



Selective measurements of isoprene and 2-methyl-3-buten-2-ol based on NO^+ 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^+ as a primary ion in a conventional PTR-MS equipped with an SRI unit. High purity of NO^+ (> 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_5H_8^+ (> 99 %) (e.g. Spanel and Smith, 1998). 232 MBO undergoes a hydroxide ion transfer reaction resulting in the major product ion channel C_5H_9^+ (> 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) ncps ppbv⁻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_3O^+ 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⁻¹ (Guenther et al., 2006) (uncertainty range: 230–700 Tg yr⁻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⁻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_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-butene-2-ol (232 MBO) in a coniferous forest in the USA. Since then many studies (e.g. Harley

et al., 1998; Schade and Goldstein, 2001; Baker et al., 2001; Kim et al., 2010) have confirmed the presence of this alcohol throughout coniferous ecosystems in the Western US. Due to the large emission source 232 MBO is sometimes also termed the “isoprene of the west”.

The ecological roles of isoprene and 232 MBO have not been entirely elucidated, but might reflect a plant’s ability to protect against oxidative stress (Loreto and Schnitzler, 2010), act as a biochemical stat (Rosenstiel et al., 2004) or mitigate high temperature exposure (Sharkey et al., 2008).

With the emergence of fast online measurement techniques, ecosystem fluxes of both species are increasingly obtained by the eddy covariance technique. Proton-transfer-reaction mass spectrometry (PTR-MS) (Hansel et al., 1995; Lindinger et al., 1998; de Gouw and Warneke, 2007) has so far been the technique of choice (e.g. Karl et al., 2001; Warneke et al., 2002; Taipale et al., 2010; Müller et al., 2010). Previous studies (Fall et al., 2001) have identified the presence of a host of biogenic C5 alcohols and aldehydes, which collisionally dissociate or dehydrate and could potentially interfere with the detection of isoprene using hydronium ion chemistry in PTR-MS. In many places isoprene dominates over most other BVOCs and these interferences are often shown to be minor (Karl et al., 2004; Warneke et al., 2010; Miszta et al., 2011); however measurements, particularly in coniferous ecosystems, can be more challenging due to the concomitant emission of isoprene and 232 MBO. In PTR-MS 232 MBO undergoes collisional dissociation and a dehydration reaction leading to the dominant ion fragment m/z 69⁺ Th (parent ion minus an H₂O group); typically about 25 % remains on the parent ion (m/z 87⁺ Th). Theoretically it should be possible to distinguish 232 MBO and isoprene, as long as a significant portion of both compounds enables investigating the ratio of the ions m/z 87⁺ Th and m/z 69⁺ Th. However this exercise becomes increasingly difficult when isoprene concentrations are comparably low (e.g. < 30 %) relative to 232 MBO.

Need for improved detection of these species is also corroborated by the fact that conventional GC (gas chromatographic) techniques can be prone to humidity and oxidant dependent detection uncertainties (Goldan et al., 1997). Baker et al. (2001) have shown that anytime a sample treatment involves heating, 232 MBO can dehydrate (e.g. GC sample treatment). Here we test the feasibility of using NO⁺ ion chemistry to selectively distinguish isoprene and 232 MBO using SRI-MS technology (selective reagent ion mass spectrometry).

2 Method and field site description

2.1 Field site and sampling inlet

The study was located at the Manitou Forest Observatory near Woodland Park, Colorado, USA (2290 m elev., lat.

39° 6′ 0″ N, long. 105° 5′ 30″ W) and took place in July 2011. The site has been described previously (e.g. Kim et al., 2010) and is representative of the montane ponderosa pine zone in the Front Range which extends from southern Wyoming to northern New Mexico. The canopy is open and of varying density, with mixed age ponderosa pine up to 100 yr old and a surface cover of grasses, sage, crocus, forbs and exposed cryptogammic soils. The average tree height surrounding the measurement tower was 18.5 m.

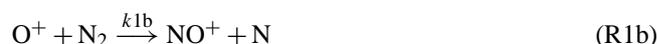
Measurements were taken from a 30 m tall tower. All instruments sampled off an approximately 35 m long Teflon line (OD: 3/8″; ID: 0.33″), pumped at a speed of about 30 L min⁻¹, so that overall delay times were measured between 3 and 5 s.

