Expedited Field Survey and Sampling Techniques for PCB Congeners and Dioxins: GIS Mapping of PCB Congeners and Dioxins in Sediments and Soils: Preliminary Assessment of Sediments on the PORTS site

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QRT 3 Activities

- Reviewing quotes from independent laboratories
- Obtained and set-up portable GC/MS in Clippinger Laboratory
- Tested GC/MS performance measures

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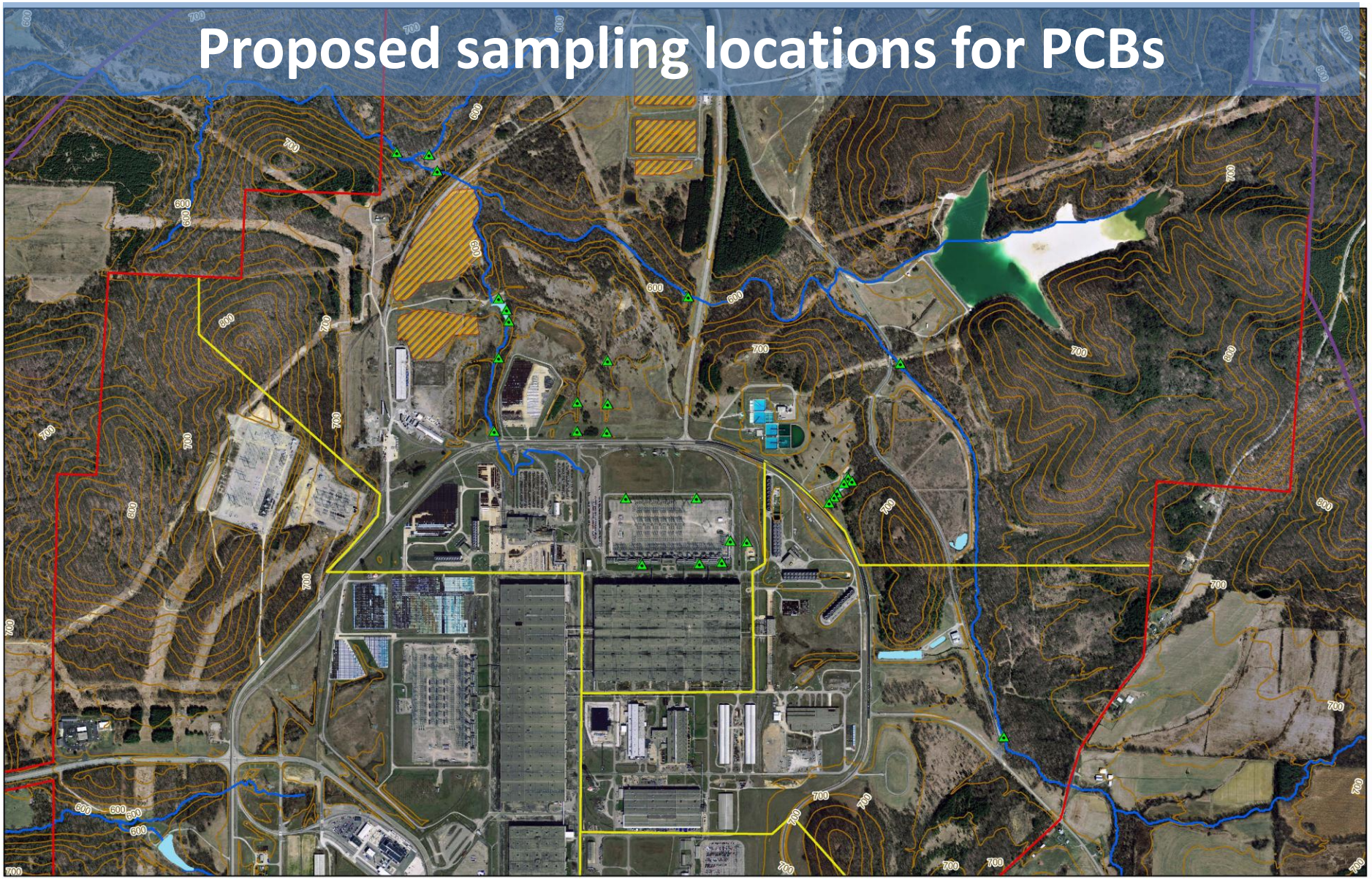
Sampling Plan

- Initial sampling planned for November 2011
- Full sampling planned for Spring 2012

Proposed sampling locations for PCBs



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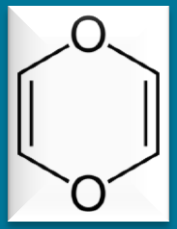
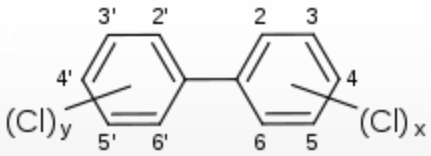
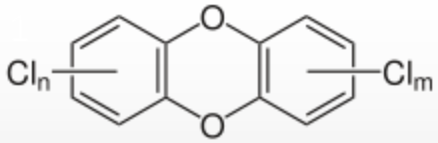
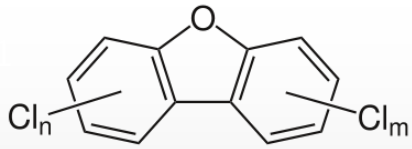
Introduction – PCBs and Dioxin



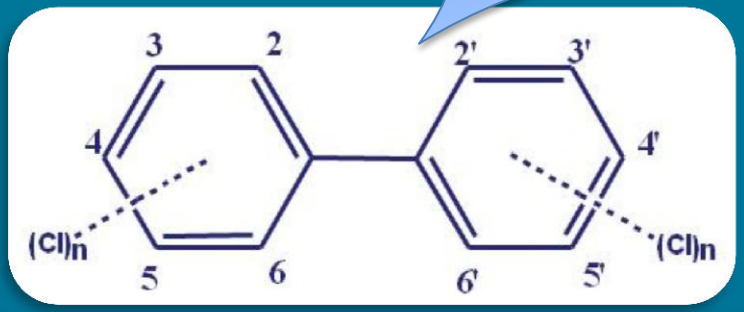
Dioxins and dioxin-like compounds

PCBs	Polychlorinated dibenzo-p-dioxins (PCDDs)	Polychlorinated dibenzofurans (PCDFs)
		
12 WHO Concern	7 WHO Concern	10 WHO Concern

Introduction - PCBs

209

PCBs -- Polychlorinated Biphenyls



STABLE

X
- Oxidation
- Reduction
- Addition
- Elimination
- Electrophilic Substitution

→

- Low reactivity
- Non-flammable
- High electrical resistance
- Stable exposed to heat & pressure

- Used as lubricants, coolants and insulators in industry
- Extremely difficult to decompose

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Introduction - PCBs

General Rules

- more Cl = more toxic
- Position of Cl affects toxicity
  - ✓ Ortho position less toxic than meta or para
  - ✓ Para + meta = "dioxin like"; flat plane molecule, particularly toxic

