Pyrolysis PLOT Cryoadsorption
or,
Headspace Sampling on Steroids

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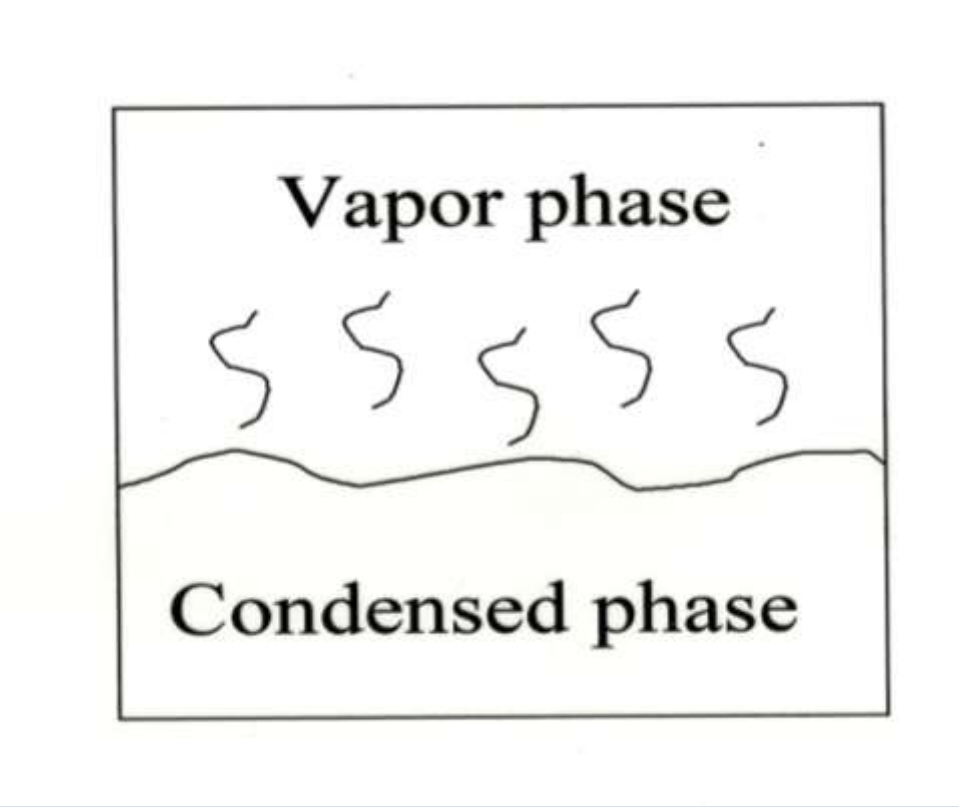
National Institute of Standards and Technology

Boulder, CO

The vapor that develops above a condensed phase:



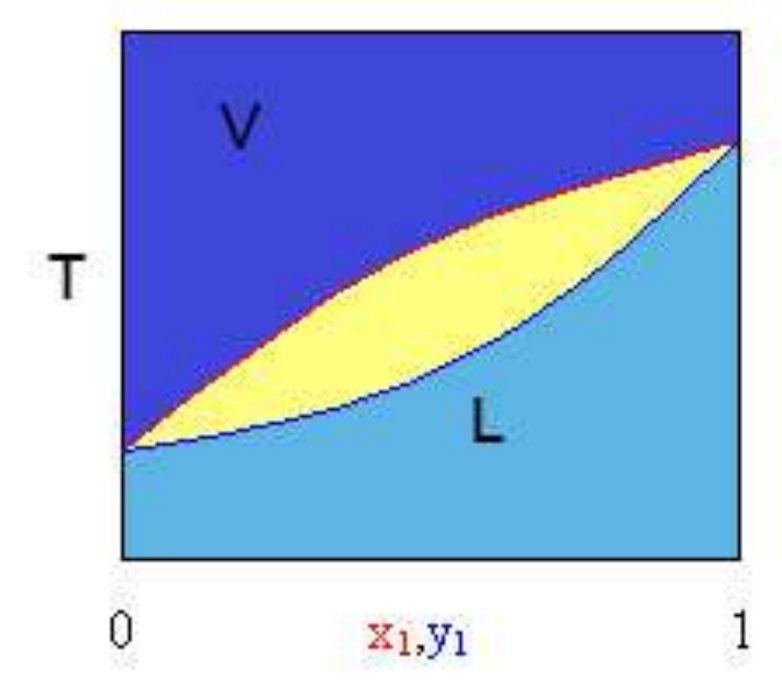
IMPORTANT FOR:

Food quality analysis

Environmental sample analysis

Natural products

Condensed phase and vapor phase composition will be different:



Thermodynamics ensures that there will be a difference

VLE is “predictable”*, VSE is less predictable

* If you have an equation of state

So, why bother with this?

- Sometimes you need to know what is in the vapor phase
  - The vapor is all you get
  - The vapor is the best way to analyze sample

The Challenge:

- The primary difficulty has always been to **obtain enough** solute (or analyte)

- Other difficulties:
  - Calibration
  - Matrix overload
  - Stability, etc.

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- Other difficulties:
  - Calibration
  - Matrix overload
  - Stability, etc.

- Purge and Trap Approach:
  - Capture what you can grab
  - Analyze it later
- SPME
  - The sample does the walking

Getting back to **pyro PLOT cryo**

What's in a Name?

- Lineage:

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    - Highly repeatable, thermodynamically consistent
      - Van't Hoff equation represents f(1/T) at 10 ppb

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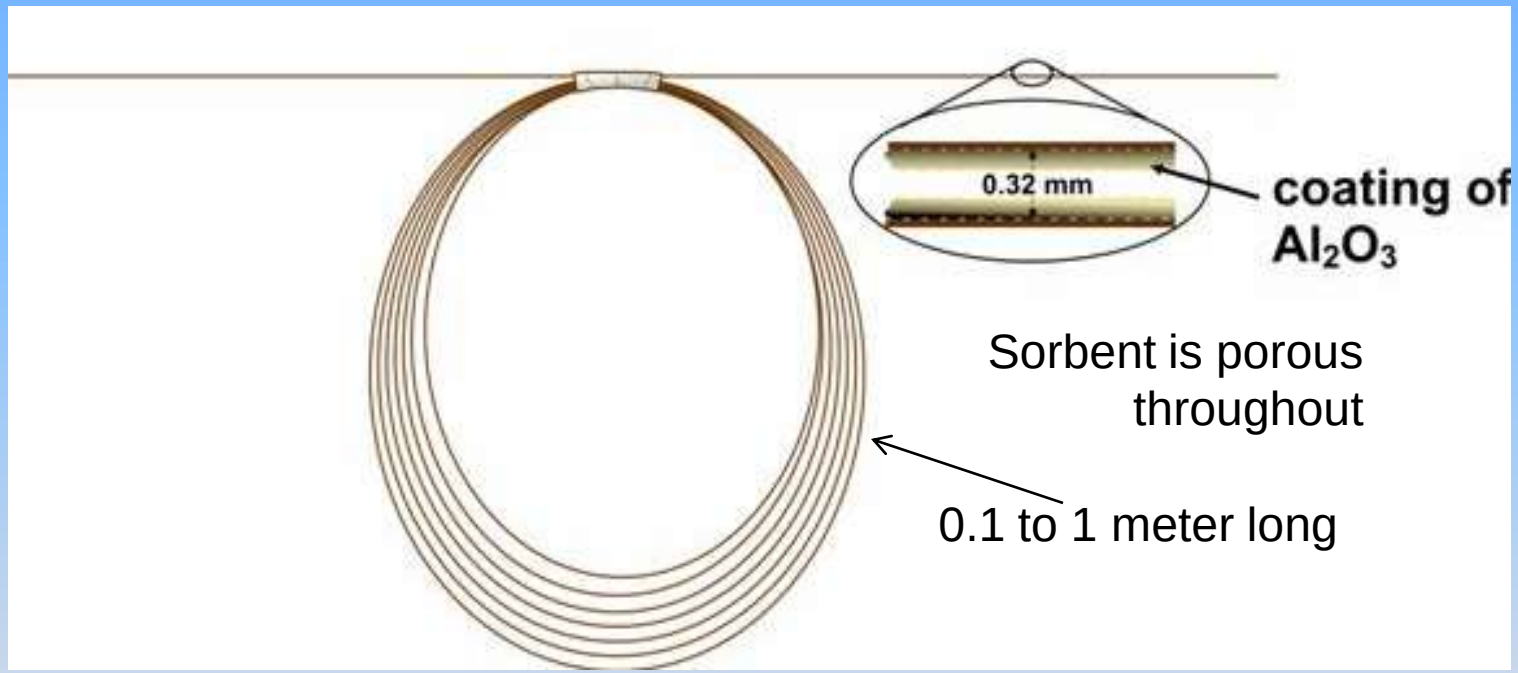
      - go/no-go at < 1 ppb
  - PLOT cryo beats SPME in a walk

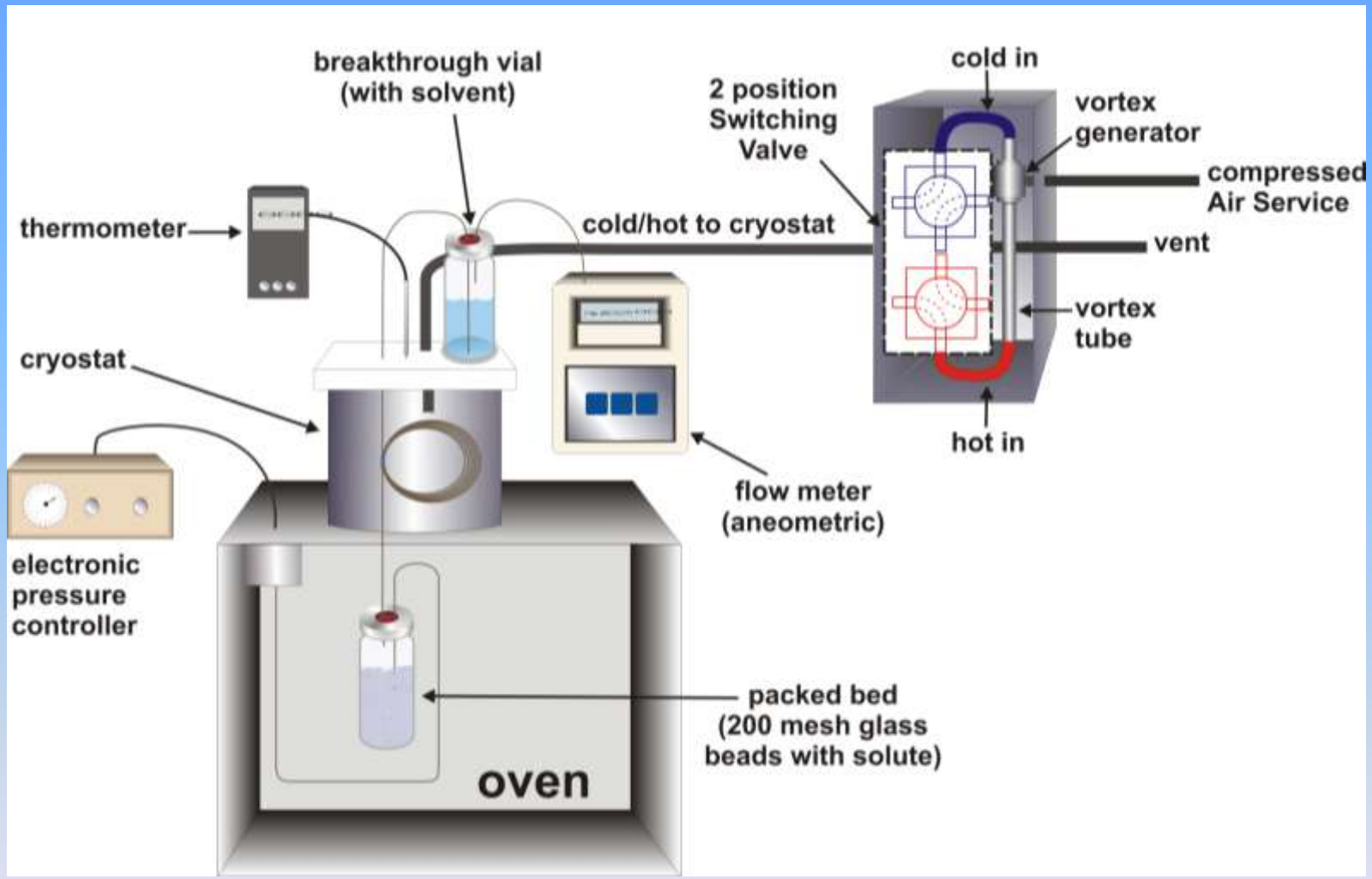
So what was PLOT Cryo?
PLOT capillary trap, in a cryoadsorber



A wide variety of sorbent phases can be used:

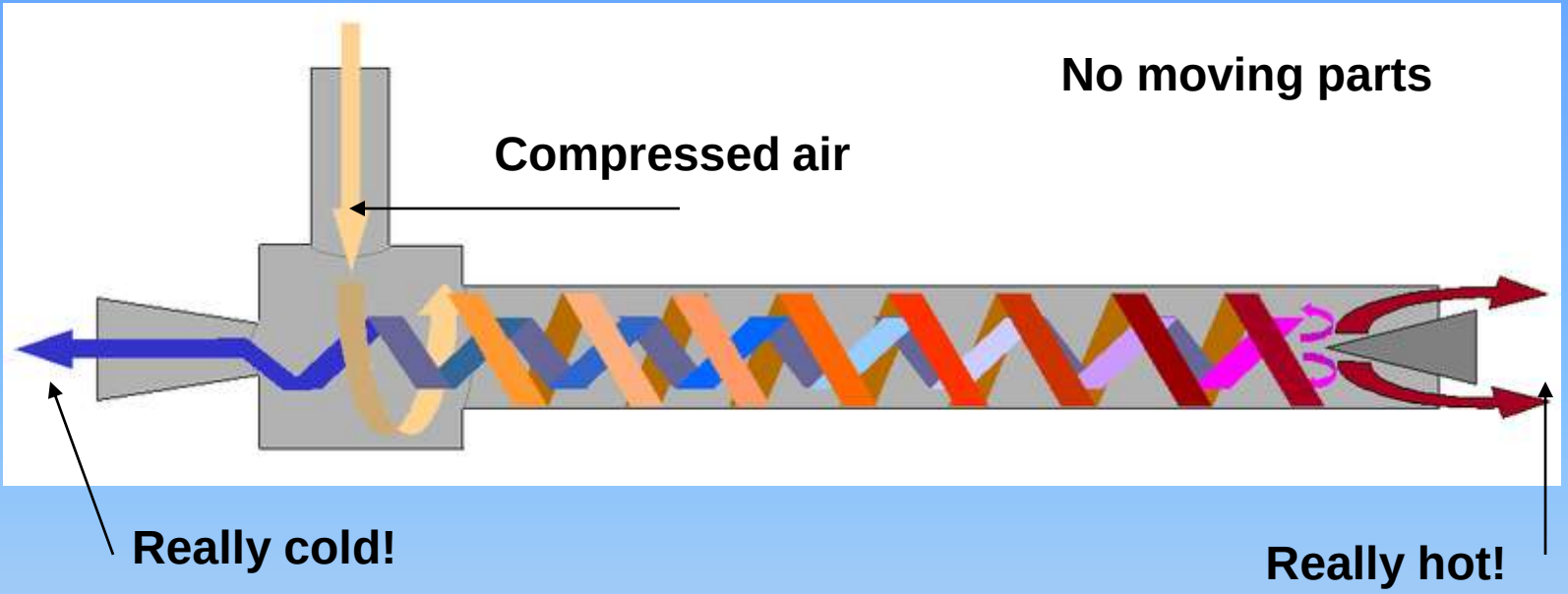
alumina, silica, polymeric, **sol-gel, clay, organoclay**,…

PLOT Capillary Cryoadsorption*



*Bruno, T.J., Simple quantitative headspace analysis by cryoadsorption on a short alumina PLOT column, *J. Chromatogr. Sci*., 47, 569-574, 2009.

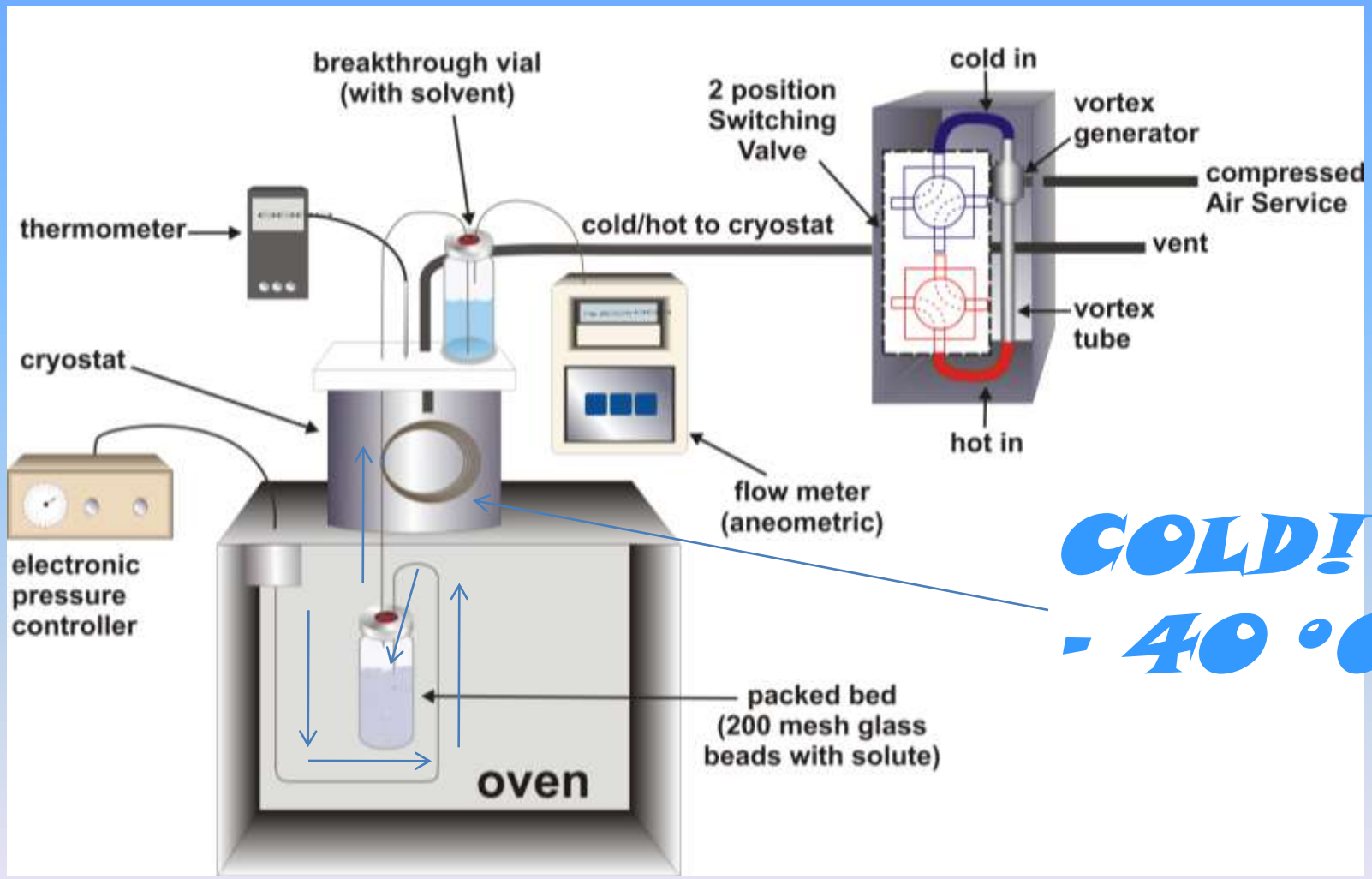
Vortex Tubes:



My Favorite Toy:

Bruno, T.J., Vortex cooling of HPLC components, *Liquid Chromatography*, Vol. 4, No. 2, pp. 134-136 (1985).
Bruno, T.J., Vortex cooling for low temperature gas chromatography, *Anal. Chem*., Vol. 58, p. 1596 (1986).
Bruno, T.J., Laboratory applications of the vortex tube, *J. Chem. Educ*., Vol. 64, No. 11, p. 987 (1987).
Bruno, T.J., Applications of the vortex tube in chemical analysis, *Proc. Contr. and Qual.*, 3, 195, 1992.
Bruno, T.J., Application of the vortex tube in chemical Analysis, Part I, *Am. Lab*., 25(12), 15 1993
Bruno, T.J., Application of the vortex tube in chemical Analysis, Part II, *Am. Lab*.,, 25(14), 14 1993
Bruno, T.J., Chromatographic cryofocusing and cryotrapping with the vortex tube, *J. Chromatographic Sci.*, 32, 112, 1994.

PLOT Capillary Cryoadsorption*



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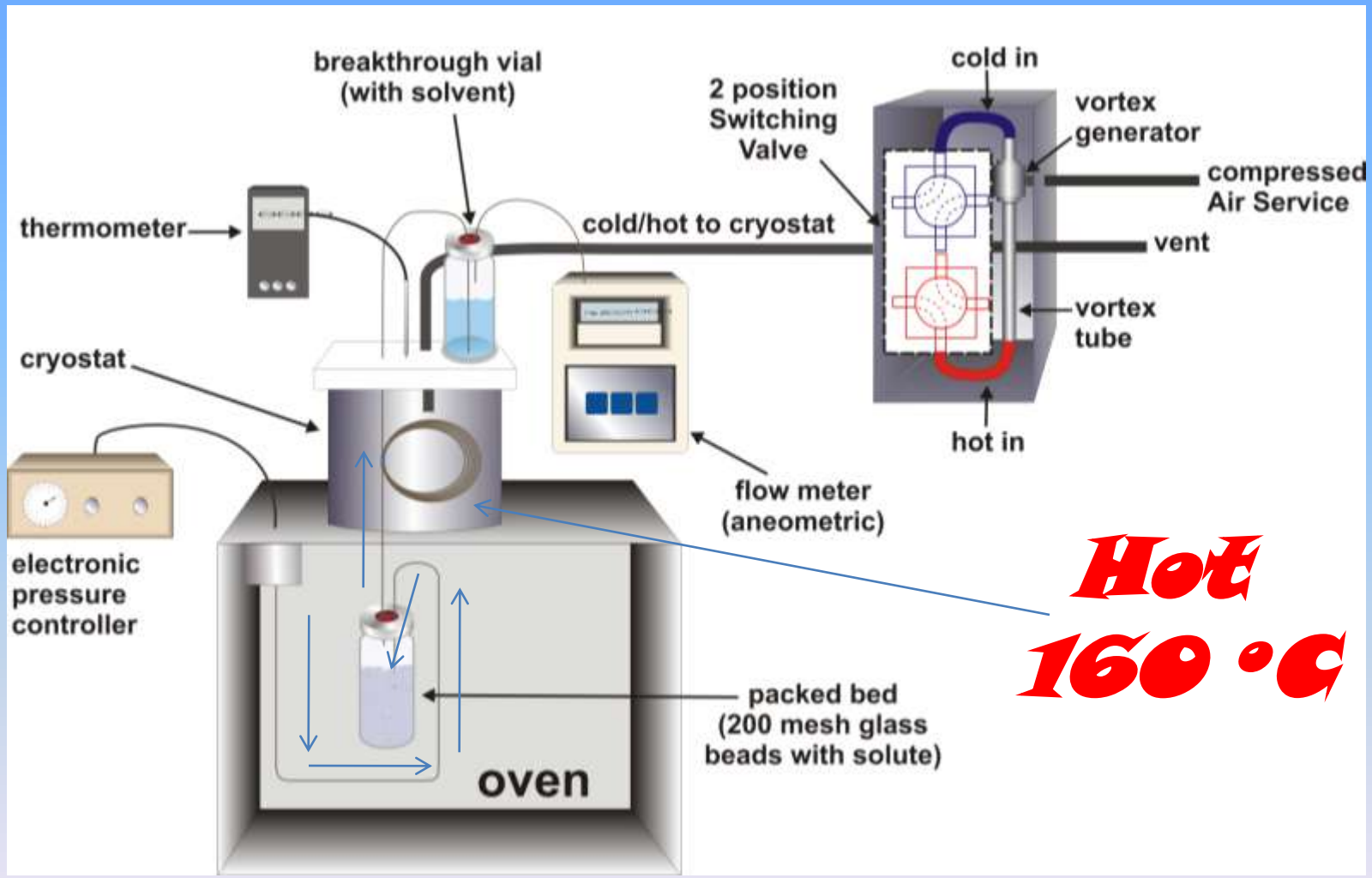
PLOT Capillary Cryoadsorption*



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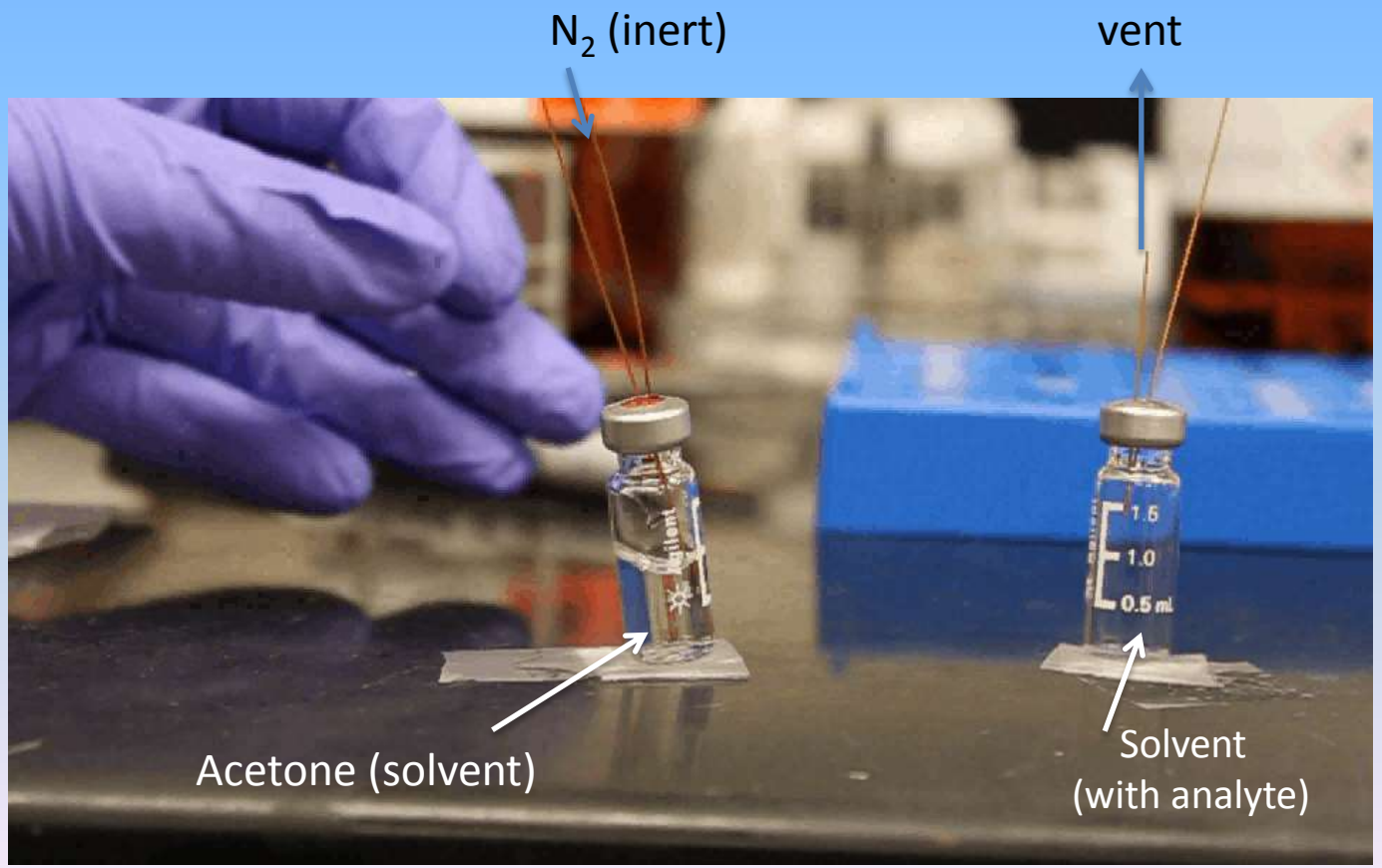
Analyte Elution



The Payoff:

Multiple PLOT Capillaries:

-tailor the sorbent to the analyte

only headspace method that

makes this possible

Application and Impact:

- Vapor composition of **explosives**
  - Lovestead, T. M., Bruno, T. J., Trace Headspace Sampling for Quantitative Analysis of Explosives with Cryoadsorption on Short Alumina Porous Layer Open Tubular Columns. ***Anal. Chem.*** **2010, 82, 5621-5627**
- Early detection of **food spoilage**
  - Lovestead, T. M., Bruno, T. J., Detection of poultry spoilage markers from headspace analysis with cryoadsorption on a short alumina PLOT column. ***Food Chemistry*** **2010, 121, 1274-1282.**
- Finding illegally **buried corpses**
  - Lovestead, T. M., Bruno, T. J., Detecting gravesoil from headspace analysis with adsorption on short porous layer open tubular (PLOT) columns. ***Forensic Science International,*** **204 156–161, 2011.**
- **Fire retardants** in auto interiors, **histamine** in shrimp, **COS** in imported drywall, **arson fire debris**,…

Now, add the pyro!

