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Dual Confirmation of EPA Method 8330 explosives using DUIS-equipped Single Quadrupole LCMS-2050 and PDA for Tandem Detection

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1. Introduction

Due to the global usage of explosives, their toxic remnants have increased in quantity over time and have found their way into the environment, including our soil, water, and sediment. EPA 8330 was designed to detect explosives along with their impurities and degradants in these matrices and typically requires two analyses to confirm the presence of contaminants in samples. The method recommends the use of a C18 column and a phenyl/biphenyl-functionalized column because of their different selectivity. We propose a method that performs UHPLC with a reversed-phase column and uses tandem PDA/MS detection so that only one injection is required to detect explosive constituents in water matrices, while complying with EPA 8330.

2. Methods

Explosives were separated using a Nexera LC and quantified by a Shimadzu SPD-M40 detector and LCMS-2050. The EPA 8330 explosives panel was run using an isocratic method consisting of 75% water and 25% methanol for 22 minutes using a Shim-pack Velox SP-C18 (2.7 µm, 2.1×100 mm) column. An EPA 8330 mix of standards was purchased from Restek. The standard was serially diluted using LCMS water from 0.001 µg/mL to 5 µg/mL for all compounds. A DUIS source was used for ionization of the explosives. Table 1 breaks down the SIMs and λ_{max} used for quantitation.

UHPLC conditions (Nexera system)
Column: Shim-pack Velox SP-C18
Mobile Phase A: 5mM ammonium acetate in H_2O
B: MeOH
Flow rate: 0.4 mL/min
Isocratic: 75%:25% (A:B)
Injection vol.: 2 µL
Column temperature: 30 °C
Detection: PDA (wavelengths in table 1)

MS conditions (LCMS-2050)
Ionization: DUIS, Negative SIM mode
Nebulizing Gas Flow: 2.0 L/min
Drying Gas Flow: 5.0 L/min
Heating Gas Flow: 7.0L/min
Desolvation Temperature: 450 °C
Desolvation Line Temperature: 200 °C

Table 1. SIMs and wavelengths used for quantitation of EPA 8330 panel

Chemical name (Polarity)	Abbreviation	SIMs	λ (nm)
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (-)	HMX	355.06	228
Hexahydro-1,3,5-trinitro-1,3,5-triazine (-)	RDX	281.05	234
1,3,5-Trinitrobenzene (-)	1,3,5-TNB	244.00	228
1,3-Dinitrobenzene (-)	1,3-DNB	168.02	241
3,5-Dinitroaniline (-)	DNA	182.03	223
Nitroglycerin (-)	NG	62.00	215
Methyl-2,4,6-trinitrophenylnitramine (-)	Tetryl	318.00	225
2,4,6-Trinitrotoluene (-)	TNT	226.01	226
2-Amino-4,6-dinitrotoluene (-)	2-Am-DNT	196.03	223
4-Amino-2,6-dinitrotoluene (-)	4-Am-DNT	196.03	226
2,4-Dinitrotoluene (-)	2,4-DNT	182.03	245
2,6-Dinitrotoluene (-)	2,6-DNT	181.03	244
Nitrobenzene (-)	NB	N.D.	266
2-Nitrotoluene (-)	2-NT	N.D.	264
3-Nitrotoluene (-)	3-NT	N.D.	273
4-Nitrotoluene (-)	4-NT	N.D.	284
Pentaerythritol tetranitrate (-)	PETN	315.00	215

3. Results

3.1. Method development

A total of 13 compounds were detected using LCMS (Fig. 1.). In contrast, 17 compounds were identified using SPD-M40. Table 3 displays the linear range, %accuracy, and the %RSD area of the lowest calibrator for each compound using both PDA and MS.

