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Comprehensive Detection and Confirmation of Explosive Residues in Soil Using a High Performance Benchtop GC-TOFMS

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Key Words: Detection, Explosive Residues, Soil, GC-MS, Time-of-Flight

Introduction

For years, gas chromatography (GC) combined with various detector types (e.g., flame ionization, mass spectrometers, electron capture, etc.) has been utilized for the detection of a variety of explosives. GC provides efficient separation while mass spectrometry adds the benefits of selectivity and compound identification through spectral similarity comparisons to commercial databases. Explosives can be difficult to analyze due to their relatively low volatility and thermal instability. However, careful adjustment of acquisition parameters results in rapid characterization of samples. Modern-day, high performance gas chromatograph time-of-flight mass spectrometers (GC-TOFMS) provide unprecedented sensitivity (ppt), extended dynamic range (10^5), and improved selectivity. The analysis of explosive residues via fast and comprehensive high performance GC-TOFMS has dramatically increased sample throughput, while simultaneously providing rich data sets with a wealth of information for explosive materials, precursors, and matrix compounds. In addition, the historical archives of comprehensive mass spectral data can be probed retrospectively using targeted processing methods once compounds of interest have been identified. In this study, we analyzed a standard mixture of explosives in soil in under five minutes (Figure 1). The analysis was facilitated by superior chromatographic resolution, use of a high performance benchtop TOFMS, and powerful software with deconvolution for untargeted and targeted data processing.
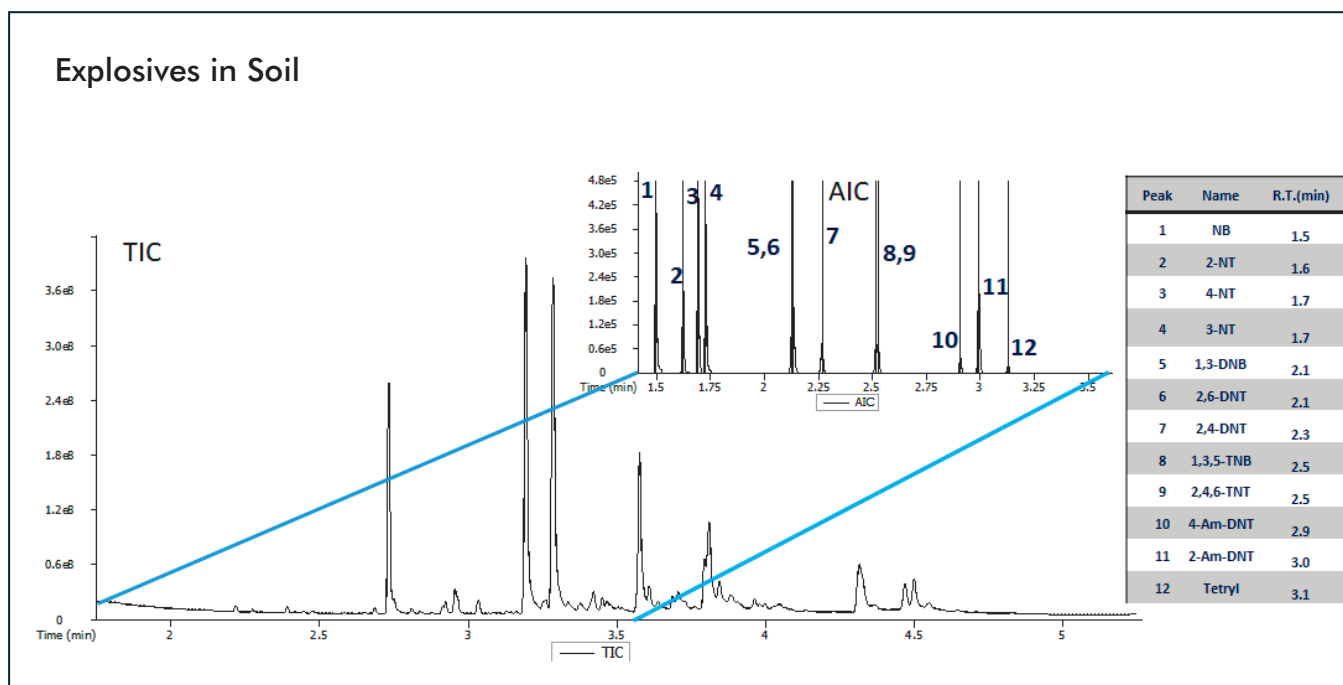

Figure 1. Total Ion Chromatogram (TIC) with an inset Analytical Ion Chromatogram (AIC) region of explosives detected in a soil sample.

