The Role of Stationary Phase Selection on Performance For Explosives Analysis Using GC–ECD*

Roderick R. Kunz†, Kerin E. Gregory, and **Dennis Hardy**
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, MA 02420

Abstract

Gas chromatography with electron capture detection (GC–ECD) analysis of explosive-related nitro organic compounds was performed using four different column stationary phases with the focus being on their impact on analyte stability and transfer efficiency during analysis. All four columns used were 6 m × 0.53 mm, and the four stationary phases were a 1.0-µm thick 5% phenyl siloxane/95% methyl siloxane non-polar phase, a 1.5-µm thick 5% phenyl siloxane/95% methyl siloxane non-polar phase optimized for explosives analysis, an intermediate polarity 0.5-µm thick trifluoropropylmethyl siloxane phase, and a proprietary intermediate polarity 0.5-µm thick phase. Although all exhibited similar recovery (as defined as the detector signal per injected mass) when new, the intermediate polarity phases maintained higher sample recovery over the course of analyzing hundreds of samples than the non-polar phases, particularly for the nitramines hexahydro-1,3,5-trinitro-1,3,5-triazine and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, for which a 7× and 3× decrease in recovery were observed, and the nitrate esters nitroglycerin and pentaerythritol tetranitrate, for which a 7× and 11× decrease in recovery were observed. For most other explosive-related compounds, the differences in recovery were between 1.5× and 3× over the same course. Although the detailed chemical formulation of the stationary phases have not been disclosed by their manufacturers, we attribute the observed differences in performance to the stability of their passivation chemistries with regard to other mobile-phase compounds contained in complex field samples. Although these effects have been qualitatively noted in the past and in response, maintenance procedures have been developed to help account for this behavior, the analyst's preference is to use an explosives analysis method that does not require these time-consuming measures. Our desire to prolong this maintenance interval provided the motivation for the assessment reported in this paper. From our assessment, we conclude that manufacturers of GC columns should focus more attention on the stationary phase and passivation chemistries that can lead to the development of a column that is better able to maintain passivation against explosive compound degradation; and users intending to perform large numbers of analyses using GC–ECD should make this a consideration when selecting a column.

* This work was supported by the U.S. Army Edgewood Chemical and Biological Center as a subcontract from the Joint Improvised Explosive Device Defeat Organization (JIEDDO) under Air Force contract FA8721-05-C-0002. Interpretations, opinions, and conclusions are those of the author and do not represent the official view of the United States government.
† Author to whom correspondence should be addressed.

Introduction

The importance of trace explosives detection in forensics, public safety, occupational exposure, and environmental science has provided a strong incentive to develop analytical capabilities useful for these many applications and has resulted in the establishment of several OSHA- and EPA-approved methods for analysis. One common analysis method is gas chromatography (GC) with electron capture detection (ECD) (1–7) and is the basis of EPA Method 8095. Since this method's development, there have been many subsequent reports on improvements that have been focused both on sensitivity (8) (i.e., the ability to detect smaller quantities of trace explosives) and on analysis selectivity (i.e., the ability to detect explosive traces in evermore contaminated matrices) (9). In addition, there have been recent studies that have focused on quantifying and improving one of the more challenging aspects of this method, namely the tendency for the explosive analytes to break down in the GC system during analysis. This phenomenon is usually attributed to the thermally activated decomposition of the more labile analytes on unpassivated surfaces inside the GC system. Reported techniques for minimizing these effects include operating at lower inlet temperature, frequent replacement of the inlet liners and gold seal, use of a replaceable, passivated guard column between the inlet and the analytical column, solvent cleaning of the inlet, and/or operating at higher flow rates (10,11). There have been additional numerous reports that indirectly address this issue by using selective solid-phase extraction (SPE) for sample preparation, which among other things cleans up the sample matrix, thereby reducing the concentration of fugitive chemicals that can reduce the system passivation (12–14). However, these approaches are separate from the more fundamental issue of column passivation stability. Although the qualitative impact of the injection inlet liner, guard column, temperature, and flow rate on analyte stability have all been documented, few reports quantify the role that column passivation itself plays in determining analyte stability. In fact, there have been far fewer reports on the role that column passivation chemistry plays in maintaining analyte stability during GC analysis than reports on the analytical column's role in retention time order and co-elution issues amongst the common explosive compounds. However, the analyte stability issue turns out to be an important factor in GC-

based explosive analyses when analyzing samples in contaminated matrices, and its impact can be best understood by the quantification equation that describes the magnitude of the electrical signal produced from a given analyte,

Signal = (Amount Injected (g) × Recovery × Detector Responsivity)

where recovery is defined here as the ratio of analyte that reaches the detector to that originally injected. As seen from this equation, maintaining high recovery is essential to maximize performance, and low recovery can partially offset the benefits of a superior detector. Thus, optimizing a GC for analysis of explosives requires a quantitative understanding of the role that the column plays in determining both the absolute analyte recovery and the long-term stability of that recovery through the GC column, particularly when analyzing large collections of samples.

