Short communication

Minimizing thermal degradation in gas chromatographic quantitation of pentaerythritol tetranitrate

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ABSTRACT

An analytical method for establishing calibration curves for the quantitation of pentaerythriol tetranitrate (PETN) from sorbent-filled thermal desorption tubes by gas chromatography with electron capture detection (TDS-GC-ECD) was developed. As PETN has been demonstrated to thermally degrade under typical GC instrument conditions, peaks corresponding to both PETN degradants and molecular PETN are observed. The retention time corresponding to intact PETN was verified by high-resolution mass spectrometry with a flowing atmospheric pressure afterglow (FAPA) ionization source, which enabled soft ionization of intact PETN eluting the GC and subsequent accurate-mass identification. The GC separation parameters were transferred to a conventional GC-ECD instrument where analytical method-induced PETN degradation was further characterized and minimized. A method calibration curve was established by direct liquid deposition of PETN standard solutions onto the glass frit at the head of sorbent-filled thermal desorption tubes. Two local, linear relationships between detector response and PETN concentration were observed, with a total dynamic range of 0.25–25 ng.

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1. Introduction

Pentaerythritol tetranitrate (PETN) is a military explosive commonly used in improvised explosive devices (IEDs) and detection of this material has become increasingly important over the last 15 years for transportation security and safety [1,2]. PETN can be difficult to detect due to its low vapor pressure and thermal lability [3]. While this motivates the development of improved PETN threat detection technologies, as target detection levels drop new challenges arise in generating and characterizing reference trace vapor streams to properly validate the efficacy and reliability of these technologies.

Standard methodology, such as EPA Method 8095, centers on solvent extraction of trace PETN from liquid or solid matrices, rather than vapor [4]. Other published laboratory methods for analysis of trace explosive vapors such as trinitrotoluene (TNT) and hexamethylenetetramine (RDX) involve collection on sorbent-filled tubes during active sampling [5–10]. The analyte is then thermally

desorbed and refocused on a cryogenically cooled gas chromatograph (GC) inlet, followed by gas chromatographic analysis. Calibration is achieved by direct liquid deposition of gravimetrically prepared standard solutions onto sorbent-filled thermal desorption tubes.

Unfortunately, PETN analysis is complicated by the fact that the molecule is thermally labile and easily degrades under the temperatures commonly used in GC analysis [11–15]. This complication has generally precluded the use of GC for PETN quantitation in favor of other methods that do not use high temperatures or thermal desorption for analysis, such as high performance liquid chromatography (HPLC) [16]. However, these alternatives require additional preparation steps that GC methods avoid by retaining samples in the gas phase throughout analysis. PETN undergoes extensive fragmentation within the electron impact (EI) source commonly used for gas-chromatography mass selective detection (GC-MS) instruments [17,18]. This fragmentation complicates identification of PETN in GC method development and introduces ambiguities that are difficult to resolve when working with low concentrations.

This work focuses on identifying and demonstrating GC conditions suitable for trace PETN analysis in a routine lab

environment. Here, an alternative ionization technique coupled with high-resolution mass spectrometry was employed to definitively assign a GC elution time to intact molecular PETN. Flowing atmospheric-pressure afterglow (FAPA) is an ambient ionization technique that directs post-plasma reagent ions to the sample to desorb and ionize analytes. FAPA has been previously demonstrated for analysis of gas-phase analytes, including from GC effluent [19]. In the negative mode, the molecular ion $[M]^-$ and nitrate-molecular ion $[M+NO_3]^-$ have been observed for PETN [20]. Thus, FAPA ionization coupled to a high-resolution mass spectrometer (HRMS) is used here as an alternate detection strategy for the GC separation to minimize fragmentation compared to EI and conclusively identify the PETN molecular ion via the high mass accuracy of the mass analyzer ($\sim$1 ppm). This approach enabled methodology from the GC–FAPA-HRMS instrument to be transferred to a conventional gas chromatograph equipped with a thermal desorption system and electron capture detection (ECD) [9,10,21] to provide simple, direct analysis of sorbent-trapped PETN on a routine basis.

