

# The DART™ Revolution: Fast, Non-Contact, Soft Ionization without Sample Preparation

by

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Until the DART era, samples could only be analyzed by mass spectrometry if they were...

- Put into a high vacuum
  - Sample loss
  - Vacuum leaks
- Dissolved in liquids and injected
  - Plumbing
  - Unwanted chemical reactions
  - Environmental loading from solvents
- Irradiated (lasers or radioactivity)
  - Safety

# Why isn't this good enough?

- **Time**
  - Time critical situations
  - You need an answer RIGHT NOW
- **Effort**
  - Dissolve/extract sample, filter, solvent choice, clean and change plumbing, etc.
- **Expense**
  - Operator cost
  - Chemicals
  - Waste disposal
  - Plumbing

# DART<sup>tm</sup> Chronology

- 2001 – Created by Laramee
- 2002 – Developed by Cody and Laramee within Restricted program
- 2003 – Chemical Warfare Agent testing
- 2003 – Limited disclosure to academic and industrial concerns
- 2004 – Demonstration of methods to militarily unique substances

# DART<sup>tm</sup> Chronology

- 2004 – DART is commercially available
- 2004 – IonSense, Inc is created
- 2005 – Patents issued, PittCon Gold Award, R&D 100 Award, TV debut
- 2005 – Publications in closed journals

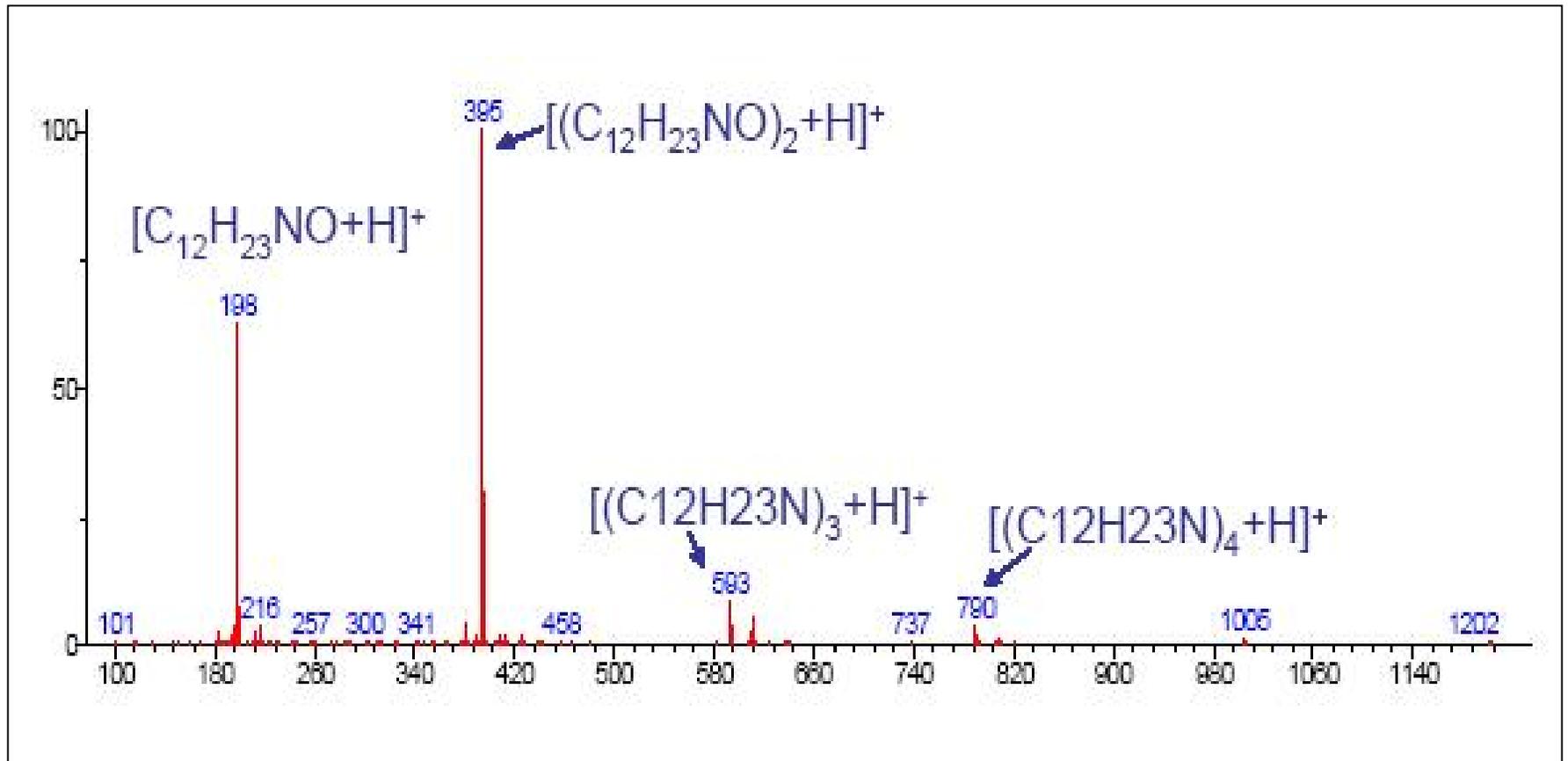
# Capabilities of DART

- Instant analysis. *Skip the prep, go direct.*
- Safe, no solvents
- Detects low-volatility analytes (pico-Torr)
- Non-contact sampling
- Samples ionize at atmospheric pressure and ambient conditions

