Supporting Information for: Broad spectrum infrared thermal desorption of wipe-based explosive and narcotic samples for trace mass spectrometric detection

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Supplemental Experimental Methods

The Venturi-assisted flow component used compressed nitrogen at 105 kPa to drive analyte flow from the IRTD through a discharge ionization region (consisting of a needle at 5 kV_{rms}) and toward the mass spectrometer inlet.

Absorbance measurements. Fourier transform infrared spectroscopy (FTIR) was used measure absorbance in the infrared spectral window for powdered forms of select narcotics (heroin and methamphetamine) and explosives (RDX and PETN), as well as the wipe substrate (PTFE-coated fiberglass) and glass-mica housing cap. Absorbance spectra were collected using an IR-microscope (IlluminatIR, Smiths Detection, Edgewood, MD, USA) operated in attenuated total reflectance (ATR) mode. A total of 128 scans were averaged with 8 cm^{-1} resolution across a range of 650 cm^{-1} to 4000 cm^{-1} (15.4 μm to 2.5 μm). Samples were evaluated by placing approximately 200 μg of powdered material on a low-e microscope slide (MirrIR, Kevley Technologies, Chesterland, OH, US) or directly from the substrate surface.

Temperature measurements. Temperature measurements of the wipe substrate were conducted with a K-type thermocouple and a custom data acquisition system (LabVIEW, National

Instruments) to qualitatively investigate the heating ramp experienced by the wipe. It is important to note that the thermocouple materials also experienced the radiative energy from the infrared emitter, skewing the quantitative temperature magnitude. The thermocouple was woven into the mesh of the wipe and inserted into the thermal desorber prior to heating. Temperature data was acquired at a rate of 40 Hz for 5 s emission durations as a function of increasing power. The system was allowed to cool to room temperature following each measurement. Wipe temperature measurements for ion mobility spectrometry (IMS) instruments (Figure S6) were conducted in the same manner, however, heating duration was dependent on duration within the constant temperature thermal desorber.

Table S1. Select compounds from the synthetic fingerprint material and corresponding dominant observed ion, mode (positive or negative), molecular mass, and *m/z* value. Preliminary peak assignments based on knowledge of compounds nominal mass, common ionization pathways, and past experiences.

Compound	***m/z***	±	**Ion Observed**	**Molecular mass**
Valine	118	+	$[M+H]^+$	117
Octanoic Acid	145	+	$[M+H]^+$	144
Valine (dimer)	235	+	$[2M+H]^+$	117
Palmitic Acid	257	+	$[M+H]^+$	256
Oleic Acid	283	+	$[M+H]^+$	282
Squalene	412	+	$[M+H]^+$	411
Tridecanoic Acid (dimer)	429	+	$[2M+H]^+$	214
Palmitic Acid (dimer)	513	+	$[2M+H]^+$	256
Hexanoic Acid	115	-	$[M-H]^-$	116
Octanoic Acid	143	-	$[M-H]^-$	144
Nonanoic Acid	157	-	$[M-H]^-$	158
Decanoic Acid	171	-	$[M-H]^-$	172
Lauric Acid	199	-	$[M-H]^-$	200
Tridecanoic Acid	213	-	$[M-H]^-$	214
Myristic Acid	227	-	$[M-H]^-$	228
Pentadecanoic Acid	241	-	$[M-H]^-$	242
Palmitic Acid	255	-	$[M-H]^-$	256
Linoleic Acid	279	-	$[M-H]^-$	280
Oleic Acid	281	-	$[M-H]^-$	282
Stearic Acid	283	-	$[M-H]^-$	284
Arachidic Acid	311	-	$[M-H]^-$	312
Decanoic Acid (dimer)	343	-	$[2M-H]^-$	172

Emitter Spectral Distribution. The near infrared emitter used here was estimated as a blackbody emitter with a spectral intensity following the Planck distribution [1]. The blackbody spectral intensity is given by:

$$I_{\lambda,b}(\lambda,T) = \frac{2hc^2}{\lambda^5[\exp(hc/\lambda k_B T)-1]} \tag{1}$$

Where, h is the Planck constant, k_B is the Boltzmann constant, c is the speed of light in vacuum, and T is the blackbody temperature. Figure S2 demonstrates the spectral intensity as a function of wavelength and temperature, along with a normalized plot to simplify visualization.

