

Supplementary Information of

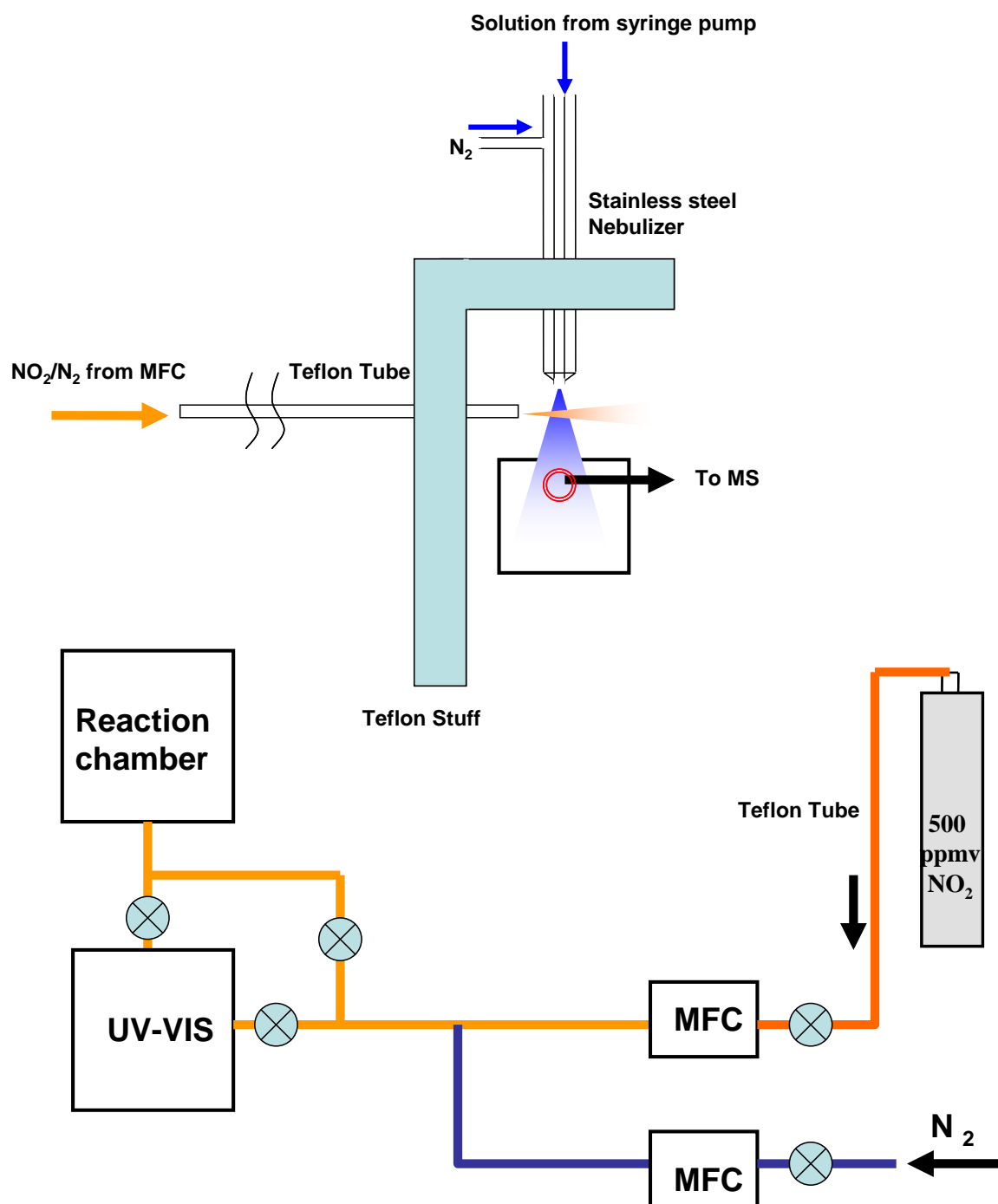
**Absorption of Inhaled NO<sub>2</sub>**

