Effects of argon on the analytical properties of a microwave-sustained, inductively coupled, atmospheric-pressure plasma

- Electronic supplementary information -

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Table S1. Fe (I) lines used for the determination of T_{exc} by Boltzmann plot method; Fundamental constants where taken from literature [25, 26]

Wavelength, nm	Excitation Energy, eV	Transition probability for spontaneous emission, s^{-1}	Statistical weight
368.411	6.09	$3.40 \cdot 10^{7}$	7
370.109	6.35	$4.90 \cdot 10^{7}$	9
370.446	6.04	$1.40 \cdot 10^{7}$	9
370.557	3.40	$3.22 \cdot 10^{6}$	7
370.925	4.26	$1.56 \cdot 10^{7}$	7
371.993	3.33	$1.63 \cdot 10^{7}$	11
372.256	3.42	$4.97 \cdot 10^{6}$	5
372.438	5.61	$1.30 \cdot 10^{7}$	7
372.762	4.28	$2.25 \cdot 10^{7}$	5
373.240	5.52	$2.00 \cdot 10^{7}$	5
373.332	3.43	$6.50 \cdot 10^{6}$	3
373.486	4.18	$9.02 \cdot 10^{7}$	11
373.713	3.37	$1.42 \cdot 10^{7}$	9
373.831	6.58	$3.80 \cdot 10^{7}$	13
374.826	3.42	$9.15 \cdot 10^{6}$	5
374.949	4.22	$7.64 \cdot 10^{7}$	9
375.361	5.48	$1.10 \cdot 10^{7}$	5
375.823	4.26	$6.34 \cdot 10^{7}$	7
376.005	5.70	$5.70 \cdot 10^{6}$	15
376.053	5.52	$5.70 \cdot 10^{6}$	5
376.379	4.28	$5.44 \cdot 10^{7}$	5
376.554	6.53	$9.90 \cdot 10^{7}$	15

Table S2. Effect of plasma gas composition on the emission line intensity of several atomic and ionic lines. All emission line data has been normalized to the respective emission intensity in a pure (100 %) nitrogen plasma; RSDs < 2% for all lines and conditions with n=5. The fraction (v/v) of argon in each of the three gas flows is given above each column: OG - outer gas flow; IG -intermediate gas flow; NG - nebulizer gas flow, ND – not determined. Color coding: blue – signal suppression, red – signal enhancement

