Comprehensive Two-Dimensional Gas Chromatography coupled with Time-of-Flight Mass Spectrometry for Broad Spectrum Organic Analysis GCxGC-TOFMS

GACID - Group for Analytical Chemistry Instrument Development

Harsh Environment Mass Spectrometry workshop
09/22/2003
Sarasota, FL

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University of Michigan

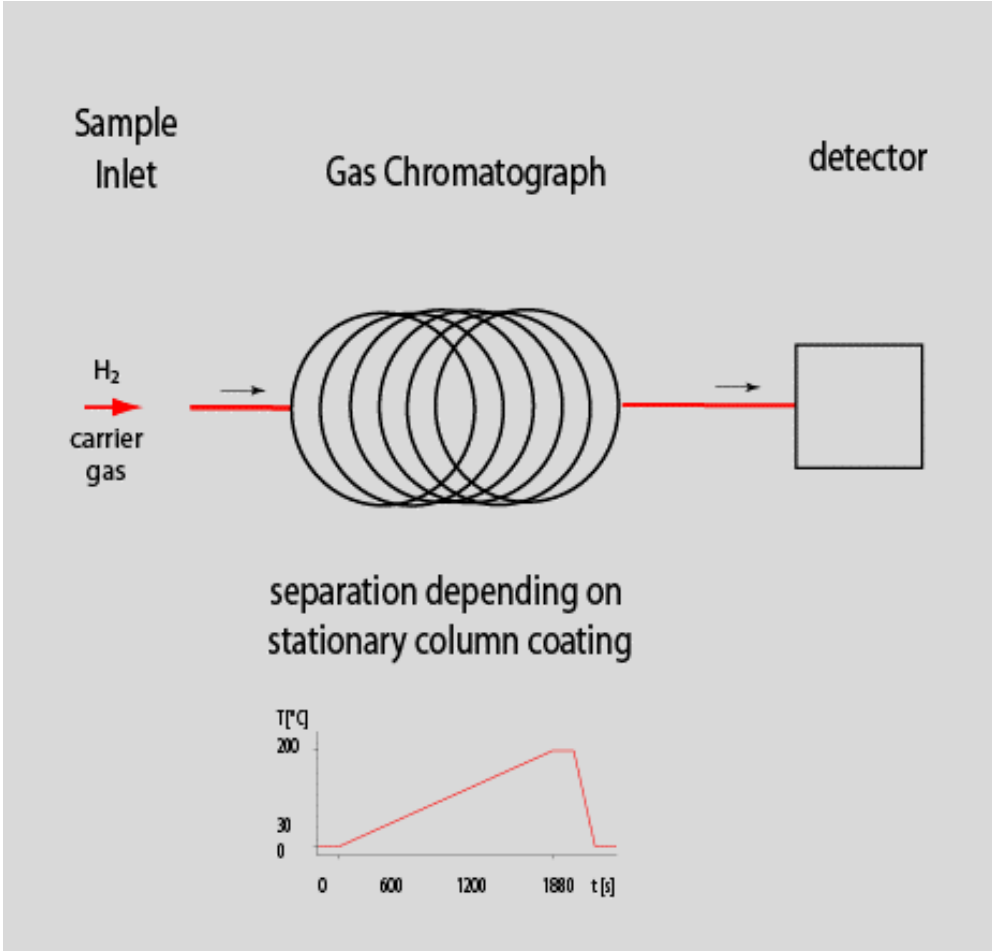
Presentation Outline

- Separation using Comprehensive 2-Dimensional Gas Chromatography (GCxGC)
  - 1-D GC versus 2-D GC
- Identification using Time-of-Flight Mass Spectrometry TOFMS
  - Capabilities of TOFMS
- Applications for GCxGC-TOFMS (selected examples)
  - Tholins
  - CWA simulants detection in gasoline
  - Breath analysis
- Field deployment at UMBS
- Subsystem development activities
  - Thermal Modulator
- Future steps
- Acknowledgement

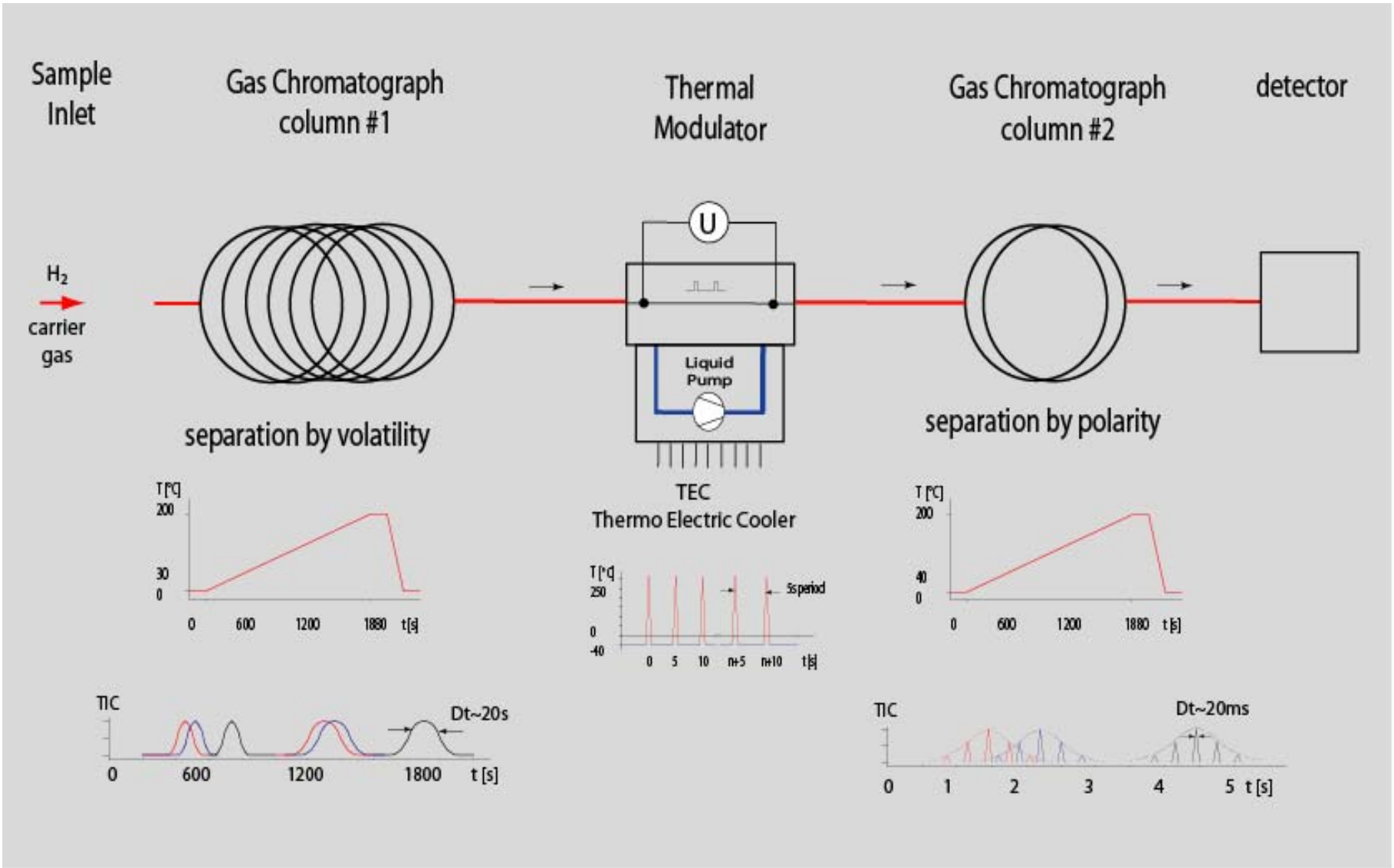
1-Dimensional Gas Chromatography (GC)

Standard 1D-GC technique

- narrow sample plug injection into the chromatographic column
- Sample transport happens in the mobile phase by the flow of an inert carrier gas
- separation of the sample occurs along the coated column with various stationary phases by interaction of the sample material with the column coating
- Retention time of the effluent is detected

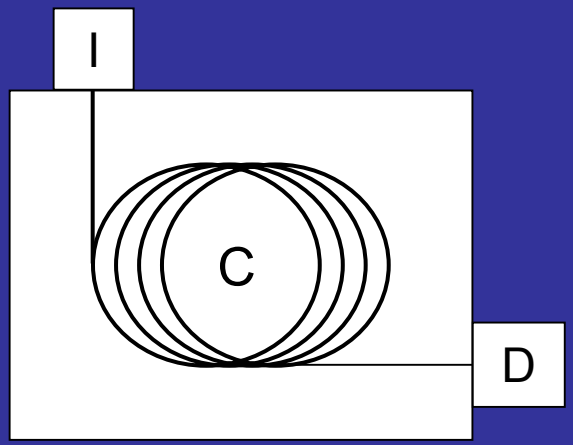


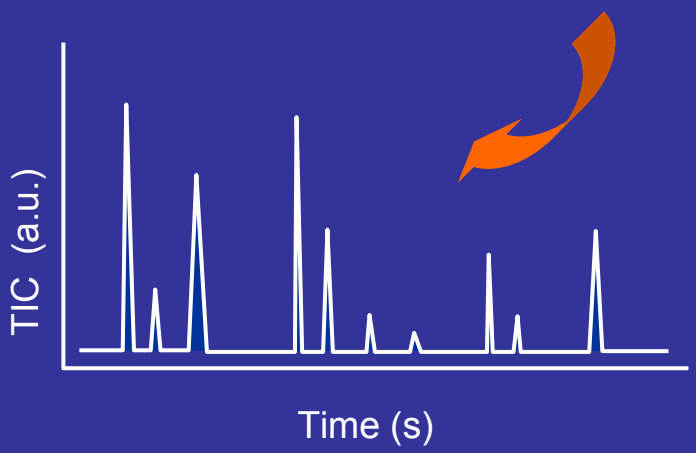
Comprehensive 2-Dimensional Gas Chromatography (GC x GC)



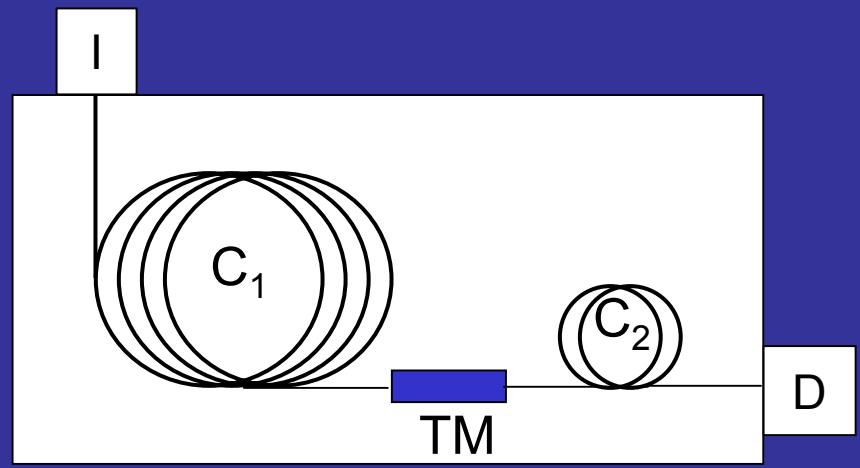
1-Dimensional versus 2-Dimensional Gas Chromatography (1/2)

