Rapid Field Identification of Street Drugs by the portable Torion® T-9 GC/MS

A rapid sample preparation and analysis of underivatized drugs like amphetamine and its precursors, included are also the drugs cocaine, heroin and MDMA, was preformed with PerkinElmer´s person-portable Torion® T-9 capilarry gas chromatograph toroidal ion trap mass spectrometer (GC/TMS).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

GC/MS is a technique, which combines two techniques, the gas chromatography and the mass spectrometry. This allows to specify a compound with the retention time and the mass spectrum, often described as a chemical fingerprint. Therefore the application field results in a broad range of sample components including drugs [1,2], their impurities and by-products [3]. Impurities like products from side reactions due to poor chemical handling during synthesis, insufficient purification of the product, contaminations of reactants/ materials/packaging generate a chromatogram, which is also a kind of chemical fingerprint, a chemical pattern. So that is why links can be made between drug seizures, drug sources and also drug trafficking routes using this chemical pattern.

Sample Preparation and Analysis

The analysis of diffrent street drugs was performed. The key compounds are listed in Table 1. If possible, the impurities in the samples were identified like solvents & precursors.

Table 1. List of Target compounds.

Compound	CAS no.	Mw (g/mol)
Amphetamine	300-62-9	135.21
Methamphetamine	7632-10-2	149.23
γ-Butyrolactone	96-48-0	86.09
Heroin	561-27-3	369.42
Caffeine	58-08-2	194.19
Cocaine	50-36-2	303.36
MDMA	42542-10-9	193.25
MDPV	687603-66-3	275.35
1-Phenyl-2-nitropropene	705-60-2	163.17

The analytes Amphetamine, γ-Butyrolactone and 1-Phenyl-2-nitropropene were extracted using Solid phase microextraction (SPME) using a Custodion™ syringe with a PDMS/ DVB fiber (film thickness 65 µm). The fiber was placed in the head space for approximately 30 seconds. For MDMA the fiber was directly immersed in the solution for approximately 5 seconds, with gentle manual agitation. For the street drug samples, containing heroin and cocaine a prototype for liquid injection, the so called `Coiled wire filament´ was used. The stainless steel coil (see Figure 1) takes a sample with the help of capillary forces. Than it is possible to inject the liquid sample or let the solvent evaporate before the injection.

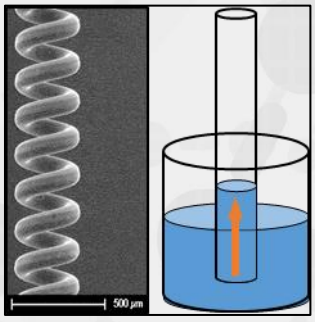

Figure 1. Scanning electron micrograph of the stainless steel coiled wire filament (left). The scheme shows the loading of the filament due to the acting capillary forces (right).

After the sampling step, the sampler was introduces into the injection port of the Torion® T- 9, where the analytes were desorbed and evaporate from the fiber due to the thermal treatment of the fiber. After that the low thermal mass GC was loaded with the sample, which is directly interfaced to a toroidal ion trap mass spectrometer (TMS) with a mass range from 43-500 Da. Both methods (see experimental

conditions) including sampling were done rapidly under 3 minutes. One `sample to sample´ cycle just took under 5 minutes.

Experimental Conditions

GC Inj. Temp: 270 °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: 250 °C
Injector Split Ratio: 10:1
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: 50-270 °C at 2 °C/s

b) Sampling: Coiled Wire Filament (CWF); prototype
GC Column Temp: 50-300 °C at 2 °C/s

Results and discussion

Figure 2. γ-Butyrolactone, also known under the name `K.O. drops´ was quick and easy detected by SPME technique and without any sample preparation. The signal at 50 s was confirmed by the mass spectrum with the molecular ion peak (M+1) m/z 87.

