

Analysis of Explosives by Chemical Ionization GC/MS

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Overview

Purpose

Analyze a number of explosive compounds, including precursors and residues, in negative chemical ionization using gas chromatography-mass spectrometry. Evaluate method optimization, chromatography concerns, and rapid identification of residues using fast GC techniques.

Methods

Standards ranging from 1 – 5000 pg/μL of selected nitroaromatic, nitramine, and nitrate ester explosives were prepared. A deuterated analogue of 2,6-Dinitrotoluene (2,6-DNT-D3) was selected as the internal standard. A matrix blank from soil was prepared and then spiked in duplicate for a matrix spike/matrix-spike duplicate analysis, and seven replicates at 50 pg/μL provided precision analysis.

Results

Linearity ranged from 1 – 1000 pg/μL for many compounds. Analysis time was less than seven minutes, with retention times ranging from 1.95 minutes for nitrobenzene to 6.31 minutes for Tetryl. Calibration curves for all compounds had a linear fit of $r^2 > 0.99$, and precision analyses ($n = 7$) of a 50 – 250 pg/μL sample showed coefficients of variation of less than 7% for all compounds.

Introduction

Identification of explosives, including residues and precursors, is important in a number of fields. These compounds can have a negative impact on the environment; therefore, their presence is typically monitored around ordnance remediation sites, as well as in areas where blasting occurs regularly, such as for avalanche control.^{1,2} Forensically, the analysis of explosives can identify source materials, determine the nature of accelerants, and evaluate potential threats. Other applications may include detection of explosives in hair, on airline boarding passes, and on other substrates. A combination of techniques are typically applied to identify trace evidence of explosives.³ These include color spot tests, X-ray examination, and IR spectrophotometry. This application explores the use of GC/MS and its role in identification of selected organic explosives.

The Finnigan™ TRACE™ DSQ™ is a quadrupole mass spectrometer that incorporates a curved prefilter, which, by reducing neutral noise, enables lower detection limits.

By using the Finnigan TRACE DSQ in negative chemical ionization selected ion monitoring mode (NCI SIM), coupled with a Finnigan TRACE GC Ultra™ equipped with a pressure-temperature programmable vaporizing inlet (PTV), explosives can be analyzed in less than 7 minutes. Vacuum chromatography facilitates analysis of the thermally labile components by reducing temperatures needed for sample elution. The use of dual solvents improves chromatography and enhances recovery for a number of analytes by solvent exchange. A vacuum interlock on the Finnigan TRACE DSQ enables the user to change between electron impact (EI) ionization mode and chemical ionization without venting the mass spectrometer. Finally, the availability of the molecular ion for 12 of the compounds allowed the use of NCI SIM on that molecular ion, which increases specificity and sensitivity when compared to EI SIM.

REF. TIME (MIN)	COMPOUND NAME	NCI SIM MASS	% RSD (N=7)	r^2	CALIBRATION RANGE (pg/μL)
1.98	*Nitrobenzene	123	3.01	0.9923	5 – 1000
2.53	*2-Nitrotoluene	137	2.18	0.9949	5 – 5000
2.76	*3-Nitrotoluene	137	5.71	0.9985	5 – 1000
2.86	*4-Nitrotoluene	137	1.66	0.9906	5 – 1000
3.61	*Nitroglycerine	62	1.89	0.9932	5 – 2500
4.00	1,3-Dinitrobenzene	168	1.49	0.9995	1 – 1000
4.07	2,6-Dinitrobenzene	182	0.15	0.9996	1 – 1000
4.05	2,6-Dinitrobenzene-D3 (Internal Standard)	185	11.0 (n = 25)	N/A	N/A
4.38	2,4-Dinitrobenzene	182	1.04	0.9997	1 – 1000
4.95	1,3,5-Trinitrotoluene	213	1.41	0.9995	10 – 1000
5.04	2,4,6-Trinitrotoluene	227	3.86	0.9978	2 – 1000
5.35	*Pentaerythritoltetranitrate (PETN)	62	3.97	0.9984	5 – 5000
5.54	Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	102	6.41	0.9955	1 – 1000
5.82	4-amino-2,6-dinitrotoluene	197	5.32	0.9999	1 – 1000
5.86	3,5-Dinitroaniline	183	5.60	0.9994	1 – 1000
6.00	2-amino-4,6-dinitrotoluene	197	6.21	0.9999	2 – 1000
6.31	2,4,6-Trinitrophenyl methyl nitramine	242	3.45	0.9970	50 – 1000

Table 1: Compound list, including retention times, NCI SIM masses, and a summary of results for precision and linearity. Compounds denoted with * were present in the standards at five times the concentration of the other analytes. The internal standard precision is for area count over all of the injections for all of the samples, including unknowns and standards.

