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PTR-QMS vs. PTR-TOF comparison in a region with oil and natural gas extraction industry in the Uintah Basin in 2013

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Abstract

Here we compare volatile organic compound (VOC) measurements using a standard Proton-Transfer-Reaction Quadrupole Mass Spectrometer (PTR-QMS) with a new Proton-Transfer-Reaction Time Of Flight Mass Spectrometer (PTR-TOF) during the Uintah Basin Winter Ozone Study 2013 (UBWOS2013) field experiment in an oil and gas field in the Uintah Basin, Utah. The PTR-QMS uses a quadrupole, which is a mass filter that lets one mass pass at a time, whereas the PTR-TOF uses a Time Of Flight mass spectrometer, which takes full mass spectra with typical 0.1 s to 1 min integrated acquisition times. The sensitivity of the PTR-QMS in units of counts per ppbv is about a factor of 10–35 times larger than the PTR-TOF, when only one VOC is measured. The sensitivity of the PTR-TOF is mass dependent because of the mass discrimination caused by the sampling duty cycle in the orthogonal-acceleration region of the TOF. For example, the PTR-QMS on mass 33 (methanol) is 35 times more sensitive than the PTR-TOF and for masses above 120 amu less than 10 times more. If more than 10–35 compounds are measured with PTR-QMS, the sampling time per ion decreases and the PTR-TOF has higher signals per unit measuring time for most masses. For UBWOS2013 the PTR-QMS measured 34 masses in 37 s and on that time-scale the PTR-TOF is more sensitive for all masses. The high mass resolution of the TOF allows for the measurements of compounds that cannot be separately detected with the PTR-QMS, such as oxidation products from alkanes and cycloalkanes emitted by oil and gas extraction. PTR-TOF masses do not have to be pre-selected allowing for identification of unanticipated compounds. The measured mixing ratios of the two instruments agreed very well ($R^2 \geq 0.92$ and within 20 %) for all compounds and masses monitored with the PTR-QMS.

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1 Introduction

The measurements of volatile organic compounds (VOCs) with Proton-Transfer-Reaction Quadrupole Mass Spectrometry (PTR-QMS) have become a standard technique in atmospheric measurements on various platforms such as ground sites, ships and aircraft, because of its high time resolution and sensitivity. The instrument has been described and characterized in great detail over the last several years (Blake et al., 2009; de Gouw and Warneke, 2007; Hansel et al., 1999, 1995; Lindinger et al., 1998a, b; Warneke et al., 2003, 2001, 2011b) and many successful inter-comparisons with other techniques such as gas chromatography mass spectrometry (GC-MS) have demonstrated the sensitivity and the selectivity of PTR-QMS (de Gouw et al., 2003; de Gouw and Warneke, 2007; Haase et al., 2012; Wisthaler et al., 2008). PTR-QMS is a chemical ionization mass spectrometry technique that detects VOCs using proton transfer reactions with H_3O^+, but has the drawback that only the nominal unit-resolution mass of one VOC at a time can be determined. To improve on the selectivity three approaches have been frequently investigated: (1) instead of H_3O^+ different reagent ions (Sulzer et al., 2012) have been used such as NO^+, O_2^+, NH_4^+ and Kr^+, (2) gas chromatographic pre-separation of VOCs prior to PTR-QMS detection (Karl et al., 2001; Warneke et al., 2003) and (3) isomers are distinguished by fragmentation patterns generated with collision induced dissociation (CID) (Warneke et al., 2004). In addition, other mass spectrometers have been used in place of the quadrupole such as ion traps (Mielke et al., 2008; Prazeller et al., 2003; Warneke et al., 2005a, b) and Time Of Flight (TOF) mass spectrometers (Blake et al., 2004; Tanimoto et al., 2007).

The PTR-TOF instrument (Graus et al., 2010; Jordan et al., 2009; Müller et al., 2010) was recently developed by the University of Innsbruck and Ionicon Analytic and is commercially available. It is aimed to improve on the time response and on the selectivity of PTR-QMS by using a high resolution TOF mass spectrometer from Tofwerk AG, which has the capability of recording mass spectra at a very high frequency (> 10 Hz) and

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with a high mass resolution ($> 4000 m/\Delta m$). This mass resolution is often sufficient to distinguish between isobaric compounds.

Here we compare a commercial PTR-TOF with a standard PTR-QMS that were operated side-by-side during a measurement campaign (UBWOS2013) in an area of oil and natural gas exploration in the Uintah Basin, Utah. We evaluate the stability, sensitivity and the detection limits of both instruments and determine which instrument is more sensitive in a given measurement mode. We also describe the advantages and the additional science that can be done with PTR-TOF using the data from the UBWOS2013 campaign.

2 Experimental

2.1 UBWOS2013 field campaign

The Uintah Basin Wintertime Ozone Study 2013 (UBWOS2013) was conducted in January and February 2013 in the Uintah Basin, Utah. This area has a very low population density, but about 10 000 active oil and natural gas wells are located within the basin. A map of the Uintah Basin study area with the oil and natural gas wells is shown in Fig. 1. This intense oil and natural gas extraction operation results in emissions of greenhouse gases, volatile organic compounds (VOCs) and nitrogen oxides (NO_x) (Gilman et al., 2013; Helmig et al., 2014; Howarth et al., 2011; Karion et al., 2013; Katzenstein et al., 2003; Kemball-Cook et al., 2010; Litovitz et al., 2013; Petron et al., 2012). The UBWOS2013 campaign was designed to investigate the unusual wintertime ozone production that was observed in basins with oil and natural gas exploration during strong inversions and snow covered surfaces (Edwards et al., 2013; Helmig et al., 2014; Schnell et al., 2009).

