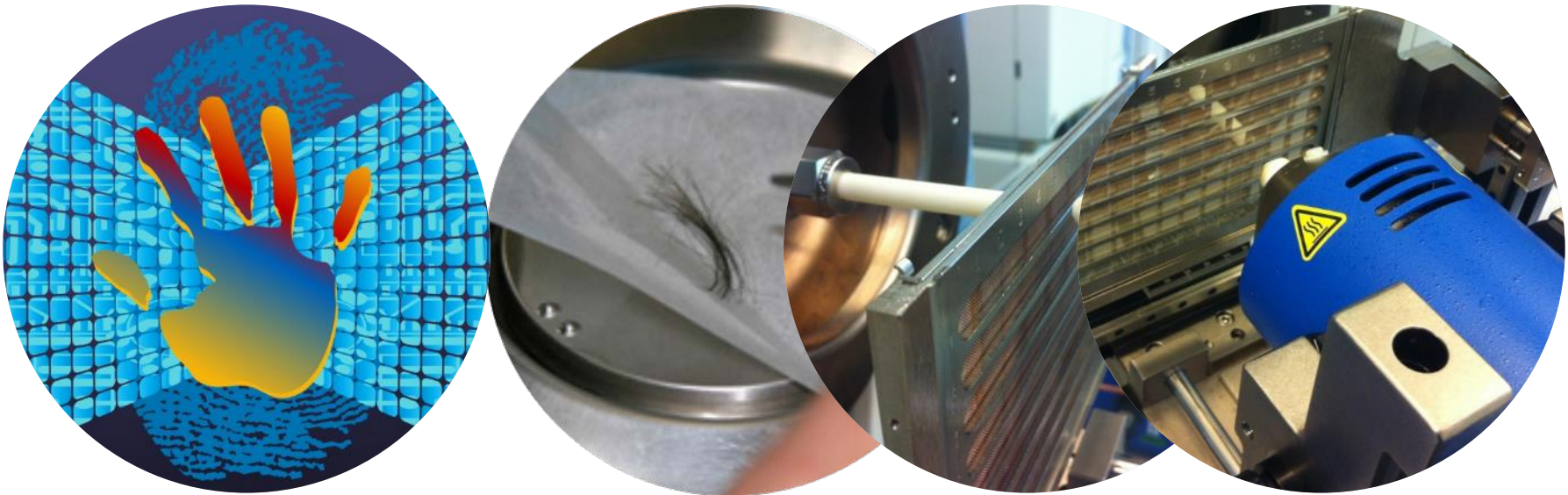


# DART MSI of drugs of abuse in hair

Wilco Duvivier, Teris van Beek, Michel Nielen

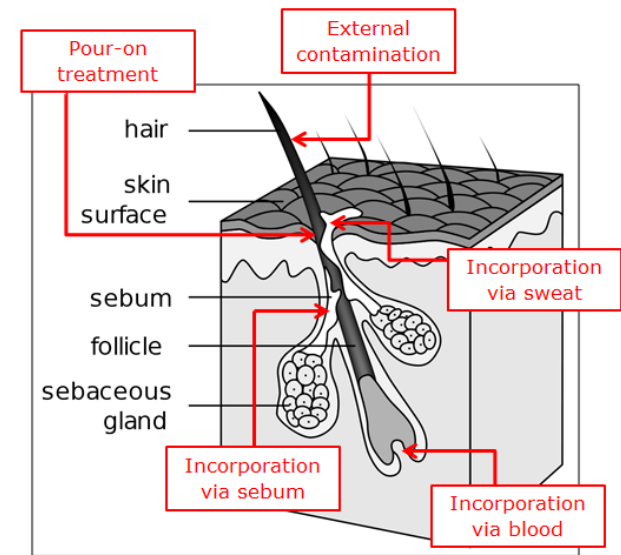
October 5, 2017



# Forensic hair evidence

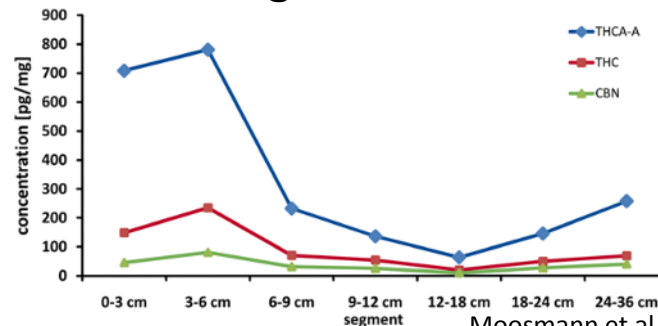
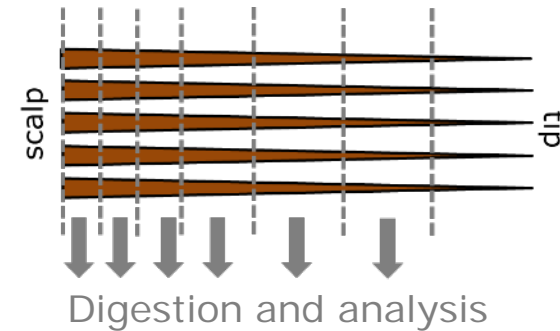
## Forensically interesting:

- Many **compounds accumulate** in **hair**
- **Prolonged detectability** versus body fluids
- **Non-invasive** sampling, **easy storage**



## Conventional hair analysis:

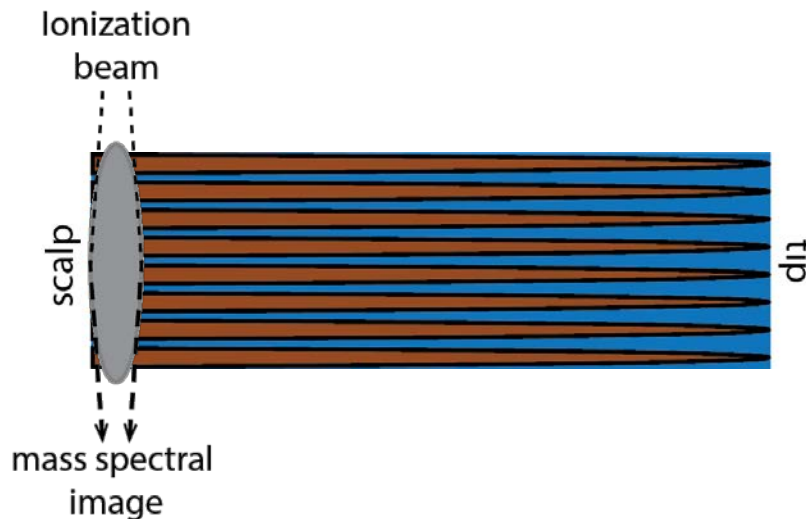
- + **Sensitive** LC- or GC-MS(/MS) analysis
- + **Segmentation** to **estimate time** of drug **intake**
- **Destructive** and **inefficient** sample preparation
- Only **rough estimated** time of drug intake (>1 month intervals)



# Hair scan concepts: hair scan

What if we..

