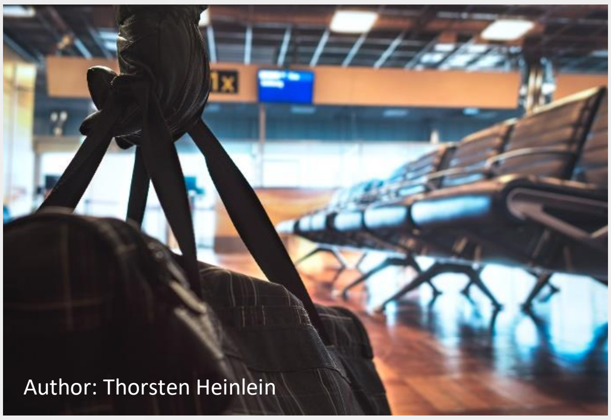
Rapid Field Identification of Explosives, tagging agents and metabolites by the portable Torion® T-9



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A rapid sampling of Explosives and associated tagging agents was preformed with PerkinElmer´s person-portable Torion® T-9 capillary gas chromatograph toroidal ion trap mass spectrometer (GC/MS). The samples were analyzed fast and reliable in combination with the Custodion™ solid phase microextraction (SPME) or the prototype, the so called *Coiled Wire Filament* (CWF).

Introduction

In this application, Explosives and associated compounds like tagging agents, metabolites, stabilizers, explosive propellants and solvents, which can included in preparation of Explosives were sampled and identified in less than 3 min.

This application note is based on PerkinElmer´s published results in `Determination of Explosive Compounds in Soil Samples Using the Torion® T-9 GC/MS with SPME sampling´[1]. The article was broadened by compounds, that were found by further searches [2, 3, 4], because sometimes it is not necessary to find the explosive material. Just a hint for that can result in rapid decision making. A good example are the tagging agents, which can detect very easily by special trained dogs.

But also metabolites, stabilizers and solvents can be a very good indicator cause not every Explosive is sufficient volatile for the detection via SPME technique or stable for the analysis via GC/MS.
To cover the disadvantage of the missing volatility the CWF was used for liquid injection.

In addition the application note shows the results in case of impossible detection of Explosives. But this shouldn´t reduce the benefit of using the portable GC/MS system Torion® T-9, it should show the complex nature of Explosives and their potential for further investigations.

Sample Preparation and Analysis

The analysis of different explosives, their metabolites and associated taggant agents was performed. The key compounds are listed in Table 1. For method a) the explosives standards were used with a concentration of 1000 µg/mL or 100 µg/mL [4] . 20 µL were placed in a 8 mL headspace vial including a headspace cap. For butyl acetate (20 µL), cyclohexanone (20 µL), dimethyl phthalate (10 µL), diethyl phthalate (10 µL) and a small amount of the solid compounds (1-Nitronaphthalene, Diphenylamine, 2-Methyl-4-Nitroaniline) was used. The 8 mL vial was heated on a heater block set at 37 °C for more than 10 min. After the equilibration the SPME fiber (DVB/PDMS; 65 µm) was exposed to the headspace for 5 min, with the fiber located in the middle of the vial. Afterwards no signal was detected with the Torion® T-9, a fresh sample was prepared heated for 1 min up to 70 °C and incubated the SPME for 5 min.
For method b) the CWF was immersed directly into the non-dissolved standards. For the Explosives Tetryl, PETN and RDX a small amount of solid was dissolved in methanol.

Experimental Conditions

GC Inj. Temp: 175 °C
GC Column: MXT-5, 5 m x 0.1 mm, 0.4 µm d_f
GC Column Temp: 50-270 °C at 2 °C/s
Transfer Line: 175 °C
Mass Analyzer: Toroidal ion trap (TMS)
TMS Mass Range: 43-500 Da
Ionization Mode: In-trap electron impact (EI)
Detector: Electron multiplier
Vacuum: Roughing and turbo molecular pumps
Mass Resolution: Less than unit mass to 230 amu, nominal unit mass to 500 amu.

Methods:

a) Sampling: Solid phase microextraction (SPME)
SPME Phase: (DVB/PDMS, 65 µm)
GC Column Temp: 40-280 °C at 2 °C/s

b) Sampling: Coiled Wire Filament (CWF); prototype
GC Column Temp: 40-280 °C at 2 °C/s

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Table 1. List of key compounds