Experimental

A simple and efficient extraction method was used for the analysis of explosives in soil.[1] Samples were collected from a location adjacent to a local parking lot. These soil samples were spiked with explosive nitroaromatic, nitroaniline, and nitroamine standards (Figure 2).[2] The standards included nitrobenzene (NB), 2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), 4-nitrotoluene (4-NT), 1,3-dinitrobenzene (1,3-DNB), 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrotoluene (2,4-DNT), 1,3,5-trinitrobenzene (1,3,5-TNB,) 2,4,6-trinitrotoluene (2,4,6-TNT), RDX or cyclonite, 2-amino-4,6-dinitrotoluene (2-Am-DNT), 4-amino-2,6-dinitrotoluene(4-Am-DNT), tetryl, and octogen (HMX).
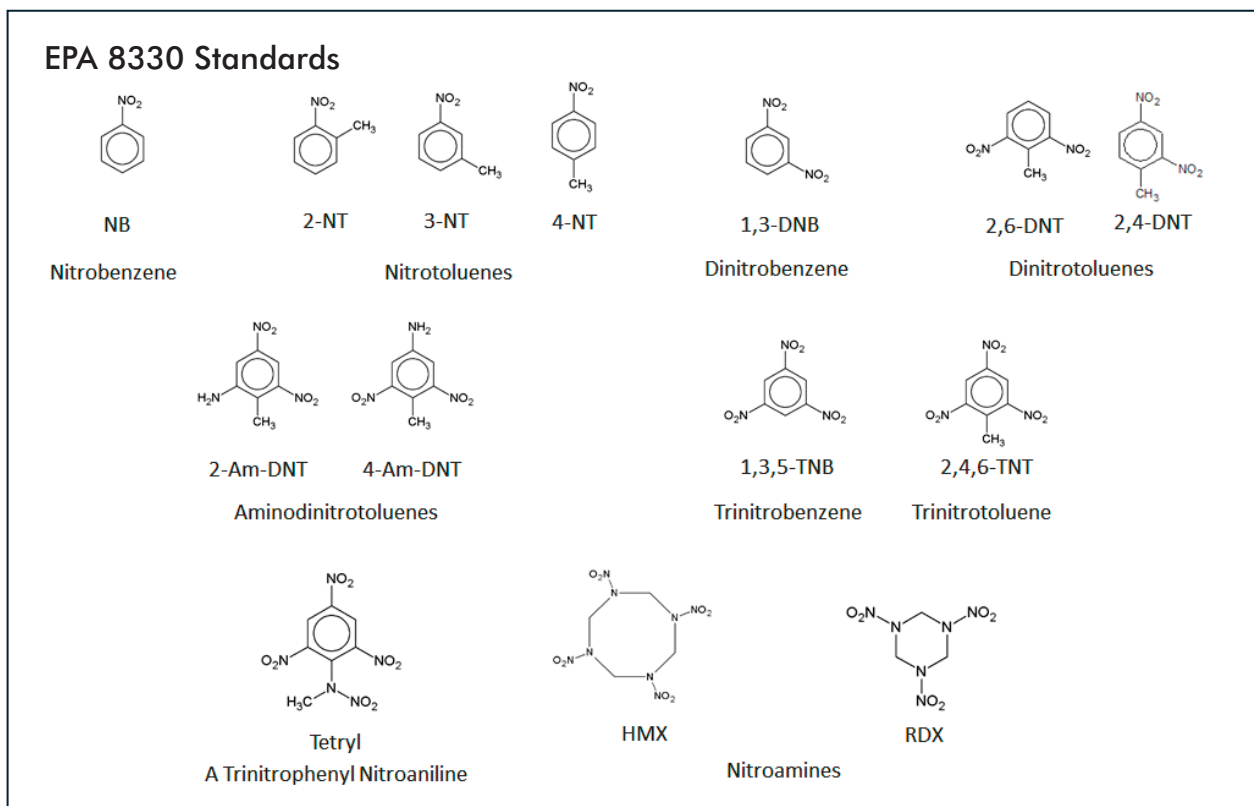

Figure 2. EPA 8330 Standards.

A small amount of soil (0.40 to 0.50 g) was placed in a 20 mL vial. 5.0 mL of acetonitrile was added and the mixture was vortexed for 10 seconds and then agitated for 5 minutes at a temperature of 30 °C. This was followed by the addition of 5.0 mL of dichloromethane and agitation for 25 minutes at 30 °C. A 3 mL aliquot of the heterogenous mixture was dried over anhydrous calcium chloride and 1 mL was transferred to a GC vial for immediate analysis using the instrumental parameters listed in Table 1. An Agilent Multimode Inlet (MMI) with a 2 mm inner diameter liner and temperature programming were used to minimize compound degradation.

