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Measuring long chain alkanes in diesel engine exhaust

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Measuring long chain alkanes in diesel engine exhaust by thermal desorption PTR-MS

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Abstract

A method using thermal desorption sampling and analysis by PTR-MS to measure long chain alkanes (C_{12} - C_{18}) and other larger organics associated with diesel engine exhaust emissions is described. Long chain alkanes undergo dissociative proton transfer reactions forming a series of fragment ions with formula C_nH_{2n+1} . The PTR-MS is insensitive to n-alkanes less than C_8 but displays an increasing sensitivity for larger alkanes. Fragment ion distribution and sensitivity is a function of drift conditions. At 80 Td the most abundant ion fragments from C_{10} to C_{16} n-alkanes were m/z 57, 71 and 85. The mass spectrum of gasoline and diesel fuel at 80 Td displayed ion group patterns that can be related to known fuel constituents, such as alkanes, alkylbenzenes and cycloalkanes, and other compound groups that are inferred from molecular weight distributions such as dihydronaphthalenes and naphthenic monoaromatics. It is shown that thermal desorption sampling of gasoline and diesel engine exhausts at 80 Td allows for discrimination against light alkanes and alkenes which are a major constituent of both exhausts, allowing for quantification of higher molecular weight alkanes from the abundance of C_nH_{2n+1} fragment ions. Using this approach, the molar abundance of C_{12} - C_{18} alkanes in diesel engine exhaust was found to be 75 % that of the total C_1 - C_4 alkylbenzene abundance. While the PTR-MS mass spectra of gasoline and diesel exhaust looked similar, the abundance of higher molecular weight compounds relative to that of C_4 -alkylbenzenes was much greater in diesel engine exhaust. The abundance patterns of compounds determined by thermal desorption sampling may allow for emission profiles to be developed to better quantify the relative contributions of diesel and gasoline exhaust emissions of larger organic compounds to urban air concentrations.

1 Introduction

Vehicle emissions are a major source of primary air pollutants that impact human health (HEI, 2010). Photochemical processing of organic compounds from vehicle emissions

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also forms ozone and increases organic particulate matter concentrations through the formation of secondary organic aerosol (SOA) (Meng et al., 1997). While the photochemistry of ozone formation is reasonably well understood, the formation of secondary organic aerosol (SOA) in urban areas is a less understood, more complex process, and it has been noted that some models significantly underestimate organic aerosol concentrations in urban areas compared to observations (de Gouw et al., 2005; Volkamer et al., 2006; Kleinman et al., 2008). This discrepancy may arise from underestimation of SOA formation rates from larger organic compounds emitted from diesel engine vehicles because diesel engine emission inventories for organic compounds are biased to the condensed phase by virtue of how emissions sampling is done (Robinson et al., 2007; Shirvastava et al., 2008). Components of organic particulate matter emitted from diesel exhaust likely partition back to the gas phase as the exhaust plume becomes diluted, creating a pool of compounds that act as precursors for SOA which would not be accounted for in emission inventories and chemical transport models (Robinson et al., 2007). These compounds have been labeled intermediate volatile organic compounds (IVOCs) to distinguish them from more volatile organic compounds (VOCs) associated with spark ignition engine exhaust. IVOCs are classified as organic compounds with a saturation vapor pressure between 1.33×10^{-4} and 1.33×10^{-1} hPa (10^{-4} and 10^{-1} Torr) at 25 °C (Robinson et al., 2007; Presto et al., 2009). For the n-alkanes this vapor pressure range corresponds to dodecane (C₁₂) through to octadecane (C₁₈) and compounds within this vapor pressure range comprise a large fraction of diesel fuel and exhaust (Han et al., 2008; Schauer et al., 1999; Siegl et al., 1999; Gentner et al., 2012). Laboratory tests have shown significant formation of SOA from long chain n-alkanes, branched alkanes, and cyclic alkanes found in diesel engine exhaust (Lim and Ziemann, 2005; Jordan et al., 2008; Samy and Zielinska, 2009; Tkacik et al., 2012). Recasting a portion of the primary organic particulate matter emissions from diesel vehicle exhaust as reactive gas phase material indeed results in significantly more SOA and better agreement with measurements (Shirvastava et al., 2008; Dzepina et al., 2009; Murphy and Pandis, 2009; Hodzic et al., 2010; Pye and Seinfeld,

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2010). However, the actual emission rates and photochemistry of these compounds is not well understood. The general importance of diesel engine emissions to urban air chemistry is gaining significance in the United States as gasoline engine roadway emissions of CO and VOCs are steadily decreasing (Parrish et al., 2009; Schneidemesser et al., 2010) while roadway diesel fuel use has been growing significantly compared to gasoline usage (Dallman and Harley, 2010). Recently Gentner et al. (2012) concluded that diesel engine vehicle emissions were more important than gasoline engine vehicle emissions as a source of SOA for urban regions in California. The opposite conclusion was drawn by Bahreini et al. (2012) for SOA formation in the Los Angeles, CA urban plume. There is a need to better quantify the abundance of organic compounds associated with diesel engine exhausts to clearly understand their role on urban air photochemistry and health.

Due to their low concentration, low volatility, and the very large number of compounds that comprise diesel exhaust, it is difficult to speciate and quantify these species in urban air (Zielinska et al., 1996). While n-alkanes are among the most abundant individual components of diesel fuel (Gentner et al., 2012; Vendeuvre et al., 2005; Isaacman et al., 2012) and exhaust (Schauer et al., 1999), branched and cycloalkanes, and monoaromatic compounds are also very abundant and would be expected to be present in urban air, though rarely reported (Lewis et al., 2000). A method is presented here to improve the quantification of the abundance of IVOC species using a thermal desorption sampler integrated into a proton transfer reaction mass spectrometer (PTR-MS). The sampling approach is to alternate VOC sampling by the PTR-MS with analysis of heavier organics collected on an adsorbent resin and analyzed by thermal desorption. In this way the abundance of IVOC compounds can be compared to the abundance of VOC compounds using the same principle of measurement. The PTR-MS identifies organics by molecular weight (MW) hence isomers are lumped together, simplifying the analysis of complex mixtures and improving detection of larger organic compounds with many isomeric forms. This paper reports the technical details of the

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with minimal disruption of the drift tube pressure. While the IVOC sample is being collected, the IVOC inlet is shut (S1 closed) and the VOC inlet is open (S2 open) to allow for VOC measurement. The VOC sample is dried by passing the sample through a -30°C cold tube and the low abundance of H_2O vapor in both measurement modes allows for operation of the drift tube at 80 Townsends (Td) to reduce fragmentation.

The temperature of the Tenax adsorbent trap was thermostated to control sampling, purging, and desorption temperatures. The desorption temperature as measured inside the trap was 230°C . The volume of air collected on the trap could be varied by controlling the sample collection time. Zero air was collected on the trap in the same manner as a sample and peak responses above the zero air signals were determined. Peak areas were integrated with custom analysis software (Wavemetrics IgorPro). The area under the desorption peak is proportional to the moles of analyte collected on the Tenax trap.

2.2 Dynamic dilution system

Species with low vapor pressures are typically not very stable as compressed gas standards. For calibrating the PTR-MS response to IVOC species a dynamic dilution system was used based on a low flow syringe pump (Harvard Apparatus). The syringe pump was used to deliver low flow rates of a neat liquid into a dilution flow of air or nitrogen. Multiple syringes could be used so that a mixture of 2 or more compounds could be created by injecting the neat liquids. The needle of a $0.5\ \mu\text{L}$ syringe pierced a septum on a stainless steel tee fitting. The liquid was evaporated from the tip of the syringe under the flow of the diluent gas. The manifold tee where the liquids were injected was temperature controlled between 30 and 80°C . Downstream of the manifold the tubing was temperature controlled to 80°C . The PTR-MS sub-sampled from this flow. It was observed that if the infusion rate was too low then evaporative loss from the needle of the syringe was greater than the infusion rate. To determine the accuracy of the dynamic dilution system, test mixtures of toluene, p-xylene, and 1,3,5-trimethylbenzene were made ranging from 1 ppbv to 1 ppmv by varying the infusion rate. These mixtures

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were sampled by the PTR-MS and the measured ion signal converted into a mixing ratio using calibrated response factors determined from a multicomponent VOC compressed gas standard containing these components (Scott-Marrin, accuracy $\pm 5\%$). The measured molar mixing ratio was compared to that calculated from the infusion rate and molar flow of the diluent air. Measured mixing ratios agreed within 15% or better for mixing ratios > 10 ppbv, giving confidence that the system could reproducibly deliver reasonably accurate test mixtures for determining n-alkane sensitivities. For the n-alkane sensitivity tests, the injections were typically performed at $0.5 \mu\text{L h}^{-1}$ and diluted by 20 slpm of dry nitrogen resulting in a mixing ratio of approximately 40 ppbv for dodecane. The lowest mixing ratios achievable were dependent on the compounds vapor pressure; lower vapor pressures allowed for lower syringe pump infusion rates. Gasoline and diesel fuel were also evaporated using this system to make test mixtures of the fuels for sampling by the PTR-MS.

