LC/MS Application Note

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Analysis of TNT, RDX, and CL-20 by APCI LC/MS/MS

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Introduction

The detection and characterization of explosives has gained the interest of various analytical laboratories and research groups around the world.

For the forensic community, trace analysis of explosive residues after arson and terrorism is of critical interest. Biologists and environmentalists monitor biotransformation of these high energy compounds when evaluating environmental contamination. Other groups, such as the munitions industry, continue to explore the synthesis of novel explosive materials. In all of these examples, investigators need an analytical methodology that is informative, sensitive, and selective as well as robust.

In this application note, LC negative ion APCI-MS/MS is used to characterize and detect trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) (Figure 1).

Instrumentation

- Varian ProStar 430 AutoSampler
- Varian ProStar 210 Isocratic Solvent Delivery Module
- Varian 1200L LC/MS with APCI source

HPLC Conditions

Column	Pursuit C18, 5 µm, 150 x 4 mm (Varian Part No. 2000-150X40)
Mobile Phase	water:isopropanol:methanol at 60:30:10 and 0.1% chloroform (isocratic)
Flow	0.8 mL/min
Injection Volume	20 µL

MS Parameters

APCI Torch Temp	450 °C
API Drying Gas	15 psi at 300 °C
API Nebulizing Gas	60 psi
Corona Current	5 µA
Capillary	40V
Housing	50 °C
Collision Gas	1.7 mTorr Argon

Compound Structures

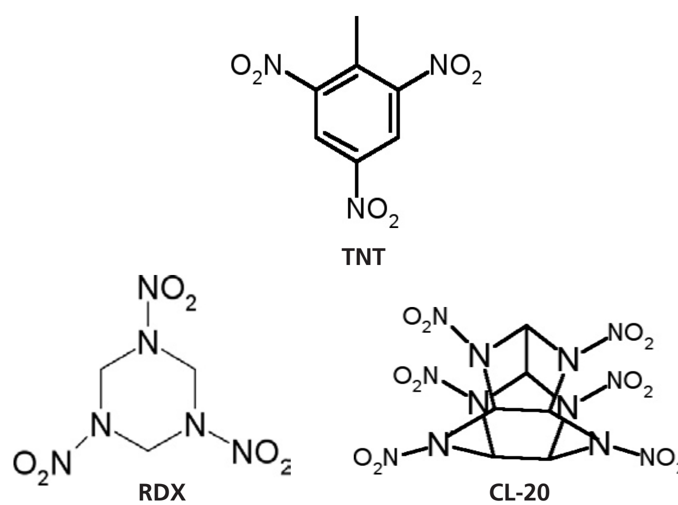


Figure 1. Structure of analyzed explosives.

MS/MS Scan Parameters

Analyte	Precursor Ion (m/z)	Product Ion (m/z)	Collision Energy (V)	Retention Time (min)
TNT	227	210	8	4.6
RDX	257	46	6	2.6
CL-20	473	154	6	4.2

Results and Discussion

TNT, a nitroaromatic, readily undergoes charge exchange to create a radical anion in the source. Unfortunately, the chemical structures of RDX and CL-20 do not make them easily amenable to atmospheric pressure ionization without the aid of additives. For this analysis, chloroform was used as a source of chlorine for adduct ion formation.

TNT collisionally dissociates through two main fragmentation pathways (Figure 2). One pathway is the loss of 17 u (OH) producing a fragment at m/z 210. In the second pathway, TNT loses an NO functional group to yield a product ion at m/z 197.

CL-20 also yields two intense product ions (Figure 3). The major product ion is m/z 154 or a loss of 319 mass units ($C_5H_5O_8N_9$). Unlike TNT and CL-20, the RDX-chlorine adduct ion dissociates mainly to yield NO_2^- fragment ions (Figure 4).

All three explosives eluted in less than 5 minutes under isocratic conditions (Figure 5). TNT and RDX were well separated while CL-20 eluted close to TNT. MS/MS, however, adds an additional selective dimension by further separating the analytes according to their unique product ions. The table on page one shows the MS/MS transitions and retentions times for this analysis.

MS/MS Spectrum for TNT

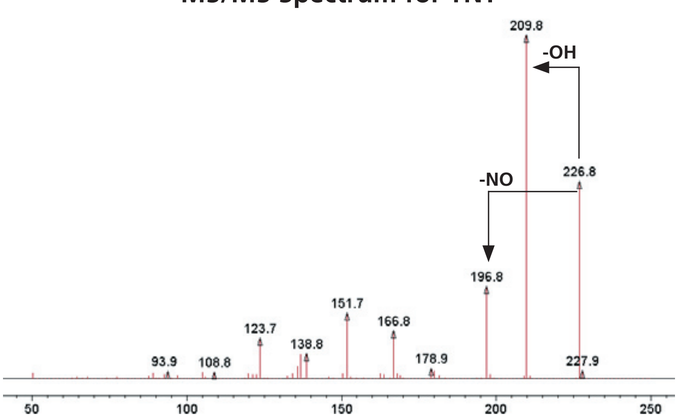


Figure 2. TNT dissociates two produce two intense product ions.

