Quantitative Comparison of Trace Organonitrate Explosives Detection by GC–MS and GC–ECD^2 Methods with Emphasis on Sensitivity*

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Abstract

Quantitative analysis of organonitrate explosive standards was performed by gas chromatography (GC) with dual electron capture detection (ECD^2) and electron-impact ionization quadrupole mass spectrometry (EI-MS) in selected ion monitoring (SIM) detection mode. A comparison of method conditions and performance parameters, including minimum detectable limit (MDL) by compound, is presented in this technical note. The GC–ECD^2 method shows an improved 30–250X sensitivity to dinitroaromatics, trinitroaromatics and RDX, in clean noise-limited backgrounds, and the GC–MS method reveals a sensitivity increase of 2–10X to high volatility mononitroaromatics, the ability to detect target analytes in complex matrices, and identify unknown compounds by mass-to-charge determination.

Introduction

The critical importance of trace explosive detection has led to the development of a variety of means to detect organonitrates using laboratory and field instrumentation. These methods range from quick colorimetric assays (1) to highly sophisticated tandem mass spectrometry (MS) (2) and time-of-flight MS methods (3), often with specialized ionization techniques (2,4). Despite the range of applications that have driven the development of these methods, the need exists to perform quality trace detection using standard low-cost gas chromatography (GC) instruments. These instruments are prevalent in laboratories around the world and commonly adapted for a wide range of analyses. The current Environmental Protection Agency approved analytical methods for organonitrate explosives detection include gas chromatography with electron capture detection (GC–ECD) Method 8095 (5), solid-phase extraction with GC–MS Method 529 (6), and high-performance liquid chromatography with ultraviolet spectrophotometric detection (HPLC–UV) Method 8330 (7). In this study, we compare detection sensitivities and performance parameters of GC–ECD with electron ionization GC–MS for explosives detection, and compare the results to those for negative chemical ionization GC–MS (8).

A modified Method 8095 with dual gas chromatography electron capture detection (GC–ECD^2) and a GC–MS method developed at the Edgewood Chemical Biological Center (Analytical Method 183) were used to analyze a large volume of calibration standards to qualify the capabilities of each technique. The use of two parallel GC columns, also described in other work (9,10), provides two retention time constraints for compound identification, which is significant in a complex sample with possible interferents. A comparison of method performance reveals

Table I. A Summary and Comparison of Experiment Parameters Important in Determining the Performance Differences Between the GC–MS and GC–ECD^2 Methods

	GC–MS	GC–ECD^2
Separation Step		
Inlet Temperature	200°C	250°C
Column i.d.	0.25 mm	0.53 mm
Column Length	5 m	6 m
Column Coating Thickness	0.25 µm	1.0 to 1.5 µm*
Column Flow Rate	2.8 mL/min	20 mL/min
Carrier Gas Linear Velocity	149 cm/s	130 cm/s
Retention Time of TNT	3.8 min	4.5 to 5.0 min*
Detection Step		
Detector	MS	ECD
Detector Pressure	$< 10^{-5}$ Torr	760 Torr (1 atm)
Detection Mechanism	70 eV electron impact cross section to form positive ions	Electron capture cross section of <0.1 eV electrons to form negative ions

*column dependent

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compound-specific detection advantages and limitations for each technique. Minimum detectable limits (MDL) for a series of organonitrate explosive compounds were carefully calculated using calibration statistics from each method, where MDL is defined as the minimum sample quantity which will produce a signal that is statistically distinguishable from the intrinsic electronic noise in the detector. Table I summarizes the experimental conditions for the GC–MS and GC–ECD^2 methods, which help to explain performance differences. GC based analyses involve three distinctly different steps: the efficiency of vaporization and transfer of analytes onto the column, the separation of the analytes in time and space on the chromatographic column, and the individual detection of each of the separated chemicals at the end of the column, which contribute to method sensitivity. Table II summarizes method differences in compound detection sensitivities which can be attributed to chemical stability during separation and the detection efficiency, including those limitations resulting from both instrument noise and chemically complex field samples termed environmental clutter.

