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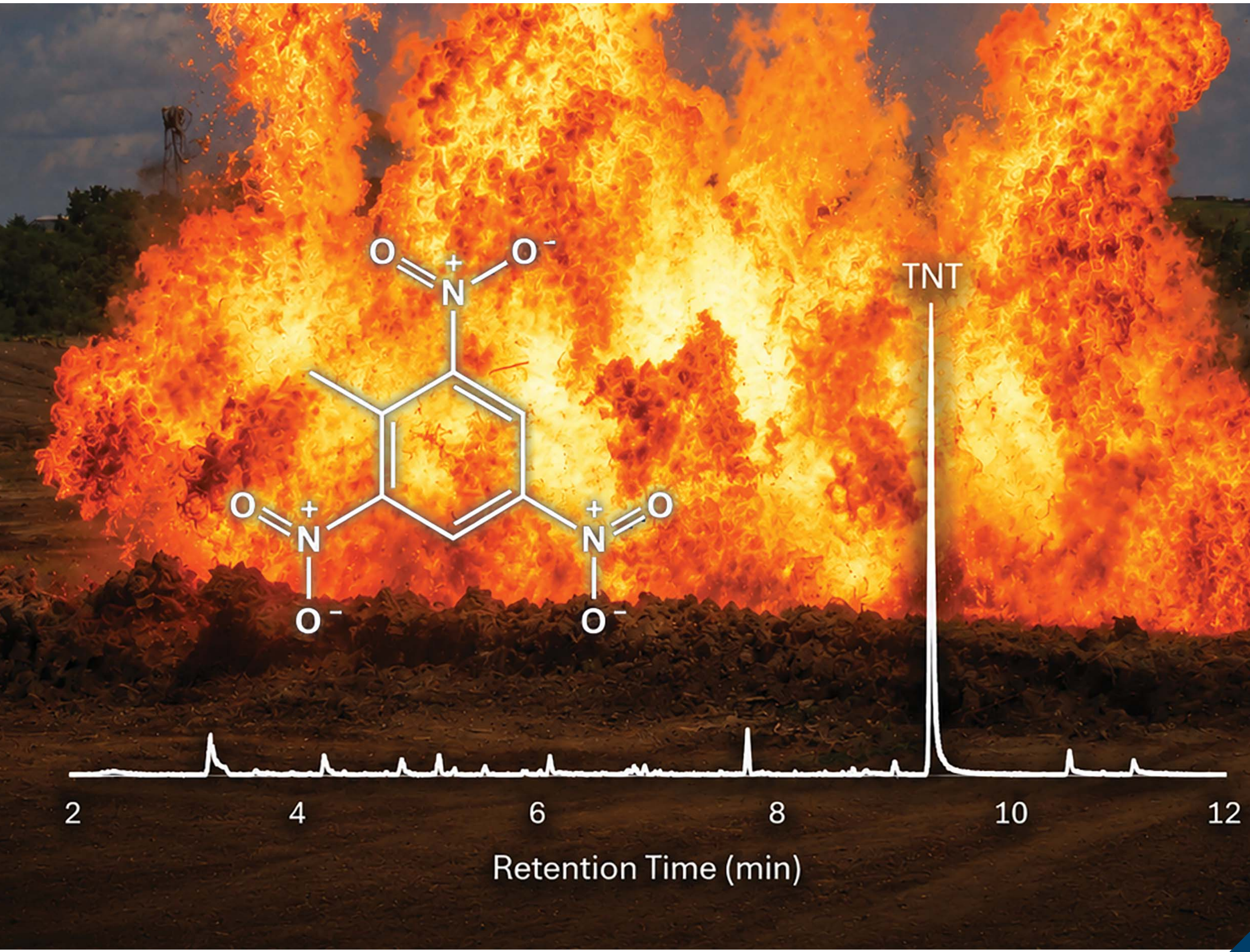

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Recovery of TNT from post-blast soil samples: effects of soil type, extraction methodology, and storage conditions

A. J. Hecker,[a] H. Upadhyaya[a] and J. V. Goodpaster *[ab]

Traditionally, determination of explosives and their decomposition products in soil samples involves a 24-hour ultrasonic solid–liquid extraction (SLE) using acetonitrile followed by a "salting out" liquid–liquid extraction (LLE). Alternatively, aqueous extracts of soil can undergo solid-phase extraction to isolate target analytes prior to liquid chromatography. Although well suited for environmental analysis and standardized by the Environmental Protection Agency (EPA), these methods can be overly labor- and time-intensive for a forensic chemist working a post-blast investigation. This highlights the need for rapid, simple, and effective alternatives. In addition, the extent to which the post-blast residues of explosives can biodegrade due to soil bacteria is not fully characterized. In this study, we introduce total vaporization-solid phase microextraction (TV-SPME) coupled with gas chromatography-mass spectrometry (GC-MS) as an alternative to traditional methods for environmental and forensic samples. To benchmark TV-SPME, more established methods including modified-immersion SPME GC-MS and immersion-SPME GC-MS were evaluated for their ability to identify TNT in both spiked and post-blast soils. Three soils with varying composition and organic matter content were spiked with TNT and analyzed to assess the impact of matrix on TNT recovery. In addition, three different storage temperatures (freezer, fridge, and room temperature) were examined to understand TNT degradation in post-blast soil. The chemical kinetics of the TNT degradation process were also explored. TV-SPME showed the greatest response for TNT present in soil. Among the spiked soils, those with higher organic content exhibited greater degradation over time. There is clear evidence of microbial degradation of TNT in post-blast soil over several weeks, which argues for immediate analysis of such samples or their storage at temperatures of at least −18 °C. These findings emphasize the importance of soil composition, extraction methodology and storage conditions when analyzing explosives in forensic and environmental samples.