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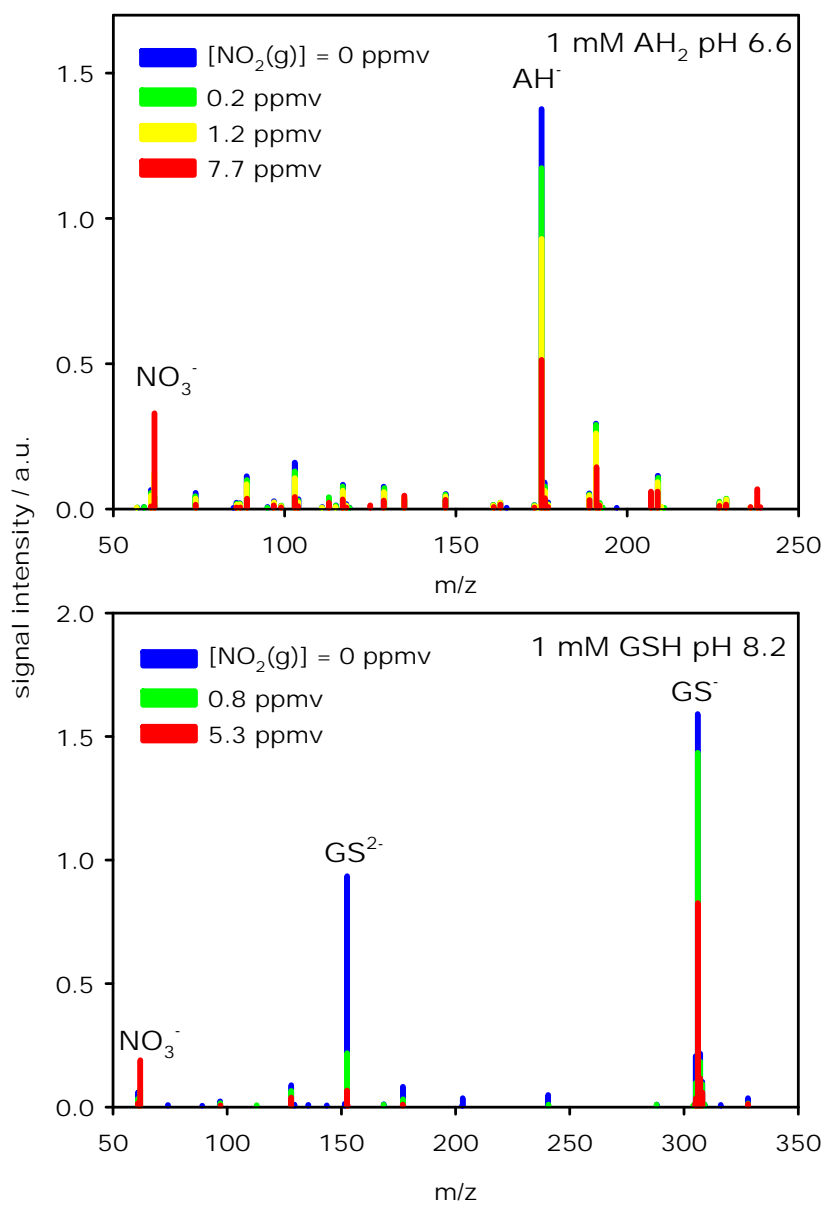
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## SI text

