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CDS Analytical

Quantitative Analysis of Explosives by Thermal Desorption–GC–MS Method

Application Note

Homeland Security

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Abstract

This application note demonstrates quantitative analysis of explosive standards by thermally desorb the sample into a GC-MS.

Introduction

With the growing public interest to military and homeland security, a reliable analytical technique for identification and quantitation of explosives is in high demand. Many methods have been proposed including colorimetric assays[1] and tandem mass spectrometry[2]. EPA has also published a standard method using GC-ECD and GC-MS[3] to detect trace explosives. These methods either require a high resolution detector that is not ready for large-scale deployments, or focus on samples in solution. Recently, there are reports[4] that established sampling protocols to collect analytes in vapor phase by using sorbent based thermal desorption tubes, followed by a quantitative GC-MS analysis. In this application note, a thermal desorption system from CDS Analytical coupled to mainstream GC-MS was tested on explosive standards spiked in thermal desorption tubes.

Experiment Setup

Camsco Tenax 1/4” x 3.5” thermal desorption tubes were the sampling device. The thermal desorber was a CDS 7550S 72-position autosampler equipped with Camsco 1/8” x 115 mm focusing trap, which was packed with 80/100 Supelcoport (3% SP-2100) and Tenax sorbent. A Shimadzu QP-2010 GC/MS system with Thermo Scientific TG-SQC capillary column was used as the separation and detection instrument. The optional Peltier cooling module was not equipped for this application. Experimental parameters are listed below:

7550S Thermal Desorber:	
Valve oven:	250 °C
GC transfer line:	0.01” ID
	200 °C
Tube purge flow:	120 mL/min
Pre-heat time:	10 s
Tube desorber:	
Rest temp.:	35 °C
Dry purge temp.:	35 °C
Dry purge time:	0.5 min
Desorb temp.:	280 °C
Desorb time:	10 min
Trap:	
Rest temp.:	40 °C
Desorb temp.:	250 °C
Desorb time:	4 min

GC:	
GC conditions	
Oven temp.:	40.0 °C
Injection temp.:	
0 min	160 °C
2 min	175 °C
4 min	270 °C
10 min	160 °C
Injection mode:	Split
Pressure:	30 psi
Split Ratio:	10.0
Temp. program:	
40.0 °C hold 6 min	
120.0 °C ramp to 100.0 °C	
40.0 °C ramp to 260.0 °C	
hold 10.5 min	

MS:

ACQ Mode: SIM (m/z = 46.00, 50.00, 51.00, 60.00, 63.00, 64.00, 65.00, 74.00, 75.00, 76.00, 77.00, 78.00, 89.00, 91.00, 92.00, 104.00, 120.00, 123.00, 137.00, 165.00, 168.00, 180.00, 183.00, 194.00, 210.00, 213.00)

Ion Source Temp.:	250.00 °C	Interface Temp.:	250.00 °C
Solvent Cut Time:	5.50 min		

Two explosive standards as nitroaromatics/nitramine mix and 3,5-dinitroaniline were purchased from Restek (Part No. 33905 and 31661). The concentration of each component were 1000 *μ*g/mL. The two standards were mixed and diluted in methanol to be the stock solution, which was then injected with different volumes onto seven pre-conditioned thermal desorption tubes. The injection was performed on the sampling end of the thermal desorption tube. The residue solvent on the tube was purged by nitrogen flow at 120 mL/min for 5 min at ambient temperature immediately after spiking. This led to 7 loaded thermal desorption tubes, each of which was spiked with 5 ng, 10 ng, 20 ng, 40 ng, 100 ng, 200 ng, and 400 ng of each compound.

Due to the unique physical properties, including high boiling point, low vapor pressures and high sticking coefficients, instrumentations need to be optimized to increase the response and resolution for the target analytes. The first optimization was that a narrow bore SilcoNert coated tubing with 0.01” I.D. was employed as the transfer line to maintain the high linear velocity of the carrier gas flow, in order to minimize the dwelling time of the analytes in the sample flow path. The second optimization was using a unique GC oven temperature program. A 6-minute initial hold at 40 °C followed by a two-step temperature ramp yield enough time for all analytes, especially the ones with high boiling point, to be completely transferred through the column with adequate separation. The last optimization was on the injection port. A programmed temperature profile from 160 °C to 270 °C was adapted to minimize the degradation of thermally labile compounds.

Results and Discussions

Figure 1 is the chromatogram of the explosive compounds mix in SIM mode. Each component of this sample had an absolute mass of 400 ng. Among the list, 2,4,6-Trinitro-N-methyl-aniline was the degradation compound from Tetryl. As shown in the figure, all compounds were adequately separated with symmetric peak shape. This data approved the cleanness and inertness of the sample flow path at elevated temperature. A system blank was followed after the sample run without observing significant amount of carryover, which shows the high efficiency of thermal desorption system to transfer all the compounds into the GC-MS.

Similar runs were performed on rest samples to draw the calibration curve for each compound. The results are depicted in Figure 2. For compounds with boiling points under 300 °C, the response factors were fit with linear curve, whereas the rest of the compounds were fit with second order polynomial regression (quadratic model), based on recommendation in EPA method 8000D and 8270E. The R^2 for all the 14 compounds was greater than 0.997.

