Selective measurements of isoprene and 2-methyl-3-buten-2-ol based on NO\textsuperscript{+} ionization mass spectrometry

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Abstract. Biogenic VOC emissions are often dominated by 2-methyl-1,3-butadiene (isoprene) and 2-methyl-3-buten-2-ol (232 MBO). Here we explore the possibility to selectively distinguish these species using NO\textsuperscript{+} as a primary ion in a conventional PTR-MS equipped with an SRI unit. High purity of NO\textsuperscript{+} (> 90\%) as a primary ion was utilized in laboratory and field experiments using a conventional PTR-TOF-MS. Isoprene is ionized via charge transfer leading to the major product ion C\textsubscript{5}H\textsubscript{8}\textsuperscript{+} (> 99\%) (e.g. Spanel and Smith, 1998). 232 MBO undergoes a hydroxide ion transfer reaction resulting in the major product ion channel C\textsubscript{6}H\textsubscript{9}\textsuperscript{+} (> 95\%) (e.g. Amelynck et al., 2005). We show that both compounds are ionized with little fragmentation (< 5\%) under standard operating conditions. Typical sensitivities of 11.1 ± 0.1 (isoprene) and 12.9 ± 0.1 (232 MBO) ncp ppbv\textsuperscript{-1} were achieved, which correspond to limit of detections of 18 and 15 pptv respectively for a 10 s integration time. Sensitivities decreased at higher collisional energies. Calibration experiments showed little humidity dependence. We tested the setup at a field site in Colorado dominated by ponderosa pine, a 232 MBO emitting plant species. Our measurements confirm 232 MBO as the dominant biogenic VOC at this site, exhibiting typical average daytime concentrations between 0.2–1.4 ppbv. The method is able to detect the presence of trace levels of isoprene at this field site (90–250 ppt) without any interference from 232 MBO, which would not be feasible using H\textsubscript{3}O\textsuperscript{+} ionization chemistry, and which currently also remains a challenge for other analytical techniques (e.g. gas chromatographic methods).

1 Introduction

Isoprene (2-methyl-1,3-butadiene) plays an important global and regional role in photochemistry and climate. It was first discovered by Rasmussen and Went (1965) and Sanadze et al. (1976) that plants can synthesize and subsequently emit this chemical. Currently the global emission strength of isoprene is estimated to be 560 Tg yr\textsuperscript{-1} (Guenther et al., 2006) (uncertainty range: 230–700 Tg yr\textsuperscript{-1}, e.g. Stevenson et al., 2006), which could exceed that of methane (IPCC, 2007). Many different VOCs are emitted into the atmosphere and together the global VOC emission source is currently estimated to be in the range of 1200–1350 Tg yr\textsuperscript{-1} (Goldstein and Galbally, 2007). Chameides et al. (1988) showed that isoprene was the single most important reactive VOC fueling ozone chemistry in the South Eastern US. Oxidation of isoprene leads to complex organic compounds, which will be oxidized further to CO\textsubscript{2}, or deposit in the form of highly soluble organic species or organic aerosol (e.g. Karl et al., 2010). It has recently been suggested that oxidation of isoprene is still poorly understood questioning our understanding of the oxidizing capacity of the atmosphere (Lelieveld et al., 2008; Hofzumahaus et al., 2009). Through these processes isoprene, along with other VOCs, exhibits a direct and indirect climate forcing on the Earth’s atmosphere.

While isoprene is a dominant emission from many deciduous ecosystems, Goldan et al. (1993) reported the ubiquitous presence of 2-methyl-3-buten-2-ol (232 MBO) in a coniferous forest in the USA. Since then many studies (e.g. Harley...
atmospheric chemistry to selectively distinguish isoprene and 232 MBO
oretically it should be possible to distinguish 232 MBO and about 25% remains on the parent ion (m/z 87 Th). The ionization were performed using a SRI-TOF-MS apparatus from Ionicon Analytik GmbH, Innsbruck (Austria) (Jordan et al., 2009a). The ionization conditions in the drift tube were controlled by drift voltage (530 V), drift temperature (60°C) and drift pressure (2.3 mbar) resulting in an E/N of about 115 Td. In NO+ mode the hollow cathode was supplied with dry, purified air entering the ionization region leading to the following ionization sequence:

\[ N^+ + O_2 \rightarrow NO^+ + O \]  
(R1a)

\[ O^+ + N_2 \rightarrow NO^+ + N \]  
(R1b)

\[ N_2^+ + O_2 \rightarrow O_2^+ + N_2 \]  
(R1c)

\[ O_2^+ + NO \rightarrow NO^+ + O_2 \]  
(R1d)

Measurements using NO+ ionization were performed using a SRI-TOF-MS 8000 apparatus from Ionicon Analytik GmbH, Innsbruck (Austria) (Jordan et al., 2009a). The ionization conditions in the drift tube were controlled by drift voltage (530 V), drift temperature (60°C) and drift pressure (2.3 mbar) resulting in an E/N of about 115 Td. In NO+ mode the hollow cathode was supplied with dry, purified air entering the ionization region leading to the following ionization sequence:

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(R1d)
where rate coefficients \(k_{1b}\) and \(k_{1c}\) are much smaller than the collisional rate (i.e. \(k_{1c} \ll k_2\)) and rate coefficients \(k_1\) and \(k_4\) proceed close to \(k_c\) (Federer et al., 1985).