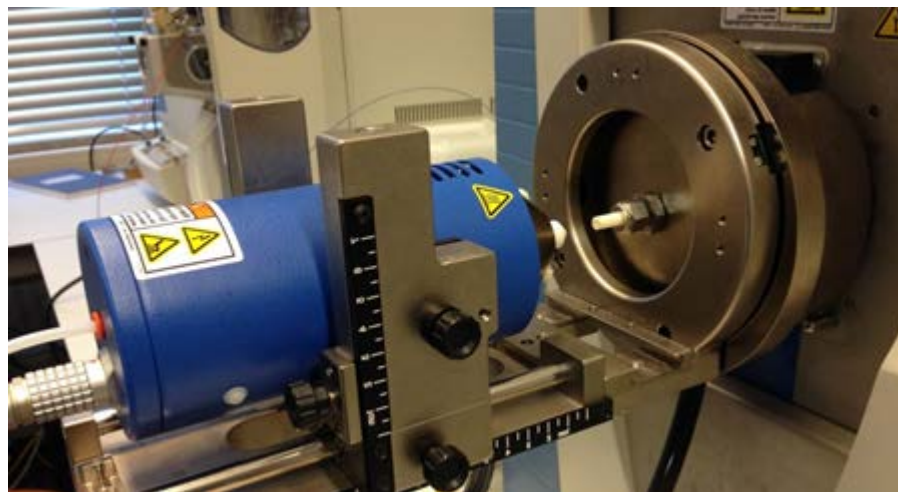
- ..could target **intact locks of hair**
- ..would **not** need MALDI **matrix** or other **sample preparation**
- ..could make hair analysis **fast** and **easy** to perform



