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ON-LINE ANALYSIS OF ORGANIC COMPOUNDS IN DIESEL EXHAUST USING PROTON-TRANSFER-REACTION MASS SPECTROMETRY

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ABSTRACT

In this study, diesel exhaust (DE) was measured in real time using a proton-transfer-reaction mass spectrometer (PTR-MS) to determine the effect of an after-treatment catalyst on gas phase volatile organic compounds (VOCs). DE after-treatment catalysts are being designed to reduce the pollutants in exhaust, which contains both particulate matter and gas phase constituents. The PTR-MS can make *in-situ* real time measurements of hydrocarbons in the air, from concentrations in the parts per million by volume (ppmV) down to the low part per trillion by volume (pptV) range. Spectrum scans were performed at varied engine loads from mass range m/z (mass to charge ratio) = 20 to 200. This showed the relative abundance of gas phase VOCs produced as the engine ran between idle mode and 80% of its maximum load. The mass spectrum was complex and appeared to be composed of aromatic species ionized by PTR ($M+1$) through the anticipated proton transfer reactions as well as unexpected alkane fragments, evidenced by a strong $14n+1$ ion pattern showing intense peaks at $m/z = 43, 57, \text{ and } 71$. A number of protonated $M+1$ masses could be identified. These compounds displayed $M+2$ peaks consistent with known ^{13}C isotopic abundance. As the engine load increased, the concentrations of over 90% of the species decreased. An attached smoke meter showed that soot concentrations increased over the same conditions. In addition, the decrease in the concentration of compounds with a larger molecular weight ($m/z > 100$) was greater than the rate that the smaller compounds experienced. This appears to be due to the affinity of VOCs, larger masses in particular, to adhere to soot particles. Further PTR-MS measurements of VOCs on soot confirmed this by producing a mass spectrum comprised of masses predominantly over 100 amu. On-line analysis of diesel exhaust by PTR-MS is a practical tool for quantifying selected organic species in diesel exhaust and should prove useful for developing better diesel exhaust after-treatment system.

INTRODUCTION

This experiment tests the applicability of the novel technology of the proton-transfer-reaction mass spectrometer (PTR-MS) to the analysis of diesel exhaust (DE). The many organic compounds present in DE make speciation and resolution of its individual constituents a very difficult task even for traditional analytical tools such as gas chromatography mass spectrometry. The power of the PTR-MS lies in its ability to do *in-situ* real time monitoring, useful for tracking rapid changes in gas phase concentrations. There is a need for real time monitoring of gas and particle composition in engine exhaust because particle composition and hydrocarbon loadings can vary rapidly as engine conditions change. Many tests of DE (for example, [1]) utilize particle filter techniques, which are capable of desorbing

volatile organic compounds (VOCs) into the air before being tested, preventing accurate analysis of compound quantity in samples.

The PTR-MS has recently been used to detect organic molecules in such applications as breath analysis and atmospheric monitoring [2] due to its capacity to continuously measure organic gasses in air in real time. This is accomplished by chemical ionization mass spectrometry using the ionization reagent H_3O^+ produced in a hollow cathode ion source. When this hydronium is accelerated through a drift tube, it reacts with organic analytes in a proton transfer reaction but not with the major components of clean air. The positive ions produced are then measured by a quadrupole mass spectrometer, with sensitivities of about 50 parts per trillion, making it suitable for trace gas analysis. This technique is comparable to atmospher-