2.3 Engine exhaust sampling

Diesel and gasoline engine exhaust were sampled from inhalation exposure chambers at the Lovelace Respiratory Research Institute in Albuquerque, NM. The diesel engine was a 5.5 kW Yanmar diesel electric generator and the gasoline engine a 1996 model General Motors 4.3-L V-6 mounted to a dynamometer. The emissions from these engines and facility description are described in more detail in McDonald et al. (2004, 2007, 2011). The facility can blend diesel and gasoline engine exhaust in different proportions and thus provided an excellent opportunity to test the IVOC thermal desorption sampler. Over a series of tests, the engine load was varied and the exhaust diluted to different extents with clean, dry air. A portion of the diluted exhaust flow was diverted through a 1.5 m^3 exposure chamber from which the PTR-MS sampled. The inlet for the PTR-MS consisted of a heat traced electropolished steel tubing (UHP Cardinal) protected by a $1.0 \mu\text{m}$ Teflon particle filter that was replaced after each experiment.

3 Results

3.1 n-alkane response

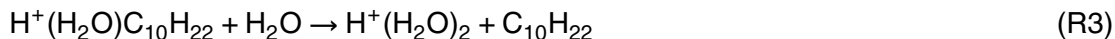
The PTR-MS instrument measures organics (R) via a proton transfer reaction with H_3O^+ producing a mass spectrum of an air sample that is ideally interpreted as an



However, many dissociative proton transfer reactions are known to occur complicating this interpretation. Reaction (R1) will be exothermic if the species R has a higher proton affinity (PA) than H_2O and exothermic proton transfer reactions occur near their collision rate limit (Bohme et al., 1979), making the PTR-MS sensitive to a wide variety of organic compounds. The proton affinity of H_2O is $166.5 \pm 2 \text{ kcal mol}^{-1}$ at 298 K (Lias et al., 1984) and the proton affinities for larger alkanes approach this value (Hunter and East, 2002). Spanel and Smith (1998) measured H_3O^+ reactions with alkanes using a selected ion flow tube. It was found that larger n-alkanes can form an adduct with the hydronium ion:



The study also observed a ligand switching reaction that occurs in the presence of water vapor that catalyzed the formation of water clusters:



In our studies with the PTR-MS instrument, adducts were observed during measurement of the n-alkanes at 80 Td but at very low abundance. There was also an increase in the m/z 37 ion abundance due to the water cluster $\text{H}^+(\text{H}_2\text{O})_2$, perhaps a result of Reaction (R3). In the PTR-MS there are also reactions that occur with O_2^+ ions created in the ion source that confound the interpretation of the PTR-MS mass spectrum

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as a simple $M + 1$ mass spectrum. O_2^+ reacts rapidly with alkanes causing extensive fragmentation (Spanel and Smith, 1998). To minimize the influence of O_2^+ , dry N_2 was used as the diluent gas in the dynamic dilution system and in thermal desorption from the adsorbent trap. Typically O_2^+ ion count rates were less than 0.1 % of the H_3O^+ count rate.

The PTR-MS response to n-alkanes was determined for 120 and 80 Td drift tube conditions by preparing known mixtures with the dynamic dilution system. The n-alkanes undergo dissociative proton transfer reactions in the PTR-MS (Jobson et al., 2005) producing fragmentation patterns similar to electron impact ionization. Figure 2 shows the fragmentation pattern for dodecane as an example of the typical pattern observed for n-alkanes. The C_8 - C_{16} n-alkanes produce a significant response and their spectra displayed similar features, yielding a pattern of fragment ions with the formula C_nH_{2n+1} for $n \geq 3$. For heptane and smaller n-alkanes there was little response and these species appear to be unreactive with H_3O^+ at these drift tube conditions. The n-alkane fragmentation pattern was a function of the Townsend number. At lower Townsend numbers there was less fragmentation into lighter ions. At 80 Td there was essentially no fragmentation to m/z 41 and 43 while at 120 Td these were two of the most abundant fragment ions.

The benefit of operating at lower Td is that the n-alkane ion signal occurs at larger ion masses allowing for better distinction between IVOC and VOC species. The ions m/z 41, 43 and 57 are common fragment ions from a wide range of species and are typically the most abundant ion signals in PTR-MS analysis of urban air. At 80 Td, approximately 70 % of the ion signal occurs at m/z 57, 71, and 85 for the C_9 to C_{16} n-alkanes. There would be significant interference from VOC compounds found in urban air for m/z 57 (from butenes) and m/z 71 (from pentenes, methacroliein, methyl vinyl ketone). To use these ions to monitor for IVOC alkanes will require a discrimination strategy to prevent interfering VOCs from being measured during thermal desorption. Our approach, described in more detail below, is to purge the Tenax trap at an elevated temperature after sample collection to remove these VOCs, then desorb the trap

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at higher temperatures to measure the heavier organics that remain. The ions m/z 85, 99, 113, and 127 may be more unique tracers of long chain alkane abundance in the atmosphere. Preliminary tests have shown that branched and iso-alkanes display similar fragmentation patterns and sensitivity as n-alkanes except there is a more significant M-1 peak for iso-alkanes, typically on the order of 10% of the total fragment ion signal.

The PTR-MS instrument's sensitivity to alkanes was determined by preparing known n-alkane and toluene mixtures using the dynamic dilution system. The sum of the normalized response at all ions was divided by the mixing ratio to get sensitivity in units of Hz ppbv^{-1} per MHz H_3O^+ (ncps). The alkane species of interest was co-injected with toluene to ensure the syringe pump was operating correctly, since an expected signal for toluene can be calculated from a known response to external gas phase standards. The n-alkane sensitivity is shown in Fig. 3. The response curve displays a dependence on the drift conditions. The PTR-MS is insensitive to alkanes with carbon numbers $< C_8$. The increase in sensitivity for alkanes $> C_7$ is consistent with the rate constant measurements of Arnold et al. (1998) which are also shown in the figure. Quantum mechanical calculations of alkane C-C bond proton affinities reveal that the more central bonds of the molecule have the largest proton affinities and for larger alkanes approach that of water at $166.5 \text{ kcal mol}^{-1} e$ (Hunter and East, 2002). The H_3O^+ + n-alkane reaction appears to be endothermic and explains why the n-alkane sensitivity is significantly lower than that of toluene. Using the summed ion signal for all $\text{C}_n\text{H}_{2n+1}$ ($n \geq 3$) fragment ions, the normalized sensitivity for dodecane at 120 Td was 2.4 ncps compared to 9 ncps for toluene. The PA of n-alkanes appears to plateau for larger alkanes and the 120 Td sensitivity curve suggests a sensitivity plateau as well for n-alkanes $> C_{14}$. At the 80 Td condition normalized sensitivities should increase due to the 150% increase in reaction time. The expected sensitivity increase was observed for toluene but not the n-alkanes. The similarity in sensitivity for C_8 - C_{11} n-alkanes at the two drift conditions may be due to the decrease in reaction rate at lower ion energies at 80 Td offsetting the increase in reaction time. At 120 Td the n-alkane sensitivity is primarily determined by the ion signal at m/z 41, 43 and 57 while at 80 Td the sensitivity is determined by

broader range of heavier ion masses, as illustrated in Fig. 2, with most of the ion signal (> 50 %) at m/z 57, 71, 85.

3.2 Diesel and gasoline fuel mass spectra

To better understand what constituents of vehicle fuels and exhausts the PTR-MS may respond to, gasoline and diesel fuel #2 used in the engine exhaust studies were measured by evaporating $5 \mu\text{L h}^{-1}$ of whole fuel into 20 slpm of dry nitrogen in the dynamic dilution system at 60°C . The PTR-MS sampled directly from this flow, by-passing the thermal desorption sampler and water trap. Gasoline is mostly comprised of hydrocarbons in the C_4 to C_{10} range compared to the C_8 to C_{25} range for diesel fuel (Han et al., 2008; Schauer et al., 1999; Lough et al., 2005; Gentner et al., 2012; Wang et al., 2005). Distinct ion groups were observed in both fuel types that can be related to different organic compound classes. Exhausts are a more complex mixture that will contain these fuel species plus oxygenated species such as aldehydes and furans, and other hydrocarbons such as alkenes, acetylene, and pyrogenic compounds (Schauer et al., 1999, 2002). Both fuels were sampled at 80 and 120 Td drift conditions and the resulting mass spectra are shown in Fig. 4. The gasoline contained 10 % ethanol by volume and ethanol appears at m/z 47 and an ethanol water cluster ion at m/z 65 in the gasoline mass spectra. The relative intensity of the peaks gives a qualitative indication of the relative molar abundance of the different constituents; the ion intensities were not corrected for differences in ion transmission efficiency and compound sensitivity. The PTR-MS mass spectrum for gasoline ends around m/z 180 while significant ion signal in the diesel fuel mass spectrum was still observed to m/z 240. There are more pronounced differences in the 120 and 80 Td mass spectra of diesel fuel than gasoline, with significant shifts to higher m/z ions for the $\text{C}_n\text{H}_{2n+1}$ and $\text{C}_n\text{H}_{2n-1}$ ion groups in diesel fuel, suggesting significant fragmentation of hydrocarbons.

