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Broad spectrum infrared thermal desorption of wipe-based explosive and narcotic samples for trace mass spectrometric detection†‡

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Wipe collected analytes were thermally desorbed using broad spectrum near infrared heating for mass spectrometric detection. Employing a twin tube filament-based infrared emitter, rapid and efficiently powered thermal desorption and detection of nanogram levels of explosives and narcotics was demonstrated. The infrared thermal desorption (IRTD) platform developed here used multi-mode heating (direct radiation and secondary conduction from substrate and subsequent convection from air) and a temperature ramp to efficiently desorb analytes with vapor pressures across eight orders of magnitude. The wipe substrate experienced heating rates up to $(85 \pm 2) \text{ }^{\circ}\text{C s}^{-1}$ with a time constant of $(3.9 \pm 0.2) \text{ s}$ for 100% power emission. The detection of trace analytes was also demonstrated from complex mixtures, including plastic-bonded explosives and exogenous narcotics, explosives, and metabolites from collected artificial latent fingerprints. Manipulation of the emission power and duration directly controlled the heating rate and maximum temperature, enabling differential thermal desorption and a level of upstream separation for enhanced specificity. Transitioning from 100% power and 5 s emission duration to 25% power and 30 s emission enabled an order of magnitude increase in the temporal separation (single seconds to tens of seconds) of the desorption of volatile and semi-volatile species within a collected fingerprint. This mode of operation reduced local gas-phase concentrations, reducing matrix effects experienced with high concentration mixtures. IRTD provides a unique platform for the desorption of trace analytes from wipe collections, an area of importance to the security sector, transportation agencies, and customs and border protection.

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Introduction

Thermal desorption and vaporization of analytes (*e.g.*, from particles and residues) lies at the foundation of target analyte introduction to many ion mobility spectrometry (IMS)^{1–4} and mass spectrometry (MS)^{5–8} trace chemical detection platforms utilized by the defense, homeland security, and forensic science sectors. Target collection is typically accomplished using dry wipe sampling, followed by the direct thermal desorption of target compounds from the wipe substrate. Commonly deployed instruments often incorporate a resistively heated chamber for thermal desorption that conductively and convectively heats the wipe and analyte. Resistance-based thermal desorption heaters typically require continuous power consumption to reach and maintain an elevated steady state

temperature (transient response to reach steady state on the order of 10 min to 30 min). Previous IMS and MS studies have demonstrated the important effects desorption temperature can have on sensitivity, making accurate and reproducible control over this component critical.^{2,3,9} The power draw to maintain these elevated temperatures can limit instrument performance as well as remote site sampling capabilities, portability, and battery life. In addition, evolving alarm algorithms and avenues for differential thermal desorption of complex matrices incorporate a temperature ramp during the desorption cycle. This implementation may provide enhanced specificity, but resistance-based thermal desorbers often include a conductive thermal mass for uniform heating that will require active cooling and/or additional delay time to return to the lower starting temperature before subsequent samples can be introduced.

In addition to conductive and convective energy transfer, radiative energy, typically in the form of laser or light emitting diode sources, has been used to desorb target analytes through photothermal and ablation-based mechanisms for chemical detection.^{10–20} The laser wavelength (typically ultraviolet to infrared: hundreds of nm to several μm) and duration (femtosecond to nanosecond)²¹ play distinct roles in the inter-

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play between direct radiation absorption and secondary thermal processes, *e.g.*, conduction from the substrate.^{10,12,14,22} Similarly, the nature of the target analyte and collection substrate spectral absorbance distributions directly influence the photothermal and/or ablation processes.^{23–25}

Laser-based desorption platforms have demonstrated powerful capabilities for the analysis of trace analytes,^{10,11,13,24} however, lasers can be expensive, require additional infrastructure, lead to excessive fragmentation at high fluence, be limited to a single wavelength of emission, require rastering over a larger wipe collection area, limit wipe material options to those that will not burn or ablate, and introduce additional safety considerations for operational users. Laser diode thermal desorption (LDTD) has also been coupled with atmospheric pressure chemical ionization for biological applications of ambient mass spectrometry, incorporating continuous infrared diode lasers in the range of 880 nm to 980 nm.^{18–20} Alternatively, filament-based infrared (IR) emitters offer tunable broad spectrum emission, rapid response times (~ 1 s), temporally discrete emission durations, and reduced costs (only requiring a power supply) and infrastructure requirements.^{25–32}

We present the implementation of a broad spectrum near infrared emitter for the thermal desorption of wipe collected target analytes. The use of a low-power radiation-based scheme demonstrates an alternative to the common resistance-based heating for thermal desorption in the trace detection arena.^{24,25,28,30} The twin tube infrared emitter at the foundation of the thermal desorption unit developed here, coupled both direct radiative heating and secondary conductive and convective heating (heating through the wipe and housing materials and air flow) of target analytes for efficient vaporization. The infrared thermal desorption (IRTD) unit was coupled to a mass spectrometer with a component using the Venturi effect to generate a low pressure region, entraining vaporized analyte out of the desorber, transporting it through a discharge ionization region and to the mass spectrometer inlet.³³ The trace detection of both volatile and semi-volatile illicit narcotics and explosives was demonstrated with the IRTD-MS system and discrete emission durations. This low-power discrete emission configuration also enabled the detection of target analytes within complex mixtures and matrices, specifically plastic-bonded explosives and exogenous narcotics from latent fingerprints. The interplay between emission power level (%) and emission duration (on the order of seconds), directly controlled the wipe substrate heating rate and maximum achieved temperatures, enabling alternative modes of operation. Manipulation of these parameters led to differential thermal desorption and temporal separation of analytes, a useful mode of operation for high concentration complex mixtures.

