

Supporting Information for:

Hydrogen Peroxide-Induced Oxidation of Mixtures of Alkanethiols and Their Quantitative Detection as Alkanesulfonates by Negative-Ion Electrospray Ionization Mass Spectrometry

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B. Supplemental Figures

Six figures that are referenced in the original article are present here:

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A. Experimental Section

Ternary Mixtures. In order to investigate ternary mixtures of C₈SH + C₁₀SH + IS, a more extensive serial dilution scheme for the standard solutions was devised. Each set of solutions consisted of eleven standards prepared by serial dilution using the following stock solutions (all in ethanolic 1.0 mM ammonium acetate): stock solution A = 2.84 mM C₈SH (50.0 μ L neat reagent in 100 mL); stock solution B = 2.32 mM C₁₀SH (50.0 μ L neat reagent in 100 mL); IS diluting solution = 1.19 mM C₅SH (15 μ L neat reagent in 100 mL). Prior to dilution with ethanol, 15 μ L neat C₅SH was added to stock solutions A and B so that the IS concentration would be identical to that for the IS diluting solution (1.19 mM). Also prior to dilution, 0.2 mL of 30% w/w H₂O₂ was added to stock solutions A and B, as well as to the IS diluting solution, in order to provide the excess oxidant necessary for complete conversion of all thiols to sulfonates. Table S-1 below displays the serial dilution scheme and the resulting concentrations of the standards. Serial dilution of the stock solutions was only performed after the mass spectral features for both the alkanethiolates and alkanesulfonates were no longer observed.

TABLE S-1: Serial Dilution Scheme for Ternary Mixtures of Alkanethiols

Compound	
C ₈ SH	octane-1-thiol
C ₁₀ SH	decane-1-thiol
C ₅ SH	pentane-1-thiol (IS)

Stock Solutions	Compound	Conc (mM)	Procedure^a	IS/Conc
A	C ₈ SH	2.84	50 μ L/100mL	C ₅ SH/1.19
B	C ₁₀ SH	2.32	50 μ L/100mL	C ₅ SH/1.19
IS Diluting Solution	C ₅ SH	1.19	15 μ L/100mL	—————

Serial Dilutions	Mixture	Conc C₈SH (mM)	Conc C₁₀SH (mM)	Conc C₅SH (mM)
C1	5.00 mL A + 5.00 mL B	1.42	1.16	1.19
C2	5.00 mL C1 + 5.00 mL IS	0.709	0.579	1.19
C3	5.00 mL C2 + 5.00 mL IS	0.355	0.289	1.19
C4	5.00 mL C3 + 5.00 mL IS	0.177	0.145	1.19
C5	5.00 mL C4 + 5.00 mL IS	0.0887	0.0724	1.19
C6	5.00 mL C5 + 5.00 mL IS	0.0443	0.0362	1.19
C7	5.00 mL C6 + 5.00 mL IS	0.0222	0.0181	1.19
C8	5.00 mL C7 + 5.00 mL IS	0.0111	0.00904	1.19
C9	5.00 mL C8 + 5.00 mL IS	0.00554	0.00452	1.19
C10	5.00 mL C9 + 5.00 mL IS	0.00277	0.00226	1.19
C11	5.00 mL C10 + 5.00 mL IS	0.00139	0.00113	1.19

^aVolumes correspond to the μ L of neat reagent in 100 mL of solution.

TABLE S-2: Typical ESI-IT-MS Operating Parameters for Quantitative Analyses

<i>Binary Mixtures</i>	$C_8SO_3^-$ (+ IS)	$C_{10}SO_3^-$ (+ IS)
Capillary Temperature (°C)	350	350
Sheath gas flow rate (arb)	20	20
Aux/Sweep gas flow rate (arb)	20	20
Spray Voltage (kV)	4.5	4.5
Capillary Voltage (V)	−11.00	−9.00
Tube Lens Offset (V)	−25.00	−30.00
<i>Ternary Mixtures</i>	$C_8SO_3^- + C_{10}SO_3^-$ (+ IS) ($C_8SO_3^-$ tune parameters)	$C_8SO_3^- + C_{10}SO_3^-$ (+ IS) ($C_{10}SO_3^-$ tune parameters)
Capillary Temperature (°C)	350	350
Sheath gas flow rate (arb)	20	20
Aux/Sweep gas flow rate (arb)	20	20
Spray Voltage (kV)	4.5	4.5
Capillary Voltage (V)	−47.00	−47.00
Tube Lens Offset (V)	−40.00	−60.00

