

Development and use of a thermal desorption unit and proton transfer reaction mass spectrometry for trace explosive detection

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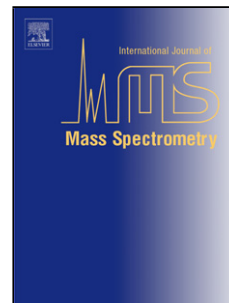
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1 Highlights:

- 2 (i) Industrial-University collaboration developing a novel Thermal Desorption Unit for
3 use with Proton Transfer Reaction Mass Spectrometer for trace explosive
4 detection;
5 (ii) Excellent recovery times (memory effects) for many explosives – typically tens of
6 seconds;
7 (iii) The first quantification of TDU/PTR-MS limits of detection for the screening of
8 explosives comparable with IMS systems for most explosives investigated;
9 (iv) Enhanced selectivity of TDU/PTR-MS instrument by changing operational
10 parameters;
11 (v) New data on the reactions of H_3O^+ with nitroglycerine, PETN and RDX;
12 (vi) Separation of compounds with the same nominal mass (i.e. TNT and NG).
13

13 **Development and use of a thermal desorption unit and proton transfer**
14 **reaction mass spectrometry for trace explosive detection: determination of**
15 **the instrumental limits of detection and an investigation of memory effects**

16

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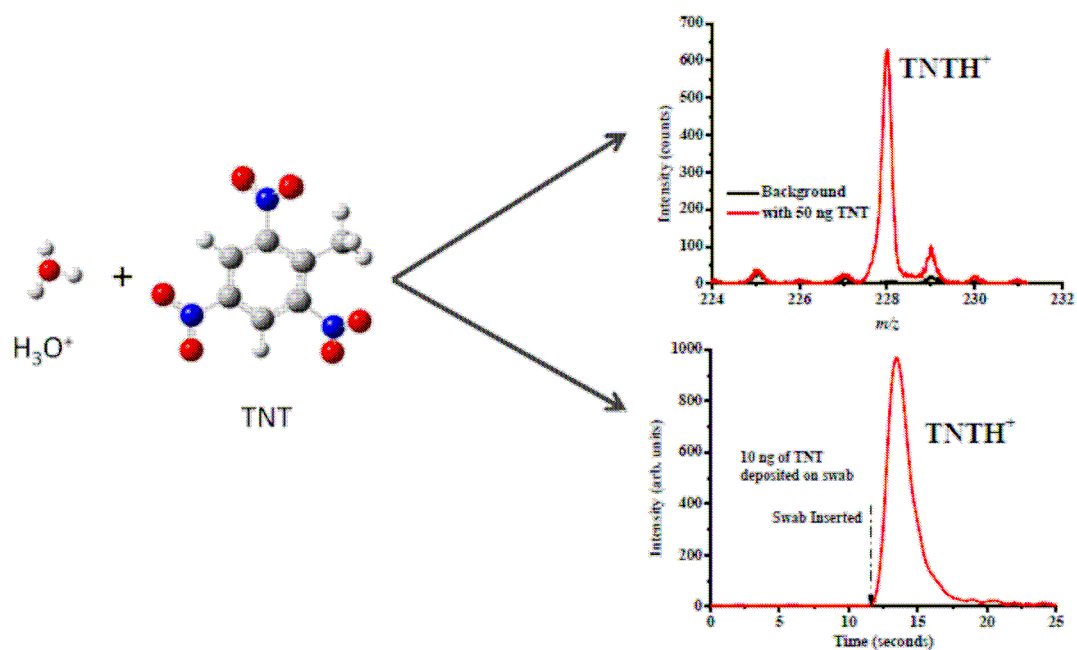
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30 **Abstract**

31 A novel thermal desorption unit (TDU) has been developed and specifically designed for the
32 detection of trace quantities of explosives using a proton transfer reaction mass spectrometer
33 (PTR-MS). For the first time details on recovery times and instrumental limits of detection
34 for the screening of explosives with this TDU/PTR-MS system are reported. We demonstrate
35 that traces (nanograms or less) of explosives deposited on swabs are desorbed within less
36 than a second upon insertion into the TDU. For a short period of time (seconds) a
37 concentration “pulse” of an explosive enters the drift (reaction) tube of the PTR-MS. This
38 temporal concentration pulse of material is monitored in real-time by recoding the product
39 ion intensities for a given explosive as a function of time. By changing the reduced electric
40 field in the drift tube region of the PTR-MS, we demonstrate how selectivity can be
41 improved. This study demonstrates that the TDU/PTR-MS instrument meets security
42 application criteria in terms of sensitivity, selectivity and recovery times.

43

44 **1. Introduction**

45 Highly selective and sensitive screening for traces of explosives in complex chemical
46 environments is important in many areas of security. A number of analytical techniques are
47 available for use in the detection of explosives. These are highlighted and compared in a
48 recent review [1], and includes ion mobility spectrometry (IMS), atmospheric pressure
49 chemical ionisation mass spectrometry and desorption electrospray ionisation-mass
50 spectrometry. IMS is the most commonly used technique found in security areas, owing to its
51 compactness and ease of operation. Its use has been critically reviewed by Ewing et al. [2]. A
52 limitation of IMS is its reliance on the temporal separation of ions in a high-pressure drift
53 tube for its selectivity. In comparison to IMS, the technique known as proton transfer reaction
54 mass spectrometry (PTR-MS) has a better selectivity owing to the use of a mass
55 spectrometer. PTR-MS has been shown to be a useful platform technology capable of
56 detecting a range of explosives [3-7] (in addition to other threat agents [8-11]). Identification
57 of explosives with a high level of confidence minimises false positives and is therefore
58 beneficial for applications in security areas. However, for PTR-MS to be adopted as an
59 analytical tool, it is not sufficient to be able to detect explosives present in trace quantities
60 with high levels of confidence, it is also necessary to do so with limited memory effects.
61 Crucially, the whole process of sampling, analysis and recovery needs to be completed within
62 tens of seconds if it is to be acceptable to security personnel and the travelling public. Until
63 now that has not been achieved with PTR-MS [4].