Experimental methods

Materials and sample preparation

Explosive and narcotic standards, including pentaerythritol tetranitrate (PETN), erythritol tetranitrate (ETN), cyclotri-

methylenetrinitramine (RDX), 2,4-dinitrotoluene (DNT), 2,4,6-trinitrophenylmethylnitramine (Tetryl), hexamethylene triperoxide diamine (HMTD), hexamethylene diperoxide diamine (HMDD), heroin, methamphetamine, 3,4-methylenedioxy-methamphetamine (MDMA), 4-methyl methcathinone (4-MMC), naphyrone, and 6-acetylmorphine (6-AM) were purchased at 1 mg mL^{-1} concentration in acetonitrile or methanol from AccuStandard Inc. (New Haven, CT, USA)[§] and Cerilliant (Round Rock, TX, USA), respectively. Standards were further diluted in acetonitrile to required concentrations. Ammonium nitrate (AN) was purchased from Sigma Aldrich (St Louis, MO, USA), dissolved to a concentration of 1 mg mL^{-1} , and diluted in water. Semtex A and C-4 plastic-bonded explosives were provided by the Transportation Security Laboratory (TSL, Atlantic City, NJ, USA) and dissolved in a mixed solvent of 32% 1,2,3-trichloropropane, 32% diacetone alcohol, 32% cyclopentanol, and 4% benzofuran by volume. Samples were either solution deposited (and solvent allowed to evaporate preceding experiments) directly onto polytetrafluoroethylene (PTFE, emissivity ~ 0.87 to 0.92)³⁴-coated fiberglass wipes (Sample Traps-ST1318, DSA Detection, LLC, Boston, MA, USA) or onto a secondary surface and then swiped. Synthetic fingerprint material and a fingerprint mold were used to directly control deposition of endogenous and exogenous compounds in artificial latent fingerprints. Details of the synthetic material composition and deposition procedures can be found in the literature.^{35,36}

Instrumentation

Broad spectrum infrared thermal desorber. The thermal desorber comprised a twin tube near infrared emitter (Heraeus Noblelight America, LLC, Buford, GA, USA) mounted within a custom aluminum housing and capped with a glass-mica ceramic (Mykroy/Mycalex, McMaster-Carr, Princeton, NJ, USA) insulating layer. An opaque quartz reflective coating (QRC) nano reflector was used to direct emitted infrared radiation toward the inserted wipe surface. The infrared emitter was controlled by an AccuPower 120 Manual power supply (Heraeus Noblelight America, LLC), which enabled direct manipulation of the percent power output and emission duration. The manufacturer specified an infrared spectral distribution in the near infrared range, with peak wavelength of $1.2 \mu\text{m}$ to $1.4 \mu\text{m}$ (Fig. S1†), filament temperature of 1800°C to 2400°C , approximately 200 kW m^{-2} maximum surface power density, and a 1 s response time.

Venturi-assisted entrainment and ionization mass spectrometry. Following thermal desorption, analyte vapors were extracted from the desorber housing through a 20 mm (long) $\times$ 6.35 mm (OD) ceramic tube by Venturi-induced flow and ionized by atmospheric pressure chemical ionization (Ion Air Jet, Exair Corporation, Cincinnati, OH, USA). This component was previously reported on in the literature,³³ coupled to a

[§]Certain commercial products are identified in order to adequately specify the procedure; this does not imply endorsement or recommendation by NIST, nor does it imply that such products are necessarily the best available for the purpose.

remote sampling extension, as the Venturi-assisted ENTrainment and Ionization (VENTI) platform. Following ionization, ions were detected by a 4000 QTRAP triple quadrupole mass spectrometer (SCIEX, Redwood City, CA, USA), for which operation parameters and details can be found below and in the ESI.†

Mass analyzer. A 4000 QTRAP triple quadrupole mass spectrometer (SCIEX, Redwood City, CA, USA) fitted with a 35 mm extended capillary interface was used in all experiments. The investigations demonstrated here primarily used the first quadrupole for scanning and the second and third quadrupoles as ion guides. System parameters included: 10 psi (69 kPa) curtain gas (N₂), 12 psi (83 kPa) ion source gas 1 (N₂), 0 psi (0 kPa) ion source gas 2, 100 °C interface temperature, ± 100 V declustering potential, ± 10 V entrance potential, and 8.3×10^{-3} Torr to 9.8×10^{-3} Torr (1.1×10^{-3} kPa to 1.3×10^{-3} kPa) operating vacuum.

Results and discussion

Infrared thermal desorption

The complete infrared thermal desorption and ionization front-end system described above is represented in Fig. 1(a) and (b). Thermal desorption and vaporization directly from

wipe substrates were achieved by infrared heating at a specified intensity (% power) and duration (in seconds). The mechanism of analyte desorption and vaporization was postulated to be a combination of both direct absorption of infrared energy and secondary thermal conduction and convection. The level of direct infrared absorption was a function of each analyte's specific absorbance spectrum. Thermal conduction and convection to the analyte resulted from the non-specific infrared energy absorption and heating of the wipe material, thermal desorber housing, and ambient air. The overall heating of the wipe material demonstrated a 2D spatial distribution centered around the typical target collection area of the wipe (visualized by PTFE-coated wipe burn patterns and copper and nickel mesh oxidation patterns – Fig. S2†). The PTFE-coated fiberglass wipes used here demonstrated temperatures up to approximately 300 °C within 5 s exposure to 100% power emission (Fig. 1(c) – measurement details in ESI†). The rapid flow generated by the Venturi effect (tens of L min^{-1})³³ resulted in effectively instantaneous transport from desorber to mass spectrometer inlet relative to the timescales for desorption and m/z scanning. The desorbed analyte molecules and ambient gas molecules were then ionized as they passed the discharge region and were transported to the mass spectrometer inlet. The short residence time between the desorber and mass spectrometer resulted in a tight packet of