- Combine an *in situ* pyrolyzer platform with PLOT cryo

Modes of Operation:

-Enhanced vaporization

-True pyrolysis

-Combined

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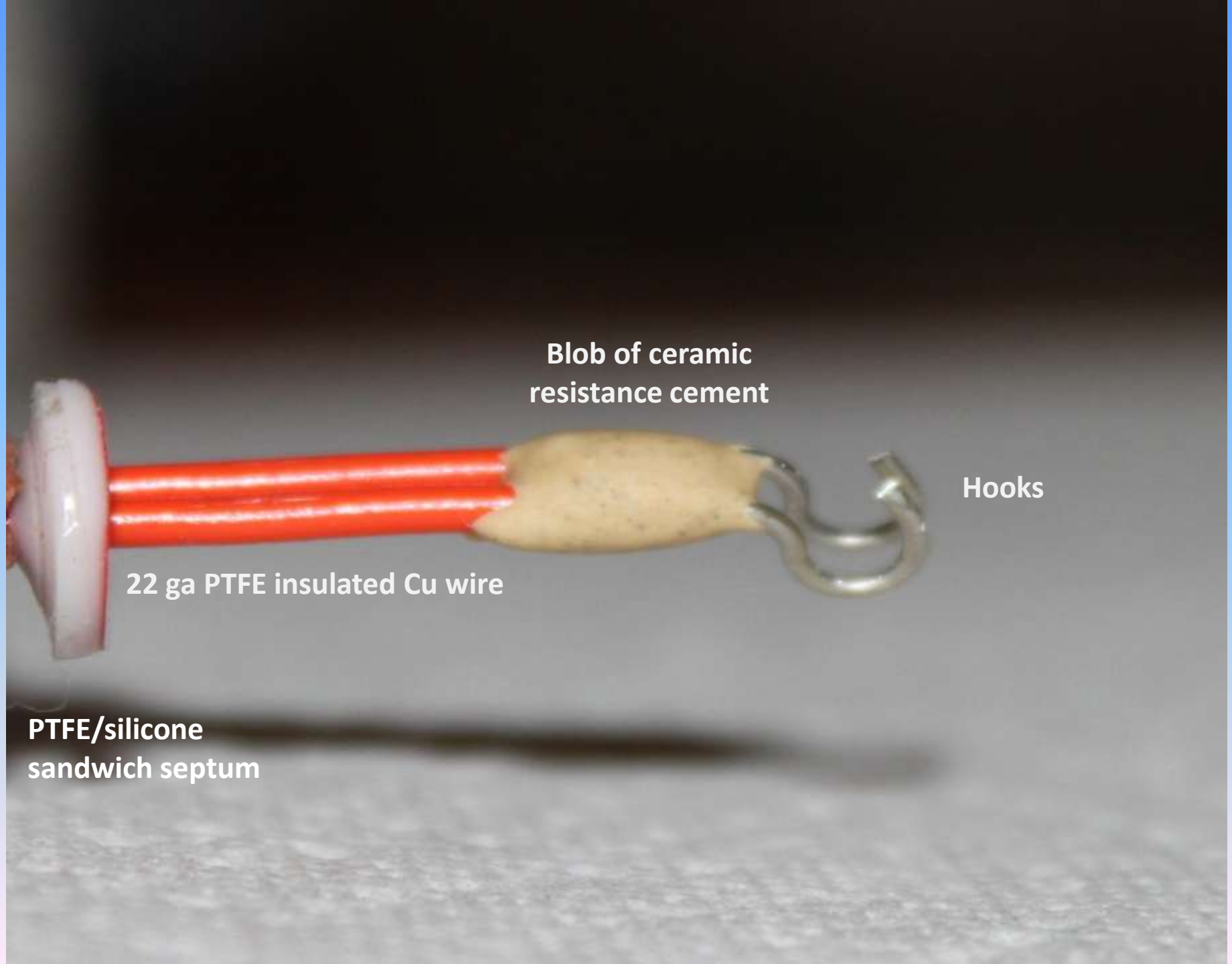
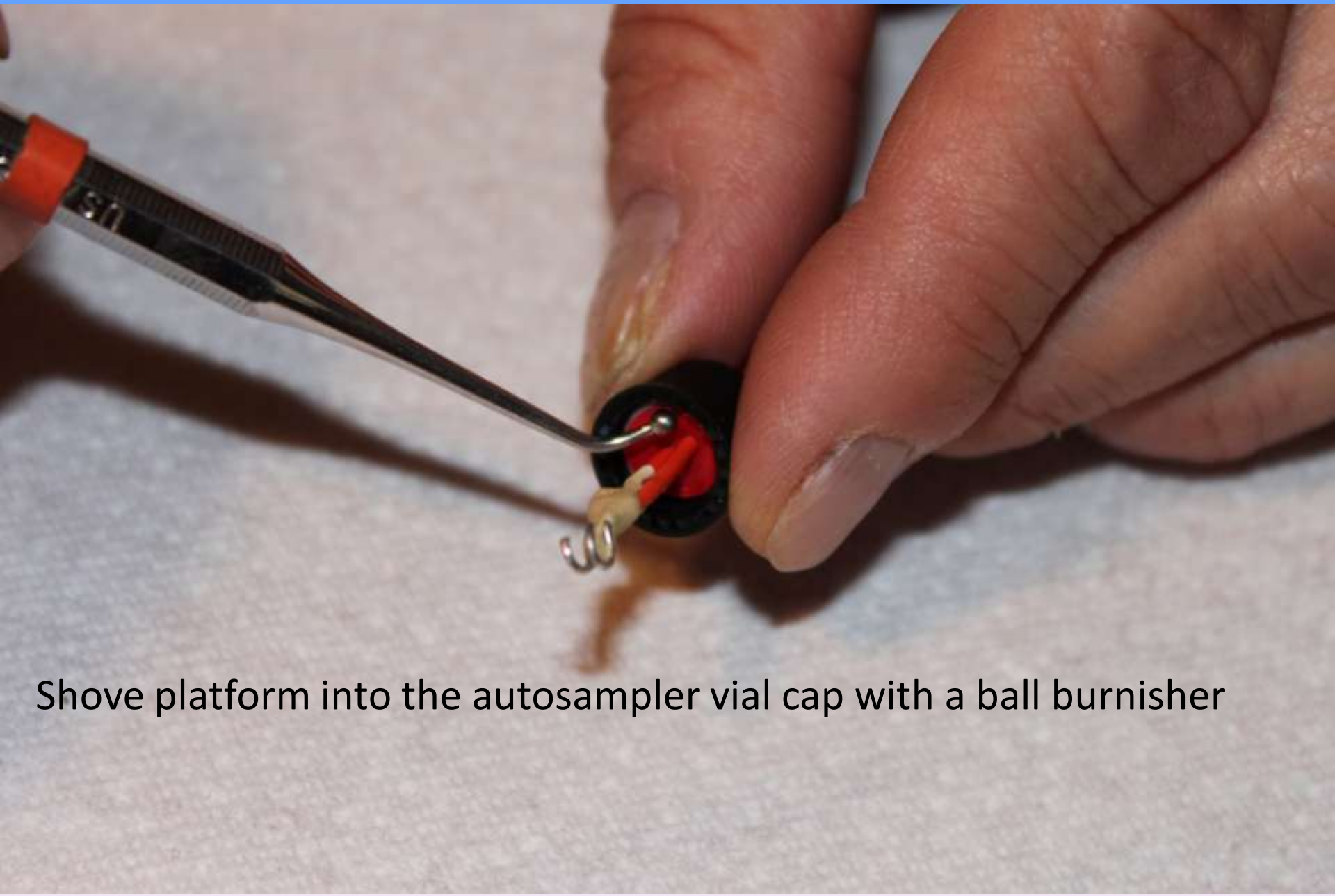
- Combine an *in situ* pyrolyzer platform with PLOT cryo

A headspace analysis method that makes it's own headspace!


Blob of ceramic
resistance cement
Hooks
22 ga PTFE insulated Cu wire
PTFE/silicone
sandwich septum



Shove platform into the autosampler vial cap with a ball burnisher

Wrap 15 winds of 0.002 in OD resistance wire around hooks; form a **basket**

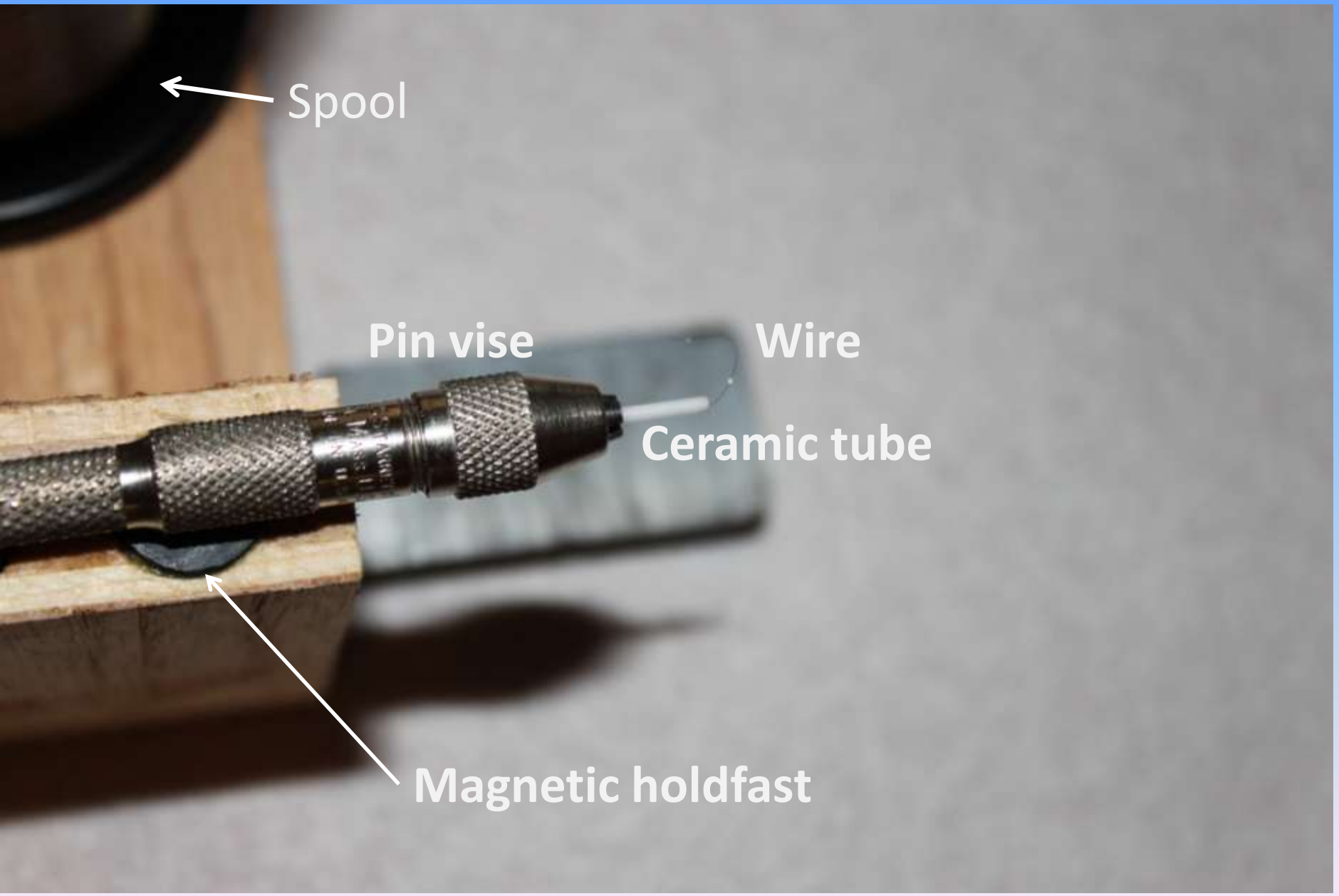
Different wires have been used:

304 SS	541 Ω/ft
NiCr	650 Ω/ft
NiCr	675 Ω/ft

0.001 in W has also been used, but it is too small to bother with.