Ambient ionization mass spectrometry

# DART ionization

**DART:** Direct Analysis in Real Time

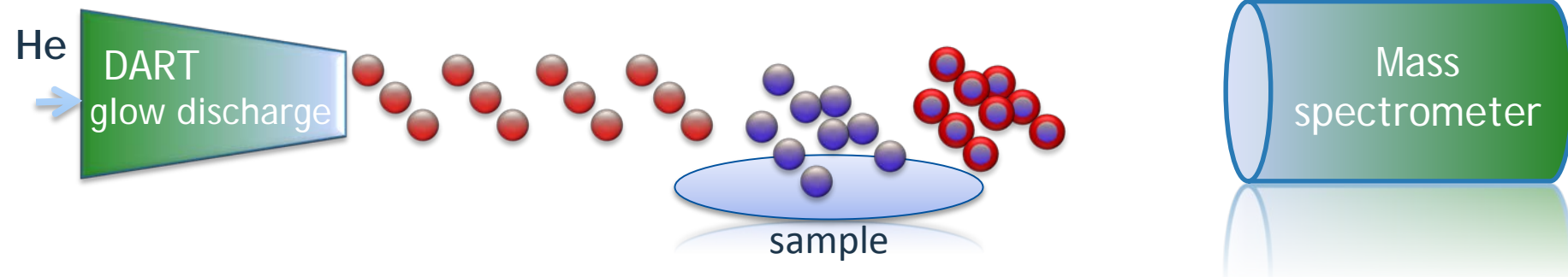


Metastable species  $\text{He}(2^3\text{S})$  ●

Analyte ●

Charged analyte ions ●

150-500 °C

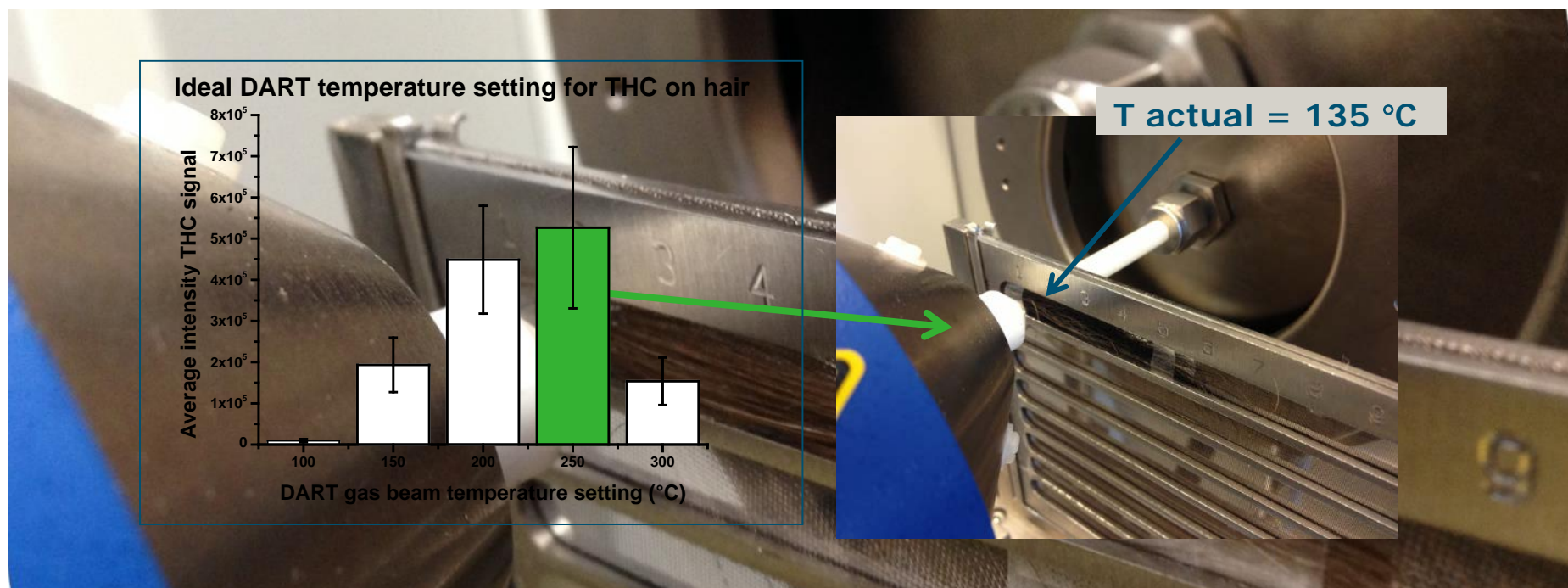


# DART hair scan method

Intact lock of hair attached to stainless steel mesh

Scanned at 0.2 mm/s, DART source at 250 °C

Orbitrap MS: ~ 1 scan per second with high mass resolution

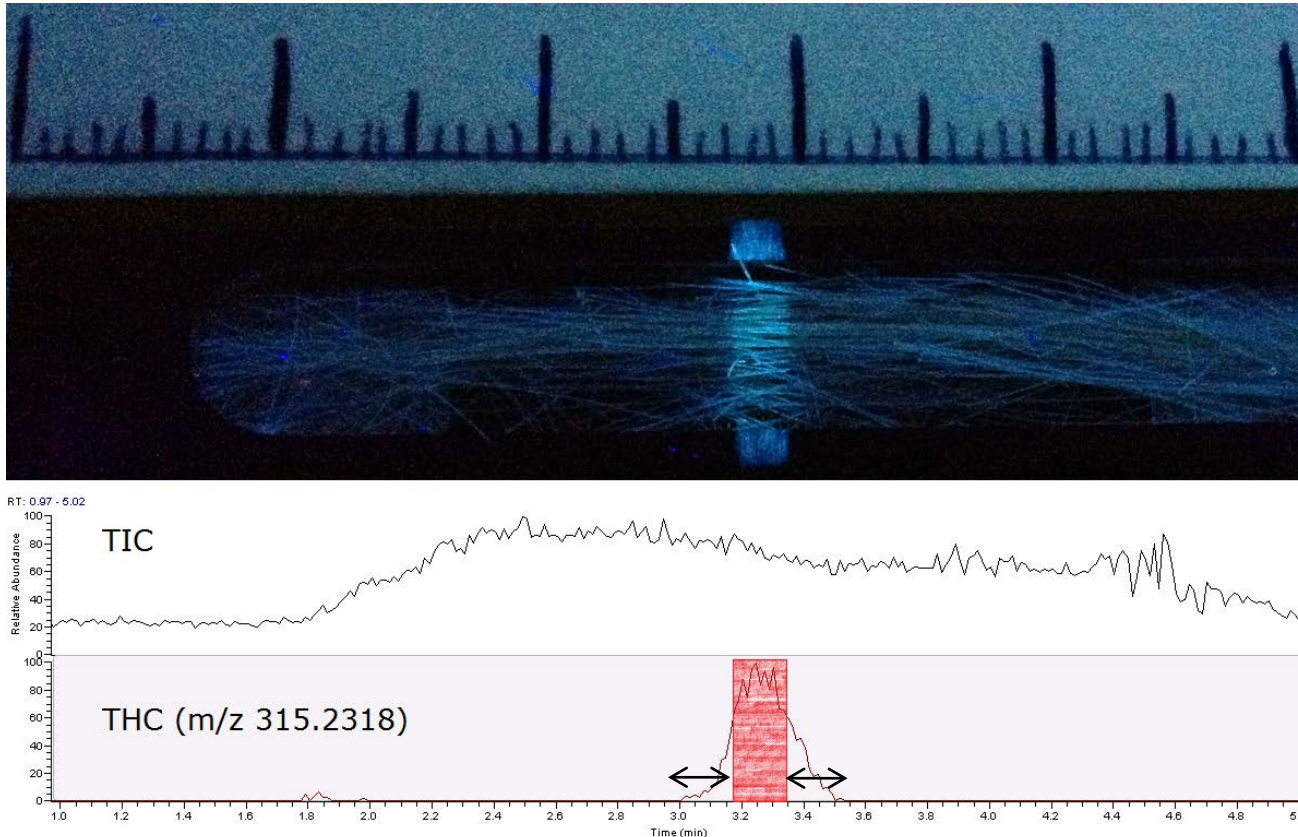


Duvivier et al., *Rapid Commun. Mass Spectrom.* **2014**, 28, 682-690



# DART-MS scan accuracy

Hair spiked with **cannabis extract** and **quinine** using **TLC-sprayer** through 2 mm slit (x-scan at 0.2 mm/s)

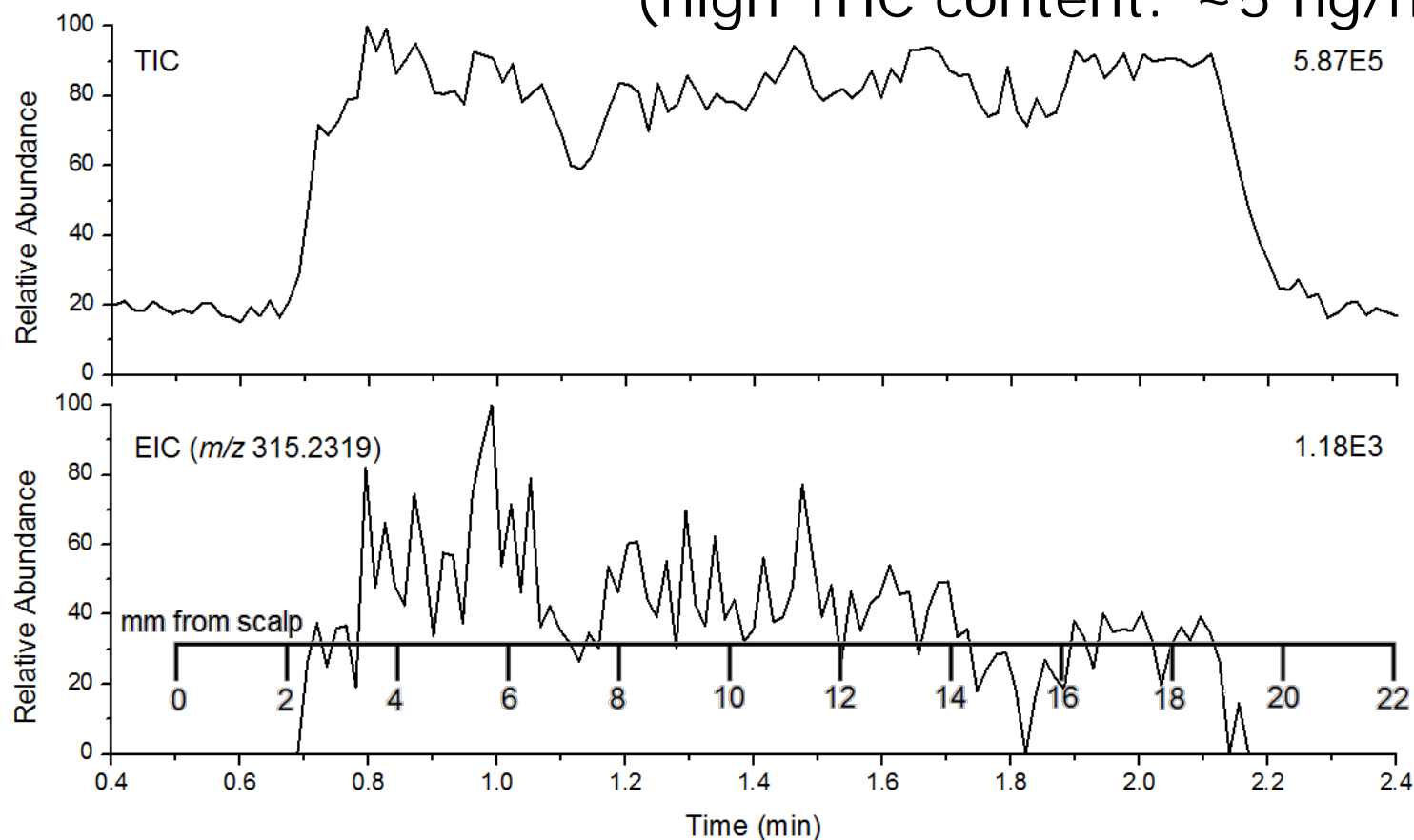


Spatial resolution: **~ 2.5 mm** (~ 1 week history) → Improvement over conventional hair analysis

