



## Interference in the PTR-MS measurement of acetonitrile at $m/z$ 42 in polluted urban air—A study using switchable reagent ion PTR-MS

Erin Dunne<sup>a,b,\*</sup>, Ian E. Galbally<sup>a</sup>, Sarah Lawson<sup>a</sup>, Antonio Patti<sup>c</sup>

<sup>a</sup> Centre for Australian Weather and Climate Research, CSIRO Marine and Atmospheric Research, PMB 1, Aspendale, Vic. 3195, Australia

<sup>b</sup> School of Applied Science, Monash University, Gippsland, Vic., Australia

<sup>c</sup> Centre for Green Chemistry, Monash University, Clayton, Vic., Australia

### ARTICLE INFO

#### Article history:

Received 30 January 2012

Received in revised form 4 May 2012

Accepted 7 May 2012

Available online 20 May 2012

#### Keywords:

Acetonitrile

Switchable reagent ion

PTR-MS

Mass interference

Urban air

### ABSTRACT

In Proton Transfer Reaction Mass Spectrometer (PTR-MS) measurements of the atmosphere, the signal at  $m/z$  42 is commonly regarded as a unique measure of acetonitrile. However, two other ions potentially contribute to the signal at  $m/z$  42. These are  $^{13}\text{C}$  isotopologues of  $\text{C}_3\text{H}_5^+$  and the product ion  $\text{C}_3\text{H}_6^+$  produced by reaction of  $\text{NO}^+$  and  $\text{O}_2^+$  (present in trace amounts in the  $\text{H}_3\text{O}^+$  reagent gas), with a number of volatile organic compounds. Thus, there is the possibility of interference in the measurement of acetonitrile at  $m/z$  42 by PTR-MS.

Interference in the measurement of acetonitrile at  $m/z$  42 was quantified in urban air over 17 days in Sydney, Australia, in summer. A PTR-MS with Switchable Reagent Ion capability was used for measurements at  $m/z$  41 and 42 in three different primary reagent ion modes,  $\text{O}_2^+$ ,  $\text{NO}^+$  and  $\text{H}_3\text{O}^+$ , to quantify the contribution of non-acetonitrile compounds to the signal at  $m/z$  42 when the PTR-MS was operating in  $\text{H}_3\text{O}^+$  reagent ion mode. Acetonitrile dominated the ion signal at  $m/z$  42; however non-acetonitrile ions contributed 5–41% of the total ion signal at  $m/z$  42. The average corrected and uncorrected acetonitrile concentrations were 120 pptv and 148 pptv respectively.

The interference in the  $m/z$  42 signal was calculated from known or interpolated concentrations of compounds identified as potential interferences. Overall the isotopologue correction is due to alkenes including isoprene with probable contributions from other compounds not measured in this study. The other component of the interference, produced by reactions of  $\text{O}_2^+$ , is due to alkanes and alkenes.

Levogluconan, a biomass burning tracer in atmospheric particulate matter was more highly correlated with the corrected acetonitrile signal than the uncorrected acetonitrile signal.

Measurements of acetonitrile by PTR-MS at  $m/z$  42 in urban air will frequently require correction because of the non-trivial concentrations of alkanes and alkenes commonly observed in urban air.

Crown Copyright © 2012 Published by Elsevier B.V. All rights reserved.

### 1. Introduction

Biomass burning is a major source of gases and particles to the atmosphere at concentrations that have a significant influence on atmospheric chemistry at local, regional and global scales [1]. Acetonitrile is almost exclusively emitted from biomass burning and has an atmospheric lifetime of many months [2]. Consequently, it is commonly used as a tracer for biomass burning. In the urban atmosphere measurements of acetonitrile are a useful indicator of the contribution to air quality of controlled and uncontrolled biomass burning, wood fuelled heating, and any other biomass combustion.

Proton transfer mass spectrometry (PTR-MS) observations have been useful in identifying biomass burning plumes and observing their transport and chemical processing [e.g., 3,4]. PTR-MS instruments are capable of detecting numerous VOCs including acetonitrile and other nitrogen-containing VOCs as well as oxygenated VOCs, aromatics and some alkenes [5,6] online with fast response and high sensitivity (sub-ppb). The principle of the PTR-MS is the utilization of proton transfer reactions from  $\text{H}_3\text{O}^+$  compounds with a proton affinity (PA)  $> \text{H}_2\text{O}$  (166.5 kcal mol<sup>-1</sup>) to produce charged products.

The ion detection system in a standard PTR-MS consists of a quadrupole mass spectrometer that separates the ions according to their mass/charge ratio ( $m/z$ ) and a secondary electron multiplier (SEM) operated in count mode that detects the number of impinging ions at each  $m/z$  channel with a mass resolution of 1 amu. The major practical limitation of PTR-MS is its inability to distinguish between ions with the same mass to charge ratio ( $m/z$ ) [7]. The low

\* Corresponding author at: Private Bag 1, Aspendale, Vic. 3195, Australia.

