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Michael Alexander is involved with instrument development in the fields of chemical ionization and mass spectrometry at the Pacific Northwest National Lab. Specifically, he is using proton transfer reaction mass spectrometry (PTR-MS) to obtain direct measurements of volatile organic compounds in air to study air pollution. Dr. Alexander served as part of an air quality campaign in Mexico City and he also collaborated with Boeing to determine how jet engine oil is broken down in high temperatures. He received his B.S. in chemistry from the University of California, Berkeley in 1979 and his Ph.D. in chemical physics from the University of Colorado in 1987. Dr. Alexander is the recipient of several awards, including DOE Mentor of the Year Award (2002), a Fitzner-Eberhardt Award nominee (2002), and a PTR-MS Collaborator, University of Innsbruck, Austria.

CHARACTERIZING THE PERFORMANCE OF A PROTON-TRANSFER-REACTION MASS SPECTROMETER WITH A RAPID CYCLING TENAX PRECONCENTRATOR

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ABSTRACT

Volatile organic compounds (VOCs) are species of interest for atmospheric modeling, worker chemical exposure and medical studies. Sometimes the required detection limits for these compounds is below the capability of existing real-time instrumentation. Preconcentrators have been implemented as an inexpensive way to amplify chemical signals and improve detection limits. Proton-transfer-reaction mass spectrometry (PTR-MS) has been used as a tool for studying low concentrations of VOCs, but it lacks the capability to differentiate chemical signal contributions from isobaric compounds. In this work, behavior of a newly designed Tenax TA preconcentrator when coupled with a PTR-MS is characterized. This novel preconcentrator design allows rapid temperature cycling, maintaining near real-time response. The preconcentrator was exposed to a sample gas of toluene in varying concentrations and loading times between and then thermally desorbed for analysis by PTR-MS. The effects of preconcentrating multiple analytes simultaneously were also investigated as well as the chromatographic effects of the preconcentrator. A linear behavior was observed when the integrated ion count rates (ICPS) from thermal desorption peaks were regressed against both varying loading times at a constant toluene concentration and varying concentrations with constant loading times. From these trends, it is possible to determine the concentration of a VOC by knowing its ICPS from thermal desorption peaks from a known preconcentration time. Peak height ion count rates representing ultimate detectability were amplified by factors up to 257 times the original signal, extending the range of the PTR-MS from 50pptv to nearly 250 parts per quadrillion. This corresponds to an ultimate sensitivity of 200 parts per quadrillion with 20 minute time resolution. Quantitative preconcentrator behavior was demonstrated using ICPS from these ion peaks and were amplified as much as 148 times their original signal. Results from multi-analyte desorption indicate that chromatographic separation is possible with a Tenax preconcentrator and further details are discussed. The dramatic increased in sensitivity with near real-time response, combined with chromatographic resolving capability opens up new areas of research requiring the detection of ultra-trace organic species using PTR-MS.

INTRODUCTION

Volatile organic compound (VOC) emissions to the atmosphere have been a topic of interest for some time now in relation to ozone formation and aerosol pollutants. The identity and fate of eventual products and destinations of organic reactions in the atmosphere is currently not well understood [1]. Industrial solvents and pollutants are commonly VOCs and their detection is important to ensure worker exposure safety limits [2]. Sometimes these

exposure guidelines are below the lower detectible concentration of common detection equipment [3]. In order to overcome this problem without purchasing more expensive equipment that would be potentially difficult to implement, preconcentrators have been used. Preconcentrators are exposed to streams of gas containing compounds of interest for certain lengths of time at a known flow rate and then trapped compounds can either be thermally desorbed or extracted by solvents [4]. Solid absorbent preconcentrators have been employed in a variety of situations to increase the sensitivity

U.S. Department of Energy Journal of Undergraduate Research

of common detection instruments such as for atmospheric study and health-related issues [2-6]. Another benefit that has been found is that if multiple analytes are adsorbed, various temperature programs can be used for chromatographic separation upon thermal desorption [6,7]. Tenax TA is an adsorbent polymer often used in preconcentrators to trap VOCs and its contents are thermally desorbed. Some of the benefits of Tenax TA compared to other sorbent materials are its stability at high temperatures, low water uptake in humid conditions, performs well with adsorbing VOCs in low concentrations, and its ability to be conditioned to give very low background interference in detection instruments [2].