It should be pointed out there are two characteristic behaviors leading to low analyte recovery through a GC system. The first is the degree of passivation of the "virgin" system. Here, a system refers to the collective wetted surfaces of the inlet, guard column, analytical column, and detector. All these components as provided by the manufacturer are nominally passivated, and from our experience this is true, as determined by the signal measured per unit mass injected. The second and more important cause of low recovery is usage-dependent, which can be thought of as recovery stability. This refers to the GC system's collective ability to maintain passivation during analysis of large volumes of samples in any of a variety of sample matrices that might introduce impurities into the GC system that re-activate the wetted surfaces. Again, the column needs to be evaluated in this regard because the inlet and guard columns can be considered consumables and be easily replaced when they become re-activated. Finally, it should be pointed out that there are several reported means to restore recovery in a heavily used system. The first procedure is to remove the first 5–10 cm of the analytical column upon evidence of loss of passivation (15). The second method is to inject a chemical that re-passivates the surfaces in situ. Some Method 8095 practitioners recommend injecting a large concentration of explosive-containing calibration solution to perform this function (16). Although this partially recovers system passivation, it does not fully restore it. There are other possible passivating agents that can be used, such as organic amines, but these agents may be specific to the passivation chemistry used by the manufacturer. Although these methods have been demonstrated to be effective at restoring performance, our wish is to identify columns where this procedure can be reduced in frequency or else altogether obviated, while maintaining acceptable chromatographic performance.

In this paper, we report GC–ECD recovery performance using four different analytical columns for a variety of explosive compounds. The data presented is derived from repeated calibration runs taken at periodic intervals that were interspersed with the measurement of field samples. Only calibration data that was acquired after replacement of the inlet liner, inlet seal, and guard column has been included to ensure that analyte recovery in the system was not limited by loss of activation of these components; and thus, we can attribute differences in recovery performance to differences in the performance of the analytical columns.

Table I. Experimental Conditions for the Four Columns Used in This Study

	Run simultaneously		Run simultaneously	
	Column 1	**Column 2**	**Column 3**	**Column 4**
Manufacturer	**Agilent**	**Restek**	**Restek**	**Restek**
Column	**DB-5**	**Rtx-200**	**TNT-1**	**Rtx-440**
Stationary Phase Composition	5% Phenyl siloxane, 95% dimethyl siloxane	Trifluoropropylmethyl siloxane	5% Phenyl siloxane, 95% dimethyl siloxane	Proprietary
Polarity	Low	Intermediate	Low	Intermediate
P/N	Agilent 125-501J	Restek Rtx-200	Restek TNT-1	Restek Rtx-440
Length	6 m	6 m	6 m	6 m
i.d.	0.53 mm	0.53 mm	0.53 mm	0.53 mm
Coating thickness	1.0 µm	1.5 µm	0.5 µm	0.5 µm
Mode	Constant flow	Constant flow	Constant flow	Constant flow
Initial flow	15.0 mL/min	15.0 mL/min	15.0 mL/min	15.0 mL/min
Nominal inlet pressure	2.94 psi	2.96 psi	2.80 psi	2.80 psi
Average velocity	130 cm/s	130 cm/s	126 cm/s	126 cm/s
Injection mode	Splitless	Splitless	Splitless	Splitless
Inlet temperature	250ºC	250ºC	250ºC	250ºC
Purge flow	199.9 mL/min	198.8 mL/min	200 mL/min	200 mL/min
Purge time	0.50 min	0.50 min	0.50 min	0.50 min
Total flow	217.1 mL/min	217.0 mL/min	217.1 mL/min	218.2 mL/min
Carrier gas	> 99.999 % He	> 99.999 % He	> 99.999 % He	> 99.999 % He
Initial Oven Temp	100ºC		90ºC	
Initial Time	2 min		1 min	
Ramp Rate 1	10.0ºC/min		30ºC/min	
Final Temperature 1	200ºC		120ºC	
Ramp Rate 2	20.0ºC/min		10ºC/min	
Final Temperature 2	250ºC		180ºC	
Ramp Rate 3	N/A		40ºC/min	
Final Temperature 3	N/A		270ºC	
Final Hold Time	2.5 min		0 min	
Total Time	17 min		10.25 min	
Detector Temperature	300°C	300°C	300°C	300°C
Makeup Flow	30 mL/min	30 mL/min	30 mL/min	30 mL/min
Makeup Gas	Nitrogen	Nitrogen	Nitrogen	Nitrogen

Experimental

EPA Method 8095 for quantitative explosives analysis by GC–ECD was used as a guideline for the methods used in this study. An Agilent 6890 GC equipped with two auto-injectors, two columns, and two micro-ECDs was used for this procedure. Table I lists the four columns used in these comparisons. Each sample analyzed was injected simultaneously on the two parallel GC columns using a refrigerated (< 8°C) 100-vial autosampler and two parallel auto-injectors.

