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Technology Transition Workshop| *José R. Almirall, Ph.D.*

Introduction to Instrumental Detection Technology (Part 2): SPME and PSPME

Outline

- **IMS detection of volatiles**
  - **Identification of volatile target compounds**
  - **Sampling and preconcentration**
  - **Delivery of sample/analytes to detector**
  - **Optimization of IMS conditions for new target compounds**
  - **Determine LODs for optimized sampling/detection**
  - **Identify sources of false +, false – and potential interferences**
- **Comparison between canine and IMS**
- **Novel geometry compatible with IMS**
- **Performance characteristics for PSPME**

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1. Identify the Volatile Chemical Markers to Target for Detection.

Category	Vapor Pressure @ STP	Boiling Point
Volatile	>0.1 torr	<100° C
Semi-Volatile	0.1 to 10^{-7} torr	100-325° C
Non-Volatile	<10^{-7} torr	>325° C

Illicit Drugs	P_v (torr)	Chemical Markers	P_v (torr)
Cocaine	1.2 x 10^{-7}	methyl benzoate	0.28 @ 20° C
MDMA	(low)	Piperonal *(3,4-methylenedioxybenzaldehyde)*	1.0 @ 87° C
Marijuana (THC)	N/A (low)	α/β –pinene, limomene, β-caryophyllene	1 to 3 @ 20° C

Pawliszyn (**2002**)

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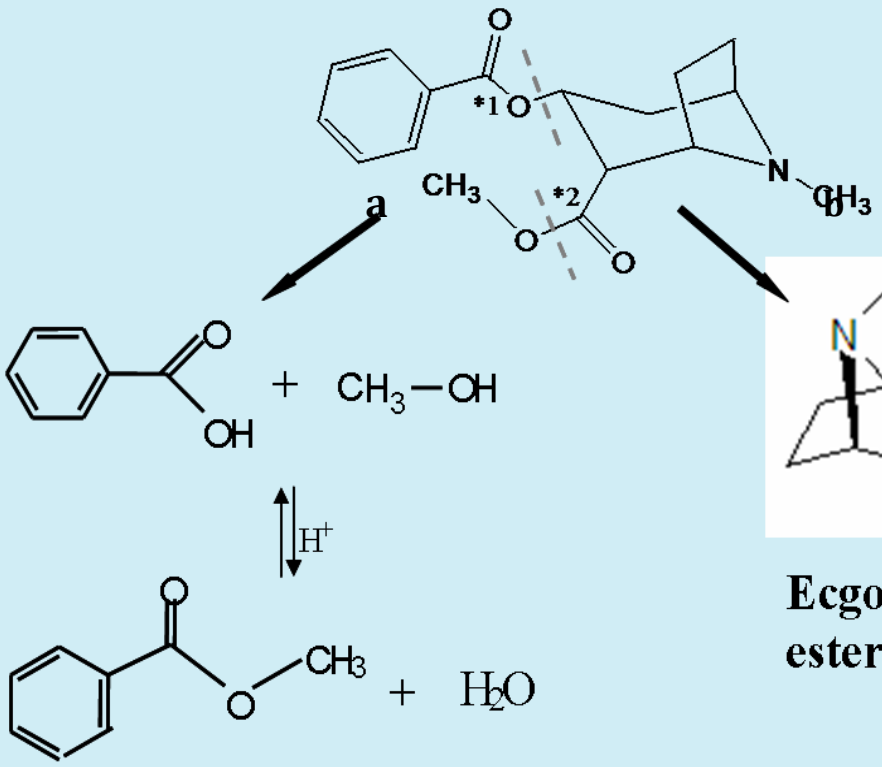
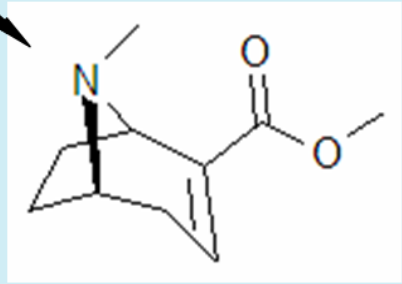
Cocaine Decomposes at *1 and *2

Cocaine
(MW=303 amu)





Ecgonidine methyl ester (MW=181 amu)

Methyl benzoate (MW=174 amu)

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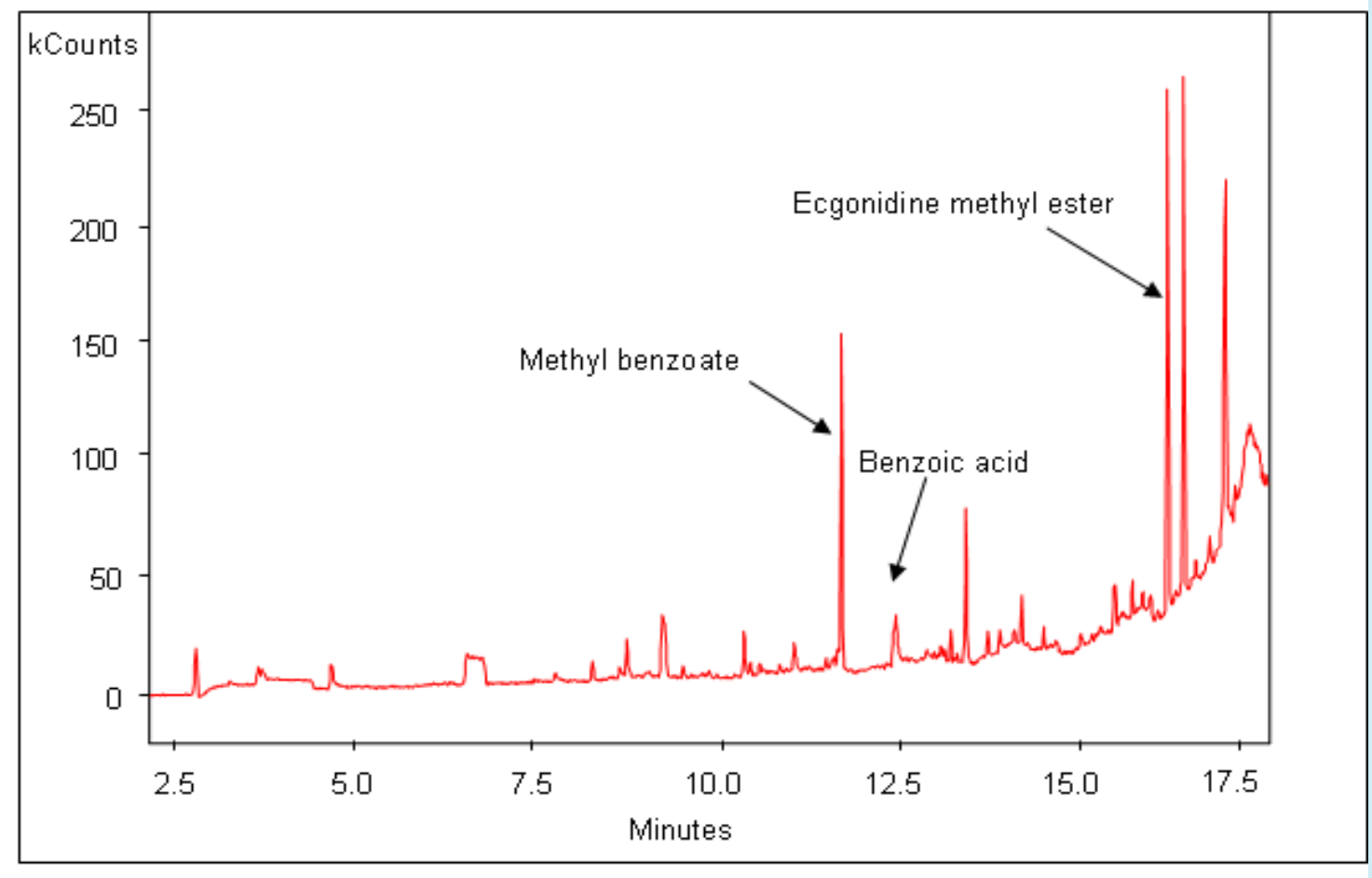
Cocaine SPME-GC/MS



- **25 g (relatively "fresh" cocaine) in gallon-sized can**
- **14hr SPME (Carboxen™-PDMS) extraction at room temperature**

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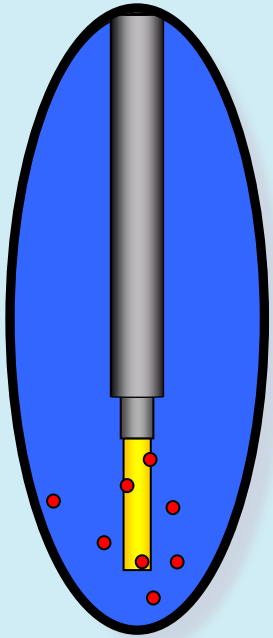
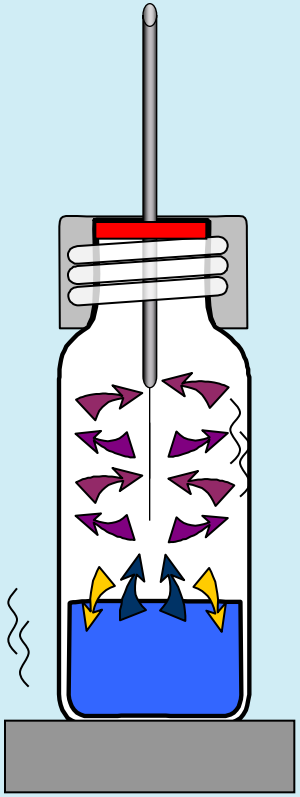
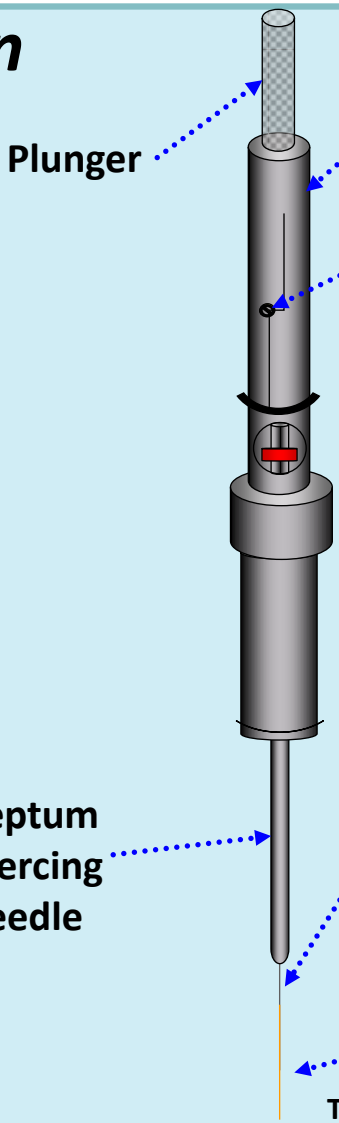
2. Sampling and Preconcentration
Solid Phase Microextraction







Advantages

- Analyte pre-concentration
- Selectivity
- Speed
- Sensitivity
- Ease of use
- Equilibrium-based

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Headspace or Air Sampling

When the sample volume is very large ($V_f << V_s$), the equation can be simplified to:

$$n = K_{fs} V_f C_0$$

- **The amount of extracted analyte is independent of the volume of the sample**
- **The amount extracted corresponds directly with the concentration in the matrix and is mediated by:**
  - **The distribution constant between the fiber and the sample (and between the sample and the headspace)**
  - **The amount of sorbent volume**

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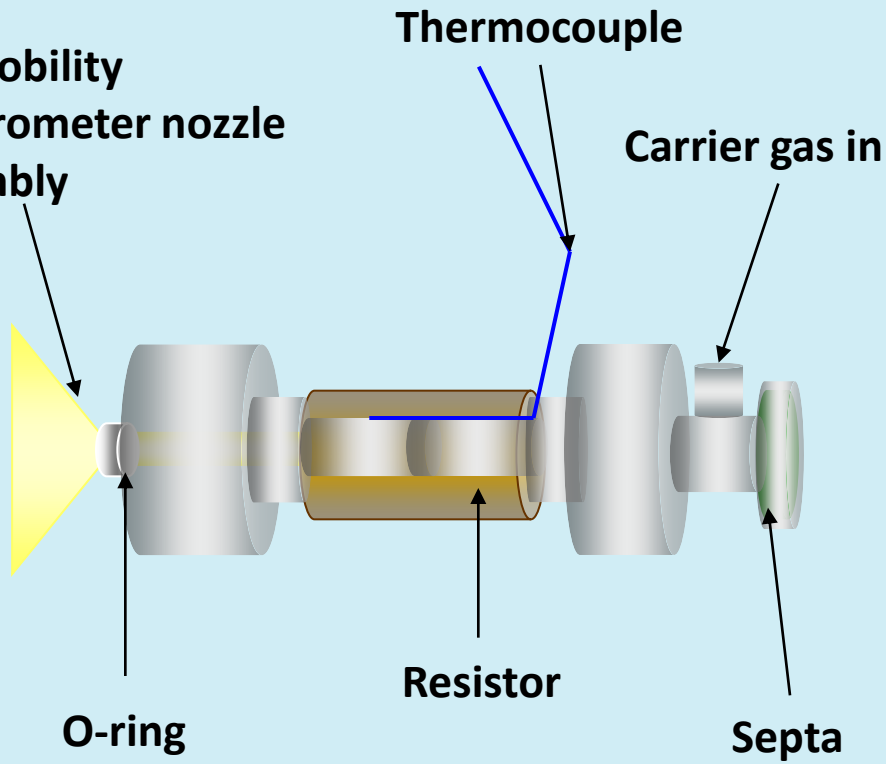
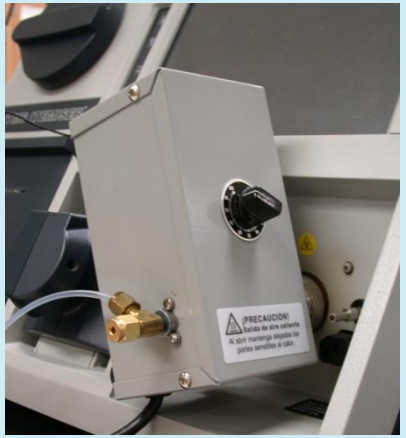
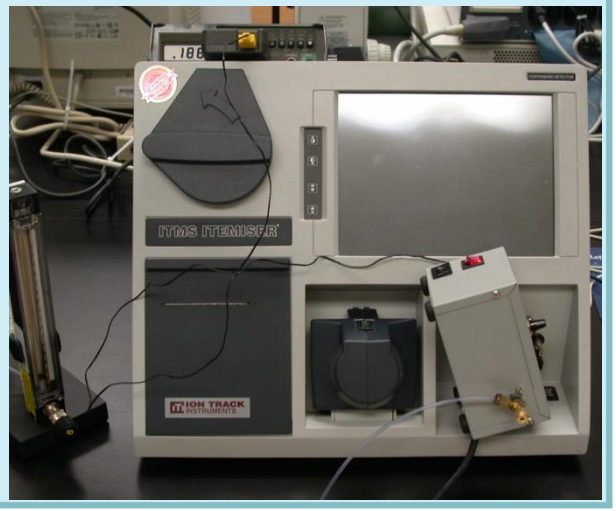
3. Delivery of Sampled Analytes to the Detector – SPME-IMS Interface

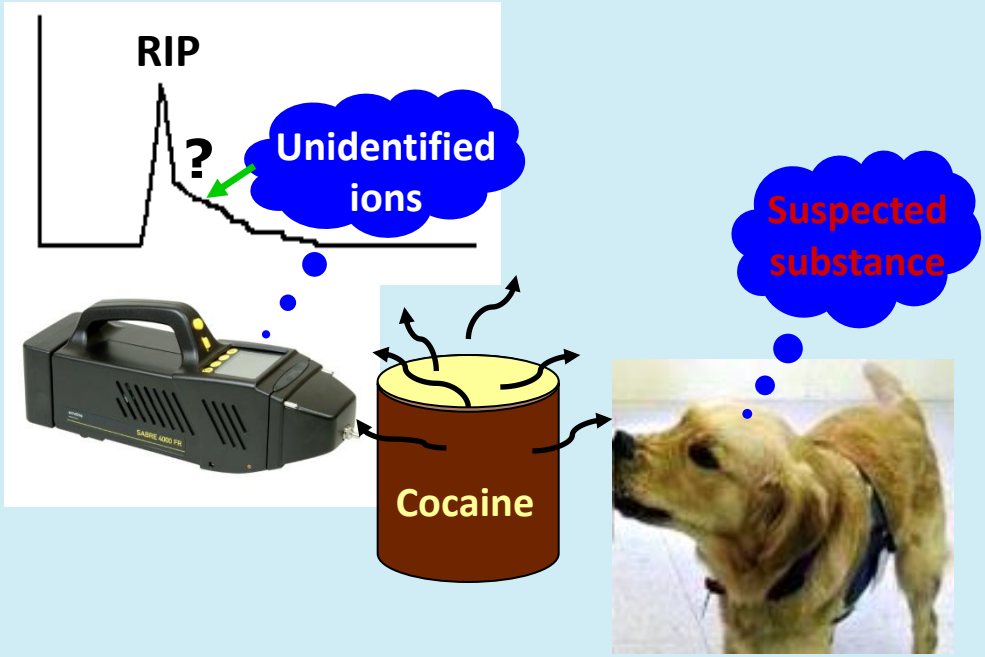






PATENT PENDING (Almirall, Florida International University)

