

**A Technology for Real-Time Monitoring of VOCs Emanating from the Hanford Tank Farms
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ABSTRACT

This study determined the viability of using Proton Transfer Reaction Mass Spectrometry (PTR-MS) as a real-time measurement technique for Compounds of Potential Concern (COPCs) that may emanate from nuclear waste tanks in the Hanford Tank Farms and that can impact worker health and environmental safety. The tests were performed on 58 volatiles and mixtures expected in the tanks, including amines & nitrosamines, furans, nitriles, aromatics, alcohols & ketones, and carbonyls, under simulated tank conditions sampled through PFC tubing up to 100 feet to reflect the field conditions of a mobile unit. These tests determined the performance efficiencies, detection limits, analytical speed, memory effects and logistical necessities of PTR-MS in tank field applications using a mobile laboratory. Results showed response times were excellent (seconds) and that losses and memory effects were negligible for most COPCs ($<<1\%$ and seconds, respectively). The only exception was dimethylamine which showed clearing times up to 45 min. Detection limits for most compounds were in the ppt_v range. High concentrations of ammonia did not affect the results appreciably, and large rapid variations in concentrations over several orders of magnitude were easily captured in seconds. Humidity effects on chlorinated compounds and formaldehyde were accommodated with a special drying system developed for this instrument. A traditional GC-MS was also mounted in the mobile laboratory for confirmatory and regulatory completeness. The PTR-MS fits under the protocols of ASTM D5314-92.

INTRODUCTION

Proton Transfer Reaction Mass Spectrometry (PTR-MS) was commercialized in 1998 by Lindinger and Mark [1]. Since that time it has been utilized in the measurement of a wide range of volatile organic compounds (VOCs) originating from sources encompassing foods and beverages, industrial hygiene, environmental, agricultural, medical, explosives, chemical warfare agents, atmospheric research, and litigation support [2-12]. The instrument can be operated in either a fixed laboratory configuration or mounted in a mobile unit for remote real time measurements. Unlike many of the portable devices used for real time measurements, the PTR-MS simultaneously delivers high sensitivity (ppt_v), high specificity (specific mass detection), wide dynamic range (10^6), and high stability.

The sensitivity provided by this mass spectrometer configuration is a result of the relatively low energy, highly efficient gas phase chemical ionization reactions that result in protonation of the VOC. Typical ionization efficiencies at 2 millibar pressure [13,14] are on the order of 10% of the neutral density of a given compound, yielding high abundances of the $[M+H]^+$ pseudo-molecular ion with minimal fragmentation. In comparison, a conventional, well-designed electron ionization source has an ionization efficiency of approximately 1:10,000 and is a function of ion source design and electron ionization cross section.

The linear dynamic range of PTR-MS spans 6 orders of magnitude from its detection limit at low parts per trillion volume (pptv) to the low to mid-parts per million volume (ppmv). The upper range of detection is limited by the concentration of precursor reagent ions available for reaction and multiplier saturation. High levels of VOCs beyond the linear dynamic range may be quantified accurately by using appropriate dilution techniques in real-time or altering experimental conditions.

METHODS

The PTR-MS instrument incorporates a drift tube reaction chamber that operates at approximately 2 mbar. The mass spectrometer is either a quadrupole or time-of-flight mass analyzer. In this study, we used a quadrupole mass spectrometer with high sensitivity ion optics that is optimal for the tank waste volatiles. The drift tube is operated at a fixed reduced electric field (E) to facilitate the movement of the ions through the system. Typical field strength to buffer gas number density (N) in the drift tube is 100-130 Td ($1 \text{ Td} = 10^{-17} \text{ V cm}^2$). Generally, reactions of H_3O^+ at 2 mbar pressure will have a tendency to produce water clusters, predominantly the $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$ species. This narrow range of Td minimizes protonated water cluster formation, limits fragmentation of the protonated molecular species due to collisional events, and provides sufficient reaction time to maximize sensitivity.