# Drug user hair samples

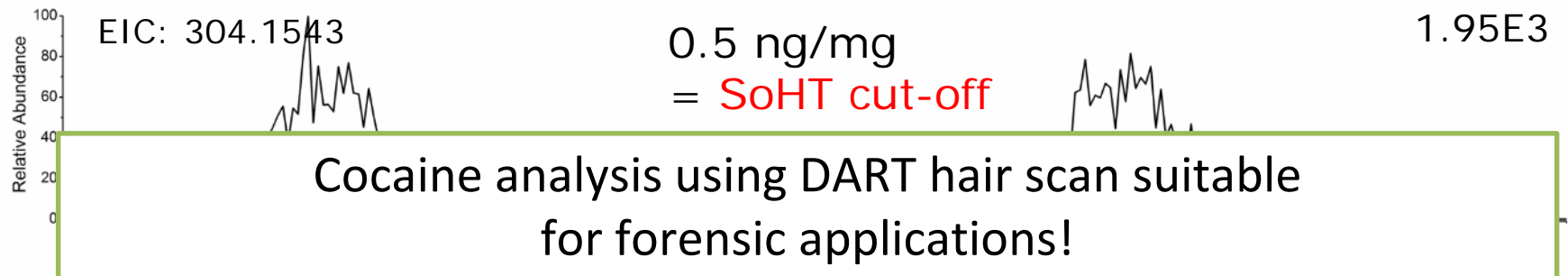
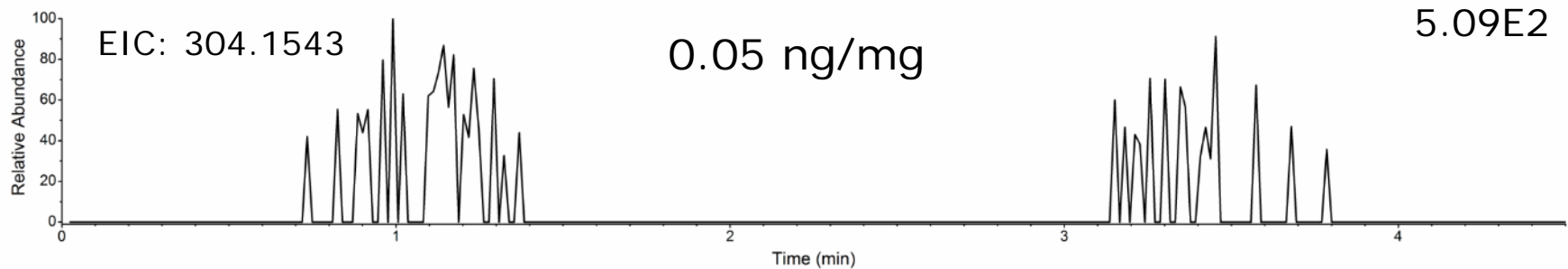
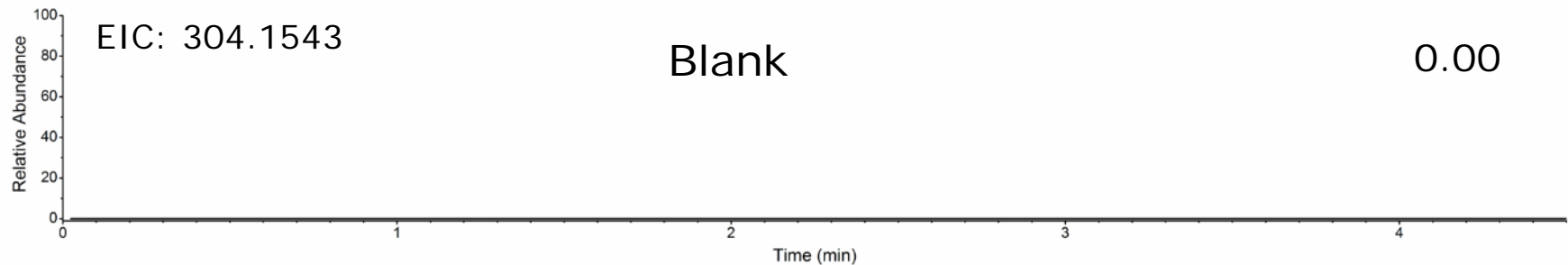
## Chronogram of chronic cannabis user hair sample

(high THC content: ~5 ng/mg)