- **Current IMS analyzers and other electronic noses are not optimized to detect volatile signature compounds**



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4. Optimize the IMS Instrumental Conditions to Detect Target Compounds

Compounds	K_o ($cm^2/V \cdot s$)	Temperature (° C)	Drift Flow ($ml \cdot min^{-1}$)	Sample Flow ($ml \cdot min^{-1}$)	Dopant	Mode
Piperonal	1.51	80	350	500	Nicotinamide	Positive
Methyl Benzoate	1.55	190	250	1000	Air	Positive
α/β-Pinene, limomene, β-caryophyllene	1.28	110	50	1000	Nicotinamide	Positive

SPME Parameters

Fiber type: Polydimethyl Siloxane (PDMS), 100µm

Interface temperature: 260° C

Interface warm up: 15 minutes

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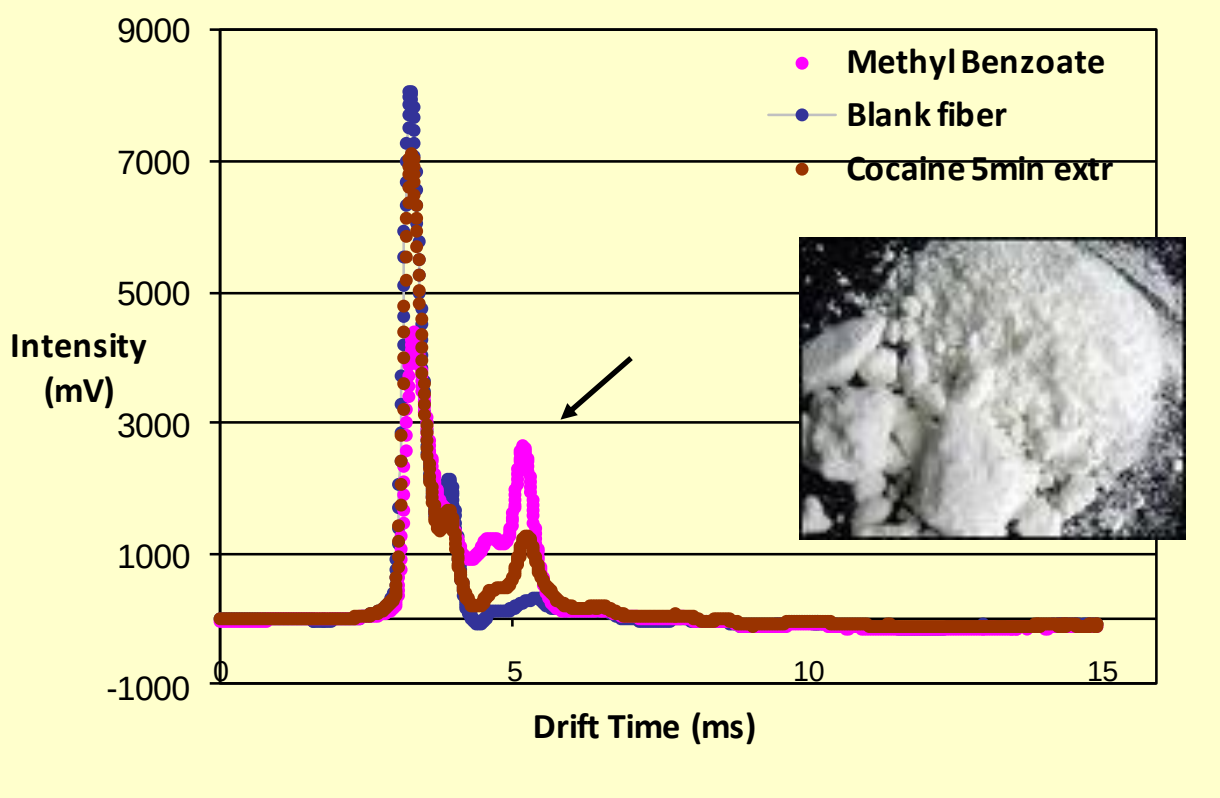
Headspace Air Sampling & Detection of Cocaine By SPME-IMS (5 Minute Extraction, Room Temp.)



0.5g of cocaine HCl in a Ziploc bag, sealed in quart can
Extracted compound was confirmed by GC/MS

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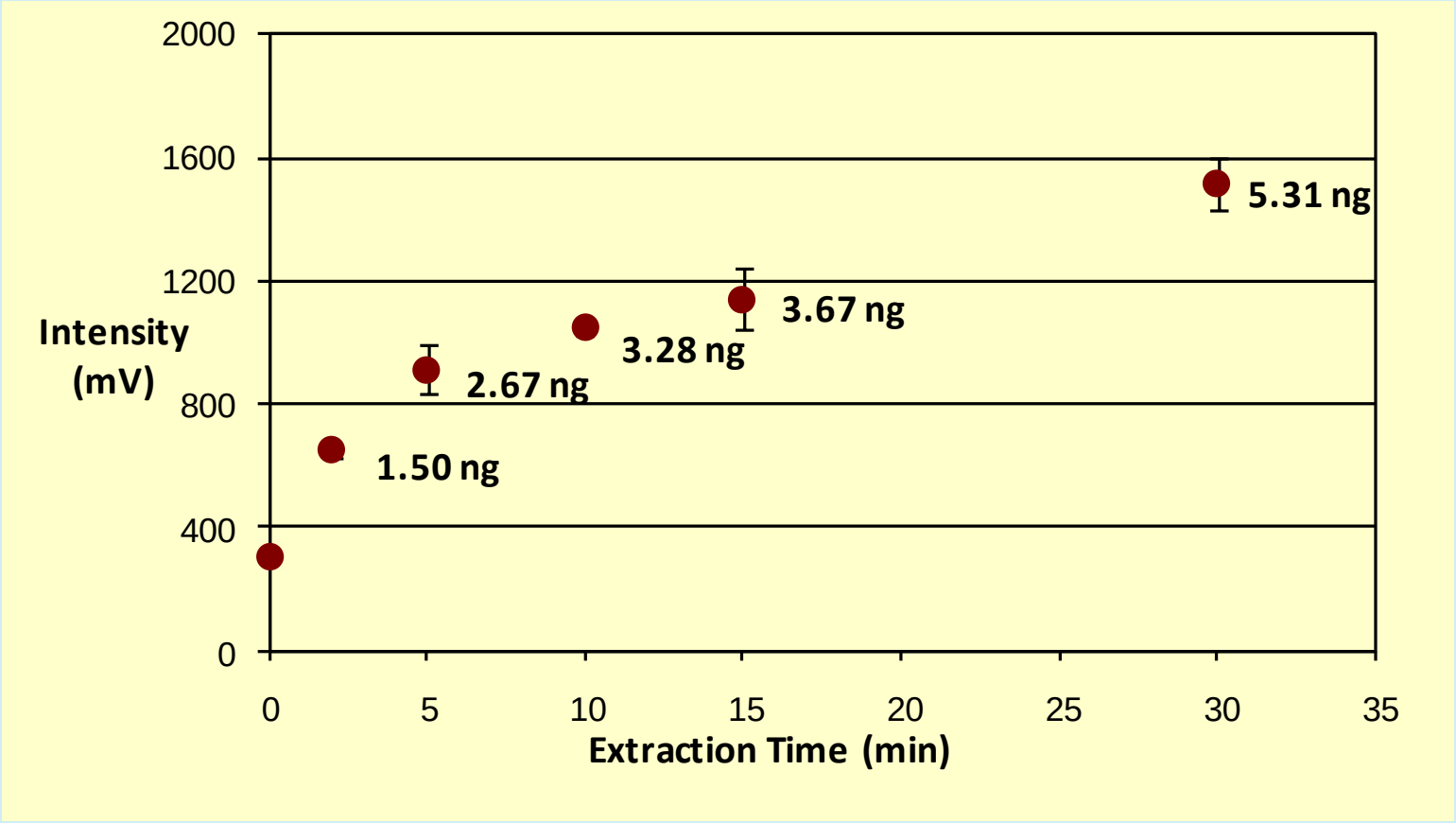
SPME Extraction Profile (Exposure Time)

Cocaine (Methyl Benzoate Detected)



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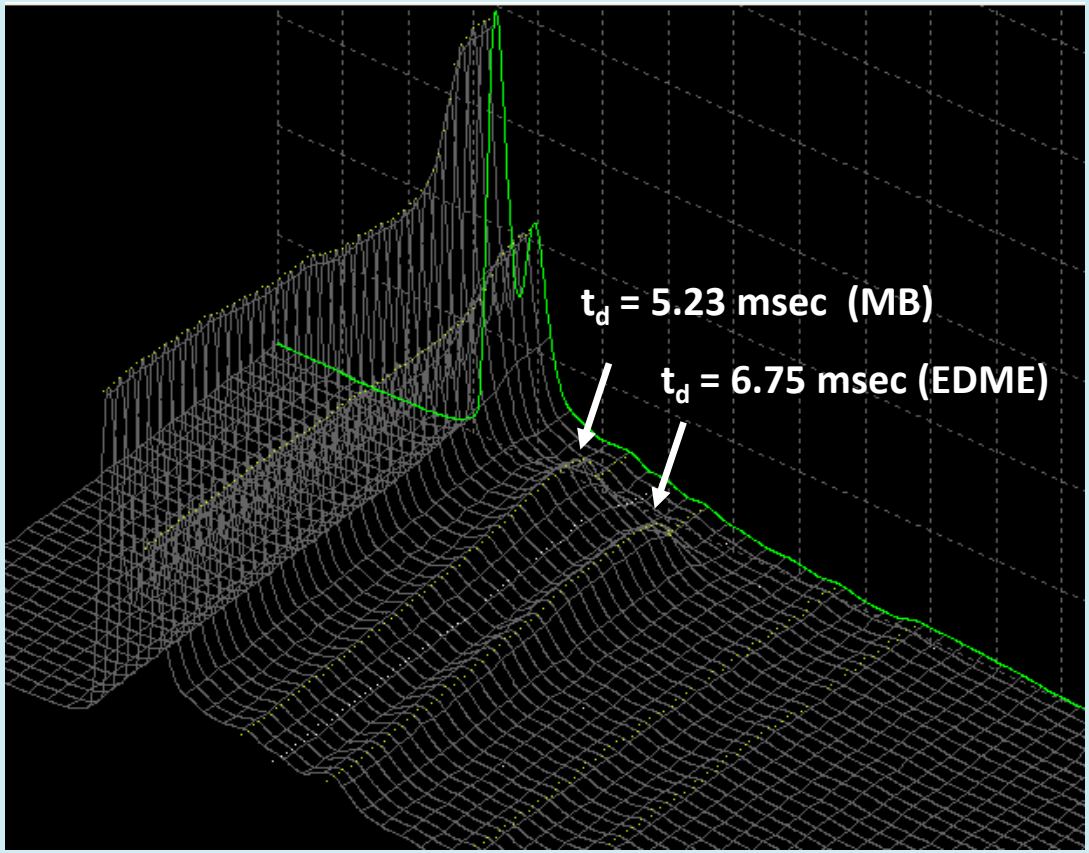
Headspace Air Sampling & Detection of Cocaine By SPME-IMS (30 Minute Extraction)



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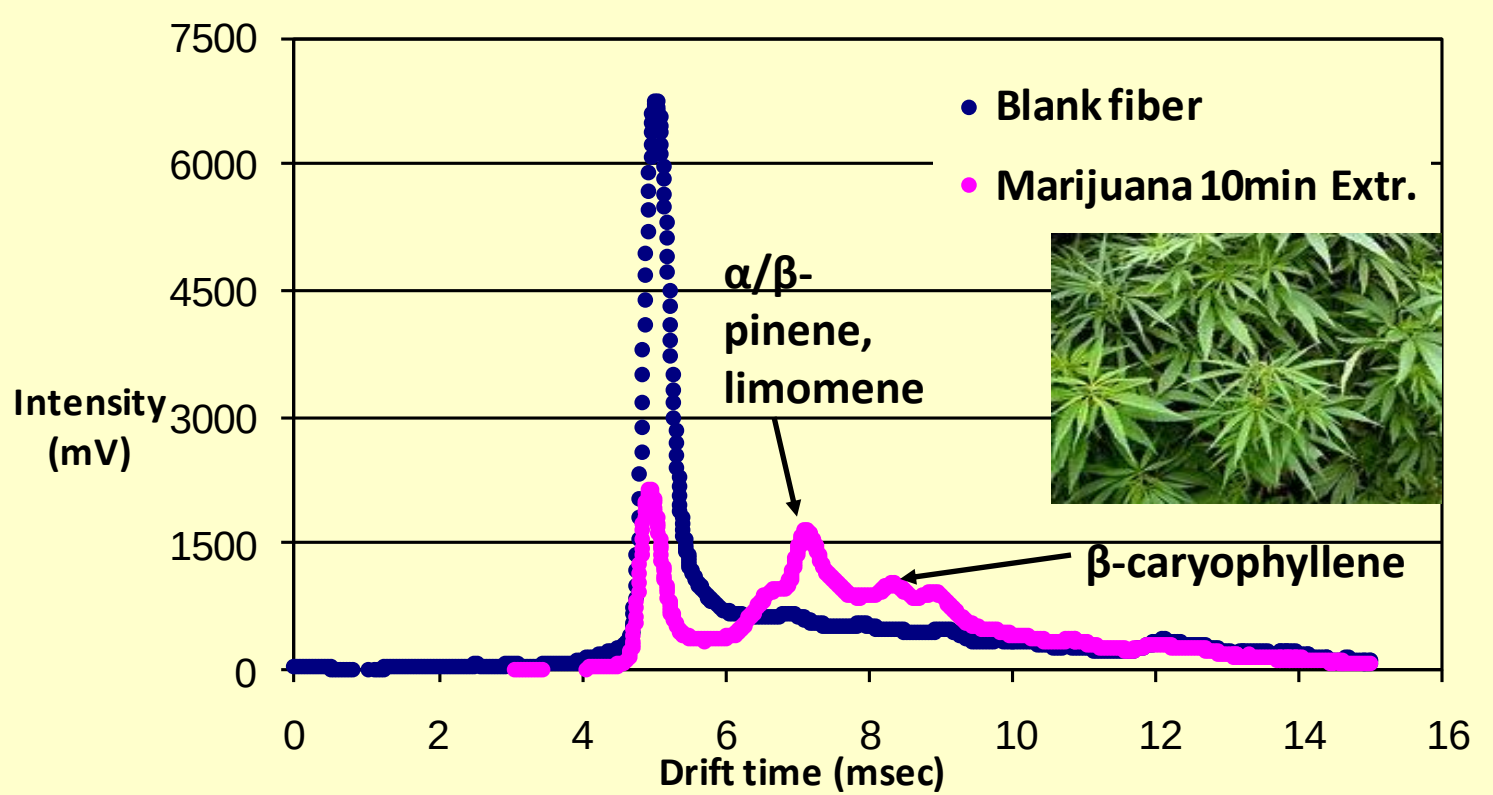
Headspace Air Sampling & Detection of Marijuana By SPME-IMS (10 Min. Extraction, Room Temp.)