The schematic of the instrument is shown in Figure 1. Important to the operation of the instrument is the ion source region. This ion source, in comparison to the conventional EI ion source, is used for the production of reagent ions used in the reactions in the drift tube rather than ionization of the target compounds of interest.

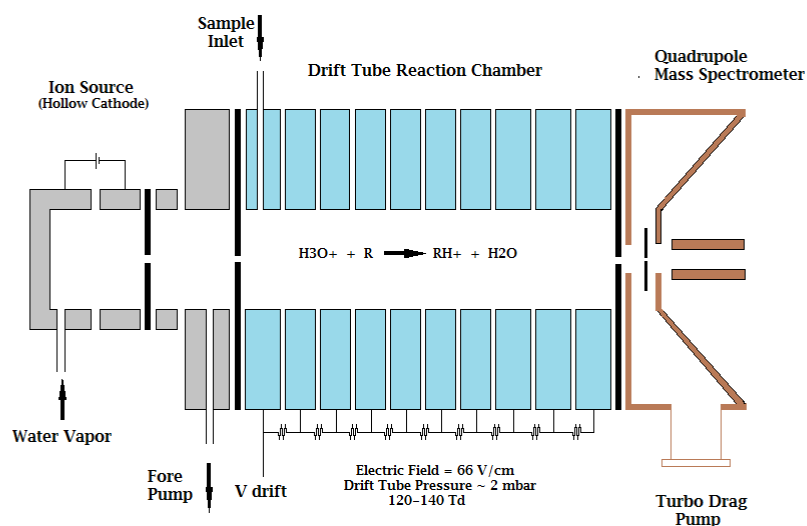
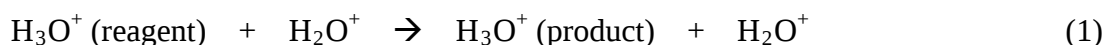


Fig. 1. A schematic representation of the Proton Transfer Reaction Mass Spectrometer.

It is important to note that reagent ion formation and protonation of the VOC occur in two physically separate zones of the instrument. A controlled flow of water vapor enters a cold

cathode discharge cell where ionization of the water initially forms a variety of species including H_2O^+ , OH^+ , O^+ , and H_2^+ . The products of the cold cathode discharge enter an intermediate reduced pressure zone where the ion population comes to a steady state equilibrium with the ultimate formation of predominantly H_3O^+ ions and H_2O . These terminal reagent ions are drawn into the drift tube where they react with the VOC. The bulk air sample containing the VOC is introduced at the high field end of the drift tube. The entire drift tube length then becomes a reaction chamber for production of desired ion signal. The resulting product ions pass through the ion optics and are focused into the mass analyzer. The instrument can be operated in full scan or single ion monitoring mode. Generally, to maximize sensitivity, the instrument is operated in single ion monitoring mode with ion dwell times ranging from 100 milliseconds to 5 seconds. The instrument has excellent stability allowing continuous data collection for days at a time.

The proton transfer ion chemistry in the drift tube between H_3O^+ and a VOC must be exothermic; that is, the VOC must have a proton affinity higher than that of water (698 kJ/mol). Hundreds of compounds of interest meet this requirement, particularly constituents potentially in the head space of the Hanford tanks. Most importantly, the main constituents of air such as nitrogen, oxygen, argon, carbon dioxide, and the aliphatic hydrocarbons have proton affinities less than that of water. These species do not react and are not observed in the resulting background. Water vapor, a significant concentration in background air, will react with the reagent ion according to:



As seen from the reaction, there is no net loss of reagent ion from the drift tube, therefore, high sensitivity is maintained.

