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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.

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

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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 (~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 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.

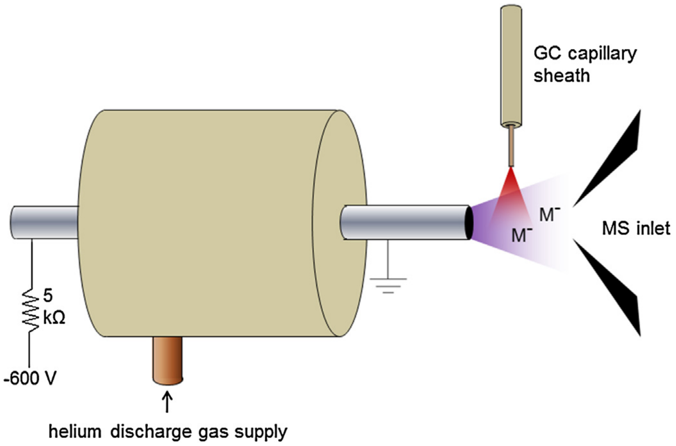

Fig. 1. Diagram of the FAPA ionization source with GC column flow introduced.

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 autosampler (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