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Short communication

Part per quadrillion quantitation of pentaerythritol tetranitrate vapor using online sampling gas chromatography–mass spectrometry

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ABSTRACT

The development of an online sampling method using programmable temperature vaporization gas chromatography with a mass spectrometer detector (PTV-GC/MS) for the analysis of trace pentaerythritol tetranitrate (PETN) vapor is presented. PETN degradation was minimized by optimizing the temperature and flow rates of the vapor sampling infrastructure. Validation of the online method was done using a previously published technique, vapor sampling with Tenax-TA thermal desorption tubes followed by analysis with a thermal desorption system coupled to a programmable temperature vaporization gas chromatograph with a micro-electron capture detector (TDS-PTV-GC/ μ ECD). Trace PETN vapor was generated using state-of-the-art instrumentation known as the TESTbed, located at the US Naval Research Laboratory. For PETN vapor concentrations in the parts per trillion_{volume} (ppt_v) range, quantitative results from the TDS-PTV-GC/ μ ECD consistently showed concentrations approximately double that measured by the online PTV-GC/MS method, indicating that sample loss due to additional exposure to the vapor sampling infrastructure occurs when using online sampling. Further utilization of the online PTV-GC/MS system allowed for the quantitation/semi-quantitation of PETN vapor concentrations as low as 260 parts per quadrillion_{volume} (ppq_v) with only 10 min of sampling time.

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1. Introduction

The effort to make security checkpoints around the world safer, more effective, and less intrusive has brought about the push to develop new technology for sensitive and selective trace explosives vapor detection. In the past two decades, the collaboration between government and academia has led to innovative instrumentation and sensors being developed that are capable of accomplishing this task [1–5]. However, in addition to the development of this new technology, it is equally important to be able to reliably generate, deliver, and validate trace vapor concentrations of analytes being sampled by these instruments [6]. Work at the US Naval Research Laboratory has brought about new analytical instrumentation designed specifically to accomplish such a task. The TESTbed couples a pneumatically modulated liquid delivery system (PMLDS) to a dual vapor delivery manifold which is housed in a custom oven. The dual manifold allows for dedicated analyte and clean air lines and can deliver a uniform, humidified vapor to six sampling ports,

simultaneously. For a complete review of the TESTbed the reader is directed to Collins et al. [7].

Pentaerythritol tetranitrate (PETN) is a military explosive that has been used in improvised explosive devices (IEDs) and is difficult to detect [8–10]. These difficulties stem from the fact that PETN has a low vapor pressure and is thermally labile, which makes it non-ideal for traditional vapor detection techniques that involve heated components to both keep analytes in the vapor phase and increase analyte mobility through the system. Only recently was work published that describes a method for analysis of PETN vapor using a thermal desorption system programmable temperature vaporization gas chromatograph with a micro-electron capture detector (TDS-PTV-GC/ μ ECD) with minimal thermal degradation [11]. This technique involves vapor sampling with sorbent filled sampling tubes, which the PETN is thermally desorbed from and collected on a cryogenically cooled inlet before entering the GC column. Prior to this, standard practice for trace PETN analysis was solvent extraction from a solid matrix followed by analysis with high performance liquid chromatography [12].

Previous work described a method to separate and detect trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX) using an online PTV inlet on a GC/MS for the purpose of rapidly validating the concentration of vapors generated with the TESTbed [13].

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Using online sampling, TNT and RDX vapor concentrations at the ppq_v level can be quantified with only 1–2 min of sampling time compared to more than 4 h of sampling time required for the sorbent tubes. Additionally, the online method offers greater precision over the sorbent tubes due to lower chemical background noise and a more uniform desorption process. The purpose of this work is to optimize an online sampling method for the quantitation of PETN vapor being generated by the TESTbed. Validation of this method is done through a comparative study between online PTV-GC/MS and TDS-PTV-GC/μECD. Through use of online sampling, trace PETN vapor concentrations in the ppq_v range can be quantified.

