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Identification of Various Controlled Substances by Headspace Chemical Analysis using Headspace Solid Phase Micro-Extraction and GC-MS

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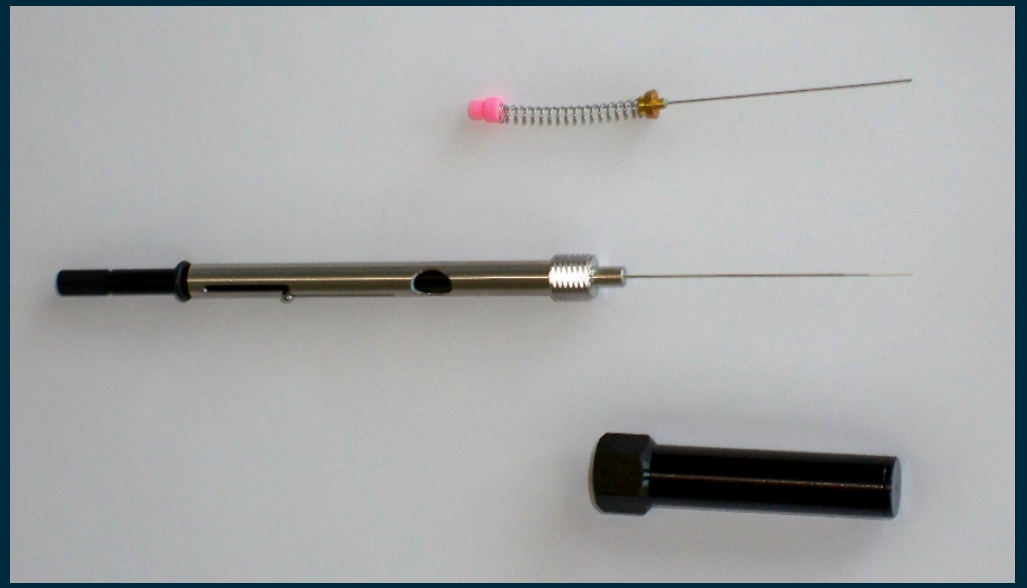
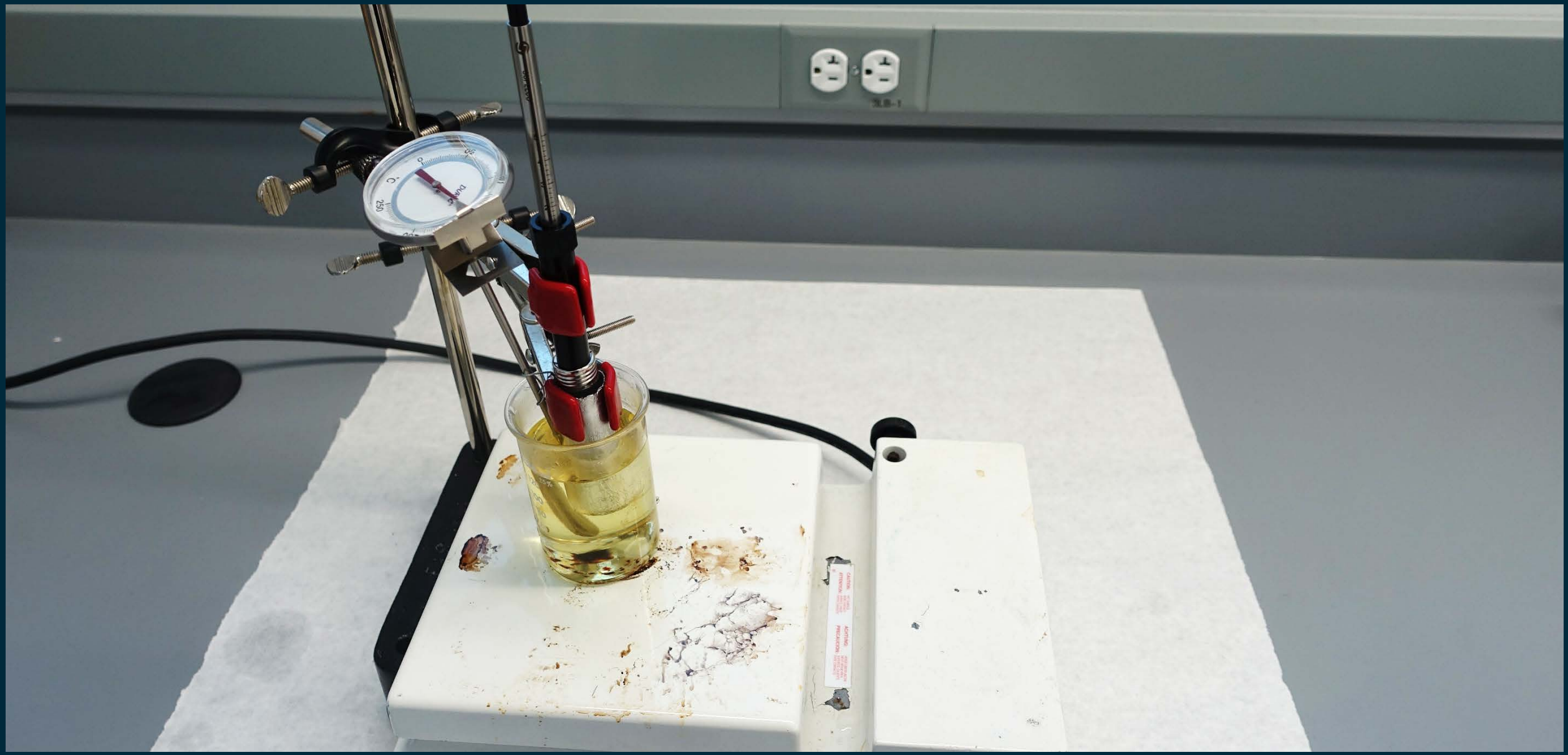
Goal

- **Improve results and preserve evidence while saving effort, time, & money**
  - Some samples are known to cause instrument problems
  - Dirty samples can cause sample carryover
  - Instrument components may need to be replaced
  - Some substances require derivatization
  - Each step in the process presents an opportunity for error

HS-SPME

- **Solid Phase Micro-Extraction Holder (Manual)**
  - Supelco
- **SPME Fiber Assembly**
  - 100 µm Polydimethylsiloxane Coating (PDMS)
- **Headspace Vials**
  - 20 mL





HS-SPME Apparatus

Chemicals

- **Synthetic cathinone standards (26)**
- **Real world case samples**
- **O-(2,3,4,5,6-Pentafluorobenzyl)hydroxylamine hydrochloride***
  - aka PFBHA
- **MSTFA**

*Kerrigan, S. Improved Detection of Synthetic Cathinones in Forensic Toxicology Samples: Thermal Degradation and Analytical Considerations; U.S. Department of Justice, 2015.

Instruments

GC-FID

- **Agilent Technologies 7890A**
- **ZB-50 Column**
- **Adjusted for Manual SPME**

GC-MS

- **Agilent 6890 series GC system**
- **DB-1MS Column**
- **Agilent 5973N Mass Selective Detector**
  - Full scan mode
- **Adjusted for Manual SPME**

Plan

- **Extraction of cathinone standards**
- **Derivatization of cathinone standards**
- **Case Samples**
  - Pills
  - Powders
  - Crystals
  - Marijuana

Extraction of Cathinones

Creating Test Samples

- **Individual Cathinones**
  - Added 20 µL (1 mg/mL) of solvated standard
  - Dried down under nitrogen
  - 26 different cathinones used