Measurements were done at the heavily instrumented Horse Pool ground site, which is also shown in Fig. 1. During UBWOS2013, cold temperatures, snow on the ground and strong temperature inversions provided ideal conditions for wintertime ozone

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production and indeed ozone mixing ratios at Horse Pool exceeded 120 ppbv on several days. Emissions from oil and natural gas exploration in the Uintah Basin are mainly alkanes, cycloalkanes and aromatics related to the natural gas (Warneke et al., 2014), but active photochemistry produces, besides ozone, many different oxygenated VOCs (oxyVOCs). The Uintah Basin presents a unique VOC mix that is an excellent test case for demonstrating the additional capabilities of PTR-TOF, because many of the photochemically produced oxyVOCs are difficult to identify with standard PTR-QMS.

2.2 PTR-QMS and PTR-TOF instruments

PTR-QMS and PTR-TOF both use similar reaction chambers, in which proton transfer reactions of H_3O^+ are used to ionize the VOCs of interest (Lindinger et al., 1998a). The main difference between the two instruments is the mass spectrometer, which is a quadrupole QMS420 from Pfeiffer Vacuum for the PTR-QMS and an orthogonal acceleration reflectron TOF-MS from Tofwerk AG for the PTR-TOF. Both instruments were housed in the same instrument trailer and sampled from a common inlet manifold that pulled 20 L min^{-1} through a 15 m long Teflon inlet.

The PTR-QMS (owned by the Chemical Sciences Division of NOAA) has been used extensively in various field and laboratory experiments including several ground based, ship and airborne deployments over the past 15 years and has been characterized and described in much detail previously (de Gouw and Warneke, 2007). During this measurement campaign standard operating conditions of 2.4 mbar and 720 V resulting in an E/N of about 125 Td in the drift tube were used. Instrument backgrounds were determined every 3 h for about 3.5 min using a catalytic converter. Calibrations were done about every other day using three different calibration standards containing VOC mixtures in nitrogen. Using the mobile organic carbon calibration system (MOCCS) system (Veres et al., 2010), formaldehyde was calibrated 5 times and the cyclohexanes twice. The results of all the calibrations from UBWOS2013 for the PTR-QMS are shown in Fig. 2a and b. Clear differences in the gas calibration standard tanks for some compounds were observed and result in an instrument accuracy of better than 20 %.

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The quadrupole is a mass filter and measures only one mass at a time. During the measurements presented here the PTR-QMS was set to measure 34 masses related to VOCs with a 1 s dwell time every 37 s. A common 1 min data format was used for all instruments during UBWOS2013 and therefore either one or two 1 s dwell time measurements were used for the 1 min data.

The PTR-TOF (owned by the University of Wyoming) is a commercial instrument that was acquired from Ionicon Analytics about 1 month before the field experiment. The operating conditions were 2.2 mbar and 600 V resulting in an E/N of about 130 Td in the drift tube. Instrument backgrounds were determined similar to the PTR-QMS every 3 h for 1.5 min using a similar catalytic converter. Calibrations were done less frequently, but the same gas standards and MOCCS system were used. The calibration results from UBWOS2013 for the PTR-TOF are shown in Fig. 2c. Only three calibrations are available and the average sensitivity value was used for the entire campaign. As will be described below, the primary ion signal in the PTR-TOF was slightly unstable over the course of the campaign, but we still estimate the accuracy to be within 20 %. In the PTR-TOF mass spectra from 1–500 amu with an extraction frequency of 250 kHz were pre-averaged and recorded as 10 s spectra, which were then further averaged to the 1 min UBWOS standard data format.

3 Inter-comparison

3.1 Sensitivity

The sensitivity determined during the calibration measurements of the PTR-QMS and the PTR-TOF is compared in Fig. 3. The standard way of expressing the PTR-QMS sensitivity is in units of ncps ppbv^{-1} (de Gouw and Warneke, 2007), which normalizes the calibration signal to 10^6 H_3O^+ primary ions. Figure 3a shows that the PTR-QMS and PTR-TOF have very comparable normalized sensitivities for the individual compounds as can be expected, because similar drift tube reaction chambers are used.

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The PTR-QMS sensitivity in ncps ppbv^{-1} is higher, because the PTR-QMS drift tube is 1 cm longer and 2.4 mbar is used in the drift tube at similar E/N compared to the PTR-TOF. Also the transmission efficiency for H_3O^+ in the PTR-QMS is smaller compared to the product ions. The PTR-TOF data were analyzed with the software package described by Müller et al. (2013) and are corrected for dead time, baseline and most notably mass discrimination. The mass discrimination is caused by the sampling duty cycle in the orthogonal-acceleration region of the TOF. The duty cycle is mass dependent, because different mass ions coming from the drift tube have a different velocity in the orthogonal accelerator. The smaller masses are faster and a larger fraction reaches the end of the orthogonal accelerator and is therefore lost there. The resulting mass discrimination is $[(m/z)_{max}/(m/z)]^{0.5}$. The normalization to the primary ions for both instruments and the mass discrimination are removed in Fig. 3b to compare sensitivities in actual count rates. The primary ion signal for the PTR-TOF used in Fig. 3b was 1.6×10^6 ions and for the PTR-QMS 25×10^6 ions, about a factor of 15 higher (see discussion of Fig. 6a). On average, the PTR-QMS is about a factor of 20 more sensitive than the PTR-TOF in cps ppbv^{-1}. The difference in sensitivity is dependent on the mass because of the mass discrimination of the PTR-TOF (Müller et al., 2013) and the transmission efficiency of the PTR-QMS (de Gouw and Warneke, 2007). The sensitivity here is expressed as cps ppbv^{-1}, but the PTR-QMS measures only one mass per second, while the PTR-TOF takes full mass spectra, which compensates for the lower sensitivity, if multiple masses are measured with the PTR-QMS. During UBWOS2013, the PTR-QMS measured 34 masses in 37 s duty cycle and the final data protocol required the use of 1 min data. In Fig. 3c the sensitivities from both instruments are compared in counts per minute per ppbv (cpmin ppbv^{-1}) and in this comparison the PTR-TOF is now the more sensitive instrument.