# Expansion of method: cocaine

Cocaine: different concentrations **spiked** on blank hair



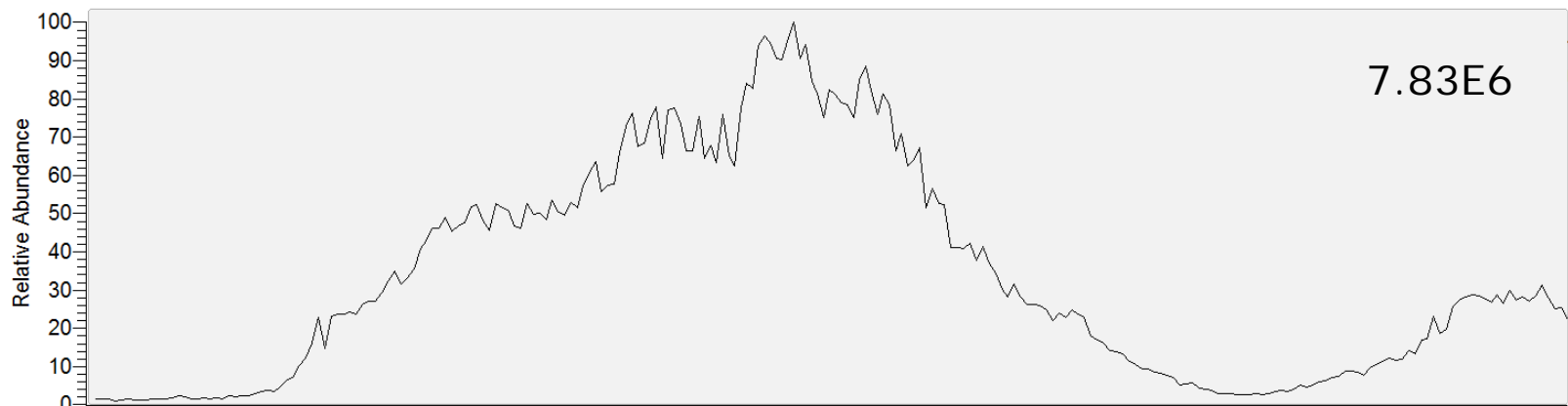


# Expansion of method: cocaine

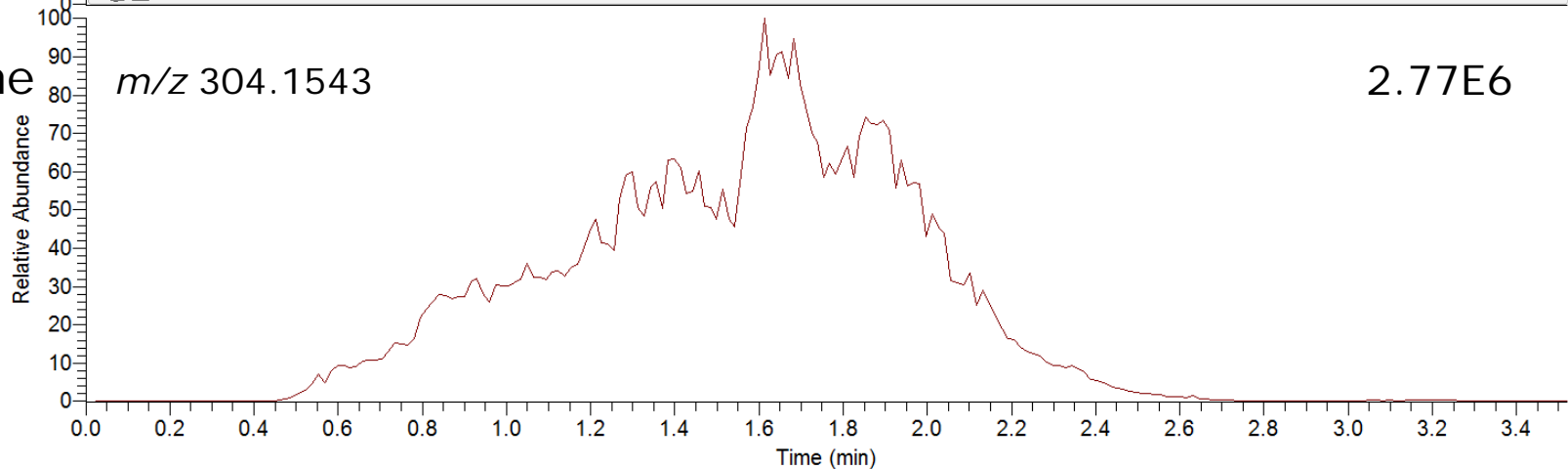
Cocaine user hair sample (> 50 ng/mg)

Reported use: 2.5 gram daily (!)

TIC



Cocaine

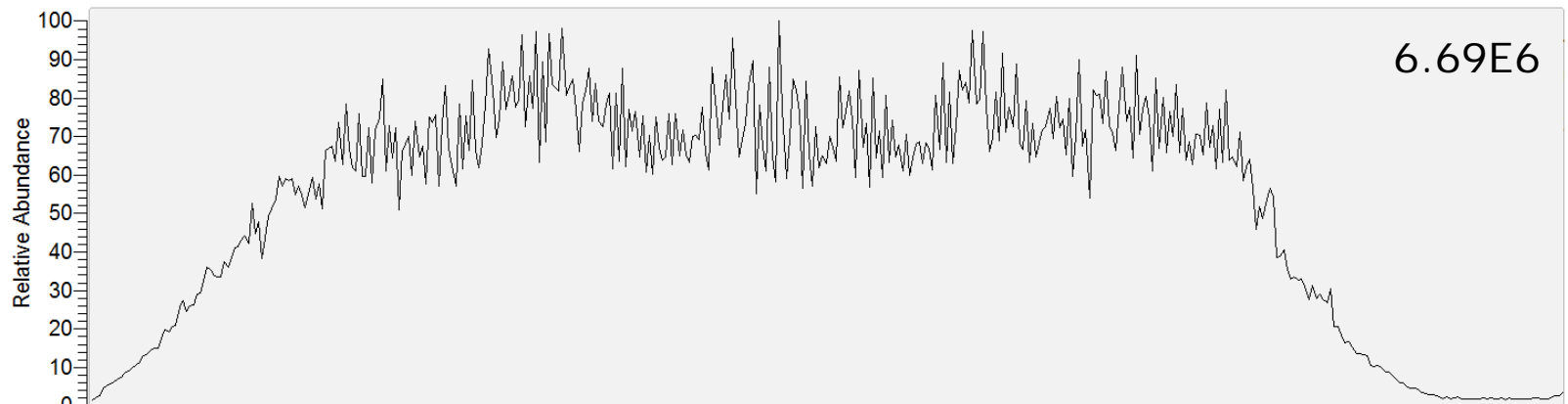


# Expansion of method: cocaine

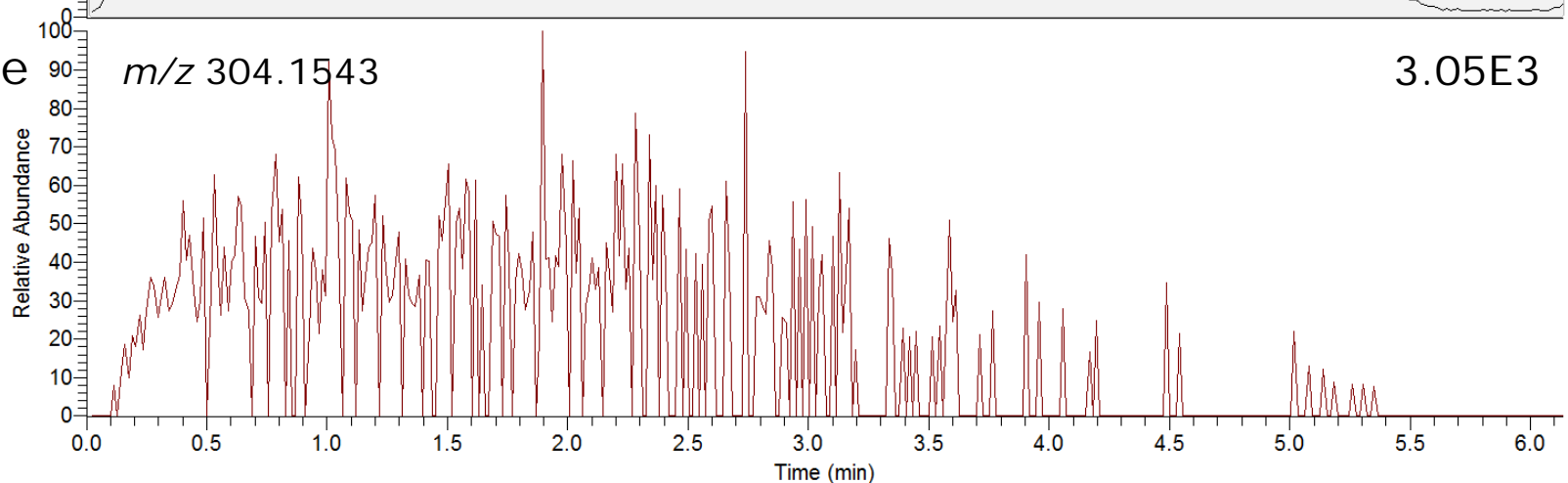
Cocaine user hair sample (0.5 ng/mg = **SoHT cut-off**)