Proton-transfer-reaction mass spectrometry (PTR-MS) has become an integral tool for studying VOCs by being capable of detecting them in low concentrations near 50 parts per trillion by volume (pptv). PTR-MS, which was developed by [8], has much literature [1,8,9] describing its methodologies and theory, so only a brief description is given here. Functionality of the PTR-MS consists of introducing a sample at 2mBar into the presence of H_3O^+ primary ions in a drift tube where the VOC is protonated if it has a proton affinity larger than that of water (165.2 kcal/mol) [8]. Once it leaves the drift tube, a linear quadrapole separates a selected mass which then collides with a secondary electron multiplier, giving a detectible signal. The utility of this type of mass spectrometry comes from relatively soft ionization and its selectiveness in what it can detect; largely only organic compounds have a greater proton affinity than water which eliminates interference from the carrier gas and most other common inorganic species found in the atmosphere. While the PTR-MS has great sensitivity, there are research areas where the required detection limits for VOC concentrations are below its detection limit. An example is very trace gas emissions from crop plants [10]. Proton transfers are also much less potent energetically than electron impact methods which results in very little fragmentation of an ionized molecule. While lack of fragmentation is useful when looking at an isolated source, it does not allow for the capability to distinguish between isobaric compounds which can be normally be done by the resulting fragmentation patterns. Because some molecules, like biogenic VOCs, share the same molecular weight, [1] points out the need for chromatographic separation prior to analysis in PTR-MS to differentiate signal contributions.

The goal of this work is to couple the preconcentrator and PTR-MS together and characterize its performance. Combining the rapid evolution of VOCs with the real-time detection capability of the PTR-MS has the potential to lower PTR-MS detection limits and help to distinguish signals between different compounds of the same molecular weight. The preconcentrator employed in this work used Tenax deposited on a nickel foam core as described [7] by a previous work. This novel setup allows for rapid, uniform heating of the Tenax allowing minimum time spread in evolution of a given VOC when heated, resulting in high preconcentration factors with near real-time response. Toluene gas solutions in nitrogen at concentrations between 50 and 1000pptv with various loading times are used to test the preconcentrative capability of a Tenax TA preconcentrator. Chromatographic trends and separation by thermal desorption are also demonstrated and discussed.

MATERIALS AND METHODS

Toluene samples were prepared by filling gas tanks with vapor generated by heating diffusion vials in a Dynacalibrator (Vici) using dry nitrogen as a carrier gas. The sample tanks were pressurized by a cylinder of ultra high pure nitrogen to approximately 100psi to provide enough sample for one run and to further dilute the toluene to a usable stock solution. Teflon permeation tubes provided another source of toluene.

The preconcentrator was fabricated according to a previous work [7] from a 12.7mm x 4.8mm x 12.7mm nickel foam core (Porvair Advanced Materials, Inc., 700 Shepherd Street, Hendersonville, NC 28792, 800-843-6105) filled with 25mg of the 60/80 mesh Tenax TA polymer (Supelco) fitted into 0.150in Inconel 600 tubing (Figure 1). The tubing containing the preconcentrator pellet was wrapped with
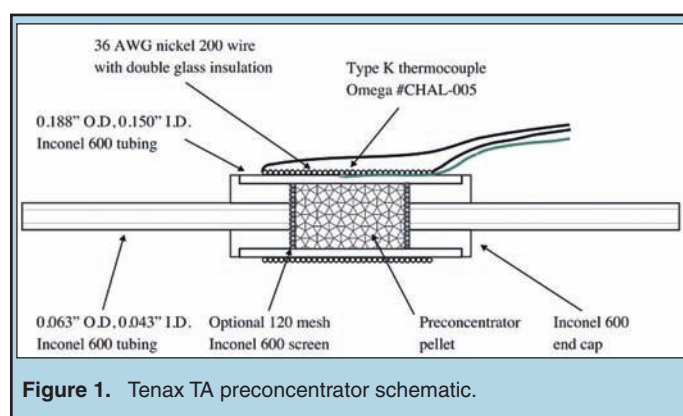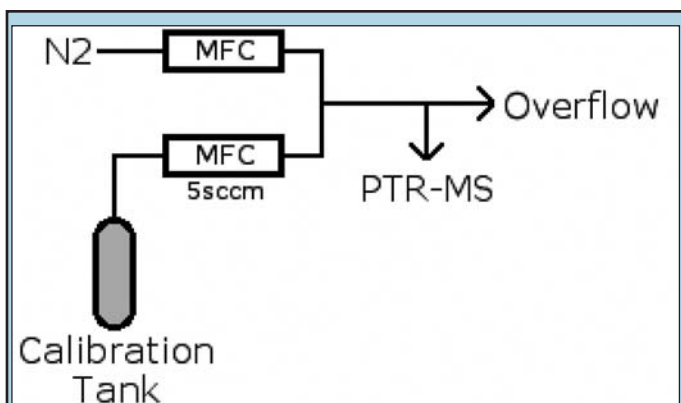