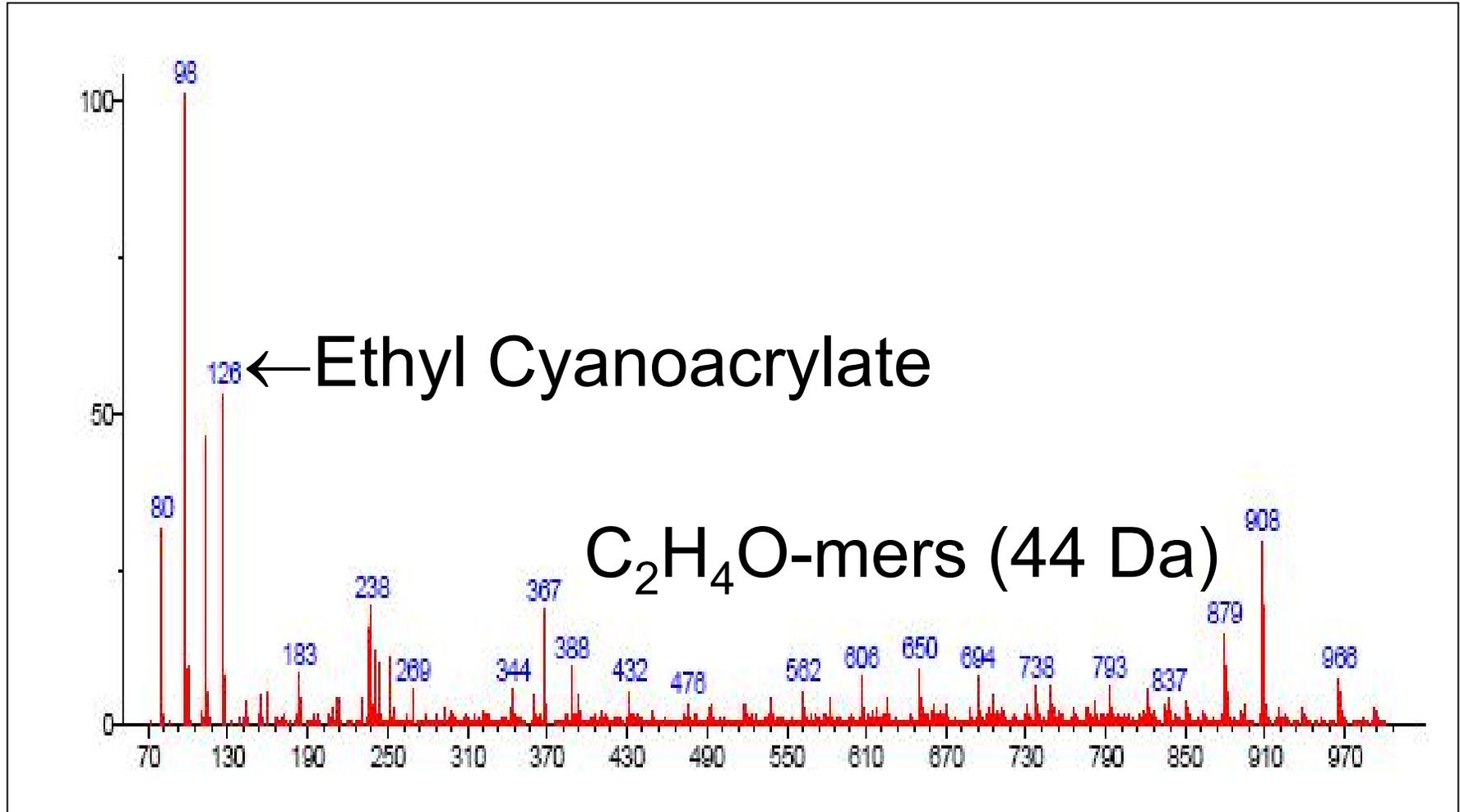
# DART Gives Clean Spectra of Polymers, Resins, Glues, etc

- Nylons
- Polypropylene and polyethylene
- Polyethylene terephthalate (PET)
- Polyesters
- Poly(methylmethacrylate) (PMMA)
- Polycarbonate
- Cellulose

