

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

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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  $\text{H}_3\text{O}^+$  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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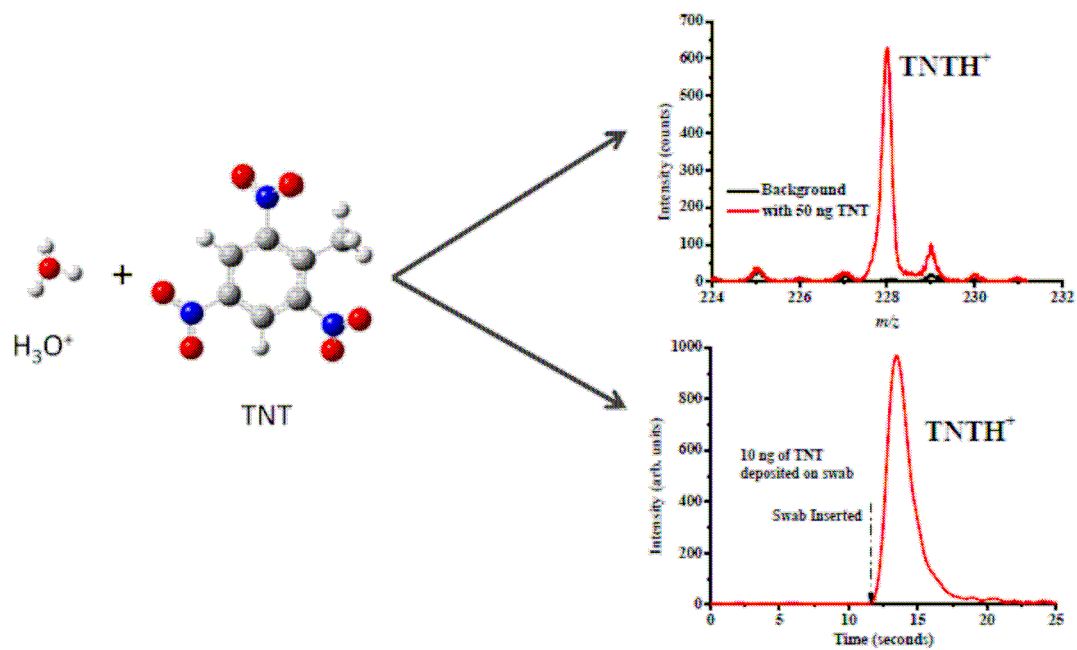
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30 **Abstract**

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

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

78 In order to overcome problems associated with memory effects and to determine  
79 instrumental LoD for the detection of trace explosives, we have developed a novel variable  
80 temperature thermal desorption unit (TDU) for use with PTR-MS. Recovery times and  
81 instrumental limits of detection (LoD) for the combined TDU/PTR-MS system are reported  
82 for a number of explosive compounds. In order of increasing molecular mass, these are  
83 ethylene glycol dinitrate (EGDN,  $m/z$  152,  $C_2H_4N_2O_6$ ), 1,3-dinitrobenzene (DNB,  $m/z$  168,  
84  $C_6H_4N_2O_4$ ), 3,4-dinitrotoluene (DNT,  $m/z$  182,  $C_7H_6N_2O_4$ ), hexamethylene triperoxide  
85 diamine (HMTD,  $m/z$  208,  $C_6H_{12}N_2O_6$ ), 1,3,5-trinitrobenzene (TNB,  $m/z$  213,  $C_6H_3N_3O_6$ ),  
86 1,3,5-trinitroperhydro-1,3,5-triazine (RDX,  $m/z$  222,  $C_3H_6N_6O_6$ ), nitroglycerin (NG,  $m/z$  227,  
87  $C_3H_5N_3O_9$ ), 2,4,6-trinitrotoluene (TNT,  $m/z$  227,  $C_7H_5N_3O_6$ ), and pentaerythritol tetranitrate  
88 (PETN,  $m/z$  316,  $C_5H_8N_4O_{12}$ ). The selection of explosives reported have been chosen because  
89 they cover a wide range of vapour pressures, ranging from the  $4.9 \times 10^{-9}$  mbar (RDX) to 0.1  
90 mbar (EGDN) at 25 °C [12]. Mass spectrometric  $m/z$  analysis of the product ions provides  
91 good selectivity. However, this paper illustrates how this selectivity can be enhanced by  
92 changing operational parameters in the drift (reaction) region.