64 The detection of many explosives is challenging because of their low vapour
65 pressures [12]. Without any sample preparation, low vapour pressure makes it very difficult
66 to introduce sufficient vapour concentrations of an explosive into the reaction region (the
67 drift tube) of a PTR-MS to make it detectable. An approach to remedy this problem was
68 adopted in this investigation. For this we have adopted a similar technique routinely used in
69 IMS, namely a pre-concentration technique followed by thermal desorption. An earlier
70 attempt of pre-concentration and thermal desorption of explosives with PTR-MS resulted in
71 limited success [4]. That study used a suction device that drew air through a fine wire mesh to
72 trap particulates of an explosive. This mesh was then ohmically heated to evaporate that
73 trapped material. A simple heated inlet tube placed close to the wire mesh carried some of the
74 desorbed material into the drift tube reactor. Although this successfully resulted in much
75 higher characteristic ion signals than had been previously obtained it suffered from a long

recovery times, with memory effects being observed of tens of minutes. No quantification in terms of the instrumental limits of detection (LoD) was possible in that previous study.

In order to overcome problems associated with memory effects and to determine instrumental LoD for the detection of trace explosives, we have developed a novel variable temperature thermal desorption unit (TDU) for use with PTR-MS. Recovery times and instrumental limits of detection (LoD) for the combined TDU/PTR-MS system are reported for a number of explosive compounds. In order of increasing molecular mass, these are ethylene glycol dinitrate (EGDN, m/z 152, $C_2H_4N_2O_6$), 1,3-dinitrobenzene (DNB, m/z 168, $C_6H_4N_2O_4$), 3,4-dinitrotoluene (DNT, m/z 182, $C_7H_6N_2O_4$), hexamethylene triperoxide diamine (HMTD, m/z 208, $C_6H_{12}N_2O_6$), 1,3,5-trinitrobenzene (TNB, m/z 213, $C_6H_3N_3O_6$), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX, m/z 222, $C_3H_6N_6O_6$), nitroglycerin (NG, m/z 227, $C_3H_5N_3O_9$), 2,4,6-trinitrotoluene (TNT, m/z 227, $C_7H_5N_3O_6$), and pentaerythritol tetranitrate (PETN, m/z 316, $C_5H_8N_4O_{12}$). The selection of explosives reported have been chosen because they cover a wide range of vapour pressures, ranging from the 4.9×10^{-9} mbar (RDX) to 0.1 mbar (EGDN) at 25 °C [12]. Mass spectrometric m/z analysis of the product ions provides good selectivity. However, this paper illustrates how this selectivity can be enhanced by changing operational parameters in the drift (reaction) region.

2. Experimental Details and Methods

2.1 Proton Transfer Reaction Mass Spectrometry (PTR-MS)

A first generation KORE Technology Ltd. Proton Transfer Reaction - Time of Flight - Mass Spectrometer (PTR-ToF-MS), manufactured in 2006, was used in this study. Details on this instrument have already been published [13, 14], and hence only a brief description is provided here. Using a needle valve, water vapour is introduced into a hollow cathode discharge where, after ionisation via electron impact and subsequent ion-molecule processes, the terminal reagent ions are H_3O^+ . These ions are transferred from the ion source into the drift tube (reaction region) of the PTR-ToF-MS. H_3O^+ ions donate their protons to compounds (M) present in the drift tube whose proton affinities are greater than that of water ($PA(H_2O) = 691 \text{ kJ mol}^{-1}$). This process can be non-dissociative (resulting in the protonated parent molecule MH^+) and/or dissociative. Dissociative proton transfer results in product ions which, depending on their m/z values, may or may not be useful for the identification of a compound with a high level of confidence. Complications other than dissociation arise because it is not only H_3O^+ ions that are produced in the ion source region. Back streaming of air from the drift tube into the ion source results in the production of other “terminal”

(impurity) ions. These cannot react with water because their recombination energies (RE) are less than the ionisation energy of water (12.6 eV), and include NO^+ (RE = 9.3 eV), O_2^+ (RE = 12.1 eV) and NO_2^+ (RE = 9.6 eV), respectively. Operating conditions are such that the total impurity ion signal level is typically less than 3% of the H_3O^+ intensity. Therefore usually these ions are of little consequence. However, we have found that NO_2^+ is a product ion from the reaction of H_3O^+ with explosives that contains a nitrate group, i.e. EGDN, NG and PETN, and with RDX. That must be taken into account when calculating the LoD using NO_2^+ .

2.2 Thermal Desorption Unit (TDU)

The TDU designed and developed for use with PTR-MS is better described as a swab crusher, which makes it unique. Unlike some other TDUs where often a poor seal is made between the inlet and outlet carrier gas flows, this design features a high-force annular “anvil” that compresses the PTFE in a ring around the edge of a swab. A schematic representation of this new TDU and “anvil” system is provided in figure 1. The force is sufficiently high to plastically deform the PTFE and convert it into a gas tight circular seal around the rim of the swab, thereby improving the transfer of material from the swab into the inlet line. The TDU is connected to a short heated stainless steel inlet system, the surfaces of which are passivated (SilcoNert® 2000 treated) to minimise adsorption, leading to the reaction chamber. Once a seal is created, a carrier gas (in this study laboratory air) is heated to the temperature of the TDU before it flows through a series of holes in a heated metal plate. This heated air then passes through the swab and into the inlet system driving any desorbed material through to the drift tube. The actual temporal duration of a “pulse” of concentration of a compound will depend on many factors including the compound’s volatility and chemical nature, the temperature of the inlet system, the carrier gas flow rate and the temperature of the inlet lines. The inlet line from the TDU to the drift tube of the PTR-MS was kept as short as possible and heated during measurements to further minimise losses onto the surfaces.

