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Application News

Rapid LC-MS/MS Analysis of 19 Explosives in Soil

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User Benefits

- Simultaneous measurement of positive and negative ions enables the analysis of 19 explosives in about 5 minutes.
- Thermally labile explosives can be detected with high sensitivity under optimized MS conditions.
- Regioisomers of nitrobenzenes can be separated under optimal LC conditions.

■ Introduction

Explosives are defined as chemical substances that decompose rapidly and release high-temperature, high-pressure gases. There are many types of explosives, including nitramines, nitrobenzenes, nitrates, and peroxides. While these are widely used for military and industrial purposes, they may remain in the environment due to accidental leakage or illegal use. In particular, soil tends to retain explosives and their residues. The analysis of these substances is useful for evidence collection in criminal investigations and for assessing environmental impacts. Traditionally, GC-MS has been widely used for the analysis of explosives. However, some compounds are prone to thermal decomposition during vaporization. Therefore, LC-MS/MS methods are increasingly being applied to such analyses.
In this study, 19 explosives listed in Table 1, including nitramine, nitrobenzene, nitrate ester, and peroxide, were analyzed in soil using LCMS-8060RX (Fig. 1).

Fig. 1 Nexera™ X3 + LCMS-8060RX

■ Sample Preparation & Extraction

Calibration standards were prepared by diluting a mixed solution of each standard with methanol to obtain concentrations equivalent to 1.0, 5.0, 10, 50, 100, 500, and 1,000 ng/mL in soil samples. The extraction method for soil samples was based on EPA 8330B[1)] (Fig. 2). First, the dried soil samples were passed through a 10-mesh sieve to remove coarse particles. The samples were weighed in 10-g portions, and 10 mL of methanol was added to each. As an internal standard (I.S.), 10 µL of a 1,2-DNB solution (50 µg/mL) was added to each sample, and a mixed solution of 19 explosives (10 µg/mL) was also added for validation. The samples were then mixed with a vortex mixer for 1 minute, shaken for 10 minutes at room temperature using a shaker, and centrifuged. The resulting supernatant was collected and filtered through a 0.45 µm filter. The filtrate was concentrated under a nitrogen stream and dissolved in 1 mL of methanol to prepare the analytical samples.

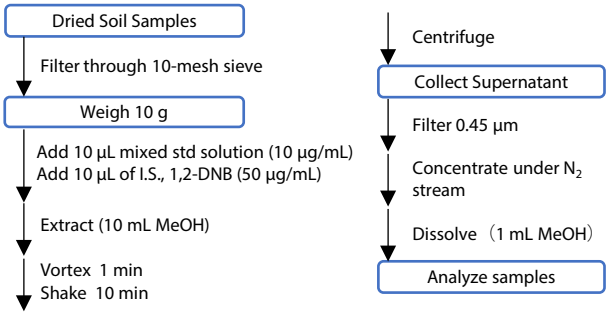

Fig. 2 Workflow for Soil Sample Pretreatment

Table 1 List of Target Compounds

Abbreviation	Compound name	Group	Formula	M.W. (monoisotopic mass)
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine	Nitramine	C3H6N6O6	222.03
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	Nitramine	C4H8N8O8	296.05
NQ	Nitroguanidine	Nitramine	CH4N4O2	104.03
TNT	2,4,6-Trinitrotoluene	Nitrobenzene	C7H5N3O6	227.02
4A-2,6-DNT	4-Amino-2,6-Dinitrotoluene	Nitrobenzene	C7H7N3O4	197.04
2A-4,6-DNT	2-Amino-4,6-Dinitrotoluene	Nitrobenzene	C7H7N3O4	197.04
2,4-DNT	2,4-Dinitrotoluene	Nitrobenzene	C7H6N2O4	182.03
2,6-DNT	2,6-Dinitrotoluene	Nitrobenzene	C7H6N2O4	182.03
TNB	1,3,5-Trinitrobenzene	Nitrobenzene	C6H3N3O6	213.00
1,3-DNB	1,3-Dinitrobenzene	Nitrobenzene	C6H4N2O4	168.02
3,5-DNA	3,5-Dinitroaniline	Nitrobenzene	C6H5N3O4	183.03
Tetryl	2,4,6-N-tetranitro-N-methylaniline	Nitrobenzene	C7H5N5O8	287.01
PA	2,4,6-Trinitrophenol (Picric acid)	Nitrobenzene	C6H3N3O7	229.00
PETN	Pentaerythritol tetranitrate	Nitrate ester	C5H8N4O12	316.01
NG	Nitroglycerin	Nitrate ester	C3H5N3O9	227.00
1,2-DNG	1,2-Dinitroglycerin	Nitrate ester	C3H6N2O7	182.02
1-MNG	1-Mononitroglycerin	Nitrate ester	C3H7NO5	137.03
TATP	Triacetone triperoxide	Peroxide	C9H18O6	222.11
HMTD	Hexamethylene triperoxide diamine	Peroxide	C6H12N2O6	208.07
1,2-DNB	1,2-Dinitrobenzene	I.S. (Nitrobenzene)	C6H4N2O4	168.02