1.4 g of marijuana sealed in a quart can

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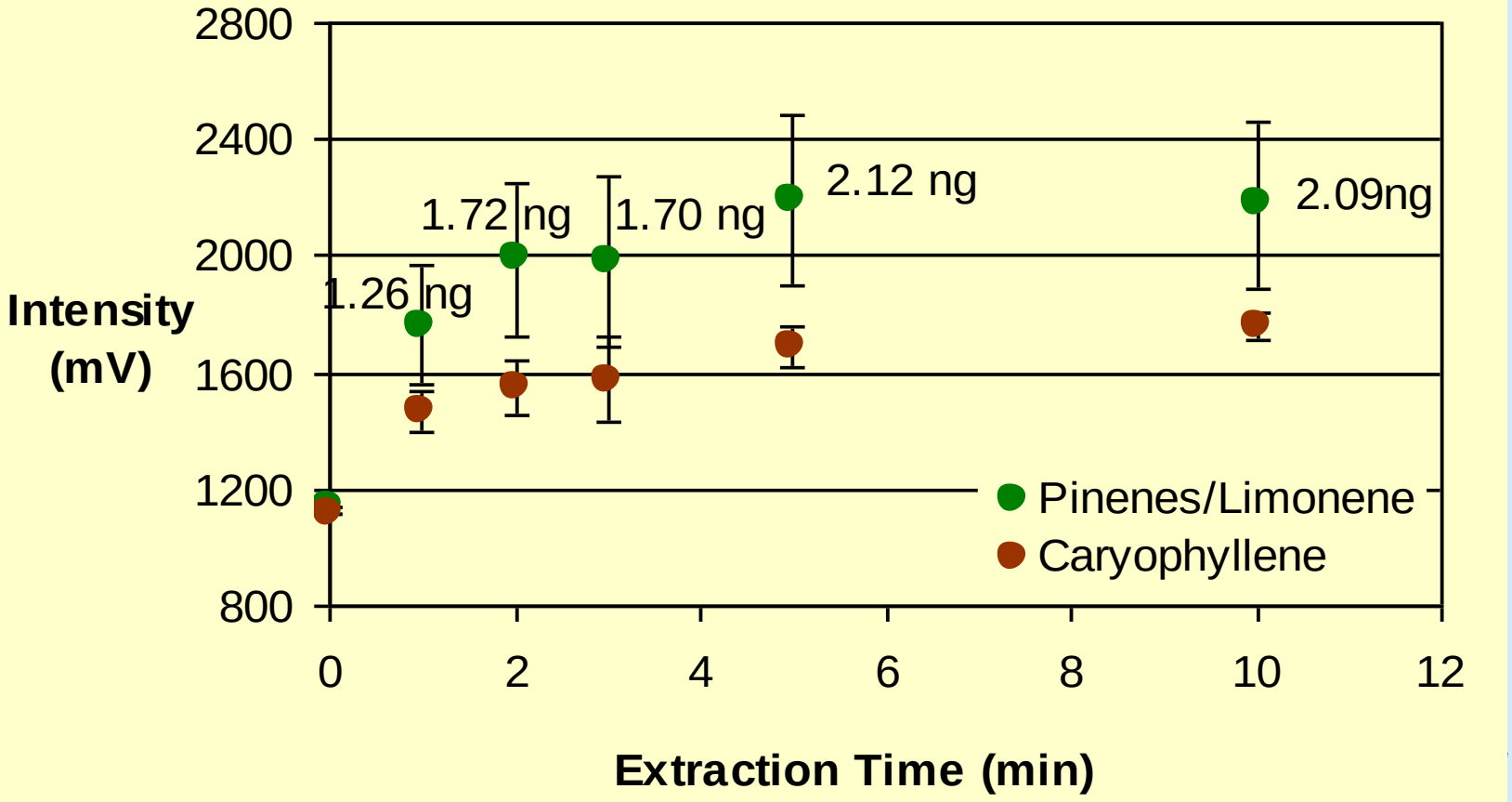
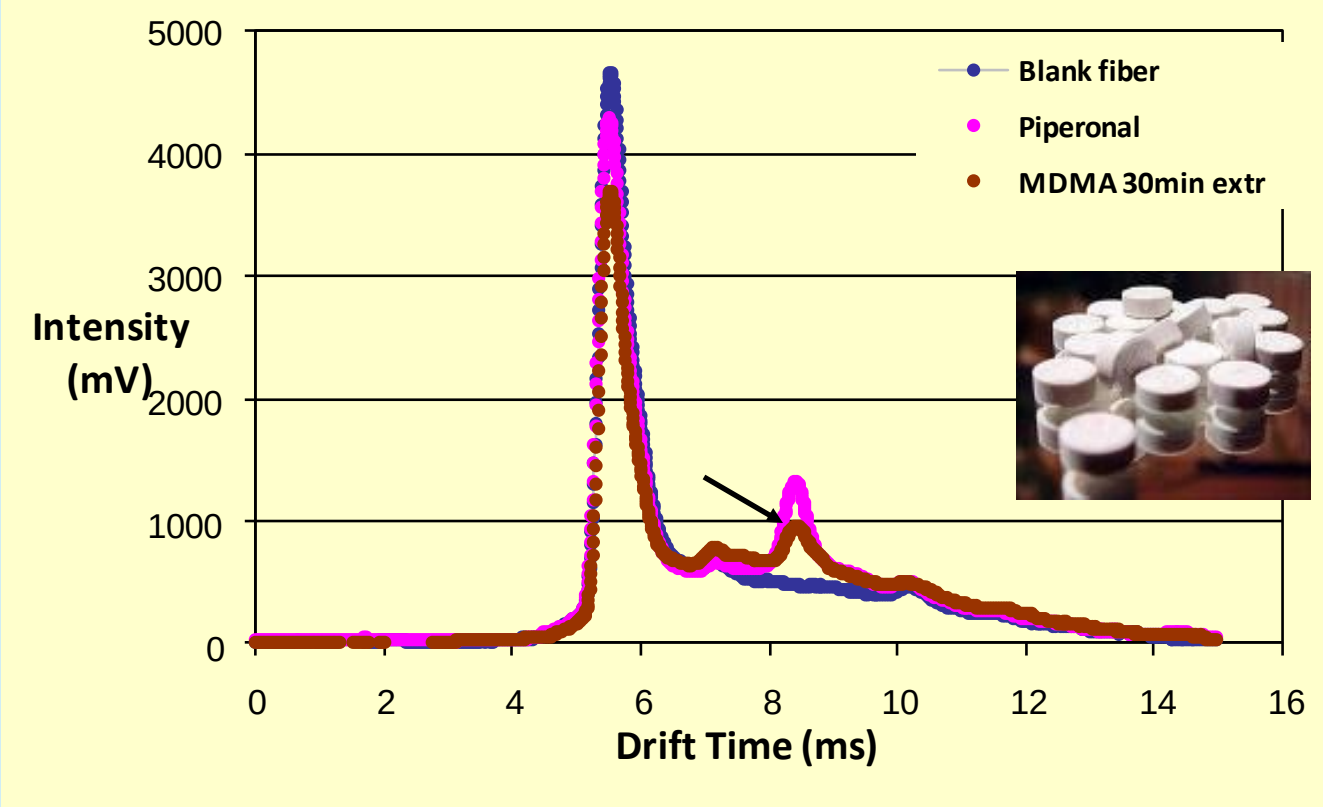
SPME Extraction Profile (Exposure Time)

Marijuana (Pinenes/Caryophyllene Detected)



Headspace Air Sampling & Detection of MDMA By SPME-IMS (30 Minute Extraction, Room Temp.)



2.3 g of MDMA sealed in quart can

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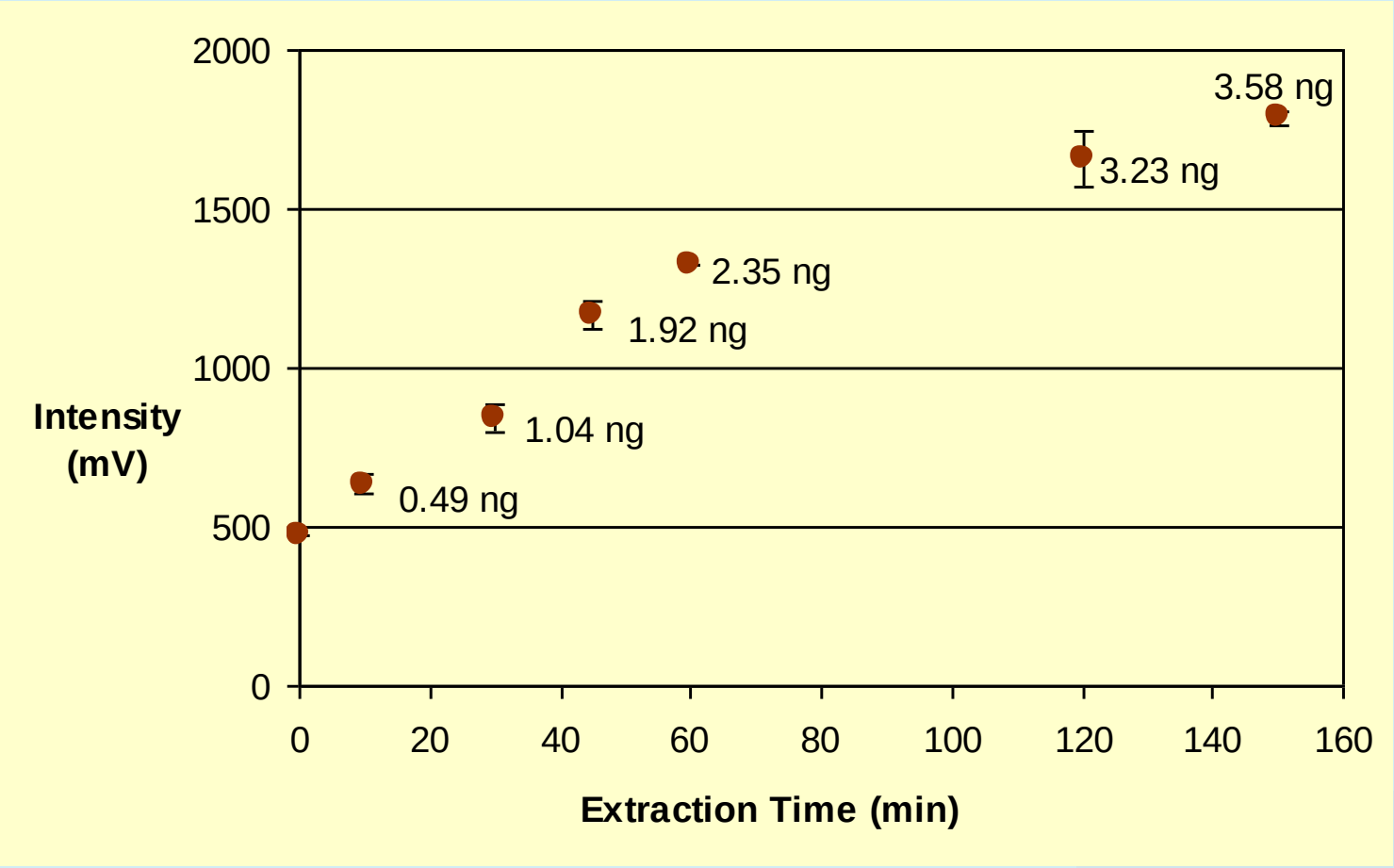
SPME Extraction Profile (Exposure time)

MDMA (Piperonal Detected)



Piperonal (Ecstasy Odor) Detection

Canine Response (%)

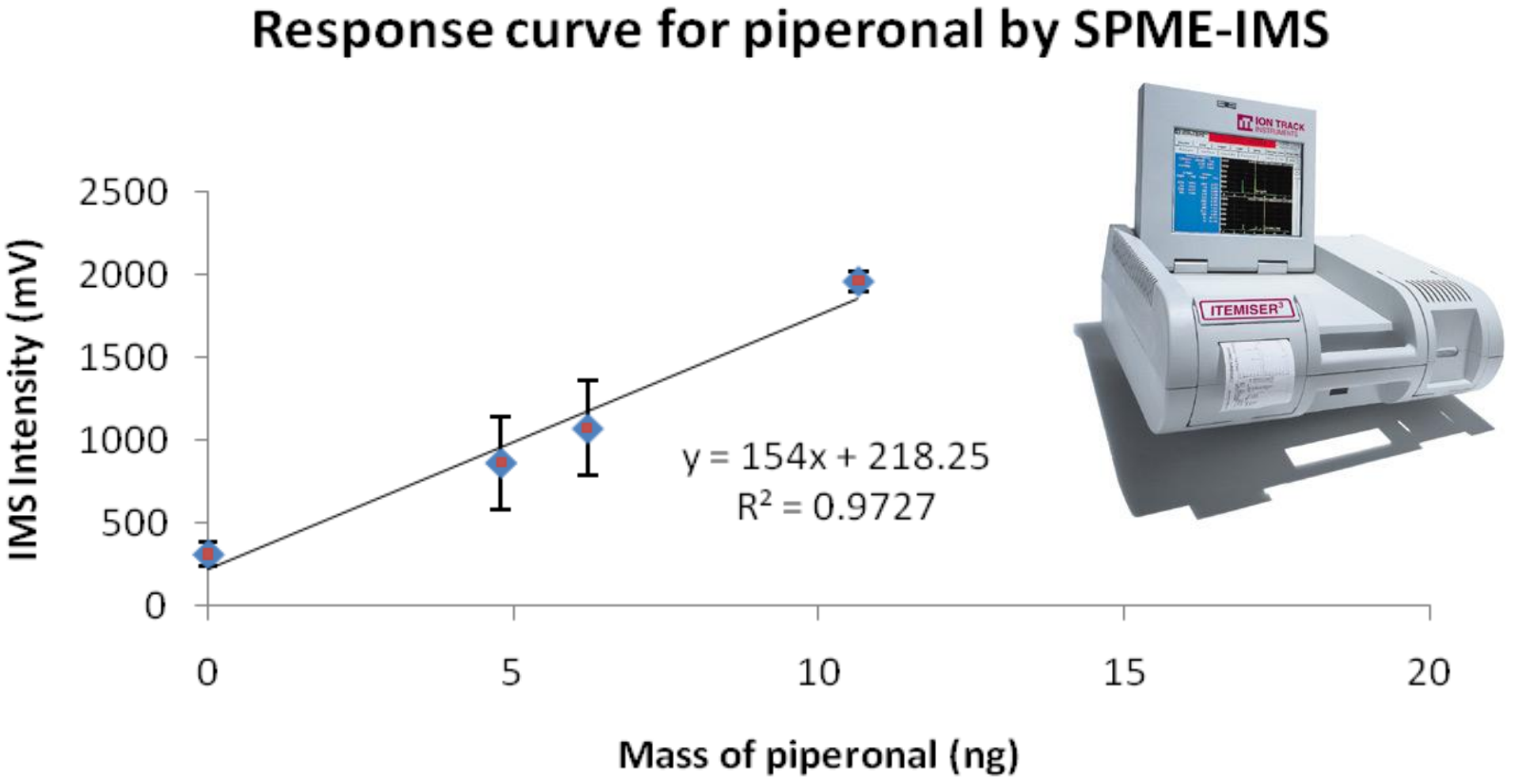
100
90
80
70
60
50
40
30
20
10
0

1
10
100
1000
10000

Permeation Rate (ng s-1)

Macias et al. (2010)

Piperonal (Ecstasy Odor) Detection (Continued)



Macias et al. (2010)

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5. Identify Potential Sources of False Positives and False Negatives

- **SPME fiber/disk absorption/adsorption competition**
- **Breakthrough (for dynamic sampling)**
- **Ionization competition**
- **Peak location interference**

Lai, Corbin and Almirall (2008)

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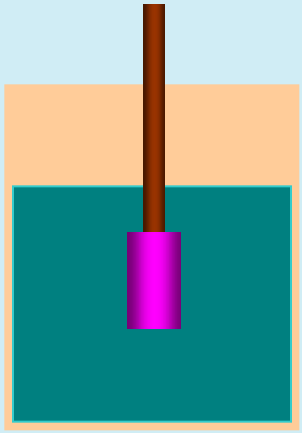
SPME Configurations

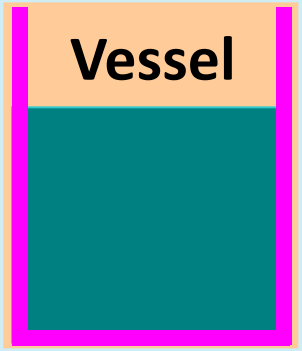


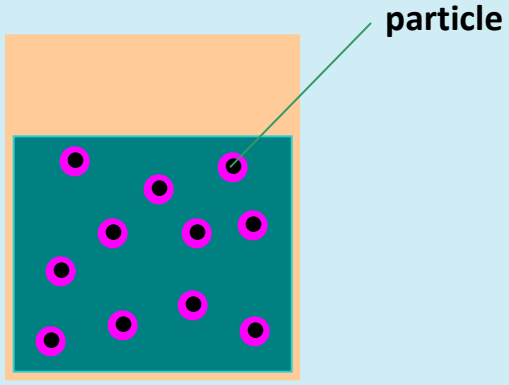
Fiber

Extraction Phase

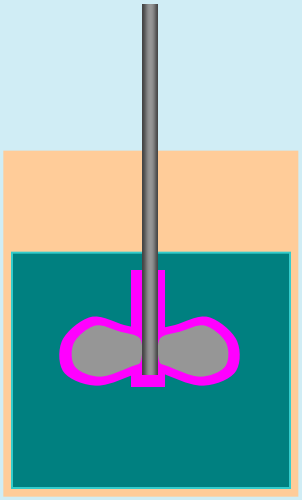
Sample

Tube

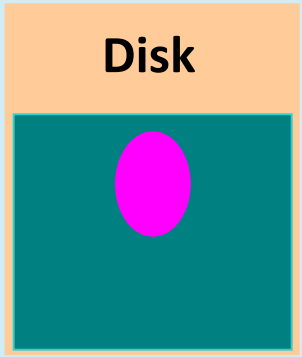




Suspended Particles



Stirrer



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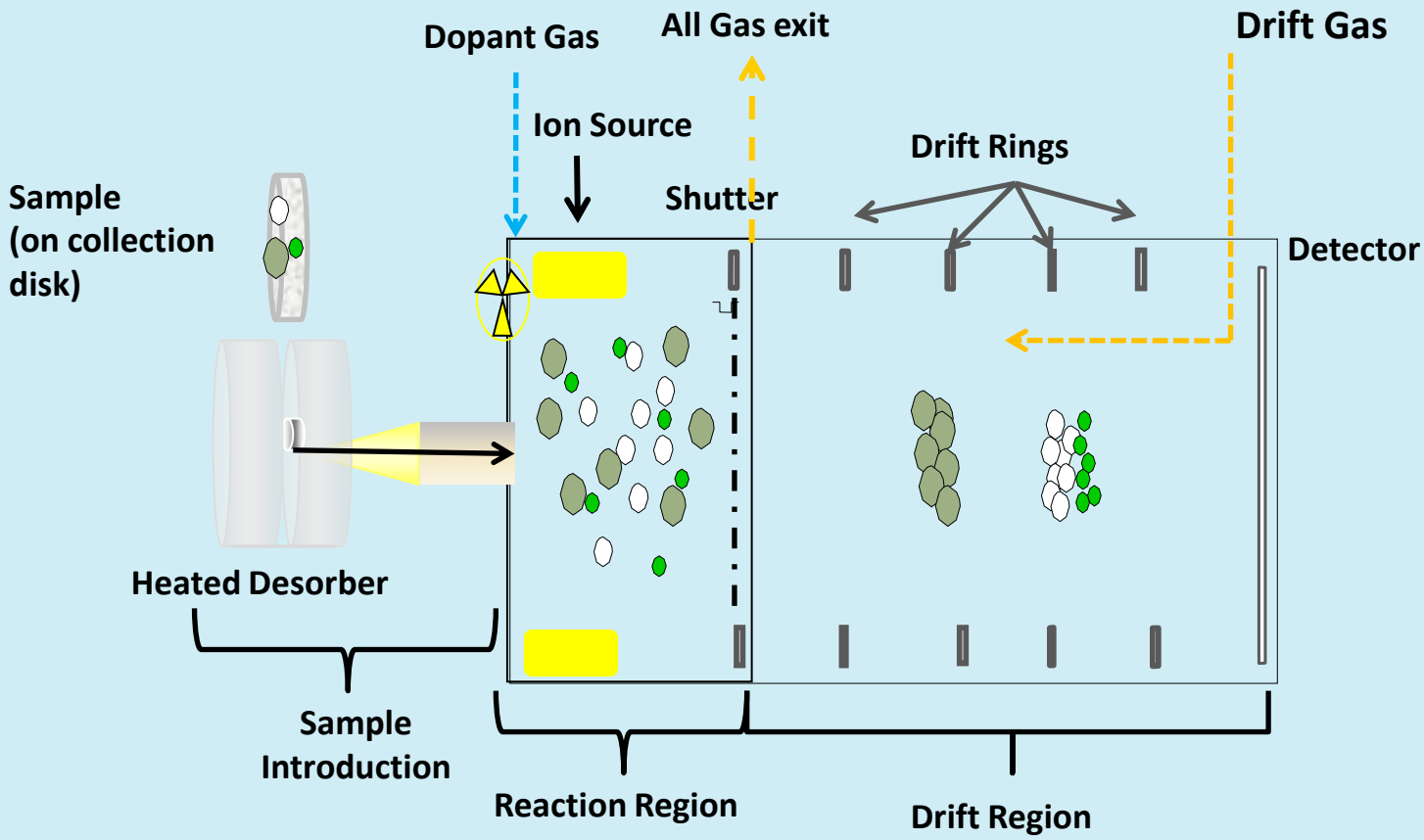
Ion Mobility Spectrometry – IMS