B. Supplemental Figures (located on following pages)

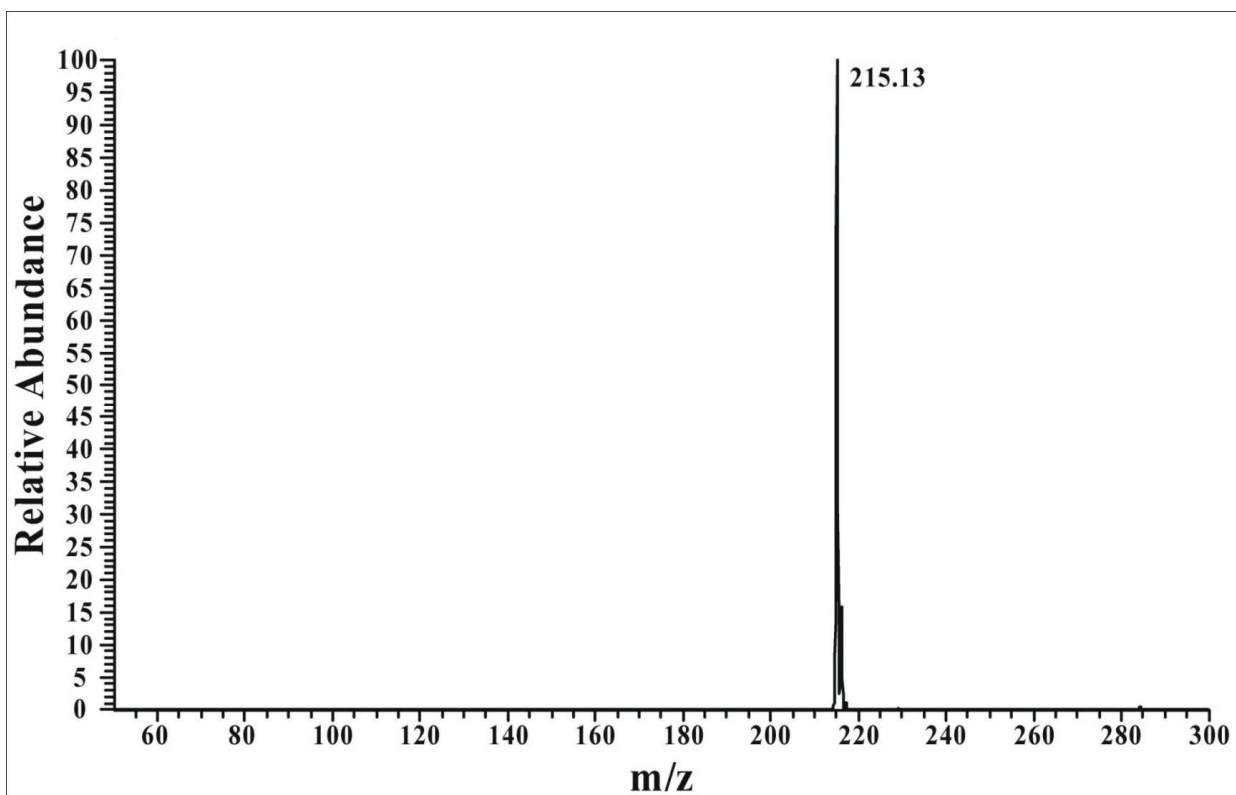


Figure S-1. Positive-ion ESI mass spectrum of n-alkanethiol mixture, consisting of C₄SH, C₈SH, C₁₀SH, C₁₂SH, and C₁₈SH (1 mM each) and Proton SpongeTM (PS = 25 mM) in methanol, showing the (M+1) peak ($m/z = 215$) associated with PS.