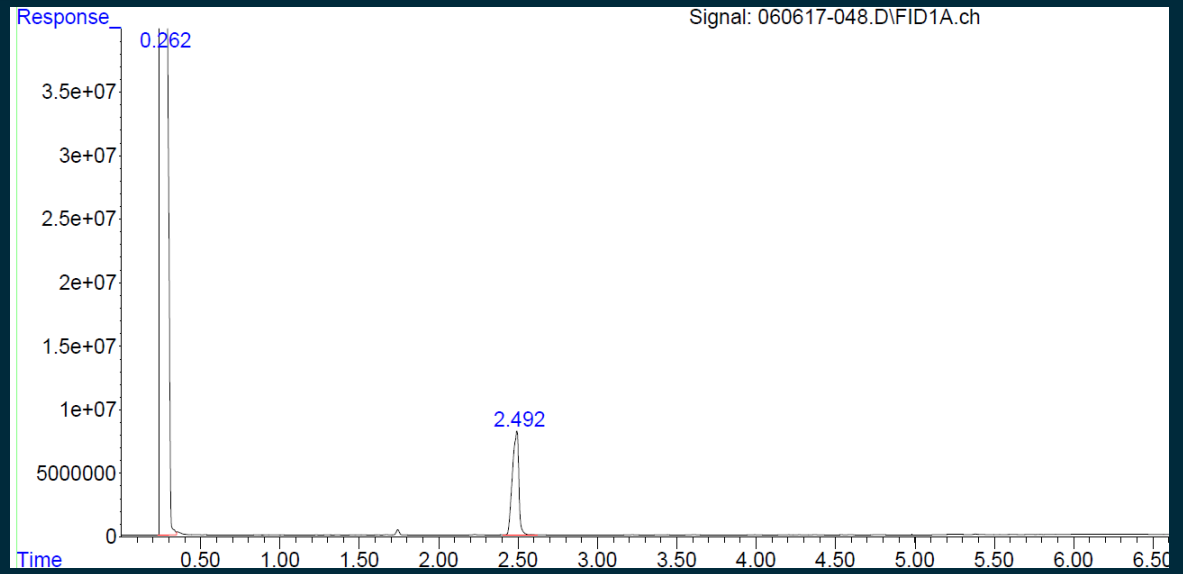
Extraction of Cathinones

Optimized Method

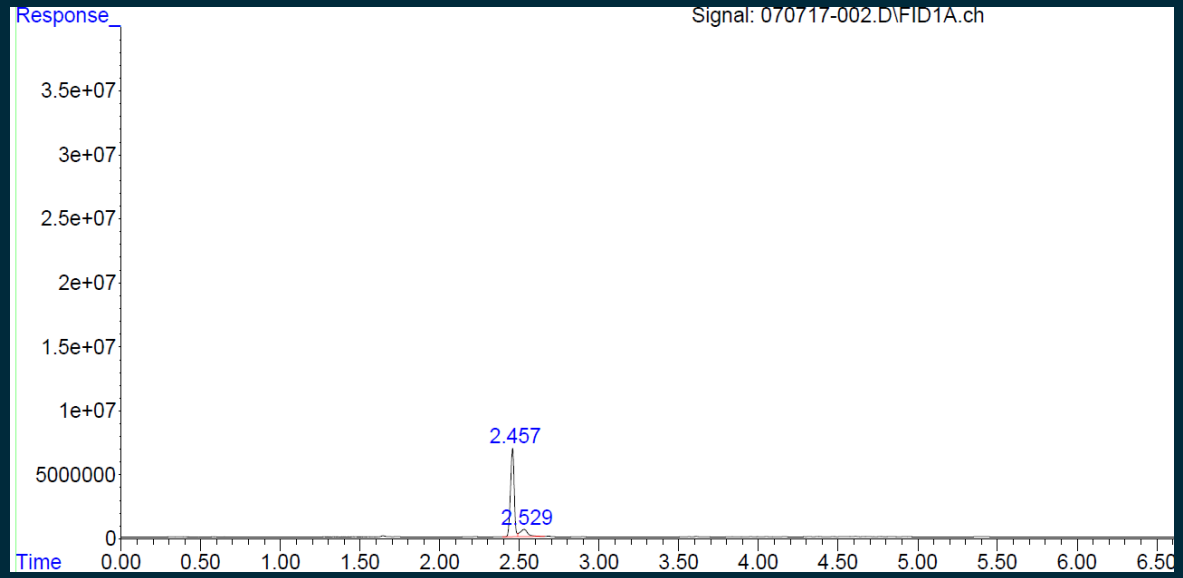
- **Fiber Conditioning**
  - Temperature: 270 °C
  - Time: 10 minutes
  - Needle Depth: 32 mm
- **Extraction**
  - Incubation Time: 5 minute
  - Temperature: 150 °C
  - Exposure Time: 1 minute

Extraction of Cathinones

4-FMC
1 mg/mL standard
Direct Injection



4-FMC
20 µg dry salt
HS-SPME Method

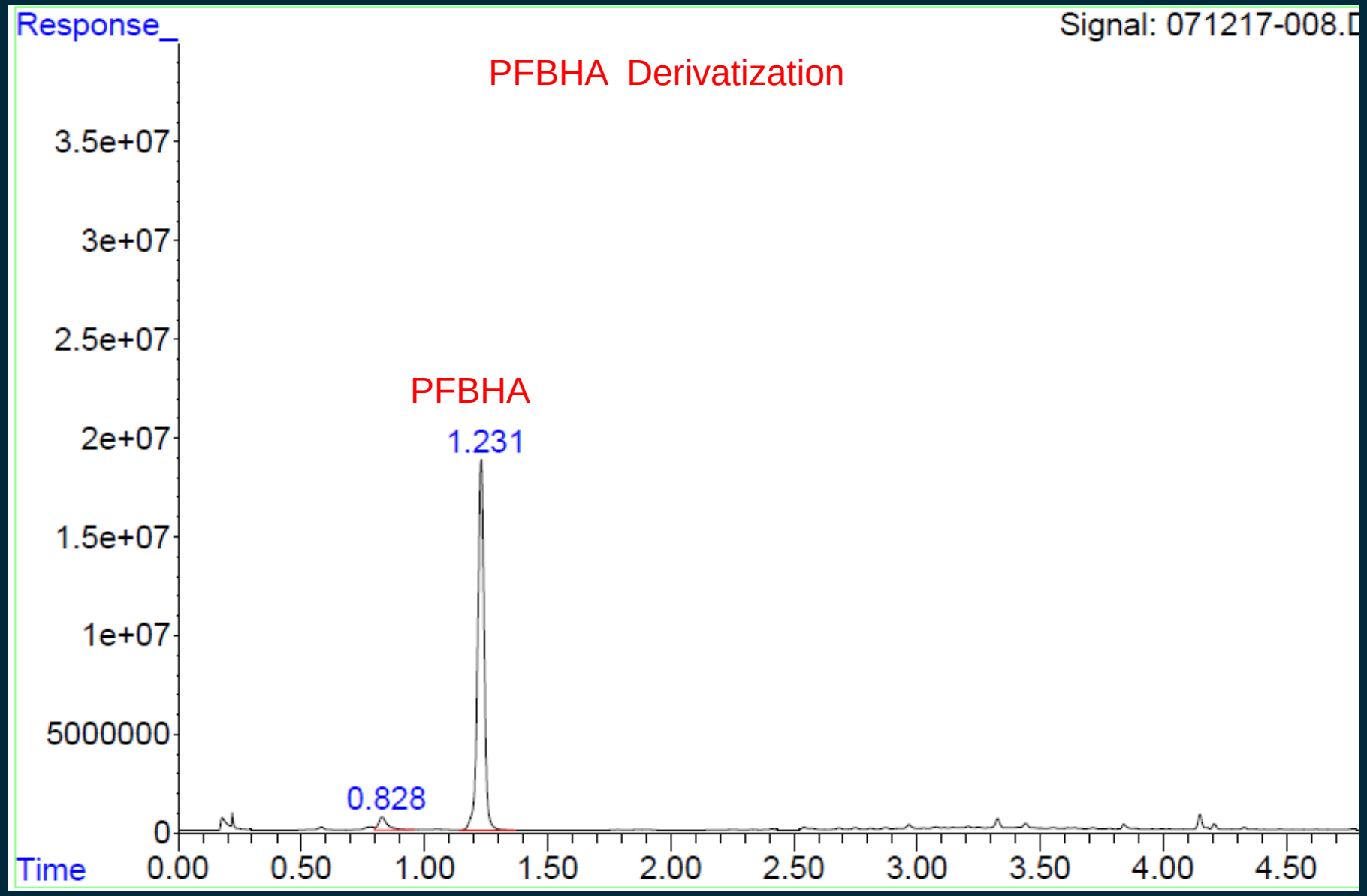


Derivatization of Cathinones

Preparation of Derivatizing Agent

- **PFBHA**
  - 1.398 mg/mL(methanol)
  - Transferred desired amount to insert
    - 10 – 100 µL
  - Dried down under nitrogen
- **Performed extraction using optimized extraction parameters**
  - Small amount of solid produced very intense peak
  - Showed PFBHA was volatile at desired temperature