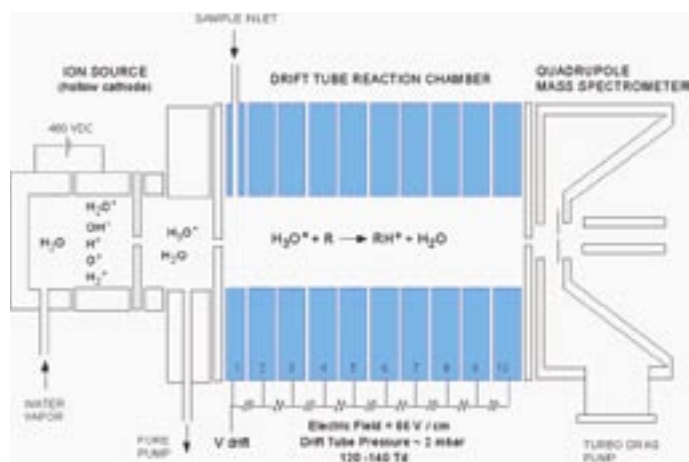


Figure 1 shows the mechanisms of the PTR-MS. Water is ionized into H_2O^+ , OH^+ , H^+ , H_2^+ , and O^+ by the ion source. These ions proceed to the right where they recombine with H_2O molecules to form H_3O^+ (hydronium) ions. Analytes enter the drift tube through the sample inlet and react with the hydronium ions as shown. Protonated species are then measured by the quadrupole mass spectrometer.

ic pressure chemical ionization (APCI) in positive ion mode. However, the PTR has a more intense production of H_3O^+ (making it more sensitive) and a simpler mass spectrum due to fewer competing ion molecule reactions. The PTR is also inherently more quantitative as will be discussed below. These advantages make it a more attractive analytical tool for diesel exhaust analysis than APCI.

The objective of this experiment was to perform on-line measurements using the PTR-MS on diesel exhaust emissions downstream of an after-treatment system in an attempt to discern a molecular weight fingerprint and reveal the composition of gas phase exhaust. Complex mixture analysis by PTR can not by itself provide resolution of individual constituents but may be the best quantitative method to date for providing real time information on selected species, such as aromatics and light oxygenated components like formaldehyde [3]. Organic compounds attached to soot particles were also measured in this study by thermal desorption of particle filters to show the relative change in concentration over varied temperatures. The application of the PTR-MS to the analysis of organics bound to particulate matter may provide important information on semi-volatiles that are difficult to quantify with other methods [4].

New regulations [5] mandate a drastic reduction of the particulate matter and sulfur content in DE within the next five years. This will require the use of diesel particulate filters, likely including catalysts of the type used here. It is therefore important that the composition of DE is understood thoroughly to reduce the harmful impact it has on the environment and human health [6]. The results of these tests could be used to help develop improved exhaust after-treatment systems and reduce the amount of pollution caused by diesel engines.

A	Mass (m/z)	m33	m45	m59	m69	m71	m79	m93	m107	m121	
B	kc 295K	26.89	37.43	39.44	19.86	40.57	19.25	21.67	21.91	24.00	
C	kADO 295K	23.33	31.17	33.29	19.61	33.00	19.25	21.36	21.91	24.00	
D	Calculated R.S. kc 295K	48.37	71.91	78.94	39.92	81.41	38.03	40.40	37.17	35.99	
E	Calculated R.S. kADO 295K	41.96	59.89	66.64	39.42	66.21	38.03	39.83	37.17	35.99	
F	Observed R.S. (cps/ppbV)	57.80	59.25	85.82	37.60	66.46	38.07	45.27	42.81	39.55	Ave

Table 1. Rows B and C show two k_i values used to determine theoretical response sensitivities (R.S.). Using equation (2), the theoretical sensitivities were calculated and appear in rows D and E in counts per second per parts per billion by volume (cps/ppbV). Row F shows an average R.S. for the observed calibration mix. The last two rows compare the observed and theoretical R.S. and give an average ratio in the last column. The ratio obtained using the kc 295K rate constant (highlighted) was the overall closest match to observed values.

MATERIALS AND METHODS

A detailed description of the PTR-MS is given by [2]; a brief explanation is given here. The PTR-MS is able to continuously measure organic gasses in air in real time by chemical ionization mass spectrometry. This is accomplished by the ionization of water into H_2O^+ , OH^+ , H^+ , H_2^+ , and O^+ ions in a hollow cathode. Figure 1 shows a rough instrument schematic. These ions then recombine with water molecules to form H_3O^+ (hydronium) ions. The hydronium ions are produced in large quantities and accelerated through a 10 cm drift tube at speeds of 905 m/s where they react with organic analytes as follows:

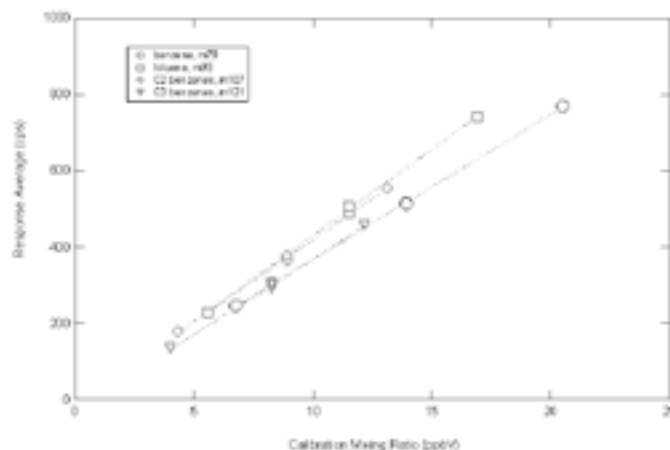


Figure 2 demonstrates the method for calculating the observed response sensitivity for four aromatic compounds. The observed response average is plotted against the known calibration mixture ratio to determine the sensitivity of the instrument. Response values are shown in Table 1.



The hydronium ion does not react with the major components of clean air such as O_2 , N_2 , CO_2 , and CH_4 . This makes it suitable for trace gas analysis, with sensitivities of about 50 parts per trillion by volume for a one second dwell time.

Positive ions are extracted from the drift tube and mass filter by a quadrupole mass spectrometer (Balzers model BG 800 451 BE) and detected with a secondary electron multiplier in pulse counting mode. The drift tube is maintained at a pres-

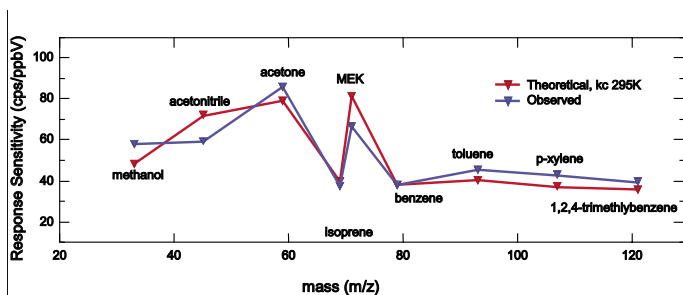


Figure 3 compares the closely matching theoretical and observed response sensitivities, calculated using equation (2). The higher the masses, the more closely the sensitivities matched overall.

sure of 2 mbar under an electric field of 66 V/cm to prevent ions from clustering with H₂O. All calibration and DE tests were run under the following conditions. Secondary electron amplifier was set at 2500 V, zero air flow at 1.0 standard liters per minute, inlet and drift tube temperatures were both 50° C, U2 was 190V, U3 was 140V, Udrift was 540V, water-flow was 4scm, and inlet line pressure was 350 mbar.

Calibration of the PTR-MS

Calibrations were performed on the PTR-MS using a multi-component gas mixture (Apel-Remier Environmental). The mixture consisted of 13 compounds from m/z 45 amu to 121 amu, including aromatic, oxygenated and biogenic molecules. A multipoint calibration was performed by varying the gas flow and diluting it into a humidified zero air flow. The flow of the calibration gas was increased in three steps from 20-60 mL/min, resulting in a concentration range between 10 and 150 parts per billion by volume (ppbV). The count rate of the analytes was recorded in number of counts per second (cps). The mean count rate at each flow was plotted against the analyte concentration known to be in the calibration gas to calculate observed response sensitivities.

Proton transfer reactions that are exothermic, such as the ones analyzed here, occur at a collisional rate constant, k_r . Collisional rate constants for ion-molecule reactions can be calculated from theory in the absence of experimentally determined values. The manufacturer of the PTR-MS (Ionicon) supplied such calculated values for most of the components in the calibration mix. The four relevant rate constants are the capture rate constant, k_c (Langevin expression), rate constants calculated from average dipole orientation theory (kADO), and two corresponding rates that take into account the non-thermal ion energy (0.13 eV) in the drift tube (k_{cEcm} and $k_{ADO Ecm}$) [8]. These tabulated rate constants (k_i) were used in the following equation to calculate theoretical response sensitivities:

$$[R_jH^+] = [R_j] [H_3O^+] k_i t (\epsilon_i/\epsilon_{H_3O^+}) \quad (2)$$

Where $[R_jH^+]$ represents the count rate of protonated analyte, $[R_j]$ is the neutral molecule concentration (number density in the drift tube at 1 ppbV), $[H_3O^+]$ is the count rate of hydronium ions, t denotes the reaction time (105×10^{-6} seconds), and $\epsilon_i/\epsilon_{H_3O^+}$ is the experimentally determined relative transmission factor (approx. 1). The theoretical and observed response rates

were then compared to find a k_i value that could be used as a reasonable estimate for those compounds which do not have published k_i values, as will be discussed later.

Analysis of Diesel Exhaust

The analysis of DE vapor was accomplished using the PTR-MS attached to a diesel generator (GenPro 4000) in the following way. From the engine, the diesel exhaust proceeded first to an emissions reducing catalyst being tested by the Diesel Emissions Facility where a large percentage of the particulate matter was removed. The remaining DE continued through two diluters in series, further diluting the exhaust by a factor of 70:1. From there, a pump pulled the diluted DE into the PTR-MS at a rate of 100mL/min for the duration of the tests. The diesel generator ran at four load settings (idle, 20%, 40% and 80%) that simulated standard engine workloads for an average of 20 cycles each. The fuel used was a Carb Diesel, low sulfur emissions (Specified HF128) type that will be used in diesel engines in California within the next few years in an effort to reduce the sulfur content of DE.

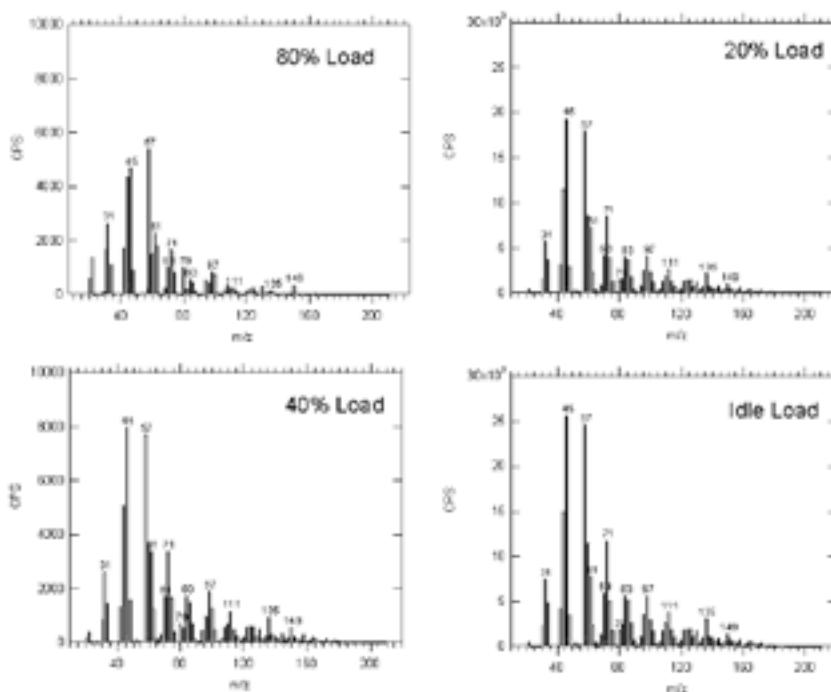
A smoke meter was also attached directly to the generator. The smoke meter measured the soot concentration in mg/m³ as load levels varied. This provided information that would later be related to the concentrations of compounds under different loads.

Investigation of Soot Samples

A collection filter (Gelman model 2220-2) was attached directly downstream of the engine exhaust portal. This was done in order to capture soot and the organic compounds adsorbed by soot so that a VOC desorption could later be performed. In this collection filter, 47mm quartz membrane filters (Gelman, lot # 53323) were collected at each load level for exactly 14 cycles. An attached sampling pump pulled air through the membrane at a constant rate of 3 liters per minute to facilitate even sampling. The collected soot filters were stored in airtight containers at approximately 10°C and later examined using the PTR-MS. In this procedure, a flow of 100 milliliters per minute N₂ was run through a stainless steel tube containing ½ a filter collected during a single engine load. The tube was then heated continuously from 25°C to 80°C and the concentrations of the analytes were recorded in real time at a dozen intervals. This was done in an attempt to observe the VOCs vaporizing off of the soot at various temperatures.