Analyses on columns 1 and 2 were performed simultaneously as were those on columns 3 and 4 (Table I). All four columns were 6 m × 0.53 mm. Column 1 was a DB-5 (Agilent Technologies, Santa Clara, CA) composed of 5% phenyl siloxane-95% methyl siloxane; column 2 was an RTX-200 (Restek, Bellefonte, PA) composed of cross-bonded perfluoropropyl siloxane; column 3 was a TNT-1 (Restek) optimized for explosives analysis and was based on 5% phenyl siloxane-95% methyl siloxane; and column 4 was an RTX-440 composed of a proprietary cross-bonded phase and optimized for inertness and analysis of semi-volatiles. Each column was connected to a 12-in section of a passivated, 0.53-mm bore guard column, which was replaced periodically as the sensitivity of the method decreased due to its surface passivation loss.

All data shown in this paper were from calibration runs acquired immediately after inlet liner, inlet seal, and guard column replacement when the system's passivation was at a maximum. Each system check consisted of a ten-point calibration curve using pre-made calibration standards resulting in injection masses of 1, 5, 10, 25, 50, 100, 250, 500, 1000, and 2000 pg from 1-µL injections of the appropriate standard concentrations purchased from either AccuStandard (New Haven, CT) or Cerilliant (Round Rock, TX). Prior to running each calibration set, duplicate injections at a concentration of 2 µg/mL (2000 pg on column) were performed to partially re-establish passivation loss from the previous day (16). Table II shows a list of all the compounds analyzed in the calibration mixes along with their abbreviations. Figure 1 shows representative chromatograms for an injection mass of 1,000 pg, and their respective retention times are listed in Table III. Retention times were experimentally determined and used for identification of each component. The retention time windows used were ± 0.03 min, and the peak areas were integrated using the software provided by the instrument. The GC–ECD data was calibrated and quantified using the Agilent MSD ChemStation Enhanced Data Analysis software package (D.01.02.16). A unique software quantification method file was created for each date on which calibration data was collected. The calibration curves were fit with a forced-origin quadratic regression using a weighting inverse to the concentration, and analytical expressions were derived for every calibration run for each compound. These calibrations were performed at least once every day, and the analytical expressions derived from each 10-point calibration curve could be used to predict the raw signal for any notional injection mass on each day of operation. Tracking this intrinsic instrument response over time allowed observation of performance trends that were correlated and attributed to events, such as exposure to a fugitive de-activating agent contained in the sample matrix, which reduces sample recovery, and exposure to high analyte concentrations, which can temporarily increase sample recovery (Note: This is separate from carryover). Figure 2 shows both the raw and calibrated daily 1,000-pg calibration runs over the course of one month for RDX on the Rtx-200 column. Although the variations in system response are calibrated out, the impact on minimum detectable limits can be significant. Thus, minimizing these response swings is essential to maintaining optimum sensitivity.

In order to isolate the column performance from all other factors causing this behavior, only calibrations that were performed after replacement of the inlet liner and/or guard column, as indicated by a decrease in signal from the previous day, were used in the analysis. In most instances, replacing the inlet liner and

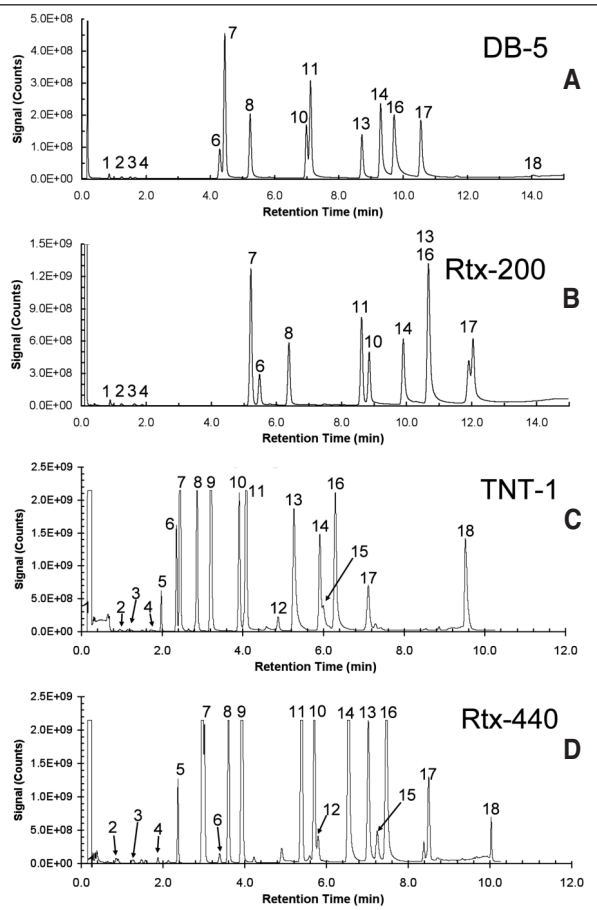

Figure 1. Sample chromatogram using DB-5 (A), RTX-200 (B), TNT-1 (C), and RTX-440 (D). The legend for the peak labels can be found in Table II.