Key Words

- Explosives
- Fast Vacuum Chromatography
- Finnigan TRACE DSQ
- Forensics
- Negative CI
- PTV

FINNIGAN TRACE DSQ METHOD

Detector Gain:	3 x 10 ⁵ e ⁻ (Multiplier Voltage = 1489 V)
Reagent Gas Type:	Methane
Reagent Gas Flow:	1.5 mL/Min
Source Temp:	200°C
Start Time:	1.50 Min
Tune Filename:	NIcIautotune
Lens 1V:	-25.0
Lens 2V:	-4.7
Lens 3V:	-25.0
Prefilter Offset V:	-14.1
Electron Lens V:	15.0
Electron Energy eV:	-70.0
Emission Current eV:	100.0

FINNIGAN TRACE GC ULTRA OVEN METHOD

Initial Temperature (Deg C):	80
Initial Time (min):	2.00
Number of Ramps:	1
Rate #1 (deg/min):	30.0
Final Temperature #1 (Deg C):	290
Hold Time #1 (min):	0.00

PTV PARAMETERS

Base Temperature:	On
Base Temperature (Deg C):	75
Mode:	PTV Splitless
Split Flow:	On
Split Flow (ml/min):	35
Splitless Time (min):	0.20
Constant Purge:	On
Evaporation Phase:	On
Cleaning Phase:	On
Ramped Pressure:	Off
Sub-ambient:	Off
Backflush:	Off
Inject Time (min):	0.1
Evaporation Rate (deg/sec):	14.5
Evaporation Temperature (Deg C):	120
Evaporation Time (min):	1.0
Transfer Rate (deg/sec):	14.5
Transfer Temperature (Deg C):	235
Transfer Time (min):	1.0
Clean Rate (deg/sec):	14.5
Clean Temperature (Deg C):	275
Clean Time (min):	1.0
Clean Flow (ml/min):	50

Figure 1: Selected instrument parameters for the Finnigan TRACE DSQ and the Finnigan TRACE GC Ultra, including the PTV inlet method.

Methods

Materials

Standards for United States EPA Method 8095 Calibration Mixes A and B were obtained from Restek Corporation (Bellefonte, PA). Table 1 lists the compounds tested. 2,6-dinitrotoluene-D3 (2,6-DNT-D3), with a deuterated methyl group, was obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA) for use as internal standard. Acetonitrile and toluene were UV grade or better, and were from Burdick & Jackson (Muskegon, MI). The analytical column was an Rtx[®]-TNT 6 m x 0.53 mm id x 1.50 µm df proprietary phase column from Restek Corp. These column dimensions are similar to those described in US EPA Method 8095.² However, the phase is designed specifically for explosive compounds. A 1.0 m x 0.1 mm id uncoated pre-column was used as a restrictor column to create a pressure drop between the inlet and the mass spectrometer. A SilTite™ mini-union (SGE, Incorporated, Austin, TX) enabled a leak-free inert connection between the analytical column and the pre-column.

Standard & Sample Prep

Improved chromatography and sensitivity were noted when toluene was used to dilute the standard curve 1:1 with acetonitrile. To accommodate this dilution, the working solution was prepared at double-concentration in acetonitrile by adding 200 µL of each stock standard to a volumetric flask, and brought to 100 mL with acetonitrile. This yielded a solution containing 10,000 pg/µL of six compounds, denoted with * in Table 1. The remaining compounds are present at a concentration of 2000 pg/µL. The 2,6-DNT-D3 stock solution was diluted to 50,000 ng/mL in acetonitrile. 10 µL of internal standard solution, added to the 1 mL standards, yielded an internal standard concentration of 500 pg/µL. To prepare a soil matrix, approximately 20 grams of soil were sonicated with approximately 50 mL acetonitrile in an ice water bath for 3 hours.³ The acetonitrile was filtered and dried to approximately 5 mL under nitrogen.

