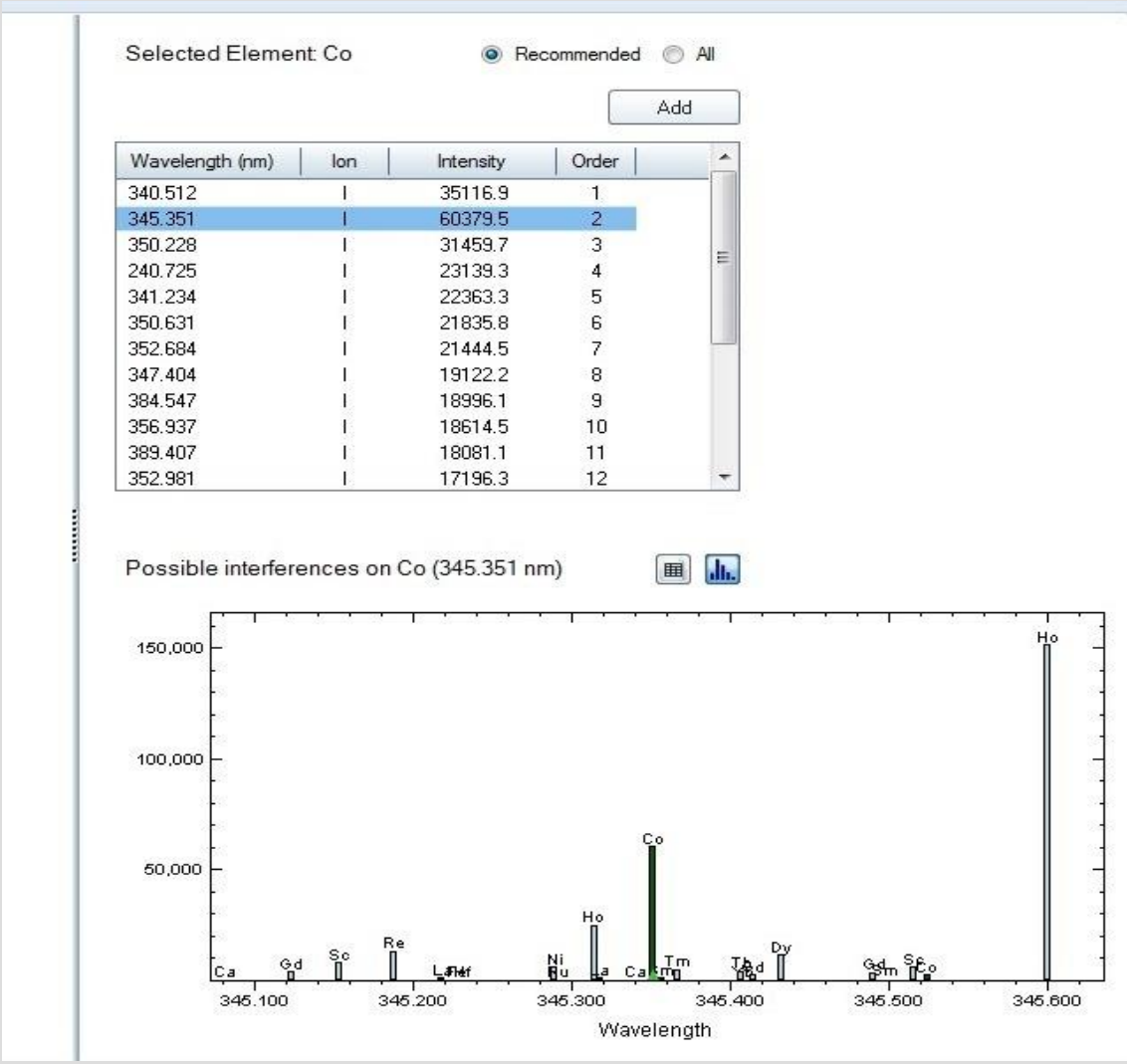
- *Set up common instrumental conditions*



2. Optimization of instrumental parameters

Cobalt

- ✓ Emission line selected: 345.351 nm
- ✓ Possible interferences are shown on graph below

