

Sample Preparation for Dioxin Analysis, Episode II: 'Tails-side of the system' & 'Fractionation'

J.-F. Focant, C. Pirard, D.G. Patterson Jr.,
E. DePauw



Mass spectrometry Laboratory
Dioxin Laboratory



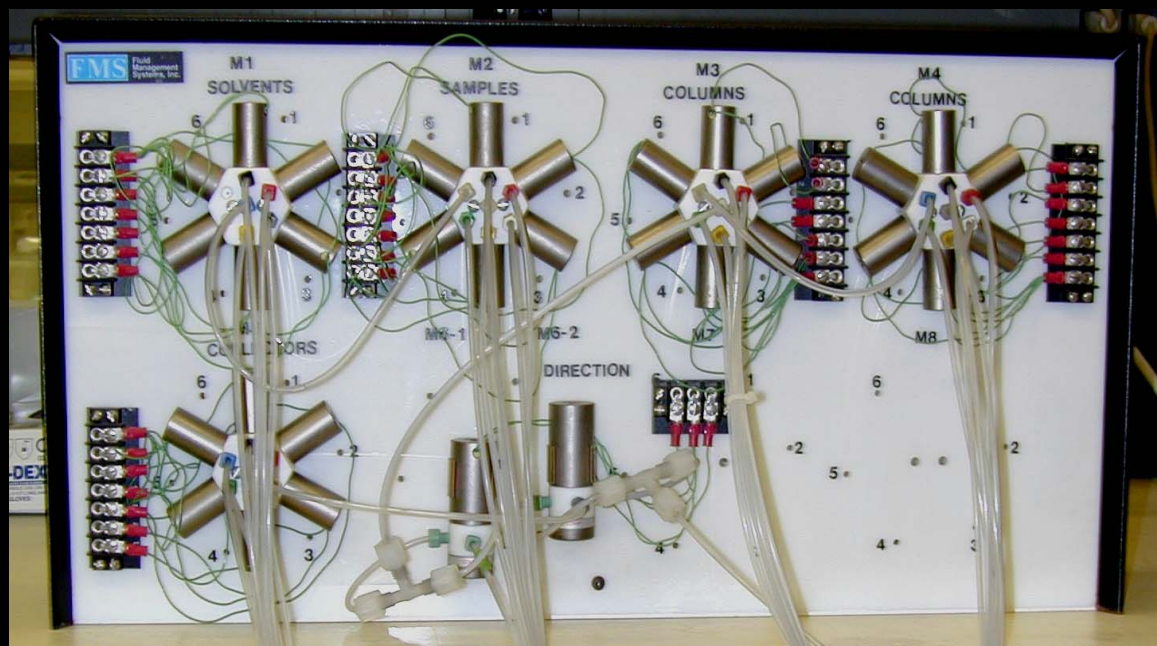
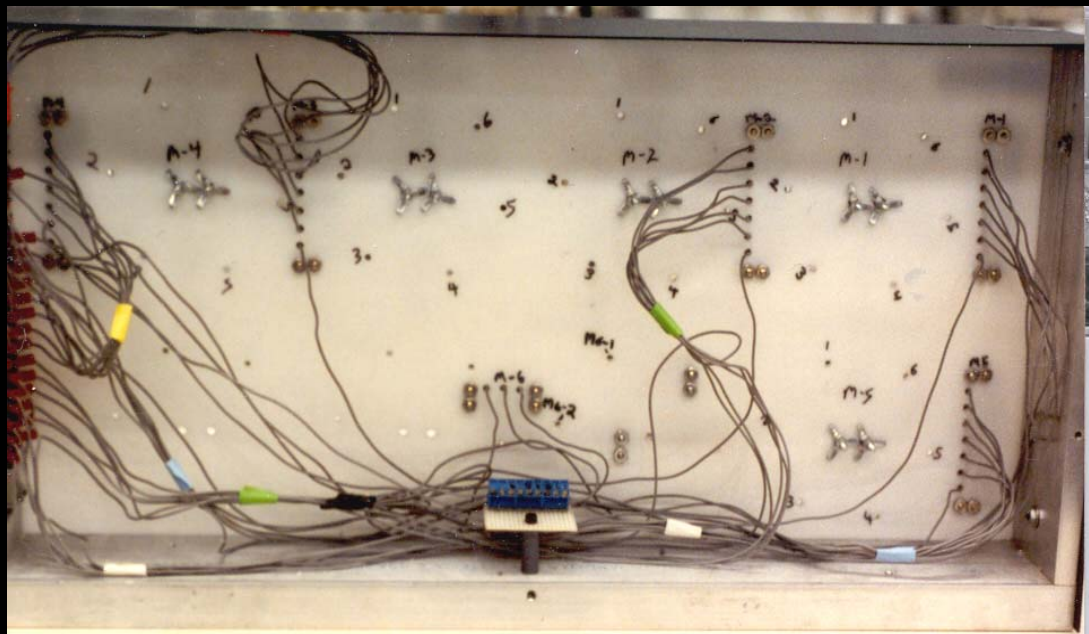
CDC, NCEH, DLS, OATB

‘Tails side of the system’

Clean-up Automation

- ✓ 1970's Smith & Stalling (LC prep.)
- ✓ 1986 Lapeza et al. (LC automation)
- ✓ 1987 FMS Inc. (Power-Prep™)
- ✓ 1991 Turner et al. (Serum)
- ✓ 1999 Rivera et al. (Environmental)
- ✓ 2000 Focant et al. (Foodstuffs)

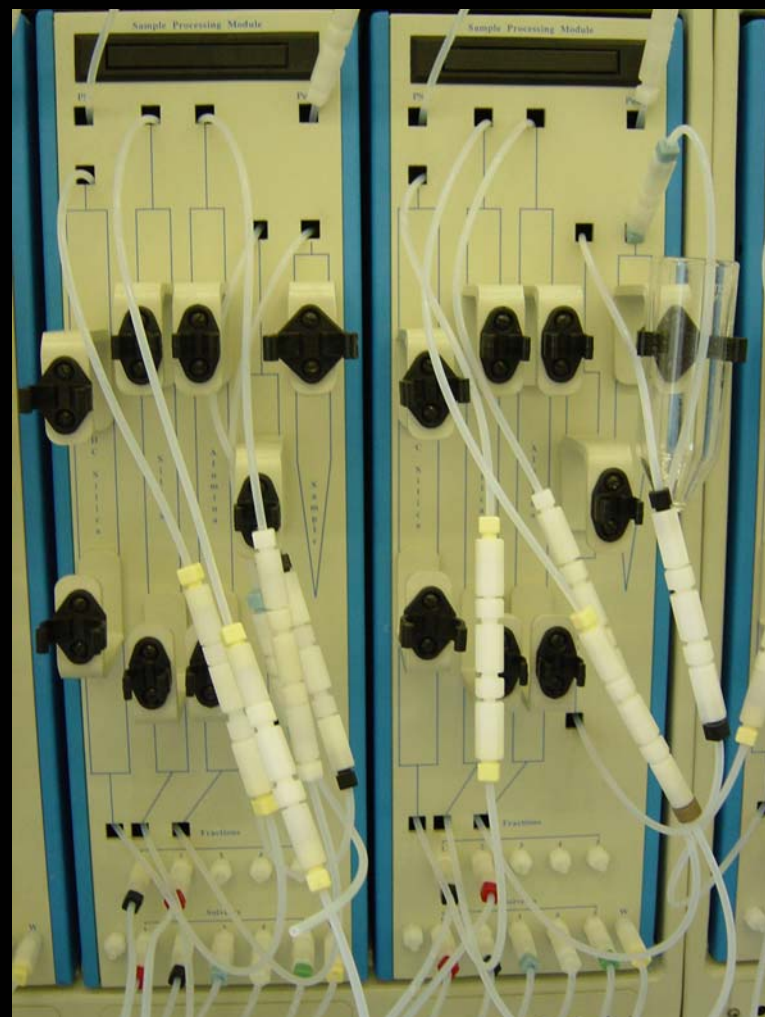
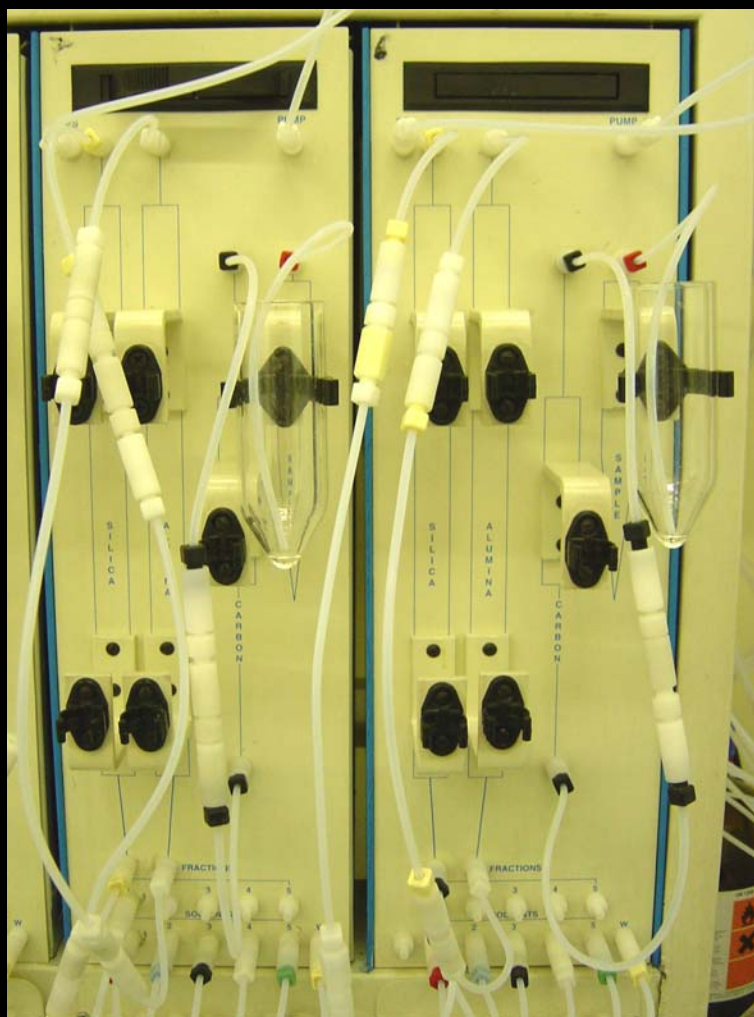
At the beginning
was...