# Nylon 12 on Glass



# A Well Known Cyanoacrylate Glue on Metal



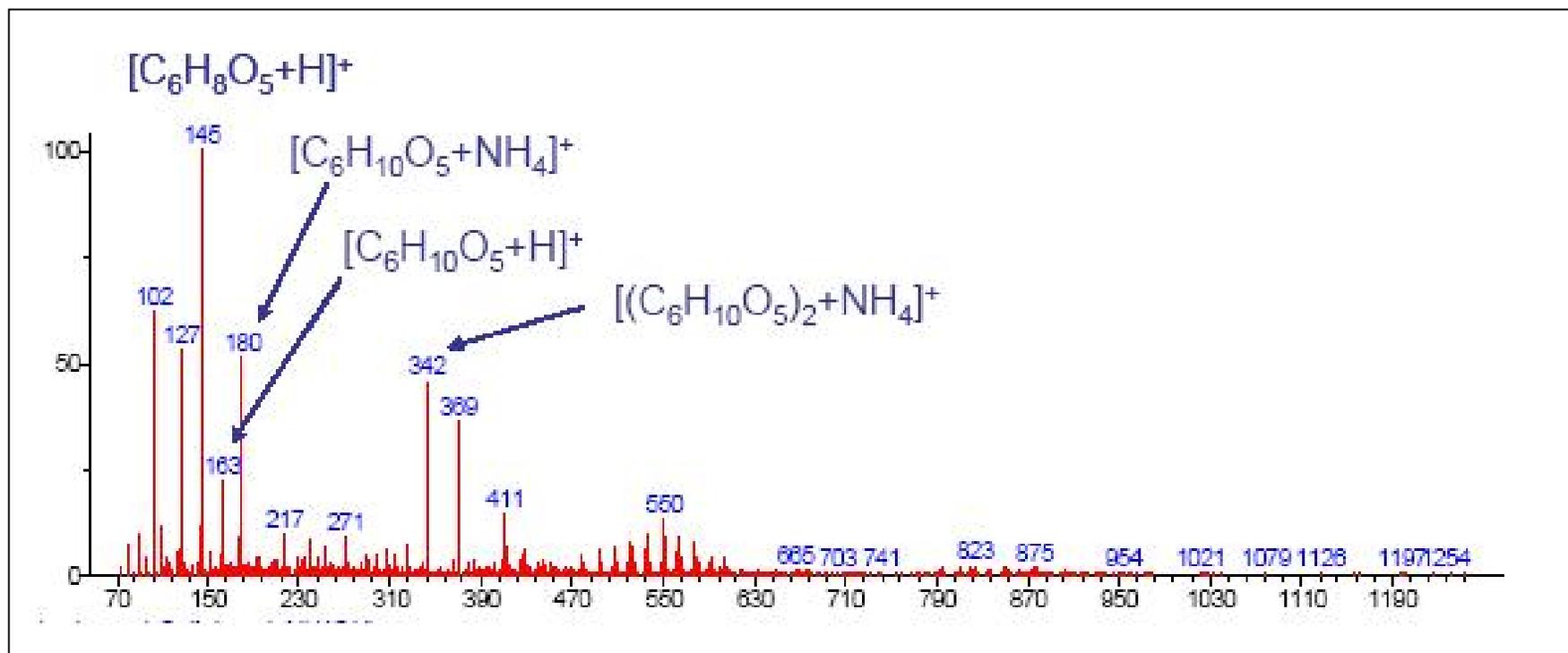
# Any Surface Works

- Insulating glass, living tissue or electrically conductive metals work equally well
- Hundreds of surfaces tested
- No known incompatible surface yet found

# Unequivocal Peak Assignment Because ...

- Exact masses are measured
- Accurate isotopic abundances assayed
- Thus, unequivocal elemental compositions are known
  
- Not so for quads or traps

# Cellulose: A 1,4-Polyglucose Polymer



# DART Reveals Internal Contents

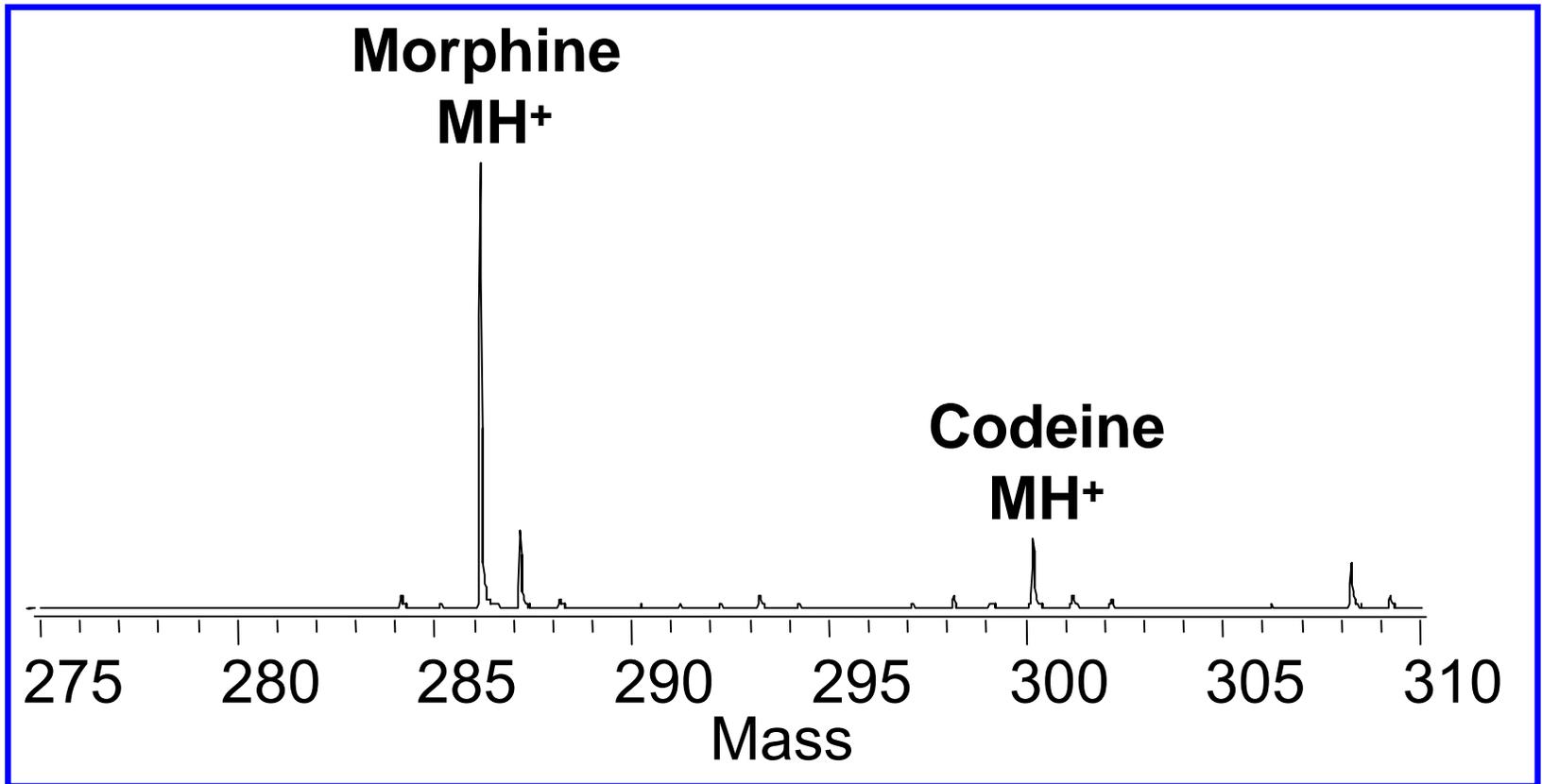
- DART penetrates seed coats
- Single poppy seed
- Narcotic alkaloids detected inside
- DART gives a clean mass spectrum