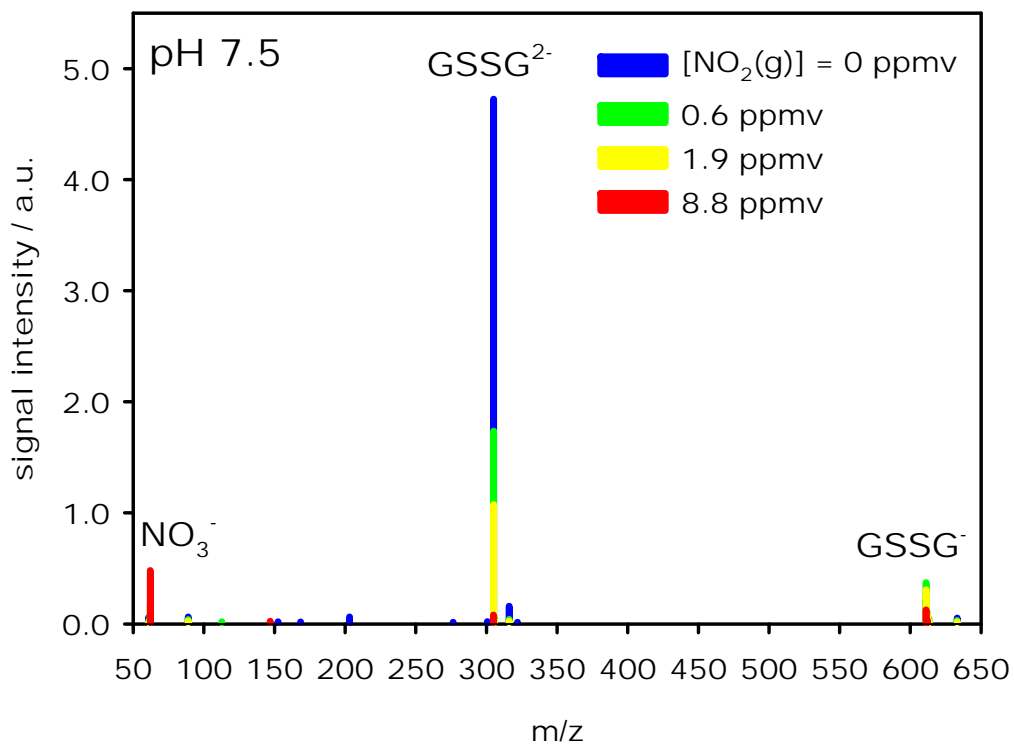
NO<sub>2</sub>/N<sub>2</sub> gas mixtures were introduced into the spraying chamber in a direction perpendicular to a stainless steel needle injector and mass spectrometer, respectively (see Fig. S1). This geometry was chosen to prevent unwanted NO<sub>2</sub> losses on the wall of the spraying chamber. The NO<sub>2</sub> concentration in the chamber was calculated from the combined NO<sub>2</sub>/N<sub>2</sub> mixture and N<sub>2</sub> drying gas flow rates. NO<sub>2</sub> concentrations were confirmed to be valid by UV absorption spectrophotometry (HP 8452) at 400 nm. The [NO<sub>2</sub>(g)] values reported in the figures throughout correspond to the concentrations actually sensed by microdroplets in the spraying chamber, which are ~13 times smaller than the values determined from UV absorbance due to further dilution by the N<sub>2</sub> drying gas. Gas flows were regulated by calibrated mass flow controllers (MKS) and a needle bulb. Typical instrumental parameters were as follows: drying gas flow rate, 13 L min<sup>-1</sup>; drying gas temperature, 340 °C; nebulizer pressure, 2 atm; collector capillary voltage, +3.5 kV; fragmentor voltage, 22 V. L-ascorbic acid (> 99 %), uric acid (> 99 %), reduced L-glutathione (> 99 %), glutathione disulfide (> 90 %), sodium nitrate (> 99 %) and sodium nitrite (> 99 %) were obtained from Sigma-Aldrich. All solutions were prepared in purified water (Resistivity = 18.2 MΩ cm) from a Millipore Milli-Q gradient water purification system. Solution pH was adjusted by adding HCl/NaOH and measured with a calibrated pH meter (VWR).



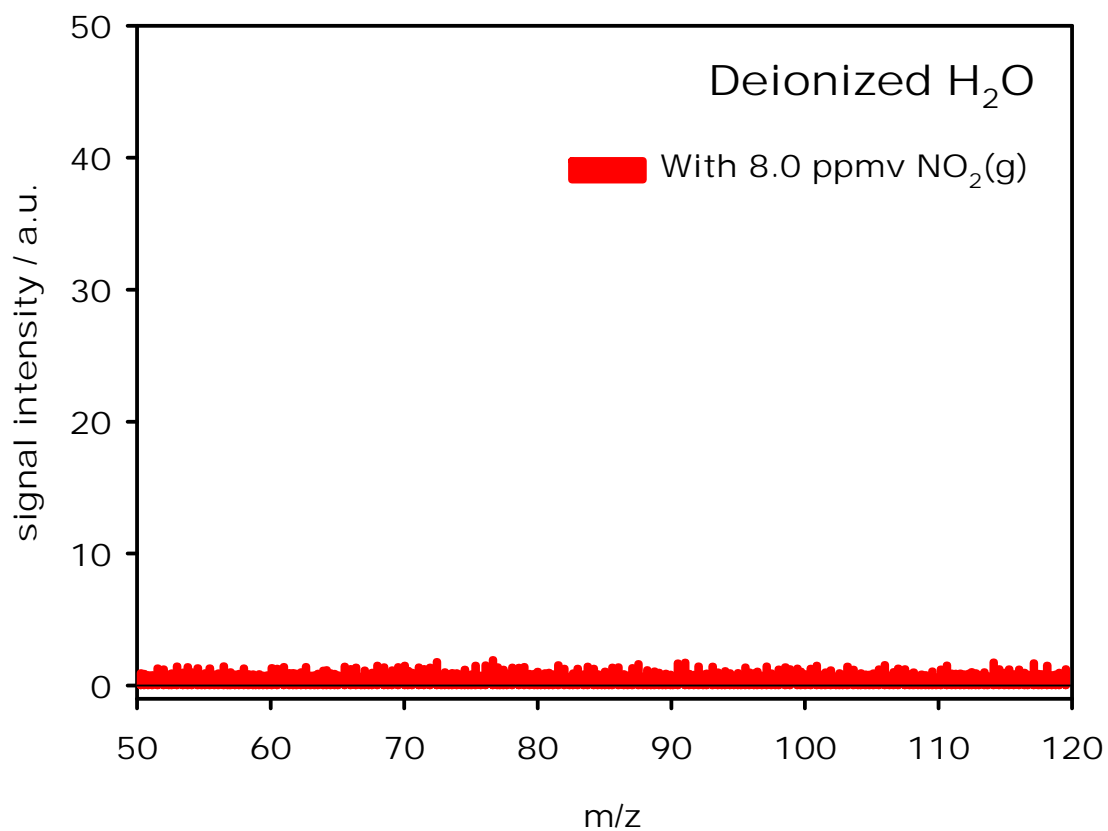
**Figure S1** Schematic diagram of the present experimental setup and  $\text{NO}_2(\text{g})$  injection system. MFC stands for mass flow controller.