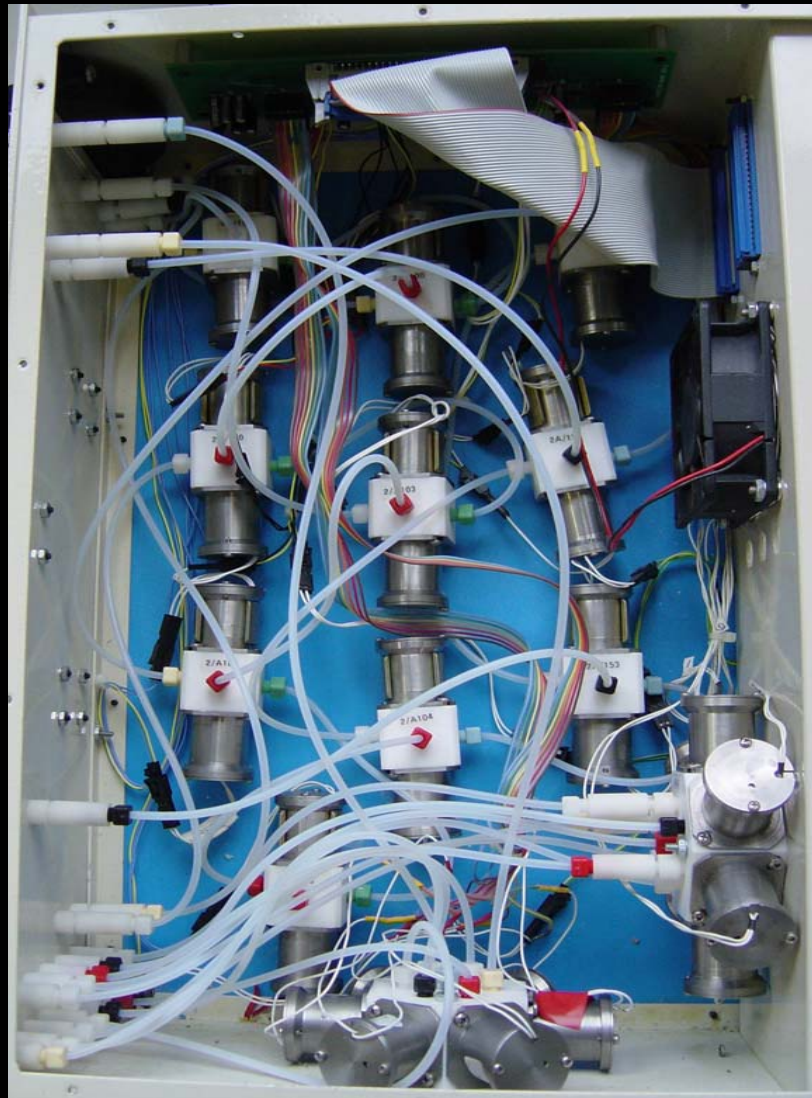
Several generations later...