compound	CAS no.	Mw (g/mol)	type	***detectable with***	
				SPME	**CWF**
Butyl acetate	123-86-4	116	Solv		
Cyclohexanone	108-94-1	98	Solv		
EGDN (Ethylene Glycol Dinitrate)	628-96-6	152	Tagging agent		
TATP (triacetone Triperoxide)	17088-37-8	222	Exp		
Nitrobenzene	98-95-3	123	prop		
2-Nitrotoluene	88-72-2	137	Tagging agent		
DMNB (2,3-Dimethyl-2,3-Dinitrobutane)	3964-18-9	176	Tagging agent		
3-Nitrotoluene	99-08-1	137	Tagging agent		
4-Nitrotoluene	99-99-0	137	Tagging agent		
Nitroglycerin	55-63-0	227	Exp		
Dimethylphthalate	131-11-3	194	Stab		
DEGDN (Diethylene glycol dinitrate)	693-21-0	196	Exp		
2,6 Dinitrotoluene	606-20-2	182	prop		
Diethyl phthalate	84-66-2	222	Stab		
1-Nitronaphthalene	86-57-7	173	prop		
2,4 Dinitrotoluene	121-14-2	182	Exp		
Trinitrotoluene (TNT)	118-96-7	227	Exp		
1,3,5 Trinitrobenzene	99-35-4	213	Met		
Diphenylamine	122-39-4	169	Stab		
2-Amino-4,6-dinitrotoluene	19406-51-0	197	Met		
4-Amino-2,6-dinitrotoluene	35572-78-2	197	Met		
2-Methyl-4-Nitroaniline	99-52-5	152	Met		
1,3-Diethyl-1,3-Diphenylurea (Ethyl centralite)	85-98-3	268	Stab		
1,3-Dimethyl-1,3-Diphenylurea(Methyl centralite)	611-92-7	240	Stab		
1,3-Dinitrobenzol	99-65-0	168	Exp		
2,4,6-Trinitrophenylmethylnitramine (Tetryl)	479-45-8	287	Exp		
RDX (Cyclonite, Hexogen)	121-82-4	222	Exp		
PETN (Nitropenta, Pentaerytrityl tetranitrate)	78-11-5	316	Exp		
TEGDN (Triethylene glycol dinitrate)	111-22-8	240	Exp		
HMTD (Hexamethylene triperoxide diamine)	283-66-9	208	Exp		
HMX (Homocyclonite, Octogen)	2691-41-0	296	Exp		

Exp = Explosive, Stab = Stabilizer, Met = metabolite, Prop = explosive propellant, Solv = Solvent.
Underlined in green (detection possible), red (not possible), grey (not needed, because was detected with SPME).

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Results & Discussion

TATP, NG, DEGDN

Figures 1-3 show the TIC and the Mass Spectrum of the most famous explosive target analytes TATP, Nitroglycerin and DEGDN sampled via SPME for 5 min up to 70 °C.

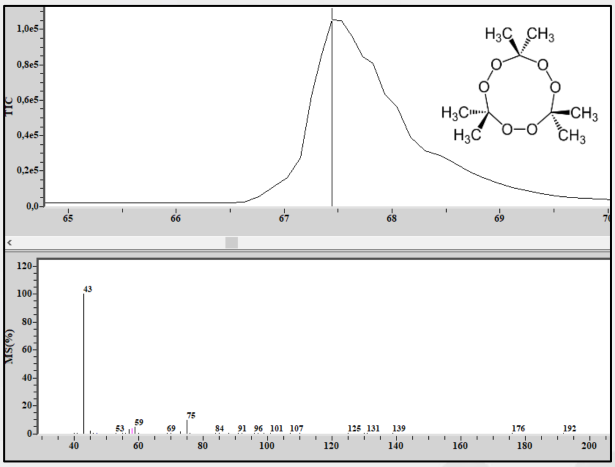

Figure 1. TIC and MS of TATP. Sampling: 5 min, 70 °C, SPME.

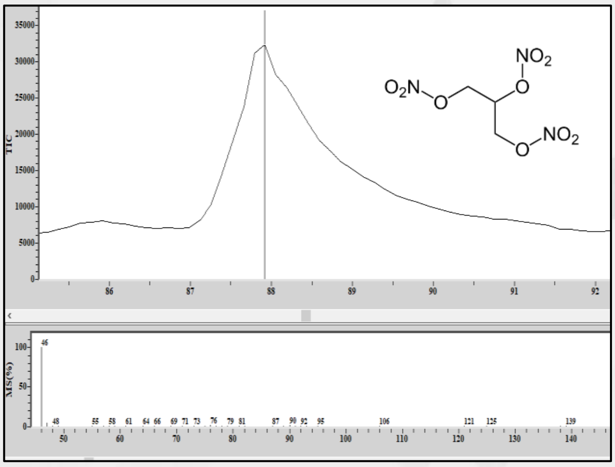

Figure 2. TIC and MS of NG. Sampling: 5 min, 70 °C, SPME.

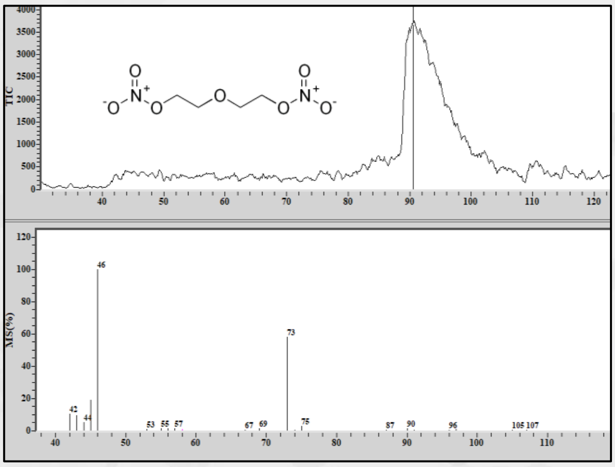

Figure 3. TIC and MS of DEGDN. Sampling: 5 min, 37 °C, SPME.

Aromatic explosives

Figures 4 a + b show the TIC and Mass Spectra of TNT and Figure 5 the Mass Spectra of the Explosives containing an aromatic structure, derivates of Dinitrotoluene and 1,3- Dinitro-benzene.

Figure 4 a shows the chromatogram and the Mass Spectrum of TNT through liquid injection.

