Supporting Information for

Electrospray Droplet Exposure to Organic Vapors: Metal Ion Removal from Proteins and Protein Complexes

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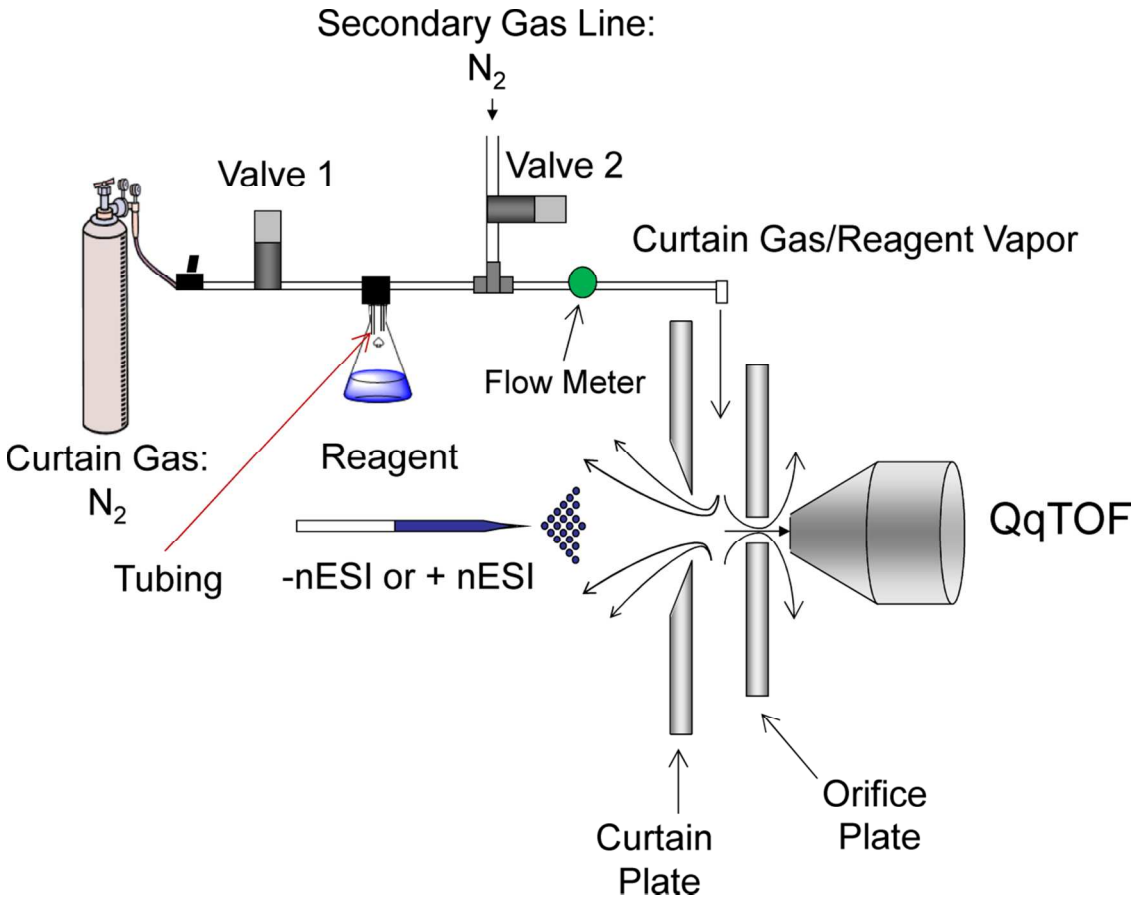
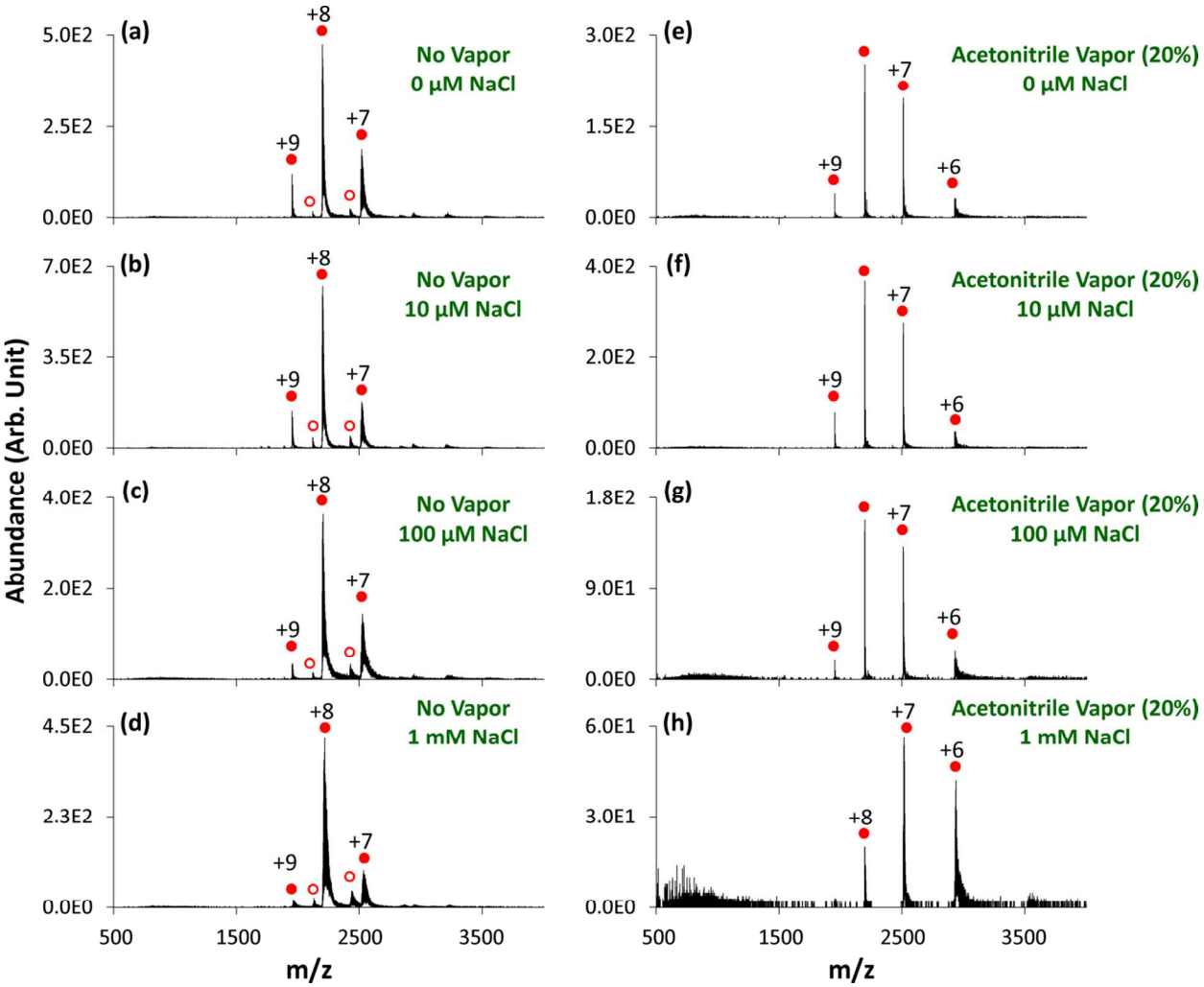