2. Material and methods

PETN trace analysis was performed by direct deposition onto sorbent-packed thermal desorption tubes (part no. 009947-000-00, Gerstel Inc. USA, Linthicum, MD) and subsequent analysis by a thermal desorption system (model TDS-3, GERSTEL Inc. USA, Linthicum, MD) coupled to a gas chromatograph (model 7890A, Agilent Technologies, Santa Clara, CA) equipped with a cryogenically cooled inlet (model CIS-4, GERSTEL Inc. USA, Linthicum, MD) and an Agilent micro electron capture detector. Sampling of trace PETN vapor streams was not conducted as part of this work, as there was no current method for reference PETN vapor generation available. Such a method is being developed in parallel to this work and will be the subject of a future communication. SiltekTM-coated glass liners (part no. 014652-005-00, Gerstel Inc. USA, Linthicum, MD) were used in the CIS-4 inlet, and a 0.53 mm ID stainless steel transfer line heated to 300 °C was used to connect the CIS-4 inlet to the TDS-3 thermal desorption system. A twenty tube auto-sampler (part no. 013200-000-02, Gerstel Inc. USA, Linthicum, MD) was attached to the front end of the TDS-3 system.

During thermal desorption of samples, the CIS was cooled to a temperature of 0 °C while the TDS-3 oven was ramped at 180 °C min^{-1} to the desorption temperature and held for 5 min. Desorption temperature and carrier gas flow rate through the sample tube were evaluated by adjusting the appropriate TDS-3 and CIS-4 method parameters, respectively. Following desorption, the CIS-4 inlet was ramped at 10 °C s^{-1} to 175 °C and held for 6 min, followed by a brief temperature ramp to 250 °C prior to cooling down for the next cycle.

Analytical standards of 100 µg mL^{-1} PETN in methanol were purchased from AccuStandard, Inc. (New Haven, CT, USA). Calibration was performed by direct deposition of 5 µL aliquots of serially diluted PETN reference solutions to the glass frit at the ends of clean thermal desorption tubes with a micropipette, followed by a 15-min delay prior to desorption and analysis to allow the solvent to evaporate.

Analyses of reference PETN solutions were also performed via direct injection onto the GC inlet in order to isolate PETN degradation effects induced by the CIS-4 GC inlet from those induced by the TDS-3 system. This was done by temporarily replacing the TDS-3 thermal desorption system with an Agilent model 7693A automatic liquid sampler (ALS) coupled to the CIS-4 GC inlet via a Gerstel septumless head (SLH) attachment. GC inlet temperatures were evaluated over a range of 175–300 °C. During each run, a 1 µL aliquot of PETN solution was injected from a 10 µL syringe with the
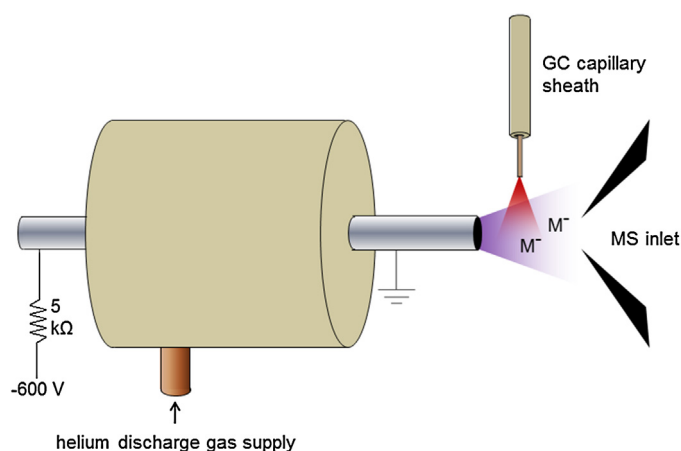

Fig. 1. Diagram of the FAPA ionization source with GC column flow introduced.

CIS-4 GC inlet in "solvent vent" mode with an initial vent flow rate of 300 mL min^{-1} which was then reduced to 100 mL min^{-1} 2.1 min after injection.