Separation of product ions by mass, charge and shape

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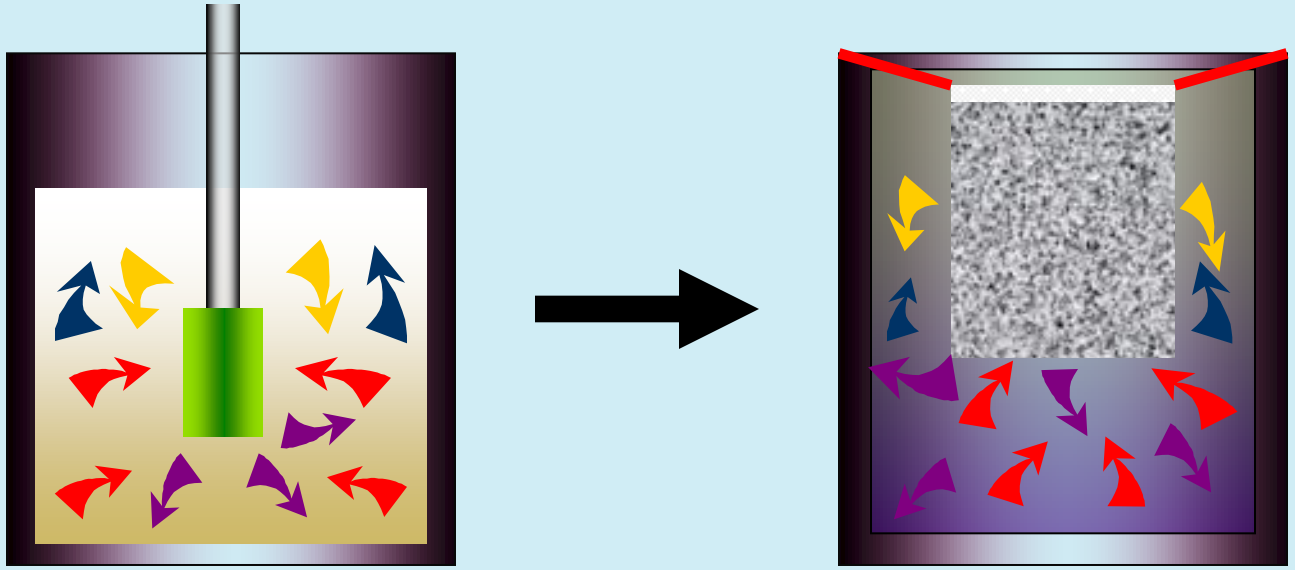
Planar SPME Geometry

- **PSPME increases surface area and capacity**
- **Reduces sampling time**
- **Geometry is amenable for IMS introduction**



Modified-syringe SPME **Planar SPME**

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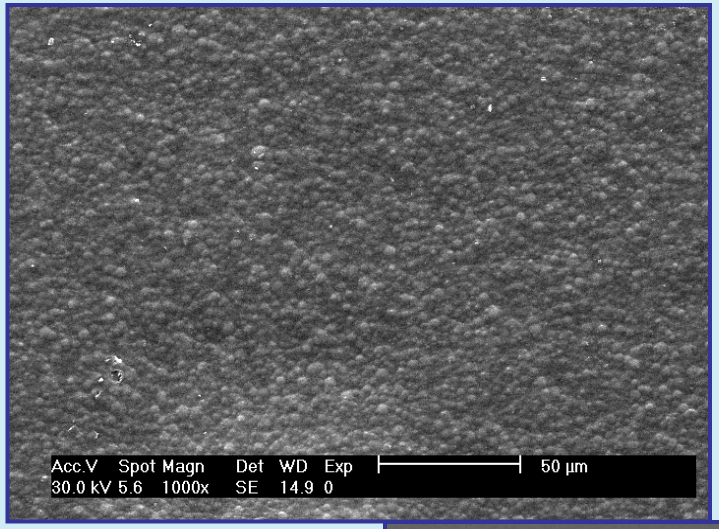
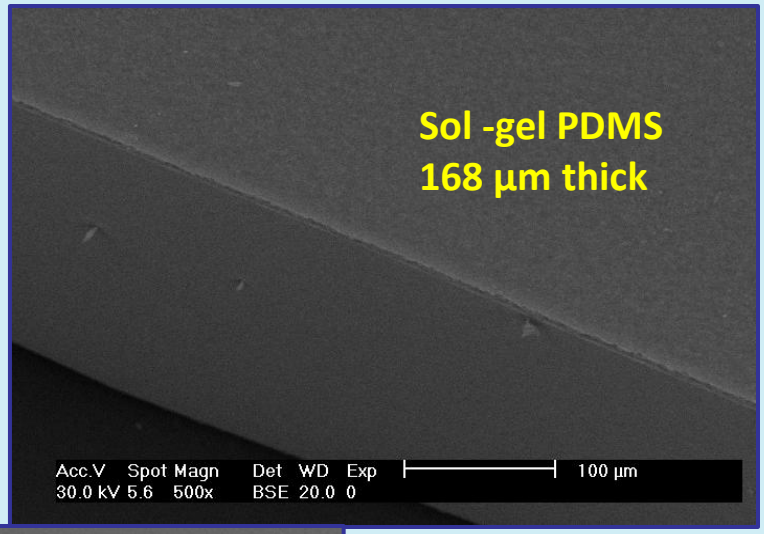
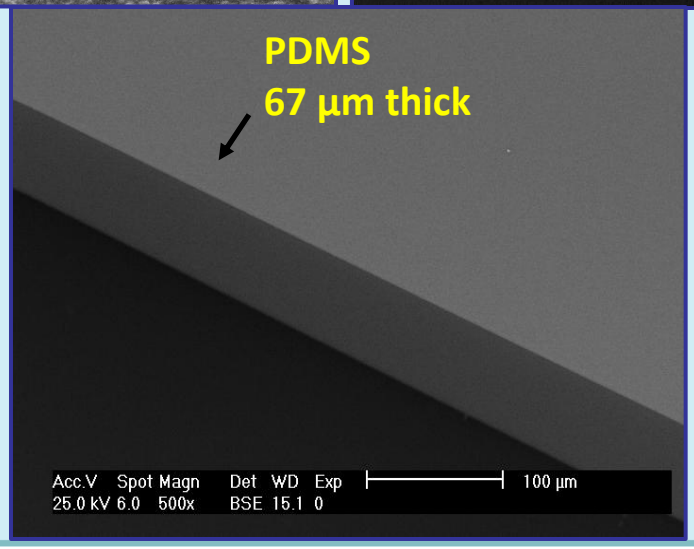
SEM of Planar SPME



Dip Coating





Spin Coating

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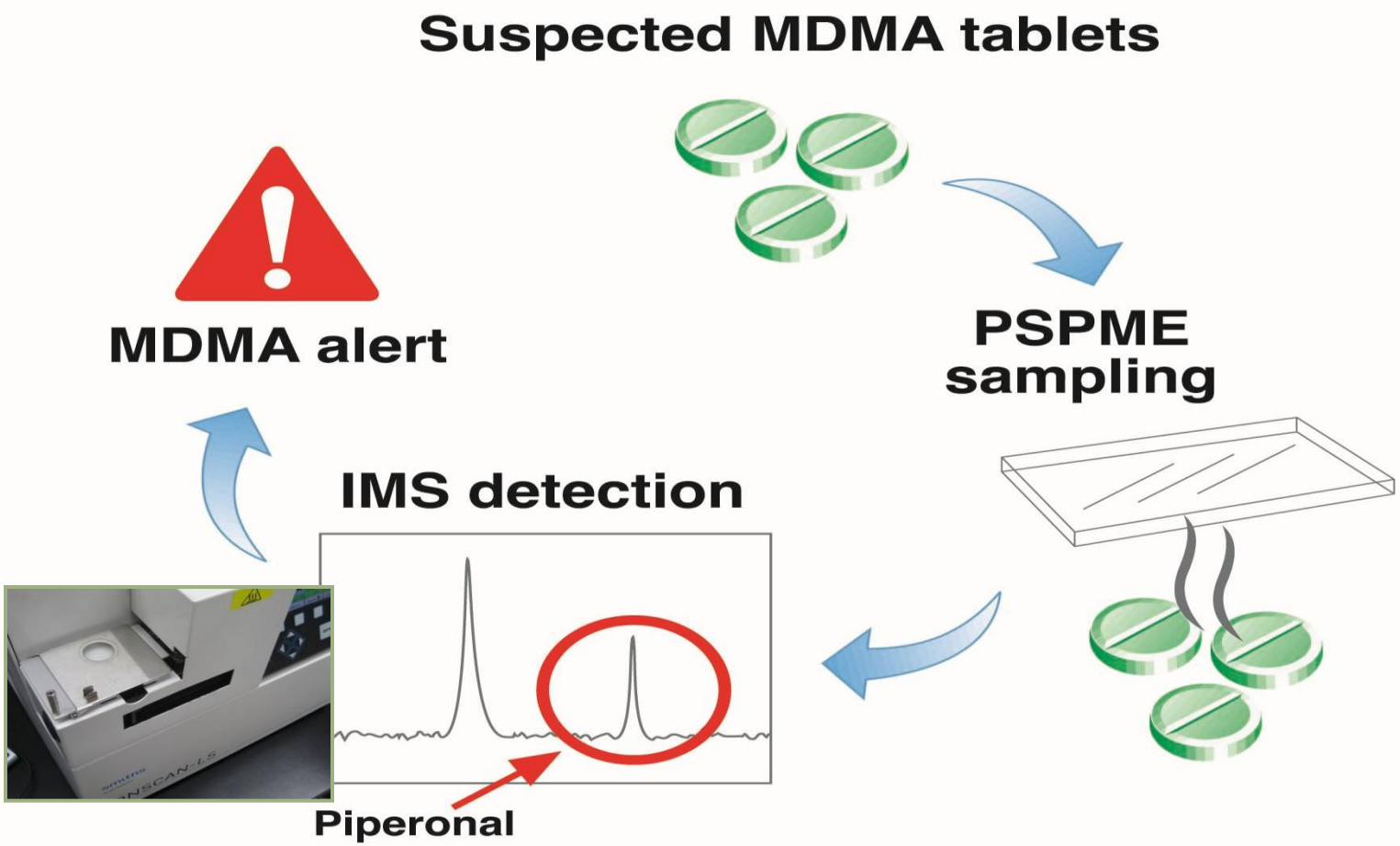
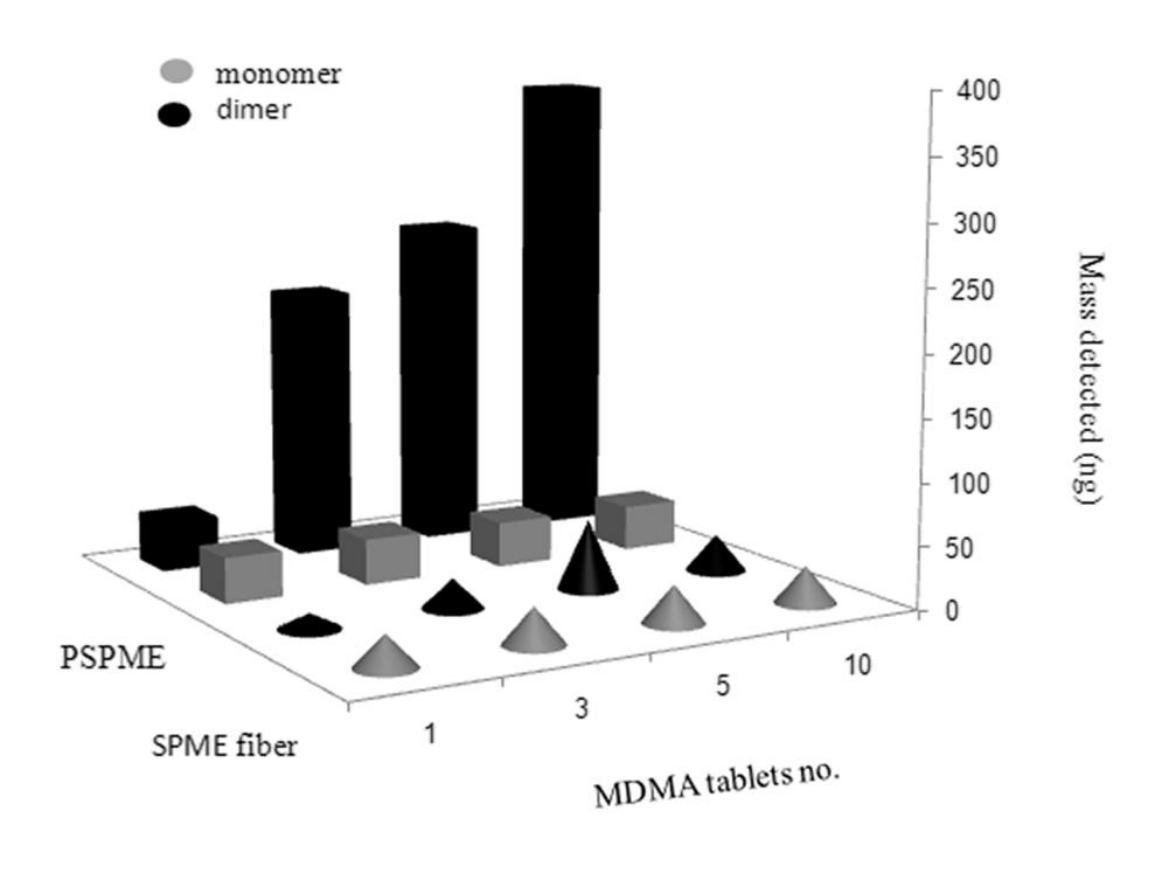
Sampling Approach



Gura et al. (2009)

MDMA Tablets – Static Sampling

(15 Min., Room Temp.)



