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Validation of Atmospheric VOC Measurements by Proton-Transfer-Reaction Mass Spectrometry Using a Gas-Chromatographic Preseparation Method

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Proton-transfer-reaction mass spectrometry (PTR-MS) has emerged as a useful tool to study volatile organic compounds (VOCs) in the atmosphere. In PTR-MS, proton-transfer reactions with H_3O^+ ions are used to ionize and measure VOCs in air with a high sensitivity and fast time response. Only the masses of the ionized VOCs and their fragments, if any, are determined, and these product ions are not unique indicators of VOC identities. Here, a combination of gas chromatography and PTR-MS (GC-PTR-MS) is used to validate the measurements by PTR-MS of a number of common atmospheric VOCs. We have analyzed 75 VOCs contained in standard mixtures by GC-PTR-MS, which allowed detected masses to be unambiguously related to a specific compound. The calibration factors for PTR-MS and GC-PTR-MS were compared and showed that the loss of VOCs in the sample acquisition and GC system is small. GC-PTR-MS analyses of 56 air samples from an urban site were used to address the specificity of PTR-MS in complex air masses. It is demonstrated that the ions associated with methanol, acetonitrile, acetaldehyde, acetone, benzene, toluene, and higher aromatic VOCs are free from significant interference. A quantitative intercomparison between PTR-MS and GC-PTR-MS measurements of the aforementioned VOCs was performed and shows that they are accurately measured by PTR-MS.

1. Introduction

Volatile organic compounds (VOCs) in the atmosphere are emitted in large quantities from a variety of different natural and anthropogenic sources (*1*). VOCs are thought to play a significant role in regional air quality by ozone and aerosol formation, in the chemistry of the global troposphere, and possibly in balancing the global carbon cycle (*2*). Proton-

transfer-reaction mass spectrometry (PTR-MS) is a novel method for online measurements of trace amounts of VOCs in air, including many oxygenated VOCs. PTR-MS was developed by Lindinger and co-workers at the University of Innsbruck (*3*) and utilizes proton-transfer reactions of hydronium ions (H_3O^+) to ionize VOCs in combination with mass spectrometric detection of the product ions. PTR-MS is a well-suited tool for studying the atmospheric chemistry of organic compounds, because it allows many important VOCs from natural and man-made origin to be measured along with their oxidation products. Three features that set PTR-MS apart from its alternatives such as GC-MS are (1) the fast time response of only seconds or less, (2) the lack of air sample preconcentration and chromatography, and (3) the capability of performing stand-alone measurements over extended periods of time. Lindinger et al. (*4*) have summarized the recent applications of PTR-MS.

In PTR-MS, only the masses of the product ions are determined, which is a valuable but certainly not a unique indicator of the identity of trace gases. It is clear that different isomers cannot be resolved in this manner. The interpretation of the mass spectra is further complicated by the fragmentation of product ions and the formation of cluster ions, which may lead to additional mass overlap (*5*). By coupling a gas chromatographic (GC) column to a PTR-MS instrument, the contributions from different VOCs to a single mass channel can be separated (*6*, *7*). In this work we have used the combination of GC with PTR-MS (GC-PTR-MS) to validate the measurements by PTR-MS of some commonly observed VOCs in the atmosphere. First, we have analyzed 75 common atmospheric VOCs contained in standard mixtures using GC-PTR-MS. As a result, a database was built up which contains the product ion masses and calibration factors for these VOCs. This database is used to address the specificity of the detection by PTR-MS for some important VOCs such as methanol, acetonitrile, acetaldehyde, acetone, and the aromatics. Second, we have analyzed 56 urban air samples from a site in Boulder, CO, using GC-PTR-MS to study how well these VOCs are resolved by PTR-MS under the most challenging conditions.

Some compounds, such as organic acids, peroxides, and peroxyacetyl nitrates (PANs), may not be detectable by GC-PTR-MS, because they may be lost in the GC column or in one of the sample preparation steps that are necessary to inject VOCs into the column. In direct-inlet PTR-MS, no sample treatment is necessary, and compounds such as the acids, peroxides, and PANs can in principle be detected (*8*, *9*). The absence of interfering peaks in the GC-PTR-MS chromatogram is, therefore, not sufficient evidence that PTR-MS uniquely measures a given VOC. Therefore, we have also intercompared quantitatively the direct-inlet PTR-MS and GC-PTR-MS measurements of methanol, acetonitrile, acetaldehyde, acetone, and the aromatics in urban air. A quantitative agreement between these two measurements definitively excludes the possibility that compounds not detectable by the GC-PTR-MS system used significantly interfere with the direct-inlet PTR-MS measurements.

2. Experimental Set-Up

2.1. PTR-MS. Lindinger et al. have described proton-transfer-reaction mass spectrometry in detail (*3*, *4*), and, therefore, only a brief description is given here. The PTR-MS consists of (1) an ion source to produce H_3O^+ ions, (2) a drift-tube reaction chamber, where the proton-transfer reactions between H_3O^+ and the different trace gases take place, and (3) a quadrupole mass spectrometer to measure the reagent

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and product ions. In the ion source, H_3O^+ ions are produced from pure water vapor in a hollow cathode discharge. A water vapor flow of $4-8$ STP cm^3 min^{-1} (STP = standard temperature of 273.15 K and pressure of 1 atm) is pumped through the source; about 5% of this flow reaches the drift tube, leading to an increased humidity of the sampled air (*10*).

Two different drift tubes were used over the course of this work. Both of them have a length of approximately 10 cm and consist of a set of stainless steel rings to set up a homogeneous electric field in the drift tube. The standard drift tube used in PTR-MS has an inner diameter of 5.0 cm, and the rings are isolated from each other with either Viton or Teflon O-rings. The residence time of air in the drift tube is about 1 s, which is one of the limiting factors to the response time of the system. The second drift tube used in this work has a conic form with an inner diameter between 4 and 2 cm and, therefore, a smaller volume, which reduces the residence time of air to about 0.3 s. The second drift tube consists of a Teflon cylinder, which houses the stainless steel rings; no O-rings are used. The conic form of the drift tube gives an electric field with a small radial component toward the symmetry axis and was designed to reduce the radial diffusion of ions toward the walls and improve signal intensities. Unfortunately the signal intensity with this specific design of a conic drift tube decreased, most probably due to a too large distance between the drift tube and the detection chamber.