The ratio of the sensitivities taken from Fig. 3b of PTR-QMS/PTR-TOF is plotted in Fig. 4a and is closely related to the mass discrimination of the PTR-TOF, which is also shown in Fig. 4a. This ratio also determines at what length of the PTR-QMS duty cycle, assuming 1 s dwell time per mass, the PTR-TOF becomes more sensitive, which is shown in Fig. 4b. For UBWOS2013, 1 min measurements are reported, in which case the PTR-TOF is more sensitive for all masses. During aircraft measurements such as done during CALNEX2010 (Warneke et al., 2011b), a duty cycle of about 17 s was used, in which case the PTR-QMS would be more sensitive for masses below 80 amu and the PTR-TOF above 80 amu.

3.2 Noise and detection limits

The detection limit of the instruments depends not only on the sensitivity, but also on the signal noise and the instrument background. The noise is the square root of the signal for all the product ions (if the gain on the multi channel plates (MCP) is set high enough). Primary ion signals are so large that undercounting has an influence on the noise and signal detection. This has been previously demonstrated for PTR-QMS (de Gouw and Warneke, 2007). For a typical PTR-TOF calibration measurement, the signal, the measured noise and the square root of the signal for some selected masses are shown in Fig. 5. For most masses the noise is basically identical to the square root of the signal as can be seen in Fig. 5 for mass 73.0656 (methyl ethyl ketone) and mass 137.133 (α-pinene). There are some exceptions, which are shown by mass 33.0349 (methanol), mass 33.0207 (O_2H^+) and mass 45.0347 (acetaldehyde). The baseline is increased near peaks with very large signals, such as the primary ions H_3O^+, O_2^+, ...), increasing the noise on masses close to these peaks. The baseline increase can be seen in a mass spectrum in Fig. 9a.

The detection limit is calculated from the sensitivity and the noise on the background signals determined using the catalytic converter measurements. The detection limits are three times ($S/N = 3$) the standard deviation of the background measurements, where 30 s averaging times for the PTR-TOF and the 37 s measurements for the PTR-QMS were used. The results are shown for a few selected compounds in Fig. 6. The detection limits are comparable for both instruments, but improve with increasing mass for the PTR-TOF as is expected due to the increase in sensitivity with mass. Two notable exceptions in Fig. 6 are methanol and acetaldehyde. In the PTR-QMS the instrument

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background is comprised of mainly O_2H^+ and methanol $\cdot H^+$ ions, which can be separated by mass in the PTR-TOF (Li et al., 2014). As a result, the PTR-TOF has a much smaller instrument background than the PTR-QMS and therefore also a lower detection limit. This effect can be observed for all compounds, where the background signal is comprised of more than one isobaric ion as for example acetonitrile (Dunne et al., 2012). The instrument background and therefore also the detection limit of the PTR-TOF for acetaldehyde was elevated during UBWOS2013, likely because the instrument was new and not run long enough for the background levels to drop.

3.3 Mixing ratios

PTR-TOF and PTR-QMS have been compared successfully recently (Kaser et al., 2013; Park et al., 2013). In Fig. 7 the inter-comparison for acetone for UBWOS2013 is shown. In the top panel the time series for acetone on mass 59 from the PTR-QMS and on mass 59.0491 from the PTR-TOF are shown together with the respective primary ion signals. Over the whole time period the acetone measurements agree very well with a slope of 1.03 and an R^2 of 0.982.

The PTR-QMS was very stable, whereas the PTR-TOF primary ion signal was variable during the campaign. The PTR-TOF instrument was new and only briefly tested in the laboratory before being deployed during the field experiment. Therefore various issues with the set-up and the software had to be resolved during the field deployment resulting in the large changes in primary ion signal and therefore sensitivity and detection limit. Most issues were the result of software instability, but also the TOF, the MCP, and the ion source had to be retuned during the experiment. For the measurements of the detection limit as described above, a period was chosen, where the primary ion signal was around 1.6×10^6 cps. At high MCP gain voltages, continuous operation and high signal intensities the detector may deteriorate relatively quickly. Excessively high gain voltages may cause a more rapid deterioration, and a more frequent re-adjustment of the MCP gain in small steps should – all other things being equal – lead to a more constant signal. The detector deterioration due to high gain operation is a necessary trade off to avoid an additional mass discrimination introduced by the MCP (Müller et al., 2014). The lower panels in Fig. 7 show the inter-comparison separated into periods, when the PTR-TOF was relatively stable in a specific mode (except the deterioration of the signal due to the MCP). For each individual period the comparison is excellent with $R^2 \geq 0.987$ and the slope varies between ±9 % of unity. For the PTR-TOF only three calibrations are available and the averages from the three calibrations were used for the whole time period. This shows that without frequent calibrations an additional error of ±10 % can be expected, if the instrument set-up is not stable during the experiment.