Derivatization of Cathinones

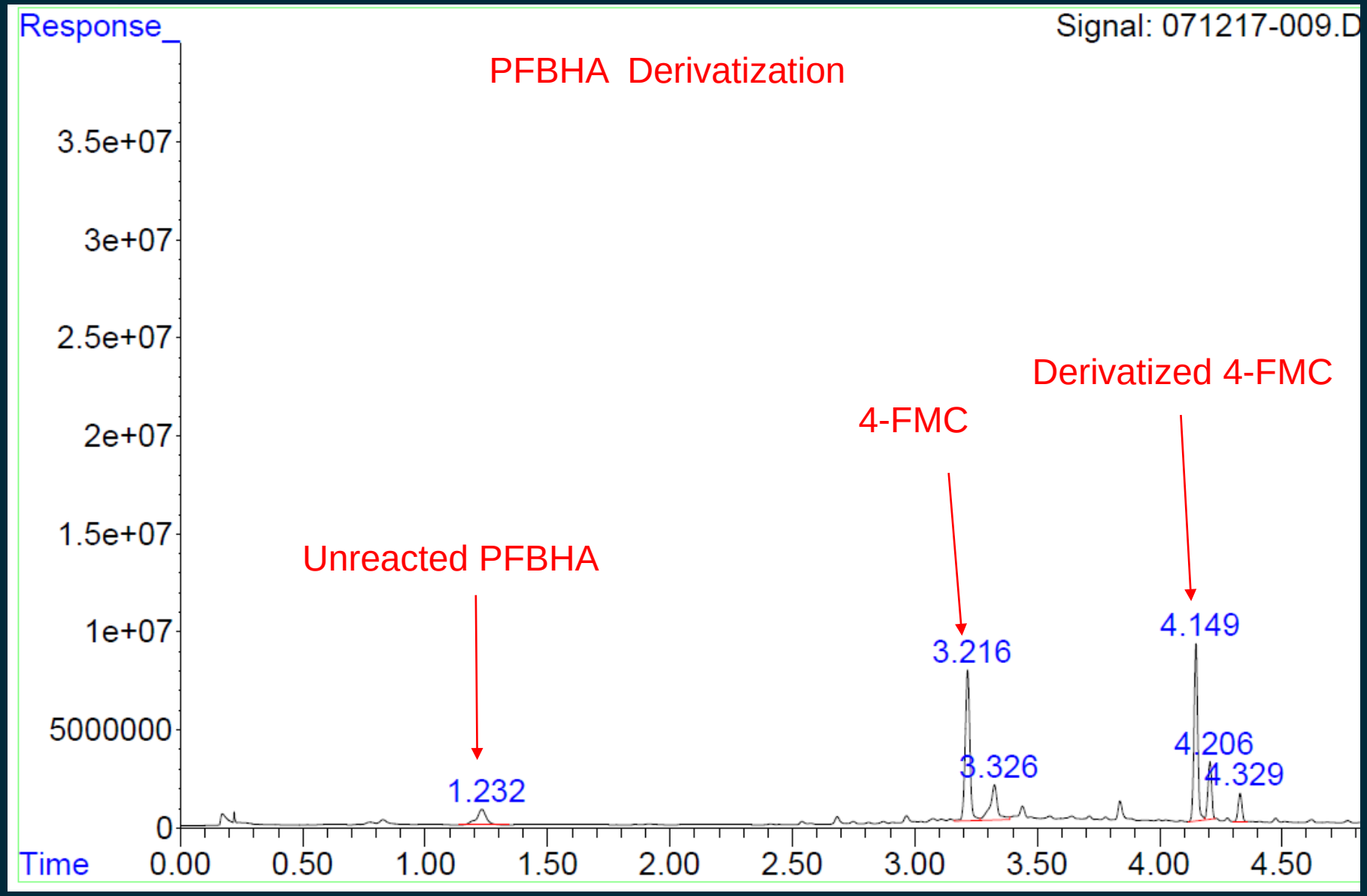


Derivatization of Cathinones

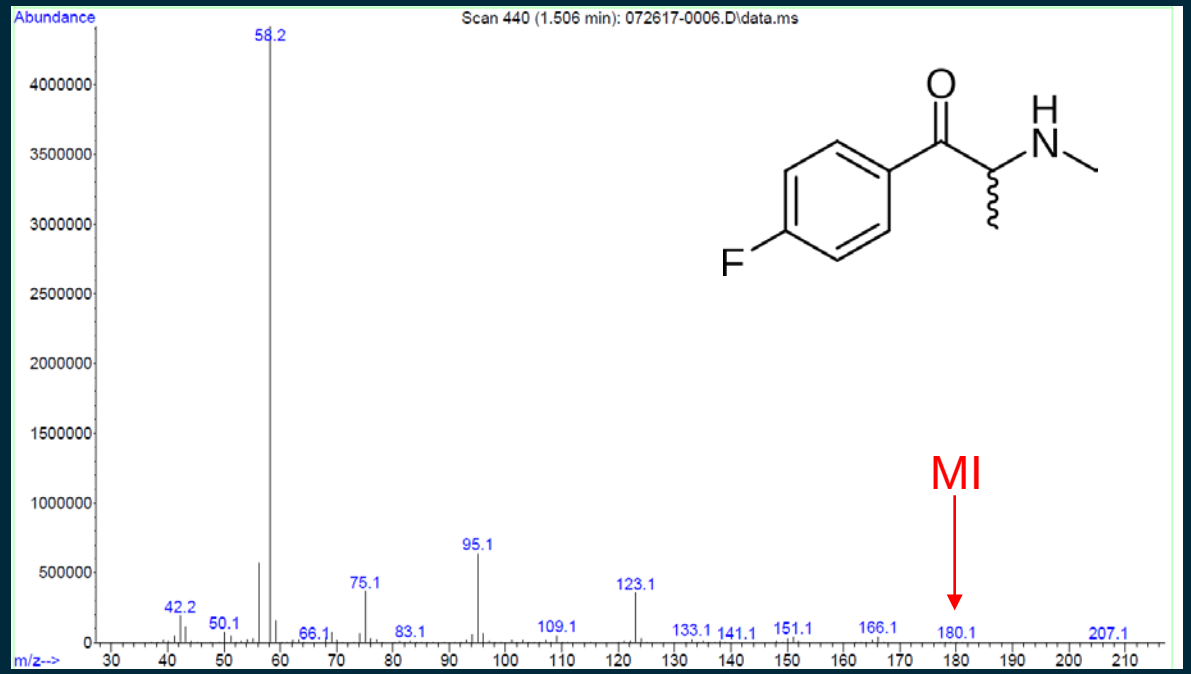
Solventless Derivatization

- **Dried PFBHA insert added to headspace vial**
- **No direct contact between agent and cathinone salt**
  - Derivatization occurs in the headspace
- **All cathinones tested**
  - Extracted for 1 minute, with 10 minute incubation period
    - Longer incubation was to encourage reaction completion
- **Amount of agent adjusted for MS runs**

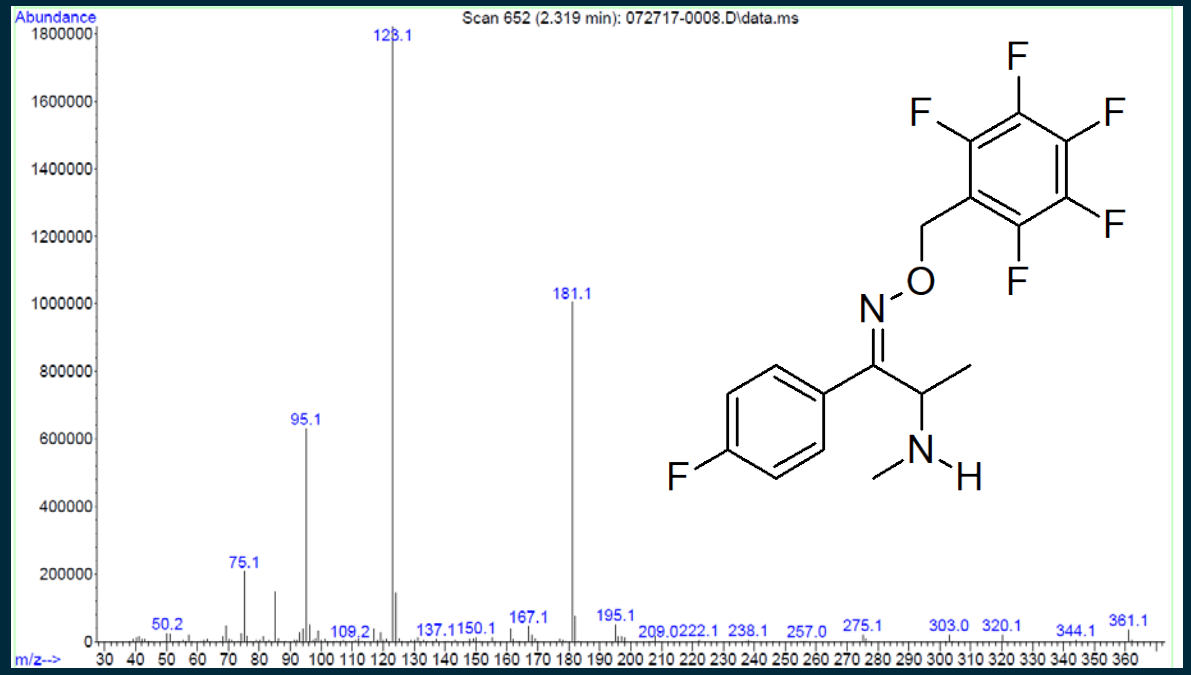
Derivatization of Cathinones



Derivatization of Cathinones



MS of 4-FMC



MS of Suspected Derivatized Product

Application to Case Samples

- **Used parameters from cathinone study**
  - Adjusted to optimize as needed

- **Sample size dependent on form**
  - Explored both minimal mass needed and what facilitated least prep

