

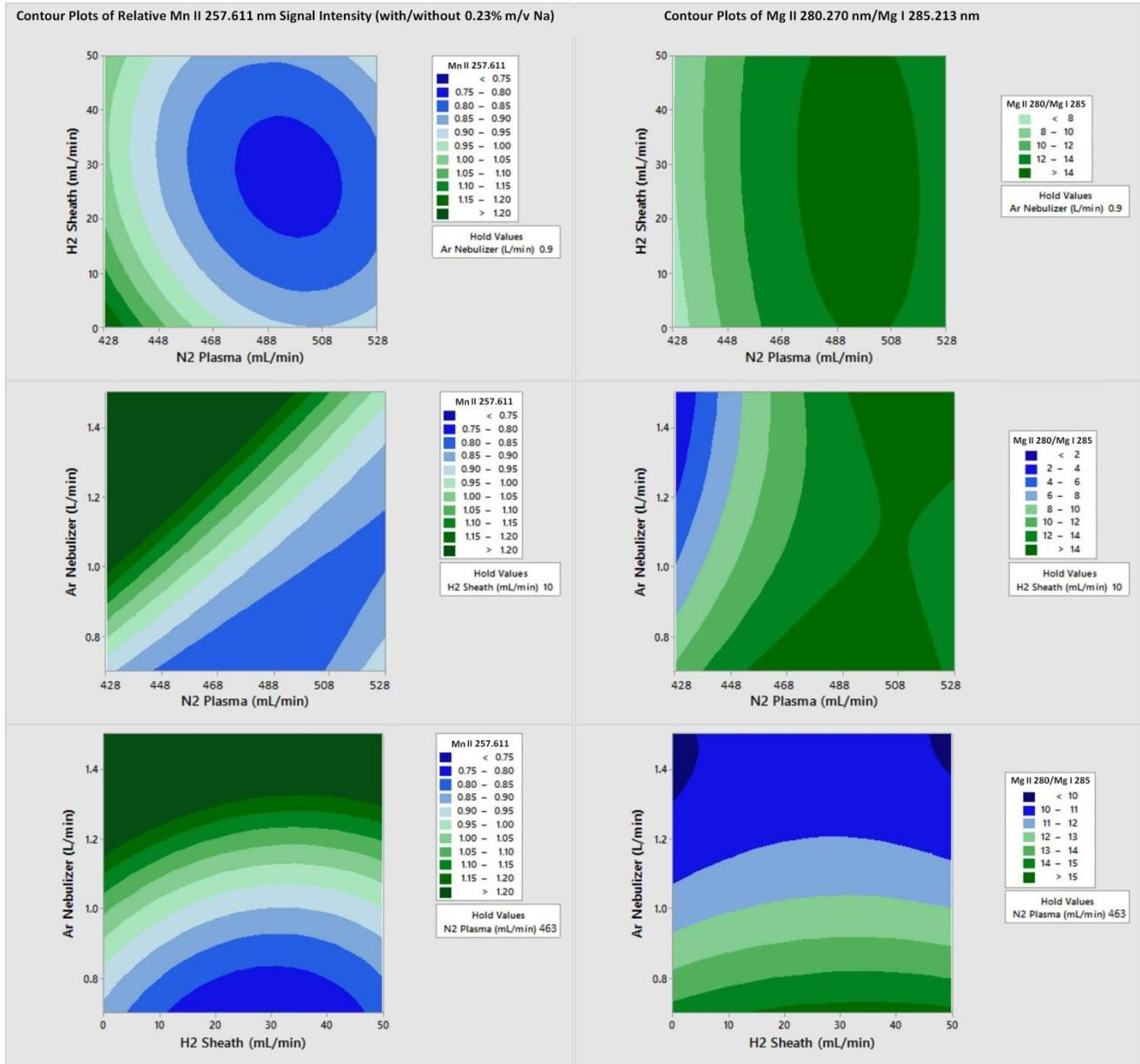
### Supplementary Information

**Table A1.** Approximate chemical composition of the LKSD, TILL and STSD reference materials.

Component	LKSD- 2 (%)	LKSD- 3 (%)	TILL- 2 (%)	TILL- 4 (%)	STSD- 1 (%)	STSD- 3 (%)	STSD- 4 (%)
SiO <sub>2</sub>	58.9	58.5	60.8	65.0	42.5	48.6	58.9
Al <sub>2</sub> O <sub>3</sub>	12.3	12.5	16.0	14.4	9	10.9	12.1
Fe <sub>2</sub> O <sub>3</sub>	6.2	5.7	5.39	5.63	6.5	6.2	5.7
CaO	2.2	2.3	1.27	1.25	3.6	3.3	4.0
Na <sub>2</sub> O	1.9	2.3	2.19	2.46	1.8	1.5	2.7
MgO	1.7	2.0	1.83	1.26	2.2	2.2	2.1
K <sub>2</sub> O	2.6	2.2	3.07	3.25	1.2	1.8	1.6
TiO <sub>2</sub>	0.6	0.5	0.88	0.81	0.8	0.7	0.8
P <sub>2</sub> O <sub>5</sub>	0.3	0.2	0.17	0.20	0.4	0.4	0.2
MnO	0.3	0.2	0.10	0.06	0.5	0.3	0.2
Loss on ignition	13.6	13.4	8.1	5.7	31.6	23.6	11.6

**Table A2.** Approximate chemical composition of the OREAS and CDN reference materials.

Component	OREAS-131B (%)	CDN-ME-9 (%)	CDN-ME-14 (%)
SiO <sub>2</sub>	44.2	47.3	44.9
Al <sub>2</sub> O <sub>3</sub>	8.66	12.3	8.2
Fe <sub>2</sub> O <sub>3</sub>	5.85	19.0	25.7
CaO	7.68	5.9	1.1
Na <sub>2</sub> O		2.4	0.7
MgO	5.35	7.2	2.1
K <sub>2</sub> O		0.9	1.8
TiO <sub>2</sub>		0.6	0.1
S	5.01	3.4	16.6
Loss on ignition		2.5	11.3



**Fig. S1.** Response surface plots from the multivariate optimization of the Ar-N<sub>2</sub>-H<sub>2</sub> mixed-gas plasma while varying the Ar nebulizer gas, the outer N<sub>2</sub> gas and the H<sub>2</sub> sheath gas flow rates. Left: effect on the blank-subtracted relative signal intensity (with/without 0.23% m/v Na) for 10 mg L<sup>-1</sup> Mn II 257.611 nm. Right: effect on the blank-subtracted ratio of Mg II 280.270 nm / Mg I 285.213 nm line intensities.