The gas inlet of the PTR-MS is described by de Gouw et al. (*7*) and consists of a pressure controlled all-Teflon tubing system. It allows the sample air to be pumped either directly to the reaction region or through a catalytic converter, which efficiently removes the VOCs from the sample to determine the system background. Approximately 15 STP cm^3 min^{-1} of sample air is pumped through the drift tube. The air and a fraction of the ions exit the drift tube through an orifice and enter a small intermediate chamber, which is pumped by a turbo pump (Pfeiffer TPD 022). The intermediate chamber separates the pressure of approximately 2 mbar in the drift tube from the high vacuum in the quadrupole chamber (10^{-5} mbar). In the intermediate chamber, ions are focused onto the opening of the quadrupole mass spectrometer (Balzers QMG422), where the ions are mass selected and counted with an electron multiplier.

The count rate of RH^+ product ions, $i(RH^+)$, can be calculated from

$$i(RH^+) = i(H_3O^+)_0(1 - e^{-k[R]t}) \approx i(H_3O^+)_0 k[R]t \quad (1)$$

where $i(H_3O^+)$ is the count rate of H_3O^+ ions, k is the proton-transfer reaction rate coefficient, $[R]$ is the number density of trace molecules in the reactor, and t is the transit time of H_3O^+ ions. It is assumed that the H_3O^+ and RH^+ ions are detected with the same efficiency. From the equation it can be seen that $i(RH^+)$ is proportional to $[R]$; in other words the signal is linearly proportional to the concentration of a trace gas. The sensitivity of PTR-MS with respect to a certain compound is defined as the number of product ions produced at a trace gas mixing ratio of 1 ppbv and at an H_3O^+ signal of 1 million normalized counts per second (ncps ppbv^{-1}) (*10*). The sensitivity can be calculated from eq 1 and can also be measured with gas standards. The PTR-MS instrument was operated at a drift pressure of 2.4 mbar and an E/N value of 106 Td, which gives a higher conversion efficiency of primary into product ions than usually used in PTR-MS. In the calculation also the transmission of the quadrupole was taken into account. A more detailed description of how the sensitivity is calculated can be found in de Gouw et al. (*7*). As was shown by Hayward et al. (*11*), the instrument noise is described by the square root of the count rate, which can be used to determine the detection limit for each compound.

Warneke et al. (*10*) have determined the detection limit and the dependence on the primary ion signal and the integration time for benzene and toluene. The determination of the detection limit for acetone is given here as a typical example. The mean background signal of acetone is around 20 ncps, and, therefore, the instrument noise is around 4.5 ncps at a 1 s integration time. So the detection limit at S/N of 2 is 9 ncps, which corresponds to 200 pptv. At a 10 s integration time the noise is 1.4 ncps and accordingly the detection limit about 65 pptv. Note here that the detection limit is determined for 10^6 primary ions and that it decreases at higher signals. The background signals are different for each mass and might also vary between measurements. Therefore, the detection limit of PTR-MS can strongly vary and can be different for other PTR-MS systems. Typical detection limits for the measurements presented here are (5 s integration time and 3×10^6 primary ions) as follows: methanol 200 pptv, acetonitrile 35 pptv, acetone 60 pptv, benzene 65 pptv, toluene 50 pptv.

A description of the VOC standards used in this work, their preparation procedure, and accuracy can be found in Goldan et al. (*12*). The uncertainties in the calculated and measured calibration factors are estimated to be 30% and 20%, respectively.

2.2. GC-PTR-MS. Goldan et al. described the GC system in detail (*12*) and only a brief summary is given here. The sample acquisition system is made of Teflon to prevent the loss of reactive and/or hydrophobic compounds. Sample air is dried to prevent freeze-up of the sample loop described below using a 50×0.64 cm o.d. PFA (perfluoro alkoxy) Teflon tube maintained at -80 °C. The mixing ratio of water vapor downstream of the trap is about 1 ppmv (parts-per-million by volume). Apart from water vapor, the trap is known to remove a small fraction of some polar compounds such as the light alcohols. Accounting for such losses is part of the normal calibration procedure. In some of the analyses, an Ascarite trap was used to remove carbon dioxide from the sample flow to minimize the peak widths in the chromatograms. Air samples are acquired by diverting the dried air stream through a 0.43-mm inner diameter open PTFE sample loop with an internal volume of approximately 100 μL. The sample loop is evacuated and then submerged into liquid nitrogen prior to the sample acquisition. As the pressure in the sample loop never exceeds 180 mbar, no liquid oxygen is accumulated despite the use of liquid nitrogen as a cryogen. In this work, samples of 600 cm^3 STP are acquired in about 10 min.