In principle, the instrument requires no calibration to deliver quantitative data. VOC concentration can be determined directly from the measurement of the reagent ion intensity and the intensity of the product ion according to the following:



$$[\text{R}_i] = \frac{[\text{RH}^+]}{k_i t [\text{H}_3\text{O}^+]}$$

where:

$[\text{RH}]^+$ = count rate of the protonated species

$[\text{H}_3\text{O}]^+$ = count rate of the reagent ion

k_i = reaction rate constant; ~ 1.5 to $4 \times 10^{-9} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$

t = reaction time; $105 \times 10^{-6} \text{ s}$

In actual practice, to insure strict adherence to quality assurance/quality control practices, the instrument is calibrated for each VOC of interest using a 5 point calibration curve with the incorporation of reagent blanks, and periodic laboratory control samples to verify operational stability. Several comparison studies between PTR-MS results and GC or light based methods have shown excellent agreement, with errors less than 20% [3,15,16].

Alternative reagent ions can be formed in the cold cathode discharge for the analysis of those compounds that have proton affinities less than water. The two most common alternate ions are NO^+ and O_2^+ . The predominant reaction is charge-exchange between the reagent ion and the compound of interest.



The driving energetics of the reaction is the difference in ionization potential between NO and R. The larger the difference in ionization potential, the more energy transferred to the product ion, generally resulting in increased fragmentation of the molecular ion. This in turn may result in lower sensitivity and an increase in non-specific ions in the spectrum where multiple compounds are being analyzed simultaneously. But the number and type of VOCs that can be observed using NO^+ is greatly increased and will include the alkanes, alkenes, CO_2 , CO, SO_2 , and N_2O .

DISCUSSION

A PTR-MS can be mounted in a mobile unit and driven to a remote site, like the tanks farms. The Mobile Organic Monitoring Lab designed and built for tank emission monitoring is shown in Figure 2 and has both a PTR-MS and a conventional GC-MS that can accept summa canisters and TDU or charcoal tubes. Samples can be obtained with a Summa canister, taken to the mobile lab and immediately analyzed on the PTR-MS as well as the GC-MS. This is an effective way of performing sample analysis but still falls within the realm of separate sample collection followed by separate sample analysis. The preferred mode of operation is to incorporate an integrated approach to the process. The PTR-MS can achieve this objective.

Our group has been evaluating the use of long sample transport lines that will permit the collection of a sample at some distance (100 to 200 ft) from the PTR-MS. The sample is pumped from the source directly to the instrument drift tube where it is analyzed. For field monitoring or for monitoring inside buildings and structures, the end of the sampling line can be walked in all directions, observing and recording the level of VOCs in the ambient air in real time,. The sampling operator can carry an electronic notepad coupled to the instrument computer system, as well as a GPS system, which displays the VOC signal from the instrument in real time to allow immediate feedback regarding the sampling event and location.

Critical to this approach is understanding the various transport properties of VOCs through a long sampling line. Parameters for evaluation include VOC loss in the transport line (adsorption effects), purging efficiency of the transport line (memory effects), and actual transport time of the VOC from the source to the instrument. Actual transport time can be readily calculated from the tube diameter, the liters of gas pumped per minute by the system, and the length of the tube. Alternatively, measurements can be made in real time by introducing a source standard into the sampling end of the line and monitoring the time required for a signal response.

We evaluated these three parameters on VOC constituents of most concern in tank emissions using an experimental set-up shown in Figure 3. Perfluoroalkoxy fluoropolymer (PFA) is a suitable material for the sample transport tube because of its inertness to a wide range of organic compounds. For this study, neat samples were introduced with a syringe pump at controlled rates and mixed with a large volume of nitrogen gas.



Fig. 2. The Mobile Organic Monitoring Lab featuring a Proton Transfer Reaction Mass Spectrometer (lower left) and a GC-MS with summa can and TDU tube capabilities.

The sample was further diluted with ambient air pumped to the instrument at a known flow rate. Various lengths and diameters of tubing were evaluated with this process. In addition, a Summa canister standard was prepared and introduced to the transport line at a known rate using a mass flow controller. This particularly useful for evaluating long narrow diameter tubing as would be used in the field. Ion signals were monitored at the PTR-MS while experimental conditions were evaluated.