2. Experimental

2.1. PETN vapor generation

PETN solutions for vapor generation were prepared using a 10 mg mL⁻¹ standard solution in organic solvent purchased from AccuStandard, Inc. (New Haven, CT, USA). An aliquot of standard solution was deposited in a 50 mL centrifuge tube and the solvent was allowed to evaporate. The remaining PETN was then reconstituted in 18 MΩ Milli-Q water. To generate a steady vapor stream of PETN, the aqueous solution was sprayed using a PMLDS, the operation of which has been described previously [14]. A polytetrafluoroethylene nebulizer (ME2020, Meinhard Glass, Golden, CO, USA) coupled to the PMLDS sprayed the solution into a heated SilcoNert coated stainless steel tube (SilcoNert, Silco-Tek, Bellefonte, PA, USA). The solution flow rate to the nebulizer was set to 60 μL min⁻¹ with an air sheath flow of 1 L min⁻¹. The stainless steel tube was operated at 100 °C to minimize degradation of PETN during the vaporization process. Once vaporized, the PETN entered the TESTbed, an analytical instrument that can deliver uniform vapor concentrations to six different sampling ports. For the purposes of these experiments, the TESTbed was prepared for the delivery of PETN vapor with a total diluent air flow of 11 L min⁻¹ at a fixed relative humidity. The TESTbed oven was programmed to a temperature of 130 °C which results in a vapor stream exiting the TESTbed at a temperature of 66 °C.

2.2. PETN vapor validation - TDS-PTV-GC/μECD

PETN vapor generated with the TESTbed is validated by adsorbing PETN vapor in a thermal desorption tube which is then analyzed by TDS-PTV-GC/μECD [11,13]. This method is considered to be the most accurate representation of the actual PETN concentration arising from the exit port of the TESTbed. Vapor samples were collected by connecting a clean Tenax-TA thermal desorption tube (part No. 009947-000-00; Gerstel GmbH & Co., KG, Mulheim an der Ruhr, Germany) to one of the TESTbed sampling ports. The backside of the sampling tube was connected to a piston flow meter (Defender 510, Bios International/Mesa Labs, Butler, NJ, USA) to measure the flow being sampled by a handheld pump (AirChek 2000, SKC, Eighty Four, PA, USA). Samples were collected at a flow rate of 100 mL min⁻¹ and the amount of sampling time varied from 30 to 300 min, depending on the expected vapor concentration. After sampling, the tubes were placed in a twenty tube auto-sampler (part No. 013200-00-02, Gerstel GmbH & Co., KG, Mulheim an der Ruhr, Germany) which was attached to a thermal desorption system (model TDS-3, Gerstel GmbH & Co., KG, Mulheim an der Ruhr, Germany). The TDS was coupled to the front end of a gas chromatograph (model 7890A, Agilent Technologies, Santa Clara, CA, USA) utilizing a cryogenically cooled PTV inlet (model CIS-4, Gerstel GmbH & Co., KG, Mulheim an der Ruhr, Germany) and a micro-electron capture detector (Agilent Technologies, Santa Clara, CA, USA).

The GC method for minimizing PETN thermal degradation on the TDS-PTV system is described by Lubrano et al. [11]. Briefly, the CIS was cooled to a temperature of 0 °C for analyte trapping. PETN samples were desorbed with a flow rate of 500 mL min⁻¹ through the tube while the TDS-3 oven was ramped at a rate of 180 °C min⁻¹ to a temperature of 200 °C where it was held for 5 min. After desorption from the tube, the CIS was ramped to 175 °C at a rate of 10 °C s⁻¹ and held for 5.25 min, followed by a quick burn off at 250 °C. After a splitless desorption from the CIS, the vapor entered the GC/μECD which was equipped with a 15-m RTX-5MS column with a 0.25 mm inner diameter and a 250 nm thick interior coating (part No. 12620; Restek Corp., Bellefonte, PA, USA). The GC oven was initially held at 80 °C for 0.5 min and then ramped to 175 °C at a rate of 20 °C min⁻¹. The flow of helium through the column was held constant at 5 mL min⁻¹.

Calibration of this system was achieved by pipetting 5 μL of PETN standard solutions onto the glass frit of a clean Tenax-TA thermal desorption tube. The tube was allowed to sit for 15 min after solution deposition to ensure all solvent had evaporated prior to analysis on the TDS-PTV-GC/μECD system.