TOXICITY

- Carcinogenesis
- Hepatotoxicity
- Chloracne
- Otitis media
- Reduced Neurodevelopment
- Bioaccumulation

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Introduction - PCBs

First manufactured in 1929 by Monsanto

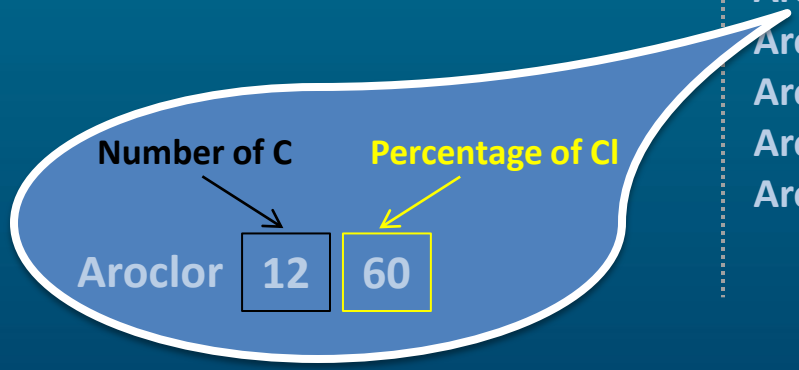
Use banned in US in 1979

A congener is a specific conformational isomer (arrangement) of $C_xH_yCl_z$

An Aroclor is a commercial name for mix of multiple congeners

Names related to PCBs

PCB congeners	Aroclor	Other trade names
209	Aroclor – 1016 Aroclor – 1242 Aroclor – 1260 Aroclor – 1221 Aroclor – 1248 Aroclor – 1268 Aroclor – 1232 Aroclor – 1254	Chlorextol Pyranol/Pyrenol Askarel • • •



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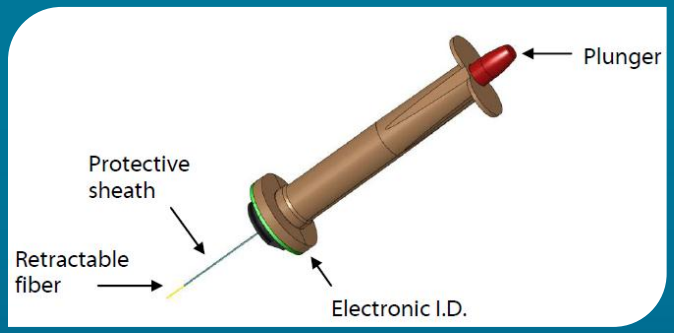
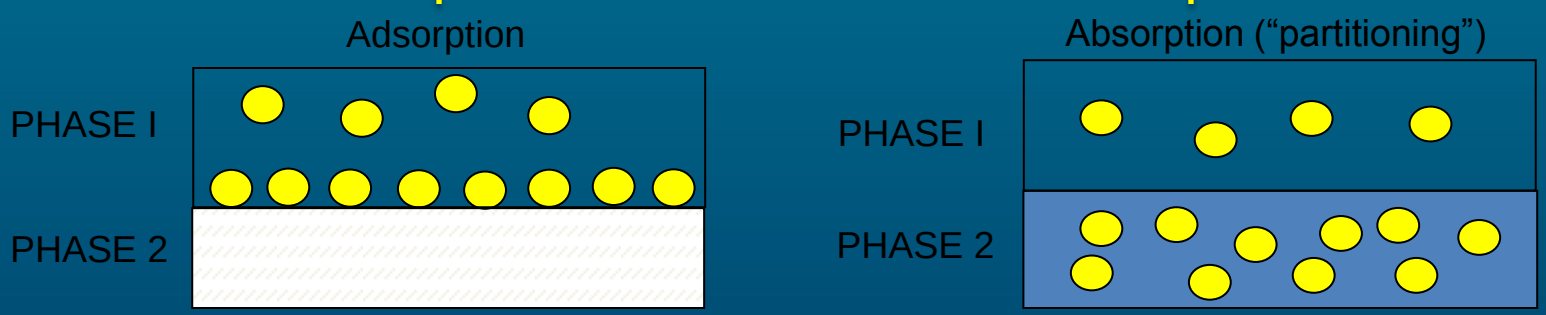
Introduction - SPME

SPME -- Solid Phase MicroExtraction



Direct Insertion (aqueous phase) or headspace SPME

Mechanisms for SPME



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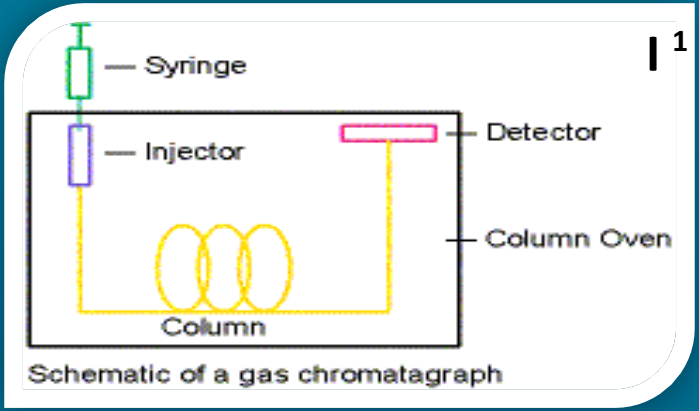
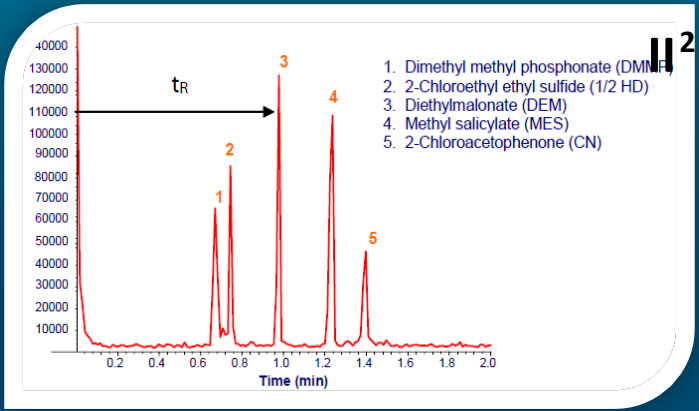
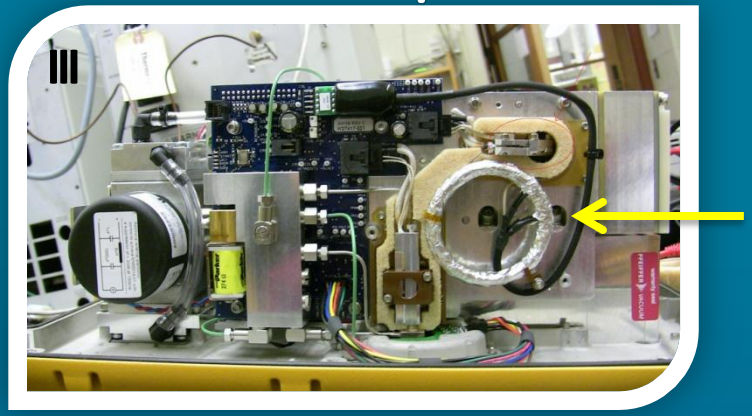
Introduction - GC