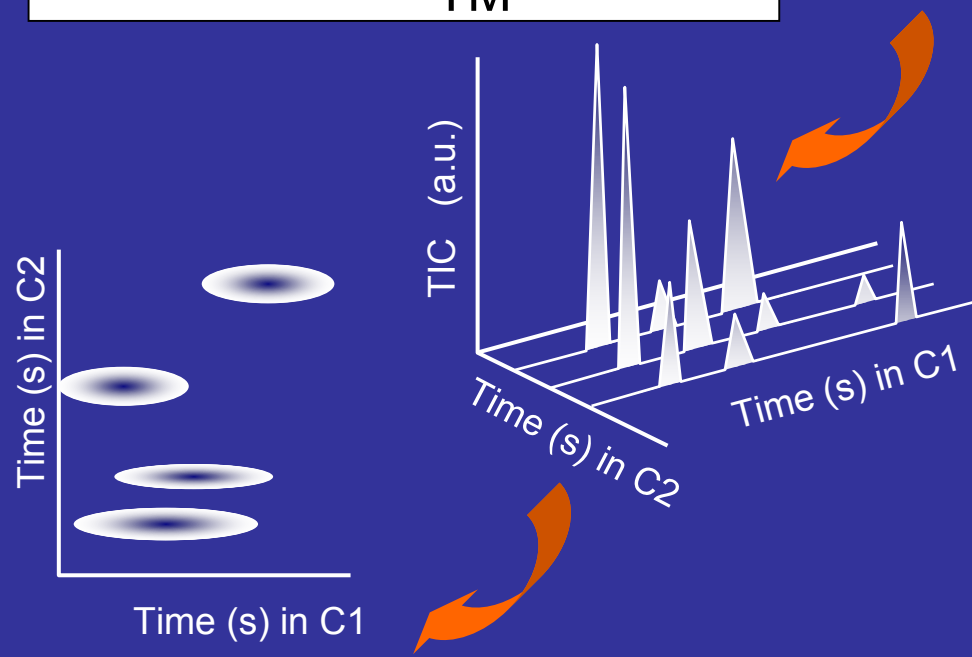
1-Dimensional GC



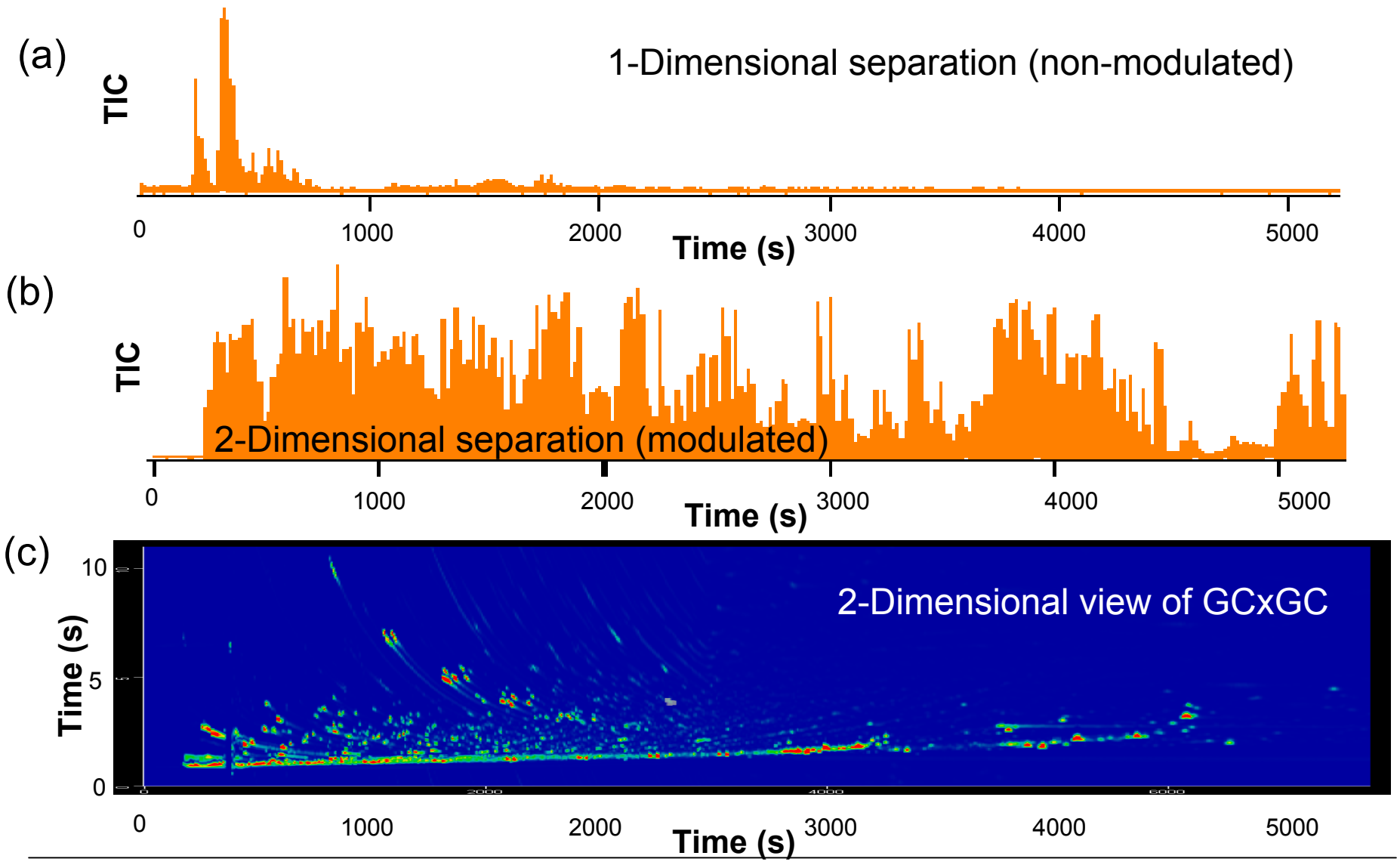


Comprehensive 2-Dimensional GC





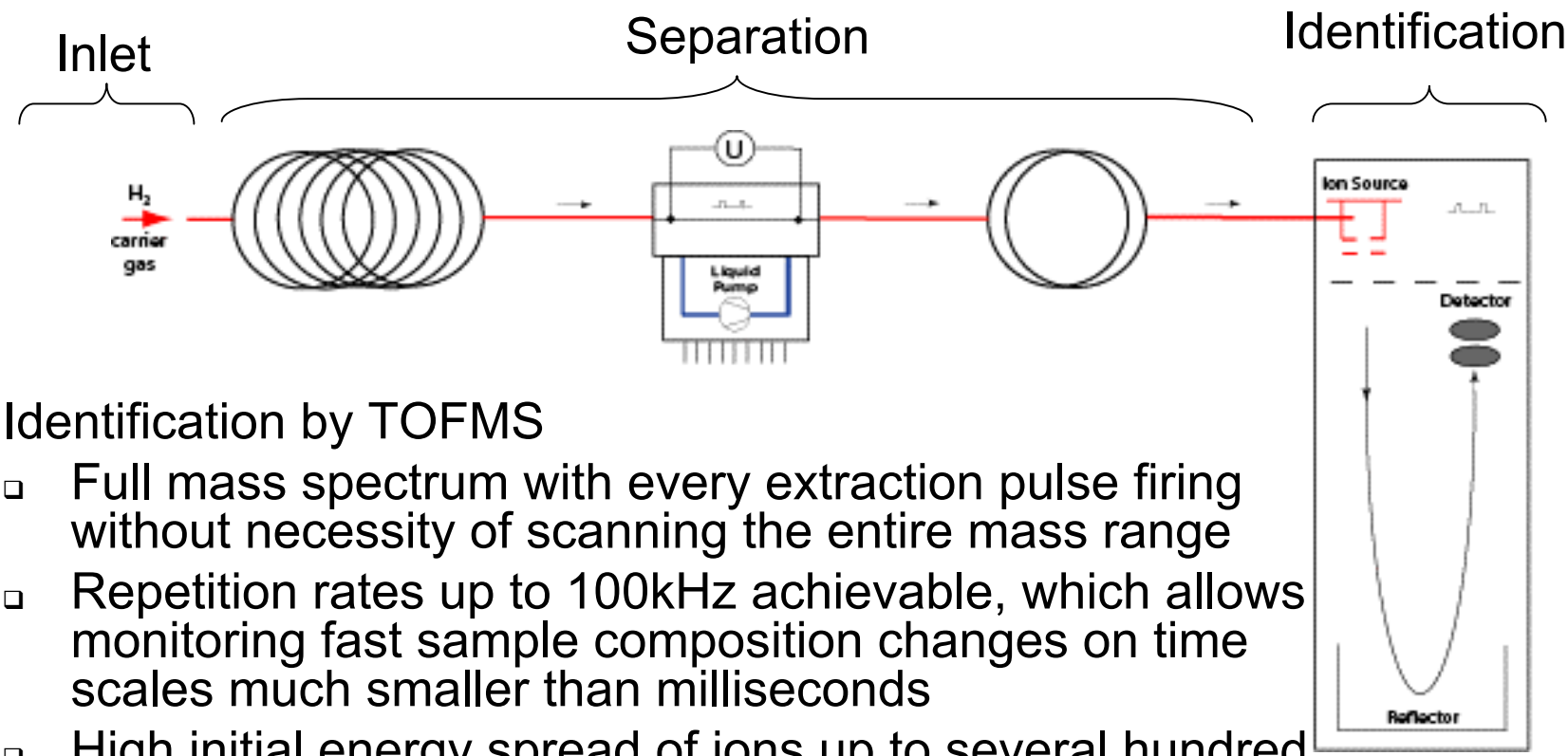
1-Dimensional versus 2-Dimensional Gas Chromatography (2/2)



Measurement capabilities of GCxGC

- Analysis of organic carbon compounds C_5 to C_{25}
- High peak capacity (several thousand peaks per chromatogram)
- Typical analysis cycle duration 30 min
- Various sampling methods are available
  - Solid samples using pyrolysis
    (10-100 μg/cycle sample material using Flash or Stepped Pyrolysis)
  - Volatile samples using direct sampling/pre-concentration
  - Liquid sampling using split/splitless injection
- Sensitivity in the low parts per trillion (ppt) range
- Increased detectability
- Linearity over more than 3 orders of magnitude (ppb - ppt)
- Thermal Modulator (TM) is key component of GCxGC
  - commercial TM require consumables
  - consumable-free TM under development