Table 1. Instrumental Parameters

Gas Chromatograph	Agilent 7890 with Multi-Mode Inlet (MMI) and 7693 Autosampler
Injection	1µL, splitless at 60 °C (0.5 min) to 200 °C at 720 °C/min
Carrier Gas	He @ 1.4 mL/min, Constant Flow
Column	DB-5MS UI, 15 m x 0.25 mm i.d. x 0.25 µm coating
Oven Program	70 °C (0.5 min), ramped 50 °C/min to 320 °C
Transfer Line	250 °C
Mass Spectrometer	**LECO Pegasus BT**
Ion Source Temperature	250 °C
Mass Range	50-450 m/z
Acquisition Rate	20 spectra/s

Results and Discussion

The detection of explosives is a vital part of law enforcement, anti-terrorism, and military activities around the world. The ideal method for detection of explosives must provide: 1) high sensitivity, 2) applicability for a wide range of explosives, 3) high selectivity to reduce false positives or negatives, 4) quick response times, and 5) minimal sample preparation or handling.[3] Typically, the analysis of explosives in soil involves complicated, time-consuming extractions with acetonitrile followed by either analysis by GC/ECD (EPA Method 8095) or HPLC/UV (EPA Method 8330). These methods often are plagued with poor results (i.e., false positives, inadequate quantification) due to coelutions and/or poor selectivity especially in complex matrices. A better analytical method would include the implementation of high-performance GC-TOFMS for comprehensive analysis of explosives. The analytical technology is ideal for the identification of explosives and their precursors in challenging matrices. Its superior chromatographic resolution, mass spectral selectivity, and high acquisition speeds for increased sample throughput facilitated the analysis of a variety of explosive sample types. A *Pegasus* BT Analytical Ion Chromatogram (AIC) for EPA 8330 standards is shown in Figure 3. The total analysis time was less than 5 minutes with retention times for explosives ranging from 1.9 to 4.2 minutes. Comprehensive data processing utilizing ChromaTOF® brand software resulted in detection of 12 out of 14 explosives with an average spectral similarity of 880/1000.
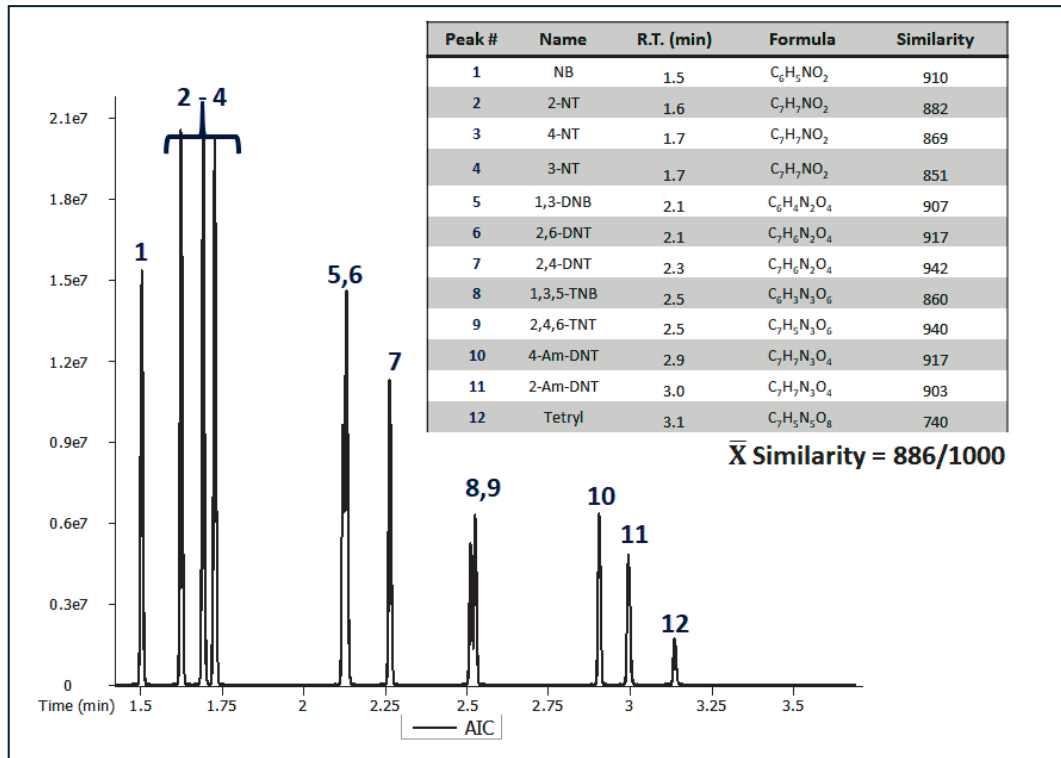

