



Applications Development Report

Determination of Explosive Compounds in Soil Samples Using the TRIDION™-9 GC-TMS with SPME Sampling

Explosives: Trinitrotoluene (TNT), 1,3-Dinitrobenzene (1,3-DNB), 2,4-Dinitrotoluene (2,4-DNT), Methyl Centralite (MCT), and Triacetone Triperoxide (TATP)

Introduction

Detection limit studies were conducted for the detection of selected explosive compounds, including TNT, 1,3-DNB, 2,4-DNT, MCT, and TATP, in soil matrices using the TRIDION™-9 GC-MS. Sampling was achieved using a DVB/PDMS SPME fiber (65 µm) which was used to collect the samples for GC injection by either direct immersion into liquid sample extracts or through exposure to the headspace of processed samples. SPME sampling was done at either ambient temperature for immersion sampling or elevated temperature (~70°C) for head space sampling. The mode of SPME sampling was determined based on (1) the concentration levels required for detection, and (2) the cleanliness of sample matrix.

(Note: Solid Phase Micro-Extraction (SPME) is a simple, common method used to sample for organics in aqueous samples. The advantages of this device are its low cost, field robustness and applicability with either liquid sample collection by direct immersion or gas-phase sampling by head space extraction. The method minimizes contamination for the GC-MS system.)

Experimental Conditions

Preparation of Standard Samples: Standard samples of the explosive test compounds used in these experiments were prepared by spiking 10 g of soil (pretreated to be free of test analytes) contained in 40 mL vials. Stock standard solutions were received from Sigma Aldrich at concentrations of 100 µg/mL for TATP and MCT and 1000 µg/mL for TNT, 2,4-DNT and 1,3-DNB in methanol/acetonitrile (1:1 v/v). Simulated test samples of the explosive compounds in soil were prepared at 0.1 µg/g (0.1 ppm) for TATP and MCT and 1 µg/g (1 ppm) for TNT, 2,4-DNT and 1,3-DNB. After addition of the explosives standards to the soil matrix, the blend was then thoroughly mixed and allowed to stand. Next, simulated test samples were extracted using acetone. 10 mL of acetone was added to the sample vial containing the soil spiked with explosives compounds and manually extracted by shaking for 3 min. A known volume of acetone extract (from 1-2 mL) was then withdrawn from the soil-solvent mixture and transferred to a clean 2 mL vial. The solvent was then evaporated under a nitrogen or helium flow with the vial placed on a heater block set at a temperature of 35-40°C. The sample extract volume was reduced until only a tiny liquid drop was observed in the bottom of the vial (*Note: the liquid is thought to be water from the soil matrix and/or water condensate from the sample preparation process*). The sample preparation pathway is shown in Figure 1.

SPME fiber sampling using either a direct immersion technique at ambient temperature or a headspace exposure technique at elevated temperature (70°C) was performed. Immersion SPME sampling is more applicable to higher analyte concentrations (>1 ppm) in cleaner samples. Headspace extraction sampling is best used for lower analyte concentrations (< 1 ppm) in dirtier samples.

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- **Immersion SPME Sampling Conditions:**

1 mL of deionized H₂O is added into the 2 mL vial following the solvent evaporation step. The extraction was conducted at ambient temperature with hand shaking using DVB/PDMS 65 μ m fiber for 2 min.

- **Headspace SPME Sampling Conditions:**

The 2 mL vial was heated on a heater block set at 70-80°C for 4 min. The SPME fiber was exposed to the headspace for 2 min. with the fiber located in the middle of the vial.

Preparation of Simulated Real-world Samples: Untreated soil samples spiked with explosive compounds were prepared following the same procedures used for the standard-spiked clean samples. These samples were prepared and used to evaluate the method for applicability to real-world samples contaminated with explosive compounds.

