**Solid Phase Excitation-Emission Matrix Spectroscopy for Combustion Generated Particulate Matter Analysis**

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**Supplemental Information**

Number of Pages: 8

Number of Figures: 9

# Particulate Matter Collection

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| Figure S1: Quartz slide coated with PDMS (left) was placed in a parallel plate electrostatic collector. Combustion-generated PM was collected directly onto the PDMS coated surface of the substrate. The substrate was used for SP-EEM analysis after collection. |

# External Excitation SP-EEM Measurement

External excitation SP-EEMs of woodsmoke at varying θ are plotted in S2 without removing the Rayleigh and Raman scattering peaks computationally. As θ increases from 0° to 50°, the intensity of woodsmoke fluorescence peaks increases; however, a greater EEM region is masked due to wider Rayleigh and Raman scattering peaks. The same is observed when θ decreases from 85° to 50°. At θ = 50°, the intensity of woodsmoke fluorescence peaks is the highest among all SP-EEMs, however, the scattering peaks block almost all the fluorescence peaks except in the region λex = 280nm – 320nm, λem = 380nm – 480nm. These masked external excitation SP-EEM features cannot be recovered using interpolation of scattering peaks as in the LP-EEMs because the scattering peaks are significantly broader compared to the fluorescence peaks. For θ = 0° or θ = 85°, the scattering peaks are narrower, the intensity of the fluorescence signal is too low.

For smaller θ, most of the light detected is reflection/scattering. As θ increases, the path of reflected/scattered light moves away from the detector, and PM fluorescence peaks are observed in SP-EEMs. For θ > 50°, as θ increases, the path of emitted fluorescence light through PDMS increases. This reduces PM fluorescence reaching the detector due to the inner filter effect.1 To balance the increasing intensity and masking of fluorescence, θ = 60° was chosen as optimum θ since, at θ = 60°, removal of scattering peaks computationally retains fluorescence peaks defining the EEM signature of woodsmoke with good intensity levels, as shown in Figure S2.

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| Figure S2: External excitation SP-EEMs of woodsmoke at varying θ. θ = 60° was chosen as an optimum angle for external excitation SP-EEM measurements.  |

# External Excitation SP-EEM Comparison of Quartz and Glass Analysis Substrates

Figure S3 shows external excitation SP-EEMs at θ = 60° recorded using glass and quartz analysis substrates. The number and relative intensity of peaks in the woodsmoke PM fluorescence signature matches well in both SP-EEMs (see Figure S3), and it does not affect external excitation SP-EEM measurements. However, this difference in transmission will affect internal excitation SP-EEM measurements where the substrate acts as a waveguide for excitation light, in which case glass analysis substrates cannot be used due to negligible transmission of UV light (λ < 300nm). Hence, we use quartz analysis substrates for internal excitation SP-EEM measurements in the main manuscript.

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| Glass Analysis Substrate | Quartz Analysis Substrate |
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| Figure S3: External excitation SP-EEMs at θ = 60° match well for glass and quartz analysis substrates. The number and relative intensity of peaks defining the woodsmoke PM fluorescence signature is similar for both SP-EEMs.  |

# Transmission Spectra for Quartz and Glass

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| Figure S4: Transmission of HSQ® 100 quartz glass (92% at 280 nm) and soda-lime glass (2% at 280 nm) with a thickness of 1 mm between 200 and 450 nm measured with a Specord 250 Plus spectrophotometer from Analytik Jena (Jena, Germany).2 |

# Interference of PDMS Fluorescence in Internal vs. External Excitation SP-EEMs

Figure S5 shows external excitation SP-EEM at optimum θ (θ = 60°), front-side emission, and back-side emission internal excitation SP-EEMs of woodsmoke PM samples without subtracting SP-EEM of a blank analysis substrate during pre-processing of EEM data. PDMS fluorescence (λex <250nm, 350nm < λem <450nm) overlaps with woodsmoke PM fluorescence. For external excitation SP-EEM, the PDMS fluorescence is negligible compared to woodsmoke PM fluorescence.

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| Figure S5: SP-EEMs of woodsmoke PM at θ = 60° without blank subtraction using three different excitation emission optics arrangements. Intensity of PDMS fluorescence (λex <250nm, 350nm < λem <450nm) compared to woodsmoke fluorescence peaks (λex > 250nm) is least in external excitation SP-EEM.  |  |
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Figure S6: PM PAH fraction for woodsmoke. GCMS concentration of 16 PAHs is divided into LMW and HMW PAH. The woodsmoke contains mainly HMW PAHs.

# References

(1) Larsson, T.; Wedborg, M.; Turner, D. Correction of Inner-Filter Effect in Fluorescence Excitation-Emission Matrix Spectrometry Using Raman Scatter. *Anal. Chim. Acta* **2007**, *583* (2), 357–363. https://doi.org/10.1016/j.aca.2006.09.067.

(2) Gross, A.; Stangl, F.; Hoenes, K.; Sift, M.; Hessling, M. Improved Drinking Water Disinfection with UVC-LEDs for Escherichia Coli and Bacillus Subtilis Utilizing Quartz Tubes as Light Guide. *Water* **2015**, *7* (9), 4605–4621. https://doi.org/10.3390/w7094605.