2.2 PTR-TOF-MS (H₃O⁺) (Proton-transfer-reaction time of flight mass spectrometer)

A Proton-transfer reaction time of flight mass spectrometer (PTR-TOF-MS) based on a high resolution time of flight mass spectrometer (HTOF-MS, Tofwerks, Switzerland) and developed at the University of Innsbruck (Graus et al., 2010) was operated using protonated water (H₃O⁺) as reagent ion. De Gouw and Warneke (2007) reviewed the operational mode for H₃O⁺ chemistry using the PTR-MS technique in detail. Here we operated the instrument at 60 °C, a drift tube voltage of 580 V and a drift tube pressure of 2.3 mbar. These conditions resulted in an E/N ratio of about 125 Townsend (Td) (E being the electric field strength and N the gas number density; 1 Td = 10⁻¹⁷ V cm²). Six minutes average concentration measurements are used for the analysis presented in this manuscript. Details about TOF-MS data acquisition and data post processing can be found in Müller et al. (2010).

2.3 SRI-TOF-MS (NO⁺) (selective reagent ionization time of flight mass spectrometer)

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:



where rate coefficients k_{1b} and k_{1c} are much smaller than the collisional rate (i.e. $k_{1c} \ll k_c$) 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 NO^+ signal was 93 % in the field and 95 % for laboratory calibration experiments. Knighton et al. (2009) have observed high purity of NO^+ production and concluded that 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 % NO_2^+ relative to NO^+ . O_2^+ and H_3O^+ varied between 2–4 % and 1–3 % respectively relative to the 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), methylethylketone (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 ppmv, 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, Netherland). 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 at 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

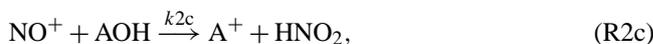
Previous ion chemistry investigations (e.g. Spanel and Smith, 1998; Amelynck et al., 2005; Jordan et al., 2009b; Knighton et al., 2009) identified four dominant reaction pathways using NO^+ as a primary ion. These include charge transfer,



hydride ion transfer,



hydroxide ion transfer,



and three body association reactions,



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. 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 NO^+ . No significant fragmentation is observed and the major product ion appears on m/z 68.0618⁺ Th, corresponding to (C_5H_8^+):



Similarly, Knighton et al. (2009) have used 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

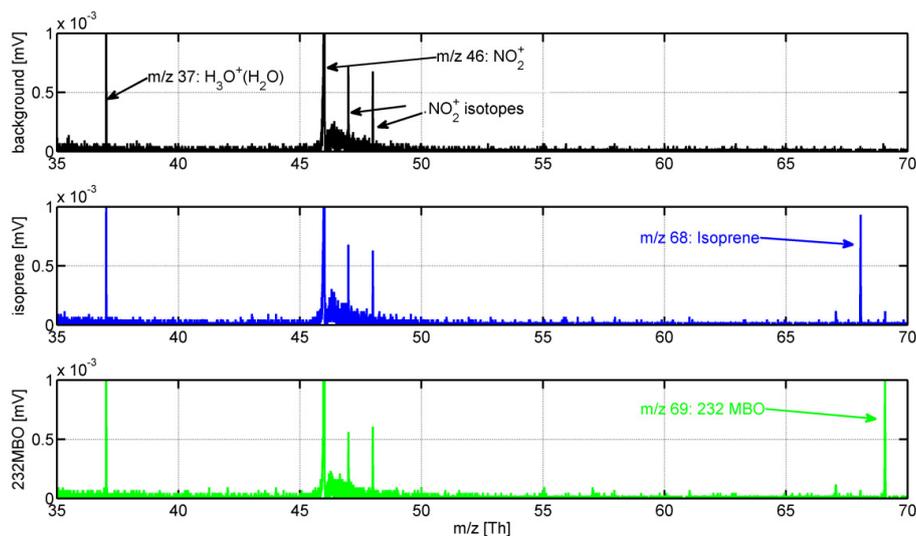


Fig. 1. Plot of the mass spectrum between m/z 35⁺ Th and m/z 70⁺ Th for a blank (top panel), an isoprene standard (middle panel) and 232 MBO standard (lower panel). Ion impurities are labelled on the top panel.

