

## Detection Limits for GC/MS Analysis of Organic Explosives\*

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**ABSTRACT:** Method detection limits are determined and compared for analysis of liquid injections of organic explosives and related compounds by gas chromatography-mass spectroscopy utilizing electron impact (EI), negative ion chemical ionization (NICI), and positive ion chemical ionization (PICI) detection methods. Detection limits were rigorously determined for a series of dinitrotoluenes, trinitrotoluene, two nitroester explosives, and one nitramine explosive. The detection limits are lower by NICI than by EI or PICI for all explosives examined, with the exception of RDX. The lowest detection limit for RDX was achieved in the PICI ionization mode. Judicious choice of the appropriate ionization mode can enhance selectivity and significantly lower detection limits. Major ions are reported for each analyte in EI, PICI, and NICI detection modes.

**KEYWORDS:** forensic science, gas chromatography-mass spectrometry, detection limits, organic explosives

Analysis of explosives trace chemical evidence in post-blast material is typically achieved through the application of multiple physical and chemical techniques (1–4). One technique of analysis involves extracting a debris sample with organic solvent to remove organic explosive trace evidence. Following appropriate cleanup procedures, the organic solvent is analyzed by gas chromatography using any one of a number of detection methods. The detection limits vary from method to method as do the analyte specificity and analysis information content. Gas chromatographic methods of analysis for trace explosive and incendiary chemicals have recently been reviewed (2,5,6). The three most sensitive detection methods for gas chromatographic analysis of explosives are thought to be electron capture detection (ECD) (7), thermal energy analyzer (TEA) (7), and negative ion chemical ionization mass spectrometry (NICI) (8–11).

Trace analysis of picogram quantities of explosives, by injection of standard mixtures, has previously been demonstrated by Douse and coworkers using a gas chromatography/electron capture detection (GC/ECD) method (12). The method utilized a 165°C injection port temperature to prevent degradative losses of the analytes. Kolla later reported an injection port temperature of 170°C to be

the optimal for giving the minimum analyte degradation and maximum analytical sensitivity for GC analysis of a series of explosives (13). Kolla also reported that thin film (<0.25  $\mu\text{m}$ ) moderate-polarity stationary phases and high carrier gas flow rates (up to tens of  $\text{mL min}^{-1}$ ) were required for optimum analyte separation and recovery.

Martz has shown that gas chromatography with negative ion chemical ionization mass spectrometric detection (GC/NICI) exhibits nanogram sensitivity levels for explosives when scanning a range of ions (14). Picogram detection levels were demonstrated for GC/NICI using selected ion monitoring. Levensen and coworkers have reported picogram detection limits for a series of five nitroaromatics by EI, NICI, and PICI detection following gas chromatographic separation (15). The detection limits were defined by a signal-to-noise ratio of three.

Mass spectrometry offers a higher information content than ECD or TEA and the use of extracted ion chromatograms and selected ion monitoring offer added discrimination in data analysis. Many forensic laboratories today have access to mass spectrophotometric detection, although NICI is probably less common than EI and PICI ionization modes due to the added expense of instruments possessing this capability. In this paper we present a study of the rigorously determined method detection limits for the analysis of a set of organic explosives by mass spectrometric detection. Limits of detection are determined on a single instrument operating in the EI, PICI, and NICI ionization modes. This work allows for a direct comparison between explosives detection limits for these commonly available mass spectral ionization modes. The method detection limits reported here were determined in a full scan mode. The full scan mode of detection was used because this method allows for the identification of a suite of explosives without *a-priori* knowledge of the sample composition. Lower detection limits can certainly be achieved for each ionization mode through the use of selected ion monitoring. Major spectral features are also given for each analyte detected by the three ionization modes and mass spectral characteristics are discussed and compared with previous reports (15).