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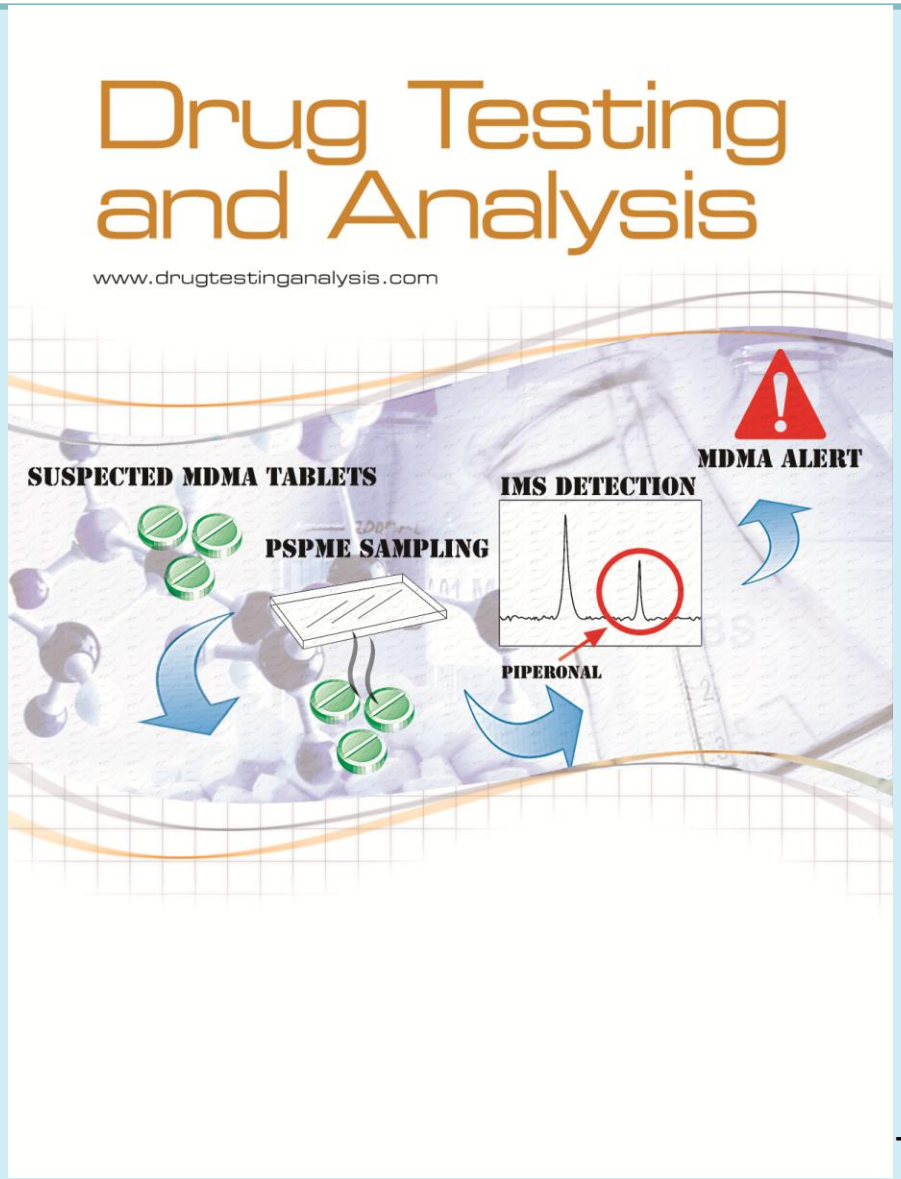

Gura et al. (2009)

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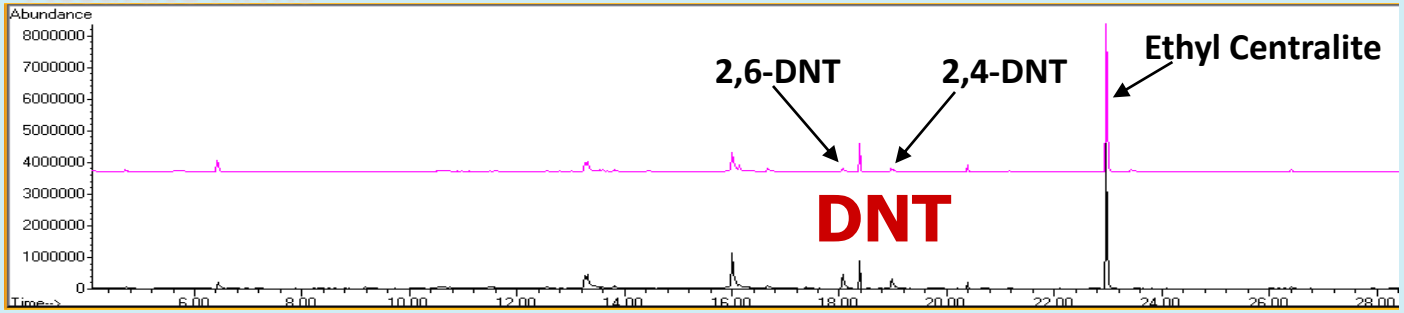
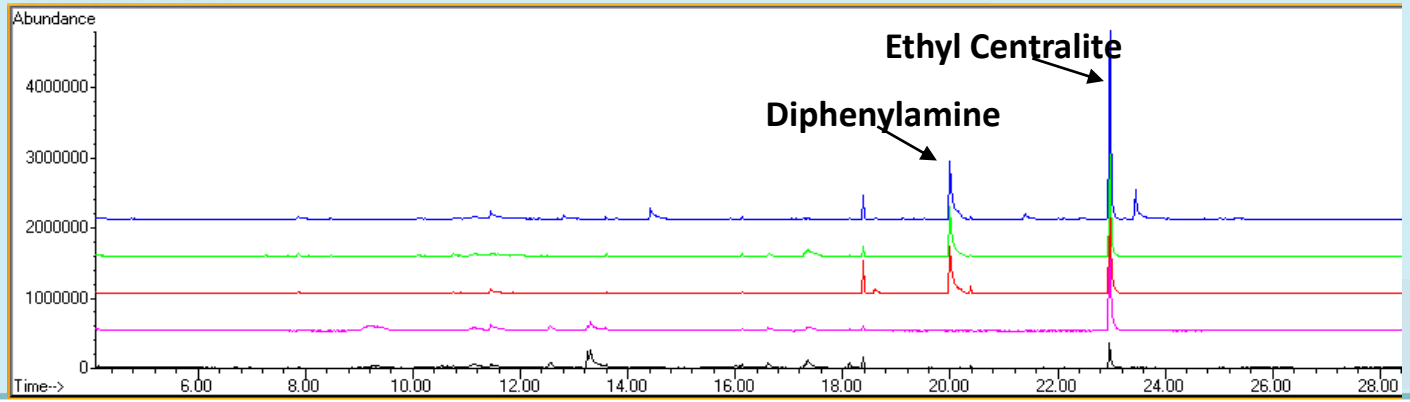
Single Based SP

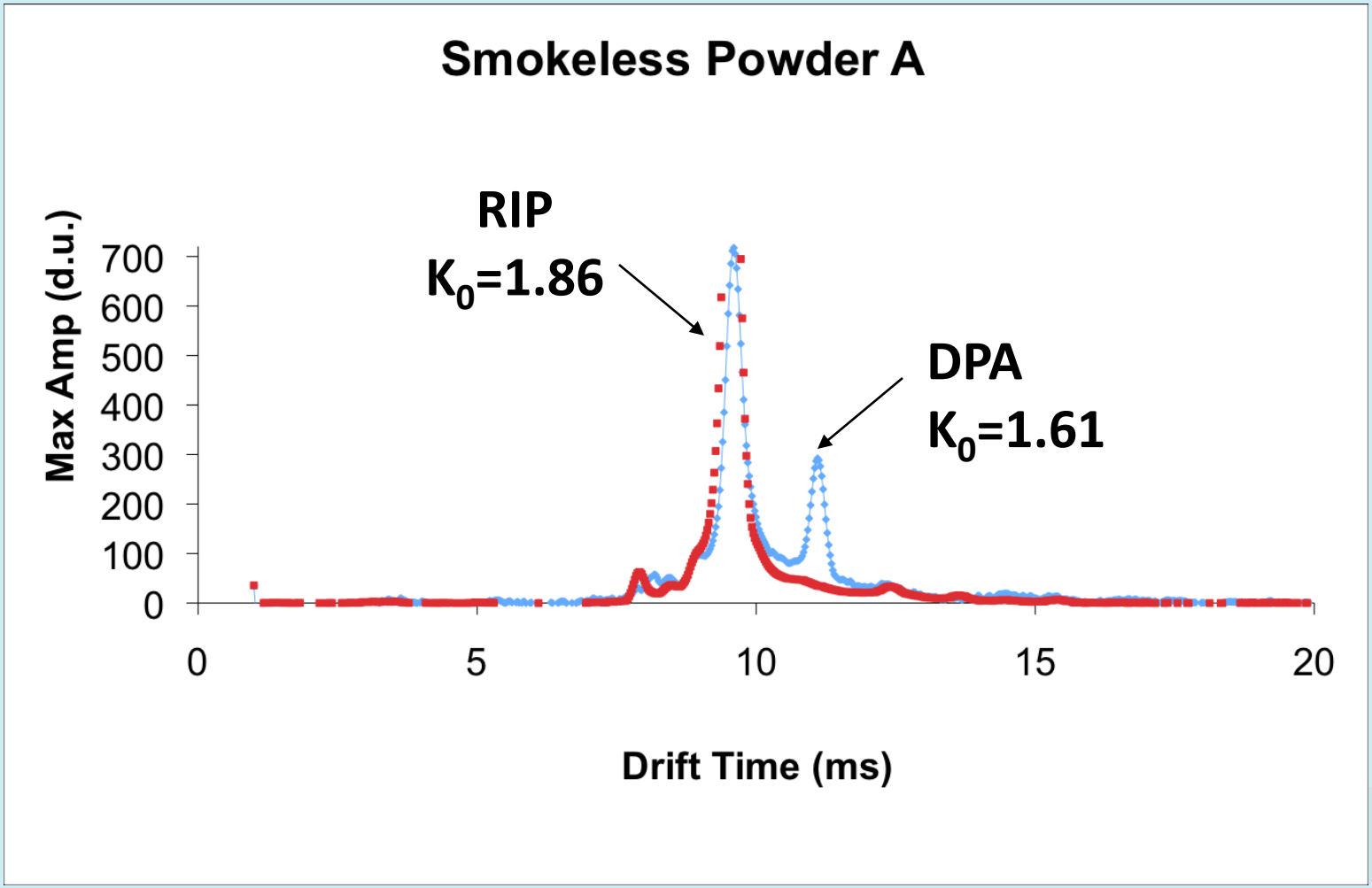
Accurate Arms



VihtaVuori



Smiths 400B – Positive Mode, Default Settings
Reactant Gas is Nicotinamide: DPA Alarm



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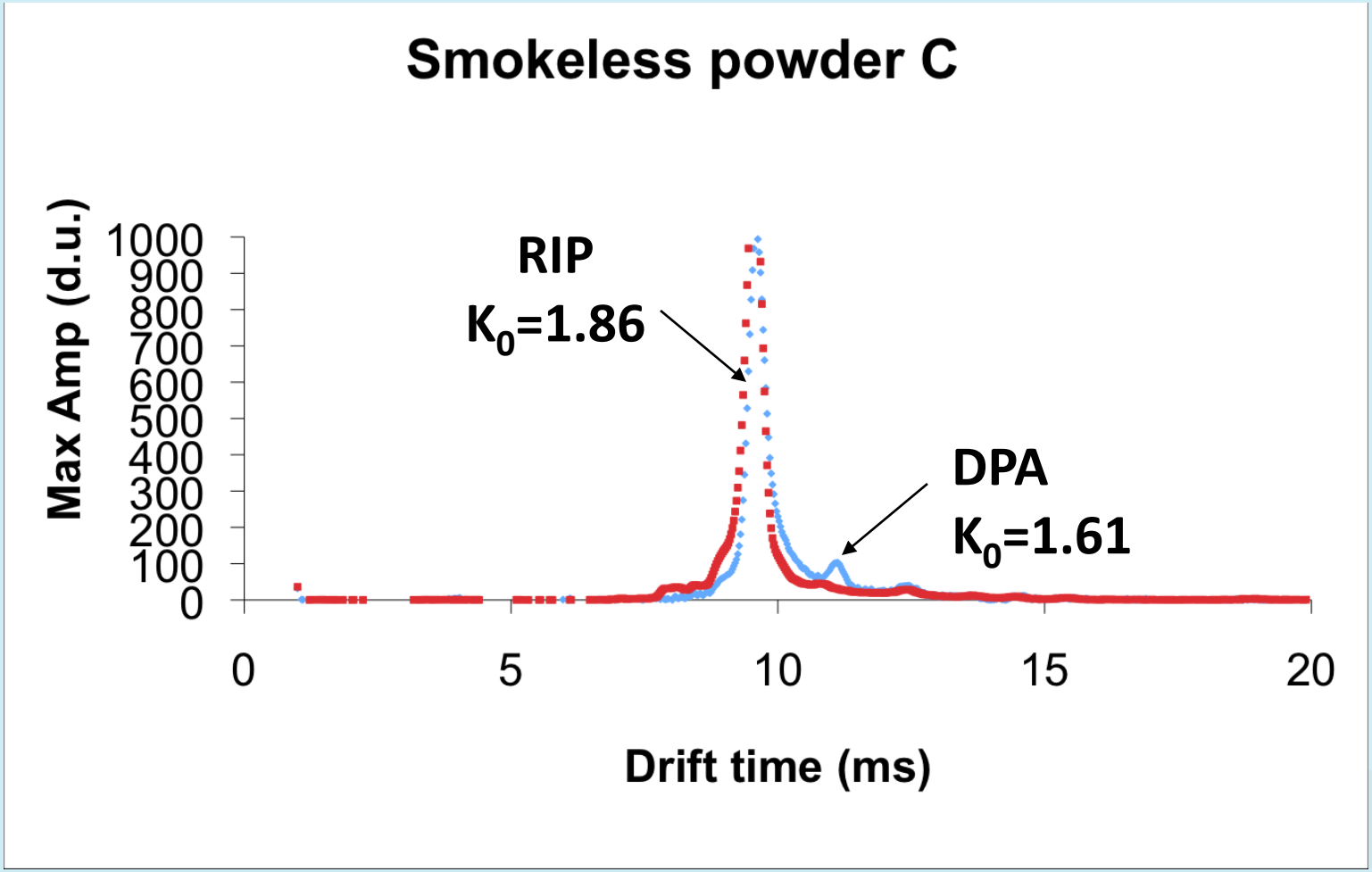
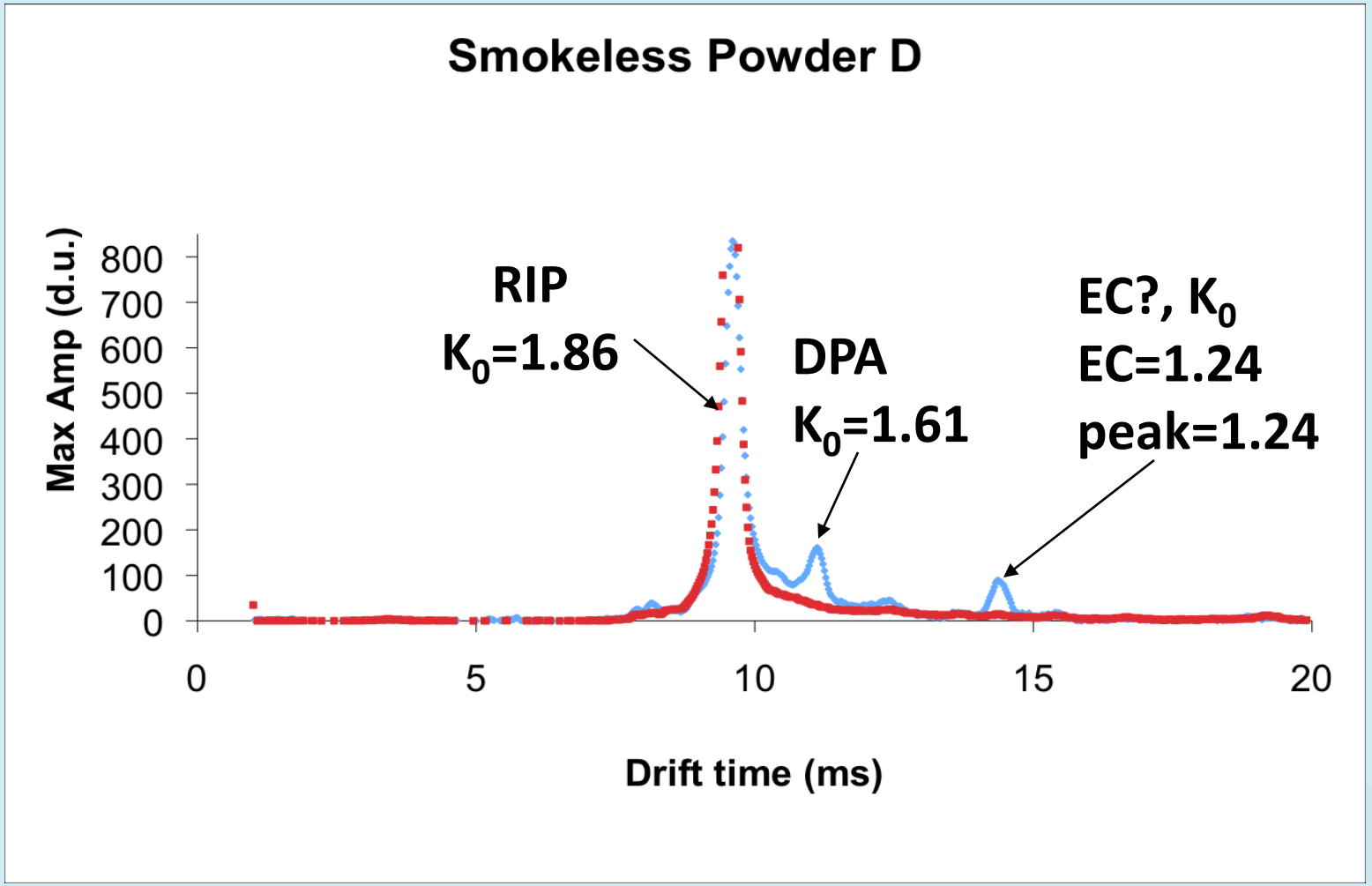
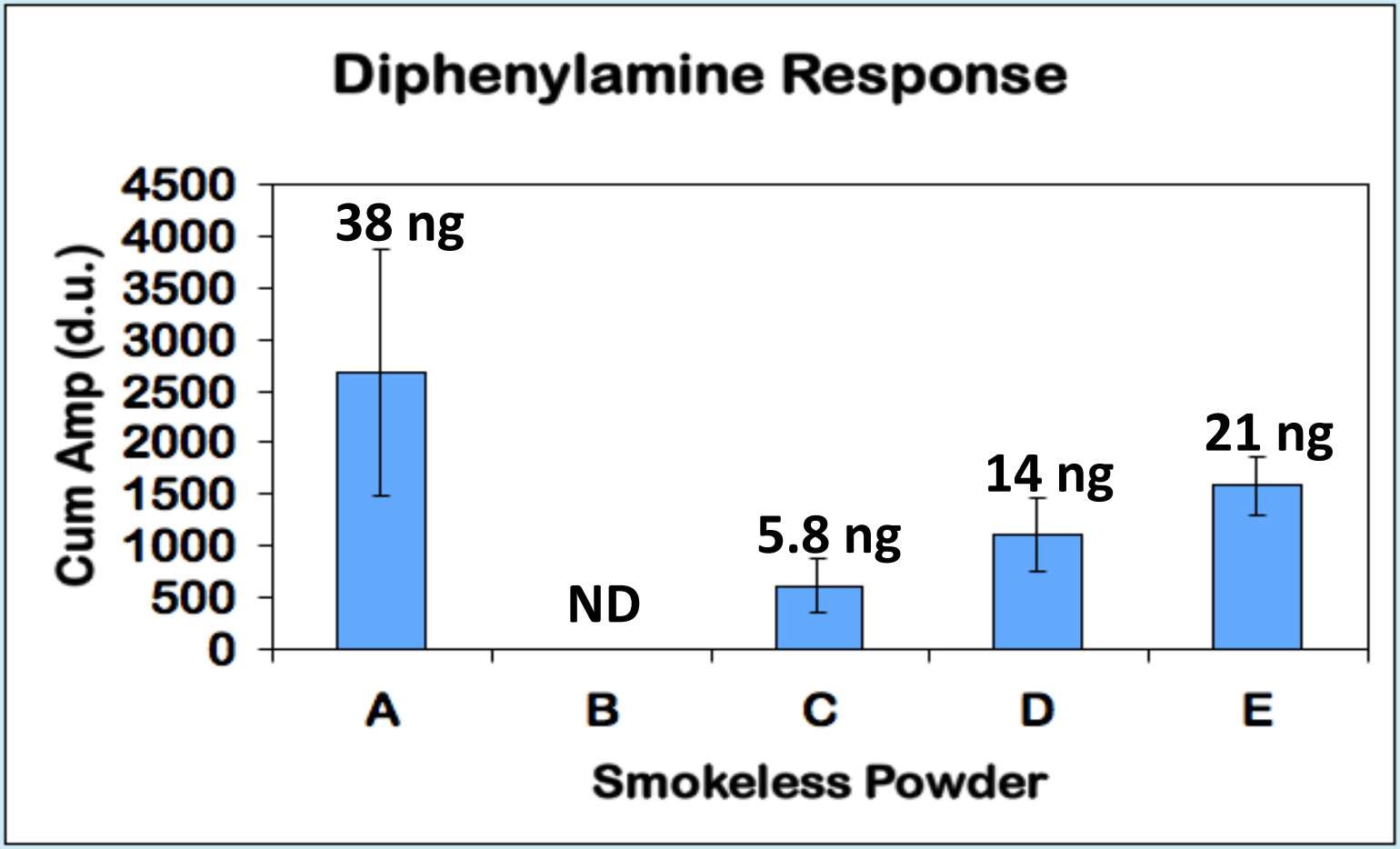