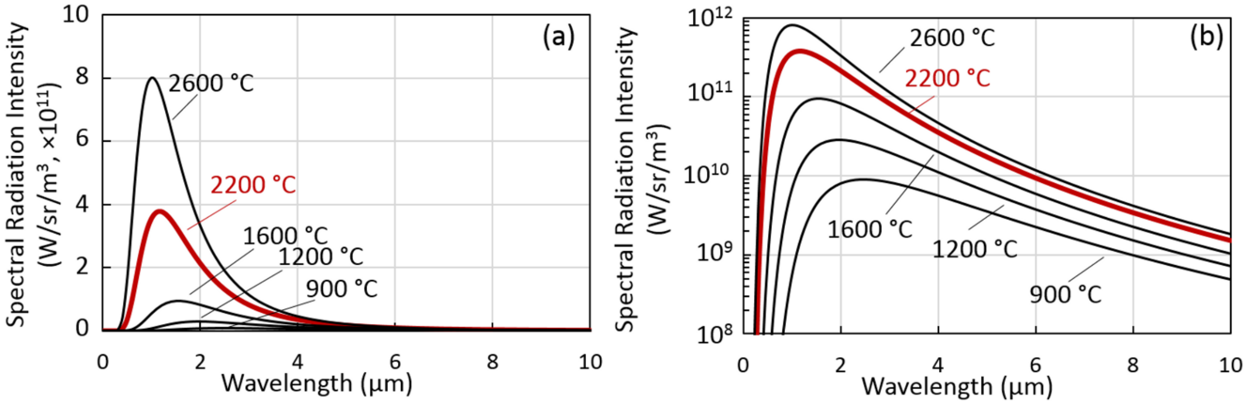


Figure S1. Spectral distributions for a range of filament temperatures based on blackbody emission ((a) linear and (b) semi-log scales). The near infrared emitter, with filament temperature of ~2200 °C as provided by manufacturer – Heraeus Noblelight, is highlighted. Details of the emitter can be found in the article text.