GC -- Gas Chromatography





Torion GC port



1. http://www.doj.state.wi.us/dles/crimelabs/images/gc-schem.gif
2. Torion user's guide
3. http://imgs.sfgate.com/c/pictures/2008/08/16/sp-oly17_ph_bolt_0498958651.jpg

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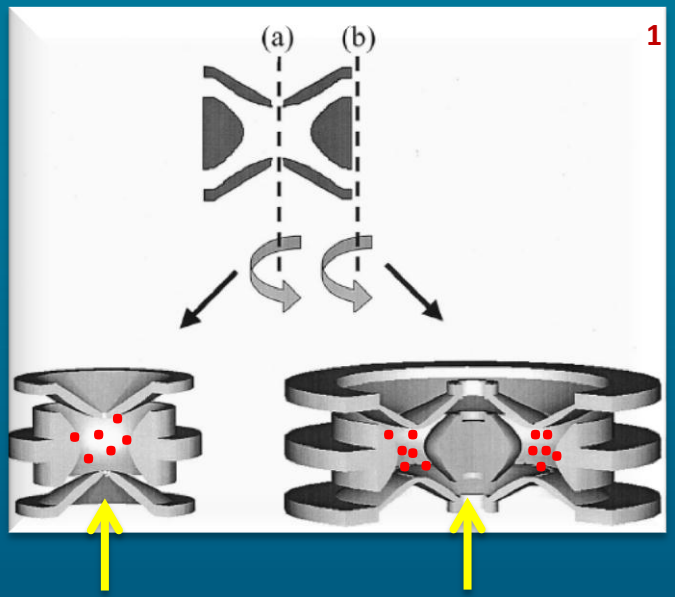
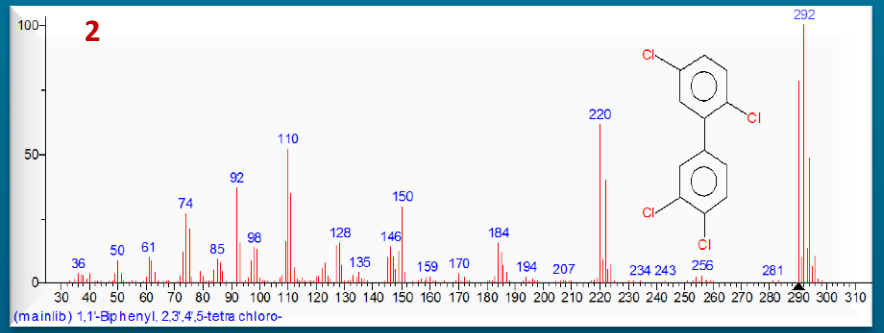
Introduction - TMS

MS -- Mass Spectrometry





High sensitivity and selectivity when couple with GC

1. Lammert, S. A., et al. (2001). International Journal of Mass Spectrometry 212(1-3): 25-40.
2. NIST Database

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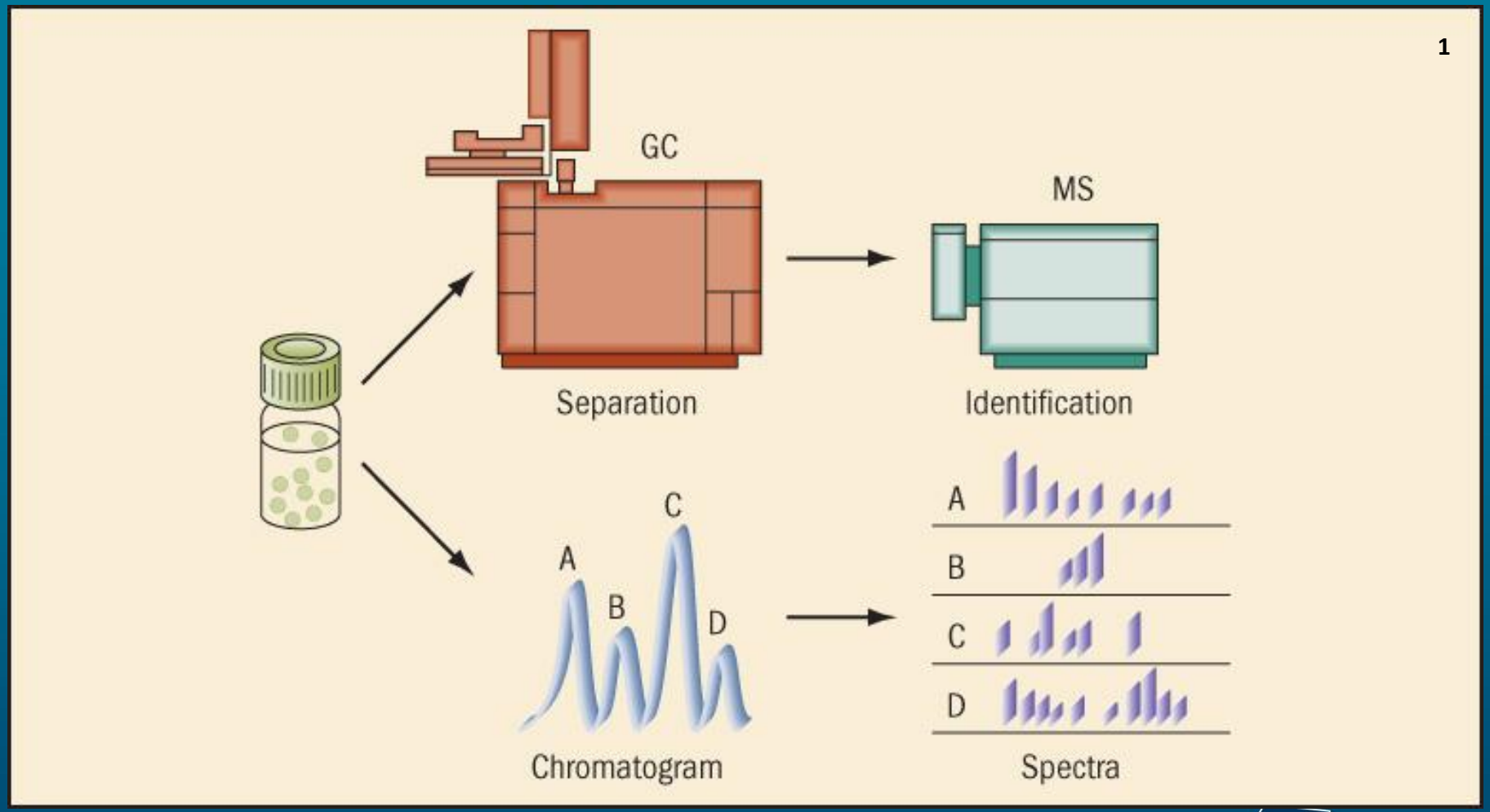
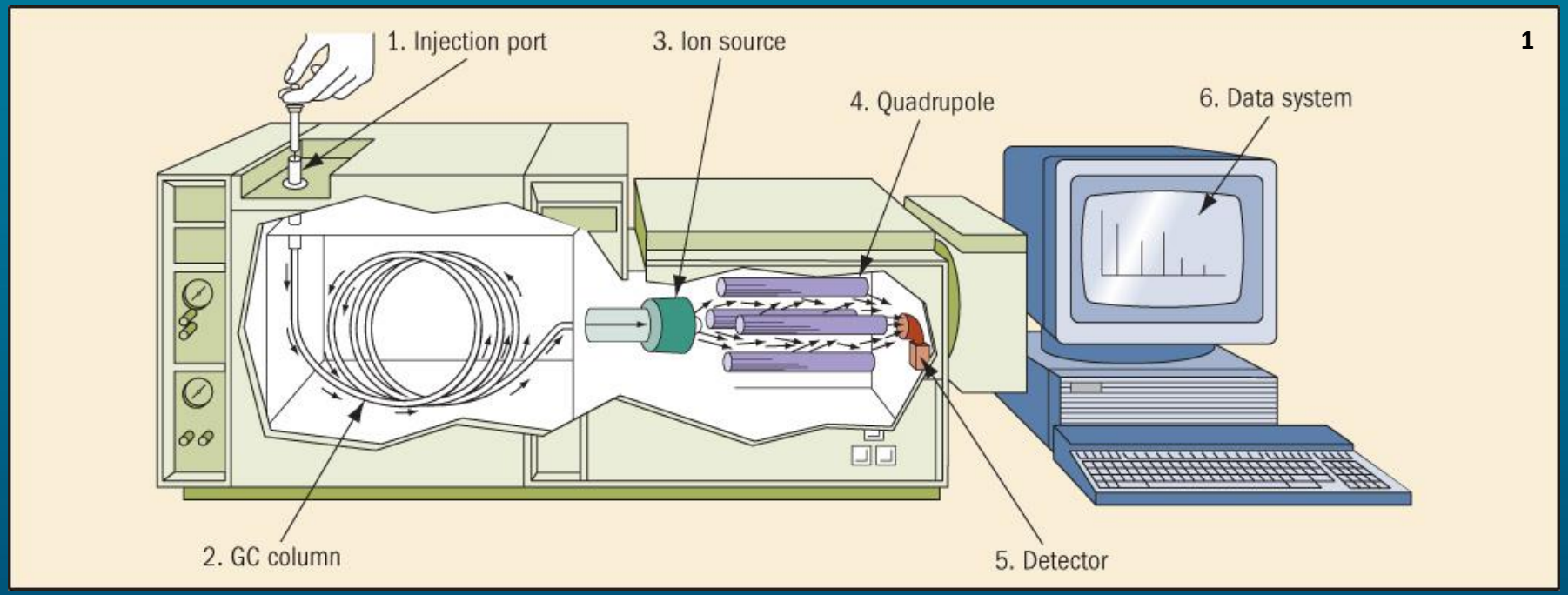
Introduction - GC coupled to MS