MS/MS Spectrum for CL-20

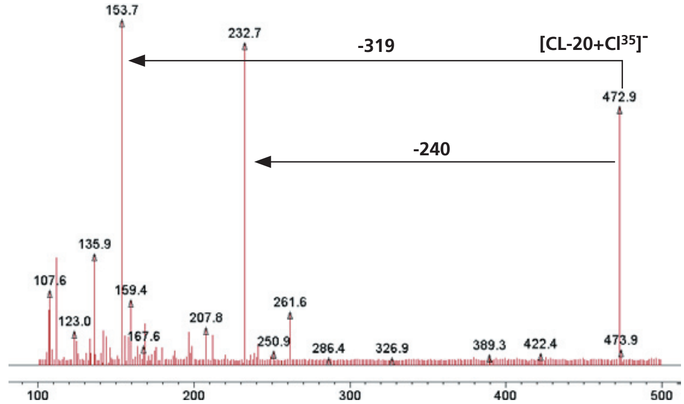


Figure 3. CL-20-chloride adduct also dissociates to produce two intense ions.

MS/MS Spectrum for RDX

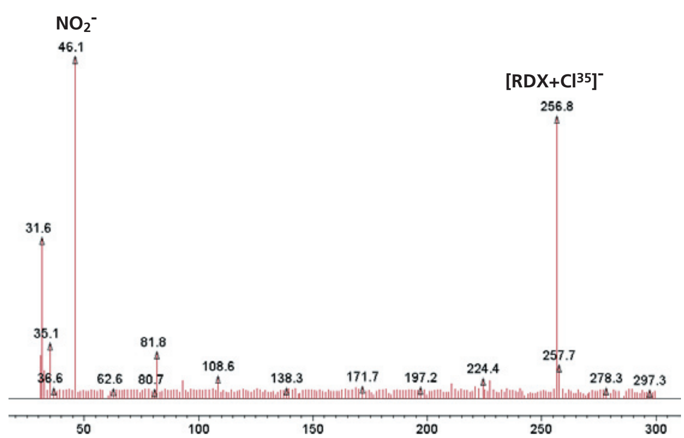


Figure 4. RDX-chloride adduct only yields one small product ion.

Ion Chromatograms for Analyzed Explosives

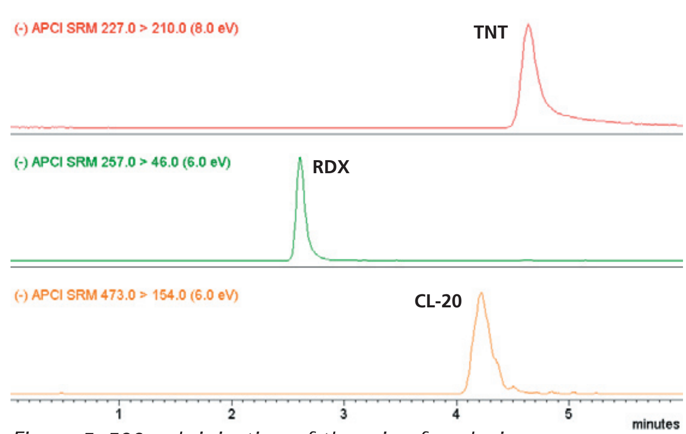
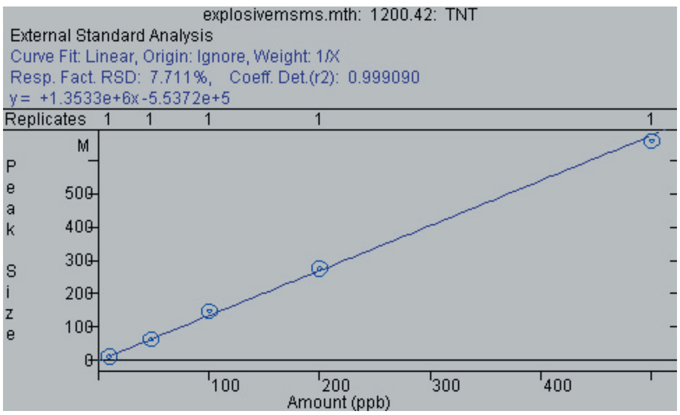


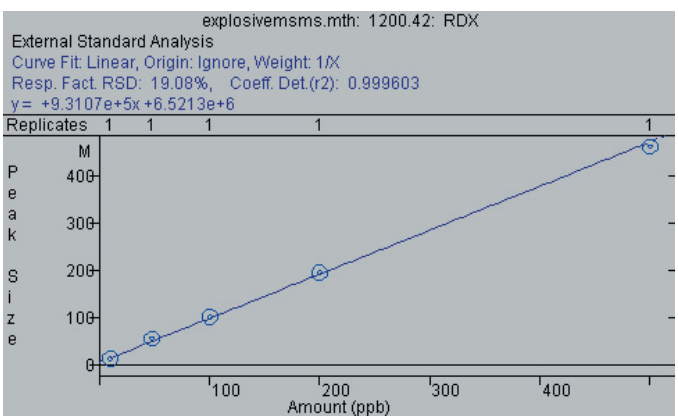
Figure 5. 500 ppb injection of the mix of explosives.