Many other masses routinely measured by PTR-QMS, where generally only one VOC contributes to the signal (methanol, acetaldehyde, benzene, toluene and many others), agreed well within the stated uncertainties with the PTR-TOF: $R^2 \geq 0.92$ and ±20 %. Benzene from the PTR-TOF and PTR-QMS agreed within 3 % and $R^2 = 0.98$. The PTR-TOF measurements of benzene were also compared with a GC-FID system; the PTR-TOF agreed with an $R^2 = 0.96$ but its results were larger by 22 %. This difference is within the stated uncertainties, but larger than observed in previous inter-comparisons (Warneke et al., 2011a). Figure 8 shows the comparison of masses 71 and 85 in ncps as examples. The PTR-TOF detects two separate peaks on each of those nominal masses and identifies their atomic compositions as *m* 71.0491 ($C_4H_6O \cdot H^+$) and *m* 71.083 ($C_5H_{10} \cdot H^+$) and *m* 85.0647 ($C_5H_8O \cdot H^+$) and *m* 85.0966 ($C_6H_{12} \cdot H^+$). The PTR-QMS correlates the best with the sum of the two compounds for both masses as expected. The sensitivity of the PTR-QMS in ncps ppb^{-1} is close to a factor of two larger than the PTR-TOF (Fig. 3a), which is reflected in the slope in Fig. 8 as well. Other compounds that were compared are H_2S, which is discussed elsewhere (Li et al., 2014), and formaldehyde. Both of those compounds have only a slightly higher proton affinity than water and have therefore much lower sensitivities and need to be calibrated frequently (Warneke et al., 2011b). Formaldehyde calibrations for the PTR-TOF are not available, but the comparison of the signals in ncps showed an $R^2 = 0.88$.

4 Mass resolution and additional science possible with PTR-TOF

One of the two main differences between PTR-QMS and PTR-TOF is the achievable mass resolution: unity for the PTR-QMS and 4000–5000 for the PTR-TOF (Graus et al., 2010). Figure 9 shows mass spectra from both instruments for the full range and four selected masses. The PTR-QMS mass spectrum is an average of three cycles, where each mass (m/z 20–200) was measured for one second each resulting in a total of 9 min measurements. The PTR-TOF spectrum is an average of all spectra over those 9 min. Figure 9 shows that at one nominal mass, as measured by the PTR-QMS, up to four nominally isobaric ions are seen in the PTR-TOF.

The composition of each nominal mass, where the PTR-TOF detected signal in ambient air, is shown in Fig. 10. In the Uintah Basin large emissions of alkanes, cycloalkanes and aromatics from the oil and gas industry result in a rather unusual VOC composition and as a result many of the observed mass peaks are hydrocarbons. Subsequent photochemical oxidation of the alkanes produced many oxygenated compounds and VOCs with up to three oxygen atoms. In Fig. 10 the gray shaded masses are the ones that were monitored with the PTR-QMS and it can be seen that for most compounds either the hydrocarbon C_xH_y or the C_xH_yO structure dominate the signal on that nominal mass. This means that in principle with PTR-QMS the same information is obtained for the dominant peak on that mass, but the molecular identity is still not known and has to be assumed from prior knowledge of the emissions or chemistry. But in many cases multiple isobaric ions contribute to the signal at a nominal mass and the PTR-TOF provides identification of VOCs that are not separable with PTR-QMS.

The photo oxidation products of some alkanes, cycloalkanes and aromatics, which are detectable with H_3O^+ ions, but have interferences on the PTR-QMS, can be quantified by PTR-TOF. The diurnal profiles for the UBWOS2013 campaign of many of those compounds are shown in Fig. 11. It can be seen that similar homologues of VOCs such as the acids, ketones or cycloketones have very similar diurnal profiles, but they are different from another. Often the signals corresponding to these compounds, especially

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$C_xH_yO_2$ structures, are very small and have the same nominal mass as C_xH_yO compounds. For example, mass 73 is mainly comprised of methyl ethyl ketone (C_4H_9O) and has a small contribution of methylglyoxal ($C_3H_5O_2$). Methylglyoxal is a very important compound in the chemistry leading to wintertime ozone exceedances in the Uintah Basin, because it acts as a radical precursor (Edwards et al., 2013). The detection of methylglyoxal is not possible with PTR-QMS, but feasible with PTR-TOF and has added greatly to our understanding of wintertime ozone formation.

5 Conclusions

PTR-TOF has been a significant step in the evolution and improvement of the PTR technique to monitor VOCs in the atmosphere, where the main advantages of the TOF are the high time resolution for full mass scans and the high mass resolution of 4000–5000 compared to the unit mass resolution with PTR-QMS. The high mass resolution allows for the identification of isobaric ions. Here we compared a standard PTR-QMS with a new PTR-TOF during the UBWOS2013 field experiment in an oil and gas field in the Uintah Basin, Utah.

The set-up of the measurements with the two instruments determines which instrument is more sensitive. The difference in sensitivity is dependent on the mass: the PTR-TOF is increasingly more sensitive with increasing mass, and at above 80 amu it becomes more sensitive than the PTR-QMS. In PTR-QMS, the masses that are monitored need to be chosen. If only one mass is measured with 1 s dwell time, the PTR-QMS is about a factor of 10–35 more sensitive depending on the mass. The number of masses monitored in PTR-QMS and the averaging times then determine which instrument is more sensitive: 10–35 masses for 1 s dwell times, again dependent on the mass, is the break-even point. During UBWOS2013 the PTR-QMS was set to monitor 34 masses in 37 s and data for both instruments were reported as 1 min averages. In this set-up the PTR-TOF is more sensitive for all masses.