1. Saferstein, R., *Criminalistics,* 9nd Ed; Prentice Hall: Upper Saddle River, NJ, 2007.

Introduction - GC coupled to MS



1

1. Saferstein, R., *Criminalistics,* 9nd Ed; Prentice Hall: Upper Saddle River, NJ, 2007.

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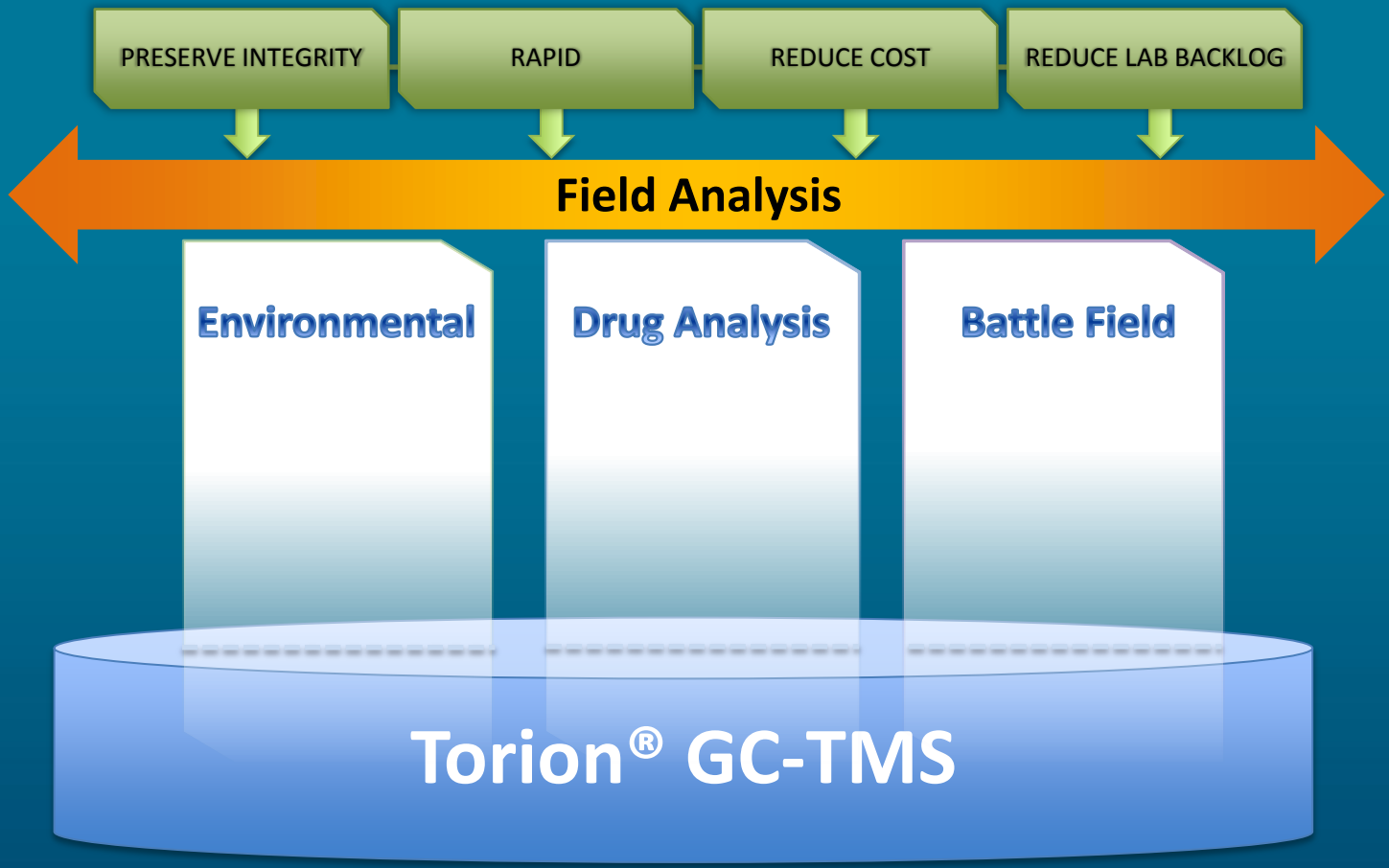
Introduction – GC-TMS



