Electronic Supplementary Information

Naturally occurring molecular species used for plasma diagnostics and signal correction in microwave-induced plasma optical emission spectrometry

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Emission spectra for CN, N₂, N₂⁺ and OH

Figs. S1 - S4 show emission spectra recorded in wavelength regions corresponding to CN, N₂, N₂⁺ and OH, respectively. The spectra were collected with the microwave-induced plasma (MIP) either on or off to demonstrate the origin of these molecular species in the N₂ plasma. The CN emission band corresponds to the B(2Σ⁺) - X(2Σ⁺) electronic transition, with a band peak at 387.147 nm. The N₂, N₂⁺, and OH emission bands correspond to the C(3Π_u) - B(3Π_g), B(2Σ⁺) - X(2Σ⁺g⁺), and A(2Σ⁺) - X(2Π_i⁺) electronic transitions, with band peaks at 337.097, 391.439, and 308.970 nm, respectively.¹

Figs. S5 - S8 show the spectra collected for these same molecular species when the instrument’s spray chamber was removed (i.e., no aqueous solution was being introduced into the plasma), as well as when distilled-deionized water or 1 % v v⁻¹ HNO₃ were introduced into the MIP. Note that N₂⁺ is originally part of the MIP (Fig. S7), while OH is mainly produced as an aqueous solution is introduced into the plasma (Fig. S8).
**Fig. S1.** Molecular emission spectra for CN recorded with the plasma off, or as a 1 \% v v^{-1} HNO_3 solution was introduced into the MIP at a nebulization gas flow rate of 0.7 L min^{-1}.

**Fig. S2.** Molecular emission spectra for N_2 recorded with the plasma off, or as a 1 \% v v^{-1} HNO_3 solution was introduced into the MIP at a nebulization gas flow rate of 0.7 L min^{-1}.
**Fig. S3.** Molecular emission spectra for N$_2^+$ recorded with the plasma off, or as a 1 % v v$^{-1}$ HNO$_3$ solution was introduced into the MIP at a nebulization gas flow rate of 0.7 L min$^{-1}$.

**Fig. S4.** Molecular emission spectra for OH recorded with the plasma off, or as a 1 % v v$^{-1}$ HNO$_3$ solution was introduced into the MIP at a nebulization gas flow rate of 0.7 L min$^{-1}$.
**Fig. S5.** Molecular emission spectra for CN recorded as 1 % v v$^{-1}$ HNO$_3$, distilled-deionized water (NGFR = 0.7 L min$^{-1}$), or no aqueous solution (no spray chamber) was introduced into the MIP.

**Fig. S6.** Molecular emission spectra for N$_2$ recorded as 1 % v v$^{-1}$ HNO$_3$, distilled-deionized water (NGFR = 0.7 L min$^{-1}$), or no aqueous solution (no spray chamber) was introduced into the MIP.
Fig. S7. Molecular emission spectra for N$_2^+$ recorded as no aqueous solution (no spray chamber), distilled-deionized water, or 1 % v v$^{-1}$ HNO$_3$ (NGFR = 0.7 L min$^{-1}$) was introduced into the MIP.

Fig. S8. Molecular emission spectra for OH recorded as 1 % v v$^{-1}$ HNO$_3$, distilled-deionized water (NGFR = 0.7 L min$^{-1}$), or no aqueous solution (no spray chamber) was introduced into the MIP.
Evaluation of individual emission signals and combinations of CN, N$_2$, N$_2^+$ and OH intensities as plasma diagnostic tools

To evaluate the efficiency of some of the MIP’s naturally occurring species as diagnostic tools, individual emission signals for CN, N$_2$, N$_2^+$ and OH, as well as their combination in the form of signal ratios (i.e. N$_2^+$/OH, N$_2^+$/N$_2$, N$_2^+$/CN, N$_2$/OH, N$_2$/CN and CN/OH) were studied. The performance criterion was the sensitivity to plasma changes caused by the introduction of high concentrations of Na into the MIP at different nebulization gas flow rates (NGFR). The molecular species were also compared with Mg II and Mg I lines, and with the Mg II/Mg I signal ratio. As shown in Figs. S9 - S12, the N$_2^+$/OH signal ratio was the most sensitive to plasma change across all conditions evaluated. For example, when the Na concentration increased from 200 to 500 mg L$^{-1}$, at a NGFR of 0.6 L min$^{-1}$, the N$_2^+$/OH signal ratio dropped more than 43 %, from 1.173 to 0.666 (absolute percent change of 43.2 %). For comparison at the same conditions, the Mg II/Mg I, N$_2^+$/N$_2$, N$_2^+$/CN, N$_2$/OH, N$_2$/CN and CN/OH ratios changed 22.3, 34.1, 21.9, 13.9, 18.6 and 27.4 %, respectively. If a more drastic change takes place, as for example with the Na concentration increasing from 0 to 500 mg L$^{-1}$ (not shown in Figs. S9 - S12), the N$_2^+$/OH signal ratio will change 65.2 %, as opposed to 33.2, 51.6, 32.1, 28.1, 40.2 and 48.7 % for Mg II/Mg I, N$_2^+$/N$_2$, N$_2^+$/CN, N$_2$/OH, N$_2$/CN and CN/OH, respectively.

Based on these results, and considering Na as a model for EIEs, which are responsible for some of the most severe matrix effects observed in MIP OES, the N$_2^+$/OH signal ratio was further studied as a diagnostic tool in the present work.
**Fig. S9.** Absolute emission signal percent change as Na concentrations in the 0 - 1000 mg L\(^{-1}\) range were introduced into the MIP at a NGFR of 0.6 L min\(^{-1}\). Species 1 - 6 correspond to Mg II (280.271 nm), Mg I (285.213 nm), CN (387.147 nm), N\(_2\) (337.097 nm), N\(_2^+\) (391.439 nm) and OH (308.970 nm), respectively.

**Fig. S10.** Absolute emission signal percent change as Na concentrations in the 0 - 1000 mg L\(^{-1}\) range were introduced into the MIP at a NGFR of 1.0 L min\(^{-1}\). Species 1 - 6 correspond to Mg II (280.271 nm), Mg I (285.213 nm), CN (387.147 nm), N\(_2\) (337.097 nm), N\(_2^+\) (391.439 nm) and OH (308.970 nm), respectively.
Fig. S11. Absolute signal ratio percent change as Na concentrations in the 0 - 1000 mg L\(^{-1}\) range were introduced into the MIP at a NGFR of 0.6 L min\(^{-1}\). Here, 1 - 7 correspond to Mg II/Mg I, N\(_2^+\)/OH, N\(_2^+\)/N\(_2\), N\(_2^+\)/CN, N\(_2\)/OH, N\(_2\)/CN, and CN/OH, respectively.

Fig. S12. Absolute signal ratio percent change as Na concentrations in the 0 - 1000 mg L\(^{-1}\) range were introduced into the MIP at a NGFR of 1.0 L min\(^{-1}\). Here, 1 - 7 correspond to Mg II/Mg I, N\(_2^+\)/OH, N\(_2^+\)/N\(_2\), N\(_2^+\)/CN, N\(_2\)/OH, N\(_2\)/CN, and CN/OH, respectively.
References