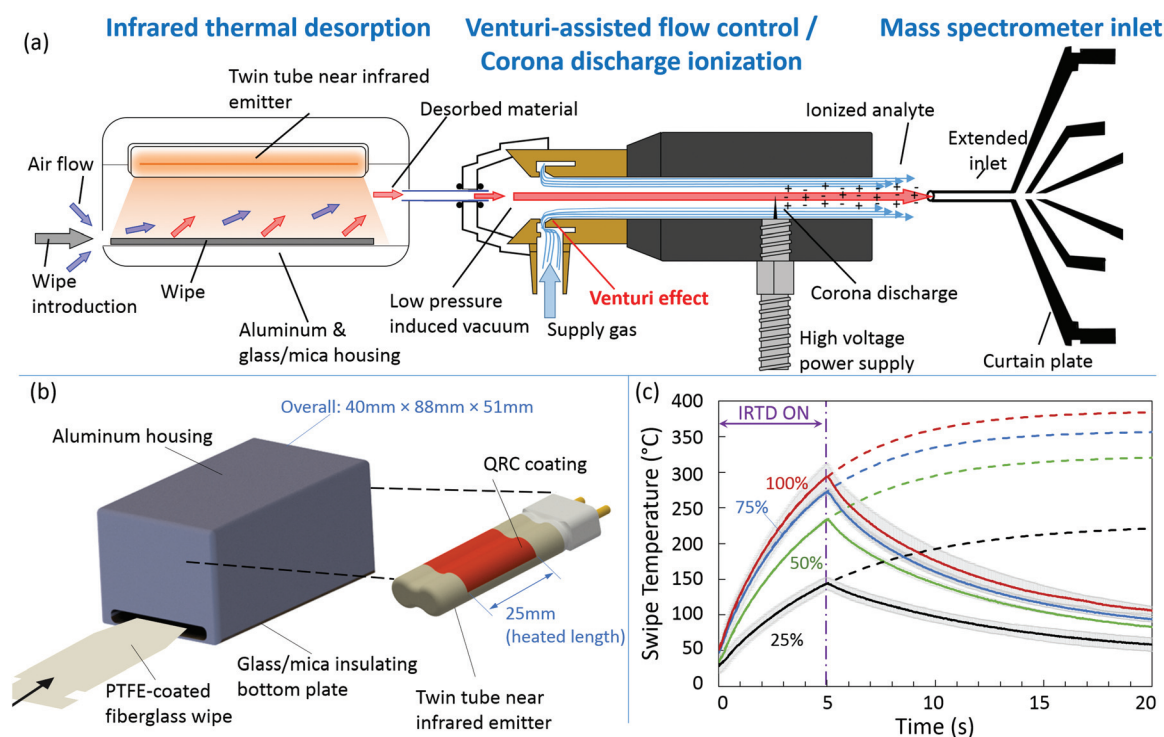


Fig. 1 Schematic representation of (a) the infrared thermal desorption (IRTD) and Venturi-assisted entrainment and ionization system comprised of the twin tube near infrared emitter, a join air amplifier and discharge chemical ionization source for both flow control and gas phase ionization, and the mass spectrometer inlet interface; and (b) the IRTD housing and emitter, including the PTFE-coated fiberglass wipe insert location, aluminum housing, and glass/mica insulating plate. Schematic not drawn to scale. (c) PTFE-coated fiberglass wipe temperature profiles for 5 s emission at 25%, 50%, 75%, and 100% power. Solid lines and uncertainty represent the average and standard deviations for triplicate measurements. Dashed lines represent exponential fit for each heating rate.

ions. Details of the induced flow effects on MS response can be found in the ESI (Fig. S3†).

The IRTD utility for discrete emission (100% power for 5 s duration) was demonstrated for select illicit narcotics and explosives, detected at trace levels in full scan mode (representative mass spectra for each – Fig. S4†). Table 1 displays the dominant ion observed and monitored for each compound, along with corresponding m/z value, deposited mass (directly onto wipe), and average signal-to-noise (S/N) ratio from triplicate measurements. Peak assignments provided here and throughout the text and ESI† are preliminary and based on knowledge of the compounds nominal mass and common ionization, as well as past experience. Here, the S/N was measured from extracted ion chromatograms for each analyte relative to 3× the standard deviation of a corresponding blank. Across the range of compounds investigated, the IRTD-MS platform demonstrated trace (single to tens of nanograms) level sensitivities in full scan mode, with enhanced sensitivities anticipated by moving to a selected ion monitoring mode of operation. Compounds such as RDX that displayed slightly poorer sensitivity, suffered from large ion distributions (adducting with Cl^- , NO_2^- , NO_3^- , and HCO_4^-) and dimerization (Fig. S4(k)†), reducing the overall fraction observed for the monitored ion. Optimization of instrument parameters (e.g., the in-source collision induced dissociation potential and dopant addition) may reduce dimerization and adduct formation to further enhance detection of the monitored ions.

The nature of the infrared heater suggests a thermal desorption mechanism coupling direct absorption of infrared radiation and secondary thermal conduction and convection from infrared heated components (wipe, desorber housing, and ambient gas). However, the explosive and narcotics compounds investigated here did not demonstrate significant absorption in the near infrared range of the emitter (Fig. S5†), suggesting minimal contribution from direct absorption. Yet, the inherent transient temperature ramp (Fig. 1(c)) during

infrared emission enabled the desorption of analytes at their optimal desorption temperature, similar to temperature programmed desorption (TPD) on a much faster timescale. The transient temperature ramp experienced by the wipe exhibited an exponential increase (Fig. 1(c)) with an initial heating rate of $(85 \pm 2)^\circ\text{C s}^{-1}$ and time constant of (3.9 ± 0.2) s (100% power), achieving approximately 300°C within the 5 s emission duration.

