Supplementary Information for "Rapid Detection of Sugar Alcohol Precursors and Corresponding Nitrate Ester Explosives using Direct Analysis in Real Time Mass Spectrometry"

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This SI contains additional representative mass spectra highlighting special case sugar alcohols, such as inositol and maltitol, as well as those used to highlight the parametric experiments that were completed. Also included are additional figures to further support the sensitivity and incorporation of dopants portions of the article.

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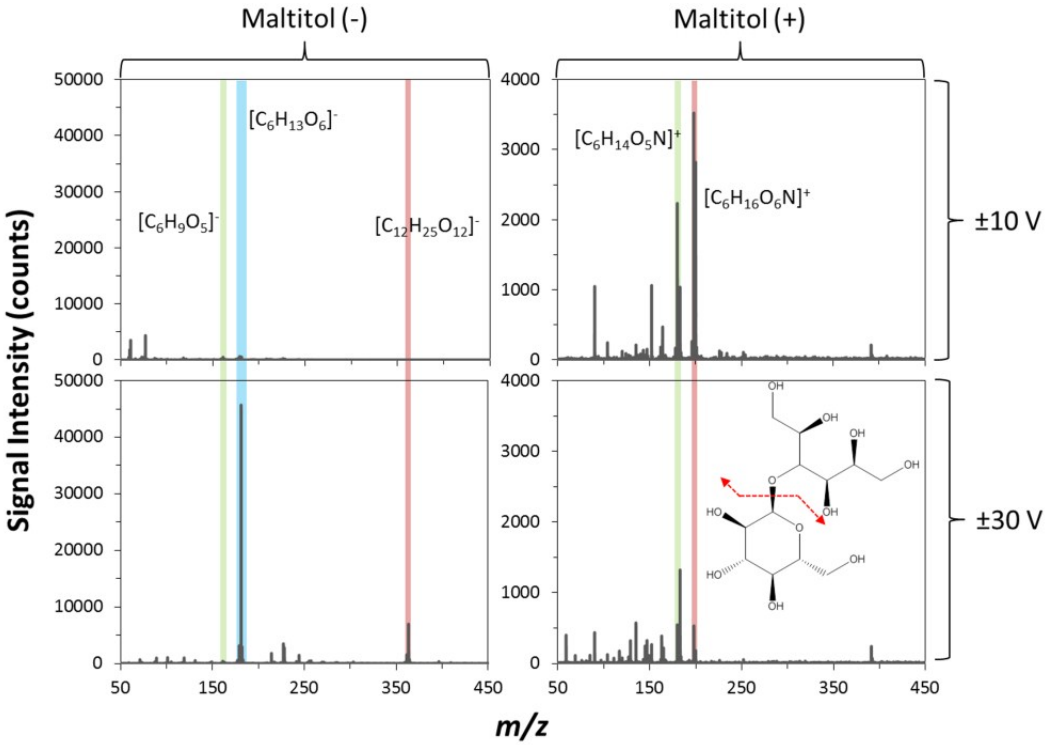

Figure S1. Negative ion (left) and positive ion (right) mass spectra of the disaccharide sugar alcohol, maltitol, at ±10 V (top) and ±30 V (bottom) first orifice plate voltages. Select peaks of interest have been identified. Inset shows the common fragmentation pathway.