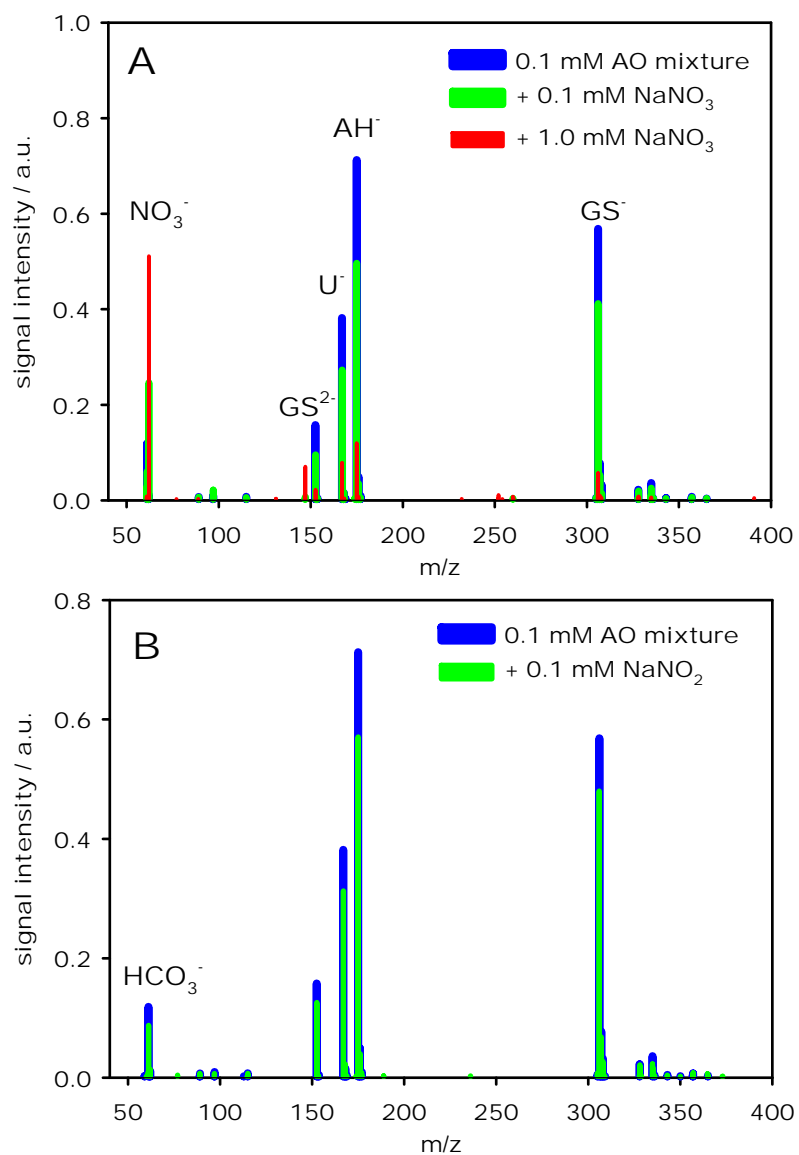
**Figure S2** Negative ion mass spectra of aqueous 1mM AH<sub>2</sub> (upper panel) or 1 mM GSH (lower panel) microdroplets in the absence/presence of NO<sub>2</sub>(g).



