

# Automated Cold-on-Column Injection and the Analysis of Explosive Residues by Negative Chemical Ionization GC/MS

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## Overview

### Purpose

An experiment was designed to investigate the use of an automated on-column injection for the analysis of explosives by gas chromatography/quadrupole mass spectrometry (GC/MS). Negative ion chemical ionization (NCI) using methane as the reagent gas was chosen based on past research using this technique.

### Methods

Standards of 17 explosives and a deuterated internal standard were prepared in acetonitrile. Injection using an automated on-column technique allowed sample introduction directly onto the column, by-passing a heated injection port, which can contribute to degradation of fragile explosive residues. The mass spectrometer, operated in NCI, was programmed for selected ion monitoring.

### Results

Chromatography and injection techniques were optimized to ensure that all components were eluted from the analytical column. Successful identification and quantification of the compounds was accomplished in a run time of ~17 minutes, including HMX.

## Introduction

Analysis of explosive residues by GC/MS is complicated by the unstable nature of the compounds themselves, which tend to decompose in the injection port. The use of a pressure-temperature programmable vaporizing inlet can overcome many of these limitations; however, certain components, particularly HMX, are inherently difficult to analyze by GC/MS, making this technique incomplete for analysis of the compounds listed in US EPA Method 8095.<sup>1</sup> Therefore, an alternate injection technique was investigated using true automated cold-on-column injection to meet the additional demands of the analysis.

A DSQ™ GC/MS system (Thermo Electron Corporation) was operated in electron capture negative chemical ionization (NCI) mode (Figure 1). The system was coupled to a TRACE GC Ultra™ with an on-column injector (OCI). The autosampler, the TriPlus™ AS, provided automated injections, using an electronically controlled motor to regulate the opening and closing of the on-column rotary valve (Figures 2 and 3). The technique was optimized for the components of EPA Method 8095, and a deuterated internal standard was used for quantification purposes.



Figure 1: The DSQ, shown with a TRACE GC Ultra. The DSQ is a dual-stage single quadrupole mass spectrometer. When operated in negative chemical ionization mode, the DSQ allowed the identification and quantification of the explosives listed in Table 1.

A limitation typically encountered when analyzing explosives by gas chromatography is the need for a high linear velocity (LV). The high LV helps prevent column-compound interactions, particularly for explosives, such as RDX and HMX. The resulting LV is then incompatible with the vacuum system of a mass spectrometer. However, for this analysis, an analytical column was located that allowed the elution of all compounds using a constant column flow of helium as the carrier gas. The flow rate of 5.0 mL/min, along with the NCI gas flow, was well within the capacity of the 200/200 L/sec split turbo pump on the DSQ.



Figure 2: The on-column injection port as shown on the TRACE GC Ultra. This injection port is configured for automatic on-column injections using software control and a motorized valve opener.

## Key Words

- Cold-on-Column Injection
- DSQ GC/MS
- Explosive Residue Analysis
- Negative Chemical Ionization
- US EPA Method 8095

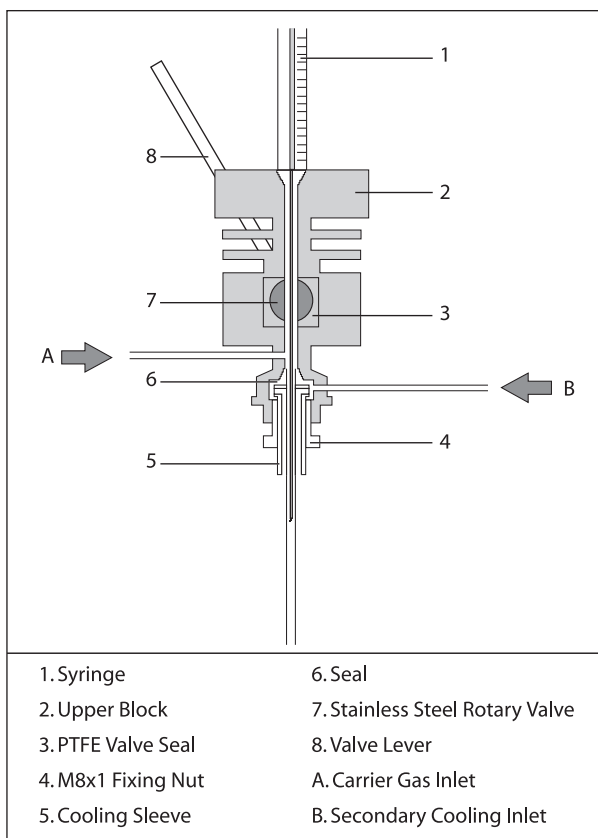


Figure 3: Schematic showing the on-column injector with the needle inserted. With this configuration, the needle enters the 0.53 mm id uncoated pre-column, allowing direct injection of the sample.

Overall, this method offered excellent specificity and sensitivity for the analysis of 17 explosives by GC/MS. On-column injection without secondary cooling was sufficiently gentle to prevent compound degradation in the injection port, peak shape was satisfactory, and detection in the pg/ $\mu$ L range for all compounds was successfully achieved.