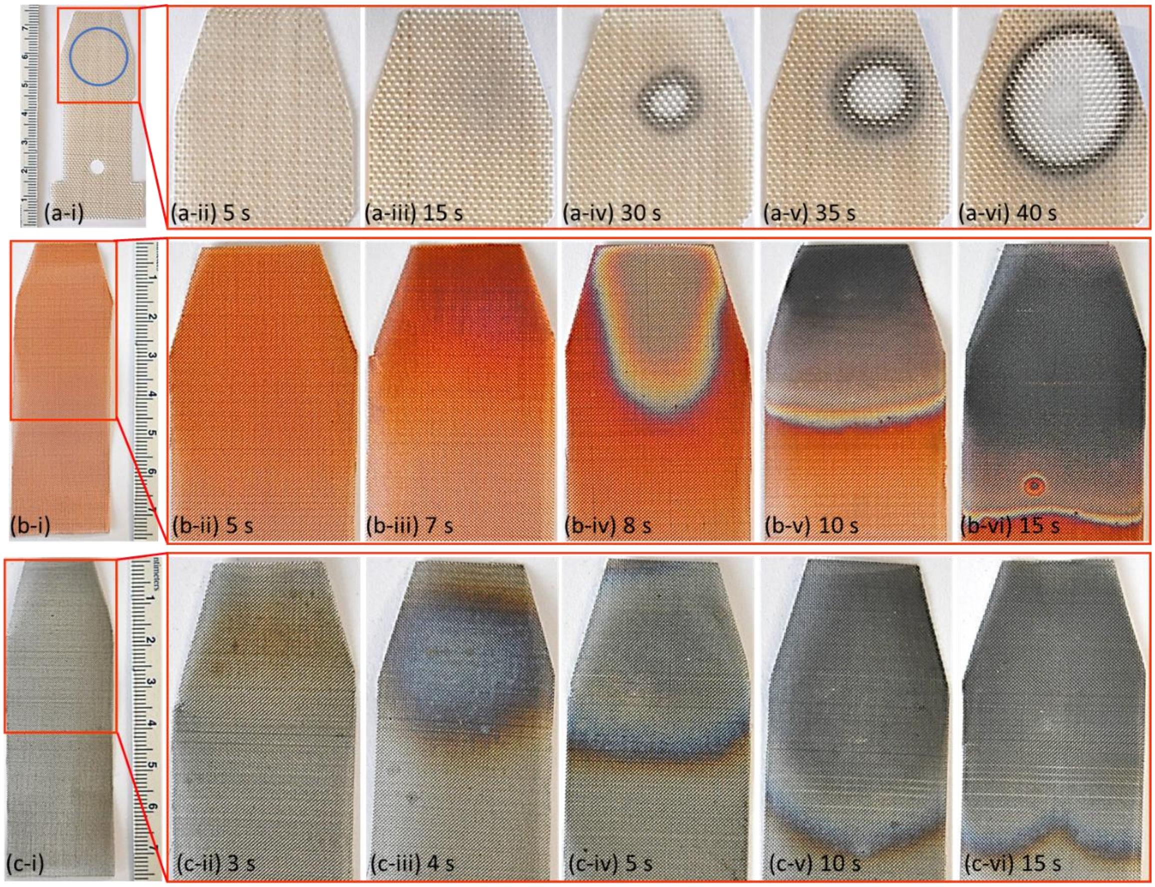


Figure S2. Visual representation of the wipe heating spatial distribution within the infrared thermal desorber for 100 % emission as a function of increasing time for (a) PTFE-coated fiberglass wipes, (b) copper mesh wipes, and (c) nickel mesh wipes. Blue circle represents the typical target collection area for wipe sampling procedures.

Figure S3 displays the observed decrease in signal of 100 ng ETN for increasing supply pressure, which correlated with increasing flow rates and further decreasing residence times (infrared emitter power and duration: 50 %, 10s). This decrease resulted from incomplete ionization of the locally high concentration of molecules and the mismatch between the temporally short ion packet and 0.5 s *m/z* window scan time (*m/z* 30 to *m/z* 600). In addition, a shift from the nitrate adduct to other adducts was experienced at higher pressures, further reducing the intensity of the monitored ion. At lower supply pressures, ETN displayed adduct formation with anion species associated with the discharge ionization, including *m/z* 319, $[ETN+OH]^-$, *m/z* 364 $[ETN+NO_3]^-$, and *m/z* 379 $[ETN+HCO_4]^-$. As the supply pressure was increased, higher levels of ambient laboratory air were entrained resulting in a shift in background anions, most notably, the increase in *m/z* 60 CO_3^- and *m/z* 77 HCO_4^- .