Validation of PETN gas chromatographic retention time was performed on a second GC (model 5890C, Agilent Technologies, Santa Clara, CA) that was coupled to a prototype FAPA source in "pin to capillary" configuration 20 positioned 5 mm from the inlet of a high-resolution mass spectrometer (LTQ Orbitrap XL, Thermo Fisher Scientific, Inc., Waltham, MA) with a translation stage. A high voltage power supply (model SL600, Spellman High Voltage Electronics, Hauppauge, NY) was connected to the FAPA electrode through a 5 kΩ ballast resistor and operated current limited at 25 mA (0.6 kV) A mass flow controller (model M100, Sierra Instruments, Monterey, CA) was connected to a compressed gas cylinder containing ultra-high purity helium and was used to provide an inlet helium flow rate of to the FAPA of 750 mL min^{-1}. The GC column was passed through a transfer line that was heated to 160 °C and mounted between the GC oven and the FAPA source, allowing the end of the GC column to be positioned transverse to the FAPA-MS axis, impinging upon the FAPA-MS axis midway between the tip of the FAPA source and the MS inlet, as shown in Fig. 1. An auto-sampler (model HT310A-E, HTA s.r.l, Brescia, Italy) was mounted and connected electrically to the GC to synchronize injection and analysis. A custom trigger cable between the GC and the HRMS in combination with the synchronized auto-sampler allowed the analysis to be initiated and coordinated from a single computer connected to the HRMS. During each run, a 1 µL aliquot of standard PETN solution was injected. The LTQ Orbitrap was operated with a maximum fill time of 25 ms, scanning mass range m/z 50–400. The inlet capillary was held at a potential of -35 V and a temperature of 275 °C The tube lens potential was set to -114 V.

Both instruments (GC–FAPA-HRMS and TDS-GC-ECD) were equipped with a 15-m RTX-5MS column with a 0.25-mm inner diameter (ID) and 250 nm film thickness (part no. 12620; Restek Corp., Bellefonte, PA). Each GC used the same optimized GC oven temperature program, regardless of sample preparation (i.e. thermal desorption tube or direct liquid injection). The GC oven was ramped at 20 °C min^{-1} to 175 °C with a 0.5 min hold time from an initial temperature of 50 °C and column flow was maintained at 5 mL min^{-1}.

3. Results and discussion

Analysis of standard solutions of PETN by GC–FAPA-HRMS confirmed that intact PETN survives analysis under the proposed GC method conditions to unambiguously identify the retention time. Example data from GC–FAPA-HRMS analysis of a 1 µL injection of
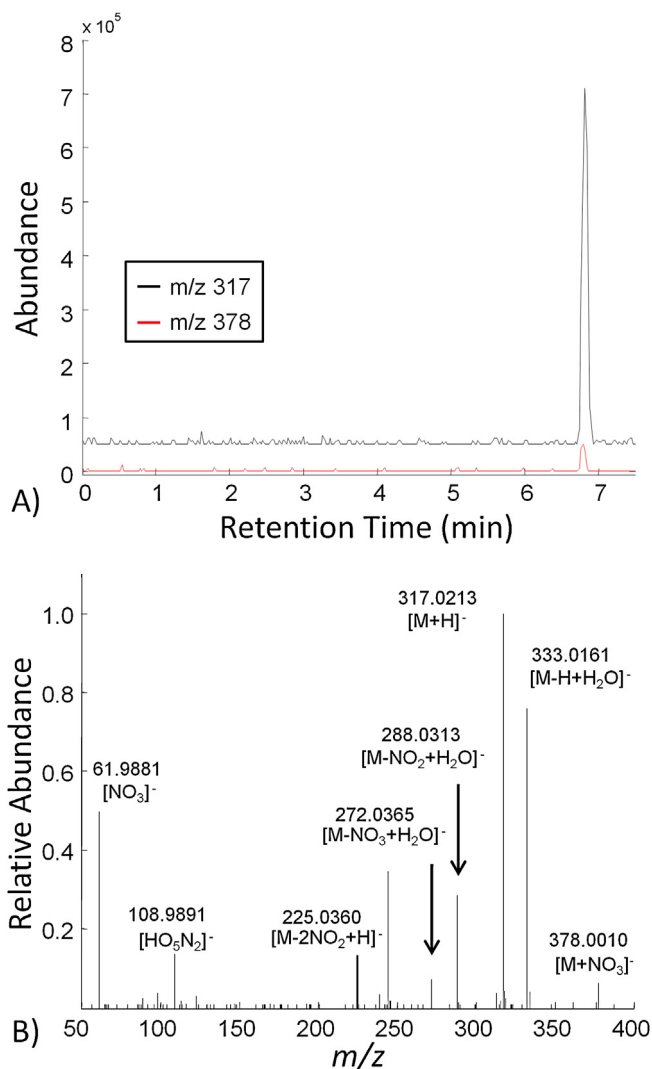
A)

B)

Fig. 2. GC–FAPA-HRMS analysis of a 100 ng injection of PETN: (A) Selected ion chromatograms of PETN molecular adducts at m/z 317 and 378. (B) Background-subtracted high-resolution mass spectrum from m/z 50–400 at retention time 6.82 min.