## Methods

### Sample Preparation

Explosives calibration standards and matrix spike mixes in acetonitrile were obtained from Restek Corporation (Bellefonte, PA). Deuterated 2,6-dinitrotoluene (methyl-D3) was received from Cambridge Isotope Laboratories, Inc. (Andover, MA). Acetonitrile, Omni-Solv<sup>®</sup> grade, from EM Science, was used for preparation of standards and extraction of soil matrix. A primary dilution standard (PDS) of explosives was prepared at a concentration of 1,000 pg/ $\mu$ L (5,000 pg/ $\mu$ L for \* components in Table 1), excluding HMX (Cerilliant Corp, Round Rock, TX), which was at a concentration of 100 ng/ $\mu$ L in the PDS. Serial dilutions of the PDS provided the calibration curve. Internal standard was spiked after standard preparation to a concentration of 50 pg/ $\mu$ L in all standards. A 70 g sample of soil was extracted by cold sonication using 100 mL of acetonitrile. The resultant extract was evaporated under N<sub>2</sub> to a volume of 10 mL. Selected components were spiked into the concentrated extract. Unspiked matrix was also analyzed.

### Instrumentation

A DSQ configured with a 200/200 L/s split turbo pump system was operated in NCI SIM mode, with methane as the reagent gas. A digital gas flow controller for the reagent gas allowed selection of 2.5 mL/min of methane. A TRACE GC Ultra was configured with an on-column injector for automatic operations. The initial GC oven temperature of 80°C was held for 5.0 min, followed by a ramp of 20°C/min to a final temperature of 225°C. A high oven temperature was avoided to prevent breakdown of the components. A constant flow of 5.0 mL/min of He provided sufficient linear velocity to ensure elution of all explosives. The TriPlus AS was configured for on-column injections with a 1.0  $\mu$ L injection volume. Instrument parameters are summarized in Table 2. The analytical column of choice was a 12 m x 0.32 mm x

RT (min)	PEAK #	NAME	MW	NCI SIM MASS	CALIBRATION RANGE (pg/ $\mu$ L)	R <sup>2</sup>
1.33	1	* nitrobenzene	123	123	5-5,000	0.9990
2.06	2	* 2-nitrotoluene	137	137	5-5,000	0.9996
2.75	3	* 3-nitrotoluene	137	137	5-5,000	0.9996
3.18	4	* 4-nitrotoluene	137	137	5-5,000	0.9994
6.60	5	* nitroglycerin	227	62	25-5,000	0.9993
7.32	6	2,6-dinitrotoluene-D3 (ISTD)	185	185		18.9% RSD
7.35	7	2,6-dinitrotoluene	182	182	1-1,000	0.9999
7.56	8	1,3-dinitrobenzene	168	168	1-1,000	0.9997
8.23	9	2,4-dinitrotoluene	182	182	1-1,000	0.9998
9.23	10	2,4,6-trinitrotoluene	227	227	50-1,000	0.9935
9.32	11	1,3,5-trinitrobenzene	213	213	50-1,000	0.9998
9.66	12	* PETN	316	62	50-5,000	0.9984
10.34	13	4-amino-2,6-dinitrotoluene	197	197	1-1,000	0.9999
10.43	14	RDX	222	102	1-50	0.9987
10.62	15	3,5-dinitroaniline	183	183	1-1,000	0.9998
10.83	16	2-amino-4,6-dinitrotoluene	197	197	1-1,000	0.9995
11.34	17	Tetryl	287	242	50-1,000	0.9980
15.69	18	HMX	296	102	100-100,000	0.9983

Table 1: List of compounds analyzed, in retention time order. Compounds denoted with "\*" were included in standard at 5X the concentration of the other components. HMX was present at 100X the concentration of the other components. The correlation coefficient for linear fits (R<sup>2</sup>) is given for target components, along with linear range in pg/ $\mu$ L. With a 1  $\mu$ L injection, this is also the amount on-column.

DSQ PARAMETERS	TRACE GC ULTRA PARAMETERS	TRIPLUS AS SETTINGS
Start Time: 1.00 min	Oven Method	Injection mode: Basic
Detector Gain: $3.0 \times 10^9$ (1,074 V)	Initial Temperature (°C): 80	Sampling parameters
Lens 1: -25.00	Initial Time (min): 5.00	Sample volume (µL): 1.0
Lens 2: -4.80	Rate #1 (deg/min): 20.0	Plunger strokes: 7
Lens 3: -25.00	Final Temperature #1 (°C): 225	Air volume (µL): 0.0
Prefilter Offset: -11.70	Hold Time #1 (min): 5.00	Pre & Post-injection dwell time (s): 0.0
Electron Lens: 10	Equilibration Time (min): 0.50	Injection dept (mm): 75
Electron Energy: -70	Left OCI Method	Injection speed (µL/sec): 10
Emission Current: 100 µA	Sec. Cooling Time (min): 1.00	Sample type: Viscous
Reagent Gas Type: Methane	Left Carrier Method Mode: Constant Flow	Post-Injection washes parameters
Source Temp: 200°C	Initial Value (mL/min): 5.00	Solvent wash vials: A + B
Reagent Gas Flow, all segments: 2.5 mL/min	Vacuum Compensation: On	Solvent cycles: 9
		Solvent Volume (µL): 10.0

Table 2: Selected instrument parameters for the DSQ, TRACE GC Ultra, and TriPlus AS.