Longitudinal dispersion of the sample in a transport line would result in decreased certainty in assigning changes in signal to concentration gradients within a structure. It is, therefore, important to maintain high linear velocities through the tube to minimize longitudinal dispersion. Typical velocities in our system are in the order of 4-7 meters per second. Compounds chosen for these experiments were those expected to show some adsorption affinity on surfaces. The data in the following experiments were obtained at approximately 22°C.

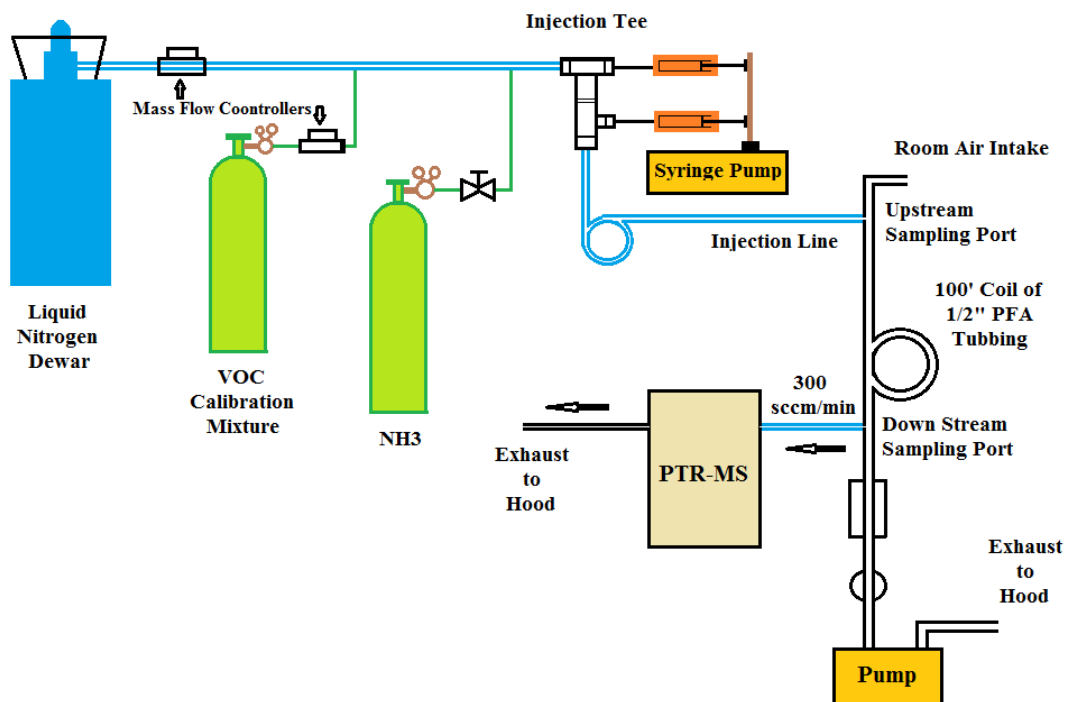


Fig. 3. The experimental setup for the evaluation of VOC response times, memory effects, and decay constants in sample transport tubes. The injection line can be moved from the upstream sampling port to the downstream sampling port to determine potential VOC losses in the tubes.

In Figure 4, hexanenitrile was used to evaluate the effects of compound loss through a 100 foot tube. The sample source was placed at the upstream end of the tube, the signal was monitored for a period of time, and then the source was removed and placed directly at the entrance to the PTR-MS. As observed, there is relatively little change in signal intensity, therefore, little compound was lost as a result of its transport through the tube.

The result of the evaluation of the onset of signal response with sample concentration changes is given in Figure 5. There is a sharp change in signal associated with the introduction of the sample through a 100-ft (30-meter) PFA tube (.376" (1 cm) i.d.). Initially, N-nitrosodimethylamine was introduced at a constant rate equivalent to 1 ppbv. The initial two dips in the signal are the result of moving the syringe pump away from the introduction line to simulate a rapid change in VOC source concentration followed by reintroduction of the source. Note that the time required for the signal change is a single cycle of the mass spectrometer as noted by the single data point between the elevated signal and baseline, approximately 5 seconds. The large signal in the middle of the figure is the result of increasing the flow of the syringe pump 10 fold, thus the more gradual increase in concentration. There is a corresponding 10 fold increase in signal intensity which is repeated by the final measurement. The higher concentration signal provides the opportunity to measure the time constant of the memory effect of various VOCs. The memory effect is essentially the time required to fully evacuate the tube between samples for a given VOC.