# Opium Alkaloids in Poppy Seeds

- Poppy seeds are a common flavoring ingredient
- Maximum morphine and codeine concentrations are 33 and 14 micrograms /g seed
- 2 milligrams opiates per ounce



# A Single Poppy Seed



# Pharmaceutical Polymers

- Internal contents of tablets are instantly revealed by DART

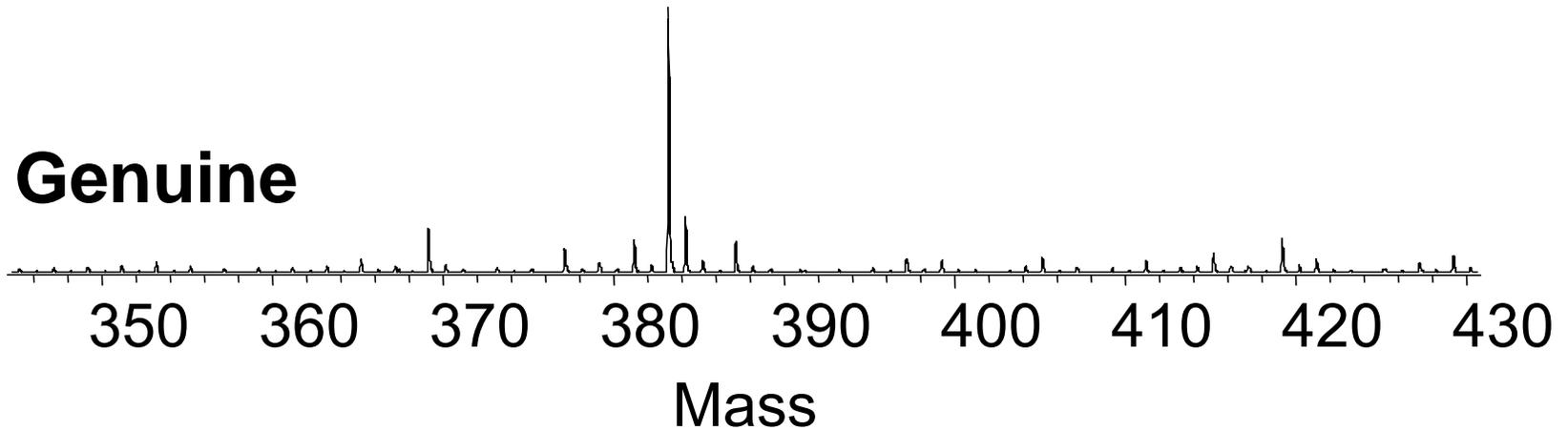
# Counterfeit Drug Detection

- Genuine Guilin B contains the antimalarial drug artesunate
- The counterfeit drug does not
- Exact mass of artesunate is 383.1705 Da

