Development of a method for the analysis of OGSR (Organic GunShot Residues) by SPME-GC- MS

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Introduction:

Forensic police is responsible for conducting different analyses to find clues to solve a case. Those analyses are performed on many elements present on the crime scene, like DNA of fingerprints that can give us example for the identity of the shooter of a murder. OGSR (Organic GunShot Residue) refers to organic particles deposited on a person and the surrounding areas of the firearm after discharge. The main goals of this project are to develop an analytical method of extraction by SPME (Solid Phase Micro Extraction) and then analyze 6 OGSR compounds by GC-MS.

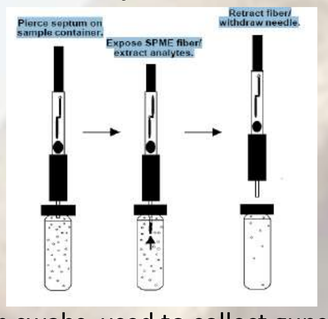
Extraction method :

SPME extraction :

This extraction technique is solvent-free, needs less reagents and could provide an increment of speed of the extraction protocol. Analytes are adsorbed on a 65 µm PDMS/DVB (Polydimethylsiloxane/Divinylbenzene) fiber and thermally desorbed into the injection device of the chromatograph.

Fiber :
PDMS-DVB

Extraction :
35 minutes
at 80°C

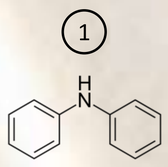


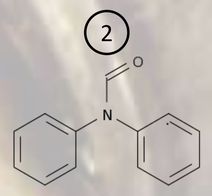
Solvent extraction : Cotton swabs, used to collect gunshot residue from a shooter's hands, are put in a vial with 100 µL of acetonitrile. We sonicate and centrifugate before evaporating under a nitrogen flow and then injecting directly in the GC-MS device.

Cotton swab samples

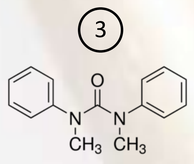
Zones of sampling for gunshot residues

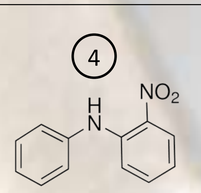
Target molecules :



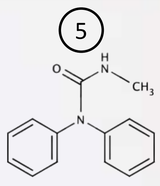


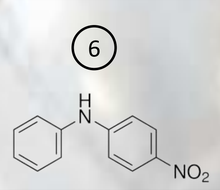
Name	Diphenylamine (DPA)	N,N-Diphenylformamide
tr (min)	10,82	12,08





Name	1,3-Dimethyl-1,3-diphenylurea	2-Nitrodiphenylamine
tr (min)	12,47	13,35





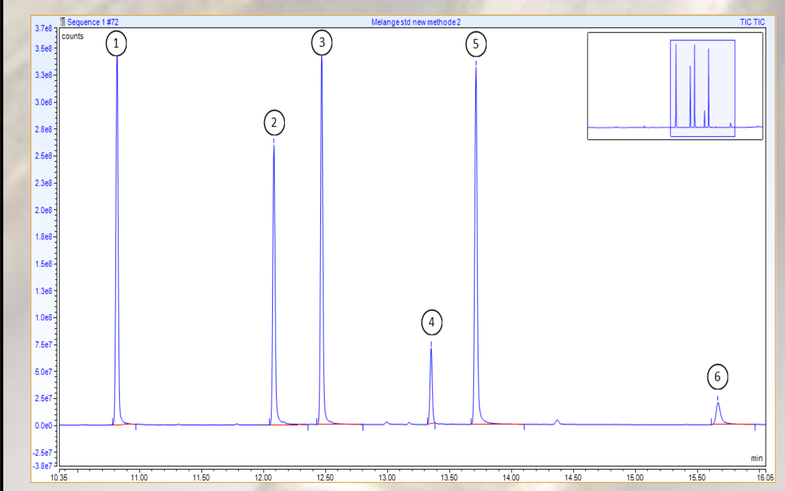
Name	3-Methyl-1,1-diphenylurea	4-Nitrodiphenylamine
tr (min)	13,71	15,67

Instrumentation and experimental conditions :

The analyses by GC-MS were performed through the operational conditions described in the table below. Our samples were collected on hands thanks to a cotton swab and the target molecules are extracted before analysis. Before dealing with our samples through GC-MS, we carried out the analysis of 6 standards (Diphenylamine, N,N-diphenylformamide, 2-nitrodiphenylamine, 4-nitrodiphenylamine, 1,3-Dimethyl-1,3-diphenylurea, 3-Methyl-1,1-diphenylurea). For all of them, a solution at 10 µg/mL was prepared.