Table II. Explosive Materials Measured and Their Abbreviations

No.	Compound	Abbreviation
1	Nitrobenzene	NB
2	2-Nitrotoluene	2NT
3	3-Nitrotoluene	3NT
4	4-Nitrotoluene	4NT
5	Nitroglycerine	NG
6	Dinitrobenzene	DNB
7	2,6-Dinitrotoluene	26DNT
8	2,4-Dinitrotoluene	24DNT
9	3,4-Dinitrotoluene	34DNT
10	Trinitrobenzene	TNB
11	Trinitrotoluene	TNT
12	Pentaerythritol Tetranitrate	PETN
13	Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX
14	4-Amino-2,6-Dinitrotoluene	4AmDNT
15	Dinitroaniline	DNA
16	2-Amino-4,6-Dinitrotoluene	2AmDNT
17	Methyl-2,4,6-Trinitrophenylnitramine	Tetryl
18	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX

guard column restored the majority of the diminished system sensitivity. In instances where it did not, performance changes were attributed to changes in the analytical column performance. It should be noted that in between the calibration runs shown in Figure 2, 50–100 field samples were analyzed; thus the trends illustrated in Figure 2 represent the performance of these columns under real-world analysis conditions. Furthermore, we were concerned that differences in the trace oxygen, water, or carbon dioxide levels in the two columns might impact performance and impart differences in the behaviors of the respective columns. However, the helium carrier gas used in both columns came from the same source, Spectra Gas (Branchburg, NJ) (99.9999% He, certificate of analysis: O_2 < 0.20 ppm, H_2O < 0.20 ppm, CO_2 < 0.08 ppm, CO < 0.06 ppm), passed through the same oxygen filter, and furthermore we monitored the baseline signal in the ECD and ensured it was identical in both columns as a leak in the inlet or guard column connection might result in an elevated ECD baseline signal. Also, to ensure that observed differences in performance were not caused by differences in the inlets or detectors, such as imperceptibly small leaks, a series of calibration runs were performed with the two GC columns cross-connected to the two inlets. Using this configuration, identical results were obtained when comparing response factors derived from calibration curves, confirming that the observed differences were due to differences in the columns and not the carrier gas, inlets, or detectors. From this, we concluded that differences in the columns could not be attributed to differences in residual oxygen, water, or carbon dioxide levels.

Results and Discussion

Under the conditions described in the Experimental section, large numbers (> 300) of GC–ECD calibration runs were performed where the principal independent variables were the column stationary phase, which is characterized by the stationary phase chemistry, deactivation chemistry, and coating thickness, and the total number of analytical samples run between calibration runs. This thus isolates and, by extension, highlights the sensitivity and stability differences in the different columns. To perform the analysis, comparison of the analytical fits to each of the 10-point calibration curves were made rather than comparing specific data points at fixed injection masses. Figure 3 shows several examples of these curves and demonstrates how the instrument's response can be described by these curve fits, thus enabling a statistically robust prediction of the

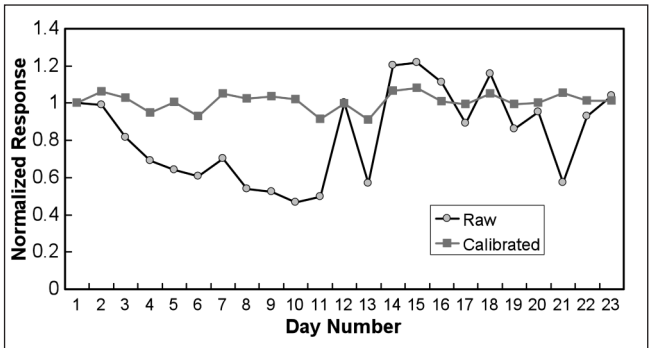

Figure 2. Data from 1,000-pg RDX injections into an Rtx-200 column each day for one month of heavy use processing soil extract samples. The large swings in raw response can be attributed to a combination of de-passivation/replacement of the inlet liner and guard column, super-imposed on a more gradual slope of column degradation. Although these response swings can have a significant impact on the minimum detectable limits, much of this behavior has little impact on the calibrated response at high analyte concentration.

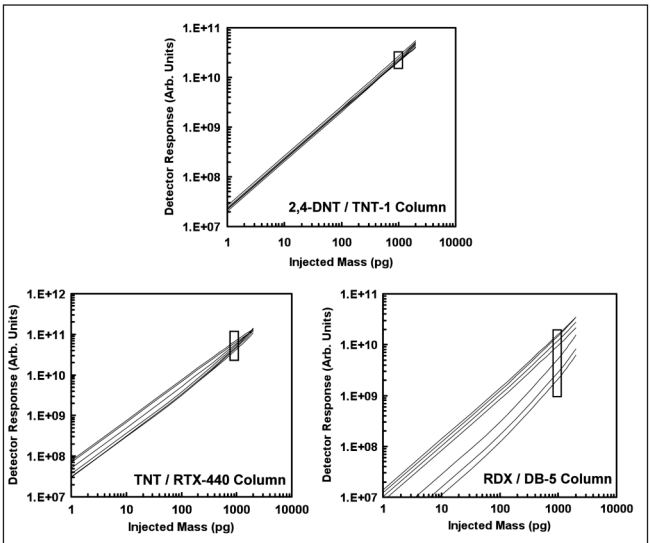

Figure 3. Summaries of selected curve-fit expressions measured over a six-week period for select compound/column combinations as indicated by the inset labels. The curve fits were derived from 10-point plots using a quadratic fit with a forced origin and a least-squares weighting proportional to the inverse of the concentration. The differences between the plots are attributed to changes in the column as it accumulates wear from processing large volumes (> 40/day) of analytical samples.

