Explosives Analysis using GC/MS

Randi S. George, BS[1]; Heather L. Harris, MFS, JD, D-ABC[1,3]; Barry K. Logan, PhD[1,2]

[1]MSFS Program, Arcadia University, Glenside, PA [2]The Center for Forensic Science Research and Education, Willow Grove, PA [3]HLH Consulting, Philadelphia, PA

Introduction

More laboratories use Gas Chromatography/Mass Spectrometry (GC/MS) than any other technology for analytical purposes. GC is advantageous in trace analysis as it has a high resolving power, resulting in more efficient separations, which lead to better identifications. MS is an accurate and reliable detector with the capability of examining a broad range of compounds and identifying them with specificity. The combination of GC with MS allows for improved separation of complex matrices and specific identification of trace analytes.

The greatest obstacles when identifying high explosive compounds by GC/MS are their high reactivity and propensity to decompose rapidly at high temperatures. At the wrong temperatures, the explosive compounds decompose and their mass spectra contain non-unique ions making it difficult to identify a specific explosive compound. In addition to the temperature challenges, active sites can be found throughout the chromatographic system attracting these explosive compounds and binding them. The explosive compounds can become bound in the inlet and column and thus never appear in the MS source to produce a spectrum.

This research involves method development using types of compounds such as: trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), cyclotrimethylenetrinitramine (RDX), nitroguanidine, and more. Optimum inlet temperatures for each of these compounds were determined in an attempt to decrease decomposition and improve chromatography.

Method

Agilent 6890 GC

- Three main inlet temperatures were tested: 250ºC, 150ºC, 80ºC
- Split injection 40:1
- Column: DB-5ms 15m x .25cm x .25um
- Oven: 40ºC; 10ºC/min to 150ºC; 15ºC/min to 250ºC, hold 5 min
- Column flow: 1.2mL/min helium

Agilent 5973 MS

- Mass range: 30-500 m/z
- MS source: 230ºC
- Transfer line: 220ºC

Acknowledgements

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Data

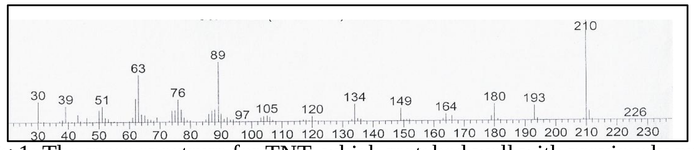


Fig 1: The mass spectrum for TNT, which matched well with previously published spectra, showing high stability in the GC.

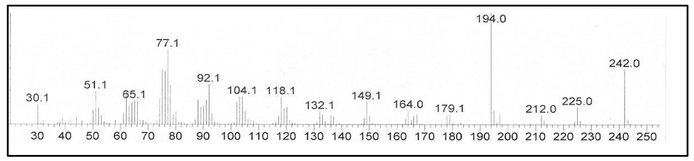


Fig 2: The mass spectrum for tetryl, which produced some variations from previous publications. Further examination showed an improved match with the spectrum of N-methylpicramide, a hydrolysis product of tetryl.

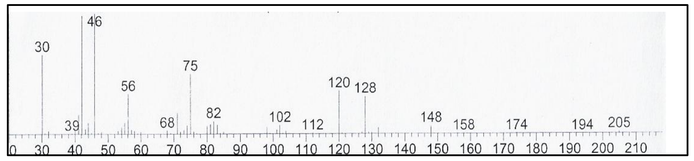


Fig 3: The mass spectrum of RDX, which consistently showed a much higher 42 peak than the literature suggests. Determination of the structural ions for each of the main peaks suggest a possible separation of the six member ring.

Table 1: Compound GC/MS data

Table 1: Retention times, top 6 mass spectra peaks, molecular weights and best inlet temperatures for each compound tested.