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1. Introduction

The recovery, identification, and quantitation of nitrated explosives in soil is a long-standing concern that is highly important for both environmental and forensic chemistry. As such, the tools and methods used in the analysis of explosives have been under development for decades, and they are very similar between the two disciplines.[1–8] The most sensitive and specific methods typically involve a separation step (*e.g.*, gas chromatography (GC), ion chromatography (IC), or liquid chromatography (LC)) coupled with mass spectrometry (MS). Despite the thermal sensitivity of some explosives, GC remains a popular technique because of its superior separation power (chromatographic resolution) and peak capacity. In GC-MS, elevated inlet and column temperatures can promote degradation or analyte loss for thermally labile energetic compounds, such as organic peroxides. However, TNT is sufficiently volatile and comparatively stable to be routinely analyzed by GC-MS when conditions are carefully controlled.

However, there are many vital differences in the typical event and sampling circumstances as well as analytical priorities of these two communities, as summarized in Table 1 below.

In the environmental context, soil contamination involving explosives can occur from a range of human activities such as mining, manufacturing, demolition, and military operations.[9–14] Such activities result in the bioaccumulation of explosives and their transformation products in the environment, which can endanger the health of the ecosystem. Commonly used military explosives include 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and pentaerythritol tetranitrate (PETN).[9] TNT and RDX are classified as potential human carcinogens and mutagens, with possible human exposure occurring through contact with contaminated

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Table 1 A comparison of environmental and forensic analysis of explosives in soil

Variable	Environmental analysis	Forensic analysis
Sampling location	Ammunition dumps, proving grounds, firing ranges, munition disposal sites, *etc.*	Criminal/terrorist bombing scenes
Exposure of soil to explosives	Chronic (many events)	Acute (single event)
Time between deposit of explosives and sample collection	Months/years	Minutes/hours
Type of analysis	Typically quantitative	Solely qualitative
Analytical targets	Parent compounds and degradation products	Parent compounds
Concentration range	Variable (bulk to trace)	Trace
Legal implications	Environmental impact, code violations, and liability	Criminal and counter-terrorism investigation

blast debris, migration of residues into groundwater after an explosion, or contamination of drinking-water sources near manufacturing facilities.[10,15–18] TNT metabolism can induce oxidative stress and damage macromolecules,[19] while RDX exposure has been linked to neurological effects including convulsions.[20,21]

Extensive research has explored microbial degradation of TNT in soil under aerobic and anaerobic conditions. Due to its stable aromatic ring, TNT can be transformed into amino-dinitrotoluene derivatives (*e.g.*, 2-amino-4,6-DNT and 4-amino-2,6-DNT) *via* microbial reduction under both aerobic and anaerobic conditions. TNT typically forms transformation products rather than undergoing complete mineralization. Effective degradation requires alternating reducing and oxidizing conditions.[22] While aerobic microbes reduce two nitro groups, full reduction of TNT requires anaerobic pathways.[23] TNT exhibits slight water solubility (130 mg L^{-1} at 20 °C) and a low $\log K_{ow}$ of 1.86, suggesting moderate mobility.[24,25] However, sorption can be influenced by soil components such as humic acids, clay, and organic matter.[10,26] For example, Haderlein *et al.* found TNT retention is enhanced *via* hydrogen bonding and ion exchange with soil colloids.[27] Furthermore, sorption tends to increase with amino group substitution, as shown by Sheremata *et al.*,[28] while Yamamoto *et al.* observed greater TNT and DNT retention in soils with higher organic carbon.[29]

In the forensic context, soil samples recovered from post-blast environments serve as critical indicators of the nature and composition of the explosive device utilized.[29–35] However, the dynamic nature of soil as a matrix complicates the extraction and identification of explosives. Organic matter, microbial populations, moisture content, and mineral composition all affect the degradation, transformation, or retention of explosive compounds over time.[10,22–28] For example, TNT sorption behavior is known to correlate with soil organic carbon and mineral content.[22,23,26–28,36]

Traditionally, post-blast soil analysis has been inspired by U.S. EPA Methods 8095 or 8330A/8330B, which are well-established protocols for the determination of nitroaromatic and nitramine explosives in soil matrices *via* a "salting out" solvent extraction and Gas Chromatography with an Electron Capture Detector (GC-ECD) or High-Performance Liquid Chromatography with an Ultraviolet detector (HPLC-UV). However, these methods have several drawbacks from the point of view of forensic analysis. They involve labor-intensive sample preparation and long extraction times, which can significantly delay analysis. The HPLC method requires two columns as separating nitrated explosives and their degradation products is only possible using capillary GC or capillary LC.[37,38] Furthermore, the detection methods (ECD and UV) are not structurally specific.