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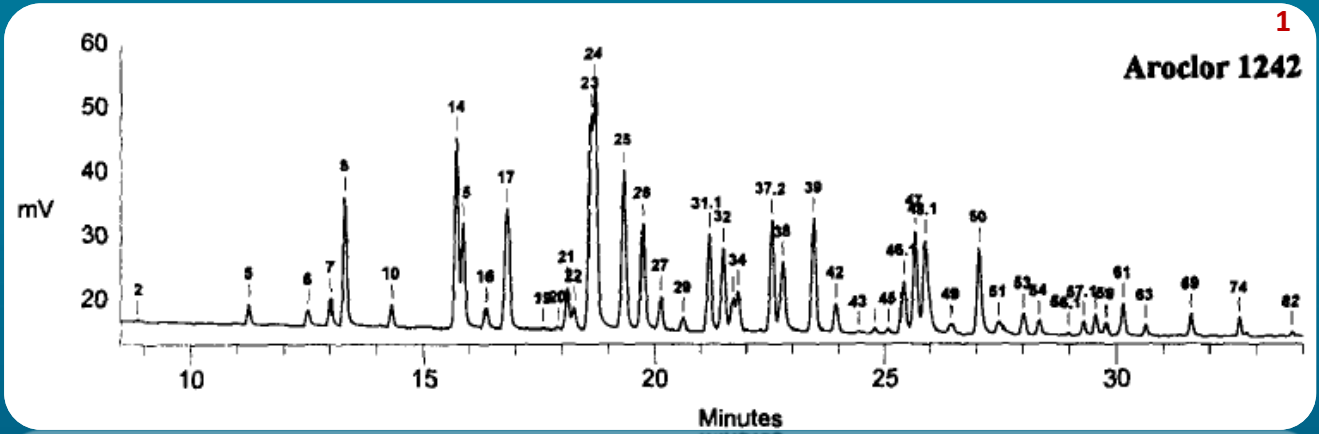
Introduction – PCB Selection

---Many congeners in an Aroclor mixture.

--- Only ~140 congeners of the 209 are found in the environment

e.g.



Chromatogram analyzed by a HP 5890 GC with DB-1 GC column

Concern 2 aspects: **Environmental fate**

Biological effect

1. Frame, G. M, et al. (1996). Chemosphere 33(4): 603-623.

Introduction – PCB Selection

WHO

Summary of WHO 1998 and WHO 2005 TEF Values [1]

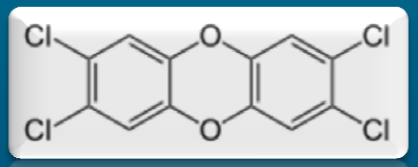
Compound	WHO 1998 TEF	WHO 2005 TEF
Chlorinated dibenzo-*p*-dioxins		
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	1	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.0001	**0.0003**
Chlorinated dibenzofurans		
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	**0.03**
2,3,4,7,8-PeCDF	0.5	**0.3**
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.0001	**0.0003**
Non-*ortho*-substituted PCBs		
3,3′,4,4′-tetraCB (PCB 77)	0.0001	0.0001
3,4,4′,5-tetraCB (PCB 81)	0.0001	**0.0003**
3,3′,4,4′,5-pentaCB (PCB 126)	0.1	0.1
3,3′,4,4′,5,5′-hexaCB (PCB 169)	0.01	**0.03**
Mono-*ortho*-substituted PCBs		
2,3,3′,4,4′-pentaCB (PCB 105)	0.0001	**0.00003**
2,3,4,4′,5-pentaCB (PCB 114)	0.0005	**0.00003**
2,3′,4,4′,5-pentaCB (PCB 118)	0.0001	**0.00003**
2′,3,4,4′,5-pentaCB (PCB 123)	0.0001	**0.00003**
2,3,3′,4,4′,5-hexaCB (PCB 156)	0.0005	**0.00003**
2,3,3′,4,4′,5′-hexaCB (PCB 157)	0.0005	**0.00003**
2,3′,4,4′,5,5′-hexaCB (PCB 167)	0.00001	**0.00003**
2,3,3′,4,4′,5,5′-heptaCB (PCB 189)	0.0001	**0.00003**

Bold values indicate a change in TEF value.

World Health Organization

TOXIC EQUIVALENCE FACTOR (TEF)

EXPRESSES THE TOXICITY OF DIOXINS, FURANS AND PCBS IN TERMS OF THE MOST TOXIC FORM OF DIOXIN, 2,3,7,8-TCDD.



2,3,7,8-Tetrachlorodibenzodioxin

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1. Van den Berg, M., et al. (2006). Toxicological Sciences 93(2): 223-241.

Introduction – PCB Selection

EPA method

Congener- Based Method

Base on all congeners—accurate, but time-consuming and costly

Aroclor-Based Method

Use selected PCBs as markers

PCB congene[a]	Aroclor 1248	Aroclor 1254	Aroclor 1260
31/28	1.25	—	—
31/118	—	0.025	—
118/203	—	149	—
138/149	—	—	0.930
149/118	0.165	0.589	22.6

1

SPECIFIC PCB CONGENERS THAT ARE MAJOR COMPONENTS IN COMMON AROCLORS[2]

Congener	IUPAC Number	Aroclor 1016	1221	1232	1242	1248	1254	1260
Biphenyl	--		X					
2-CB	1	X	X	X	X			
2,3-DCB	5	X	X	X	X	X		
3,4-DCB	12	X		X	X	X		
2,4,4'-TCB	28*	X		X	X	X	X	
2,2',3,5'-TCB	44			X	X	X	X	X
2,3',4,4'-TCB	66*					X	X	X
2,3,3',4',6-PCB	110						X	
2,3',4,4',5-PCB	118*						X	X
2,2',4,4',5,5'-HCB	153							X
2,2',3,4,4',5'-HCB	138							X
2,2',3,4,4',5,5'-HpCB	180							X
2,2',3,3',4,4',5-HpCB	170							X

*Apparent co-elution of: 28 with 31 (2,4',5-trichlorobiphenyl)
66 with 95 (2,2',3,5',6-pentachlorobiphenyl)
118 with 149 (2,2',3,4',5',6-hexachlorobiphenyl)

This table is not intended to illustrate all of the congeners that may be present in a given Aroclor, but rather to illustrate the major congener components.

