

Supporting Information

Non-Proximate Detection of Explosives and Chemical Warfare Agent Simulants by Desorption Electrospray Ionization Mass Spectrometry

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Abstract: Additional information regarding sample analysis and preparation is provided. Also, additional data is included for the chemical warfare agent simulant DMMP at distances of 2 mm, 1 and 3 meters from the mass spectrometer.

Source parameters are summarized elsewhere.¹ Ions were sampled and analyzed using a Thermo Finnigan LTQ mass spectrometer in both positive and negative ion modes. Certified standards for all explosives except TATP and Composition C4 were used to prepare the samples by dilution in methanol to the desired concentration. TATP was synthesized as described in the literature,² and it showed a melting point of 97-98 °C, consistent with reported values.^{3,4}

Figure S-1a shows the positive ion DESI spectrum of 0.5 ng of DMMP deposited within an area of 1 cm² on paper with the DESI source placed at a distance of 2 mm from the mass spectrometer. The most significant adducts ions occur at m/z 147 and m/z 271, corresponding to the [DMMP + Na]⁺ and [2DMMP + Na]⁺ adducts respectively as confirmed by tandem MS. At 1 meter from the mass spectrometer (Fig S-1b), the relative abundances for the ions at m/z 147 [DMMP + Na]⁺ and m/z 271 [2DMMP + Na]⁺ were inverted, showing the dimer as the favored species probably due to collisions with other molecules during transfer to the mass spectrometer, which stabilize the complex, or to [DMMP + Na]⁺ adduct ions that prefer to recombine with other neutral DMMP molecules. At 1 meter, a significant reduction in the background ion population is observed as compared to the mass spectrum taken at 2 mm from the mass spectrometer. An ion at m/z 229 is also observed in the mass spectrum and corresponds to a background ion that survived transport to the mass spectrometer. The absolute abundance of the ion at m/z 271 was decreased 2 orders in magnitude as compared to the absolute abundance obtained at 2 mm from the mass spectrometer. At 3 meters from the mass spectrometer, the only ion present in the mass spectrum of 3 ng DMMP deposited in 1 cm² on paper was the dimer [2DMMP + Na]⁺ at m/z 271, showing the absolute absence of background ions from the spectrum (Fig S-1c). The absolute abundance for this adduct ion was further decreased another order in magnitude as compared to the absolute abundance obtained at 1 meter from the mass spectrometer.

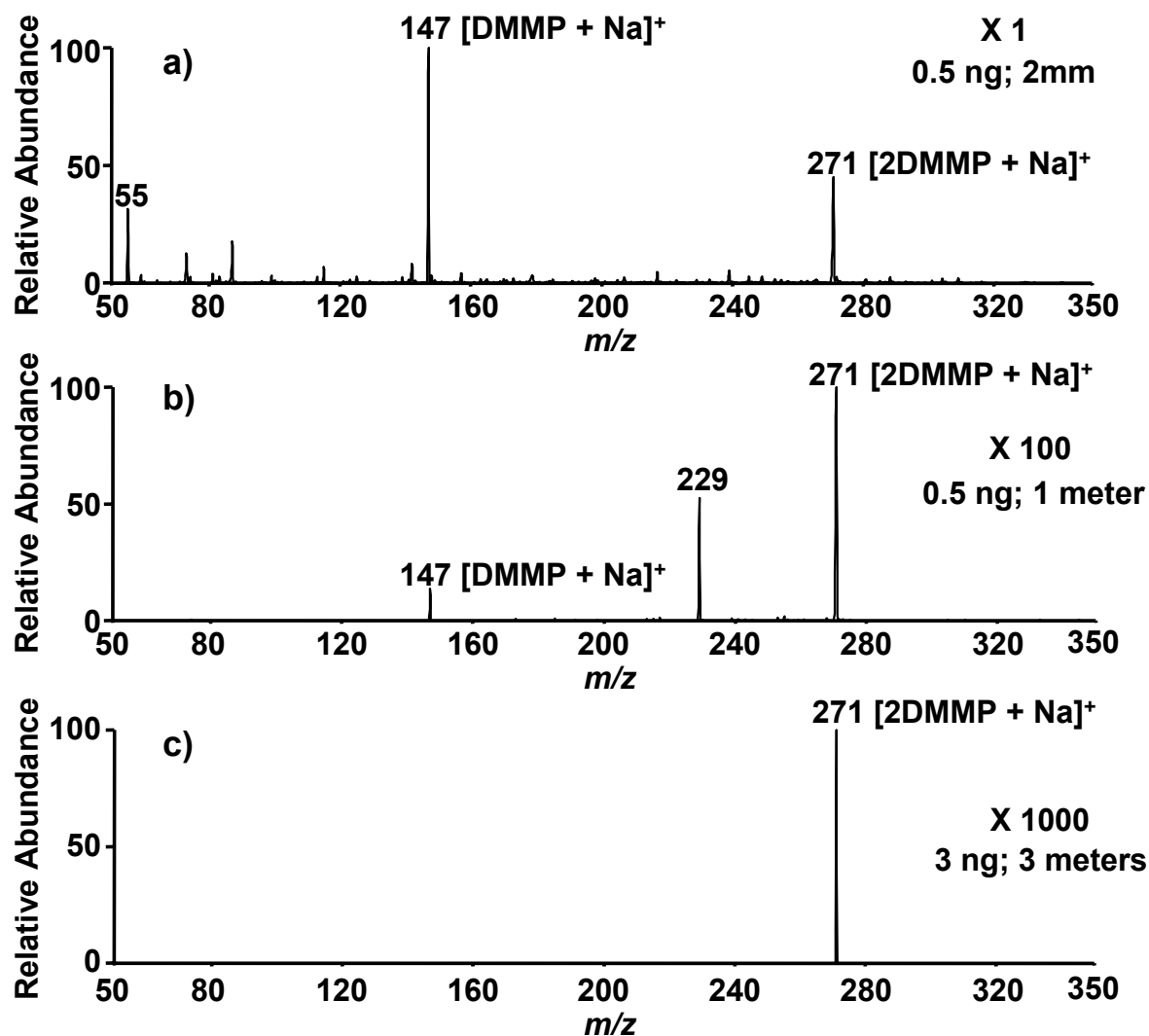


Figure S-1 Positive ion DESI spectrum of 0.5 ng DMMP deposited on 1 cm² of paper analyzed at a distance of 2 mm (a) and 1 meter (b) from the mass spectrometer. Methanol/water (50:50) was used as the spray solvent. (c) Positive ion DESI spectrum of 3 ng DMMP deposited on 1 cm² of paper at a distance of 3 meters from the mass spectrometer.

- 1 I. Cotte-Rodriguez, Z. Takáts, N. Talaty, H. Chen, and R. G. Cooks, *Anal. Chem.*, 2005, **77**, 6755-6764.
- 2 N. A. Milas and A. Golubovic, *J. Am. Chem. Soc.*, 1959, **81**, 6461-6462.
- 3 H. K. Evans, F. A. J. Tulleners, B. L. Sanchez, and C. A. Rasmussen, *J. Forensic Sci.*, 1986, **31**, 1119-1125.
- 4 J. C. Oxley, J. L. Smith, K. Shinde, and J. Moran, *Propellants, Explos., Pyrotech.*, 2005, **30**, 127-130.