Previous generation

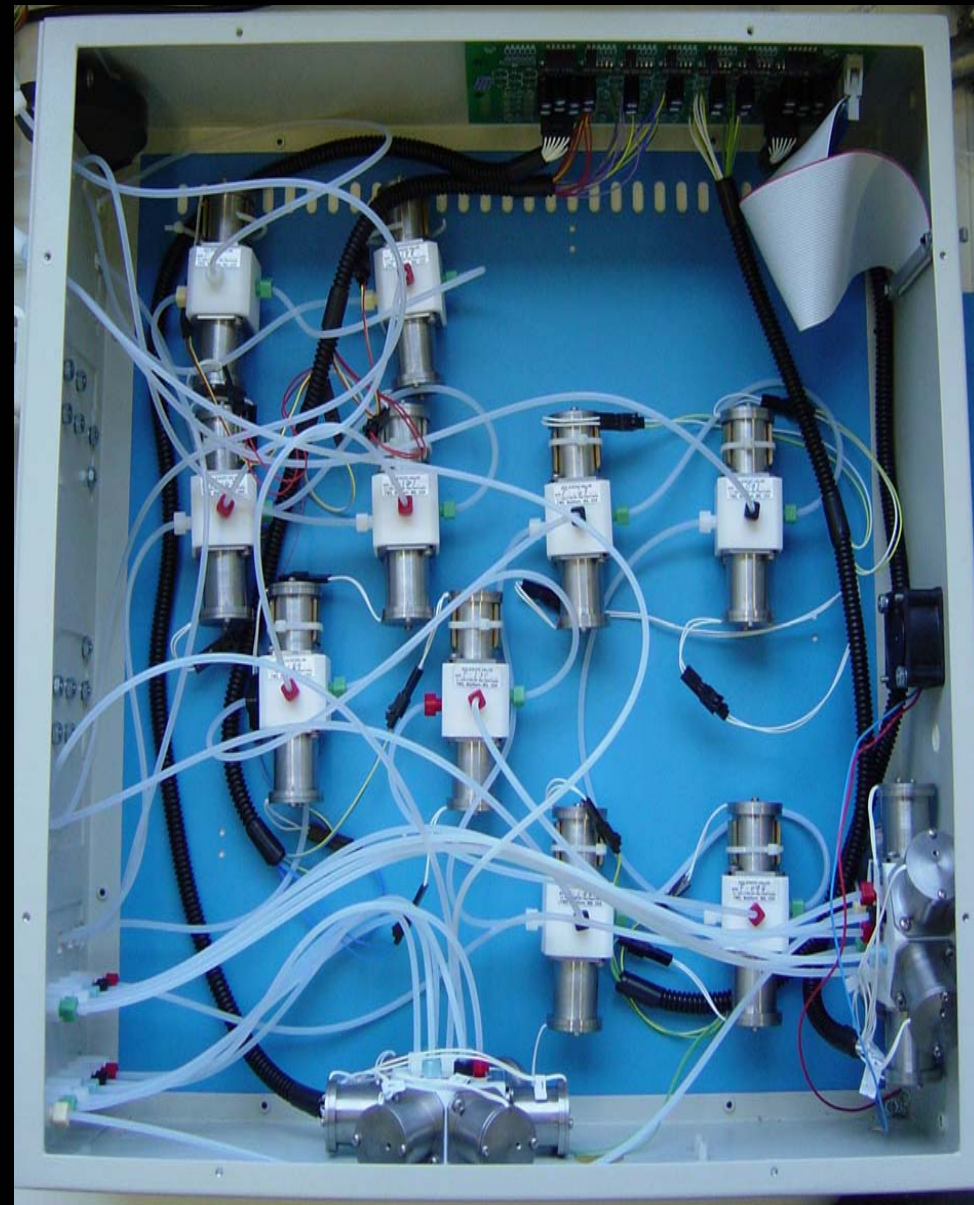
Current generation



Previous generation



Current generation



Current
generation



Previous
generation

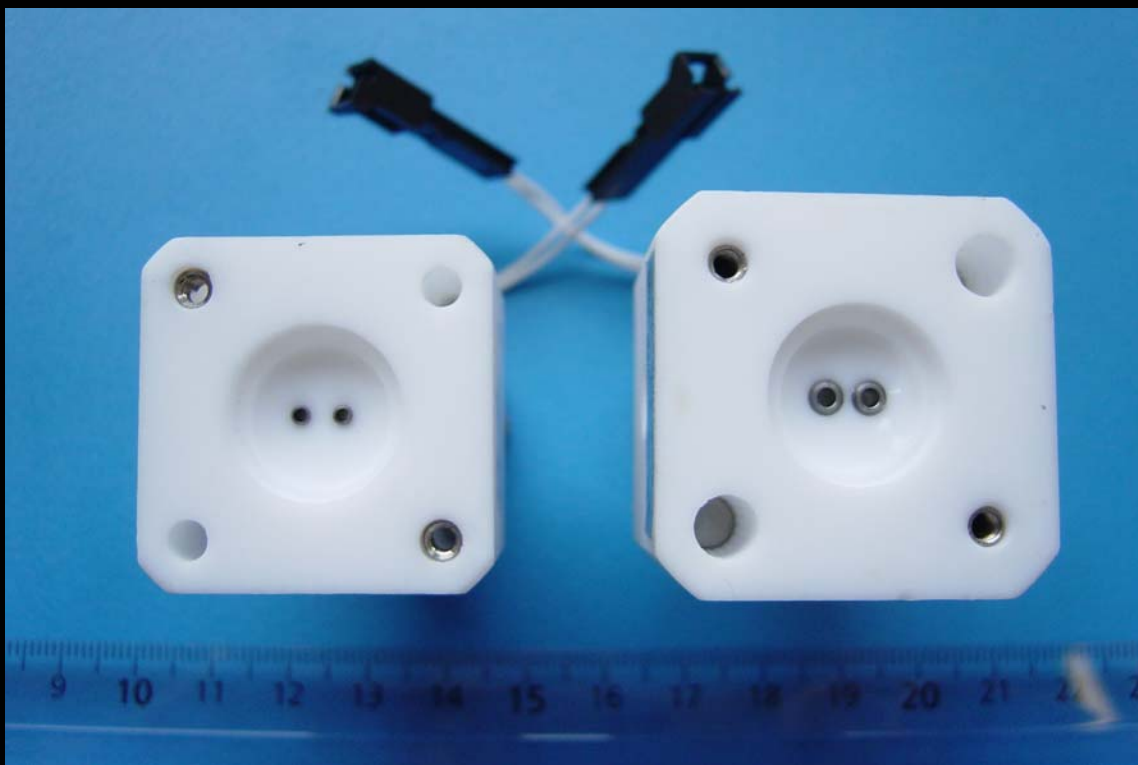
Previous generation

Current generation

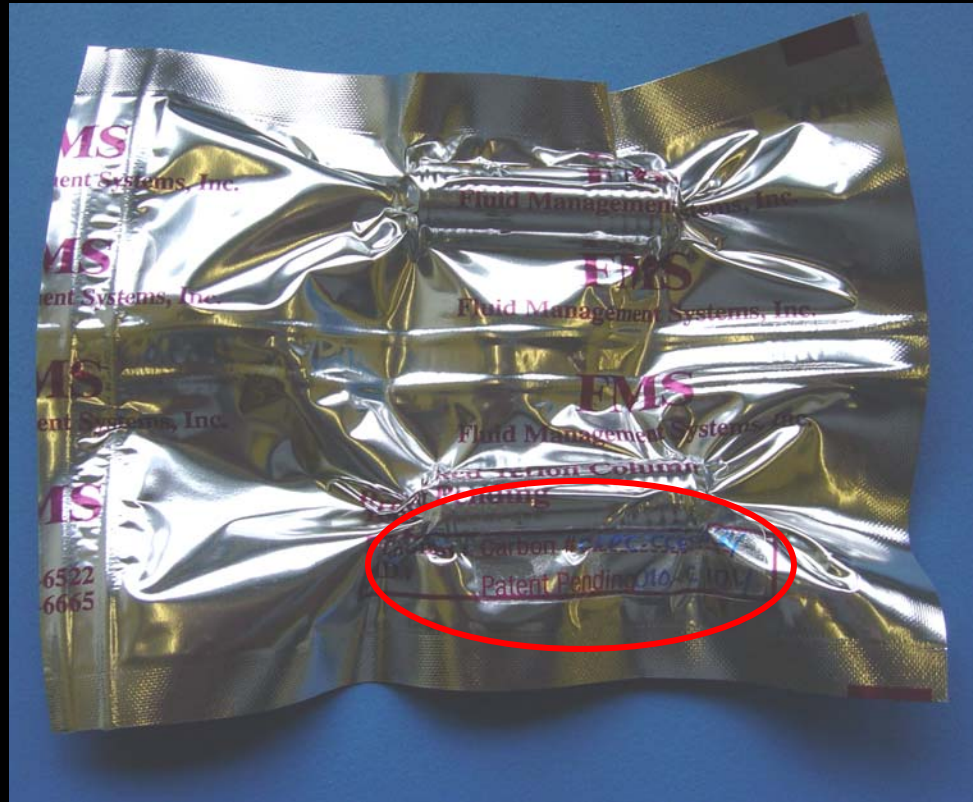


Previous generation

Current generation



Tracability by Lot



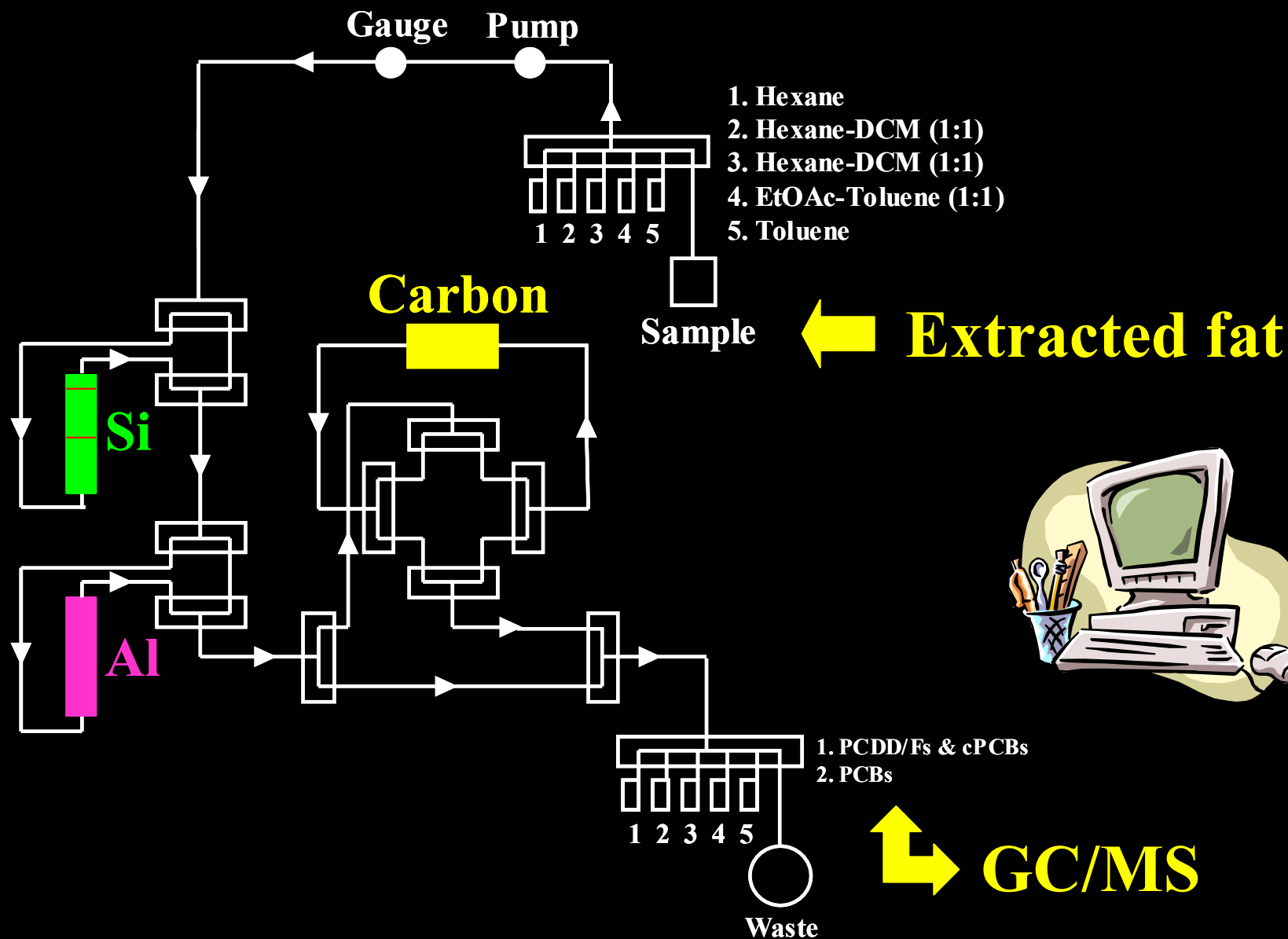
- ✓ Good stability
- ✓ Good lot-to-lot reproducibility
- ✓ New « PCB-free » columns...

