B121 High Speed High Resolution GC/MS of High Explosives

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Attendees will learn the use of high speed GC/MS to perform rapid, efficient, and reliable analysis and identification of trace levels of high explosives in post-blast debris.

High speed high resolution GC/MS has the potential to be a powerful tool in routine analysis by increasing sample throughput and improving laboratopry productuivity. Significant savings in time and money can be acheived through this technique without sacrficing sepration efficiency. This presentation will impact the forensic community and/or humanity by providing useful for the fast analysis of organic explosive mixtures in postblast investigation where a short "time-to-result" is urgently required.

Introduction: The rapid, sensitive, and specific identification of trace levels of high explosives has taken center stage with the escalating threat of terrorist acts worldwide. High speed high resolution GC/MS has the potential to be a powerful tool in explosive analysis by increasing sample throughput (save time and money) and improving laboratory productivity.

This paper focuses on a faster separation of a mixture of 14 organic explosives with improved resolution compared to the conventional method. It explores the scope and limitations of the speeding approaches for the analysis of high explosives. The objective is to demonstrate that rapid analyses are possible and can be achieved without sacrificing resolution and separation efficiency.

Three columns were used in this study: the conventional long middle bore column (30 m x 0.25 mm x 0.25 µm), a short middle bore column (10 m x 0.25 mm x 0.25 µm), and a short narrow bore column (10 m x 0.1 mm x 0.1 µm). Different speeding approaches were adopted and each of their significance and impact in reducing the analysis time was evaluated by comparing the column efficiency, peak resolution, areas, heights, and widths. The speeding approaches used include:

(a) Fast temperature programming
(b) Higher initial oven temperature
(c) Increased carrier gas velocities
(d) Pressure programming
(e) Decreased length, bore size, and film thickness of columns

The effects of a temperature programmed injection temperature on peak broadening and sample decomposition were also investigated using a programmable temperature vaporiser (PTV). Peak resolution, areas, heights, and widths obtained under PTV conditions were compared to those performed using various constant injection temperatures.

Materials and Methods:

Instrumentation

The analyses were carried out using a GC/MS with programmable temperature vaporiser (PTV). Three columns were used:

(a) HP-5MS (30 m x 0.25 mm x 0.25 µm)
(b) PTE-5MS (10 m x 0.25 mm x 0.25 µm)
(c) DB-5 (10 m x 0.1 mm x 0.1 µm)

The analytes were injected into the PTV at isothermal temperature and with temperature programming, using different ramp rates.

Analytes: The explosive mixture used in this study comprises of a 70 ppm solution of nitroglycerin (NG), ethylene glycol dinitrate (EGDN), 2-nitrotoluene, 3-nitrotoluene, 4-nitrotoluene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, 2,4,6-trinitrotoluene (TNT), 4-amino-2,6-dinitrotoluene, 2-amino-4,6-dinitrotoluene, nitrobenzene, 1,3-dinitrobenzene, 1,3,5-trinitrobenzene, and cyclotrimethylene trinitramine (RDX).

Results and Discussion:

Characteristics of analytes

The 14-component explosive mixture comprises of analytes which are thermally labile (requiring low injection temperature) and those which are non-volatile with high boiling points (requiring high injection temperatures).

Conventional GC/MS

Conventional GC/MS for the analysis of high explosives is performed using a long middle bore DB-5MS column (30m x0.25mm x 0.25 µm) at an injector temperature of 150°C and oven temperature of 50 to 200°C at 15°C/min. The analysis time is 14.8 minutes. The objective of this study is to apply various speeding approaches to reduce this long analysis time to achieve a short "time-to-result" analysis.

High speed GC/MS

(a) Injection system

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Sample introduction is the most critical step in high speed GC because it affects band broadening. The advantage of a PTV is that it combines a cool injection step with controlled vaporisation. The smaller i.d. liner of the PTV can also be heated or cooled more rapidly and this helps to reduce peak broadening.
There was poor sensitivity of the high boiling point analytes at an isothermal injection temperature of 100°C while thermally labile components decomposed at higher temperatures. On using a PTV temperature program from 100 to 250°C, the decomposition of the thermally labile analytes was greatly reduced and better detection limits of the higher boilers were obtained. The ramp rate for the PTV was investigated at the various temperature programming rates from 50°C/min to 250°C/min. At low ramp rates, resolution was poor for two critical pairs. There was a marked improvement in peak separation, peak shape, area, and height at higher ramp rates. Hence, PTV was employed in all the analysis with the three columns.