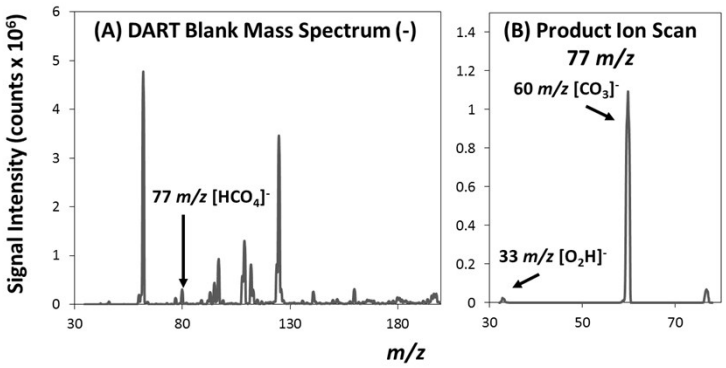

Figure S2. MS/MS mass spectra for the confirmation of the 77 *m/z* adduct species as $[HCO_4]^-$. Both a blank full scan mass spectrum (A) and a product ion scan of 77 *m/z* (B) are shown. The product ion scan supports the formation of the $[HCO_4]^-$ ion over the alternative $[HN_2O_3]^-$ due to the lack of nitrogen species in the product ion scan even though there is abundant nitrate in the blank mass spectrum (A). Both the blank mass spectrum and product ion scan were obtained by coupling the DART-SVP source to an ABSciex QTrap4000 with a Vapur® interface. Identical DART parameters were used with the exception of N_2 as the analysis gas instead of He. Additional parameters for the QTrap included 68.9 kPa curtain gas, no ion source gases, an inlet temperature of 150 °C, a mass scan range of 30 *m/z* to 200 *m/z* at a rate of 1 scan/s, 20 eV collision energy, and a declustering potential of -75 V.

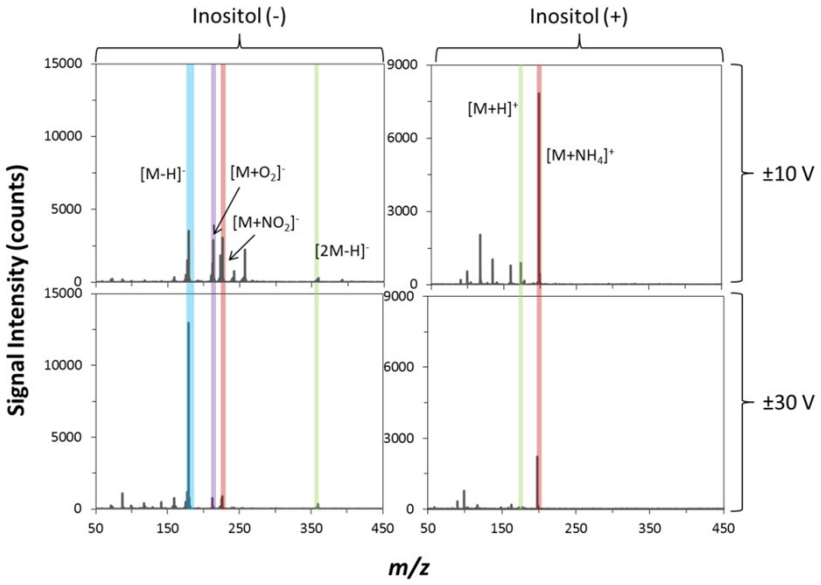

Figure S3. Negative ion (left) and positive ion (right) mass spectra of the ringed monosaccharide sugar alcohol, inositol, at both ±10 V (top) and ±30 V (bottom) first orifice plate voltages. Select peaks of interest have been identified.

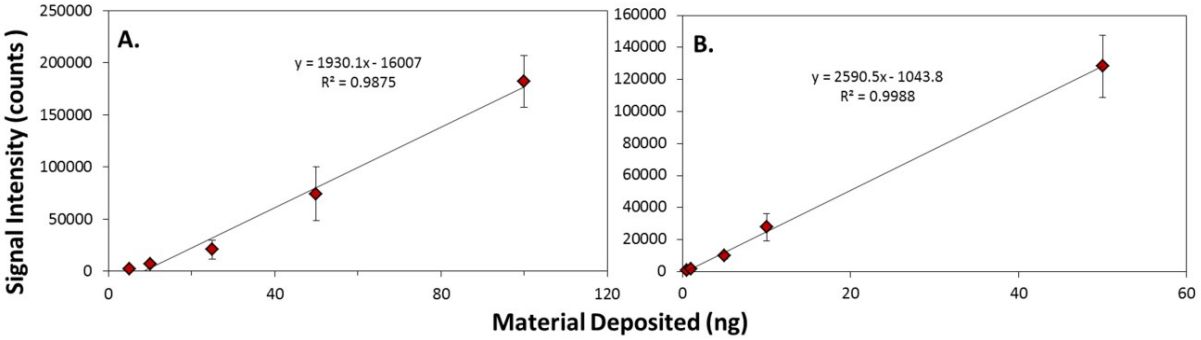

Figure S4. Linear response curves for xylitol (A.) and pentaerythritol (B.). Uncertainty is expressed as the standard deviation of four replicate measurements.