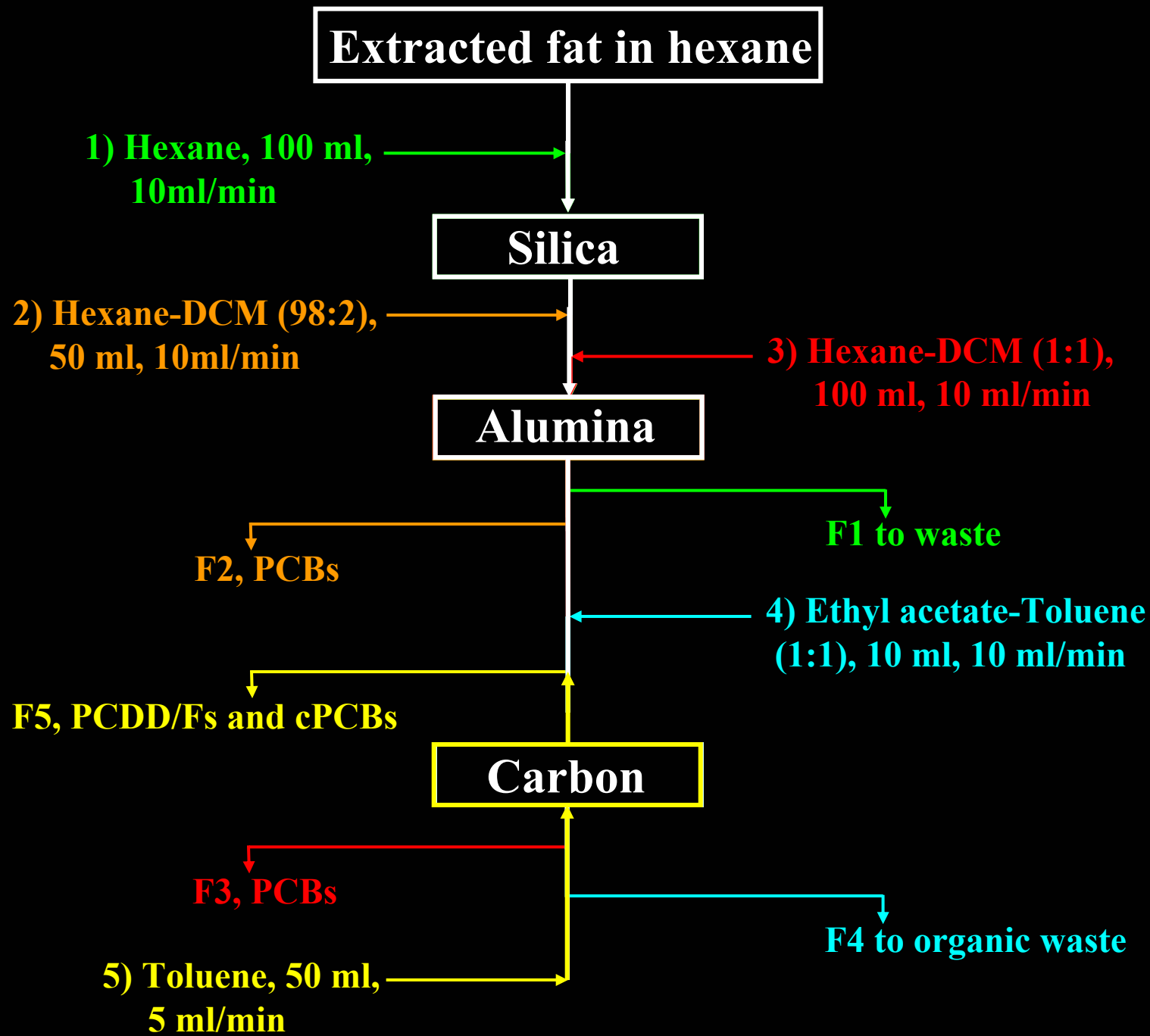
Grocery (wish) list

<u>Items</u>	<u>Price (\$)</u>
✓ Power-prep system (P5) ≈ HCDS (\$22), Si (\$18), Al (\$15), C (\$12)	90,000
✓ Soxhlet	50
✓ PLE (ASE)	50,000
✓ GC-HRMS	300,000
✓ GC-QISTMS	150,000
✓ GCxGC-TOFMS	200,000

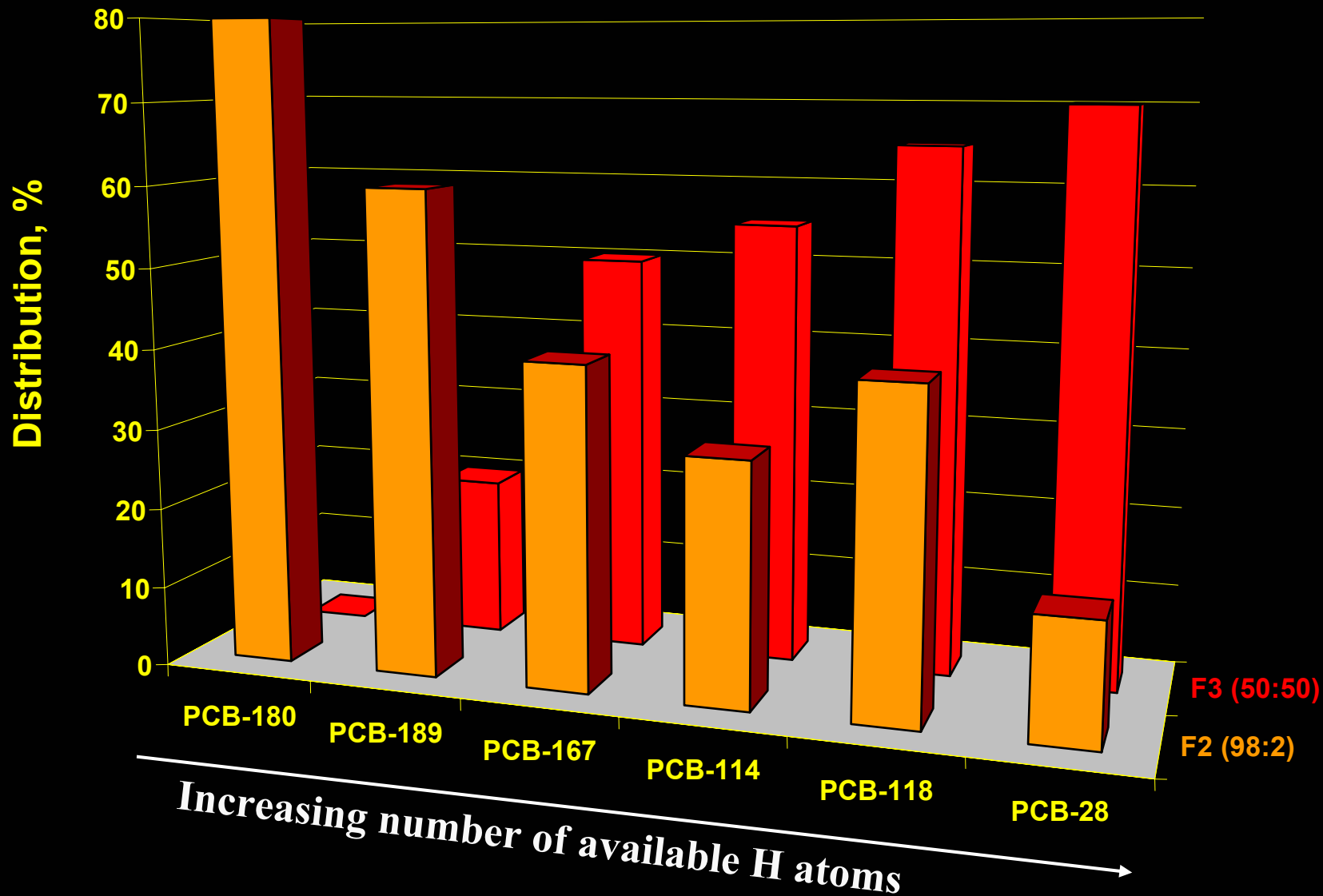
‘Fractionation’