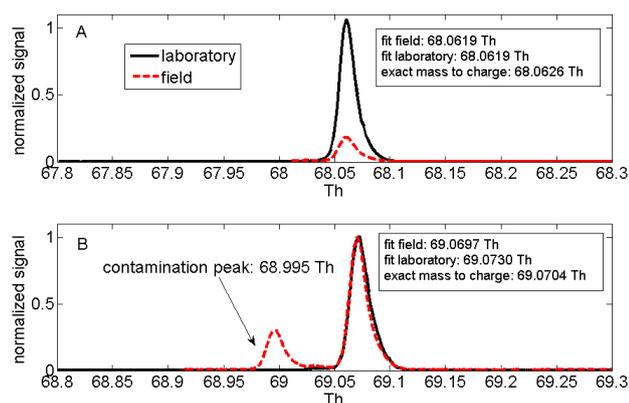
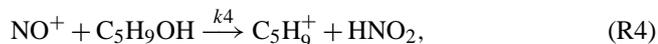


Fig. 2. Observed mass spectra for field and laboratory measurements depicting the molecular ion distribution on m/z 68⁺Th (A) and m/z 69⁺Th (B). Spectra are normalized by the 232 MBO count rate.

($KE_{cm} = 0.16$ 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



(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 ($C_5H_9^+$); isoprene

is observed on m/z 68.0626⁺ Th. These measured signals are accurate to within 7×10^{-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 4×10^6 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_3O^+ 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

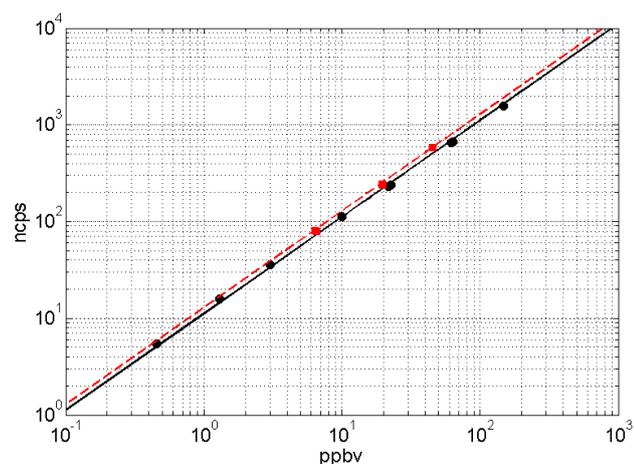


Fig. 3. Multipoint calibration curve for isoprene (black) and 232MBO (red). Regression lines yield 11.1 ± 0.1 ncps ppbv $^{-1}$ and 12.9 ± 0.1 ncps ppbv $^{-1}$ for isoprene and 232 MBO respectively.

of 2.0×10^{-9} cm 3 s $^{-1}$. Similarly for 232 MBO, the calculated normalized sensitivity (for NO $^+$ mode) would correspond to a reaction rate coefficient of 2.3×10^{-9} cm 3 s $^{-1}$. At thermal energies (~ 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 1.7×10^{-9} cm 3 s $^{-1}$ and 2.3×10^{-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 ~ 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