GCxGC-TOFMS

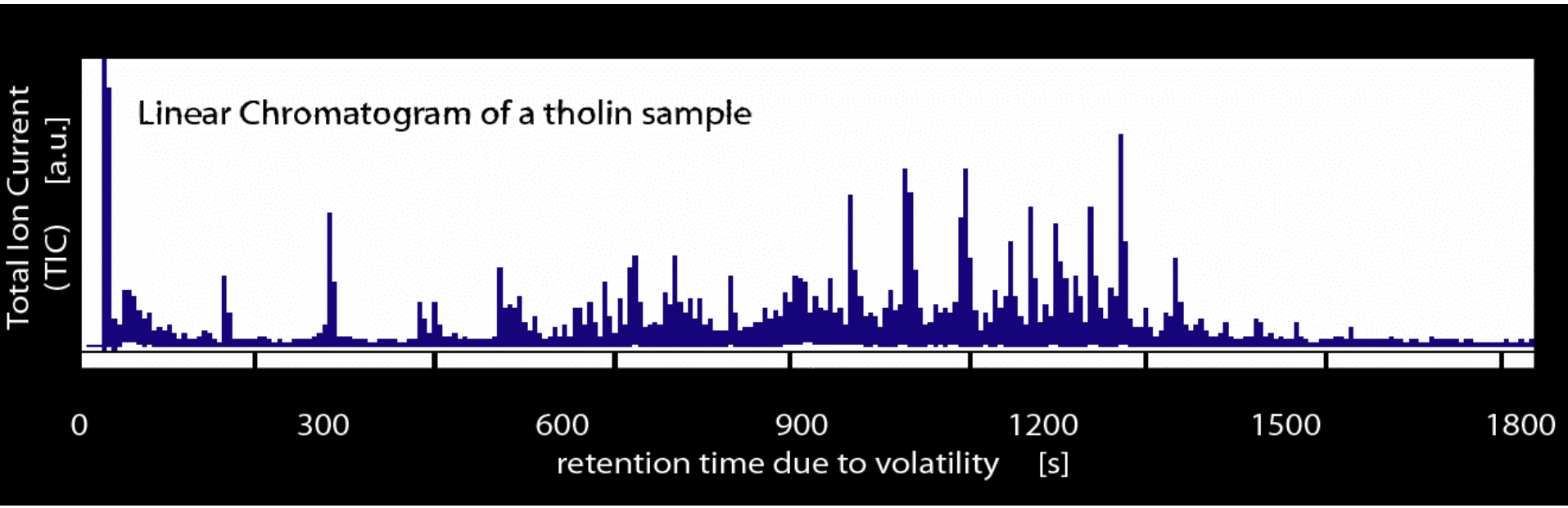


Identification by TOFMS

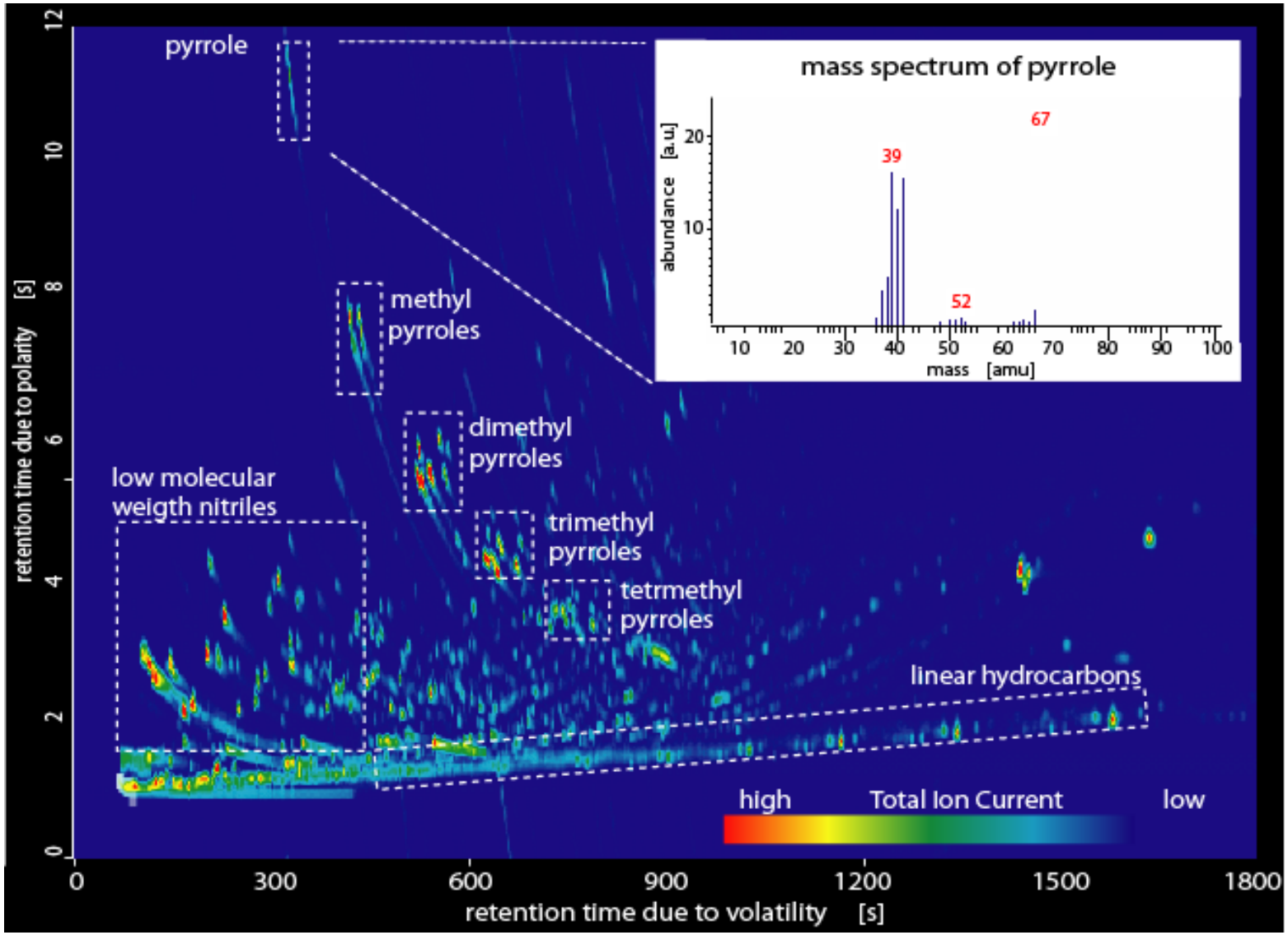
- Full mass spectrum with every extraction pulse firing without necessity of scanning the entire mass range
- Repetition rates up to 100kHz achievable, which allows monitoring fast sample composition changes on time scales much smaller than milliseconds
- High initial energy spread of ions up to several hundred eV is admissible
- Neither static nor dynamic magnetic fields are required
- Performance depends mainly on electrical circuits rather than mechanical alignment
- Mass scale calibration for TOFMS is simple and reliable

Chromatogram of tholins using GCxGC-TOFMS technique (1/2)

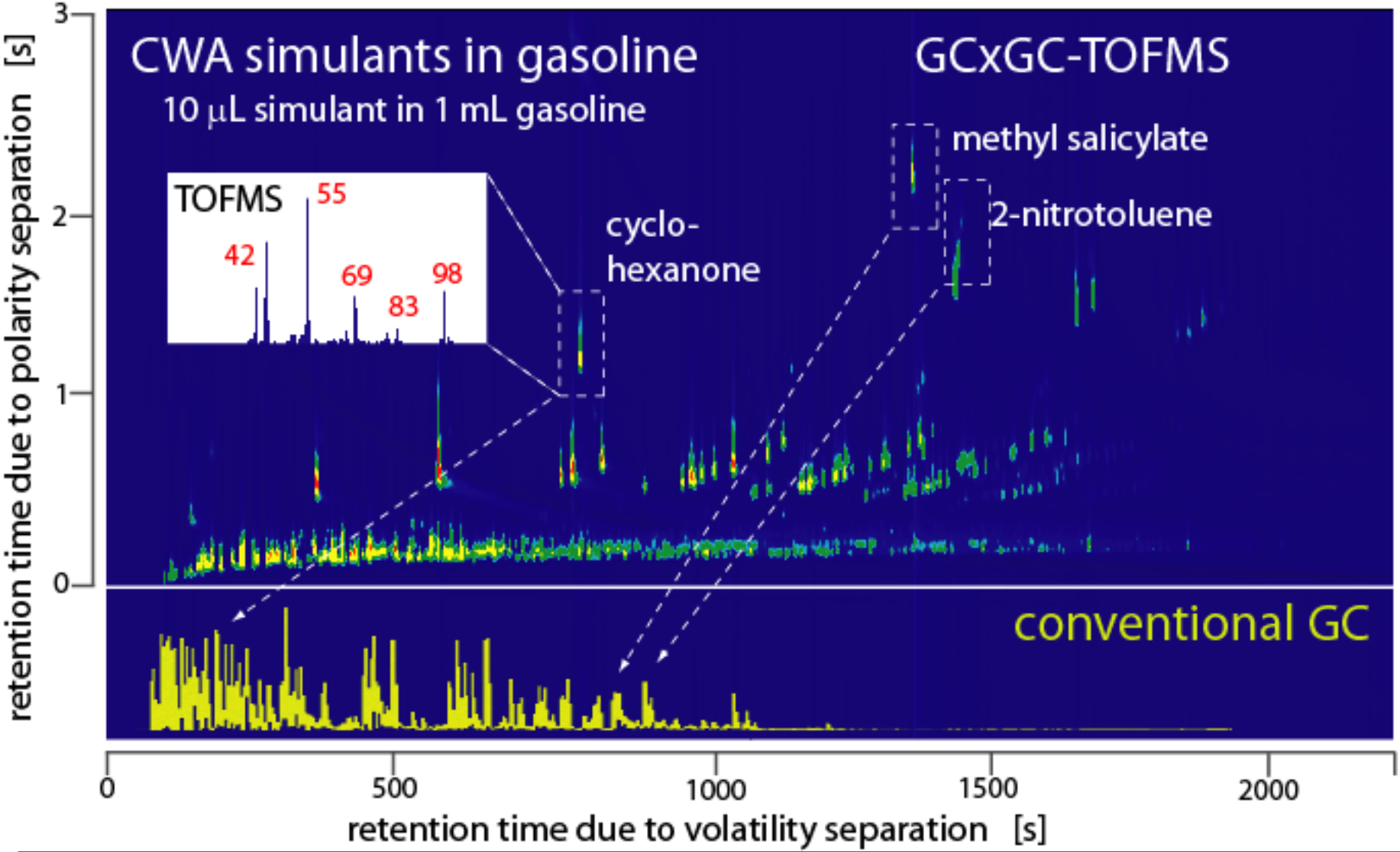
sample (tholin) analyzed by commercial laboratory equipment (LECO Corp.) using pyrolysis injection (CDS).



Chromatogram of tholins using GCxGC-TOFMS technique (2/2)