Case Samples

Pills

- **Whole tablets used for testing**
  - Adderall
  - Soma
  - Ecstasy

Powders

- **Cocaine**
  - Different cutting agents greatly impacted extraction efficacy

Crystals

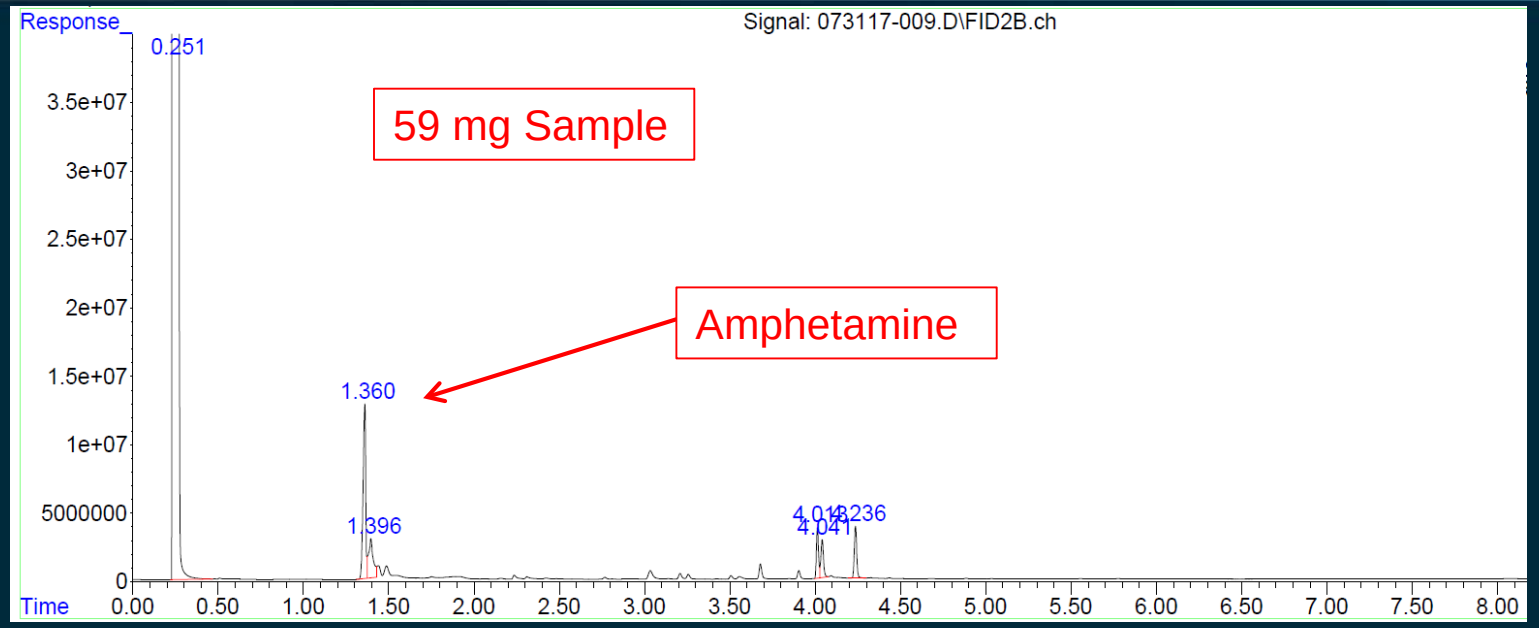
- **Methamphetamine and “bath salts”**
  - Small crystal samples used
  - Very volatile relative to other specimens

Botanicals

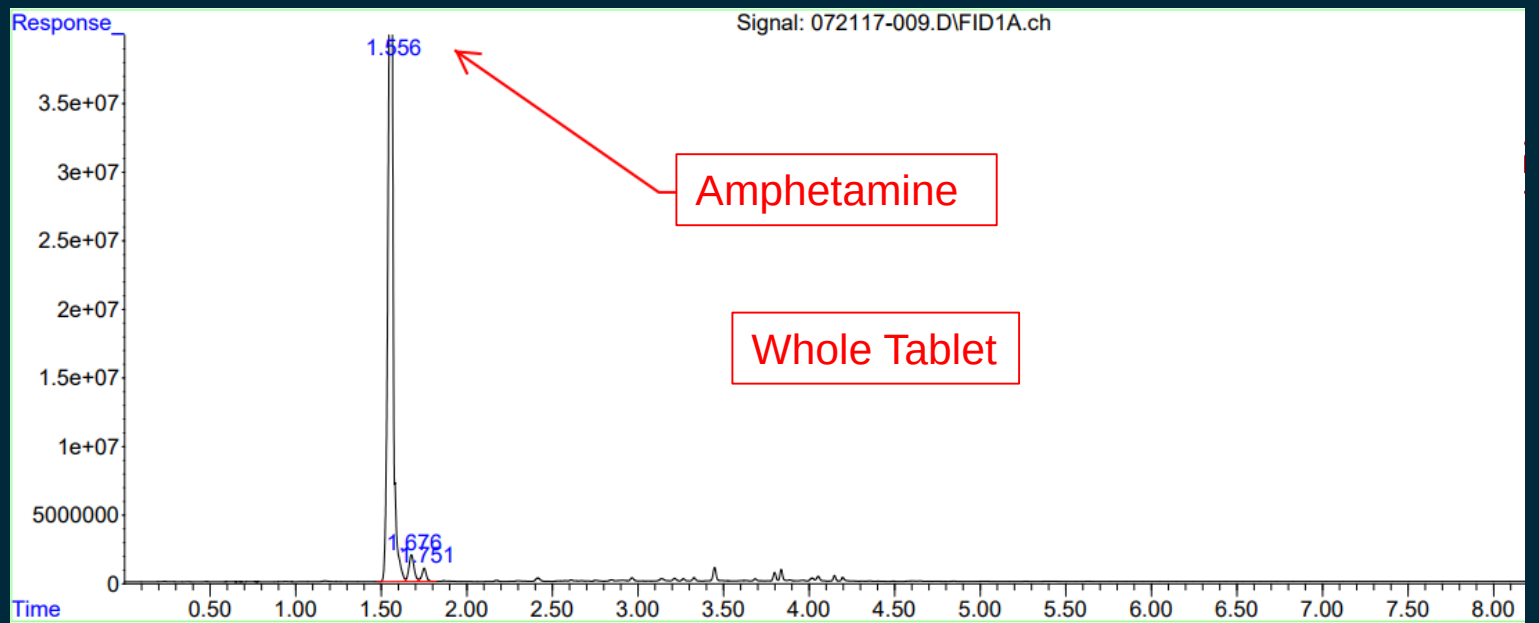
- **Marijuana**
  - Whole bud tested
  - Headspace MSTFA derivatization explored