The rapid transient heating from infrared emission eliminated some limitations seen with classical conduction-based thermal desorbers held at single temperatures, specifically variability in the optimal temperature for analyte desorption and maximum achievable temperatures. Under most circumstances, the range of analyte volatility results in a need for higher temperatures to effectively desorb less volatile compounds.^{2,3,9} Generally, higher vapor pressure compounds are more volatile and will thermally desorb at lower temperatures. Classical resistance-based thermal desorbers held at a single temperature exhibit much slower heating of the inserted wipe substrate. For example, a PTFE-coated fiberglass wipe inserted into the Itemiser DX and Ionscan 400B IMS thermal desorbers set to 230°C experienced an approximately 40°C s^{-1} initial heating rate and achieved only about 150°C within 5 s and 200°C within 10 s (Fig. S6†). The slower heating rates limited the efficiency of thermally desorbing low vapor pressure compounds.

The select narcotics investigated here demonstrated comparable trace detection sensitivities (Table 1), however, they represented a wide range in volatility. For example, methamphetamine has a phase interface vapor pressure eight orders of magnitude higher than heroin (10^{-2} kPa vs. 10^{-10} kPa; at 25°C). Trace detection of narcotics (IMS and MS), vaporized using classic conduction-based thermal desorbers at a constant temperature in the range of 200°C to 240°C , typically exhibited superior performance for the volatile methamphetamine relative to heroin.^{2,5} The comparable sensitivity

Table 1 Dominant ion and associated signal-to-noise ratio (S/N) for trace level detection of illicit narcotics and explosives using IRTD-MS in a full scan mode (m/z 30 to m/z 600) at 100% power, 5 s duration, and 105 kPa Venturi flow supply pressure. Values represent deposited mass and average S/N ratio from triplicate measurements

Compound	Classification	MW (g mol ⁻¹)	VP ^a (kPa) ³⁷	±	Ion observed	m/z	Mass (ng)	S/N
Illicit narcotics								
Methamphetamine	Stimulant	149	2.17×10^{-2}	+	$[\text{M} + \text{H}]^+$	150	2	4
MDMA	Stimulant	193	2.13×10^{-4}	+	$[\text{M} + \text{H}]^+$	194	2	11
4-MMC	Synthetic cathinone	177	7.19×10^{-4}	+	$[\text{M} + \text{H}]^+$	178	1	5
Naphyrone	Synthetic cathinone	281	7.24×10^{-8}	+	$[\text{M} + \text{H}]^+$	282	1	14
Heroin	Opioid	369	1.01×10^{-10}	+	$[\text{M} + \text{H}]^+$	370	1	9
Explosives								
HMDD	Peroxide	176	9.04×10^{-4}	+	$[\text{M} + \text{H}]^+$	177	3	8
HMTD	Peroxide	208	6.07×10^{-6}	+	$[\text{M} + \text{H}]^+$	209	3	14
DNT	Nitroaromatic	182	4.16×10^{-5}	–	$[\text{M} - \text{H}]^-$	181	2	19
Tetryl	Nitroaromatic	287	1.60×10^{-8}	–	$[\text{M} - \text{NO}_2]^-$	241	2	6
ETN	Nitrate ester	302	8.00×10^{-6}	–	$[\text{M} + \text{NO}_3]^-$	364	10	11
PETN	Nitrate ester	316	1.08×10^{-9}	–	$[\text{M} + \text{NO}_3]^-$	378	2	8
RDX	Nitramine	222	4.91×10^{-10}	–	$[\text{M} + \text{NO}_2]^-$	268	10	5
AN	Inorganic oxidizer	80	1.49×10^{-6}	–	$(\text{HNO}_3)\text{NO}_3^-$	125	50	6

^a Estimated using EPI Suite™ v4.11, US EPA, 2014.

demonstrated here was a direct result of desorption at their optimal temperatures and increased achievable temperatures. This was demonstrated by the sequential thermal desorption of methamphetamine, MDMA, naphyrone, and then heroin from a multi-component mixture (100 ng each). Fig. 2 displays the extracted chronograms and cumulative signal distributions for each compound (methamphetamine: m/z 150, MDMA: m/z 194, naphyrone: m/z 282, and heroin: m/z 370, all $[M + H]^+$) and mass spectra from select timepoints. Cumulative distributions were fit with an error function and exhibited time constants for desorption (time to reach half maximum) of 3.6 s, 3.9 s, 4.7 s, and 5.0 s for methamphetamine, MDMA, naphyrone, and heroin, respectively. For this example, the order of desorption directly followed decreasing compound vapor pressure (Table 1). The distribution for the low vapor pressure heroin indicated the possibility for signal enhancement by increasing the emission duration past 5 s. The temporal separation of compounds can be exploited further for complex mixture analysis by manipulating the infrared emission power and duration, and will be discussed in the next section.

The IRTD-MS system also demonstrated sensitive detection of trace analytes from complex mixtures, including plastic-bonded explosives and latent fingerprints. Fig. 3(a) and (b) display representative negative mode mass spectra for 250 ng of C-4 and Semtex A. The background spectra resulting from the solvent mixture was subtracted from each (Fig. S7†). The C-4 chemical composition comprised of the explosive RDX (~91%), plasticizer – dioctyl adipate (DOA, ~5.3%), binder – polyisobutylene (~2.1%), and process lubricant – mineral oil

(~1.6%). The RDX component was observed clearly and formed adducts with chlorine (present from the dissolution solvent residue after evaporation), nitrite, and nitrate anions, as well as an unidentified anion at m/z 137 present in the solvent spectra. In addition, the DOA plasticizer was identified in the positive mode mass spectrum (Fig. 3(a) inset). Similarly, the explosive components of Semtex A (~76% PETN and ~5% RDX) were observed in negative mode. However, no identifiable peaks could be attributed to the Semtex binder (styrene-butadiene co-polymer) or plasticizer (tributyl citrate).