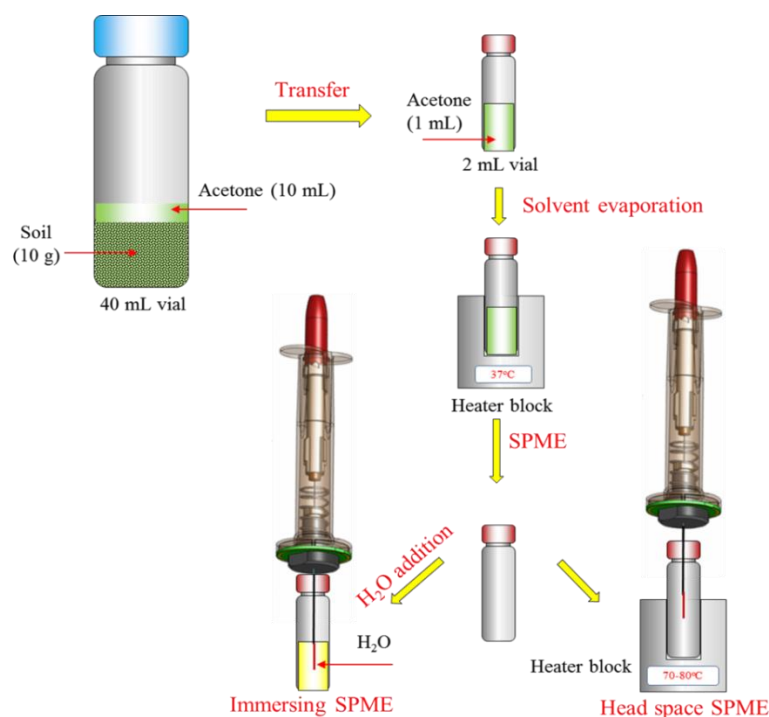


Figure1: Sample preparation and SPME sampling steps used for explosive in soil.

The SPME fiber syringe used to collect the samples was inserted into the TRIDION-9 GC-TMS injection port where the target analytes were desorbed into a split-splitless injector (270°C, 20 s splitless) coupled with a low thermal mass metal-clad capillary GC column (MXT-5, 5 m x 0.1 mm, 0.4 μ m df). After an initial 10 second hold at 50°C, the GC temperature was increased at 2°C/sec to 270°C with 10s hold for a total run time of 130 sec. The capillary GC is coupled to a TMS detector having a mass range of 43-500 m/z.

Results

Figures 2-6 show the TIC and RIC chromatograms of the explosive target analytes in soil at 0.1 and 1 $\mu\text{g/g}$. The analytes were sampled by SPME headspace and analyzed by GC-MS.

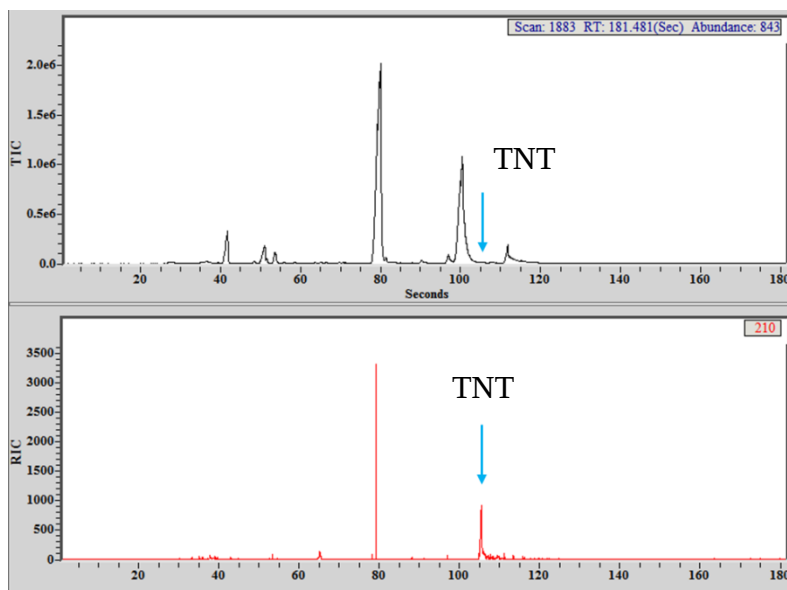


Figure 2. TIC and RIC (m/z 210) chromatograms of TNT in soil at 1 ppm.