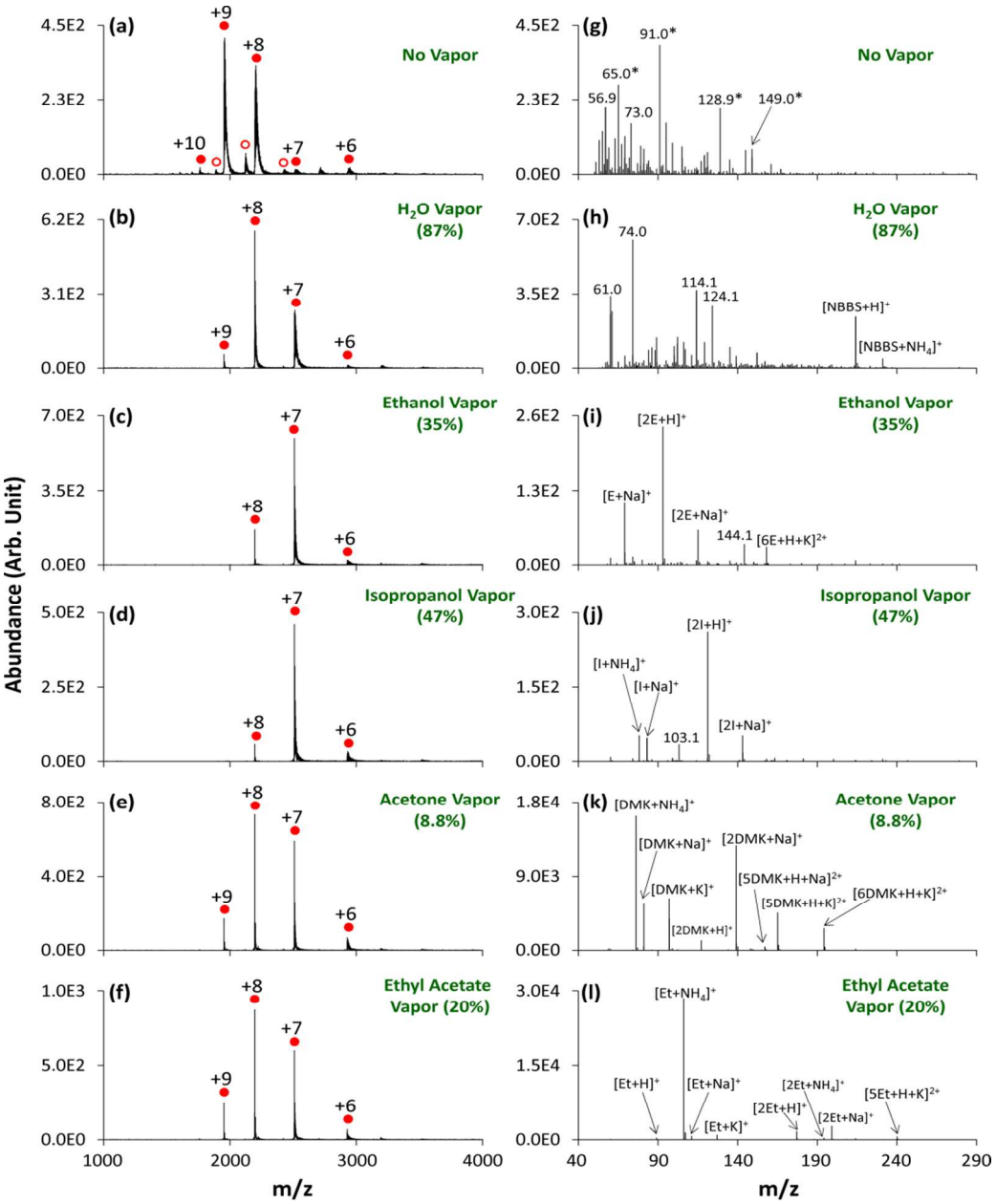
Supporting Information: Supplemental Figures S1-S5



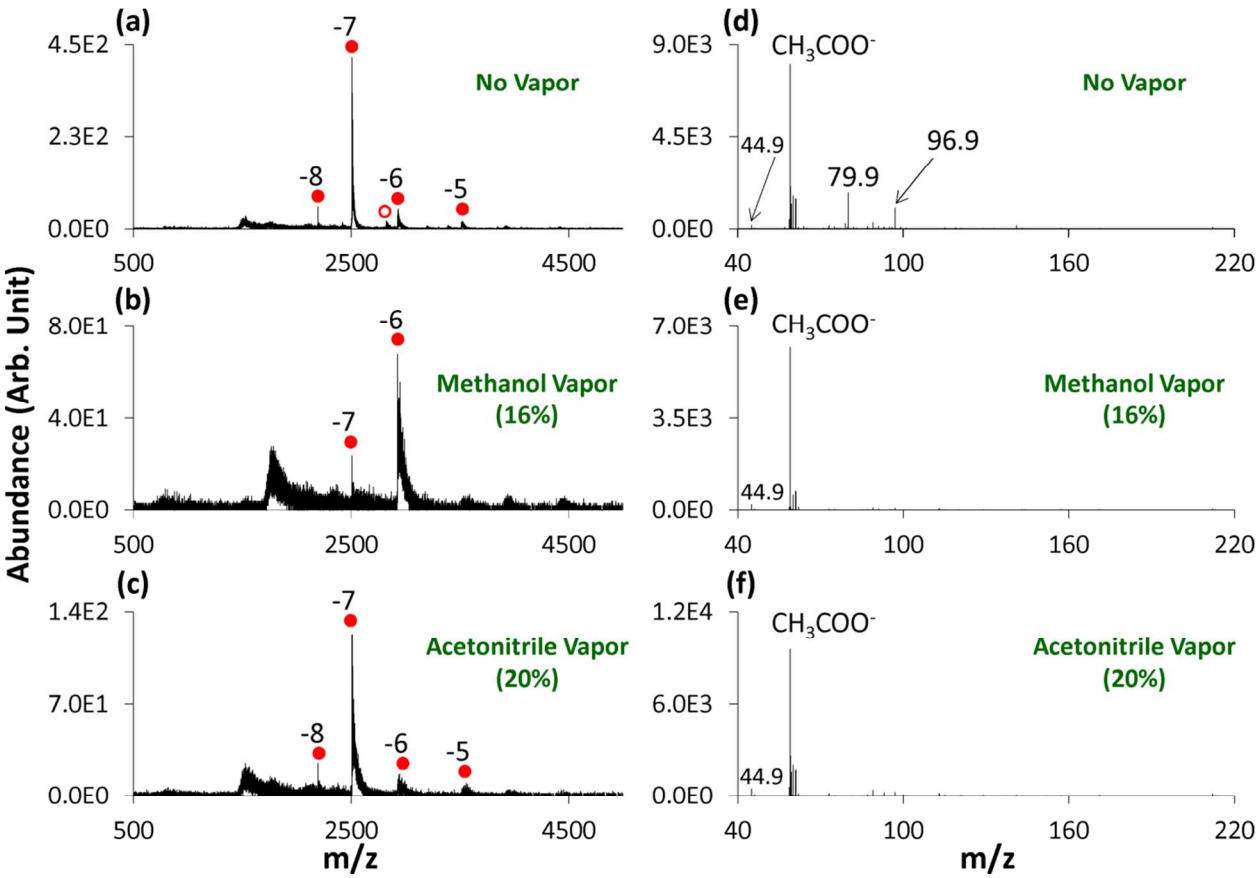
Supplemental Figure S-1. Diagram of Vapor Introduction Setup. Using Swagelok valve 1, a desired amount of N_2 curtain gas is directed across a 125-mL Erlenmeyer flask containing reagent. Above the flask, there is tubing, which allows N_2 to enter the flask and tubing that allows N_2 entrained with reagent vapor to exit the flask. A secondary N_2 gas line, which is controlled using Swagelok valve 2, is used to bring the total flow rate of curtain gas/reagent vapor to 1.1 L/min as measured using a flow meter. The curtain gas containing reagent vapor is exposed to nanoelectrospray ionized (nESI) droplets between the curtain plate and the orifice plate of a QqTOF.