Comprehensive analysis of diesel fuel has shown that approximately 70 % by mass is composed of saturated compounds, of which 30 % are n-alkanes and branched alkanes, and 21 % cycloalkanes, and 18 % of the fuel by mass is monoaromatic com-

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pounds, with no contribution from alkenes (Venduevre et al., 2005; Gentner et al., 2012). The series of ions in diesel fuel corresponding to masses C_nH_{2n+1} for $n \geq 3$, as listed in Table 1, are attributed to alkanes and these masses are shown as black bars in Fig. 4. Significant differences in the relative ion intensity for the alkane fragment ions are observed between the 120 and 80 Td conditions. Alkanes are also a significant component of gasoline but the PTR-MS is relatively insensitive to alkanes with less than 8 carbons. For summer blends of gasoline, alkanes with 8 or more carbon atoms comprise about 30 % of the total alkane composition on a molar basis (Lough et al., 2005; Gentner et al., 2012) and these compounds would produce a signal at the C_nH_{2n+1} ion masses. Contributions to signal at m/z 57, 71, and 85 could also be due to C_4 – C_6 alkenes. These species comprise a much smaller molar fraction of whole gasoline, on the order of 4 % (Lough et al., 2005; Gentner et al., 2012) but the PTR-MS is much more sensitive to these species than alkanes. Given the negligible response of the PTR-MS to C_4 – C_7 alkenes, and the low molar abundance of C_3 – C_6 alkenes and alkanes $> C_8$ in gasoline, the gasoline PTR-MS mass spectrum of gasoline is thus dominated by the alkylbenzene constituents, in particular toluene (m/z 93) and the xylene isomers (m/z 107).

The prominent group of ions with mass formula C_nH_{2n-1} ($n \geq n$) was attributed to alkyl substituted cycloalkanes as listed in Table 1 and indicated as green bars in Fig. 4. Gentner et al. (2012) have reported the presence of C_7 to C_{25} cycloalkane compounds in diesel fuel, with mass fractional contribution by carbon number ranging from 0.15 % for C_7 compounds to 2.2 % for C_{10} , C_{11} , and C_{12} compounds, diminishing to 1.1 % for C_{18} compounds, the apparent upper limit of our experimentally observable range. As noted in Table 1, this ion group comprised 17.7 % of the total ion signal for diesel fuel at 80 Td and 5.4 % for gasoline, with ions m/z 69, 83, 97, 111 and 125 the most abundant. Laboratory tests confirmed that cycloalkanes yield these ions at 80 and 120 Td drift tube conditions. At 80 Td these compounds yielded an M-1 ion as the major fragment ion. For example, methylcyclohexane and 1,2-dimethylcyclohexane yielded M-1 ions at m/z 97 and m/z 111 respectively with greater than 85 % total ion abundance.

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Cyclohexane also yielded a strong M-1 ion signal at m/z 83, but a more intense $M + 1$ ion at m/z 85. The compound 1,3,5-trimethylcyclohexane produces an M-1 ion at 80 Td but fragments at 120 Td to yield m/z 69 as the most abundant ion. Cyclohexane has a proton affinity less than that of H_2O and our tests suggest the PTR-MS is more sensitive to alkyl substituted cyclohexanes, implying they have greater proton affinity. For diesel fuel at 80 Td, the ion signal for this group was more intense than the corresponding alkane ion at a similar mass. The ion intensity for this group was relatively uniform from m/z 97 to m/z 153, and then decreased rapidly to the heaviest ion measured at m/z 237, corresponding to a C_{17} compound.

The alkylbenzene compounds identified as blue bars in Fig. 4 and listed in Table 1 are also prominent in diesel fuel mass spectra, comprising 20 % of the total ion signal at 80 Td. Ion signal for these species ranges from m/z 79 (benzene) to m/z 233 indicating a C_{18} alkylbenzene. Most of the ion intensity was at m/z 121 and 135 corresponding to alkylbenzene compounds with 9 and 10 carbon atoms respectively; these are identified as C_3 -alkylbenzenes and C_4 -alkylbenzenes to indicate the number of carbon atoms in the alkyl groups attached to the benzene ring. The Gentner et al. (2012) analysis of diesel fuel reports the most abundant aromatics by carbon number are C_{10} compounds at 2.4 % by weight carbon, decreasing gradually to 0.8 % abundance for C_{18} compounds, the limit of our observable range, down to 0.2 % for C_{25} compounds. Examination of the alkylbenzene ion abundance relative to m/z 149 showed that fragmentation of higher molecular weight aromatics was occurring as evidenced by much larger abundance of m/z 79, 93, and 107 ions at 120 Td than at 80 Td. At 120 Td m/z 79 was a factor of 7 more abundant, m/z 93 was 3 times more abundant, and m/z 107 was 1.4 times more abundant. The relative abundance of m/z 135 and ions larger than m/z 149 were very similar for the two drift conditions, within 5 %, with the exception of m/z 233 which was a factor of 2 higher at 80 Td. Tests performed on fragmentation patterns for a suite of methyl, ethyl, n-propyl, i-propyl, and n-pentyl alkyl substituted benzene compounds have shown that few compounds fragment at the 80 Td drift field energies, exceptions being compounds with isopropyl groups. For example, 10 % of p-cymene

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fragments to produce at ion at m/z 93. At 120 Td a greater degree of fragmentation was observed and m/z 79 and m/z 93 were common fragment ions. The occurrence of an ion at m/z 79 (benzene) in diesel fuel may be entirely due to fragmentation of larger alkylbenzene compounds. It was also observed that some aromatic compounds (i.e. n-pentylbenzene, 1,3-diisopropylbenzene, 2,2-dimethyl-1-propylbenzene) yielded significant fragmentation to m/z 43. Operating the PTR-MS at lower Td values will provide a higher fidelity measure of alkylbenzene mass distribution in diesel fuel given the prevalence of higher molecular weight alkylbenzene compounds. The alkylbenzene compounds are isobaric with the tricycloalkanes compounds identified as being present in diesel fuel by Gentner et al. (2012) though ranging from a factor of 2 less abundant for C_{18} to a factor of 20 less abundant for C_{10} .

An ion group with a formula $C_{n+9}H_{2n+11}$ ($n \geq 0$) makes up 14 % of total diesel fuel ion signal at 80 Td but less than 2 % of the gasoline mass spectra as shown as red bars in Fig. 4 and listed in Table 1. If the ion signal pattern can be interpreted as an $M + 1$ mass spectrum then this group could be a series of alkyl substituted indane (C_9H_{10}) and 1,2,3,4-tetrahydronaphthalene (tetralin, $C_{10}H_{12}$) compounds. Laboratory tests demonstrated that at 80 Td indane and tetralin yield $M + 1$ ions at m/z 119 and 133 respectively, with no fragmentation. Such compounds are comprised of a benzene ring fused to a cycloalkane structure. The presence of such naphthenic monoaromatics has been reported in diesel fuel (Vendeuvre et al., 2005, 2007). Ions at m/z 91 and 105 may also belong to this series, possessing a 3 or 4 member alkyl ring structure respectively. The ring structure is isobaric with an alkene functional group but there are few reports of alkenes being prominent in diesel fuel.

About 8 % of the diesel fuel mass spectrum is comprised of an ion group with mass formula $C_{n+5}H_{2n+7}$ ($n \geq 0$). This group contributes less than 1 % of the ion signal in the gasoline mass spectrum. These compounds may be bicycloalkanes (C_8H_{14} , C_9H_{16} , $C_{10}H_{18}$) and related alkyl substituted compounds. Bicycloalkanes with 10 or more carbon atoms have been identified as a significant constituent in diesel fuel (Gentner et al., 2012). Laboratory experiments at 80 Td demonstrated that decahydronaphtha-

lene ($C_{10}H_{18}$) yields an $M-1$ ion at m/z 137 with no fragmentation. At 120 Td there was significant fragmentation to m/z 67, 81 and 95 accounting for 1, 50, and 11 % of the signal respectively with 38 % of the response at m/z 137. Naphthalene and alkylsubstituted naphthalenes with mass formula $C_{n+10}H_{2n+9}$ ($n \geq 0$) and dihydronaphthalenes, $C_{n+10}H_{2n+11}$, both yield $M+1$ ions at 80 Td as demonstrated in laboratory tests. These compounds comprise a small fraction of the fuel ion signal. Their masses and total group ion signal abundance are listed in Table 1.