Next, an artificial fingerprint, laden with 100 ng of heroin and its corresponding metabolite, 6-acetylmorphine (6-AM), was deposited onto a representative automobile surface (clear-coated aluminum) and swiped, collecting analyte. IRTD at 100% for 5 s resulted in clear positive mode mass spectra, demonstrating the protonated heroin and 6-AM compounds (Fig. 3(c)). In addition, a number of endogenous fingerprint components were observed, including the amino acid valine (m/z 235 $[2M + H]^+$), fatty acids – palmitic (m/z 257 $[M + H]^+$) and oleic (m/z 283 $[M + H]^+$), and squalene (m/z 412 $[M + H]^+$). A similar artificial fingerprint laden with 2 μ g of each PETN and ETN was deposited and swiped for analysis in negative mode at 50% power for a 10 s duration. The collection efficiency of the PTFE-coated fiberglass wipes used here was on the order of single percentages as demonstrated in prior work,^{38,39} estimating detection levels of single to tens of nanograms for the exogenous compounds. The nitrate adducts of both explosives were observed (Fig. 3(d)) as well as a range of endogenous fingerprint compounds. A more complete table

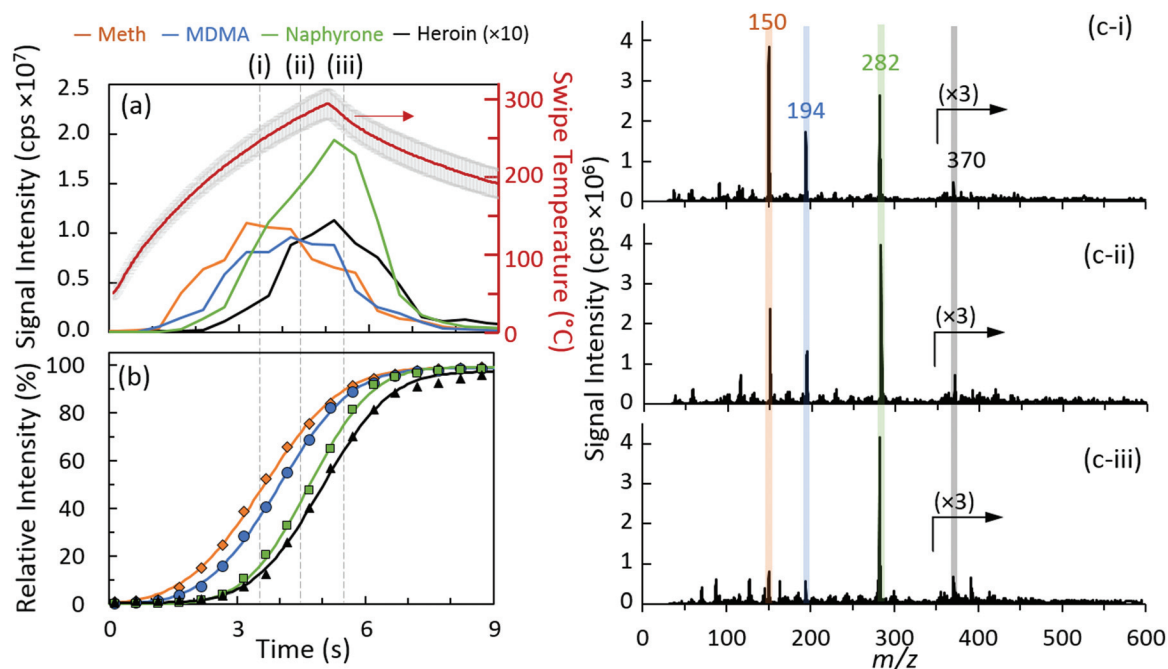


Fig. 2 (a) Extracted ion chronograms and (b) cumulative distributions from a mixture of 100 ng each of methamphetamine (m/z 150 $[M + H]^+$), MDMA (m/z 194 $[M + H]^+$), naphyrone (m/z 282 $[M + H]^+$), and heroin (m/z 370 $[M + H]^+$) for thermal desorption by infrared emission at 100% power and 5 s duration. Overlaid PTFE-coated fiberglass wipe temperature profile for 5 s infrared emission at 100% power from Fig. 1(c). (c) Individual mass spectra from timepoints (i)–(iii) identified in parts (a) and (b) with vertical dashed lines.