Adderall GC-FID

Methanol Extraction

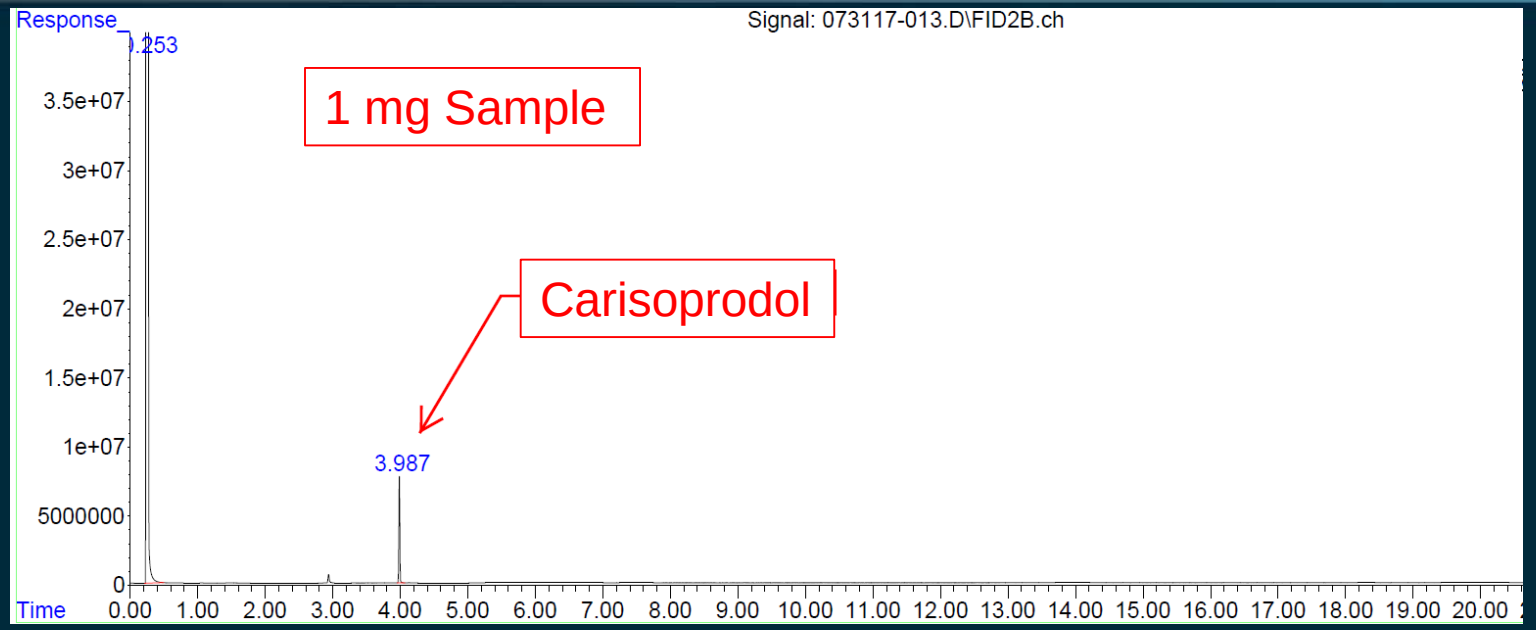


HS-SPME Method

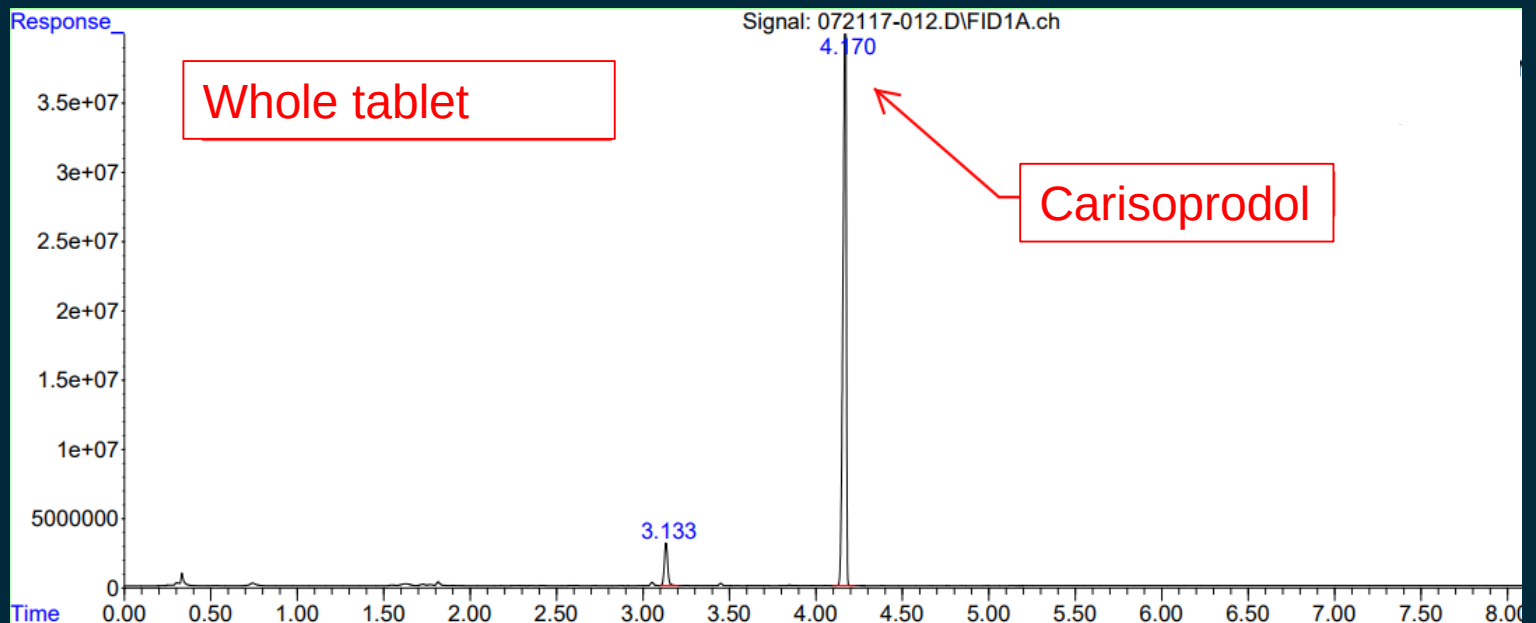


Soma GC-FID

Methanol Extraction

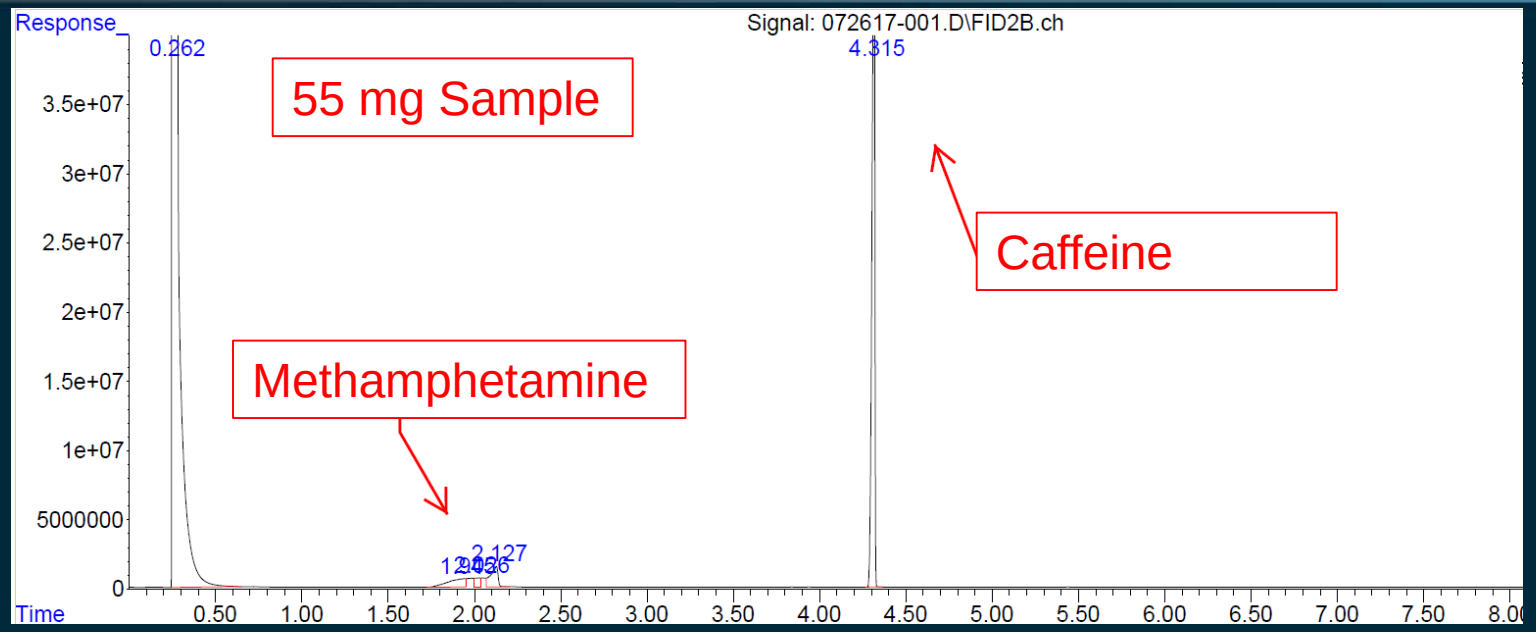


HS-SPME Method

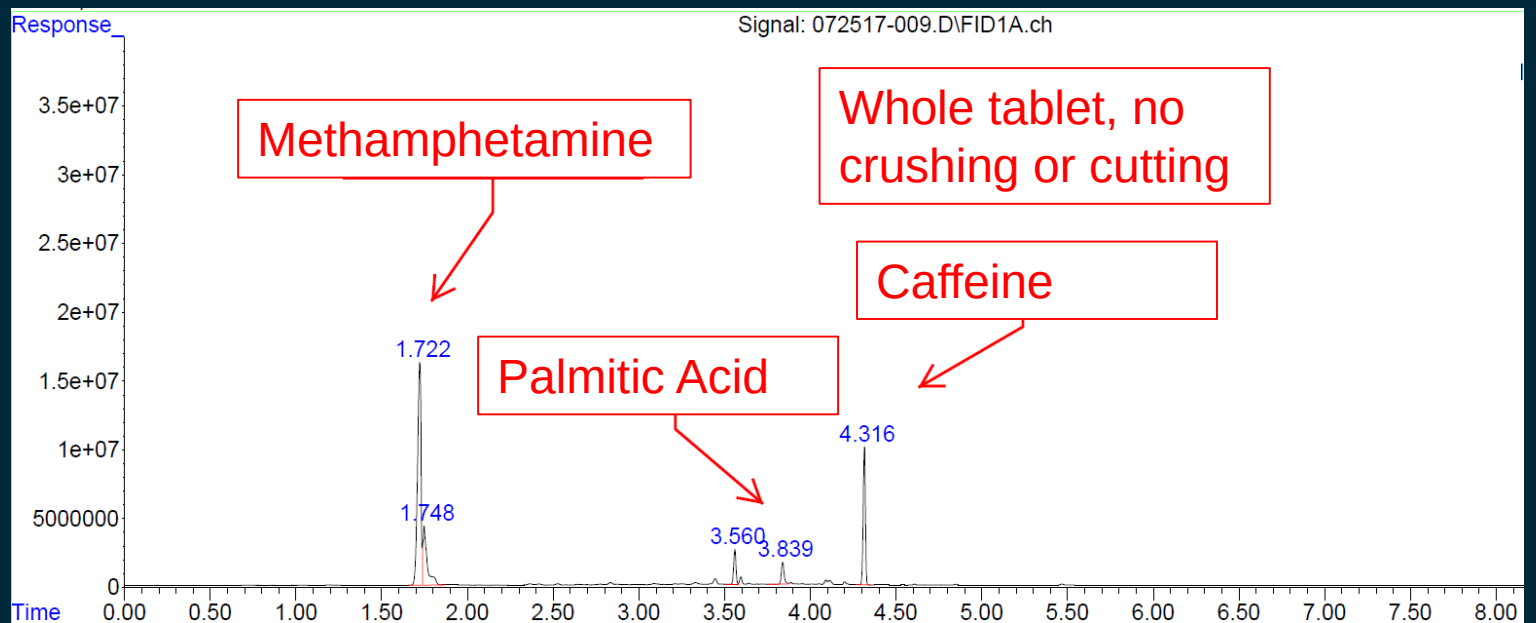


Ecstasy GC-FID

Methanol Extraction

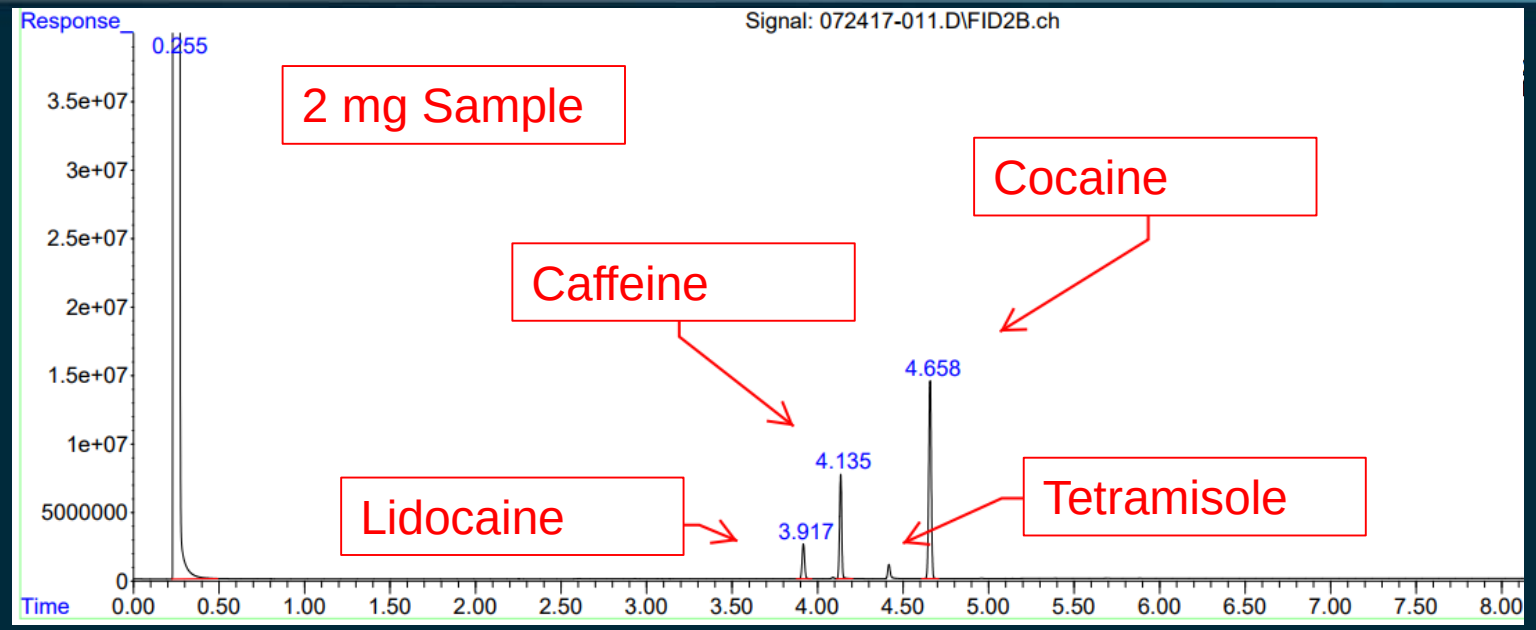


HS-SPME Method

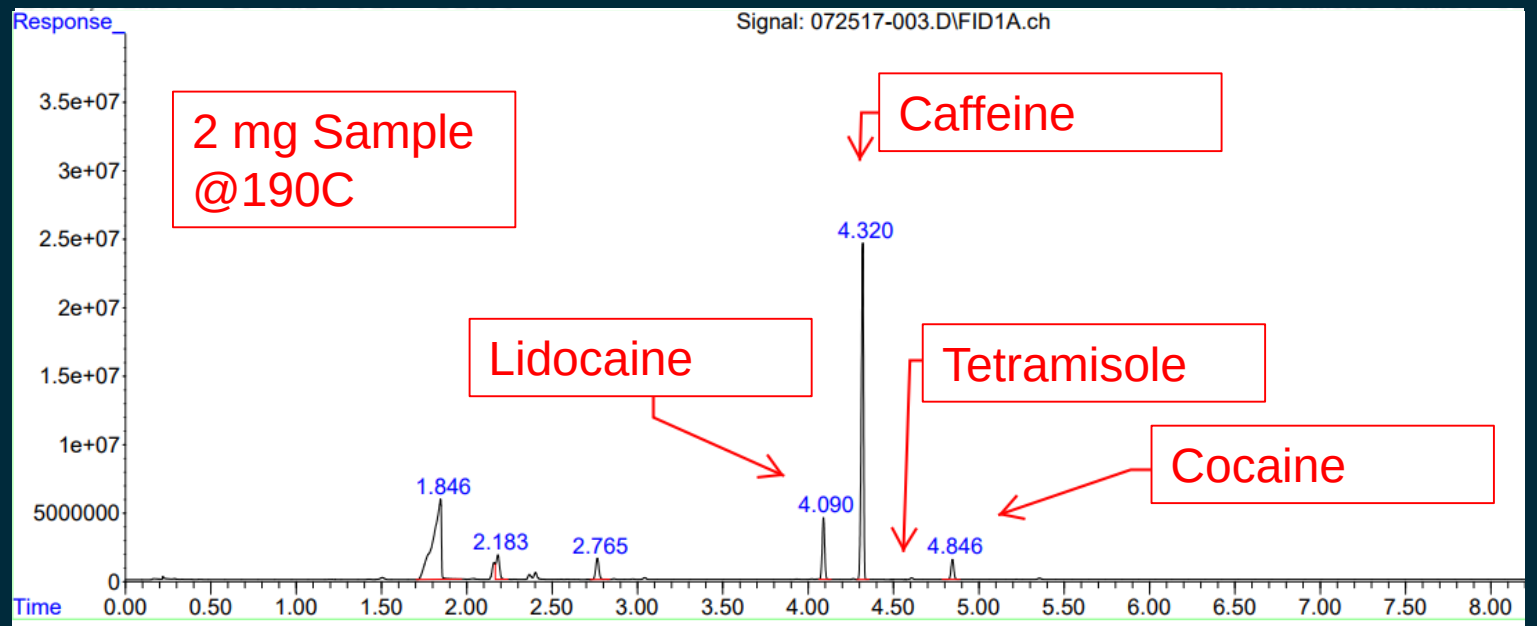


Cocaine Case GC-FID

Methanol Extraction

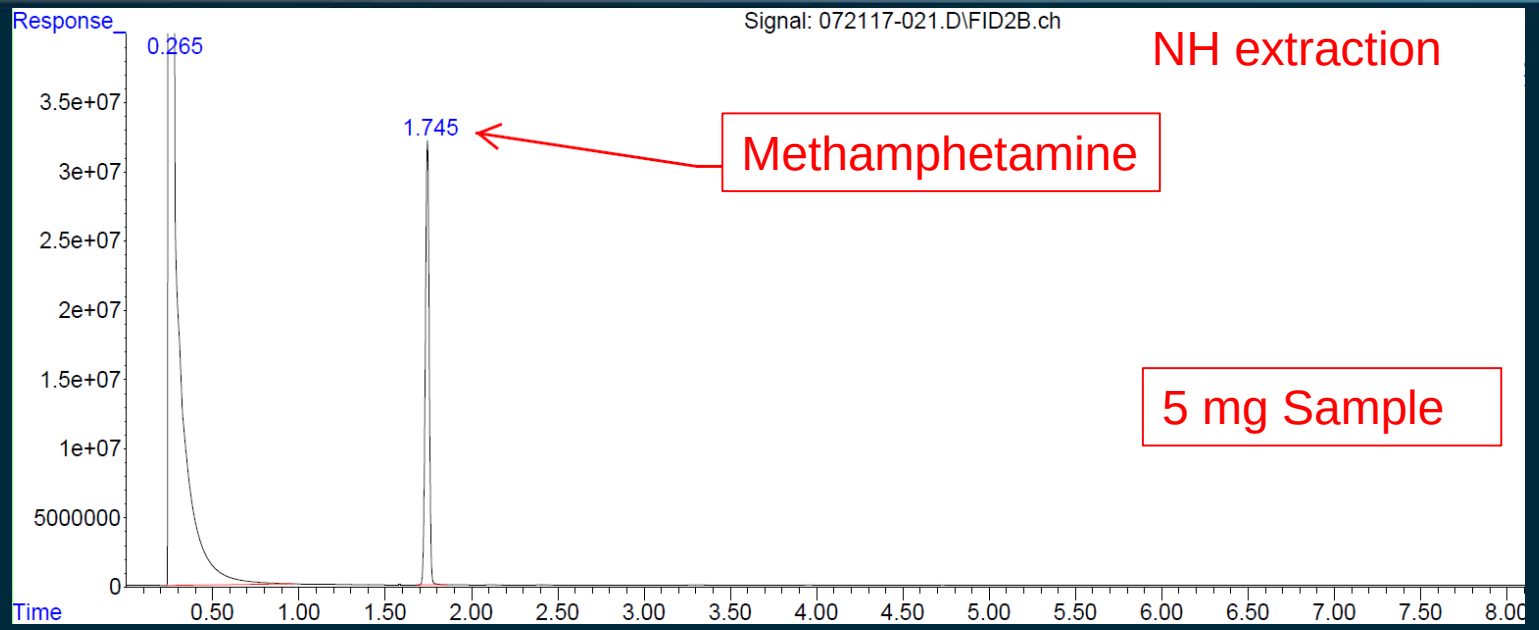


HS-SPME Method

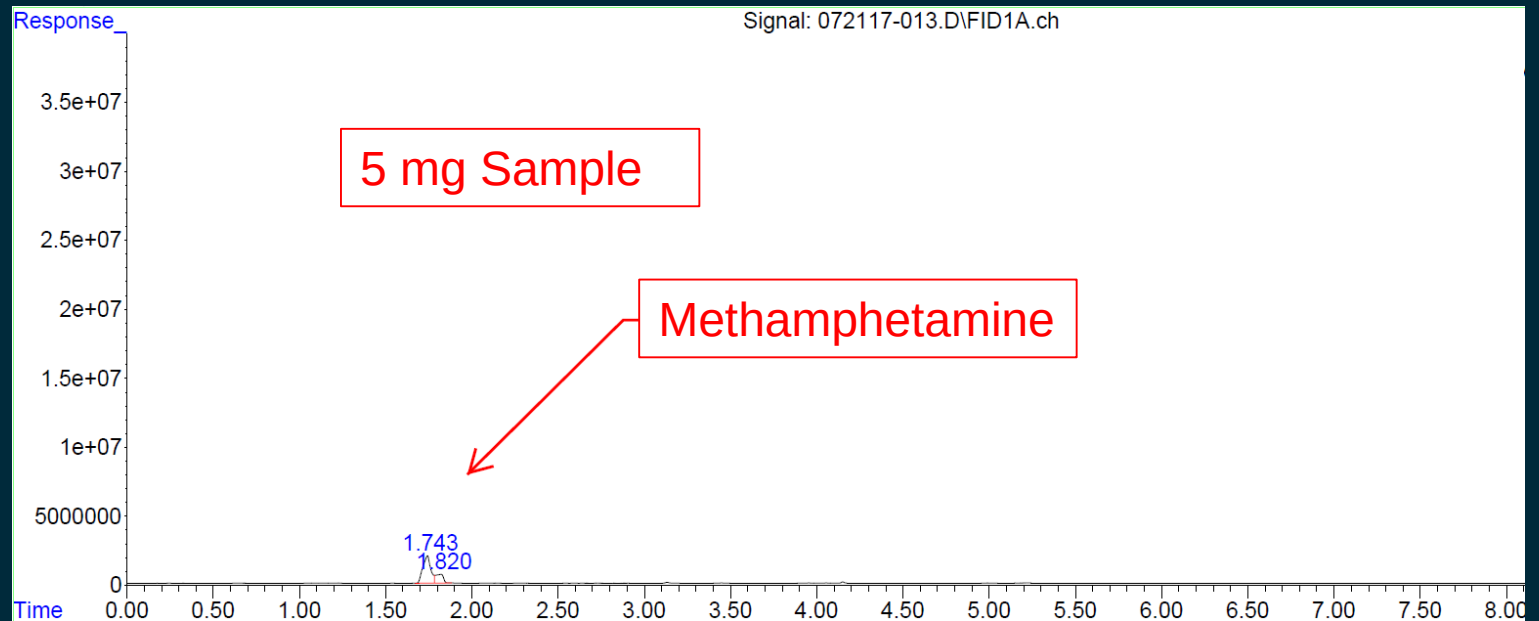


Methamphetamine GC-FID