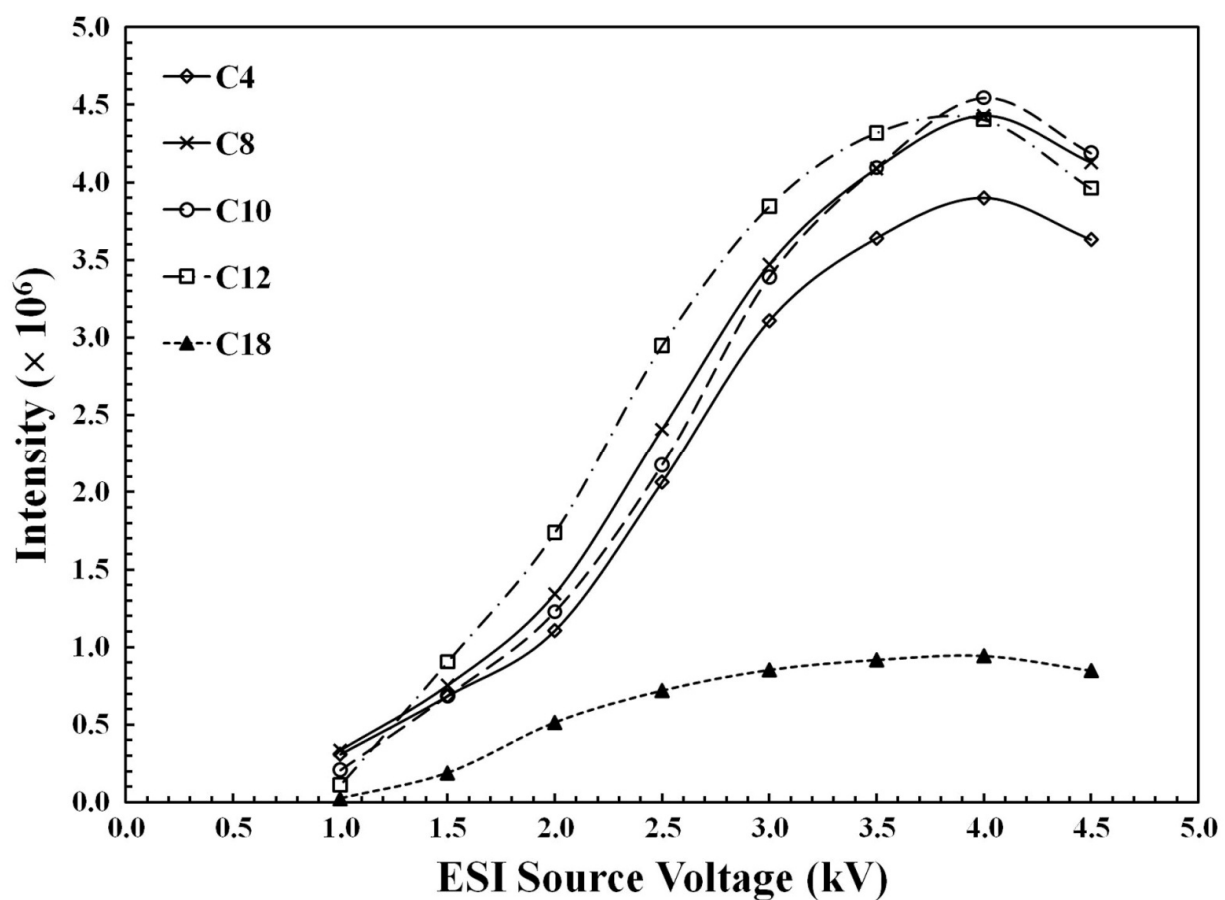


Figure S-2. Effect of ESI source voltage (V_s) on the absolute intensities of various n-alkanesulfonates (monomers) observed by negative-ion ESI-IT-MS. Spectra acquired from an n-alkanethiol mixture consisting of C_4SH , C_8SH , $C_{10}SH$, $C_{12}SH$, and $C_{18}SH$ (1 mM each) and H_2O_2 (25 mM) in methanol. Capillary temperature = 250 °C; flow rate = 30 $\mu L/min$.