2.3 Operational Parameters

All measurements were taken under the same operational conditions, namely the TDU, inlet tubing and drift tube were maintained at temperatures of 140 °C, 150 °C and 100 °C (maximum possible with the current drift tube heating system), respectively. The drift tube pressure was set at 1.1 mbar. The only variable was the operating drift tube voltage, which was adjusted to provide an appropriate reduced electric field which resulted in the best

sensitivity for each explosive investigated. (The reduced electric field value is the ratio of the electric field strength (E) and the gas number density (N), and is given in units of Townsend (Td) ($1 \text{ Td} = 10^{-17} \text{ V cm}^2$.)

2.4 Explosive Compounds

Single component standards for the explosives used in this study were purchased from AccuStandard Inc., New Haven, CT. Typically, these standards contained 1 mg of an explosive placed in 1 ml of either acetonitrile (AcN) or a mix of AcN and methanol (MeOH). RDX and TNT came in an AcN: MeOH (1:1) mix. PETN and DNT were delivered in MeOH. EGDN and HMTD (both at 0.1 mg) were supplied in AcN. NG (0.1 mg) came supplied in a 1 ml solution of ethanol. However, O_2^+ reacts with ethanol to form an ion at m/z 46 via dissociative charge transfer, which complicates the analysis. Therefore, we purchased a sample of NG (100 μg) dissolved in AcN (1 ml) from Dr. Ehrenstorfer GmbH, Augsburg, Germany. The results for NG presented in this paper are all taken using that sample. Samples were diluted in the appropriate solvent(s) (HPLC grade) to provide the required quantity of an explosive. Typically 1 μl of a solvent containing the required mass of an explosive was spotted onto a PTFE swab of diameter 3.5 cm. This swab came prepared from the manufacturer (ThermoFisher Scientific) and was mounted on rectangular cardboard for easy insertion into our TDU.

2.5 Determining Instrumental Limits of Detection

The instrumental limit of detection (LoD) for a given m/z is taken to be the situation when the signal intensity in that channel exceeds the background noise level by factor of three. The background signal will be m/z dependent, because of ion signals resulting from various chemical impurities in different concentrations present in the instrument and/or as a result of unreactive ions coming from the hollow cathode ion source. To calculate the LoD for a compound M we have used the expression:

$$\text{LoD} = \frac{3\sigma_{\text{Background}}}{\epsilon_M},$$

where $\sigma_{\text{Background}}$ is the standard deviation of a blank swab and ϵ_M is the instrument's sensitivity for compound M in counts per second (determined by integrating the ion signal over the temporal peak) per ng of explosive placed on a swab. To test for linearity, the amount of explosive deposited on a swab was varied from as low as 0.06 ng up to 1000 ng. (The actual range depended on the explosive being investigated.) Precision of the technique

was evaluated in terms of repeatability and reproducibility. Repeatability determinations involved measurements of 5 replicates consecutively, while reproducibility determinations were 5 replicates over 5 different days, with each replicate being the mean of three measurements. We used five times the limit of detection for each of the compounds to evaluate these parameters.

3. Results

3.1 Product ions

Table 1 provides a list of product ions detected at a given E/N for each explosive. For the majority of the explosives investigated the protonated parent was detected (EGDN, DNB, DNT, HMTD, NG, TNB, TNT and PETN). However, in addition to the protonated parent for the nitrate esters (EGDN, NG and PETN) a more dominant product ion at m/z 46 (NO_2^+) was also observed. RDX was the only explosive compound in this study for which no protonated parent signal was observed, instead the product ions NO_2^+ , $\text{CH}_3\text{N}_2\text{O}_2^+$ (m/z 75 (dominant at the E/N used)) and $([\text{RDX-HONO}]\text{H}^+)$ (m/z 176) were detected.

3.1 Instrumental Limits of Detection

Table 1 also presents the instrumental LoD values. These have been obtained from calibration plots of the type shown in figure 2, which is for TNT. Large variations in LoD are found. The lowest LoD obtained is for DNT at 0.07 ± 0.01 ng. This is followed by DNB (0.13 ± 0.02 ng), TNB (0.14 ± 0.02 ng) and TNT (0.15 ± 0.01 ng). For RDX, a LoD of 6 ± 2 ng is obtained using the product ion at m/z 75. The calculated LoD for NG is found to be 2.0 ± 0.2 ng when using the protonated parent signal at m/z 228, but somewhat higher when using the fragment ion signal at m/z 46 (12 ± 2 ng).

3.2 Memory Effects

For the majority of compounds investigated it was found that the ion signal at the m/z being used to identify an explosive had returned to background levels within tens of seconds. EGDN, DNT and HMTD showed the least memory effects. This is illustrated for DNT in figure 3. This figure shows a chromatographic spectrum (product ion intensity versus time) for the protonated parent signal that resulted from 1 ng of DNT desorbed from a swab. For comparison, figure 4 shows the temporal intensity profiles of the dominant product ions at m/z 46 and 75 resulting from RDX. Although the product ion signals for RDX do not return

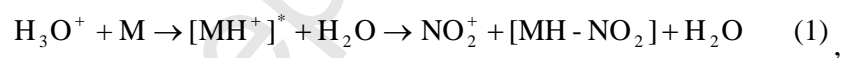
to background values as quickly as those obtained for the other explosives, by approximately 60 seconds the ion signal intensities have dropped to approximately 5% of their peak values.