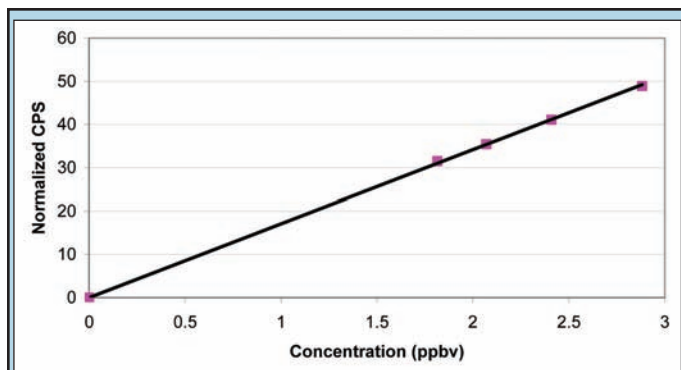**Figure 1.** Tenax TA preconcentrator schematic.

a type K thermocouple (#CHAL-005, Omega, Stamford, CT, 800-848-4286) on the inner-most layer and approximately 61cm of 36 AWG nickel 200 double glass insulated wire (Pelican Wire Company, Inc., Naples, FL, 941-597-8555) was wrapped around the outside to act as a resistive heater. The assembly was then coated with an insulating zircon-based cement and Teflon tubing was connected to the Inconel tubing. Custom LabVIEW™ software written in a previous work [7] was used to control the resistive heater.

The proton-transfer-reaction mass spectrometer (PTR-MS) was calibrated for toluene by using a gas cylinder with a standardized toluene concentration connected to a gas dilution system shown in Figure 2. The standard toluene gas was diluted with dry nitrogen gas. All gas flows were controlled with mass flow controllers and the dilution flow was varied from 800 to 200sccm in 100sccm decrements to yield different toluene concentrations. The PTR-MS settings were U_{drift} = 540V, P_{drift} = ~2.0mBar, and multiplier voltage was 3400V. Dwell time for toluene (m/z 93) was 1 second and hydronium (m/z 21) was 500 milliseconds. The resulting data was linearly regressed to an equation, as shown in Figure 3, and was used to determine toluene concentrations for the remainder of the experiment.

Flow from the sample gas tanks was regulated by a mass flow controller which could be diluted further by nitrogen flow from another mass flow controller. From the resulting diluted flow, 30sccm of it was diverted and regulated to a gas switching apparatus by a mass flow controller. The output of the switching apparatus was
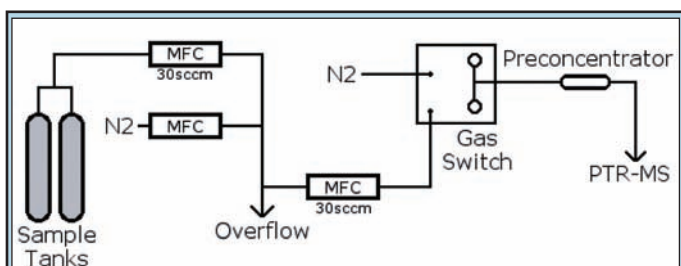
Figure 2. This is the experimental setup used to calibrate the PTR-MS for toluene. Static flow rates are indicated. MFC = mass flow controller

