

Characterization of Two Wastewaters for Explosives Using On-Column Injection and Gas Chromatography—Time-of-Flight Mass Spectrometry

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1. Introduction

The United States Environmental Protection Agency (EPA) recently published draft Method 8095, *Explosives By Gas Chromatography*. This gas chromatography/electron capture detector (GC/ECD) method was developed to determine the concentrations of numerous explosives and their degradation products in waters and soils. The method is non-specific since it uses ECD, and coelutions on the primary GC columns thwart the measurement of all of the Method 8095 compounds in one analysis. Confirmation columns are recommended to enhance the specificity of the method.

A better approach is to use a selective column that resolves all Method 8095 compounds, combined with mass spectrometry for additional specificity. On-column injection preserves the response for explosive compounds that are thermally labile, such as the nitrate esters (i.e. nitroglycerin, PETN). This application note describes the results from the on-column injection, fast GC—Time-of-Flight Mass Spectrometry (TOFMS), of explosive standards and two wastewater extracts.

2. Experimental Conditions

Gas Chromatography/Mass Spectrometry

Instrumental conditions are listed below. A Press-Tight connector (Restek Corporation) was used to connect the retention gap and analytical column. A new on-column injector liner developed by Restek was used in the PTV injector slot of an Agilent 6890 Gas Chromatograph to permit autosampler needle insertion into the 0.53 mm retention gap. The injector was programmed to remain 5°C above the GC oven during the analysis.

Standards

Method 8095 Standards (Restek)

Materials and Methods

Gas Chromatography: Agilent 6890

Retention Gap:

5 m x 0.53 mm Siltek-deactivated guard column (Restek)

Column:

10 m x 0.32 mm x 0.91 μ m Rtx-TNT (Restek)

Carrier:

Helium at 5 ml/minute, constant flow

Injection:

1 μ l on-column at 85°C (tracks 5° above GC oven)

Oven Program:

80°C (0.5 minute) to 260° at 15°/minute

Mass Spectrometry: LECO Pegasus III GC-TOFMS
Ionization: Electron ionization at 70eV
Source Temperature: 180°C
Stored Mass Range: 45 to 350 u
Acquisition Rate: 10 spectra/second

Data Processing

LECO ChromaTOF software with Automated Peak Find and Deconvolution

Extraction of Wastewaters

Duplicate wastewaters were obtained from an explosives-contaminated site. One was stored in the refrigerator for approximately 6 months. The other was frozen at the time of collection and thawed just prior to extraction.

EPA Method 3535a was used to extract the samples. 200 ml of each sample were passed through a styrene divinylbenzene (SDB) extraction cartridge. 4 ml of acetonitrile were used to elute extracted components from the SDB cartridge, followed by final dilution to exactly 5 ml with acetonitrile. A white precipitate formed on mixing the diluted extract, and was removed with a 0.45 μ m PTFE syringe filter.

3. Results

A GC-TOFMS chromatogram of an explosives standard on an Rtx-TNT column is shown in Figure 1. The analysis was performed at a constant carrier flow of 5 ml/minute, which puts the linear velocity around 140 cm/second; extremely high and way above optimum for most separations. However, it is important to minimize the time that thermally labile compounds spend in the column. The run time for tetryl is around 8 minutes. HMX, which is not shown in this chromatogram, elutes at about 11 minutes. All Method 8095 compounds are baseline resolved by the Rtx-TNT column, except for 2,6-dinitrotoluene and 1,2-dinitrobenzene (an alternate surrogate compound) under the conditions used for this work. These compounds are easily differentiated on the basis of their mass spectra. Although it would be possible to achieve a shorter analysis for some of the Method 8095 compounds by using faster GC oven-programming, the nitrate esters (e.g. nitroglycerin, PETN) would thermally degrade prior to their elution from the column.