Table III. Retention Times for all the Measured Analytes on All Four Columns*

No.	Compound	DB-5 RT (min)	Rtx-200 RT (min)	TNT-1 RT (min)	Rtx-440 RT (min)
1	NB	0.834	0.898	0.656	0.861
2	2NT	1.226	1.267	0.953	1.251
3	3NT	1.496	1.673	1.146	1.573
4	4NT	1.641	1.910	1.506	1.877
5	NG	N.M.†	N.M.	1.979	2.366
6	DNB	4.289	5.495	2.357	3.388
7	26DNT	4.440	**5.217**	2.447	**2.980**
8	24DNT	5.239	6.392	2.867	3.606
9	34DNT	N.M.	N.M.	3.220	3.946
10	TNB	6.964	8.860	3.914	5.703
11	TNT	7.102	**8.624**	4.087	**5.400**
12	PETN	N.M.	N.M.	4.876	5.795
13	RDX	8.677	10.678	5.268	7.024
14	4AmDNT	9.269	**10.002**	5.910	**6.546**
15	DNA	N.M.	N.M.	5.989	7.242
16	2AmDNT	9.713	10.678	6.292	7.473
17	Tetryl	10.565	12.052	7.110	8.500
18	HMX	14.032	N.M.	9.517	10.030

* The values in bold indicate differences in retention-time order with respect to the compared column.
† Not measured.

detector response for any given injection mass. For example, the average response amplitude and variance for a given compound/column combination could be determined from a collection of analytical curve fits, such as those shown in Figure 3 and the amplitude and standard deviation of the predicted GC–ECD responses determined for a given injection mass (inset boxes on Figure 3). In this way, statistically rigorous comparisons of the time-dependent performance of each column can be made because each of these calibration runs were performed between 50 to 100 field samples. Figures 4–8 show the results comparing the amplitude and variability of the predicted detector response to 1,000 pg of analyte for each of the four columns. From these figures, we can see that few compounds exhibit statistically identical responses in all four columns, and that for the most part, the intermediate polarity columns designed for semi-volatiles gave the highest recovery and the greatest sensitivity. The greatest response differences were for the nitramines RDX and HMX (Figure 8); their thermal instability and reactivity resulted in intermediate polarity phases that led to significantly better recoveries. Table IV summarizes the results from Figures 4–8 along with a tabulation of the response variances. The normalized response amplitudes in Table IV demonstrate the relative system sensitivities to these compounds, whereas the tabulated variances represent the recovery stability over the six-week period in which these measurements were performed. A comparison of the responses for the four columns is plotted in Figure 9 for all compounds tested. From this figure, it is clear that the two 5% phenyl siloxane/95% methyl siloxane columns (DB-5 and TNT-1) exhibit somewhat similar performance, except for a few compounds including TNT, which results in a signal two-fold higher in the TNT-1 column. However, both the Rtx-200 and Rtx-440 columns outperform the DB-5 with the Rtx-440 doing so by an average of a factor of two and up to a factor of six for RDX.

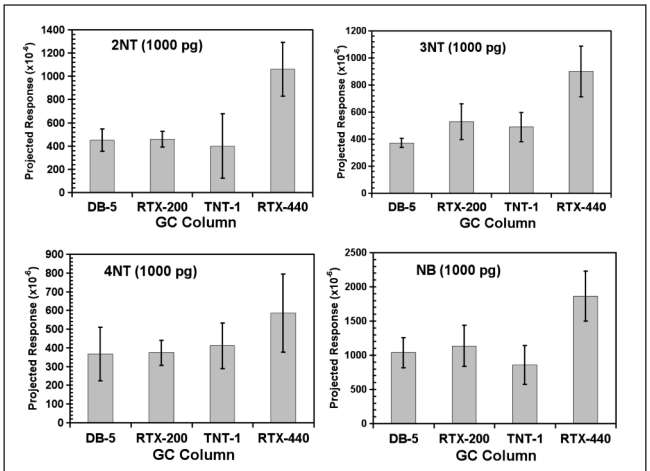

Figure 4. Bar graphs showing the predicted average response (bar height) and 1σ response variance (error bar) for mononitro aromatic explosive-related compounds. These values were determined from a collection of > 20 10-point calibration runs collected over a six-week period of running analytical samples. The differences in bar height represent differences in analyte recovery through the GC columns.