The instrument utilized in this study is equipped with a dynamically adjustable source valve, which can be used to control the gas exchange rate in the ion-source via a differential pumping stage (e.g. Jordan et al., 2009b). The achieved purity of the \(\text{NO}^+\) signal was 93% in the field and 95% for laboratory calibration experiments. Knighton et al. (2009) have observed high purity of \(\text{NO}^+\) production and concluded that \(\text{NO}_2^+\) formation can be largely suppressed by adjusting the ion source extraction voltage. Here settings of 6–8 mA ion current, an extraction voltage of 120 V and a source valve setting of 35% led to a fraction of about 1% \(\text{NO}_2^+\) relative to \(\text{NO}^+\). \(\text{O}_2^+\) and \(\text{H}_3\text{O}^+\) varied between 2–4% and 1–3% respectively relative to the \(\text{NO}^+\) signal.

The sampling time per channel in the TOF was set to 0.2 ns, amounting to 174 499 channels for a mass spectrum up to about 428.5 Th. More detail on data acquisition and treatment can be found in Cappellin et al. (2012).

### 2.4 Calibration setup

A custom built calibration system was used to dilute gravimetrically prepared VOC standards including isoprene and 232 MBO. Gas standard 1 was gravimetrically prepared and provided by NOAA according to protocols published by Montzka et al. (1993). The standard contained methanol (1.89 ppmv), acetonitrile (2.00 ppmv), acetaldehyde (3.53 ppmv), acetone (1.99 ppmv), methylvinylketone (1.1 ppmv), limonene (2.1 ppmv), 2-methyl-3-buten-2-ol (2.2 ppmv), pyrrole (2.1 ppmv), benzene (1.49 ppmv), toluene (2.3 ppmv), methylmethylethylketone (2.2 ppmv) with an uncertainty of ±5%. Gas standards 2 and 3 were gravimetrically prepared in house and contained isoprene (gas standard 2: 7.25 ppmv; gas standard 3: 147.2 ppbv) and camphene (gas standard 2: 4.87 ppbv; gas standard 3: 96.6 ppbv). Both standards were cross-validated with GC-FID based on a NIST traceable hydrocarbon standard with an uncertainty of ±5% (Greenberg and Zimmerman, 1984). Gas standard 4 was gravimetrically prepared by Apel-Riemer Environmental Inc. (CO, USA) and contained isoprene (10 ppbv) and camphene (10 ppbv) with an uncertainty of ±5% each. All VOC standards were prepared in ultrapure nitrogen.

Zero air was obtained by flowing ambient air through a small membrane pump (KNF, model MPU 2099-N8611.07, USA) pressurizing a flow controller (1 slm, Bronkhorst, model: F-201CV-K0ABD-22-V, the Netherlands), which was connected to a catalytic converter. Gas standards were selectively connected to a second flow controller (10 sccm, Bronkhorst, model: F-201CV-020-ABD-22-V, Netherlands). The outflow from both flow controllers was connected via PFA Teflon fittings allowing a dynamic dilution range between 1/1000 and 1/10. Large flows were calibrated using a dry calibration system (Bios International, model DCL-MH, USA) and small flows (< 10 sccm) were calibrated using the bubble meter technique. The uncertainty due to the dynamic dilution system is estimated to be ±10%, leading to a combined uncertainty of ±15%. This setup allowed performing calibration experiments under ambient humidity (30% RH). Calibration experiments under dry conditions (< 1% RH) were performed by passing dry zero air through the dilution flow controller.