■ Analytical Conditions

The LC-MS/MS analytical conditions are summarized in Table 2, and the retention times and transitions for each compound are listed in Table 3. It was found that peroxides and nitramines tend to form positive ions, whereas the other compounds tend to form negative ions. Since nitrate esters and peroxides are particularly prone to thermal decomposition, it was necessary to set the MS interface temperature low. On the other hand, nitramine peaks tended to tail at interface temperatures below 250 ˚C. Therefore, the interface temperature was set at 270 ˚C to achieve sufficient sensitivity and acceptable peak shapes for each compound.

Furthermore, the LC conditions were optimized to separate nitrobenzenes, which include many regioisomers, within a short analysis time. The MRM chromatograms are shown in Fig. 3.

■ Results

Standard solutions diluted with methanol were prepared at concentrations equivalent to 1.0, 5.0, 10, 50, 100, 500, and 1,000 ng/mL, and linearity was evaluated. PETN and TATP were detectable at 5.0 ng/mL, whereas the other 17 compounds were detectable at 1.0 ng/mL (Fig. 4). The calibration curves were weighted by 1/C. The correlation coefficients (R) for all compounds were 0.995 or higher, indicating good linearity (Table 4). To evaluate intra-day accuracy and repeatability, soil samples spiked to 10 ng/mL for each compound were analyzed (n = 5). Representative MRM chromatograms are shown in Fig. 5. Accuracy ranged from 70% to 120% (Fig. 6), and %RSD values, which indicate repeatability, were 9.1% or less. These results indicate that the proposed method provides sufficient linearity, accuracy, and repeatability for the analysis of explosives in soil.

Table 2 Nexera and LCMS-8060RX Conditions

[HPLC conditions] (Nexera X3)		
Column	:	Shim-pack Velox Biphenyl (100 mm × 2.1 mm I.D., 2.7 µm) P/N: 227-32015-03
Column oven	:	30 ˚C
Solvent A	:	5 mM ammonium formate + 0.1 % formic acid in water
Solvent B	:	MeOH
Flow rate	:	0.3 mL/min
Time Program (%B)	:	60 % (0-1.5 min) → 90 % (5.0-6.0 min) → 60 % (6.0-8.0 min)
Injection volume	:	2 µL
[MS conditions] (LCMS-8060RX)		
Ionization	:	APCI, Positive/Negative mode
Nebulizing gas flow	:	4 L/min
Drying gas flow	:	5 L/min
DL temp.	:	150 ˚C
Heat block temp.	:	200 ˚C
Interface temp.	:	270 ˚C