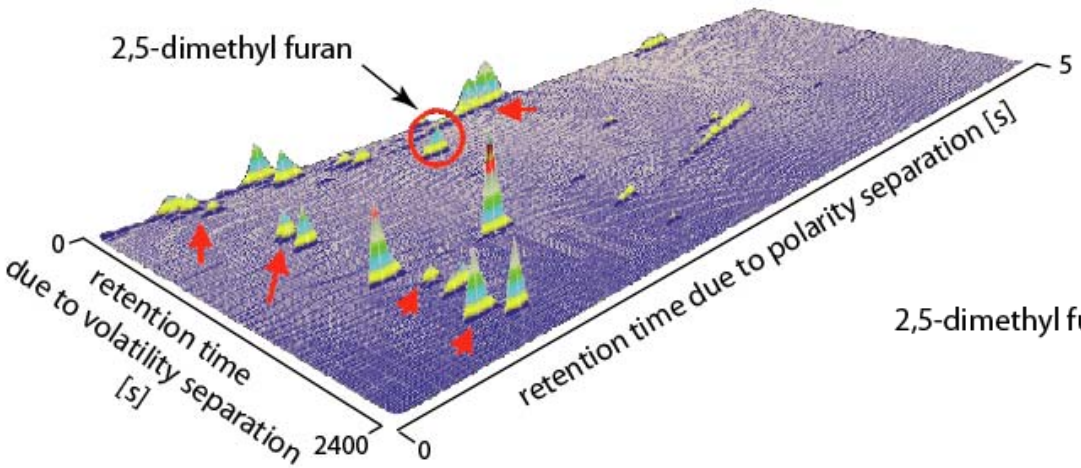


Chemical Warefare Agent Simulants in Complex Organic Mixtures

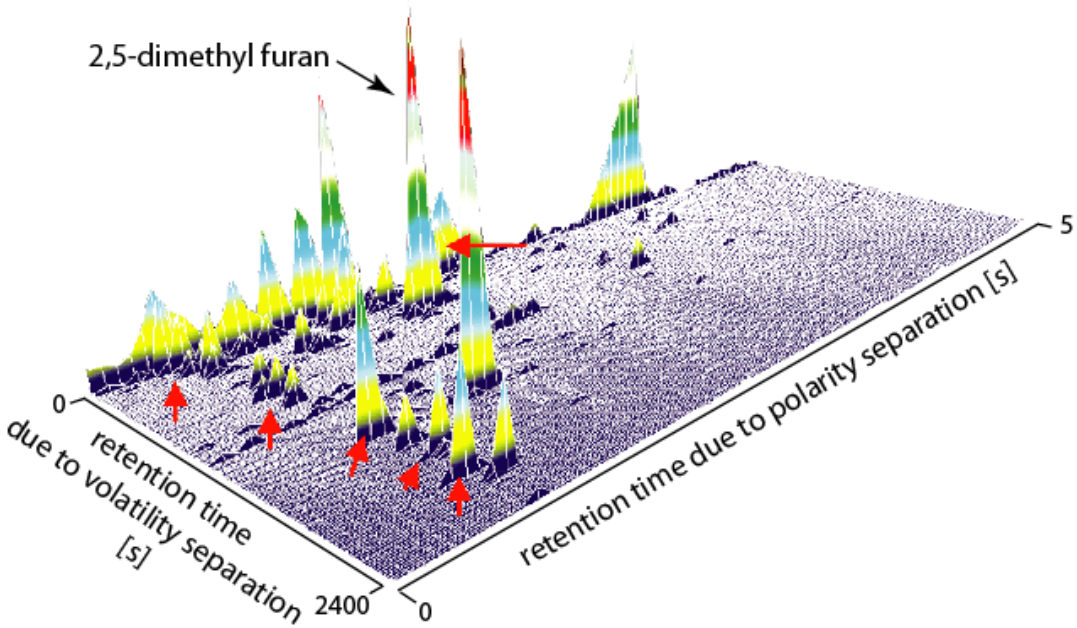


Human Breath Analysis

Human breath analysis before smoking

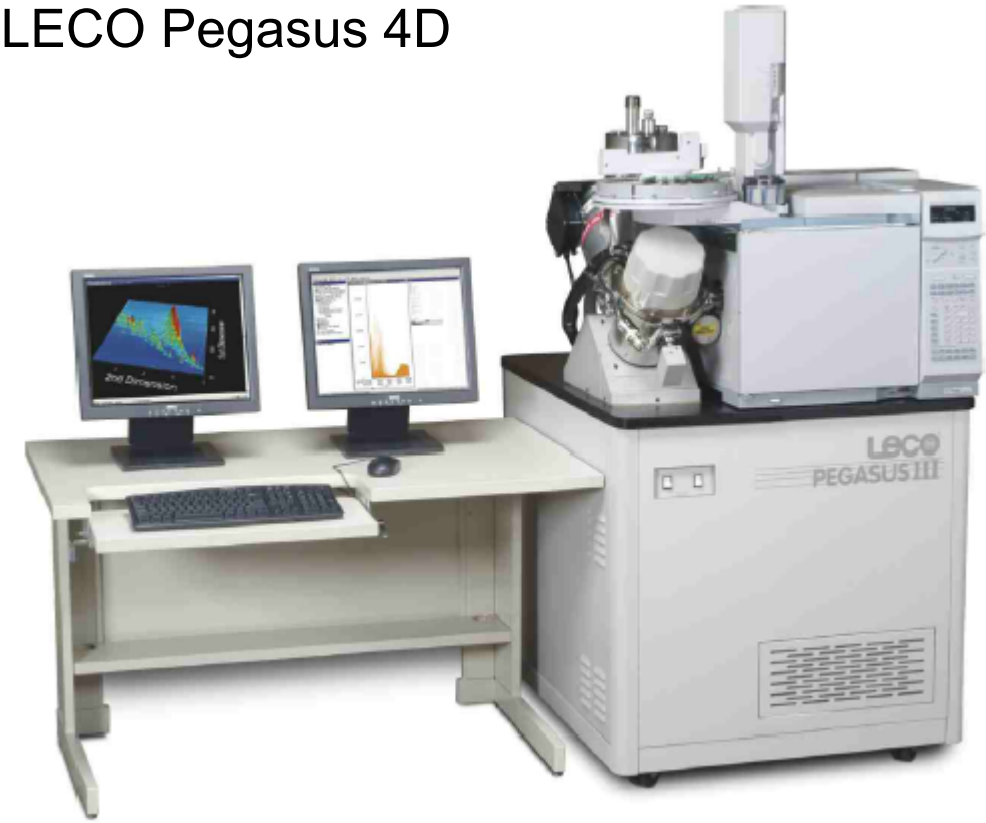


Human breath analysis shortly after smoking



Commercial GCxGC-TOFMS

LECO Pegasus 4D



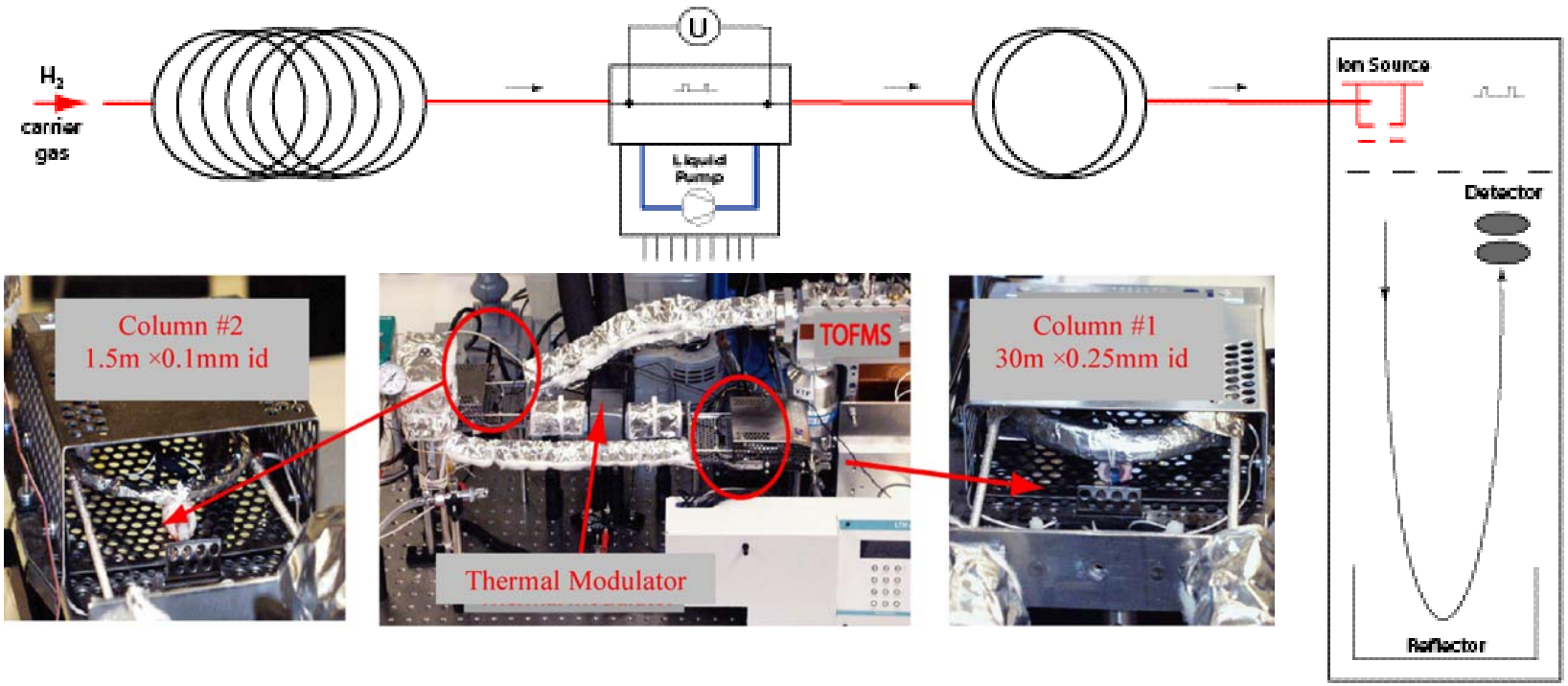
GCxGC – TOFMS

- Resource intensive liquid LN_2 cooled four jet Thermal Modulator (dewer of LN2 /week)

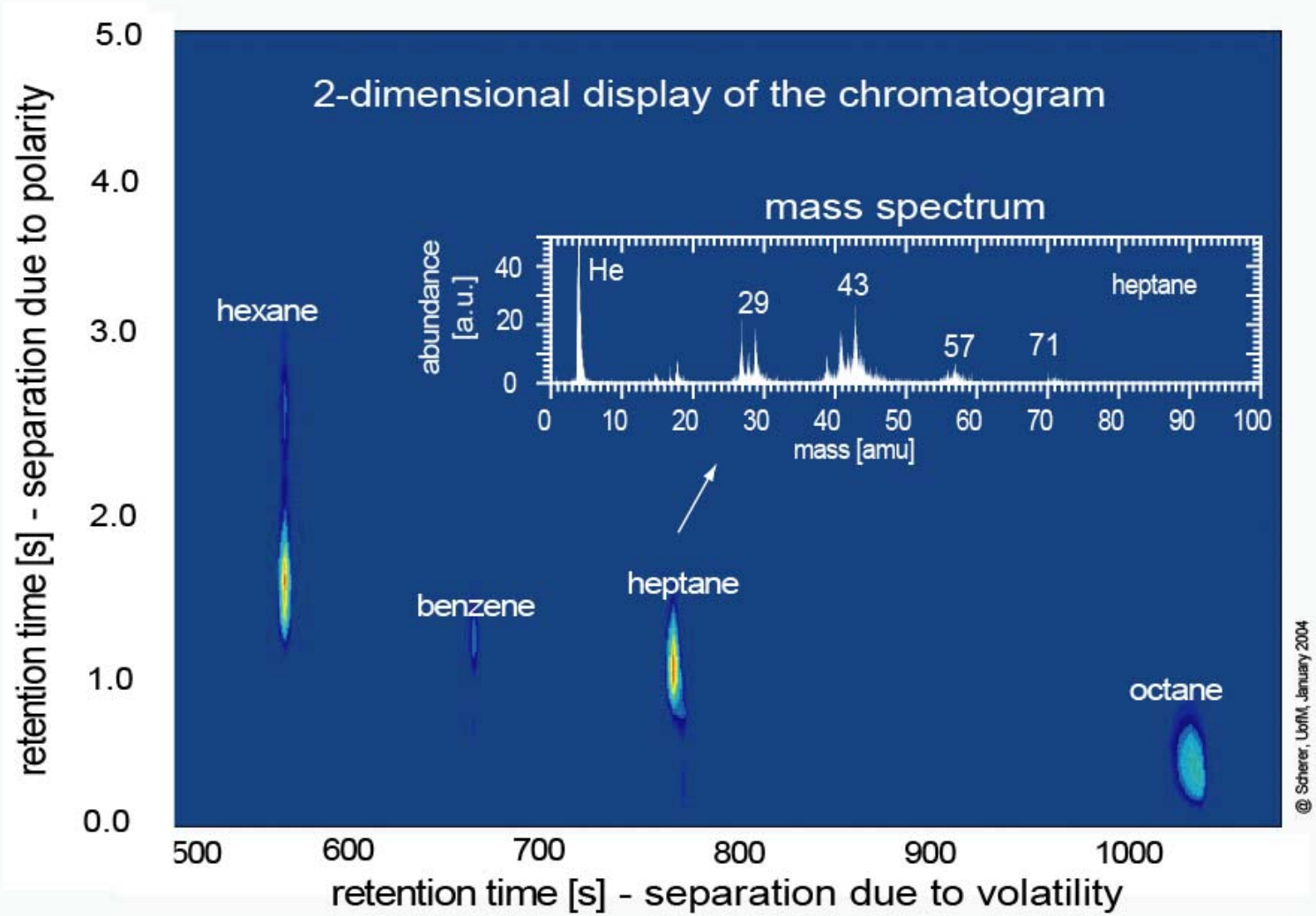
GCxGC–TOFMS breadboard using closed-loop air-cooled TM

GCxGC – TOFMS breadboard

- Custom made pre-concentrator
- Integrated packaged columns (RVM Scientific)
- Custom made closed-loop air-cooled consumable-free TM
- TOFMS (Ionwerks)



