Development and testing of a novel micro-Raman probe and application of calibration method for the quantitative analysis of microfluidic nitric acid streams

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Supporting Information

Detection Limits: A comparison of the Raman probes used in this study shows that when held at the same power level there is a decrease in signal intensity when moving toward a more narrow beam. Although there is still sufficient intensity with the narrowed beam diameter to identify and quantify materials present in solution. Figure S-1 compares the decreasing Raman intensity associated with the NO_3^- peak from aqueous HNO_3 as the laser beam diameter is decreased from 125 µm to 70 µm, and as the path length is decreased.

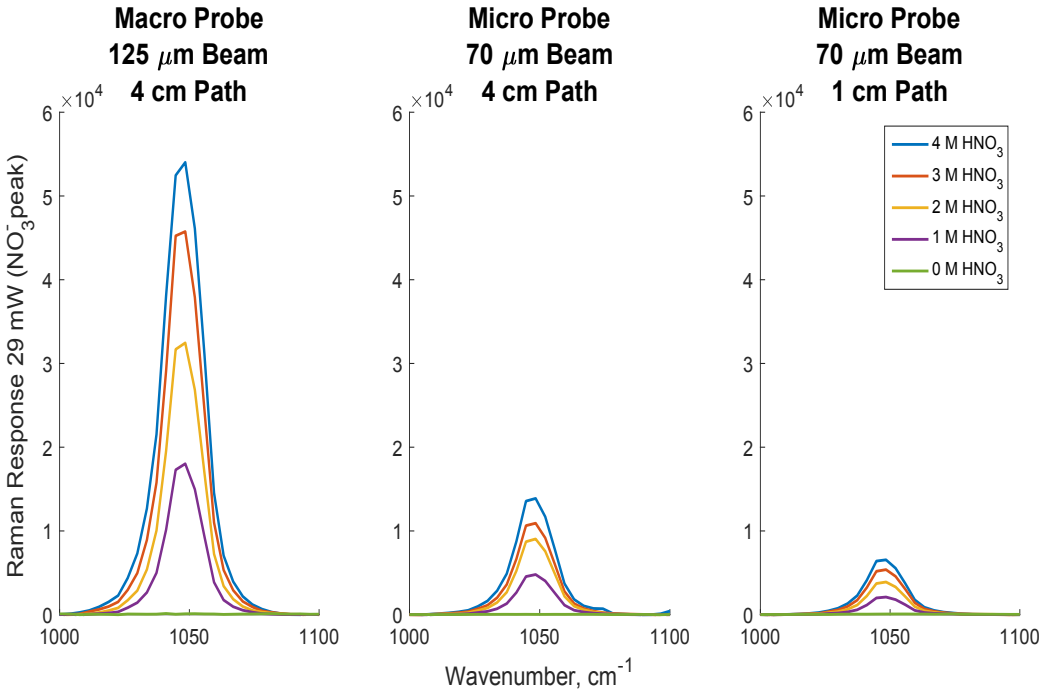

Figure SI-1: Comparison of Raman spectra collected on the 125 µm macro probe and the 70 µm micro probe. A 4 cm path length was available for samples recorded using 2 dram glass vials, while the path length was reduced to 1 cm for samples recorded in the 8 µL flow cell.