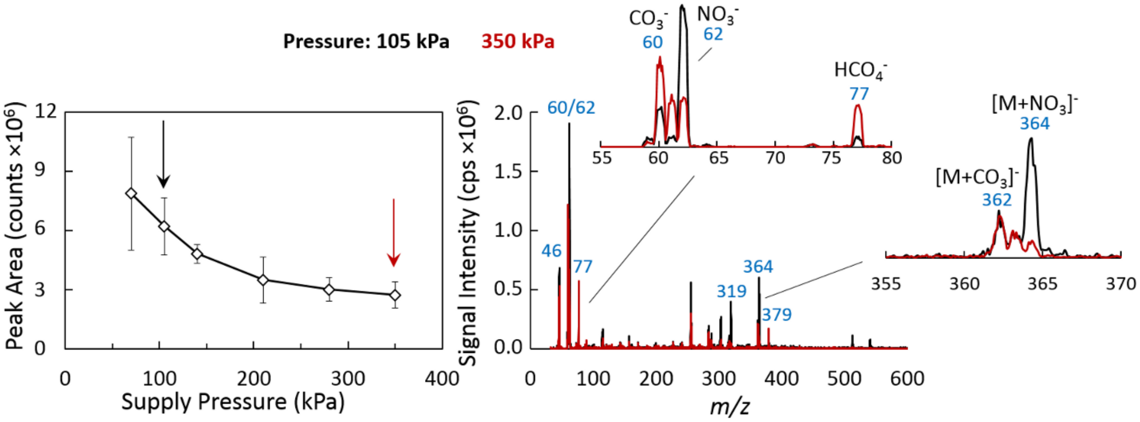
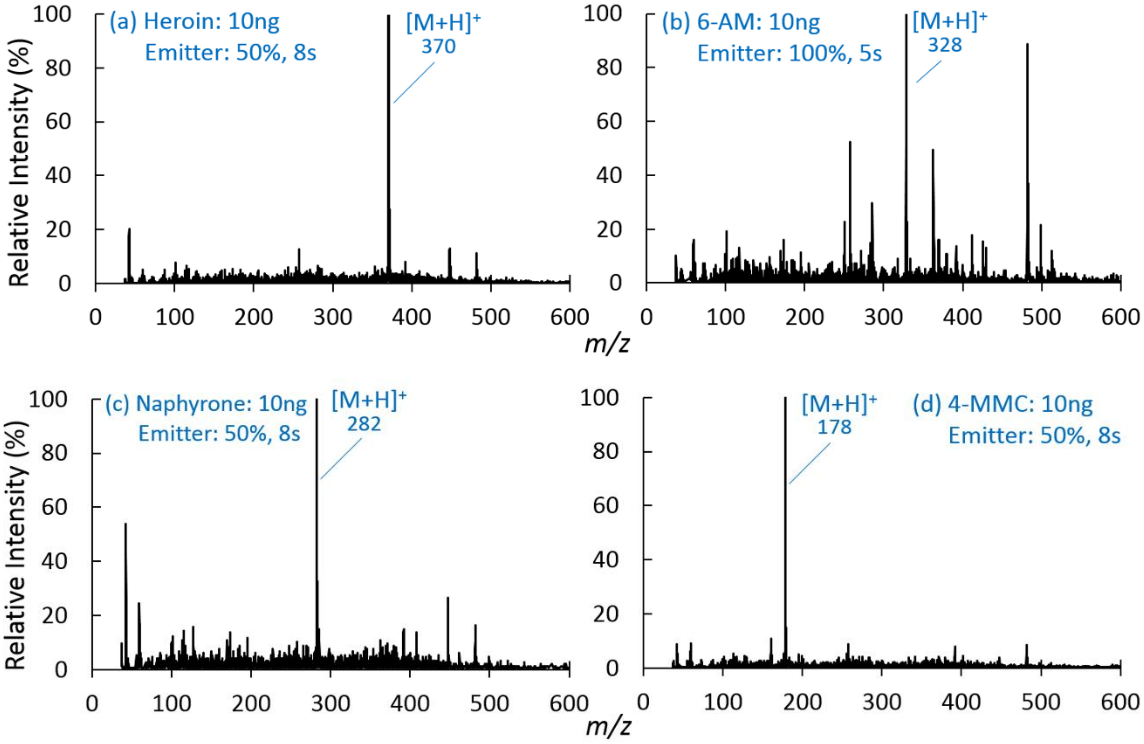
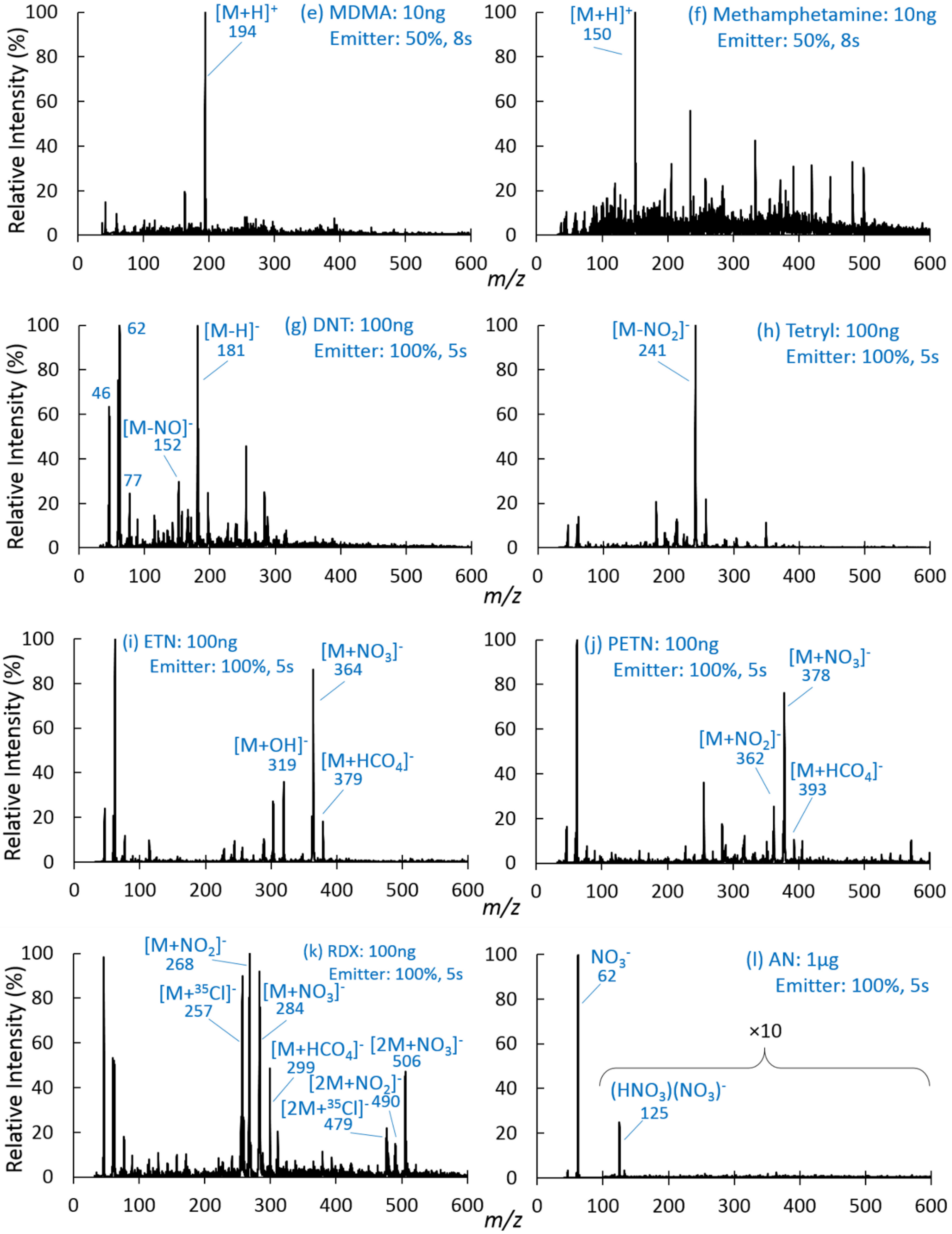