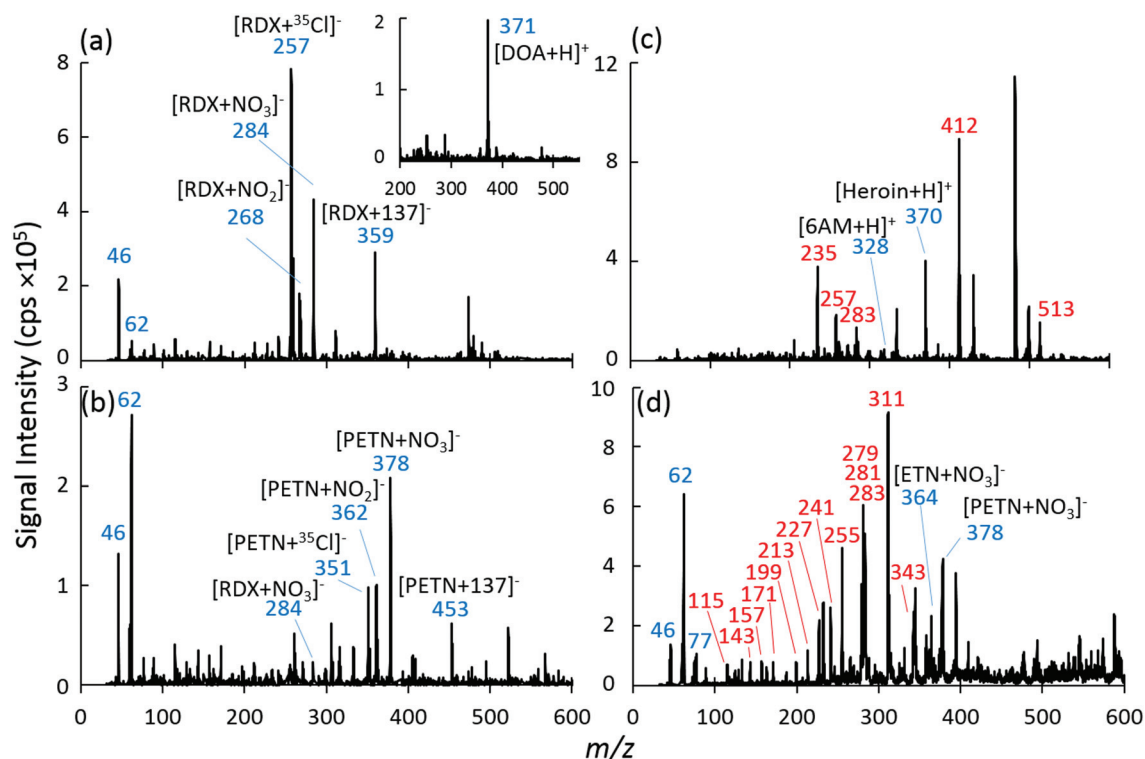


Fig. 3 Representative mass spectra for (a) 250 ng C-4 (100% power/5 s duration/negative mode/solvent background subtracted), (b) 250 ng Semtex A (100%/5 s/negative mode/solvent background subtracted), (c) 100 ng heroin and 100 ng the metabolite 6-AM deposited onto a clear coat finished car part within an artificial fingerprint and swiped (100%/5 s/positive mode), and (d) 2 µg PETN and 2 µg ETN deposited onto a car part within a fingerprint and swiped (50%/10 s/negative mode). Red labels represent endogenous fingerprint material components, for which detailed peak assignments can be found in the ESI Table S1.† Inset in part (a) represents the positive mode C-4 spectra and associated plasticizer component.

identifying the peaks associated with the fingerprint components observed in positive (Fig. 3(c)) and negative (Fig. 3(d)) modes can be found in the ESI (Table S1†). During the analysis of these complex mixtures, differences in the temporal desorption profiles of various compounds were observed, indicating an avenue for differential thermal desorption based separation.

A brief energy consumption comparison between infrared heating (discrete emission durations) and a commercial resistance-based thermal desorber was conducted under two hypothetical scenarios – the first for a field portable instrument requiring discrete single sample analysis, and a second for continuous high-throughput operation at a screening station. Under the discrete emission mode of operation, a single 5 s duration at 100% power ((3.9 ± 0.1) A and (110 ± 5) V, measured with ac current clamp meter) required approximately 2150 J. Comparatively, a commercial resistance-based thermal desorber (part of the Itemiser DX, Morpho Detection) required approximately 2250 J ((2.5 ± 0.3) A and (15 ± 1) V) to operate at steady state for 60 s – roughly a single sampling and clear-down period. However, this heater required a roughly 30 min transient warm-up period, consuming approximately 83.7 kJ ((3.1 ± 0.1) A and (15 ± 1) V). This comparison demonstrated the significant utility of a discretely emitting thermal desorber for field portability – no required warm-up period

resulting in 40-fold less energy consumption. Alternatively, we considered a hypothetical high-throughput screening station for which samples were analyzed every 60 s for approximately 8 hours of a 24 hours period. However, commercial resistance-based desorbers typically remain heated for the full 24 hours. Under these conditions, infrared heating operated with discrete emission durations would require approximately 1.03 MJ compared to 3.32 MJ for the resistance-based operation, a 3-fold reduction in energy consumption.

Temporal separation – differential thermal desorption

With the above demonstration of the IRTD-MS platform for rapid, short duration and efficient power-consumption thermal desorption of a range of trace analytes and complex mixtures, we next investigated alternative modes of operation through manipulation of the main parameters driving thermal desorption, the infrared emission power and duration. These parameters directly controlled the heating rate and maximum temperatures experienced by the wipe substrate. Fig. 4 displays the results of investigations varying the infrared emission power and emission duration for 50 ng ETN samples (monitoring the nitrate adduct: m/z 364 $[\text{ETN} + \text{NO}_3]^-$), demonstrating clear interplay between these parameters. Increasing the emitter power for constant duration (*e.g.*, 10 s), resulted in an asymptotic increase in signal (Fig. 4(a)). Notably, altering the