Peak #	Name	R.T. (min)	Formula	Similarity
1	NB	1.5	$C_6H_5NO_2$	910
2	2-NT	1.6	$C_7H_7NO_2$	882
3	4-NT	1.7	$C_7H_7NO_2$	869
4	3-NT	1.7	$C_7H_7NO_2$	851
5	1,3-DNB	2.1	$C_6H_4N_2O_4$	907
6	2,6-DNT	2.1	$C_7H_6N_2O_4$	917
7	2,4-DNT	2.3	$C_7H_6N_2O_4$	942
8	1,3,5-TNB	2.5	$C_6H_3N_3O_6$	860
9	2,4,6-TNT	2.5	$C_7H_5N_3O_6$	940
10	4-Am-DNT	2.9	$C_7H_7N_3O_4$	917
11	2-Am-DNT	3.0	$C_7H_7N_3O_4$	903
12	Tetryl	3.1	$C_7H_5N_5O_8$	740

$\overline{X}$ Similarity = 886/1000

Figure 3. AIC of explosive standards at 500 pg/µL.

Calibration curves for various explosives were produced using *ChromaTOF*. Excellent linearity from 0.1 to 100 ppb (r >0.99) with lower detection limits obtained for the majority of explosives used in this study. Representative calibration curves for three of the explosive standards are displayed in Figure 4.
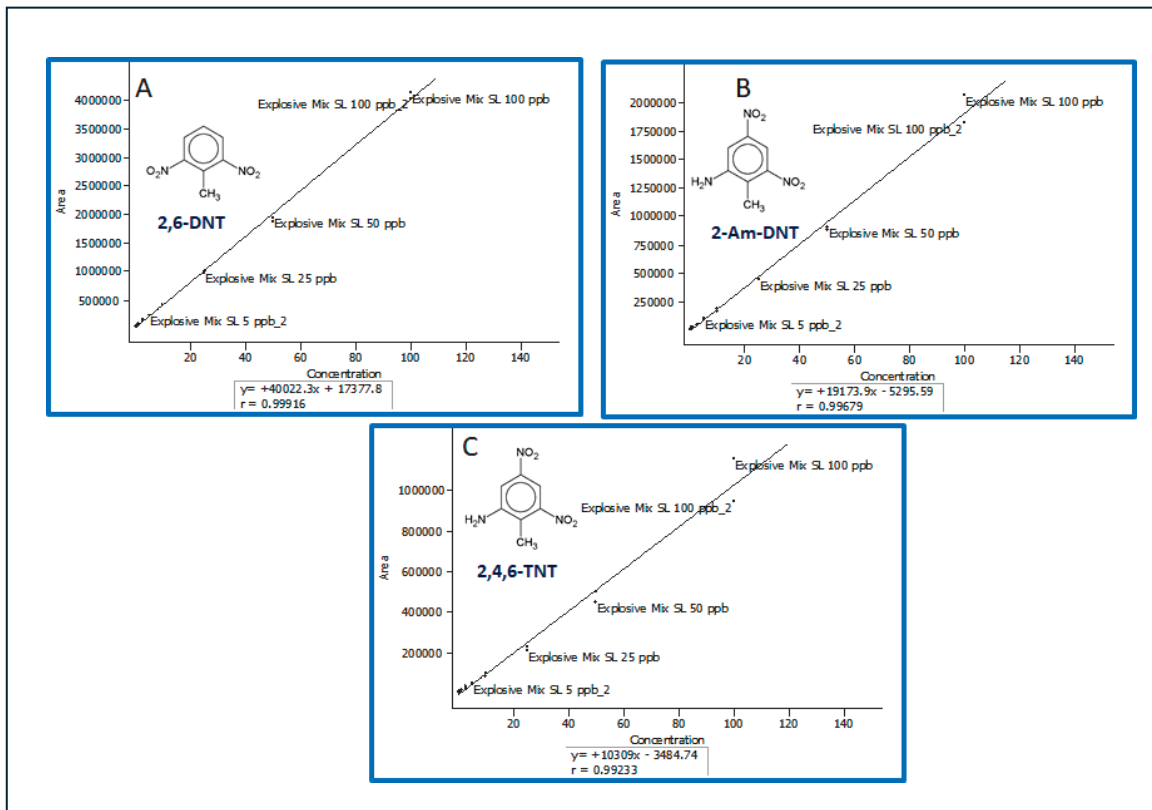
Figure 4. Calibration curves for A) 2,6-DNT, B) 2-Am-DNT, and C) 2,4,6-TNT (0.1 to 100 ppb).