A calibration curve was prepared in 1 mL acetonitrile at nine levels. Additionally, a 1.0 mL soil matrix blank, along with two matrix spike samples (50 µL of working standard plus 950 µL of unspiked, extracted soil matrix) were prepared. 10 µL of the working internal standard solution was added to each vial. Prior to injection, 200 µL of the prepared standards and matrix samples were mixed with 200 µL toluene in new autosampler vials. Following this dilution, the final internal standard concentration was 250 pg/µL. The concentration of the calibrators ranged from 1 – 1000 pg/µL for most components and from 5 – 5000 pg/µL for the six denoted components.

Instrumentation

A Finnigan TRACE GC Ultra equipped with a PTV was coupled with a Finnigan TRACE DSQ outfitted with a 250 L/s turbopump and chemical ionization. The Finnigan TRACE DSQ was operated in NCI SIM, following the use of a negative CI Autotune. Methane (1.5 mL/min) was used as the reagent gas. The NCI SIM masses monitored

are listed in Table 1. An AS 2000 autosampler was programmed to inject 2 μL of sample, with a 3-second pre- and post-injection delay. Method parameters for the Finnigan TRACE DSQ and the Finnigan TRACE GC Ultra are summarized in Figure 1.

Results

Table 1 summarizes the key results from the analyses of explosives on the Finnigan TRACE DSQ. Six compounds were linear from 1 pg to 1000 pg/ μL , while the majority were linear from 5 – 1000 pg/ μL or higher. Furthermore,

for a series of seven replicate injections of a 50 – 250 pg/ μL sample, the % RSD's of the calculated concentrations were less than 6.5% for all of the compounds, with the % RSD for 2,6-Dinitrotoluene at 50 pg/ μL less than 1%.

Figure 2 depicts the NCI SIM masses for four representative components, along with calibration curves, for each. All of the components studied had a linear fit, with correlation coefficients > 0.99. NCI enabled monitoring of the [M]⁻ mass for most compounds, although [NO₃]⁻ (*m/z* 62) was the most abundant ion for both nitroglycerine and PETN.