For the other compounds studied, DNB, TNB, NG, TNT and PETN, memory effects were found to be slightly greater than those found for explosives such as DNT, but significantly less than that observed for RDX. Typically background levels were reached in approximately 20 seconds. To illustrate this, figure 5 (a) shows the temporal profiles of NGH^+ and NO_2^+ for 50 ng of NG taken at an E/N of 80 Td, which is the best value of the reduced electric field in terms of sensitivity for detecting the protonated parent. To demonstrate the effect of E/N on the product ion branching ratios, figure 5 (b) shows the identical NG product ions being monitored, but this time taken at a higher reduced electric field of 180 Td. Figures 6 (a) and (b) show the corresponding results for TNT at E/N values of 80 Td and 180 Td, respectively, using a swab onto which 50 ng of TNT was placed.

4. Discussions

4.1 Product ions and improved selectivity

Compared to IMS, PTR-MS provides more selectivity because of the mass spectral analysis. However, product ions are not necessarily unique for a given explosive. In this study NO_2^+ is a product ion that comes from all of the nitrate esters. This product ion results from the formation of a hydroxyl group upon proton transfer and the subsequent elimination of a nitro group in the form of NO_2^+ :



where $\text{M} = \text{EGDN}$, NG , or PETN . However, the observation of it and the protonated parent makes it possible to identify explosives with a high level of confidence. An example of this is its use to discriminate between TNT and NG. These two compounds have the same nominal protonated mass. However, TNT reacts with H_3O^+ to produce only the protonated parent. The absence of an NO_2^+ product ion provides a simple method to distinguish between NG and TNT (compare figures 5 and 6). Even if TNT and NG are both present, the unusual increase of the TNTH^+ signal with increasing E/N [7] means that it is possible to determine if both compounds are present. This serves to demonstrate how changes in operational parameters can be used effectively to improve the instrumental selectivity.

4.2 TDU/PTR-MS instrumental limits of detection and comparisons with other instruments

The LoD values obtained for various explosives demonstrate that the TDU/PTR-MS system provides an analytical technique with sensitivities comparable to those achieved by Ion Mobility Spectrometry [18, 19]. The actual LoD values we have obtained are either lower (TNT (150 pg)) or slightly higher (RDX (6 ng), PETN (600 pg) and NG (2 ng)) than those often found for IMS. For example, Fetterolf et al. [21] have reported IMS LoD for RDX, TNT and PETN of 200 pg and for NG 50 pg. Another study using Electrospray Ionisation (ESI)-IMS reported LoD values for TNT, TNB, RDX, and EGDN to be 15 ng, 1.54 ng, 40 ng and 190 ng, respectively [22]. More recently, an IMS was interfaced with solid phase microextraction (SPME) [23], for which a LoD of 160 pg for TNT has been reported. (PETN and RDX were detected by the SPME-IMS, but not reproducibly and hence no LoD values are provided in that paper.) Using a corona discharge ionisation IMS system, Lee et al. [18] report LoD values for RDX, TNT, and PETN to be 100 pg, 1 ng, and 500 pg, respectively. Lower LoD values are possible with other types of instrumentation such as those that use liquid chromatography combined with MSⁿ techniques. These can also provide superior selectivity compared to IMS and PTR-MS [24, 25]. However, improved sensitivity and selectivity come at the expense of simplicity and costs. Furthermore, MSⁿ techniques can only look for one compound at a time. Therefore, even leaving aside the added complexity and allowing for the fact that it is possible to switch mass peaks quite quickly, this will limit the number of targets that can be covered in a brief thermal desorption event. These MSⁿ techniques are further unsuitable for general use in security areas, because of the long detection cycle as a result of the chromatographic techniques involved. Thus chromatography and MSⁿ techniques will have limited practical use as analytical devices in security areas. In comparison, IMS and PTR-MS can be used as rapid analytical instruments for the detection of single or multiple threat agents.

4.3 Cycle times

High sensitivity and selectivity, discussed above, are necessary but not sufficient for an analytical instrument to be of use in security areas. Another key property for an instrument to have is a rapid cycle time, whereby desorption, transfer, ionization, detection and removal of explosives take place within tens of seconds. This requires that instrumental memory effects are of the same timescale. We have demonstrated that the combination of a purposely built TDU and short heated inlet lines leading to the reaction chamber of a PTR-MS have resulted

in memory effects that are small (tens of seconds). The only exception we have found is for the explosive RDX. The longer memory effect found for RDX are not associated with the TDU, but is a result of the compound not being efficiently transferred to the drift tube owing to surface effects. (This was verified by removing the swab containing the RDX from the TDU and replacing it with a clean swab.) However, even for RDX, recovery times are not too severe, being approximately 1 minute. We are currently working on improvements to the heating of the inlet and drift tube to try to reduce this.

5. Conclusions

This study detailed the use of a novel thermal desorption system specifically designed for application with PTR-MS to detect compounds with low volatilities such as explosives. This has resulted in a step change in the performance of PTR-MS for use as a detector for traces of explosives. We have demonstrated that a first generation PTR-MS combined with a specifically designed and manufactured TDU has achieved sensitivities (nanograms) that are sufficiently low to meet current security application criteria [26]. However, recent improvements in the sensitivity of PTR-MS instruments, including the development of an ion funnel system [17], means that even lower LoD should be possible with a TDU/PTR-MS system.

Given the size and pumping requirements for PTR-MS, IMS instrumentation is less expensive and easier to use, especially when portable compact analytical devices are all that are required. These give IMS some distinct advantages over PTR-MS. However, PTR-MS has the distinct advantage of being more selective. We have demonstrated in this paper how this selectivity can be enhanced by manipulating the ion chemistry via changes in the operational parameters of the instrument, such as E/N to modify ion-molecule collisional energies and hence the intensities of the product ions.