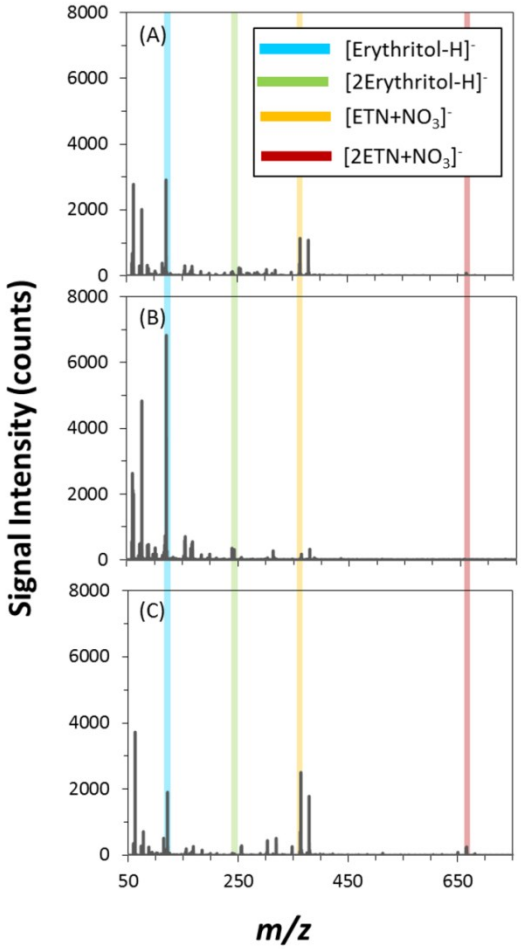

Figure S5. Representative negative ion mass spectra of mixtures containing varying levels of erythritol and erythritol tetranitrate (ETN). The mixtures represented contain 50 ng of each (A), 50 ng of erythritol in the presence of 5 ng ETN (B), and 5 ng erythritol in the presence of 50 ng ETN (C). Select peaks relating to erythritol (blue and green) and ETN (orange and red) are highlighted.

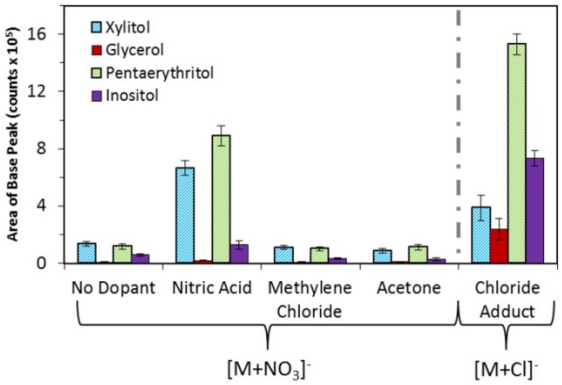

Figure S6. Peak area of the nitrate adduct $[M+NO_3]^-$ of select sugar alcohols in the presence of various dopant species (left of the dotted line). The plot highlights the increase in the nitrate adduct ion signal in the presence of nitric acid. Also depicted is the response of the chloride adduct peak $[M+Cl]^-$ when methylene chloride was introduced as the dopant (right of the dotted line). In all instances, the peak area is the average of four 100 ng deposits that were interrogated until complete consumption. Uncertainty is expressed as the standard deviation of four replicate samples.