304 SS works fine.

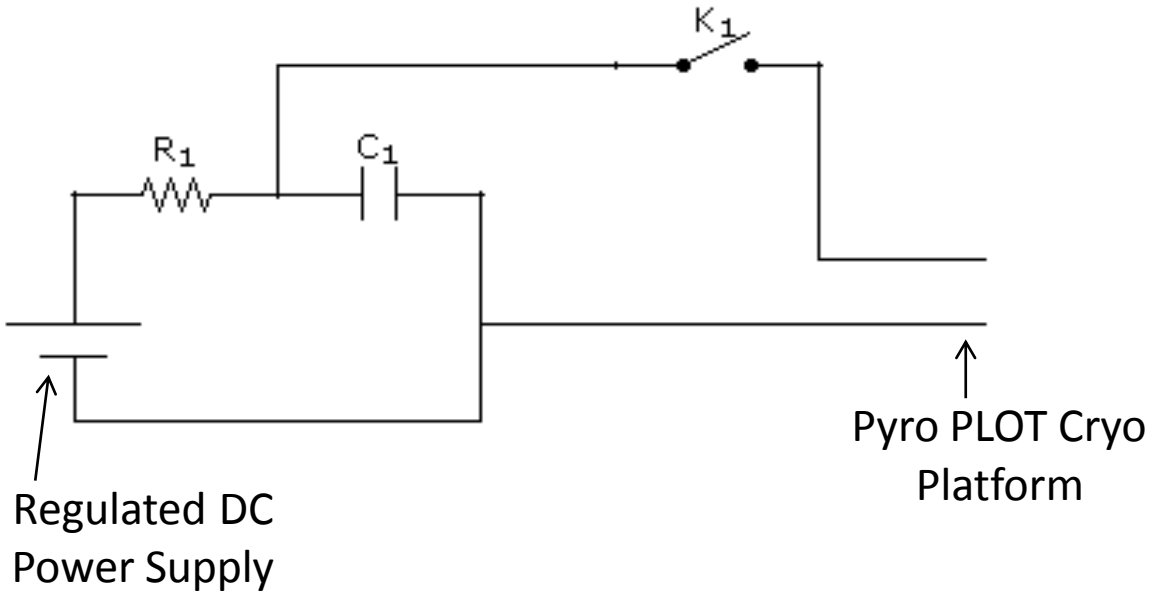
A custom made bobbin winder makes quick work!


Spool
Pin vise
Wire
Ceramic tube
Magnetic holdfast

Ready for Action

Firing Circuit

Couldn’t be simpler, a spot welder!



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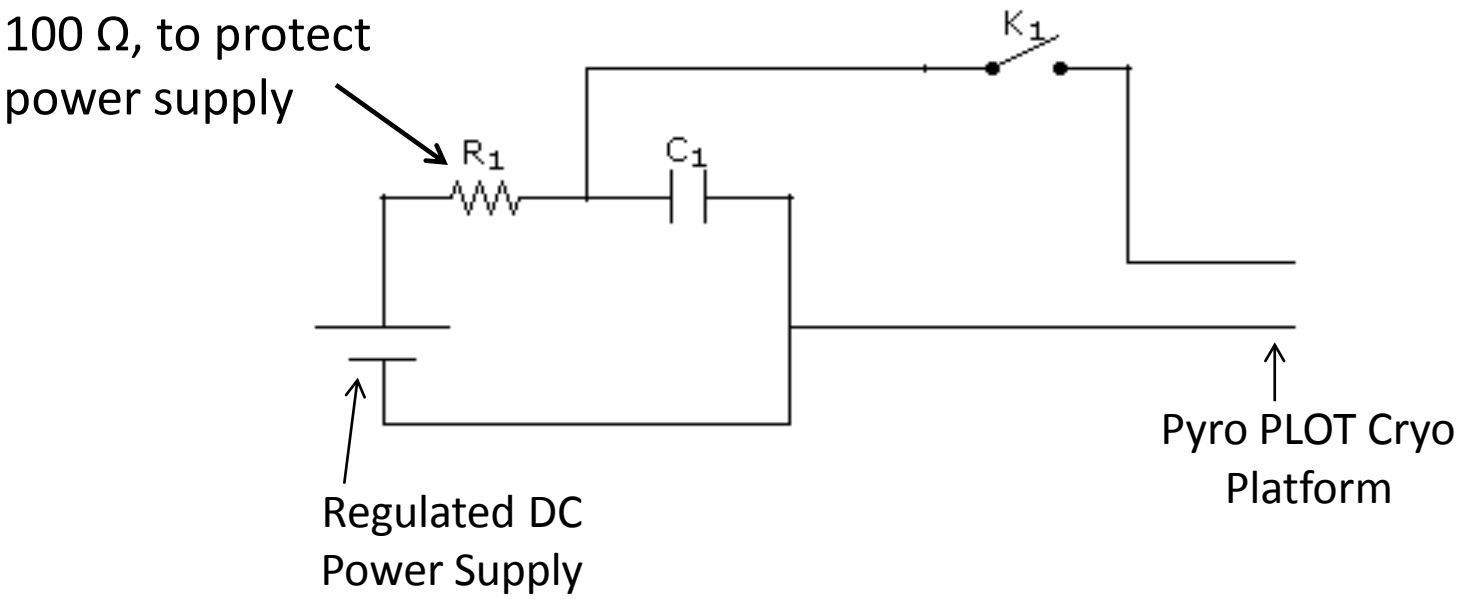
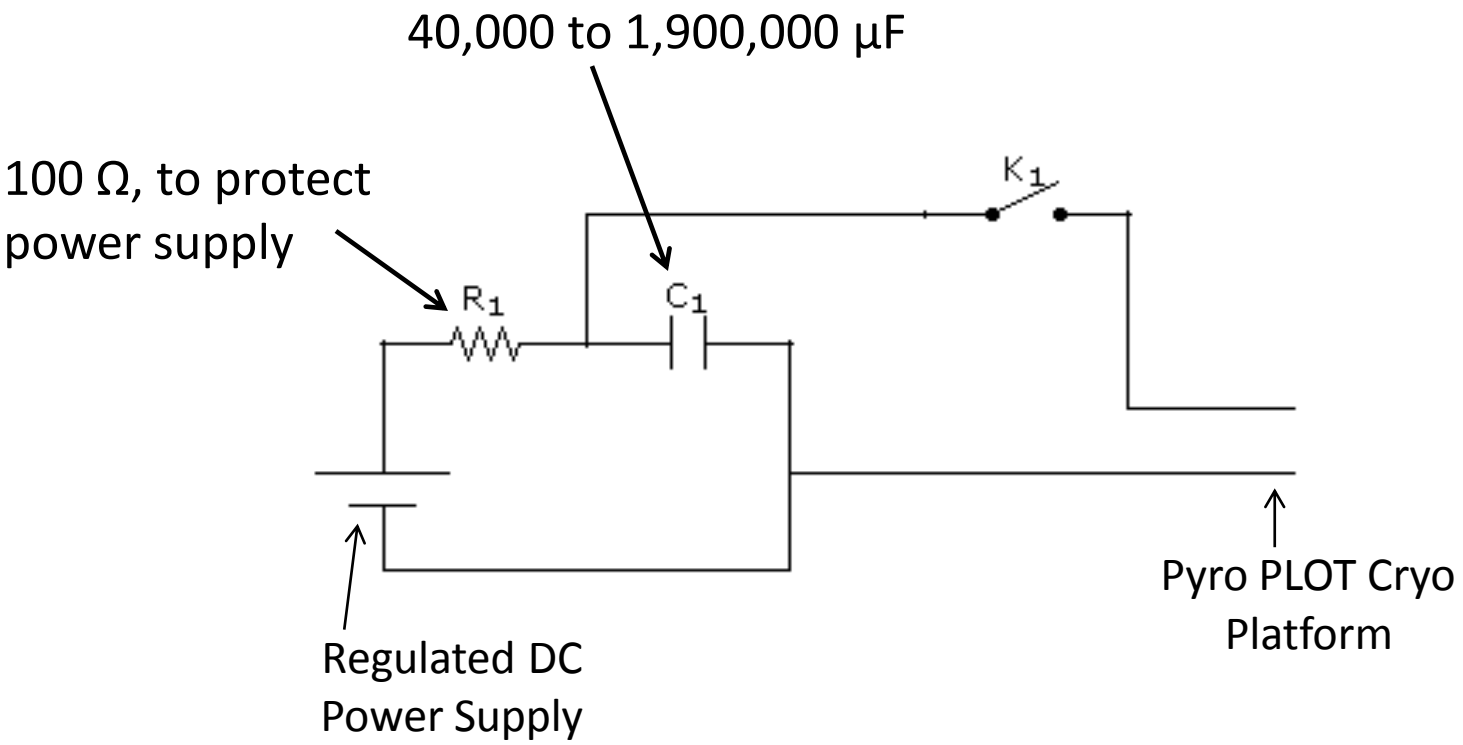


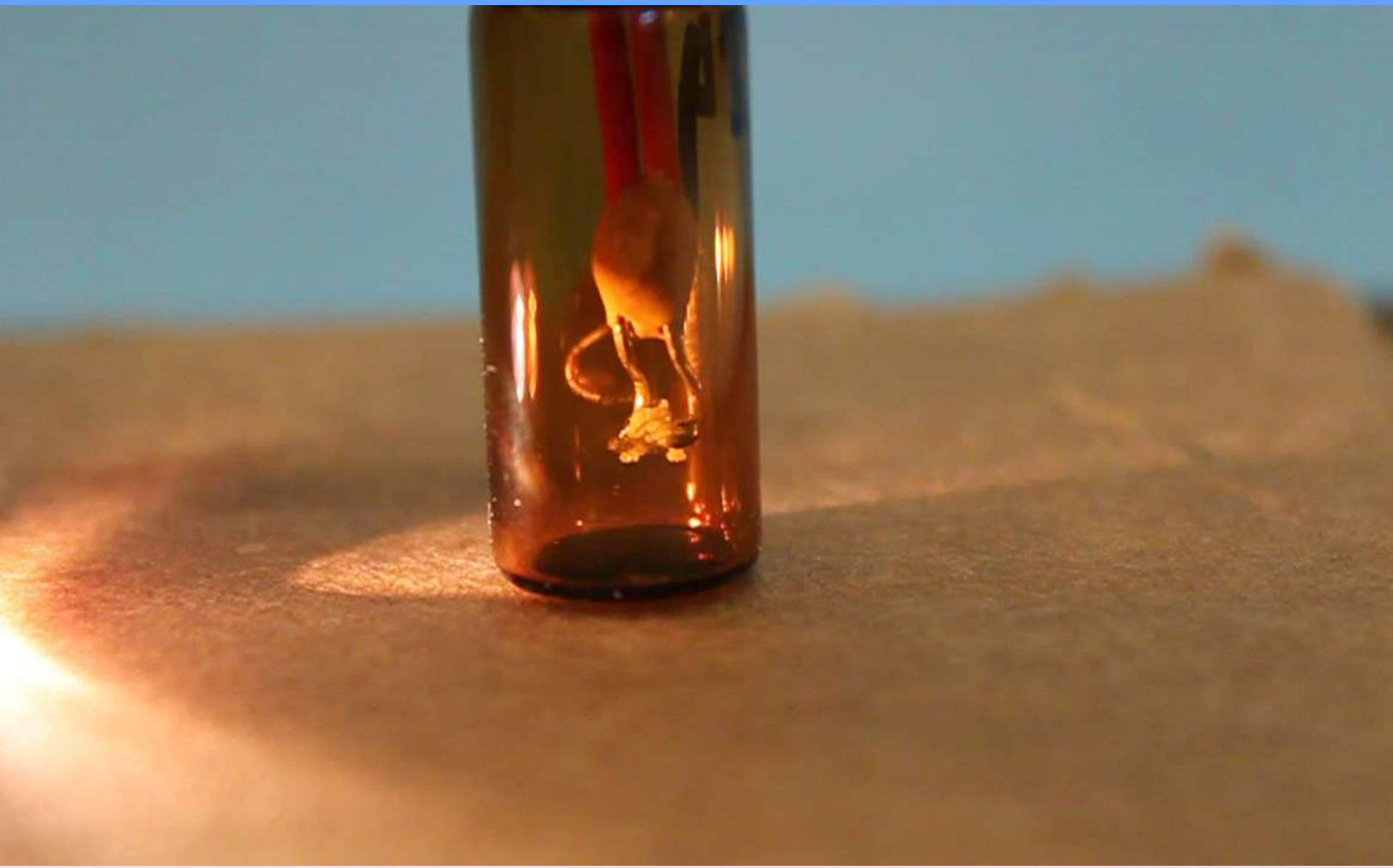
Firing Circuit

Couldn't be simpler, a spot welder!