As another step of system evaluation in quantitative analysis, the reproducibility of the method were performed by running eight replicates at 20 ng concentration. The RSDs were averaged at 7% for the 14 compounds.

Table 1 summarized all the testing data, where all the compounds, including the challenging 2,4,6-trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX), yield satisfactory results.

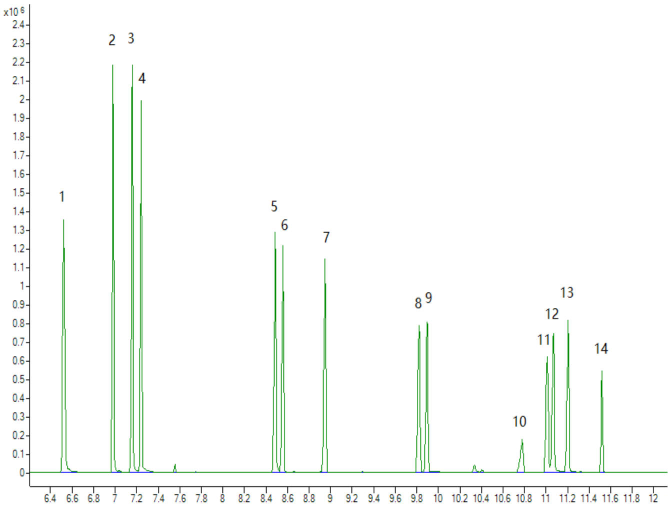

Figure 1. Chromatography of the explosive standards at 400 ng concentration (green line). The peak number corresponds to: 1 nitrobenzene, 2 2-nitrotoluene, 3 3-nitrotoluene, 4 4-nitrotoluene, 5 1,3-dinitrobenzene, 6 2,6-dinitrotoluene, 7 2,4-dinitrotoluene, 8, 1,3,5-trinitrobenzene, 9 Trinitrotoluene, 10 RDX, 11 4-amino-2,6-dinitrotoluene, 12 3,5-dinitrobenzenamine, 13 2-Amino-4,6-dinitrotoluene, 14 2,4,6-Trinitro-N-methyl-aniline. The blue line is the system blank after this sample run.

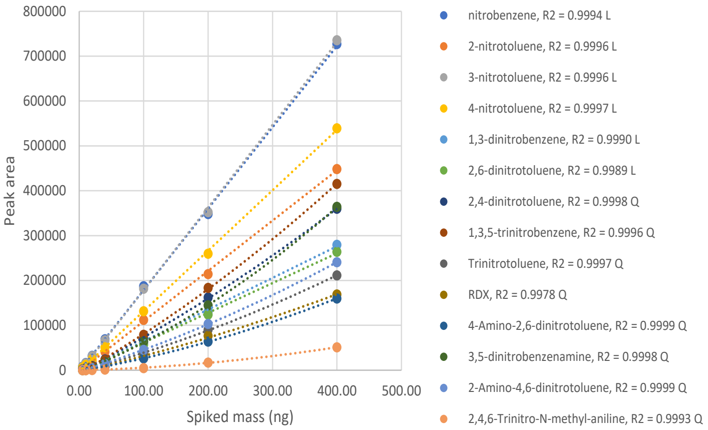

Figure 2. Calibration curves for the explosive standards by TD-GC-MS

Conclusions

A thermal desorption-GC-MS method was tested on quantitative study of 14 explosive standards that all have high boiling points over 200 °C. Some of these compounds are even thermally labile. The testing data, based on reproducibility and linearity, approved this system in quantification study of explosives in the vapor phase. The data also implied that this system is more than capable to handle other less challenging organic compounds with high boiling points.

Table 1: All the 14 compounds with corresponding boiling point, fitting model, the coefficient of determination and data precision.

Compound	**Boiling point (°C)**	**Regression**	**R^2**	**RSD% (20 ng, n=8)**
nitrobenzene	211	Linear	0.9994	4.77
2-nitrotoluene	224	Linear	0.9996	5.87
3-nitrotoluene	232	Linear	0.9996	4.87
4-nitrotoluene	238	Linear	0.9997	6.68
1,3-dinitrobenzene	296	Linear	0.9990	3.66
2,6-dinitrotoluene	289	Linear	0.9989	2.87
2,4-dinitrotoluene	300	Quadratic	0.9998	3.49
1,3,5-trinitrobenzene	315	Quadratic	0.9996	4.71
Trinitrotoluene	240	Quadratic	0.9997	4.48
RDX	353*	Quadratic	0.9978	13.81
4-Amino-2,6-dinitrotoluene	346*	Quadratic	0.9999	8.34
3,5-dinitrobenzenamine	398	Quadratic	0.9998	11.50
2-Amino-4,6-dinitrotoluene	360*	Quadratic	0.9999	8.20
2,4,6-Trinitro-N-methyl-aniline	365*	Quadratic	0.9993	14.39

* predicted; experimental value unavailable

References

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