Table II. Summary of Strengths and Limitations of GC–MS and GC–ECD^2 to Detection of Nitro-organic Compounds in Both Clean Laboratory and Contaminated Field Samples*

Detection Sensitivity For	GC–MS (ECBC AM-183)	GC–ECD^2
Mononitrates (NB, 2NT, 3NT, 4NT)	High sensitivity (To single pg on column)	Moderate sensitivity (100s of pg on column)
Dinitro compounds (26DNT, 34DNT, 24DNT, 2AmDNT, 4AmDNT)	High sensitivity (10s to 100s pg on column) Precision and accuracy decrease below 100 pg for most compounds listed.	High sensitivity (To single pg on column, particularly in clean matrices)
Trinitro compounds RDX, TNT, Tetryl	Moderate sensitivity (above 100 pg on column) Least sensitive to RDX below 100 pg on column.	High sensitivity (To single pg on column, particularly in clean matrices)
PETN	Thermally unstable, but can still be detected by identifying its decomposition products	Thermally unstable, and challenging to identify using its decomposition products
HMX	Decomposes on column and hence low signal levels observed, but can still be detected	Decomposes on column and hence low signal levels observed, can only be detected in clean samples and at large (> 100s of pg) quantities
Chemically clutter-rich field samples	Mass selective detector minimizes decrease in sensitivity due to clutter	Clutter minimizes sensitivity especially in cases of clutter signals in both column channels

*The differences stem from a combination of chemical stability during separation and detection efficiency.

Experimental

Method calibration

The daily calibration run for both GC–ECD^2 and GC–MS methods used for quantitation consisted of a set of common components in the standard mixtures (AccuStandard, Inc., New Haven, CT) which included nitrobenzene (NB), 2-nitrotoluene (2NT), 3-nitrotoluene (3NT), 4-nitrotoluene (4NT), 2,6-dinitrotoluene (26DNT), 1,3-dinitrobenzene (DNB), 2,4-dinitrotoluene (24DNT), 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), 4-amino-2,6-dinitrotoluene (4AmDNT), 2-amino-4,6-dinitrotoluene (2AmDNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), pentaerythritol tetranitrate (PETN), and 2,4,6-trinitrophenylmethylnitramine (Tetryl), indirectly via detection of *n*-methylpicramide (NMPD), over a range of concentrations in acetonitrile. The GC–MS method also included 3,4-dinitrotoluene (3,4-DNT) and 3,5-dinitroaniline (3,5-DNA).

Table III. Quantitating and Confirming Ions for SIM GC–MS

Compound	Quantitating Ion	Confirming Ion A	B	C	D
NB	123	77	93	51	
2NT	120	65	91	93	137
3NT & 4NT	137	93	91	65	
13DNB	168	75	92		
26DNT	165	89	148		
24DNT	165	89	119	182	
135TNB	75	213	120	167	
246TNT	210	89	180	134	
PETN	46	30	56	76	
RDX	128	120	75	148	205
4AmDNT	180	197	104		
35DNA	183	64	91		
2AmDNT	180	197	104		
Tetryl	194	212	225	242	

GC–MS Method

An Agilent 6890 gas chromatograph with an Agilent 5973 electron-impact ionization (EI) quadrupole mass spectrometer (Santa Clara, CA) was used in this protocol equipped with a Phenomenex Zebron ZB-5MS (5 m × 0.25-mm i.d. × 0.25-µm film thickness or equivalent) column (Torrance, CA). A short column with a small inner diameter was selected to minimize the transit time of the analyte on column. In order to achieve the conditions listed in Tables IV and VII (shown and discussed later), the MS must be equipped with a high capacity pump.) A series of eight calibration standards prepared in acetonitrile containing 15 target analytes and corresponding internal standard was analyzed by GC–MS. Nominal standard concentrations were 10, 25, 50, 100, 250, 500, 1000, and 2000 ng/mL. Approximately 250 ng/mL of the internal standard, 3,4-DNT, was added to all calibration standards. All stock solutions were remade every three months. The dilutions from those stock solutions were remade every month unless a stability study showed a longer storage time was acceptable. All solutions were stored at or below 8°C in an autosampler or secured freezer.

MS acquisition was performed in SIM mode programmed with the quantitating and confirming ions listed in Table III. A typical SIM GC–MS chromatogram, displayed as the sum of the recorded ions, is shown in Figure 1. During analysis, the thermal degradation product N-methylpicramide (NMPD) was monitored to indirectly detect 2,4,6-trinitrophenylmethylnitramine (Tetryl) (11). Also, two PETN degradants, resulting from the sequential loss of peripheral nitrate groups, were identified via GC–MS as pentaerythritol trinitrate and pentaerythritol dinitrate. These compounds, having ions in common with PETN, elute at earlier retention times. Method analytical time was approximately 8.5 min with a total cycle time of approximately 14 min. Approximately 34 samples and related quality assessors could be analyzed in an 8-h time period.