Comprehensive processing of complex soil samples included non-targeted peak finding and spectral similarity searches using large, well-established databases (Figure 5). GC-TOFMS analysis provided more detailed sample information compared to other instrumental techniques such as HPLC-UV, GC-ECD, or GC-MS utilizing targeted processing. For example, the soil sample used in this qualitative study contained relatively large quantities of polyaromatic hydrocarbons, carbazoles, and dibenzothiophenes (Table 2). This was not surprising, since the samples were collected near an asphalt parking lot.

The average spectral similarity and absolute mass delta values for the representative compounds listed in Table 2 were 924/1000 and 0.01 respectively. The high quality spectral data produced by high performance GC-TOFMS is clearly illustrated for two of these compounds: carbazole and anthracenedione (Figure 6).
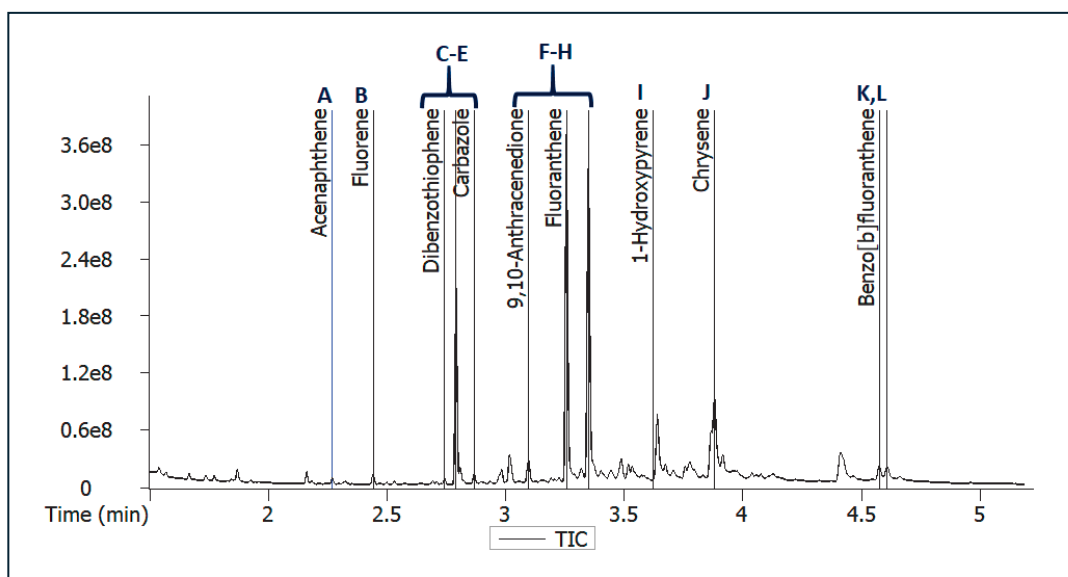

Figure 5. TIC: In addition to explosives, several other representative non-targeted compounds were identified in the soil.

Table 2. List of representative non-explosives in soil extract

Peak	Name	R.T. (min)	Similarity	Obz m/z	Calc m/z	m/z Δ (Da)
A	Acenaphthene	2.3	949	154.07	154.08	-0.01
B	Fluorene	2.4	915	166.07	166.08	-0.01
C	Dibenzothiophene	2.7	945	184.03	184.03	-0.01
D	Anthracene	2.8	952	178.07	178.08	-0.01
E	Carbazole	2.9	936	167.07	167.07	-0.01
F	9,10-Anthracenedione	3.1	893	208.05	208.05	0.00
G	Fluoranthene	3.3	964	202.08	202.08	0.00
H	Pyrene	3.3	927	202.07	202.08	0.00
I	1-Hydroxypyrene	3.6	775	218.07	218.07	-0.01
J	Chrysene	3.9	957	228.09	228.09	0.00
K	Benzo[b]fluoranthene	4.6	935	252.09	252.09	0.00
L	Benzo[k]fluoranthene	4.6	941	252.09	252.09	0.00