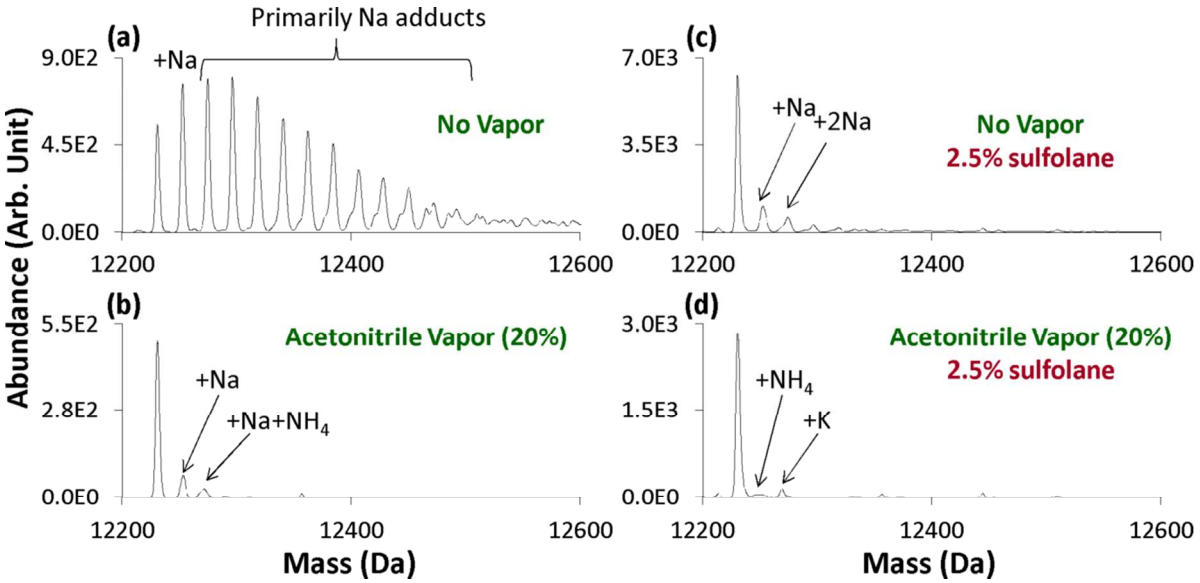
Supplemental Figure S-2. Positive nESI of 10 µM holomyoglobin prepared in (a) 1 mM ammonium acetate with no added NaCl, (b) 10 µM NaCl, (c) 100 µM NaCl, and (d) 1 mM NaCl with no reagent vapor exposure and with acetonitrile vapor (20%) exposure, respectively (e)-(h). Holomyoglobin peaks are denoted with the red filled circle symbol (●) while apomyoglobin peaks are denoted with the red open circle symbol (○).



Supplemental Figure S-3. Positive nESI of 10 μM holomyoglobin prepared in 1 mM ammonium acetate with (a) no vapor, (b) 87% water vapor, (c) 35% ethanol vapor where E denotes an ethanol molecule, (d) 47% isopropanol vapor where Ip deonotes an isopropanol molecule, (e) 8.8% acetone vapor where DMK denotes an acetone molecule, and (f) 20% ethyl acetate vapor where Et represents an ethyl acetate molecule with spectra obtained at the respective low m/z range (g)-(l). Holomyoglobin peaks are denoted with the red filled circle symbol (●) while apomyoglobin peaks are denoted with the red open circle symbol (○). N-butylbenzenesulfonamide (NBBS) is a plasticizer contaminant present in the tubing within the instrument. * In spectrum (f), the m/z 65 is $C_5H_5^+$, the m/z 91.0 is $C_7H_7^+$, the m/z 128.9 is protonated naphthalene, and m/z 149.0 is protonated phthalic anhydride. These peaks are most likely contaminates derived from the instrument tubing.



Supplemental Figure S-4. Negative nESI mass spectra of holomyoglobin (10 μM) present in ammonium acetate (1 mM) with (a) no vapor, (b) 16% methanol vapor, and (c) 20% acetonitrile vapor with spectra obtained for respective low m/z ions (d-f). In spectra (d)-(f), the m/z 44.9 ion is attributed to $[HCO_2]^-$. In spectrum (d), the m/z 96.9 ion is either $[H_2PO_4]^-$ or $[HSO_4]^-$ whereas m/z 79.9 is $[SO_3^{\bullet}]^-$. The m/z 44.9, 79.9, and 96.9 ions are attributed to contaminants derived from the myoglobin stock purchased from Sigma. Holomyoglobin peaks are denoted with the red filled circle symbol (●) while apomyoglobin peaks are denoted with the red open circle symbol (○).



Supplemental Figure S-5. Deconvoluted positive nESI mass spectra of cytochrome c (10 μM) prepared in NaCl (1 mM) and ammonium bicarbonate (10 mM) (a) and (b) in addition to 2.5% sulfolane (c) and (d). The nESI droplets were exposed to no vapors (a) and (c) and 20% acetonitrile vapor (b) and (d).