### Experimental

#### Apparatus

GC/MS analysis was performed on a Hewlett-Packard 5989 Gas Chromatograph/Mass Spectrometer (quadrupole) operating in three ionization modes: electron impact (EI), positive ion chemical ionization (PICI), and electron capture negative ion chemical ionization (NICI). Methane gas was used as reagent gas in both PICI and NICI. The instrument was tuned using the manufacturer's procedure and the electron multiplier voltage was set 200 V above the

<sup>1</sup> Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, PO Box 2008, MS 6100, Oak Ridge, TN.

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tune value for analysis in each ionization mode. The pertinent instrument operating parameters are listed in Table 1.

The gas chromatograph was fitted with a 12 m HT5 column (5% phenyl polycarbonate siloxane, Scientific Gas Engineering, Inc., Austin, TX) with a 0.22 mm I.D. and a 0.1  $\mu\text{m}$  film thickness. An initial temperature of 70°C was held for 3 min, followed by a temperature increase to 185°C at a rate of 8°C min<sup>-1</sup> and a subsequent increase to 250°C at a rate of 25°C min<sup>-1</sup>. The final temperature was held for 5 min. The carrier flow rate of 1.2 mL min<sup>-1</sup> was determined to allow for analysis of the less stable analytes (i.e., PETN) without degradation on the column. The injection port and transfer line temperatures were 170°C and 260°C, respectively. In a typical analysis, a 2  $\mu\text{L}$  sample of a standard solution was injected (splitless for 2 min).

### Reagents

Diethyleneglycol dinitrate (DEGN [693-21-0]) was obtained from Trojan Corporation (Spanish Fork, UT). Dinitrotoluenes (DNT) and 1,3-dinitronaphthalene (DNN [606-37-1]) were purchased from Aldrich Chemical Co. (Milwaukee, WI). This study included 2,6-DNT [606-20-2], 2,4-DNT [121-14-2], 2,3-DNT [602-01-7] and 3,4-DNT [610-39-9]. Benzene and 2,5-DNT [619-15-8] were purchased from Fisher Scientific Co. (Pittsburgh, PA). Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX [121-82-4]) and 2,4,6-trinitrotoluene (TNT [118-96-7]) were supplied by the Naval Explosive Ordnance Disposal Technical Division at the Naval Surface Warfare Center (Indian Head, MD). Pentaerythritol tetranitrate (PETN [00078-11-5]) was from the U.S. Army Standard Analytical Reference Material Repository, U.S. Army Environmental

Center (Aberdeen Proving Ground, MD). All explosives were used as received without further purification.

Acetonitrile was obtained from EM Science (Gibbstown, NJ) and used to prepare stock solutions containing DEGN (0.85 mg mL<sup>-1</sup>), 2,6-DNT (6.30 mg mL<sup>-1</sup>), 2,5-DNT (11.90 mg mL<sup>-1</sup>), 2,4-DNT (16.20 mg mL<sup>-1</sup>), 2,3-DNT (6.00 mg mL<sup>-1</sup>), 3,4-DNT (7.80 mg mL<sup>-1</sup>), TNT (6.60 mg mL<sup>-1</sup>), PETN (2.70 mg mL<sup>-1</sup>), RDX (5.20 mg mL<sup>-1</sup>), and DNN (3.70 mg mL<sup>-1</sup>). Stock solutions were stored at 0°C and used to prepare mixtures of known concentrations in benzene for method detection limit determinations.

### Results and Discussion

To determine the precision of the liquid injection method, six solutions were prepared, each containing all of the explosives analytes and DNN as an internal standard. Two microliters of a given solution were injected to give the range of column loadings for each analyte reported in Tables 2 to 4. The loading of the internal standard was 37 ng for each sample. At least three replicate analyses were performed for each of the six solutions. The average response for the total ion abundance and the percent relative standard deviation (%RSD) was determined for each analyte at each loading for EI, PICI, and NICI detection. The observed ranges in %RSD are listed in Tables 2 to 4 as a measure of the precision of the method. The larger %RSD values listed in the tables resulted from analyte loadings that approached the limit of detection (discussed below). The largest overall %RSD was determined for DEGN detection by EI (Table 1).