Table 3 Retention Times and MRM Transitions of Target Compounds

Compound name	Retention time (min)	Polarity	Precursor ion (*m/z*)		Quantifier ion (*m/z*)	Reference ion1 (*m/z*)	Reference ion2 (*m/z*)
NQ	0.789	Positive	$[M+H]^+$ = 105.0	>	59.0 (CE -14 V)	43.0 (CE -24 V)	-
1-MNG	0.840	Negative	$[M+CHCOO]^-$ = 182.0	>	45.0 (CE 22 V)	62.0 (CE 6 V)	-
1,2-DNG	1.093	Negative	$[M+CHCOO]^-$ = 227.0	>	45.0 (CE 10 V)	62.0 (CE 6 V)	-
HMX	1.164	Negative	$[M+CHCOO]^-$ = 341.0	>	147.1 (CE 9 V)	174.2 (CE 10 V)	100.0 (CE 10 V)
PA	1.252	Negative	$[M-H]^-$ = 228.0	>	182.0 (CE 18 V)	198.3 (CE 16 V)	63.0 (CE 26 V)
RDX	1.330	Negative	$[M+CHCOO]^-$ = 267.0	>	46.0 (CE 8 V)	92.0 (CE 6 V)	-
HMTD	1.376	Positive	$[M+H]^+$ = 209.1	>	88.0 (CE -12 V)	145.1 (CE -8 V)	-
NG	1.854	Negative	$[M]^-$ = 227.0	>	62.0 (CE 10 V)	45.0 (CE 8 V)	-
3,5-DNA	2.091	Negative	$[M-H]^-$ = 182.0	>	94.0 (CE 20 V)	124.0 (CE 16 V)	152.1 (CE 17 V)
4A-2,6-DNT	2.444	Negative	$[M-H]^-$ = 196.0	>	119.1 (CE 17 V)	149.0 (CE 17 V)	-
1,2-DNB	2.549	Negative	$[M]^-$ = 168.0	>	138.0 (CE 14 V)	107.9 (CE 15 V)	-
2A-4,6-DNT	2.583	Negative	$[M-H]^-$ = 196.0	>	136.0 (CE 28 V)	119.1 (CE 17 V)	-
PETN	3.357	Negative	$[M]^-$ = 316.0	>	62.0 (CE 30 V)	46.0 (CE 24 V)	-
1,3-DNB	3.452	Negative	$[M]^-$ = 168.0	>	138.0 (CE 14 V)	107.9 (CE 15 V)	-
TATP	3.766	Positive	$[M+H]^+$ = 240.0	>	43.0 (CE -18 V)	74.0 (CE -8 V)	-
2,6-DNT	3.894	Negative	$[M]^-$ = 182.0	>	152.1 (CE 12 V)	45.9 (CE 24 V)	-
Tetryl	4.246	Negative	$[M+CHCOO]^-$ = 288.0	>	194.0 (CE 12 V)	212.0 (CE 10 V)	207.0 (CE 22 V)
2,4-DNT	4.368	Negative	$[M]^-$ = 182.0	>	45.9 (CE 24 V)	152.1 (CE 12 V)	137.1 (CE 12 V)
TNB	4.411	Negative	$[M]^-$ = 213.0	>	183.1 (CE 13 V)	95.0 (CE 23 V)	125.0 (CE 19 V)
TNT	4.801	Negative	$[M-H]^-$ = 226.0	>	196.1 (CE 12 V)	76.0 (CE 22 V)	88.0 (CE 18 V)