There has been some development of more rapid extraction techniques that maintain comparable levels of sensitivity and extraction efficiency.[39,40] For example, portable devices for analysis of soil containing explosive residues on site, however these devices have not yet been adopted for routine analysis.[41–44]

Currently, contaminated soil samples are collected and transported to laboratories for analysis. The reality in forensic science laboratories is that evidence that is gathered from crime scenes is stored at room temperature for days, weeks, or even months due to case backlogs. This can have a devastating effect on some evidence types when soil is involved. For example, the loss of ignitable liquids in soil during storage due to microbial degradation is well studied.[45–53]

Prior research has utilized Liquid Chromatography-Mass Spectrometry (LC-MS) and Gas Chromatography-Mass Spectrometry (GC-MS) for analysis of soil contaminated with TNT.[13,54–56] Furton *et al.* in 2000 utilized gas chromatography with an electron capture detector (GC-ECD) and HPLC-UV for analysis of contaminated soil samples.[32] Commonly used sample preparation methods include liquid–liquid extraction (LLE), and solid phase extraction.[22,29,57–59] These extraction methods are considered time consuming, expensive, and not always effective for trace-level detection in complex matrices which demands a rapid and affordable extraction technique.[13,32,59,60]

Solid-phase microextraction (SPME) has emerged as a solvent-free, rapid, and sensitive technique for the recovery of explosives from aqueous and solid matrices.[30,32,33,56] Particularly, variations such as headspace and immersion-SPME have demonstrated utility in capturing volatile and semi-volatile explosive residues.[33,56,61] SPME utilizes a thin polymer coated fused silica fiber for extraction of volatile organic compounds (VOCs) from a matrix.[57] On completion of the extraction process, the fiber gets thermally desorbed in the heated injection port of the GC. SPME is highly sensitive, rapid, and can be automated making it an attractive extraction technique for analysis of VOCs present in complex matrices.[58,59,62] New techniques such as total vaporization-solid phase microextraction (TV-SPME), immersion SPME and single drop microextraction (SDME) have been developed to maximize the availability of analytes for absorption onto the SPME fiber, leading to improved extraction efficiency and detection limits.[63,64]

In TV-SPME, the sample is completely vaporized before adsorption of analytes onto the fiber takes place resulting in the partitioning of the analyte between the vapor phase and the SPME fiber. The partitioning of the analyte between vapor phase and fiber also eliminates the need for filtering the sample. This allows more analytes in the vapor to get adsorbed onto the fiber leading to improved sensitivity. To achieve complete vaporization, analytes are dissolved in a solvent and a specific volume of this aliquot is placed in a headspace vial for analysis.[65] Various studies in the last few years have utilized TV-SPME for analysis of explosives, polyaromatic hydrocarbons (PAH), lipids, and controlled substances.[66–69] Recent advancements in TV-SPME include vacuum assisted TV-SPME (VA-TV-SPME) coupled with GC-FID (Gas Chromatography-Flame Ionization Detector) for environmental applications, including PAH determination in river water samples, showing high accuracy and precision.[70]

Previous studies involving analysis of TNT in soil can be classified into three types: (1) spiked soil studies where soil is spiked with a standard solution of TNT,[25,34,61,71] (2) analysis of post-blast soil containing TNT from a blast site,[31,72–76] and (3) analysis of TNT contaminated soil obtained from an environmental site.[32,76–81] Of these categories, environmental contamination studies are particularly common, likely because runoff- and waste-related samples frequently contain higher concentrations of energetic compounds than post-blast residues, making them more amenable to detection and method development. As a result, fewer studies have focused specifically on the detection and characterization of trace explosive residues in true post-blast soil samples. To highlight the relative scarcity of post-blast GC-MS-based approaches, previously reported GC studies involving post-blast soil are summarized in Table 2.

Table 2 Summary of previously reported GC-based studies involving post-blast soil analysis[a]

Instrumentation	Explosives	Extraction technique	Ref.
GC-ECD	TNT RDX	SLE LLE SPME	32
GC-ECD	PETN	SLE SPME	33
GC-TEA GC-MS	TNT C-4	SLE	35
GC-TEA	NG	SLE	82
GC-TID GC-ECD	TNT RDX HMX	SLE	83
GC-FID	TNT	SLE LLE SPME	84
GC-ECD	PETN NG TNT RDX HMX	SPE	85
GC-ECD GC-MS	C-4 NG R-Salt TNT PETN RDX Tetryl HMX	SPE SLE	86
GC-MS	TNT	SLE	87
GC-ECD GC-MS	NG TNT PETN RDX	SLE LLE SPME	88
GC-MS	PETN	SLE SPE	89

[a] ECD: electron capture detector, TEA: thermal energy analyzer, SLE: solid liquid extraction, LLE: liquid–liquid extraction, SPME: solid-phase microextraction, SPE: solid-phase extraction.