Figure 3. Calibration curve for toluene. The regression is forced through the origin.

thermally ramped from 25°C to 200°C linearly in 20 seconds by running electrical current through the 36 AWG heater wire. The peak temperature was held for 10 seconds before the preconcentrator was allowed to conventionally cool by aid of a cooling fan. Once the preconcentrator reached a temperature of 30°C, the thermal cycle restarted. A complete thermal cycle finished in about 150s. Thermal cycles continued until observed toluene ion count peaks were at consistent, minimal heights, then sample loading commenced on the next thermal cycle.

Toluene vapor concentrations of 56, 199, 534, and 975 parts per trillion by volume were then flowed in turn through the preconcentrator at 30sccm for loading times of 60, 150, 300, 600, and 1200 seconds. After each loading time, the thermal cycle previously described was performed with the exception that only dry nitrogen gas was flowed through the preconcentrator during the cool down process by the gas switching apparatus. Toluene ion count rates were observed by the PTR-MS during the thermal cycle with a dwell time of 1 second. This procedure was performed 5 times for loading times of 60, 150, and 300 seconds and 3 times for the loading times of 600 and 1200 seconds.

The toluene vapor source was then changed with a standard gas calibration tank that contains various gases outlined in Table 1.

Species	Protonated m/z	Concentration, ppbv	Temperature at Peak Height for 120s Ramp, °C
Methanol	33	641	58.0
Acetonitrile	42	515	73.8
Acetone	59	390	70.9
Isoprene	69	405	80.1
Methyl Vinyl Ketone Methacrolein	71	727	92.7
Methyl Ethyl Ketone	73	272	95.9
Benzene	79	362	108.5
Toluene	93	299	133.7
p-Xylene	107	232	158.9
1,2,4-Trimethylbenzene	121	215	171.5
α-Pinene	137	179	89.6

Table 1. Contents and concentrations of VOC mixture tank. Temperature and peak data is provided from a 120s ramp time.

connected to the preconcentrator, which in turn was connected to the PTR-MS. Operation of the switching apparatus was controlled by the same LabVIEW™ software [7]. The length of the tube from the preconcentrator to the PTR-MS was minimized to 3cm to retain sharp count rate peak shape during gas analysis with the PTR-MS. The setup is outlined in Figure 4. The intake flow of the PTR-MS was adjusted to 30sccm.

Figure 4. This is the experimental setup used to load the preconcentrator. Static flows rates are indicated. (MFC = mass flow controller)

Prior to starting a perconcentration loading time test for a particular toluene concentration, the sample vapor concentration was measured by the PTR-MS in the absence of the preconcentrator for 100 cycles. The preconcentrator was then reconnected in series to the PTR-MS and was thermally cycled with a dry nitrogen flow of 30sccm. During a thermal cycle, the preconcentrator was

The flow from the tank was regulated to 5sccm and the nitrogen dilution flow to 1500sccm by mass flow controllers resulting in a dilution factor of 3.3%. The same cleaning procedure used prior to running the tests for varied loading times was carried out. The same loading and thermal cycle sequence previously performed was used with the exceptions that the loading time remained constant at 300 seconds and the thermal ramping time was varied to 20, 40, 60, 90, and 120 seconds. During the thermal ramping process all organic species' count rates were monitored simultaneously by the PTR-MS with a dwell time of 100 milliseconds.

RESULTS

Data points acquired during the calibration phase for each dilution were recorded and averaged (arithmetic mean) over the 50 cycles. Toluene count rates were normalized to 1,000,000 H_3O^+ count rates averaged (arithmetic mean) over the same cycles. The resulting normalized ion counts per second were plotted and linearly regressed against toluene concentration, resulting in the equation displayed in Figure 2. The concentrations of toluene for the samples used in this work were determined from this regressed formula.