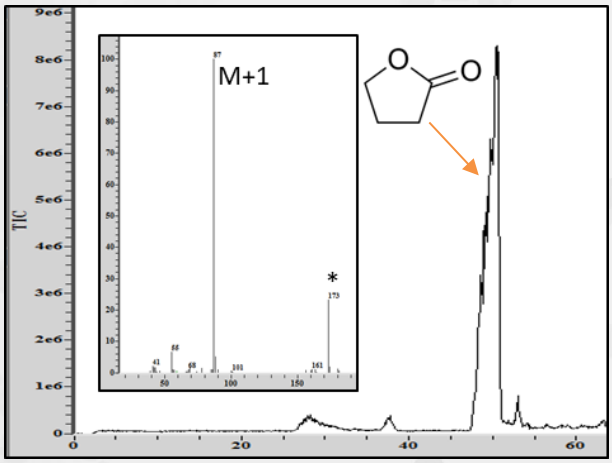

Figure 2. Total Ion Chromatogram & Mass Spectrum of a street sample, containing γ-Butyrolactone with the molecular ion peak (M+1) m/z 87. The signal marked with asterix (*) is a product of recombined ions in the ion trap.

Figure 3. Amphetamine was very easy detected by SPME technique. The signal at 69 s was confirmed by the mass spectrum with the molecular ion peak (M+2) m/z 137. The signals marked with asterix (*) are products of recombined ion in the ion trap. This is a well-known phenomenon of the ion trap technique.

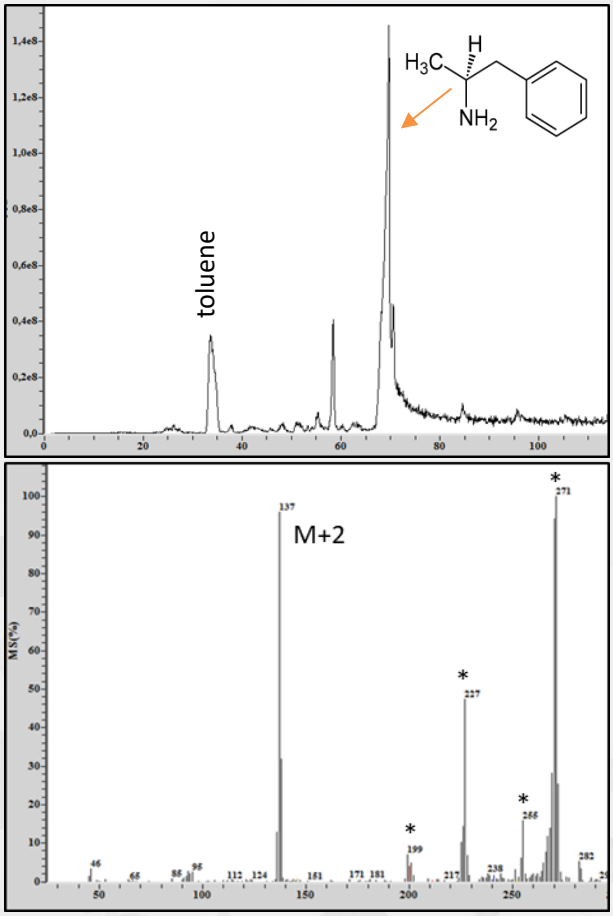

Figure 3. Total Ion Chromatogram & Mass Spectrum of a street sample, containing Amphetamine with the molecular ion peak (M+2) m/z 137. The signals marked with asterix (*) are products of recombined ions in the ion trap.

Figure 4. 1-Phenyl-2-nitropropene (P2NP) is a precursor of amphetamine and will synthesized from benzonitrile.

The signal at 92 s was confirmed by the mass spectrum with the molecular ion peak (M+1) m/z 164. In this case the SPME technique shows the advantage over other sampling techniques, again. No sample preparation was necessary, just putting the SPME fiber into the gas phase of the sample, which was located in a glass vial. By evaluating the signals with the associated mass spectra ethyl acetate (solvent), benzaldehyde (precursor) and benzonitrile (solvent) were identified.