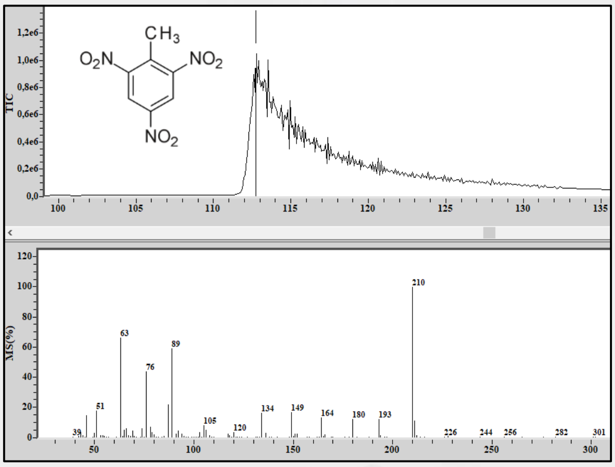

Figure 4 a. TIC and MS with the charateristic basic ion peak m/z 210 of TNT. Sampling: CWF.

Sampling via SPME yielded in signals with low intensity (Figure 4 b).

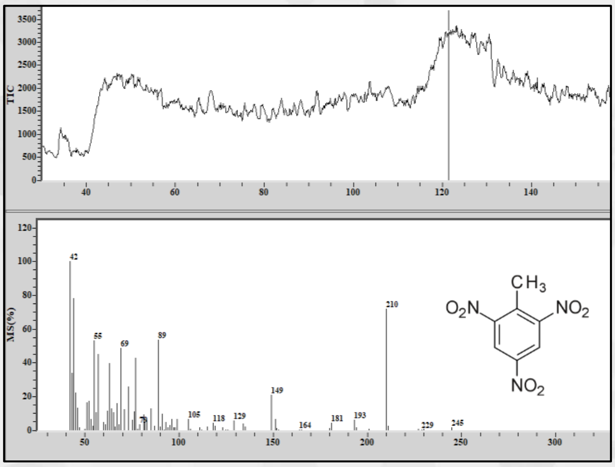

Figure 4 b. TIC and MS with the characteristic basic ion peak m/z 210 of TNT. Sampling: 5 min, 37 °C, SPME.

In this case the samples (2, 4- Dinitrotoluene, 2, 6- Dinitrotoluene, 1,3-Dinitrobenzene) first were analyzed with CWF, checked the retention time plus Mass Spectrum and than confirmed the results obtained by SPME sampling. Figure 5 shows the Mass Spectra of each compounds. Experiments with 70 °C incubation were not performed.