2.3. PETN vapor validation – online PTV-GC/MS

Direct PETN vapor sampling onto a cryogenically cooled PTV inlet (model CIS-4, Gerstel GmbH & Co., KG, Mulheim an der Ruhr, Germany) was achieved by connecting a heated transfer line (Clayborn Hot Tube, Clayborn Labs, Truckee, CA, USA) from a sampling port on the TESTbed to the six way valve system of the PTV inlet. Presented here are the optimized values for the online PTV-GC/MS system. The optimization process is discussed in detail later in the text. The temperature and flow rate of sample through the transfer line were set to 80 °C and 300 mL min⁻¹, respectively. The CIS was secured to the back inlet on the GC and the housing of the six way valve system was set to a temperature of 200 °C. The CIS was cooled to a temperature of 10 °C using an ethanol water mixture in a Peltier cooling system (UPC Plus, Gerstel GmbH & Co., KG, Mulheim an der Ruhr, Germany) for PETN vapor trapping and the vapor stream was sampled directly onto the inlet liner for either 5 or 10 min depending on the concentration. Following adsorption, the CIS was ramped at a rate of 10 °C s⁻¹ to a temperature of 175 °C and held for 5.25 min, followed by a rapid burn off at 250 °C for 0.1 min. After desorption, the vapor passed through an identical, but separate make and model GC to that used with the TDS-PTV-GC/μECD system (model 7890A, Agilent Technologies, Santa Clara, CA, USA). The GC was operated with an optimized split ratio and a column flow of 5 mL min⁻¹. The GC oven was set to an initial temperature of 80 °C and held there for 0.5 min followed by a ramp to 175 °C at a rate of 20 °C min⁻¹ and held for 0.5 min, giving a total run time of 5.75 min.

The MS (model 5975C, Agilent Technologies, Santa Clara, CA, USA) was run using chemical ionization in negative ion mode with methane as the reagent gas. The auxiliary line connecting the GC to the MS was set to a temperature of 250 °C and both the MS quad and source were set to 120 °C. Analysis of the PETN vapor was done with the MS operating in selective ion monitoring (SIM) mode. The three ion channels monitored for PETN are *m/z* 46, 62, and 240, none of which correspond to the PETN molecular ion due to the harsh ionization process. However, previous research using flowing atmospheric pressure afterglow ionization, a milder ionization source, has shown that molecular PETN traverses the entirety of the GC column under the given conditions despite its tendency to undergo degradation [11]. A schematic diagram of the entire online sampling experimental set up can be found below in Fig. 1.

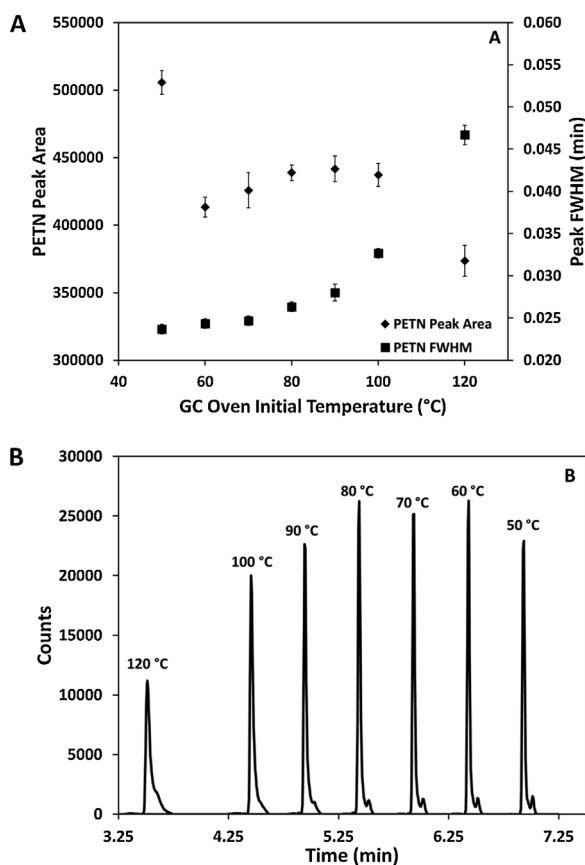
Calibration of this system was done with direct injections of serially diluted standard solutions onto the front inlet which consisted of a standard Agilent split/splitless inlet. The injection volume was

Table 1
Measured PETN vapor concentration via TDS-PTV-GC/ μ ECD analysis as a function of PETN solution concentration. The error represents a standard deviation of $N = 10$.