PCB 153 was used as potential indicator of Aroclor weathering[1]

1. Sather, P. J., M. G. Ikonomou, et al. (2001). Environmental Science & Technology 35(24): 4874-4880.
2. EPA method 8082a

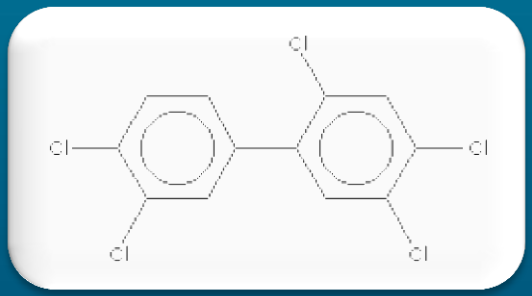
Introduction – Retention Indices

RI -- Retention Indices

C #	7	8	9	10	…
RI	700	800	900	1000	…

e.g. 2,4,5,3',4'-Pentachlorobiphenyl

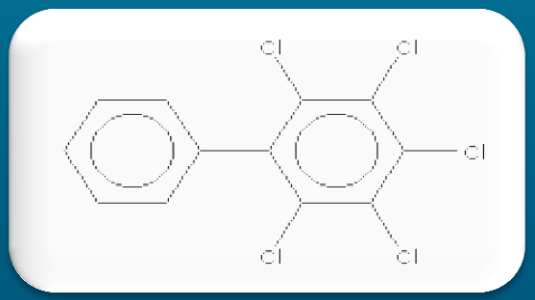
Formula: $C_{12}H_5Cl_5$



RI: 2275

2,3,4,5,6-Pentachlorobiphenyl

Formula: $C_{12}H_5Cl_5$



RI: 2110

All information above comes from http://webbook.nist.gov

2,3,4,5,6-Pentachlorobiphenyl will elute between C_{21} and C_{22}
2,4,5,3',4'-Pentachlorobiphenyl will elute between C_{22} and C_{23}

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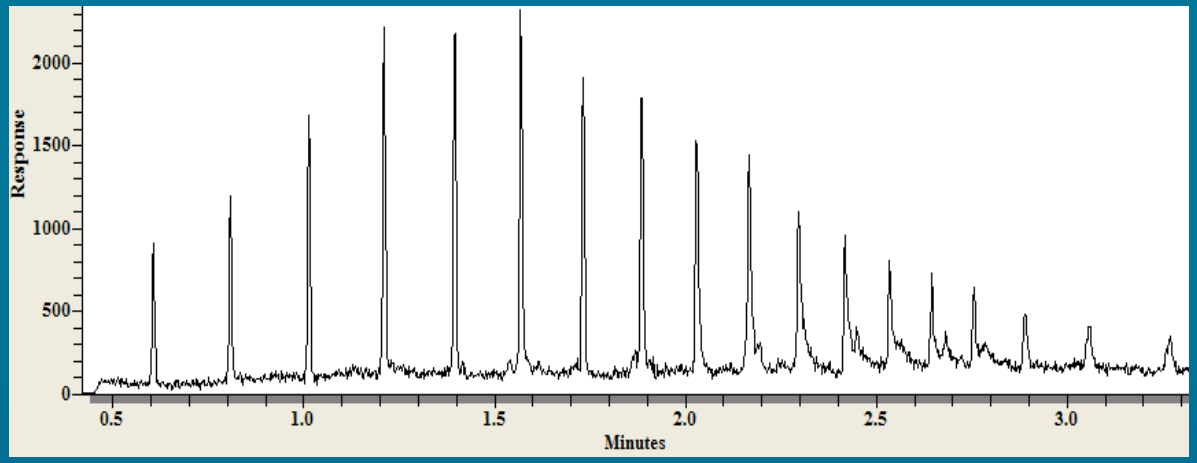
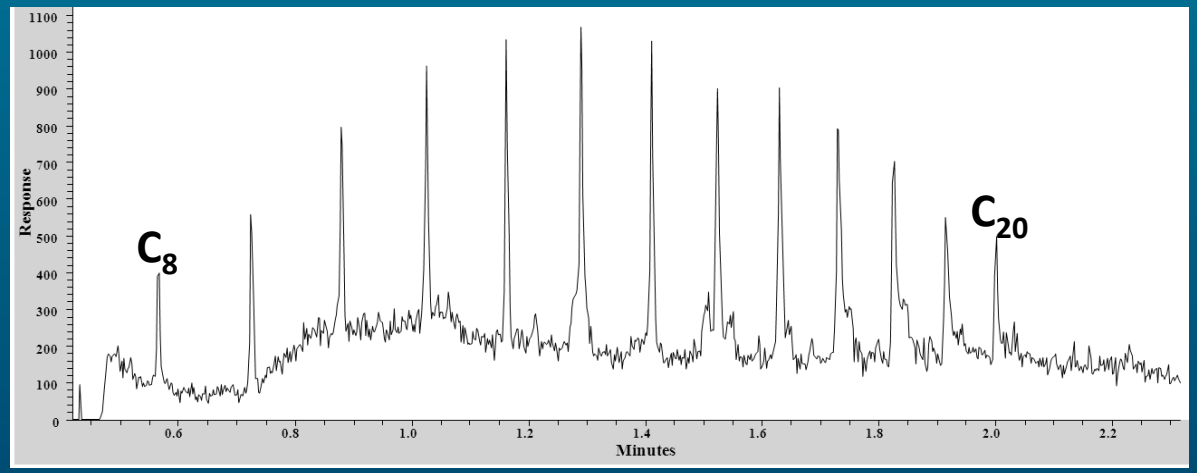
Results: Mix of n-alkanes on Torion GC/TMS



TIC chromatogram for Alkane standard solution (C7~C30)

GC temperature gradient:
- Initial T: 50 ℃; Hold time : 10 s
- End T: 270 ℃; Hold time: 40 s
- T ramp rate: 1.5 ℃/s
- Flow rate: 200



TIC chromatogram for Alkane standard solution (C8~C20)

GC temperature gradient:
- Initial T: 50 ℃; Hold time : 10 s
- End T: 270 ℃; Hold time: 10 s
- T ramp rate: 2 ℃/s
- Flow rate: 180