a 100 μg mL^{-1} PETN reference solution are shown in Fig. 2. Under the GC oven parameters described above and a GC inlet temperature of 175 °C, a single chromatographic peak was observed as well as several background ions which appeared throughout the GC run. Fig. 2A shows selected ion chromatograms at m/z 378 and 317, offset for clarity. The background-subtracted mass spectrum at 6.8 min is shown in Fig. 2B. The formula of the ion at m/z 378 was identified by accurate mass as [C$_5$H$_8$N$_5$O$_{15}$]$^-$, corresponding to the nitrated molecular adduct [M+NO$_3$]$^-$. Likewise, the formula of the ion at m/z 317 was identified as [C$_5$H$_9$N$_4$O$_{12}$]$^-$ corresponding to the most abundant molecular adduct [M+H]$^-$ [22]. Other major ions within the spectrum correspond to PETN molecular fragment adducts such as [M+OH]$^-$ at m/z 333 and [M-NO$_2$+H$_2$O]$^-$ at m/z 288. These results indicate that intact PETN elutes at 6.8 min in the GC method.

The GC oven temperature ramp and flow rate parameters were transferred to the TDS-GC-ECD instrument, where subsequent experiments were performed to understand the relationship between thermal desorption method parameters and PETN degradation. Thermal degradation of PETN within the GC inlet was evaluated by varying the maximum inlet temperature over a range
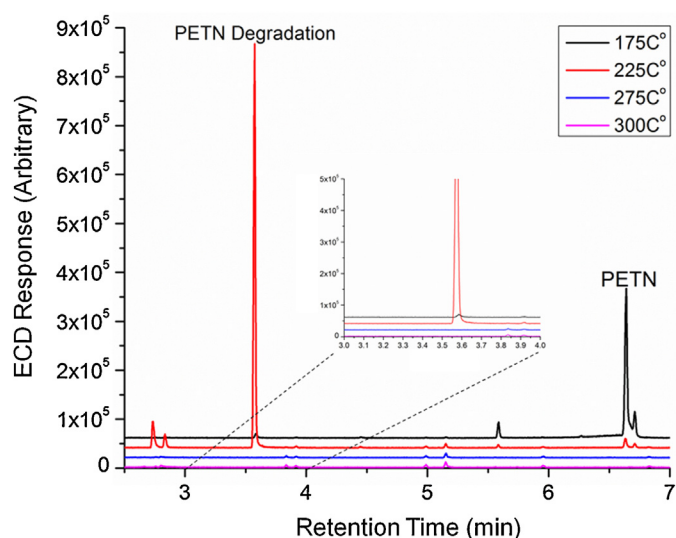

Fig. 3. GC-ECD chromatograms from direct injections of 100 ng PETN at varying maximum inlet temperatures to probe PETN thermal degradation. Chromatogram baselines are offset for clarity.

of 175–300 °C and observing the resulting chromatograms from direct injection of PETN standard solutions, shown in Fig. 3. Due to minor variations between instruments, the retention time of PETN was observed at 6.6 min rather than 6.8 min. Minimal degradation is seen at an inlet temperature of 175 °C, but when the inlet temperature is increased to 225 °C, additional PETN degradant peaks are observed, the largest occurring at a retention time of 3.6 min. When the inlet is heated to 275 °C, both the PETN peak and degradation product peaks disappear completely, which suggests that the PETN and initial degradation products have further degraded into smaller molecules that are not retained by the GC column.

Thermal desorption parameters were evaluated by direct deposition of 50 ng of PETN (5 μL of 0.1 mg mL^{-1} standard solution) onto cleaned thermal desorption tubes and allowing the solvent to evaporate during a 15 min delay prior to analysis by TDS-GC-ECD. Thermal desorption temperature, flow rate, and time were sequentially optimized as shown in Fig. 4. As shown in Fig. 4A, TDS desorption temperatures of 175, 200, and 225 °C all yielded signal due to both PETN and PETN degradant (as observed by the degradant peak at 3.6 min) and increased desorption temperature led to an increase in signal for both. A temperature of 200 °C was selected to reduce the amount of degradation occurring in the TDS while maximizing the amount of desorbed PETN. The effect of TDS desorption flow rate is shown in Fig. 4B. Signal due to the PETN degradant decreases while that due to PETN dramatically increases as the desorption flow rate is increased. Total desorption flow was limited to 500 mL min^{-1} in order to minimize gas consumption. Finally, the impact of TDS desorption time is shown in Fig. 4C. It can be seen that a desorption time of 3 min appears to provide equivalent signal to longer desorption times. Under optimized TDS conditions, desorption and analysis of varying amounts of PETN standard resulted in additional chromatographic peaks at 5.6, 2.9, 3.6, and 4.5 min whose area tracked with PETN, indicating that these were likely PETN degradants. The largest degradant peak occurred at 5.6 min, presenting areas approximately 20% that of the PETN peak.