Ready for Action

Ready for Actio



Some Interesting Examples

- From: forensics, explosives, fuels, polymers, reactions, bioproducts
- All samples were collected by Pyro PLOT cryo, **30 second sweeps**
- Vials at **room temperature**
- Analyses were done by 1 mL acetone elution, then **GC-MS**

Analysis of Cosmetics

A Forensic Science Measurement Challenge

- Two aspects
  - DNA recovery in lip cosmetics
  - Cosmetics transfer to clothing and persons

Base
oils, siloxanes, surfactants,

Additives
coloring agents, bases, bulking agents, sunscreens, and additives

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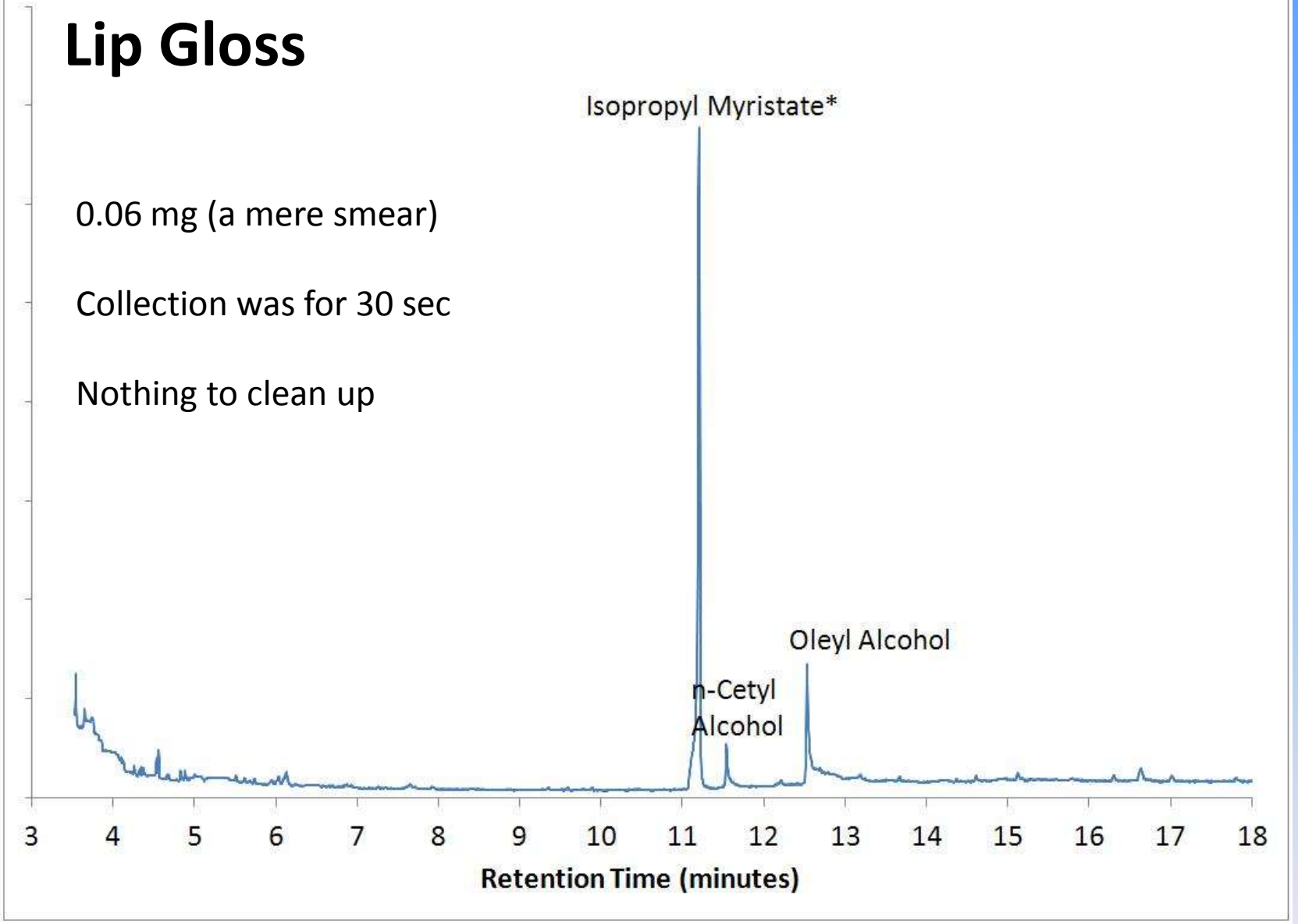
Lip Gloss



0.06 mg (a mere smear)

Collection was for 30 sec

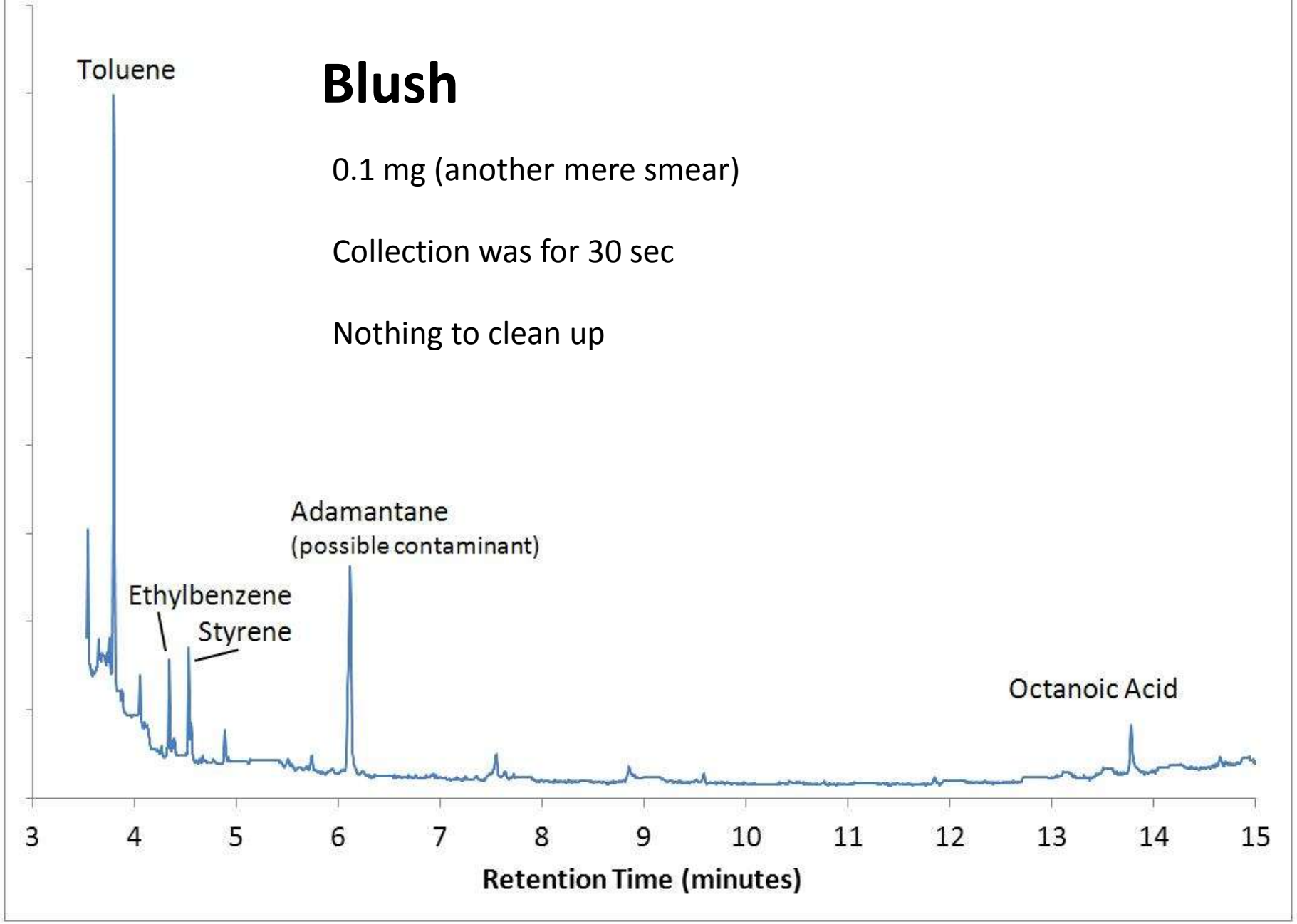
Nothing to clean up

Blush

0.1 mg (another mere smear)

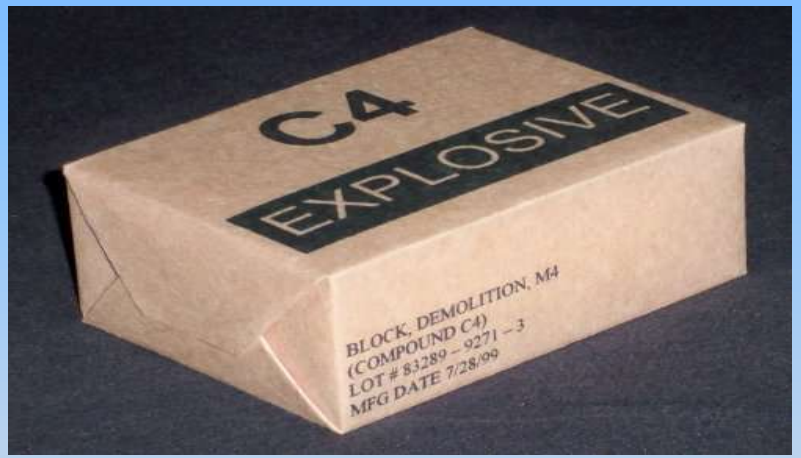
Collection was for 30 sec

Nothing to clean up



Vapor composition of explosives:

- TSA required the ability to measure and predict the vapor composition above explosives



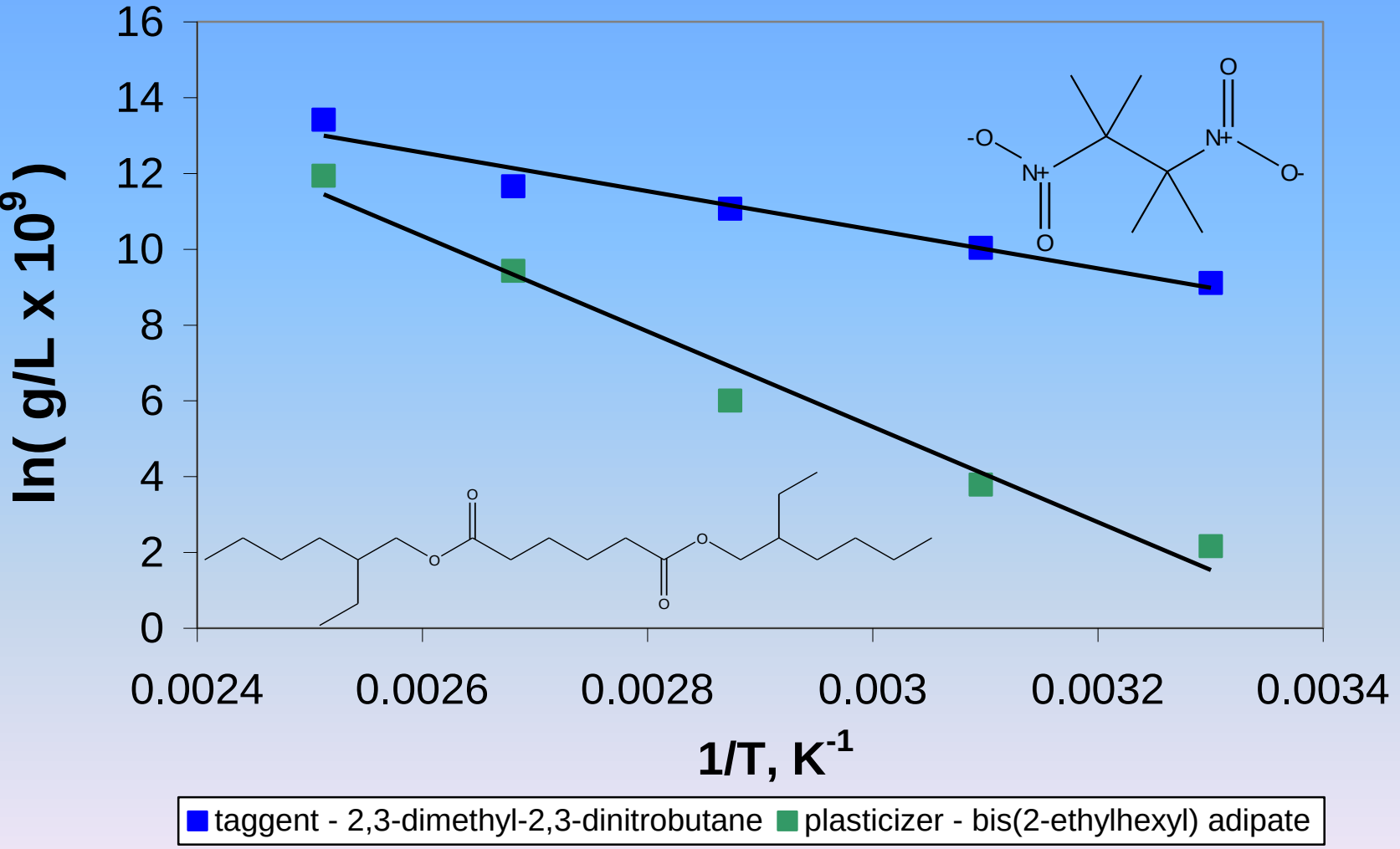
- For the certification of in-the-field equipment

Lovestead, T. M., Bruno, T. J., Trace Headspace Sampling for Quantitative Analysis of Explosives with Cryoadsorption on Short Alumina Porous Layer Open Tubular Columns, *Anal. Chem.* 2010, 82, 5621-5627.