Reported use: **twice a month** 0.5-1 gram

TIC

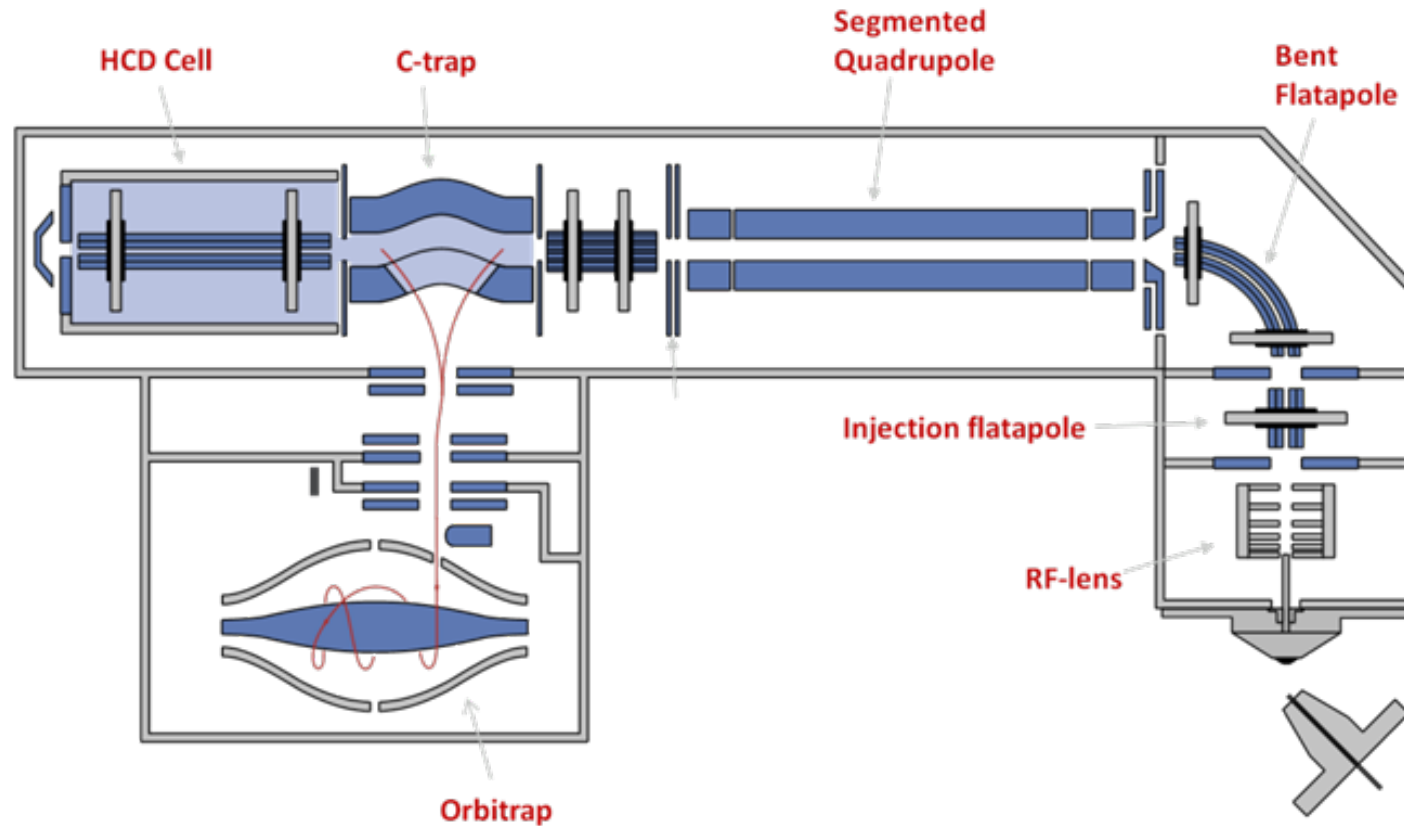


Cocaine



# Confirmation by MS/MS

## Q-orbitrap instrument (Thermo Q-Exactive)



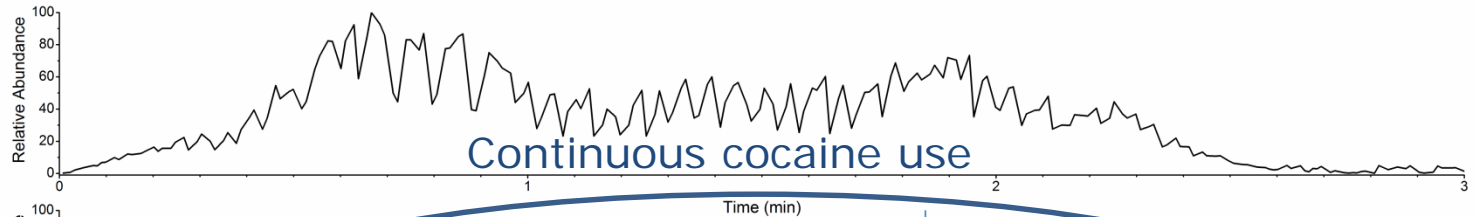
Data dependent MS/MS:  $m/z$  of known compounds in inclusion list,  
when detected: selected for fragmentation in HCD cell

→ Full scan and MS/MS data  
also retrospective !

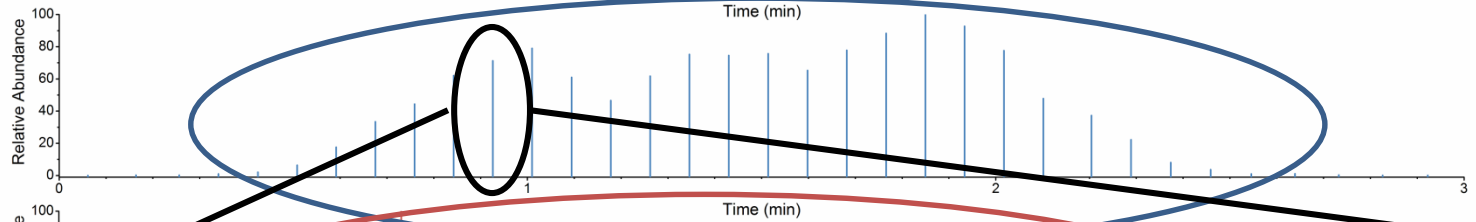
# Confirmation by MS/MS

Cocaine user hair sample

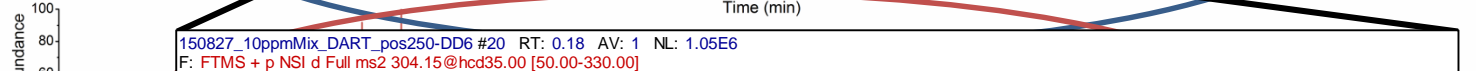
TIC  
(full scan)