Element, emission line	Total line energy, eV	Relative line intensity, %	Emission line intensity normalized to a pure nitrogen plasma										
			OG: 0% IG: 0% NG: 44%	OG: 0% IG: 0% NG: 100%	OG: 0% IG:33% NG: 0%	OG: 0% IG: 67% NG: 0%	OG: 0% IG:100% NG: 0%	OG: 0% IG:100% NG: 100%	OG: 14% IG:100% NG: 100%	OG: 29% IG:100% NG: 100%	OG: 43% IG:100% NG: 100%	OG: 57% IG:100% NG: 100%	OG: 71% IG:100% NG: 100%
Al (I) 396.152 nm	3.1	100	0.41	0.73	0.99	0.99	0.98	1.12	1.12	1.08	1.01	0.91	0.76
As (I) 189.042 nm	6.6	100	0.38	0.66	1.00	1.00	0.99	1.35	1.29	1.23	1.18	1.07	0.90
As (I) 193.759 nm	6.4	74	0.37	0.65	0.99	0.98	0.96	1.32	1.32	1.28	1.21	1.11	0.94
B (I) 249.677 nm	5.0	50	0.36	0.59	1.01	1.00	1.00	0.99	0.97	0.92	0.87	0.83	0.75
B (I) 249.773 nm	5.0	100	0.36	0.58	1.01	1.00	1.00	1.00	0.97	0.91	0.87	0.83	0.74
Be (I) 234.861 nm	5.3	53	0.32	0.50	1.01	1.00	1.00	0.85	0.80	0.73	0.67	0.59	0.48
Be (II) 313.042 nm	13.3	100	0.47	0.78	1.00	1.00	0.98	1.34	1.29	1.25	1.24	1.22	1.12
Bi (I) 222.825 nm	5.6	32	0.16	0.33	0.99	0.99	1.01	0.92	0.93	0.93	0.88	0.80	0.74
Bi (I) 223.061 nm	5.6	100	0.17	0.36	1.01	1.00	1.00	0.94	0.95	0.91	0.87	0.81	0.71
Ca (II) 393.366 nm	9.3	100	0.17	0.37	1.00	1.00	0.99	1.05	1.12	1.06	1.01	0.93	0.80
Ca (II) 396.847 nm	9.2	49	0.17	0.35	1.01	1.00	0.99	1.04	1.05	1.00	0.95	0.89	0.75
Cd (II) 214.438 nm	14.8	28	0.21	0.42	0.98	0.97	0.97	1.29	1.25	1.22	1.15	1.04	0.85
Cd (II) 226.502 nm	14.5	22	0.22	0.44	0.99	0.97	0.98	1.34	1.34	1.32	1.29	1.24	1.11
Cd (I) 228.802 nm	5.4	100	0.22	0.38	0.99	0.99	0.98	0.92	0.89	0.84	0.77	0.68	0.56
Co (II) 228.616 nm	13.7	87	0.18	0.40	0.98	0.99	0.99	1.12	1.12	1.12	1.10	1.08	0.99
Co (II) 238.892 nm	13.5	76	0.19	0.41	0.98	0.99	0.98	1.14	1.14	1.17	1.17	1.16	1.09
Co (I) 344.364 nm	4.1	100	0.19	0.40	0.98	1.00	0.97	0.88	0.88	0.82	0.84	0.78	0.75
Cr (II) 205.552 nm	12.8	35	0.16	0.34	0.99	0.98	0.96	1.01	1.05	1.02	0.97	0.89	0.75
Cr (II) 267.716 nm	12.9	60	0.15	0.34	1.00	1.00	0.99	1.07	1.09	1.07	1.03	0.97	0.86
Cr (II) 283.563 nm	12.7	100	0.15	0.34	0.99	0.99	0.98	1.04	1.05	1.02	0.99	0.93	0.81
Cu (I) 324.754 nm	3.8	100	0.23	0.44	1.01	1.00	1.00	0.90	0.89	0.86	0.83	0.81	0.75
Cu (I) 327.396 nm	3.8	45	0.24	0.46	1.00	1.00	0.99	0.90	0.93	0.91	0.89	0.86	0.80
Fe (II) 238.204 nm	13.1	70	0.17	0.33	0.98	0.96	0.93	0.99	0.97	0.96	0.94	0.89	0.78
Fe (II) 239.562 nm	13.1	48	0.16	0.34	0.98	0.95	0.92	0.98	0.96	0.97	0.94	0.90	0.79
Fe (II) 259.941 nm	12.7	100	0.16	0.33	0.98	0.96	0.93	0.97	0.94	0.94	0.94	0.92	0.83
K (I) 766.491 nm	1.6	100	1.08	1.16	0.93	0.94	1.03	1.57	1.62	1.80	1.99	2.06	2.02
Li (I) 670.78 nm	1.8	100	0.66	1.03	1.01	1.01	0.97	1.38	1.45	1.37	1.28	1.17	0.99
Mg (II) 280.270 nm	12.1	100	0.17	0.31	1.00	0.99	0.99	0.77	0.76	0.71	0.67	0.60	0.50
Mg (I) 285.213 nm	4.3	64	0.29	0.49	1.01	1.00	1.00	0.81	0.80	0.73	0.65	0.55	0.41
Mn (II) 257.611 nm	12.2	100	0.15	0.31	1.00	0.99	0.98	0.92	0.93	0.88	0.85	0.78	0.68
Mn (II) 259.373 nm	12.2	83	0.15	0.31	1.00	0.99	0.98	0.92	0.92	0.88	0.85	0.79	0.69
Mn (I) 403.076 nm	3.1	28	0.34	0.69	1.00	1.01	1.00	1.10	1.16	1.11	1.05	0.97	0.87