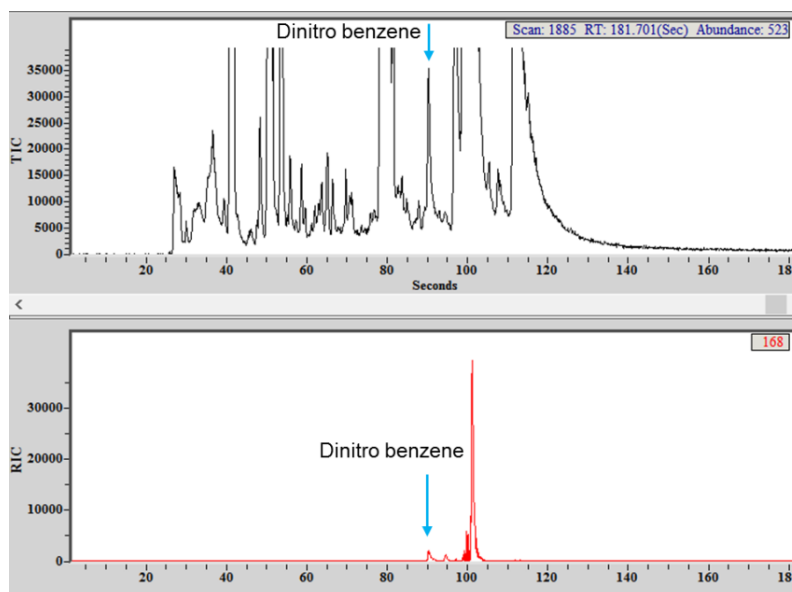


Figure 3. TIC and RIC (m/z 168) chromatograms of 1,3-DNB in soil at 1 ppm.

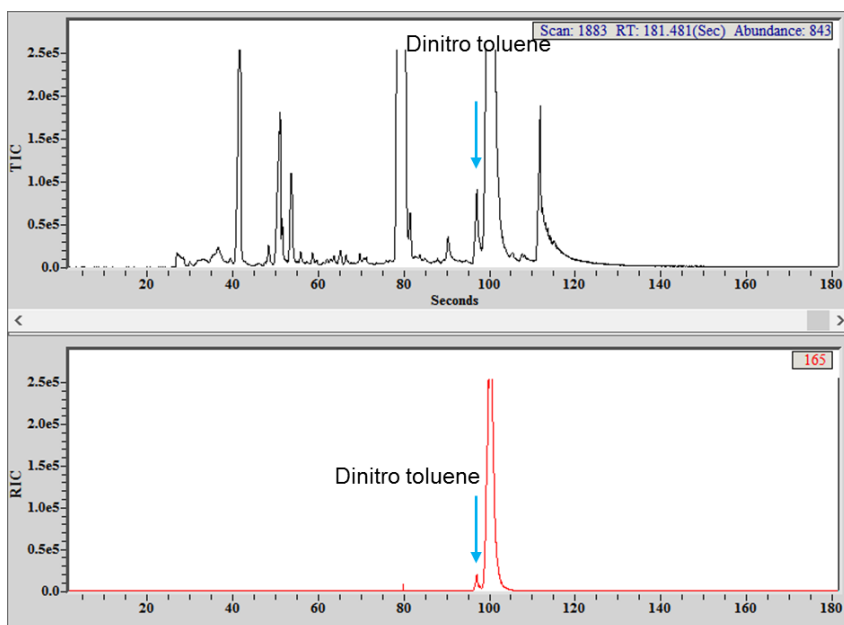


Figure 4. TIC and RIC (m/z 165) chromatograms of 2,4-DNT in soil at 1 ppm.