Cocaine



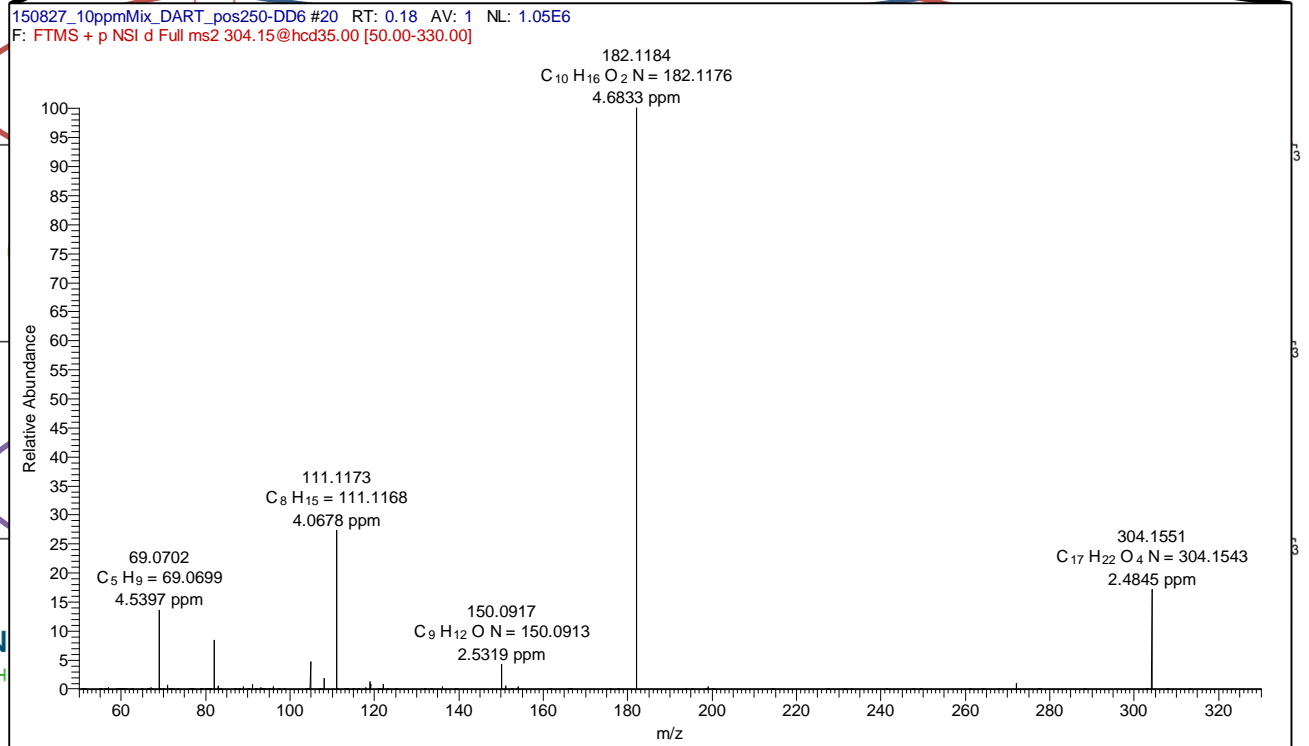
Amphetamine



THC

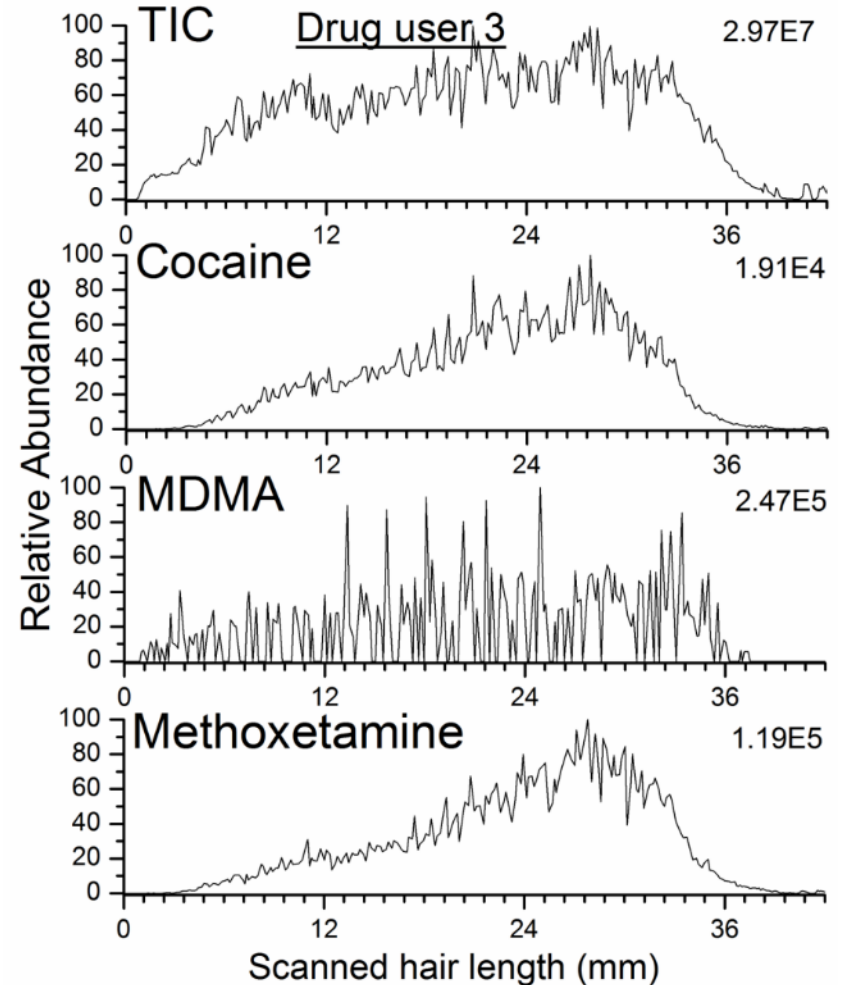
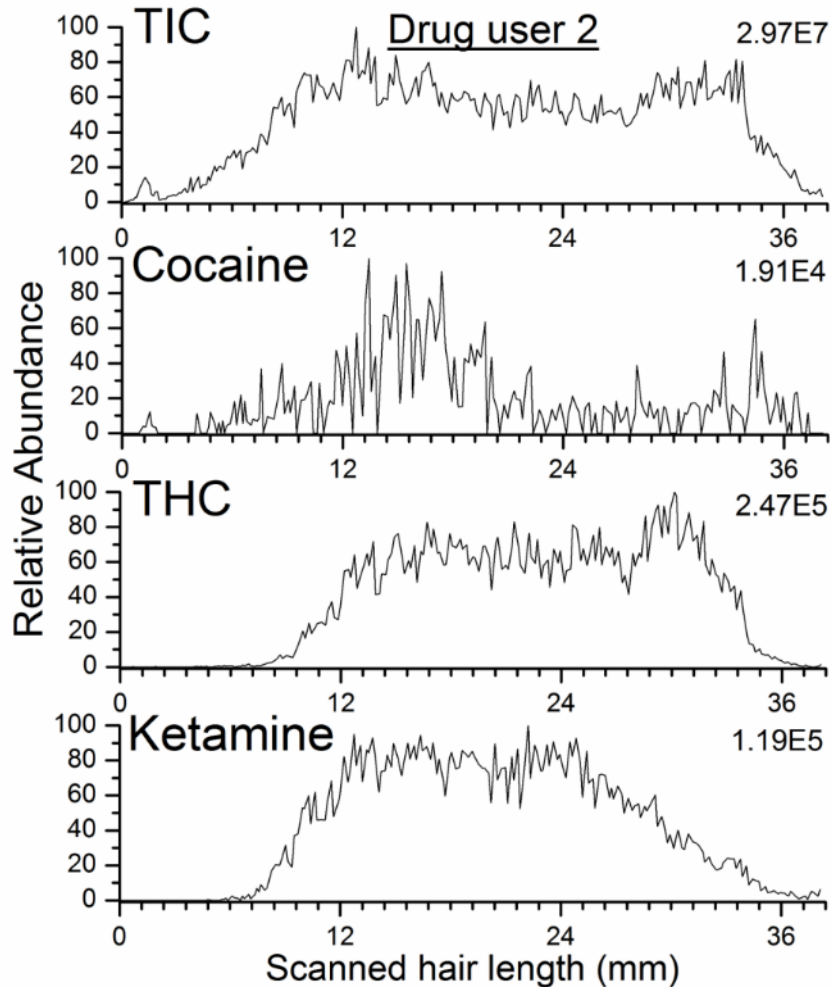