Figure S3. IRTD-MS integrated signal for the ETN nitrate adduct as a function of flow inducing supply pressure (50 % power / 10s / 100 ng samples). Inset displays representative mass spectra for 105 kPa and 350 kPa supply pressures. Identified ion correspond to *m/z* 46 NO_2^-, *m/z* 60 CO_3^-, *m/z* 62 NO_3^-, *m/z* 77 HCO_4^-, *m/z* 319 $[ETN+OH]^-$, *m/z* 364 $[ETN+NO_3]^-$, and *m/z* 379 $[ETN+HCO_4]^-$. Data points and uncertainty represent the average peak area and standard deviations for five replicate measurements.




Relative Intensity (%)
m/z
[M+H]+ 194
(e) MDMA: 10ng
Emitter: 50%, 8s
[M+H]+ 150
(f) Methamphetamine: 10ng
Emitter: 50%, 8s
62
46
[M-NO]- 152
77
[M-H]- 181
(g) DNT: 100ng
Emitter: 100%, 5s
[M-NO2]- 241
(h) Tetryl: 100ng
Emitter: 100%, 5s
(i) ETN: 100ng
Emitter: 100%, 5s
[M+NO3]- 364
[M+OH]- 319
[M+HCO4]- 379
(j) PETN: 100ng
Emitter: 100%, 5s
[M+NO3]- 378
[M+NO2]- 362
[M+HCO4]- 393
[M+NO2]- 268
(k) RDX: 100ng
Emitter: 100%, 5s
[M+35Cl]- 257
[M+NO3]- 284
[M+HCO4]- 299
[2M+NO3]- 506
[2M+NO2]- 490
[2M+35Cl]- 479
NO3- 62
(l) AN: 1µg
Emitter: 100%, 5s
×10
(HNO3)(NO3)- 125
0
20
40
60
80
100
0
100
200
300
400
500
600