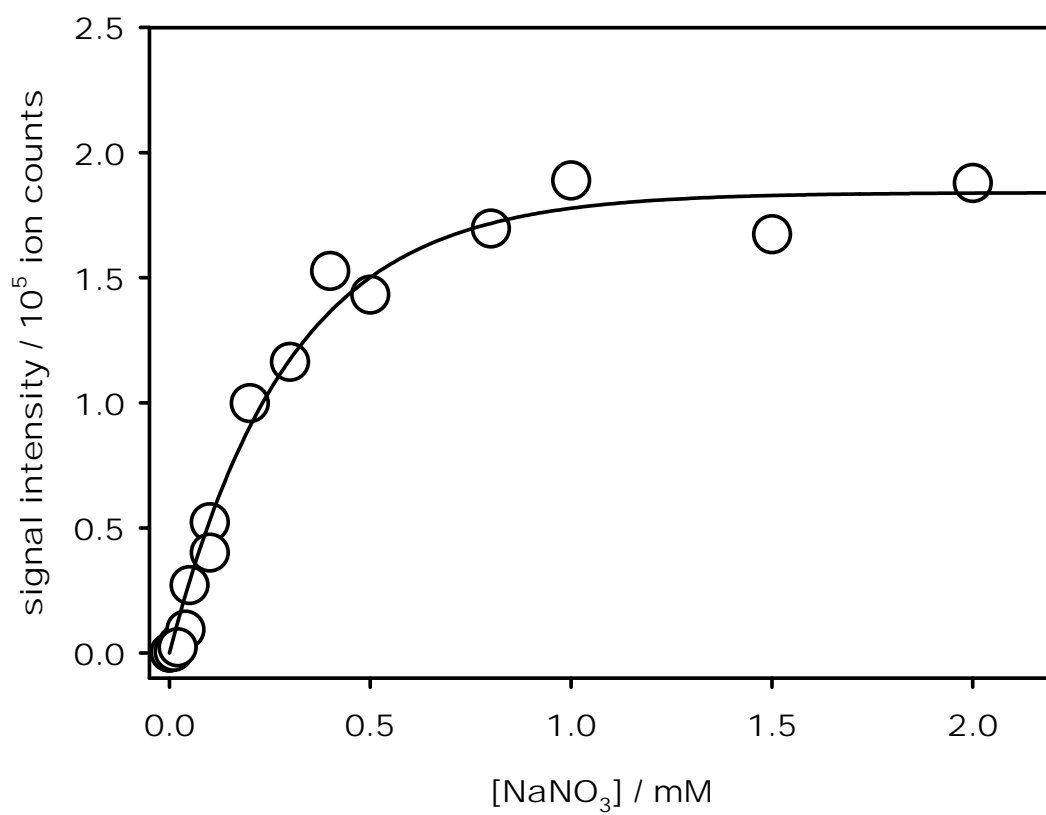
**Figure S3** Negative ion mass spectra of 0.2 mM GSSG microdroplets at pH 7.5 in the absence/presence of NO<sub>2</sub>(g). Note that GSSG<sup>-</sup> radical (m/z = 610) is *not* observed.



**Figure S4** Negative ion mass spectra of deionized MilliQ-water microdroplets at pH 7 in the presence of 8 ppmv NO<sub>2</sub>(g). Note that *no* NO<sub>3</sub><sup>-</sup> (m/z = 62) is observed.