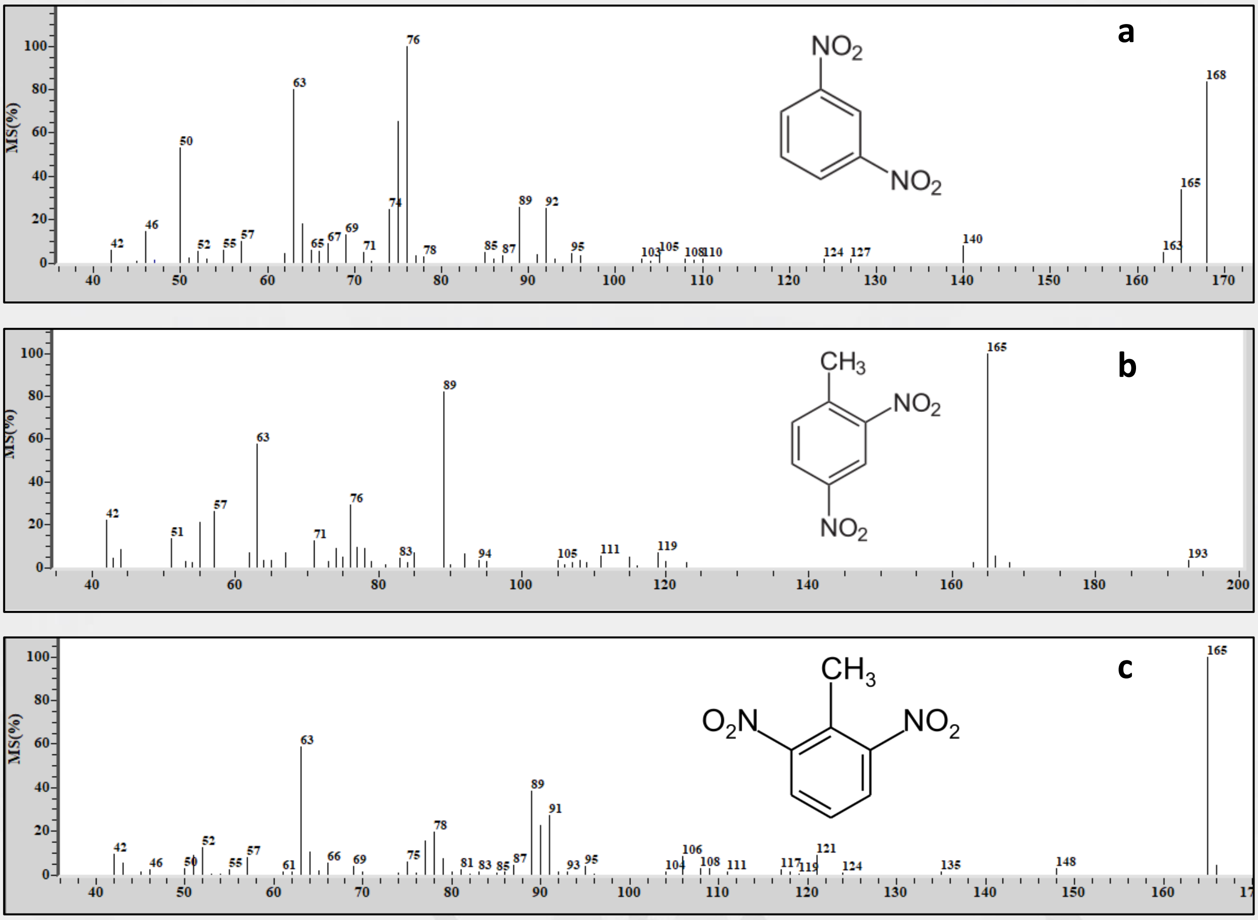

Figure 5. Mass Spectrum with the molecular ion peak m/z 168 for 1, 3-Dinitrobenzene (a), m/z 165 for 2, 4-Dinitrotoluene (b) and 2, 6-Dinitrotoluene (c). Sampling: 60 s, 37 °C, SPME.

Metabolites of TNT and related structures

For the compounds 1, 3, 5-Trinitrobenzene, the two derivates of Amino-dinitrotoluene and 2-Methyl-4-Nitroaniline a detection via headspace technique (37 °C and 70 °C) led to no positive result. Just the liquid injection with the *Coiled Wire Filament* yielded for every substances in an identification, confirmed each time with a well-defined Mass Spectrum (Figure 6).

However, detection by means of headspace is also not absolutely necessary, since these substances usually occur in the ground in the immediate vicinity of blasting funnels [3], which were created by bombing during the two World Wars. The TNT contained therein and the partially highly soluble metabolites must be extracted prior to the analysis.

Thus, the CWF provides a very good tool for on-site analysis and an initial assessment of the environmental impact of the area [3].

Tagging agents

In the production process, plastic explosives are labeled by adding odorous substances (*tagging agents*) in order to be able to find them more easily by means of tracking dogs or suitable detection devices. Such taggants are easily attainable substances with a relatively high vapour pressure, e. g. EDGN, DMNB and derivates of Nitrotoluene.

Figures 7 & 8 show the TIC and the Mass Spectrum of the tagging agents EDGN and DMNB sampled via SPME for 5 min up to 70 °C.