Investigation of Alkane Fragmentation

To aid in the interpretation of the DE mass spectrums, another set of tests was run on the PTR-MS. Four alkane species (decane, dodecane, hexadecane, and butylcyclohexane) were analyzed individually in order to unambiguously determine the mass spectra created by each compound. A permeation device (1/16" Teflon tubing sealed at both ends) was used to heat a few microliters of analyte within a glass tube



Figures 4a – d are DE mass spectra and show the increase in gas phase compound concentration with decreasing engine load. Shown are mass scans between 20 and 210 m/z. The PTR-MS measured count rates (cps) at each m/z value for 1 second and updates the mass spectrum approximately every 90 seconds.

as N₂ was pumped through to the PTR. The inlet tubes on the PTR-MS were also heated to avoid analyte condensation as the compounds flowed to the drift tube. In this experiment the precise count rate was not sought. A general picture of the mass spectrum was needed, therefore exact volumes of the analyte varied. These tests determined alkane fragmentation patterns in the drift tube.

RESULTS AND DISCUSSION

Calibration of the PTR-MS

The sensitivity calculations proved useful for quantitative analysis of DE. The observed response sensitivity showed a direct linear correlation between the calibration mixture ratio and the PTR-MS response average (Figure 2). These sensitivities also allowed the use of collisional rate k_i values for compounds whose rate constants are not known. The theoretical k_c 295K rate constant (295K refers to the temperature at which the reaction takes place) gave calculated sensitivities within 20% of observed sensitivities (Figure 3 and Table 1) and was used to calculate a correction factor for all masses. This correction factor was used to take into account the average difference between the theoretical and observed sensitivities. Including the correction factor, f , the new equation for calculating the count rate of the analyte is:

$$[R_i H^+] = f [R_i] [H_3O^+] k_i t (\epsilon_i / \epsilon_{H_3O^+}) \quad (3)$$

It was then possible to convert the signal received in cps into ppbV, which is easier to interpret.

Analysis of Diesel Exhaust

The mass spectrum that resulted from the DE was complex and not easily decipherable. While many of the masses remain unidentified, over 20 species and many more fragments have been revealed by patterns that appear in the spectrum. The most notable trend is in the decrease of compound concentration as the load increases. (Figures 4a-4d) Over 90% of the masses show marked decrease in concentration as the load increases. This decrease in compound concentration coincided with an increase in soot concentration as measured by the smoke meter attached directly downstream of the engine. (Figure 5) It is reasonable to assume that as the concentration of soot increases, more of the semi volatile VOCs partition to the soot. This is further reinforced by the decrease in concentration of compounds with larger masses ($m/z > 100$) at a greater rate than the smaller mass compounds.

The larger masses would most likely partition to soot more easily than the smaller ones because of their predominantly less volatile nature.

Less visually obvious from the mass spectrums are the isotopic ratio patterns of aromatic compounds that ionize according to the process described in equation (2). A number of M+1 masses corresponding to aromatic species ionized by PTR could be identified, including C₂ through C₆ benzenes, naphthalene, and dimethylnaphthalene. (Figure 6) These compounds displayed M+2 peaks consistent with known ¹³C isotopic abundance. (Figure 7) Deviance from the appropriate ratio shows contamination of a molecular weight peak with other