The relative contributions from each of these compound classes can be illustrated in Fig. 5 which shows the PTR-MS mass spectrum for diesel fuel measured at 80 Td over the C_{12} to C_{14} carbon number range. Sensitivities for unsaturated compounds will likely be similar and thus the relative ion abundance reflects relative molar composition for a particular carbon number. The figure shows a similar pattern of group abundance for the different carbon number ranges, arranged by mass from the least saturated compounds (naphthalenes) to the most saturated compounds (alkanes). The identifications are tentative and need to be verified by more specific analytical techniques, but suggest that soft ionization by H_3O^+ may be useful for characterizing the compound group composition of diesel fuel. In this analysis the naphthenic monoaromatics, possibly alkylsubstituted tetralin compounds, are more abundant than the equivalent carbon number alkylbenzenes in the C_{12} to C_{14} range.

3.3 Diesel and gasoline exhaust mass spectra

Representative mass spectra of diesel and gasoline engine exhaust are shown in Fig. 6. Ions are grouped and color coded by compound classes as was done for the fuel. The data were collected at 80 Td in VOC mode using a -30°C dehumidifier to remove water vapor and to some extent, depending on exhaust concentrations, lower volatility organics. Shown are ions measured in selective ion measuring mode of the PTR-MS and include major ions from the compound groups identified in diesel fuel plus ions attributed to oxygenated species known to be emitted in exhaust such as formaldehyde (m/z 31), acetaldehyde (m/z 45) and acetone + propanal (m/z 59). The diesel

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engine was operated under a low engine load, the gasoline engine was under a typical engine load and both exhausts were diluted with similar flows of dry air. For a similar level of dilution, gasoline exhaust displayed much higher concentrations of VOCs. For both engine types the major organic compounds in exhaust have been reported to be aldehydes, light alkenes and alkanes, and alkybenzenes (Hoekman, 1992; Schauer et al., 1999, 2002; Schmitz et al., 2000; Smith et al., 2002; Jobson et al., 2005). The exhaust composition is thus significantly different than the fuel composition, particularly for diesel exhaust, where a large fraction of the mass emission rate is comprised of low molecular weight compounds not present in the fuel. This compositional change is reflected in the PTR-MS mass spectrum with prominent peaks associated with aldehydes and ketones (m/z 31, 45, 59, 73), light alkenes (m/z 43, 57, 71), and alkylbenzenes (m/z 79, 93, 107, 121, 135). The PTR-MS mass spectrums of the diesel and gasoline engine exhaust thus appear quite similar. Table 2 compares the percentage of ion signal found for selected ions within the different compound groups for the fuel and exhaust. For PTR-MS measurements of long chain alkanes and other IVOC species associated with engine exhaust in urban air, it will be necessary to both discriminate against the very abundant light alkenes which produce interfering ions for the measurement of IVOC alkanes and to preconcentrate the air sample to improve detection of the much lower abundant IVOC range species. For example, the ion signal for IVOC alkylbenzenes with carbon numbers of 10 or greater is about 2 orders of magnitude less than xylenes at m/z 107. This need motivates thermal desorption sampling that can both discriminate against volatile alkenes and preconcentrate IVOC compounds.

3.4 Thermal desorption sampling

Figure 7 shows an example of the thermal desorption peak from the trap as described in Sect. 2.1. Shown is a time series of the 1,3,5-trimethylbenzene ion signal from a calibration gas test mixture. The test mixture was measured in VOC mode, passing through the -30°C water trap, while a 257 cc air sample was simultaneously being collected on the Tenax trap over a sampling period of 6 min, as indicated by the shaded area under

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the trap flow rate in the figure. After sample collection, the trap was purged with dry N₂ for 4.5 min to remove traces of air, then the gas sampling valve was rotated to connect the trap to the drift tube. After 30 s of settling time the trap was heated to 230 °C in 65 s under a 25 sccm carrier N₂ flow. To demonstrate the trapping efficiency and equivalent sensitivity for the 2 modes, the area under the desorption peak (A2) can be shown to be equal to the area under the VOC trace (A1) accounting for the differences in air volume sampled. The product of IVOC sample collection time in seconds multiplied by the *m/z* 121 normalized count rates in VOC mode yields area A1 of 50 000 counts. The air flow through the drift tube is 25 sccm corresponding to a 150 cm³ volume of air sampled into the drift over the IVOC sample collection time. The VOC air sample volume is thus 58 % the size of the IVOC air sample volume. Multiplying the IVOC area A2 of 88 420 counts by the ratio of sample volumes yields an equivalent area of 51 600 counts, only 3 % larger than area A1. The peak area A2 is determined from the start of the desorption heating time to when the ion signal reaches the background count rate. As in VOC mode, humid zero air is collected on the Tenax trap in the same manner as an air sample and desorbed to determine background area counts.

In VOC mode the molar mixing ratios for some compound X_j in nmol mol⁻¹ (ppbv) are determined from the measured ion count rates by:

$$\text{VOC} : X_j = \frac{S_{(i)} - \text{bkg}_{(i)}}{\text{ncps}_{(i)} \times \text{MHzH}_3\text{O}^+} \quad (1)$$

where S and bkg are the measured and background ion count rates (Hz), and ncps is the normalized sensitivity for the compound in units of Hz ppbv⁻¹ per MHz H₃O⁺. For IVOC mode a similar relationship holds to convert peak areas to molar mixing ratios but this must account for the air volume sampled.

$$\text{IVOC} : X_j = \left[\frac{\text{AC}_{(i)} - \text{bkgAC}_{(i)}}{\text{nAC}_{(i)} \times \text{MHzH}_3\text{O}^+} \right] / \text{moles air sample} \quad (2)$$

where AC represents the area under the sample ion peak, bkgAC the background area, and nAC is the sensitivity of the PTR-MS to the compound i in units of area counts per nmol. Since the drift tube kinetics don't change between VOC and IVOC modes, the intrinsic sensitivities are the same, and nAC sensitivities can be calculated from VOC sensitivities. For example, a nominal VOC sensitivity of 10 Hzppbv^{-1} per MHz H_3O^+ and a 25 sccm air sample flow into the drift tube yields an 80 Td nAC sensitivity value of 5.4×10^5 area counts n mol^{-1} per MHz H_3O^+ at 80 Td. For n-dodecane the sensitivity shown in Fig. 3 of 1.7 Hzppbv^{-1} per MHz H_3O^+ yields a nAC sensitivity of 9.14×10^4 area counts n mol^{-1} per MHz H_3O^+ , or 538 area counts ng^{-1} per MHz H_3O^+ .

3.5 VOC discrimination

By purging the Tenax trap before desorption, the light alkenes and other VOCs can be removed to make identification of IVOC alkanes and other species tractable. Several desorption purge temperatures were tested to find the optimum temperature for VOC discrimination without significant loss of IVOC alkane species. A 150°C purge temperature was chosen as this provided effective removal of interfering VOC compounds while limiting losses of C_{12} and larger alkanes. Figure 8 shows an example of the effectiveness of the trap purge for several species. Methacrolein, benzene, toluene, p-xylene, 1,2,4-trimethylbenzene, 1,2,3,5-tetramethylbenzene, decane, dodecane, and pentadecane were sampled onto the trap and subjected to two purge temperatures of 30°C and 150°C . Given the breakthrough volumes for these compounds, no loss would be expected for the 30°C purge and this temperature was used as a reference to compare to other desorption temperatures. Methacrolein, benzene and toluene were removed by the 150°C purge flow with 98 ± 7 , 99 ± 5 and $97 \pm 5\%$ reduction in their respective peak areas. The purge flow at 150°C effectively removed alkanes and alkenes $< \text{C}_9$ and n-aldehydes $< \text{C}_7$. Decane, dodecane, and pentadecane peak areas were reduced by 84, 52, and 7.5% respectively. The noticeable offset of the pentadecane desorption peaks in Fig. 8 is due to the migration of pentadecane further along the

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Tenax adsorbent bed with the 150 °C purge flow. The IVOC thermal desorption sampler thus measures alkanes from the C_{12} - C_{18} range with the upper range limited by the ability to effectively transfer low volatility compounds through PTR-MS sample lines and valves.