Therefore, based upon an extensive literature search, this study has been preceded by only five publications that utilized GC-MS and only one study that combined GC-MS and SPME. In this study, TV-SPME has been used for analysis of post-blast and spiked soil contaminated with TNT. To the best of our knowledge, this is the first instance of soil analysis using TV-SPME. The purpose of this work is to develop a robust, highly sensitive and rapid TV-SPME technique for analysis of contaminated soil. To benchmark performance, TV-SPME is evaluated against established methods including immersion-SPME GC-MS and modified immersion-SPME GC-MS for TNT recovery in spiked soils. In tandem, the role of organic content in spiked soil analysis and various storage conditions in the post-blast soil analysis have also been assessed.

2. Materials and method

2.1 Chemicals

Acetonitrile (analytical grade) and 1,4-dinitrobenzene were purchased from Fisher Scientific. Cast boosters (TNT) and pentaerythritol tetranitrate (PETN) were purchased from Omni Explosives using a Bureau of Alcohol, Tobacco, Firearms, and Explosives (ATF) User of explosives license issued to the corresponding author. A standard solution of 2,4,6-trinitrotoluene (1000 mg mL^{-1} in acetonitrile) was obtained from Restek. A 1 mg per mL solution of cast booster was also prepared by dissolving 1 mg cast booster in 1 mL of acetonitrile. A 1 mg per mL standard solution of 4-amino-2,6-DNT in acetonitrile was obtained from Agilent technologies. Additionally, 1 mg per mL solutions of 1,4-dinitrobenzene and 2,4-dinitrotoluene in acetonitrile were also prepared for analysis.

2.2 Consumables

4 oz amber glass jars were purchased from Fisher Scientific to collect soil samples. 20 mL headspace vials and 2 mL liquid injection vials were purchased from Restek. 100 µm PDMS Smart SPME arrows with an outer diameter of 1.10 mm were purchased from Agilent Technologies. A 2 mm splitless SPME

inlet liner was purchased from Restek. 10 mL plastic syringes were purchased from BD Syringe and 25 mm syringe filters (0.45 µm, PTFE, non-sterile) were purchased from Fisher Scientific. Metal spoons were purchased from Meijer. Miracle-Gro Indoor Potting Mix was obtained from Home Depot. Local Indiana soil was obtained from a nearby residential property in Indianapolis, IN. Sandy loam soil was obtained in North Dakota and purchased from Agvise Laboratories.

2.3 Calibrants and standards

Calibrants comprising of 10 ppm, 5 ppm, 1 ppm, 500 ppb and 250 ppb concentrations of TNT in DI water were prepared by diluting a 1000 ppm standard solution of TNT in acetonitrile for immersion SPME GC-MS analysis. 20 mL of solution was placed in a nominal 20 mL headspace vial (actual capacity was 22 mL). Triplicates of each concentration were analyzed and blank vials (containing DI water) were run before and after each sample.

Calibrants comprising of 10 ppm, 5 ppm, 1 ppm, 500 ppb and 250 ppb concentrations of TNT in DI water containing 25% NaCl were prepared by diluting a 1000 ppm standard solution of TNT in acetonitrile for modified immersion SPME GC-MS analysis. 7.5 mL of solution was placed in a headspace vial. Triplicates of each concentration were analyzed, and blank vials (containing DI water with 25% NaCl) were run before and after each sample.

Calibrants comprising of 10 ppm, 5 ppm, 1 ppm, 500 ppb and 250 ppb concentrations of TNT in acetonitrile were prepared by diluting a 1000 ppm standard solution of TNT in acetonitrile for total vaporization analysis. To determine the sample volume used to achieve total vaporization the following equation was used:

$$V_{\mathrm{s}} = \left(\frac{\left(10A - \dfrac{B}{T+C}\right)}{RT}V\right)\left(\frac{M}{\rho}\right) \tag{1}$$

In this equation, V_s is the volume of the liquid extract, A, B and C are the Antoine constants for the solvent vapor pressure, R is the ideal gas constant (L bar K^{-1} mol^{-1}), T is the temperature (K), V is the volume of the vial (in mL), M is the molar mass of the solvent (g mol^{-1}), and p is the density of the solvent (g mL^{-1}).[65] A volume of 9 µL was calculated at a temperature of 40 °C using the equation and then transferred into a headspace vial for analysis. Triplicates of each concentration were analyzed with blank vials containing air run before and after each sample.

A one-gram sample of cast booster was analyzed *via* HS-SPME. Standard solutions (1000 mg mL^{-1} in acetonitrile) of 4-amino-2,6-dinitrotoluene (4-A-2,6-DNT), 1,4-dinitrobenzene (1,4-DNB), and 2,4-dinitrotoluene (2,4-DNT) were analyzed *via* TV-SPME.

Method performance on the analysis of spiked soils was evaluated based on the efficiency of workflow and percent recovery of TNT. Percent recovery was determined using the following equation:

$$\text{Percent recovery} = \frac{\text{calculated concentration of analyte}}{\text{spiked concentration of analyte}} \times 100 \tag{2}$$

2.4 Post-blast soil preparation and storage

2.4.1 Soil detonation setup. The setup and detonation of all explosives was completed by the Indiana State Police Bomb Squad. One pound of cast booster was wrapped in PETN-based detonating cord and placed in five different sites, approximately 12–15 feet apart from one another. About 10 feet of PETN based detonating cord was run from the cast booster to blasting caps. Shock tube was used to set up a delay between the blasting caps. The delay between blasting caps was 200 milliseconds (ms) and the main charge delay from the blasting cap was 5400 ms. A wireless initiator was used to set off the explosion. A schematic of the setup is provided in Fig. 1.