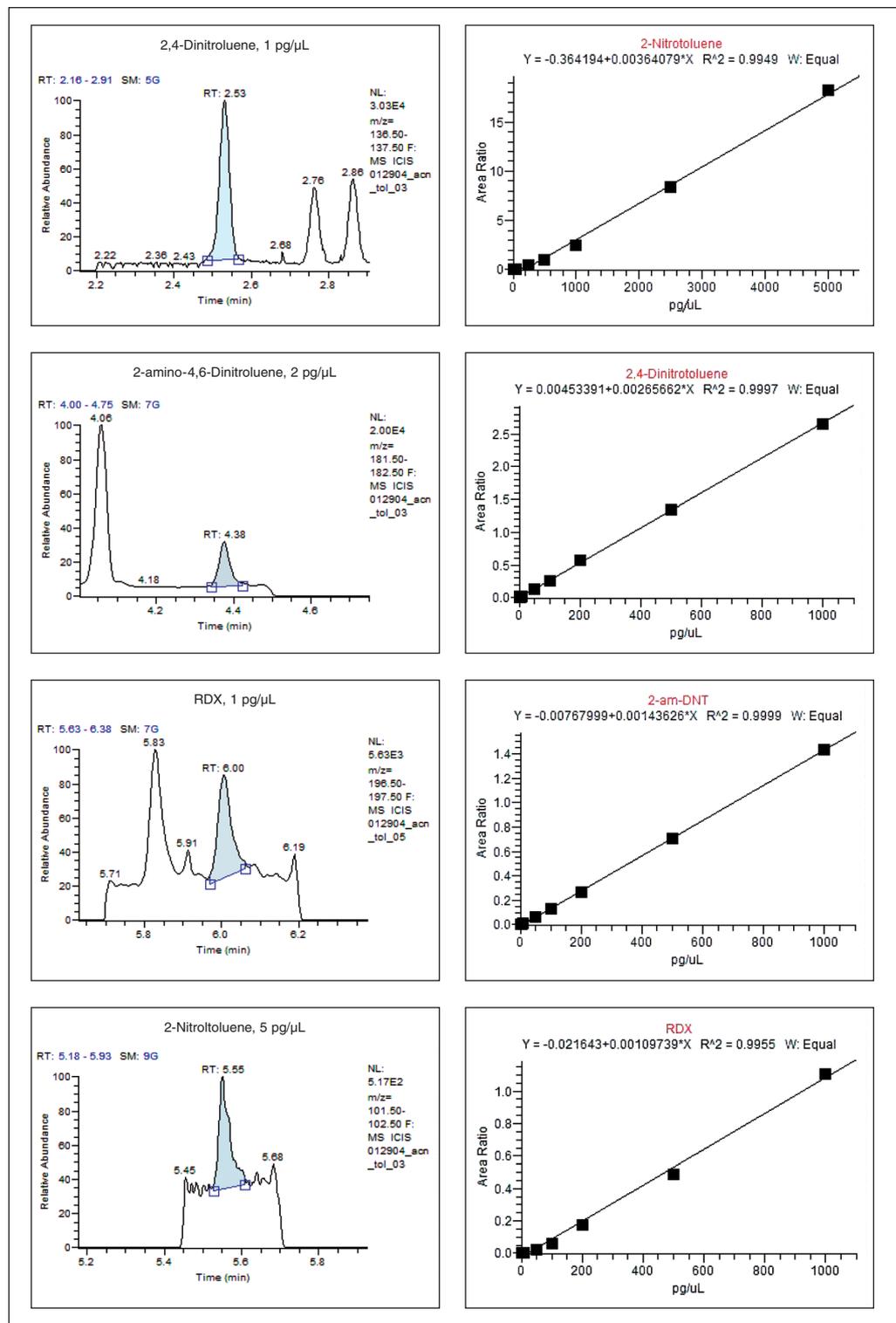


Figure 2: Calibration curves from Xcalibur™ Quan Browser and extracted ion chromatograms for selected compounds. The ion chromatogram depicts the quantitation ion for the lowest point of the curve for that compound.

Due to the high speed of vacuum chromatography, the entire run time was approximately seven minutes. The last compound, Tetryl, eluted at a retention time of 6.31 minutes. Optimization of chromatography was required due to the short run times. Standards prepared in neat acetonitrile displayed split peaks in the middle of the run, or poor chromatography in the earlier components, depending upon the injection technique used. By incorporating toluene to provide a solvent exchange effect and operating the PTV in a cold splitless mode, chromatography was improved across the course of the run. Additionally, the toluene affords better recovery for some of the components. This improvement is shown in Figure 3, which compares the area count for m/z 62 for nitroglycerine at 10 $\mu\text{g}/\mu\text{L}$ in acetonitrile to the area count for the same concentration in 1:1 acetonitrile:toluene. This improvement is particularly noticeable at lower concentrations.

Method development was facilitated by the vacuum interlock on the Finnigan TRACE DSQ. Samples were originally acquired in EI mode to optimize chromatography and ensure compound identities. Then, without venting, the Finnigan TRACE DSQ was switched to CI mode by exchanging the EI ion volume for a CI ion volume through the interlock. Continued method development in CI mode allowed further refinement of chromatographic and GC/MS conditions.

Conclusion

A method for the rapid identification of 16 different nitramine, nitrate ester, and nitroaromatic organic explosives was developed using NCI SIM as the detection method, and vacuum gas chromatography provided the sample separation. Optimization of chromatography, including the use of a solvent exchange, was a critical component for use of the vacuum technique. Acetonitrile as a single solvent was incompatible with vacuum chromatography. Aberrant peak shapes, peak splitting, or high baselines interfered with quantitation. However, by diluting 1:1 with toluene, these problems were eliminated. The resulting method offers sensitivity in the low $\text{pg}/\mu\text{L}$ range, equivalent to low ng/kg in soil.

