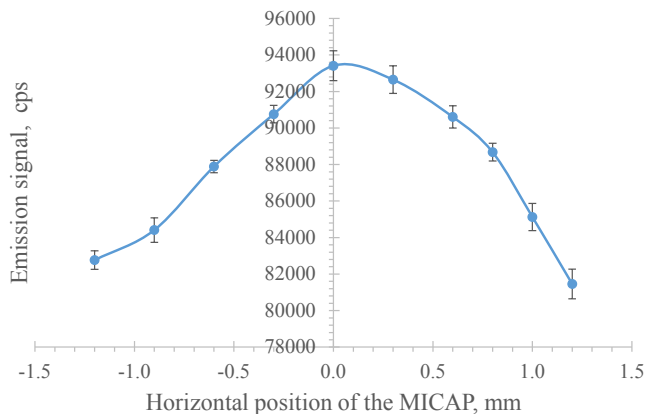
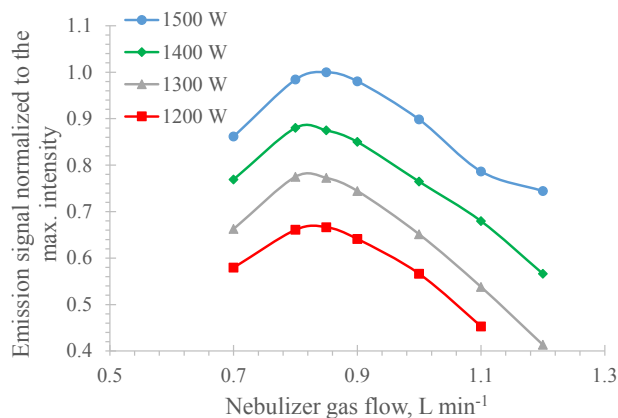


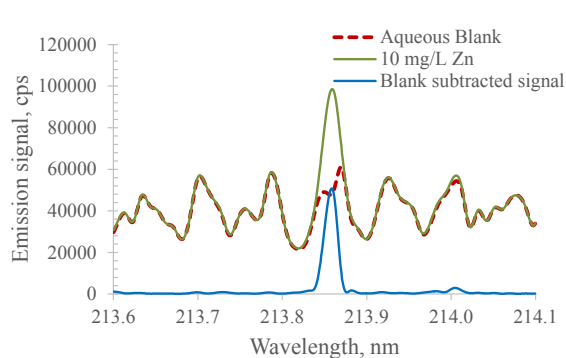
Electronic supplementary information



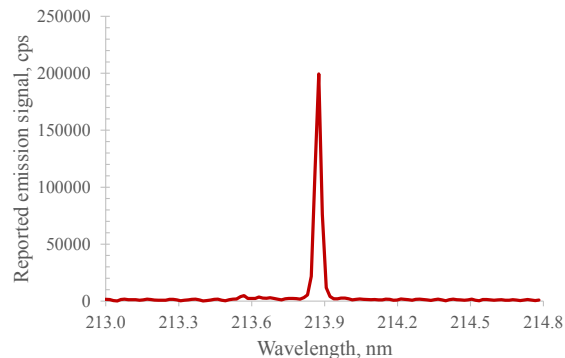
ESI Figure 1. Mn (II) 257.611 nm emission line signal as a function of the horizontal position of the MICAP with respect to the spectrometer (n=5; 1 mg L⁻¹ Mn; 1000 W)



ESI Figure 2. Normalized Mn (II) 257.611 nm emission line signal (1 mg L⁻¹ Mn) as a function of nebulizer gas flow and microwave power; SDs are not plotted for clarity but all RSD's < 2% (n=5); intensity data have been normalized to the maximum measured signal (0.85 L min⁻¹ and 1500 W)

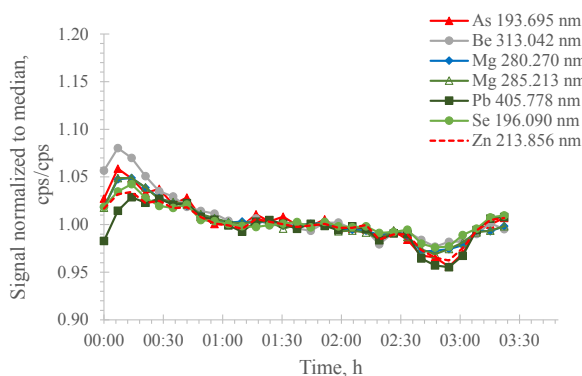


a)