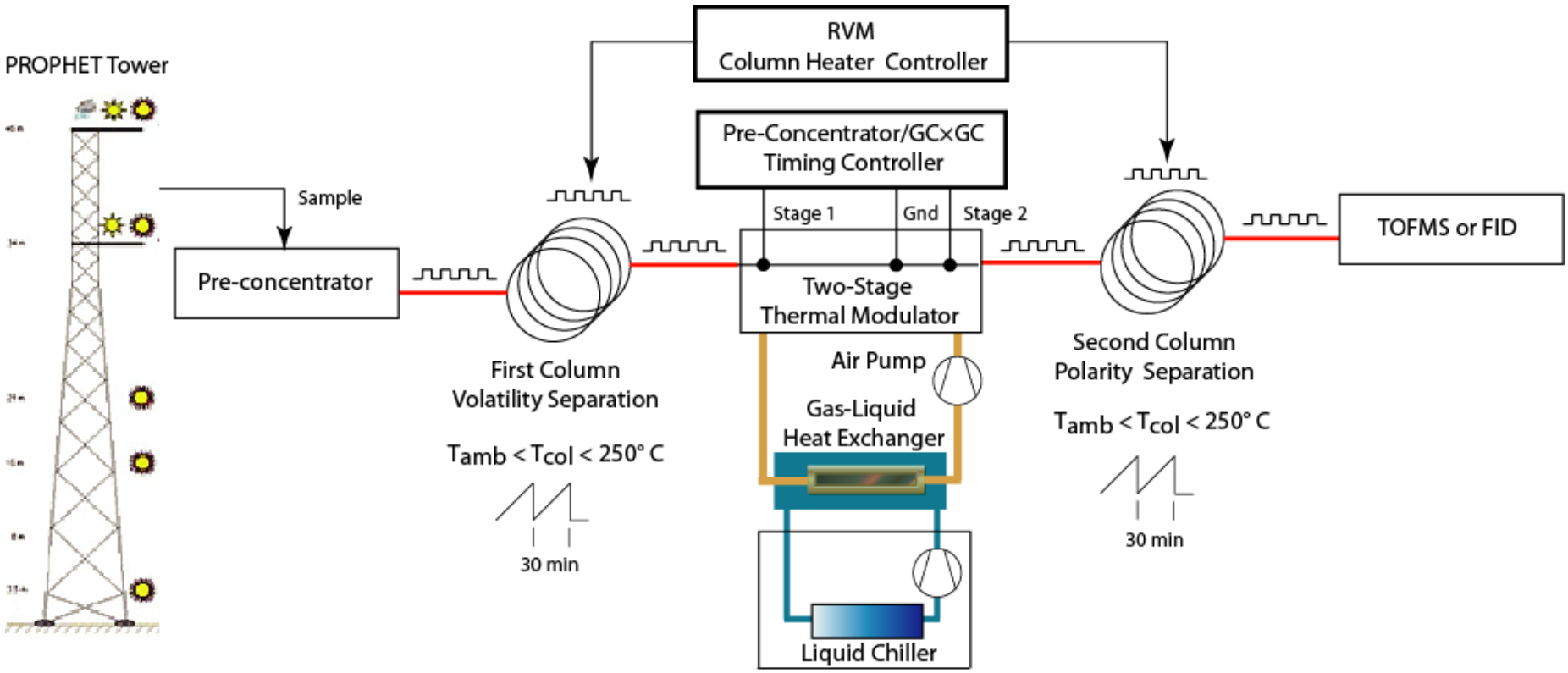
Breadboard results of GCxGC - TOFMS



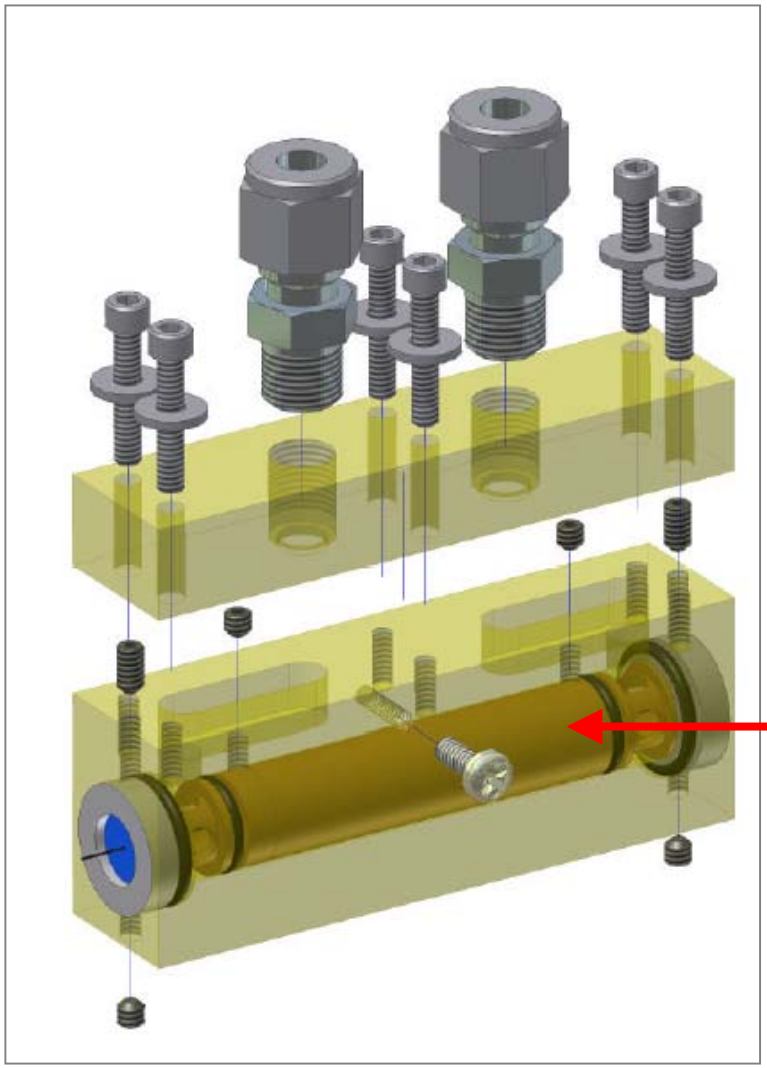
Field deployment of the GCxGC-TOFMS breadboard

GCxGC–TOFMS breadboard field deployed during summer 2005 campaign at the PROPHET tower laboratory at the University of Michigan Biological Station (Northern Michigan); refer to poster from Judy Yu

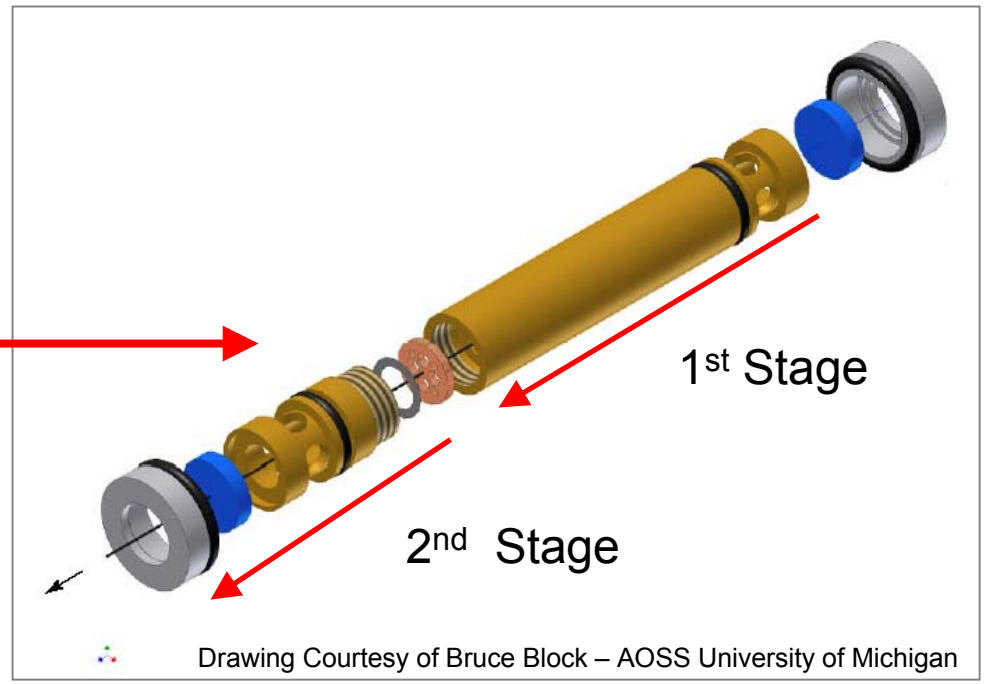
Measurement Goal: VOCs and isoprene measurements



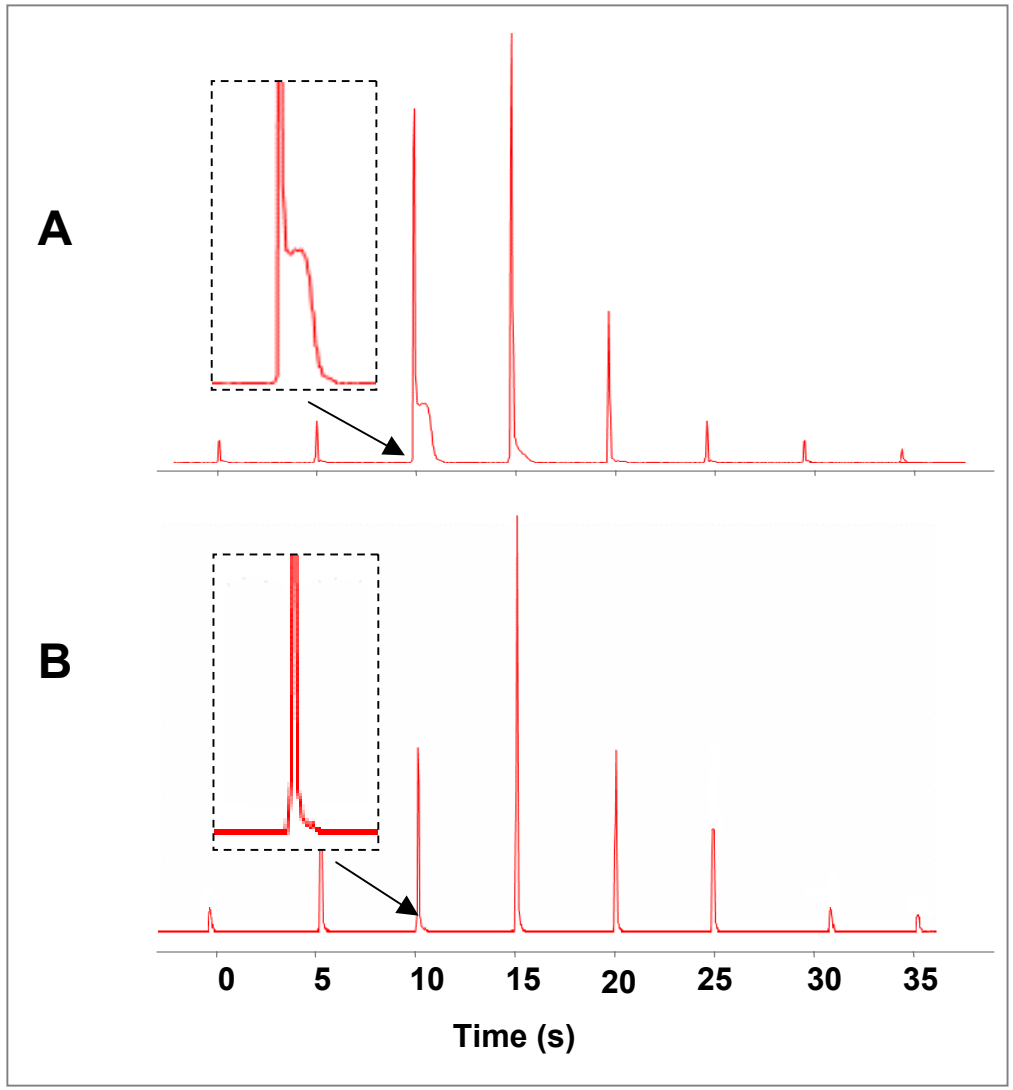
2-Stage Thermal Modulator



- Two-Stage Thermal Modulator designed and prototyped at the University of Michigan
- Set Industry Standard for Modulators
- Two-Stage will eliminate sweep through



Single Stage versus 2-Stage Thermal Modulator



Single-Stage Air-Cooled

- limited quantitative analysis
- Breakthrough observed
- Peak Tailing as concentration inside modulator increases

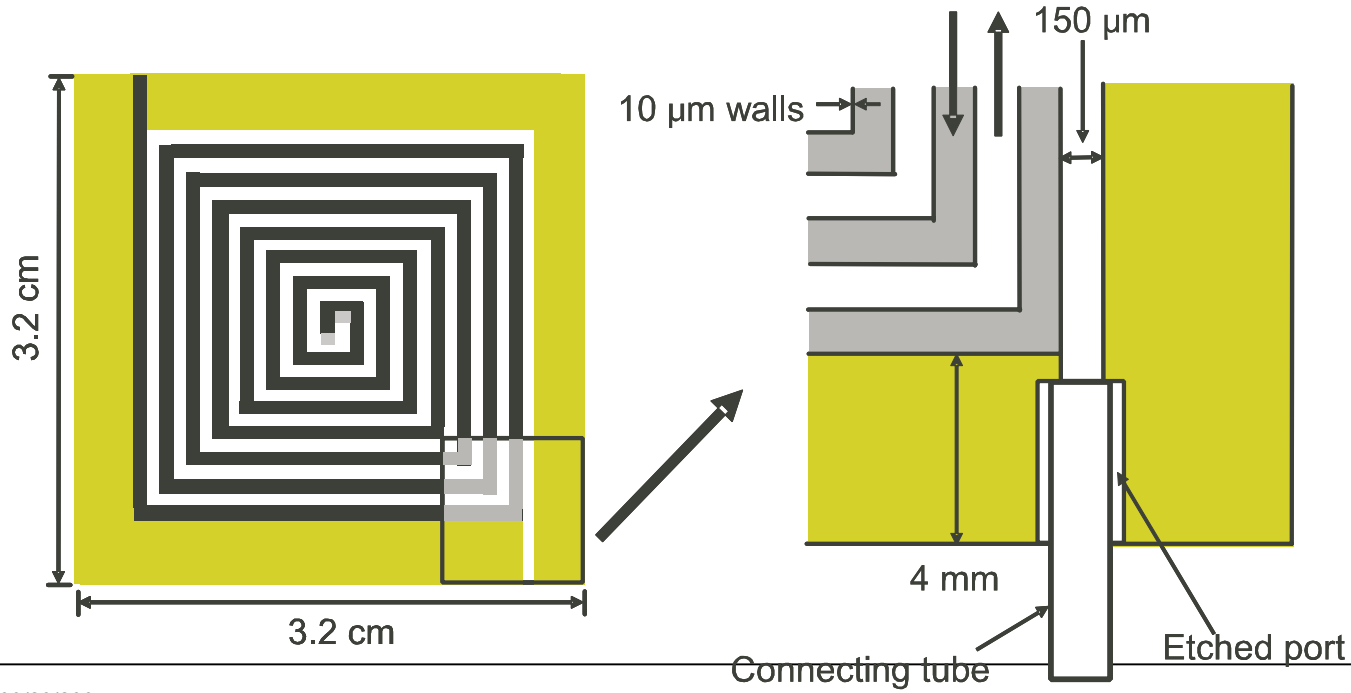
Two-Stage Air-Cooled

- Improved quantitative analysis
- Minimal Breakthrough
- No Peak Tailing

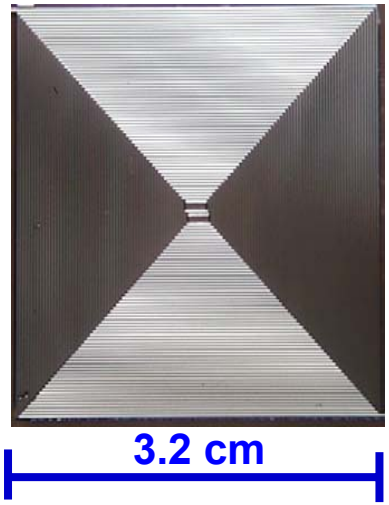
1 ppm Octane

Future of GCxGC using Micro-Fabricated Columns

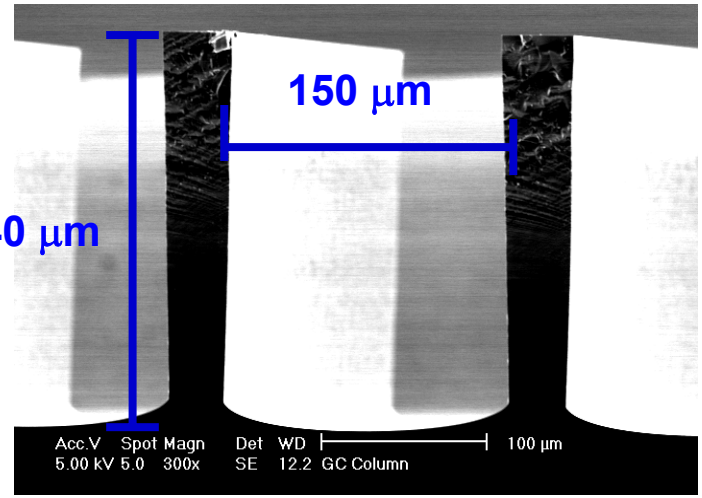
- Further miniaturize the separation section by using MEMS technology for the GCxGC subsystem
- Decrease physical size as well as reduce resource requirements with on-chip heating
- Collaboration with the WIMS center at UofM

