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Short communication

Applications of proton transfer reaction time-of-flight mass spectrometry for the sensitive and rapid real-time detection of solid high explosives

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ABSTRACT

Using recent developments in proton transfer reaction mass spectrometry, proof-of-principle investigations are reported here to illustrate the capabilities of detecting solid explosives in real-time. Two proton transfer reaction time-of-flight mass spectrometers (Ionicon Analytik) have been used in this study. One has an enhanced mass resolution ($m/\Delta m$ up to 8000) and high sensitivity (~50 cps/ppbv). The second has enhanced sensitivity (~250 cps/ppbv) whilst still retaining high resolution capabilities ($m/\Delta m$ up to 2000). Both of these instruments have been successfully used to identify solid explosives (RDX, TNT, HMX, PETN and Semtex A) by analyzing the headspace above small quantities of samples at room temperature and from trace quantities not visible to the naked eye placed on surfaces. For the trace measurements a simple pre-concentration and thermal desorption technique was devised and used. Importantly, we demonstrate the unambiguous identification of threat agents in complex chemical environments, where multiple threat agents and interferents may be present, thereby eliminating false positives. This is of considerable benefit to security and for the fight against terrorism.

1. Introduction

Fears of terrorism and the requirement to detect dangerous chemicals in low concentrations is leading to an ever-increasing need for reliable, real-time and sensitive detection of a wide range of substances that are a threat to the safety of our society. The chemicals that need to be detected in trace quantities range from explosives, through to narcotics and chemical and biological agents. The ability to quickly and accurately identify these hazardous compounds, particularly within a complex chemical environment, is vital to any nation's needs for its fight against crime and terrorism. An obvious need for such detection is for airport security [1]. Consequently, considerable effort has been focused on the direct detection of threat agents in trace quantities on a passenger and on carry-on and checked luggage. The detection of residual traces may indicate that a passenger had been in recent contact with a threat agent; it is particularly difficult to make a bomb without contaminating people and objects [1].

The major technological requirements for the detection of trace quantities of threat agents in real-time include rapid cycle time and high sensitivity and selectivity. A rapid cycle time, whereby sampling, analysis, processing of data and recovery occurs within tens of seconds, is crucial for high throughput and for the technology to be tolerated by the travelling public and the airlines. A rapid recovery time is required for the elimination of memory effects so that a large number of passengers and their luggage can be quickly processed. High sensitivity is particularly important when dealing not only with small quantities of threat agents but also with threat agents, such as solid explosives, which have extremely low vapour pressures. High selectivity is needed to reduce the number of false positives and negatives. In addition to these requirements any instrument used must also be able to detect a large range of possible (multiple) threat agents in complex chemical environments.

There are a number of technologies available for security applications based on the analysis of volatile organic compounds (VOCs) emitted by threat agents, but none succeed in achieving all of the above requirements. The current technologies most commonly employed for the detection of threat agents include Gas Chromatography-Mass Spectrometry (GC-MS) and Ion Mobility Spectrometry (IMS), with IMS being the technology most deployed. GC-MS has a number of limitations. Not least is its inherent reliance on chromatographic columns, making it difficult for one GC-MS to be able to handle the detection of a large range of VOCs. There are also issues of long cycle times and potentially the complex mass spectra to analyse, wherein the parent VOC is rarely observed. IMS operates at atmospheric pressure, is rapid and highly sensitive, and is therefore currently the preferred technology used in secu-

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rity applications [2,3]. Its major limitation is associated with its inherent poor selectivity, which results in frequent false positives through detection of another chemical, such as solvents, resulting in a change in the mobility spectrum similar to that of a threat agent.

The disadvantages of the poor selectivity associated with IMS, whilst retaining its major advantage of sensitivity, have been overcome by the recent development of high resolution and high sensitivity proton transfer reaction time-of-flight (PTR-ToF) mass spectrometers [4–6]. It is therefore of interest to test the capabilities and performance of these spectrometers for the detection of threat chemical agents in trace quantities in the environment, which is of considerable benefit for the prevention of crime and for improved security.

In this short communication we present proof-of-principle measurements for the detection of solid explosives from their VOCs emissions using two types of PTR-ToF mass spectrometers. One is an instrument (PTR-TOF 8000) that has recently become commercially available from Ionicon Analytik [4–6]. This has an extremely high mass resolution (up to approx. 8000 m/Δm) and high sensitivity (as low as a few pptv). The second instrument is currently being developed by Ionicon Analytik, with an enhanced sensitivity compared to the PTR-TOF 8000 version whilst still retaining high resolution capabilities (up to 2000 m/Δm), and is referred to as the PTR-TOF 2000.