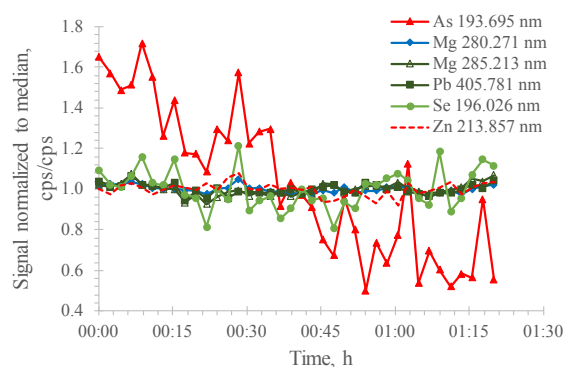


b)

ESI Figure 3. Spectrum of 10 mg L⁻¹ Zn at 213.856 nm recorded with a) MICAP and b) Hammer cavity MIP-OES. The well isolated emission line of Zn in spectrum b) clearly shows the effectiveness of the mathematical background subtraction. Note, that due to the different optical resolution of the used spectrometers (18 pm for MICAP; 30 pm for Hammer cavity MIP-OES) the wavelength interval shown in a) is smaller than in b).



a)



b)

ESI Figure 4. Variation of the emission signals of selected lines of As, Be (only for MICAP), Mg, Pb, Se and Zn determined using a) MICAP and b) Hammer cavity MIP-OES. The signals were normalized to the respective median signal of each line; SDs not plotted for clarity but RSD's < 2% (n=5); 10 mg L⁻¹ of each element. Note the different scaling of the y axis

ESI Table 1. MICAP and ICP-OES: Limits of detection (LOD; calculated by blank method) and limits of quantification (LOQ; calculated by calibration method) of selected emission lines determined by MICAP (nitrogen as plasma gas) and ICP-OES (argon as plasma gas); lines were no emission signal above 3 σ of the background was obtained at the highest calibration standard are marked with "no signal"

Element, emission line	Total line energy, eV	MICAP operated with N ₂		MICAP operated with air		ICP-OES	
		LOD, $\mu\text{g L}^{-1}$	LOQ, $\mu\text{g L}^{-1}$	LOD, $\mu\text{g L}^{-1}$	LOQ, $\mu\text{g L}^{-1}$	LOD, $\mu\text{g L}^{-1}$	LOQ, $\mu\text{g L}^{-1}$
Ag (I) 328.068 nm	3.8	4	8	1	6	0.8	4
Ag (I) 338.289 nm	3.7	8	10	2	6	3	5
Al (II) 167.078 nm	13.4	50	70	no signal	no signal	0.6	11
Al (I) 396.152 nm	3.1	1	9	1	5	2	6
As (I) 189.042 nm	6.6	300	400	no signal	no signal	6	14
As (I) 193.759 nm	6.4	200	300	no signal	no signal	7	14
As (I) 228.812 nm	6.8	100	200	no signal	no signal	1	4
B (I) 249.677 nm	5.0	10	30	no signal	no signal	4	24
B (I) 249.773 nm	5.0	8	10	200	300	0.8	8
Ba (II) 233.527 nm	11.2	10	20	200	1000	0.4	5
Ba (II) 455.404 nm	7.9	0.1	2	0.1	2	0.05	3
Be (I) 234.861 nm	5.3	1	2	10	10	0.1	4
Be (II) 313.042 nm	13.3	2	2	80	90	0.2	3
Bi (II) 190.241 nm	15.9	no signal	no signal	no signal	no signal	10	20
Bi (I) 222.825 nm	5.6	400	500	no signal	no signal	20	30
Bi (I) 223.061 nm	5.6	100	200	700	800	8	10
Ca (II) 317.933 nm	13.2	20	20	200	600	1	6
Ca (II) 393.366 nm	9.3	0.2	2	0.1	3	0.5	3
Ca (II) 396.847 nm	9.2	0.2	2	0.1	2	0.5	3
Cd (II) 214.438 nm	14.8	40	60	no signal	no signal	0.5	4
Cd (II) 226.502 nm	14.5	30	50	no signal	no signal	0.8	4
Cd (I) 228.802 nm	5.4	10	20	no signal	no signal	1	4
Co (II) 228.616 nm	13.7	30	60	no signal	no signal	1	5
Co (II) 238.892 nm	13.5	20	30	no signal	no signal	0.8	5
Cr (II) 205.552 nm	12.8	80	90	no signal	no signal	0.8	4
Cr (II) 267.716 nm	12.9	30	40	no signal	no signal	0.5	4
Cr (II) 283.563 nm	12.7	20	30	no signal	no signal	4	9
Cu (I) 324.754 nm	3.8	4	5	6	9	2	6
Cu (I) 327.396 nm	3.8	7	10	7	9	2	5
Fe (II) 238.204 nm	13.1	20	30	no signal	no signal	0.7	4
Fe (II) 239.562 nm	13.1	10	20	no signal	no signal	0.5	4
Fe (II) 259.941 nm	12.7	4	10	no signal	no signal	0.4	4

