Applications of switching reagent ions in proton transfer reaction mass spectrometric instruments for the improved selectivity of explosive compounds

Philipp Sulzer[a], Bishu Agarwal[a,b], Simone Jürschik[a], Matteo Lanza[a], Alfons Jordan[a], Eugen Hartungen[a], Gernot Hanel[a], Lukas Märk[a], Tilmann D. Märk[a,b], Ramón González-Méndez[c], Peter Watts[c], Chris A. Mayhew[c,*]

[a] IONICON Analytik Gesellschaft m.b.H., Eduard-Bodem-Gasse 3, A-6020 Innsbruck, Austria
[b] Institut für Ionenphysik und Angewandte Physik, Leopold-Franzens Universität Innsbruck, Technikerstr. 25, A-6020 Innsbruck, Austria
[c] School of Physics and Astronomy, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

ARTICLE INFO

ABSTRACT

Here we demonstrate the use of a switchable reagent ion proton transfer reaction mass spectrometry (SRI-PTR-MS) instrument to improve the instrument's selectivity for the detection of the explosive compounds 2,4,6 trinitrotoluene (TNT), 1,3,5 trinitrobenzene (TNB), pentaerythritol tetranitrate (PETN), and cyclotrimethylenetrinitramine (RDX). Selectivity is improved owing to the production of different product ions resulting from changes in the reagent ion-molecule chemistry. To be of use as an analytical tool for homeland security applications, it is important that the reagent ions (and hence product ions) can be rapidly changed (within seconds) from H_3O^+ to another dominant ion species if the technology is to be acceptable. This paper presents measurements that show how it is possible to rapidly switch the reagent ion from H_3O^+ to either O_2^+ or NO^+ to enhance selectivity for the detection of the four explosives named above. That switching reagent ions can be done quickly results from the fact that the recombination energies of O_2^+ and NO^+ are less than the ionisation potential of H_2O, i.e. charge transfer cannot occur which otherwise would result in ions that can react efficiently with water (e.g. $H_2O^+ + H_2O \rightarrow H_3O^+ + OH$) leading to H_3O^+ becoming the dominant reagent ion. Reaction processes observed are non-dissociative charge transfer (O_2^+ with TNT and TNB), dissociative charge transfer (O_2^+ with TNT) and adduct formation (NO^+ with PETN and RDX). O_2^+ is found to be unreactive with PETN and RDX, and under the conditions operating in the reaction region of the PTR-MS only a low signal associated with $NO^+ \cdot TNT$ was observed. No $NO^+ \cdot TNB$ was detected.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The potential of terrorists to use explosives and chemical warfare agents focuses our attention on the need to detect dangerous agents in low concentrations reliably, in real-time and with high sensitivity and selectivity. This is particularly a challenging task when only trace concentrations of threat compounds with low vapour pressure, such as explosives, are present on exposed surfaces in complex chemical environments.

The most commonly deployed chemical analysis technology for the detection of threat agents in trace amounts in security areas is Ion Mobility Spectrometry (IMS) [1,2]. Despite its sensitivity and robustness, IMS has certain disadvantages; the most critical is its limited chemical specificity. This can cause false positive signals resulting from the erroneous identification of harmless interferents

as a threat agent. The rapid detection of traces of threat agents adhered to people or objects with a high level of confidence (low rate of false positives) in ambient air with a sensitivity that equals or surpasses that of IMS, but has a superior selectivity requires a new analytical approach.

Prior to this work, two other studies have appeared in the literature based on the use of ion-molecule reactions in low-pressure reaction environments for the detection of explosives [3,4] using reagent ions other than H_3O^+. Both of these earlier studies have focused on the unstable explosive triacetone triperoxide (TATP), $C_9H_{18}O_6$. A selected ion flow tube-mass spectrometry (SIFT-MS) study by Wilson et al. [3], using thermal H_3O^+, O_2^+, and NO^+ as the reagent ions, claimed that only NO^+ reactions with TATP showed product ions that provided "unequivocal evidence" for the presence of a TATP-based explosive. Shen et al. [4], using a proton transfer reaction quadrupole mass spectrometer with either H_3O^+ or NH_4^+ as the reagent ions, showed that TATP could be detected by either identifying (weakly) $TATP \cdot H^+$ (proton transfer from H_3O^+) or $TATP \cdot NH_4^+$ (association reaction with NH_4^+) by using a suitable reduced electric field in the drift tube.

* Corresponding author. Tel.: +44 121 414 4729; fax: +44 121 414 4577.
E-mail address: c.mayhew@bham.ac.uk (C.A. Mayhew).

In a series of recent papers we have highlighted the potential of the platform technology proton transfer reaction mass spectrometry (PTR-MS) for the detection of explosives [5–8], in addition to other threat agents [9–12]. Having mass spectrometric capabilities, this technology of course has improved selectivity compared to IMS owing to its ability to generate protonated parent species, i.e. an ion is produced with an m/z which is observed at one atomic mass unit above that of the neutral species. Although, an observed m/z at where MH^+ is expected (M being the neutral analyte) provides a greater confidence in an assignment, an m/z does not provide a unique indicator for the identity of trace gases in an air sample, because for low resolution mass spectrometers, i.e. those using quadrupole filtering, it can only provide a nominal m/z value. This causes problems if isomeric or isobaric compounds are present in the environment because they have the same nominal mass (isobaric) or identical mass (isomeric). High resolution mass spectrometers can be used to separate out isobaric compounds. However this adds considerably to the cost of an analytical instrument. Furthermore, it is not just isobaric/isomeric compounds that can cause problems in the interpretation of mass spectra. Product ions resulting from fragmentation, clustering, and secondary ion-molecule reactions can also cause complications for accurate assignments and hence in the unambiguous detection of a compound.