[PETN] ($\text{ng } \mu\text{L}^{-1}$)	Theoretical Vapor Concentration (ppt_v)	Sampling Time (min)	Measured Vapor Concentration (ppt_v)	Vaporization Efficiency (%)
0.01	4.8	240	2.6 ± 0.2	68
0.1	48	30	31 ± 2	65
0.5	240	30	149 ± 6	62
1.0	480	30	320 ± 11	67

Table 2
Experimental conditions used to generate and quantify trace vapor streams of PETN using online PTV-GC/MS. The error represents a standard deviation of $N = 10$.

[PETN] ($\text{ng } \mu\text{L}^{-1}$)	Solution Flow Rate ($\mu\text{L min}^{-1}$)	TESTbed Air Flow (L min^{-1})	Sample Time (min)	Theoretical Vapor Concentration (ppt_v)	Measured Vapor Concentration (ppt_v)	Vaporization Efficiency (%)
0.001			10	0.48	0.26 ± 0.02	55
0.01			10	4.8	1.57 ± 0.04	33
0.1	60	11	10	48	15.7 ± 0.2	33
0.5			5	240	90 ± 1	38
1.0			5	480	166 ± 2	35

**Fig. 3.** A) Effect of GC oven initial temperature on the PETN peak characteristics. The error bars represent a standard deviation of $N = 3$. In some cases, the error bars are obscured by the size of the data marker. B) Chromatograms of PETN at select GC oven initial temperatures.

Further optimization of the online sampling method focused on reducing the duty cycle of each run. To reduce this time, the GC oven initial temperature was systematically increased and the PETN peak area, full width at half max (FWHM), and retention time were observed as a function of initial GC oven temperature, which is shown in Fig. 3A. As the oven temperature increases the PETN peak area initially decreases, then remains steady over the middle of the temperature range before decreasing again at the maximum temperature while the FWHM increases nonlinearly.

Fig. 3B shows the individual chromatograms from each GC oven temperature. As the temperature increases, the resolution

decreases between the PETN peak and the shoulder peak that immediately follows. Due to the decrease in resolution coupled with the increase in the FWHM at higher temperatures, an initial GC oven temperature of 80°C was chosen, reducing the GC analysis time by ~ 1.5 min.

3.2. Vapor validation: comparison between TDS-PTV-GC/ μ ECD and online PTV-GC/MS

PETN vapor streams in the ppt_v vapor concentration range were analyzed using both the TDS-PTV-GC/ μ ECD system and the online PTV-GC/MS system for direct comparison. The results of sampling PETN off the TESTbed using Tenax-TA thermal desorption tubes and TDS-PTV-GC/ μ ECD analysis are shown in Table 1. Previous reports indicated that the low temperature of the nebulizing system leads to carryover when transitioning from high to low concentrations [13]. Therefore, any chance of carryover was eliminated by running water blanks until there was no PETN signal before transitioning to a lower concentration. Following this routine, the TDS-PTV analysis showed a consistent vaporization efficiency, which is defined as the percentage of the measured vapor concentration to the theoretical value, of approximately 65% for all PETN concentrations. The losses observed in PETN are associated with incomplete nebulization as a result of operating the nebulizer at a temperature of 100°C to minimize degradation during vaporization.

Shown in Table 2 are the parameters used to generate PETN vapor ranging from 166 ppt_v to 260 ppt_v along with the measured PETN vapor concentrations determined using the online PTV-GC/MS. While the sampling time for the Tenax-TA filled sorbent tubes varied between 30–300 min, the online PTV method required sampling times of only 5–10 min. Like previous reports for TNT and RDX [13], the online PTV method displayed higher precision in the measured PETN vapor concentration for all nebulized solution concentrations. This is attributed to a much more uniform desorption process from the online PTV inlet liner compared to desorption from thermal desorption tubes.