There are two recent ion-molecule reaction studies presented in the literature dealing with the detection of VOC emissions from explosives [7,8]. Both of these are associated with detecting the unstable explosive triacetone triperoxide (TATP), $C_9H_{18}O_6$. One is a selected ion flow tube (SIFT) study by Wilson et al. [7] who used thermal H_3O^+, O_2^+, and NO^+ as reagent ions. They concluded that only NO^+ reactions with TATP showed product ions that provide unequivocal evidence for a TATP-based explosive. A later study by Shen et al. used a proton transfer reaction quadrupole mass spectrometer with H_3O^+ or NH_4^+ as the reagent ions [8]. They showed that by using a suitable reduced-electric field in the drift tube of the PTR chamber, TATP could be readily identified. Whilst the above two earlier studies have demonstrated the capabilities of using ions as probes to VOC emissions from explosives, they are limited to a highly volatile explosive, with TATP having a high vapour pressure at room temperature (5.25×10^{-2} Torr at room temperature—the highest of most commonly used explosives) [9]. By way of comparison, the vapour pressures of solid explosives are considerably less, making their detection by headspace analysis that much more difficult. A more recent SIFT study dealing with emissions from a number of industrial explosives (EMSIT1, Ostravit C, Perunit 28E and Permonex V19) was briefly presented at a conference [10]. That study rarely observed parent molecular ions. Only in the case of those explosives containing highly volatile compounds (namely ethylene glycol dinitrate (EGDN) and nitroglycerine (NG)) were parent explosive molecules (EDGN and NG) identified. To our knowledge, reported here are the first ion-molecule investigations applying PTR-MS technology to detect trace quantities of solid explosives with very low vapour pressures at room temperature.

A number of solid explosives have been used in this study; namely, and in order of increasing molecular weight, 1,3,5-Triazine hexahydro-1,3,5-trinitro (RDX, $C_3H_6N_6O_6$), 2,4,6-trinitrotoluene (TNT, $C_6H_2(NO_2)_3CH_3$), 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX, $C_4H_8N_8O_8$), and pentaerythritol tetranitrate (PETN, $C_5H_8N_4O_{12}$) in addition to the general-purpose plastic explosive Semtex A (containing 6% RDX and 94% PETN).

2. Experimental details

Since the successful launch of Ionicon's PTR Quadrupole Mass Spectrometer system in the mid-1990s [4,11], there has been a considerable growth in the use and exploitation of proton transfer reaction mass spectrometry for trace gas analysis in various chemical and physical environments, and in particular for the detection of VOCs at low concentrations [12–17]. The recent development of high resolution and high sensitivity PTR-ToF mass spectrometers will only enhance this growth and development in analytical chemistry.

In addition to the benefits associated with the higher resolution achievable with ToF-MS compared to quadrupole mass spectrometers (namely in the PTR-TOF 8000 version the ability to easily separate isobaric ions), there is the added benefit of being able to record all ions simultaneously—thereby eliminating the need to select a subset of ions for monitoring as is required for quadrupole-based experiments. In addition, and again unlike quadrupole mass spectrometer systems, the sensitivity of ToF systems does not decrease with increasing molecular ion mass, making ToF systems particularly suitable for the detection of high weight molecular ions.

The first reported use of a PTR-ToF-MS for analytical purposes was by Blake et al. in 2004 [18]. Subsequently there are a number of papers in the literature illustrating the successful use of PTR-ToF-MS instruments [19–21]. Crucially, however, the two PTR-ToF mass spectrometers used in this study both surpass any of the other instruments referred to in the above papers in terms of their sensitivity and selectivity.

The PTR-TOF 8000 has already been described in detail in a recent publication [6]. The PTR-TOF 2000 system differs from the 8000 version primarily in the type of ToF-MS interfaced to the PTR.