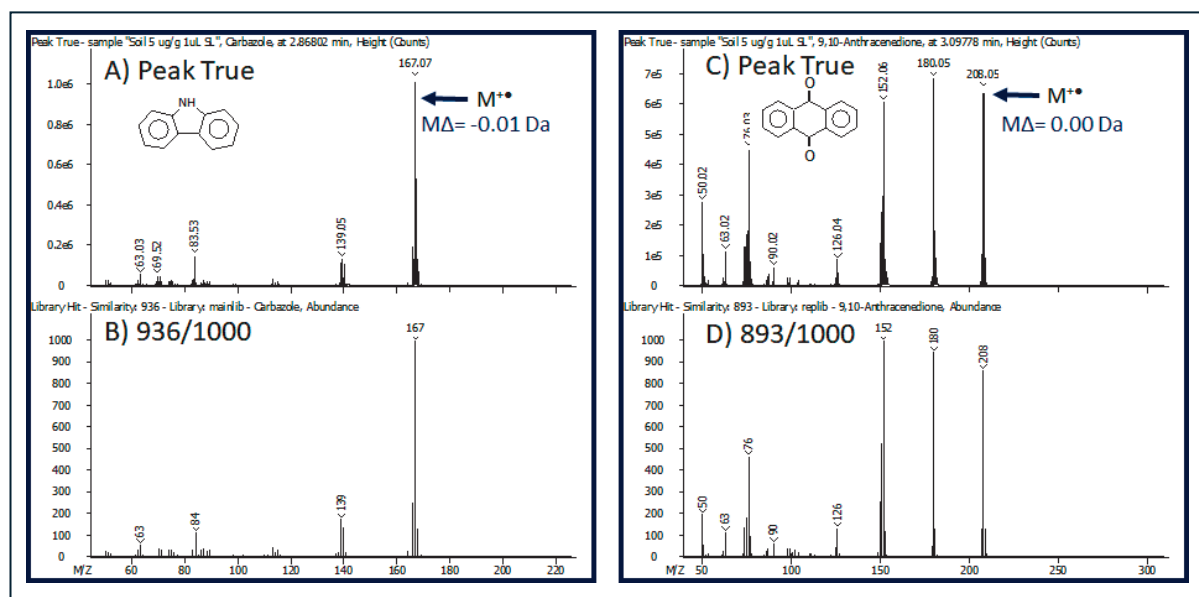$$\overline{X} \text{ Similarity} = 924/1000$$

Figure 6. Peak True and library mass spectral data for carbazole (A, B) and anthracenedione (C, D).

An extra dimension of separation, deconvolution, is required for shorter acquisition times since chromatographic peak coelutions are common. The clear advantage of producing Peak True (deconvoluted) mass spectral data is illustrated in Figure 7 where *ChromaTOF* provided "clean" Peak True spectra for the coeluting compounds 2-NT and p-toluidine (spectral similarity values of 887 and 889/1000).
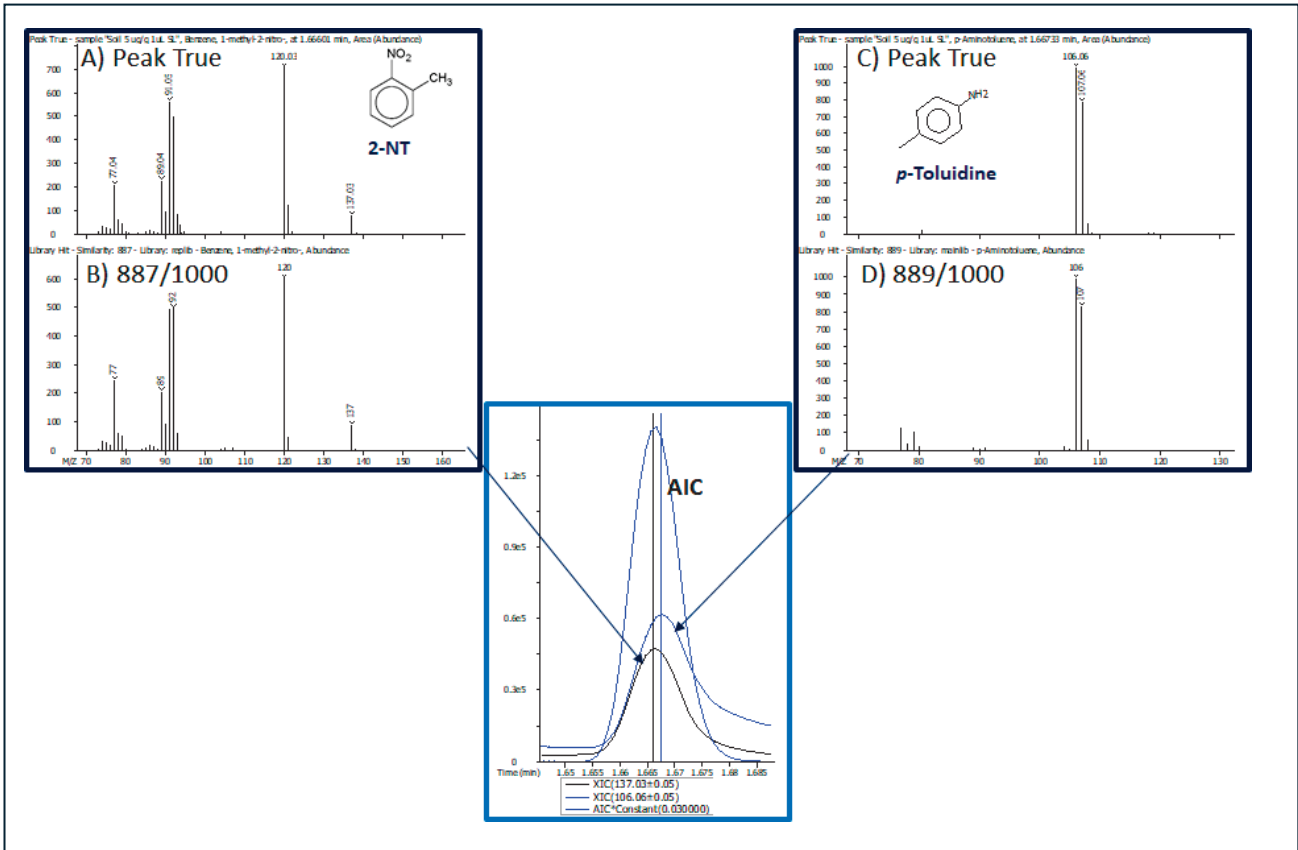
Figure 7 AIC showing coeluting compounds in a soil sample (bottom). Peak True and library mass spectral data for 2-NT (A, B) and p-toluidine (C,D).