GC–ECD^2 Method

An Agilent 6890 gas chromatograph equipped with two auto-injectors, inlets, columns, and dual micro-electron capture detectors was used for this procedure. Each set of two identical samples were run simultaneously on the two parallel GC columns, using a refrigerated (< 8°C) 100-vial autosampler and two parallel auto-injectors. Column 1 (Agilent 125-501J) was a 6-m DB-5, 0.53-mm bore, 1-µm film thickness column, and column 2 (Restek 15067-119) was a 6-m Rtx-200, 0.53-mm bore, 1.5-µm film thickness column. Each column was connected to a 12-inch section of 0.53-mm-bore guard column which was replaced periodically as the sensitivity of the method decreased from surface passivation loss. A ten-point calibration was used for each compound using injection masses of 1, 5, 10, 25, 50, 100, 250, 500, 1000, and 2000 pg from 1-µL injections of the appropriate standard concentrations. New calibration standards were prepared every 4 weeks using only qualified HPLC-grade acetonitrile and stored in a freezer below 8°C when not housed in the refrigerated autosampler tray. Sample chromatograms for the two GC columns are shown in Figure 2.

Overall, the GC–ECD^2 method run-time was approximately 15 min. In an eight-hour time period, approximately 20 samples and related quality assessors could be analyzed.

A custom analysis program compared results from each of the two GC columns, referred to as "detection channels" and if, for a given compound, a peak appeared within its respective retention time window on both columns and the integrated areas were within 50% of each other, a positive identification for that compound was assigned with an area equal to the average of the two columns. If the relative areas for the two columns' responses were more than 50% different, a positive identification was still assigned but now with an area equal to the lesser of the two columns' responses. If a peak was identified in only one or neither of the two columns, a negative identification for that compound was assigned.

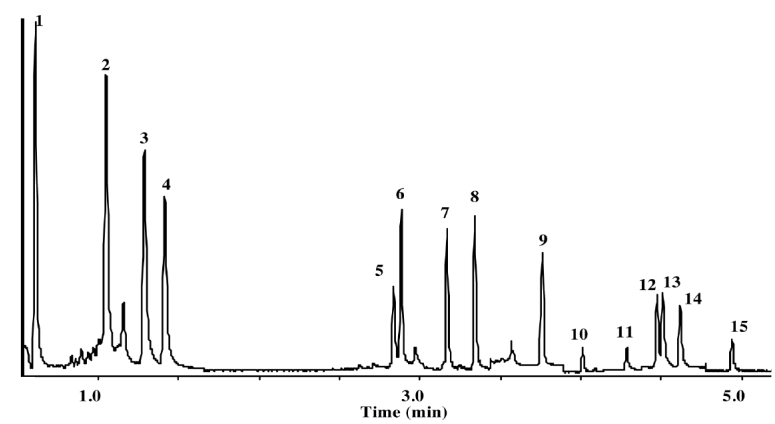

Figure 1. Typical SIM GC-MS total ion chromatogram collected for a 250 pg injection using a ZB-5MS column: Nitrobenzene (1), 2-Nitrotoluene (2), 3-Nitrotoluene (3), 4-Nitrotoluene (4), 1,3-Dinitrobenzene (5), 2,6-Dinitrotoluene (6), 2,4-Dinitrotoluene (7), 1,3,5-Trinitrobenzene (8), TNT (9), PETN (10), RDX (11), 4AmDNT (12), 3,5-DNA (13), 2AmDNT (14), and Tetryl (15-NMPD). The calibration standard contained 250 ng/mL 3,4-DNT (8) as an internal standard.

GC–ECD^2 versus GC–MS method conditions

Experimental conditions, such as GC inlet and oven settings, which contribute to the transfer efficiency of analytes from injector to detectors for both GC–ECD^2 and GC–MS methods are listed in Table IV. The injection port temperature was decreased in the GC–MS method to reduce analyte degradation within the inlet. The inlet liner used in both methods was a drilled uniliner type. The inlet temperature, injection mode, and type of inlet liner will