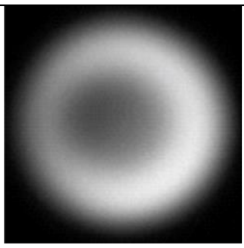
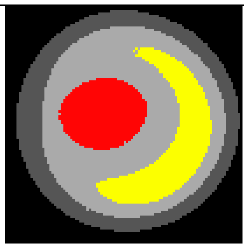
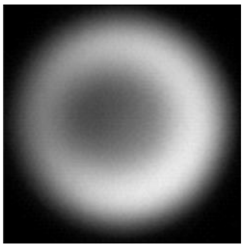
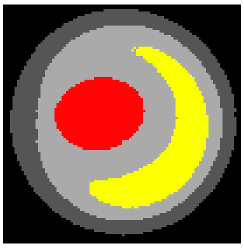
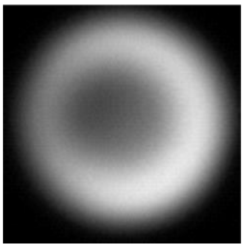
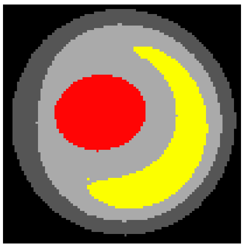
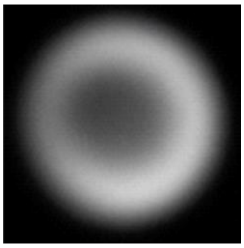
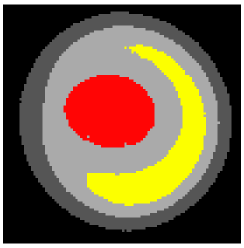
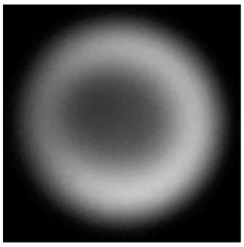
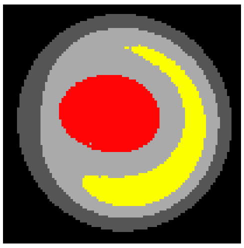
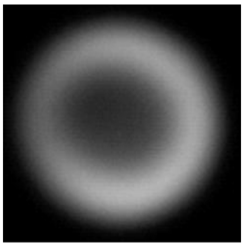
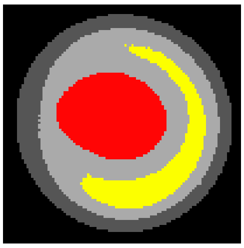
Element, emission line	Total line energy, eV	Relative line intensity, %	Emission line intensity normalized to a pure nitrogen plasma										
			OG: 0% IG: 0% NG: 44%	OG: 0% IG: 0% NG: 100%	OG: 0% IG:33% NG: 0%	OG: 0% IG: 67% NG: 0%	OG: 0% IG:100% NG: 0%	OG: 0% IG:100% NG: 100%	OG: 14% IG:100% NG: 100%	OG: 29% IG:100% NG: 100%	OG: 43% IG:100% NG: 100%	OG: 57% IG:100% NG: 100%	OG: 71% IG:100% NG: 100%
Mo (II) 281.615 nm	13.2	40	0.13	0.31	0.98	0.99	0.99	1.10	1.12	1.11	1.10	1.06	0.98
Mo (II) 281.615 nm	3.3	100	0.25	0.54	0.99	0.99	0.99	0.96	0.98	0.96	0.91	0.84	0.76
Na (I) 588.995 nm	2.1	100	0.99	1.34	1.03	1.03	1.01	1.57	1.66	1.66	1.63	1.48	1.27
Na (I) 589.592 nm	2.1	52	0.99	1.32	1.02	1.03	1.00	1.56	1.63	1.63	1.58	1.44	1.22
Ni (II) 231.604 nm	14	10	0.19	0.41	0.96	0.94	0.93	1.17	1.25	1.29	1.26	1.24	1.16
Ni (I) 232.003 nm	5.3	20	0.21	0.38	1.00	0.99	0.99	0.87	0.88	0.84	0.81	0.74	0.65
Ni (I) 352.454 nm	3.5	100	0.09	0.45	0.95	0.94	0.98	0.82	0.93	0.93	0.83	0.91	0.87
P (I) 177.495 nm	7.0	58	0.60	0.98	1.01	1.01	1.00	1.58	ND	ND	ND	ND	ND
P (I) 178.287 nm	7.0	40	0.59	0.96	1.00	1.01	1.00	1.57	ND	ND	ND	ND	ND
P (I) 213.618 nm	7.2	100	0.59	0.94	0.99	0.99	0.97	1.63	ND	ND	ND	ND	ND
Pb (II) 220.353 nm	14.8	14	0.12	0.32	0.95	0.97	0.95	1.24	1.24	1.17	1.12	1.00	0.85
Pb (I) 405.778 nm	4.4	100	0.25	0.52	0.99	1.00	0.99	1.00	1.02	0.97	0.91	0.81	0.69
S (I) 180.731 nm	6.9	100	0.64	1.01	0.99	1.00	0.97	1.56	ND	ND	ND	ND	ND