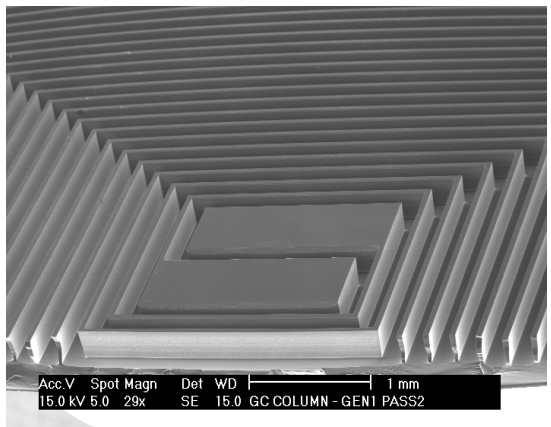


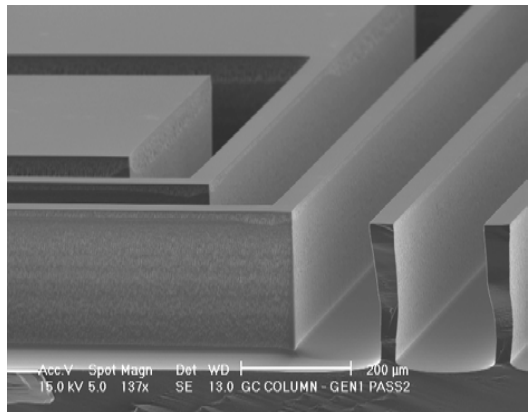
Future of GCxGC using Micro-Fabricated Columns



- Capillary length 3m
- Chip size (3.2cmx3.2cm)
- cross section
  150 µm wide x 240 µm deep
- Side ports etched in Si for more mechanical stability
- Etched back structure for reduced thermal mass

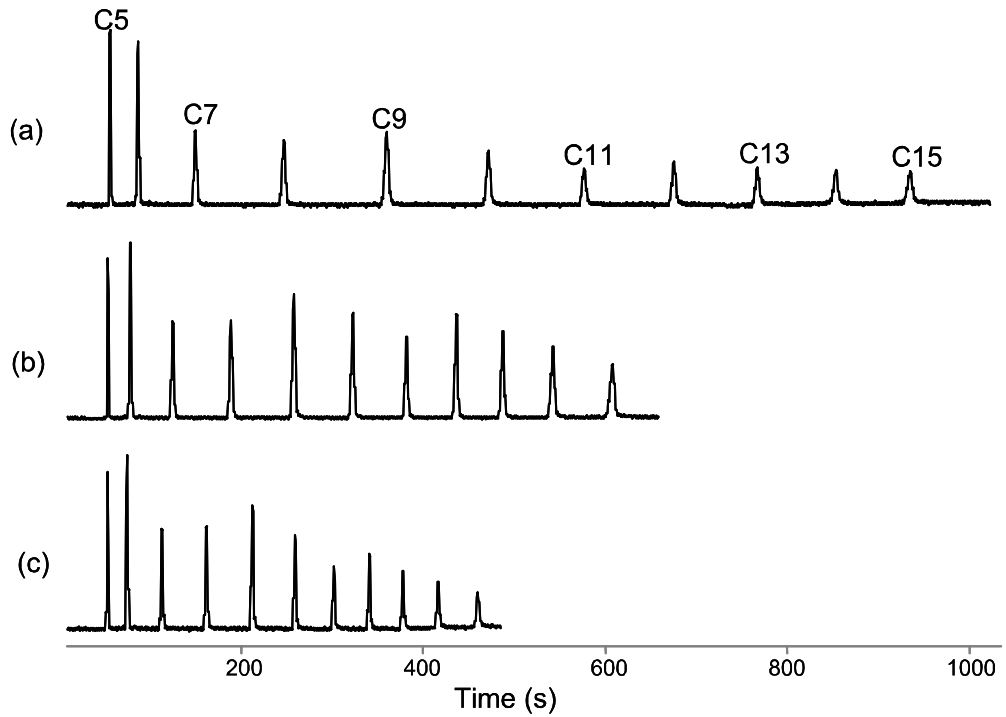






Future of GCxGC using Micro-Fabricated Columns

- Separation of series of n-alkanes (C_5 to C_{15}) at 3 temperature programs
  a) 10 K/min
  b) 20 K/min
  c) 30 K/min
- Design of a meso-scale TM using thermo-electric cooling and resistive heating attached to columns in MEMS technology



The GACID Team

… By the enthusiastic effort of the following team members at the University of Michigan the results have been made possible …

College of Engineering

Charlie Hasselbrink

Atmospheric, Oceanic, and Space Sciences

Hunter Waite

Megan McGuigan

Bruce Block

Stefan Scherer

Chemistry

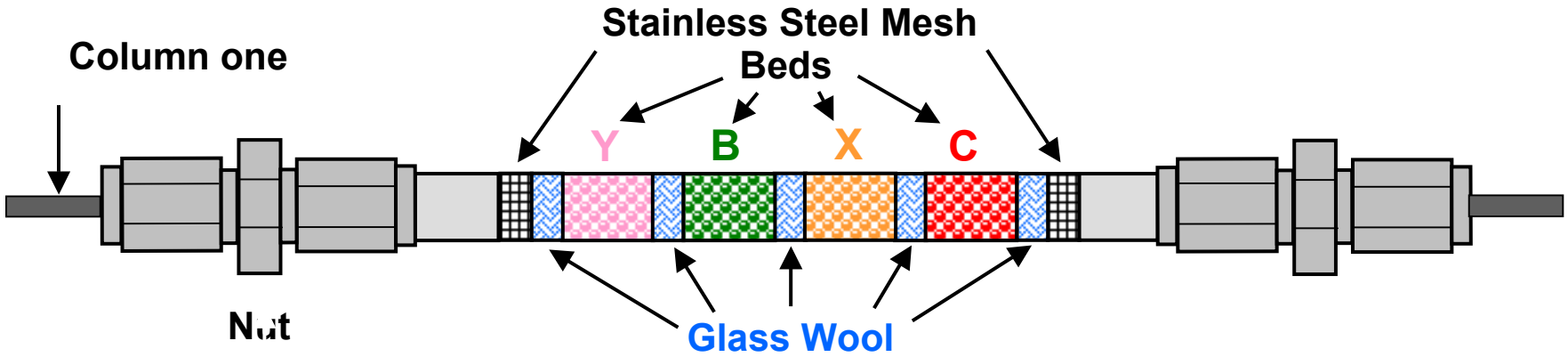
Richard Sacks

Amy Payeur

PT Stevens

Mark Libardoni

Pre-Concentrator



Gas Flow During Sample Collection

Gas Flow During Sample Desorption

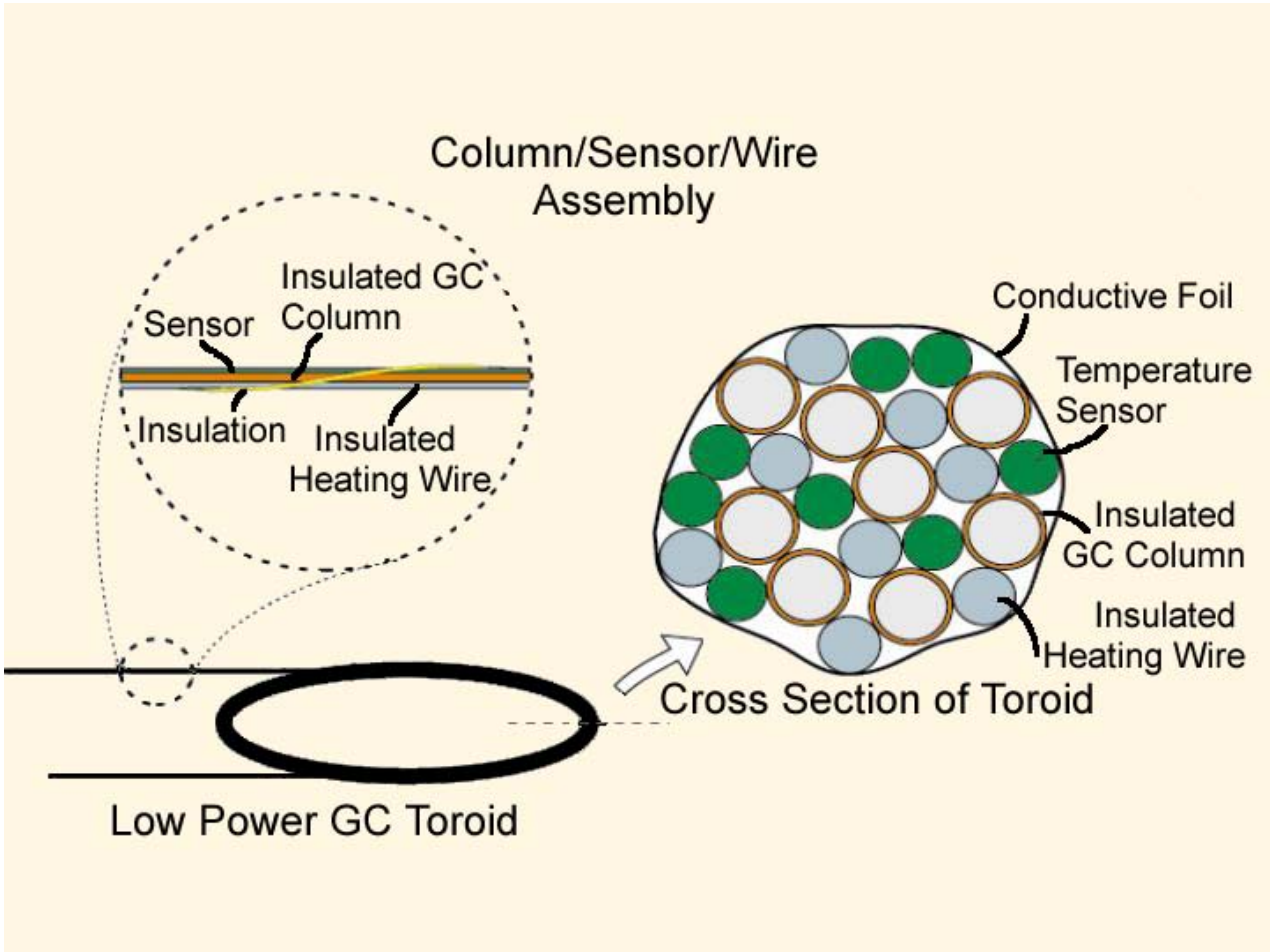
	Symbol	Adsorbent	Adsorbent Strength	Application
Carbon Molecular Sieve	C	Carboxen 1000	Strongest	C_2 to C_5
Graphitized Carbon	X	Carbopack X	Stronger	C_3 to C_5
↓	B	Carbopack B	Weaker	C_5 to C_{12}
	Y	Carbopack Y	Weakest	C_{12} to C_{20}