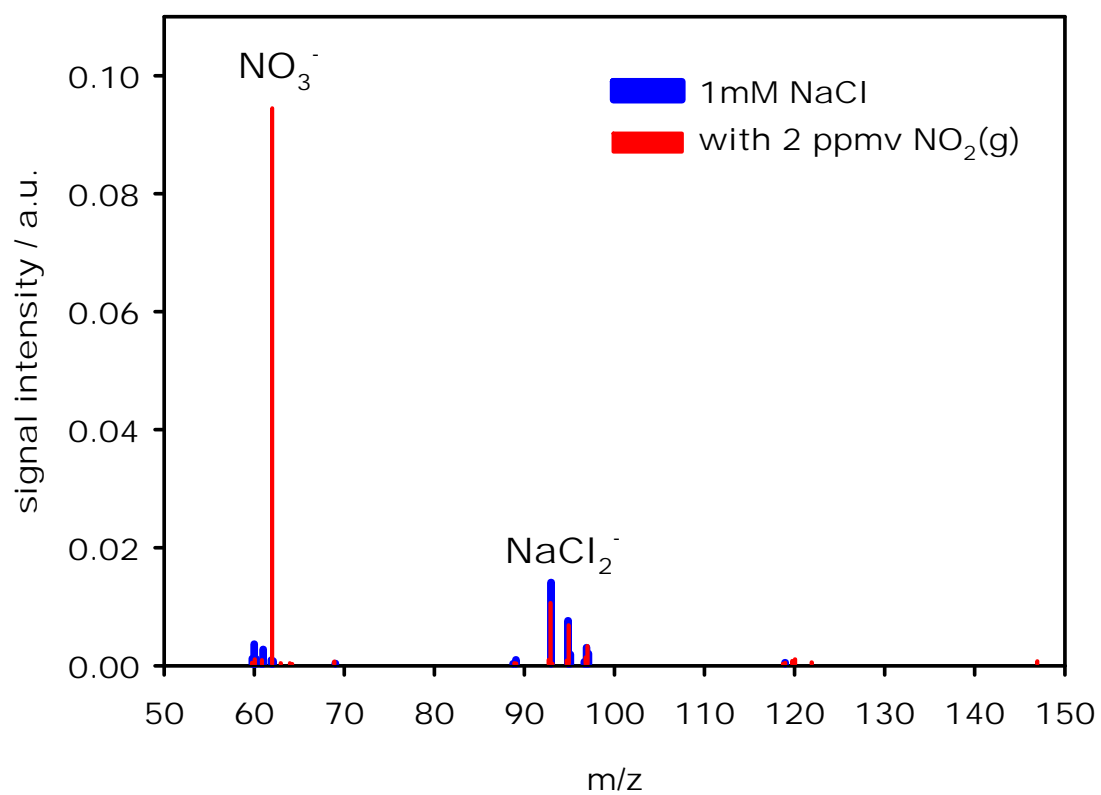


**Figure S5** Negative ion mass spectra of 0.1 mM equimolar mixture microdroplets at pH 7.1 A) added NaNO<sub>3</sub>(aq) or B) NaNO<sub>2</sub>(aq).