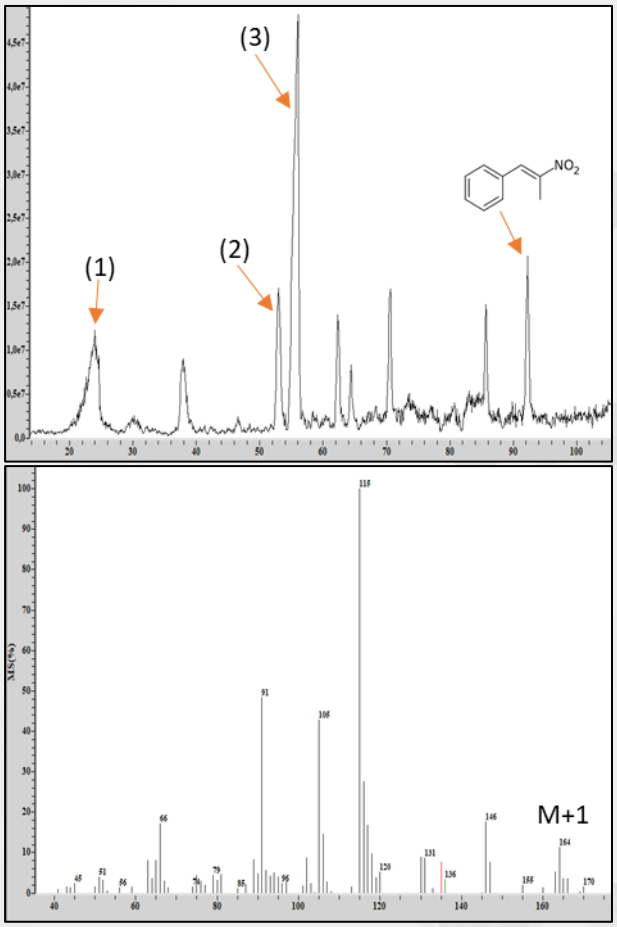

Figure 4. Total Ion Chromatogram & Mass spectrum of a sample, containing the precursor for amphetamine PN2P with the molecular ion peak (M+1) m/z 264 and associated solvents & precursors: (1) Ethyl acetate (2) benzaldehyde (3) benzonitrile.

Figure 5. 3, 4-Methylendioxymethamphetamine (MDMA), commonly known as ecstasy, was confirmed with a retention time of 98 s and the molecular ion peak (M+1) m/z 194. The immersion and a gentle manual agitation for a view seconds was enough to get a significant signal for the identification of MDMA (1 mg/mL in water).

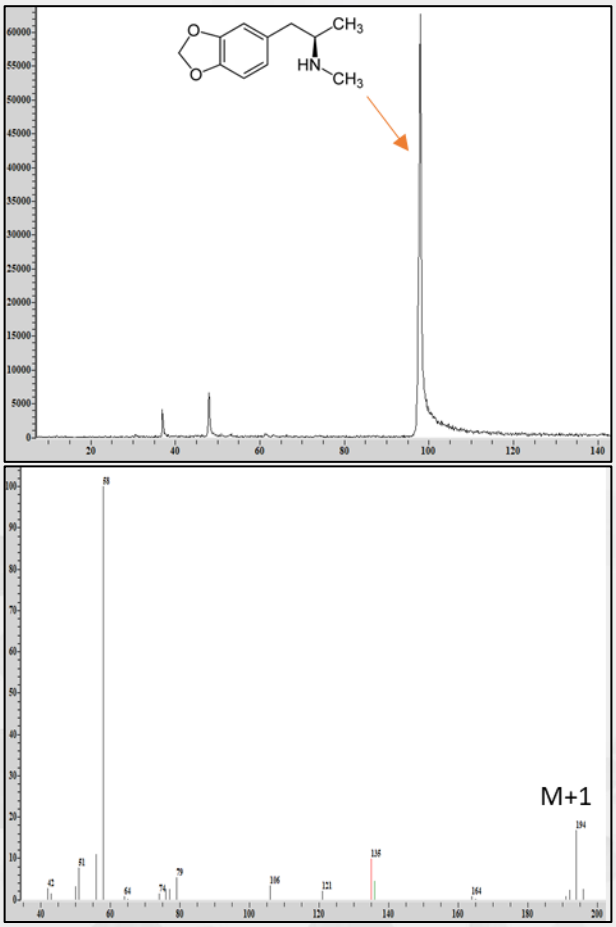

Figure 5. Total Ion Chromatogram & Mass Spectrum of a MDMA sample (1 mg/mL) with the molecular ion peak (M+1) m/z 194.