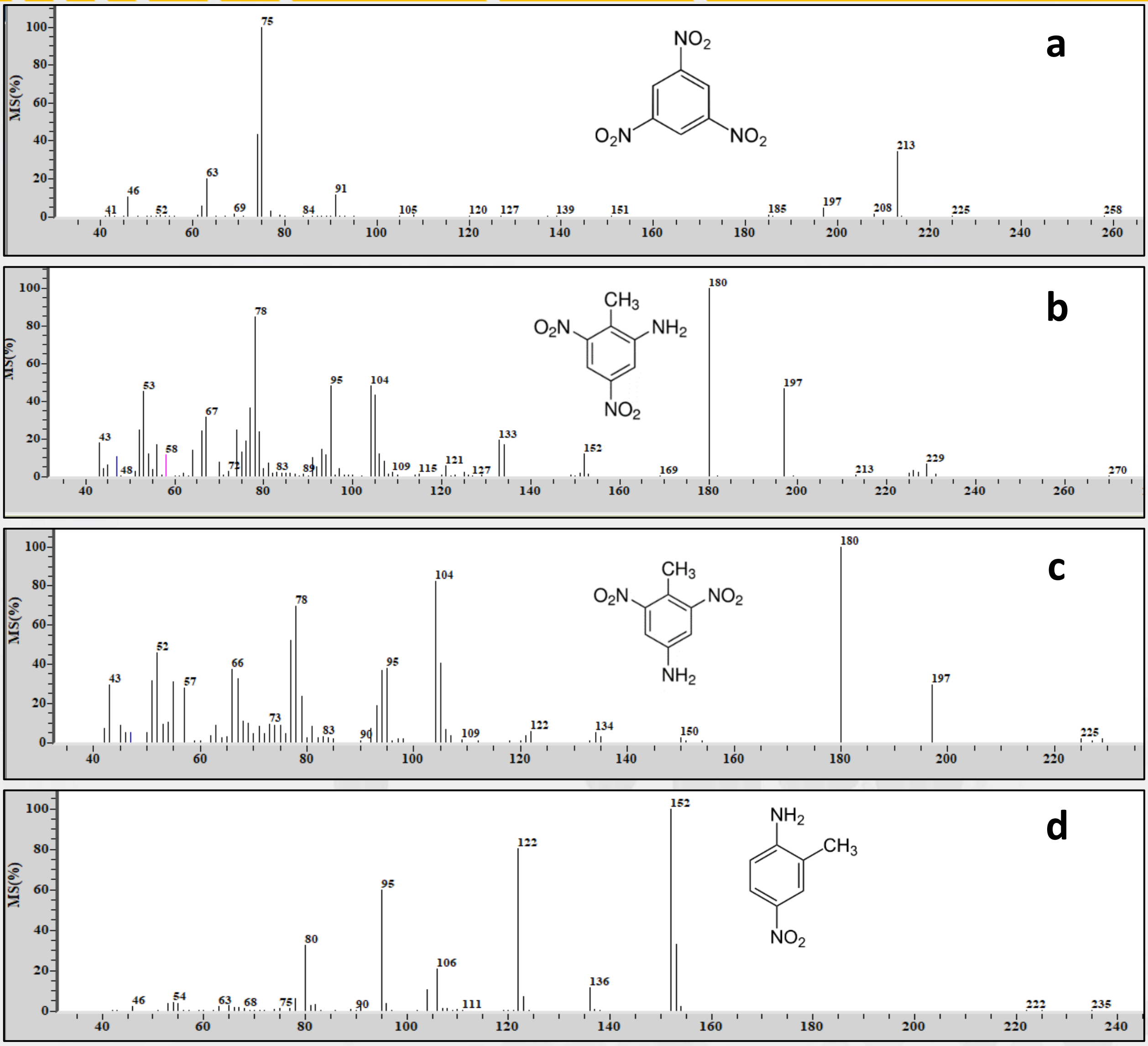

Figure 6. Mass Spectrum with the molecular ion peak m/z 213 for 1,3,5-Trinitrobenzene (a), m/z 197 for 2-Amino-4,6-dinitro-toluene (b) and 4-Amino-2,6-dinitrotoluene (c) and 2-Methyl-4-Nitroaniline (d). Sampling: CWF.

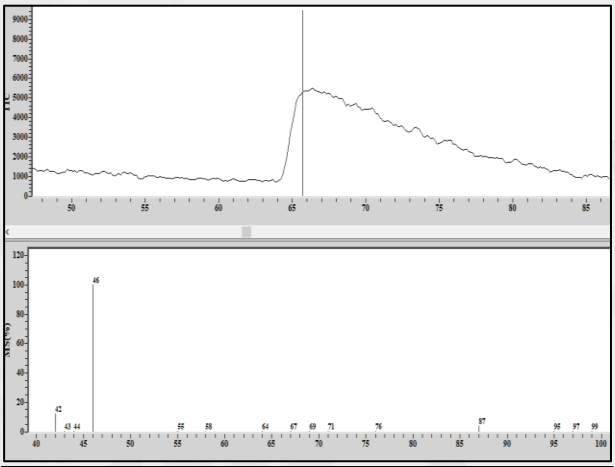

Figure 7. TIC and MS of EGDN. Sampling: 5 min, 70 °C, SPME.

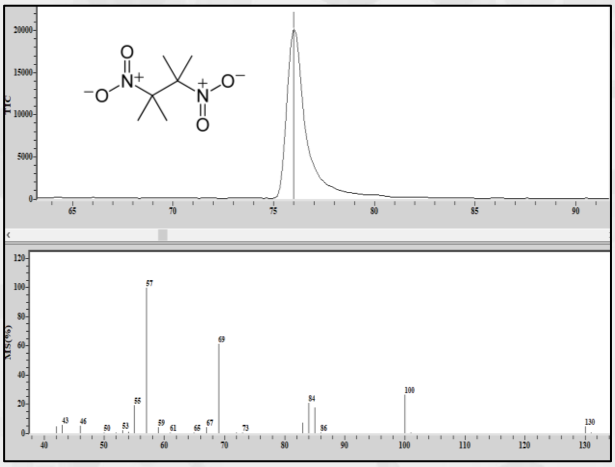

Figure 8. TIC and MS of DMNB. Sampling: 5 min, 70 °C, SPME.

For both compounds it was possible to reach a markedly signal, although the used concentration of the naturally readily decomposable compounds was very low. The incomplete Mass spectra result in the properties of EGDN and DMNB and further experiments are needed with higher concentrations to confirm the already preformed experiments by the detection of the molecular ion peak.

The stable tagging agents 2-Nitrotoluene, 3-Nitro-toluene and 4-Nitrotoluene could much more easier detected via SPME technique, with an incubation time of 60 s and a temperature up to 37 °C.

Figures 9 - 11 show the TIC and the Mass Spectrum of the three derivates of Nitrotoluene.

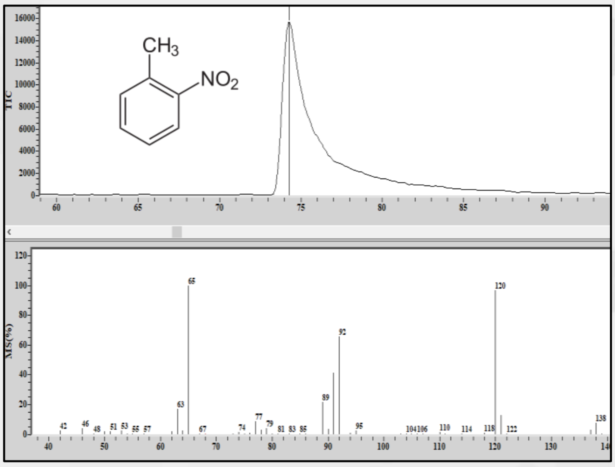

Figure 9: TIC and MS with the molecular ion peak m/z 138 (M+1) for 2-Nitrotoluene.

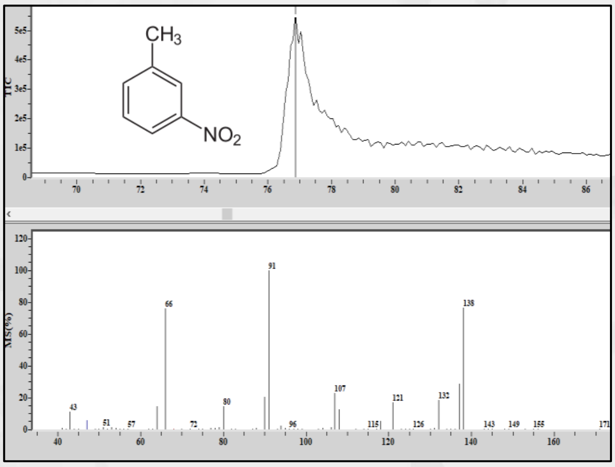

Figure 10: TIC and MS with the molecular ion peak m/z 138 (M+1) for 3-Nitrotoluene.