The high mass resolution of the PTR-TOF showed that many masses monitored with the PTR-QMS had contributions from only one ion, but that many others had contributions from up to four different isobaric ions. This capability gives the PTR-TOF the ability to measure small oxidation products of the main emissions from the oil and gas development (alkanes, cycloalkanes and aromatics) that play an important role in the formation of ozone. These compounds were previously not measurable by PTR-QMS.

Overall the two instruments agreed for measured mixing ratios very well for all compounds where calibration gases were available and for measured count rates for all other compounds ($R^2 \geq 0.92$ and within 20 %). For masses, where more than one isobaric ion contributes to the signal, the PTR-QMS agreed with the sum of those ions observed with the PTR-TOF.

The additional analytical capabilities and the sensitivity of the current PTR-TOF version are clearly a major advance in PTR technology for VOC analysis compared to the standard PTR-QMS instruments. For measurements on aircrafts, where PTR-QMS instruments excel by commonly monitoring only a few selected ions and thus achieve high sensitivities, PTR-TOF instruments could still be improved in sensitivities to achieve the same detection limits as PTR-QMS instruments. A promising new development for a sensitivity improvement of PTR-TOF has recently been shown by Sulzer et al. (2014), which could make PTR-TOF the ideal instrument for aircraft measurements as well.

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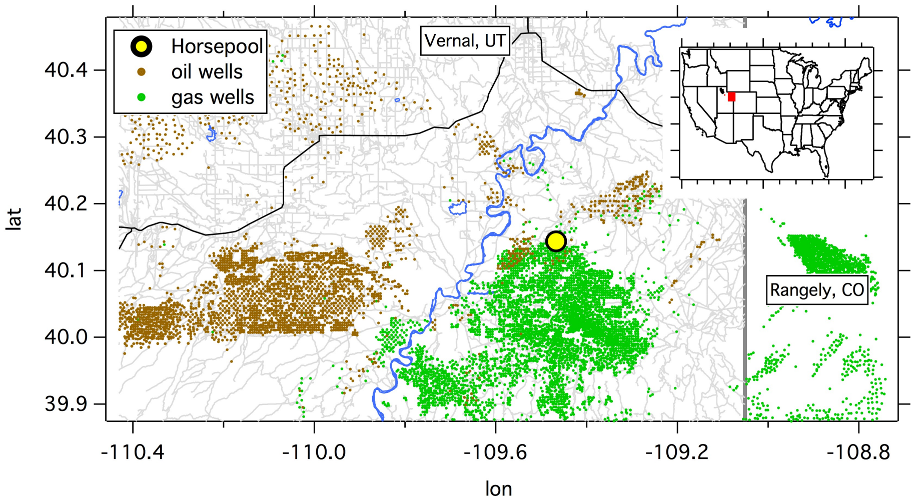

Figure 1. Map of the study area with the Horse Pool ground site in the Uintah Basin, Utah.

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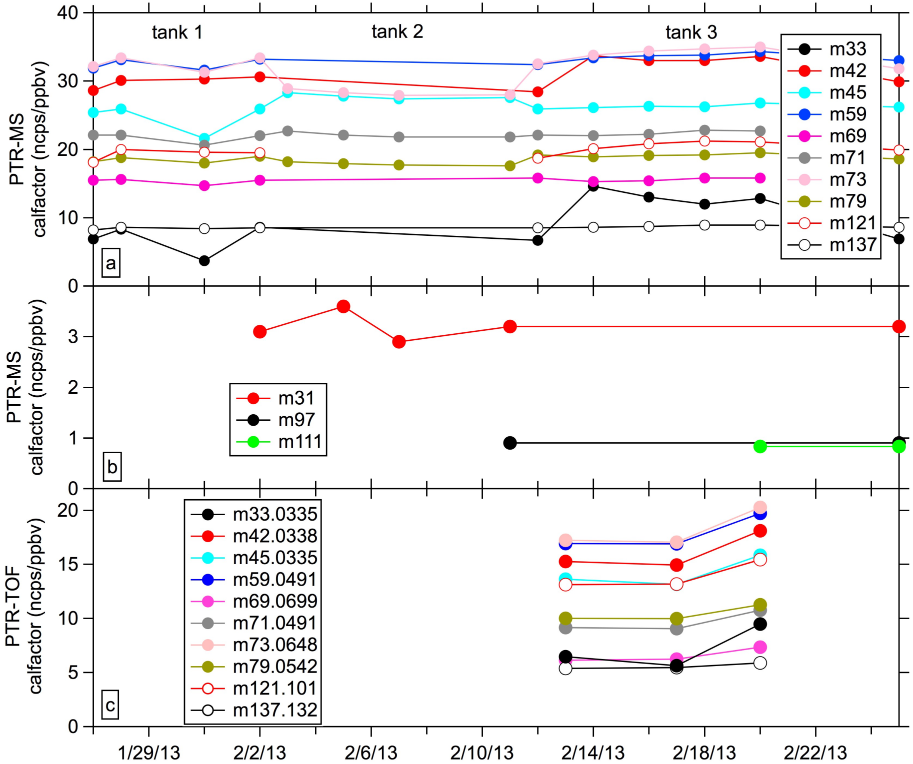

Figure 2. (a) Multiple VOC PTR-QMS calibration using three different calibration gas tanks during UBWOS2013: methanol (*m* 33), acetonitrile (*m* 42), acetaldehyde (*m* 45), acetone (*m* 59) isoprene (*m* 69), methacrolein (*m* 71), methylethylketone (*m* 73), benzene (*m* 79), 1,3,5-trimethylbenzene (*m* 121) and *α*-pinene (*m* 137). **(b)** PTR-QMS calibrations using the MOCCSS cart for formaldehyde (*m* 31), methylcyclohexane (*m* 97) and dimethylcyclohexane (*m* 111). **(c)** PTR-TOF calibration for the same compounds as in **(a)** during UBWOS2013.