The pre-blast and post-blast areas were measured, as shown in Fig. 2. Soil samples were gathered from post-blast craters within the measured parameters. Metal spoons were used to gather the soil samples, which were then placed in 4-ounce amber glass jars. Care was taken to avoid contamination by using a new spoon for every pre- and post-blast soil collection. Rocks with visible charring were also collected and stored in 4-ounce amber glass jars.

2.4.2 Storage conditions. All pre- and post-blast samples were initially stored in a freezer at −18 °C within 2 hours of collection and remained under these conditions for 3 months prior to analysis. Pre- and post-blast soil from site 1 and site 2 remained in the freezer after the 3-month storage period. Pre- and post-blast soil from site 3 and site 4 were moved from the freezer to a refrigerator three months after the initial sampling. The fridge was kept at 4 °C. Pre- and post-blast soil from site 5 was moved from the freezer to room temperature three months after the initial sampling. The average room temperature was 24.1 °C. The rocks were collected and stored in the freezer. Samples were removed from their storage condition only for short periods of time during sampling.

2.5 Sample preparation and extraction

2.5.1 TV-SPME. Triplicates containing one gram of pre- and post-blast soil were placed in 20 mL headspace vials and 2 mL acetonitrile was added to each vial. The vials were vortexed for

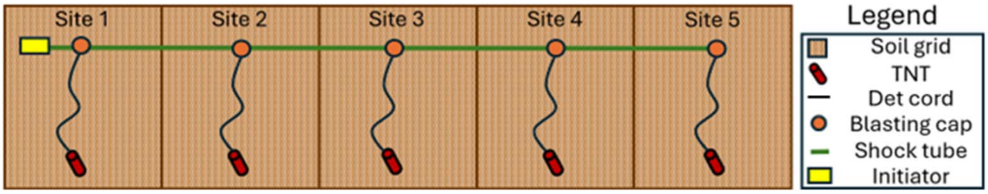

Fig. 1 TNT blasting setup grid.

Fig. 2 Site 1 area measurement pre-blast (left) and post-blast (right) of cast booster.

15 minutes and 9 μL of extracts obtained were transferred to clean headspace vials. 9 μL was chosen as the volume as per eqn (1). Blank vials containing air were run before and after each sample. Pre-blast soil samples were screened for the presence of TNT to ensure that the soil did not contain any prior to the blast. The same extraction procedure was followed for all spiked soil samples.

For spiked soil, all soil types (*i.e.*, Miracle Gro soil, sandy loam and local soil) were kept at room temperature. For each soil type, one gram of soil was collected in a headspace vial and 10 μL of 1000 ppm standard of TNT in acetonitrile was added to the vial. Triplicates of each soil type were prepared in a similar fashion, and the vials were sealed and kept aside for 12 hours to equilibrate.

2.5.2 Immersion SPME.

Triplicates containing one gram of pre- and post-blast soil were placed in headspace vials and water was added until each vial was full. The vials were hand shaken for 2 minutes. Blank vials containing water were run before and after each sample. The same extraction procedure was followed for all spiked soil samples.

For spiked soil, all soil types (*i.e.*, Miracle Gro soil, sandy loam and local soil) were kept at room temperature. For each soil type, one gram of soil was collected in a headspace vial and 10 μL of a 1000 ppm standard of TNT in acetonitrile was added to the vial. Triplicates of each soil type were prepared in a similar fashion, and the vials were sealed and kept aside for 12 hours to equilibrate.

2.5.3 Modified immersion SPME.

Triplicates of charred rock from site 1 were washed with 5 mL of acetonitrile in a 100 mL beaker and shaken for 15 minutes *via* vibration table, then allowed to settle for 10 minutes. The rocks were removed with tweezers and 75 μL of the solution was added to 7.5 mL of water containing 25% NaCl. Blank vials containing DI water with 25% NaCl were run after each sample.

No post-blast soil samples were extracted using this method. For spiked soil, all soil types (*i.e.*, Miracle Gro soil, sandy loam and local soil) were kept at room temperature. For each soil type, one gram of soil was collected in headspace vial and 10 μL of a 1000 ppm standard of TNT in acetonitrile was added to the vial. Triplicates of each soil type were prepared in a similar fashion, and the vials were sealed and kept aside for 12 hours. For extraction, 2.5 mL of acetonitrile was added to each vial. The vials were shaken *via* shaker table for 15 minutes then allowed to settle for 10 minutes. 75 μL of the supernatant was extracted and dispensed into a clean headspace vial containing 7.5 mL of water containing 25% NaCl. Blank vials containing DI water with 25% NaCl were run before and after each sample.

2.6 Instrumental analysis

2.6.1 GC-MS parameters.

Analysis was performed on an Agilent 7890B GC coupled to an Agilent 5977B Mass Selective Detector. A PAL RTC 120 autosampler was employed for all experiments. An Agilent HP-1MS Ultra Inert Column (15 m long) with an inner diameter of 0.250 mm and a 0.25 μm film thickness was used. All analysis was done in negative ion chemical ionization mode. A flow rate of 2 mL min^{-1} was chosen.