With PLOT Cryo:

- 100 - 200 mg samples
- Collection for 2.5 to 6 hrs
- At 50 to 150 ^{o}C

Recovered mass (grams per liter x 10^9) from tagged C-4



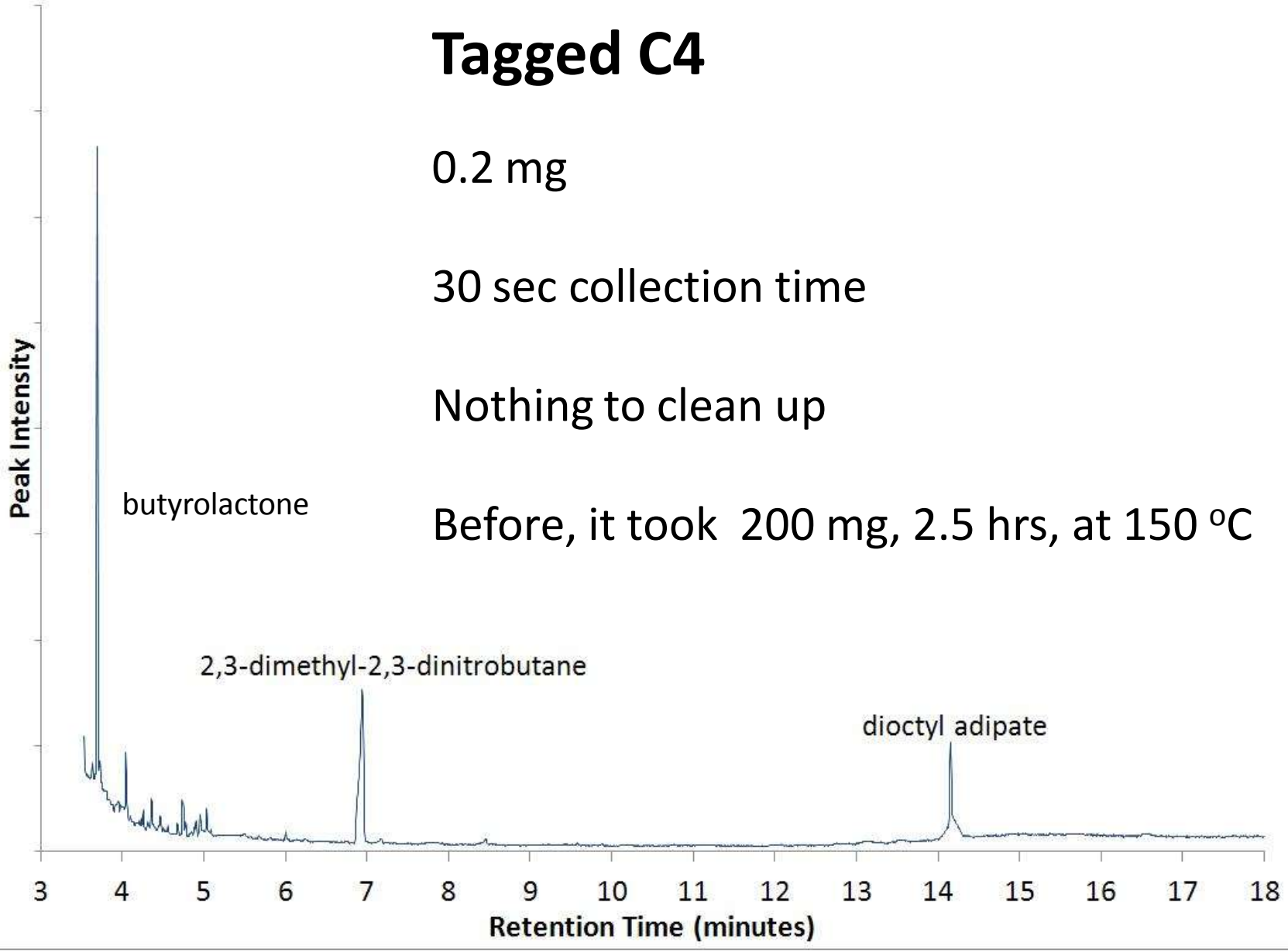
Tagged C4

0.2 mg

30 sec collection time

Nothing to clean up

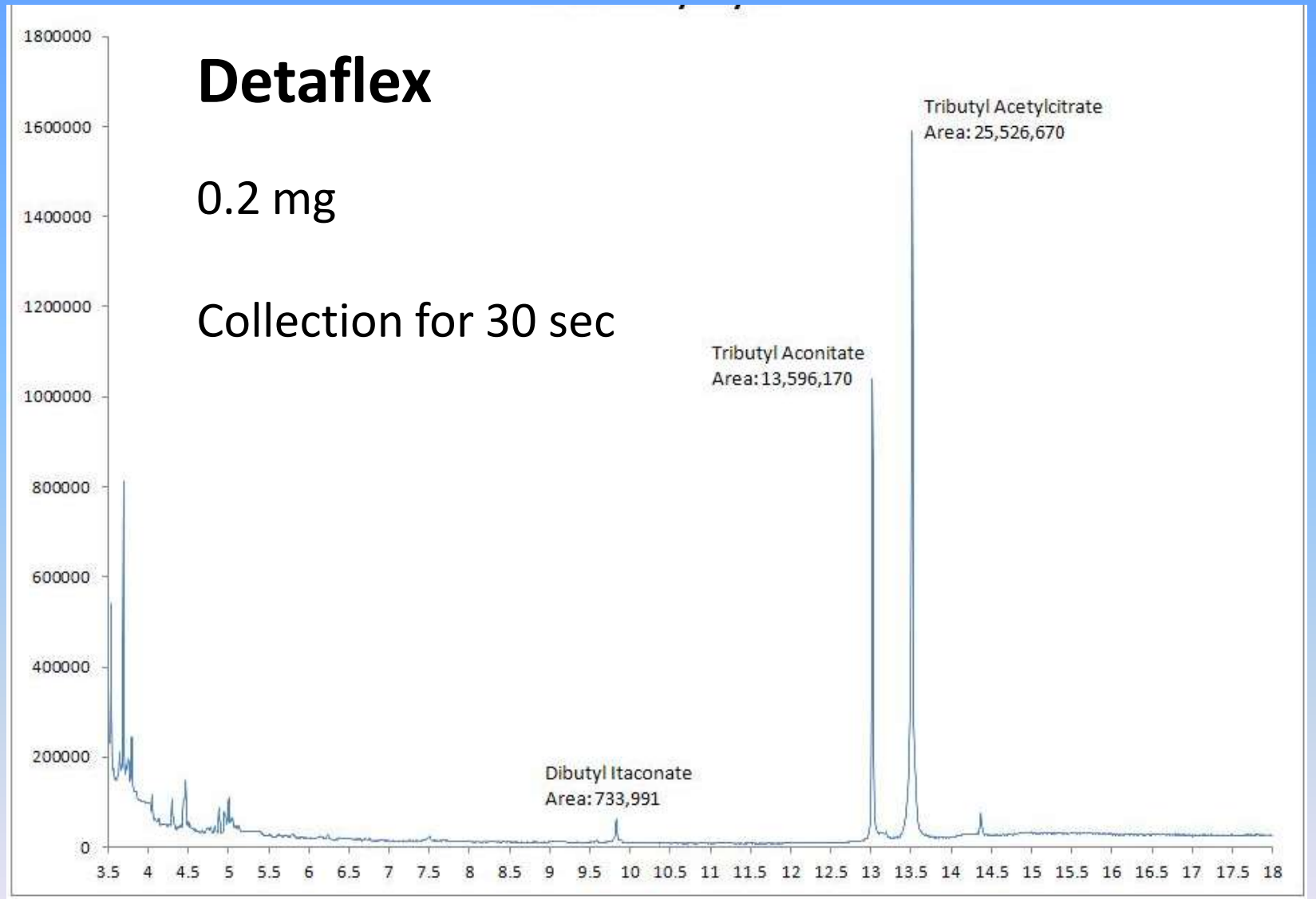
Before, it took 200 mg, 2.5 hrs, at 150 °C



Detaflex

0.2 mg

Collection for 30 sec



Semtex, the choice of the discriminating terrorist

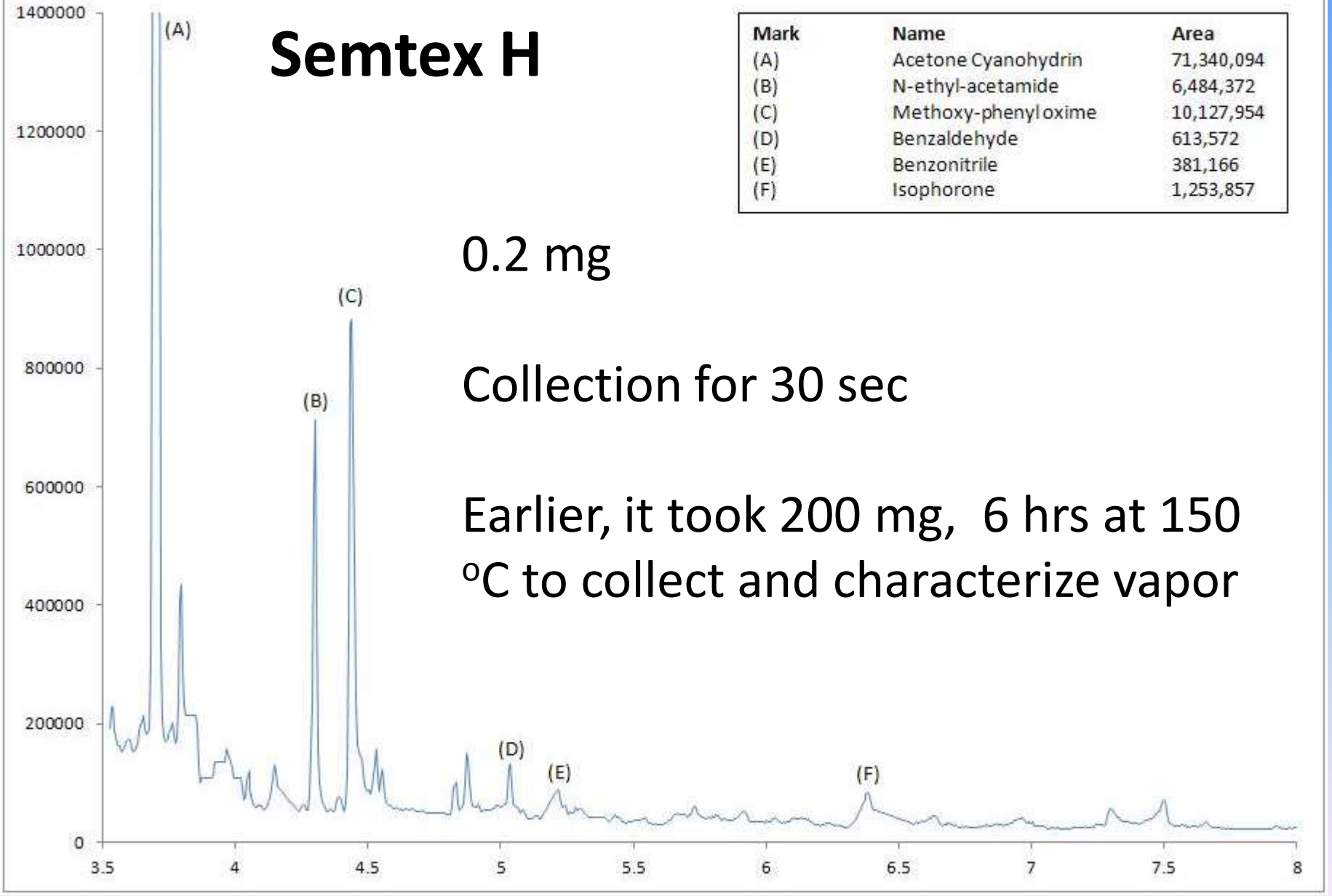
Very difficult to detect, on purpose

Clipper Maid of the Seas – Departs Heathrow on Dec. 21, 1988, operating as Pan Am 103

With:

Semtex H

Mark	Name	Area
(A)	Acetone Cyanohydrin	71,340,094
(B)	N-ethyl-acetamide	6,484,372
(C)	Methoxy-phenyl oxime	10,127,954
(D)	Benzaldehyde	613,572
(E)	Benzonitrile	381,166
(F)	Isophorone	1,253,857



0.2 mg

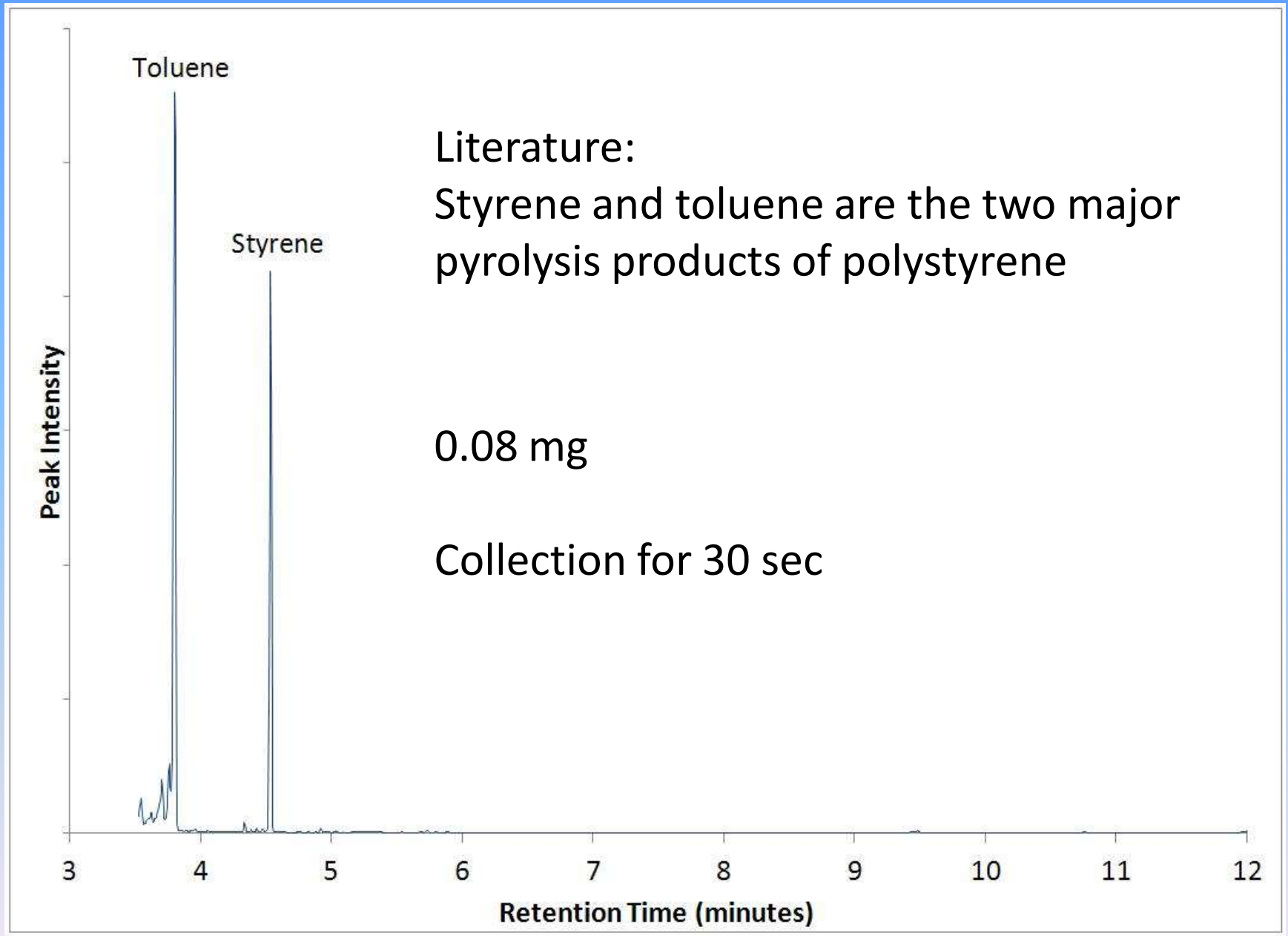
Collection for 30 sec

Earlier, it took 200 mg, 6 hrs at 150 ^{o}C to collect and characterize vapor

Pyrolysis of polystyrene

- Start with a packing peanut
- Mash it into a disk with a dental amalgam carrier

- Place in pyro basket, and FIRE!