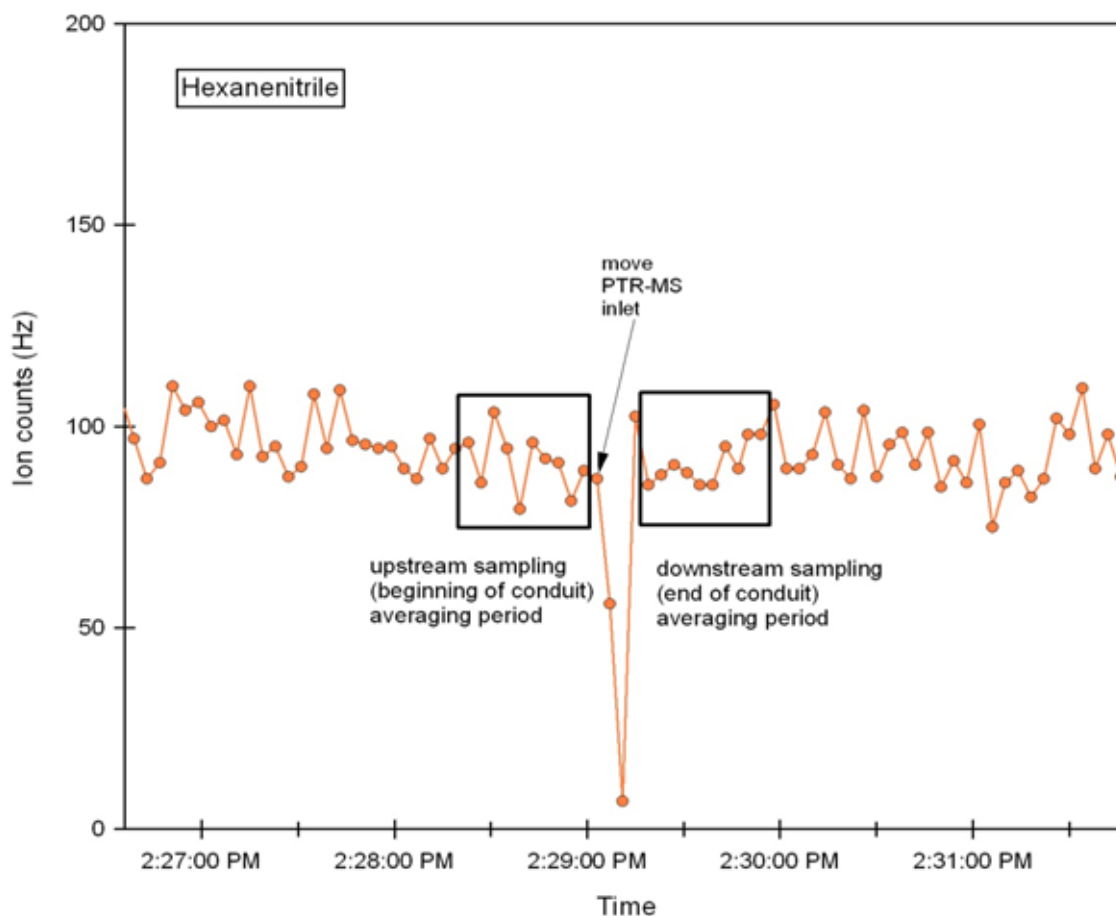


Fig. 4. An example of the determination of potential losses due to adsorption effect for hexanenitrile. The sample injection line was moved from the upstream sampling port to the downstream sampling port. The signal remains the same indicating that there are minimal losses. The concentration of hexanenitrile is approximately 1 ppbv.