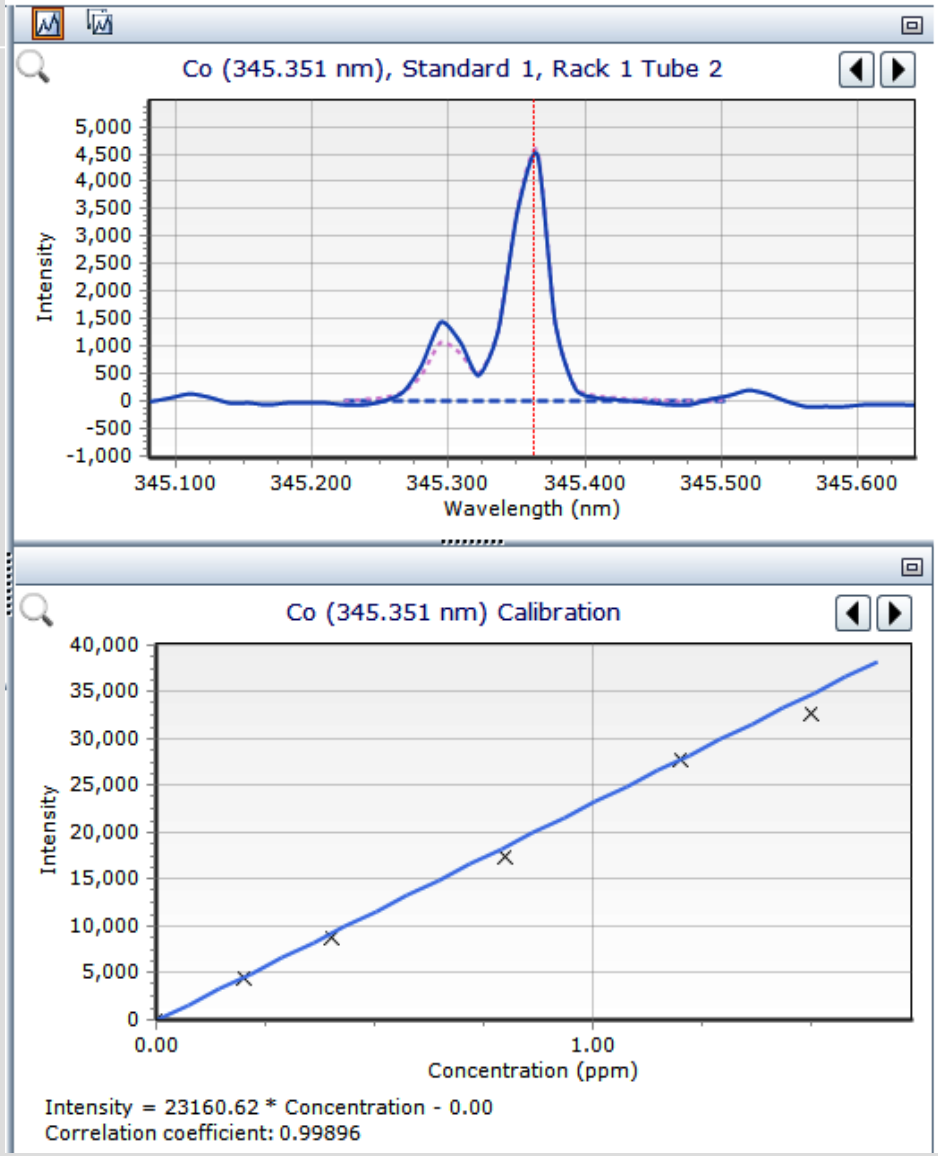


Wavelength (nm)	Ion	Intensity	Order
340.512	I	35116.9	1
345.351	I	60379.5	2
350.228	I	31459.7	3
240.725	I	23139.3	4
341.234	I	22363.3	5
350.631	I	21835.8	6
352.684	I	21444.5	7
347.404	I	19122.2	8
384.547	I	18996.1	9
356.937	I	18614.5	10
389.407	I	18081.1	11
352.981	I	17196.3	12

2. Optimization of instrumental parameters

- ✓ Viewing position and nebulizer pressure optimized prior to analysis using sample solutions (matrix effect included)
- ✓ Calibration fit: linear with blank subtraction
- ✓ Concentration intervals for Co:

  0 – 1.50 ppm



2. Optimization of instrumental parameters

Chromium

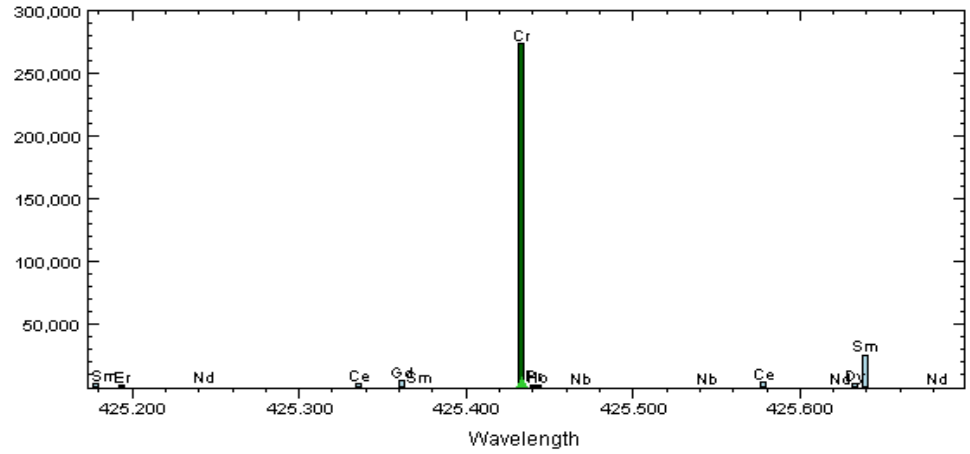
- ✓ Emission line selected: 425.433 nm
- ✓ Possible interferences are shown on graph below

Selected Element: Cr Recommended All

Add

Wavelength (nm)	Ion	Intensity	Order
425.433	I	273540.4	1
357.868	I	212267.6	2
427.480	I	210416.3	3
359.348	I	182831.0	4
428.972	I	153595.5	5
360.532	I	129968.1	6
520.844	I	101895.7	7
520.604	I	71082.6	8
520.452	I	43963.2	9
283.563	II	13330.7	10
540.979	I	12404.2	11
302.158	I	11201.1	12

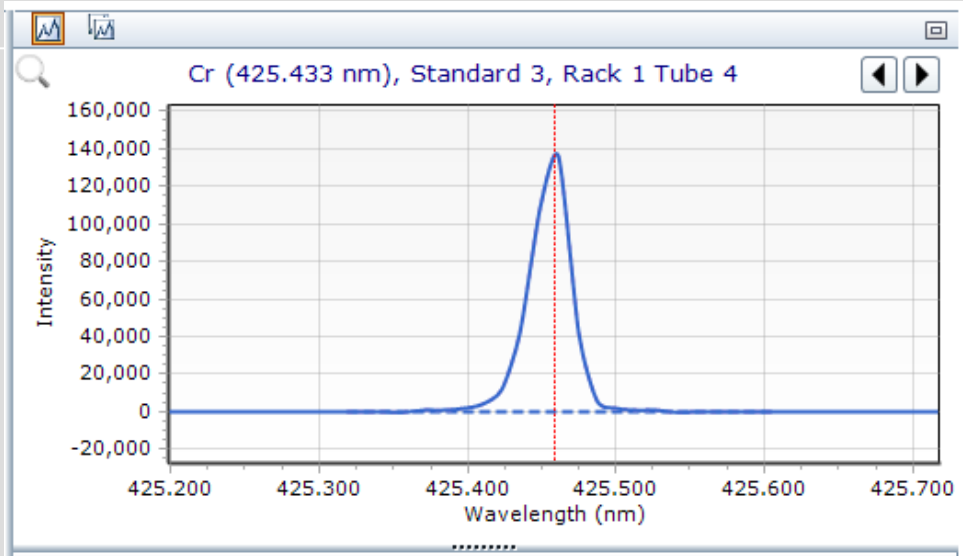
Possible interferences on Cr (425.433 nm)