Both instruments have identical hollow cathode ion sources and drift tubes, and therefore a description of the PTR is valid for both instruments. H_3O^+ reagent ions are produced from water vapour introduced as a reagent gas into the hollow cathode from a liquid water sample holder via a mass flow controller. These reagent ions, under the influence of a voltage gradient, pass through a small orifice into the adjacent drift tube section, where the analyte is introduced (via a gas inlet system with an adjustable flow of between 50 and 1000 sccm and an adjustable temperature of between 40 and 150 °C). The operating pressure in the drift tube is usually maintained between 2.2 and 2.4 mbar whilst the drift tube voltage and temperature can be varied between 400–1000 V and 40–120 °C, respectively. The voltage applied across the drift tube is used to adjust the ratio of electric field strength (E) to molecular number density (N), and is usually selected to minimise fragmentation of product ions whilst ensuring a high H_3O^+ signal. Within the drift tube proton transfer reactions occur between H_3O^+ ions and any VOCs present in the sample whose proton affinities are greater than that of H_2O. The protonated VOCs (and fragment ions if present) are then sampled through an orifice at the end of the drift tube and focused, via a specially designed transfer lens system, into the pulse extraction region of the orthogonal acceleration reflectron ToF mass spectrometer. Here ions are accelerated into the ToF section at a typical repetition rate of up to approximately 80 kHz. The mass-to-charge ratios of the ions are determined from the flight times measured and each extraction pulse generates a complete mass spectrum for the time interval (mass range) chosen. Each mass spectrum is then processed by a fast data acquisition board in combination with a desk top computer.

Of interest is a comparison of the sensitivities of the two instruments. This is illustrated in Fig. 1, which shows the counts per seconds achievable for VOC concentrations at the level of 1 ppbv over the mass range 79–181 amu. This figure was obtained by using a calibration gas standard (mixture from Restek) with both instruments operating in V-mode (one reflection). For these calibration measurements the drift tubes were maintained at a temperature of 60 °C and pressure of 2.3 mbar with an applied voltage of 600 V, resulting in a reduced-electric field E/N value of 129 Td

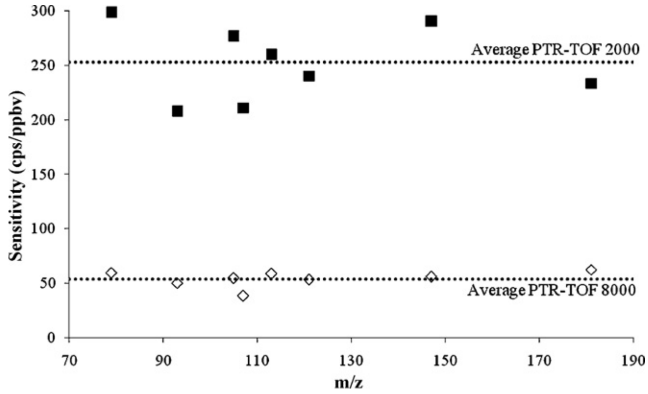

Fig. 1. Comparisons of sensitivity (counts per second per ppbv) between the PTR-TOF 8000 (resolution up to 8000) and the PTR-TOF 2000 (resolution up to 2000) over the range *m*/*z* 79–181 determined at *E*/*N* = 129 Td. The relative standard deviation about the mean values of 54 cps/ppbv (PTR-TOF 8000, H_3O^+ signal intensity of 1.0×10^6 cps) and 254 cps/ppbv (PTR-TOF 2000, H_3O^+ signal intensity of 1.6×10^6 cps) is 14% for both instruments. The calibration gas used for these measurements contained benzene (100 ppbv), toluene (100 ppbv), styrene (92 ppbv), ethyl benzene and o, m and p-xylene (400 ppbv), 1,2,4- and 1,3,5-trimethylbenzene (199 ppbv), 1,2-, 1,3- and 1,4-dichorobenzene (300 ppbv) and 1,2,4-trichlorobenzene (99 ppbv).

(1 Td = 10^{-17} V cm^2). By taking an average value of the measurements a value for the sensitivities of the two instruments can be determined. The PTR-TOF 8000 is found to have a sensitivity of 54 ± 7 cps/ppbv (H_3O^+ signal intensity of 1.0×10^6 cps) and the PTR-TOF 2000 has a sensitivity of 254 ± 35 cps/ppbv (H_3O^+ signal intensity of 1.6×10^6 cps), both across the range *m*/*z* 79–181 amu. The errors represent one standard deviation, which provide the same relative standard deviation about the mean of 14%.

To record the VOCs emitted from the solid explosives at room temperature, a small quantity of a particular threat agent was placed in a closed glass vial. Laboratory air was then drawn through a charcoal filter into the glass vial, passed over the sample and drawn simultaneously into one of two inlet lines. Thus both instruments were operated in parallel in order for them to be sampling the threat agents under identical conditions. The sample inlet lines (1/16th in. peek, internal diameter 1 mm (VICI AG International)) were both of approximately 1 m in length and passed from the sample to the PTR inlet system. They were heated and maintained at 120 °C to minimize surface adsorption. The drift tubes were maintained at 90 °C.