The linearity of the liquid injection method was determined from the averaged ratios of the instrument response for each analyte relative to the response for the internal standard. The average response ratios were plotted against the analyte to internal standard concentration ratios and linear regression was used to obtain calibration curves. The resulting linearities ( $r^2$ ) and slopes are given in Tables 2 to 4 for EI, PICI, and NICI detection, respectively. Greater than 96.8% of the variance was accounted for by the linear model in all cases and greater than 99% of the variance was accounted for in most cases.

The method limit of detection (LOD) values, given in Tables 2–4, represent the lowest analyte concentration in a sample that can be detected, but not quantified (16). In this work the LOD is calculated as 3.3 (SD/S), where SD is the standard deviation of the response near the detection limit and S is the slope of the calibration curve (16). The LOD values in Tables 2 to 4 are liquid injection method limits of detection (16,17). A standard *t*-test was used to insure that the fitted intercept from each calibration curve was not different from zero at the 95% confidence level. The slope of each calibration with the intercept forced to zero was used to calculate

TABLE 1—Mass spectrometer parameters used for detection limit determinations in EI, PICI and NICI ionization modes.

Mass Spectrometer Parameter	Ionization Mode		
	EI	PICI	NICI
Source temperature (°C)	200	150	150
Quadrupole temperature (°C)	100	100	100
Electron energy (eV)	70	230	230
Electron multiplier (V)	2302	2562	1834
Emission current ( $\mu\text{A}$ )	300	300	300
Full scan mass range scanned (AMU)	29–400	60–500	40–400
Mass scan rate (scan/sec)	1.2	1.6	1.6
Reagent gas pressure (Torr)	na*	1.2	1.2

\* Not applicable.

TABLE 2—Validation data for the analysis of explosives by GC/EI.

Analyte	Reproducibility (%RSD)	Calibration Slope	Calibration Linearity ( $r^2$ )	Method Limit of Detection (ng)	Method Limit of Quantitation (ng)	Conc. Range (ng/ $\mu\text{L}$ )
DEGN	10–42	0.855	0.998	2.31	7.01	1.30–66.09
2,6-DNT	4–12	0.689	0.998	0.78	2.36	1.60–17.58
2,5-DNT	3–12	0.623	0.997	1.80	5.47	2.01–22.14
2,4-DNT	3–11	0.659	0.998	1.37	4.16	2.74–30.13
2,3-DNT	5–15	0.741	0.998	1.45	4.39	1.52–16.74
3,4-DNT	3–13	0.748	0.999	1.47	4.45	1.98–1.76
TNT	5–9	0.657	0.997	0.71	2.14	2.79–30.69
PETN	6–15	0.249	0.999	2.75	8.33	4.12–209.93
RDX	3–14	0.422	0.999	3.36	10.17	4.74–241.82

TABLE 3—Validation data for the analysis of explosives by GC/PICI.

Analyte	Reproducibility (%RSD)	Calibration Slope	Calibration Linearity ( $r^2$ )	Method Limit of Detection (ng)	Method Limit of Quantitation (ng)	Conc. Range (ng/ $\mu$ L)
DEGN	12–25	1.348	0.999	1.20	3.62	1.30–66.09
2,6-DNT	7–18	1.150	0.983	1.40	4.25	0.84–17.58
2,5-DNT	8–28	0.997	0.998	1.89	5.72	1.05–22.14
2,4-DNT	7–20	0.979	0.993	1.77	5.37	1.43–30.13
2,3-DNT	6–18	1.441	0.979	1.20	3.63	0.80–16.74
3,4-DNT	5–29	1.296	0.993	1.70	5.14	1.04–21.76
TNT	4–22	0.645	0.994	1.32	4.01	1.46–30.69
PETN	2–18	0.144	0.996	2.38	7.21	4.12–209.93
RDX	3–16	0.846	0.999	0.64	1.92	4.74–241.82

TABLE 4—Validation data for the analysis of explosives by GC/NICI.