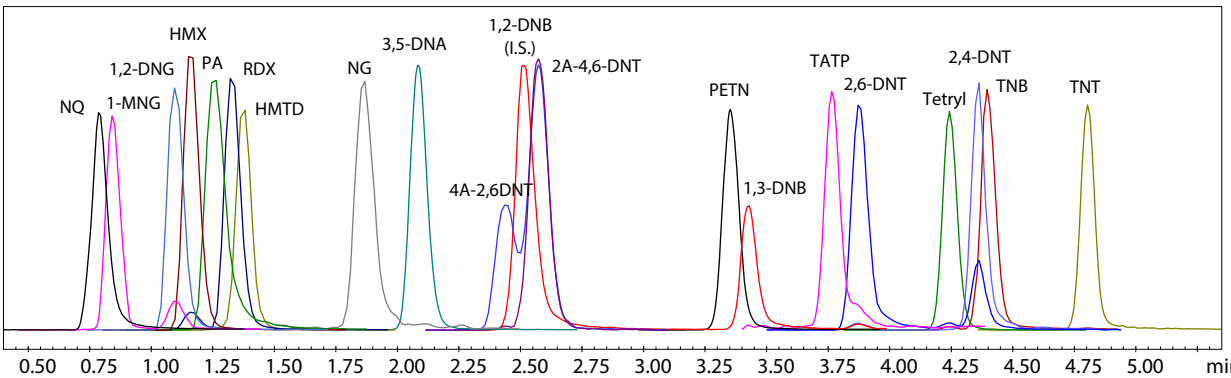

Fig. 3 MRM Chromatograms of the 19 Target Compounds and the Internal Standard

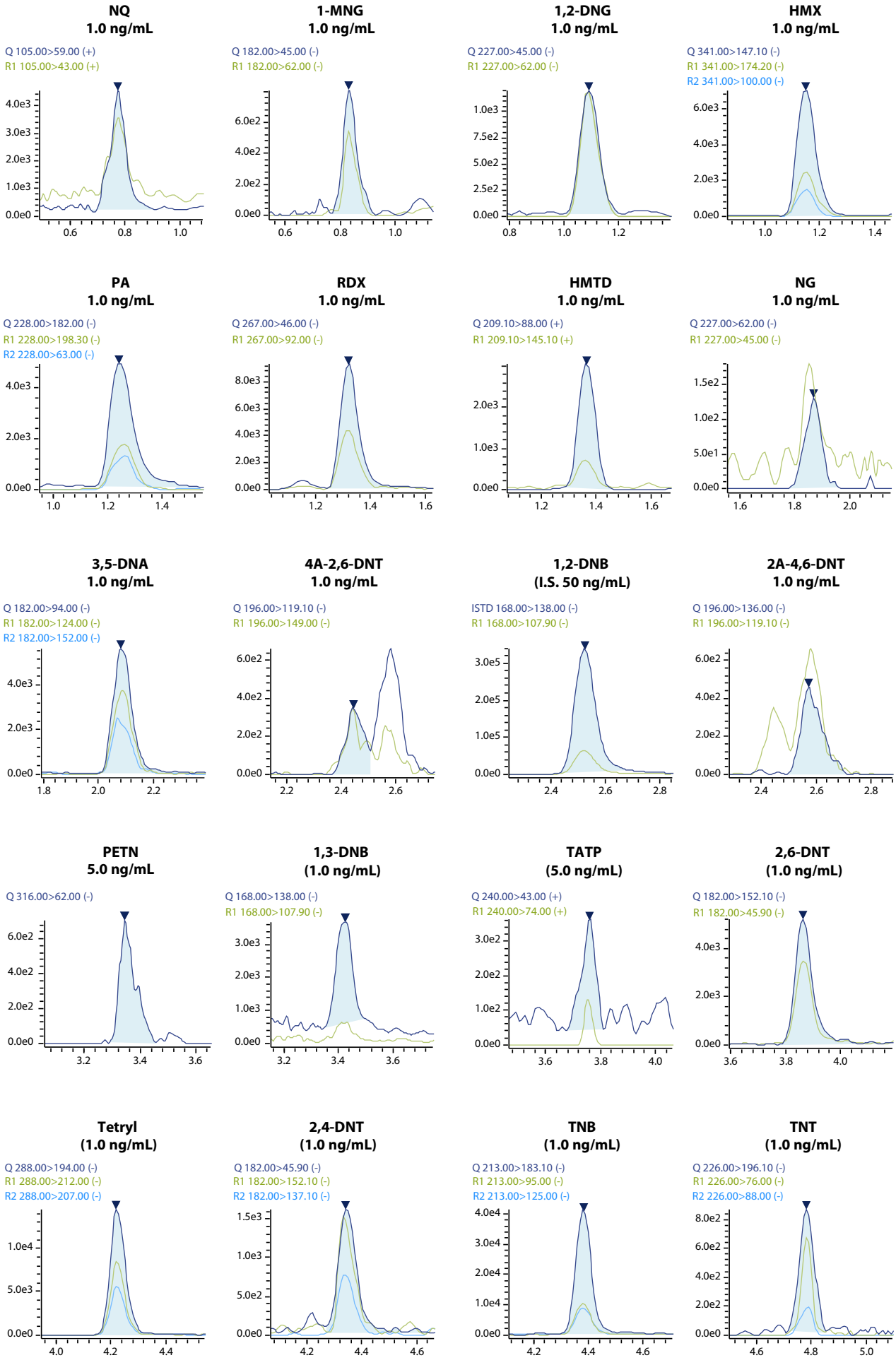

Fig. 4 MRM Chromatograms at the Lowest Calibration Concentrations

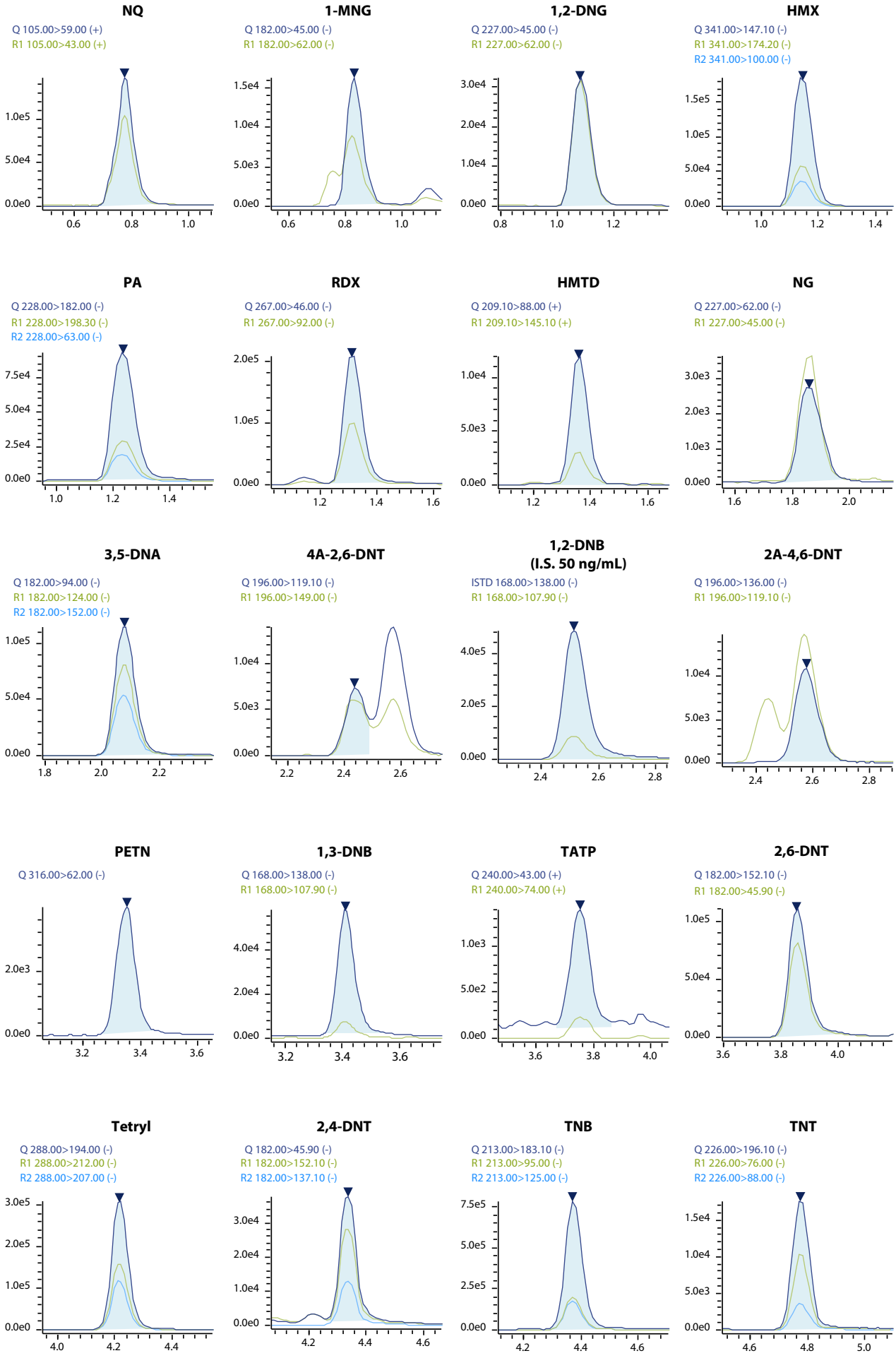

Fig. 5 MRM Chromatograms of Soil Samples Spiked with the Mixed Standard Solution (10 ng/mL)

Table 4 Calibration Range and Linearity

Compounds	Calibration range ng/mL	Correlation coefficient R
NQ	1.0 – 1000	0.9965
1-MNG	1.0 – 1000	0.9996
1,2-DNG	1.0 – 1000	0.9996
HMX	1.0 – 1000	0.9998
PA	1.0 – 1000	0.9991
RDX	1.0 – 1000	0.9978
HMTD	1.0 – 1000	0.9973
NG	1.0 – 1000	0.9998
3,5-DNA	1.0 – 1000	0.9983