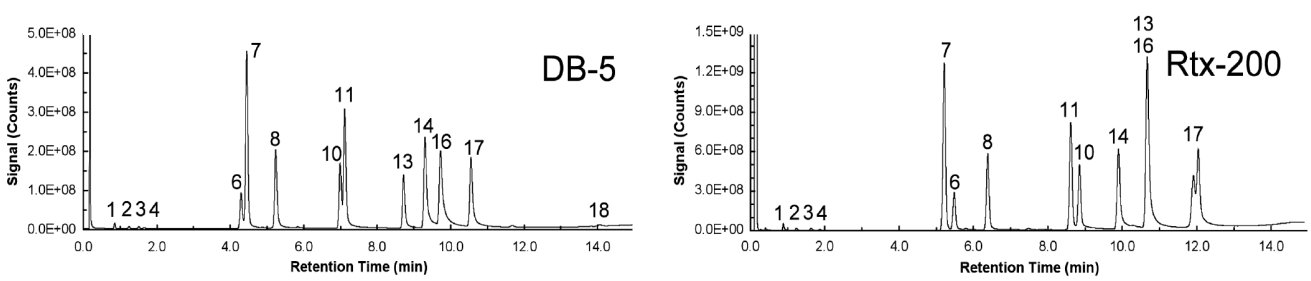

Figure 2. GC–ECD^2 data collected using a DB-5 column and an RTX-200 column for a 1-ng injection of a 14-component explosive mix. Peak identifications are: nitrobenzene (1), 2-nitrotoluene (2), 3-nitrotoluene (3), 4-nitrotoluene (4), 1,3-dinitrobenzene (6), 2,6-dinitrotoluene (7), 2,4-dinitrotoluene (8), trinitrobenzene (10), TNT (11), RDX (13), 4AmDNT (14), 2AmDNT (16), Tetryl (17-NMPD), and HMX (18).

affect the stability of particular compounds (e.g., PETN and NG) and the amount loaded on column. In the GC–MS method, compounds flow at a higher velocity through a smaller diameter column in a MS system using a turbo vacuum pump. The retention time for each analyte in both methods are listed in Table V and demonstrate the overall reduced elution time of components using the GC–MS conditions versus those used for the GC–ECD^2. Subsequent improvements in the GC–ECD^2 method have reduced the retention time to those compared to the GC–MS method (15).

Results and Discussion

In order to provide a direct comparative study of the sensitivity of each method by compound, the MDL was calculated for each analyte using a widely accepted method as described in literature (12–14) The measurement was performed using the entire analytical method, including all sampling, extraction, and analysis steps. A series of replicate measurements are performed using a single analyte concentration. From this, the MDL for a single measurement can be calculated as:

$$MDL = t_{(0.01, n-1)} s_C \quad \text{Eq. 1}$$

where $t_{(0.01, n-1)}$ is the t-distribution for a significance test at the 99% level for N measurements, and s_C is the standard deviation of the instrument response for the N different replicate experiments performed at concentration C. The MDL as derived this way indicates that if the true concentration of a single unknown sample is below the reported MDL, there will be a 99% chance that the instrument will report that it is not detected, or stated differently, there will be a 99% probability that the result will be statistically identical to a blank sample of zero concentration. For an unknown sample repeated n times, the MDL resulting from averaging the n measurements is reduced by $n^{0.5}$.

Table IV. Comparison of Experimental Conditions for GC–ECD^2 and GC–MS Methods

	GC–ECD^2 Method Conditions		GC–MS Method Conditions
	Column 1	Column 2	Column 1
Manufacturer	Agilent	Restek	Phenomenex
Column	DB-5	Rtx-200	ZB-5MS
Stationary Phase Composition	5% Phenyl siloxane, 95% dimethyl siloxane	Trifluoropropylmethyl siloxane bonded phase	5%-Phenyl-arylene, 95% dimethyl polysiloxane
Polarity	Low	Intermediate	Low
P/N	Agilent 125-501J	Restek RTX-200	Zebron ZB-5MS
Column Length	6 m	6 m	5 m
Column i.d.	0.53 mm	0.53 mm	0.25 mm
Coating thickness	1.0 µm	1.5 µm	0.25 µm
Mode	Constant flow	Constant flow	Constant flow
Initial flow	15.0 mL/min	15.0 mL/min	2.8 mL/min
Nominal inlet pressure	2.94 psi	2.96 psi	~5.4 psi
Average velocity	130 cm/s	130 cm/s	149 cm/s
Injection mode	Splitless	Splitless	Splitless
Injection Volume	1 µL	1 µL	1 µL
Inlet temperature	250°C	250°C	200°C
Purge flow	199.9 mL/min	198.8 mL/min	initially off – @ 1.00 min, 50 mL/min @ 2.0 min, 20 mL/min
Purge time	0.50 min	0.50 min	see purge flow above
Solvent Delay	NA	NA	1.10 min
Total flow	217.1 mL/min	217.0 mL/min	55.4 mL/min
Carrier gas	> 99.999% He	> 99.999% He	> 99.999% He
Initial Oven Temp	100°C		50°C
Initial Time	2 min		0.20 min
Ramp Rate 1	10.0°C/min		15°C/min
Final Temp 1	200°C		85°C
Ramp Rate 2	20.0°C/min		35°C/min
Final Temp 2	250°C		150°C
Ramp Rate 3	N/A		25°C/min
Final Temp 3	N/A		250°C
Final Hold Time	2.5 min		0.0 min
Total Time	17 min		8.39 min
Detector Temp	300°C	300°C	280°C (MSD Transfer Line)
Makeup Flow	30 mL/min	30 mL/min	NA
Makeup Gas	Nitrogen	Nitrogen	NA