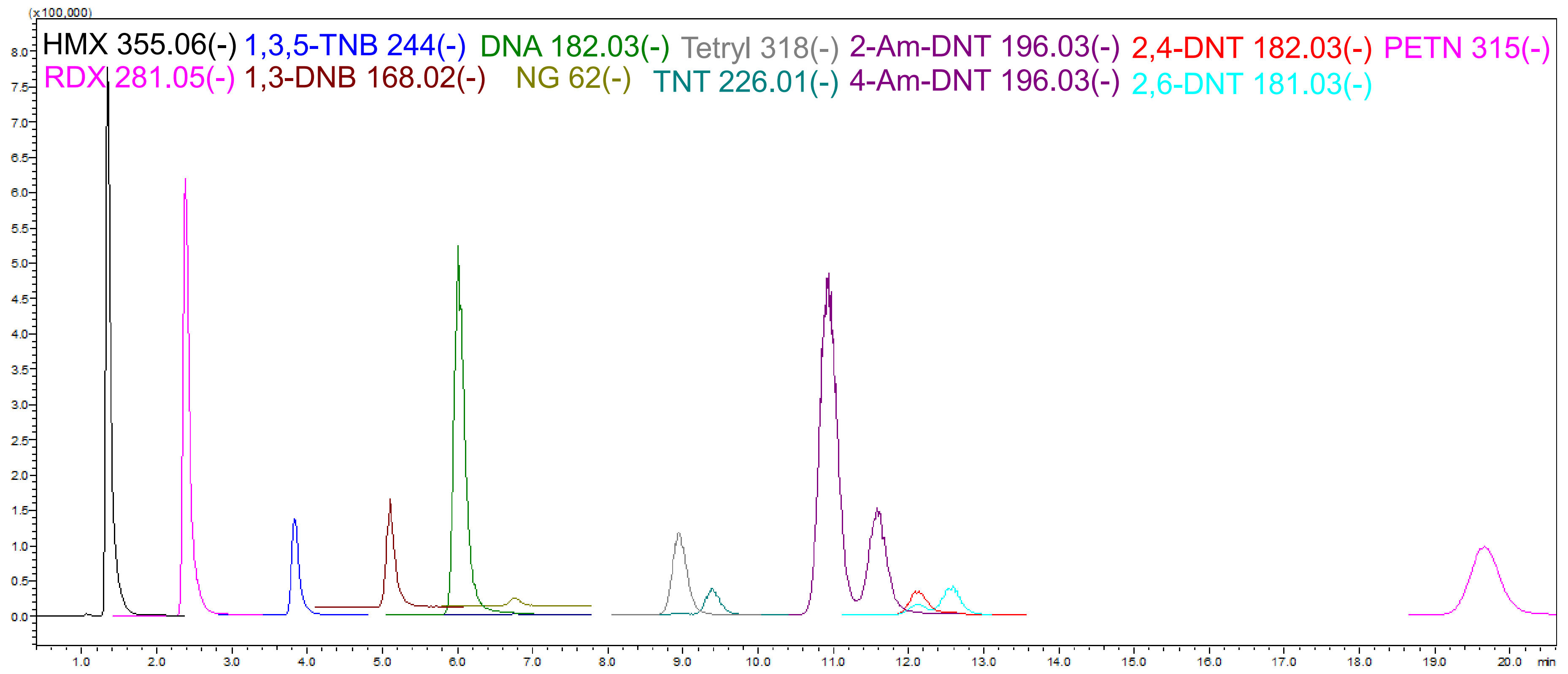
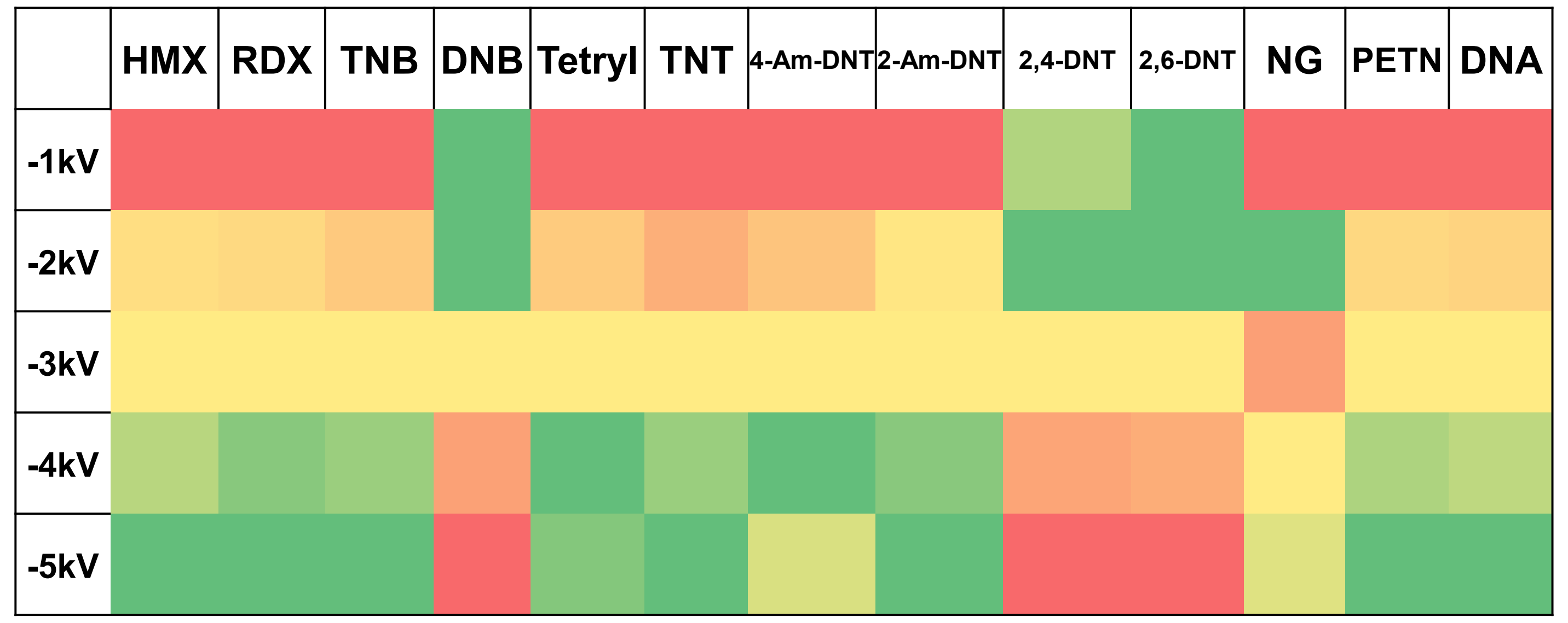