Count rate peak areas obtained from thermal ramping of the preconcentrator were obtained by numerically integrating over 6 points using the trapezoid method. The selected points for the peak started 2 data points before the highest recorded count rate for that particular run. The average time integrated for each peak was approximately 8.2 seconds. All peaks belonging to the same toluene concentration and loading time were averaged (arithmetic mean). This process was used for determining the areas of all peaks in this work. Peak areas were divided by the interval of time over which they were measured to calculate integrated ion counts per second.

Table 2 compares the preconcentration factors of toluene for peak height and normalized integrated ion count rate methods

	60s Loading		150s Loading		300s Loading		600s Loading		1200s Loading	
	NICPS	Height	NICPS	Height	NICPS	Height	NICPS	Height	NICPS	Height
56pptv	11	16	17	27	30	51	58	102	113	189
199pptv	8	14	16	27	25	46	54	101	92	157
534pptv	10	16	21	34	38	63	69	118	132	242
975pptv	10	17	21	35	39	65	78	151	148	257

Table 2. Comparison of preconcentration factors of ICPS and ion peak height calculation methods for the loading times and concentrations used. NICPS = Normalized Integrated Counts Per Second

calculated by dividing either the normalized integrated counts per second or normalized peak heights by the original normalized ion count rate. Mean peak heights from the same concentration and preconcentration time are used in this calculation.

Figure 5 is a compressed time plot of the peaks recorded from a 20s thermal ramp with a 150s loading time at 56pptv. The deviation of peak heights in the figure is due to small variations in peak width. The true measure of reproducibility is integrated peak area as discussed later. Temperature is included in the graph for reference.

Figure 6 is a composite that demonstrates typical variation of ion count peaks with different loading times for the same concentration (56pptv). Time between the peaks is compressed.

The integrated ion count rates from each loading time belonging to the same toluene concentration were plotted against the respective loading time. This plot was then linearly regressed to demonstrate the relationship between integrated ion count rates and loading times. A graph of all concentrations is shown in Figure 7. In a similar manner, Figure 8 shows the linear correlation between toluene concentration and integrated ion count rates for each loading time.

Table 1 is a list of the contents and concentrations of the gas mixture used to test the chromatographic ability of the
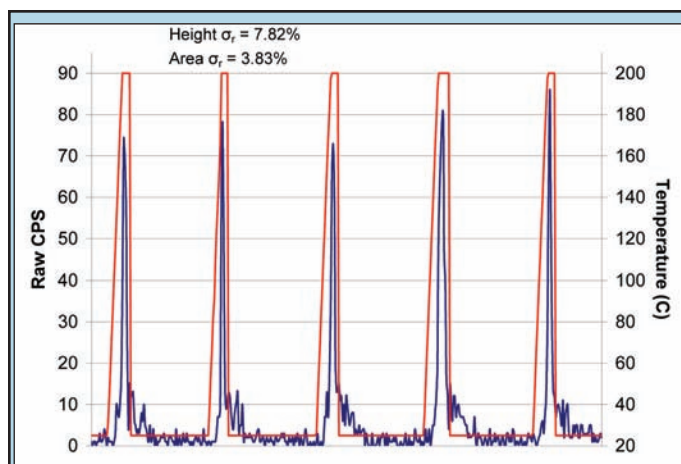
Figure 5. Demonstration of repeatability. Toluene peaks resulting from 20s thermal desorption from 150s of loading time at 56pptv are in blue. Target temperature for the thermal ramps is shown in red. Time between the peaks is condensed for greater peak detail. Relative standard deviations are shown for peak areas and heights.
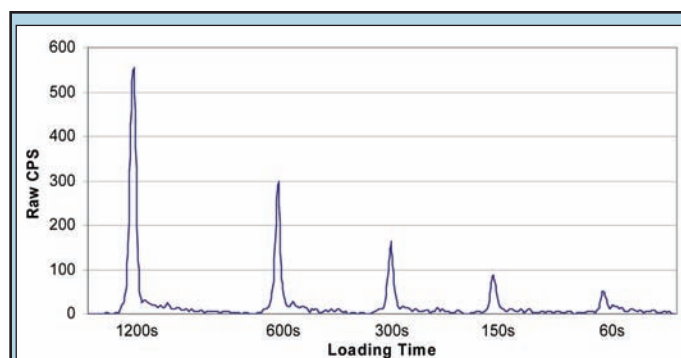