93

## 94 **2. Experimental Details and Methods**

### 95 **2.1 Proton Transfer Reaction Mass Spectrometry (PTR-MS)**

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



110 (impurity) ions. These cannot react with water because their recombination energies (RE) are  
111 less than the ionisation energy of water (12.6 eV), and include  $\text{NO}^+$  (RE = 9.3 eV),  $\text{O}_2^+$  (RE =  
112 12.1 eV) and  $\text{NO}_2^+$  (RE = 9.6 eV), respectively. Operating conditions are such that the total  
113 impurity ion signal level is typically less than 3% of the  $\text{H}_3\text{O}^+$  intensity. Therefore usually  
114 these ions are of little consequence. However, we have found that  $\text{NO}_2^+$  is a product ion from  
115 the reaction of  $\text{H}_3\text{O}^+$  with explosives that contains a nitrate group, i.e. EGDN, NG and PETN,  
116 and with RDX. That must be taken into account when calculating the LoD using  $\text{NO}_2^+$ .

117

## 118 **2.2 Thermal Desorption Unit (TDU)**

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

137

## 138 **2.3 Operational Parameters**

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

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

147

## 148 **2.4 Explosive Compounds**

149 Single component standards for the explosives used in this study were purchased from  
150 AccuStandard Inc., New Haven, CT. Typically, these standards contained 1 mg of an  
151 explosive placed in 1 ml of either acetonitrile (AcN) or a mix of AcN and methanol (MeOH).  
152 RDX and TNT came in an AcN: MeOH (1:1) mix. PETN and DNT were delivered in MeOH.  
153 EGDN and HMTD (both at 0.1 mg) were supplied in AcN. NG (0.1 mg) came supplied in a 1  
154 ml solution of ethanol. However,  $\text{O}_2^+$  reacts with ethanol to form an ion at  $m/z$  46 via  
155 dissociative charge transfer, which complicates the analysis. Therefore, we purchased a  
156 sample of NG (100  $\mu\text{g}$ ) dissolved in AcN (1 ml) from Dr. Ehrenstorfer GmbH, Aurburg,  
157 Germany. The results for NG presented in this paper are all taken using that sample. Samples  
158 were diluted in the appropriate solvent(s) (HPLC grade) to provide the required quantity of an  
159 explosive. Typically 1  $\mu\text{l}$  of a solvent containing the required mass of an explosive was  
160 spotted onto a PTFE swab of diameter 3.5 cm. This swab came prepared from the  
161 manufacturer (ThermoFisher Scientific) and was mounted on rectangular cardboard for easy  
162 insertion into our TDU.

163

## 164 **2.5 Determining Instrumental Limits of Detection**

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

171

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

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

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

182

### 183 **3. Results**

#### 184 **3.1 Product ions**

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

192

#### 193 **3.1 Instrumental Limits of Detection**

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

201

#### 202 **3.2 Memory Effects**

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

210 to background values as quickly as those obtained for the other explosives, by approximately  
 211 60 seconds the ion signal intensities have dropped to approximately 5% of their peak values.

212 For the other compounds studied, DNB, TNB, NG, TNT and PETN, memory effects  
 213 were found to be slightly greater than those found for explosives such as DNT, but  
 214 significantly less than that observed for RDX. Typically background levels were reached in  
 215 approximately 20 seconds. To illustrate this, figure 5 (a) shows the temporal profiles of  
 216  $\text{NGH}^+$  and  $\text{NO}_2^+$  for 50 ng of NG taken at an  $E/N$  of 80 Td, which is the best value of the  
 217 reduced electric field in terms of sensitivity for detecting the protonated parent. To  
 218 demonstrate the effect of  $E/N$  on the product ion branching ratios, figure 5 (b) shows the  
 219 identical NG product ions being monitored, but this time taken at a higher reduced electric  
 220 field of 180 Td. Figures 6 (a) and (b) show the corresponding results for TNT at  $E/N$  values  
 221 of 80 Td and 180 Td, respectively, using a swab onto which 50 ng of TNT was placed.