After the acquisition is complete, an automated system injects the sample directly onto the analytical column: the liquid nitrogen is removed, the sample loop is heated to 100 °C in 8 s, and a 6-port valve transfers the VOCs from the loop into the carrier gas stream. The gas chromatographic separation takes place on a 60 m $\times$ 0.25 mm i.d. capillary column with a 1-μm thick 5% phenyl/methylsilicone bonded stationary phase (J&W DB-5) and a 2 STP cm^3 min^{-1} He carrier gas flow. The analytical column was temperature programmed from 40 °C to 200 °C at 6 °C min^{-1}. The effluent from the column was mixed with 60 STP cm^3 min^{-1} of synthetic air and transferred through a 50 cm $\times$ 0.32 cm o.d. PFA Teflon line to the PTR-MS, where the effluent was measured in selected ion mode to detect the separately emerging compounds. The addition of synthetic air is required (1) to have sufficient sample flow in the PTR-MS and (2) to operate the system with mostly air instead of He, which could alter the ion–molecule reaction kinetics significantly. The sensitivity of the GC-PTR-MS combination was defined similarly to the PTR-MS sensitivity as peak area per ppbv (units ncps s ppbv^{-1}) and was measured using diluted gas standards. We estimate the detection limit of the GC-PTR-MS combination to be peaks with heights twice the
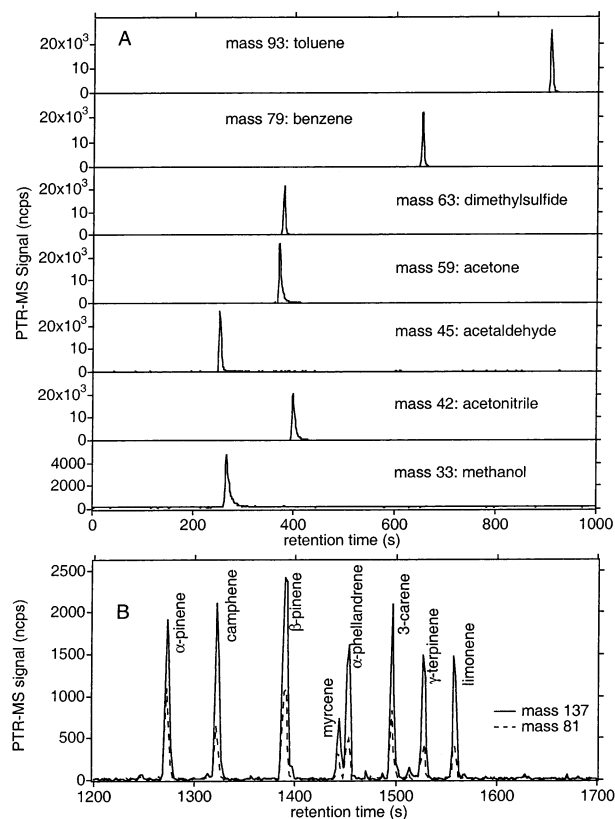
FIGURE 1. (A) GC-PTR-MS chromatogram for a calibration mixture containing methanol, acetonitrile, acetaldehyde, acetone, DMS, benzene, and toluene. (B) GC-PTR-MS chromatogram from a calibration mixture containing eight isomeric monoterpenes.

standard deviation of the background signal. The areas of such peaks can be estimated, and the concentration can be calculated using the measured sensitivity. Typical detection limits for the measurements presented here are as follows: methanol 40 pptv, acetonitrile 5 pptv, acetone 7 pptv, benzene 4 pptv, toluene 3 pptv.

3. Results and Discussion

3.1. Response Time of the PTR-MS. Figure 1 shows some typical examples of GC-PTR-MS chromatograms found for standard gas mixtures. The results shown here were obtained using the standard drift tube with Teflon O-rings. The chromatogram in Figure 1A shows the result of a measurement of a mixture that contained acetonitrile, acetaldehyde, acetone, dimethyl sulfide (DMS), benzene, and toluene at mixing ratios of around 2.5 pbbv and methanol at around 1.25 ppbv. Given in Figure 1A are the measurement results for seven different masses, all showing only one peak corresponding to one of the compounds from the standard gas. Figure 1B, in contrast, shows part of a chromatogram of a gas standard that contains eight different isomeric monoterpenes. These compounds all produce ions at mass 137 and a smaller fragment at mass 81. Obviously, the monoterpenes cannot be measured separately using PTR-MS; at best the sum of the individual concentrations can be determined if the sensitivities for the individual compounds are approximately the same. GC-PTR-MS proves to be a useful method to determine the fragmentation patterns of the individual compounds. With only a PTR-MS analysis of a synthetic sample it can be difficult to distinguish between smaller fragments produced from the analyte of interest and impurities contained in the source material.

Figure 1A shows that the peaks for some compounds, such as methanol and acetone, are wider than others. From

GC-FID (flame ionization detection) measurements done with the same system, it is known that the full width at half-maximum (fwhm) of the peaks is around 5 s and that only the methanol peak has a wider and nonsymmetric shape. It was found that memory effects in the drift tube of the PTR-MS are responsible for the observed broadening of other peaks. The transfer of effluent from the GC column to the PTR-MS could be another factor but was shown to have a negligible influence on the peak shape by coupling the GC column directly with the drift tube. GC-PTR-MS thus proved to be a good way to study the PTR-MS response time, as narrow pulses of many different compounds can be produced.

The observed peak shape for given compounds was found to be dependent on two factors as illustrated by the results in Figure 2, which shows the peak shapes and widths for methyl ethyl ketone (MEK), acetone, and toluene for different drift tube configurations. First, the O-ring material can be important depending on the VOC. The peak shape for ketones in particular and to a lesser extent aldehydes and alcohols is much improved when Teflon O-rings are used as opposed to Viton. In contrast, the peak shape for hydrocarbons such as the aromatics and monoterpenes is hardly affected by the O-ring material. It was found that, although many of the peaks are broadened using Viton O-rings, the peak areas were not significantly affected: evidently these compounds are adsorbed and later released by the Viton but not permanently lost. Second, the pressure in the drift tube determines the residence time of vapors in the instrument, which evidently has an effect on the peak widths. At higher pressures the drift tube is exposed to the sample gas longer and uptake of vapors by the O-rings is more significant. To minimize memory effects, Teflon O-rings were used in most of this work. The small volume Teflon drift tube gave an even better result. This might be due to the shorter residence time of the gas in this drift tube.

3.2. GC-PTR-MS Analyses of Standard Gas Mixtures. A total of 75 VOCs contained in standard gas mixtures were investigated using PTR-MS and GC-PTR-MS. These particular VOCs were chosen because they might be detected in the atmosphere. For each compound we determined the retention time using a standard capillary GC analysis program, the product ion distribution, and the sensitivities both for the PTR-MS and GC-PTR-MS measurements (Table 1). The major product ions were determined by analyzing the standard gases directly with the PTR-MS, and the identification of the product ions was confirmed using GC-PTR-MS analyses, which was especially necessary in more complex standard gas mixtures. The PTR-MS instrument was run in selected-ion mode for the GC-PTR-MS analyses, and, therefore, it cannot be entirely ruled out that some smaller fragments ($<5\%$) were overlooked.