Memory effects are expected to vary somewhat between compounds due to the differences in interactions with the surface of the tube material. It is also expected to be exponential (1st order kinetics). Knowledge of the memory effect is an important parameter for determining the temporal resolution required for obtaining and utilizing data from different samples. Ideally, memory effects will not change with concentration. If they do, then signal decay time constants would need to be determined for each compound at various concentrations.

Figure 5 shows the memory effect of a 10 ppbv concentration of N-nitrosodimethylamine (the two large signals in the figure). Note that there is minimal retention effect as the concentration decays toward the baseline. The data in the curve can be used to establish decay constants for all compounds. In this case, the constant for N-nitrosodimethylamine is approximately 25 seconds. It is noteworthy that 90% of the signal is lost within 2 instrument data cycles. Decay constants are readily calculated from the last 10% of the measured response shown on the tailing edge of the signal.

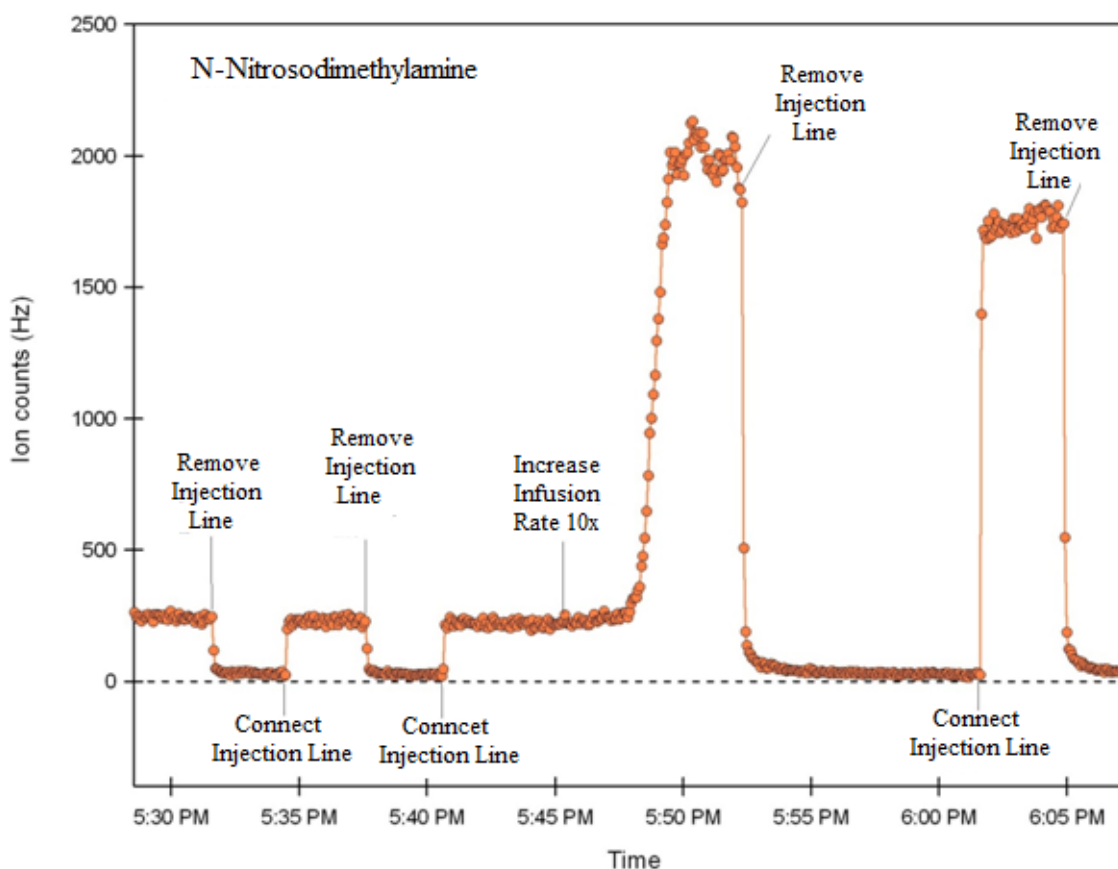


Fig. 5. Reproducibility and concentration variations for 1 ppbv of N-Nitrosodimethylamine through a ½" 100' PFA tube. The first two dips in the signal show the rapid loss and onset of signal when the sample source is removed from the upstream injection port shown in Figure 2. The large signal in the center of the figure is from the 10 fold increase in the infusion rate from the syringe pump. Decay constants are determined from the tailing edge of the signal when the sample injection line is removed from the system.

The decay constant for relatively surface inert compounds such as benzene, toluene, xylenes, PCE, and TCE are all nearly the same at approximately 18 seconds. Dimethylamine, a compound that is known to be highly surface active, has a decay constant of 1170 seconds. In general, compounds with similar functional groups and structure have similar decay constants. The theoretical decay constant is approximately 5 seconds, based on a 1st order kinetic response, for purging the tube under this particular set of experimental conditions.

From the results presented here, most compounds are expected to show some loss to the walls of the tube with initial transport through the tube. After a short period of time, it is expected that the observed concentration will come to a steady state representative of the concentration at the source. This is observed in both Figures 5 and 6. Table I lists the decay constants of several compounds representing several different chemical classifications of importance to the tank farms.

Figure 6a shows the steady state measurements of approximately 400 pptv of 2,5-dimethylfuran from the infusion system in Figure 3. Attempts to measure decay constants at these low levels becomes problematic due to diminished signal strength. The visual appearance of Figure 6a would suggest that the decay constant is faster than what is observed at higher concentration. In reality, the apparent fast decay is more a function of trying to measure the signal near its experimental detection limit. Figure 6b shows the improved response after optimization of experimental parameters by reducing the number of ions monitored to a single ion specific to 2,5-dimethylfuran and increasing its dwell time to improve the signal-to-noise. The result was a significant improvement of the response factor for this compound. At these low levels, the decay constant is essentially the same as observed at higher concentrations.

The decay constant can also be used to estimate the time required for a measured signal to come to equilibrium after a concentration change or moving a line from one location to another. The time constant for achieving a steady state measurement should be similar to the time constant for signal loss with removal of the VOC source. Fixed location measurements of concentration should always be taken.