Figure 1. Representative chromatogram of 13 explosive compounds using SIM acquisition.

Ionization of some compounds proved difficult. Challenging analytes included 2,4-DNT, 2,6-DNT, and 1,3-DNB. Changes in source temperatures were considered to improve ionization; however, more thermally labile compounds may degrade with higher temperatures. Interface voltage was optimized to improve ionization. The results of this analysis are shown in Table 2.

Table 2. Shows the results of interface voltage optimization for 11 explosives listed in EPA 8330, where red cells are the largest response and green are the least intense.



	HMX	RDX	TNB	DNB	Tetryl	TNT	4-Am-DNT	2-Am-DNT	2,4-DNT	2,6-DNT	NG	PETN	DNA
-1kV	🟥	🟥	🟥	🟩	🟥	🟥	🟥	🟥	🟩	🟩	🟥	🟥	🟥
-2kV	🟨	🟨	🟧	🟩	🟧	🟧	🟧	🟨	🟩	🟩	🟩	🟨	🟨
-3kV	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟧	🟨	🟨
-4kV	🟩	🟩	🟩	🟧	🟩	🟩	🟩	🟩	🟧	🟧	🟨	🟩	🟩
-5kV	🟩	🟩	🟩	🟥	🟩	🟩	🟨	🟩	🟥	🟥	🟨	🟩	🟩

3.2. Quantitative analysis

A total of 13 compounds were detected using LCMS (Fig. 1.). In contrast, 17 compounds were identified using SPD-M40. Table 3 displays the linear range, %accuracy, and the %RSD area of the lowest calibrator for each compound using both PDA and MS.

Table 3. Calibration curve of explosives analytes with the reported linear range, %accuracy, and the %RSD area of the lowest calibrator

Compounds	PDA				MS			
	Linear Range (µg/mL)	R²	Accuracy (%)	LOQ %RSD (Height)	Linear Range (µg/mL)	R²	Accuracy (%)	LOQ %RSD (Conc.)
HMX	0.02-5	0.999	71.7-101.7	4.20	0.001-5.00	0.996	87.89-125.36	9.70
RDX	0.05-5	0.999	74.1-101.4	3.81	0.001-5.00	0.993	81.84-113.00	2.65
1,3,5-TNB	0.1-5	0.999	71.1-100.4	0.07	0.01-5.00	0.983	87.03-129.17	5.28
1,3-DNB	0.05-5	0.999	71.7-112.8	9.27	0.05-5.00	0.974	71.75-121.67	6.37
DNA	0.05-5	0.999	70.6-111.7	4.60	0.002-5.00	0.998	90.00-116.54	5.62
NG	0.2-5	0.997	92.5-129.8	5.28	2-5	0.931	91.4-105.4	3.35
Tetryl	0.2-5	0.998	70.0-101.7	3.39	0.01-5.00	0.979	89.00-129.87	3.79
TNT	0.2-5	0.998	71.6-101.7	2.85	0.05-0.1	0.941	92.80-108.07	6.36
2-Am-DNT	0.2-5	0.999	72.7-100.6	1.77	0.002-5.00	0.997	91.17-110.28	0.87
4-Am-DNT	0.05-5	0.999	71.4-101.5	4.99	0.005-5.00	0.986	87.32-124.80	1.89
2,4-DNT	0.05-5	0.999	77.1-103.2	9.92	0.05-5.00	0.974	84.43-123.41	5.93
2,6-DNT	0.1-5	0.998	71.7-130.0	17.6	0.05-5.00	0.985	72.17-126.82	5.20
NB	0.5-5	0.996	77.0-104.2	7.26	N.D.	N.D.	N.D.	N.D.
2-NT	0.5-5	0.999	73.1-106.4	3.30	N.D.	N.D.	N.D.	N.D.
3-NT	0.2-5	0.999	79.0-123.8	6.68	N.D.	N.D.	N.D.	N.D.
4-NT	0.2-5	0.999	70.1-105.1	9.88	N.D.	N.D.	N.D.	N.D.
PETN	2.00-5.00	0.999	93.6-125.6	0.51	0.05-5.00	0.996	91.14-108.29	10.66

Representative LOQ chromatograms of each analyte are shown in Figure 2. The LOQ is defined as the lowest end of the linear range with S/N greater than 10.