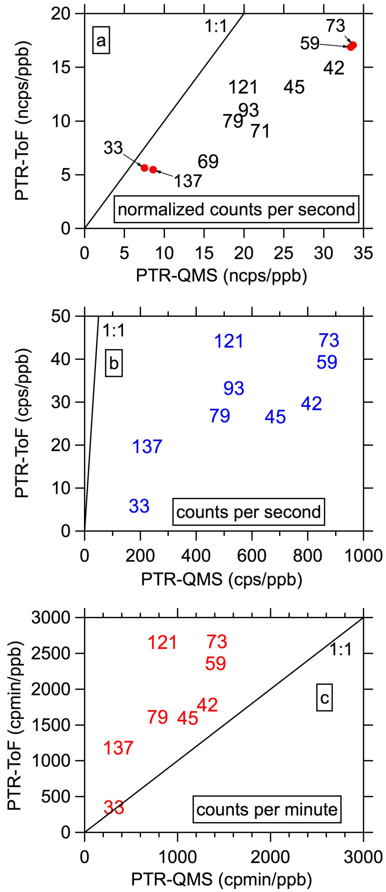

Figure 3. (a) PTR-QMS and PTR-TOF sensitivity in ncps ppbv^{-1} normalized to 1×10^6 H_3O^+ ions. **(b)** Sensitivity in cps ppbv^{-1} with PTR-QMS 25×10^6 and PTR-TOF 1.6×10^6 H_3O^+ ions. **(c)** Sensitivity in cpmin ppbv^{-1} with PTR-QMS measuring 37 ions. The numbers in **(a)**, **(b)** and **(c)** are the nominal mass of the calibrated compounds.

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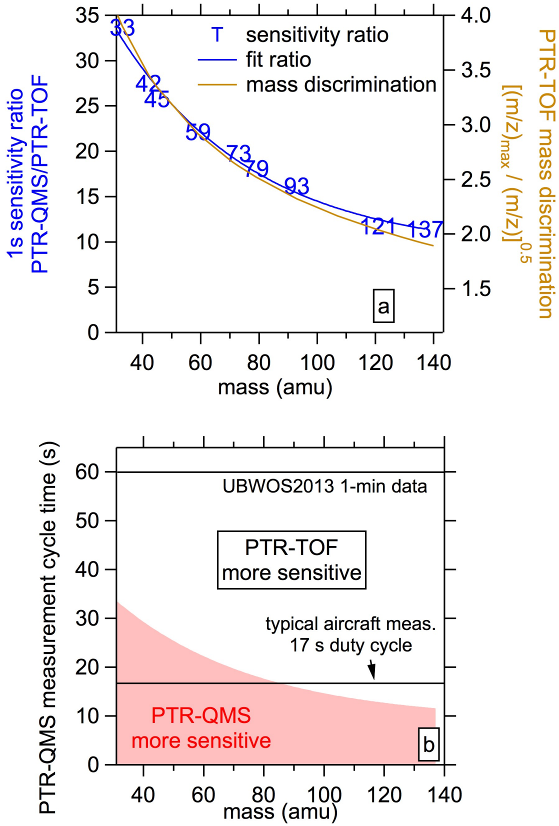

Figure 4. (a) The ratio of the 1 s sensitivities of PTR-QMS/PTR-TOF together with the PTR-TOF mass discrimination. **(b)** A mass dependent curve showing the length of the PTR-QMS measurement cycle, where the PTR-QMS is as sensitive as the PTR-TOF (identical to the fit in **a**). In aircraft measurements a duty cycle of 17 s is typical (PTR-TOF more sensitive above mass 80) and at ground sites 1 min measurements are typical (PTR-TOF more sensitive for all masses).

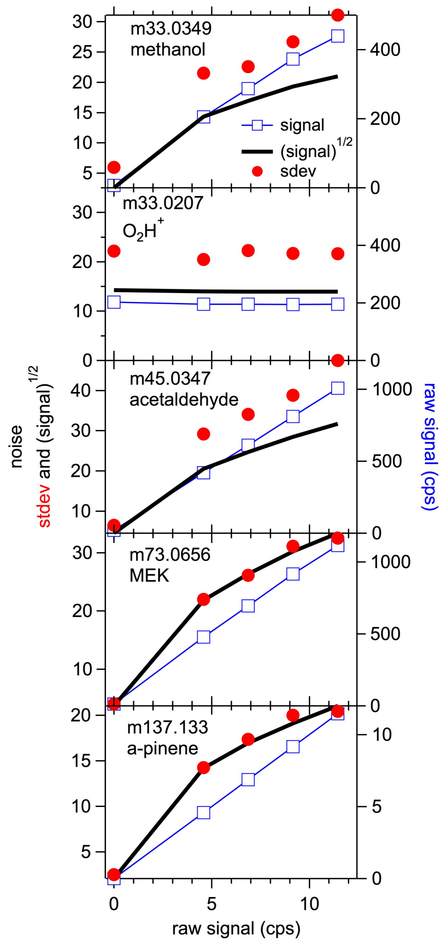

Figure 5. Signal, $(\mathrm{signal})^{1/2}$, and standard deviation of the signal (noise) during a typical PTR-TOF calibration measurement for some selected masses.