### 3 Results

#### 3.1 Ion chemistry

Previous ion chemistry investigations (e.g. Spanel and Smith, 1998; Amelynck et al., 2005; Jordan et al., 2009b; Knighton et al., 2009) identified four dominant reaction pathways using \(\text{NO}^+\) as a primary ion. These include charge transfer,

\[
\text{NO}^+ + \text{AH} \xrightarrow{k_{2a}} \text{AH}^+ + \text{NO}, \tag{R2a}
\]

hydrde ion transfer,

\[
\text{NO}^+ + \text{AH} \xrightarrow{k_{2b}} \text{A}^+ + \text{HNO}, \tag{R2b}
\]

hydroxide ion transfer,

\[
\text{NO}^+ + \text{AOH} \xrightarrow{k_{2c}} \text{A}^+ + \text{HNO}_2, \tag{R2c}
\]

and three body association reactions,

\[
\text{NO}^+ + \text{A} + \text{N}_2 \xrightarrow{k_{2d}} (\text{NO}^+) \cdot \text{A} + \text{N}_2. \tag{R2d}
\]

The ionization potential (IP) of NO (IP: 9.26 eV) is often much lower than for common VOCs detected in the atmosphere. Therefore Reaction (R2a) only proceeds in selected cases. One such example is isoprene, exhibiting an IP of 8.84 eV. \(\text{NO}^+\) ionization via charge transfer can typically be regarded as “soft”, leading to very little or no fragmentation (e.g. Spanel and Smith, 1998). Figure 1 shows the mass spectrum over a relevant range (\(m/z = 35^+\) Th to \(m/z = 70^+\) Th) for a blank and an isoprene and 232 MBO standard. Figure 2a depicts a zoomed portion of the mass spectrum of the specific ions for isoprene ionized by \(\text{NO}^+\). No significant fragmentation is observed and the major product ion appears on \(m/z = 68.0618^+\) Th, corresponding to (\(\text{C}_3\text{H}_8^+\)):

\[
\text{NO}^+ + \text{C}_3\text{H}_8 \xrightarrow{k_3} \text{C}_3\text{H}_8^+ + \text{NO} \tag{R3}
\]

Similarly, Knighton et al. (2009) have used \(\text{NO}^+\) to selectively measure an anthropogenic pollutant (1,3 butadiene) and isoprene via charge transfer and reported negligible fragmentation for both compounds.

Due to the low IP of NO, many reactions will proceed via hydride ion transfer (R2b) or hydroxide ion transfer (R2c). Association (i.e. clustering) reactions (R2d) are largely suppressed under standard SRI-MS operating conditions (i.e. 115 Td) as a consequence of the high collisional energy.
Fig. 1. Plot of the mass spectrum between \( m/z \) 35\(^+\) Th and \( m/z \) 70\(^+\) Th for a blank (top panel), an isoprene standard (middle panel) and 232 MBO standard (lower panel). Ion impurities are labelled on the top panel.

Fig. 2. Observed mass spectra for field and laboratory measurements depicting the molecular ion distribution on \( m/z \) 68\(^+\) Th (A) and \( m/z \) 69\(^+\) Th (B). Spectra are normalized by the 232 MBO count rate.

\[ \text{(KE}_{cm} = 0.16 \text{ eV). This is an important difference compared to other chemical ionization mass spectrometers, where collisional dissociation cells are often de-coupled from the reaction region, leading to potential nonlinear behavior masked by ligand switching reactions (Eisele et al., 1992).} \]

The reaction between NO\(^+\) and 232 MBO proceeds via hydroxide ion transfer according to

\[ \text{NO}^+ + \text{C}_3\text{H}_5\text{OH} \xrightarrow{k} \text{C}_3\text{H}_5\text{O}^+ + \text{HNO}_2. \]  

\[ \text{(R4)} \]

(Amelynck et al., 2005).

Figures 1 and 2b show mass spectra of 232 MBO ions measured during field and laboratory experiments. The major product ion (>98\%) for 232 MBO is detected on molecular ion \( m/z \) 69.0704\(^+\) Th corresponding to (C\(_3\)H\(_3O\))\(^+\); isoprene is observed on \( m/z \) 68.0626\(^+\) Th. These measured signals are accurate to within 7 \times 10^{-4} Th of the exact molecular ion. During field experiments a contamination peak at \( m/z \) 68.995\(^+\) Th was present, which was absent during laboratory investigations. The nature of this peak remains unclear, but it was confirmed as internal contamination, when it remained high after passing ambient air through a catalytic converter. The peak did not interfere with any of the presented analysis.