It is appreciated that for this study we have introduced an analyte under the most advantageous way possible. However, the important goal of this paper is to demonstrate the TDU/PTR-MS system in terms of its efficiency and cycle time, which has been achieved. It is necessary to characterise a new instrument using ideal conditions, before considering complicating factors such as real samples and real-world sampling. Additional further work now needs to be undertaken to investigate the complexity of working with “real-world” sampling. This includes testing the instrument by wiping surfaces contaminated with known quantities of an explosive, using interference tests and determining throughput rate. Other studies are also needed to determine whether thermal decomposition of an explosive occurs.

Thus details on the ideal temperatures (or range of temperatures) at which the TDU/PTR-MS should be operated for optimal conditions for a given explosive would be obtained.

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Table 1

Calculated limits of detection (LoD) for the explosives investigated in this study presented in order of increasing molar mass. The product ions resulting from the reaction of H_3O^+ with a given explosive and their corresponding nominal m/z values are presented at given E/N values. The E/N value used for a given explosive was found to provide the best sensitivity. The linear dynamic range in nanograms (ng) is given for each explosive and the corresponding regression coefficient (r^2) provided. The precision of the method was evaluated by the determination of the repeatability and reproducibility in terms of relative standard deviation (RSD).

425 **Table 1**

Explosive	Product Ion, nominal m/z	E/N (Td)	Linear dynamic range (ng)	r^2	LoD (ng)	Repeatability (RSD %) (n=5)	Reproducibility (RSD %) (n=5)
EGDN	EGDNH ⁺ , 153	110	10-300	0.9982	4.4 ± 0.5	13.8	19.0
	NO ₂ ⁺ , 46			0.9910	7.2 ± 0.6	9.2	16.1
1,3-DNB	DNBH ⁺ , 169	170	0.5-25	0.9981	0.13 ± 0.02	2.9	7.7
3,4-DNT	DNTH ⁺ , 183	140	0.3-25	0.9982	0.07 ± 0.01	5.0	3.7
HMTD	HMTDH ⁺ , 209	90	1-500	0.9996	0.74 ± 0.08	3.8	5.2
1,3,5-TNB	TNBH ⁺ , 214	210	0.2-25	0.9980	0.14 ± 0.02	3.9	6.5
RDX	[RDX-HONO]H ⁺ , 176	110	50-1000	0.8938	36 ± 6	0.5	17.7
	CH ₃ N ₂ O ₂ ⁺ , 75			0.9974	6 ± 2	2.8	23.1
	NO ₂ ⁺ , 46			0.9993	14.9 ± 0.8	3.1	7.1
NG	NGH ⁺ , 228	80	15-500	0.9763	2.0 ± 0.2	9.6	10.8
	NO ₂ ⁺ , 46			0.9849	12 ± 2	6.6	6.5
2,4,6-TNT	TNTH ⁺ , 228	180	0.25-50	0.9974	0.15 ± 0.01	1.2	2.9
PETN	PETNH ⁺ , 317	110	15-500	0.9996	0.6 ± 0.1	2.0	3.9
	NO ₂ ⁺ , 46			0.9953	14 ± 1	12.4	16.4

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Figures

Figure 1. Schematic cross-section of the KORE Technology Ltd. thermal desorption unit. The laboratory air is heated as it travels through the heating block to the temperature of the block. This heated air is then dispersed across the surface area of the swab via a series of equally spaced holes (the pepper pot) directed towards the swab. The passage of the air heats the swab resulting in thermal desorption of material placed on it. This material is carried through by the gas flow to the drift tube reactor.

Figure 2. Illustrative calibration curve. This shows the normalised ion counts (relative to 10^6 H_3O^+ counts per second) of protonated TNT (m/z 228) versus mass (ng) spotted onto a swab prior to thermal desorption. The linear fit shown has $r^2 = 0.9974$.

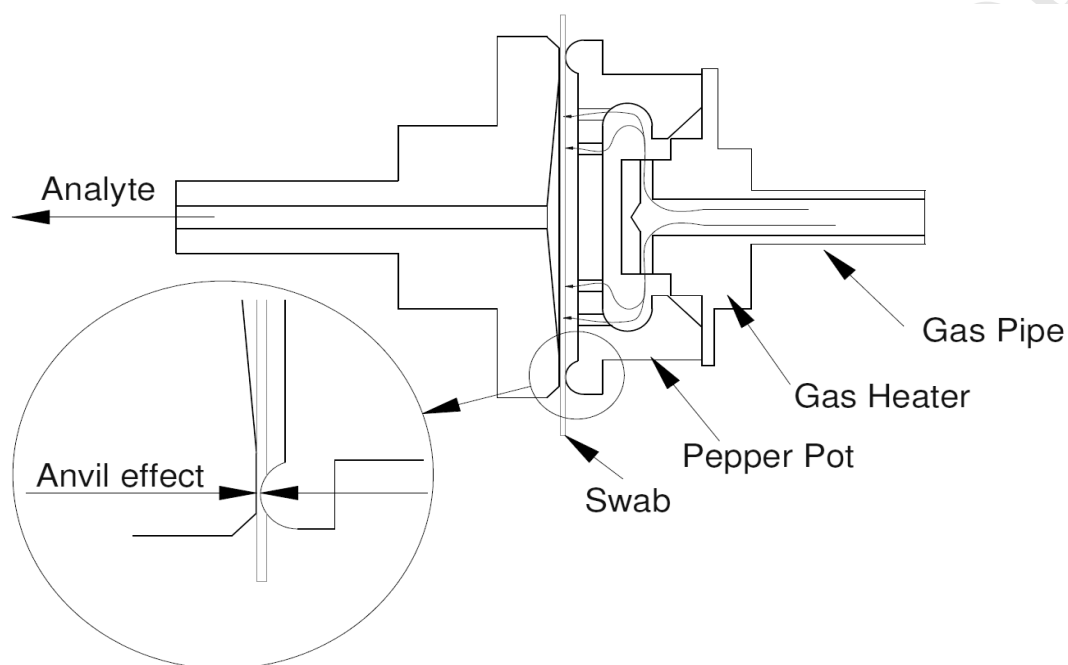
Figure 3. Thermal desorption chromatographic spectrum for 1 ng DNT deposited onto a clean swab. This is a plot shows the intensity of DNTH^+ as a function of time from just before and after insertion and compression of the swab.