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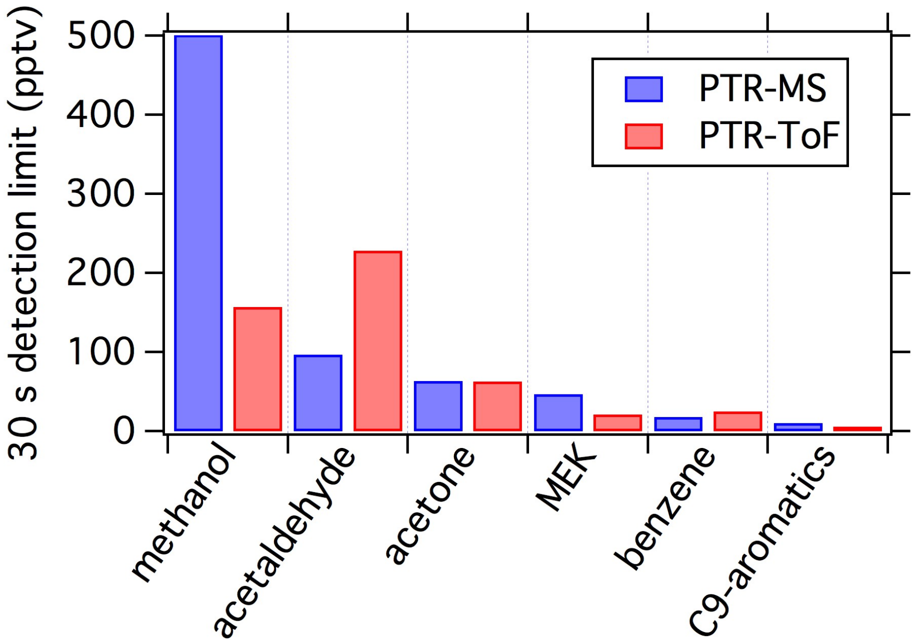

Figure 6. PTR-QMS and PTR-TOF 30 s detection limits during UBWOS2013.

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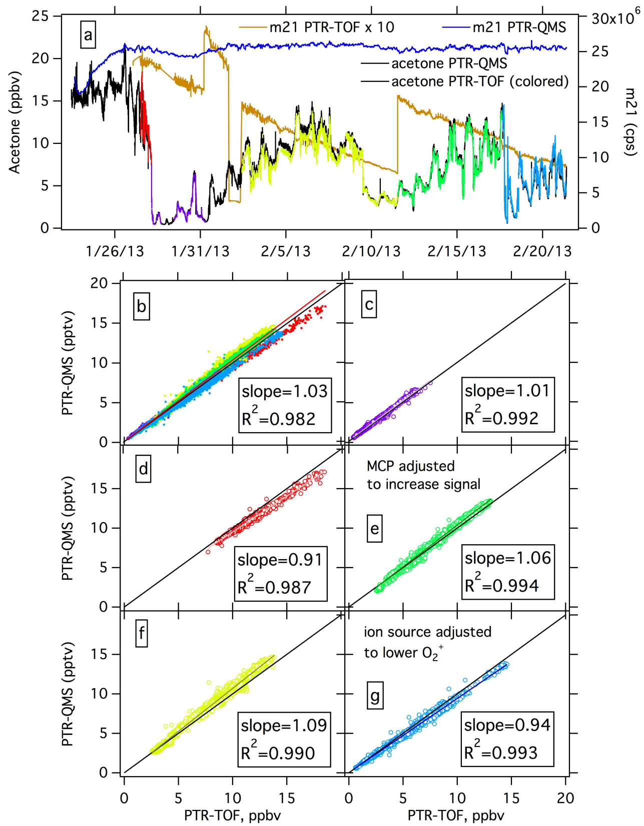

Figure 7. PTR-QMS and PTR-TOF acetone inter-comparison during UBWOS2013: **(a)** time series of the PTR-TOF and PTR-QMS primary ions and acetone. The color code of the PTR-TOF acetone signal indicates, when the PTR-TOF was relatively stable. **(b)** Scatter plot of PTR-QMS and PTR-TOF acetone for the whole campaign. **(c–g)** Scatter plots for separate stable periods of the PTR-TOF.

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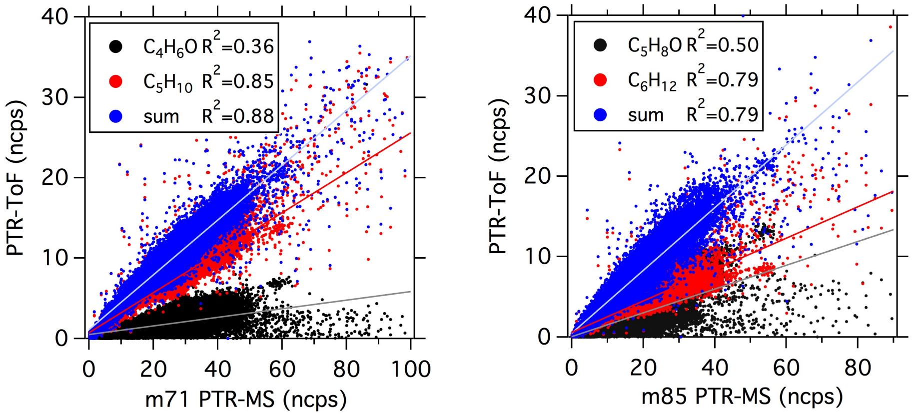

Figure 8. PTR-QMS and PTR-TOF inter-comparison for mass 71 and mass 85 during UB-WOS2013.