Figure 6. Composite of typical desorption peaks from indicated loading times at 56pptv. Thermal ramp time is 20s. Time between the shown peaks was compressed for better peak clarity.
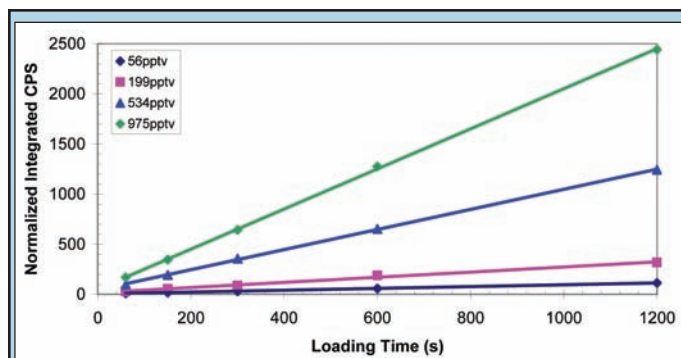

Figure 7. Linear regression of normalized, integrated CPS (counts per second) of toluene against preconcentrator loading times for the toluene concentrations used.

preconcentrator. The temperature at which each compound had its maximum ion count rate from the 120s ramp is provided to show the order of desorption for the various compounds.

Figures 9 and 10 show the behavior and comparison of the organic species described in Table 2 when different thermal ramp times are performed. The count rate for each data point was
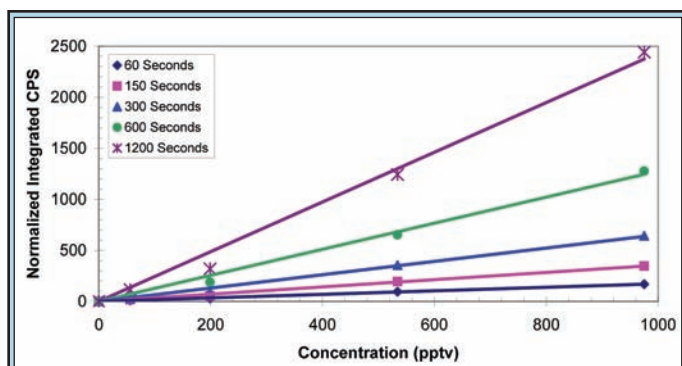
Figure 8. Linear regression of normalized, integrated CPS (counts per second) of toluene against the concentrations used for each preconcentrator loading time. The regressions are forced through the origin.
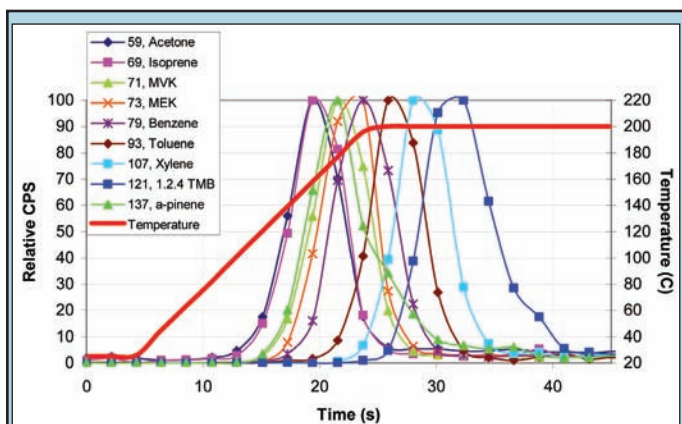
Figure 9. Time and temperature of peak separations for listed organic species over a 20s thermal ramp. Peaks are normalized to their maximum height. MVK = methyl vinyl ketone, MEK = methyl ethyl ketone, 1.2.4 TMB = 1,2,4-trimethylbenzene.
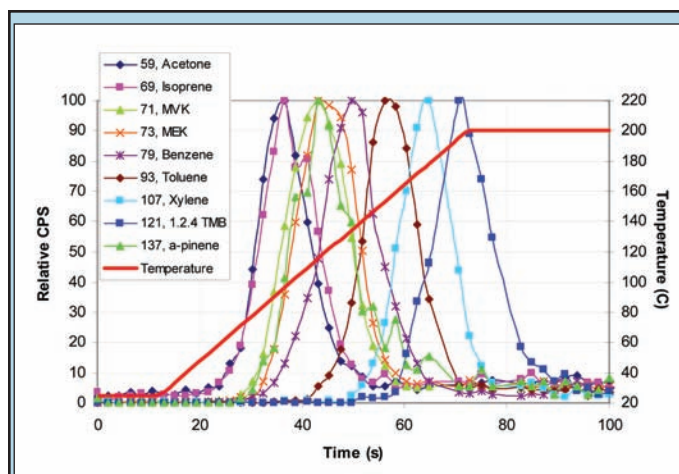
Figure 10. Time and temperature of peak separations for listed organic species of a 60s thermal ramp. Peaks are normalized to their maximum height. MVK = methyl vinyl ketone, MEK = methyl ethyl ketone, 1.2.4 TMB = 1,2,4-trimethylbenzene
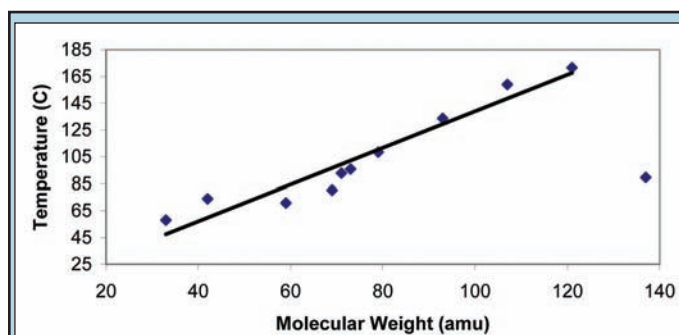
Figure 11. Temperature at maximum count rate height against molecular weight. A line is regressed to show a trend. Mass 137 (α-pinene) exhibits atypical behavior and was excluded in the calculation of the trend line.