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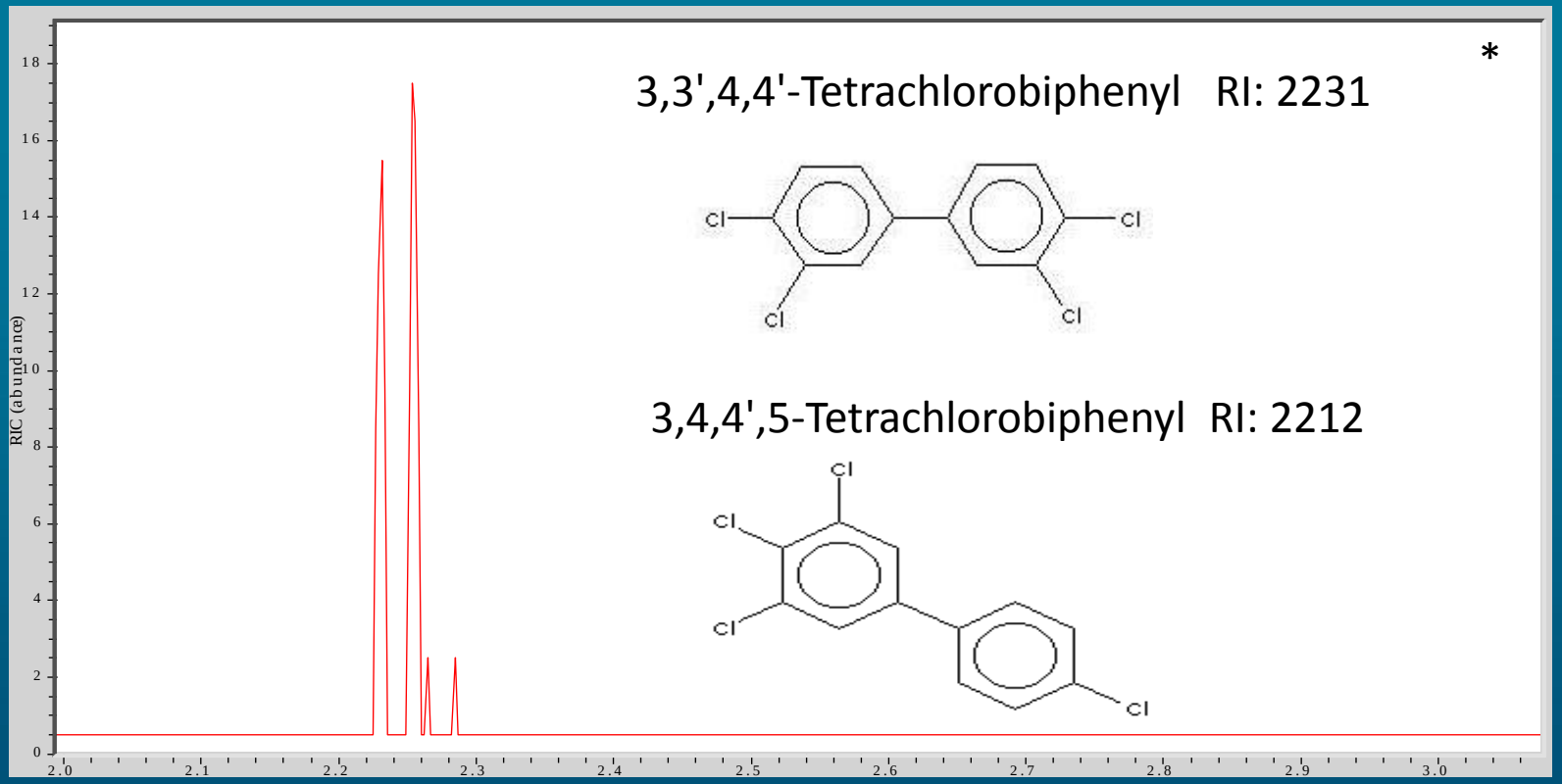
Results: WHO PCB mix standards on Torion GC/TMS



RIC of selected ion m/z 292 for WHO PCB mix standards

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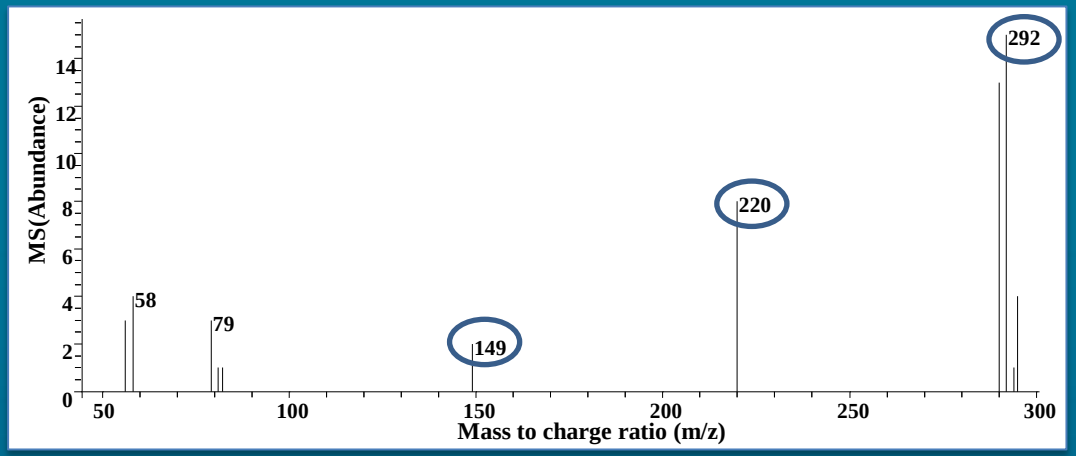
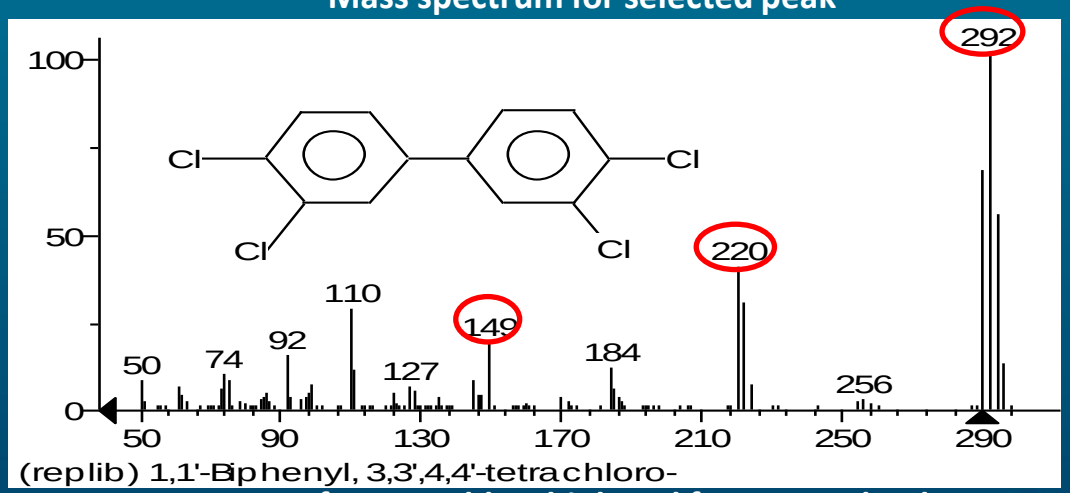
* NIST webbook database http://webbook.nist.gov