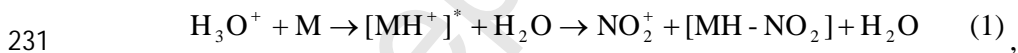
222

## 223 4. Discussions

### 224 4.1 Product ions and improved selectivity

225 Compared to IMS, PTR-MS provides more selectivity because of the mass spectral analysis.  
 226 However, product ions are not necessarily unique for a given explosive. In this study  $\text{NO}_2^+$  is  
 227 a product ion that comes from all of the nitrate esters. This product ion results from the  
 228 formation of a hydroxyl group upon proton transfer and the subsequent elimination of a nitro  
 229 group in the form of  $\text{NO}_2^+$ :

230



232

233 where  $\text{M} = \text{EGDN}$ ,  $\text{NG}$ , or  $\text{PETN}$ . However, the observation of it and the protonated parent  
 234 makes it possible to identify explosives with a high level of confidence. An example of this is  
 235 its use to discriminate between TNT and NG. These two compounds have the name nominal  
 236 protonated mass. However, TNT reacts with  $\text{H}_3\text{O}^+$  to produce only the protonated parent. The  
 237 absence of an  $\text{NO}_2^+$  product ion provides a simple method to distinguish between NG and  
 238 TNT (compare figures 5 and 6). Even if TNT and NG are both present, the unusual increase  
 239 of the  $\text{TNTH}^+$  signal with increasing  $E/N$  [7] means that it is possible to determine if both  
 240 compounds are present. This serves to demonstrate how changes in operational parameters  
 241 can be used effectively to improve the instrumental selectivity.

242

243 **4.2 TDU/PTR-MS instrumental limits of detection and comparisons with other**  
244 **instruments**

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

269

270 **4.3 Cycle times**

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

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

284

## 285 **5. Conclusions**

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

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

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

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

313

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324

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412 Applications **1999**, NIJ Guide 100-99.

414 **Table 1**

415 Calculated limits of detection (LoD) for the explosives investigated in this study presented in  
416 order of increasing molar mass. The product ions resulting from the reaction of  $\text{H}_3\text{O}^+$  with a  
417 given explosive and their corresponding nominal  $m/z$  values are presented at given  $E/N$   
418 values. The  $E/N$  value used for a given explosive was found to provide the best sensitivity.  
419 The linear dynamic range in nanograms (ng) is given for each explosive and the  
420 corresponding regression coefficient ( $r^2$ ) provided. The precision of the method was  
421 evaluated by the determination of the repeatability and reproducibility in terms of relative  
422 standard deviation (RSD).

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425 **Table 1**

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

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427

428 **Figures**

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

435 Figure 2. Illustrative calibration curve. This shows the normalised ion counts (relative to  $10^6$   
436  $\text{H}_3\text{O}^+$  counts per second) of protonated TNT ( $m/z$  228) versus mass (ng) spotted onto a swab  
437 prior to thermal desorption. The linear fit shown has  $r^2 = 0.9974$ .

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

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

443 Figure 5. Logarithmic thermal desorption chromatographic spectra for 50 ng of NG. The  
444 intensities of the product ions at  $m/z$  228 ( $\text{NGH}^+$ ) and  $m/z$  46 ( $\text{NO}_2^+$ ) are shown at  $E/N$  values  
445 of (a) 80 Td and (b) 180 Td.

446 Figure 6. Logarithmic thermal desorption chromatographic spectra for 50 ng of TNT with  
447 channels  $m/z$  228 and 46 being monitored at the  $E/N$  values of (a) 80 Td and (b) 180 Td. Only  
448 one product ion results from the reaction of  $\text{H}_3\text{O}^+$  with TNT,  $\text{TNTH}^+$  at  $m/z$  228.

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450 Figure 1.