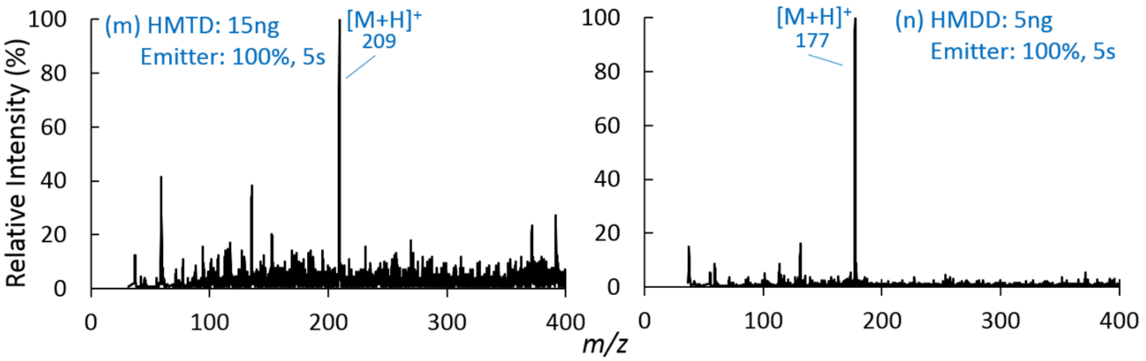
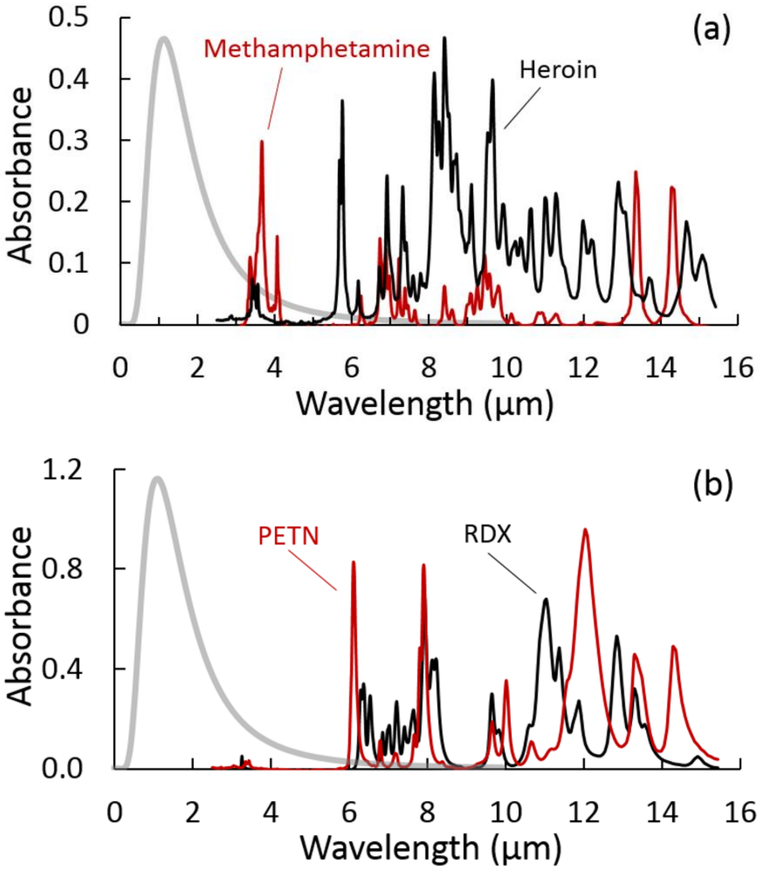


Figure S4. Representative mass spectra for (a) heroin, (b) 6-AM, (c) naphyrone, (d) 4-MMC, (e) MDMA, (f) methamphetamine, (g) DNT, (h) Tetryl, (i) ETN, (j) PETN, (k) RDX, (l) AN, (m) HMTD, and (n) HMDD using the IRTD-MS system with various emitter parameters.