In an attempt to understand the reasons for the observations in Figures 4–9, a more detailed comparison of the analysis conditions was made. Previous reports (3,4) have suggested that greater flow velocities and shorter elution times result in decreased thermal degradation and greater recovery. Table III shows there were differences in the retention times stemming from the differences in stationary phase thickness, where the TNT-1 and Rtx-440 columns where only 0.5-µm thick compared to the DB-5 (1.0 µm) and RT Rtx-200 (1.5 µm) columns. These differences resulted in elution times that were 3–5 min shorter for most of the slower eluting explosive compounds. However, our analysis showed that the shortened elution time had only a minor effect on the sensitivity as compared to the column's stationary phase composition and/or passivation chemistry. It should be pointed out that the incrementally higher ceiling temperature used for the two 0.5-µm thick stationary phases could not explain these differences either as all the compounds except HMX had eluted by the time the temperature surpassed 250°C, which was the ceiling temperature for the DB-5 and Rtx-200 columns.

Having established that the column's stationary phase and/or passivation

Table IV. Comparison of the Normalized Responsivity and Response Variance for Selected Explosive Compounds on the Four Indicated Analytical Columns*

	DB-5		Rtx-200		TNT-1		Rtx-440	
	Normalized responsivity	Variance	Normalized responsivity	Variance	Normalized responsivity	Variance	Normalized responsivity	Variance
NB	1.28 ± 0.27	0.21	1.41 ± 0.37	0.26	1.06 ± 0.35	0.33	2.31 ± 0.45	0.19
2NT	0.56 ± 0.12	0.21	0.57 ± 0.08	0.15	0.49 ± 0.34	0.70	1.31 ± 0.28	0.22
3NT	0.46 ± 0.04	0.09	0.65 ± 0.16	0.25	0.60 ± 0.13	0.22	1.11 ± 0.23	0.21
4NT	0.45 ± 0.18	0.39	0.46 ± 0.08	0.18	0.51 ± 0.15	0.30	0.72 ± 0.26	0.36
NG	N.M.	N.M.	N.M.	N.M.	2.4 ± 2.1	0.86	17.9 ± 10.5	0.59
DNB	9.4 ± 2.1	0.22	16.2 ± 1.6	0.10	12.8 ± 3.8	0.30	3.3 ± 1.3	0.40
26DNT	50.1 ± 5.2	0.10	52.2 ± 7.4	0.14	60.6 ± 4.1	0.07	100.0 ± 13.7	0.14
24DNT	24.3 ± 1.9	0.08	29.8 ± 3.1	0.11	31.8 ± 4.7	0.15	43.9 ± 5.5	0.13
34DNT	N.M.	N.M.	N.M.	N.M.	67.9 ± 6.3	0.09	96.6 ± 13.8	0.14
TNB	16.1 ± 5.1	0.31	27.9 ± 3.2	0.11	19.4 ± 5.9	0.30	41.6 ± 7.4	0.18
TNT	26.5 ± 8.8	0.33	24.9 ± 4.2	0.17	45.2 ± 12.7	0.28	63.7 ± 21.8	0.34
PETN	N.M.	N.M.	N.M.	N.M.	1.5 ± 0.6	0.40	16.0 ± 8.6	0.54
RDX	11.0 ± 6.9	0.63	71.9 ± 9.3	0.13	22.2 ± 16.6	0.75	64.8 ± 28.2	0.43
2AmDNT	35.8 ± 7.7	0.22	71.7 ± 10.1	0.14	47.3 ± 10.0	0.21	82.0 ± 10.7	0.13
4AmDNT	24.1 ± 5.3	0.22	32.6 ± 4.3	0.13	32.2 ± 8.9	0.28	48.3 ± 6.6	0.14
Tetryl	23.2 ± 7.8	0.33	32.7 ± 12.9	0.39	18.9 ± 7.2	0.38	35.8 ± 9.4	0.26
HMX	4.3 ± 3.1	0.72	1.0	N/A	6.7 ± 7.5	1.12	12.9 ± 13.6	1.05

* These data were derived from the mean response to 1,000 pg of each of the explosives, as calculated separately from either seven (DB-5 and Rtx-200) or twelve (TNT-1 and Rtx-440) individual 10-concentration calibration curves spanning 1–2,000 pg. The calibration curves were performed immediately after replacement of the inlet liner and guard column on separate days over a span of six weeks. Thus, differences in response and variance can be attributed to the performance of the analytical columns. The data in this table was derived from 38 separate 10-point calibration curves for 380 total GC runs and 6,040 individual peak integrations. Normalization was performed with respect to the 2,6-DNT response on the Rtx-440 column.