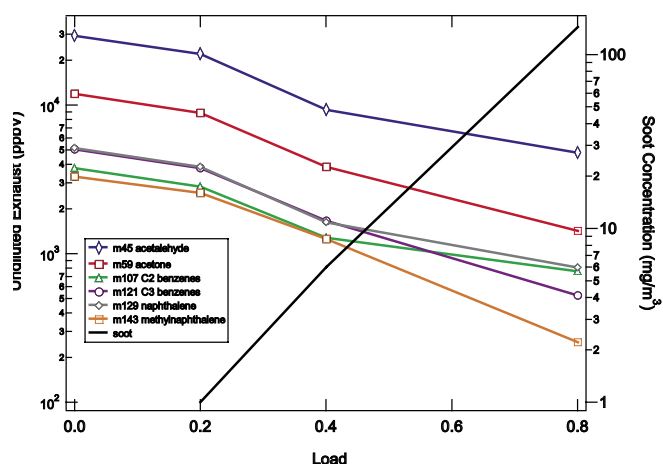


Figure 5 illustrates the increase in soot concentration as many of the gas phase constituents decrease. At less than a 20% load, soot concentration was negligible.

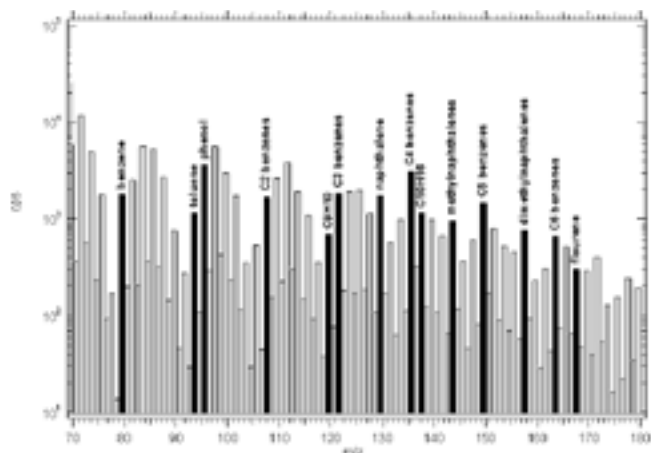


Figure 6 shows aromatic species that have been identified by their $^{13}\text{C}/^{12}\text{C}$ isotopic ratios.

ions containing a different number of carbon atoms. Several other compounds (e.g. formaldehyde and acetaldehyde) that are known to be present in DE based on previous reports of diesel exhaust composition determined by gas chromatography mass spectrometry [1] and have previously been shown to be free of interference in the PTR mass spectrum [3] were also identified.

Investigation of Soot Samples

The analyzed soot-coated filters showed a very different mass spectrum than that seen with the gas phase exhaust. (Figure 8) The filters' mass spectrum was shifted dramatically towards the higher masses, with the apex of the curve approximately 80 amu higher than the gas phase mass spectrum. While the filters collected at higher loads contained a smaller concentration of nearly all masses, this can be attributed to the DE temperature increase at higher load levels. As the generator's load increased, so did the temperature of the exhaust leaving the engine, likely volatilizing many of the VOCs into the gas phase.

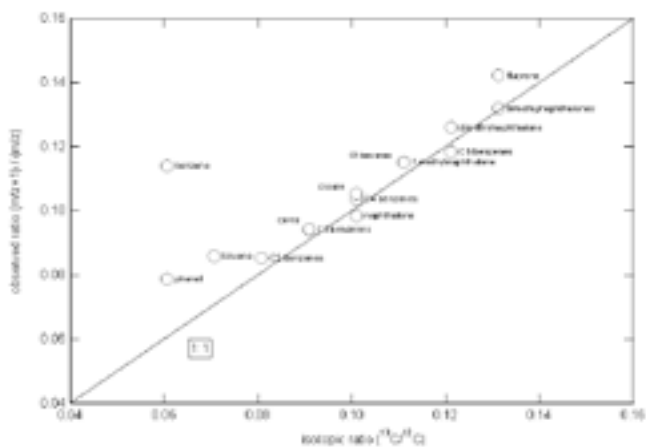


Figure 7 shows the ratio of aromatic ^{13}C and ^{12}C isotopes. The black line represents where the exact theoretical ratio falls (1 to 1).