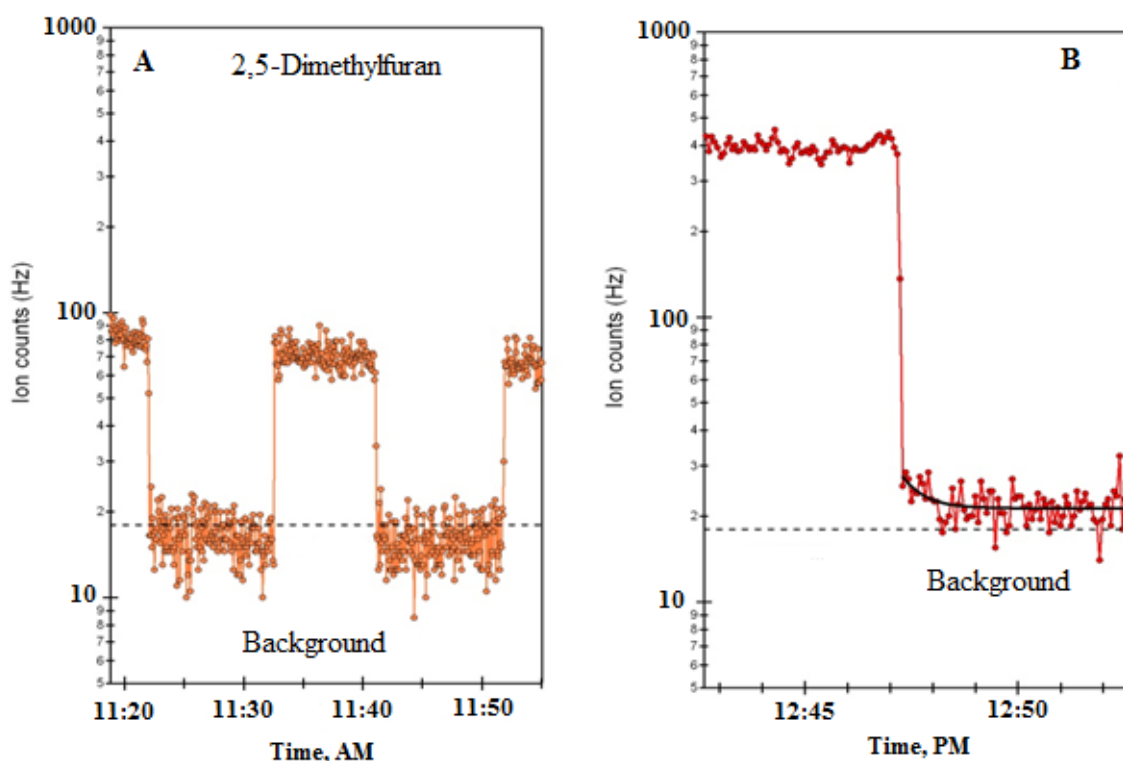


Fig. 6. (a) The steady state measurements of approximately 400 pptv of 2,5-Dimethylfuran from the infusion system in Figure 2. In (b), the experiment has been modified to improve signal stability to better define the decay slope. This also resulted in an increase in sensitivity. At these low levels, the decay constant is fast and approaches the expected theoretical 1st order kinetic response for the purging of the tube.

TABLE I. Measured signal decay time constants for approximately 10 ppbv concentration in a 0.376" i.d. 100' PFA tube at a flow of 25 liters per minute.

Compound	Decay Time Constant (sec)		Compound	Decay Time Constant (sec)
Nitrosamines			Aromatics	
N-nitrosodimethylamine	25 ± 2		benzene	18 ± 7
N-nitrosodiethylamine	31 ± 4		pyridine	200 ± 6
N-nitrosodipropylamine	96 ± 5			
N-nitrosopyrrolidine	109 ± 5		Alcohols & Ketones	
N-nitrosopiperidine	51 ± 3		2-hexanone	50 ± 11
			4-methyl-2-hexanone	25 ± 5
Furans			Nitriles	
furan	NA		butanenitrile	47 ± 2
2,5-dimethylfuran	30 ± 16		hexanenitrile	31 ± 2
2-pentylfuran	20 ± 4			
Amines				
dimethylamine	1170 ± 370			

CONCLUSIONS

Proton Transfer Reaction Mass Spectrometry (PTR-MS) is ideally suited to real-time measurements of volatile organic compounds in waste tanks such as at the Hanford site, as well as for groundwater releases into the vadose zone, building vapor intrusion from soils, and above ground vapor releases. In PTR-MS, a proton transfers from H_3O^+ to gas-phase organic compounds with a proton affinity greater than water such as acetone or BTEX. The protonation is soft and fragmentation is infrequent. There are no reactions with the primary components of air, such as N_2 , O_2 , Ar, and CO_2 , so interferences are less common and detection limits are in the mid to low parts per trillion by volume. Air samples are introduced directly into the instrument with no need of a carrier gas or dilutions. Long sampling lines can be used to transport the sample from the source to the instrument with no sensitivity loss, a critical capability in tank farm and other hazardous situations.

This study demonstrated excellent performance with respect to the dozens of volatiles expected in the Hanford tanks, including amines & nitrosamines, furans, nitriles, aromatics, alcohols & ketones, and carbonyls, under simulated tank conditions sampled through PFC tubing up to 100 feet to reflect the field conditions of a mobile unit and optimized for worker safety at the site. These tests determined the performance efficiencies, detection limits, analytical speed, memory

effects and logistical necessities of PTR-MS in tank field applications using a mobile laboratory.

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