3.2 NO\(^+\) calibration with SRI-TOF-MS

Figure 3 shows results from a typical calibration experiment performed for isoprene (black) and 232 MBO (red) at standard conditions (here defined as 115 Td). For isoprene data from 3 different standards (gas standard 2, 3 and 4) were included. The 3 point calibration curve for 232 MBO was based on gas standard 1. Each set of calibrations included two repetitions. Table 1 summarizes results for isoprene and 232 MBO, which exhibit typical normalized sensitivities of 11.2 ± 0.1 ncps ppbv\(^{-1}\) and 12.9 ± 0.1 ncps ppbv\(^{-1}\) respectively. For a NO\(^+\) primary ion count rate of 4 \times 10^6 cps, the corresponding actual sensitivities would be on the order of 44.8 cps ppbv\(^{-1}\) and 51.6 cps ppbv\(^{-1}\) for isoprene and 232 MBO. These values are comparable to sensitivities obtained with a similar PTR-TOF-MS instrument using H\(_3\)O\(^+\) ionization: Graus et al. (2010) for example reported sensitivities for isoprene on the order of 44.4 cps ppbv\(^{-1}\). Jordan et al. (2009a) reported typical normalized sensitivities for aromatic compounds (e.g. benzene and 1,3,5-trichlorobenzene) in the range of 11–13 ncps ppbv\(^{-1}\). Normalized sensitivities for isoprene reported here (for NO\(^+\) mode) are about a factor of 2 lower than those reported by Knighton et al. (2009). The value presented here would fall close to the theoretically expected value assuming a rate coefficient
of $2.0 \times 10^{-9}$ cm$^3$ s$^{-1}$. Similarly for 232 MBO, the calculated normalized sensitivity (for NO$^+$ mode) would correspond to a reaction rate coefficient of $2.3 \times 10^{-9}$ cm$^3$ s$^{-1}$. At thermal energies ($\sim 0.025$ eV) Spanel and Smith (1998) and Amelynck et al. (2005) reported rate constants for the (isoprene + NO$^+$) and [232 MBO + NO$^+$] reactions of $1.7 \times 10^{-9}$ cm$^3$ s$^{-1}$ and $2.3 \times 10^{-9}$ cm$^3$ s$^{-1}$ respectively. The present data suggest that the reaction of NO$^+$ with these VOCs proceeds at the collisional limiting value under typical SRI-MS conditions, here characterized by a center of mass energy ($KE_{cm}$) of $\sim 0.16$ eV.

Figure 4 depicts the dependence of normalized sensitivities as a function of collisional energy ($E/N$), expressed in units of Td. For this experiment the drift tube pressure was held constant at 2.3 mbar and the drift voltage was varied between 400 V and 600 V. Isoprene (black) closely follows a predicted slope based on the change in reaction time, while 232 MBO (red) exhibits a more pronounced change as a function of $E/N$. Regression lines fitted through the measured data are depicted by the solid lines with individual regression coefficients listed in the figure caption. For proton transfer reactions Cappellin et al. (2012) showed that the reaction rate coefficient for 232 MBO can vary as a function of $E/N$. The pink dash-dotted line in Fig. 4 represents a case, where we applied the same functional dependence for the reaction rate coefficient. In order to probe any potential interference we performed a test where separate mixtures of 232 MBO and Isoprene were added to a sample flow of 1.5 lpm (Fig. 5). A 6.7 ppbv concentration of 232 MBO was added at measurement cycle 30. At cycle 67 an isoprene mixing ratio of 41.6 ppbv was added to this flow. Isotopic ratios of isoprene were subtracted from $m/z$ 69. At cycle 150 the 232 MBO concentration was increased to 26.3 ppbv. The isoprene and 232 MBO standard addition was subsequently turned off as indicated on the graph. This test suggests that selective measurement of these chemical species can be performed interference free and could also potentially be used for conventional PTR-MS applications.

### 3.3 Field measurements

A field test was performed between 8 and 16 August 2011, when a PTR-TOF-MS was operated in standard H$_3$O$^+$ mode (Kaser et al., 2012), while the a SRI-TOF-MS instrument was operated in NO$^+$ mode. Figure 6 depicts diurnal cycles averaged over the entire 8 day period. The sum of isoprene and 232 MBO measured by both instruments agrees well (blue and green trace, upper panel). As confirmed before (Kim et al., 2010; Kaser et al., 2012) 232 MBO (red) is the dominant biogenic VOC at this site. Isoprene is depicted in black and exhibits typical daytime concentrations of about 200–250 pptv. As expected for light dependent biogenic VOC (BVOC) emissions, the concentration of isoprene and 232 MBO rapidly declines after sunset. The lower panel shows the ratio between isoprene and 232 MBO with an
is ionized via charge transfer, while 232 MBO undergoes a hydroxide transfer reaction. SRI-MS allows the interference free detection of both species using conventional PTR-MS technology, which is prone to collisional dissociation and dehydration of 232 MBO interfering with the detection of isoprene using conventional H$_3$O$^+$ ionization. The proposed method will also help to assess uncertainties of conventional gas-chromatography associated with the detection of isoprene in the presence of 232 MBO. Field measurements confirm 232 MBO as an important BVOC emitted from a coniferous ecosystem in Colorado. Our measurements also show the presence of trace amounts of isoprene. These findings will pave the way for more selective measurements of these compounds, which are often concomitantly emitted in semi-arid ecosystems throughout the Western United States.

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