Figure 6. A sample of a street drug containing cocaine was dissolved (1 mg/ mL in methanol) and sampled with the CWF. Due to the lower volatility and the higher interactions with the stationary phase of the GC column the end temperature of the GC program was increased from 270 °C to 300 °C. Afterwards it was possible to get a signal for cocaine with a retention time of 136 s and the molecular ion peak (M+1) m/z 303. To check the performance of the CWF, the sampling and injection were done 5 times. The chromatogram in Figure 6 shows results with a very good reproducibility of the sampling technique.

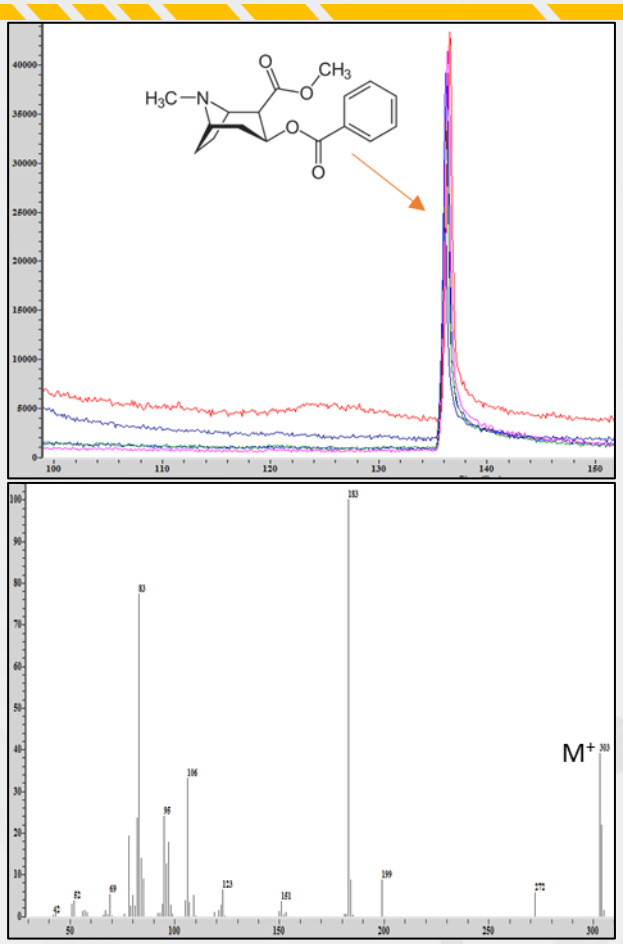

Figure 6. Total Ion Chromatograms of 5 time injection & Mass Spectrum of a cocaine street sample (1 mg/ mL in methanol).

Figure 7a-c. A sample of a street drug containing heroin was dissolved (1 mg/ mL in methanol) and sampled with the CWF. Like cocaine the end temperature of the GC program was increased from 270 °C to 300 °C. Afterwards it was possible to get a signal for heroin with a retention time of 170 s (Figure 7a) and the molecular ion peak (M+1) m/z 379 (Figure 7c). Next to heroin the usual additive caffeine was detected with a retention time of 118 s and the molecular ion peak (M+1) m/z 195.

Figure 7a also shows the very good performance of the prototype CWF with very congruent retention times and peak shapes of caffeine and heroin.

The usual additive paracetamol couldn´t found due to the amphoteric character. But also to find the component is not required.

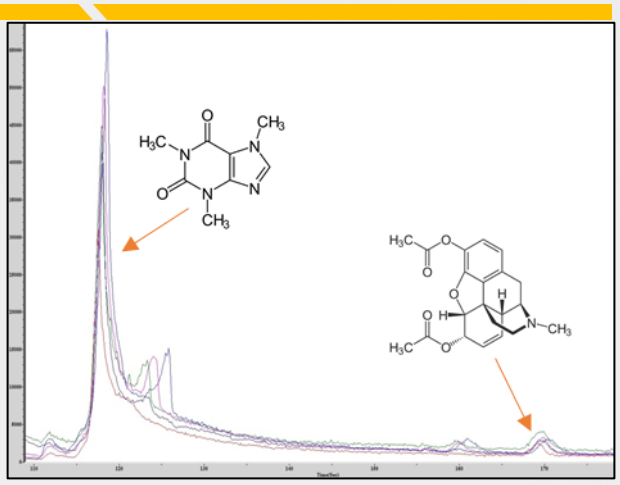

Figure 7a. Total Ion Chromatograms of 5 time injection of a heroine street sample (1 mg/ mL in methanol), contains heroine and the usual additive caffeine.