It is clear from Table 1 that the proton-transfer reaction between H_3O^+ ions and VOCs is in many cases nondissociative, so that only the protonated product ion is detected. Notable exceptions are the alcohols, heavier than methanol and, to a lesser extent, the aldehydes, heavier than propanal, which fragment as a result of the proton-transfer by giving up a water molecule. This fragmentation was already reported in earlier studies (13, 14). Among the 75 compounds in Table 1, there are a number of masses that are unique for one specific compound: mass 33 (methanol), mass 41 (propyne), mass 42 (acetonitrile), mass 45 (acetaldehyde), mass 63 (DMS), and mass 105 (styrene). Other masses such as 121 (C9-benzenes) or 137 (monoterpenes) are indicative of a class of similar compounds and could be used as a sum measurement, if the sensitivity for the individual compounds is similar.

Although only a modest number of atmospheric VOCs were detected, the information in Table 1 is a useful aid in the identification of the product ion masses observed by
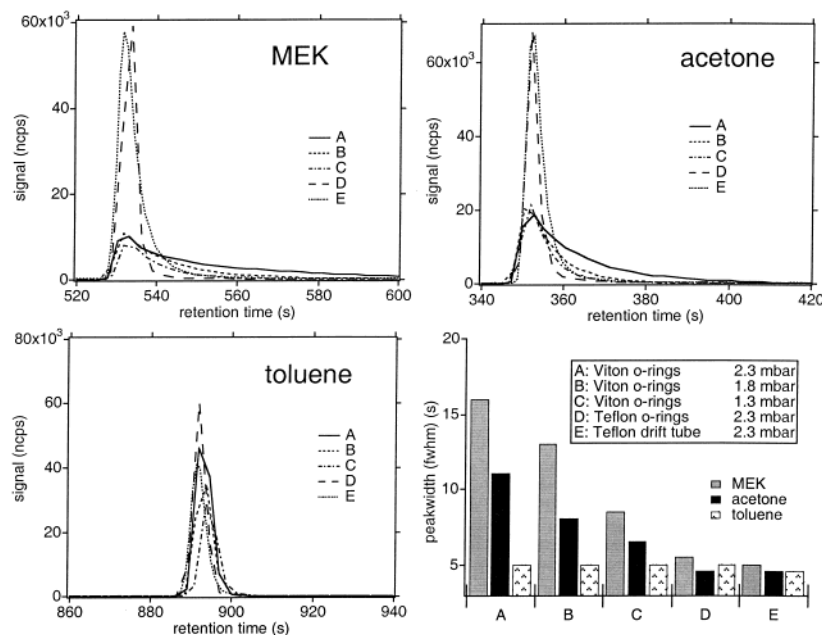
FIGURE 2. Peak shape and width for methyl ethyl ketone (MEK), acetone, and toluene for different drift tube configurations.

PTR-MS. For many compounds, possible interferences can be ruled out based on a general understanding of the air mass composition. For example, toluene, emitted mainly from vehicle exhaust, is detected at 93 amu. The only interferences from Table 1 are chloroacetone, usually not abundant with high mixing ratios in the atmosphere, and α- and β-pinene, emitted by plants, for which mass 93 is only a minor fragment. It can be expected, therefore, that mass 93 can be predominantly attributed to toluene, except in air masses that are recently impacted by biogenic emissions and show highly insignificant anthropogenic pollution. Other examples include the masses 59 and 73, which are produced, respectively, from acetone/propanal and methyl ethyl ketone/butanal. As the aldehydes are much shorter lived in the atmosphere than the ketones, it is therefore expected that mass 59 and 73 signals can be predominantly attributed to the ketones in most air masses (*7*). Notably, all 75 VOCs shown in Table 1 could be resolved by a combination of retention time and PTR-MS product ions.

3.3. Calibration Factors. Included in Table 1 are the calibration factors for the PTR-MS and GC-PTR-MS measurements determined experimentally from the standard mixtures. The linearity of the response was verified for all compounds by diluting the standard gases with varying amounts of synthetic air. Warneke et al. have presented more details on the PTR-MS calibration and characterized the sensitivity vs sample humidity (*10*). The sensitivity of the PTR-MS is also calculated using the proton-transfer rate coefficient and the reaction time from eq 1 and is listed in Table 1 as PTR-MS (*k*). The rate coefficients were taken from Spanel and Smith (*15*) and references therein. Most of the gas standards used contained a large number of different compounds, some of them isomers. Using these mixtures it is not possible to determine the PTR-MS calibration factors for the different isomers. Some compounds listed in Table 1 were contained in more than one gas mixture, in which case the average is given. The calibration factors differed in multiple detections around 20−30%.

Assuming that VOCs are not lost in any of the sample preparation steps of the GC-PTR-MS analysis, the calibration factor for the GC-PTR-MS is directly related to that of the PTR-MS. Figure 3A shows the comparison between the two calibration factors for the VOCs in Table 1. The dashed line in Figure 3A shows the result of a linear fit of a line to the
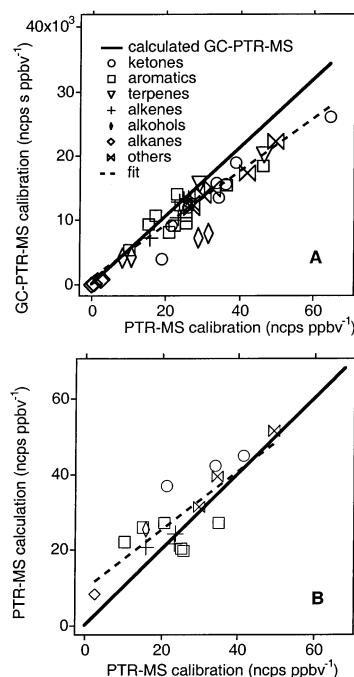

FIGURE 3. (A) Comparison of the PTR-MS and the GC-PTR-MS calibration factors, determined by calibration measurements of standard gas mixtures, for many different VOCs and a fit through the data (dashed line). The solid line is the calculation of the GC-PTR-MS sensitivity using the PTR-MS response under the assumption of no loss in the GC system. (B) Comparison of the measured calibration factors using standard gas mixtures on the *x*-axis and the theoretical calibration factors of the PTR-MS on the *y*-axis calculated using the rate coefficient for the proton transfer and the reaction time in eq 1.