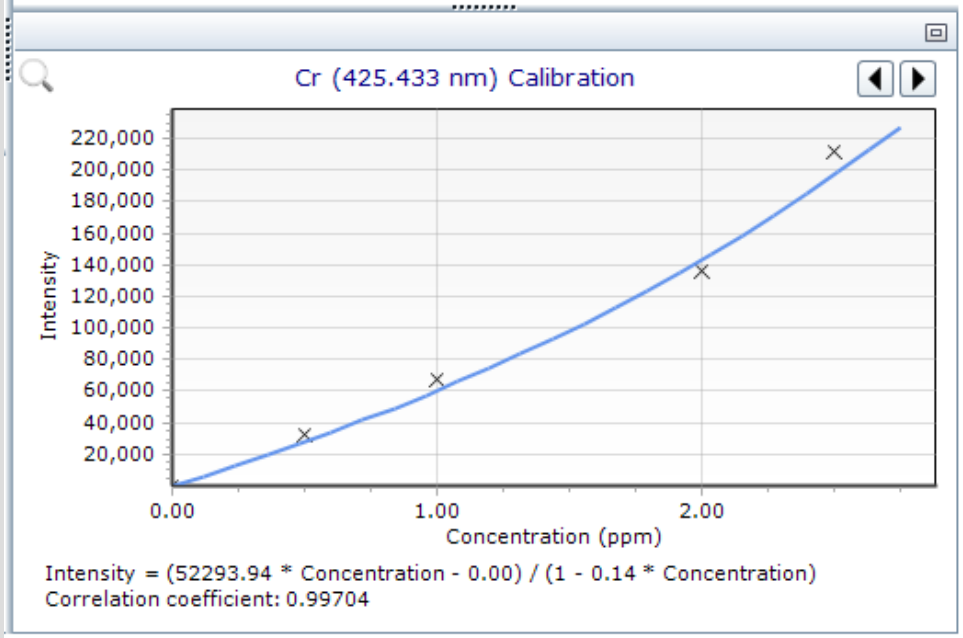


2. Optimization of instrumental parameters

- ✓ Viewing position and nebulizer pressure optimized prior to analysis using sample solutions (matrix effect included)
- ✓ Calibration fit: rational with blank subtraction
- ✓ Concentration intervals for Cr:

  0 – 2.50 ppm





2. Optimization of instrumental parameters

Copper

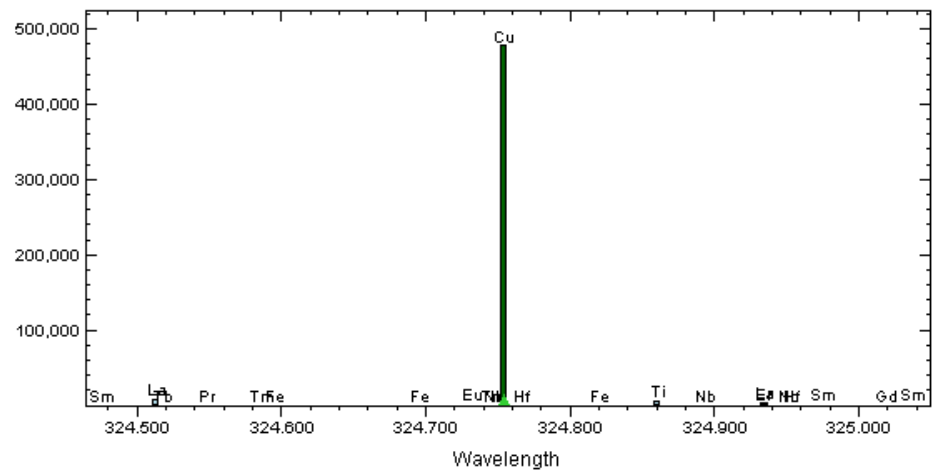
- ✓ Emission line selected: 324.754 nm
- ✓ Possible interferences are shown on graph below

Selected Element: Cu Recommended All

Add

Wavelength (nm)	Ion	Intensity	Order
324.754	I	477458.5	1
327.395	I	245232.7	2
510.554	I	7105.1	3
217.895	I	3732.7	4
223.008	I	3053.0	5
216.510	I	2413.5	6
218.172	I	2326.5	7
219.958	I	2090.8	8
521.820	I	2009.4	9
316.968	I	1758.9	10
578.213	I	1753.8	11
222.570	I	1751.3	12

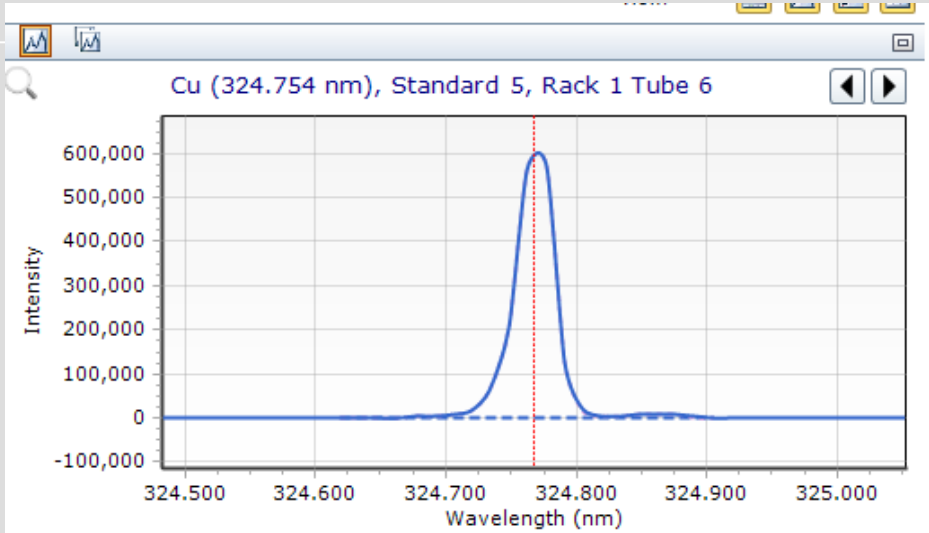
Possible interferences on Cu (324.754 nm)

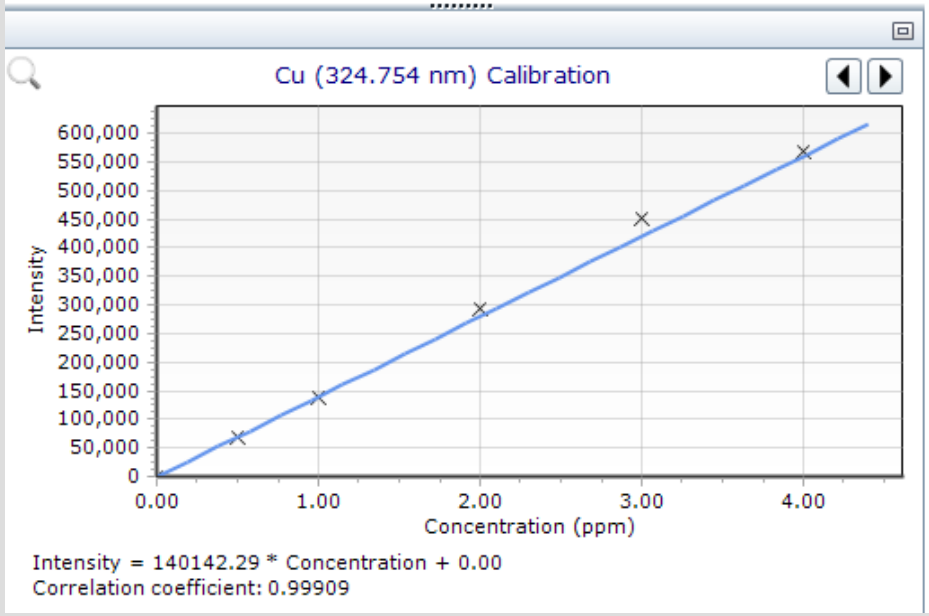


2. Optimization of instrumental parameters

- ✓ Viewing position and nebulizer pressure optimized prior to analysis using sample solutions (matrix effect included)
- ✓ Calibration fit: linear with blank subtraction
- ✓ Concentration intervals for Cu:

  0 – 4.0 ppm





2. Optimization of instrumental parameters

Iron

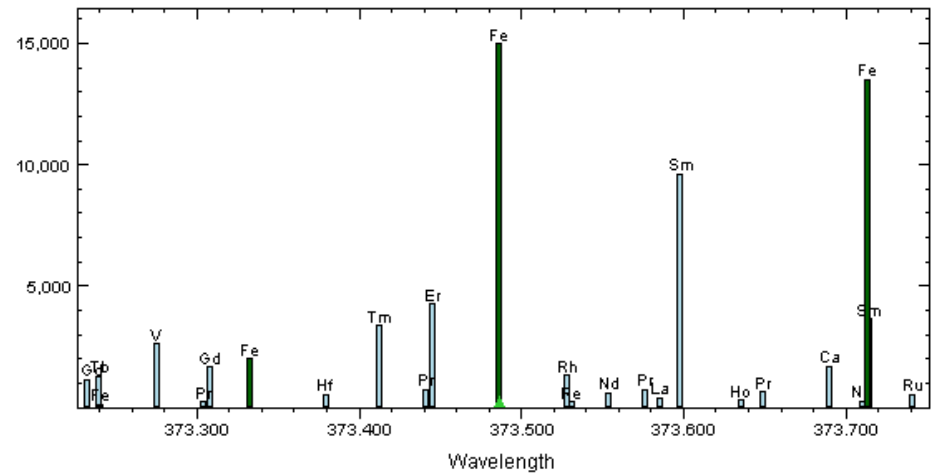
- ✓ Emission line selected: 373.486 nm
- ✓ Possible interferences are shown on graph below

Selected Element: Fe Recommended All

Add

Wavelength (nm)	Ion	Intensity	Order
371.993	I	16875.6	1
259.940	II	6819.3	2
373.486	I	14977.3	3
385.991	I	15401.6	4
373.713	I	13533.4	5
358.119	I	12912.6	6
302.064	I	12696.8	7
382.043	I	12088.8	8
374.949	I	10385.4	9
374.547	I	8789.9	10
438.354	I	7951.8	11
382.588	I	7763.9	12

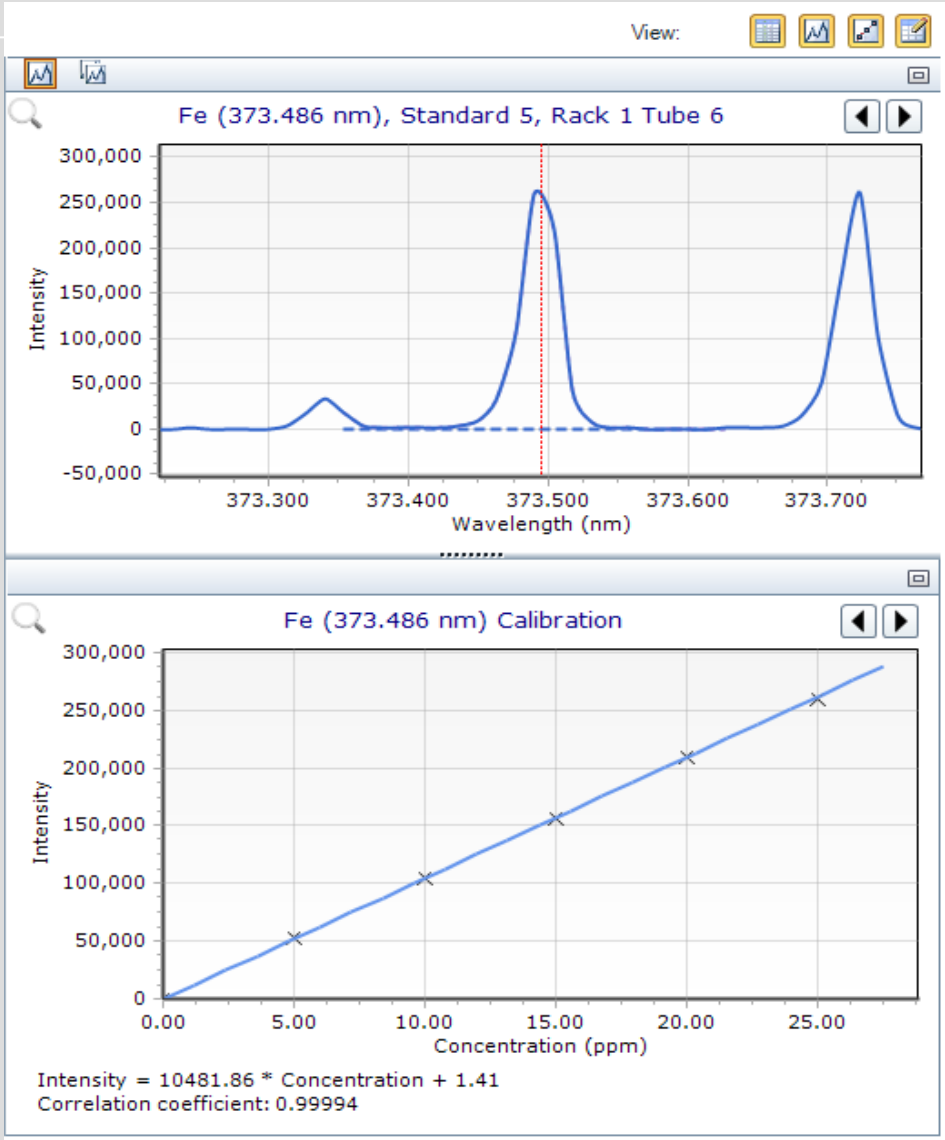
Possible interferences on Fe (373.486 nm)



2. Optimization of instrumental parameters

- ✓ Viewing position and nebulizer pressure optimized prior to analysis using sample solutions (matrix effect included)
- ✓ Calibration fit: linear with blank subtraction
- ✓ Concentration intervals for Fe:

  0 – 25 ppm



2. Optimization of instrumental parameters

Mangan

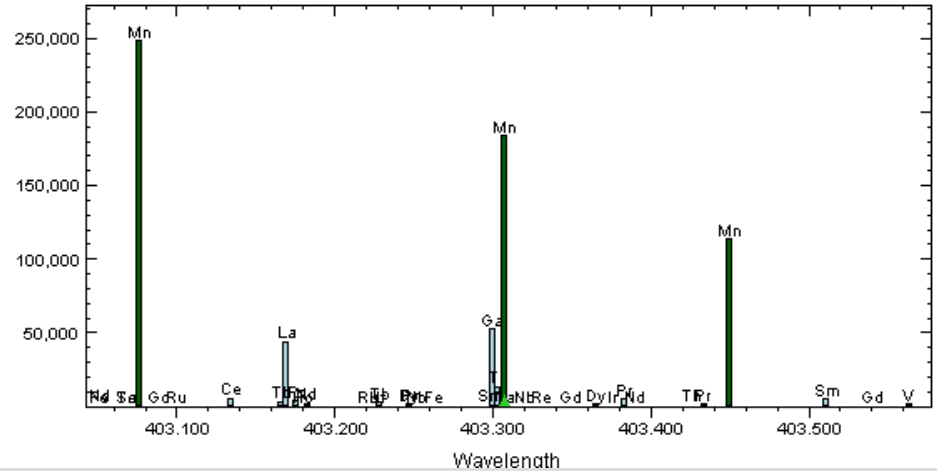
- ✓ Emission line selected: 403.307 nm
- ✓ Possible interferences are shown on graph below

Selected Element: Mn Recommended All

Add

Wavelength (nm)	Ion	Intensity	Order
403.076	I	248229.4	1
403.307	I	183876.2	2
257.610	II	140320.0	3
279.482	I	128520.7	4
259.372	II	118435.0	5
403.449	I	113710.2	6
279.827	I	104348.6	7
260.568	II	97027.9	8
280.108	I	68317.4	9
294.920	II	27932.4	10
293.931	II	18848.0	11
293.305	II	10719.1	12

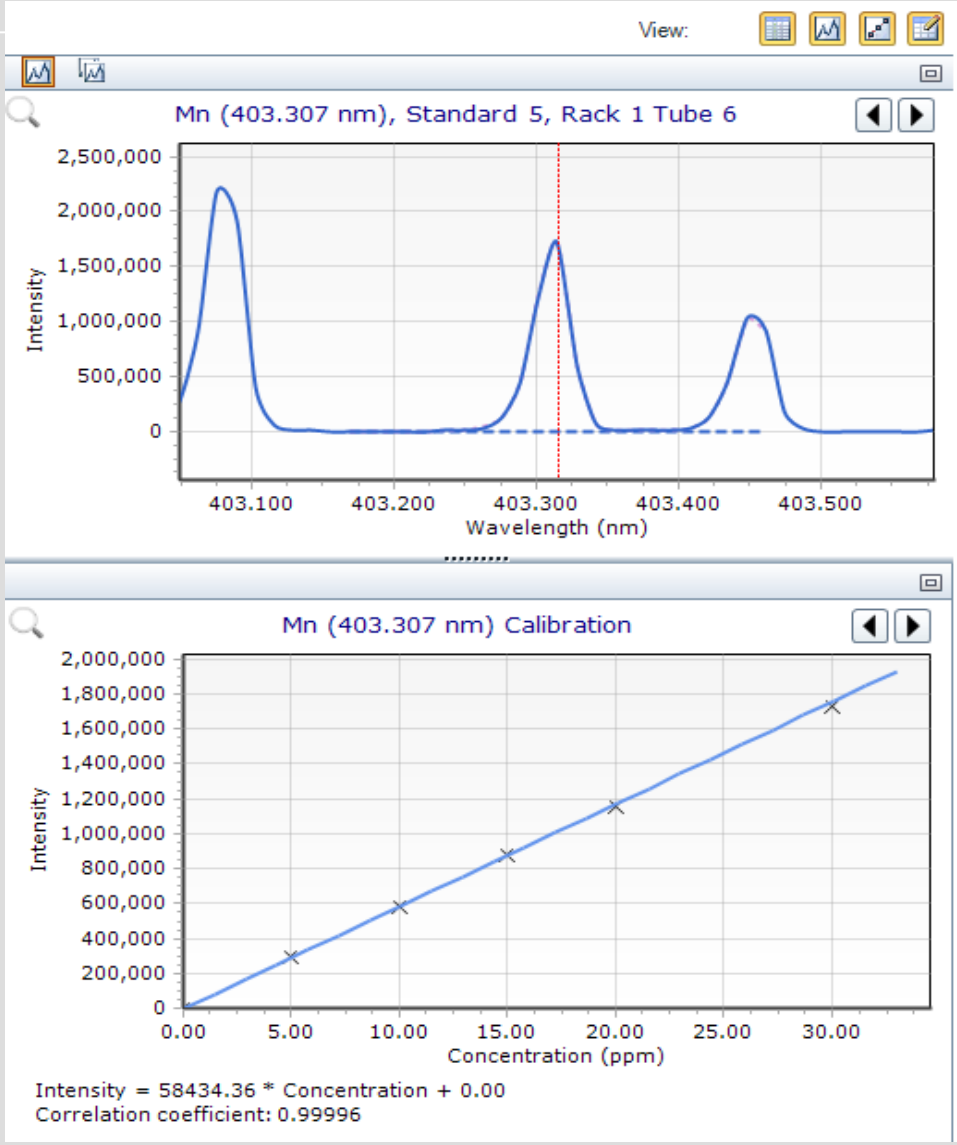
Possible interferences on Mn (403.307 nm)



2. Optimization of instrumental parameters

- ✓ Viewing position and nebulizer pressure optimized prior to analysis using sample solutions (matrix effect included)
- ✓ Calibration fit: linear with blank subtraction
- ✓ Concentration intervals for Mn:

  0 – 30 ppm



2. Optimization of instrumental parameters

Nickel

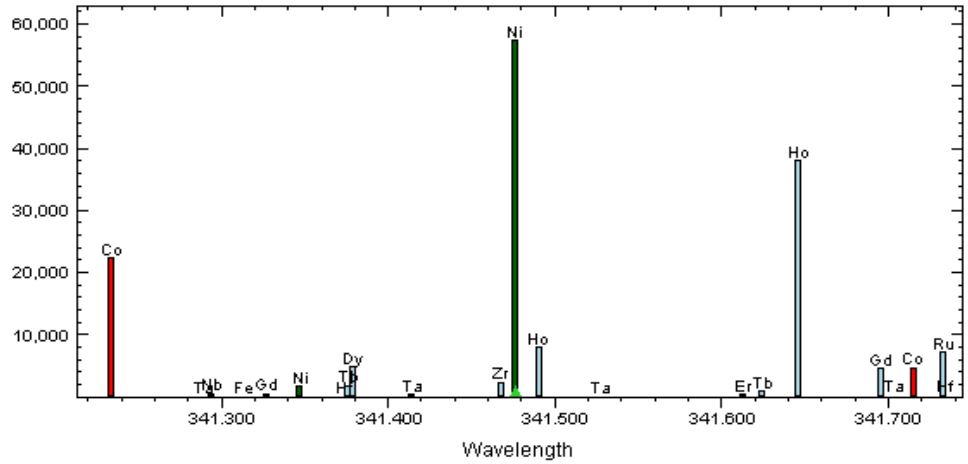
- ✓ Emission line selected: 341.476 nm
- ✓ Possible interferences are shown on graph below

Selected Element: Ni Recommended All

Add

Wavelength (nm)	Ion	Intensity	Order
352.454	I	77567.8	1
341.476	I	57306.4	2
361.939	I	37622.5	3
351.505	I	37432.8	4
349.295	I	29919.4	5
346.165	I	29807.0	6
305.082	I	28111.5	7
345.846	I	23693.7	8
300.248	I	23042.5	9
310.155	I	21877.3	10
344.626	I	20005.2	11
232.003	I	16363.9	12

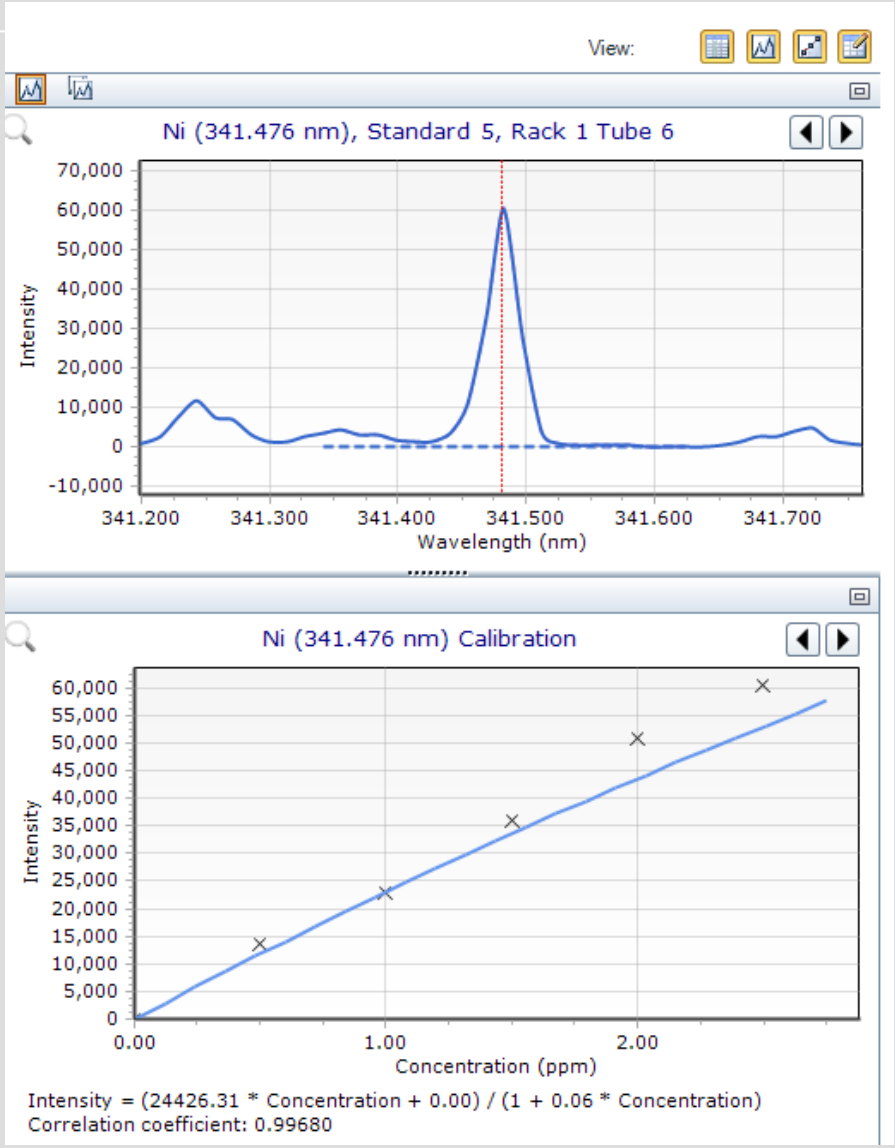
Possible interferences on Ni (341.476 nm)



2. Optimization of instrumental parameters

- ✓ Viewing position and nebulizer pressure optimized prior to analysis using sample solutions (matrix effect included)
- ✓ Calibration fit: rational with blank subtraction
- ✓ Concentration intervals for Ni:

  0 – 2.5 ppm



2. Optimization of instrumental parameters

Vanadium

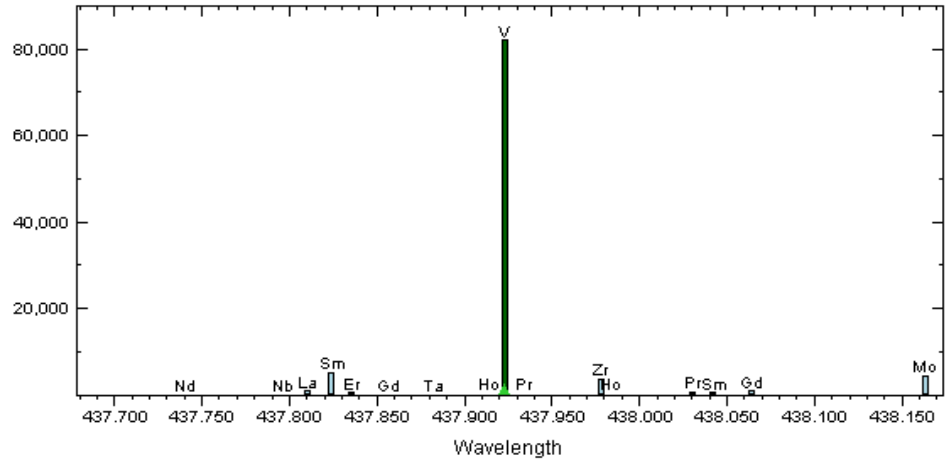
- ✓ Emission line selected: 437.923 nm
- ✓ Possible interferences are shown on graph below