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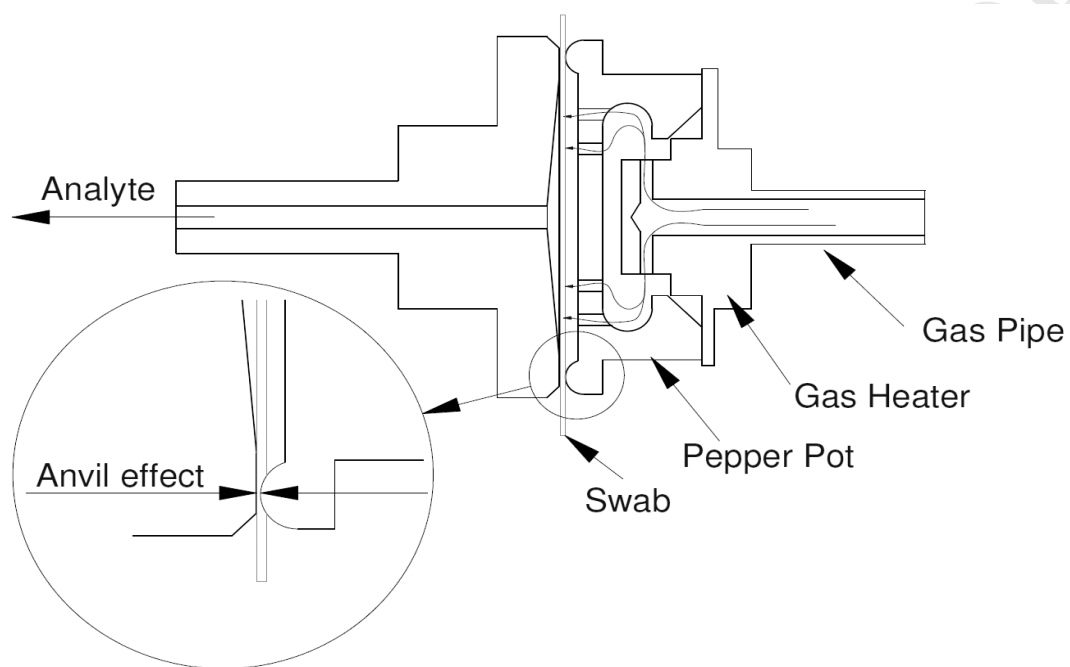
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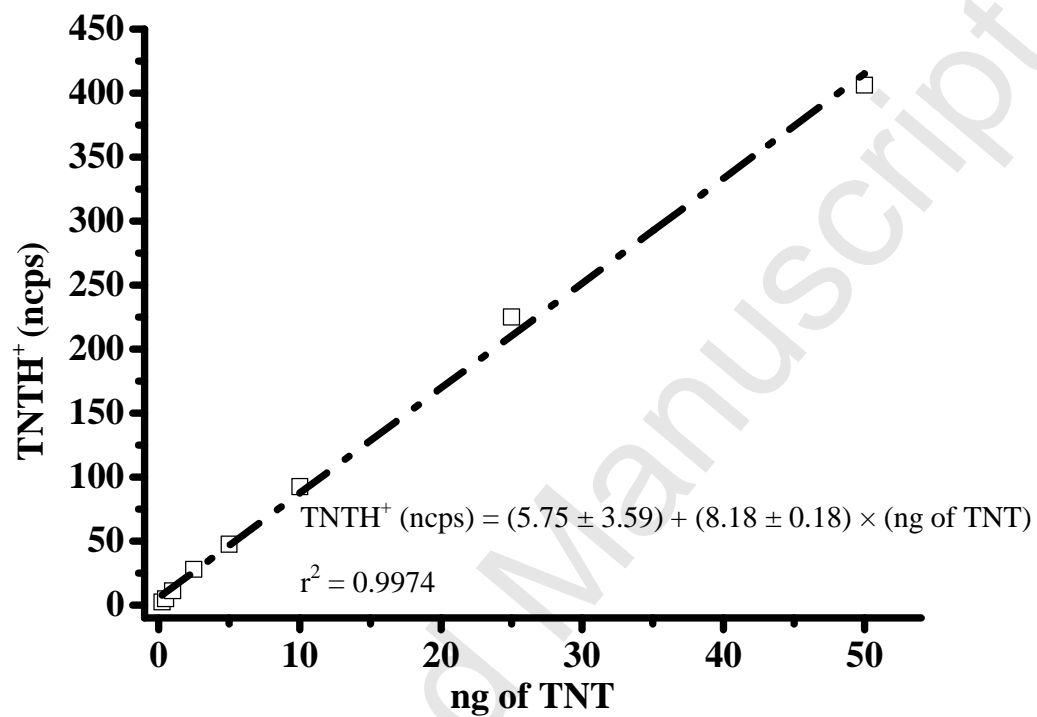
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464 Figure 2.