Critical to the measurements involving the explosives was the uniform heating of the sample, inlet lines and PTR chamber, because of the condensable nature of the explosives. It was observed that if any cold spots were present, the signal corresponding to the protonated parent would significantly diminish.

Given the low vapour pressures associated with the solid explosives, additional procedures were adopted to help obtain higher VOC concentrations. This involved devising and utilizing a simple pre-concentrator and thermal desorption system. Basically, this involved passing high flows of air at room temperature over the solid samples or over trace quantities placed on a surface and through a fine stainless steel wire mesh for approximately 5 s to collect small quantities of the explosive via adsorption. The mesh consisted of 325 × 325 wires per inch, with each wire having a diameter of 0.0014 of an inch (Small Parts Inc., Florida, USA). The heated inlet line to either the PTR-TOF 8000 or PTR-TOF 2000 was then placed within a few mm to the wire mesh. The mesh was then heated for typically 5–10 s by passing a current through it in order to reach temperatures of between 100 and 150 °C. The resulting high molecular weight VOCs released in a much more concentrated form during the heating were then monitored as a function of time.

For the investigations involving trace quantities on a surface, 2–3 particles of an explosive were placed onto a latex glove. The particles were then gently rubbed on the surface of that glove and then returned to their container. The glove was brushed-off so that no residue of the explosive was visible on the glove prior to passing air over its surface.

In addition to the above, we also performed a simple swipe procedure in an attempt to duplicate the type of process used for IMS systems in airports. For this procedure a small quantity of an explosive was rubbed on a cardboard surface, and then returned to its container. The surface was brushed-off and, as for the glove, no visible deposits could be seen on the cardboard's surface. A metal mesh was then rubbed over the cardboard surface for a few seconds to pick-up any residue of the explosive. The mesh was then subsequently heated as before to 100–150 °C and the corresponding VOC emissions monitored as a function of time.

All of the explosives used in this study were obtained from the Austrian Army.

3. Results

All of the solid explosives investigated in this study are in wide use today, with TNT being the most widely used. HMX, which is chemically related to RDX, is generally employed in solid-fuel rocket propellants and in high performance warheads. Semtex A is a general-purpose plastic explosive containing predominantly PETN, and is one of the most powerful explosives known.

3.1. Headspace measurements above samples of solid explosives at room temperature

This part of the investigation serves to illustrate the sensitivity of the PTR-TOF 8000 and 2000 instruments to detect solid explosives without any heating or any form of pre-concentration followed by thermal desorption. Here the headspace above a small quantity of explosive (typically less than 1 g) placed in a glass vial and maintained at room temperature was sampled and analysed. By monitoring the intensity of the protonated parent molecular ion we were able to detect RDX, TNT, HMX, PETN and Semtex A. To illustrate this we present in Fig. 2(a)–(d) the mass spectra recorded using the PTR-TOF 8000 instrument obtained from headspace analysis (at 30 °C) above RDX, TNT, HMX and PETN, respectively, at the *m*/*z* value corresponding to the associated protonated molecular parent (223.0427, 228.0257, 297.0543 and 317.0217, respectively). (A spectrum for Semtex A is not given because it is identical to that of PETN.) Fig. 3 shows measurements for TNT taken simultaneously on the PTR-TOF 8000 and 2000 instruments. The figure clearly demonstrates the differences in the sensitivities and resolutions of the two instruments. That the signal intensity for the PTR-TOF 2000 measurement is not five times that recorded for the PTR-TOF 8000 instrument, as expected from the sensitivity measurements, is attributed to differences in the heated inlet sampling lines. Fig. 3 also serves to demonstrate that the mass accuracy (i.e., accurate assignment of the peak position) is similar for both instruments.

Worthy of comment is the observation that the signal intensity corresponding to protonated TNT shows a dramatic increase in intensity (Fig. 2(b)) upon changing the applied drift tube voltage from 400 V (corresponding to an *E*/*N* value of approximately 90 Td) to 600 V (corresponding to an *E*/*N* value of approximately 140 Td), whilst the opposite is true for PETN (Fig. 2(d)). For PETN this is presumably because as *E*/*N* increases fragmentation of the protonated parent molecule occurs. Significant fragmentation of the protonated TNT (i.e., a decrease in signal intensity) is only observed after a drift tube voltage of 760 V has been applied, corresponding to an *E*/*N* of approximately 180 Td. We were unable to