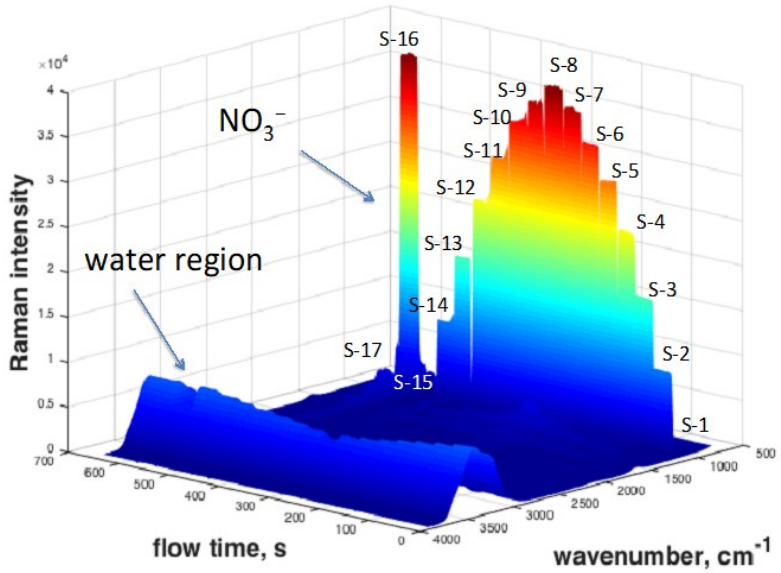

Figure SI-2: The sequence of Raman spectra recorded by the micro-Raman probe as a function of time for a series of HNO_3 solutions passed through a 70 µL flow cell (aperture diameter 3 mm). The 648 spectra recorded during the flow run are presented sequentially along the flow time axis in the order they were recorded. The spectra were recorded over a spectral range of 750 cm^{-1} to about 4000 cm^{-1}.

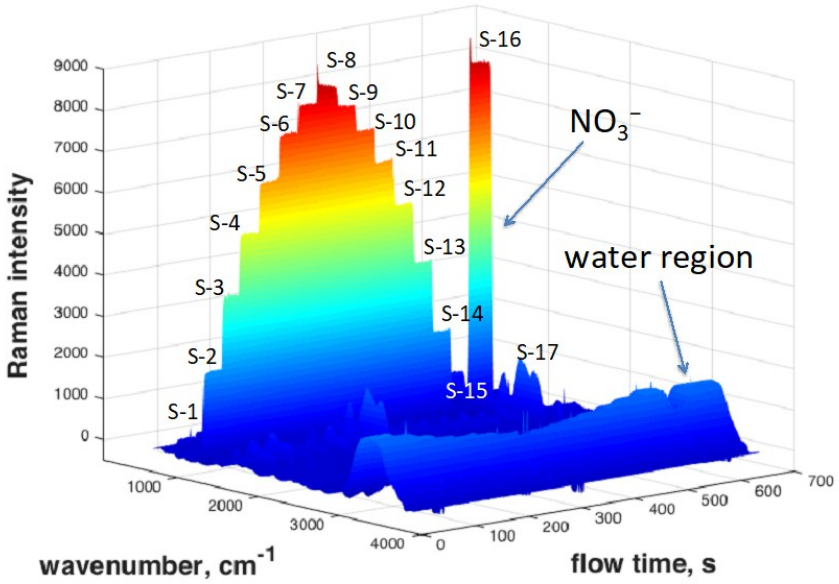

Figure SI-3: The sequence of Raman spectra recorded by the micro-Raman probe as a function of time for a series of HNO_3 solutions passed through a 8 µL flow cell (aperture diameter 3 mm). The 648 spectra recorded during the flow run are presented sequentially along the flow time axis in the order they were recorded. The spectra were recorded over a spectral range of 750 cm^{-1} to about 4000 cm^{-1}.

Static Samples for Training Sets: Large volume spectra taken of static HNO_3 solutions were analyzed using 2 dram Fisherbrand® borosilicate threaded glass vials. This allowed 5 mL of solution to be analyzed by Raman spectroscopy while providing a very long sampling path of about 4 cm. The set of Raman spectral standards were recorded using the glass vials positioned immediately above the probe (See Figure S-1, left).

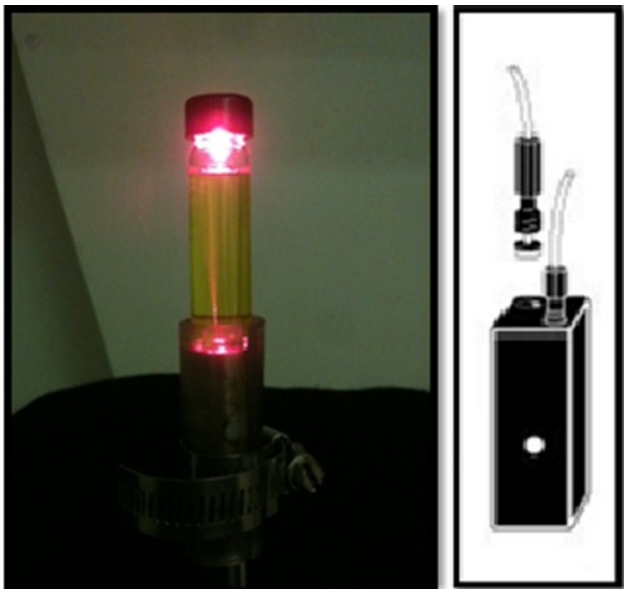

Figure SI-4. Left – Glass vial (2 dram) containing a solution sample positioned above the Raman probe using a plastic collar to secure the sample. Right—Schematic diagram of a Starna™ 585.3-Q-10-Z15 micro flow cell showing aperture and ports for solution flow through.