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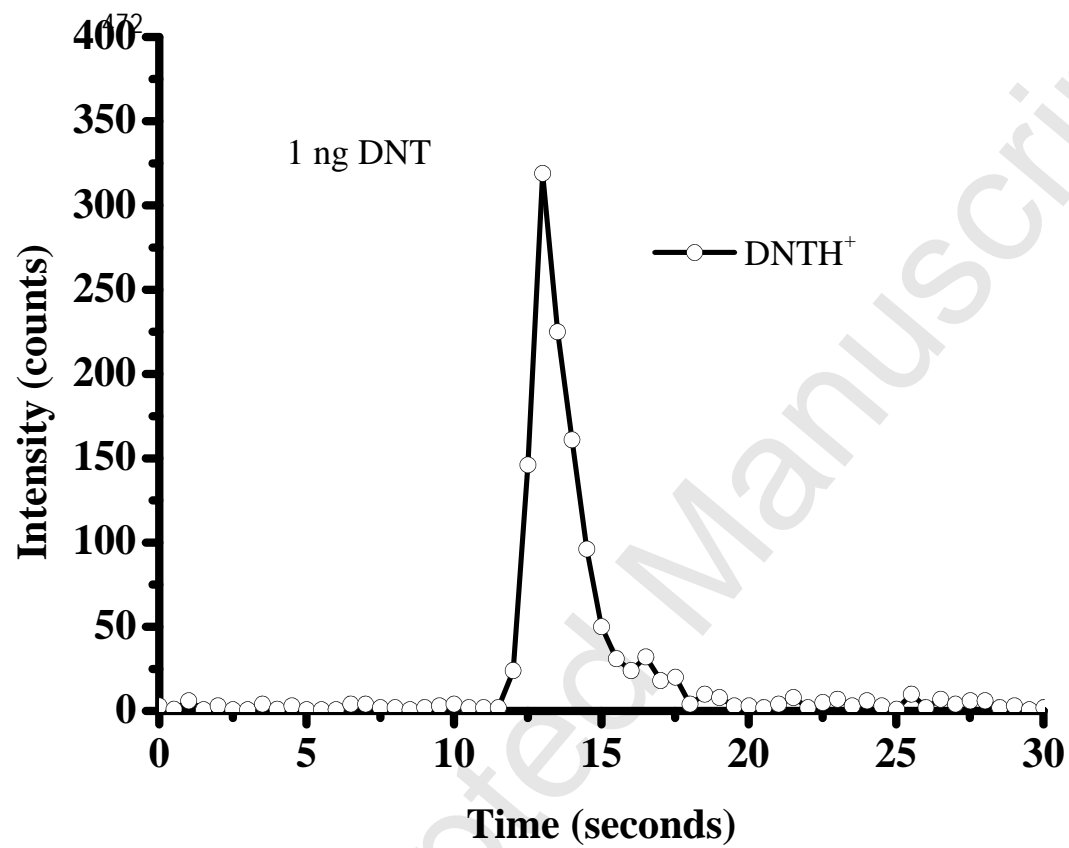
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469 Figure 3.

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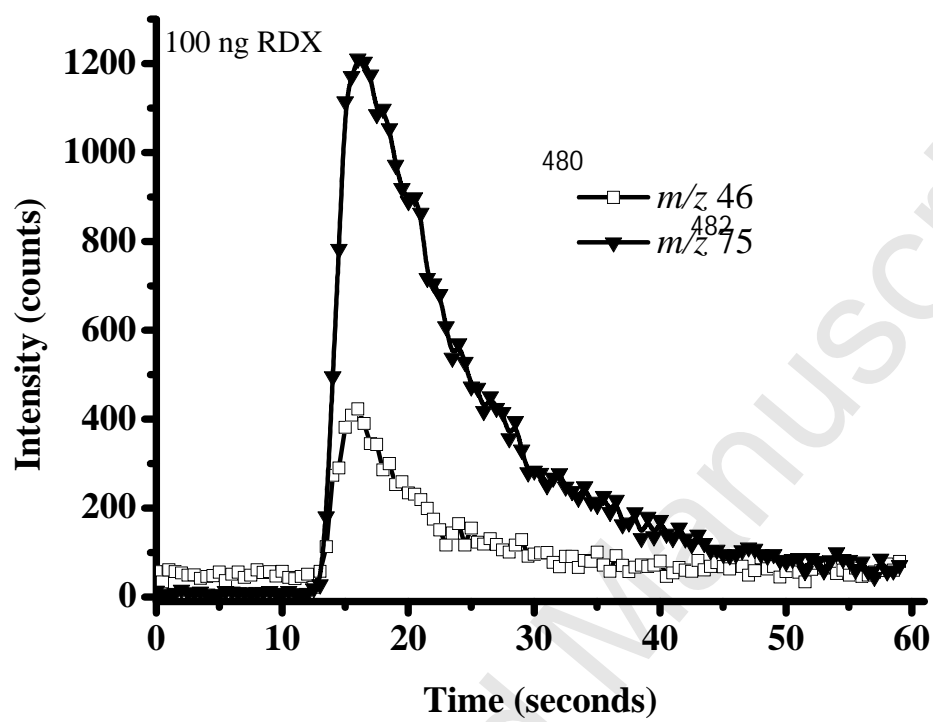