S (I) 182.034 nm	6.9	60	0.66	1.02	0.99	1.00	0.99	1.59	ND	ND	ND	ND	ND
Sb (I) 206.833 nm	6.0	67	0.20	0.38	1.06	1.04	1.07	1.10	0.93	0.94	0.91	0.85	0.74
Sb (I) 217.581 nm	5.7	82	0.16	0.34	1.00	1.00	0.99	0.99	0.96	0.95	0.94	0.85	0.79
Sb (I) 231.147 nm	5.4	100	0.17	0.35	1.00	0.98	0.94	0.98	1.02	0.99	0.95	0.90	0.82
Sc (II) 361.384 nm	10	100	0.14	0.29	1.01	1.01	1.00	0.88	0.88	0.85	0.81	0.74	0.64
Sc (II) 424.683 nm	9.8	38	0.14	0.30	1.01	1.00	1.01	0.87	0.88	0.85	0.82	0.77	0.67
Se (I) 196.09 nm	6.3	100	0.43	0.74	0.99	0.98	0.98	1.41	1.35	1.30	1.20	1.09	0.91
Se (I) 203.985 nm	6.3	72	0.44	0.75	0.97	0.98	0.99	1.42	1.42	1.32	1.22	1.10	0.92
Sr (II) 407.771 nm	10.4	100	0.17	0.35	1.00	1.00	0.99	1.10	1.16	1.12	1.05	0.94	0.80
Sr (II) 421.552 nm	10.3	51	0.16	0.34	1.01	1.02	1.01	1.10	1.16	1.13	1.08	0.97	0.83
Ti (II) 307.864 nm	10.9	22	0.13	0.27	0.99	0.99	0.98	0.87	0.88	0.85	0.81	0.75	0.65
Ti (II) 334.941 nm	10.6	100	0.13	0.30	1.00	1.00	1.00	0.90	0.93	0.90	0.88	0.83	0.75
Ti (II) 336.121 nm	10.5	93	0.14	0.31	1.00	0.99	1.00	0.90	0.94	0.92	0.89	0.85	0.76
Tl (I) 276.787 nm	4.5	100	0.37	0.71	1.01	1.01	1.01	1.22	1.23	1.17	1.10	0.97	0.79
V (II) 292.464 nm	11.4	25	0.14	0.31	0.99	0.99	0.98	0.94	0.96	0.95	0.91	0.87	0.76
V (II) 309.311 nm	11.1	100	0.13	0.30	1.00	0.99	1.00	0.94	0.95	0.92	0.89	0.86	0.76
V (II) 311.071 nm	11.1	62	0.14	0.31	1.00	1.00	0.99	0.94	0.94	0.92	0.89	0.87	0.79
Zn (II) 202.548 nm	15.5	22	0.38	0.67	0.99	0.99	0.98	1.57	1.53	1.47	1.41	1.30	1.08
Zn (II) 206.191 nm	15.4	14	0.38	0.68	0.99	0.99	0.98	1.58	1.53	1.48	1.45	1.34	1.11
Zn (I) 213.856 nm	5.8	100	0.25	0.39	0.99	0.99	0.97	0.85	0.80	0.74	0.66	0.57	0.44
Area of the analyte channel normalized to a pure nitrogen plasma, %			99 ± 4	101 ± 3	105 ± 3	109 ± 3	115 ± 4	107 ± 3	104 ± 5	111 ± 4	124 ± 3	141 ± 3	161 ± 3
Mg ratio (Mg (II) 280.27 nm / Mg (I) 285.213 nm)			0.9	1.0	1.6	1.6	1.6	1.5	1.5	1.6	1.6	1.7	1.8