Custom designed Thermal Modulator

Dual stage Thermal Modulator
- resistively heated -air-cooled

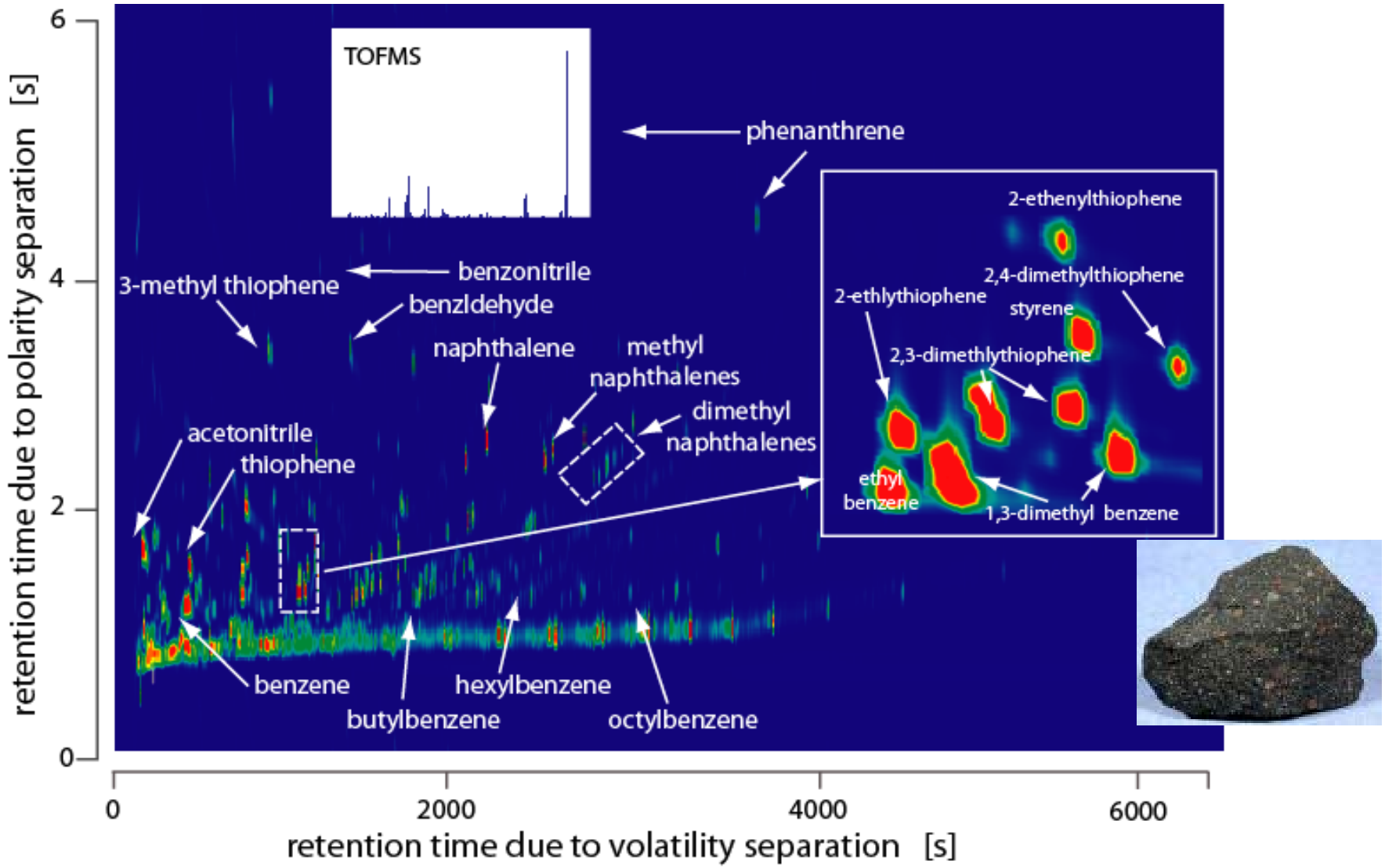
Gas Chromatographic columns

RVM Scientific integrated columns

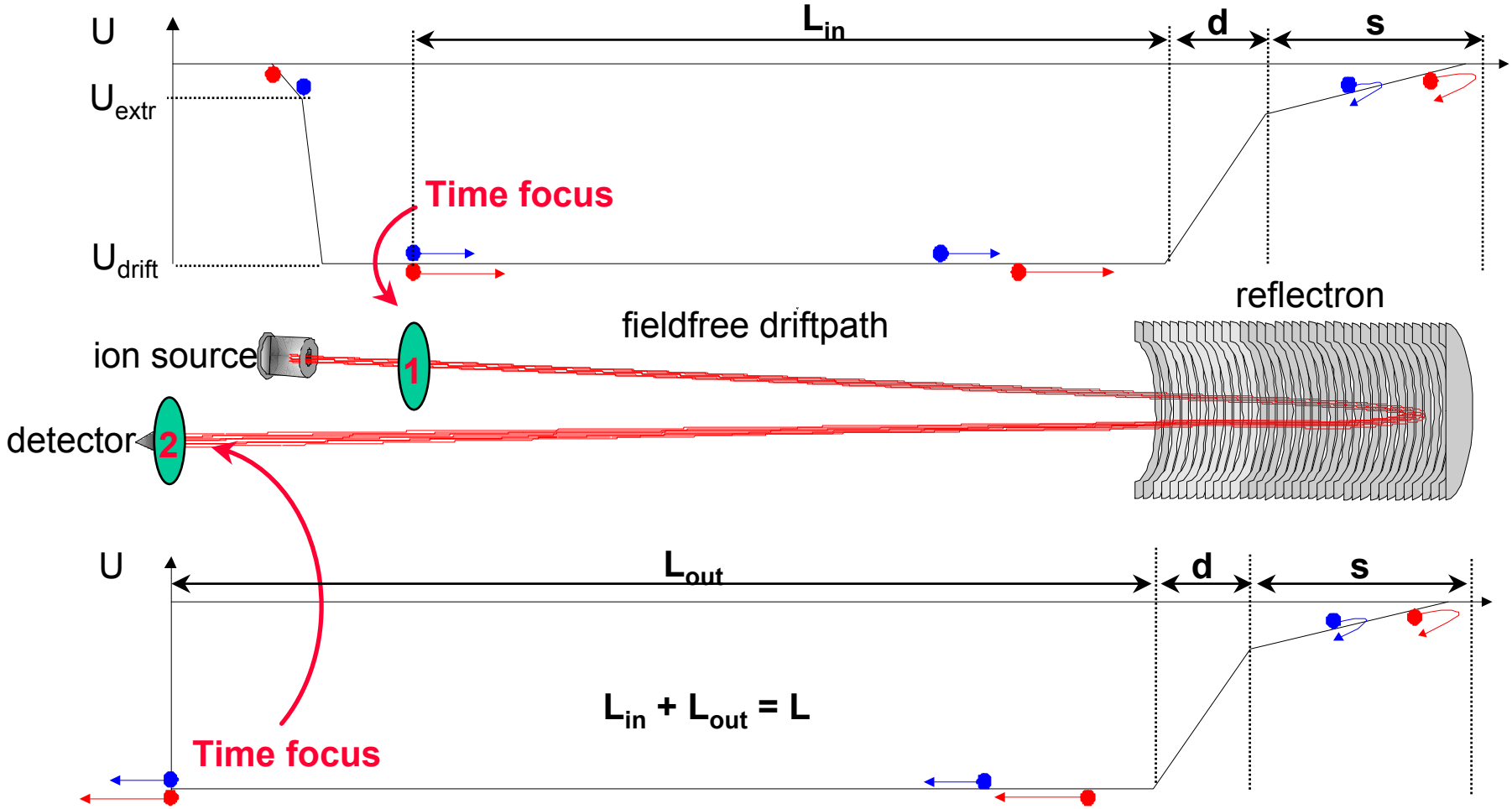


Add photo of the RVM columns

Murchinson Meteorite analysis using Pyrolysis-GCxGC-TOFMS

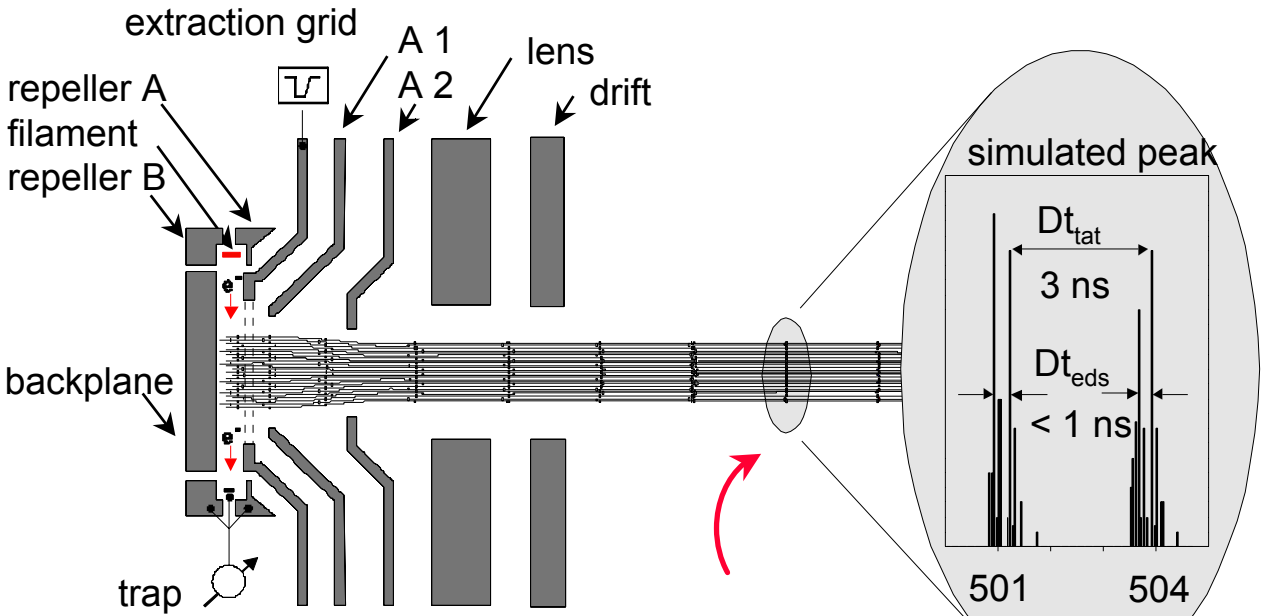


Time-of-Flight principle

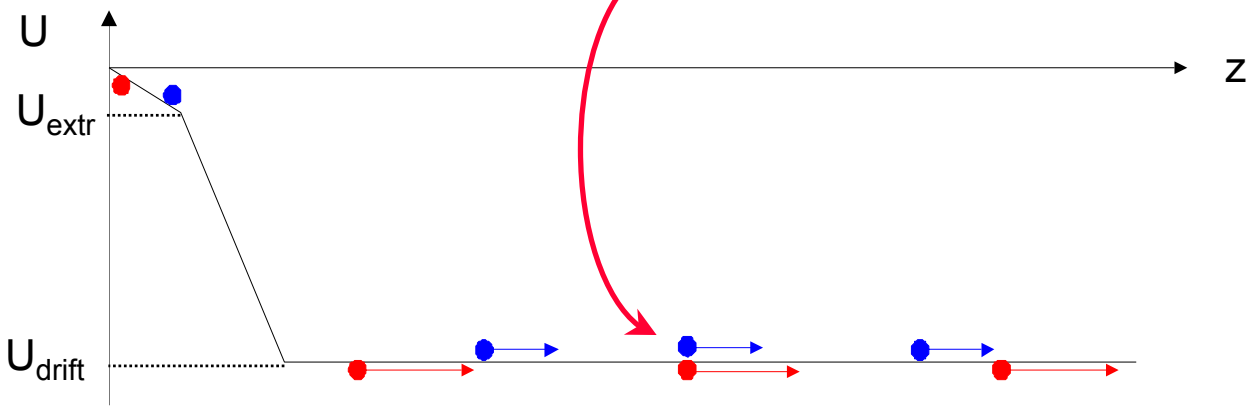


Mamyrin *et al.*, 1972

Electron Impact Storage Ion Source



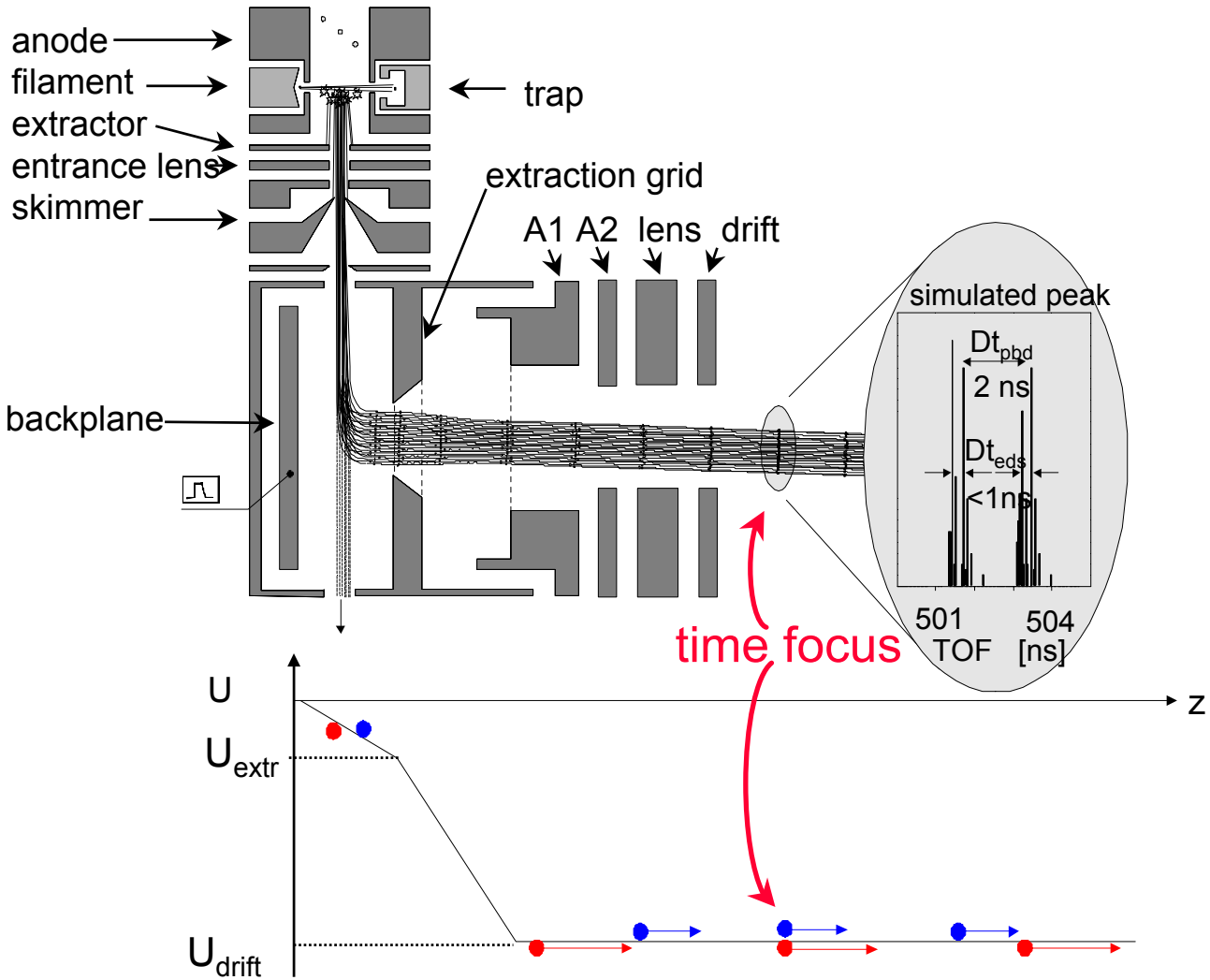
1. Time focus

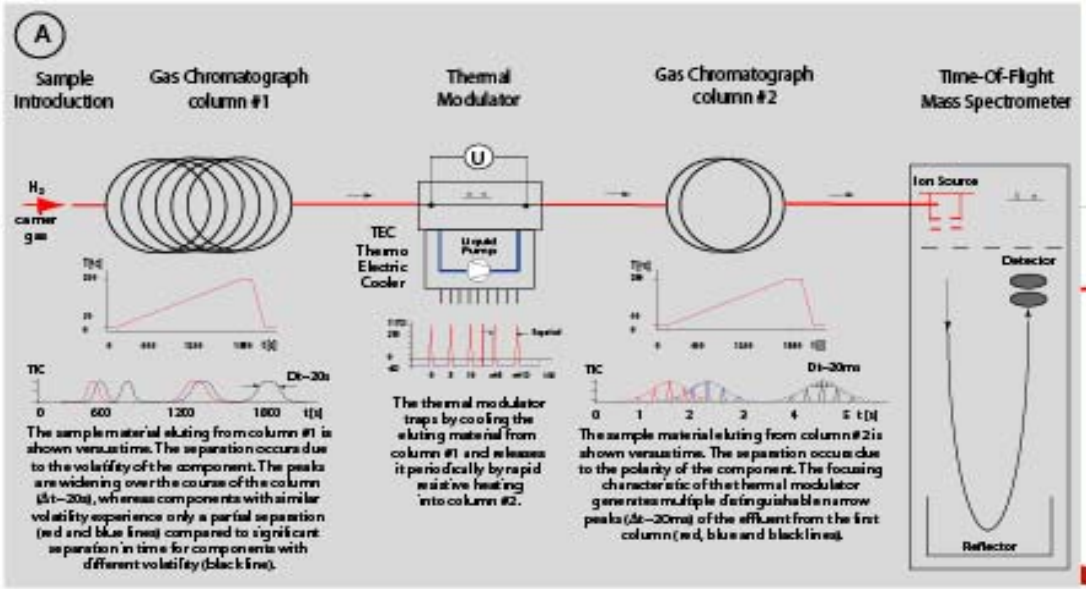


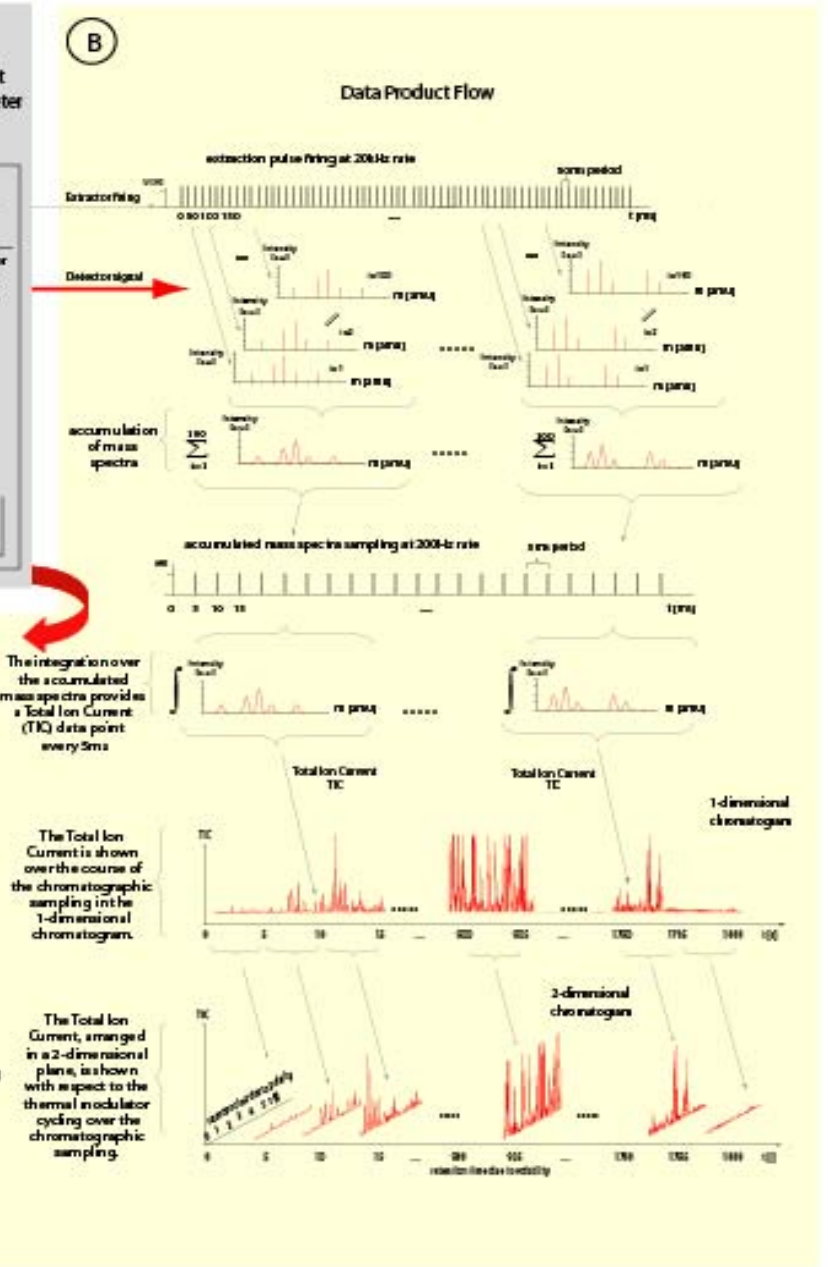
turn-around time

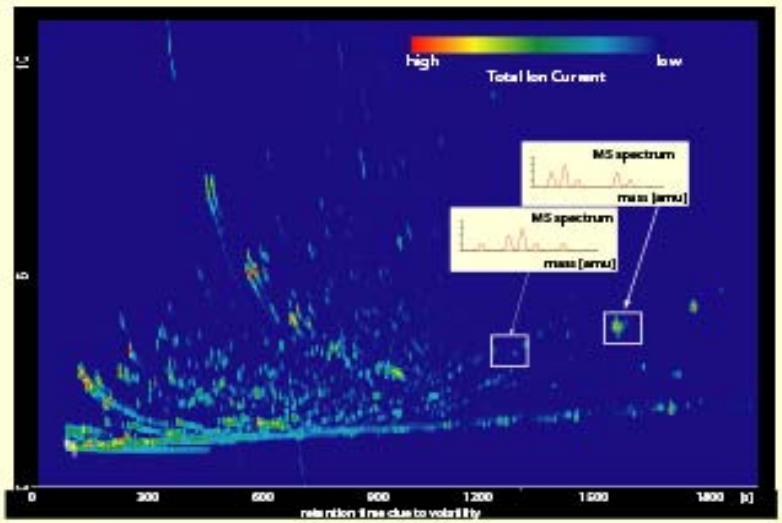