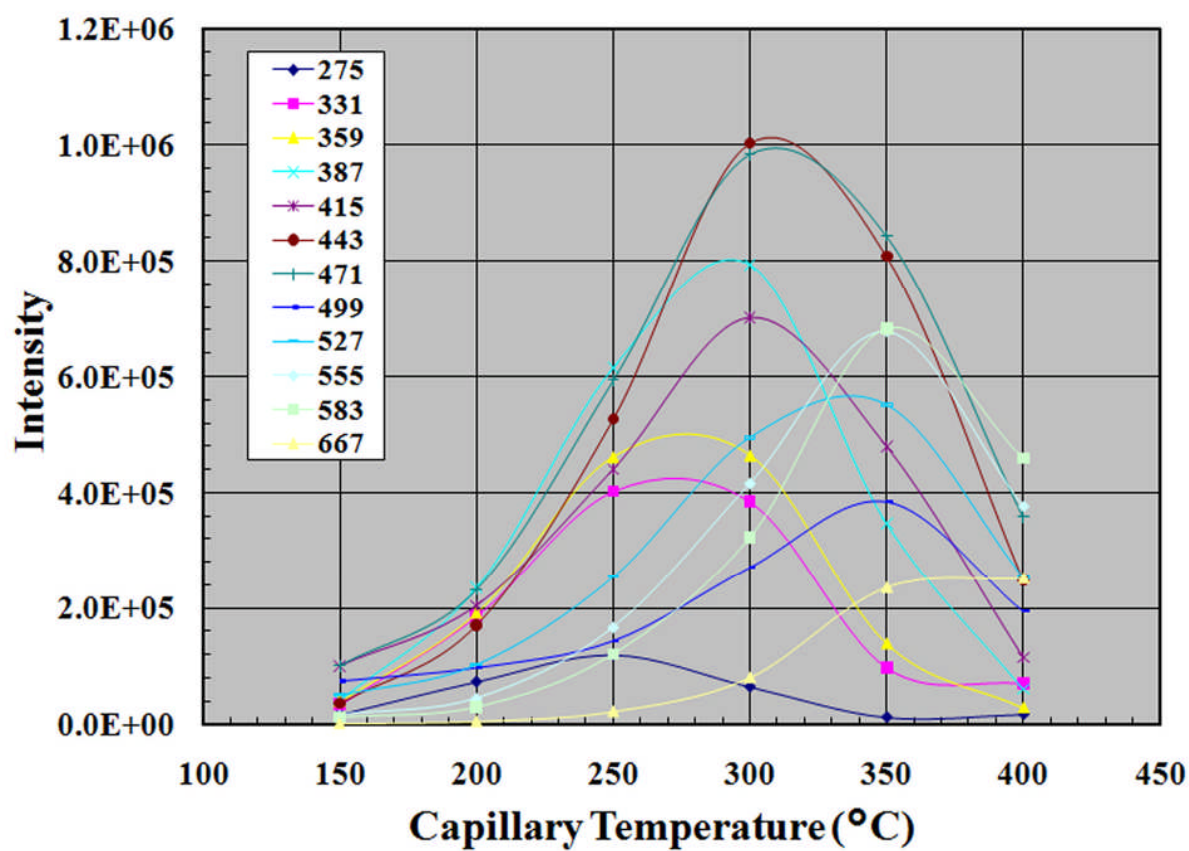


Figure S-3. Effect of ion transfer capillary temperature on absolute ESI-IT-MS intensities of alkanesulfonate dimeric adducts. Plot includes both hetero- and homodimers (see Table 1 from text for nominal m/z assignments). ESI source voltage = 4.5 kV.