Compounds	Calibration range ng/mL	Correlation coefficient R
4A-2,6-DNT	1.0 – 1000	0.9994
2A-4,6-DNT	1.0 – 1000	0.9998
PETN	5.0 – 1000	0.9981
1,3-DNB	1.0 – 1000	0.9998
TATP	5.0 – 1000	0.9972
2,6-DNT	1.0 – 1000	0.9978
Tetryl	1.0 – 1000	0.9953
2,4-DNT	1.0 – 1000	0.9969
TNB	1.0 – 1000	0.9981
TNT	1.0 – 1000	0.9977

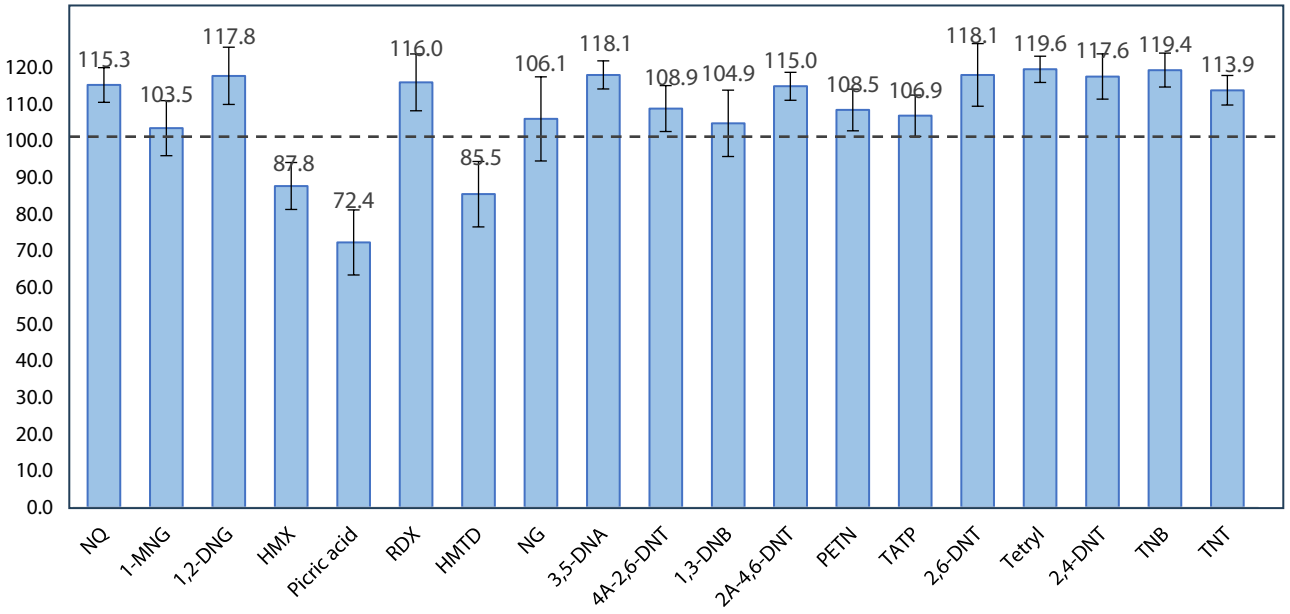

Fig. 6 Accuracy and Repeatability of Target Compounds in Spiked Soil Samples (n = 5)

■ Summary

In this study, we developed a rapid LC-MS/MS method for the simultaneous measurement of positive and negative ions for 19 explosives in soil. Nitrobenzenes, including their regioisomers, could be detected within approximately 5 min under optimized LC conditions. In addition, optimized MS conditions provided high sensitivity for nitrate esters, which are particularly prone to thermal decomposition. As a result, 17 of the 19 target compounds, including thermally labile compounds, were detectable at 1.0 ng/mL. Furthermore, the results of intra-day variability tests using soil samples spiked to 10 ng/mL demonstrated that this method provides sufficient performance for soil analysis.

<References>

1) U.S. EPA. 2006. "Method 8330B (SW-846): Nitroaromatics, Nitramines, and Nitrate Esters by High Performance Liquid Chromatography (HPLC)," Revision 2. Washington, DC.

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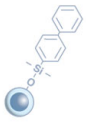

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