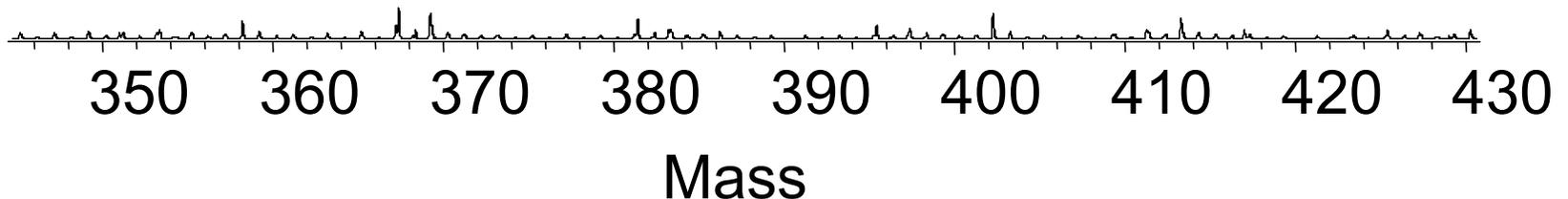
# Genuine vs. Counterfeit Drug

Artesunate  
383.1705 Da

**Genuine**



**Counterfeit**

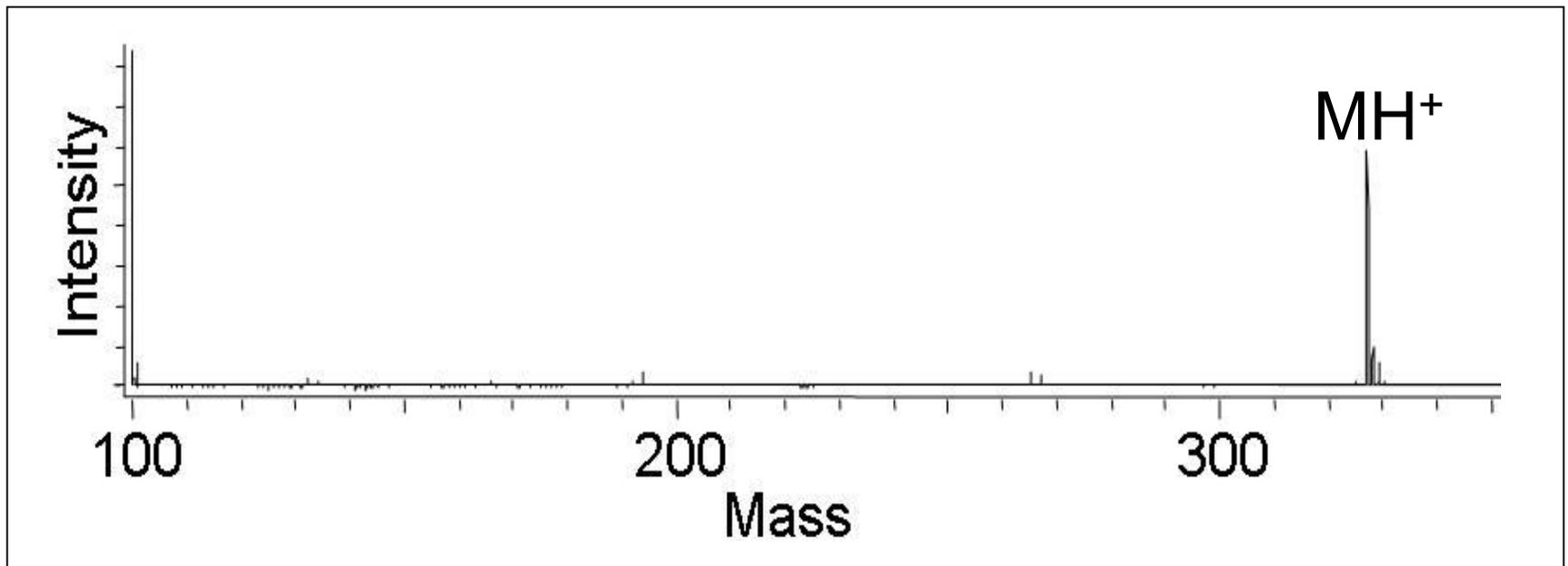


# Findings

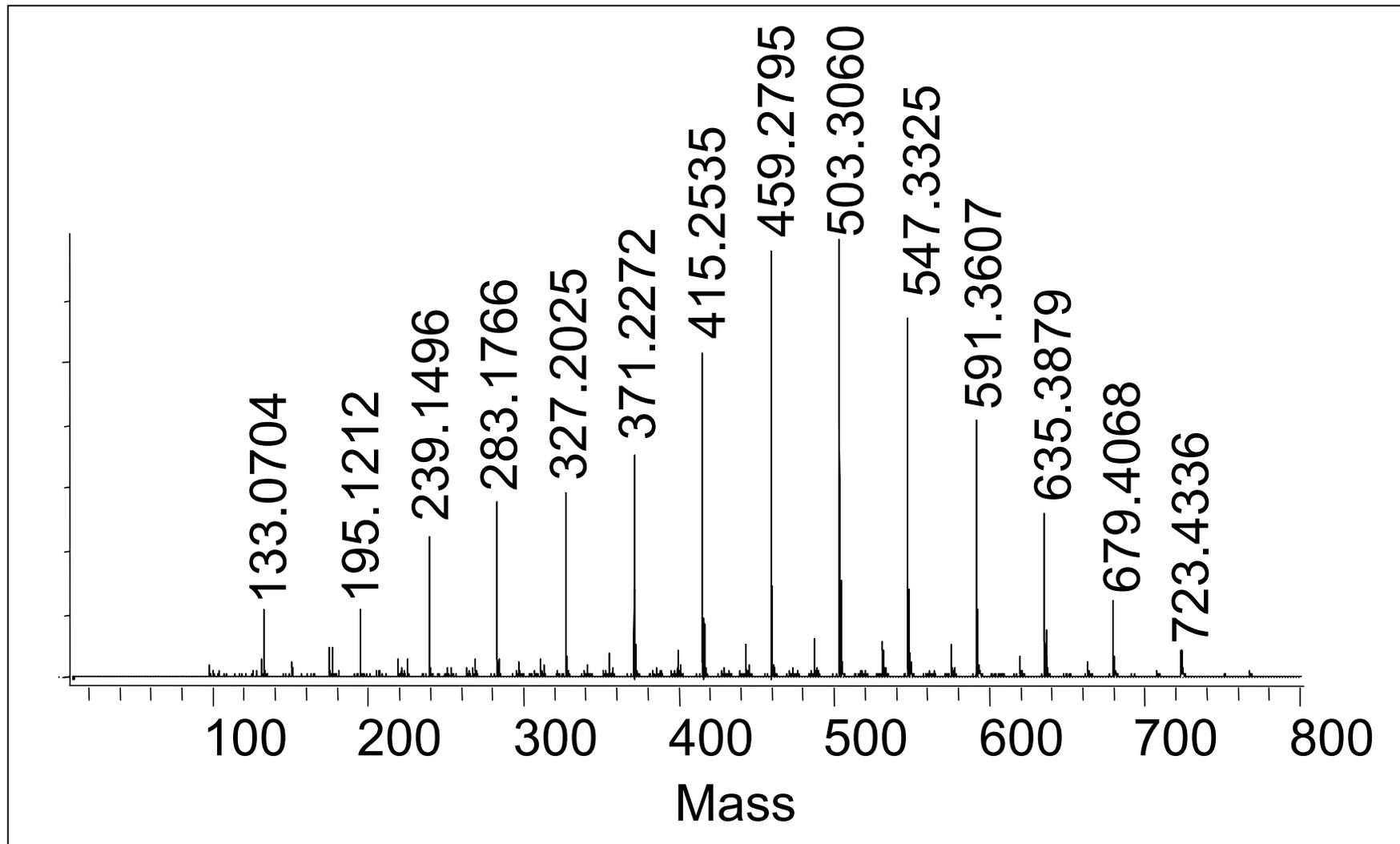
- Authentication of drug within 2 seconds
- Criminal evidence is preserved because tablet does not need to be opened
- No solvents, no gas chromatograph
- No sample preparation