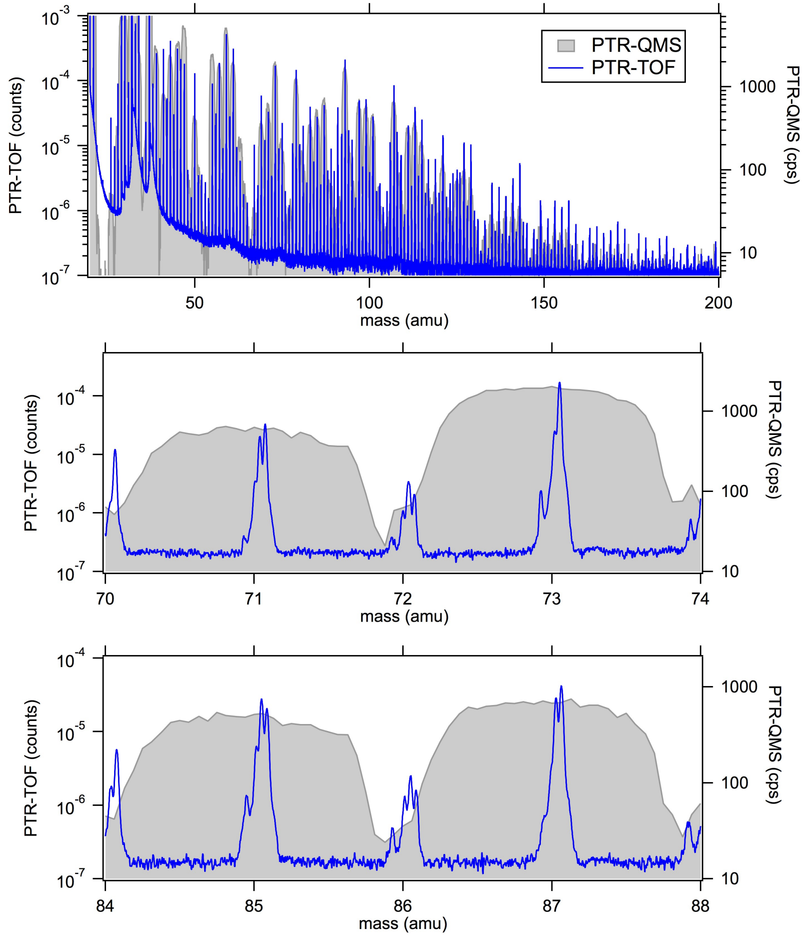

Figure 9. PTR-QMS and PTR-TOF mass scans.

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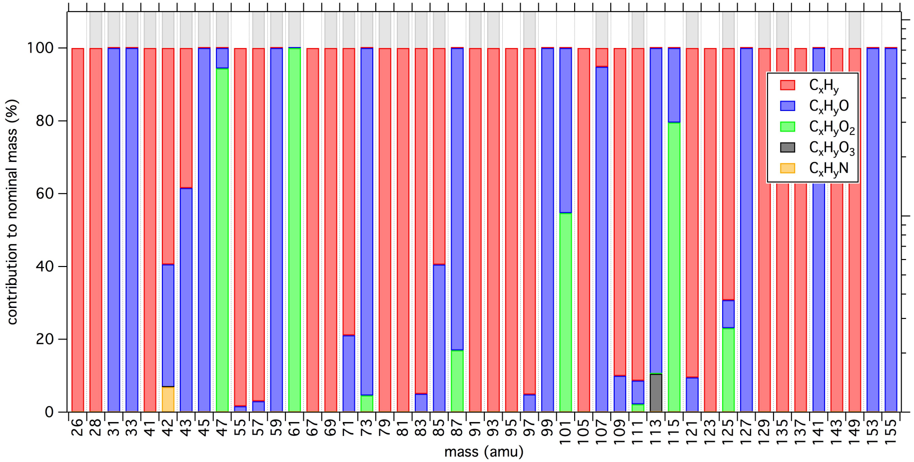

Figure 10. PTR-TOF mass contributions for all the masses that showed ambient signal during UBWOS2013. The grey bars on top indicate the masses that were monitored with the PTR-QMS.

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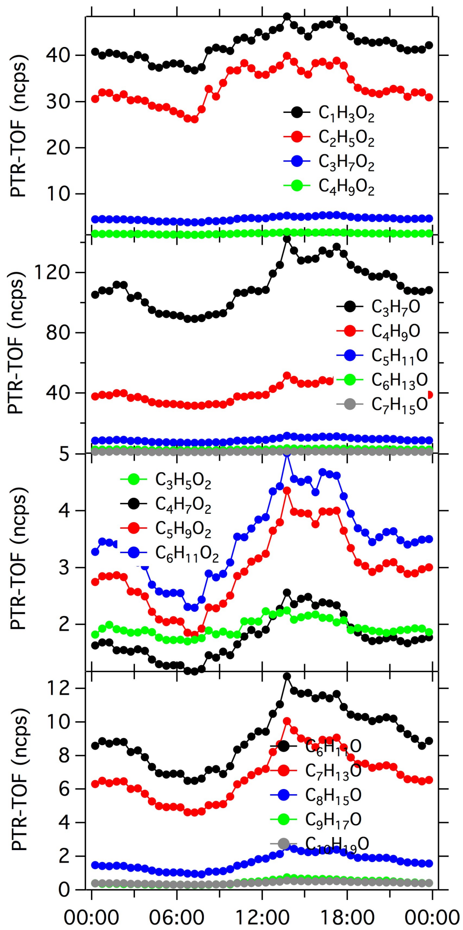

Figure 11. PTR-TOF diurnal variation of selected oxygenated VOCs during UBWOS2013. Many of those compounds cannot be unambiguously identified with PTR-QMS.

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