normalized to the maximum value recorded for that specie for that run. The temperature line is included for reference.

Data taken from the 120s ramp was taken to plot molecular weight against the temperature at which each VOC had its maximum count rate and is shown in Figure 11. A linear regression was done to show the observed relationship between molecular weight and temperature at peak height.

DISCUSSION AND CONCLUSIONS

Current PTR-MS instruments are able to detect some VOCs with a lower limit of approximately 50pptv. This detection limit can be improved when a preconcentrator is used to collect a sample VOC over a brief collection time and then desorb the analyte to the PTR-MS in a short time. Our results showed that a preconcentrator can successfully increase the lower sensitivity of a PTR-MS by 2 orders of magnitude with a 1200s loading time. With the smallest concentration at the shortest loading time tested (56pptv at 60s), we increased the signal from 0.996 normalized counts per second to 10 normalized integrated counts per second, an amplification by a factor of 11.

Calibration of the PTR-MS was done with a standardized mixture gas tank and diluted with nitrogen by mass flow controllers.

Proton transfer efficiencies for toluene were not accounted for in this calibration because another work showed that such considerations ultimately integrate themselves into the calibration curve when standardized gases are used [9].

The data presented in Figure 5 demonstrates the repeatability of the desorption peaks for a set loading time and toluene concentration. The peaks slightly vary in heights due to the time resolution of the PTR-MS. Due to this limitation, we chose to take data from the peaks by numerically integrating their area using a trapezoidal method rather than ratios of peak height and width. Further justification for integrating can be found in the standard deviations for the particular series in Figure 5; the standard deviations for the peak area and peak heights were 3.83% and 7.82%, respectively. The consistent temperature of thermal desorption is also observed in the figure. Peak tails were observed after each thermal desorption which can clearly be seen in Figures 5 and 6. This phenomenon is noted in another work [7].

Integrating over the peaks also reduces the calculated preconcentration factors by averaging over the entire range of concentrations emitted during heating. Table 2 compares the preconcentration factors for normalized peak height and normalized integrated ion count rate methods. Recent developments [12]

improving the time resolution of PTR-MS can eliminate the need for peak integration allowing full utilization of preconcentrator capability. With a preconcentration time of 1200s, the detection limits are improved from about 50pptv to nearly 250 parts per quadrillion.