measured calibration factors, whereas the solid line represents the expected relationship assuming no losses in the GC system. It is clear that the two lines have similar slopes, indicating that losses in the GC system are small. From a comparison between the slopes of the two lines, it is estimated that on average 20% of the sample is lost. Three of the compounds are clearly lower than the solid line: methanol, 2-methyl-3-buten-2-ol, and bromoacetone. The polar alco-

TABLE 1. Compounds Used for Calibration, Their Product Ion Distribution (Product Ion Mass with the Relative Abundance in Brackets), the Retention Time in the GC Column, the GC-PTR-MS Sensitivity in ncps·s/ppbv Measured with Standard Gas Mixtures (GC-PTR-MS), the PTR-MS Sensitivity in ncps/ppbv Measured with Standard Gas Mixtures (PTR-MS), the PTR-MS Sensitivity Calculated from the GC-PTR-MS Calibration Using the Linear Fit from Figure 3A (PTR-MS (GC)), and the PTR-MS Sensitivity Calculated Using the Rate Coefficients of the Proton Transfer Reaction k and the Reaction Time in the Drifttube (PTR-MS (k))

compound	major product ions [amu]	retention time [s]	measurement GC-PTR-MS [ncps·s/ppbv]	measurement PTR-MS [ncps/ppbv]	calculation PTR-MS (GC) [ncps/ppbv]	calculation PTR-MS (k) [ncps/ppbv]
acetylene	27 (100)	180		0.1		
propylene	43 (85), 41 (15)	188	7900	16	16.6	20.7
propyne	41 (100)	199	18550		43.1	23.4
cyclopropane	43 (100)	203	4440		9.0	18.7
1,3-butadiene	55 (100)	230	11200	23.4	24.2	21.7
trans-2-butene	57 (100)	232	8290		17.4	21.6
acetaldehyde	45 (100)	238	13900	34.5	30.9	39.2
cis-2-butene	57 (100)	243	9730		20.7	
methanol	33 (100)	251	5130	15.9	10.5	25.4
1,2-butadiene	55 (100)	262	11560		25.1	26.1
3-methyl-1-butene	71 (80), 43 (20)	266	13430		29.7	
1-pentene	71 (85), 43 (15)	299	11250		24.3	23.7
2-methyl-1-butene	71 (80), 43 (20)	307	11360		24.6	
ethanol	47 (50), 29 (50)	317	3459	3	7.0	25.9
trans-2-pentene	71 (80), 43 (20)	319	10400		22.3	
isoprene	69 (100)	330	14000	25.8	31.1	19.8
cis-2-pentene	71 (80), 43 (20)	330	12740		27.9	
2-methyl-2-butene	71 (79), 43 (21)	335	11500		24.9	23.7
propanal	59 (100)	345	15830		35.8	33.3
acetone	59 (90), 43 (10)	353	19725	41.5	47.5	45.0
2-propanol	43 (100)	365	13740		30.4	25
dimethyl sulfide	63 (100)	378	13950	30	31.0	31.2
cyclopentene	69 (100)	393	11220		24.2	
acetonitrile	42 (100)	399	22200	49.5	53.7	51.3
cyclopentane	71 (100)	405	990		2.0	
methyl tertiary butyl ether	89 (0.2), 57 (89.8), 73 (10)	425	15550	32.5	35.1	
methacrolein	71 (100)	465	20440		48.5	
n-butanal	73 (43), 55 (57)	510	24250		60.1	35.1
methyl vinyl ketone	71 (100)	514	15690		35.5	
methylcyclopentane	85 (100)	518	2500		5.0	0
1,3-hexadiene	83 (100)	522	13420		29.6	
methyl furan	83 (100)	523	14665		32.8	
methyl ethyl ketone	73 (100)	530	16540	34.1	37.9	42.4
2-methyl-3-buten-2-ol	87 (19), 69 (71)	568	7980	31.4	23.4	
benzene	79 (100)	634	12500	25.0	27.5	20.5
cyclohexene	83 (100)	643	13970	23.7	31.0	24.3
3-methyl-2-butanone	87 (100)	682	14563		32.5	
methylcyclohexane	99 (14), 57 (86)	737	206	0.7	0.4	0
pentanal	87 (22), 69 (78)	745	16875		38.6	33.3
2-pentanone	87 (100)	750	5710		11.7	36
3-pentanone	87 (100)	767	20487		48.7	36
chloroacetone	95 (25), 93 (75)	781	12084	25.8	26.3	
toluene	93 (100)	887	16850	35.0	39.0	27.2
octane	71 (61), 57 (39)	900	910	2.8	1.8	8.3
hexanone	101 (100)	958	9242	21.3	19.6	37
bromoacetone	139 (50), 137 (50)	987	3990	18.9	4.0	
hexanal	101 (43), 83 (57)	997	12970		28.5	37
ethylbenzene	107 (98), 79 (2)	1122	15645	20.7	36.5	27.1
m-, *p*-xylene	107 (100)	1142	12180	15.2	26.7	26.0
styrene	105 (100)	1209	4720		9.6	
o-xylene	107 (99.7), 105 (0.3)	1210	5405	10.2	11.1	22.2
heptanal	115 (48), 97 (48)	1245	6136		12.7	
iso-propylbenzene	121 (44), 79 (56)	1270	10300		22.1	
α-pinene	137 (62), 93 (7), 81 (31),	1272	15980	29	37.0	
1,2,3-trimethylbenzene	121 (100)	1321	14200		31.6	31.3
n-propylbenzene	121 (91), 79 (9)	1344	11500		24.9	31.3
3-ethyltoluene[a]	121 (100)	1359				
4-ethyltoluene[a]	121 (100)	1363				
decane	99 (45), 85 (19), 71 (15), 57 (21)	1376		2		0
1,3,5-trimethylbenzene	121 (100)	1377	14540		32.5	25.1
β-pinene	137 (67), 93 (7), 81 (26)	1390	20138	46.7	47.6	
2-ethyltoluene	121 (100)	1412	14790		33.1	
3-carene	137 (75), 81 (25)	1454	20756		49.4	
benzaldehyde	107 (100)	1444	3333	7.9	6.7	34.2
1,2,4-trimethylbenzene	121 (100)	1445	11110		24.1	29.6
α-limonene	137 (80), 81 (20)	1453	10940	10.9	23.6	
tert-butylbenzene	135 (50), 79 (50)	1475	1520		3.0	
octanal[a]	129 (68), 111 (32)	1484				
sec-butylbenzene	135 (100)	1501	480		0.9	