Element, emission line	Total line energy, eV	MICAP operated with N ₂		MICAP operated with air		ICP-OES	
		LOD, $\mu\text{g L}^{-1}$	LOQ, $\mu\text{g L}^{-1}$	LOD, $\mu\text{g L}^{-1}$	LOQ, $\mu\text{g L}^{-1}$	LOD, $\mu\text{g L}^{-1}$	LOQ, $\mu\text{g L}^{-1}$
K (I) 766.491 nm	1.6	1	8	no signal	no signal	6	10
Li (I) 670.780 nm	1.8	0.1	3	0.02	2	0.1	7
Mg (II) 280.27 nm	12.1	0.3	3	10	20	0.08	4
Mg (I) 285.213 nm	4.3	0.6	3	2	3	0.6	6
Mn (II) 257.611 nm	12.2	3	5	100	400	0.1	4
Mn (II) 259.373 nm	12.2	1	3	40	50	0.09	1
Mn (I) 403.076 nm	3.1	2	9	4	5	3	7
Mo (II) 202.030 nm	13.2	no signal	no signal	no signal	no signal	2	5
Mo (II) 281.615 nm	12.8	30	40	no signal	no signal	4	7
Mo (I) 379.825 nm	3.3	20	30	no signal	no signal	6	10
Na (I) 588.995 nm	2.1	5	8	1	5	3	10
Na (I) 589.592 nm	2.1	5	7	2	5	2	10
Ni (II) 231.604 nm	14.0	100	200	no signal	no signal	1	5
Ni (I) 232.003 nm	5.3	60	70	no signal	no signal	4	7
Ni (I) 352.454 nm	3.5	60	100	no signal	no signal	5	9
P (I) 177.495 nm	7.0	200	1000	no signal	no signal	10	50
P (I) 178.287 nm	7.0	300	900	no signal	no signal	20	50
P (I) 213.618 nm	7.2	400	600	no signal	no signal	9	40
Pb (II) 220.353 nm	14.8	no signal	no signal	no signal	no signal	3	9
Pb (I) 405.778 nm	4.4	20	40	20	40	20	30
S (I) 180.731 nm	6.9	1000	2000	no signal	no signal	60	70
S (I) 182.034 nm	6.9	1000	4000	no signal	no signal	50	100
Sb (I) 206.833 nm	6.0	300	600	no signal	no signal	7	10
Sb (I) 217.581 nm	5.7	200	300	no signal	no signal	9	10
Sb (I) 231.147 nm	5.4	100	200	200	600	1	5
Se (I) 196.09 nm	6.3	500	600	no signal	no signal	10	20
Se (I) 203.985 nm	6.3	800	1000	no signal	no signal	20	30
Sr (II) 407.771 nm	10.4	0.05	2	0.1	2	0.02	3
Sr (II) 421.552 nm	10.3	0.07	3	0.2	3	0.03	3
Ti (II) 307.864 nm	10.9	6	10	70	80	4	6
Ti (II) 334.941 nm	10.6	4	7	6	8	0.2	3
Ti (II) 336.121 nm	10.5	20	30	20	30	10	20
Tl (II) 190.864 nm	12.6	no signal	no signal	no signal	no signal	8	10
Tl (I) 276.787 nm	4.5	50	60	no signal	no signal	10	20
V (II) 292.464 nm	11.4	20	30	no signal	no signal	2	4
V (II) 309.311 nm	11.1	7	10	30	40	0.4	3
V (II) 311.071 nm	11.1	20	20	20	40	1	4
Zn (II) 202.548 nm	15.5	70	60	no signal	no signal	0.2	8
Zn (II) 206.191 nm	15.4	200	300	no signal	no signal	0.5	10
Zn (I) 213.856 nm	5.8	20	30	no signal	no signal	0.9	8