(b) Long middle bore column (30 m x 0.25 mm x 0.25 µm)
It was observed that only the initial oven temperature has some impact on reducing analysis time but overall results of the other speeding approaches are relatively insignificant with some loss of resolution. Although increasing the ramp rate produced significant changes in analysis time, peak separation was poor and hence, faster temperature programming rates could not be implemented in this analysis.

(c) Short middle bore column (10 m x 0.25 mm x 0.25 µm)
An effective way to reduce analysis time is to reduce the column length. Increasing the ramping rate from the conventional 15°C/min to 70°C/min produced the most significant change in analysis time with good resolution. Combining all the speeding approaches resulted in a significant reduction in analysis time by 80%.

(d) Short narrow bore column (10 m x 0.1 mm x 0.1µm)
Narrow bore columns with thin films are more efficient and have better resolution. It is also possible to work at higher linear gas velocities with less loss in efficiency. Increasing the ramping rate from the conventional 15°C/min to 70°C/min produces very significant changes in analysis time. The shortening of column length, constant pressure programming and higher initial oven temperature produced marginal reductions in analysis. Combining all the speeding approaches resulted in a significant reduction in analysis time by 80%.

Comparison of the three columns

(a) Analysis time
There was a significant 4.5 fold reduction in analysis time for both the short middle and short narrow bore columns but a marginal 1.5 fold reduction was obtained for the long middle bore column.

(b) Column efficiency
Plate height was used as a measure of the efficiency of the columns. Plate heights obtained for the 3 columns were similar.

(c) Peak width and resolution
The peak widths were similar for the two short columns, which were only ½ the width of the peaks obtained for the long middle bore column. The resolution-calculations were carried out using the two critical pairs. The two short columns gave good resolution for the two peak pairs and a baseline separation of these pairs was obtained. The data indicate that the gain in speed was achieved without sacrificing resolution.

(d) Repeatability
There is usually a concern that high speed GC will produce peaks that are not ideal in shape with the presence of fronting and tailing, poor baseline resolution or poor precision of the retention

times and peak areas and heights with faster temperature programming. To determine the precision of the high speed GC method, six repeated injections of the explosive standard mixture were performed. From the results obtained, the repeatability of the retention times, peak areas, and heights in high-speed analyses were found to be satisfactory.%RSD of these parameters for the columns were found to be similar to each other.

(e) Limits of detection (LODs)
Better LODs were observed for the narrow bore column. This is probably due to the increased signal to noise ratio for the much narrower peaks.

(f) Limiting factors
The use of high speed GC is usually hindered by a lack of instrumentation. A high power GC oven is required to allow for high programming rates up to 100°C/min. Pressure can also become a limiting factor for a number of speeding approaches. The use of shorter columns is limited by the minimum inlet pressure required for stable operation of the carrier gas system while long narrow bore columns require sufficiently high pressures. The use of columns with a reduced i.d. is one of the most logical approach for high speed GC but sample capacity has to be compromised. Sample capacity of a column with small i.d.s is lower than that of a middle bore column. Sample matrix

Sixteen different materials were swabbed with acetone and the swabs were concentrated and analysed using the narrow bore column. The materials tested include: metals, plastics, paper, polymeric materials, wool, soil, sand, tape, and rubber. Only two materials gave co-eluting interference with two of the analytes. A plastic container had a co-eluting peak with TNT and the chromatographic profile of newspaper had a peak that coeluted with EGDN.

Conclusion: This new technique allows the Criminalistics Laboratory to perform rapid, efficient, and reliable

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identification of trace levels of organic explosive residues in post-blast exhibits without sacrificing resolution and separation efficiency. There is a significant decrease in analysis time by 4.5 fold (from 14.8 minutes to 3.3 minutes) Fast temperature programming rates significantly decreased the analysis time, much more than other speeding approaches. Compared to conventional GC techniques, a significantly higher sample throughput is now possible. The new approach has the additional advantages of lower limits of detection, better peak separation, and resolution and a reduction in thermal degradation.

High Speed GC/MS, Programmable Temperature Vaporiser, Fast Temperature Ramping

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