As Table 2 shows, the measured vapor concentration determined by the online PTV method is approximately half the value determined from the TDS-PTV method for all vapor streams generated in the ppt_v range. Attenuation in the vapor concentration observed with the online PTV method can be attributed to inefficiencies in both sampling and desorption. Due to the thermal lability of PETN, some of the vapor handling infrastructure is maintained at much lower temperatures compared to traditional vapor phase experiments in an effort to preserve molecular PETN. Consequently, this causes some PETN to be sequestered by irreversible surface interactions at these temperatures while in transit to the

inlet, similar to what was observed in the transfer line. The other component of the online system that contributes to the observed attenuation is the six way valve that controls adsorption and desorption in the CIS. The high surface to volume ratio of the plumbing within the six way valve system must be maintained at 200 °C to prevent the system from clogging and distorting flow. As a result, PETN experiences some amount of degradation, which adds to the sample loss observed with the online system. In addition, PETN must pass through the six way valve system again during desorption before reaching the column which adds another transport step and complicates the desorption process. This also highlights the main difference in the desorption techniques between the two methods. For TDS-PTV analysis, the inlet is operated in splitless mode and vapor is desorbed directly into the column, whereas the online PTV system requires a split ratio in order to move the vapor through the valve again before entering the column.

Although there is disagreement between the two methods, one must consider that the main purpose of the TESTbed is for the evaluation of explosive vapor sensors and detection equipment. This requires rapid validation of vapor concentrations which cannot be achieved with thermal desorption tube sampling techniques in a timely manner. In this light, online sampling is the better choice for achieving this purpose. Using an appropriate correction factor, the online sampling method yields semi-quantitative results with respect to the concentration of vapor being delivered to the sample ports of the TESTbed for PETN vapor concentrations of ppt_v and higher. However, as the vapor concentration decreases, there is an increase in vaporization efficiency which may indicate that the online sampling method approaches quantitative results for sub ppt_v concentrations.

3.3. Pp_q_v vapor generation and quantification

Vapor concentrations in the pp_q_v range were analyzed using only the online PTV method due to excessively long sampling times required for the thermal desorption tubes. Care was taken to eliminate carryover when transitioning to lower concentrations using the same methodology as described previously.

Initial efforts were aimed at keeping the sampling time constant at 5 min for all concentrations. However, it was found that when the PETN spraying solution concentration was $\leq 0.1 \text{ ng } \mu\text{L}^{-1}$, the vaporization efficiency became dependent on sampling time. At higher concentrations there is more PETN available to passivate the surface of the vapor handling infrastructure which allows for efficient collection with shorter sampling times. However, as the concentration decreases, there is less PETN available and more time is needed for passivation of those surfaces to achieve efficient collection on the CIS liner. Although this leads to a longer duty cycle for each run, longer sampling increases the overall amount of material collected on the CIS which leads to improved S/N ratios for the pp_q_v measurements. That being said, sampling times longer than 10 min failed to improve S/N ratios for vapor concentrations lower than 260 pp_q_v. The cause of the jump in vaporization efficiency for the lowest concentration is unknown at this time, however we hypothesize that there is an increase in desorption efficiency as the concentration decreases from ppt_v to pp_q_v.

4. Conclusions

This manuscript reports a method for PETN trace vapor analysis using an online PTV-GC/MS system. The degradation of PETN was minimized by optimizing temperatures and flow rates through

the vapor handling infrastructure required with online sampling. The online PTV-GC/MS analysis was validated through comparison with a previously reported method using Tenax-TA thermal desorption tubes with TDS-PTV-GC/ μ ECD analysis. The additional vapor handling infrastructure required with online sampling caused sample loss, resulting in measured vapor concentrations which were approximately half that determined by the TDS-PTV method. However, with a proper correction factor, online sampling can be used as a semi-quantitative method for ppt_v concentrations. Sub ppt_v PETN vapor concentrations were realized using online sampling, going as low as 260 pp_q_v with only 10 min of sampling time. At this concentration there was an observed increase in the vaporization efficiency, indicating that online sampling may be quantitative at pp_q_v levels. Moving forward, this method will allow for rapid PETN vapor validation in the independent testing of explosive detection instrumentation using the TESTbed.

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