chemistries are the most likely determinant in the observed sensitivity differences, a better understanding of the chemistries would be needed to offer a detailed mechanism. Unfortunately, the proprietary nature of the column composition and, in particular, the columns' passivation chemistries make drawing detailed structure-activity relationships difficult. One possible approach to this limitation would be to perform mass spectrometric analysis of each column at different points in their life cycles and to correlate the composition of the "bleed" fraction with the column's recovery performance. Unfortunately, such data is not available for the results in this study, so drawing specific conclusions based on "bleed" chemistry is not possible. However, we can conclude from our data that the largest differences in sensitivity were observed for the nitramines RDX and HMX and the nitrate esters nitroglycerin (NG) and pentaerythritol tetranitrate (PETN). Because the difference between columns increases with the amount of use, we attribute these differences more so to stability of the passivation chemistry than to intrinsic differences in stationary phase chemistry. This is supported by our observations that these differences between columns appear sooner when analyzing complex soil extracts as compared to relatively clean surface swipe extracts, suggesting that some component in the soil extract accelerates loss of passivation in the columns. Thus, it is possible that use of a longer guard column, such as extending the length from one foot to three feet, might slow the column degradation, or periodic injection of the appropriate repassivating agent would tend to extend column lifetime, although the preference would be to avoid or at least prolong the interval over which this is needed.

Finally, Figure 10 shows a comparison between TNT-1 and Rtx-440 columns for two sets of columns, showing that this behavior is roughly similar between different column lots. This was tested because, although the manufacturer discloses the basic stationary phase chemistry, the details of the passivation chemistry are typically not disclosed and thus might cause column-to-column variability.

In summary, we have shown that the stationary phase and/or passivation chemistries used in GC separation of nitro organic explosives can have as much as a five-fold impact on the sensitivity. This effect is in addition to previously reported determinants to analyte recovery such as flow rate, inlet temperature, inlet passivation, and guard column usage. Although reliable

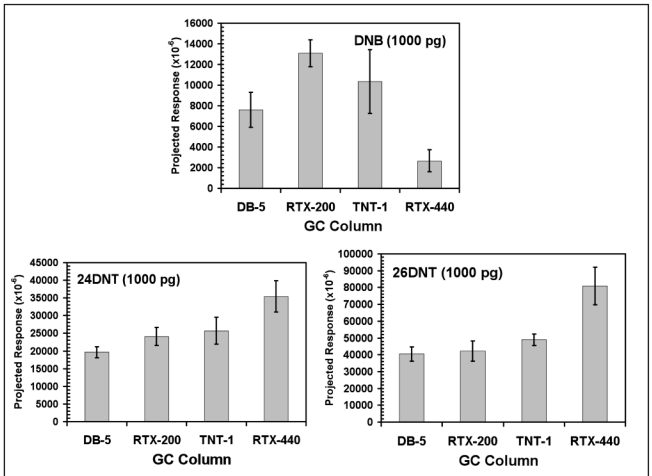

Figure 5. Bar graphs showing the predicted average response (bar height) and 1σ response variance (error bar) for dinitro aromatic explosive-related compounds. These values were determined from a collection of > 20 10-point calibration runs collected over a six-week period of running analytical samples. The differences in bar height represent differences in analyte recovery through the GC columns.

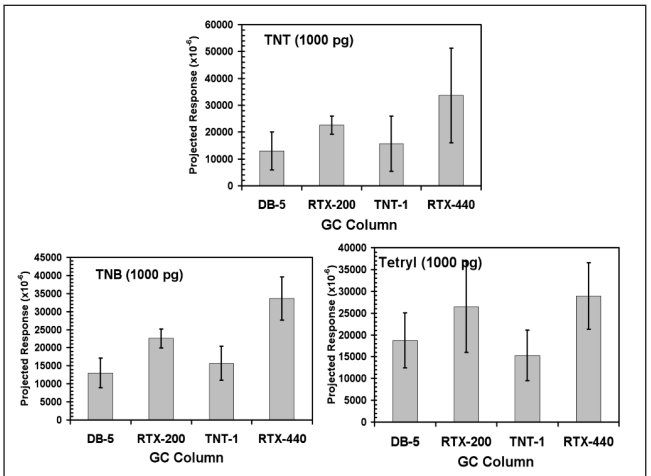

Figure 6. Bar graphs showing the predicted average response (bar height) and 1σ response variance (error bar) for trinitro aromatic explosive-related compounds. These values were determined from a collection of > 20 10-point calibration runs collected over a six-week period of running analytical samples. The differences in bar height represent differences in analyte recovery through the GC columns.

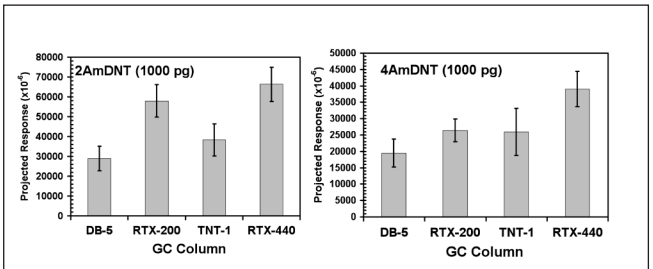

Figure 7. Bar graphs showing the predicted average response (bar height) and 1σ response variance (error bar) for aminoaromatic explosive-related compounds. These values were determined from a collection of > 20 10-point calibration runs collected over a six-week period of running analytical samples. The differences in bar height represent differences in analyte recovery through the GC columns.