Table VI presents MDLs for standard calibration solutions analyzed and quantified over different dates of routine field sample analysis. These MDLs encompass some variability in method performance statistics stemming from daily use and allow a representative comparison for expected performance. The listed MDLs were calculated from calibration samples that were run comingled with field samples. The statistics in Table VI were generated for eight common organonitrate compounds, including five dinitroaromatics, two trinitroaromatics and RDX. The series of plots in Figure 3 compares response statistics for the same eight calibration compounds for both analytical methods. The mean and standard deviation of the reported mass were normalized to the actual injected mass during calibration for the eight compounds. This figure is a graphical comparison of precision and accuracy of both methods over a similar concentration range for a select set of compounds. Thoughmethod performance is comparable at the higher injection loadings shown, the GC–ECD^2 method proved to have better recovery of these eight nitroaromatic compounds at lower injection loadings with two confirmatory output channels, especially in extractions of clean matrices or standard calibration solutions.

In a subsequent set of experiments to be described in detail in an upcoming publication (15), a different confirmatory pair of columns (Restek Rtx-TNT1 and Rtx-440, Bellefonte, PA) was used to quantify the mononitroaromatic compounds via

Table V. Retention Times for All the Measured Analytes on Three Columns *

Compound	GC–ECD² DB-5 RT (min)	GC–ECD² RTX-200 RT (min)	GC–MS ZB-5MS RT (min)
NB	0.834	0.898	1.09
2NT	1.226	1.267	1.54
3NT	1.496	1.673	1.77
4NT	1.641	1.910	1.90
DNB	4.289	**5.495***	3.33
26DNT	4.440	**5.217**	3.38
24DNT	5.239	6.392	3.66
34DNT	N.M.*	N.M.	3.84
TNB	6.964	8.860	4.25
TNT	7.102	8.624	4.26
PETN	N.M.	N.M.	4.51
RDX	8.677	9.908	4.78
4AmDNT	9.269	10.002	4.97
DNA	N.M.	N.M.	5.00
2AmDNT	9.713	10.678	5.11
Tetryl/NMPD	10.565	12.052	5.44
HMX	14.032	N.M.	N.M.

* Values in bold indicate differences in retention time order with respect to the primary GC–ECD² column. Certain compounds not present in the standard for the listed technique are marked as not measured (N.M.).

GC–ECD². Though the GC oven ramp was optimized specifically to run this pair simultaneously, and the column coating thickness was reduced to 0.5 µm, observed selectivities and retention indices were quite similar to the original column pair (DB-5 and Rtx-200). Therefore, the results would closely approximate the sensitivity of the method to the mononitrates. Table VII provides a quantitative MDL comparison of GC–ECD² versus GC–MS for four common mononitrates. The response statistics generated for the mononitrate compounds by only the GC–MS method are reported in Figure 4. The GC–MS method was superior in sensitivity to mononitroaromatic compounds, which were not quantified by the initial columns used for the GC–ECD² during these experiments.