Automated Clean-up System

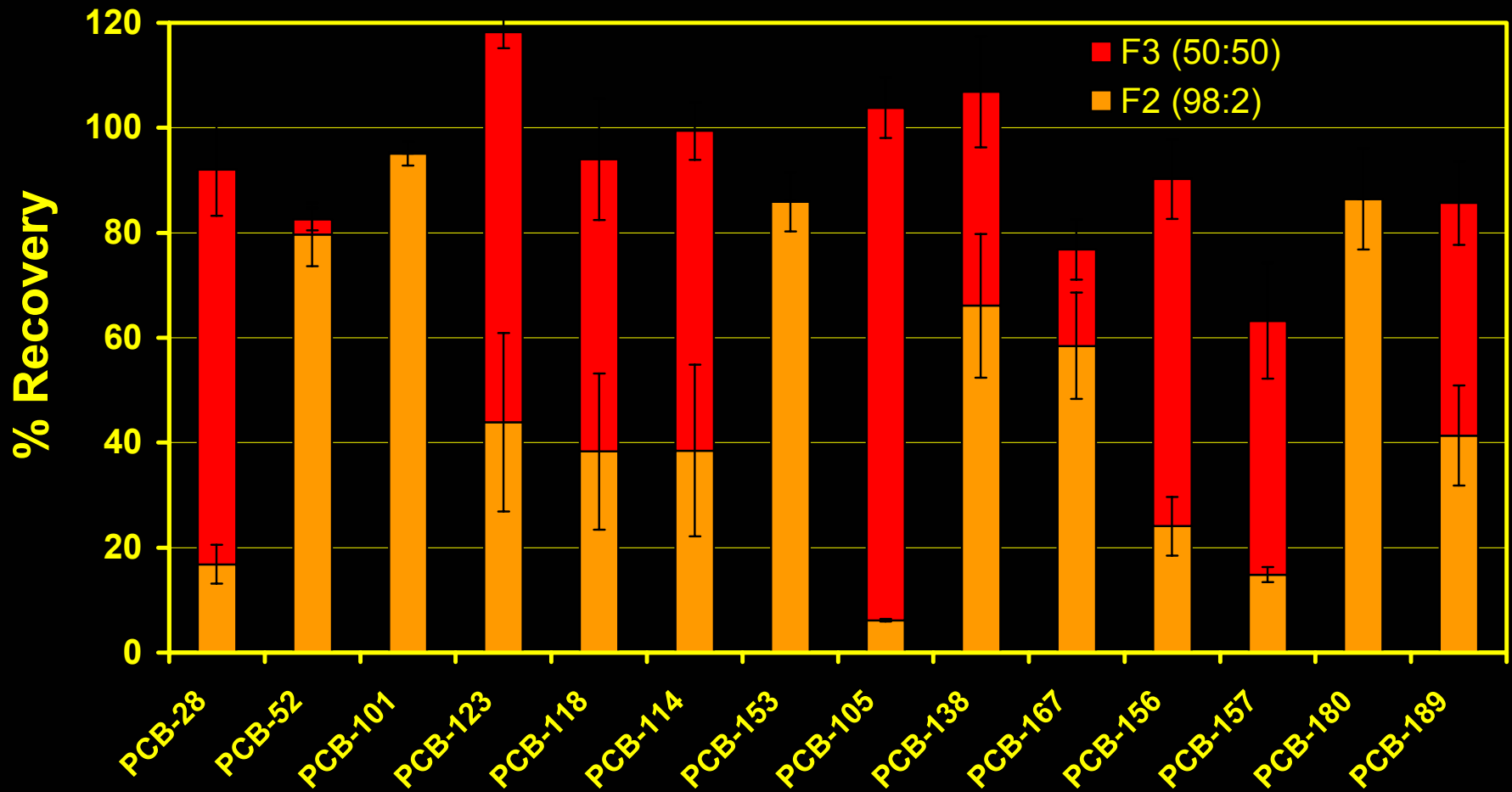




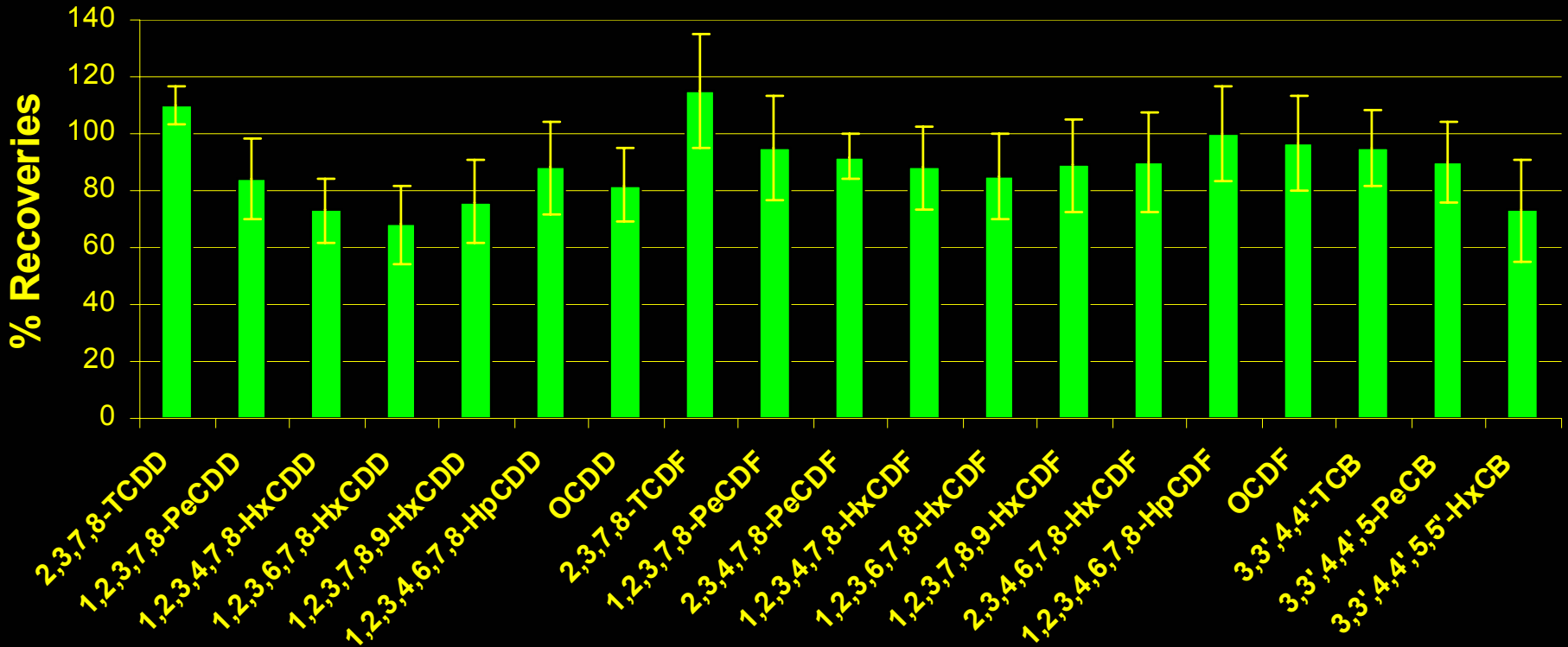
Distribution of PCBs



PCB Recovery rates



PCDD/F Recovery rates



In accordance with QA/CC criteria

LOQ investigation

- ✓ LOQ for some PCBs can be relatively poor due to the quantity of solvent used
- ✓ If the Hx-DCM 98/2 step is removed, PCBs are collected after the Carbon column
 - ➔ reduced amount of solvent
 - ➔ improved LOQs

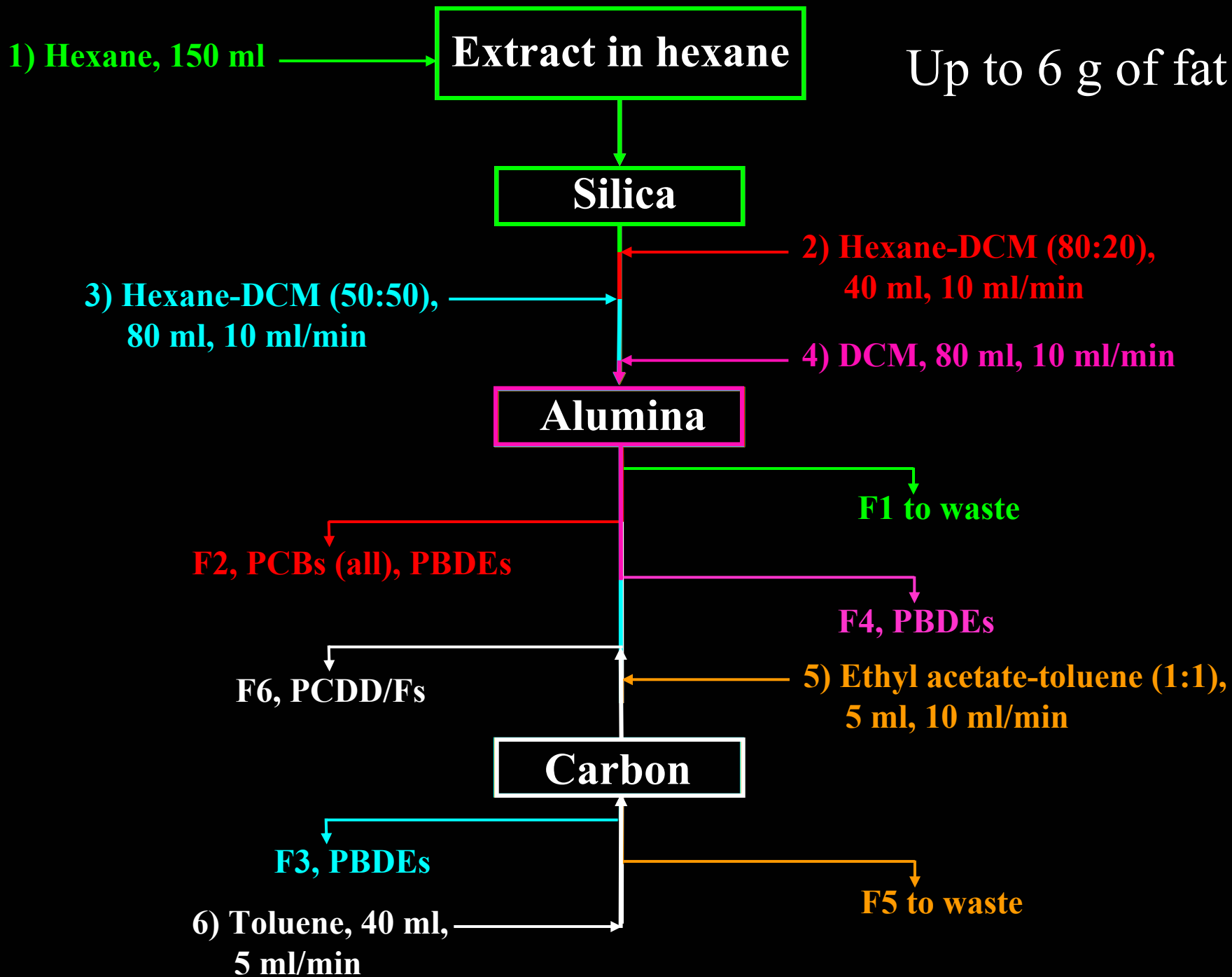
BUT:

mono-*ortho*-CBs are difficult to get on of the carbon

- ➔ lots of Hx-DCM 1/1 required
- ➔ poor LOQs



Other programs needed



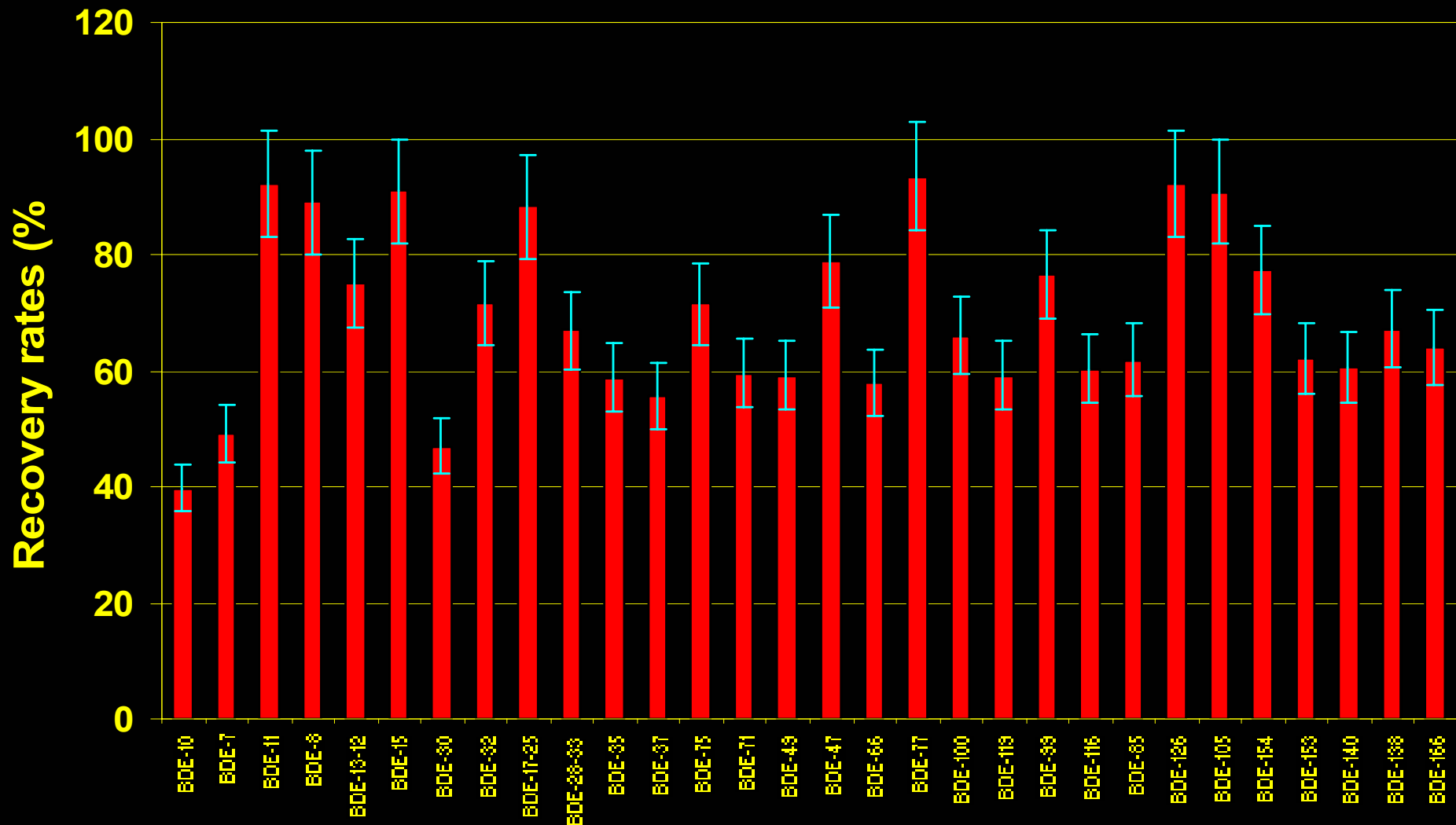
Elution profile (PBDEs)

Congeners	Ratio hexane/dichloromethane (%)			Congeners	Ratio hexane/dichloromethane (%)		
	80/20	50/50	0/100		80/20	50/50	0/100
	F2	F3	F4		F2	F3	F4
DiBDEs				PeBDEs			
10		x		100	x		
7		x		119	x		
11			x	99	x		
8			x	116		x	
13-12			x	85	x		
15			x	126		x	
TriBDEs				HxBDEs			
30		x		105		x	
32		x		154	x		
17-25		x		153	x		
28-33		x		140	x		
35		x	x	138	x		
37		x	x	166		x	
TBDEs							
75		x					
71	x						
49		x					
47	x						
66		x					
77		x					

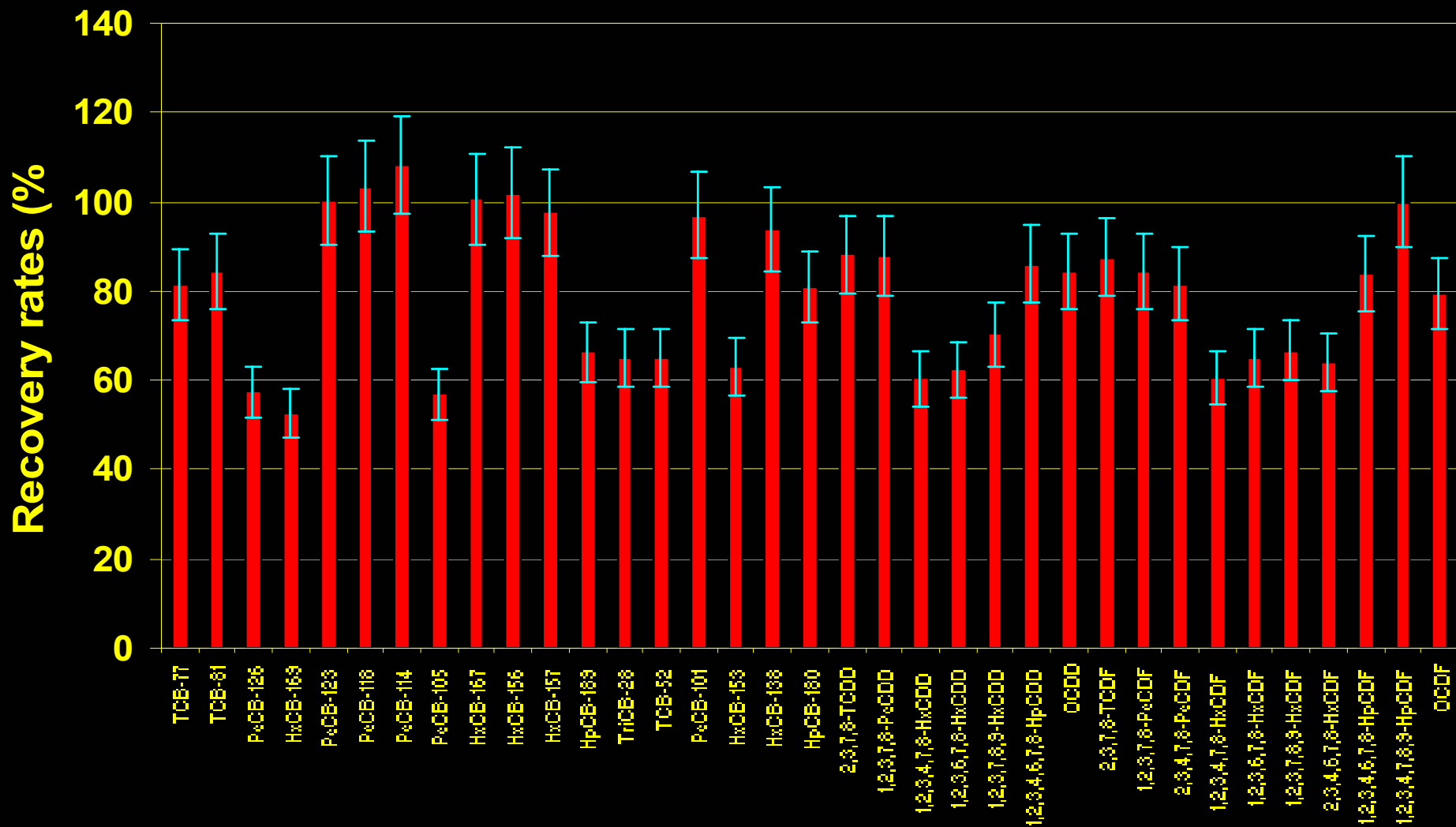
Elution profile (PCBs, PCDD/Fs)