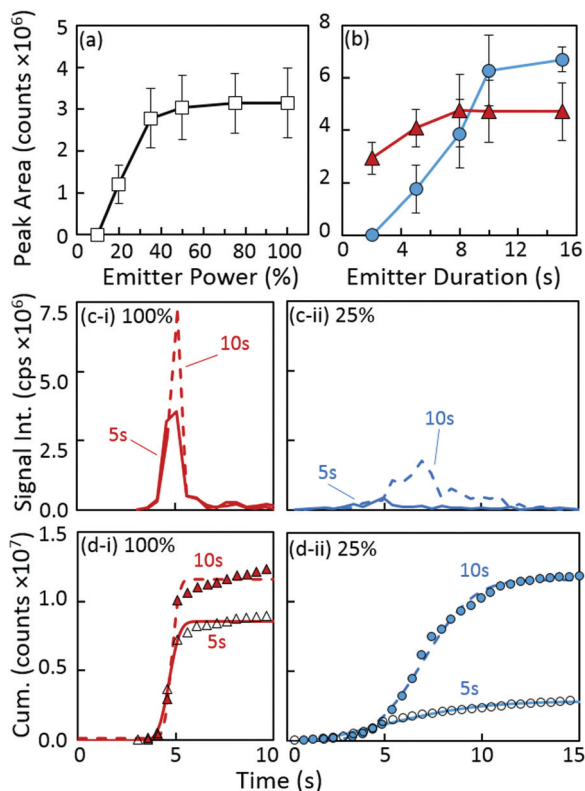


Fig. 4 IRTD-MS integrated signal for the ETN nitrate adduct as a function of (a) emitter power level (140 kPa/10 s/50 ng samples) and (b) emitter duration for $\blacktriangle$ - 100% and $\bullet$ - 25% power (140 kPa/100 ng samples). Representative (c) extracted ion chromatograms (XICs) and (d) cumulative intensity distributions for ETN (nitrate adduct) analyzed with infrared emitter parameters of (i) 100% and (ii) 25% power with (—) 5 s and (---) 10 s durations. Data points and uncertainty represent the average peak area and standard deviations derived from extracted ion chromatograms for triplicate measurements.

infrared emission power enabled direct manipulation of the transient temperature profile the wipe experienced (Fig. 1(c)). For example, the PTFE-coated fiberglass wipe heating rate increased and response time constant decreased from $(35 \pm 1)^\circ\text{C s}^{-1}$ and (5.7 ± 0.1) s to $(85 \pm 2)^\circ\text{C s}^{-1}$ and (3.9 ± 0.2) s for 25% *versus* 100% power emission, respectively (Fig. 1(c) – exponential fit: heating rate taken as derivative at time = 0 s). The increasing heating rate led to reducing the temporal MS response. The asymptotic response in Fig. 4(a) was an artifact of competing time scales for thermal desorption, analyte transport, and MS scan time. Limitations in the sampling rate, ionization efficiency, and mass range scanning rate restricted further signal enhancements.

Fig. 4(b) displays the trade-off between high power and short duration (high heating rate) *versus* low power and long duration (low heating rate) infrared emission for 100 ng ETN samples as a function of both power and duration. For example, at 100% emitter power, a modest asymptotic increase in signal was detected for increased emitter durations from 2 s up to 8 s. However, at 25% power, no signal was obtained for a

2 s emitter duration, due to insufficient wipe temperatures for thermal desorption, but a more dramatic increase in signal from 5 s to 15 s was observed. Fig. 4(c) and (d) present the temporal response, in the form of the ETN nitrate adduct extracted ion chromatograms (XICs) and cumulative intensity distributions (derived from the XICs and fit with an error function), for 5 s and 10 s emission durations, each at 25% and 100%. The presence of ETN became visible just before the 5 s emission duration ended. The higher heating rate (100% power) still achieved significant thermal desorption within the 5 s emission. The increase in duration to 10 s enabled the high heating rate to further increase the temperature of the wipe substrate and enhanced the ETN signal (Fig. 4(c-i) and (d-i)). However, at 25% power, the low heating rate and lower achieved wipe temperature led to very little ETN desorption within 5 s. Further increase in emission duration to 10 s enabled higher wipe temperatures to be achieved, leading to more complete desorption of ETN (Fig. 4(c-ii) and (d-ii)). At 100% power, both emitter durations yielded temporally short ETN signal intervals (extent of extracted ion peak from chromatogram: ~ 2 s). However, at 25% power, the increased emitter duration significantly increased the ETN signal interval (up to approximately 8 s to 10 s) and overall magnitude (counts). Finally, on average, the total integrated signal for certain low power (lower wipe heating rate) and long emission duration settings surpassed that of high power (high wipe heating rate) and short emission settings (Fig. 4(a)), an aspect previously observed for IMS thermal desorption.³ This result was attributed to the increase in the desorption timescale, providing more efficient ionization (reducing ionization saturation from highly concentrated sample plugs) and mass spectrometric detection.

The direct and simple manipulation of the emitter power and duration enabled unique control over the thermal desorption process. As introduced above in Fig. 2, the transient heating ramp yielded the sequential desorption of analytes based on their chemical and physical properties. Control over the emitter power and duration was used to further enhance this differential thermal desorption. For example, as demonstrated in Fig. 5, regulating the emitted power enabled preferential thermal desorption and detection of the more volatile HMDD from a simple binary mixture of HMDD and HMTD. Emitter powers of 10% and 20% at 10 s durations, thermally desorbed HMDD without desorbing HMTD (black arrows indicate the initiation of infrared emission). Upon further increase in power to 35%, both HMDD and HMTD were desorbed. However, their desorption was virtually sequential, enabling differential thermal desorption within a single experiment.

The variations in the effective temperature ramp and resulting temporal profile achieved by manipulating the emitter power and duration enabled a level of differential thermal desorption separation ahead of MS analysis that becomes especially useful for the analysis of complex matrices. This was demonstrated with swiped collections of latent artificial fingerprints from representative automobile surfaces, similar to experiments displayed in Fig. 3. The spectra in Fig. 3(c) represents the analysis of this collection at 100% infrared emitter