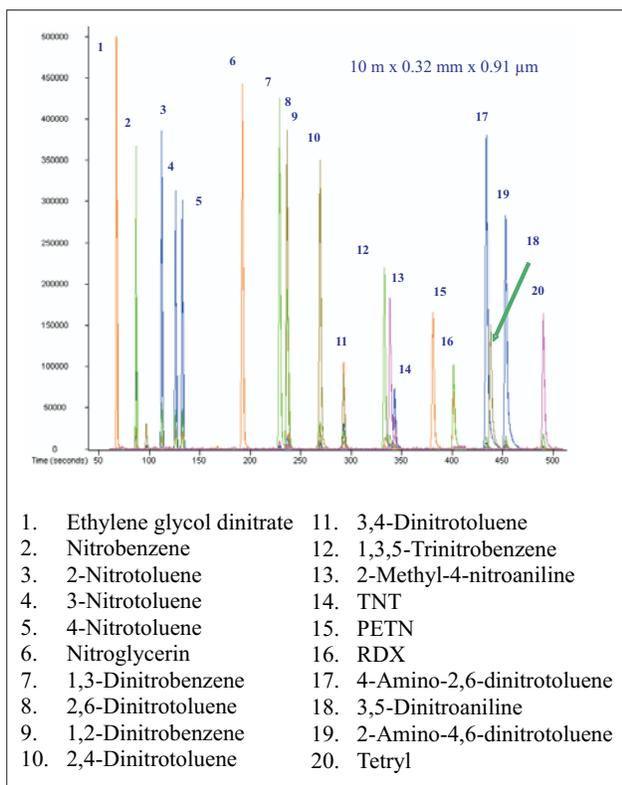


Figure 1. Fast GC-TOFMS chromatogram of explosives on Rtx-TNT. Tetryl elutes at just over 8 minutes.

Wastewater total ion chromatograms (TICs) are shown in Figure 2. The frozen wastewater contained TNT (2,4,6-trinitrotoluene), but the refrigerated wastewater did not contain this explosive. Both waters contained aminodinitrotoluenes—common degradation products of TNT—while the refrigerated water contained additional degradation components—the diaminonitrotoluenes. It is likely that the TNT in the refrigerated wastewater was totally transformed to its degradation components.

The components were easily located in the extracts, since they are the major peaks in the TIC. But what about minor components, those that exist below the TIC, but may still be important to locate and identify, either because they are toxic, or are indicators of biodegradation, etc.? The Peak Find and Deconvolution algorithms available through ChromaTOF, and enabled by the speed and spectral reproducibility of TOFMS, make locating small peaks just as easy. Production of deconvoluted mass spectra is followed by library searching for compound identification. Table 1 lists nitrogen compounds automatically located in the wastewater extracts.

Table 1. Nitrogen compounds in wastewater extracts located by Peak Find.

Pentylpyrole	TNT
Methylthiopyridine	RDX
Chloroaniline	Nitrobenzenediamine
Nitroaniline	Diaminonitrotoluenes
Dichlorobenzeneamine	Aminodinitrotoluenes
Dinitrotoluene	Dinitroaniline
Diaminotriazole	HMX

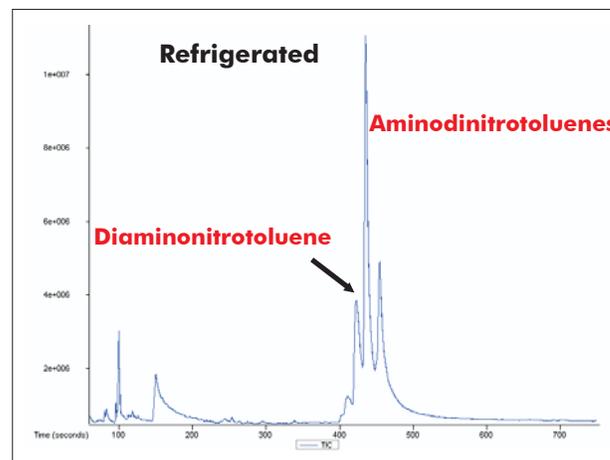
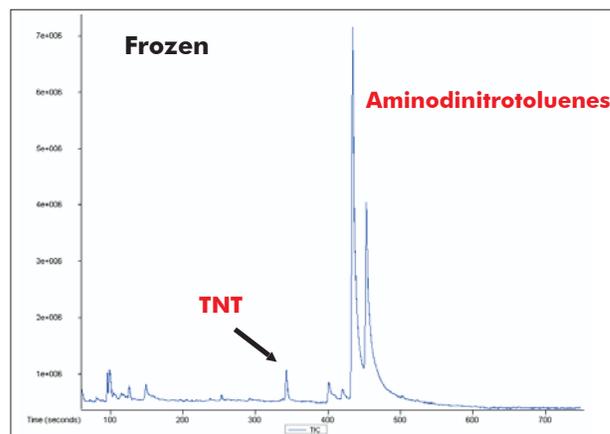


Figure 2. Total ion chromatograms for wastewater extracts showing TNT and its degradation compounds.

A good example of locating a small peak in the presence of a big peak is given by the coelution of 4-amino-2,6-dinitrotoluene and 3,5-dinitroaniline in one of the wastewater extracts (Figure 3). There is at least an order-of-magnitude difference in the concentrations of these compounds, represented graphically by the aminodinitrotoluene (blue) being off-scale versus the small dinitroaniline (red) peak. The coeluted spectrum, taken at the dinitroaniline retention time, represents mostly the aminodinitrotoluene; you can barely see the presence of a 183 m/z ion, the molecular ion of the dinitroaniline. Fortunately, the ChromaTOF software not only locates the peak, but also produces an excellent deconvoluted mass spectrum, that is fully library searchable.