The performance differences in the two methods could be attributed to both the differences in separation and detection methods. The single most important aspect of separation in these methods was the efficiency with which each respective chemical is transferred to the detector through both the injection port and the column. Explosives are prone to chemical decomposition on certain surfaces, particularly at high temperature. This process can be so severe that it consumed most, or even all, of the analyte before it reached the detector, thereby reducing the effective sensitivity a great deal. Thus, care was taken to passivate all wetted surfaces, particularly the inlet liner and the GC column's stationary phase, thereby eliminating opportunities for decomposition. This can be further minimized by using high flow rates, and large-bore, low surface-area-to-volume ratio columns. These factors favor the GC–ECD² method with its higher flow rate and larger bore column. The GC–MS method cannot support these conditions as the maximum column flow rate is limited by the pumping speed of the vacuum chamber housing the mass spectrometer detector. From a chromatographic standpoint, the GC–ECD² method is superior for trace explosives detection. However, the flow rate limitations placed on the column by the MS detector were more than compensated for by the superior performance and clutter-rejection capabilities of the MS.

Each explosive chemical detected using these methods yielded a different response during detection. Figure 5 is a graphical comparison of all the MDL data previously listed for both techniques. Three clusters of compounds emerged as a function of method sensitivity: mononitroaromatics, aminodinitroaromatics/trinitroaromatics/RDX, and dinitroaromatics. With an electron capture detector, the capture cross-section for forming a negative ion was up to 100 times lower for a mononitroaromatic compound as compared to a trinitroaromatic compound. This stemmed from the electronegativity of the nitro groups and the stability of the molecular anions that were formed after electron

Table VI. Summary of Method Minimum Detectable Limits (MDLs) Derived from Equation 1 for Eight Common Organonitrates*

Compound	GC Column	GC–ECD² Method† CS§ Mass Reported (pg)	GC–ECD² Method† CS§ MDL** (ng)	GC–ECD² Method† CS§ (C1 and C2) Effective MDL** (ng)	GC–MS Method‡ CS§ Mass Reported (pg)	GC–MS Method‡ CS§ MDL** (ng)
DNB	1	5.97 ± 1.22	1.71	0.82	30.23 ± 8.42	24.8
	2	5.77 ± 1.52	2.13			
26DNT	1	6.15 ± 0.85	1.19	0.48	29.11 ± 9.84	29.0
	2	5.79 ± 0.67	0.93			
24DNT	1	6.06 ± 0.90	1.26	0.13	34.17 ± 5.26	15.5
	2	5.44 ± 0.76	1.06			
TNB	1	4.46 ± 1.71	2.39	1.21	13.52 ± 19.75	58.3
	2	4.55 ± 1.81	2.54			
TNT	1	5.45 ± 4.20	5.88	1.94	47.54 ± 25.58	75.5
	2	7.35 ± 2.21	3.09			
RDX	1	5.21 ± 0.87	1.22	0.44	37.63 ± 39.81	109.0
	2	5.53 ± 1.61	2.26			
4AmDNT	1	5.40 ± 068	0.95	0.36	47.28 ± 18.13	53.5
	2	5.46 ± 0.70	0.98			
2AmDNT	1	5.63 ± 1.21	1.70	0.85	43.41 ± 22.53	66.5
	2	5.43 ± 1.77	2.48			

* The dual-column GC–ECD² and GC–MS noise-limited MDLs were determined from direct injection of pure calibration samples for head-to-head comparison. These data do not take into account clutter sources from field samples which may adversely impact the GC–ECD² while having little or no effect on analysis by the highly selective GC–MS method.
† Noise-Limited Performance (n = 23)
‡ Noise-Limited Performance (n =16; RDX, n =35)
§ CS = Calibration standards
** Assumes a 500-mL extract volume and an injection volume of 1 mL. For the on-column MDLs, divide this number by 500. This is the MDL independent of sample recovery variance and environmental clutter.

attachment. In contrast, the response functions for these same compounds to the MS were more similar, with a variability of only a factor of 3 or 4 from compound to compound, compared to the factor of 100 variation observed in the ECD. Thus, the MS was more sensitive to the mononitroaromatics, but the ECD is more sensitive to the trinitroaromatics. The selected column chemistries and method conditions are reported as the method of record during this study; however, sensitivities to particular compounds may be improved using other columns or method conditions (15).