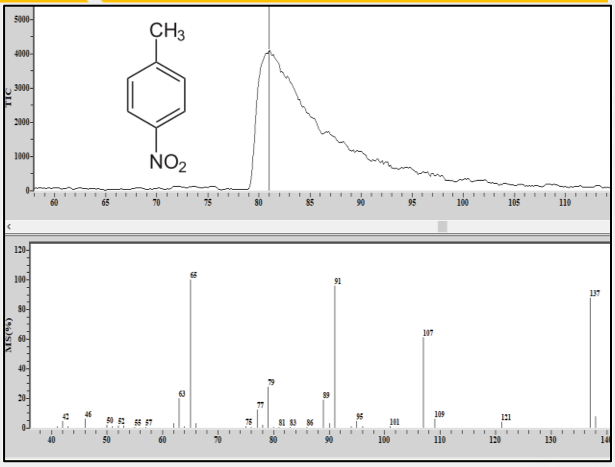

Figure 11: TIC and MS with the molecular ion peak m/z 137 for 4-Nitrotoluene.

With a retention time of 74 s, 77 s and 81 s (2-Nitro- 3-Nitro-, 4-Nitrotoluene) the device is able to separate the three components from each other and differentiates them according to their mass spectra.

Stabilizers & Phthalates

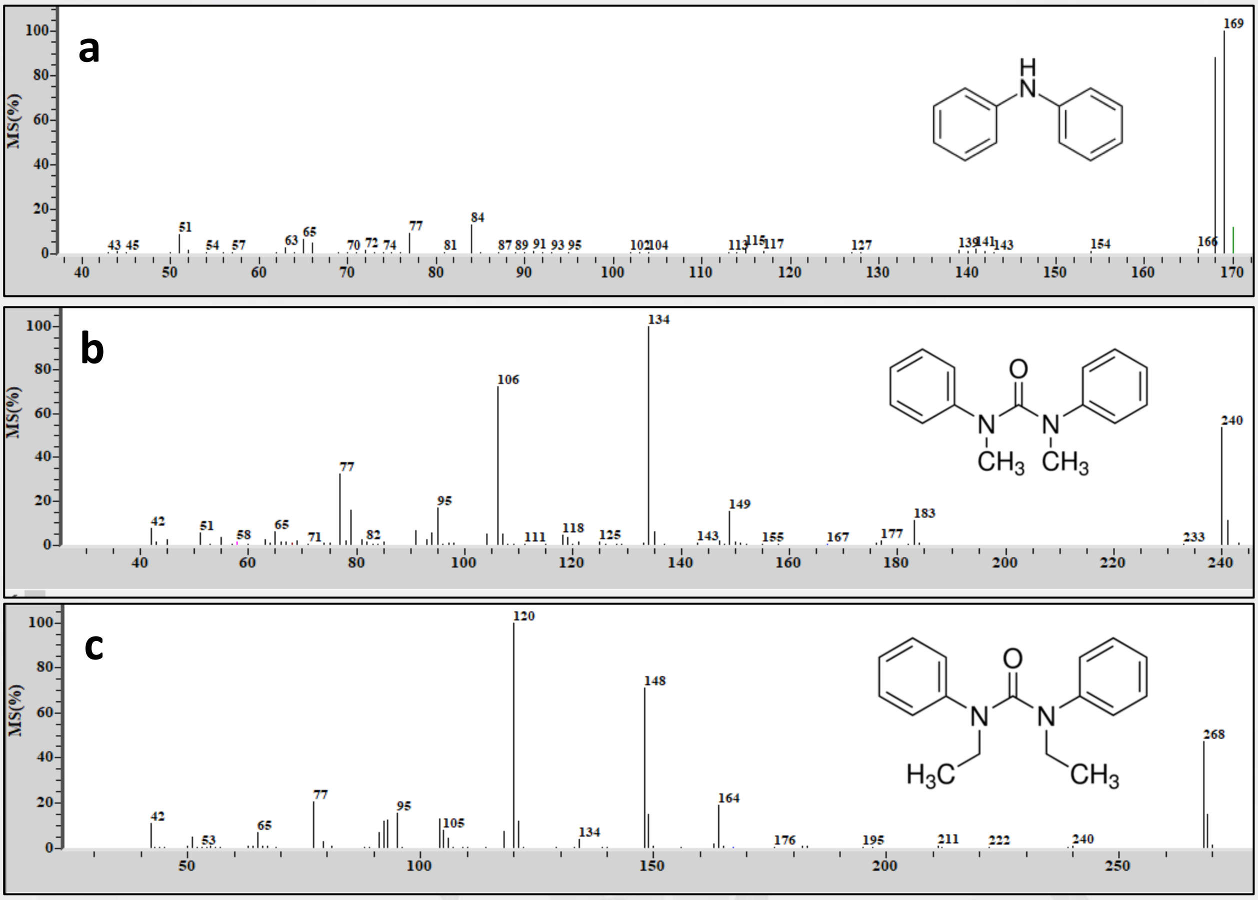

Figure 12: MS with the molecular ion peak m/z 163 for Diphenylamine (a), m/z 240 for Methyl centralie (b) and m/z 268 for Ethyl centralite (c).