For SPME, the incubation temperature was set at 40 °C for 3 minutes. Extraction was done for 15 minutes and the SPME arrow was conditioned for 10 minutes. The initial front inlet temperature was set at 40 °C and ballistically ramped at 900 °C per minute to 250 °C. The initial oven temperature was set as 40 °C, held for one minute, followed by a ramp of 15 °C per minute until a final temperature of 200 °C was achieved. A final hold time of 1 minute led to a total run time of 12.6 minutes.

Following GC separation, the samples were analyzed using an Agilent 5977B Mass Selective Detector with the following parameters: negative CI, with methane as reagent gas, with the methane flow rate set at 40% total flow. A mass range of 40–400 *m*/*z* was used.

3. Results and discussion

3.1 Calibration curves and performance comparison

Calibration curves were constructed using unweighted ordinary least squares (OLS) with a free intercept. To compare the performance of the various methods for TNT both the sample concentration and the instrument response (peak area and signal-to-noise) were calculated. In addition, the linear range

Table 3 Summary of calibration curve parameters and analytical performance metrics for TNT obtained by immersion-SPME GC-MS, modified immersion-SPME GC-MS, and TV-SPME GC-MS

Method	LLOL	ULOL	Slope (ppm^{-1})	Linearity (R^2)	RSD (%)	S/N (250 ppb)	Extrapolated LOD
Immersion SPME GC-MS	250 ppb	10 ppm	395 902	0.99	2.13	124	5.5 ppb
Modified immersion SPME GC-MS	250 ppb	10 ppm	563 447	0.99	9.44	164	4.5 ppb
TV-SPME GC-MS	250 ppb	10 ppm	681 533	0.99	30.14	516	1.5 ppb

was defined as the lower and upper limit of linearity, with the lower limit of linearity corresponding to the limit of quantitation (LOQ). Linearity was defined as the coefficient of determination (R^2) for a plot of peak area *versus* concentration. Given that the methods evaluated differed in the amount of material that was introduced on column, the S/N of the LLOL of the GC-MS methods is also included. The limit of detection (LOD) was estimated by plotting signal-to-noise *versus* signal, fitting a linear response line, and extrapolating to the signal at an S/N of 3, which was then used to calculate the LOD concentration. Percent relative standard deviation (% RSD) was calculated at 250 ppb to assess method precision (Table 3).

3.2 Spiked soil samples

A chromatographic peak corresponding to TNT in the spiked soil samples was confirmed by the mass fragments and comparison to the retention time (9.7 minutes) of a TNT peak obtained from a 1 gram sample of undetonated cast booster (Fig. 3).

The comparison of soil type for the analysis of TNT-spiked soil *via* GC-MS is presented in Fig. 4. Extraction was performed after the spiked soils sat at room temperature for 12 hours.

Fig. 4 showed that the immersion method was less efficient in recovering TNT compared to modified immersion, reflecting its susceptibility to higher matrix interference due to direct fiber-soil contact. The latter method demonstrated improved performance, which can be attributed to the effective extraction of TNT facilitated by acetonitrile and subsequent salting-out. TV-SPME demonstrated the same enhanced extraction efficiency which aligns with the ability of TV-SPME to concentrate analytes from the headspace, reducing matrix effects that may occur in other commonly used methods. The complete vaporization of the extract limits direct contact between the SPME fiber and the soil matrix allowing for the analytes to be isolated in the vapor phase. Additionally, the analyte of interest should be readily available in the vapor phase, negating the need for extract filtration. This makes TV-SPME advantageous as it minimizes competitive adsorption that may otherwise originate from matrices such as organic matter and other particulate solids present in soil.

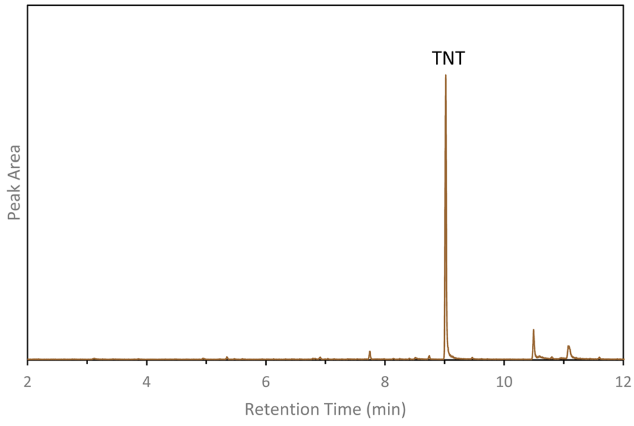

Fig. 3 Example GC/NICI MS chromatogram of TNT recovered from a spiked soil sample and analyzed *via* TV-SPME.

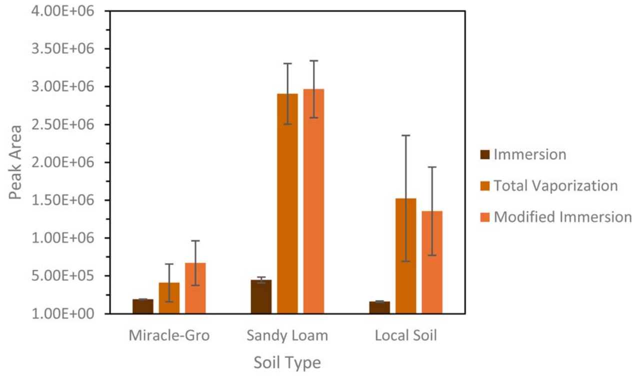

Fig. 4 Comparison of soil type and extraction methods used to analyze TNT spiked soil *via* GC-MS.