Flow Procedure: Raman spectra for the HNO_3 solution flow sequences that paired 125 µm and 70 µm laser beam diameter probes with 70 µL and 8 µL micro fluidic cells were recorded for the same series of concentrations as they were passed through the flow cell. The 70 µL and 8 µL flow cells were produced by Starna® Cells, Inc., and were fitted with an inlet port and capillary tubes that allow solutions to enter from the lower rear of the cell, flow through the sampling chamber, and exit the port toward the top front of the cell. The aperture is 3 mm in diameter for the 70 µL cell, and 1 mm for the 8 µL cell. The Teflon capillary tubes are compatible with insertion of a size 21 hypodermic needle to inject the contents of a syringe into the cell without leakage.

Each flow cell was paired with a Raman probe via a series of adjustable translation stages as shown in Figure 3. Using these adjustments, the probe could be positioned optimally in any of the XYZ directions to analyze samples flowing through the cell.

In order to produce a continuous flow of solutions through the flow cell for analysis, a set of 18 – 5 mL Luer Lock syringes were set up to hold 3.0 mL of each solution. The solution concentrations and injection sequence can be seen in the following tables proceeding from low concentration to high concentration, and then back down (syringes 1 through 15):

Table S-1. Training Set and Flow Solution Concentrations

Training Set		**Flow Set**			
Sample ID	Actual Conc., M	Sample ID	HNO_3 Conc., M	Sample ID	HNO_3 Conc., M
T-1	0	S-1	0	S-10	4.8398
T-2	0.5102	S-2	0.9716	S-11	3.9546
T-3	1.0046	S-3	1.9089	S-12	2.9182
T-4	1.9623	S-4	2.9182	S-13	1.9080
T-5	2.9645	S-5	3.9546	S-14	0.9716
T-6	3.9512	S-6	4.8398	S-15	0
T-7	5.8655	S-7	5.9421	S-16	8.0273
T-8	7.9483	S-8	8.0273	S-17	0
		S-9	5.9421	S-18	0

Filling the flow cell chamber and lines requires approximately 0.33 mL of solution. Using 3.0 mL of each solution for the flow experiment provided approximately 9 volume turn-overs in the cell. The flow rate was hand controlled and timed to flow each mL of solution in the syringe to a 1 minute cycle of a timer, thus resulting in a flow rate of 1mL/min. Error in the flow rate was estimated to be up to 15%.

There was a 20 to 30 second pause between each sample to switch syringes and reset the spectrometer. A Raman spectrum was recorded every 5 seconds for the 3 minute flow period for a total of 36 spectra per solution.

Model Results: The top panels in Figure SI-5 (A and B) presents the results of modeling the macro-Raman probe (laser diameter 125 μm) paired with the 70 μL flow cell. The top left plot (Figure SI-5A) shows the strong ability to predict the concentration as it changes with time, and the top right plot (Figure SI-5A) indicates the there is a very good correlation between the model prediction and the known values. The middle panels of Figure SI-5 (C and D) present a comparison of the known flow solution concentration and the predicted concentration for the macro-Raman paired with a smaller 8 μL flow cell. Again there is a very close correlation between the measured concentrations for the solutions used and that predicted by the model from the recorded spectra (the flat step segments of the progression). The bottom panels in Figure SI-5 (E and F) represent the comparison between the chemometric prediction of solution concentration flowing through the 8 μL flow cell measured with the micro-Raman (laser diameter 70 μm) and the known concentration values. Figures SI-5E and SI-5F are important plots for this study because the comparisons between the predicted and known values are in close agreement, and compare favorably to those in the prior experiments (shown in Figures SI-5A/B and SI-5C/D) using the

applied macro-Raman probe.