473 Figure 4.

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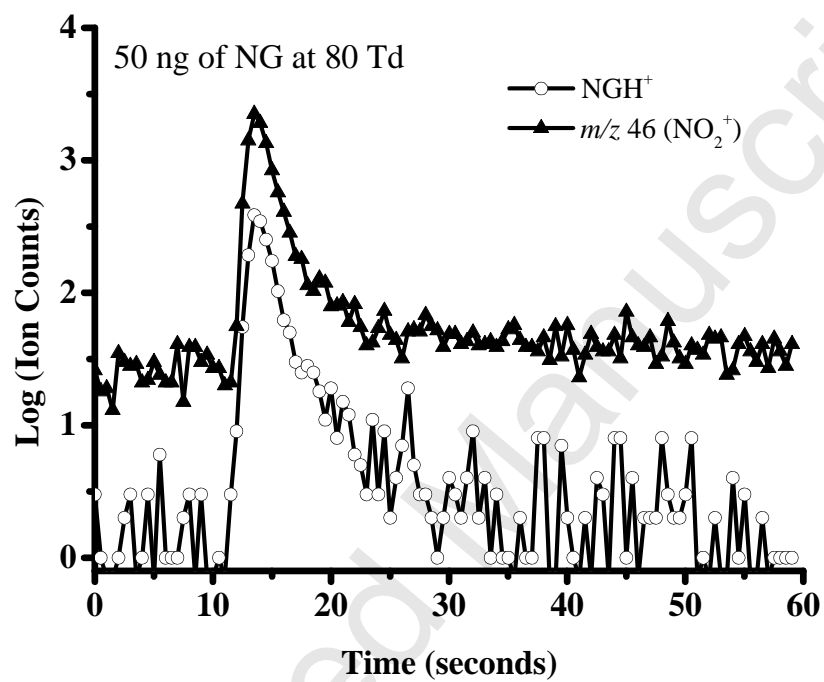




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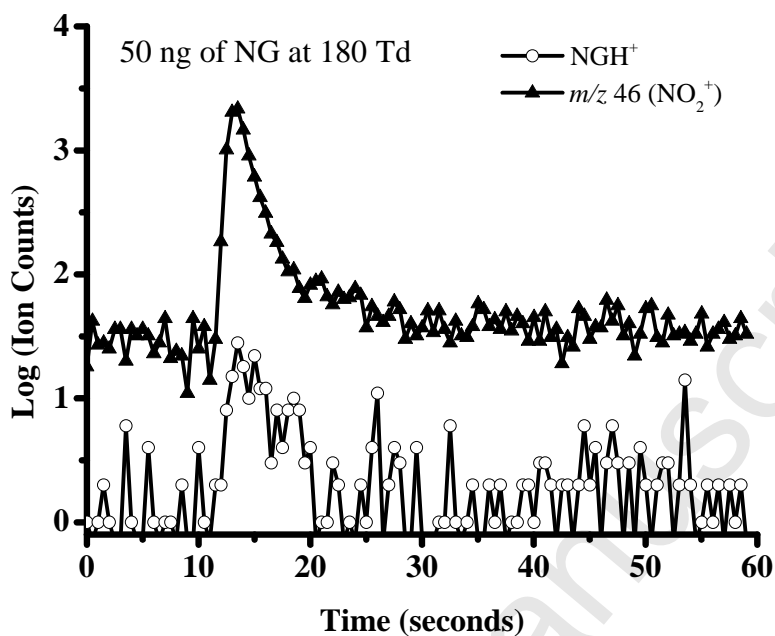
484 Figure 5.