Selected Element: V Recommended All

Add

Wavelength (nm)	Ion	Intensity	Order
309.311	II	94468.9	1
437.923	I	81952.6	2
310.229	II	74857.6	3
438.472	I	64163.4	4
311.070	II	51223.8	5
438.997	I	42627.0	6
318.397	I	38819.2	7
411.178	I	38197.5	8
311.837	II	37670.5	9
292.401	II	34901.5	10
312.528	II	30806.4	11
318.539	I	29410.7	12

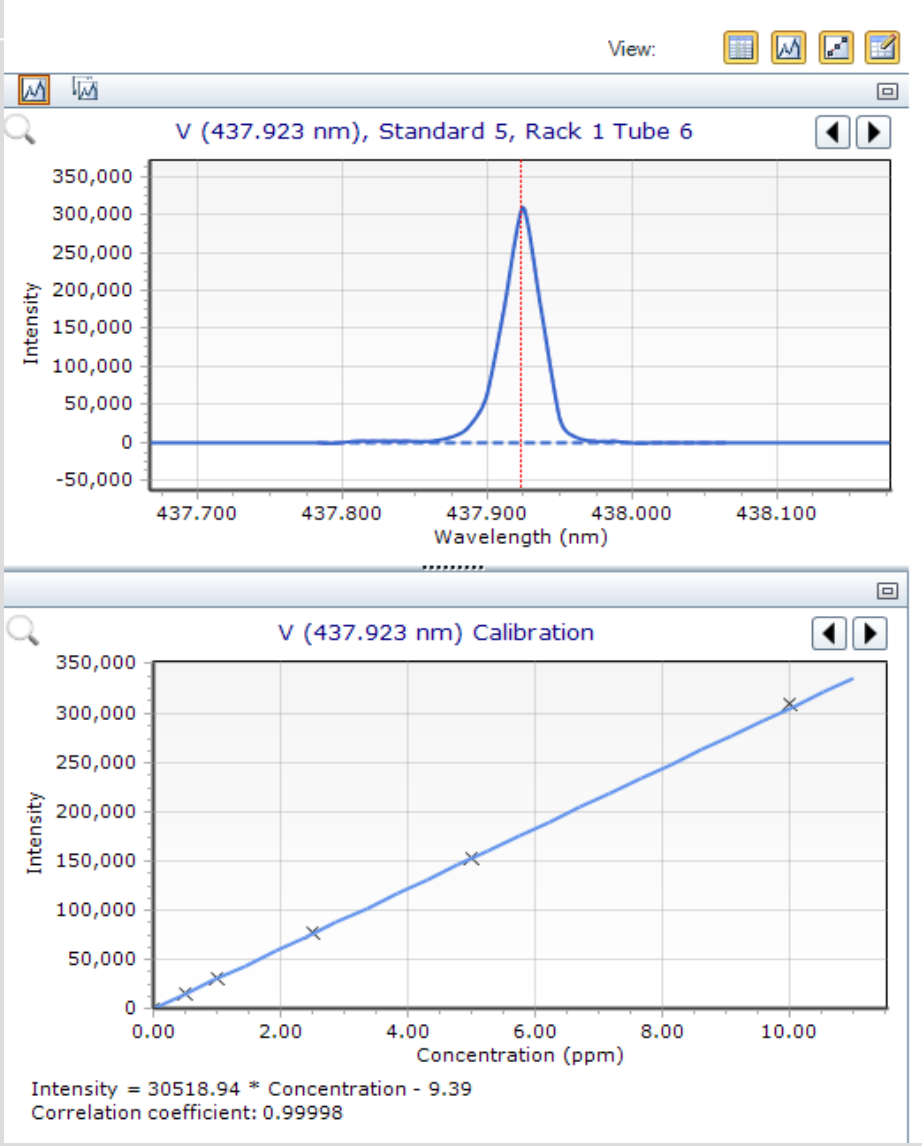
Possible interferences on V (437.923 nm)



2. Optimization of instrumental parameters

- ✓ Viewing position and nebulizer pressure optimized prior to analysis using sample solutions (matrix effect included)
- ✓ Calibration fit: linear with blank subtraction
- ✓ Concentration intervals for V:

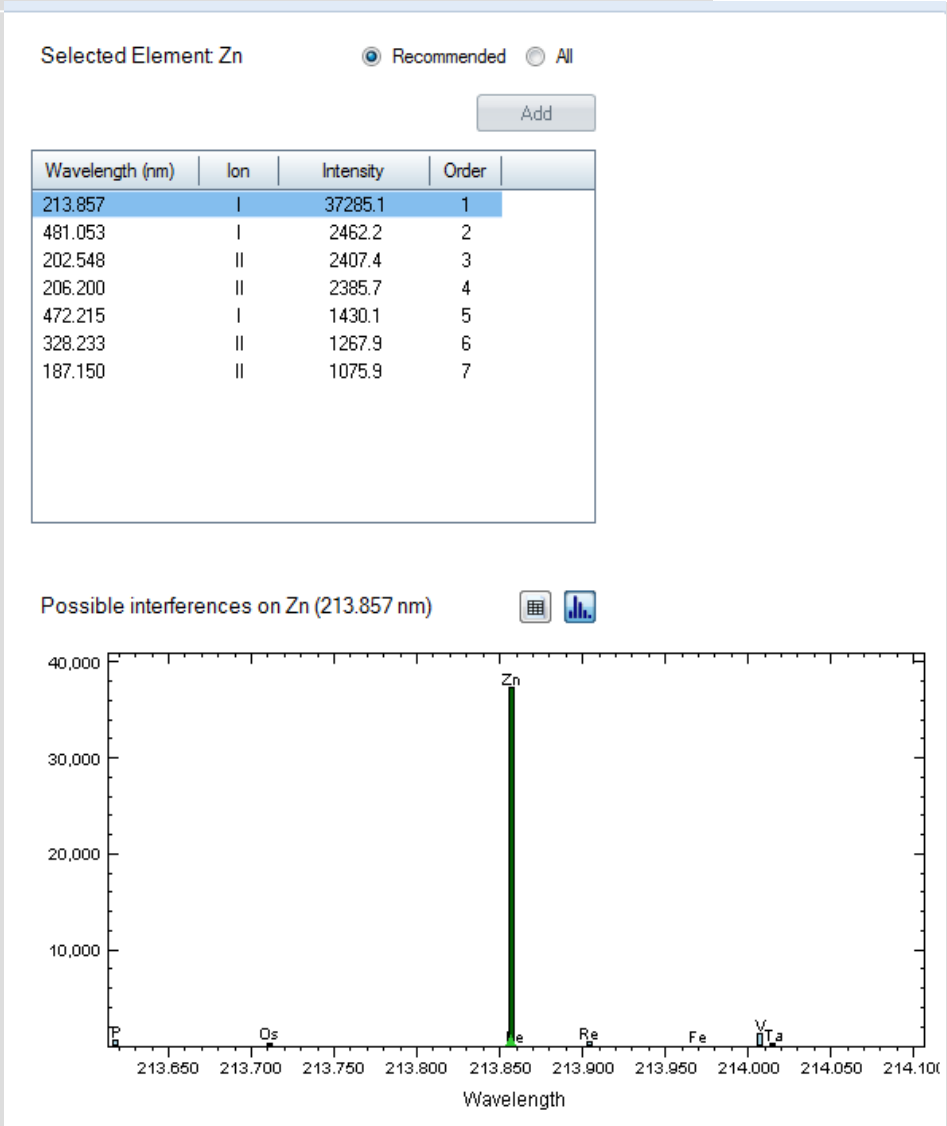
  0 – 10 ppm



2. Optimization of instrumental parameters

Zinc

- ✓ Emission line selected: 213.857 nm
- ✓ Possible interferences are shown on graph below

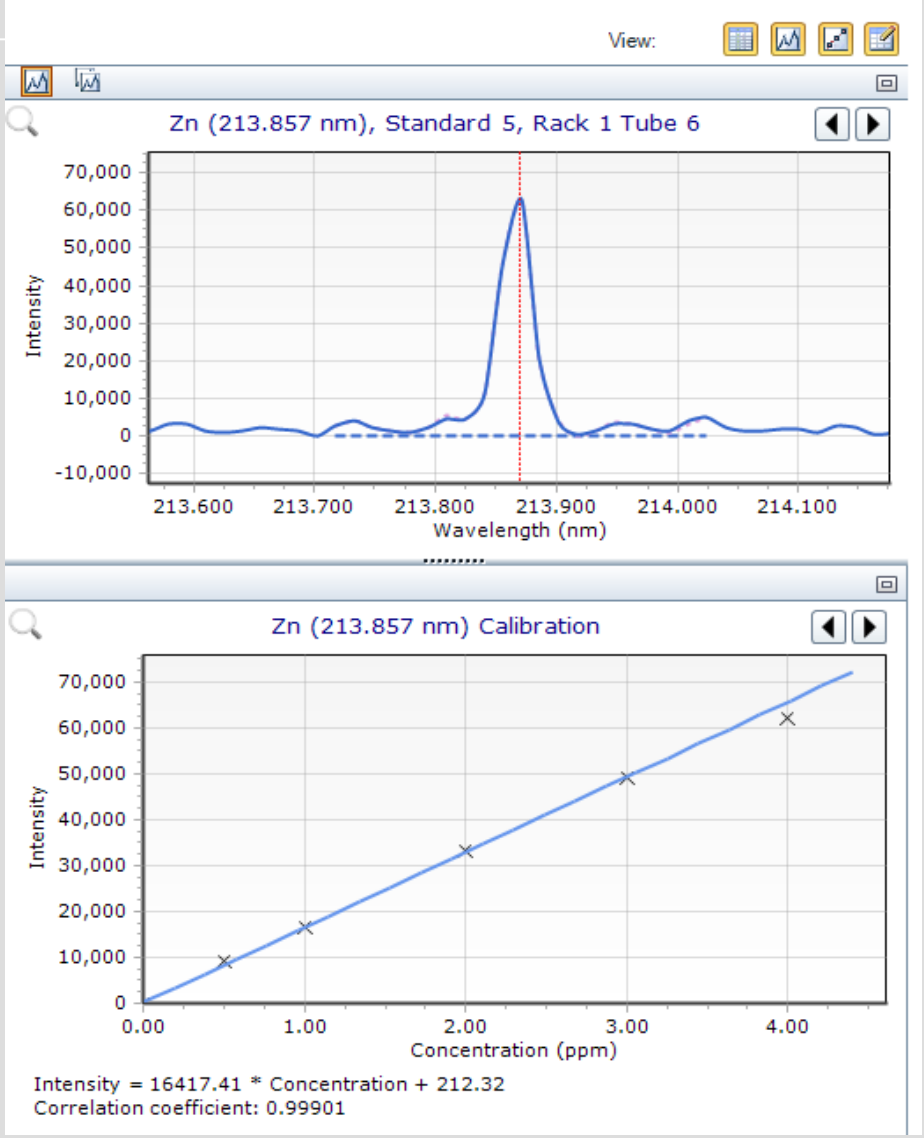


Wavelength (nm)	Ion	Intensity	Order
213.857	I	37285.1	1
481.053	I	2462.2	2
202.548	II	2407.4	3
206.200	II	2385.7	4
472.215	I	1430.1	5
328.233	II	1267.9	6
187.150	II	1075.9	7

2. Optimization of instrumental parameters

- ✓ Viewing position and nebulizer pressure optimized prior to analysis using sample solutions (matrix effect included)
- ✓ Calibration fit: linear with blank subtraction
- ✓ Concentration intervals for Zn:

  0 – 4 ppm



3. Results

- Nisan 2015 Soil reference material; TUBITAK UME
- 6 replicates for analytes

	Co	Cr	Cu	Fe	Mn	Ni	V	Zn
REFERENCE VALUE mg/kg	22.7	161	38.4	42650	778	109	140	86.9
MPAES VALUE mg/kg	24.75	153.02	36.41	40736	813.57	106.41	132.89	88.44
s	0.64	4.33	0.32	566	6.40	1.44	2.01	0.98
Δ	2.05	7.98	2.00	1913	35.57	2.59	7.11	1.54

4. Further steps

- Instrumental parameters for several elements need to be improved
- Reference values will be validated by comparison between laboratories using different detection techniques
- MWP-AES method analyses of selected analytes in soil will be compared with ICP-MS or IDMS

4. Further steps

- Measurement uncertainty budget to be obtained using empirical approach intra-laboratory validation and usage of comparison data for bias estimation

$$u_c = \sqrt{{u_{prec}}^2 + {u_{bias}}^2}$$

- The main sources of uncertainty:

✓ Purity of chemicals

✓ Plasma stability

4. Further steps

- Usage of high purity chemicals minimises the occurrence of spectral interferences
- Uncertainty from instrumental sources controlled by QC samples

Questions?

Thank you for your attention!

More about IMBIH at:

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