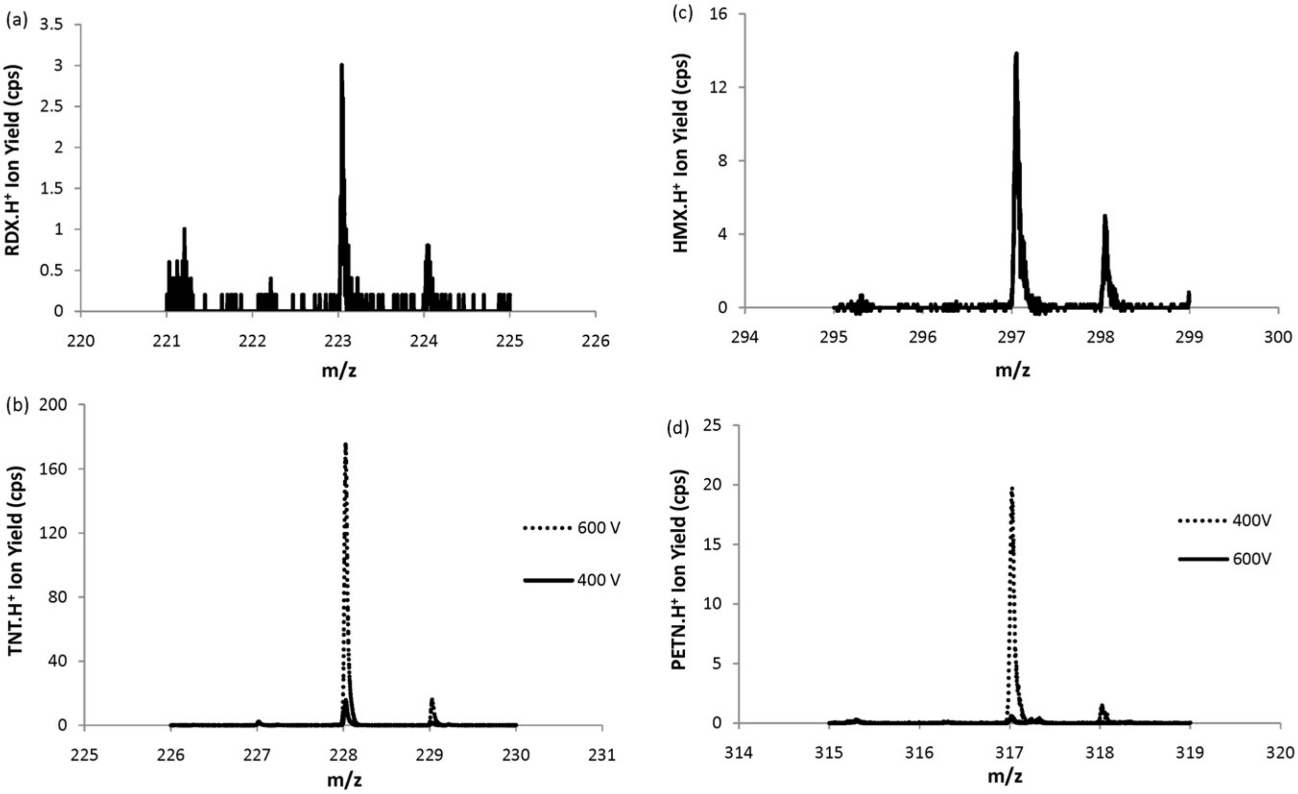

Fig. 2. PTR-TOF 8000 analysis of the headspace above (a) RDX, (b) TNT and (c) HMX and (d) PETN placed in an enclosed environment at room temperature. The mass spectra show the signal intensities for the protonated parent molecules (*m*/*z* 223.04 for RDX, *m*/*z* 228.03 for TNT, *m*/*z* 297.05 for HMX and *m*/*z* 317.02 for PETN), recorded at *E*/*N* = 91 Td (drift tube voltage = 400 V). The associated ^{13}C isotope peaks are clearly observable on the figures, although for RDX and HMX the intensity of this peak does not agree with the isotopic abundance. Thus the peaks at approximately 224 and 298 for RDX and HMX, respectively, cannot only be associated with the ^{13}C isotope of the protonated parent. In addition to the measurements at *E*/*N* = 91 Td, the peak intensities for protonated TNT and PETN are also shown for *E*/*N* = 144 Td, corresponding to an applied drift tube voltages of 600 V. Note the dramatic rise is the THT·H$^+$ signal intensity as the drift voltage (*E*/*N*) is increased, whilst that for PETN·H$^+$ decreased. Such dramatic increases in the protonated parent ion with increasing *E*/*N* have never been observed in any PTR-MS study. For all the spectra shown, any background signals at the *m*/*z* corresponding to the protonated explosives were found to be negligible compared to the intensity of the signals obtained.

observe any conclusive *E*/*N* dependence on RDX and HMX for these headspace measurements owing to the associated low signal intensity of the protonated parent. However, later measurements using a pre-concentration technique (see below) show that the intensities of the protonated RDX and HMX molecular ions as a function of *E*/*N* show a similar behaviour to that observed for PETN.

