

## OVERVIEW

### Purpose

- Identify and quantify HMX, RDX and TNT in surface water samples
- New Laser Diode Thermal Desorption (LDTD) ionization source for mass spectrometry
- Negative APCI combined to tandem mass spectrometry
- Fast sample-to-sample run time
- Compare with traditional LC-UV detection method for contaminated surface water samples

### Method

- Extraction method according to EPA Method 8330B
- Tested concentration range : 0.01 ng/mL to 1000 ng/mL
- LDTD-APCI-MS/MS analysis : Laser Diode Thermal Desorption coupled with triple quadrupole mass spectrometer

### Results

- Excellent linearity ( $R^2 > 0.99$ )
- No matrix effect and carryover
- Excellent selectivity
- Lower detection limit than LC-UV analysis
- 90 times faster than traditional chromatographic separation based methods

## 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 (Figure 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 and compared to the actual LC method using UV detection.

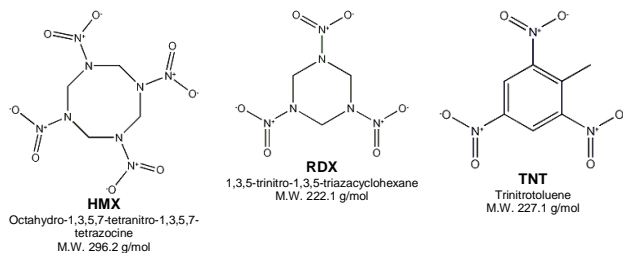


Figure 1 Chemical structure of studied explosive materials

## METHODS

### Instrumentation

- LDTD model T-960, Phytrox Technologies (Figure 2)
- Thermo Scientific TSO<sup>2</sup> Quantum™ Ultra AM

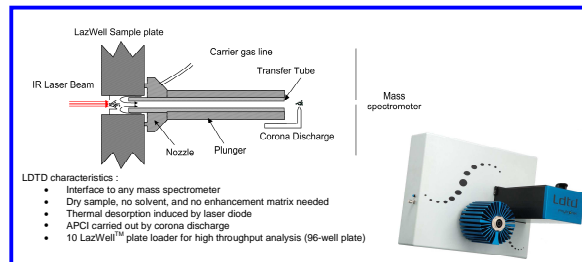


Figure 2 LDTD ionization source for mass spectrometry

### LDTD Parameters

- Laser power pattern
  - Hold at 0 % for 3 s (stabilization)
  - Increase to 32 % in 1 s
  - Hold at 32 % for 3 s
  - Decrease to 0 % in 0.05 s
  - Hold at 0 % for 3 s
- Carrier gas flow : 4.0 L/min (Air)
- Carrier gas temp. : 27 °C
- Corona voltage value : -6 kV (HMX), -4 kV (RDX, TNT)
- Deposited sample vol. : 5 µL

### MS Parameters

- Collision gas pressure : 1.5 mTorr (Argon)
- Scan time : 0.05 s
- Scan width : 0.7 amu
- Q1 width : 0.7 amu
- Q3 width : 0.7 amu

Table 1 MS MRM Parameters

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

### Sample preparation

- Water samples are treated according to the EPA Method 8330B

### LC-UV sample analysis

- Column : Supelcosil LC-8 250 mm x 3 mm, 5 µm (held at 25°C)
- Injection vol. : 20 µL
- Mobile phase : Water/Isopropyl alcohol (85:15)
- Flow : 0.75 mL/min
- Wavelength : 230 nm (HMX and TNT), 205 nm (RDX)

## RESULTS

### LDTD-APCI Explosives Mass Spectra

The LDTD-APCI process does not involve any mobile phase or enhancement matrix (like MALDI), no explosive-adduct with halide or solvent is observed.

The negative-ion LDTD mass spectra of RDX and TNT show stable ions at molecular mass [RDX-H]<sup>-</sup> and [TNT-H]<sup>-</sup> respectively. The negative-ion LDTD mass spectra of HMX show linear molecular ion [HMX-H]<sup>-</sup> at concentration below 0.7 ng/mL. As the concentration increases over 0.7 ng/mL, the ion [HMX+NO<sub>2</sub>]<sup>-</sup> is produced, affecting the linear behaviour of the molecular ion [HMX-H]<sup>-</sup>. The sum of [HMX-H]<sup>-</sup> and [HMX+NO<sub>2</sub>]<sup>-</sup> signals is then used to cover a mass range over 0.7 ng/mL.