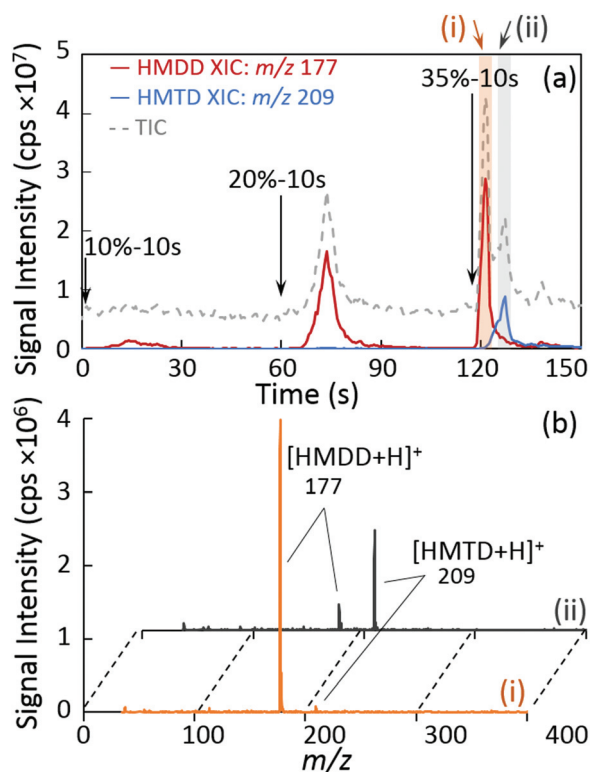


Fig. 5 IRTD-MS detection HMDD (100 ng) and HMTD (100 ng) peroxide-based explosives at multiple infrared emission power and duration combinations (10%/10 s, 20%/10 s, and 35%/10 s). (a) Total ion and extracted ion chromatograms (TIC and XICs) of $[\text{HMDD} + \text{H}]^+$ (m/z 177) and $[\text{HMTD} + \text{H}]^+$ (m/z 209). Black arrows indicate initiation of infrared emission. Mass spectra extracted from the chronogram for times corresponding to the (b-i) orange (orange spectrum trace) and (b-ii) gray boxes (black spectrum trace).

power and 5 s duration. As demonstrated in Fig. 6, the cumulative intensity XICs for a range of the synthetic fingerprint material peaks as well as heroin and its metabolite 6-AM demonstrated a short temporal response for 100% power and 5 s duration. The separation between the initially desorbed smaller (*e.g.*, endogenous octanoic acid) and larger fingerprint compounds (*e.g.*, exogenous heroin) was on the order of seconds (Fig. 6). Shifting from the high power and short duration configuration to a lower power and longer duration, *i.e.*, 25% and 30 s, enabled the temporal distribution of analytes to be extended. This temporal extension allowed for increased separation of the smaller and larger components (on the order of 10's of seconds), providing an avenue for differential thermal desorption separations of complex mixtures. Fig. 6(b) demonstrates mass spectra from the beginning and end of the thermal desorption period, separating low mass components (*e.g.*, endogenous valine) from higher mass components, including the exogenous heroin peak. Differential thermal desorption also reduced the instantaneous number of compounds and local concentration of analyte molecules within the ionization region, reducing ionization suppression effects often observed with high concentration complex mixtures.

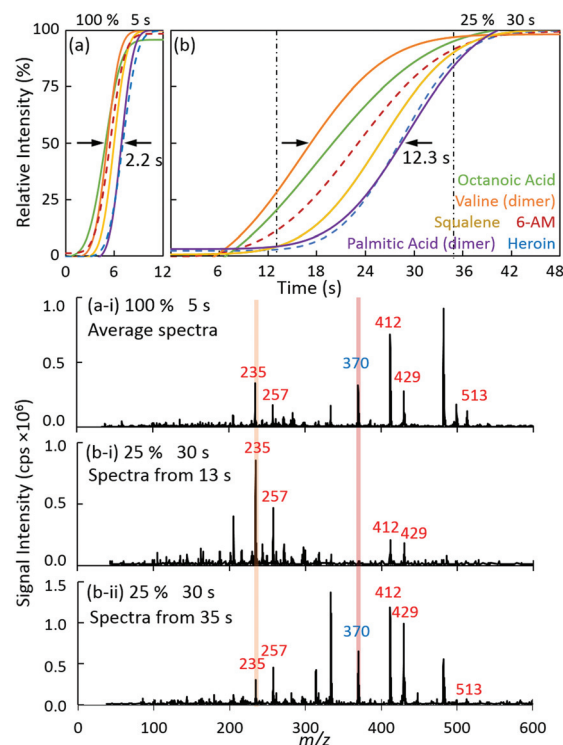


Fig. 6 Normalized cumulative distributions from extracted ion chronograms of endogenous fingerprint compounds, octanoic acid (m/z 145 $[\text{M} + \text{H}]^+$), valine (m/z 235 $[\text{2M} + \text{H}]^+$), squalene (m/z 412 $[\text{M} + \text{H}]^+$), 6-AM (m/z 328 $[\text{M} + \text{H}]^+$), palmitic acid (m/z 513 $[\text{2M} + \text{H}]^+$), and the exogenous heroin (m/z 370 $[\text{M} + \text{H}]^+$) for infrared emitter configurations of (a) 100% power, 5 s duration and (b) 25% power, 30 s duration. (c) Average mass spectra from (a) 100% power and 5 s duration. Individual mass spectra from timepoints (d) 13 s and (e) 35 s for (b) 25% power and 30 s duration. Timepoints are indicated in (b) with vertical dashed lines.

Conclusions

The thermal desorption and vaporization of wipe collected target analytes remains paramount to trace chemical detection systems employed by the security sector, customs and border protection, corrections and prisons, and transportation agencies. The development and characterization of a broad spectrum near infrared emitter for rapid thermal desorption of nanogram levels of narcotics and explosives was presented here. This system enabled multi-mode heating (direct radiative and secondary conductive) and an intrinsic temperature ramp on the timescale of seconds, representing alternative mechanisms of thermal desorption for trace detection. The discrete emission duration and rapid return to ambient temperature conditions requires no warm-up period and allows for efficient power consumption under both single-sample field portable (40-fold less energy) and continuous high-throughput screening scenarios (3-fold less energy). The ease with which the emission power level and duration can be manipulated offers direct control over the temperature ramp, enabling differential thermal desorption for upstream separation and enhanced specificity. Differential thermal desorption may play an impor-

tant role as alarm algorithms evolve to include desorption profiles. The progression of broad spectrum infrared thermal desorption offers unique capabilities to the trace detection arena.

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