Figure 4. Thermal desorption chromatographic spectra for 100 ng of RDX. The product ion intensities for m/z 75 and m/z 46 as a function of time are shown.

Figure 5. Logarithmic thermal desorption chromatographic spectra for 50 ng of NG. The intensities of the product ions at m/z 228 (NGH^+) and m/z 46 (NO_2^+) are shown at E/N values of (a) 80 Td and (b) 180 Td.

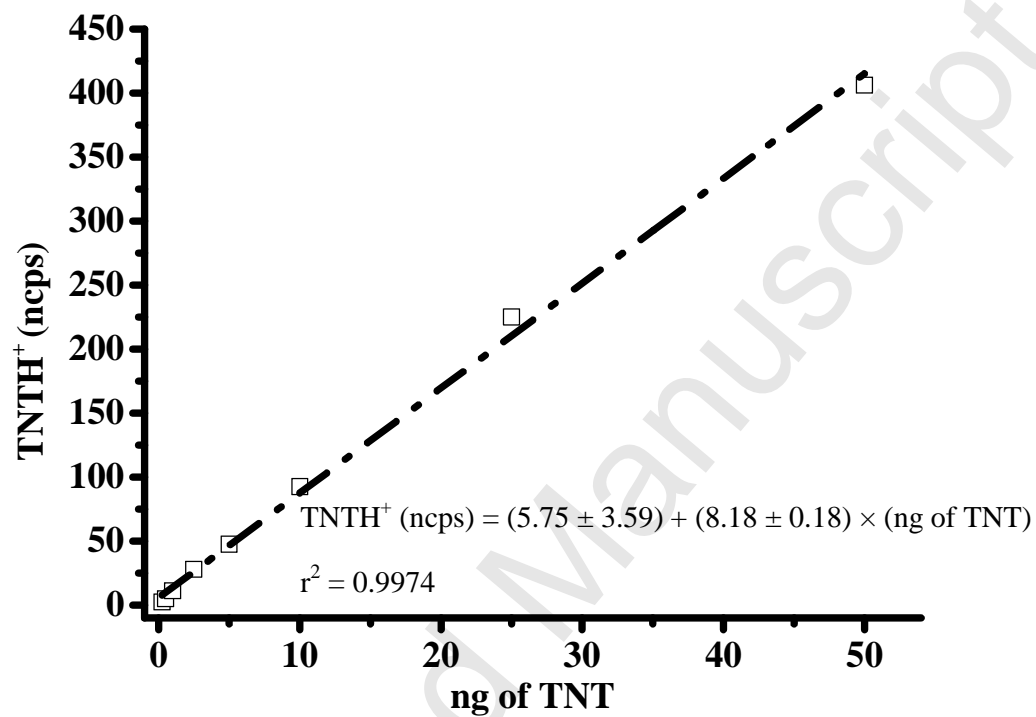
Figure 6. Logarithmic thermal desorption chromatographic spectra for 50 ng of TNT with channels m/z 228 and 46 being monitored at the E/N values of (a) 80 Td and (b) 180 Td. Only one product ion results from the reaction of H_3O^+ with TNT, TNTH^+ at m/z 228.

Figure 1.



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464 Figure 2.



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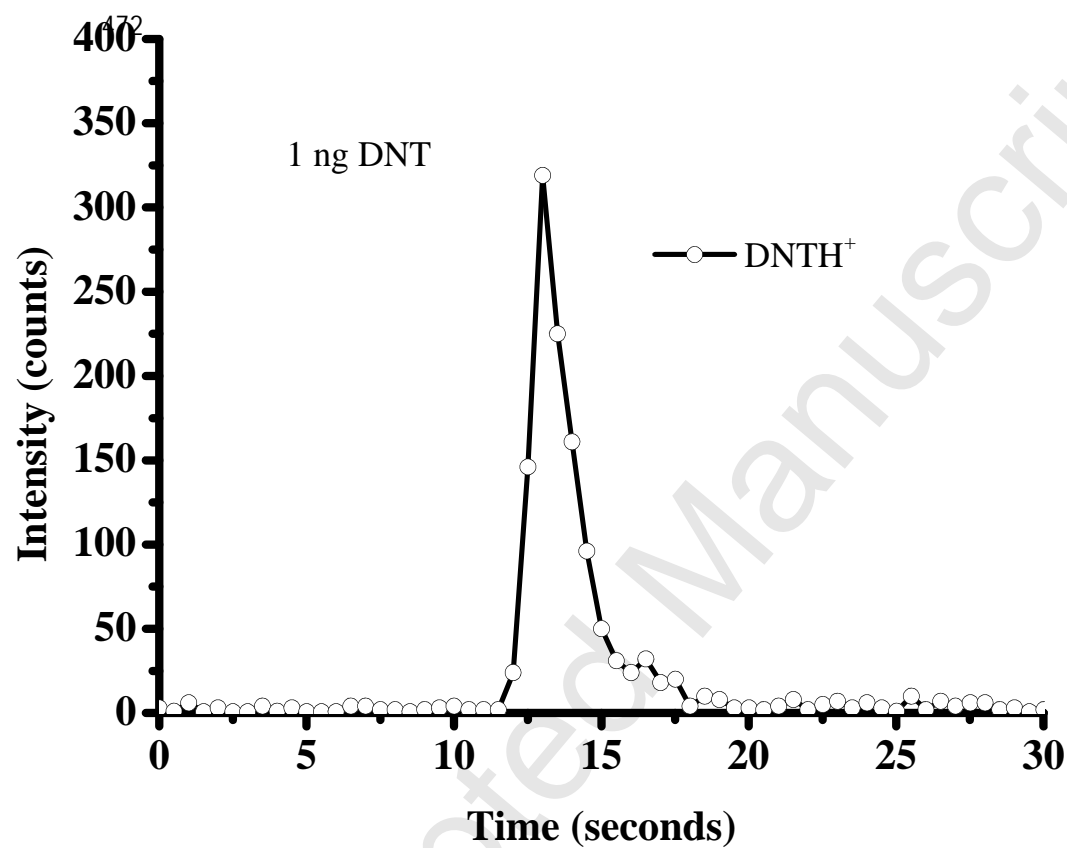
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469 Figure 3.