For comparison of soil type effect, Table 4 summarizes the percent recovery of TNT across three distinct soil types using immersion SPME, modified immersion SPME, and TV-SPME.

TNT recovery varied across different soil types. The TNT recovery was highest in sandy loam soil followed by local soil and Miracle-Gro soil. The observed results can be attributed to several factors, including extraction efficiency, organic content, and microbial content of the soil. Miracle-Gro soil, which has the highest organic content of approximately 70–90%, likely facilitated increased microbial degradation, leading to lower TNT recovery.[90] The local soil's organic composition was unknown but given that it was collected from a site with no visible plant growth in Indianapolis in October, it likely contained less organic material than Miracle-Gro but more than sandy loam soil, which had a measured organic content of 2.3%.[91] The lower organic content of sandy loam soil limited microbial degradation, resulting in the highest TNT recovery among the tested soil types.

Table 4 Percent recovery of TNT in different soil types using various analytical methods

Method	Sandy loam soil (%)	Miracle Gro soil (%)	Local soil (%)
Immersion GC-MS	12.72 ± 0.95	6.34 ± 0.15	5.59 ± 0.22
Modified immersion GC-MS	76.41 ± 9.46	18.39 ± 7.40	35.70 ± 14.74
TV-SPME GC-MS	69.27 ± 22.41	15.41 ± 0.74	66.05 ± 24.94

Together, the peak area responses and percent recoveries indicate that extraction efficiency is method-dependent; thus, the choice of extraction technique must be considered alongside soil organic content when interpreting TNT recovery.

3.3 Post-blast samples

3.3.1 Soil samples. Immersion SPME methods were unable to detect any TNT from post-blast soil samples. The results presented in Fig. 5 show the effect of different storage conditions on the recovery of TNT from post-blast soil samples analyzed using TV-SPME GC-MS. On day 0, freezer and fridge-stored samples exhibited similar TNT recovery, but as time progressed, the freezer-stored samples retained higher TNT levels compared to those stored in the fridge. Room temperature storage led to the fastest degradation, with no TNT detected by day 21, while both fridge and freezer-stored samples still contained TNT through day 28, but none was recovered after this point. Additionally, no explosives were detected in the pre-blast soil samples, confirming that TNT residues were introduced solely from the explosion.

The observed degradation trends are primarily attributed to microbial activity, which plays a significant role in breaking down TNT in environmental samples.[9] Warmer temperatures at room temperature storage accelerate microbial activity, leading to faster degradation of TNT and complete loss by day 21. Refrigeration and freezing slow microbial activity, extending the detectability of TNT, with the freezer being the most effective in preserving residues. This pattern of detection agrees with previous studies which have shown that storage at lower temperatures lowers the rate of metabolism of bacteria contained in the jar which results in slower rate of reduction of TNT's nitro groups.[34] However, degradation was not entirely prevented, as the TNT signal continued to decrease over time even in frozen samples. This is likely because samples were analyzed at room temperature, meaning they spent periods outside of cold storage where microbial activity could temporarily resume.

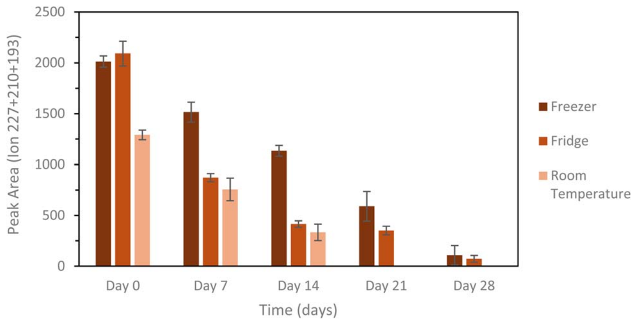

Fig. 5 Comparison of storage type of post-blast soil sampled every 7 days analyzed *via* TV-SPME.

Quantifying ion 227 and qualifying ions 210 and 193 are distinctive fragment ions of TNT frequently used in mass spectrometric analysis. As shown in Fig. 6, the CI mass spectral ions of TNT arise from formation of the molecular anion and subsequent characteristic fragmentation pathways. TNT produces a characteristic molecular radical anion at *m*/*z* 227, corresponding to $[\mathrm{M}]^{\bullet-}$, through electron capture by the highly electron-deficient aromatic ring. This is favored because TNT contains three strong electron-withdrawing nitro groups, which give the molecule a high electron affinity and stabilize the resulting negative ion. A second characteristic ion is observed at *m*/*z* 210, corresponding to $[\mathrm{M}-\mathrm{OH}]^-$. This fragment is commonly attributed to loss of $^\bullet$OH following rearrangement of the molecular radical anion, aided by the nitro substituents and the methyl group on the ring. An additional ion at *m*/*z* 193 is also observed and is consistent with a second $^\bullet$OH loss.