Fig. 5A shows the optimized temperature parameters utilized in the final PETN quantification method. These temperature parameters along with a thermal desorption flow of 500 mL min^{-1} were used to generate the ECD calibration curves shown in Fig. 5B, again
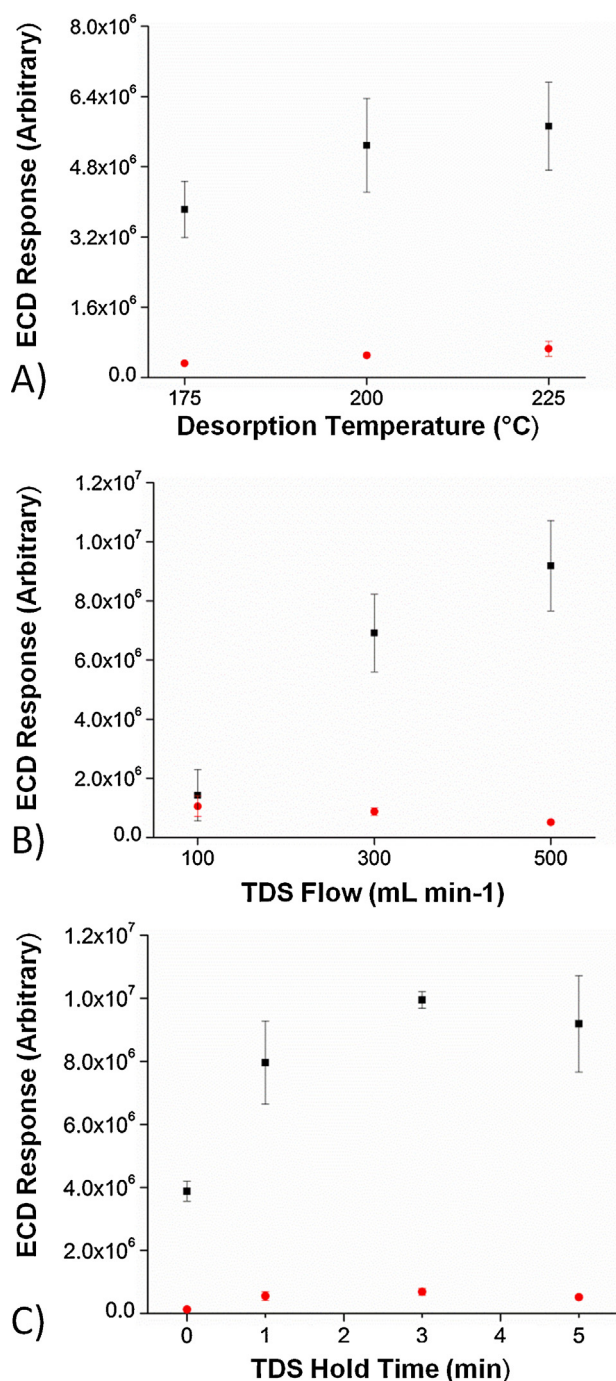
Fig. 4. Evaluation of TDS parameter space for 50 ng sample of PETN standard solution deposited on the glass frit of a Tenax TA thermal desorption tube. Error bars represent one standard deviation of three replicate runs ($N = 3$). Black squares indicate average PETN peak area and red circles represent average peak area of the PETN degradant at a retention time of 3.6 min. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. (A) Final TDS/CIS/GC run temperatures. (B) TDS/GC/ECD calibration curve produced from liquid deposition method over a range of 0.25–25 ng, error bars represent one standard deviation of three replicate runs ($N = 3$). The inset depicts a zoomed region containing calibration samples from 0.25–5 ng. Separate linear calibration functions are necessary due to an apparent reduction in sensitivity in samples less than 5 ng.