The single most important capability of the mass spectrometer, operating in scan mode, was its ability to identify the molecular structure of the detected compound by virtue of its simultaneous detection of all the mass fragments comprising the "fingerprint" of each chemical. From a data standpoint, consider the ECD as a single "channel" detector and the method using dual ECDs as a two "channel" detector, resulting from the different separations in the primary and confirmatory columns. In contrast, the GC–MS method scanned between 42 different masses in SIM mode that corresponded to the most abundant mass fragments formed after electron ionization of these compounds. The power of a 42-channel detector compared to a 2-channel detector in detecting unknown compounds using scan mode, or sensitive and selective determination of known targets in the presence of a highly chemically cluttered background. For this reason, GC–MS is often considered the optimal technique for chemical analysis. In addition, published work shows SIM mode negative chemical ionization MS offers improved selectivity of explosives over matrix interferences and sensitivity down to the 1–5 pg range for most compounds discussed here (8). The average sensitivity to organonitrate explosives of the GC–ECD^2 method remains superior to published MS data (2). Our recommendation is, when available, to employ a combination of optimized MS and ECD methods for organonitrate explosives analysis. They are excellent complements to one another especially in complex matrices.

Table VII. Summary of Method Minimum Detectable Limits (MDLs) Derived from Equation 1 for Four Common Mononitrates*

		GC–ECD^2 Method†			GC–MS Method‡	
		CS§		CS§ (C1 and C2)	CS§	
Compound	GC Column	Mass Reported (pg)**	MDL†† (ng)	Effective MDL (ng)	Mass Reported (pg)‡‡	MDL** (ng)
NB	1	71.8 ± 27.1	42.9	14.4	17.90 ± 2.26	3.16
	2	77.2 ± 23.2	36.6			
2NT	1	59.8 ± 28.8	45.5	23.7	19.24 ± 1.74	2.43
	2	72.1 ± 17.7	28.0			
3NT	1	59.7 ± 21.6	34.1	17.1	21.38 ± 2.83	3.95
	2	62.6 ± 5.3	24.2			
4NT	1	66.4 ± 33.2	52.5	8.6	23.88 ± 3.94	5.50
	2	46.7 ± .4	19.6			

* The dual-column GC–ECD^2 and GC–MS noise-limited MDLs were determined from direct injection of pure calibration samples for head-to-head comparison. The GC–ECD^2 data appearing in this table were collected using the Restek Rtx-TNT1 and Rtx-440 confirmatory column pair.
† Noise-Limited Performance (n = 23)
‡ Noise-Limited Performance (n =16; RDX, n =35)
§ CS = Calibration standards
** Injected mass 50 pg.
†† Assumes a 500-mL extract volume and an injection volume of 1 mL. For the on-column MDLs, divide this number by 500. This is the MDL independent of sample recovery variance and environmental clutter.
‡‡ Injected mass 23 pg.

Conclusions

In comparison, GC–ECD^2 versus GC–MS demonstrated particular strengths and weaknesses in the detection of organonitrates explosives. This technical note summarizes these attributes and describes