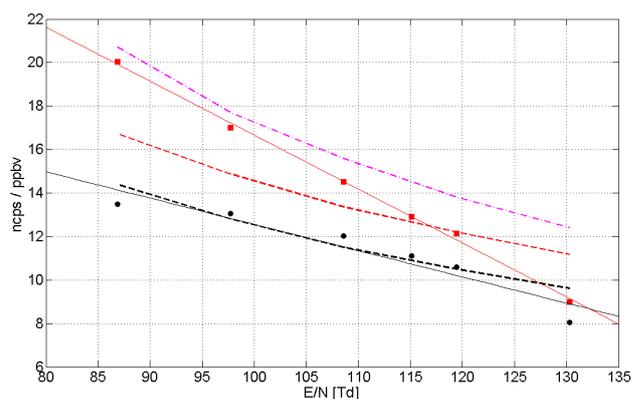


Fig. 4. Normalized sensitivities plotted as a function of E/N . Isoprene (black) and 232 MBO (red) exhibit higher sensitivities at lower collisional energies. The dashed lines indicate a theoretically calculated response curve based on a change in reaction time for a constant rate coefficient; the pink dash-dotted line indicates the case using a varying rate coefficient for 232 MBO; the thin solid lines depict a linear fit ($y = a \cdot x + b$) through measured data yielding the following fitting coefficients: Isoprene: $a = -0.12$, $b = 24.6$ and 232 MBO $a = -0.25$, $b = 41.5$.

Table 1. Normalized sensitivities in ncps ppbv $^{-1}$ ($:= 1 \times 10^6 \times \text{VOC}^+ [\text{cps}]/\text{NO}^+ [\text{cps}] \text{ppbv}^{-1}$) obtained for a drift pressure of 2.3 mbar, a drift voltage of 530 V and a drift tube temperature of 60 °C corresponding to $E/N = 115$ Td.

Humidity	Isoprene	232 MBO
Humid 30 % RH	11.1 ± 0.1	12.9 ± 0.1
Dry < 1 % RH	11.2 ± 0.1	12.6 ± 0.1

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

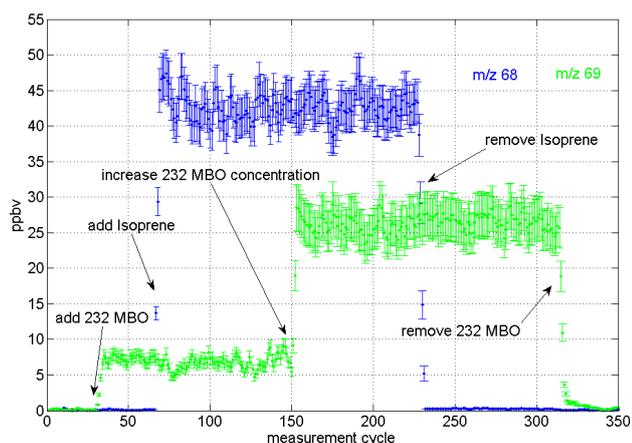


Fig. 5. Interference test: each measurement cycle represents a 1.5 s time interval; 232 MBO (green) and Isoprene (blue) concentrations are varied as indicated in the graph. Error bars represent 1σ .

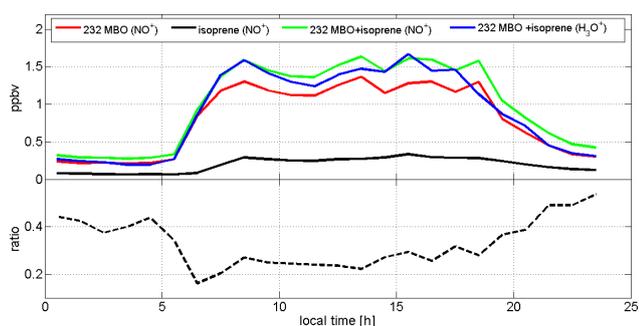


Fig. 6. Diurnal concentrations of isoprene and 232 MBO using two PTR-TOF-MS instruments (upper panel); one instrument was operated in H_3O^+ mode depicting 232 MBO + isoprene (blue trace); the other instrument was operated in NO^+ mode separating 232 MBO (red) and isoprene (black). The sum of the two is also plotted for comparison (green trace). The lower panel depicts the ratio between isoprene and 232 MBO.

average daytime value of about 0.2. The ratio increases to about 0.5 during night, which could be indicative of different emission patterns between these BVOCs or the influence of non-local isoprene sources. For the 2011 campaign the OH reactivity due to isoprene would amount to up to 40 % relative to that of 232 MBO for typical daytime conditions. Future eddy covariance measurements are needed to elucidate emission patterns of these two species in more detail at this site.

4 Conclusions

We have demonstrated that two dominant biogenic VOCs (isoprene and 232 MBO) can be selectively measured by selective reagent ionization mass spectrometry (SRI-MS) based on NO^+ ionization. Our results confirm that isoprene

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_3O^+ 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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