Alternatively, comprehensive soil sample data was processed using Target Analyte Finding (Figure 8). Target Analyte Finding (TAF) leverages retention times with fragment and/or molecular ions for trace analysis and rapid processing of large datasets. Twelve explosives were detected in the complex soil sample and the results after TAF processing are shown in Figure 9. This TAF processing approach takes less than 12 seconds per data file.
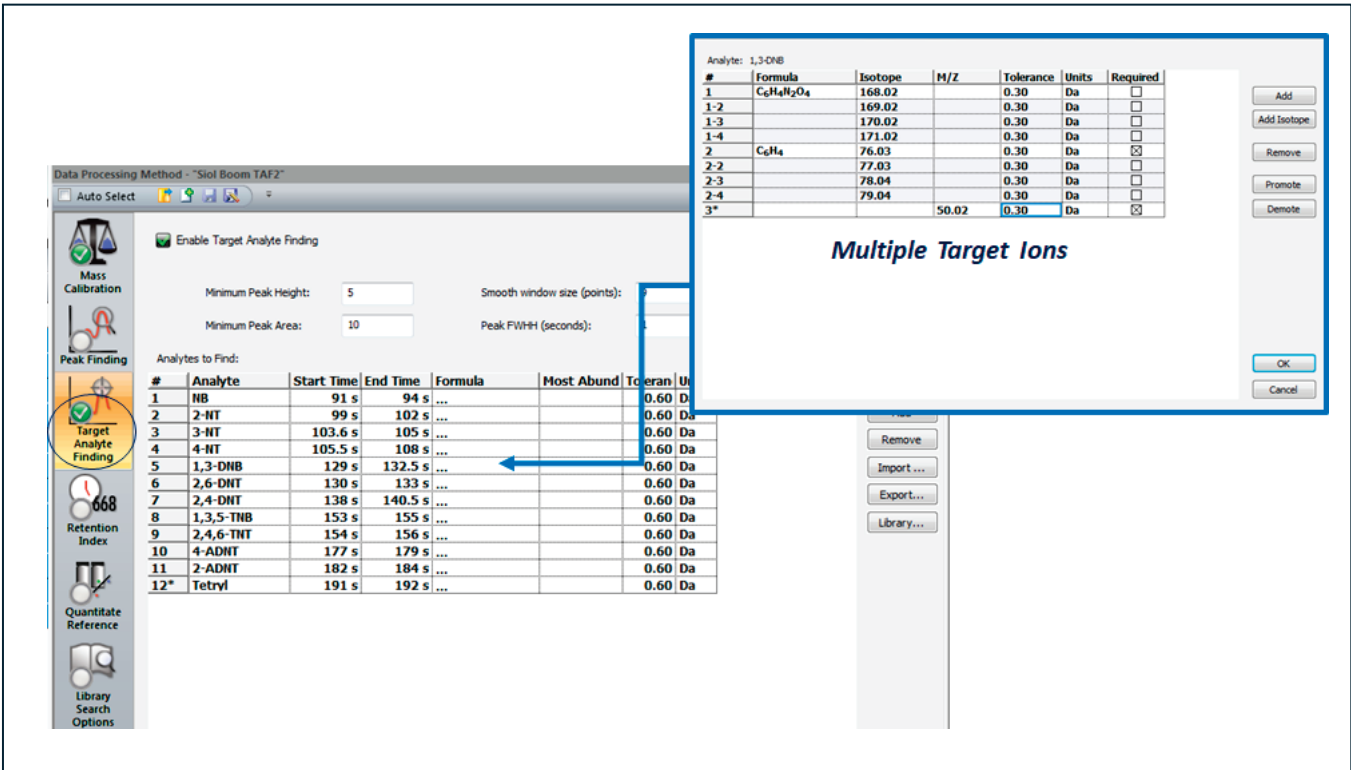