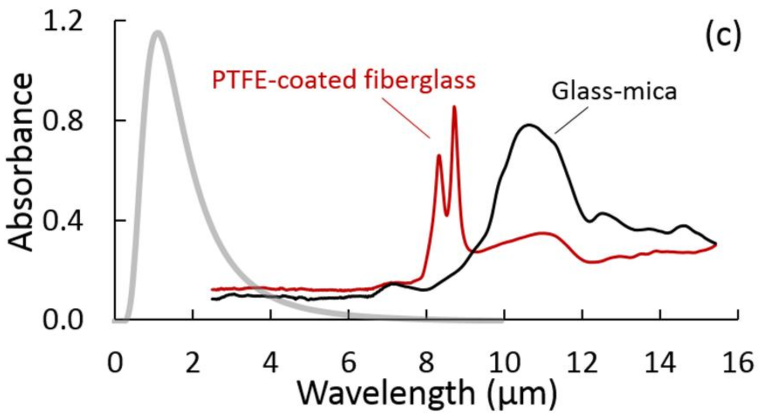


Figure S5. FTIR absorbance spectrum of 200 µg powdered samples of (a) methamphetamine and heroin, (b) PETN and RDX, and (c) the bulk PTFE-coated fiberglass weave wipe and glass-mica substrates. Details of the FTIR spectra collection can be found above. Gray traces represent the spectral distribution for infrared emission from a filament at ~2200 °C (Figure S1).

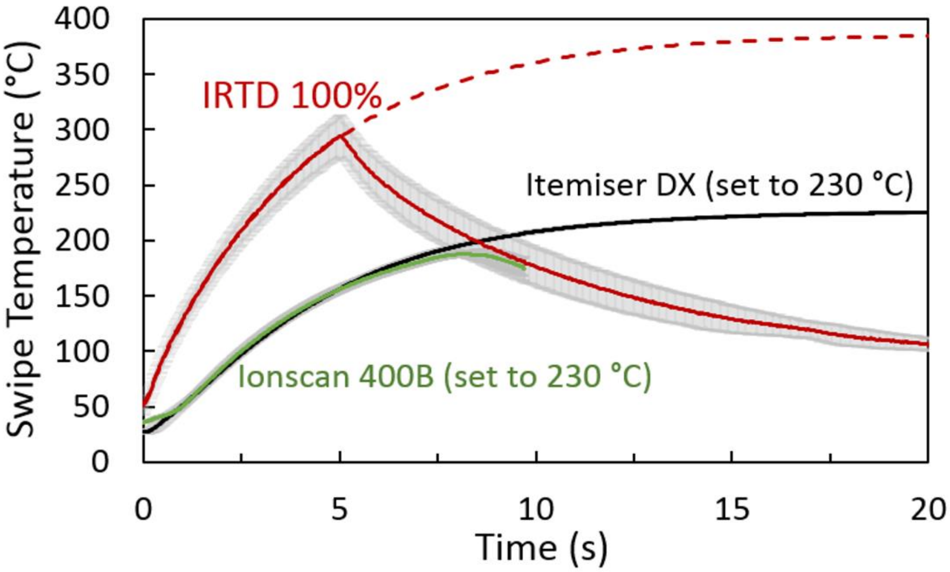


Figure S6. PTFE-coated fiberglass wipe temperature profiles for 5 s emission at 100% for IRTD, and the Itemiser DX and Ionscan 400B IMS thermal desorbers set at 230 °C. Solid lines and uncertainty represent the average and standard deviations from replicate measurements. Dashed line represents an exponential fit to the wipe heating rate for IRTD. Details of the measurement can be found above.

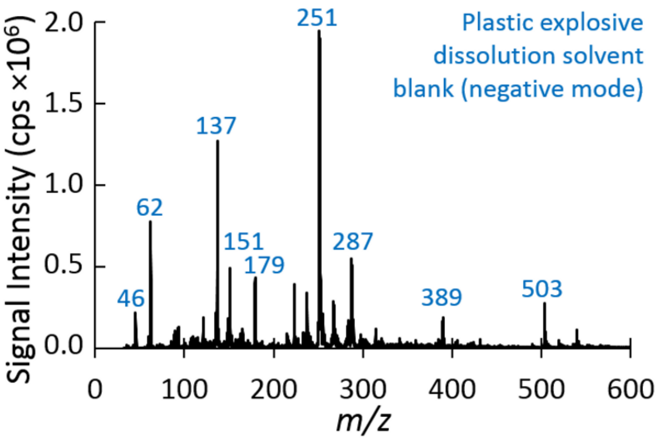


Figure S7. Representative negative mode mass spectra for the plastic-bonded explosive dissolution solvent (32 % trichloropropane, 32 % diacetone alcohol, 32 % cyclopentanol, and 4 % benzofuran by volume) for infrared emission of 100 % power and 5 s pulse.

References

[1] Incropera, F.P., D.P. DeWitt, T.L. Bergman, et al., *Fundamentals of Heat and Mass Transfer*. 6th ed. 2007, USA, John Wiley & Sons.