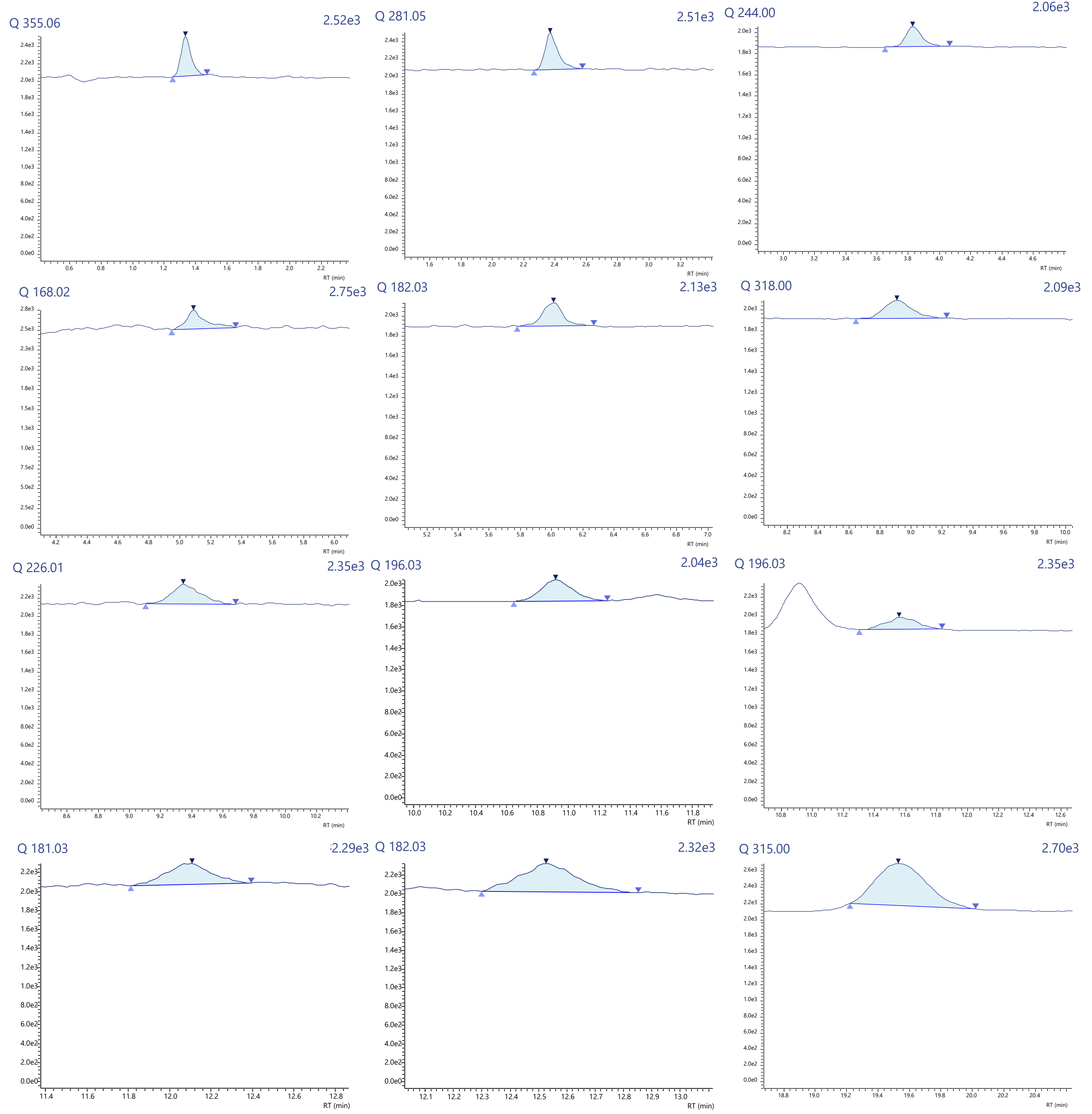


Figure 2. Representative chromatograph at LOQ for each PFAS analyte. The LOQ concentration can be found in Table 3.

4. Conclusion

In this study, we show a method that utilizes a single injection, unlike the traditional analysis methods for EPA method 8330. We successfully implemented the use of tandem detection with PDA and SQ-MS, providing the optimal signal for these conditions. Selecting the λ_{max} allowed us to quantitate explosive analytes down to 0.02 µg/mL, while the LCMS-2050 was utilized to confirm the mass of the explosives, making this single-injection method compliant with EPA 8330 requirements for secondary confirmation.

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