While 10 ppb was the lowest calibration point (Figure 6), single digit ppb levels can be easily attained with further optimization of ion source conditions (Figure 7).

The benefits of MS/MS are readily observable as the concentration of the explosives decrease. For example, a 1 ppb injection of CL-20 in SIM mode is not as discernable when compared to the MS/MS ion chromatogram at the same concentration (Figure 8).

Calibration Curves for Analyzed Explosives





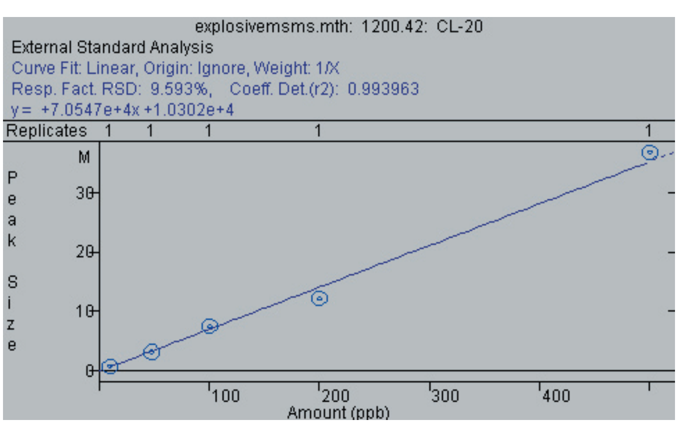


Figure 6. Good linearity was achieved for all compounds over a concentration of 10 ppb to 500 ppb.

LOD Study of Explosives Mix

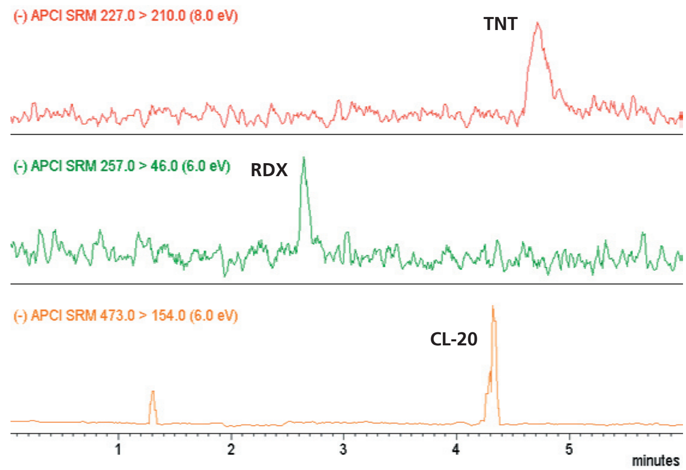


Figure 7. With a 1 ppb injection of explosives mix, TNT and RDX were at the LOD while the LOD for CL-20 could be significantly lower.

Comparison of SIM vs. MS/MS

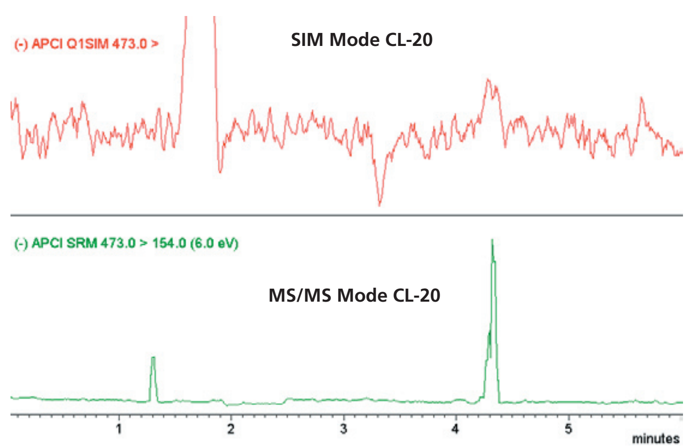


Figure 8. With a 1 ppb injection, baseline noise obscures the CL-20 peak in the SIM mode while an excellent signal-to-noise is achieved with MS/MS.

Conclusion

APCI-MS/MS is effective in the determination of explosives. The addition of an organochloro compound significantly enhances the detection limits of RDX and CL-20 through adduct ion formation. The added selectivity of MS/MS ensures reliable analysis of these compounds, especially at trace concentrations.

These data represent typical results.
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