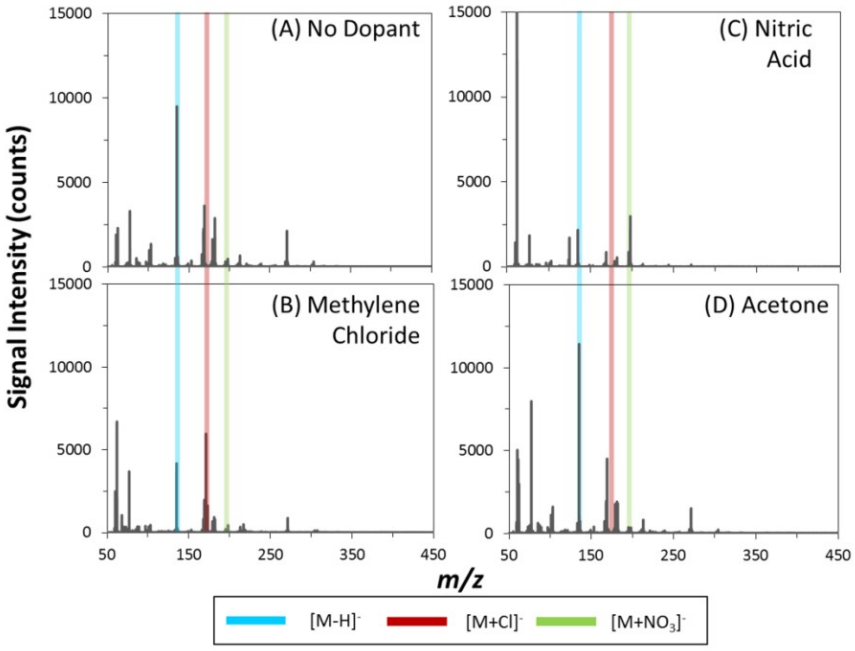

Figure S7. Representative negative ion mass spectra of 100 ng deposits of pentaerythritol (MW: 136 Da) without the presence of a dopant (A) and in the presence of the dopants that were examined: methylene chloride (B), nitric acid (C), and acetone (D). Select peaks related to pentaerythritol and the adducts formed in the presence of the dopants are highlighted. "M" refers to a pentaerythritol molecule.

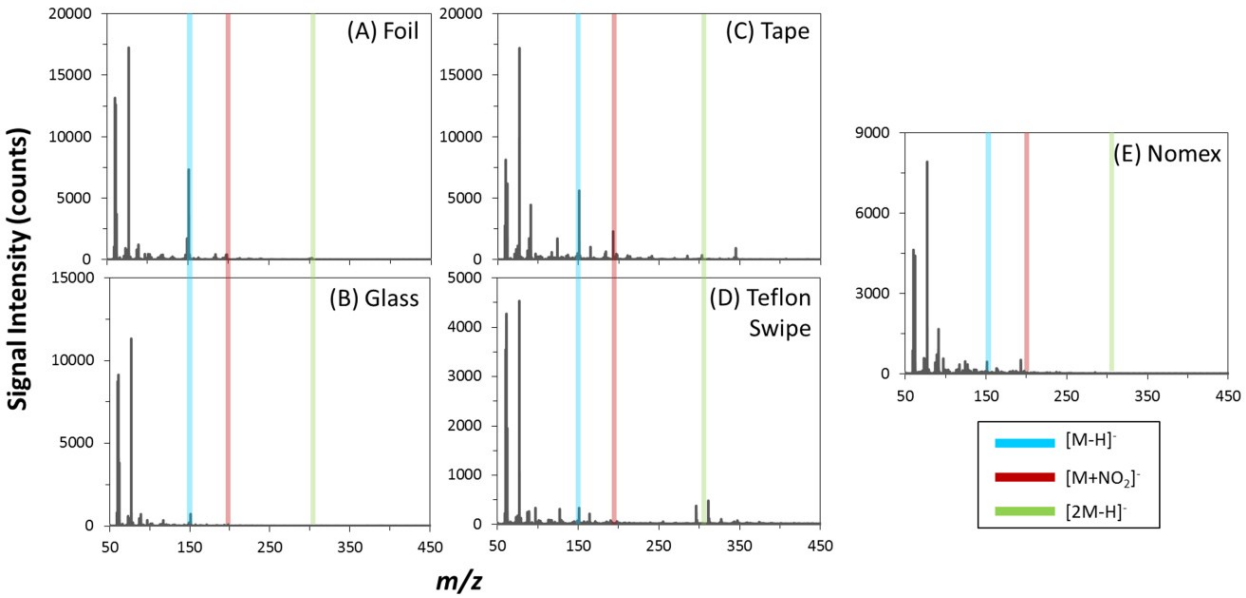

Figure S8. Representative negative ion mass spectra for 100 ng deposits of xylitol (MW: 152 Da) off a number of different surfaces. The surfaces analyzed include aluminum foil (A), a glass microscope slide (B), a piece of adhesive tape (C), a PTFE-coated fiberglass weave swipe (D), and a Nomex swipe (E). Select peaks relating to xylitol are highlighted. "M" refers to a xylitol molecule.

§ Certain commercial products are identified in order to adequately specify the procedure; this does not imply endorsement or recommendation by National Institute of Standards and Technology, nor does it imply that such products are necessarily the best available for the purpose.