References

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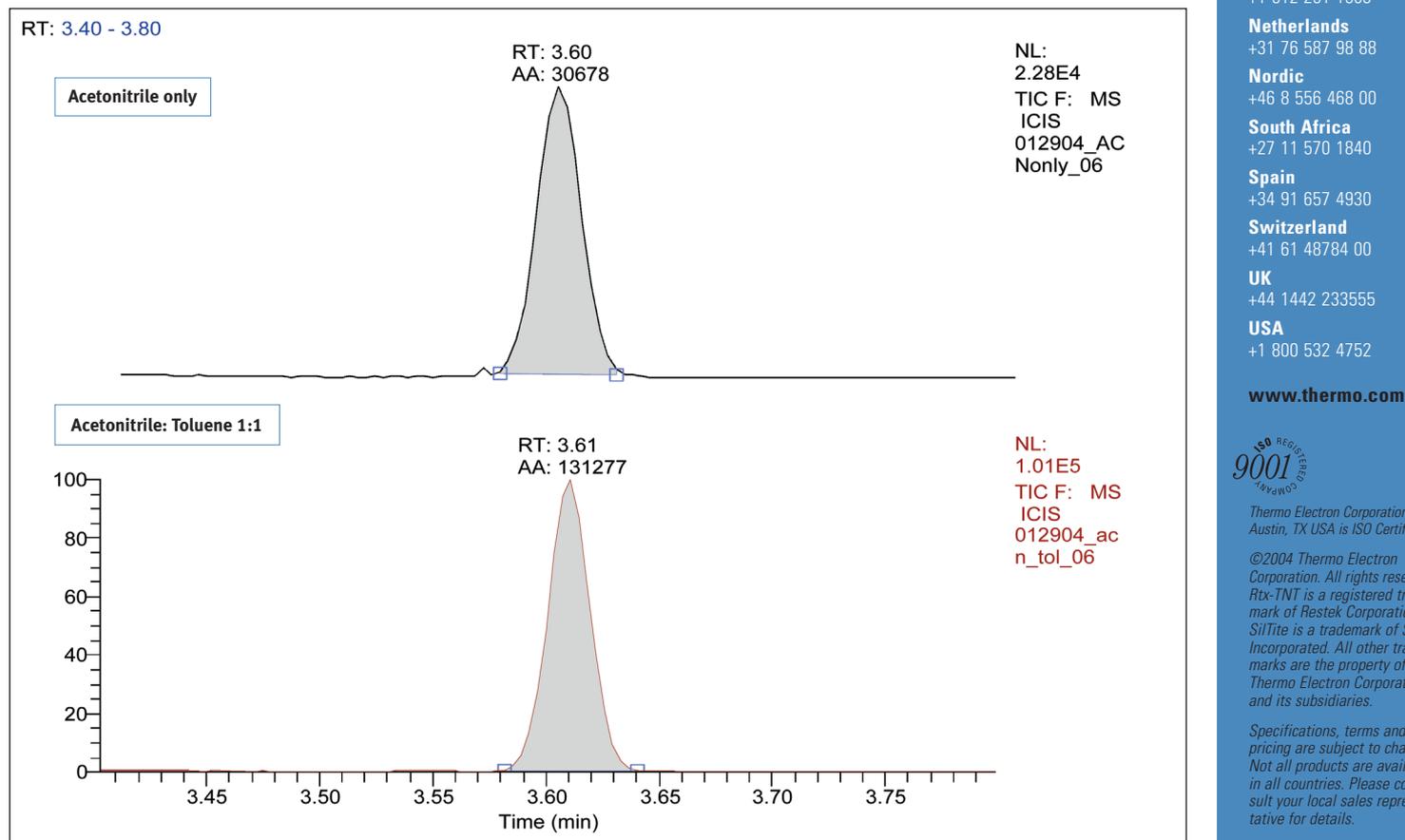


Figure 3: Comparison of recovery improvements through use of toluene in standard preparation: The top trace (black) depicts 10 $\text{pg}/\mu\text{L}$ of nitroglycerine in acetonitrile, while the lower trace (maroon) shows the same compound at the same concentration in a solution of 1:1 acetonitrile: toluene. The area count for m/z 62 in ACN:Toluene 1:1 is over 4 times greater than at the same concentration in ACN only.

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