Base/Hexane Extraction

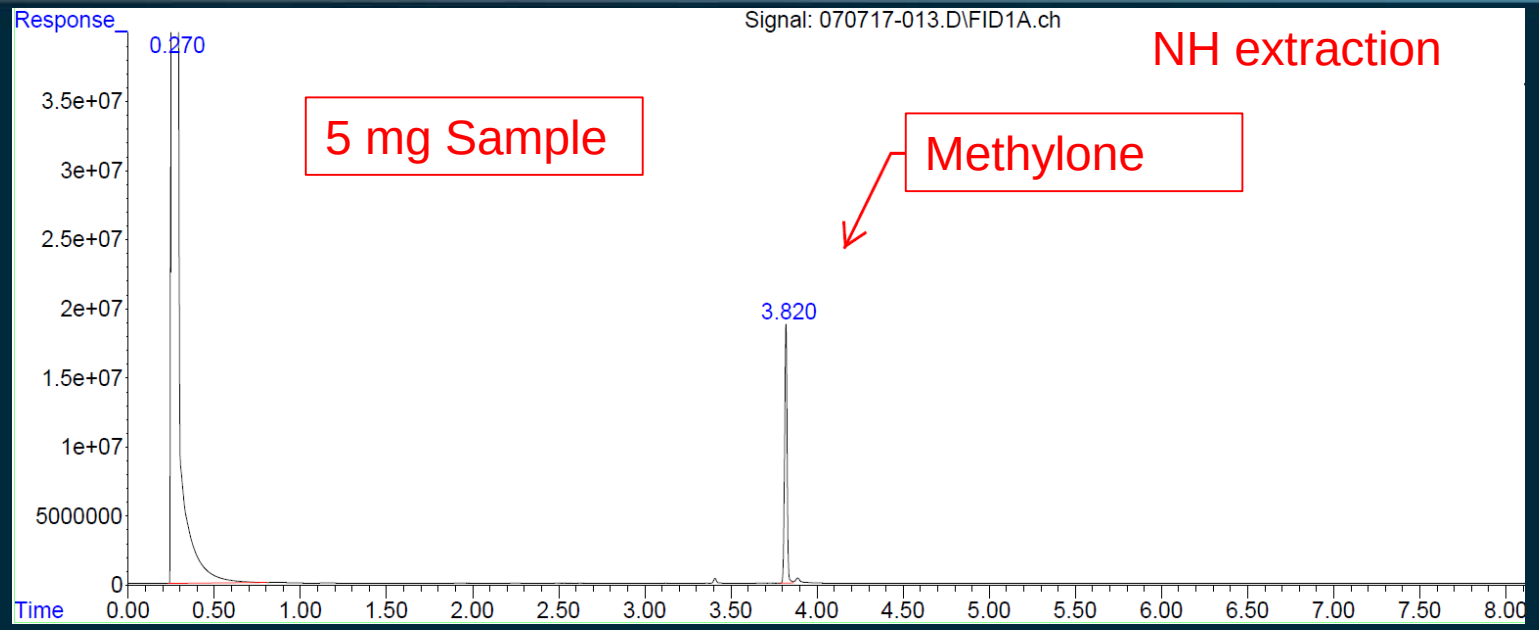


HS-SPME Method

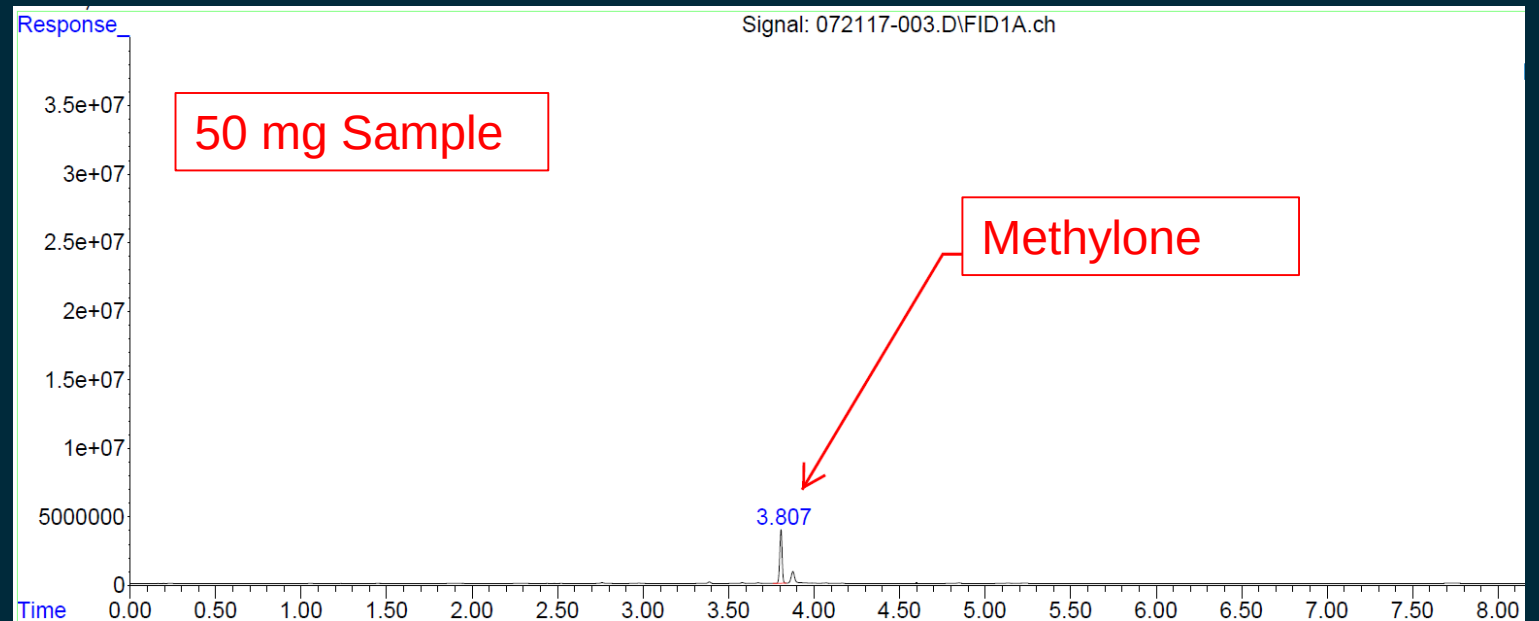


Methylone GC-FID

Base/Hexane Extraction

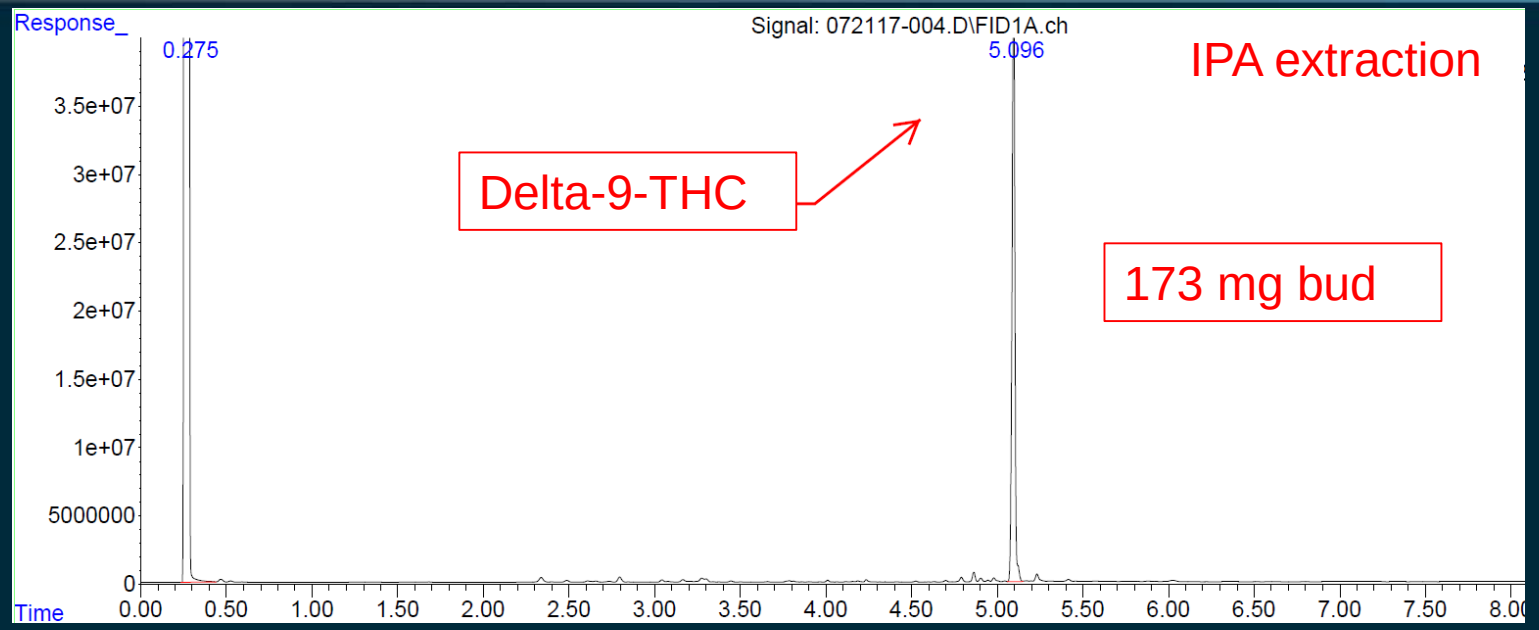


HS-SPME Method

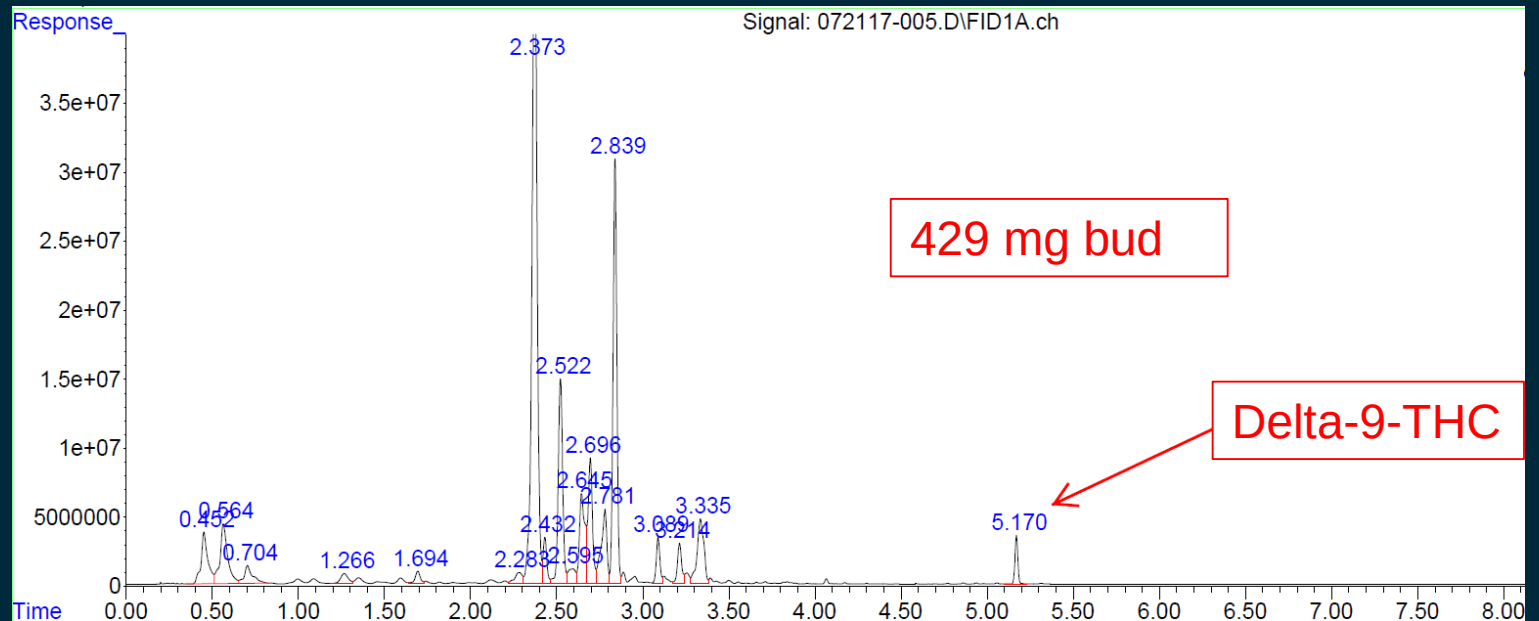


Marijuana GC-FID

Isopropyl Alcohol Extraction



HS-SPME Method



Conclusions

- **Many controlled substances can be extracted using HS-SPME**
  - Extraction can occur at microgram levels
  - Can extract from variety of matrices
  - Minimal sample preparation
  - No wet chemistry, most items remained physically intact
- **Minimal carryover**
- **No single catch all method**
  - Analyte volatility varies
- **Higher temperatures could extract additional analytes**
- **Derivatization can occur in the headspace**
  - Rapid derivatization

Continuing Project

- **High capacity SPME fibers**
- **Derivatization optimization**
- **Extraction optimization for alternative matrices**
- **Additional controlled substances**
- **Automation**

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Thank you!

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Cathinone Standards

- **2,3-Methylenedioxypyrovalerone**
- **2,3-Pentylone**
- **2,4-Dimethylethcathione**
- **2,4-Dimethylmethcathinone**
- **2-Methoxymethcathinone**
- **3-Fluoromethcathinone**
- **3-Methylbuphedrone**
- **3-Methylethcathinone**
- **3-Methylmethcathinone**
- **4-Bromomethcathione**
- **4-Chloromethcathinone**
- **4-Ethylmethcathinone**
- **4-Fluorormethcathinone**
- **4-Methylbuphedrone**
- **4-Methylmethcathinone**
- **α-PVP**
- **Cathinone**
- **Dimethylone**
- **Dipentylone**
- **Ethylone**
- **Eutylone**
- **MDPBP**
- **MDPV**
- **Methedrone**
- **Methylone**
- **PV8**

- Cayman Chemical