According the stabilizers, the detection was possible with the SPME and an incubation time of 5 min at 70 °C for the centralites and 37 °C for Diphenylamine. Broadened, but clear signals (data not shown) has shown a retention time of 109 s (diphenylamine), 120 s (Methyl centralite) and 123 s (Ethyl centralite). The corresponding Mass Spectra are shown in Figure 12.

Phthalates/plastilizers are included in the group of stabilizers although they have a different purpose. However, both groups of substances occur in explosives and can give an indication of the presence of these.

According the phthalates the detection was possible with SPME, 30 s incubation and 37 °C. Figure 13 only shows the Mass spectra for Dimethyl phthalate (rt 97 s) and for Diethyl phthalate (rt 106 s), because the signals are very broadened.

The investigations demonstrated a separation and identification of the two plasticizers.

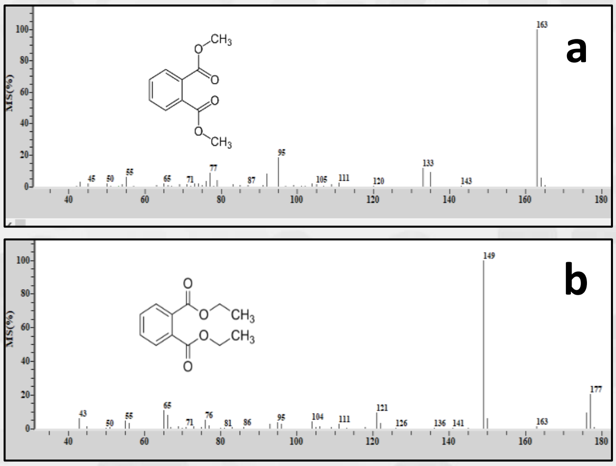

Figure 13: MS with the basic ion peak m/z 163 for Dimethyl phthalate (a) and m/z 177 for Diethyl phthalate (b).

Propellants & accompanying substances

As described above for the plasticizers and stabilizers propellants and accompanying substances can provide a hint for the presence of explosive mixtures.

Two investigated propellants 1-Nitronaphthalene (see Figure 14) and Nitrobenzene (see Figure 15) as well as two solvents commonly used for explosive synthesis Butyl acetate (see Figure 16) and Cyclohexanone (see Figure 17) can be detect very easily with SPME technique.

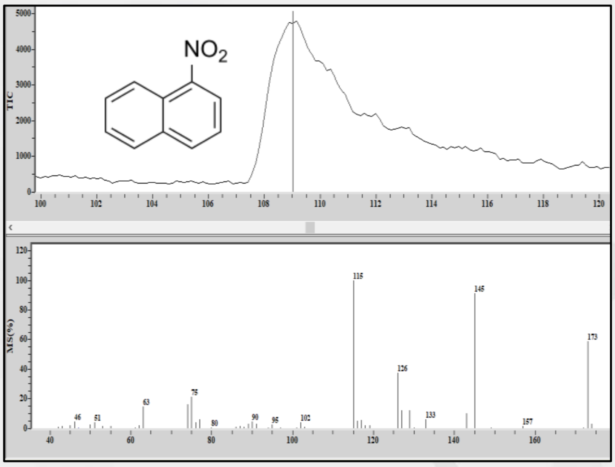

Figure 14: TIC and MS with the molecular ion peak m/z 173 for 1-Nitronaphthalene. Sampling: 5 min, 37 °C, SPME.

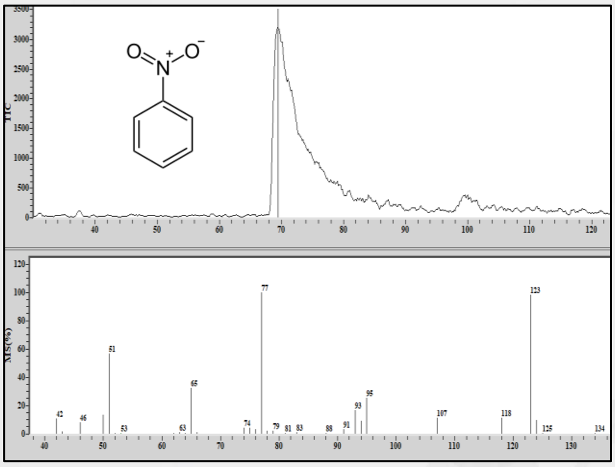

Figure 15: TIC and MS with the molecular ion peak m/z 123 for Nitrobenzene. Sampling: 60 s, 37 °C, SPME.

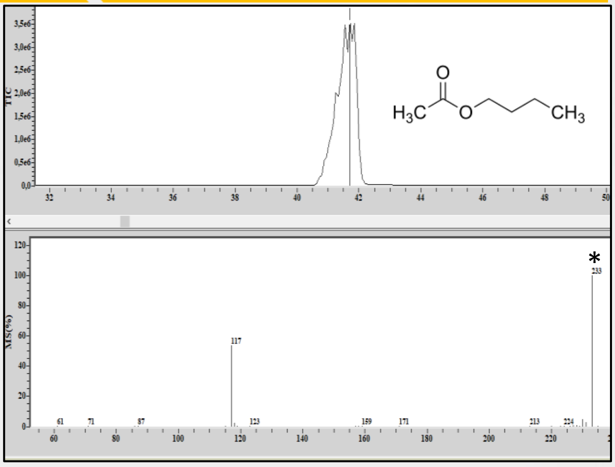

Figure 16: TIC and MS with the molecular ion peak m/z 117 (M+1) for Butyl acetate. The signal marked with asterix (*) is a product of recombined ions in the ion trap. Sampling: 10 s, 37 °C, SPME.