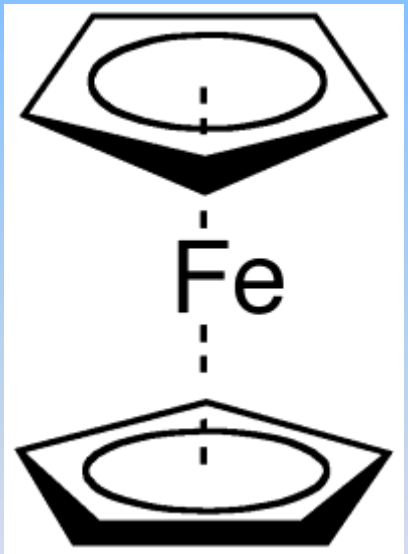
Literature:
Styrene and toluene are the two major pyrolysis products of polystyrene

0.08 mg

Collection for 30 sec

Antiknock Additive in Gasoline

- TEL is out, but others are in
  - Ferrocene is one



RMM = 186.04
T_{melt} = 174 °C
T_{boil} = 249 °C

"therapeutic" dose: 20 mg/L

Antiknock Additive in Gasoline

- TEL is out, but others are in
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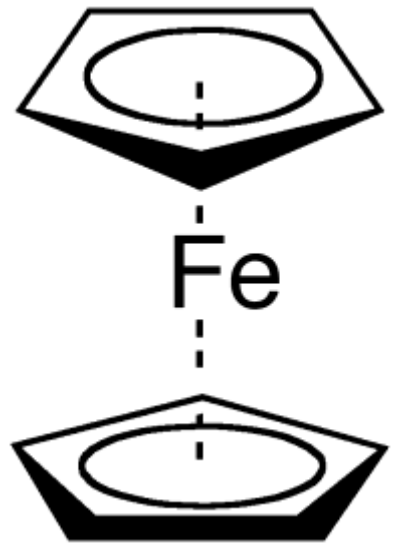
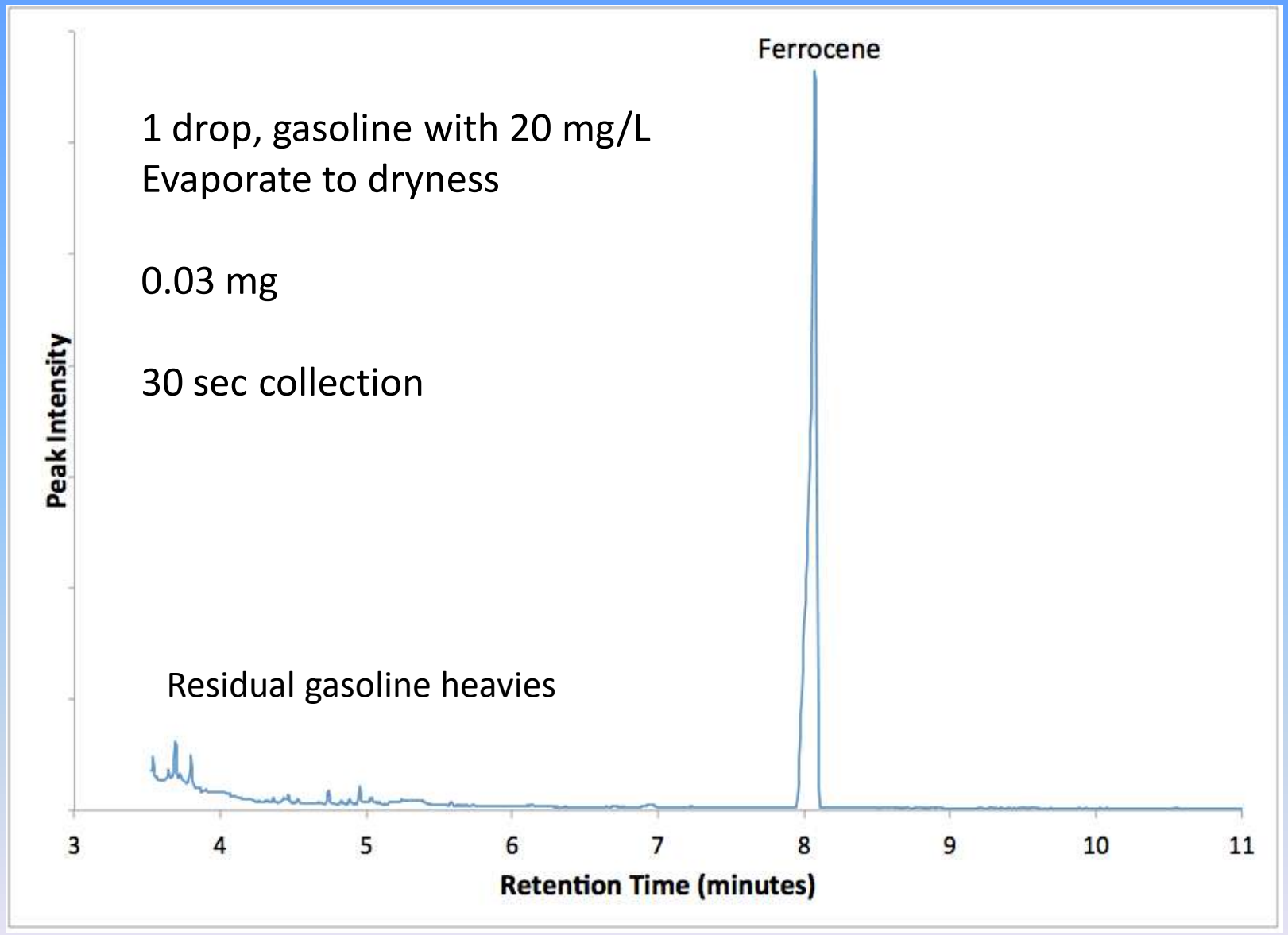


RMM = 186.04
T_{melt} = 174 °C
T_{boil} = 249 °C

Analysis* of fuels with this additive take 30 min

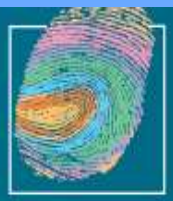
*Bruno, T.J., Baibourine, E., Analysis of organometallic gasoline additives with the composition-explicit distillation curve method, *Energy & Fuels*, 24, 5508-5513, 2010.


Ferrocene
1 drop, gasoline with 20 mg/L
Evaporate to dryness
0.03 mg
30 sec collection
Residual gasoline heavies
Peak Intensity
3
4
5
6
7
8
9
10
11
Retention Time (minutes)

Pharma:

This product information is intended for U.S. residents only.

COUMADIN®
(Warfarin Sodium Tablets, USP) Crystalline



1 mg 2 mg 2.5 mg 3 mg 4 mg 5 mg 6 mg 7.5 mg 10 mg

October 25, 2011
COUMADIN® (warfarin sodium) Crystalline Certain Lots of 2 mg and 5 mg Tablets Recall Information

May 26, 2011
COUMADIN® (warfarin sodium) Crystalline Certain Lots of 2.5 mg, 4 mg, 7.5 mg, and 10 mg Tablets Recall Information

May 2, 2011
COUMADIN® (warfarin sodium) Crystalline 5 mg Tablets Recall Information

July 12, 2010
COUMADIN® (warfarin sodium) 1 mg Blister Packs Recall Information

Coumadin.com is currently undergoing a redesign. Please visit us again in the future.

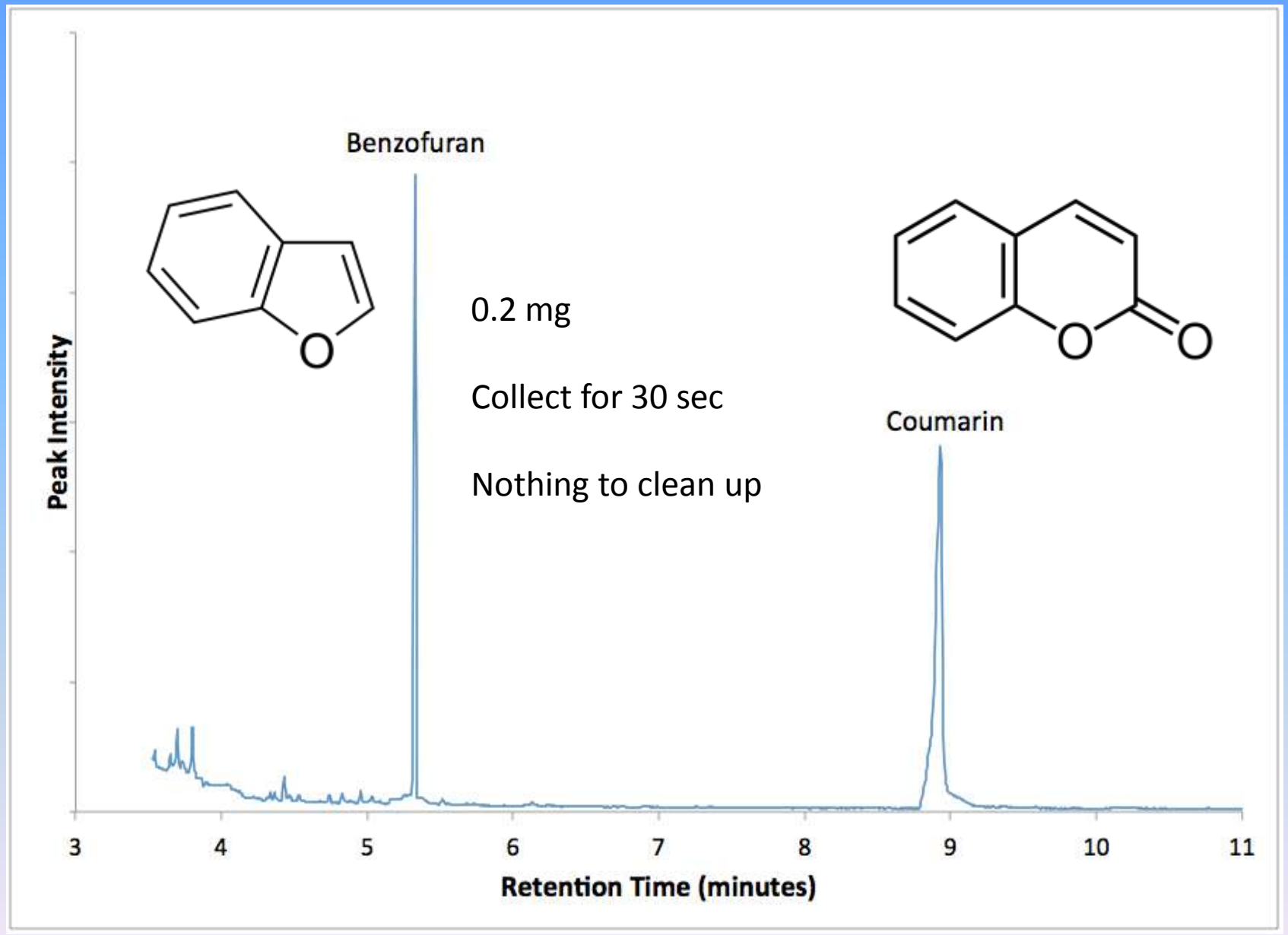
IMPORTANT SAFETY INFORMATION

WARNING: COUMADIN can cause bleeding which can be serious and sometimes lead to death. Call your doctor or seek immediate medical care if you have signs or symptoms of bleeding. For more information, please see the U.S. Full Prescribing Information and Medication Guide.