Given the complexity of alkane composition in diesel fuel and exhaust, whole diesel fuel might be a better standard to calibrate PTR-MS sensitivity to the alkane species of interest. Given the mass composition of C_8 - C_{18} alkanes in diesel fuel reported by Gentner et al. (2012), a sensitivity of 2.6 Hz ppbv⁻¹ per MHz H_3O^+ was determined from the sum of the C_nH_{2n+1} ions observed from diesel fuel measured by the IVOC sampler under the 150 °C purge condition. This value accounts for losses of alkanes in the purge and represents the average PTR-MS sensitivity to these compounds at 80 Td. This value is larger than n-alkane sensitivities shown in Fig. 3, and requires further investigation of branched alkane sensitivities and total molar abundance of alkanes in diesel fuel to reconcile this difference. Our method sensitivity is 1.5 Hz ppbv⁻¹ per MHz H_3O^+ . This value does not account for losses of longer chain alkanes in the purge. The 1.5 Hz ppbv⁻¹ per MHz H_3O^+ sensitivity factor was used to estimate IVOC alkane abundance in exhaust.

Figure 9 illustrates the discrimination against light alkenes in engine exhaust by the thermal desorption sampler. Shown in the figure is a time series of the C_nH_{2n+1} ion group response associated with alkenes and larger alkanes present in diesel and gasoline engine exhaust. The exhausts were analyzed by alternating between VOC mode sampling using a -30 °C dehumidifier and IVOC mode sampling using 150 °C purge to remove volatile compounds. The IVOC sample size was 135 mL. The same suite of ions was measured in both modes with dwell times for m/z 43, 57, 71, 85, and 99 of 50 ms and dwell times for m/z 113 and 127 of 100 ms. The exhausts were diluted by a similar amount so the ion signals reflect differences in absolute organic compound emission rates from these engines. Much higher VOC mode responses were observed in gasoline exhaust for the lighter ions m/z 43, 57, 71, 85, attributed to emissions of propene, butenes, pentenes, and hexenes respectively. In IVOC mode the

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signal for these ions is greatly diminished because these volatile compounds are effectively purged from the trap before desorption into the PTR-MS drift tube. The small remaining signal was attributed to the IVOC alkanes. The IVOC mode ion signal for the larger alkane ions m/z 99, 113, 127 was more prominent relative to the VOC mode signal. The m/z 127 ion displayed a greater response in diesel exhaust, consistent with larger mass emissions of $> C_{12}$ alkanes in diesel exhaust than gasoline exhaust (Schauer et al., 1999, 2002). Alkanes and alkenes are major constituents of engine exhausts making up about 60 % of gasoline exhaust (Schauer et al., 2002) and 12 % of the diesel exhaust non-methane organic gas mass emission rate (Schauer et al., 1999). The PTR-MS is insensitive to alkanes C_7 or smaller in size, which make up approximately 18 % of the gasoline exhaust emissions and 2 % of the diesel exhaust. Additionally, the IVOC sampling mode discriminates against alkanes and alkenes $< C_9$. It is thus estimated that only 1 % of the total alkane and alkene emissions from gasoline engine exhaust is measurable by IVOC mode sampling. For diesel engine exhaust, IVOC mode sampling measures approximately 26 % of the total alkane and alkene emission rate.

3.6 Vehicle exhaust IVOC mixing ratios and source fingerprint

Sensitivities were applied to convert VOC and IVOC mode data from diesel exhaust sampling at 80 Td into molar mixing ratios (ppbv). Sensitivities were determined from calibrations from a gas standard or dynamic dilution experiments. For compounds that were not readily available, the sensitivity was estimated from compounds with a known response and similar mass by accounting for differences in the calculated collisional rate constants (Su, 1988). Mixing ratios of selected species in diluted diesel exhaust are shown as a bargraph in Fig. 10 to illustrate relative molar abundance of the largest ion signals from the compound groups listed in Table 2. It was assumed that the m/z 43, 57, 71 and 85 ions measured in VOC mode represent the corresponding C_3 , C_4 , C_5 , C_6 alkenes, although these are common fragment ions. IVOC alkanes are represented as a separate bar. The oxygenated compounds formaldehyde (m/z 31), acetaldehyde

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(m/z 45), and acetone + propanal (m/z 59), the light alkenes, and the alkylbenzenes are the most abundant families in the VOC mode. The most abundant species in diesel exhaust are reported to be formaldehyde and acetaldehyde (Schauer et al., 1999). In Fig. 10, the most abundant compounds are propene (m/z 43) and butenes (m/z 57), ions whose abundance may be enhanced due to fragmentation from other compounds.

The mixing ratio pattern observed in the IVOC mode in Fig. 10 illustrates discrimination against the volatile species (oxygenates, alkenes, cycloalkanes) and comparable mixing ratios to those measured in VOC mode for high molecular weight compounds. The light alkylbenzenes (m/z 79, 93) are essentially removed with the 150 °C purge, so the limited response was attributed to fragmentation of larger alkylbenzenes. The difference between VOC and IVOC mixing ratios at m/z 79, 93, 107, and 121 are 97, 95, 80, and 63 % respectively which are similar to the corresponding removal rates observed in Fig. 8 of 99, 97, 86, and 65 %. The heavy alkylbenzene (m/z 149, 163) mixing ratios were similar in both the VOC and IVOC modes as be expected for lower volatility species that aren't removed by the Tenax trap purge. Good agreement was also observed for the bicycloalkane responses at m/z 123 and 137 and the naphthenic monoaromatic responses at m/z 133 and 147, with the IVOC mixing ratios being within 15 % of the VOC missing ratios. Improvements in detection from the IVOC sampler were observed at the naphthenic monoaromatic ion m/z 175 and the naphthalene ion m/z 157, with the IVOC mixing ratio being larger than the VOC mixing ratio by 40 % and 130 % respectively.

The alkane mixing ratios were determined from summing up the m/z 57, 71, 85, 99, and 113 thermal desorption ion responses and applying the diesel fuel based sensitivity factor 1.5 Hz ppbv^{-1} per MHz H_3O^+ . Uncertainty in the fuel based alkane sensitivity arises from uncertainty in the reported molar abundance of alkanes by carbon number (not well quantified in the literature), the potential for interfering ion fragments from other compound groups (thought to be small), and in assuming that the molar abundance of C_{12} – C_{18} alkanes in fuel is similar to that found in exhaust. The calculated IVOC alkane mixing ratio of 150 ppbv is similar to the sum total of the C_1 – C_4 alkylben-



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zenes (m/z 93, 107, 121, 135) mixing ratio of 198 ppbv. This data can be compared to that reported by Schauer et al. (1999) where the molar ratio of the total C_{12} to C_{18} n-alkane emission rates to the reported C_1 - C_3 alkylbenzene compound emission rates was 0.20. In our experiment the ratio of the IVOC alkane mixing ratio to the total C_1 - C_3 alkylbenzene (m/z 93, 107, 121) mixing ratios was 0.90. The difference could be attributed to the presence of isoalkanes that would be observed by the IVOC sampler, but were not reported by Schauer et al. (1999). It is also interesting to compare the alkylbenzene abundance to the other aromatic compound groups. The sum total of the major naphthenic monoaromatic compounds (m/z 119, 133, 147, 161, 175) was 66 ppbv, and sum total of naphthalene group (m/z 129, 143, 157) was 41 ppbv. Together these compounds account for about half the molar abundance of the more routinely measured VOC alkylbenzene compounds.

Figure 11 displays the IVOC thermal desorption peak area response for selected ions relative to that of m/z 135. The m/z 135 ion, attributed to C_4 -alkylbenzene compounds, is abundant in both diesel and gasoline exhaust. A clear difference was observed between the diesel and gasoline exhaust relative abundance. In general, the gasoline exhaust ratios to m/z 135 were a factor of 10 lower than the diesel exhaust, reflecting the larger mass emission rate of higher molecular weight compounds in diesel exhaust. The relative abundance pattern for each engine exhaust type can potentially be used as a source fingerprint to quantify the relative contributions of diesel and gasoline engine exhausts to organic compound concentrations in urban air. For this study, it was found that a mixture containing diesel and gasoline engine exhaust yielded compound abundance ratios between the two pure exhaust source ratios as shown in the figure. The observed exhaust mixture ratio could be reasonably well estimated from the source ratios as defined by the following equations:

$$R_i = (x \times D_i) + (y \times G_i) \quad (3)$$

$$x + y = 1 \quad (4)$$

where R_i is the observed ratio at m/z mass i , D_i and G_i are the exhaust fingerprint ratios observed in the diesel and gasoline exhaust at mass i , and x and y are the fractions of diesel and gasoline exhaust in the mixture. For example, the figure shows observed ratios of 50 : 50 mixture of diesel and gasoline engine exhaust and a fit based on Eq. (3) using x and $y = 0.5$. The good agreement suggests there is the potential to quantify the relative contributions of diesel and gasoline engine exhausts in urban air using IVOC compound measurements by PTR-MS.