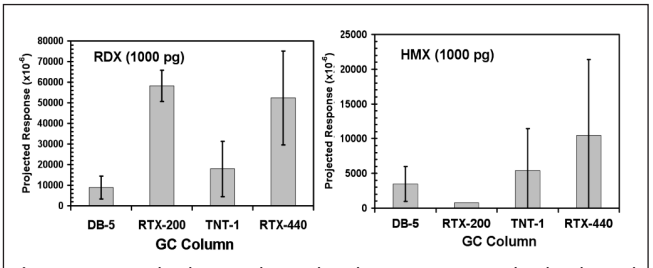

Figure 8. Bar graphs showing the predicted average response (bar height) and 1σ response variance (error bar) for nitramine explosive-related compounds. These values were determined from a collection of > 20 10-point calibration runs collected over a six-week period of running analytical samples. The differences in bar height represent differences in analyte recovery through the GC columns.

quantitative analysis of explosives using GC is challenging, strict adherence to recommended procedures and careful column selection can provide a suitable capability. Also, the manufacturers of GC columns should focus more attention on the stationary phase and passivation chemistries that can lead to the development of a column that is better able to maintain passivation. Finally, a detailed study to determine the optimum guard-column length for GC–ECD analysis of explosives would prove useful, where it might be determined that the optimal guard column length depends on trade-offs between the matrix purity on one hand and cost and through-put on the other.

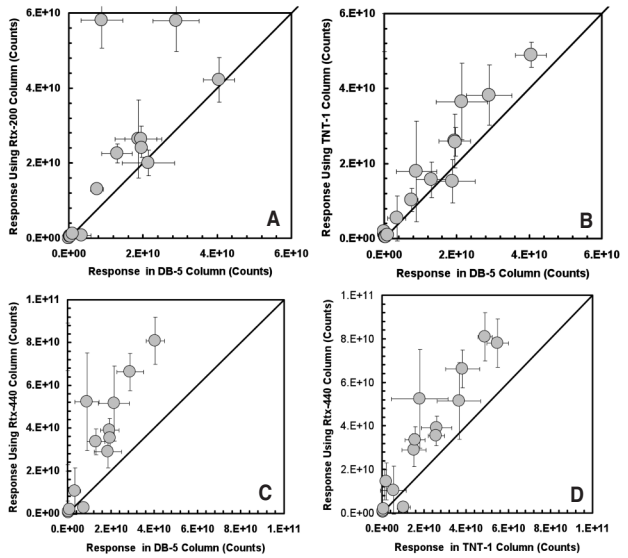

Figure 9. Comparison of the (A) Rtx-200, (B) TNT-1, (C) and Rtx-440 columns to a DB-5 column and (D) Rtx-440 to a TNT-1 column for 1,000 pg injection masses. Each data point represents the predicted response for one of the calibrated explosive compounds (Table IV), each derived from a collection of > 20 10-point calibration runs collected over a six-week period of running analytical samples. The solids lines indicate an equal response observed in each of the compared columns.

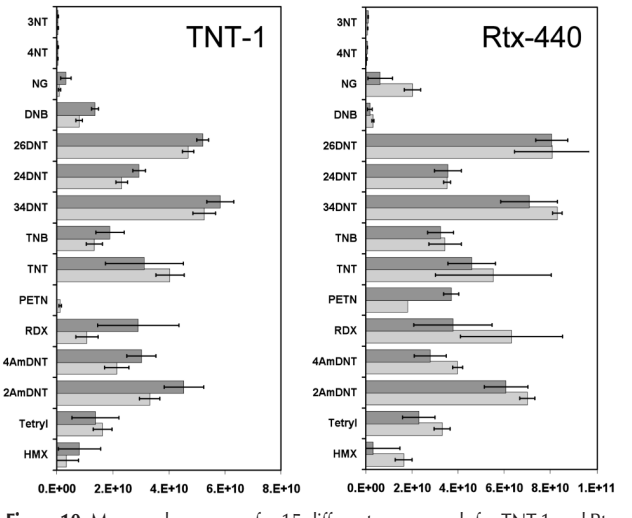

Figure 10. Measured responses for 15 different compounds for TNT-1 and Rtx-440 by comparing columns from two different manufacturing lots.

Acknowledgments

The authors would like to thank Dr. Way Fountain of the U.S. Army Edgewood Chemical and Biological Command (ECBC) for encouragement, guidance, and technical support. The authors also thank the journal reviewers for their helpful comments in preparing the final version of this manuscript. This work was supported by the U.S. Army Edgewood Chemical and Biological Center via sub-contract from the Joint Improvised Explosive Device Defeat Organization (JIEDDO) under Air Force contract FA8721-05-C-0002.

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Manuscript recieved March 24, 2009:
revision received June 9, 2009.