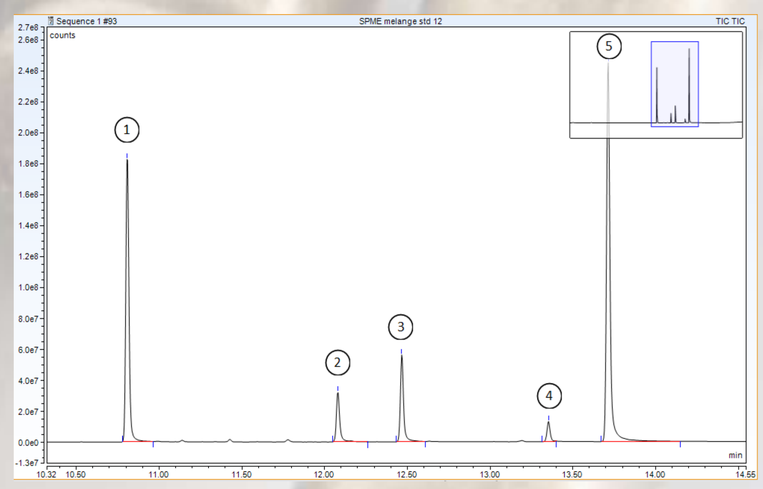
Experimental conditions	
Column	TG-5MS (30 m x 0.25 mm , 0.25 µm) 95% dimethyl, 5% diphenylpolysiloxane
Carrier gas	Helium (1 mL/min)
Injector	Splitless (30s) / Split ratio 1/50
Thermal Gradient	50 – 240 °C (15°C/min), 280°C (30°/min)
Ionisation	+70 eV Electronic Impact
Analyzer	Single Quadrupole
Mode	Full Scan
Logiciel	Chromeleon 7

Results :



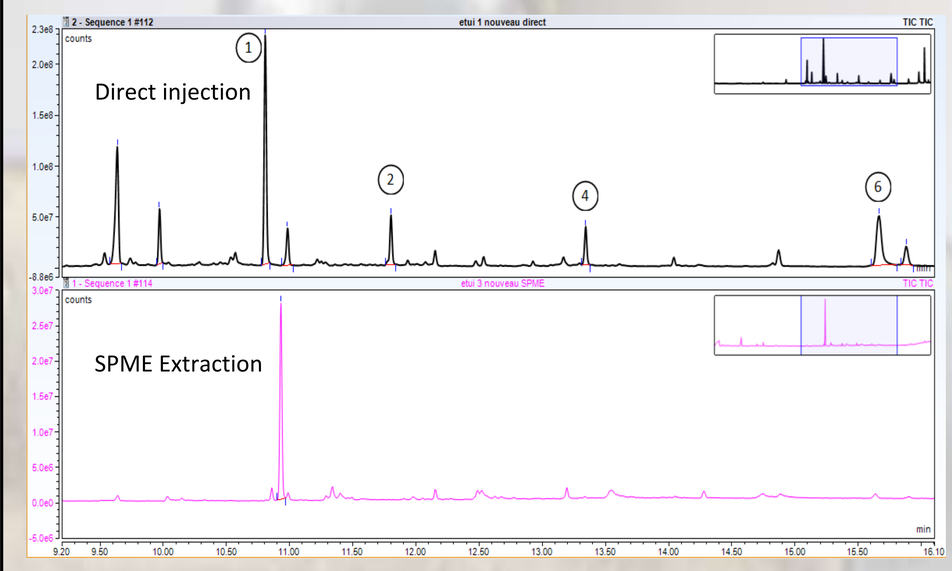
Chromatogram of standards solution with direct injection

→ Obtaining peaks for all standards with different retention times



Chromatogram of standards solution with SPME extraction

→ Obtaining 5 peaks of standards (4-Nitrodiphenylamine is not absorbed on the fiber)



Chromatogram's comparison of a direct injection and SPME extraction of a bullet socket

–> 2-Nitrodiphenylamine and 4-Nitrodiphenylamine could decompose to DPA under the influence of temperature.

– > No molecules of interest were detected on the cotton swab samples, either by SPME or by solvent extraction.

–> By direct injection of OGSR extracted from a bullet socket, we saw 4 molecules of interest instead of 6.

–> With SPME extraction, we did not see any of the molecules of interest.

Conclusion:

SPME is an efficient extraction technique for the standards (5 out of 6) but did not work for our samples.
GC-MS is a reliable and efficient method for the analysis of our 6 OGSR target compounds. However, an Orbitrap detector could be used to improve sensitivity and lower detection and quantification limits. In addition, the analysis of the samples must be carried out quickly after collection as the present compounds volatilize. More concentrated samples or a better sampling method with solvent could be explored.

Acknowledgments:

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References :

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