Behavior of the preconcentrator is found to be very linear with respect to varying loading times at constant concentrations or toluene concentrations at constant loading times as shown in Figures 7 and 8. This dual linear behavior demonstrates the potential utility of the preconcentrator-PTR-MS combination in real-world applications. Figure 8, which indicates that for any of the loading times shown, it is possible to determine the concentration of a sample by its integrated ion count rate. However, because both figures show a linear trend, it is possible to determine the concentration of a sample by its integrated count rate with any 2 loading times by plotting the slopes of the regressions in Figure 7 against their concentrations and use that regression to determine the concentration by the slope between the 2 arbitrary loading times. This linearity is presumed to hold true for the low toluene concentrations and loading times here as the total accumulation of toluene in the Tenax is far below its saturation point.

The resulting peaks as seen in Figure 9 demonstrate two important analytical capabilities of the preconcentrator. The mean time from the beginning of the thermal ramp to the time of toluene's maximum peak height was 22s for any thermal desorption peak with a 20s ramp time. In the presence of various other organic species, the time from the beginning of the thermal ramp to toluene's peak height in Figure 9 was 21.6s. The difference of 0.4s can be attributed to the time resolution of the sampling rate of the PTR-MS, which was about 2s per cycle. The close relationship of these times indicate that the temperature of desorption of an analyte is unaffected by the presence of other molecules in the Tenax preconcentrator. The chromatographic property of the preconcentrator can be seen in both Figures 9 and 10. The difference in these plots show that the slower the temperature is increased, the greater the resolving power between the peaks. This observation supports the findings of another work [7]. However our results show that as the thermal ramp time is increased, the peaks become consistently shorter and wider at the base. Temperatures determined to correspond with maximum peak height for a particular species should be only taken as an approximation as there is a short time delay for the gas to travel from the preconcentrator to the drift tube of the PTR-MS. Longer ramp times yield more accurate temperatures at maximum thermal desorption as it makes the delay less significant. An attempt was made to reduce the length of the tubing between the preconcentrator and the PTR-MS in the experimental setup as much as possible to minimize this time delay and peak widening.

It is of interest to note the order in which each of the organic species desorbed from the preconcentrator. The plot shown in Figure 11 shows a linear trend of increasing maximum desorption temperature with molecular weight. These results differ from another work [6] which show order of thermal desorption is greatly influenced by boiling points rather than molecular weight. However α-pinene (m/z 137) distinctly deviates from this linear relationship found in the figure. It is because of this deviance that the utility exists to allow separation of certain chemical compounds of the same molecular weight. The light weight organic species methanol and acetonitrile broke though the preconcentrator easily and did not show distinct peaks upon thermal desorption. This is consistent with the behavior of Tenax TA described elsewhere [4]. Further investigations will be necessary to study the mechanism of thermal desorption in Tenax TA to determine the order of elution among a set of VOC analytes.

The results of this work show that a Tenax TA preconcentrator can be used to extend the lower detection limits of a PTR-MS while giving it the advantage to chromatographic separation of analytes. Another benefit of this type of preconcentrator is its ability to reduce water vapor in a sample. Other works [9,11] have shown that humidity effects can water clusters to form in the drift tube which hinder proton transmission rates to aromatic hydrocarbons like toluene. Although this experiment was performed in dry nitrogen gas, a Tenax preconcentrator could help alleviate some of this problem where sampling conditions contain humidity since it is fairly hydrophobic [2] and would not adsorb water with the VOCs of interest contained within the sample stream. Samples could then could be purged with a dry gas like nitrogen when desorption into the PTR-MS occurs to avoid sensitivity issues.

Further investigations into the characterization of other types of preconcentrators with PTR-MS would be beneficial to help determine which preconcentrator technology would be best suited for a particular task. Studies should not only include their capacitive capabilities for certain compounds but also chromatographic behaviors. Like gas chromatograph columns, different preconcentrators may resolve some types of organic species' peaks better than others. The improvements in sensitivity and chromatographic ability to resolve peaks demonstrated in this work can potentially open up a greater number of applications for detecting time-resolved ultra-trace gas emissions by PTR-MS.

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