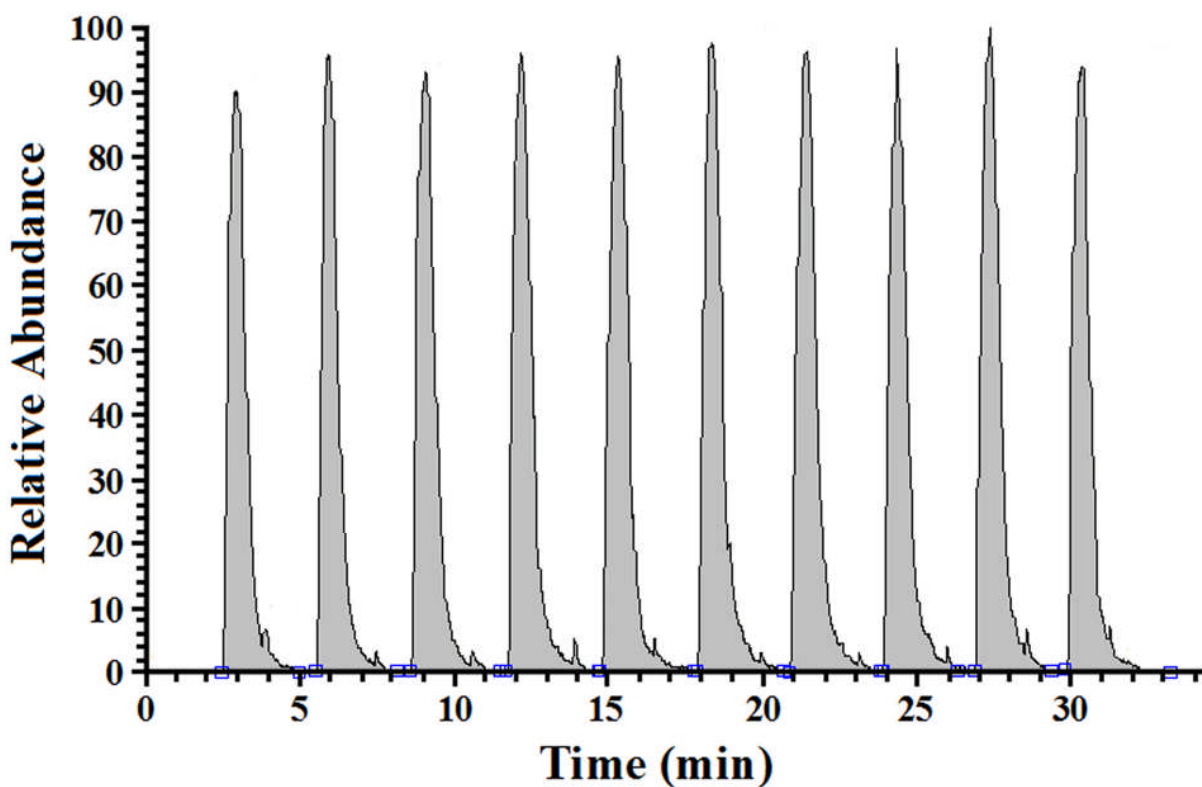


Figure S-4. Plot of the measured $C_8SO_3^-$ peak intensity (at m/z 193) as a function of time for a typical set of ten 20.0- μ L loop injections from a ternary alkanethiol standard solution (0.177 mM C_8SH + 0.145 mM $C_{10}SH$ + 1.189 mM C_5SH IS), showing the level of reproducibility associated with our sample injection method. Integrated areas for each injection (shaded regions) were determined and used for plotting the calibration data.