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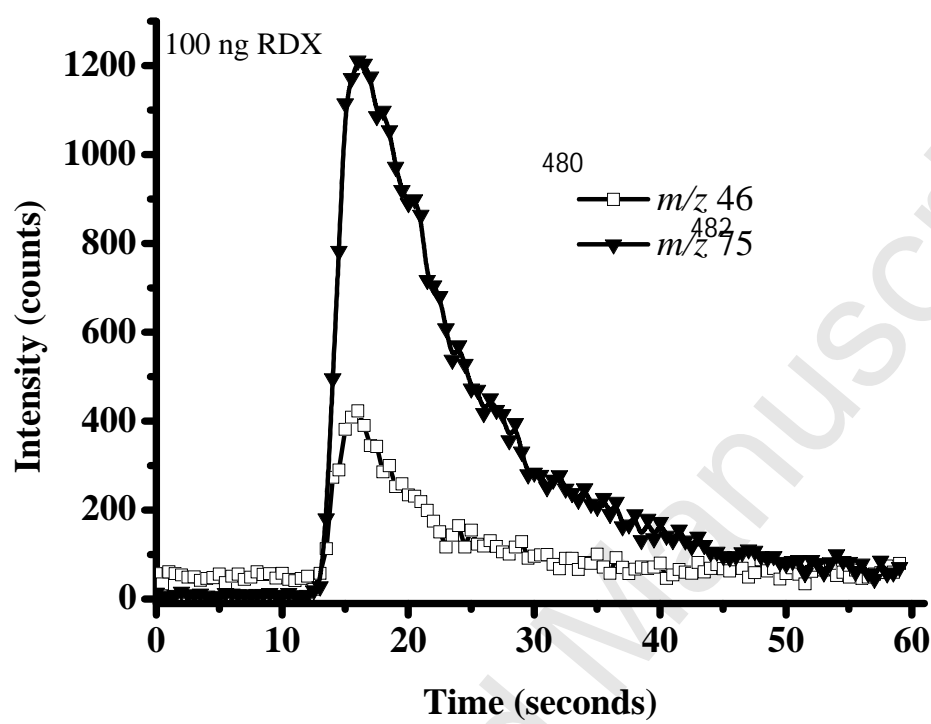


473 Figure 4.

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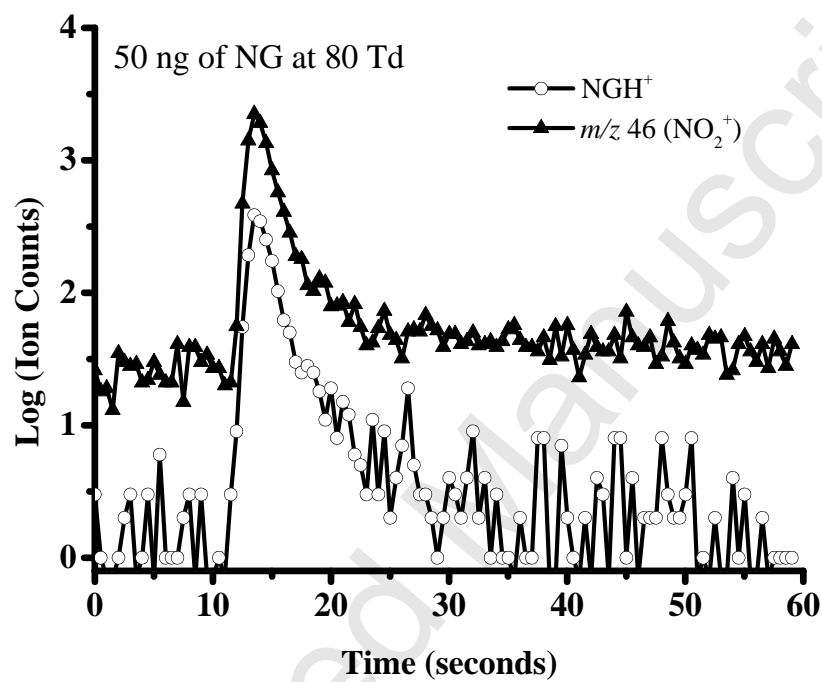
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484 Figure 5.