4 Conclusions

Analysis of gasoline and diesel fuel and gasoline and diesel engine exhaust was performed to determine if the PTR-MS instrument could be used to quantify long chain alkanes and other IVOC compounds associated with diesel exhaust emissions. Laboratory experiments show the PTR-MS sensitivity to n -alkanes increases with compound carbon number with negligible sensitivity to n -alkanes smaller than C_8 . For larger n -alkanes, the sensitivity is much less than expected if these compounds react at the collisional rate limit with H_3O^+ . Sensitivities do not increase with decreasing drift tube Townsend number, suggesting the proton transfer reaction with larger alkanes is endothermic. The n -alkanes fragment to a common set of ions with formula C_nH_{2n+1} as well as m/z 41. The relative intensity of the fragment ions was a function of drift field strength; at lower Townsend values more ion intensity occurred in larger masses and some branched alkanes yielded significant M-1 ions. Laboratory tests of fragmentation patterns imply that cycloalkanes ($C_{n+6}H_{2n+7}$: m/z 69, 83, 97, 111, 125) and naphthenic monoaromatics ($C_{n+9}H_{2n+11}$: m/z 119, 133, 147 etc.) are important constituents in both fuel and exhaust. A diesel fuel based sensitivity factor of 2.6 Hz ppbv^{-1} per MHz H_3O^+ was calculated for C_{12} - C_{18} alkanes at 80 Td drift condition.

A thermal desorption sampler was added to the PTR-MS drift tube, allowing for normal VOC measurements as well as sample collection and desorption of heavier organics from a Tenax TA adsorbent. In this analytical approach the PTR-MS drift tube

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was operated at 80 Td for both VOC sampling and thermal desorption analysis to reduce fragmentation. The thermal desorption sampler discriminated against VOC compounds by using a high temperature purge before direct desorption into the PTR-MS drift tube using dry N₂ carrier gas. By implementing a purge, VOC compounds that would interfere with the measurement of C₁₂-C₁₈ long chain alkanes were removed. In diluted diesel engine exhaust IVOC alkane mixing ratios were measured to be 76 % of the sum total of C₁-C₄ alkylbenzene abundance, and therefore comprise a significant amount of precursor material for secondary organic aerosol formation. Thermal desorption sampling and low Townsend number PTR-MS analysis is a viable approach for providing quantitative information on the total abundance of long chain alkanes and aromatics species in diesel exhaust. While diesel and gasoline engine exhaust composition of volatile components were similar, the abundance patterns IVOC compounds were quite different. The abundance patterns of IVOC compounds may allow for emission profiles to be developed to better quantify the relative contributions of diesel and gasoline exhaust emissions to urban air concentrations of organic compounds.

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Table 1. Percent of total ion signal for the different groups in diesel and gasoline fuels.

Compound Group	Mass Formula	Td 80 Base Ion	m/z	Diesel Td 120	Diesel Td 80	Gasoline Td 120	Gasoline Td 80
alkanes	C_nH_{2n+1}		43, 57, 71, 85, 99, 113, 127, 141, 155, 169	43.30 %	23.20 %	36.80 %	31.10 %
cycloalkanes	C_nH_{2n-1}	$M - 1$	69, 83, 97, 111, 125, 139, 153, 167, 181	17.10 %	17.70 %	5.30 %	5.40 %
bicycloalkanes	$C_{n+5}H_{2n+7}$	$M - 1$	123, 137, 151, 165, 179, 193	8.20 %	8.20 %	0.60 %	0.50 %
alkylbenzenes	$C_{n+6}H_{2n+7}$	$M + 1$	79, 93, 107, 121, 135, 149, 163, 177, 191	10.50 %	20.10 %	47.90 %	42.20 %
naphthenic monoaromatics	$C_{n+9}H_{2n+11}$	$M + 1$	119, 133, 147, 161, 175, 189, 203	7.40 %	14.30 %	1.70 %	1.40 %
dihydro-naphthalenes	$C_{n+10}H_{2n+11}$	$M + 1$	131, 145, 159, 173, 187, 201	0.80 %	1.70 %	0.10 %	0.10 %
naphthalenes	$C_{n+10}H_{2n+9}$	$M + 1$	129, 143, 157, 171, 185	0.80 %	1.70 %	0.90 %	1.30 %
Sum of ion signal				88 %	87 %	93 %	82 %

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Table 2. Comparison of fuel and exhaust composition at 80 Td Td.

Group	Formula	Measured m/z	Diesel Fuel	Diesel Exhaust	Gasoline Fuel	Gasoline Exhaust
oxygenated alkanes/alkenes	C_nH_{2n+1}	31, 33, 45, 47, 59	19.7%	50.3%	45.1%	51.1%
cycloalkanes	C_nH_{2n-1}	43, 57, 71, 85, 99, 113, 127	20.3%	19.4%	20.6%	16.4%
alkylbenzenes	$C_{n+6}H_{2n+7}$	69, 83, 97, 111, 125, 139	15.3%	4.3%	3.6%	3.3%
		79, 93, 107, 121, 135, 149, 163, 177, 191	21.9%	22.3%	28.6%	26.6%
unknown (<i>bicycloalkanes</i>)	$C_{n+5}H_{2n+7}$	81, 95, 109, 123, 137, 151, 165	6.1%	2.5%	0.3%	1.3%
naphthenic monoaromatics	$C_{n+9}H_{2n+11}$	119, 133, 147, 161, 175, 189	15.1%	0.9%	0.9%	1.0%
naphthalenes	$C_{n+10}H_{2n+9}$	129, 143, 157, 171	1.6%	0.3%	0.8%	0.3%

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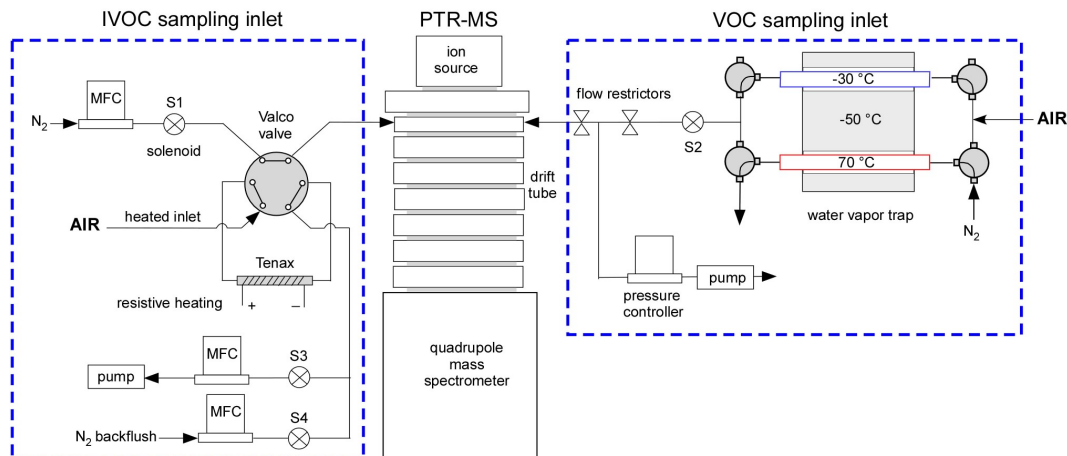


Fig. 1. Plumbing schematic showing thermal desorption sampler for IVOC compounds and VOC sampling system with water vapor trap.

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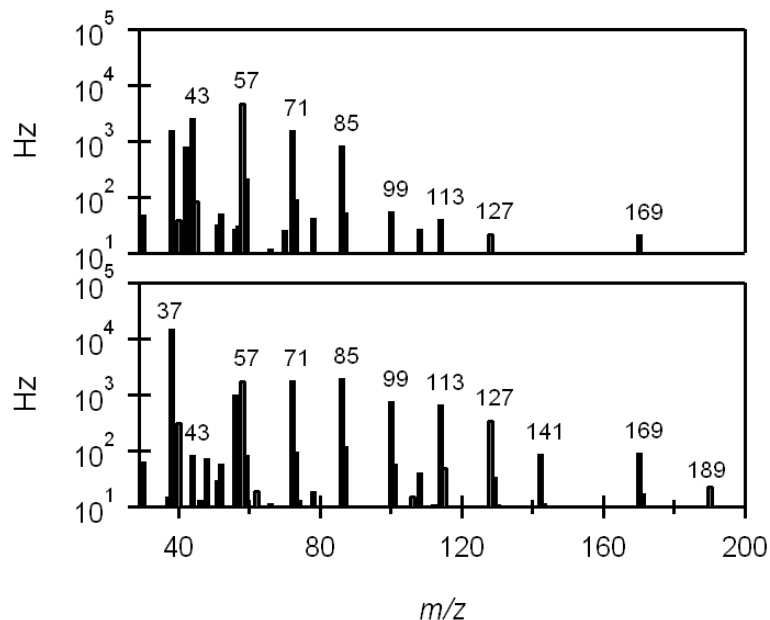


Fig. 2. PTR-MS raw mass spectrum of dodecane ($C_{12}H_{26}$) at 120 Td (upper panel) and 80 Td (lower panel) drift tube conditions. A clear pattern of C_nH_{2n-1} ion fragments is evident. At 80 Td the M-1 ion (m/z 169) is more intense. The m/z 189 ion is attributed to the $M \cdot H_3O^+$ cluster.