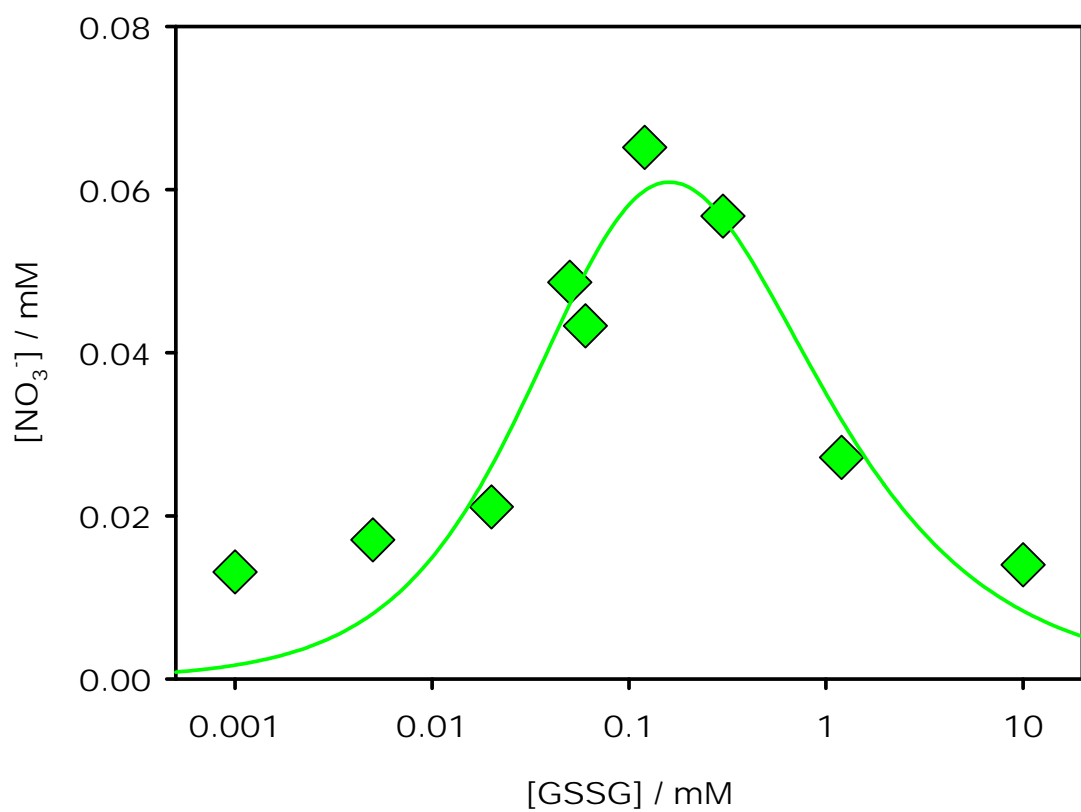


**Figure S6** Plot of the  $m/z = 62$  signal intensity vs.  $[\text{NaNO}_3]$  at  $\text{pH} \sim 7$ .

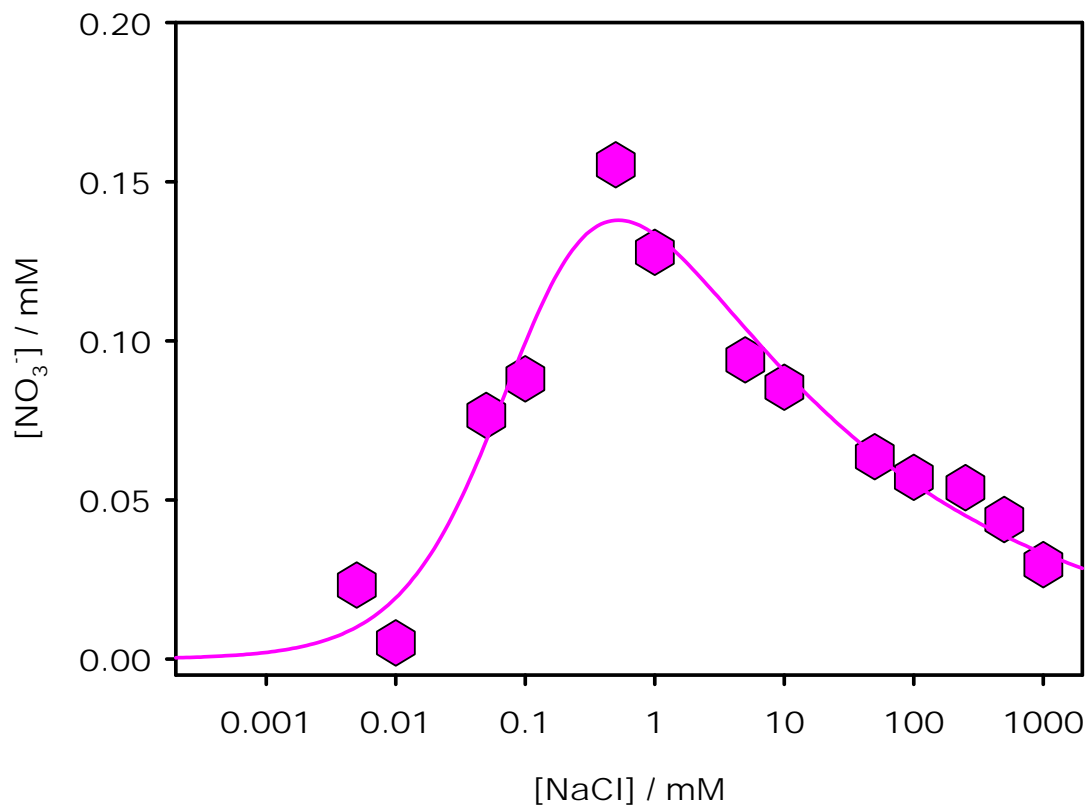




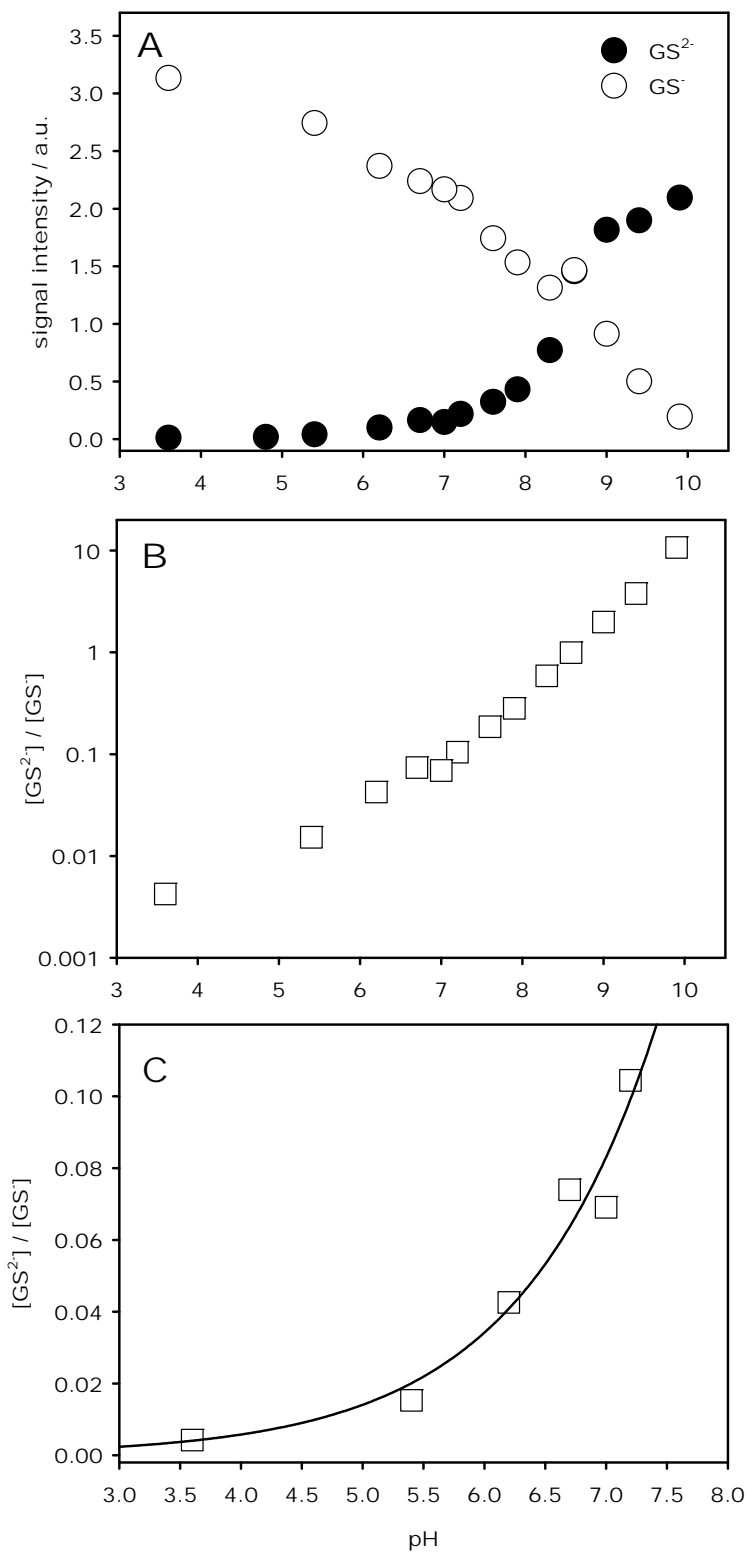
**Figure S7** Negative ion mass spectra of 1 mM NaCl microdroplets at pH 7 in the absence/presence of NO<sub>2</sub>(g).



**Figure S8** [NO<sub>3</sub><sup>-</sup>] vs. [GSSG] plots derived from 10<sup>-3</sup> to 10 mM GSSG microdroplets at pH ~7 in the presence of 2 ppmv NO<sub>2</sub>(g).



**Figure S9** [NO<sub>3</sub><sup>-</sup>] vs. [NaCl] plots derived from 10<sup>-2</sup> to 10<sup>3</sup> mM NaCl microdroplets at pH ~7 in the presence of 2 ppmv NO<sub>2</sub>(g).



**Figure S10** A) signal intensities of  $GS^{2-}$  and  $GS^-$  in 1mM GSH microdroplets as a function of bulk pH, B) The  $[GS^{2-}]/[GS^-]$  ratio as a function of bulk pH, C) Expansion around pH 3-8. Fitting curve is an exponential fitting in this pH range.