Smiths 400B – Positive Mode, Default Settings

Reactant Gas is Nicotinamide: DPA Alarm



DPA: Planar Sol-Gel PDMS



Smiths Ionscan® 400B

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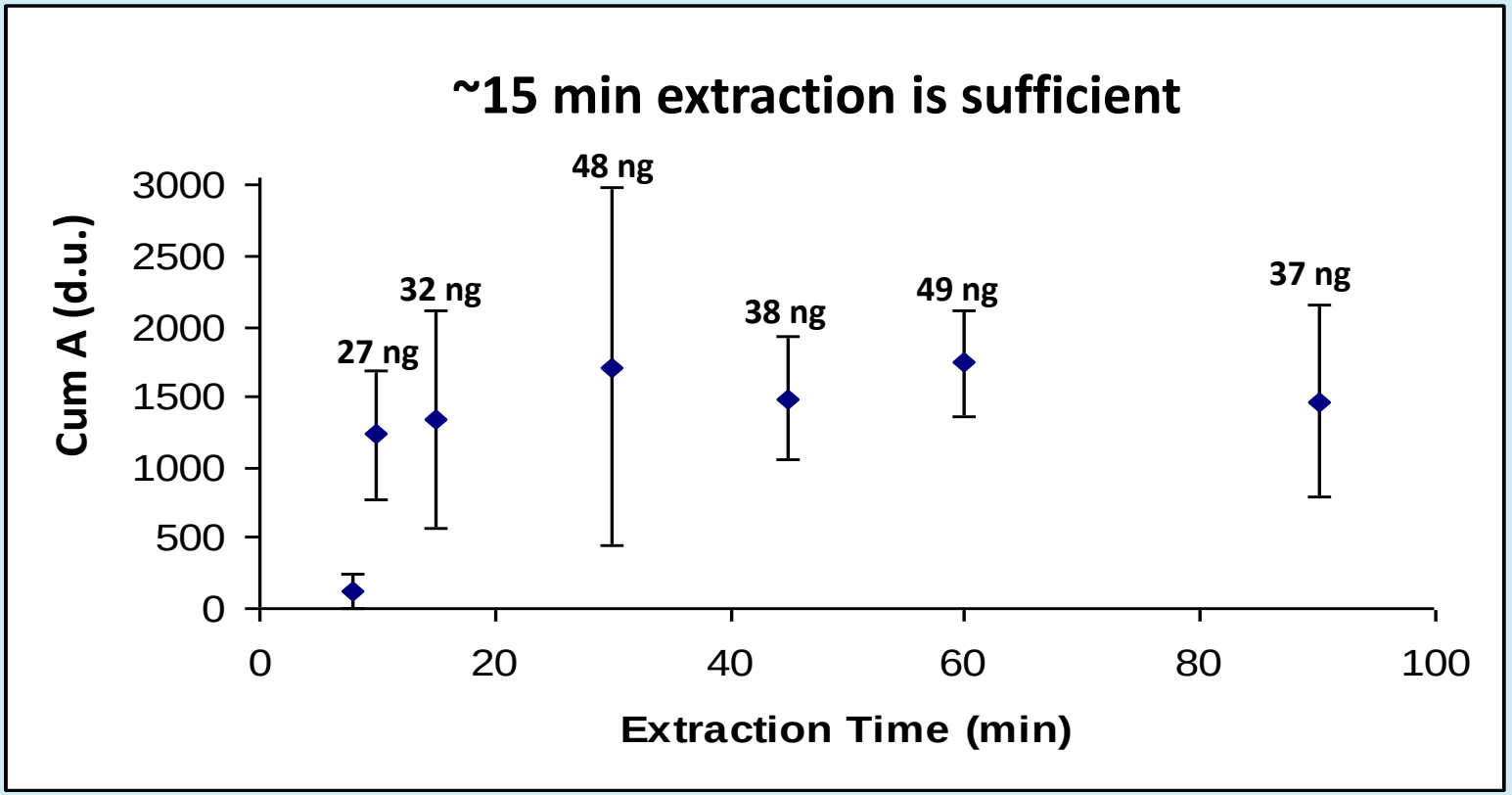
DPA Extraction Curve

Planar Sol-Gel PDMS: Smiths Ionscan® 400B



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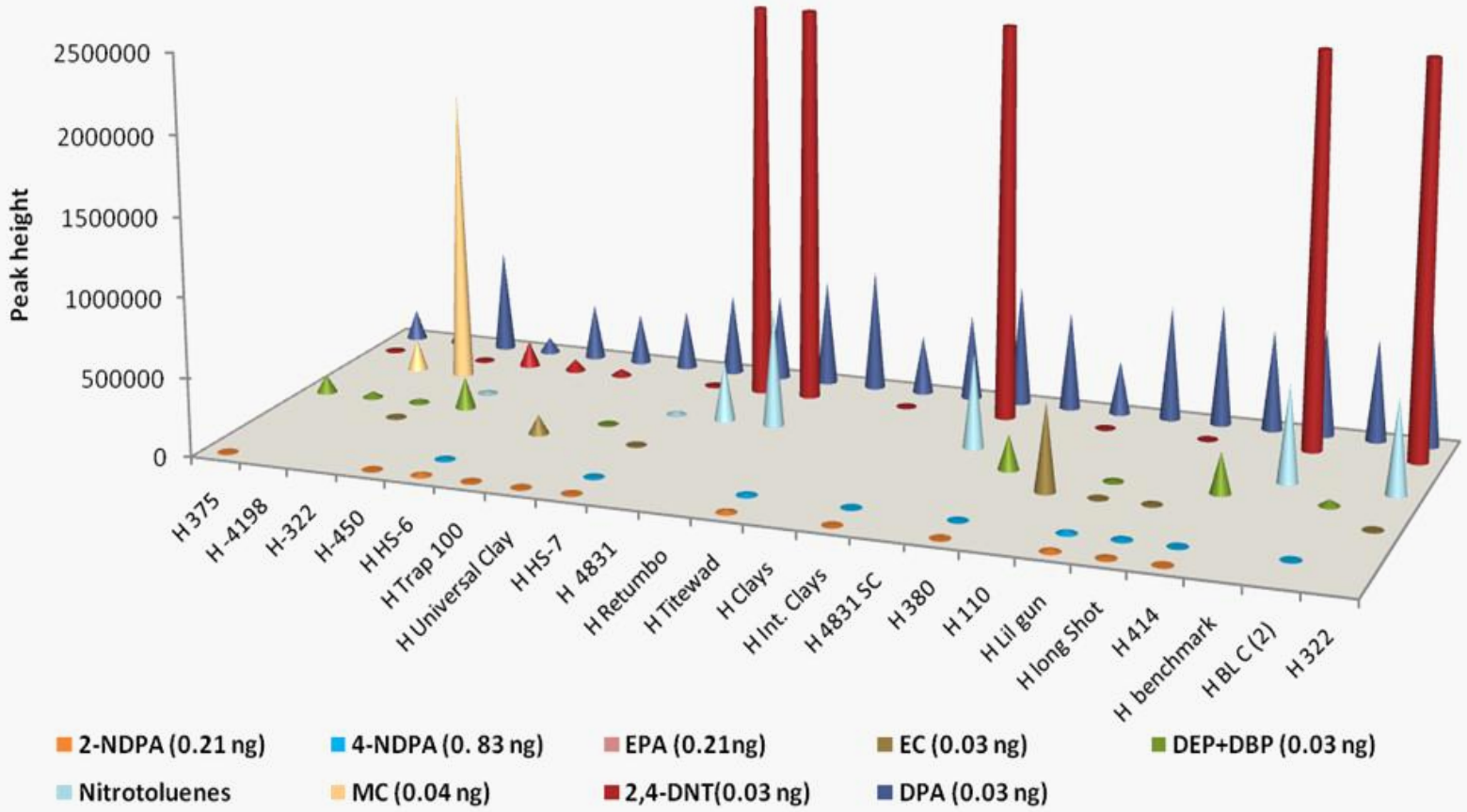
Smokeless Powder Headspace Profiles



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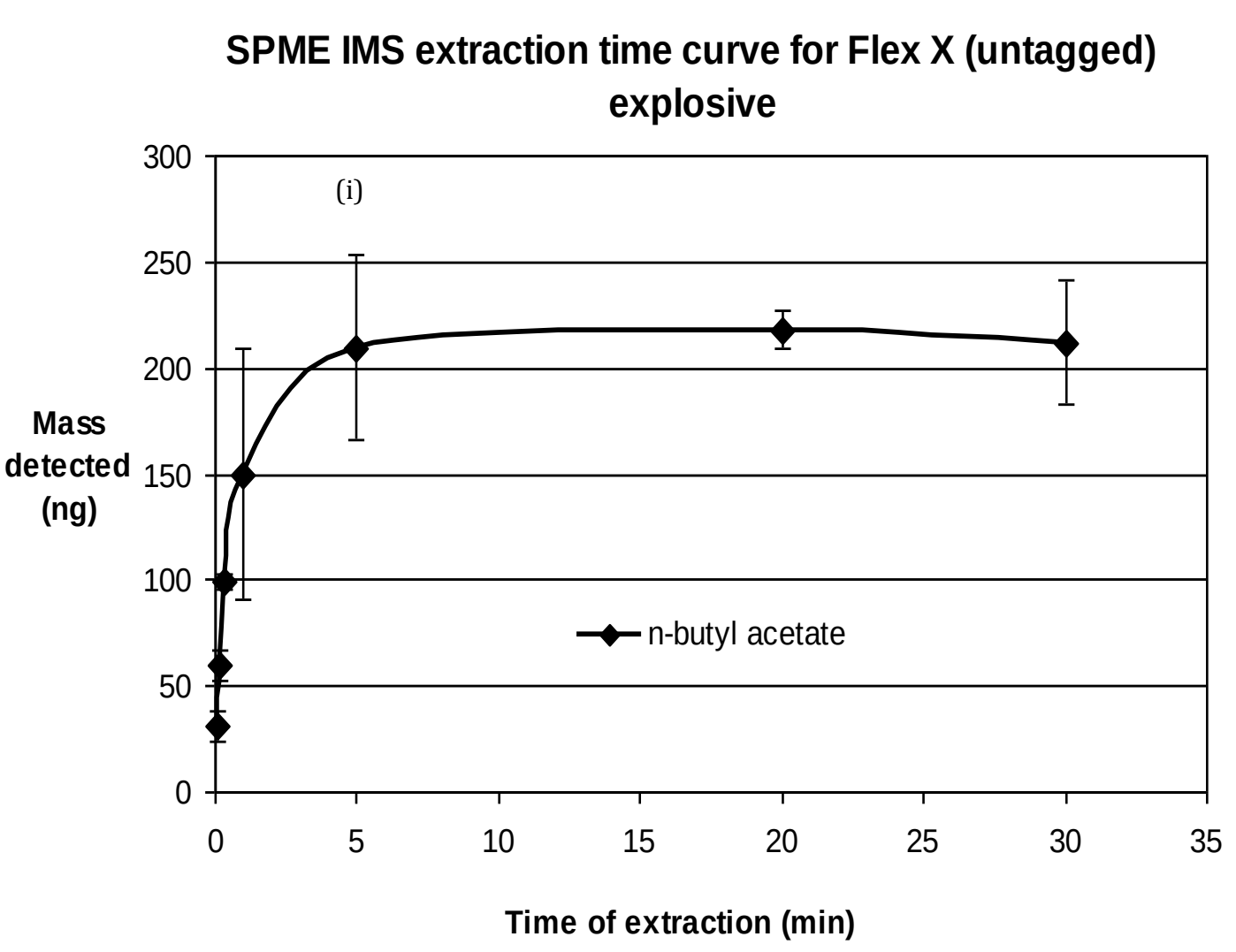

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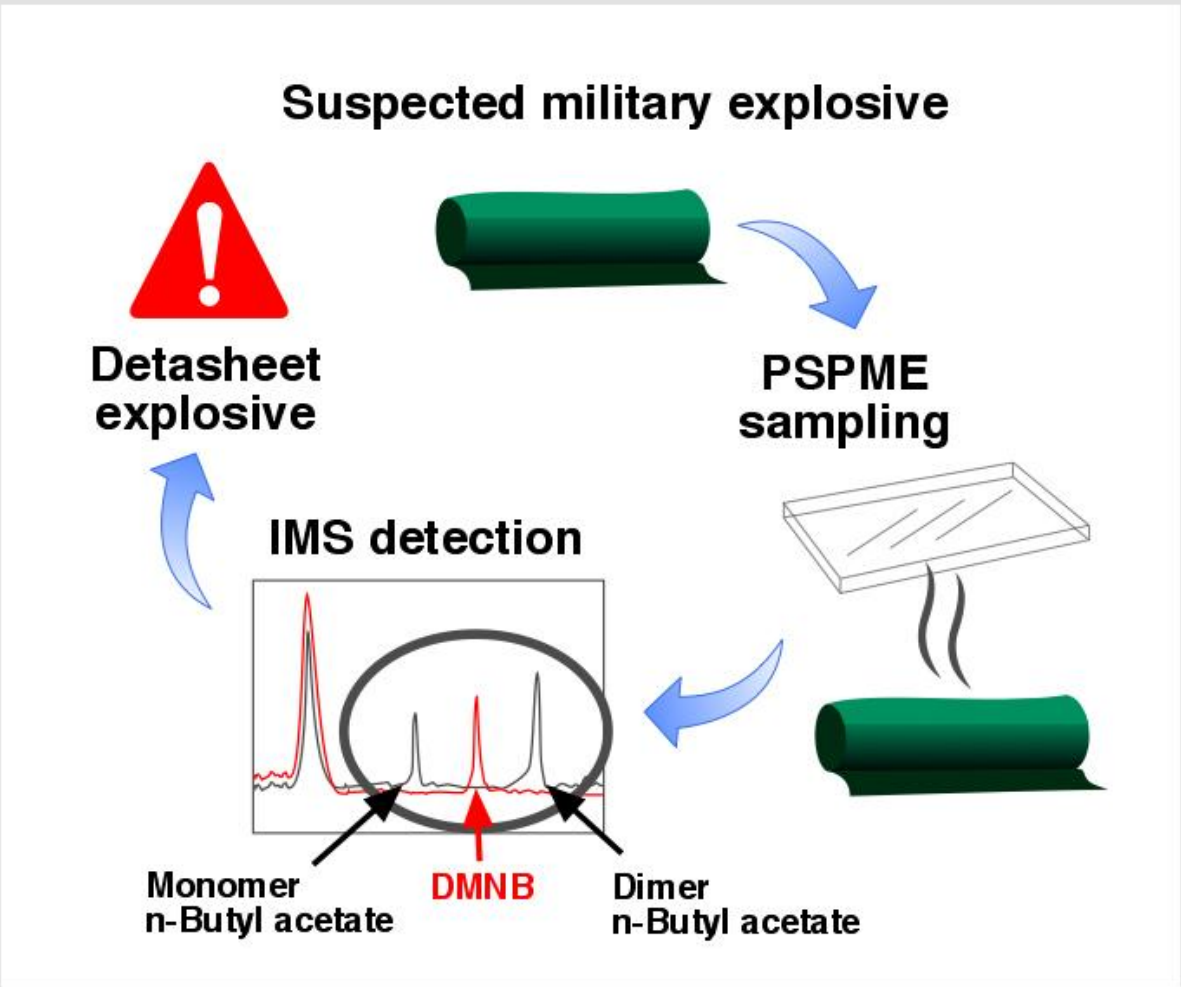
Detection of Plastic Explosives With a Universal Setting