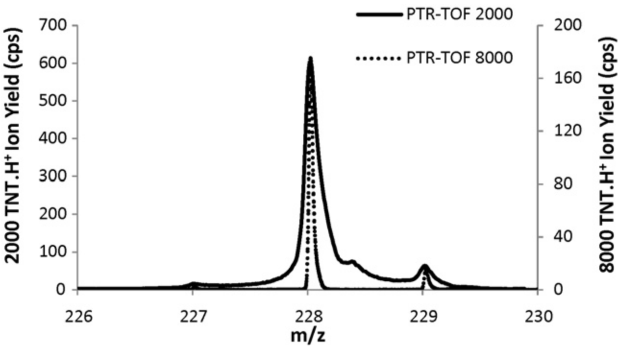

Fig. 3. Mass spectra of the protonated TNT parent molecules taken on both the PTR-TOF 8000 and 2000 instruments comparing the resolutions and detection sensitivities of the two instruments. The VOC emissions above room temperature TNT were sampled in to the PTR chambers under identical conditions (both drift tubes were maintained at 600 V, 90 °C and 2.3 mbar corresponding to *E*/*N* = 141 Td). The shoulder observed in the PTR-TOF 2000 spectrum just to the right of the main peak is not observed in the PTR-TOF 8000 spectrum, and is considered to be an impurity in the PTR-TOF 2000 system. All of the mass spectra presented in this figure were obtained by using a 5 s integration time.

The dramatic increase in the protonated TNT intensity as a function of *E*/*N* (changing by about an order of magnitude over approximately a 300 V change in drift voltage) is anomalous, and therefore warrants further discussion.

No value for the proton affinity (PA) of TNT is available in the literature. However, in a recent electrospray experiment it was noted that TNT does not give a signal with a methanol/water spray solution, probably because its proton affinity is much lower than that of methanol (754 kJ mol^{-1}) [22]. In agreement with this, DFT calculations (B3LYP 6-31 + G(d,p)) [23] with the GAUSSIAN03 PROGRAM by us provide a value of PA(TNT) (with the proton on the para NO_2) to be 744 kJ mol^{-1}. Confidence in this value is provided from the calculation of PA(H_2O) using the same basis set, providing a value of 684 kJ mol^{-1} (accepted literature value is 697 kJ mol^{-1}). Thus proton transfer from H_3O^+ to TNT is highly exothermic. Therefore the increase in signal intensity of TNT·H$^+$ as *E*/*N* increases cannot be attributable to energetic issues. Some of the increase with *E*/*N* can be attributed to the increase in the H_3O^+ signal as more of protonated water dimers fragment to protonated water monomers and neutral water as *E*/*N* increases. The PA(H_2O)$_2$, determined by us to be 842 kJ mol^{-1} by using the same basis set as above, is greater than that of TNT, and therefore cannot react with TNT via a proton transfer process. Thus the increase in H_3O^+ number density with increasing *E*/*N* caused by fragmenting $H_3O^+ \cdot H_2O$ to H_3O^+ and H_2O should result in a greater sensitivity to the detection of TNT. However, any such increase in the H_3O^+ intensity is far too small to account for the observed order of magnitude increase in the TNT·H$^+$ signal intensity. A possible answer to this anomaly is that neutral TNT clusters, and not monomers, are being formed in the gas phase, and it is these that are being sampled into the PTR and being protonated. Collisional-induced dissociation could then occur within the drift tube resulting in the protonated monomers. However, no protonated TNT clusters have been observed in the ToF mass spectra (measured over the range 0–3500 amu) at any applied drift tube voltage, thereby ruling out this possibility. To investigate if the phenomenon is due to the chemistry associated with proton transfer to nitroaromatic systems, we sampled 2,4 dinitrotoluene ($CH_3C_6H_3(NO_2)_2$) into the PTR and monitored the protonated parent signal as a function of *E*/*N*. We found that the signal remained relatively constant when increasing the voltage applied across the drift tube from 400 V to 600 V. Therefore, the *E*/*N* intensity dependence appears to be peculiar to protonated TNT. Further investigations are required to understand this interesting result.