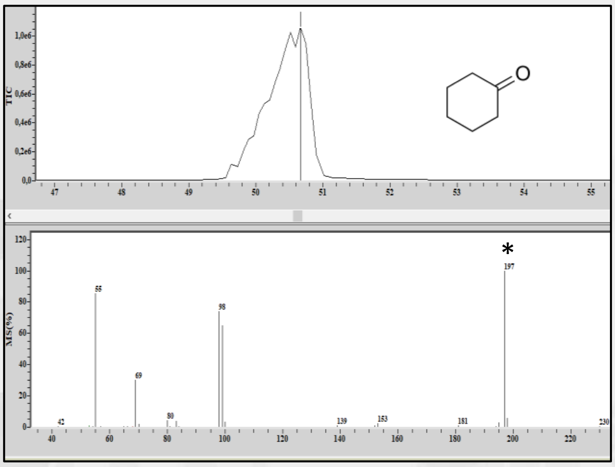

Figure 17: TIC and MS with the molecular ion peak m/z 98 for Cyclohexanone. The signal marked with asterix (*) is a product of recombined ions in the ion trap. Sampling: 10 s, 37 °C, SPME.

Tetryl & RDX

The detection of Tetryl and RDX was only possible via liquid injection. Figures 18 shows the TIC and Mass Spectra of Tetryl.

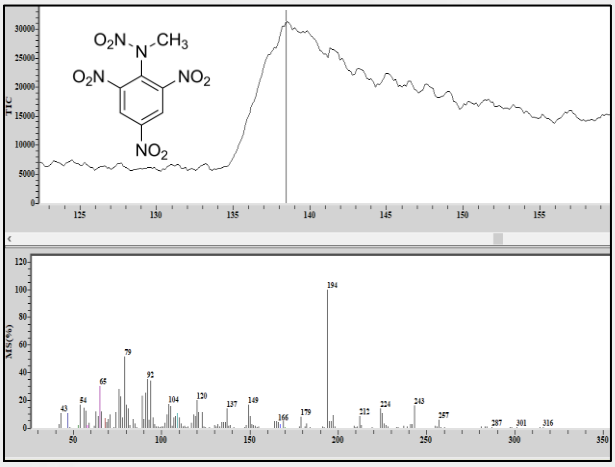

Figure 18. TIC and MS with the characteristic basic ion peak m/z 257 of Tetryl. Sampling: Liquid injection, CWF.

RDX shows (Fig. 19) a reproducible signal in the TIC with a rt of 98 s. The Mass Spectrum shows signals of m/z 46, 57, 71, 85.

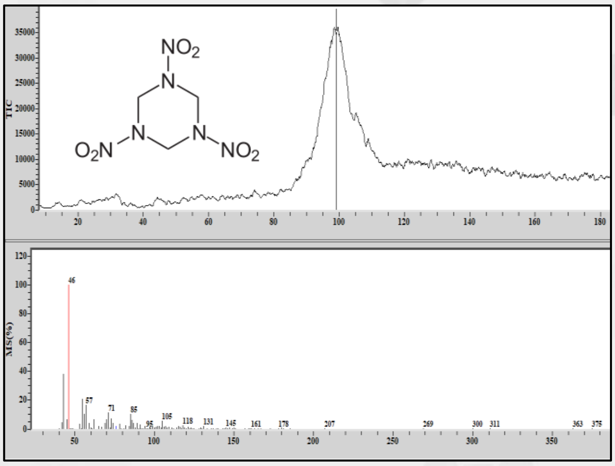

Figure 19. TIC and MS of Tetryl. Sampling: Liquid injection, CWF.

Conclusions

An On-field environment, a benefit of the portable GC/MS analysis is the ability to screen samples which allows only positive samples to be forwarded to the lab for a complete analysis segment. Thereby it is decreasing and saving time and money.

With PerkinElmer´s person-portable Torion® T-9 the operator is able to detect a series of explosives and their accompanaying substances like tagging agents, stabilizers, plasticizers and solvents commonly used explosive synthesis. Butyl acetate and Cyclohexanone are only picked out in a series of further solvents, each of which has a certain volatility, which allows an easy detection without a special sample preparation.

Method applicability for other explosive compounds, such as TEGDN, PETN, HMTD and HMX was not successful (data not shown) and require additional work. Usually the purity of their standards is checked by HPLC [4]. The suitability of the GC/MS system first should be tested in further experiments with higher substance concentrations to develop a method in a second step. Otherwise, other already known detection techniques must be used [2].

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References

[1] Application note, PerkinElmer Inc., *Determination of Explosive Compounds in Soil Samples Using the Torion® T-9 GC/MS with SPME sampling*.

[2] Ph.D. thesis, Martin Härtel, 2017, *Studies Towards the Gas-Phase Detection of Hazardous Materials by Vapor Pressure Measurements with the Transpiration Method in Combination with Vacuum Outlet GC/MS*.

[3] Bayerisches Landesamt für Umwelt, Praxisteil, 2009, *Arbeitshilfe für die Untersuchung von Sprengplätzen* (only in german).

[4] AccuStandard Explosive Standards Reference Guide 2016.

Acknowledgements

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