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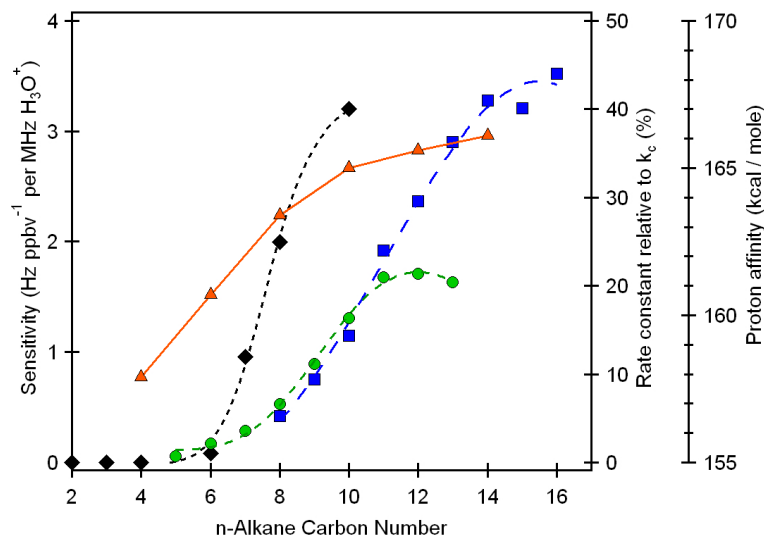


Fig. 3. n-Alkane sensitivity (left axis) for 120 Td (blue squares) and 80 Td (green circles) compared to measured H_3O^+ + n-alkane rate coefficients (black diamonds) by Arnold et al. (1998) expressed as a percentage of collision rate limit (right axis). Also shown is the proton affinity (red triangles) determined by Hunter and East (2002).

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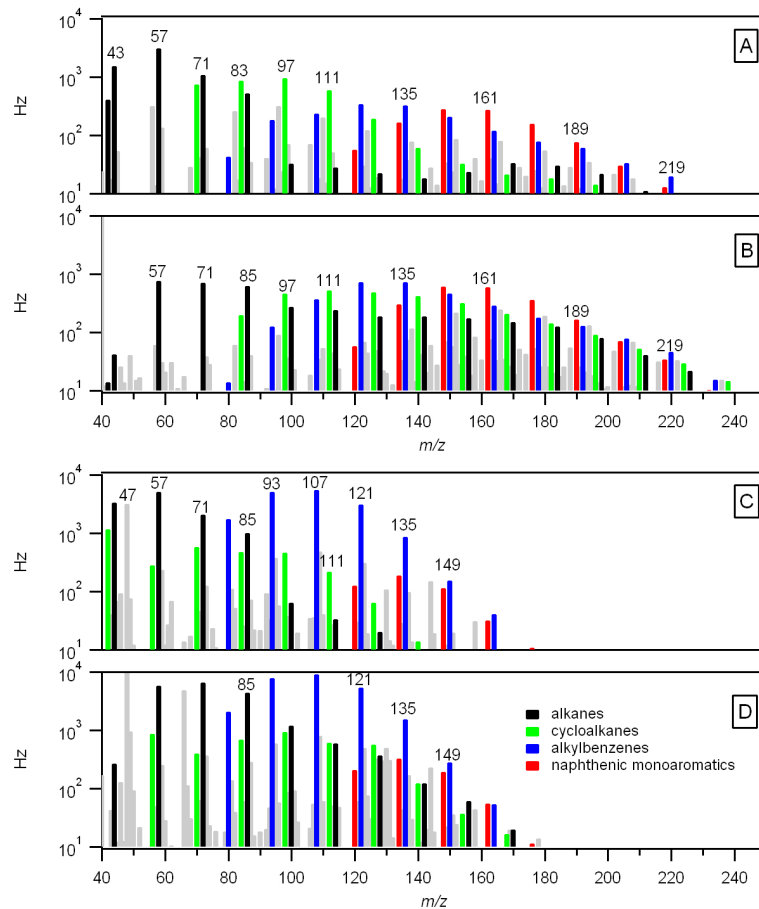


Fig. 4. PTR-MS mass spectrum of diesel fuel #2 at 120 Td (A) and 80 Td (B) and gasoline at 120 Td (C) and 80 Td (D). Ion signal has been color coded to assign ions to common fragmentation patterns that identify common organic compound classes.

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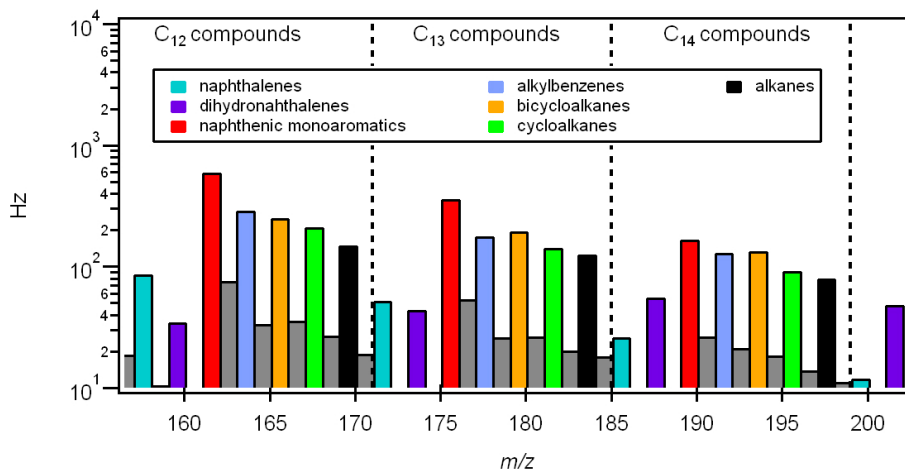


Fig. 5. Examination of the C_{12} - C_{14} compound range ion signal pattern for diesel fuel. Peaks have been tentatively identified as belonging to 1 of 7 compound groups that differ by the degree of unsaturation, ranging from naphthalenes to alkanes.

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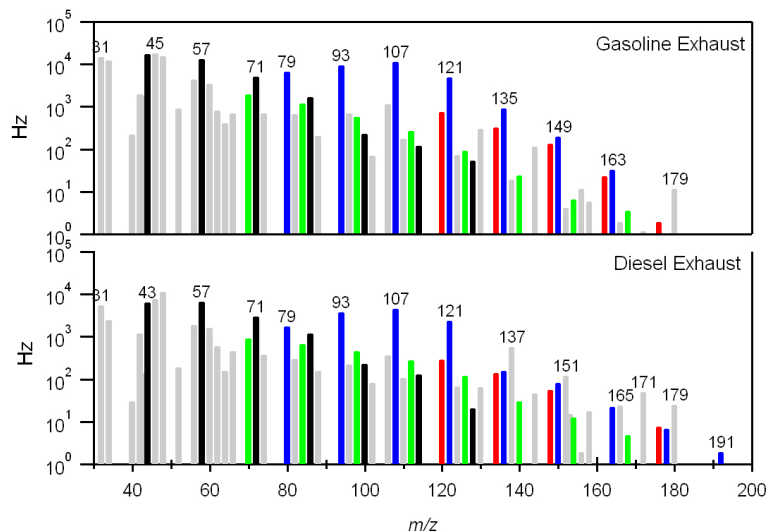


Fig. 6. PTR-MS mass spectrum of gasoline exhaust (top panel) and diesel exhaust (bottom panel) at 80 Td. Ion signal has been color coded to assign ions to common fragmentation patterns that identify common organic compound classes: alkane fragment ions (black), alkylbenzenes (blue), cycloalkane fragment ions (green) and naphthenic monoaromatics (red).

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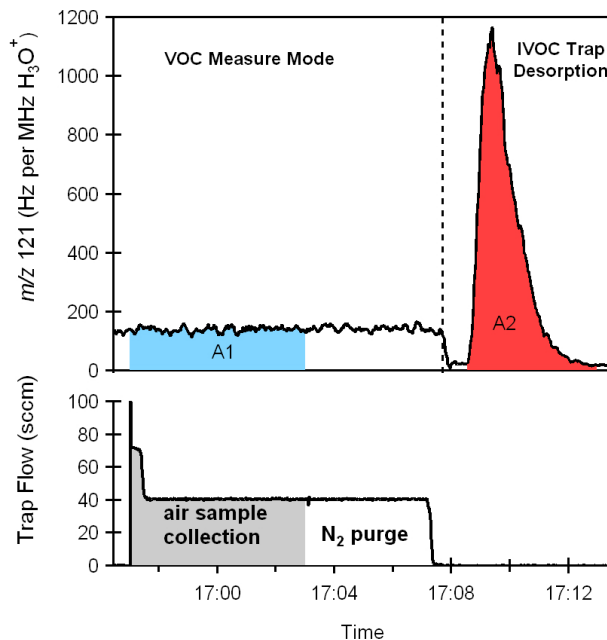


Fig. 7. Upper panel shows a time series of the 1,3,5-trimethylbenzene ion signal (m/z 121) from a prepared test mixture as measured in VOC mode passing through the water trap and from desorption of a 257 cc air sample of the test mixture collected on the Tenax trap (red shading). The bottom panel shows the gas flow through the Tenax trap. The shaded area A1 in VOC mode corresponds to the IVOC sample collection time.