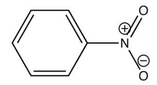
• Lo Tº RT = retention time of 80ºC inlet
• Mid Tº RT = retention time of 150ºC inlet
• High Tº RT = retention time of 250ºC inlet
• m/z = top 6 ions
• MW = molecular weight of the compound

* = poor/no chromatography

Compound	Lo Tº RT	Mid Tº RT	High Tº RT	m/z	MW	Best Inlet
TNT	13.049	13.052	13.041	210, 89,63,193,180,134	227	any
2,4 DNT	11.413	11.419	11.406	165,89,63,90,119	182	any
3,4 DNT	12.058	12.062	12.139	182,30,89,63,78,52	182	mid/lo
2,6 DNT	10.522	10.515	10.501	165,89,63,90,77,78	182	mid/lo
1,3 DNG	8.303	8.303	8.319	46,31,30,76,43,44	182	any
TNB	12.652	12.722	12.738	75,74,30,213,120,63	213	any
1,2 DNB	*	9.625	*	168,63,50,76,74	168	mid
1,3 DNB	*	9.377	*	168,76,75,50,122	168	mid
RDX	14.499	14.423		42,46,30,75,56,128	222	lo
HMX	*	*	*		296	
tetryl	15.523	15.533	15.544	194,77,242,75,76,92	287	mid
EGDN	4.758	4.747	4.715	46,30,76,31,43	152	any
PGDN	5.066	5.023	5.039	46,43,90,30,76,57	166	mid/hi
PETN			8.028	46,30,42,44,43	316	high
Picric acid	13.85	13.85	13.898	229,62,91,30,53,63	229	mid
nitroguanidine	*	*	16.154	58,104,44,43,42,31	104	high
BTTN	10.753	10.747	10.769	46,76,30,43,31	241	high
2,2'dndp	*	17.513	17.557	259, 168, 167, 196, 166, 139	259	mid/hi
2,4 dndp	*	17.718	17.751	259, 167, 166, 139, 168, 139	259	mid
4,4'dndp	*	*	21.771	259, 167, 166, 183, 229,139	259	high
2,4'dndp	*	18.215	18.296	259, 166, 167, 154, 139, 140	259	hi/mid
1mng	6.123	*	*	61,43,46,31,44,30	137	lo
2mng	6.614	6.614	6.641	31,61,46,43,32,30	137	hi
E. Centralite	14.287	14.282	14.303	120,148,77,268,121,104	268	any
3nt	*	7.143	*	91,137,65,63,39, 77	137	mid
4nt	7.03	7.019	7.068	91,137,65,107,77,63	137	any
2nt	6.247	6.242	6.291	120,65,91,92,89,77	137	any
2amino dnt	*	15.2	*	78,180,197,104,77,52	197	mid
4amino dnt	*	14.843	*	180,104,197,78,105,52	197	mid
BTDN	*	9.145	*	46,76,73,43,44	197	mid
Ammonium Picrate	*	14.098	14.136	30,62,229,91,53,50	246	mid/hi

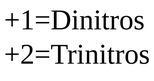
Structures & Classes

Benzene Explosives

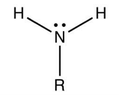


R=NitroBenzene

+1=Dinitros
+2=Trinitros



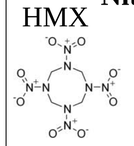
Toluenes

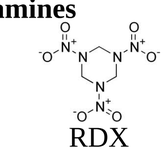


Aminos

Nitroamines

HMX

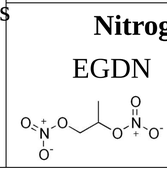


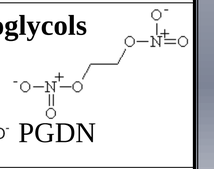


RDX

Nitroglycols

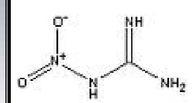
EGDN



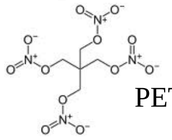


PGDN

Misc. High Explosives



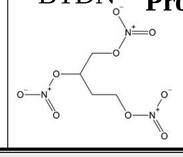
Nitroguanidine

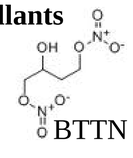


PETN

BTDN

Propellants





BTTN

Results/Conclusions

Results

- Inlet temperature had a significant impact on the chromatography.
- TNT and related compounds were not affected by differing inlet temperatures.
- Tetryl produced a mass spectrum for N-methyl picramide, a product of tetryl hydrolysis, which was expected from reports in the literature.
- RDX mass spectrum shows possible ring breakdown resulting in a lower level of m/z 76 and higher 42.
- HMX did not produce any chromatography. This is consistent with reports in the literature.
- EGDN and PGDN mass spectra were closely related, so great care needs to be taken to identify these compounds.

Conclusions

- It is important in GC/MS analysis of explosives and related compounds to use a deactivated inlet liner to ensure that these compounds enter the column.
- Careful selection of the inlet temperature optimizes chromatography for many of these compounds allowing for improved identification.