Click here for the updated U.S. Full Prescribing Information, including **Boxed WARNING on bleeding risk**

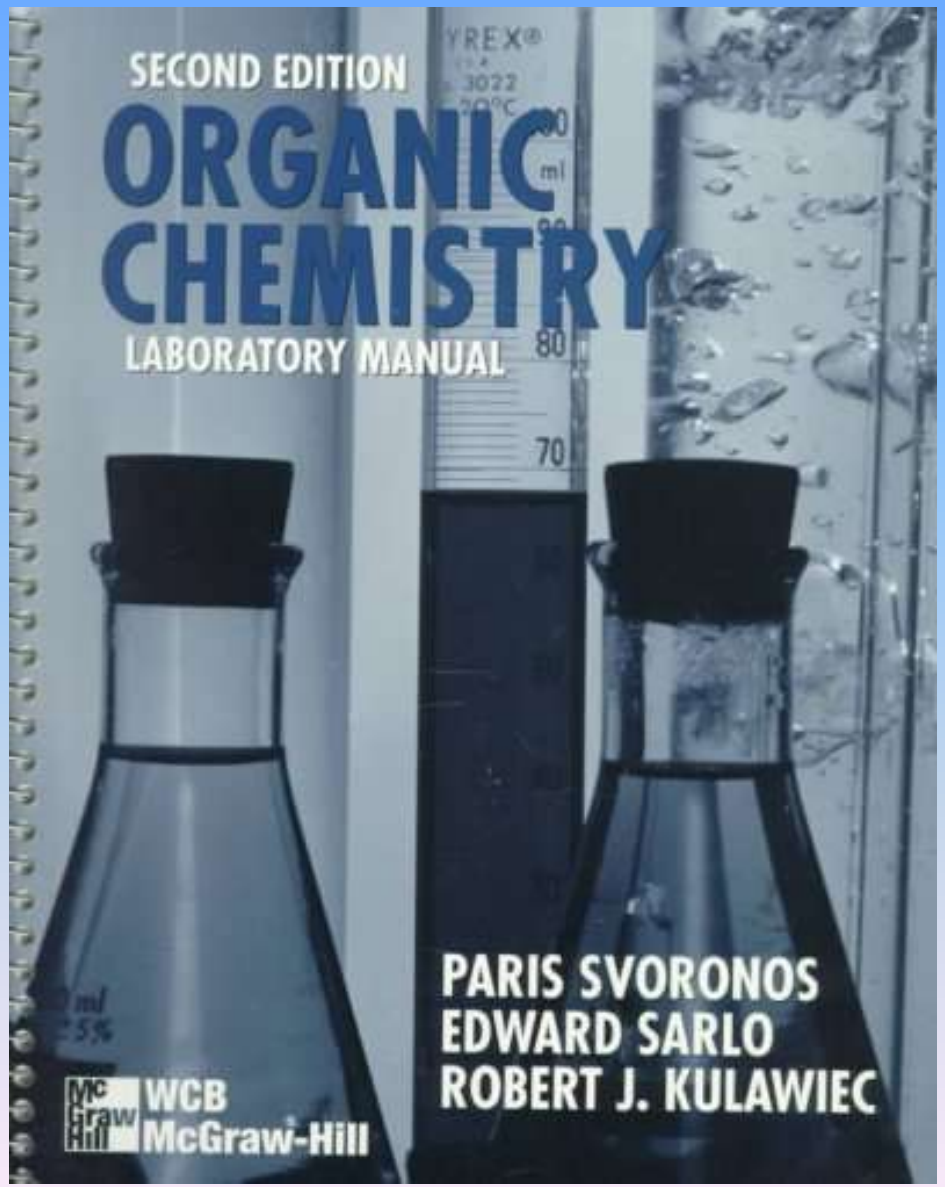
Click here for the updated Medication Guide from the U.S. Full Prescribing Information

Privacy Policy | Legal Notice


Benzofuran
Coumarin
0.2 mg
Collect for 30 sec
Nothing to clean up
Peak Intensity
3
4
5
6
7
8
9
10
11
Retention Time (minutes)

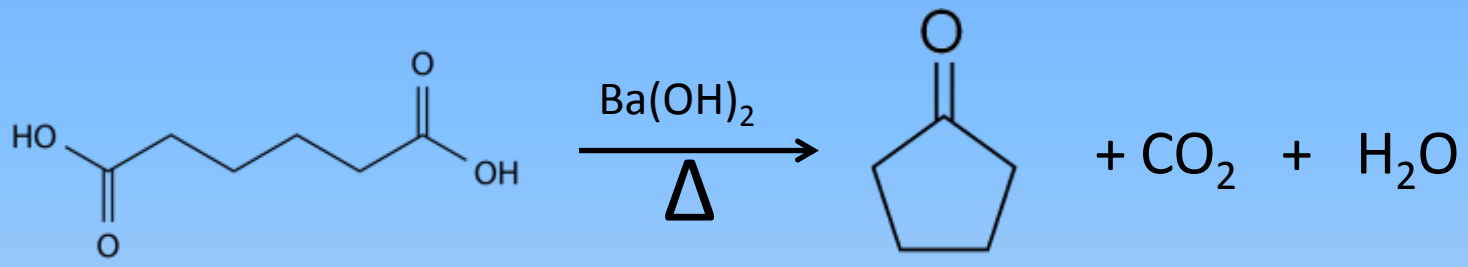
Microscale Reaction Platform

Chapter 18, Carbanions
page 231



Microscale Reaction Platform

Cyclization Reaction (carbanions and α,β-unsaturated carbonyls)

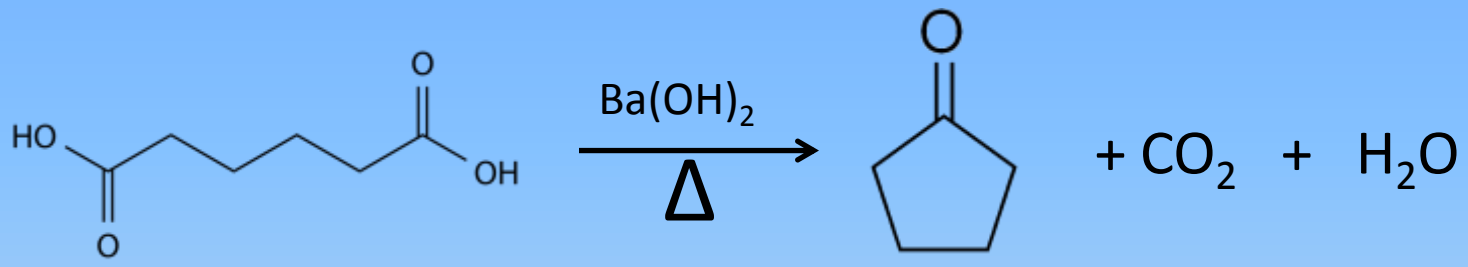


adipic acid

cyclopentanone

Microscale Reaction Platform

Cyclization Reaction (carbanions and α,β-unsaturated carbonyls)



adipic acid cyclopentanone

21.8 g adipic acid, 1.5 g $Ba(OH)_2$, put into distillation flask, attach condenser

Insert a **400 ºC** Hg/glass thermometer

Heat until solids melt (295 ºC)

Ask the DSRs:

21.8 g adipic acid, 1.5 g $Ba(OH)_2$, put into distillation flask, attach condenser

Insert a **400 °C** Hg/glass thermometer

Heat until solids melt (295 °C)

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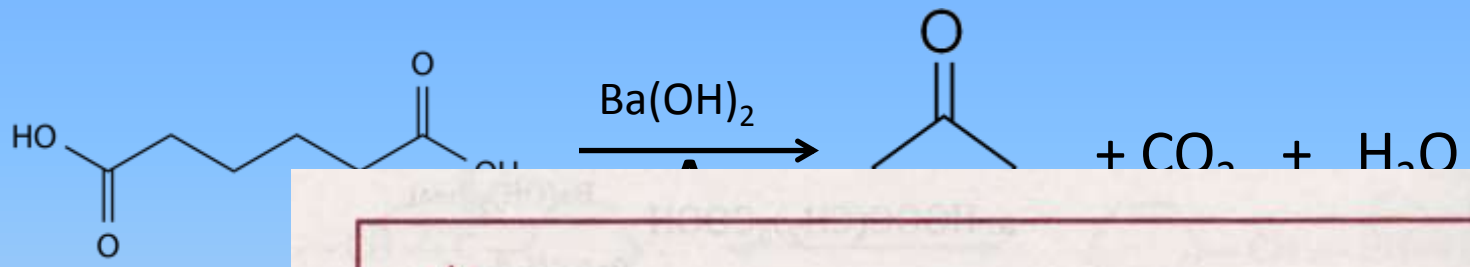


adipi

21.8 g

SAFETY TIPS

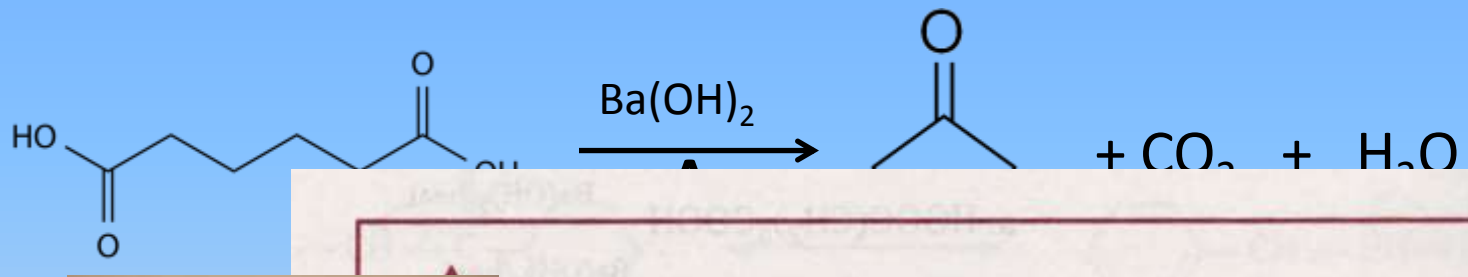
The high temperature (295°C) of the pyrolysis reaction might break the thermometer, especially if it is defective. If this happens, add sulfur powder to the round-bottomed flask (after cooling). The contents should then be disposed of properly by the instructor.

Insert a 400 °C thermometer

Heat until solids melt (295 °C)

Microscale Reaction Platform

Cyclization Reaction (carbanions and α,β-unsaturated carbonyls)



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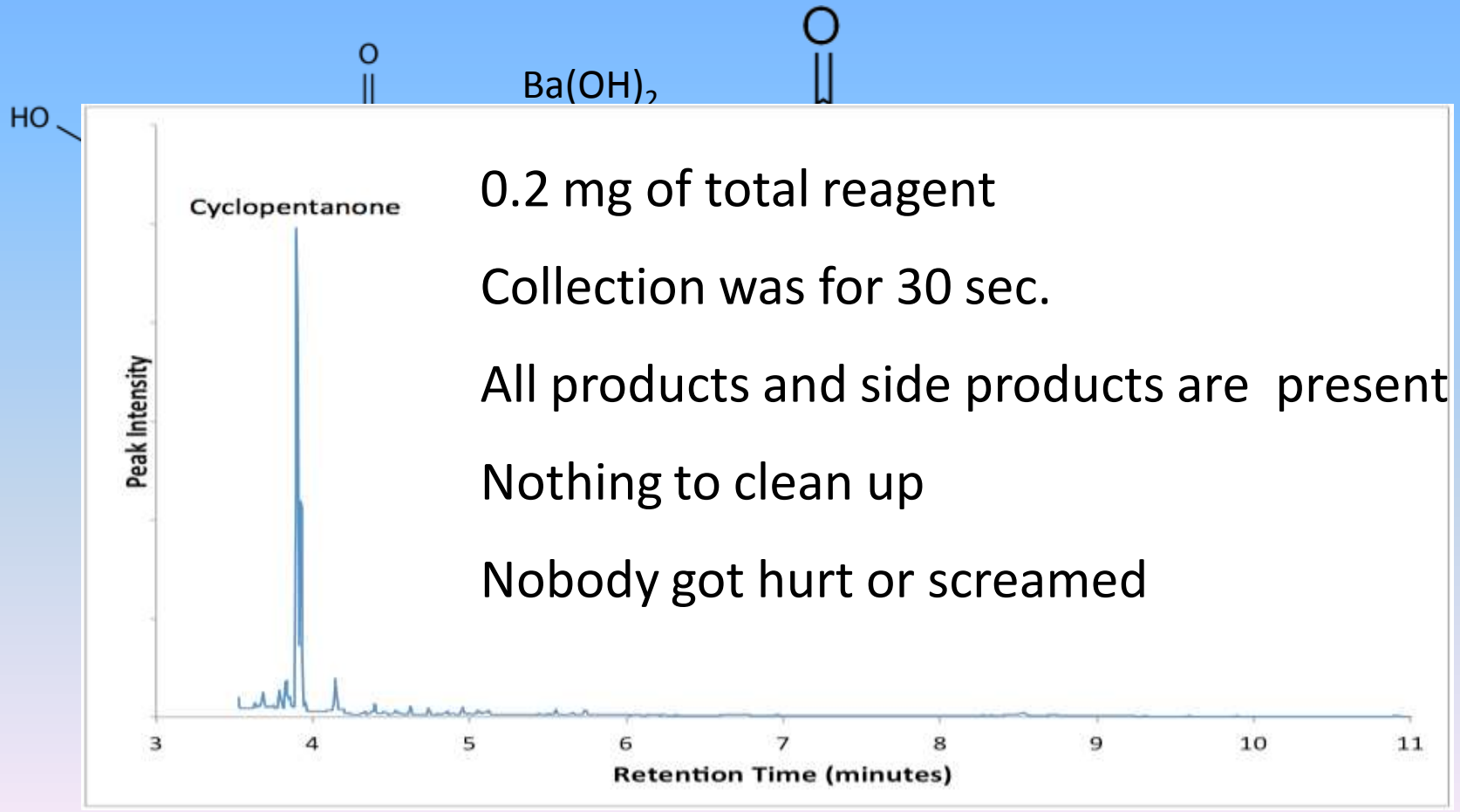
Microscale Reaction Platform

Cyclization Reaction (carbanions and α,β-unsaturated carbonyls)



0.2 mg of total reagent

Collection was for 30 sec.

All products and side products are present

Nothing to clean up

Nobody got hurt or screamed

$ Bottom Line $

$ 0.16 + 0.10 + 0.20 = $ 0.46
Use it once, then toss

$10, use over and over

Circuit, one time cost, $ 100

Next Steps:

- Provisional patent has been filed
- NIST-PRC recommended full filing
- Commercial Partners have been identified
    - ACS Regional Meeting

- Extend capabilities
  - Wick stick for liquids
  - KBr for FTIR; Krytox® for FTIR; $C_3D_8O_3$ for NMR
- Optimize resistance and capacitance

Acknowledgements

- Jessica Nichols, NIST SURF student

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- Other Methods that might appear similar:
  - Pyrolysis GC
    - Larger samples, complex chromatograms, the injector is perpetually dirty, you're stuck with GC.
  - Pyrolysis MS
    - Larger samples, the ion source is perpetually dirty, very unreliable*, you're stuck with MS

*I had one as an MS retrofit; it came with 12 fused silica crucibles, I used it a few times and excessed it, and I still have some crucibles in the drawer.