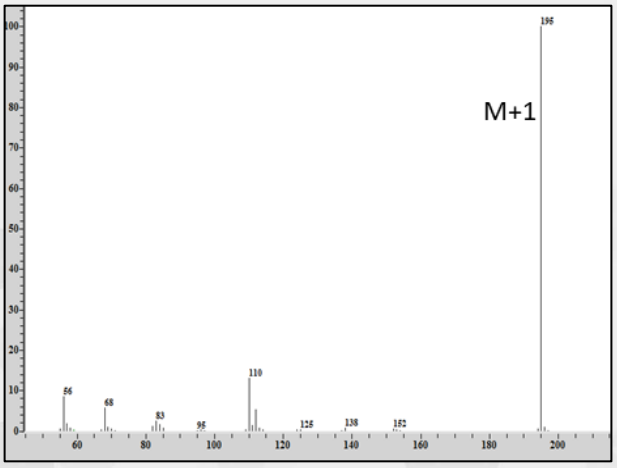

Figure 7b. Resulting Mass Spectrum of caffeine of the street drug sample heroin with the molecular ion peak (M+1) m/z 195.

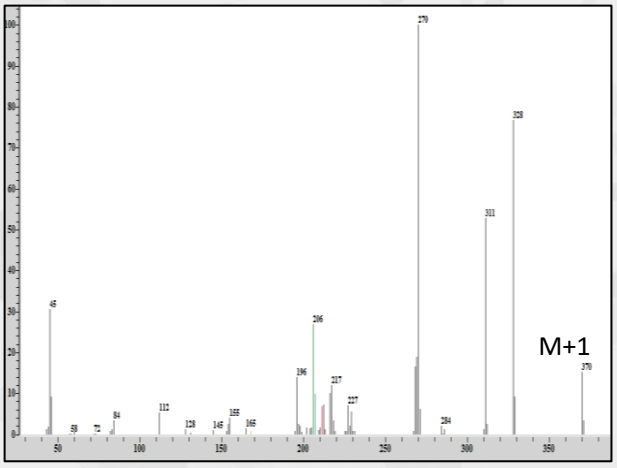

Figure 7c. Resulting Mass Spectrum of heroin of the street drug sample heroin with the molecular ion peak (M+1) m/z 379.

Investigated samples of methamphetamine (*crystal*) and MDPV (methylenedioxypyrovalerone) (data not shown) has shown a very pure chromatogram with a retention time of 72 s and the molecular ion peak (M+1) m/z 150 for methamphetamine and 132 s for MDPV. For MDPV just the base peak of m/z 126 was found, but the MS pattern matches with the NIST library.

Results and Discussion

Analysis of street drugs is possible using the person-portable Torion® T-9 of PerkinElmer under 5 minutes. In combination with the different sampling options it is possible to cover a wide range of sample types:

To use the SPME technique via head space is recommended for volatile substances like γ- Butyrolactone and solvents in general. Also it is possible to immerse the fiber directly in the solution with gentle manual agitation (MDMA).

This could also be done with samples containing amphetamine, adding a drop of ammonium hydroxide (~ pH 10) will form the free base and improve the peak shape of the signal in the chromatogram.

The prototype *Coiled Wire Filament* (CWF) has shown (Figure 6 & 7a) a high reliability in relation to sampling and injection. The retention times have a good match and the peak shapes of each signal are congruent.

The chromatogram of the sample, containing PN2P (Figure 4) is a good example for the chemical pattern mentioned before. To figure out the drug trafficking routes indicators like benzaldehyde (precursor), benzonitrile (solvent, contamination) could be used.

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.

References

[1] Tebbet, I. (ed.) 1999, Gas Chromatography in Forensic Science, Ellis Horwood Limited, West Sussex England.
[2] Karch, S. B. (ed.), 2007, Drugs of Abuse, Taylor and Francis Group, Boca Raton, Florida.
[3] Cheng, J.Y.K., Chan, M.F. Chan, T.W. and Hung, M.Y., 2006, Impurity profiling of ecstasy tablets seized in Hong Kong by gas chromatography mass spectrometry, Forensic Science International, Vol. 162, No. 1, pg. 87-94.

Acknowledgements

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