



Determination of HMX, RDX, and TNT Using LDTD-APCI MS/MS Detection : 10 seconds per sample

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Keywords: LDTD-APCI MS/MS; Explosive; HMX; RDX

Introduction

Trace analysis of explosives is of major importance to evaluate the health risk associated with the release of explosives from military sites and former ammunition plants into the environment. Moreover, military activities and manufacturing and handling explosives have contaminated soils, sediments, surface water, and groundwater with HMX, RDX and TNT (**Fig. 1**) in and around military sites. Although many methods have been published for the detection of explosive, few of these describe the quantitative analysis of HMX, RDX and TNT in tandem mass spectrometry using molecular ion [M-H]⁻.

We have developed a high throughput method to detect, identify and quantify HMX, RDX and TNT in contaminated surface water from military sites. The performance of the new Laser Diode Thermal Desorption ionization source combined to tandem mass spectrometry is evaluated.

Goals

- Illustrate the efficiency of the LDTD-APCI source to analyze explosive materials by obtaining typical APCI MS spectrum in negative ionization mode;
- Develop rapid LDTD-APCI MS/MS screening and quantifying methods to detect HMX, RDX, and TNT in 10 seconds per sample.

Instrumentation

- Phytronix Technologies LDTD-APCI ionization source (model T-960);
- Thermo Scientific Corporation TSQ[®] QuantumTM Ultra AM.

LDTD ionization process

The LDTD source uses an infrared laser diode to desorb samples that have been dried into a well of the LazWellTM (96-well plate). The desorbed gas phase molecules is carried over by a carrier gas into a corona discharge region to undergo APCI and then transferred directly into the mass spectrometer.

Samples Preparation

Standard explosives solution were prepared from the stock solutions. Dilution was performed in a H₂O:CH₃OH (25:75) solution at a concentration range from 0.01 ng/mL to 1000 ng/mL.

Surface water samples were treated according to the EPA method 8330B. A volume of 5 μ L was directly deposited into a well of the LazWellTM plate and was allowed to dry at room temperature.

LDTD Parameters

| | |
|-------------------------|--|
| Stabilization Time | 3 s |
| Laser Power Pattern | Ramp 0 to 35 % in 1 s Hold at 35 % for 3 s Hold at 0 % for 3 s |
| Carrier Gas Flow | 4.0 mL/min (Air) |
| Carrier Gas Temperature | 27 $^{\circ}$ C |

MS Parameters

| | |
|------------------------|------------------------------------|
| Collision Gas Pressure | 1.5 mTorr (Argon) |
| Scan Time | 0.05 s |
| Q1 and Q3 Width | 0.1 amu |
| Needle Voltage | -6 kV (HMX) -4 kV (RDX and TNT) |
| Sweep Gas Flow | 1 arbitrary unit |

MRM Parameters

| Compound | Precursor ion | Q1 (<i>m/z</i>) | Q3 (<i>m/z</i>) | Collision Energy (V) |
|----------|-----------------------------------|----------------------|----------------------|-------------------------|
| HMX | [M+NO ₂] ⁻ | 342 | 46 | 22 |
| | [M-H] ⁻ | 295 | 46 | 25 |
| RDX | [M+NO ₂] ⁻ | 268 | 46 | 22 |
| | [M-H] ⁻ | 221 | 46 | 10 |
| TNT | [M-H] ⁻ | 226 | 46 | 22 |

LDTD-APCI Explosives Mass Spectra

The negative-ion LDTD mass spectra of RDX and TNT show stable ions at molecular mass [RDX-H]⁻ and [TNT-H]⁻ respectively. The negative-ion LDTD mass spectra of HMX show linear molecular ion [HMX-H]⁻ at concentration below 0.7 ng/mL. As the concentration increases over 0.7 ng/mL, the ion [HMX+NO₂]⁻ is produced. Unlike ESI and APCI, Laser Diode Thermal Desorption allows easy tandem mass spectrometric analysis on RDX and TNT using [M-H]⁻ as precursor ion.

Calibration Curve

The negative-ion LDTD mass spectra of RDX show stable [RDX-H]⁻ ion and a linear behaviour over a concentration range of 0.03 to 15 ng/mL (Fig. 1A) is observed. The dynamic range for TNT using [TNT-H]⁻ ion is from 0.10 to 100 ng/mL (Fig. 1B).