compound	major product ions [amu]	retention time [s]	measurement GC-PTR-MS [ncps·s/ppbv]	PTR-MS [ncps/ppbv]	calculation PTR-MS (GC) [ncps/ppbv]	PTR-MS (k) [ncps/ppbv]
1,2,3-trimethylbenzene	121 (100)	1521	14200		31.6	31.3
1,3,-diethylbenzene	135 (100)	1557	9026		19.1	
1,4,-diethylbenzene[a]	135 (100)	1572				
n-butylbenzene[a]	135 (95), 79 (5)	1576				
1,2,-diethylbenzene	135 (100)	1595	12950		28.5	
1,2,4,5-tetramethylbenzene	135 (100)	1719	1400		2.8	

[a] The concentrations for these compounds in the standard gas mixtures were not known.

hols are expected to suffer some loss in the water trap as reported by Goldan et al. (12). Also, the methanol peak was found to be the widest peak in the GC-FID measurements indicating a different interaction between this compound and the stationary phase of the column, which could also explain some loss. Using the GC-PTR-MS calibration factors and the fit shown by the dashed line in Figure 3A, we have estimated the PTR-MS calibration factors, listed as PTR-MS (GC) in Table 1.

In Figure 3B the measured PTR-MS calibration factors (directly determined or, if unavailable, determined from the GC-PTR-MS calibration factor) are compared with the calibration factors calculated from the proton-transfer rate coefficient using eq 1. It is clear that there is a reasonable agreement. The dashed line shows the result of a linear fit to the data, whereas the solid line indicates the 1:1 relationship. The dashed line has a slope of 0.89 and an offset of 6.5. The agreement between the data and the 1:1 relationship demonstrates that calculated calibration factors are reasonably accurate. The offset in the fit and the scatter of the data in Figure 3B, however, shows the importance of calibration measurements for the best possible accuracy.

In Figure 3B and Table 1 it can be seen that for some compounds the calculation and the calibration differ by more than 30%. The reason for this is that some compounds might not be completely stable in the calibration mixtures (e.g.: methanol) or that some of the fragments might have been overlooked. Ethanol, for example, seems to have a fragment on mass 19, which is not detectable because of the H_3O^+ primary ion signal.

Some of the VOCs in Table 1, like acetylene and the alkanes, have a lower proton affinity (PA) than that of water. Proton transfer between H_3O^+ and these compounds is, therefore, endothermic and inefficient. Indeed, Table 1 shows that the sensitivity of PTR-MS for these compounds is very low, i.e., only a few percent of the sensitivity toward oxygenated VOCs. Nevertheless, in air masses with high concentrations of non-methane hydrocarbons, their contribution to the signal at masses such as 43, 57, and 71 amu may be non-negligible.

3.4. GC-PTR-MS Analyses of Urban Air Samples. As a next step, we performed GC-PTR-MS analyses of 56 air samples collected at an urban site in Boulder, CO, to investigate the specificity of PTR-MS measurements of some common VOCs in more complicated air samples. Ambient air was sampled directly in a liquid nitrogen cooled sample loop as described in section 2.2. An example of a GC-PTR-MS analysis is shown in Figure 4. Most of the measured single ion chromatograms are dominated by one peak with secondary peaks on the order a few percent at most. The findings at the different masses are described in more detail below.

All chromatograms at mass 33 amu showed one peak only attributed to methanol. Indeed, no other VOCs have been identified so far that are detected at 33 amu by PTR-MS (see Table 1).
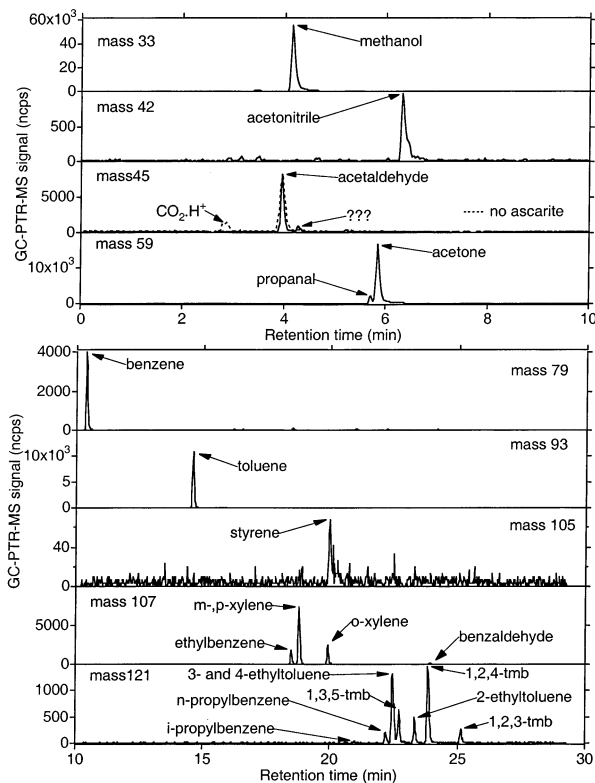

FIGURE 4. A typical GC-PTR-MS chromatogram of ambient air for all measured compounds (tmb stands for trimethylbenzene).