Results: WHO PCB mix standards on Torion GC/TMS



Mass spectrum for selected peak



Mass spectrum for Tetrachlorobiphenyl from NIST database

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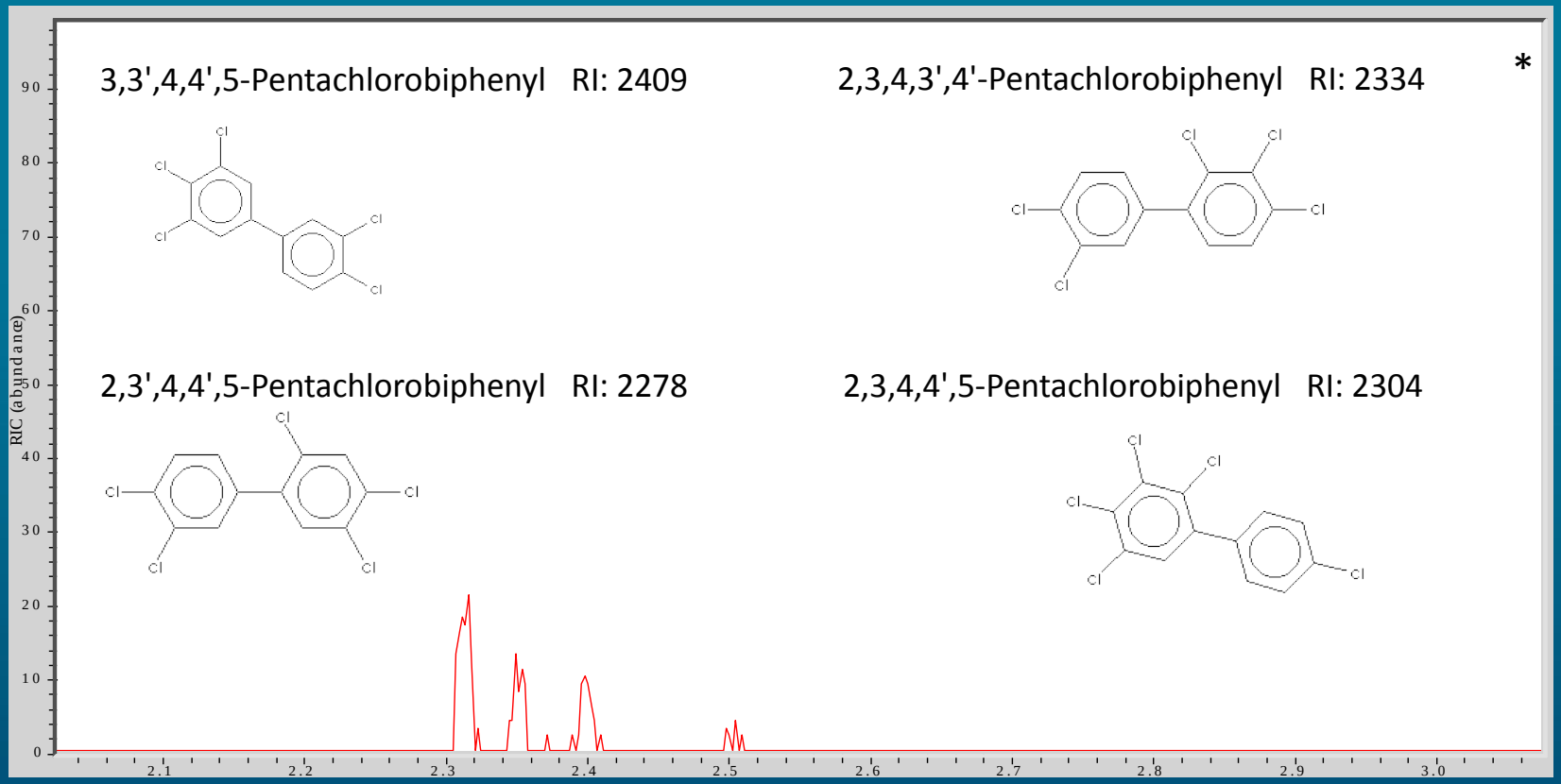
Results: WHO PCB mix standards on Torion GC/TMS



RIC of selected ion m/z 326 for WHO PCB mix standards

* NIST webbook database http://webbook.nist.gov

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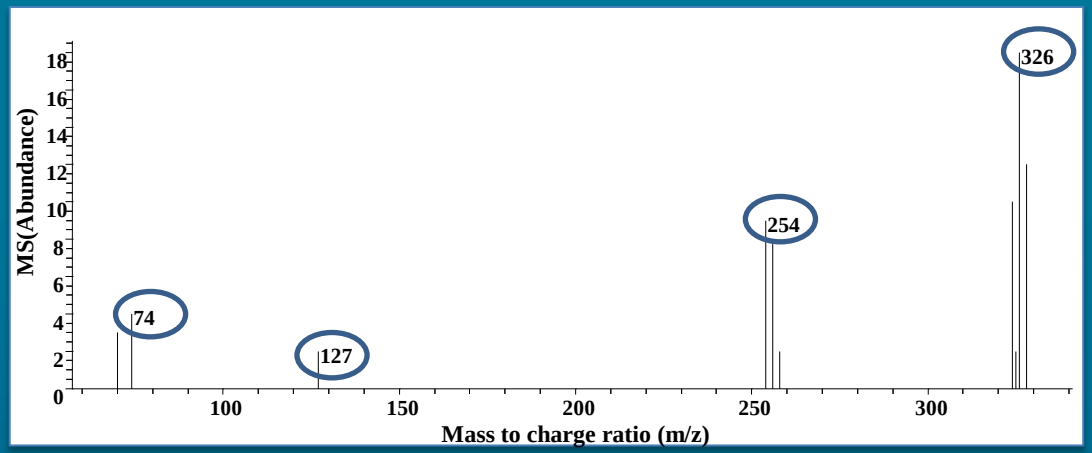
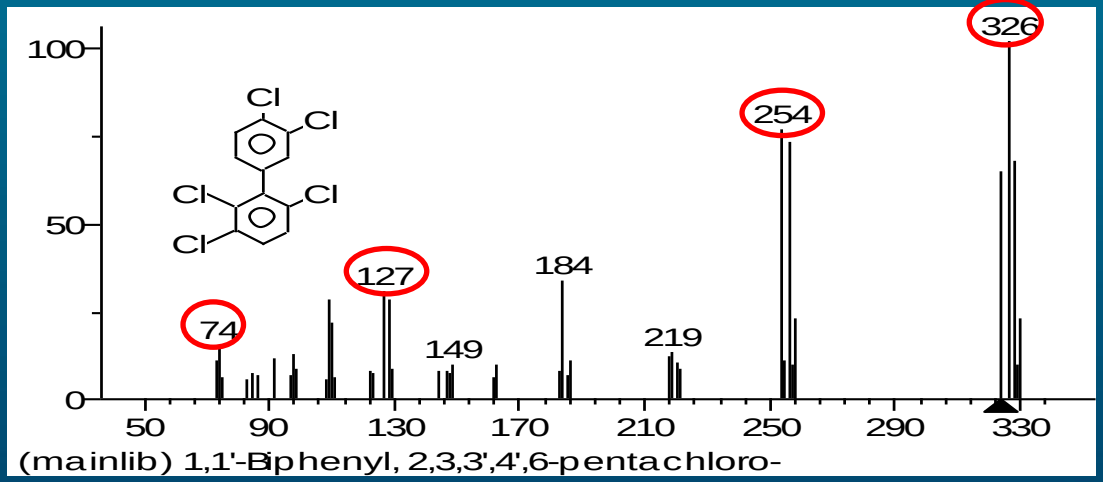
Results: WHO PCB mix standards on Torion GC/TMS



Mass spectrum for selected peak



Mass spectrum for Pentachlorobiphenyl from NIST database

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Future Work

One

- Optimize parameters

Two

- Test the instrument with WHO PCB mix standard
- Then EPA 8082A PCB mix standard solution

Three

- Analyze field samples

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Current Problems

Currently….

- Leaking
- Interference
- Signal

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Acknowledgments

Dr. Stephen A. Lammert (Torion)

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Questions/Discussion

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