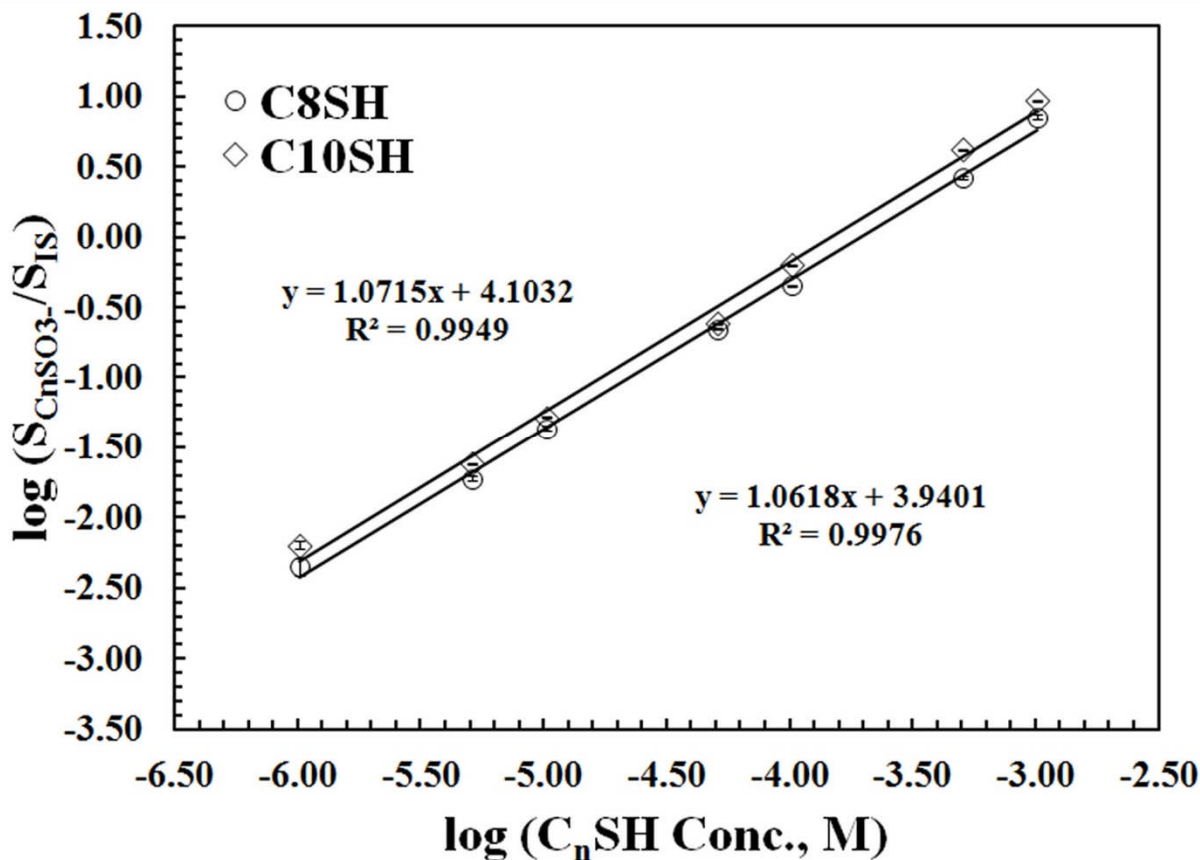


Figure S-5. Linear dynamic range observed by negative-ion ESI-IT-MS for C_8SO_3^- or $\text{C}_{10}\text{SO}_3^-$ in binary solutions with C_5SO_3^- (1.00 mM) as the internal standard (IS). The range of concentrations extends from 1.02 to 0.00102 mM. Data point symbols are enlarged so that the error bars are not obscured. All error bars represent 95% confidence intervals for 8-10 loop injections from each solution. ESI source voltage = 4.5 kV; capillary temperature = 350 °C. For C_8SO_3^- , linear regression of only the central five points yields a slight improvement in the quality of the fit ($y = 1.0597x + 8.8790$, $R^2 = 0.9996$). For $\text{C}_{10}\text{SO}_3^-$, leaving out the center and lowest concentrations (at 51.2 μM C_{10}SH and 1.02 μM C_{10}SH , respectively) yields a small improvement in the linear regression ($y = 1.1226x + 9.5876$, $R^2 = 0.9997$).