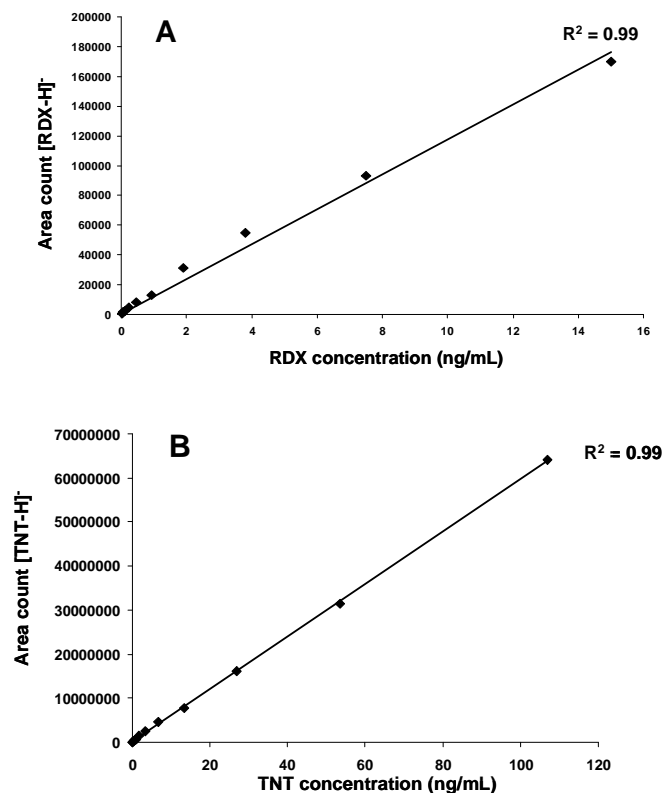


Figure 1 Calibration curve for A) RDX and B) TNT analysis

For HMX, the summation of [HMX-H]⁻ and [HMX+NO₂]⁻ area count results in a linear relationship with HMX concentration allowing quantification in a linear range from 0.03 to 55 ng/mL (Fig. 2).

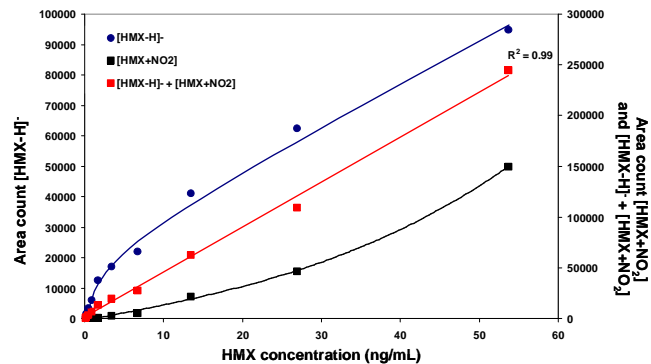


Figure 2 Calibration curve for HMX

Limit of Detection

The low background signal recorded with LDTD-MS/MS allows the detection of explosive material at concentrations as low as 0.01 ng/mL for HMX and RDX (20 fg analyzed), and 0.02 ng/mL for TNT (20 fg analyzed) (Figure 3).

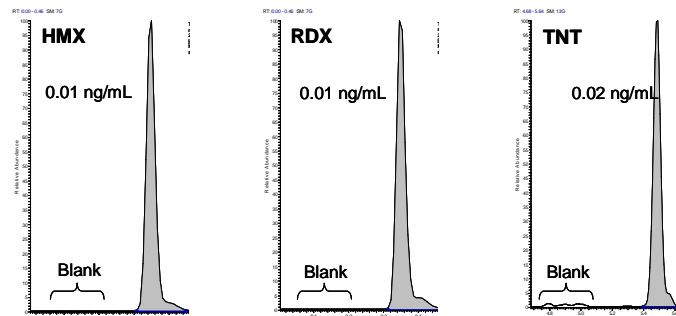


Figure 3 Desorption profiles for blank and low-concentration explosive samples

Contaminated Surface Water from Military Sites

Ten surface water samples, provided by the Defence Research and Development Canada, were analyzed using the LDTD-MS/MS method and shows TNT concentration from 0.20 to 0.44 ng/mL in 4 samples. TNT was also detected (concentration between 0.02 and 0.1 ng/mL) in 3 samples.

Conclusion

The method using LDTD-APCI-MS/MS to identify and quantify HMX, RDX and TNT shows excellent results. The complete analysis (10 seconds per sample) leads to high throughput routine analysis and successful detection and quantification of TNT in contaminated surface water samples at low concentration.

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