Figure 8. Target Analyte Finding processing method for explosives in soil.
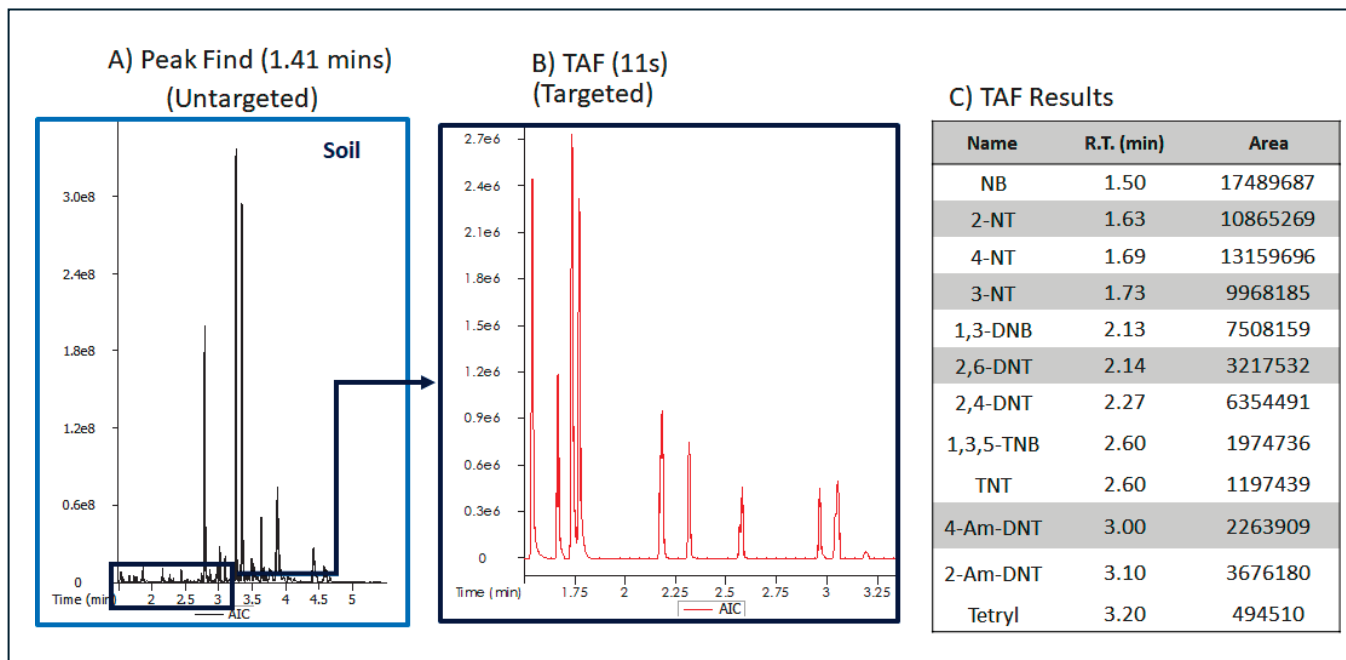
A) Peak Find (1.41 mins)
(Untargeted)

B) TAF (11s)
(Targeted)

C) TAF Results

Name	R.T. (min)	Area
NB	1.50	17489687
2-NT	1.63	10865269
4-NT	1.69	13159696
3-NT	1.73	9968185
1,3-DNB	2.13	7508159
2,6-DNT	2.14	3217532
2,4-DNT	2.27	6354491
1,3,5-TNB	2.60	1974736
TNT	2.60	1197439
4-Am-DNT	3.00	2263909
2-Am-DNT	3.10	3676180
Tetryl	3.20	494510

Figure 9. Target Analyte Find processing results for explosives in soil.

Conclusion

A combination of a simple but effective extraction technique and GC with high performance TOFMS resulted in quick and confident identification of explosives in soil samples. Linear calibration curves for representative explosives demonstrate the system's ability to effectively perform quantitation. The *Pegasus* BT provided comprehensive, high quality spectral data that was processed using either Peak Find for complete untargeted results or TAF to increase throughput and facilitate trace analysis of explosives.

References

[1] Holmgren E., Ek S. and Colmsjo A., *J. Chromatogr. A,* **2012,** *1222,* 109-115.
[2] EPA 8330 standards (Cat. No. 31450 and 31451 were purchased from Restek Corporation, 110 Benner Circle Bellefonte, PA 16823.
[3] Takats Z., Cote-Rodriguez I., Talaty N., Chen H. and Cooks R.G., *Chem. Commun.,* **2005,** 1950-1952.