The ability to detect HMX by simply sampling the headspace above a solid sample at room temperature is remarkable given that the vapour pressure of this compound is the lowest of any of the solid explosives. At 25 °C its vapour pressure has been extrapolated to be 1.6×10^{-13} Torr (corresponding to concentrations in the ppqv). In comparison at 25 °C the vapour pressures of RDX, TNT and PETN are significantly higher being 1.4×10^{-9}, 3.0×10^{-6}, and 3.8×10^{-10} Torr, respectively [24]. The vapour detection of Semtex A at room temperature is also worthy of comment. Semtex A is a general-purpose plastic explosive containing PETN (95%) and RDX (5%) contained in a complex elastomeric matrix. Presumably this matrix would serve to suppress the already small vapour pressure associated PETN, yet a signal corresponding to the protonated parent is observed.

To facilitate the vapour detection of plastic explosives such as Semtex, high volatile taggants are commonly added to the bulk explosive during manufacture. These include ethyleneglycol dinitrate, 2,3-dimethyl-2,3-dinitrobutane (DMNB) and mononitrotoluene (o and p), and which one is added depends on the country of origin of manufacture. For our Semtex A sample a small signal associated with protonated DMNB was observed (protonated molecular mass at *m*/*z* 177.0875). However, for the drift tube voltages applied (400–600 V) the strongest mass peak associated with DMNB is not the protonated parent but a fragment ion occurring at *m*/*z* 130.0868, which presumably results from the loss of HONO from $(DMNB{\cdot}H^+)^*$. In addition to DMNB being emitted from Semtex A, we also observed a relatively strong signal corresponding to cyclohexanone (protonated *m*/*z* 99.0810). In fact cyclohexanone was observed to be an emitted VOC from all of the solid explosives investigated in this study, with RDX showing the most intense protonated cyclohexanone peak. In agreement with our observations, there are reports in the literature that cyclohexanone is an important trace component in the vapour emitted by military grade Composition-B (a castable mixture of RDX and TNT), and has been detected outside of intact metallic and non-metallic antitank mines charged with Composition-B [25,26]. Given that cyclohexanone is not a common trace gas in the atmosphere, the results of this present work and the previous studies raise the possibility of using cyclohexanone as a general marker for solid explosives. Although it cannot be used to uniquely identify an explosive, detection sensitivities lower than that required for the parent explosive molecules can be used.

3.2. Use of pre-concentrator and thermal desorption for the detection of solid explosives

As mentioned in Section 2 a relatively simple form of pre-concentrator and thermal desorption system was developed to see if improvements in the signal intensity of the protonated parent explosive ion could be achieved and to investigate if extremely small quantities of explosives could be detected by this technique. To reduce the possibility of cold spots in the sampling inlet system, only the PTR-TOF 8000 instrument was used in this part of the study.