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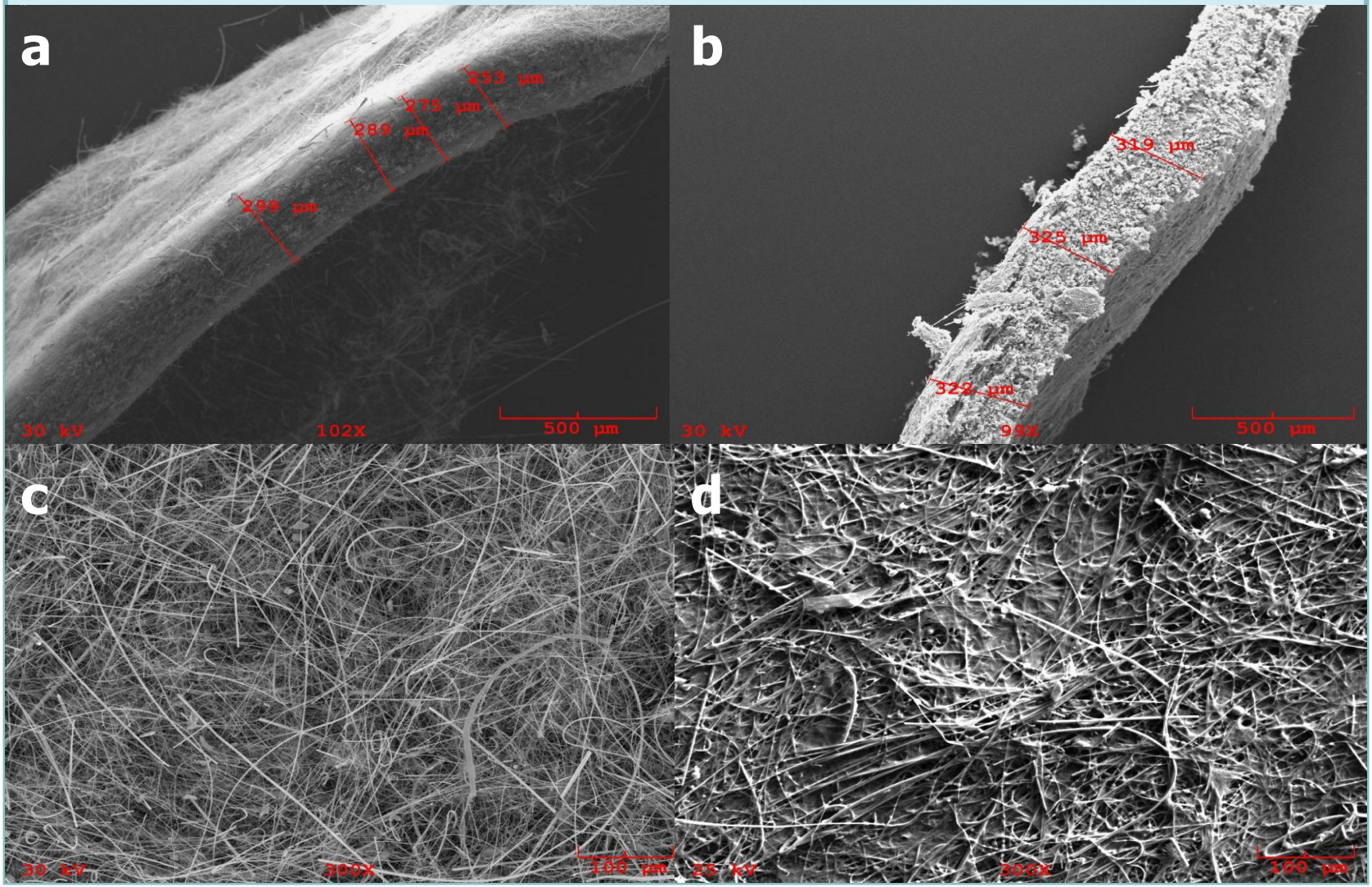
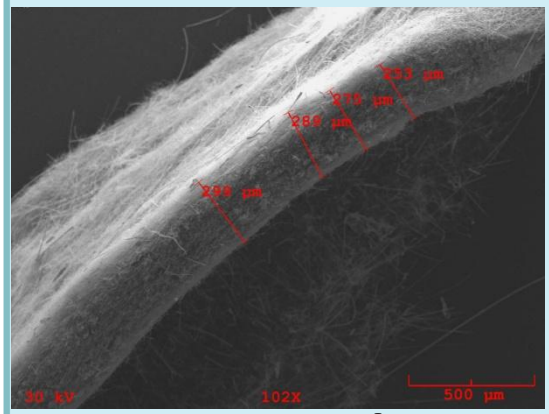
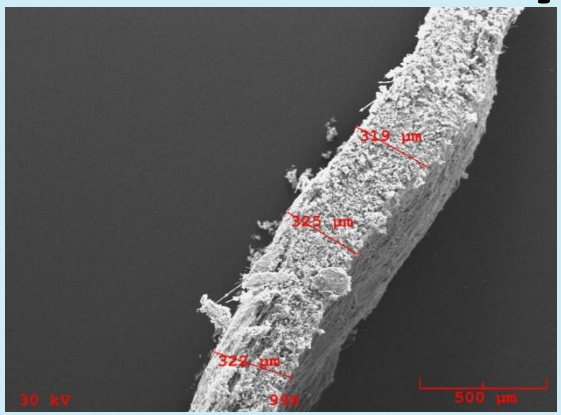
Dynamic PSPME SEM Characterization



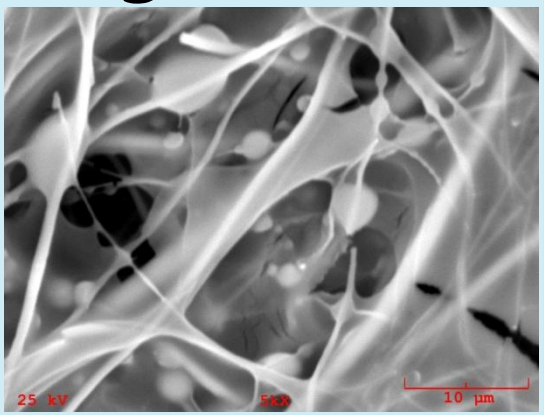
Dynamic Planar SPME Sampling



uncoated



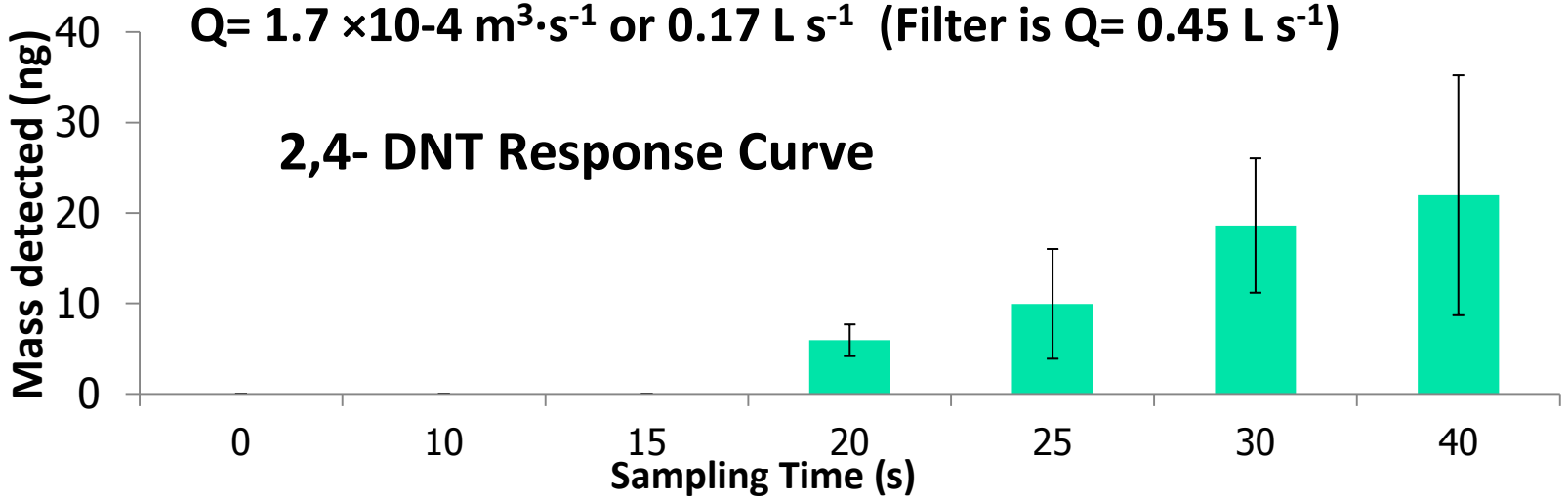
coated



coated

Sampling Time using 2,4-DNT COMPS (~ 14 ng/s)

Q= 1.7 ×10-4 $m^3 \cdot s^{-1}$ or 0.17 L s^{-1} (Filter is Q= 0.45 L s^{-1})



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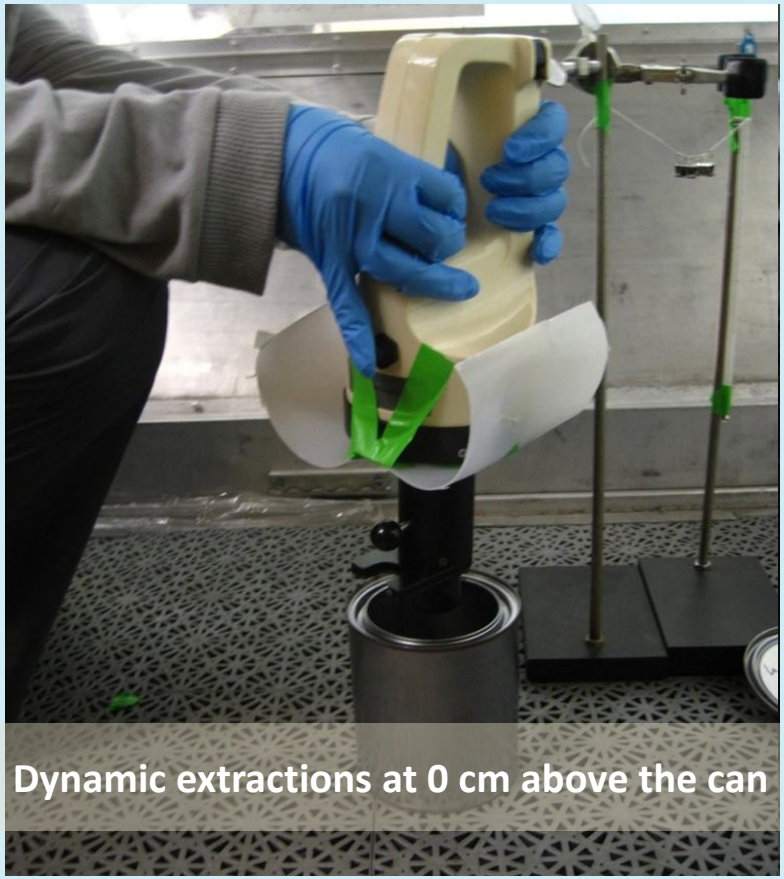
Dynamic Extractions (0.17 L s^{-1})

- **Smokeless powders**
  - **500 mg of All Unique**
  - **500 mg of IMR® 4198**
- **Instruments**
  - **Smiths Detection**
  - **IONSCAN-LS®**
- **Extraction device**
  - **Planar SPME glass filters**



Dynamic extractions at 0 cm above the can

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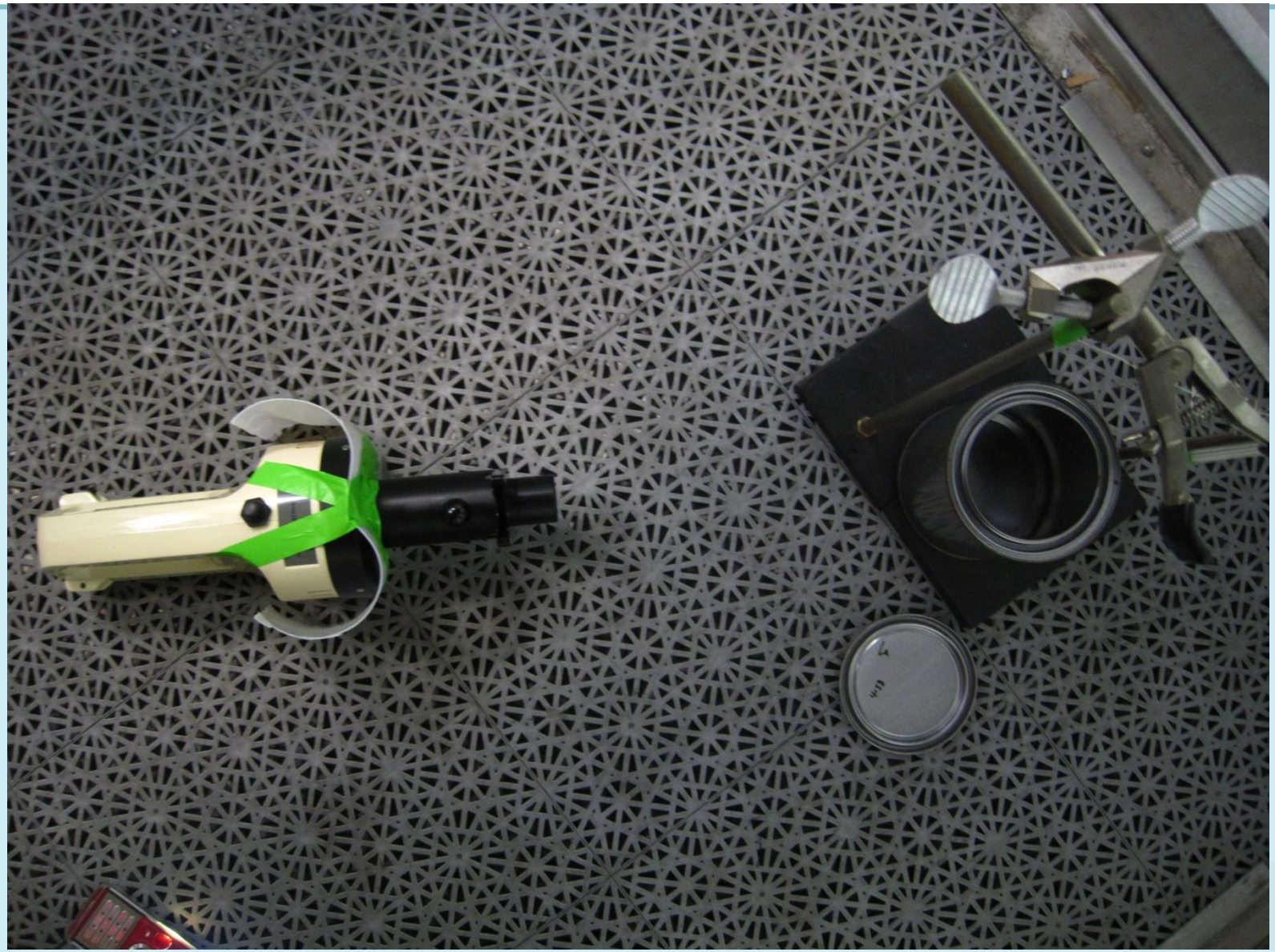