The chromatogram at mass 42 amu shows a major peak due to acetonitrile (CH_3CN) and some very minor peaks, which we attribute, from the retention times, to the light C_3 and C_4 alkanes. These can be ionized by reactions with O_2^+ ions, which are formed in the PTR-MS by backflow of air from the drift tube to the discharge ion source. However, O_2^+ is typically only present at a few percent of the H_3O^+ signal, and the $C_3H_6^+$ fragment at 42 amu is only a minor fragmentation channel, which explains the low sensitivity of PTR-MS for the small alkanes. For all of the samples we studied, acetonitrile was by far the dominant peak in the chromatogram at mass 42 amu even though the alkane levels in many samples were in the ppbv range due to the strong influence of automobile emissions.

The chromatogram at mass 45 amu shows a major peak from acetaldehyde (CH_3CHO). A minor peak at short retention times is attributed to CO_2. For some of the chromatograms, we used an Ascarite filter to remove CO_2 from the airflow upstream of the sampling loop. In these cases, the CO_2 peak was removed from the chromatogram, as shown in Figure 4. Also, the peak width of all peaks is reduced when using Ascarite. This is because the CO_2 in the sample freezes in the sample loop and there are noticeable increases in the time required to transfer the sample into the GC column. Evidently,

CO_2 can be ionized in the PTR-MS by forming HCO_2^+ ions. These ions readily react with water vapor and are, therefore, not stable in the drift tube. Their presence in the mass spectra can only be explained if the ions are formed in the lower-pressure, intermediate chamber between the drift tube and the mass spectrometer. The sensitivity of PTR-MS toward CO_2 is low, and it is not expected to interfere with the detection of acetaldehyde. Also, a catalytic converter is used in PTR-MS to determine the background impurities in the system. Because the catalyst does not remove CO_2, its contribution to the 45 amu signal is, in principle, properly accounted for. A second minor peak was in some cases observed at longer retention times as shown in Figure 4. This peak has, so far, not been identified.

The chromatogram at mass 59 amu shows a large peak attributed to acetone and a smaller one from propanal. It is clear that acetone and propanal cannot be separated using PTR-MS. In most chromatograms the observed propanal peak was only a small fraction of the acetone peak or not visible at all. Propanal has a much shorter atmospheric lifetime (9 h vs 5 weeks) and most likely a smaller atmospheric source than acetone. Propanal is not expected, therefore, to significantly interfere with PTR-MS measurements of acetone in most air masses.

In the remaining chromatograms in Figure 4 all the peaks are attributed to aromatic compounds. The chromatograms recorded at masses 79, 93, and 105 amu all show only one peak attributed to benzene, toluene, and styrene, respectively. The chromatograms at masses 107 and 121 amu show, in all cases, several peaks attributed to the C8- and C9-aromatics, respectively. Ethylbenzene, the three xylene isomers, and benzaldehyde are all detected at mass 107 amu. These VOCs have common sources in car exhaust and have a similar atmospheric reactivity. PTR-MS measurements at 107 amu can, therefore, still be useful as a sum measurement of these compounds. Apart from direct emission, benzaldehyde can be produced from the atmospheric oxidation of toluene. As toluene has a longer atmospheric lifetime than the C8-aromatics, one can expect that the relative contribution of benzaldehyde to the chromatogram at 107 amu is more important in samples that are more photochemically processed. The chromatogram at mass 121 shows a total of seven peaks, which are identified as different propylbenzene, ethyltoluene, and trimethylbenzene isomers. As in the case of the C8-benzene isomers, these aromatic compounds have a common source in car exhaust and have a similar atmospheric lifetime. It is expected, therefore, that a measurement at mass 121 can be regarded as the sum of C9-aromatics isomers.

3.5. Intercomparison between PTR-MS and GC-PTR-MS Measurements. As explained in the Introduction, it is imaginable that atmospheric VOCs such as organic acids, peroxides, PANs, and VOCs with more than one functional group can be detected by PTR-MS but not using GC-PTR-MS because they are lost in the GC system. Therefore, the absence of interfering peaks in the chromatograms in Figure 4 is only partial proof that the direct-inlet PTR-MS measurements of methanol, acetonitrile, acetaldehyde, acetone, and the aromatic hydrocarbons in Figure 4 are free from interference. To resolve this question we have quantitatively compared the direct-inlet PTR-MS measurements of these VOCs with the results from GC-PTR-MS analyses of samples acquired simultaneously.

Figure 5 illustrates how the sampling was done. Over the course of 2 days, urban air was sampled into the PTR-MS, and the mixing ratios of methanol, acetonitrile, acetaldehyde, and acetone, and the aromatic hydrocarbons were measured. Figure 5A shows the measurement results for benzene presented by solid circles. Once an hour, a 10 min integrated sample was acquired from the same inlet into the sample
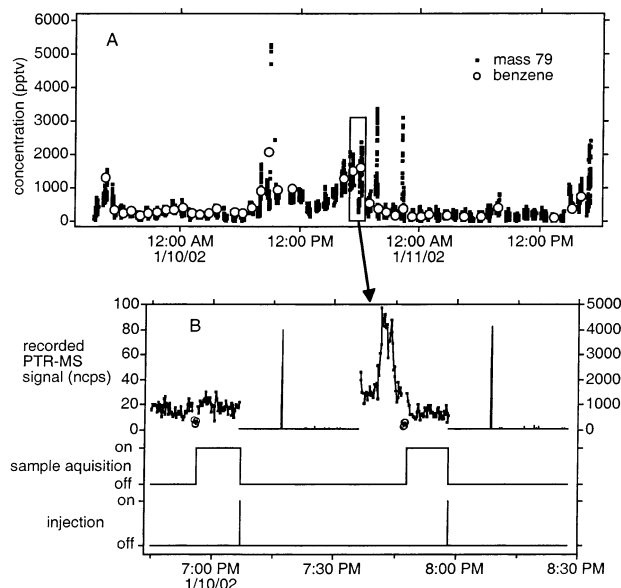

FIGURE 5. (A) Atmospheric mixing ratio of benzene in Boulder, CO, determined with simultaneous PTR-MS and GC-PTR-MS measurements. **(B)** The PTR-MS signal for mass 79 during two measurement cycles. The chromatogram is on the right axis and the online measurement (small squares) including the background determination using the catalytic converter (larger circles) on the left axis in the upper panel. In the lower panel the time is indicated, where the GC sample was acquired and injected.