MDMA



# Retrospective data analysis

Multiple drugs detected with different trends



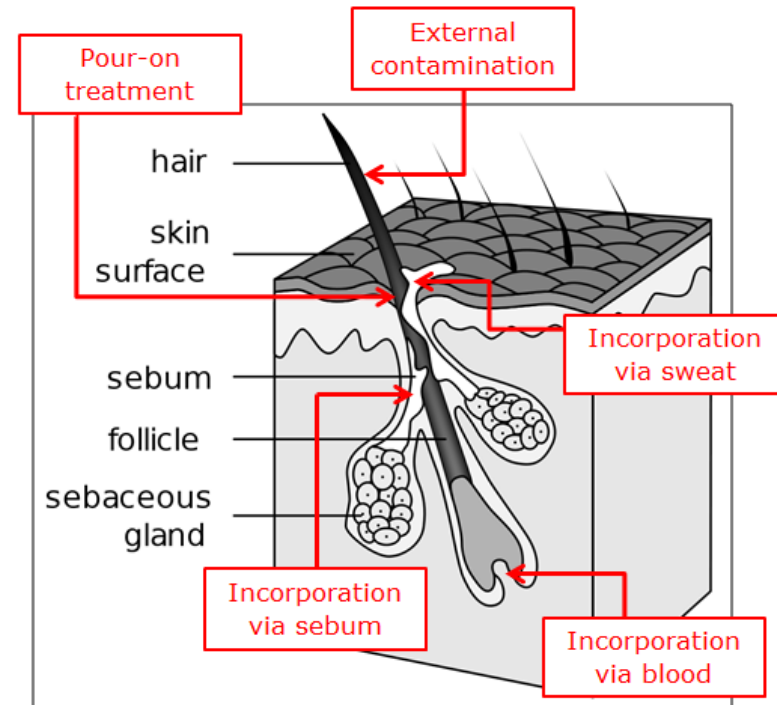


# External contamination or incorporated THC?

**External contamination** is a major issue in forensic hair analysis

**What** is measured using the DART-MS hair scan?

- Incorporated compounds, or
- External contamination



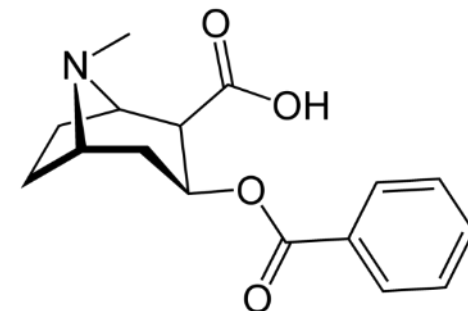
<<http://www.rapgenius.com>>



<<http://www.picstopin.com>>

# Metabolite detection

Cocaine user hair sample



$m/z$  290.1387

Cocaine

$m/z$  304.1543

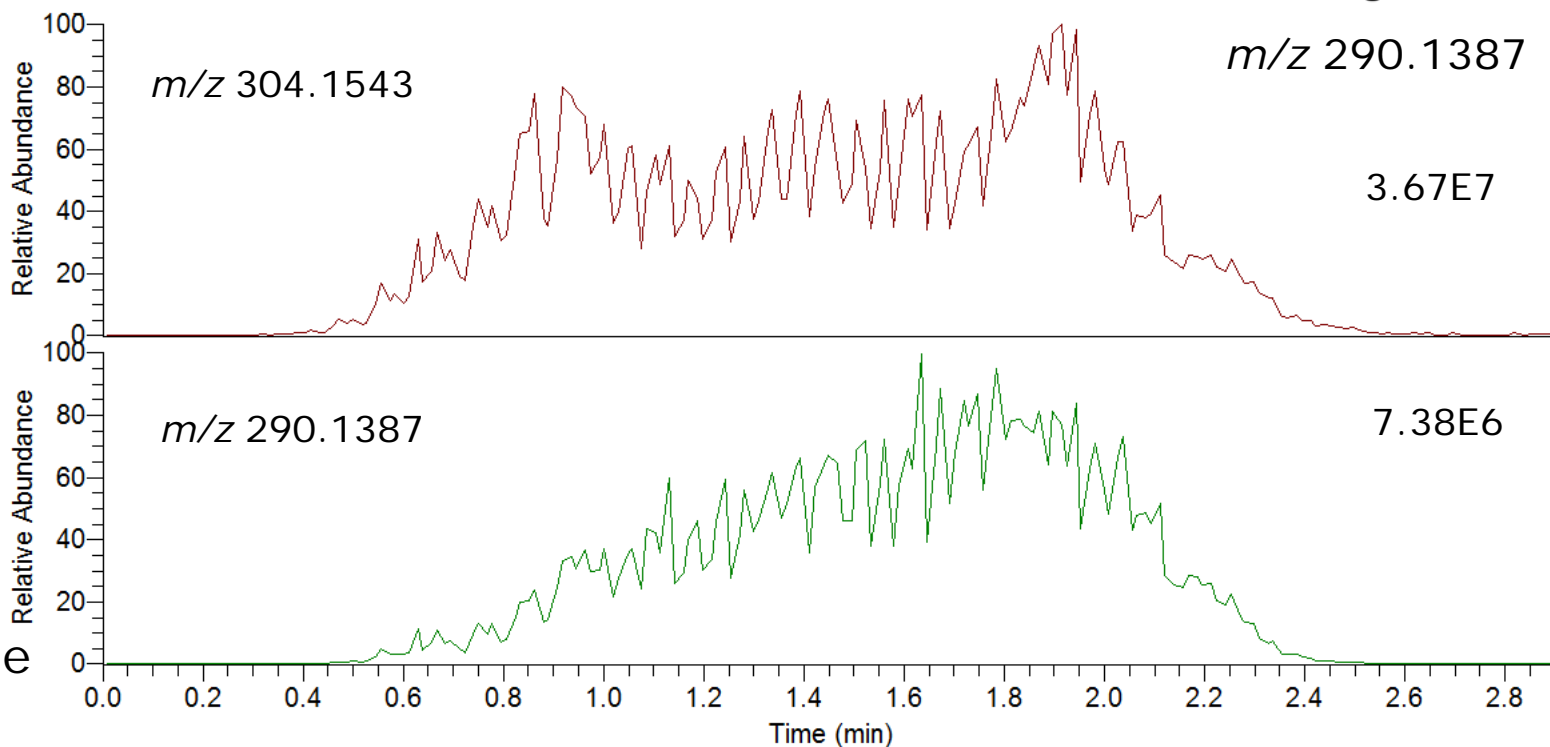
3.67E7

Benzoyl-ecgonine

$m/z$  290.1387

7.38E6

main  
metabolite



BZE at 20% of cocaine intensity shows that detected cocaine is incorporated, not from external contamination

# Conclusions

- ✓ **Direct** analysis of **intact** locks of hair, with sufficient sensitivity and better time resolution
- ✓ **Analysis time** in the order of **minutes**
- ✓ **Targeted** analysis with **confirmation** by **exact mass** and data dependent **product ion scans**
- ✓ Multiple **additional** hits found using **retrospective data analysis**
- ✓ **Metabolite detection** proves measurement of **incorporated compounds**



## Acknowledgments



Wilco Duvivier  
Michel Nielen



Thijs Meijer  
Saskia Sterk



Netherlands Organisation for Scientific Research