0.25 µm TRACE TR-8095 column (P/N 260P123P, Thermo Electron Corporation). A 1.5 m x 0.53 mm i.d. pre-column was used for desolvation.

## Results

Methane NCI resulted in the creation of molecular ions [M]<sup>-</sup> for most of the explosives. SIM was chosen to enhance sensitivity of the method, and, when available, the molecular ion was used for SIM confirmation and quantification of the explosives. In other cases, the most prominent ion from the NCI full scan spectrum was used as the SIM ion. For components such as PETN and nitroglycerin, this mass, *m/z* 62, corresponds to [NO<sub>3</sub>]<sup>-</sup>, which, by itself may not be sufficient for identification. However, combined with retention time information, positive identification of these components is supported.

All components were identified and quantitated across the calibration ranges described in Table 1, with the associated linear correlation coefficient also included. The use of the on-column injection coupled with careful selection of the analytical column allowed confirmation of even fragile explosive components. Figure 4 depicts extracted ion chromatograms at the lowest calibration point for two explosives, 3-nitrotoluene and HMX.

Reasonable peak shapes were achieved for most of the components. However, it was noted that at higher concentrations, HMX displayed peak broadening that could be associated with column overload. However, at lower concentrations, the peak shape of HMX was excellent, as shown in Figure 4. Nitrobenzene and the single nitrotoluenes (2, 3 and 4-) are virtually unretained in this column configuration, and yet they also have excellent peak shapes and linear ranges. The matrix spike sample gave excellent quantitative results, and the chromatogram for this spiked sample is shown in Figure 5.

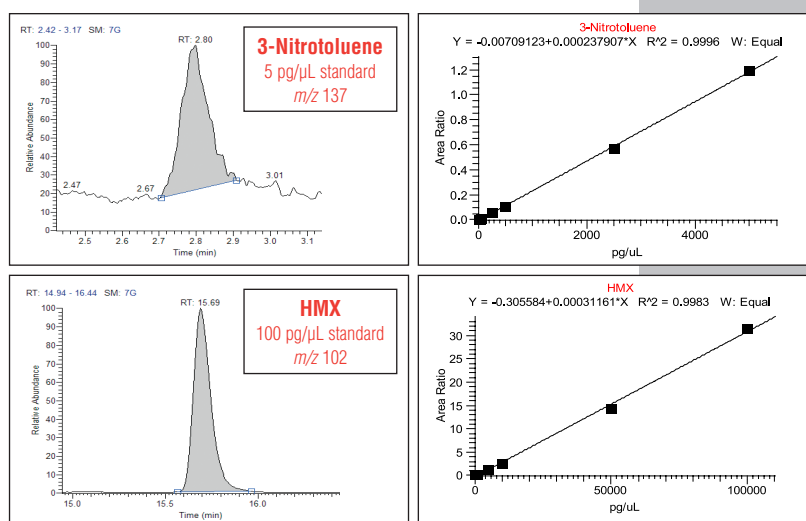


Figure 4: Extracted ion chromatograms for the quantification mass at the lowest calibration level for 3-nitrotoluene and HMX are shown. Also included are the corresponding linear calibration curves, demonstrating linearity across a broad range for both compounds.

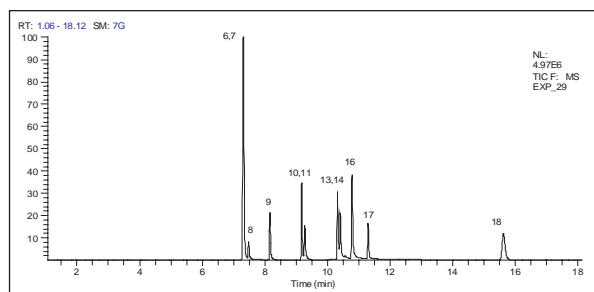


Figure 5: Total ion chromatogram for a soil extract spiked to contain 200 pg/µL of certain components (HMX at 2,000 pg/µL). Peak labels correspond to Table 1.

## Conclusions

- The DSQ operated in NCI SIM, with methane as reagent gas, offers reliable sensitivity and specificity for the identification and quantitation of nitrate ester, nitramine, and nitroaromatic explosives and residues.
- On-column injection coupled with correct column selection provides an excellent means of transferring thermally labile and unstable explosives onto the column, allowing satisfactory peak shape for all components, including RDX and HMX.

## Reference

1. US EPA Method 8095: Explosives by Gas Chromatography, Revision 0. November, 2000.

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