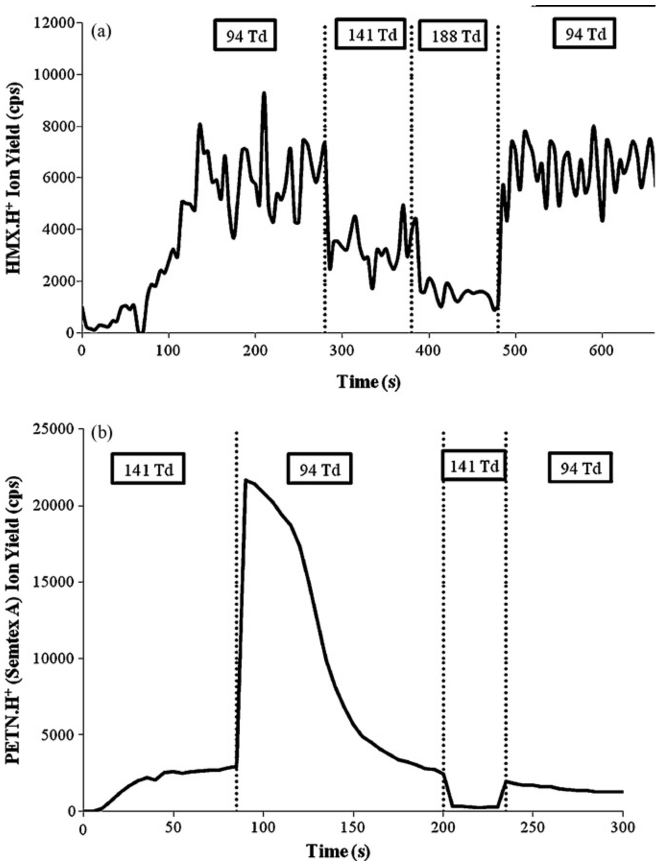

Fig. 4. (a) Detection of HMX traces on a latex glove. Illustrated are the time evolution of the intensity of the protonated HMX signal prior to (approximately 0–20 s) and following heating (approximately 20–30 s) of the pre-concentrator wire mesh and the variation in signal as the voltage applied across the drift tube is changed; 400, 600 and 800 V, corresponding to *E*/*N* = 94, 141 and 188 Td, respectively. (b) The time evolution of a swipe test measurement for trace quantities of Semtex A placed on the surface of a cardboard sheet (heating of mesh from approximately 10 s until 20 s). Illustrated on the figure are changes in the signal intensities corresponding to protonated PETN (the major constituent of Semtex A) upon changing the drift voltage to change the *E*/*N* value. The cycle time used to obtain the data shown in this figure was 1.4 s.

In the first procedure a few particles of an explosive were gently rubbed on the surface of a latex glove used by one of the researchers, and then the glove was dusted-off, so that no particles of the explosives could be seen on the glove. As mentioned earlier, air at a high flow was then passed over the glove and then through a stainless steel wire mesh, which was then heated to between 100 and 150 °C close to the sample inlet lines. Following successful measurements of TNT and RDX, the detection of HMX was then attempted. Fig. 4(a) shows the time evolution of the intensity of the protonated HMX parent signal prior to and following heating of the mesh and variation in signal intensity as the voltage across the drift tube is altered. This figure not only provides evidence of the detection of trace quantities of HMX by PTR-TOF techniques but also illustrates the dependence of signal intensity on *E*/*N*.

The second procedure consisted of an explosive rubbed onto a cardboard surface and then wiped clean (again no residue was visibly apparent). A swipe test was made by rubbing a stainless steel wire mesh over the surface for a few seconds and then heating the mesh to approximately 120 °C close to the entrance of the heated inlet system. RDX, TNT, PETN and Semtex A were all easily observed. This is illustrated in Fig. 4(b) for PETN being emitted from Semtex A. Even HMX showed a discernable increase in signal.

4. Conclusions

Two PTR-ToF-MS instruments from Ionicon Analytik were used for this study [4]. The recently developed and commercially available PTR-TOF 8000 has enhanced high resolution (up to $8000\,m/\Delta m$) and high sensitivity [6], whereas the PTR-TOF 2000, which is currently under development, has enhanced sensitivity (approximately five times better than the 8000 instrument) whilst retaining high resolution (up to $2000\,m/\Delta m$). These two instruments surpass other PTR-ToF-MS instruments reported in the literature for trace gas analysis in terms of their selectivity and sensitivity.

In this paper we have illustrated the capabilities of the PTR-TOF 8000 and 2000 instruments to be used in real-time to rapidly detect a broad range of solid explosives whose concentrations in air at 25 °C range from ppqv (HMX) to ppbv (TNT). The high sensitivities of the instruments permit the relatively easy detection of threat agents in trace quantities and the high resolution permits a high level of confidence in their identification—thereby eliminating false positives or negatives.

When using the heated inlet system for this study great care had to be taken to ensure that there were no cold spots anywhere—otherwise the signal associated with the protonated parent molecular ion of a given explosive was dramatically reduced. Furthermore, traces of explosives were still observed to be present in the inlet system many tens of minutes after the vapour of a particular explosive had been introduced into the sample inlet lines. Whilst the development of a suitable sample inlet system for compounds such as solid explosives is not the aim of this study – rather it is to demonstrate that PTR-ToF mass spectrometry can be used to unambiguously identify threat agents – it is an issue that will need to be addressed if PTR-ToF mass spectrometry is to be of use in security and forensic applications. A suitable inlet system with fast recovery time needs to be developed in order to carry this project forward.

The results have shown that PTR-ToF-MS can be used to unambiguously identify traces of explosives either from the VOCs in the headspace above solid samples at room temperature or from traces present on surfaces such as cardboard or rubber with a fast cycle time of collection and analysis (tens of seconds). Similar experiments dealing with chemical warfare agents are in progress, the results of which will be presented in a later paper.

To conclude, we have demonstrated a successful new method for the rapid detection of a broad range of solid explosives in trace quantities in what potentially could be complex chemical environments (e.g., multiple threat agents or other VOCs present in the air sample). This is of significance for potential security and forensic applications.

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