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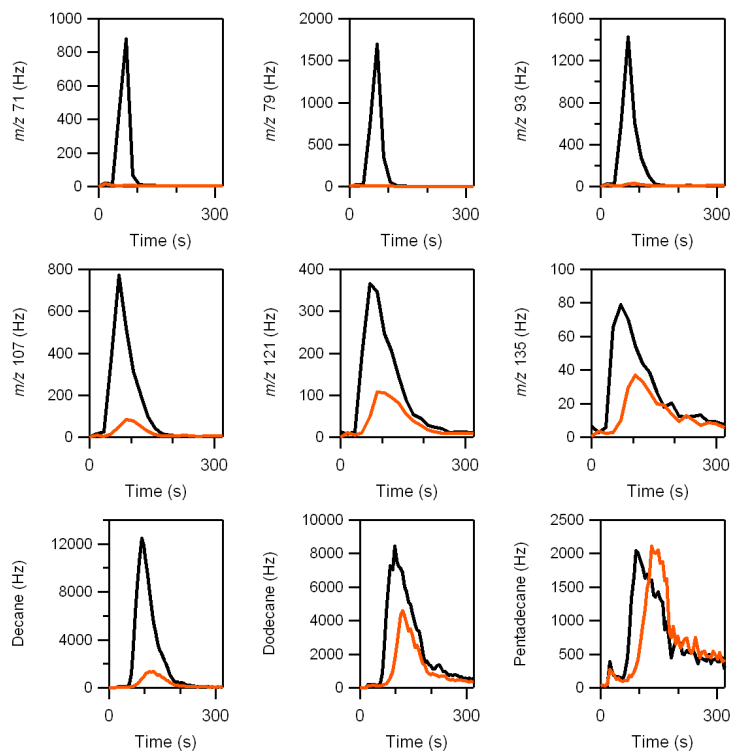


Fig. 8. PTR-MS IVOC mode desorption peaks of selected compounds comparing the 30 °C (black trace) and 150 °C (red trace) purge temperatures. Shown are: methacrolein (m/z 71), benzene (m/z 79), toluene (m/z 93), p-xylene (m/z 107), 1,2,4-trimethylbenzene (m/z 121) and 1,2,3,5-tetramethylbenzene (m/z 135), decane (m/z 57, 71, 85, 99), dodecane (m/z 57, 71, 85, 99), and pentadecane (m/z 57, 71, 85, 99). The ion signal (Hz) is normalized to MHz H_3O^+ .

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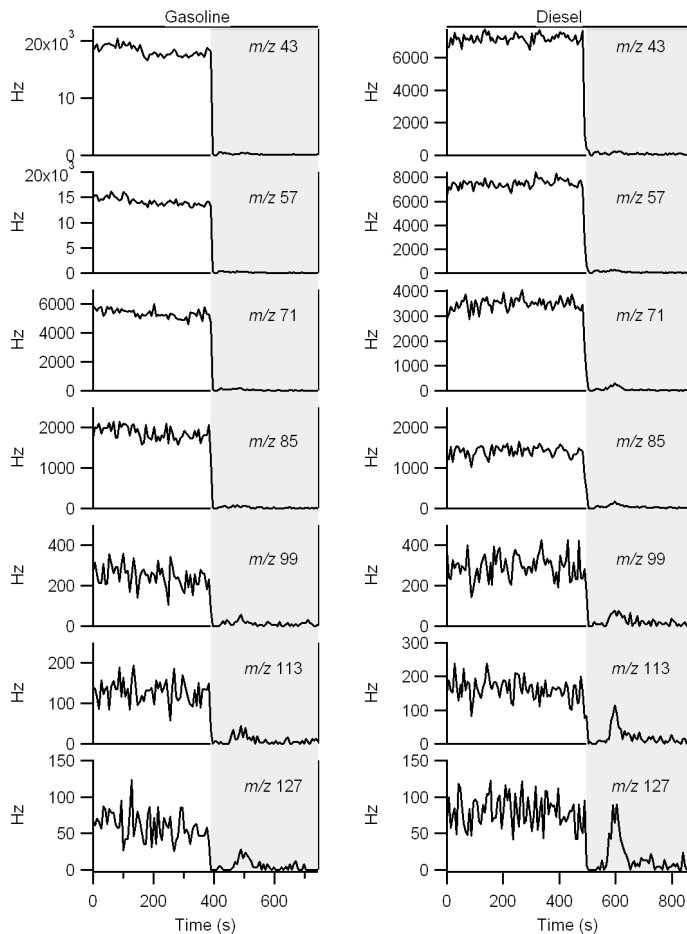


Fig. 9. Time series of measurements showing VOC and IVOC signals in gasoline (left panels) and diesel (right panels) exhaust. The IVOC mode signal is indicated by the grey shaded area. The ion signal (Hz) is normalized to MHz H_3O^+ .

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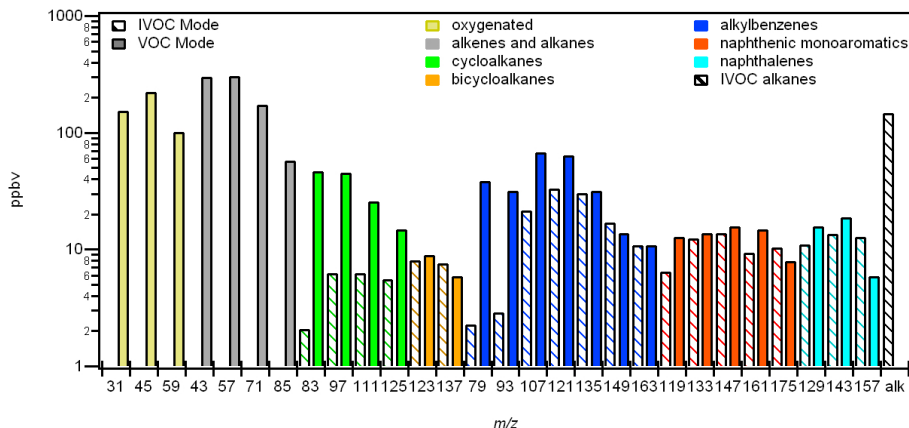


Fig. 10. Diluted diesel exhaust mixing ratios illustrating abundance of compounds measured by the PTR-MS by VOC (solid bars) and IVOC (striped bars) sampling modes.

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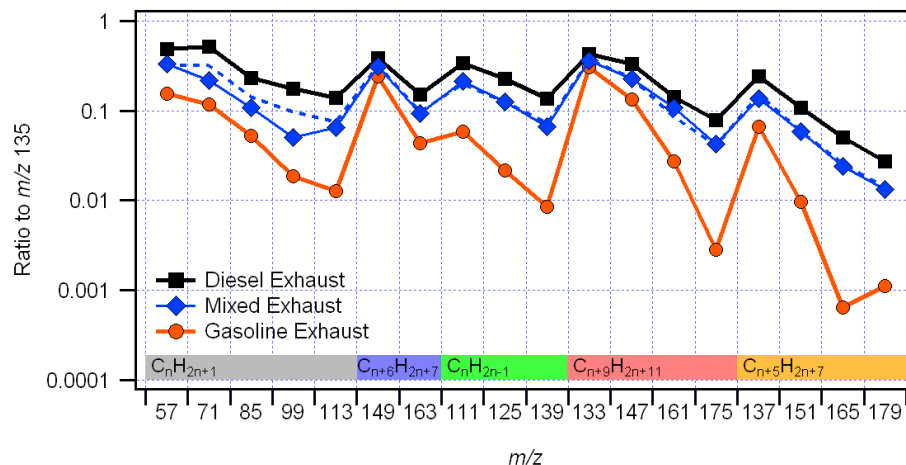


Fig. 11. PTR-MS IVOC mode exhaust fingerprints observed for diesel exhaust (black squares), gasoline exhaust (red circles), and an approximately 50 : 50 mixture (blue diamonds). The dashed line is a calculated exhaust fingerprint of a 50 : 50 mixture of gasoline and diesel exhaust given the source profiles shown. Color bands indicate compound group: alkane fragment ions (grey), alkybenzenes (blue); cycloalkane fragment ions (green), naphthenic monoaromatics (red); bicycloalkanes (orange).

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