Table S3. Limits of detection (LOD; calculated by blank method) and limits of quantification (LOQ; calculated by calibration method) of selected emission lines determined with pure nitrogen or combined argon / nitrogen supply (pure argon in nebulizer- and intermediate gas flow; pure nitrogen in the outer gas flow) as plasma gas

Element, Emission line	Total line energy, eV	N_2 MICAP		Ar / N_2 MICAP	
		LOD, µg L^{-1}	LOQ, µg L^{-1}	LOD, µg L^{-1}	LOQ, µg L^{-1}
Ag (I) 328.068 nm	3.8	4	8	10	20
Ag (I) 338.289 nm	3.7	8	10	5	20
Al (I) 396.152 nm	3.1	1	9	6	12
As (I) 189.042 nm	6.6	300	400	200	300
As (I) 193.759 nm	6.4	200	300	200	300
B (I) 249.677 nm	5	10	30	10	20
B (I) 249.773 nm	5	8	10	4	10
Ba (II) 233.527 nm	11.2	10	20	10	20
Ba (II) 455.404 nm	7.9	0.1	2	0.1	3
Be (I) 234.861 nm	5.3	1	2	1	4
Be (II) 313.042 nm	13.3	2	2	2	3
Bi (I) 222.825 nm	5.6	400	500	300	500
Bi (I) 223.061 nm	5.6	100	200	100	200
Ca (II) 317.933 nm	13.2	20	20	20	30
Ca (II) 393.366 nm	9.3	0.2	2	0.2	3
Ca (II) 396.847 nm	9.2	0.2	2	0.2	3
Cd (II) 214.438 nm	14.8	40	60	30	40
Cd (II) 226.502 nm	14.5	30	50	30	50
Cd (I) 228.802 nm	5.4	10	20	3	20
Co (II) 238.892 nm	13.5	20	30	30	40
Cr (II) 205.552 nm	12.8	80	90	30	50
Cr (II) 267.716 nm	12.9	30	40	20	30
Cr (II) 283.563 nm	12.7	20	30	10	20
Cu (I) 324.754 nm	3.8	4	5	6	9
Cu (I) 327.396 nm	3.8	7	10	8	20
Fe (II) 238.204 nm	13.1	20	30	20	30
Fe (II) 239.562 nm	13.1	10	20	20	30
Fe (II) 259.941 nm	12.7	4	10	6	8
K (I) 766.491 nm	1.6	1	8	9	30
Li (I) 670.780 nm	1.8	0.1	3	0.2	3
Mg (II) 280.27 nm	12.1	0.3	3	1	4
Mg (I) 285.213 nm	4.3	0.6	3	1	3
Mn (II) 257.611 nm	12.2	3	5	3	5
Mn (II) 259.373 nm	12.2	1	3	2	5
Mn (I) 403.076 nm	3.1	2	9	5	11
Mo (II) 281.615 nm	13.2	30	40	20	30
Na (I) 588.995 nm	2.1	5	8	0.4	2
Na (I) 589.592 nm	2.1	5	7	1	3
Ni (II) 231.604 nm	14	100	200	50	70
Ni (I) 232.003 nm	5.3	60	70	30	50
Ni (I) 352.454 nm	3.5	60	100	40	100
P (I) 177.495 nm	7	200	1000	100	500
P (I) 178.287 nm	7	300	900	400	600
P (I) 213.618 nm	7.2	400	600	200	500

Element, Emission line	Total line energy, eV	N_2 MICAP		Ar / N_2 MICAP	
		LOD, µg L^{-1}	LOQ, µg L^{-1}	LOD, µg L^{-1}	LOQ, µg L^{-1}
Pb (I) 405.778 nm	4.4	20	40	30	70
S (I) 180.731 nm	6.9	1000	2000	1000	2000
S (I) 182.034 nm	6.9	1000	4000	2000	4000
Sb (I) 206.833 nm	6	300	600	100	200
Sb (I) 217.581 nm	5.7	200	300	90	100
Se (I) 196.09 nm	6.3	500	600	300	400
Sr (II) 407.771 nm	10.4	0.05	2	0.1	2
Sr (II) 421.552 nm	10.3	0.07	3	0.1	3
Ti (II) 307.864 nm	10.9	6	10	8	20
Ti (II) 334.941 nm	10.6	4	7	5	12
Ti (II) 336.121 nm	10.5	20	30	30	50
Tl (I) 276.787 nm	4.5	50	60	20	50
V (II) 292.464 nm	11.4	20	30	20	30
V (II) 309.311 nm	11.1	7	10	3	10
V (II) 311.071 nm	11.1	20	20	30	40
Zn (II) 202.548 nm	15.5	70	60	20	50
Zn (II) 206.191 nm	15.4	200	300	100	200
Zn (I) 213.856 nm	5.8	20	30	20	30

Table S4. Effect of argon concentration in the outer gas flow on a MICAP (1000 W microwave power; 0.9 L min^{-1} N_2 nebulizer gas flow, 0.6 L min^{-1} N_2 intermediate gas flow; 14 L min^{-1} outer gas flow); position, setup and magnification of the camera remained unchanged for all images.

Averaged camera image (3000 images averaged)	Segmented camera image (4 levels of luminance)	Gas composition of the outer gas flow
		100 % N_2
		86 % N_2 + 14 % Ar (v/v)
		71 % N_2 + 29 % Ar (v/v)
		57 % N_2 + 43 % Ar (v/v)
		43 % N_2 + 57 % Ar (v/v)
		29 % N_2 + 71 % Ar (v/v)