Workshop – TUNTWIN project – Institute of Analytical Sciences





Liberté Égalité Fraternité

# Mass spectrometry as an investigation tool :

# Focus on the chemical division of the Forensic Police Laboratory in Lyon

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# Service National de Police Scientifique

- French Service of Scientific Police = « service à compétence nationale » of the Ministry of Interior (2021)
- 4 000 public servants in France
- Field samples / laboratory analysis / files comparison
- 627 local services + 56 technical platform (police stations)
- A network of 5 laboratories
- Working for the police and gendarmerie and justice
- Experts (article 157-2 from the code of criminal procedure)





POLICE SCIENTIFIOUE



DE L'INTÉRIEUR ET DES OUTRE-MER



# Multidisciplinarity



















# **Chemical Division of Lyon's Laboratory**



- ✓ Road security✓ Compoud
- identification
- ✓ Forensic analyses



 ✓ Identification, quantification and substance profiling
 ✓ Trace analysis on all kind of matrices



#### Fire/Explosion

- ✓ Fire : Searching for causes and traces of accelerant
- ✓ Explosion : determination of the nature of the devices
- ✓ Teargas

### Goal : Provide the fastest and most comprehensive response to the investigation services





### Use of mass spectrometry : to do what ?

- GC-MS et GC-MS/MS
- LC-MS/MS
- Identification
- Quantification
- Method validation
- Accredited tests (in accordance with the standard ISO/IEC 17025:2017)





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# Search for drug traces on bank bills

- Captured money linked with drug trafficking ?
- Drug traces on bank bills with irregular presence ?
- Contamination depending on denomination (€, \$), extraction and analysis methodology
- Cocaine → quantitative analysis
- Other drugs  $\rightarrow$  qualitative analysis
- Remaining contamination on € bank bills (sampling with banque de France) → cocaine rate evaluation













GC-MS/MS Agilent (2011) GC 7890A - QqQ 7010 – Mass Hunter Column : 35MS-15m-0.25mm-0.25µm

gain of a factor of 25 and 50 in terms of sensitivity between MS and MS/MS

Search for drug traces on bank bills

Analytical methodology

- Manual bills count and selection
- Extraction : wiping (compress) with EtOH
- GC-MS/MS analysis (MRM mode)
- Run of ~ 10 minutes
- LOD in MS : cocaine, THC, heroin = 250 ng/mL
- LOD in MS/MS : cocaine = 5 ng/mL and THC, heroin = 10 ng/mL





# Toxicology and road safety

• Fighting against road insecurity



DrugWipe

- Decree n° 2016-1152 (08/24/2016) : fight against driving after using substances or plants classified as drugs
- $\rightarrow$  allows saliva confirmation
- Ministerial decision on 12/13/2016
   → sets the rules for screening test, analytical equipment and minimum detection threshold
- Drugs :
  - opiates, cocaine and amphetamines derivatives (OCA)
  - THC (9-tetrahydrocannabinol)







# Drugs in saliva

### Difficulty with volumetry



- Quantitative method :
   LOQ OCA = 5 ng/mL LOQ THC = 1 ng/mL
- Positive or negative results for applicants

# Integration/automation for sample preparation step



Transcend – Altis QqQ - Thermo (2022 + 2017)

- Automatic samples cleaning (TurboFlow technology)
  - 2 channels of analysis
    - Multiplexing





# Toxicology and road safety

In progress ... :

**OCA in saliva & OCA + cannabinoids in blood and urine** → backup system + automated sample preparation





LC-MS/MS 8060 - Shimadzu (2022) with 2 online preparation systems

- online extraction SPE
- CLAM : precipitation and ultra-filtration for blood samples





# Toxicology and road safety

In progress ... :

#### Cannabinoids and synthetic cannabinoids in saliva, blood, urine



(Gerstel-RIC)



GC-MS/MS TQ8040NX (Shimadzu)

Dilutions, derivations, liquid/liquid extraction, SPE, DPX (Dispersive solid phase extraction), addition of standards ...

Centrifugation, evaporation, fast stirring

Decrease of sample quantity (micro-sampling)





# **Explosives detection by LC-MS/MS**

- Organic explosives analysis → HPTLC + GC-MS
- GC-MS analysis for some explosives → low sensitivity
- Development of a fast, sensitive and specific analytical method
- Nitric esters, nitramines, peroxides, nitrosamine, additives
- Difficulty with Electrospray ionisation



Victor Hugo street attack – Lyon - 2019



Paris Dakar – Saudi Arabia - 2022





# **Explosives detection by LC-MS/MS**

- Separation and detection of 12 explosives
- Separation in 16 minutes :
  - Column PFP 100 x 2,1 mm x 1,9  $\mu m$  , 40°C
  - 10µL injected
  - Water + ammonium formate + formic acid
  - MeOH + ammonium formate + formic acid



Ultimate 3000 – TSQ Quantum Access MAX Thermo (2011 + 2015)







# **Explosives detection by LC-MS/MS**

• Identification of 4 compounds non detectable with GC-MS (HMX, ETN, N-NDPA, HMTD)

Compound	LOD GC-MS (µg/mL)	LOD LC-MS/MS (µg/mL)
EC	0,05	0,0007
MC	0,05	0,0004
DPA	0,05	0,25
RDX	1	0,4
НМХ	-	0,4
2-NDPA	0,1	12
4-NDPA	0,25	0,04
N-NDPA	-	1
PETN	10	5
ETN	-	5
HMTD	-	0,25
R-Salt	0,25	2



• Next : integration of other compounds in the method, purification step after acetone solid/liquid extraction and before injection in LC-MS/MS





#### What's next?



#### Analytical challenges

- Sensitivity thresholds for the detection of compounds in complex and diverse matrices
  - \* LOD for THC in saliva ≤ 1 ng/mL (legislative framework, minimum detection threshold)
  - \* Drugs traces on all kind of supports (handbags, straw, knife, packaging ...)
  - \* Explosives traces on diverses matrices (clothes, nuts, blood ...)





#### What's next?



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- Development and implementation of a **tool** for the comparison of chromatographic profiles
  - Volatile substances (fires)
  - \* Standardisation of comparison criteria





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  - Volatile substances (fires)
  - \* Standardisation of comparison criteria
- Identification of knowed and unknowed compounds
  - \* Xenobiotics in forensics toxicology
  - \* New Synthetic Products (NPS)





# What's next about sensitivity ?





#### Sample preparation (micro-extractions)

Availability of samples in terms of quantity Multiplicity of analytical techniques



### Specificity

→ Extraction : decrease matrix effects (purification step)

HMTD, identification in LC-MS/MS only

→ Analysis :  $MS \rightarrow MS/MS$ 





From targeted to non-targeted

### What's next about identification ?



#### High Resolution Mass Spectrometry (HRMS)

Coupling LC with Q-ToF or Q-Orbitrap Identification and quantification of xenobiotics in biological matrices Ready-to-use method





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From targeted to non-targeted

Recherche > d'une liste ciblée (limitée)

> Recherche d'inconnus (illimitée)

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### Benchtop RMN (60 MHz)

Identification, structural elucidation and profiling for NPS Database creation Drugs quantification



Spinsolve 60 MHz – Magritek ANR project with Nantes University (2019-2023)



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#### Multi-technical approach

Correlation of results between analytical techniques Comparaison with databases Prediction of MS/MS and RMN spectra In silico fragmentation tools



Recherche



Spinsolve 60 MHz – Magritek ANR project with Nantes University (2019-2023)





# Thank you for your attention