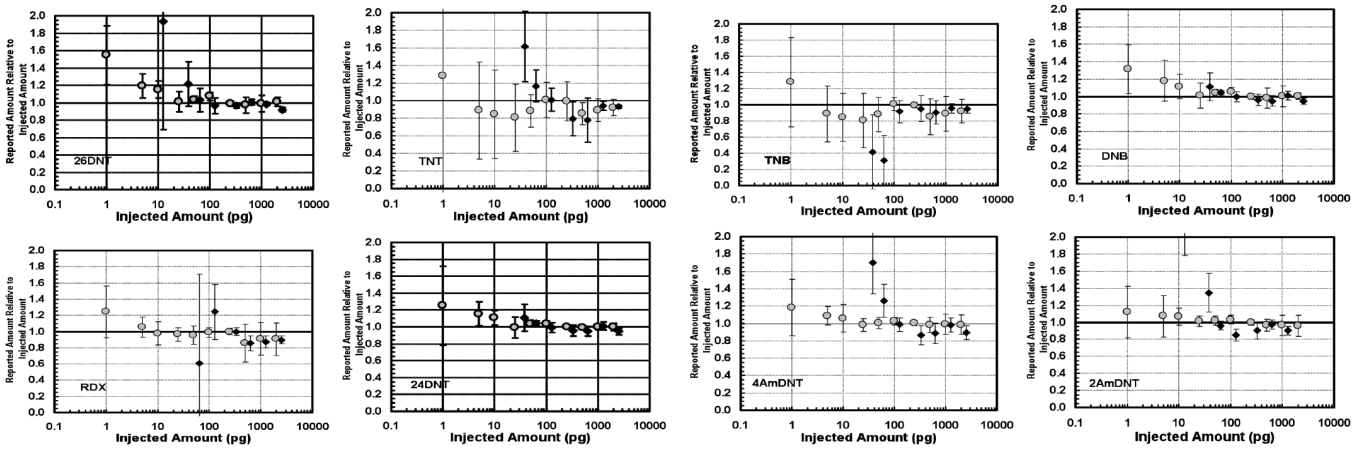

Figure 3. Summary of all calibration data for 8 compounds common to both GC–ECD^2 and GC–MS methods, including 2-amino dinitrotoluene (2AmDNT), 4-amino dinitrotoluene (4AmDNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), trinitro-toluene (TNT), 1,3,5-trinitrobenzene (TNB), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), and 1,3-dinitrobenzene (DNB), which is normalized to the injection mass. Each point represents the normalized reported mean with error bars for one standard deviation. Diamonds = SIM GC–MS results, Circles = GC–ECD^2 results when outputs from both GC columns are combined using the logical AND function.

analytes and circumstances where one method would be preferred over the other. In clean matrices, the GC–ECD[2] method, whose response is a function of electron capture cross section, maintains high sensitivity for di- and tri-nitrated compounds, including TNT and RDX, and utilizes two complementary GC columns for simultaneous confirmatory analysis based on unique retention time windows to quantify each calibrated compound. However, the mononitrate compounds show very low sensitivity via GC–ECD[2]. The GC–MS detection of explosives employs a high velocity flow rate through the GC to an electron-impact ionization quadrupole MS, which minimizes the loss of analyte through the column and boasts a high sensitivity to the mono- and di-nitroaromatics and allows identification of unknowns in scan mode. For high clutter scenarios, the mass spectral technique offers SIM detection mode which prevents the need for any confirmatory analysis and reduces sensitivity loss.

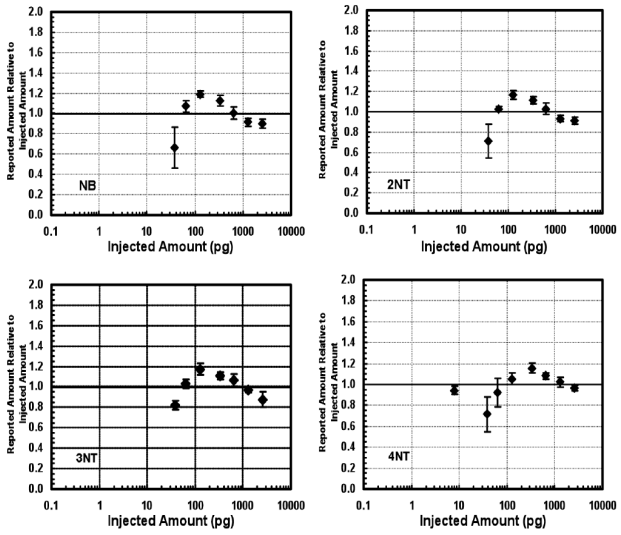

Figure 4. Summary of calibration data for 4 mononitrate compounds as measured by the GC–MS method, including nitrobenzene (NB), 2-nitrotoluene (2NT), 3-nitrotoluene (3NT), and 4-nitrotoluene (4NT). The reported values are normalized to the injection mass. Each point represents the normalized reported mean with error bars for one standard deviation.

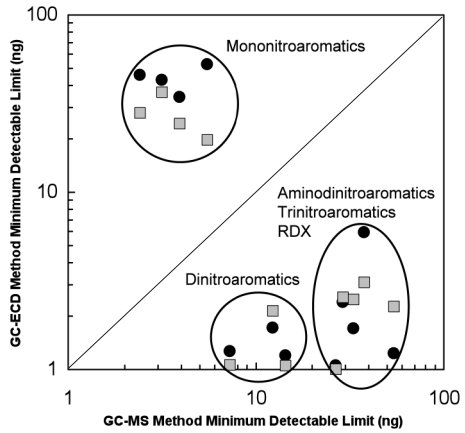

Figure 5. Graphical comparison of GC–ECD[2] and GC–MS method minimum detectable limits. This representation clearly demonstrates three clusters of compounds as a function of method sensitivity: mononitroaromatics, aminodinitroaromatics/trinitroaromatics/RDX, and dinitroaromatics. The 1:1 diagonal line designates equivalent method sensitivity. Data above the diagonal indicates superior GC–MS performance and data below the diagonal signifies greater GC–ECD[2] (column 1: black circle; column 2: grey square) sensitivity to these compounds.

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