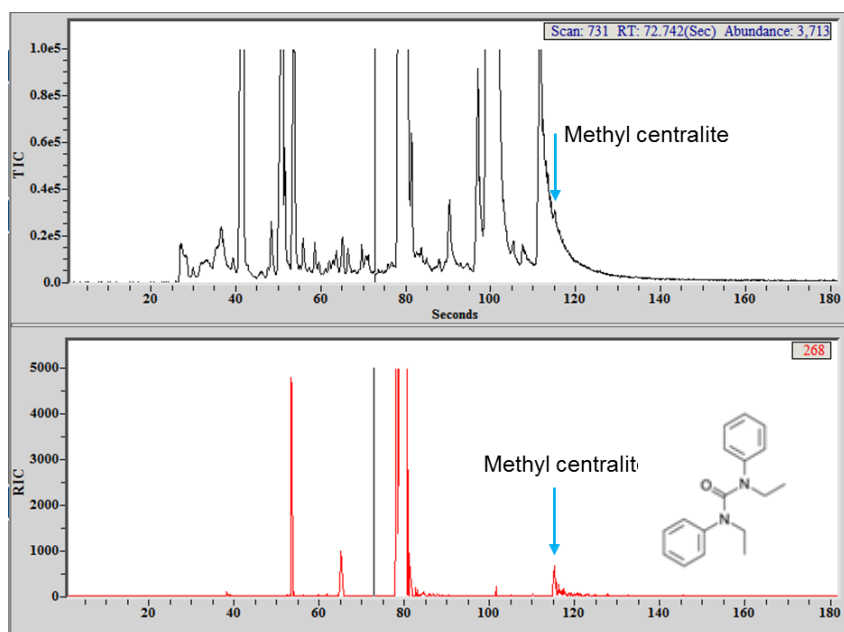


Figure 5. TIC and RIC (m/z 268) chromatograms of MCT in soil at 0.1 ppm.

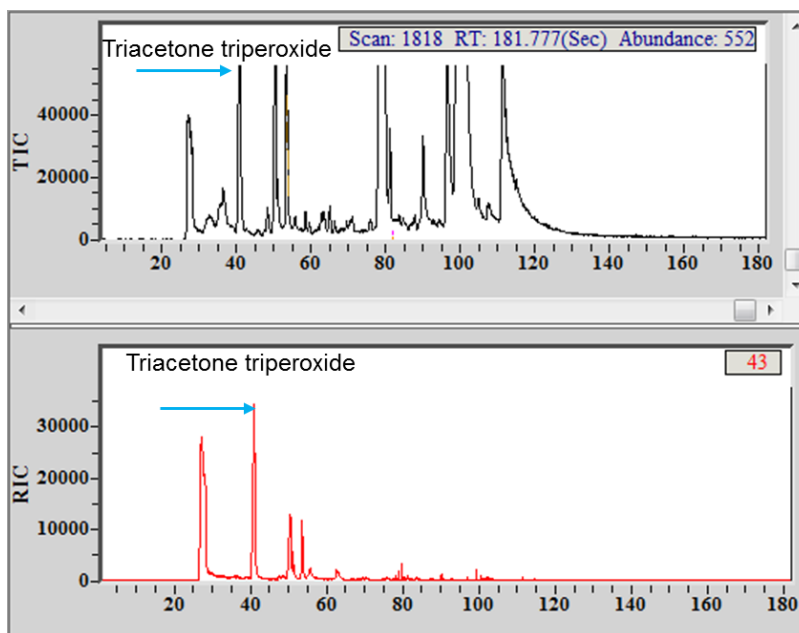


Figure 6. TIC and RIC (m/z 210) chromatograms of TATP in soil at 0.1 ppm.

In the immersion SPME method the results indicated that the sensitivities for MCT and 2,4-DNT were improved while those of TNT, TATP and 1,3-DNB were reduced significantly (data not shown). In addition, when dirty soil samples are tested, the SPME fiber may be degraded due to less-volatile or non-volatiles substances accumulation.

Conclusions

The headspace SPME method gave better detection limits for the explosive analytes studied in this report. The results shown above demonstrate that 1 ppm of TNT, 1,3-DNB, and 2,4-DNT and 0.1 ppm of TATP and MCT can be detected in soil samples. This method takes ~20 min to perform, including both sample preparation and GC-MS analysis. Calibration curves could be developed using internal standards spiked into the extraction solvent during the sample preparation steps to provide quantitative data for targeted explosive compounds in soil matrices.

The information included in this report clearly demonstrates the applicability to analyze soil samples for those explosive compounds tested. Method applicability for other explosive compounds, such as RDX and PETN, would require additional work.