# Large Acetylcholinesterase Inhibitors

- No known vapor pressure
- 100 nanograms gave 1,000,000 signal intensity and signal-to-noise ratio of 500,000



# Poly Ethylene Glycol 600



# Surface Sampling Hypothesis

- Metastables have lots of energy in a small package
- W54 nuclear warhead over 10 square miles releases 2 millijoules (mJ) per  $\text{mm}^2$
- $2^3\text{S}$  metastable helium has 3 mJ per  $\text{mm}^2$
- Nanoscopic surface heating
- Thus, analyte desorbs



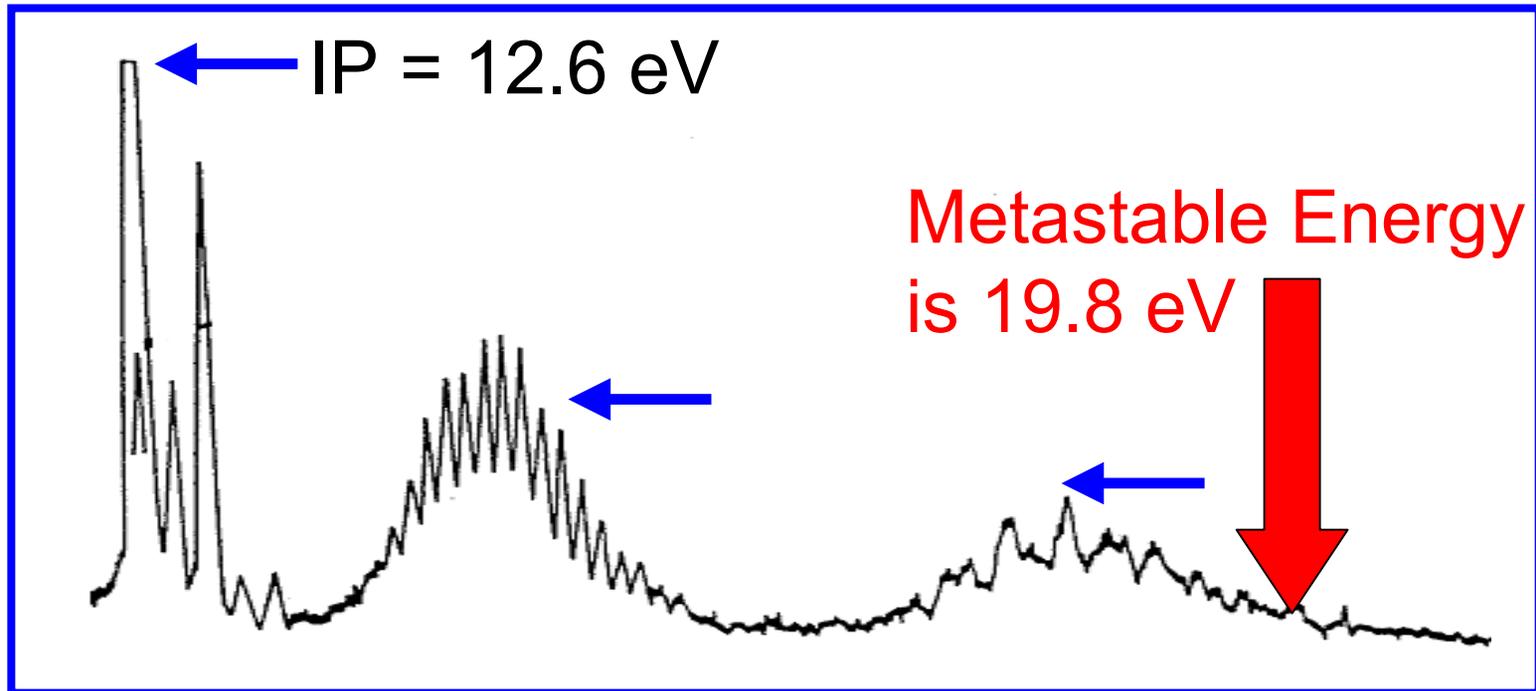
# Proton Transfer Hypothesis:

Metastables react with atmospheric water to make  $MH^+$

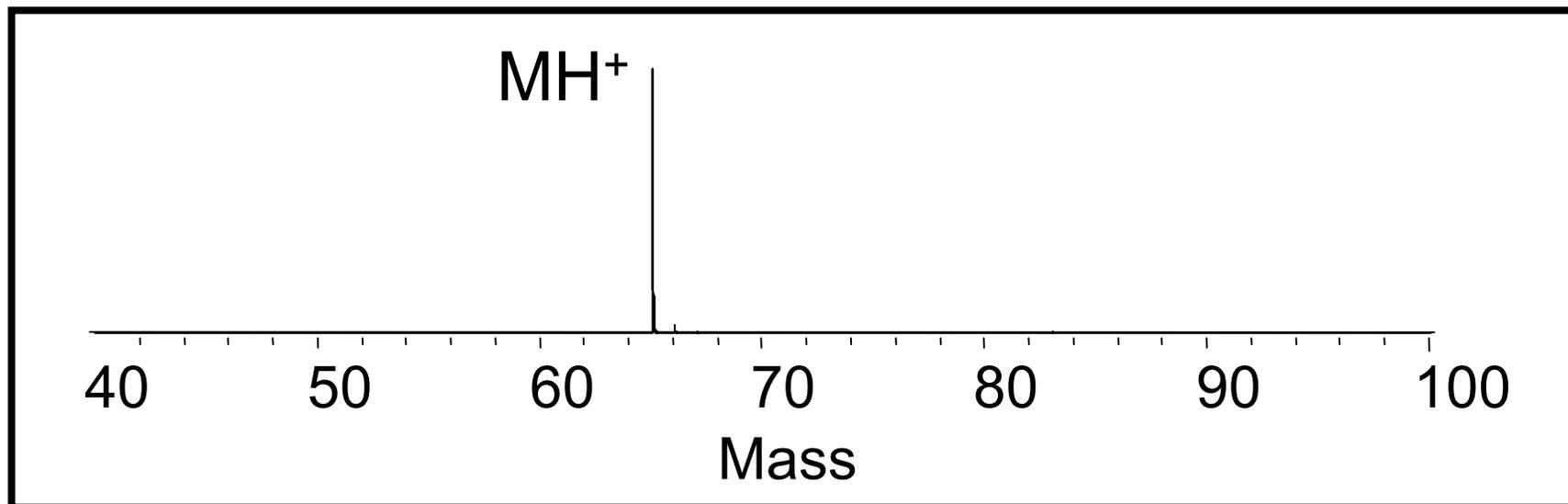
- $He(2^3S) + H_2O \rightarrow H_2O^{+\bullet} + He(1^1S) + e^-$
- $H_2O^{+\bullet} + H_2O \rightarrow H_3O^+ + OH \cdot$
- $H_3O^+ + M \rightarrow MH^+$
- Cross section is  $10^{10}$  barns or  $100 \text{ \AA}^2$
- Thus, this reaction is very likely to occur

# Why is the cross section so high?

- Because energy is plentiful (red arrow)
- Many places to put energy (blue arrows)
- Ultraviolet photoelectron spectrum of water