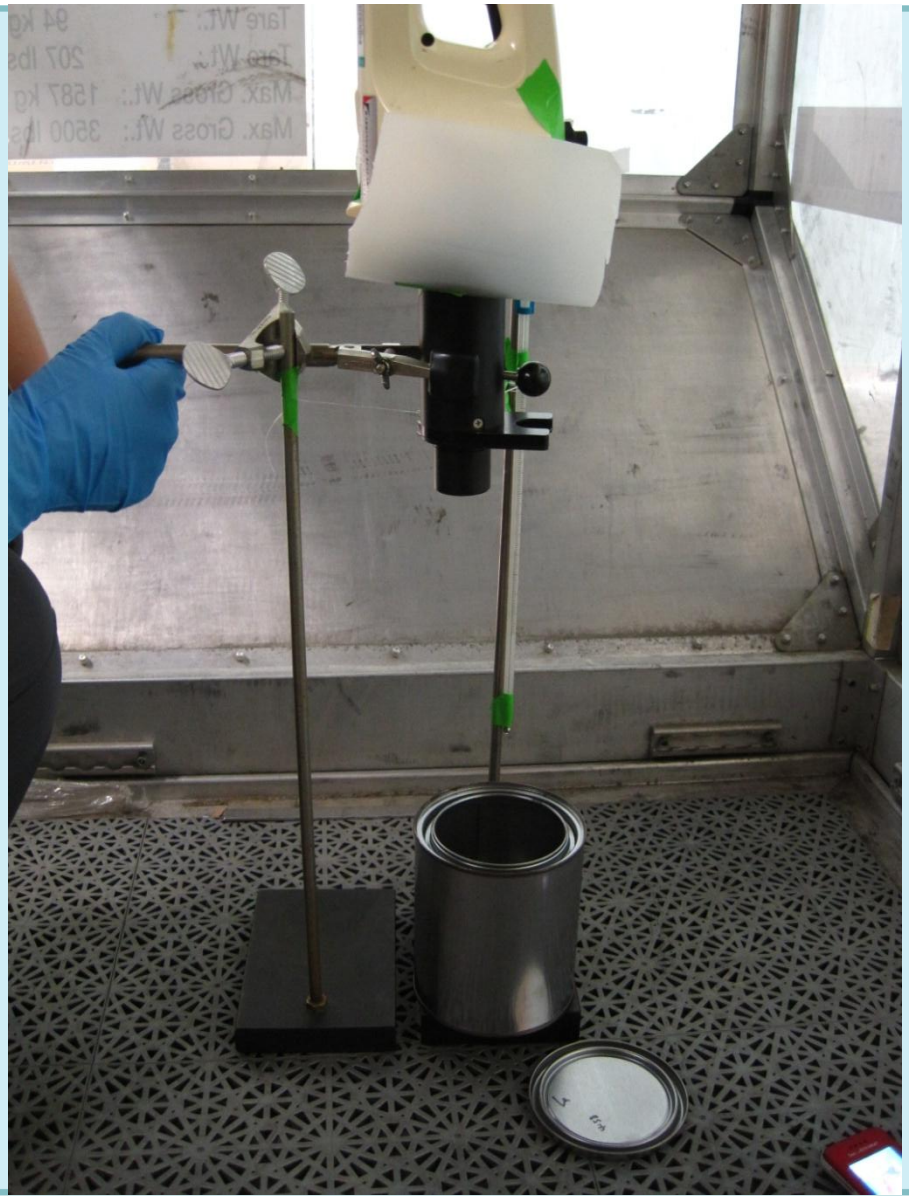

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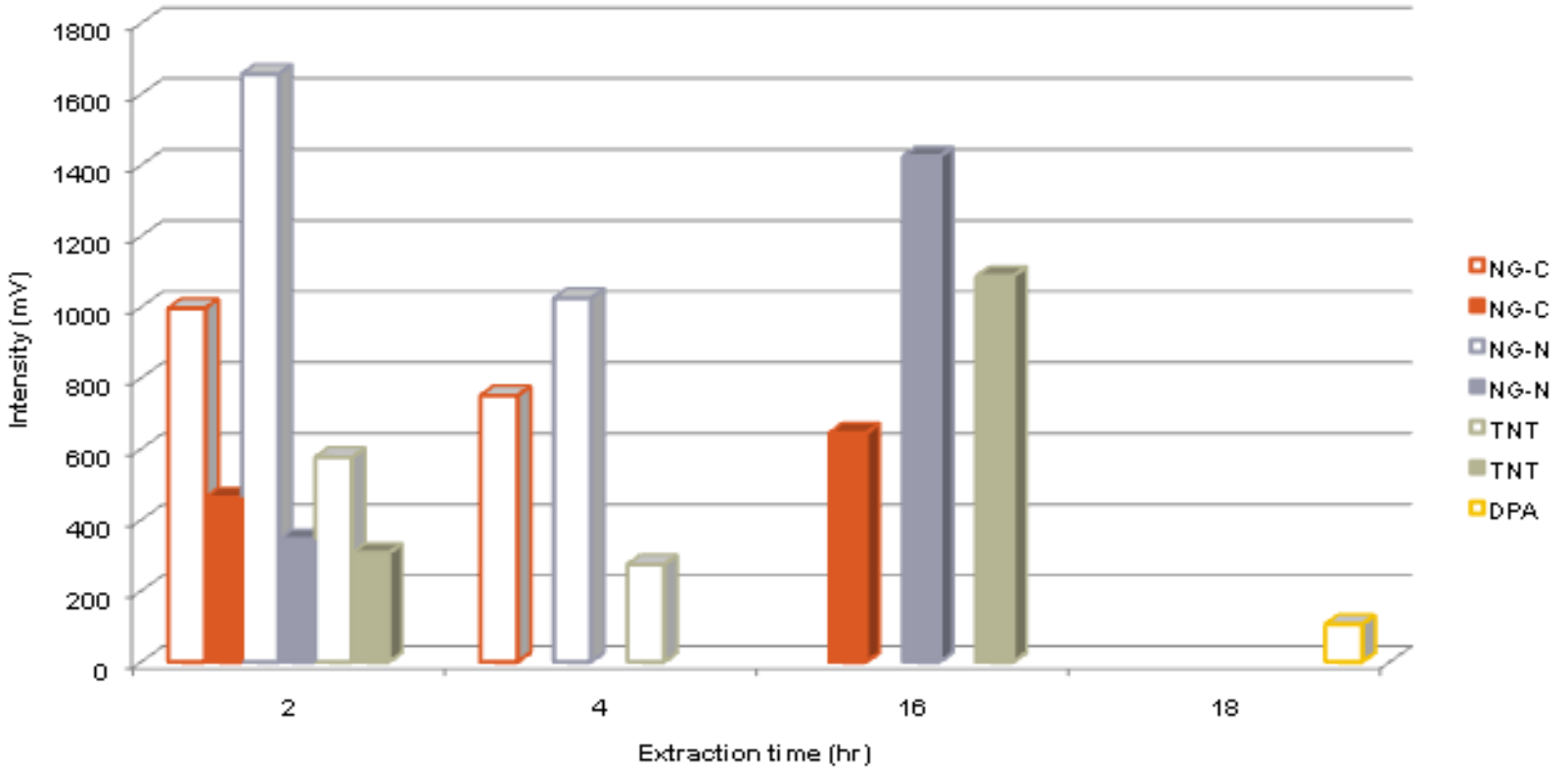
SP and Pentolite Static Extractions (100 mg)



***white bars = 20cm above can; shaded bars = ~150cm (~5ft)**

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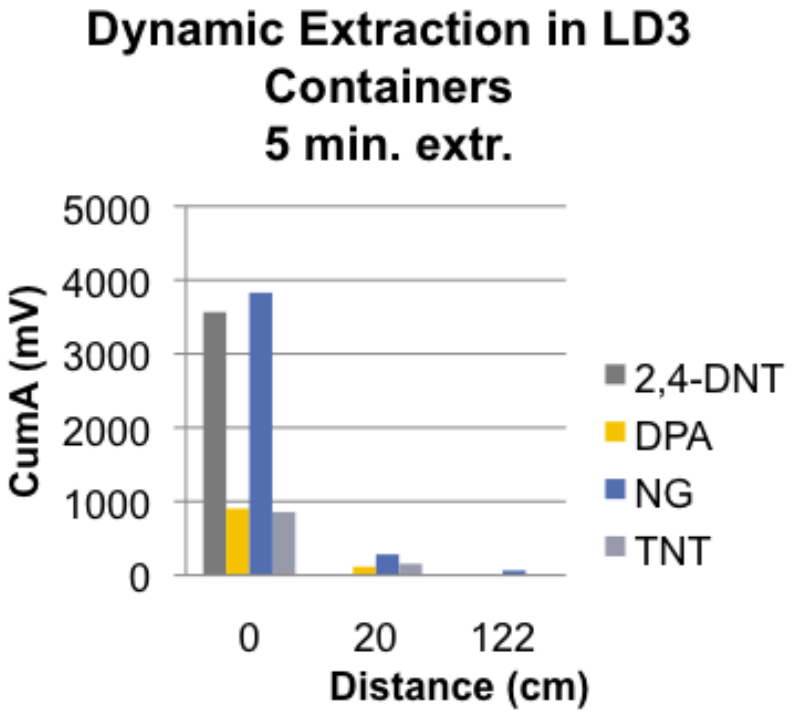
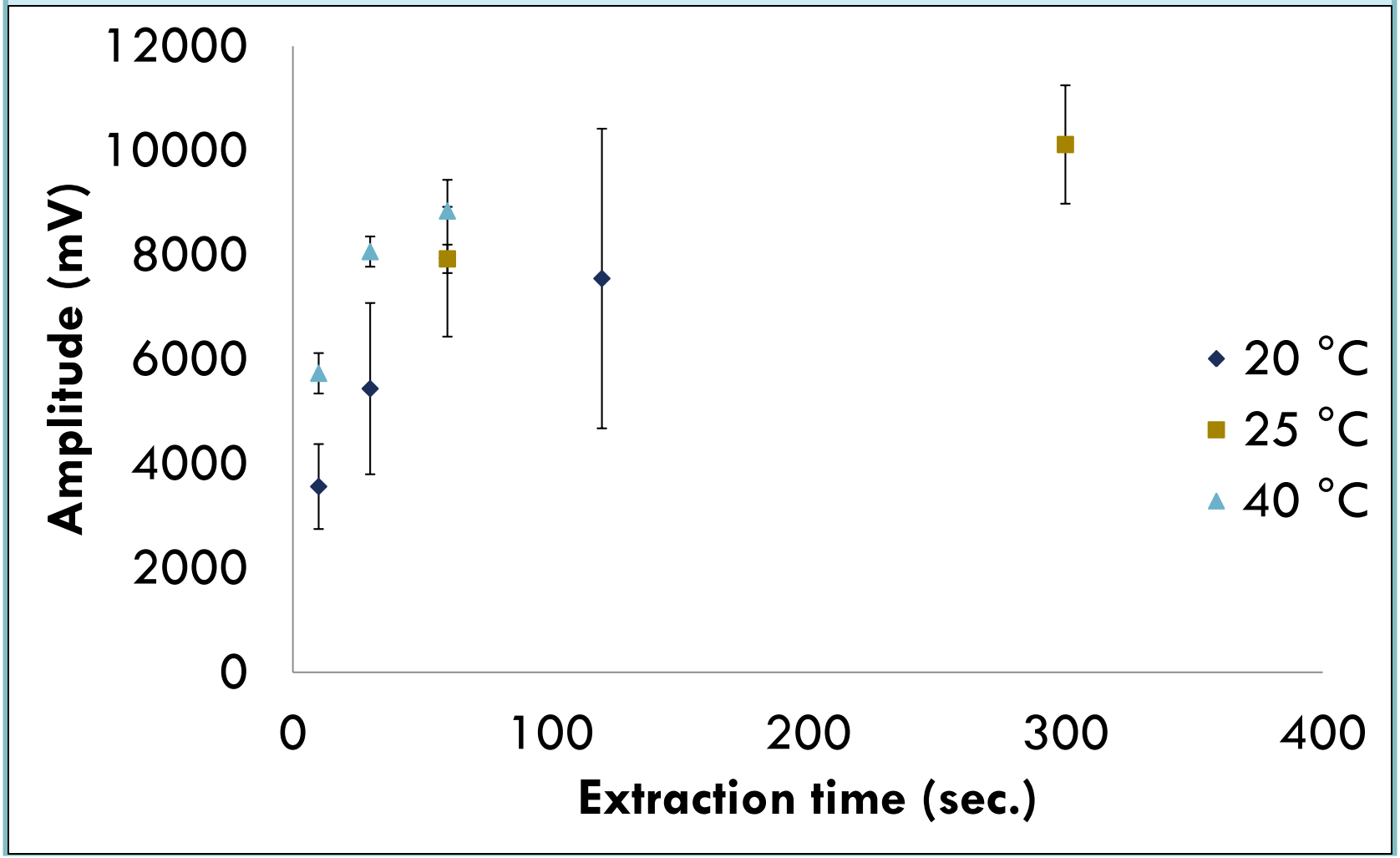
SP/Pentolite Dynamic Mode Extractions

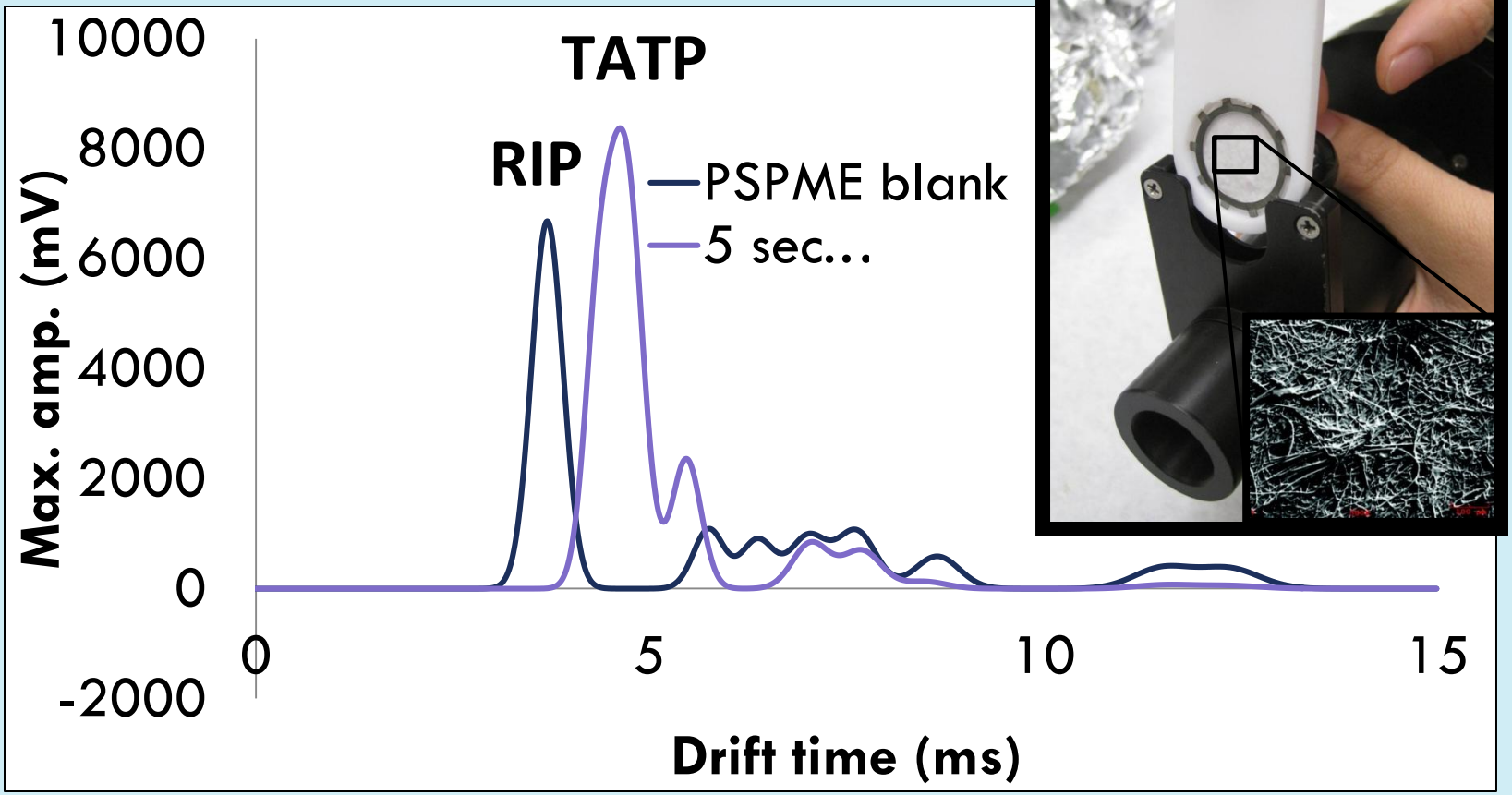
Smokeless Powders	Compound	Distance (cm)	Extraction time (min)	Signal (CumA)
IMR 4198	2,4-DNT	0	2	3565
		20	2	--
			5	--
	DPA	0	5	270
		On floor	2	173
All Unique	DPA	0	5	904
		20	5	116
		On floor	4	515
	NG-C	0	2	772
		20	2	286
			5	291
		4 ft	5	--
		On floor	2	--
	NG-N	0	2	3829
		20	2	365
			5	283
		4 ft	5	65
		On floor	2	--
	TNT	0	2	856
		20	2	156
			5	--
		4 ft	5	--
		On floor	2	60



Static Extraction of 10 mg of TATP



Dynamic Extraction – 10 mg TATP



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Conclusions

- **IMS can be used for detection of volatiles**
  - **Identification of volatile target compounds**
  - **Sampling and preconcentration**
  - **Delivery of sample/analytes to detector**
  - **Optimization of IMS conditions for new target compounds**
  - **Identify sources of false +, false – and potential interferences**
- **IMS detectors can complement canines**
- **Novel PSPME geometry is compatible with IMS**
- **PSPME enhances performance (sensitivity)**

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*Almirall Group – *IMS research*

***Dr. Patty Diaz, Dr. Hanh Lai, Dr. Monica Joshi, Wen Fan, Dr. Sigalit Gura, Howard Holness and Mimy Young**

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Questions?

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