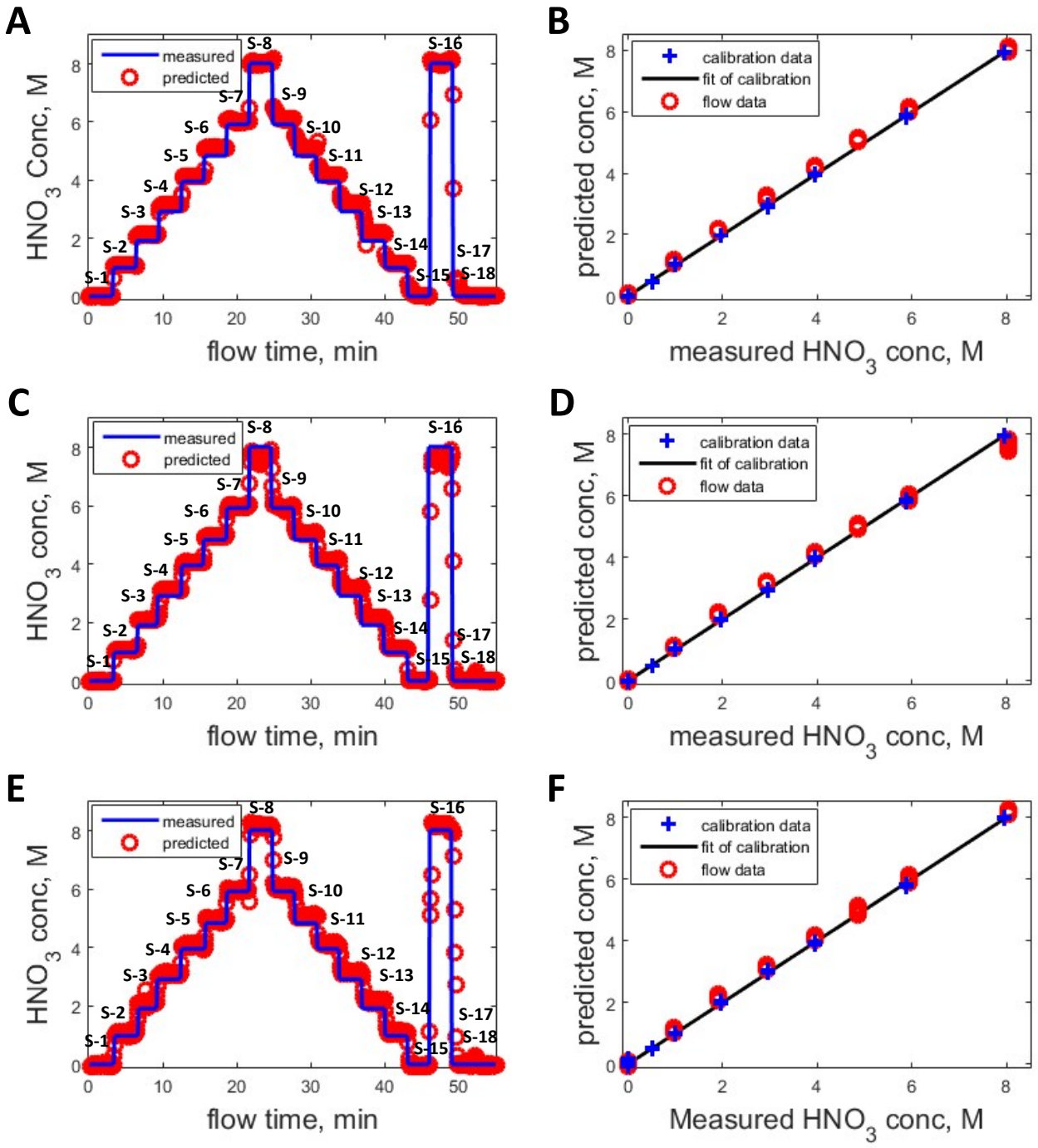

Figure SI-5: (A) PLS model results and (B) model fit for the macro Raman probe paired with the 70 µL flow cell; (C) PLS model results and (D) model fit for the macro Raman probe paired with the 8 µL flow cell; (E) PLS model results and (F) model fit for the micro Raman probe with the 8 µL flow cell.