Congeners	Hexane/DCM (%)		Congeners	Hexane/DCM (%)	
	80/20 (F2)	Toluene Back-flush (F6)		80/20 (F2)	Toluene Back-flush (F6)
PCBs			PCDDs		x
non-ortho			2,3,7,8-TCDD		x
TCB-77	x		1,2,3,7,8-PeCDD		x
TCB-81	x		1,2,3,4,7,8-HxCDD		x
PeCB-126	x		1,2,3,6,7,8-HxCDD		x
HxCB-169	x		1,2,3,7,8,9-HxCDD		x
mono-ortho			1,2,3,4,6,7,8-HpCDD		x
PeCB-123	x		OCDD		x
PeCB-118	x		PCDFs		
PeCB-114	x		2,3,7,8-TCDF		x
PeCB-105	x		1,2,3,7,8-PeCDF		x
HxCB-167	x		2,3,4,7,8-PeCDF		x
HxCB-156	x		1,2,3,4,7,8-HxCDF		x
HxCB-157	x		1,2,3,6,7,8-HxCDF		x
HpCB-189	x		1,2,3,7,8,9-HxCDF		x
Aroclor 1260			2,3,4,6,7,8-HxCDF		x
TriCB-28	x		1,2,3,4,6,7,8-HpCDF		x
TCB-52	x		1,2,3,4,7,8,9-HpCDF		x
PeCB-101	x		OCDF		
HxCB-153	x				
HxCB-138	x				
HpCB-180	x				

Recovery rates PBDEs



Recovery rates PCBs-PCDD/Fs

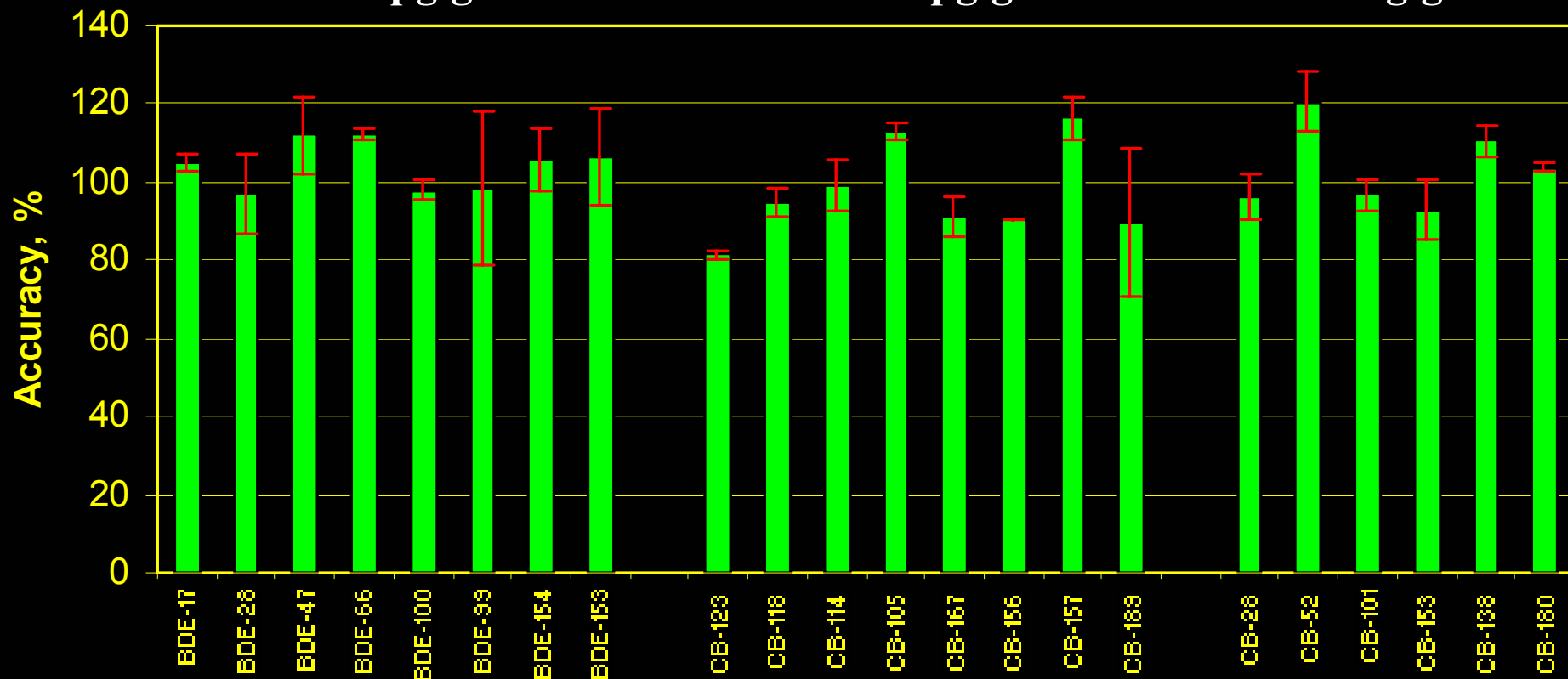


Accuracy PBDEs, PCBs

PBDEs
100-200 pg/g fat

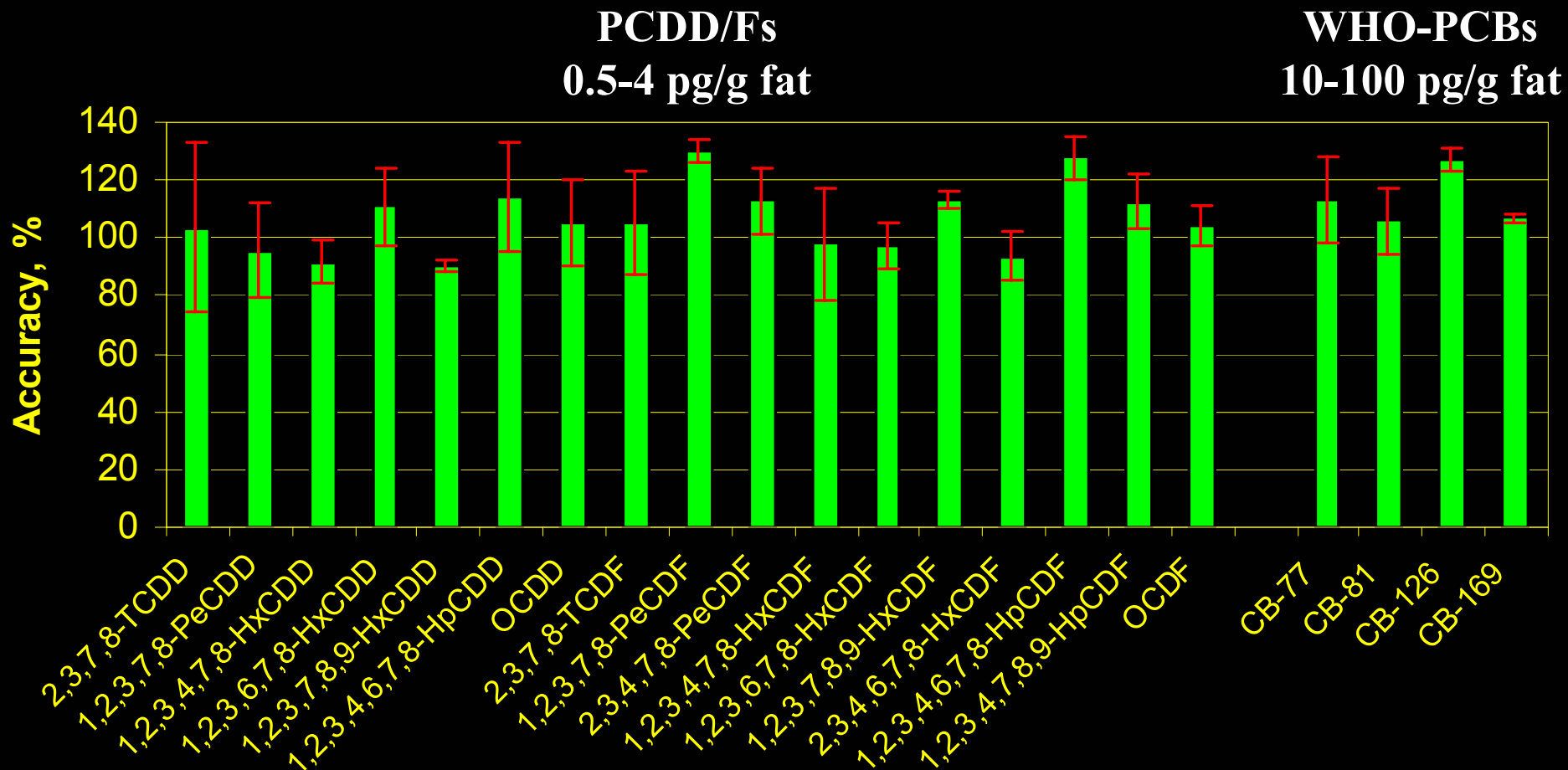
WHO-PCBs
80-350 pg/g fat

Marker-PCBs
1-2.5 ng/g fat



'in-house' beef fat QC samples (triplicates)