These ions were used to identify TNT along with comparing their retention times with total and extracted ion chromatograms. To ascertain their presence in the soil samples, standard solutions of 4-A-2,6-DNT, 1,4-DNB, and 2,6-DNT were also examined; however, none of these were detected in the post-blast soil samples.

To determine the rate of degradation and half-life of TNT in post-blast soil, eqn (3) was utilized where C is the concentration at time (t), C_0 is the initial concentration, and k is the rate constant (equal to the slope of the curve of $\ln(C/C_0)$ *vs.* time).

$$\ln\left(\frac{C}{C_0}\right) = kt \tag{3}$$

However, as shown in Fig. 7, a plot of $\ln(C/C_0)$ *vs.* time was not found to be linear. This indicates that the decay does not follow first-order kinetics and that TNT degradation is not solely concentration-dependent. Instead, the process may reflect

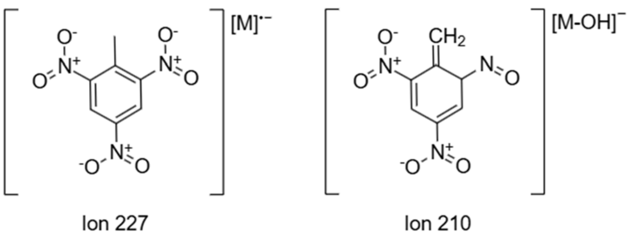

Fig. 6 Characteristic fragment ions of TNT produced in CI MS.

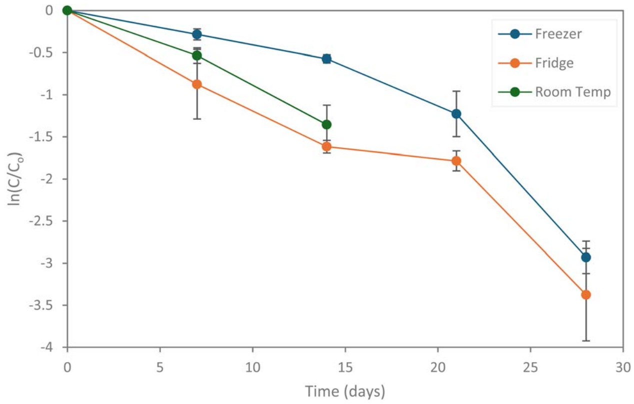

Fig. 7 Plot of $\ln(C/C_0)$ *versus* time showing deviation from linearity consistent with multiple stage decay for all storage conditions.

a multiple-phase degradation process where the degradation rate changes over time.

This observation aligns with previous studies by Miyares and Jenkins (2000) and Jenkins *et al.* (2001) which reported biphasic degradation of TNT in soil attributing to changes in microbial environment and sorption to soil components such as organic matter in different temperature conditions which can reduce its bioavailability and slow down degradation as seen in the freezer samples.[92,93]

3.3.2 Rock samples.

Neither immersion SPME nor TV-SPME could detect TNT on any of the rock samples that were gathered. However, in one instance, modified immersion SPME indicated the presence of TNT on post-blast rock samples. The presence of TNT was based on retention time comparison with an authentic reference standard and extracted ion chromatograms of ions m/z 227 and m/z 210, which are characteristic fragment ions of TNT commonly used in mass spectrometric analysis. The success of modified immersion compared to immersion SPME can be attributed to the addition of NaCl in the extraction process. The NaCl helps force TNT into the aqueous phase, enhancing its extraction efficiency.

4. Conclusion

In the present study, TV-SPME was successfully demonstrated as a rapid, simple, and sensitive technique for the extraction of TNT from post-blast and spiked soil samples. Evaluation of different storage conditions (freezer, refrigerator, and room temperature) showed that TNT could be reliably detected in soil stored at lower temperatures for up to 28 days, supporting the use of refrigerated or frozen storage for post-blast soil samples. A multi-phase degradation pattern was observed under all storage conditions, suggesting that TNT degradation does not follow simple first-order kinetics and may be influenced by both concentration and intermittent microbial activity.

In addition to analyzing post-blast soil samples, three soil types with varying organic and microbial content were spiked with TNT and analyzed using TV-SPME alongside comparative extraction methods. The soil with the lowest organic content (sandy loam) showed the highest TNT recovery, followed by local soil and Miracle-Gro, further supporting that higher organic content promotes increased analyte retention, degradation and, hence, decreased recovery.

Overall, these findings highlight that both extraction methodology and soil composition play critical roles in TNT recovery, emphasizing the necessity of carefully considering soil type and storage conditions when developing and applying analytical protocols for explosive residue analysis. It is important to consider that since soils were spiked with standard solution of TNT in acetonitrile, the recoveries may differ for actual contaminated samples.

Further studies can evaluate the extraction efficiency of TV-SPME for spiked soil samples stored at different temperature conditions to identify patterns in degradation of TNT with respect to differing soil content. It is also likely that TNT will not adhere to the soil as firmly over time as it is following direct spiking. In addition, a comparison with EPA methods could be conducted to evaluate their efficiency.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data for this article are available at IUI DataWorks at https://researchdata.iu.edu/resourcecatalog/iui-dataworks/index.html.

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