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

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ABSTRACT

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

1. Introduction

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

The detection of many explosives is challenging because of their low vapour pressures [12]. Without any sample preparation, low vapour pressure makes it very difficult to introduce sufficient vapour concentrations of an explosive into the reaction region (the drift tube) of a PTR-MS to make it detectable. An approach to remedy this problem was adopted in this investigation. For this we have adopted a similar technique routinely used in IMS, namely a pre-concentration technique followed by thermal desorption. An earlier attempt of pre-concentration and thermal desorption of explosives

with PTR-MS resulted in limited success [4]. That study used a suction device that drew air through a fine wire mesh to trap particulates of an explosive. This mesh was then ohmically heated to evaporate that trapped material. A simple heated inlet tube placed close to the wire mesh carried some of the desorbed material into the drift tube reactor. Although this successfully resulted in much 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 [13–15], 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^+ [16]. 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 ($PA(H_2O) = 691$ 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.
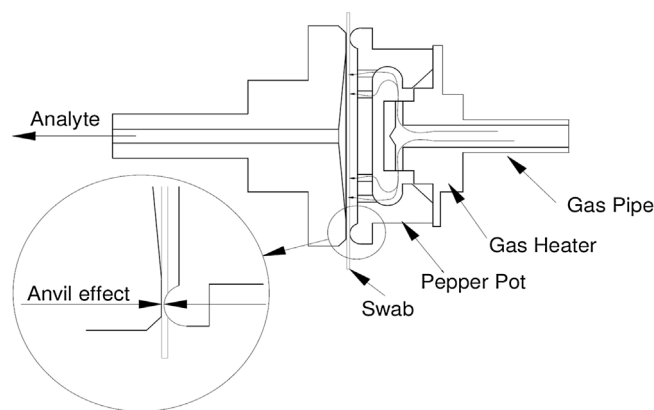

Fig. 1. Schematic cross-section of the KORE Technology Ltd. thermal desorption unit. The laboratory air is heated as it travels through the heating block to the temperature of the block. This heated air is then dispersed across the surface area of the swab via a series of equally spaced holes (the pepper 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.

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 Fig. 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 Td = 10^{-17} V cm^2).