Tel.: +61 3 9239 4428; fax: +61 3 9239 4444.

E-mail address: [Erin.Dunne@csiro.au](mailto:Erin.Dunne@csiro.au) (E. Dunne).

selectivity of PTR-MS needs to be considered when measuring air with complex VOC mixtures, such as urban air and smoke plumes, which contain many different VOCs with the same molecular or fragment ion mass.

In the identification of a signal from PTR-MS, one must consider the contributions to a particular  $m/z$  ratio from a number of reaction pathways involving constituents of the sample being analysed and the multiple components of the reagent ion matrix. These contributions include:

- Product ions with molecular mass plus one due to proton addition.
- Product ions from fragmentation of molecular ions following proton transfer.
- Product ions that are isotopologues including those containing  $^{13}\text{C}$ ,  $^{18}\text{O}$ ,  $^{35}\text{S}$ , etc.
- Product ions from reactions with the impurity reagent ions  $\text{O}_2^+$ ,  $\text{NO}^+$  and  $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ .

The ion source of the PTR-MS instrument is a hollow cathode that produces  $\text{H}_3\text{O}^+$  ions via electron impact ionization of water vapour. The ion source is tuned to produce reagent  $\text{H}_3\text{O}^+$  ions with a purity of >95% but there are always some  $\text{O}_2^+$ ,  $\text{NO}^+$ ,  $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_n$  and other ions present in the reagent ion matrix as a result of air back-streaming into the ion source. The instrument manufacturer (Ionicon Analytik GmbH) suggests that <2% of  $\text{O}_2^+$  and  $\text{NO}^+$  impurities is optimal.

PTR-MS mass spectra can be further complicated by the presence of these trace reagent ions including  $\text{O}_2^+$ ,  $\text{NO}^+$ ,  $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_n$  in the reagent ion matrix. As well as proton transfer from the  $\text{H}_3\text{O}^+$  primary reagent ion, the other trace constituents in the reagent ion matrix ( $\text{O}_2^+$ ,  $\text{NO}^+$ , and  $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_n$ ) also undergo chemical ionization reactions involving proton transfer, charge transfer, association reactions and hydride ion transfer, depending on the VOCs and other constituents within the sample.

The majority of PTR-MS instruments are operated with  $\text{H}_3\text{O}^+$  as the only primary chemical ionization reagent ion. Recently, Jordan et al. [8] described a modified PTR-MS system with a switchable reagent ion capability (SRI + PTR-MS) which allows switching between 3 primary reagent ions:  $\text{H}_3\text{O}^+$ ,  $\text{O}_2^+$  and  $\text{NO}^+$ . In each mode there was always 3 or 4 reagent ions present in the reagent ion matrix: a primary reagent ion present at a purity of ~95% and 2 or 3 trace reagent ion species.

The use of other primary reagent ions  $\text{O}_2^+$  and  $\text{NO}^+$  in PTR-MS with switchable reagent ion capability was designed by Jordan et al. [8] for the separation of isomers and identification of VOCs previously indistinguishable with ionization via  $\text{H}_3\text{O}^+$  alone. Measurements using the 3 different reagent ions can also be used to determine interference from  $\text{O}_2^+$  and  $\text{NO}^+$  reaction products when the PTR-MS is operating with  $\text{H}_3\text{O}^+$  as the primary reagent ion and  $\text{O}_2^+$  and  $\text{NO}^+$  are trace constituents in the reagent ion matrix.

In atmospheric measurements the PTR-MS signal at  $m/z$  42 is commonly regarded as a unique measure of acetonitrile [7]. However, two other ions potentially contribute to the signal at  $m/z$  42. These are  $^{13}\text{C}$  isotopologues of  $\text{C}_3\text{H}_5^+$  and the product ion  $\text{C}_3\text{H}_6^+$ .

In this paper we examine the interferences in the measurement of acetonitrile in the urban atmosphere, and quantify the interference.

## 2. PTR-MS selectivity at $m/z$ 42

When the PTR-MS is operating with  $\text{H}_3\text{O}^+$  as the primary reagent ion, there are 12 possible reaction pathways that yield four different product ions with  $m/z$  42:  $\text{CH}_3\text{CNH}^+$ ,  $\text{C}_3\text{H}_6^+$ , and the  $^{13}\text{C}$  isotopologues of  $\text{CH}_3\text{CN}^+$  and  $\text{C}_3\text{H}_5^+$ . The reaction pathways and product

ions that may contribute to the signal at  $m/z$  42, and to the either the measurement of acetonitrile or interference with acetonitrile measurement, are listed in Table 1. Each reaction pathway is discussed in turn.