$$\Delta t_{tat}(m) = 2 \cdot \frac{\sqrt{2mU_0}}{q\,E_{extr}}$$

Orthogonal Extraction Ion Source





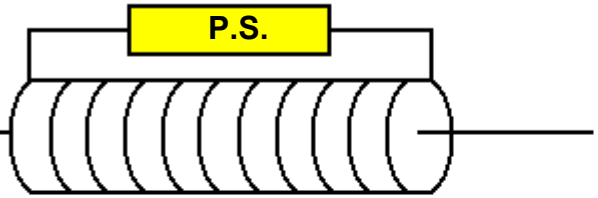




The deconvoluted chromatographic data is displayed in the 2-dimensional retention time plane. The corresponding mass spectrum is available for each chromatographic data point.

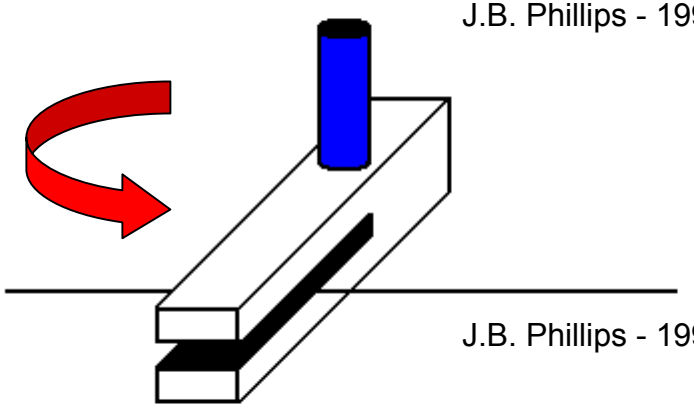
Thermal Modulators: Overview of techniques

A



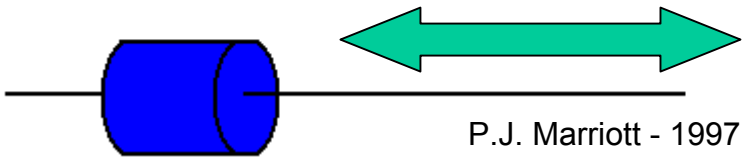
J.B. Phillips - 1991

B



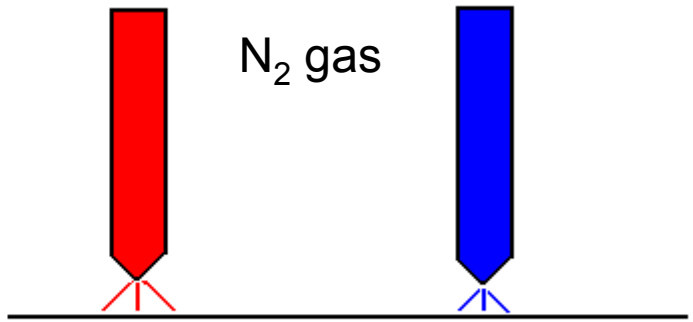
J.B. Phillips - 1993

C



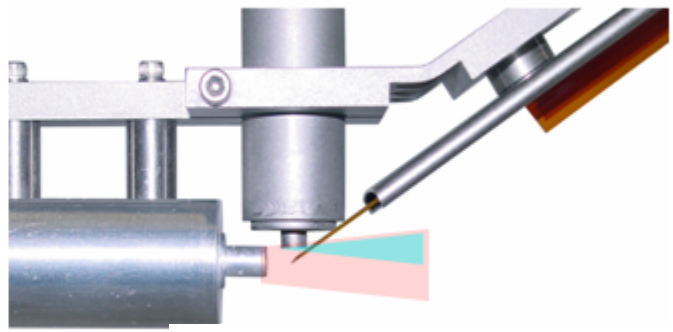
P.J. Marriott - 1997

D



E.B. Ledford and J. Beens - 2000

E



E.B. Ledford - 2002