Unlike ESI and APCI, Laser Diode Thermal Desorption allows easy tandem mass spectrometric analysis on RDX and TNT using [M-H]<sup>-</sup> as precursor ion.

### Calibration Range and Linearity

At low HMX concentration (< 1 ng/mL), the molecular ion [HMX-H]<sup>-</sup> shows linear behaviour in relation with the concentration. However, a break-up in this linear relationship is observed when the [HMX+NO<sub>2</sub>]<sup>-</sup> ion starts to be detected. The summation of [HMX-H]<sup>-</sup> and [HMX+NO<sub>2</sub>]<sup>-</sup> area count results in a linear relationship with HMX concentration allowing quantification in a linear range from 0.03 to 55 ng/mL (Figure 3).

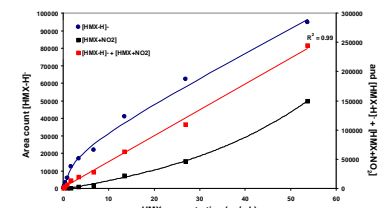


Figure 3 Calibration curve for HMX analysis

The negative-ion LDTD mass spectra of RDX show stable [RDX-H]<sup>-</sup> ion and a linear behaviour over a concentration range of 0.03 to 15 ng/mL (Figure 4A) is observed. The dynamic range for TNT using [TNT-H]<sup>-</sup> ion is from 0.10 to 100 ng/mL (Figure 4B).

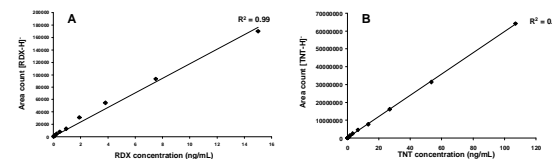


Figure 4 Calibration curve for A) RDX and B) TNT analysis

## REFERENCES

<sup>1</sup> Rapid Commun. Mass Spectrom. 2006, 20: 2222-2226  
<sup>2</sup> Rapid Commun. Mass Spectrom. 2002, 16: 1883-1891

### Limit of Detection

The LDTD-APCI process produces a low background signal for blank samples which 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 5). The corresponding LC-UV detection limit is 0.1 µg/mL (2ng on-column). Reported LC/MS/MS LOD is 25 pg/L for HMX, 5 ng for RDX and 5 fg for TNT (on-column)<sup>2</sup>.

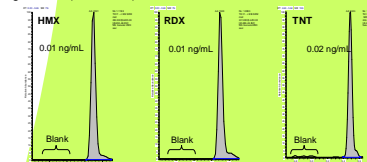


Figure 5 Desorption profiles for blank and low-concentration explosive samples

### Surface Water Analysis

Ten surface water samples were analyzed using the classic LC-UV method at Defence Research and Development Canada laboratories (DRDC Valcartier) and with the LDTD-MS/MS in the laboratories of Phytrox Technologies. The LC-UV method did not detect any explosive (limit of detection of 0.5 ng/mL). However, using the LDTD-MS/MS to perform the analysis, TNT was detected in 3 samples (#5, #7 and #10) and quantified in 4 more samples (#4, #6, #8, and #9) (see Figure 6). The TNT calculated concentrations found in the samples by the LDTD-MS/MS system are reported in Table 2.

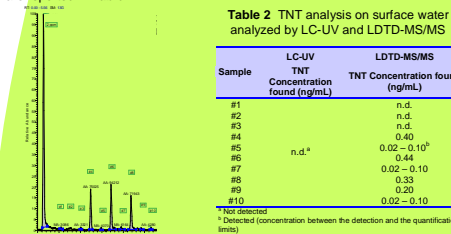


Figure 6 Desorption profile for ten surface water samples

Sample-to-sample run time for LDTD-MS/MS explosive analysis is performed in 10 seconds which is 90 times faster than classic chromatographic separation prior to the explosive detection, for which the sample-to-sample time is about 15 minutes.

## CONCLUSIONS

- Sample-to-sample run time is 90 times faster with LDTD than chromatographic separation based MS methods
- Successful LDTD-MS/MS analysis of RDX and TNT ([M-H]<sup>-</sup> ions) and of HMX ([M-H]<sup>-</sup> + [M+NO<sub>2</sub>]<sup>-</sup>)
- Excellent linearity on calibration curve for all tested explosives
- High concentration working range starting from 0.02 ng/mL to 100 ng/mL
- Low detection limits achieved
- Real surface water successfully analyzed using the LDTD-MS/MS technology