Analyte	Reproducibility (%RSD)	Calibration Slope	Calibration Linearity ( $r^2$ )	Method Limit of Detection (ng)	Method Limit of Quantitation (ng)	Conc. Range (ng/ $\mu$ L)
DEGN	10–35	0.519	0.969	0.75	2.28	0.65–11.02
2,6-DNT	5–38	2.927	0.982	0.21	0.63	0.17–2.93
2,5-DNT	5–43	2.788	0.979	0.17	0.50	0.22–3.69
2,4-DNT	4–23	1.348	0.982	0.18	0.55	0.30–5.02
2,3-DNT	5–36	3.649	0.979	0.16	0.49	0.16–2.79
3,4-DNT	1–221	2.357	0.984	0.10	0.32	0.21–3.63
TNT	3–27	1.668	0.976	0.19	0.58	0.30–5.12
PETN	3–21	0.188	0.994	0.78	2.36	2.06–34.99
RDX	2–14	0.637	0.964	1.11	3.37	2.37–40.30

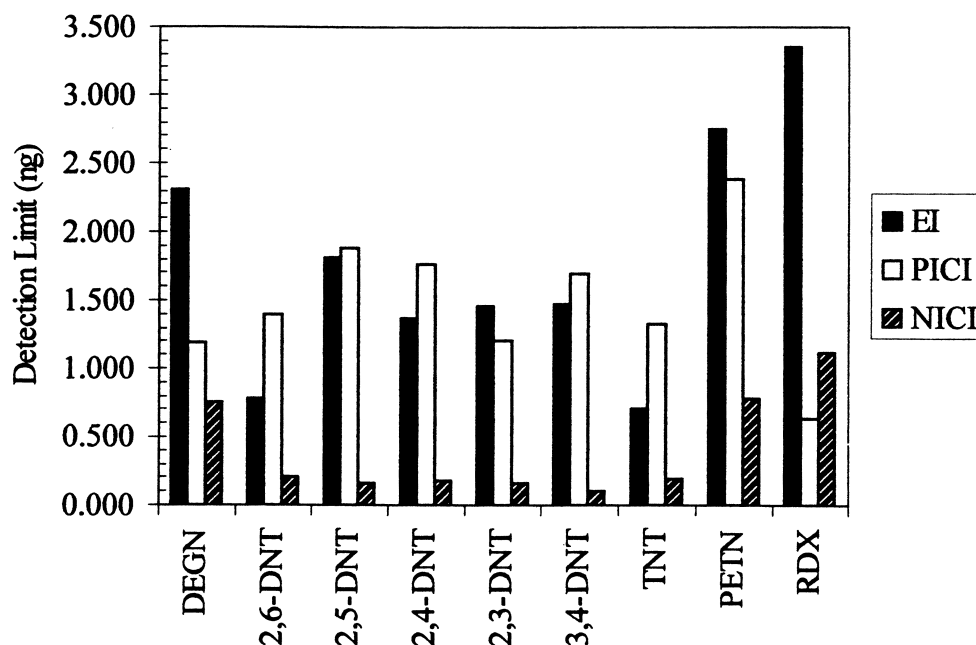


FIG. 1—LOD in ng for each explosive detected by ionization method EI, NICI, and PICI.

the LOD. A graphical comparison of the LOD for each explosive detected by each ionization method is given in Fig. 1. The lowest LOD values for the analytes included in this study are generally achieved by NICI. The one exception is the detection of RDX, where PICI gives the lowest LOD. EI generally gives the highest LOD, although the values are less than a factor of 20 higher than the NICI values. The LOD values determined for 2,6-DNT in this

work are considerably higher than those previously reported based on an estimated signal-to-noise ratio of 3 (15).

The method limit of quantitation (LOQ) is the lowest analyte concentration that can be quantified in a sample with acceptable precision and accuracy (22). The LOQ values given in Tables 2 to 4 are defined as:  $LOQ = 10(SD/S)$ . The largest LOQ was determined by EI for RDX as 10.17 ng. Although these values appear to



TABLE 5—Continued.