485 (a)



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487 (b)

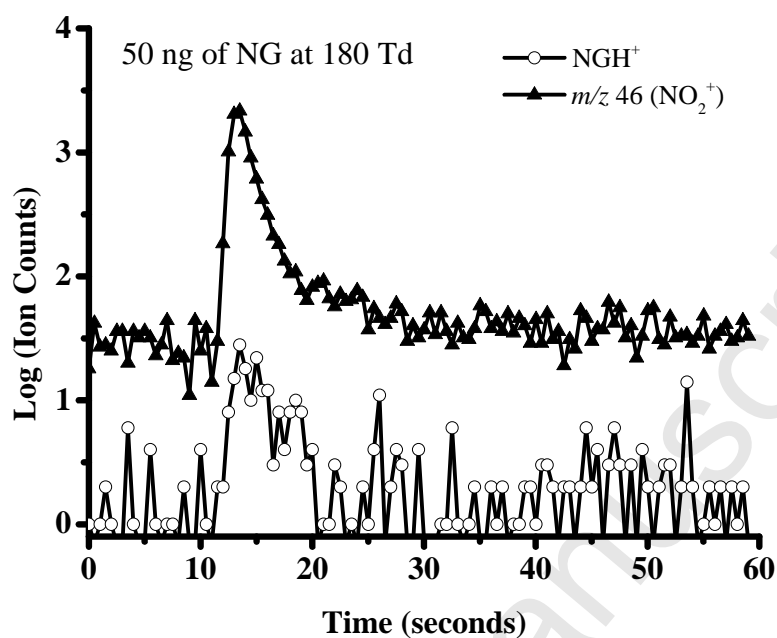
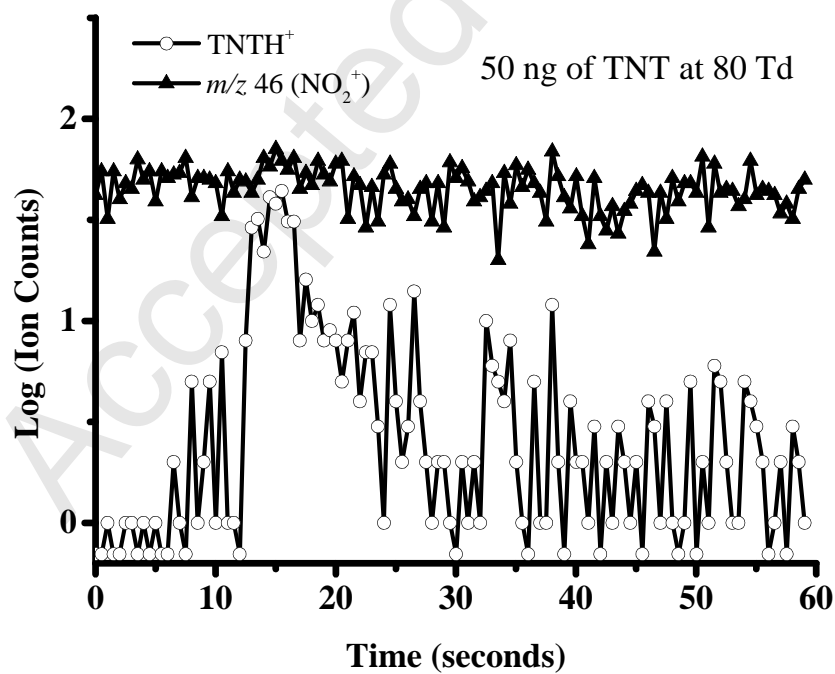
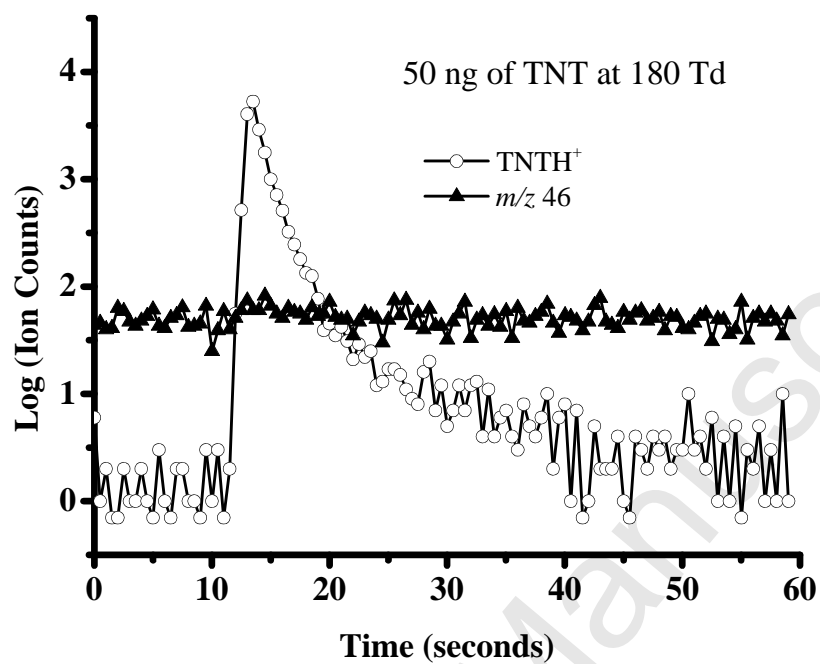


Figure 6.

(a)



(b)



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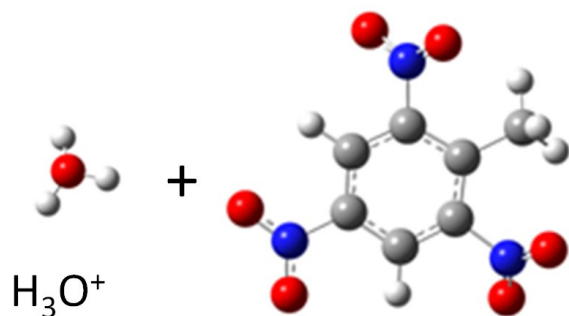
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5'

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H_3O^+

TNT