4. Conclusions

While previous studies have indicated PETN thermally degrades at temperatures above 110 °C, this work has demonstrated intact PETN can survive thermal desorption from sorbent sampling tubes and subsequent GC analysis. A high-resolution mass spectrometer configured with a FAPA ambient-ionization source, was used to confirm the retention time of intact PETN in a GC separation through accurate mass identification of intact PETN molecular adduct ions. A calibration method for trace PETN quantitation from sorbent tubes was developed and optimized using a standard GC equipped with an ECD detector and a thermal desorption system with a cryogenically cooled inlet system. Variation of method parameters confirmed that higher temperatures and lower flow rates were generally associated with increased PETN degradation and reduced sample recovery. In particular, it was observed that elevating GC inlet temperatures resulted in increased PETN degradation, while increased desorption flow was associated with improved PETN recovery. A straightforward interpretation of these data is that the extent of PETN degradation is driven by both the rate of degradation induced by elevated temperatures as well as the duration of time over which the PETN is exposed to elevated temperatures. The experimental results suggest that at sufficiently high flow rates, PETN does not reside in the inlet or GC oven long enough to induce the significant thermal degradation expected at

by direct deposition of reference PETN standard solutions onto the glass frit of clean thermal desorption tubes. Ten PETN sample loadings from 0.25 to 25 ng were analyzed. A reduction in sensitivity was observed at the lower end of the calibration range, possibly due to in part to losses in the thermal desorption-based sample introduction process. Separate piecewise linear fits of ECD response to the calibration standards between 5 and 25 ng and to those between 0.25 and 5 ng are shown.
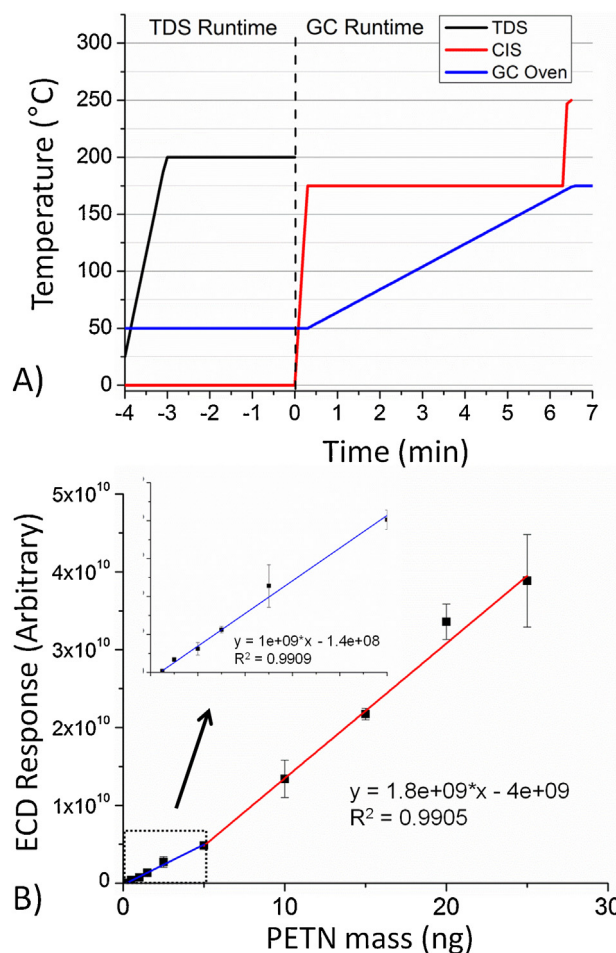
temperatures greater than 110 °C, and that, in general, careful consideration to reduce analyte residence time in heated zones is a useful strategy to compensate for elevated temperatures required in GC analysis.

The analytical method developed in this work demonstrated a dynamic range of two orders of magnitude (0.25–25 ng PETN per sample) although separate linear calibration functions were required for the low and high ends of the calibration range. Sensitivity at the lower end of the calibration range was roughly half that of the upper end, Selectivity of the method was not evaluated, but will be driven by the degree to which PETN can be chromatographically separated from the other components of the sample matrix. The observed dynamic range, while not large in absolute terms, is theoretically sufficient for practical characterization of reference trace vapor streams in the low parts-per-trillion range by sorbent tube sampling. While there is currently no standard method for generating reference trace vapor streams of PETN, work developing such is underway at NRL and will be the subject of future communications.

Authors' contribution

All authors have given approval to the final version of the manuscript.

Acknowledgments

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