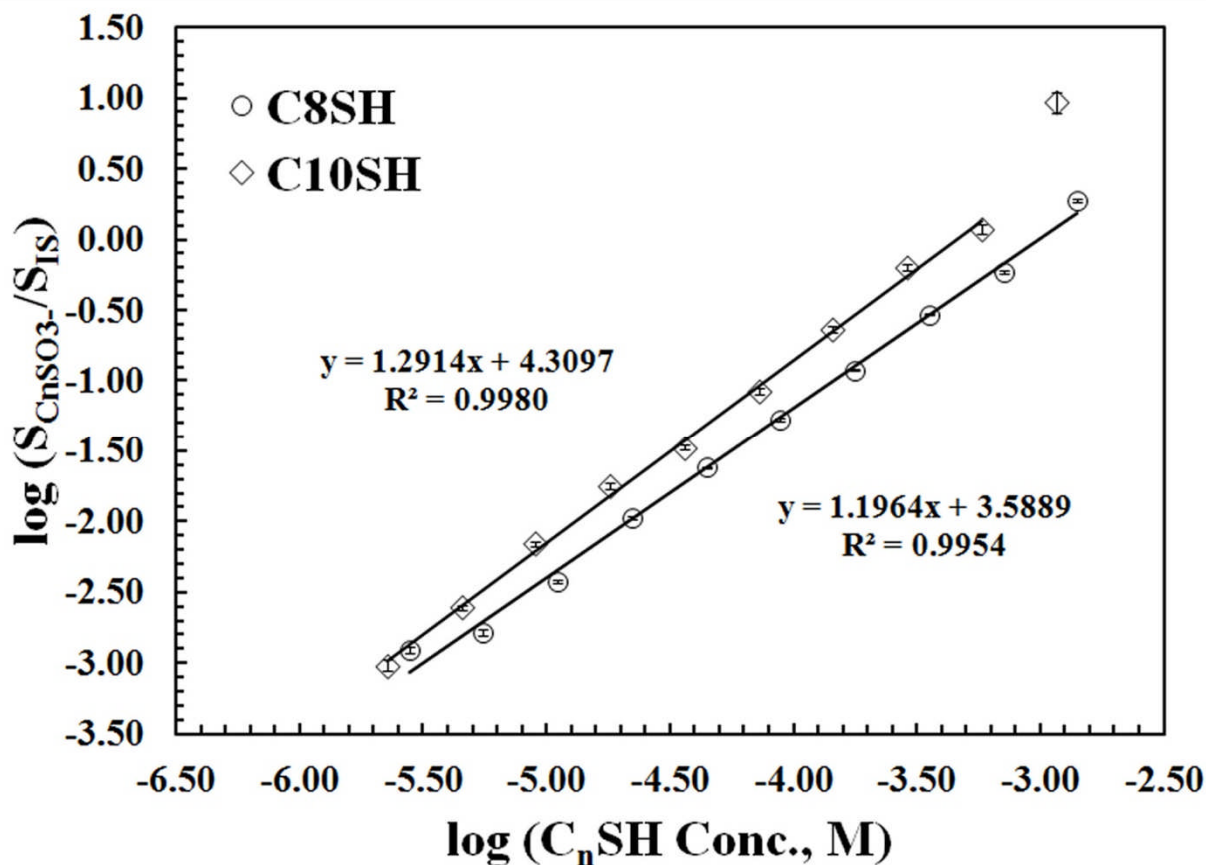


Figure S-6. Linear dynamic range observed by negative-ion ESI-IT-MS for $C_8SO_3^-$ or $C_{10}SO_3^-$ in ternary solutions containing both compounds with $C_5SO_3^-$ (1.19 mM) as the IS. The $C_8SO_3^-$ concentration range extends from 1.42 to 0.00139 mM; the $C_{10}SO_3^-$ concentration range extends from 1.16 to 0.00113 mM. Data point symbols are enlarged so that the error bars are not obscured. Note that the linear regression for the ternary $C_{10}SO_3^-$ data reflects only the lowest nine concentrations. All error bars represent 95% confidence intervals for 8-10 loop injections from each solution. ESI source voltage = 4.5 kV; capillary temperature = 350 °C.