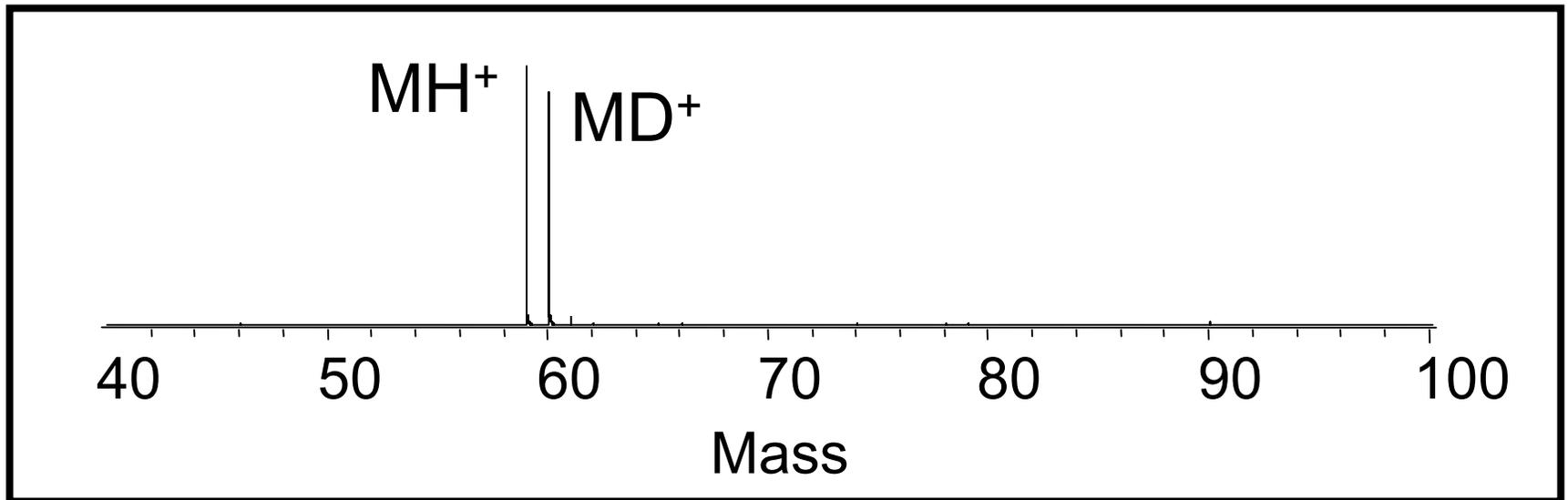


# Isotopic Labeling Evidence: Acetone -d<sub>6</sub> in atmospheric water



- Thus, ionizing hydrogen arises from atmospheric water

# Reverse Labeling Evidence: Acetone in atmospheric D<sub>2</sub>O



- Both MH<sup>+</sup> and MD<sup>+</sup> are seen because all atmospheric water vapor was not excluded

# Explosives: Our Other Research Product

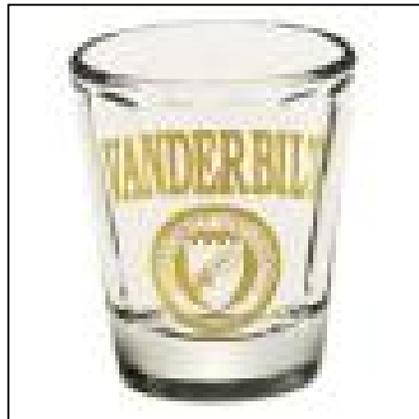
- HMTD is a terrorist explosive
- No method development with DART
- DC Metro rail card
- [DART Movie HMTD.exe](#)

# Ultra Low-Volatility Chemicals are Easy to Detect by DART

- Peak height is independent of sample volatility
- Peak height depends on amount
- DART provides  $MH^+$  molecular ions, diagnostically most useful

# One part-per-trillion (ppt) is...

- One ounce of whiskey in Loch Ness
- 5 ppt is the vapor pressure of RDX or PETN at room temperature and atmospheric pressure. HMX is 60 times less volatile.



# Peak Heights are Independent of Vapor Pressure !

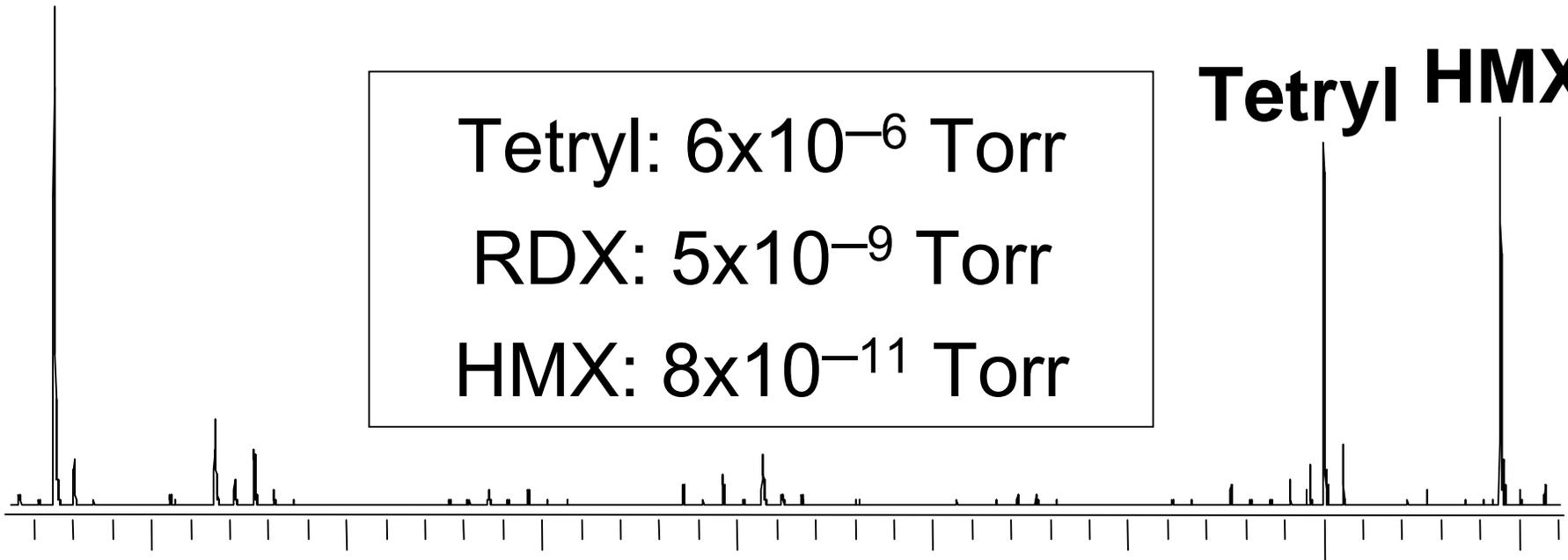
**RDX**

**Tetryl HMX**

Tetryl:  $6 \times 10^{-6}$  Torr

RDX:  $5 \times 10^{-9}$  Torr

HMX:  $8 \times 10^{-11}$  Torr



1  $\mu\text{g}$  of each on fingertip, 15th fingerprint

# Take Home Messages...

- Analytes detected in seconds
- Signal strength independent of volatility
- Surface sampling at atmospheric pressure without prep
- No solvents and no waste!

# Just for Fun: A Movie ...

See Salt & Vinegar

- [Movie Salt & Vinegar](#)

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