Analyte	EI		PICI		NICI	
	m/z	% Abundance	m/z	% Abundance	m/z	% Abundance
RDX	46	100	149	100	102	100
	42	98	75	64	129	80
	30	91	103	55	176	30
	75	42	85	23	268	25
	56	31	69	13	46	17
	128	24	133	11	324	15
	71	23	104	9	130	4
			150	9	103	4

be large relative to the instrument limit of detection, they are 70 to 700 times smaller than the amounts of TNT reported post-blast on a 1 m<sup>2</sup> steel plate located 10 m from dynamite blasts (18). The lowest LOQ was determined by NICI for 3,4-DNT as 0.32 ng.

In order to make an equitable comparison between the three modes of analysis (EI, PICI, and NICI), the LOD and LOQ values for each analyte were determined based on the ion abundance obtained with the electron multiplier voltage set at 200 V above the tuned value (as listed in Table 1). However, the background associated with NICI is virtually zero at the electron multiplier voltage of 1834 V. We expect that when the electron multiplier is set as high as 1000 V above the NICI tuned value, the background would still be low enough to increase the sensitivity by at least one order of magnitude. Thus the LOD and LOQ would be much lower than those listed in Table 4 for NICI.

A list of the major ions (m/z) and their relative abundance for each analyte determined by EI, PICI, and NICI are given in Table 5. The general fragmentation pattern observed for the nitroaromatics in each ionization mode agree with those previously reported by Levensen (15). EI spectra for all the analytes are consistent with those listed in the NIST/EPA/NIH Mass Spectral Data Base (19). Ions corresponding to  $[M-NO_2]^+$  are the most prominent ions for all the nitroaromatics except for 3,4-DNT. The molecular ion is the most prominent ion for 3,4-DNT, a unique characteristic for this isomer. However, the nitroesters (DEGN, PETN) and the nitramine (RDX) produced very few diagnostic ions in the EI spectra. The most abundant ions for those compounds are m/z 46 and 30 (for ions NO<sub>2</sub>, and NO).

In the PICI spectra, with the exceptions of PETN and RDX, all analytes exhibit protonated ions  $[M+1]^+$  and adduct ions  $[M+C_2H_5]^+$  and  $[M+C_3H_5]^+$ , which are characteristic ions observed when methane is used as a reagent gas (20). The protonated fragment ion (m/z 149) corresponding to  $[MH-CH_2N(NO_2)]^+$  is the most abundant ion for RDX (21). The most prominent ion for PETN is m/z 85; the fragment identity is unknown. In addition, ions for  $[MH-NO]^+$  were also observed for all the nitroaromatics, which is consistent with the observation reported elsewhere (20).

In the NICI spectra, molecular ions were detected for all the nitroaromatics. Fragment ions corresponding to  $[M-NO]^-$  and  $[M-OH]^-$  were also observed for those compounds, as also reported elsewhere for dinitrotoluenes (11,22). Molecular ions were not detected for the nitroesters (DEGN, PETN), or for the nitramine (RDX). Instead, highly fragmented ions  $[NO_3]^-$  (m/z 62) were detected as the most abundant ion for DEGN and PETN, in addition to adduct ions  $[M+NO_2]^-$  and  $[M+NO_3]^-$ . The most abundant

ion for RDX is m/z 102, which has previously been reported to be due to  $[CH_2N(NO_2)CH_2N]^-$  (23). The adduct ion m/z 268 corresponding to  $(M+NO_2)^-$  is also observed for RDX, in accord with earlier reports (24).

## Conclusion

NICI gives the lowest detection limits for each of the explosives examined in this paper, with the exception of RDX. Detection limits in the MS scanning mode are highly dependent on the chemical structure of the explosive and vary from the low picogram range to a few nanograms. The use of NICI generally gives a factor of less than 10 decrease in LOD relative to EI and PICI, although larger decreases in LOD were observed for 3,4-DNT.

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## Additional information and reprint requests:

Michael E. Sigman, Ph.D.  
Chem. and Anal. Sci. Div.  
Oak Ridge National Lab.  
P.O. Box 2008 MS 6100  
Oak Ridge, TN 37831-6100