loop of the GC-PTR-MS system. During this acquisition period, the PTR-MS continued to analyze the ambient air, so that a direct comparison was possible between the online PTR-MS measurement and the result of the GC-PTR-MS analysis. After each 10 min GC acquisition period, the accumulated air sample was injected into the column, and simultaneously the inlet of the PTR-MS was diverted from the ambient air inlet to the output from the GC column, using an automated Teflon valve system. From that moment on, the PTR-MS analyzed the column effluent, and a chromatogram was recorded in approximately 30 min. Afterward this whole cycle started all over again (see Figure 5B). From the area beneath the peaks in each chromatogram, the VOC mixing ratio was determined using the calibration factors given in Table 1. The GC-PTR-MS results for benzene are given by the open circles in Figure 5A, and it is clear that they agree well with the results from the direct-inlet PTR-MS measurements (solid circles). It should be noted that rapid concentration changes cannot detected with GC-PTR-MS, if they occur between the 10 min GC acquisition time, as can be seen in two mass 79 peaks on the second day.

In Figure 6, the results from the GC-PTR-MS analyses are compared with the results from the direct-inlet PTR-MS measurements performed simultaneously. The 2 days covered by the experiment were good for an intercomparison, because relatively low and high atmospheric VOC concentrations were observed. Lower concentrations were found when the prevailing winds came from the sparsely populated mountain area west of Boulder and high concentrations were found during periods when the wind came from the east over areas with intensive cattle farming and the city of Boulder itself. In Figure 6 the correlations are plotted on a log–log scale to also allow the smaller concentrations to be seen. An orthogonal distance regression, taking errors in both coordinates into account, is used to determine the linear correlation coefficients. It can be seen that the correlation between the two measurements is in general good: the square of the linear correlation coefficient, R, ranges from 0.75 for styrene and 0.77 for acetonitrile to 0.99 for toluene and the
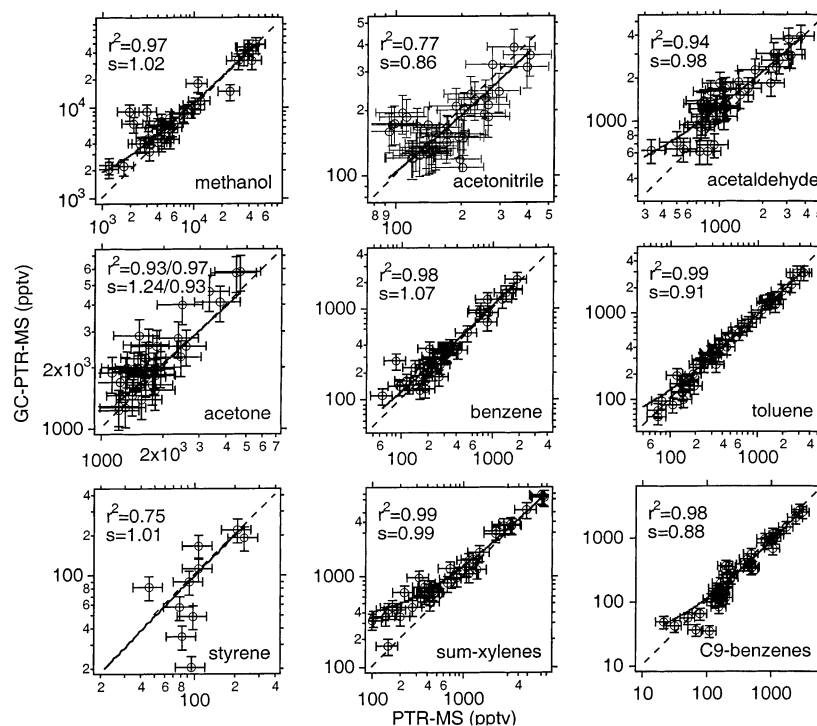
FIGURE 6. Intercomparison of PTR-MS with GC-PTR-MS.

C8-aromatics. The reduced correlation for styrene and acetonitrile is most likely due to the low mixing ratios of these compounds, in which case the low ion count rates in the PTR-MS instrument limit its precision. In general the data agree reasonably well with the 1:1 relationship indicated by the dashed line in each of the plots.

In the case of acetone, the GC-PTR-MS measurement was generally somewhat higher than the direct-inlet PTR-MS measurement: the slope of the fit in Figure 6 is 1.24. It was found that the agreement between the two measurements improved after the Ascarite filter was removed from the GC-PTR-MS sample inlet: the slope of the fit for those points only was 0.91. Evidently, the Ascarite releases some acetone, which can influence the measurements of that compound.

In case of the C8- and C9-aromatics, the surface areas of all the peaks in the chromatograms were added and compared with the direct-inlet PTR-MS measurements at the masses 107 and 121 amu, respectively. For the direct-inlet PTR-MS measurement, the calibration factor used was obtained from the calibration factors for the different isomers in Table 1, weighted with a typical relative abundance of the isomers. The calibration factors for the different isomers can be significantly different, and, therefore, the PTR-MS measurement of the C8- and C9-aromatics does rely on some a priori knowledge of the relative abundance. It should be mentioned, however, that the dependence on the relative abundances is rather weak, and the associated uncertainty in the overall calibration factor is estimated to be less than 5%.

It should be noted here that for most compounds the concentrations stayed well above the detection limit and, therefore, did not reach a level where the agreement between the two methods significantly degraded. Besides styrene, only toluene and the C9-benzenes showed concentrations below 100 ptv, but the agreement is still reasonable for both compounds at this level, so it cannot be determined down to which concentration levels selective measurements of the observed species can be performed.

We can conclude from Figure 6 that the quantitative agreement between the direct-inlet PTR-MS and GC-PTR-MS measurements is satisfactory for methanol, acetonitrile, acetaldehyde, acetone, and the C6−C9 aromatics at con-

centration levels typically observed in urban and semirural areas. Combined with the fact that the chromatograms resulting from the GC-PTR-MS analyses (Figure 4) do not show interfering peaks, this proves that these VOCs can be accurately measured using direct-inlet PTR-MS.

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