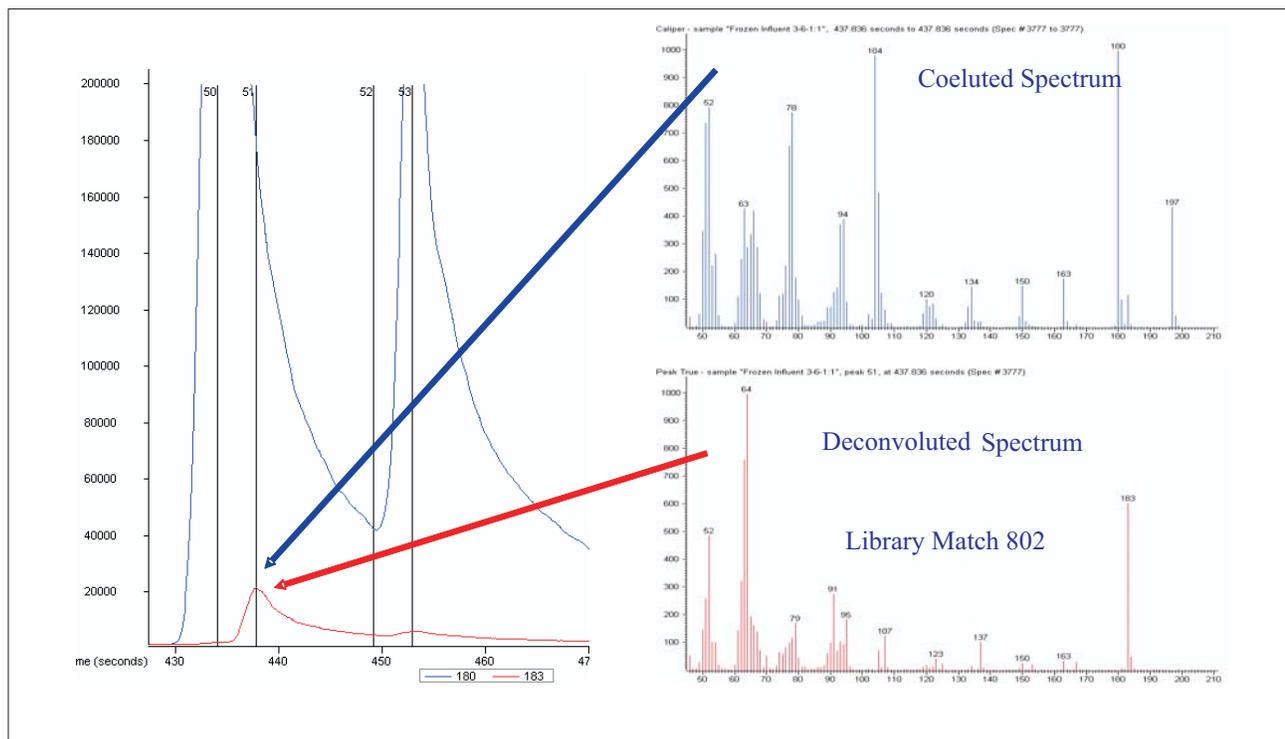


Figure 3. Peak Find and Deconvolution for a small peak (3,5-dinitroaniline) in the presence of a large peak (4-amino-2,6-dinitrotoluene). The top (coeluted) spectrum represents mainly the aminodinitrotoluene, even though the spectrum was taken at the dinitroaniline retention time, due to the huge concentration differential. The bottom spectrum, the deconvoluted dinitroaniline, shows a good NIST library match.

4. Conclusions

Using a selective GC column and TOFMS, all Method 8095 explosive compounds can be unequivocally determined in standards and wastewater extracts. On-column injection and a mass spectrometer capable of handling at least 5 ml/min GC carrier flow help minimize the thermal degradation of explosive compounds.

TOFMS, with its acquisition speed and spectral reproducibility, allows powerful, automated Peak Find and Deconvolution routines, resulting in more complete and accurate characterization of complex samples.

5. References

SW-846 On-Line, Test Methods for Evaluating Solid Wastes

Method 3535A Solid-Phase Extraction (SPE)
<http://www.epa.gov/epaoswer/hazwaste/test/3xxx.htm>

SW-846 On-Line, Test Methods for Evaluating Solid Wastes

Draft Update IVB of SW-846 On-Line

Method 8095 Explosives by Gas Chromatography
<http://www.epa.gov/epaoswer/hazwaste/test/up4b.htm>

SW-846 On-Line, Test Methods for Evaluating Solid Wastes

Method 8330 Nitroaromatics and Nitramines by HPLC
<http://www.epa.gov/epaoswer/hazwaste/test/8xxx.htm>