When the PTR-MS used in this study was exposed to a prepared pure gaseous standard of acetonitrile, a single product ion was observed at  $m/z$  42, most likely  $\text{CH}_3\text{CNH}^+$ . The PA of acetonitrile ( $186.2 \text{ kcal mol}^{-1}$ ) is not sufficient for exothermic proton transfer with  $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})$  reagent ions (PA ( $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})$ ) =  $195.7 \text{ kcal mol}^{-1}$ ) [9], so this reaction pathway does not influence the signal at  $m/z$  42. The contributions to the ion signal at  $m/z$  42 may result from dissociative ligand switching reactions with  $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})$  (reaction 2, Table 1), however the protonated product usually co-occurs with the non-dissociative ligand switching product  $\text{CH}_3\text{CNH}^+\cdot\text{H}_2\text{O}$  ( $m/z$  60) which is not observed in the mass spectra. Thus, reaction pathway 2 is unlikely to be significant.

$\text{O}_2^+$  ions undergo charge transfer reactions with compounds whose ionization energies are >12.06 eV, including some that yield product ions of  $\text{C}_3\text{H}_6^+$  at  $m/z$  42 (reactions 3 and 4, Table 1). Laboratory studies using  $\text{O}_2^+$  chemical ionization have observed molecular and fragment ions at  $m/z$  42 amu as a result of reactions with  $\text{C}_3$ – $\text{C}_5$  alkanes and alkenes [10–12].

Measurements using PTR-MS with gas chromatographic pre-separation of urban air samples observed peaks in the chromatogram at mass 42 attributed to reactions of  $\text{O}_2^+$  impurity ions with  $\text{C}_3$ – $\text{C}_4$  alkanes [7]. When the PTR-MS used in this study, operating with  $\text{O}_2^+$  as the primary reagent ion, was exposed to a pure gaseous standard mixture of 12  $\text{C}_2$ – $\text{C}_5$  hydrocarbons (ethane, ethene, propane, propene, *n*-butane, *cis*-2- and *trans*-2-butene, *n*-pentane, isopentane, *cis*-2- and *trans*-2-pentene, isoprene), the  $m/z$  42 signal was 11% of the total ion signal (the sum of the ion signals for all  $m/z$  in the range 14–200 amu excluding reagent ion signals). Thus, contributions to the signal at  $m/z$  42 due to reactions 3 and 4 are possible.

Laboratory studies using  $\text{NO}^+$  as the primary reagent ion have observed a product ion at  $m/z$  42 from charge transfer reactions of  $\text{NO}^+$  with cyclopropane and 1-butene [12,13]. When the PTR-MS used in this study, operating with  $\text{NO}^+$  as the primary reagent ion, was exposed to a pure gaseous standard mixture of 12  $\text{C}_2$ – $\text{C}_5$  hydrocarbons, the  $m/z$  42 signal was 3% of the total ion signal. Contributions to the signal at  $m/z$  42, due to reactions 5 and 6, are therefore possible.

The  $m/z$  41 ion signal is often significantly larger than the  $m/z$  42 signal when sampling urban air as there are many reaction pathways involving  $\text{H}_3\text{O}^+$ ,  $\text{O}_2^+$  and  $\text{NO}^+$  and common atmospheric VOCs that will yield a product ion at  $m/z$  41 (reactions 7–10). The most likely product ion at  $m/z$  41 is  $\text{C}_3\text{H}_5^+$ . As a result of the natural  $^{13}\text{C}$  isotopic abundance, a component of the signal at  $m/z$  41 will be detected at  $m/z$  42 as the  $^{13}\text{C}$  isotopologues of the  $^{12}\text{C}$  compound  $\text{C}_3\text{H}_5^+$ . The natural  $^{13}\text{C}$  isotopic abundance is 1.109%; thus, for a given  $\text{C}_3$  compound, 3.3% of the signal at  $m/z$  41 will appear at  $m/z$  42 due to the isotopologues. Therefore, contributions to the signal at  $m/z$  42 from reactions 7–10 are possible.

When the PTR-MS used in this study, operating with  $\text{H}_3\text{O}^+$  as the primary reagent ion, was exposed to a pure gaseous standard of  $\text{C}_2$ – $\text{C}_5$  hydrocarbons mentioned previously, a dominant peak at  $m/z$  41 was observed that constituted 37% of the total ion signal. A fragment ion signal at  $m/z$  41 was also observed when this PTR-MS, operating with  $\text{H}_3\text{O}^+$  as the primary reagent ion, was exposed to individual prepared gaseous standards of pure isoprene, acetaldehyde,  $\text{C}_3$  and  $\text{C}_4$  alcohols, and  $\text{C}_4$  and  $\text{C}_5$  formate esters. Product ions at  $m/z$  41 have been observed as a result of reactions with  $\text{H}_3\text{O}^+$  for methacrolein and 1-butene [13], propyne [7] and  $\text{C}_4$ – $\text{C}_9$  saturated and unsaturated alcohols [14,15]. Thus all of these compounds contribute through their fragmentation to  $m/z$  41, and their single  $^{13}\text{C}$  isotopologue to the signal at  $m/z$  42.

Download English Version:

<https://daneshyari.com/en/article/1192785>

Download Persian Version:

<https://daneshyari.com/article/1192785>

[Daneshyari.com](https://daneshyari.com)