485 (a)



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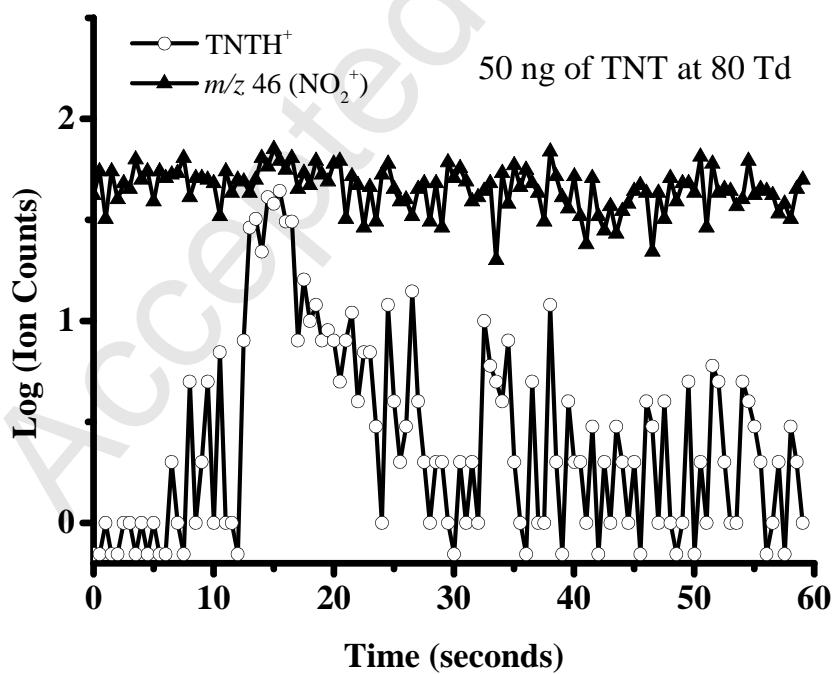
487 (b)



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490 Figure 6.

492 (a)



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511 (b)

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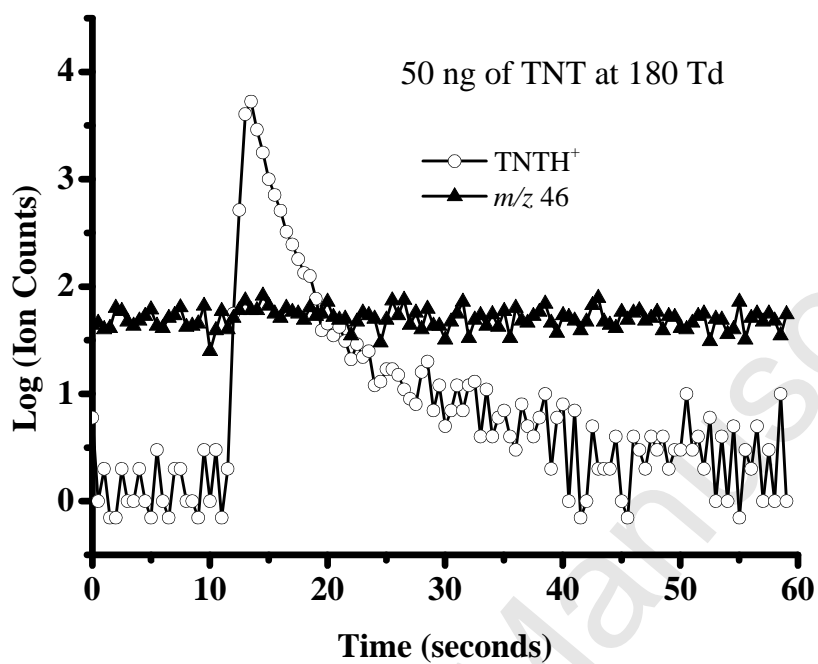
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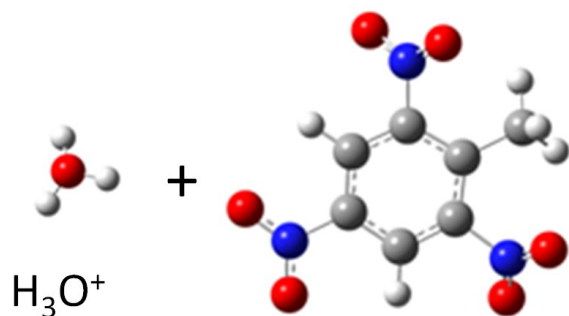
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 $\text{H}_3\text{O}^+$ 

TNT