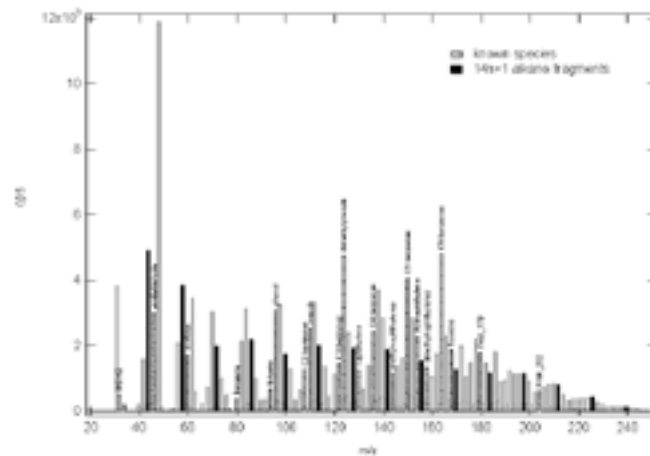


Figure 8 illustrates the mass spectrum of VOCs on soot. Note the shift of the apex of the curve by almost 80 masses higher than the DE in gas phase. Also shown are some of the compounds that have been identified by methods described earlier.

Investigation of Alkane Fragmentation

Another dominant trend is the cycle of peaks that occurs every 14 masses. (Figure 9) This pattern corresponds closely with the $14n+1$ fragmentation pattern of long n-alkanes in electron impact mass spectrometry (EI-MS). While the PTR does not use the hard ionization process of EI-MS, it was first assumed that some of these alkanes were reacting with the small percentage of O_2^+ ions produced along side the H_3O^+ ions. In all tests run, the O_2^+ concentration in the drift tube was kept below 2% of all ions present. However, the neat fuel is comprised of over 90% alkanes, which could have accounted for the large peaks seen at $14n+1$ masses. Further investigation of the reactions of individual alkanes at 0% O_2^+ concentration proved this hypothesis wrong. The fragmentation pattern occurred regardless of the O_2^+ concentration in the drift tube. This shows that long chain alkanes can break apart in the drift tube and yield $14n+1$ fragments although the fragmentation mechanism is not fully understood.

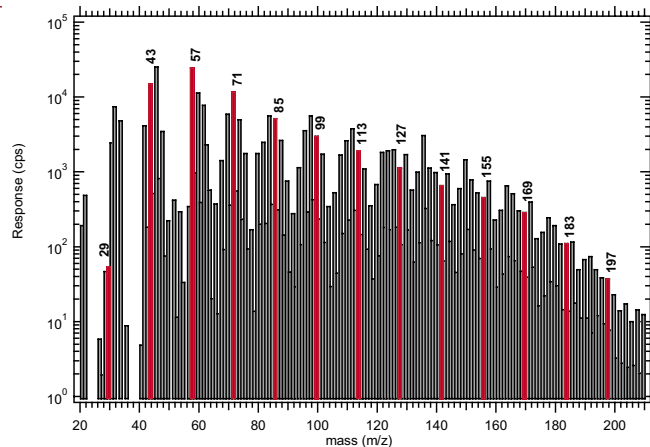


Figure 9. The red bars show peaks in counts per second, corresponding to typical $14n+1$ fragmentation of large alkanes ($>C_7$)

CONCLUSION

Analysis of DE is a promising new application for the PTR-MS and these experiments have shown that it can be a useful tool for data collection of this type. Many of the observations made here could lead to new technologies in catalyst production that would reduce gas phase pollutants as well as VOCs on particulate matter. As industry and government agencies strive to meet strict new regulations on DE, it is crucial to understand the composition and desorption patterns of this toxic compound. It is the author's hope that this study will aid in further investigations into the properties of gas and particle phase diesel emissions.

As shown in these experiments, the fragmentation of large alkanes in the PRT-MS provides another piece of the complex puzzle of deciphering the mass spectrum of DE and other gasses containing alkenes. Until now, it was assumed that these fragmentation patterns would not take place under the soft ionization process of the PTR. While the reactions behind the fragmentation are still unclear, the fact that large alkanes do fragment is necessary for the analysis of the mass spectra produced. Though the mass spectrum of DE, when viewed with the PTR-MS, can be difficult to analyze, this observation provides much information to those willing to spend some time deciphering the peaks. The patterns identified in these experiments should give a solid base for further investigations of VOCs in diesel exhaust.

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