To improve selectivity of PTR-MS, we have recently shown that H_3O^+ drift-tube ion-molecule chemistry for the explosives 2,4,6 trinitrotoluene (TNT: $C_7H_5N_3O_6$, m/z 227) and 1,3,5 trinitrobenzene (TNB: $C_6H_3N_3O_6$, m/z 213), can be discriminated by changing E/N [8]. The aim of this paper is to demonstrate how the switching of reagent ions from H_3O^+ to NO^+ or O_2^+ can also be used to enhance selectivity, not only for TNT and TNB, but also for cyclotrimethylenetrinitramine (RDX: $C_3H_6N_6O_6$, m/z 222) and pentaerythritol tetranitrate (PETN: $C_5H_8N_4O_{12}$, m/z 316). However, an important practical aspect for analytical detection in real-world environments is that to be applicable, a switchable reagent ion source used to enhance the selectivity must be able to change from one reagent ion to another rapidly (within seconds). We shall show that this is possible for switching between H_3O^+, NO^+ and O_2^+.

2. Experimental details

2.1. Background

For this project a PTR-TOF-MS instrument (PTR-TOF 8000, ION-ICON Analytik GmbH) was used owing to its availability. Its high mass resolution capabilities were not required for the measurements undertaken in this investigation. Details on the technology can be found in previous publications [8,13] and therefore only details on the experimental procedures used in this study will be provided. The measurement procedure for the explosives involved drawing air through a charcoal filter into a glass vial (through a septum in the lid), which contained a small amount of the solid explosive (typically 1–3 mg). The air passed over the sample and was drawn into a tube connected to the inlet system of the PTR-TOF-MS. The glass vial, sample inlet line and the drift tube of the PTR-TOF 8000 were maintained at approximately 100 °C. The uniform heating of the inlet lines and PTR chamber is critical to measurements involving solid explosives because of their condensable nature.

2.2. Switching reagent ions

H_3O^+, NO^+ or O_2^+ reagent ions were produced by flowing water vapour, air or oxygen, respectively, via a computer controlled mass flow controller into a hollow cathode discharge source. Of course it is relatively straightforward to have any number of flow controllers connected to the inlet of the hollow cathode if one wishes to switch between gases/vapours for introduction into the hollow cathode discharge source. However, we only had two mass flow controllers available during the study. One of these flow controllers was used for water vapour only and the other was either used with air for NO^+ production or with O_2 to generate O_2^+.

Reagent ions, under the influence of a voltage gradient, passed through a small orifice from the hollow cathode ion source into an adjacent drift tube reaction section, where the explosive analyte under investigation was introduced via the gas inlet system mentioned above. When using NO^+ and O_2^+ as the reagent ions, H_3O^+ was also produced owing to some residual water vapour on the surfaces of tubing going to and in the hollow cathode ion source, but this always resulted in an ion intensity of less than 5% found for that of the dominant reagent ion signal after several seconds. For O_2^+ another contaminant ion observed was NO_2^+. Although this was less than 1% of the O_2^+ signal intensity, and its intensity decreased with increasing reduced electric field, E/N (the ratio of the electric field applied down the drift tube to the air number density in the drift tube), this still represented a significant signal intensity in comparison to the product ion signal intensities resulting from reactions with trace explosives in the reaction region, and therefore care must be taken when detecting nitro aromatic compounds because NO_2^+ is often used as a marker for nitroaromatic explosives.

2.3. Sensitivity details

It is generally found in PTR-MS work, with a few reported exceptions [5,8], that when using H_3O^+ as a reagent ion the sensitivity for detection of an analyte decreases with increasing E/N as a result of factors such as decreased reaction time and fragmentation of the protonated parent molecule. The intensities of the product ions produced from reactions with O_2^+ and NO^+ with all of the explosives investigated in this study have been found to follow this trend. The main difference when using reagent ions other than H_3O^+ is that the drift tube may be operated at even lower E/N values than can be used when relying on water chemistry, which results in improved sensitivity in terms of normalised counts per second (ncps). In the case of H_3O^+, its signal intensity drops dramatically for E/N values much below 90 Td (depending on humidity) owing to the formation of protonated water clusters ($H_3O^+ \cdot (H_2O)_n$ ($n \geq 1$)), thereby limiting the E/N values that can be used. However, it must be appreciated that the actual value of E/N to be used is a competition between obtaining a high intensity reagent ion signal, reaction time and limiting fragmentation. To decide on the most appropriate E/N value for a given instrument it is necessary to review the cps (not ncps) and select the E/N that provides the most intense production signal.

With regard to the sensitivity, it is important to take into account changes in reagent ion signal intensity as a function of E/N. Therefore for some of the measurements presented in this paper we have used the normalised counts per second. This refers to the intensity obtained for an ion at a given m/z by integrating over the spectral line, dividing by the integrated reagent ion signal and multiplying by 10^6.

3. Results and discussion

Before investigating the capabilities of fast switching, we first investigated the reaction of the reagent ions NO^+ and O_2^+ with each of the explosives as a function of E/N to determine its effect on the sensitivity of measurements and to investigate possible fragmentation channels. Therefore this will be described first.