Accuracy PCDD/Fs, cPCBs



‘in-house’ beef fat QC samples (triplicates)

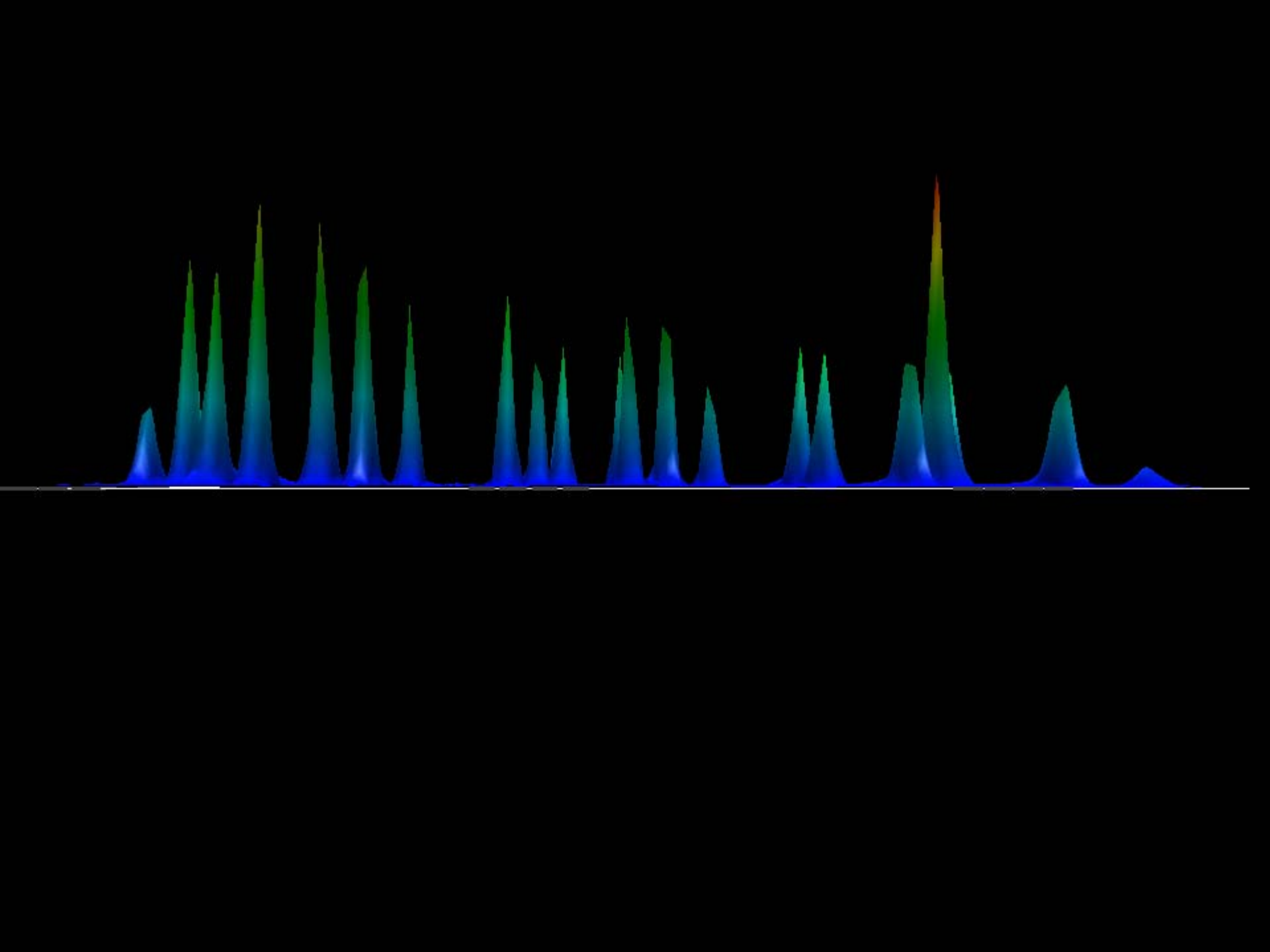
Method LODs

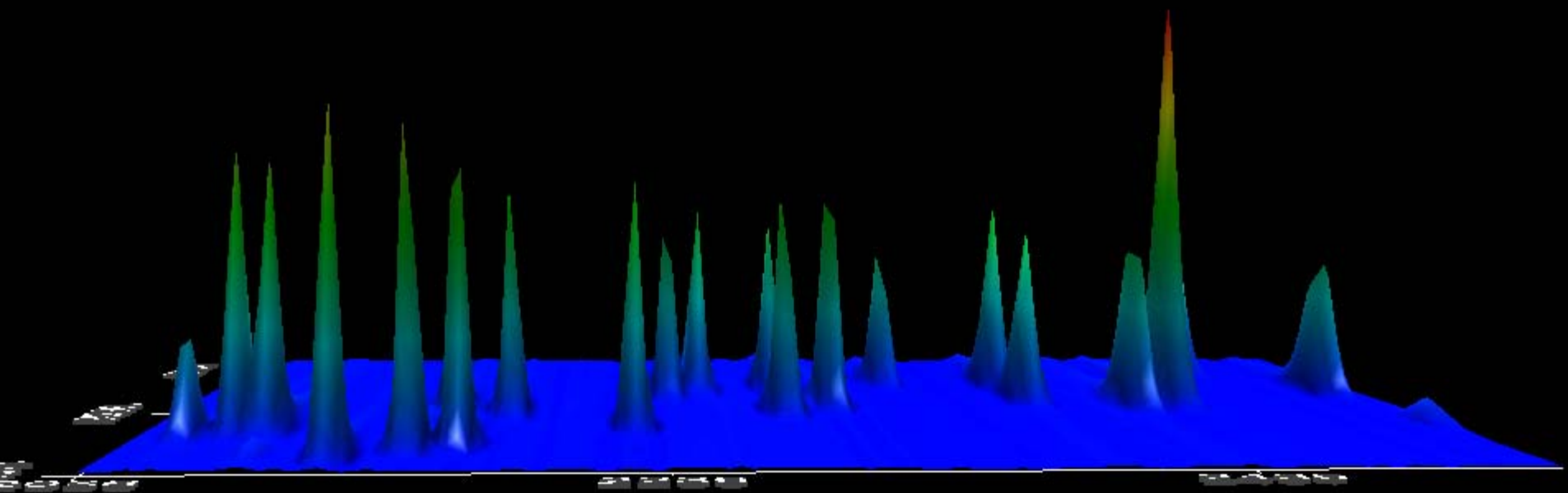
	Method LODs	Recoveries (%)		Method LODs	Recoveries (%)
PCDD/Fs (pg/g fat)			PCB-52	1.78	65
2,3,7,8 TCDD	0.1	70	PCB-101	0.83	97
1,2,3,7,8 PeCDD	0.15	85	PCB-153	0.25	63
1,2,3,4,7,8 HxCDD	0.17	62	PCB-138	0.41	94
1,2,3,6,7,8 HxCDD	0.15	64	PCB-180	0.15	81
1,2,3,7,8,9 HxCDD	0.16	66	Mono-ortho PCBs (ng/g fat)		
1,2,3,4,6,7,8 HpCDD	0.69	99	PCB-105	0.03	57
OCDD	5.32	66	PCB-114	0.1	108
2,3,7,8 TCDF	0.12	101	PCB-118	0.16	104
1,2,3,7,8 PeCDF	0.1	88	PCB-123	0.3	100
2,3,4,7,8 PeCDF	0.14	87	PCB-156	0.02	102
1,2,3,4,7,8 HxCDF	0.11	72	PCB-157	0.08	98
1,2,3,6,7,8 HxCDF	0.11	73	PCB-167	0.45	101
1,2,3,7,8,9 HxCDF	0.11	70	PCB-189	2.73	66
2,3,4,6,7,8 HxCDF	0.13	68	PBDEs (pg/g fat)		
1,2,3,4,6,7,8 HpCDF	0.69	112	BDE-28	50.23	67
OCDF	0.19	69	BDE-47	64.15	79
Non-ortho PCBs (pg/g fat)			BDE-66	15.29	58
PCB-77	18.88	91	BDE-100	16.75	66
PCB-81	8.47	81	BDE-99	39.85	77
PCB-126	1.58	84	BDE-85	15.11	62
PCB-169	0.1	72	BDE-154	8.56	77
Marker PCBs (ng/g fat)			BDE-153	17.89	62
PCB-28	2.38	65			

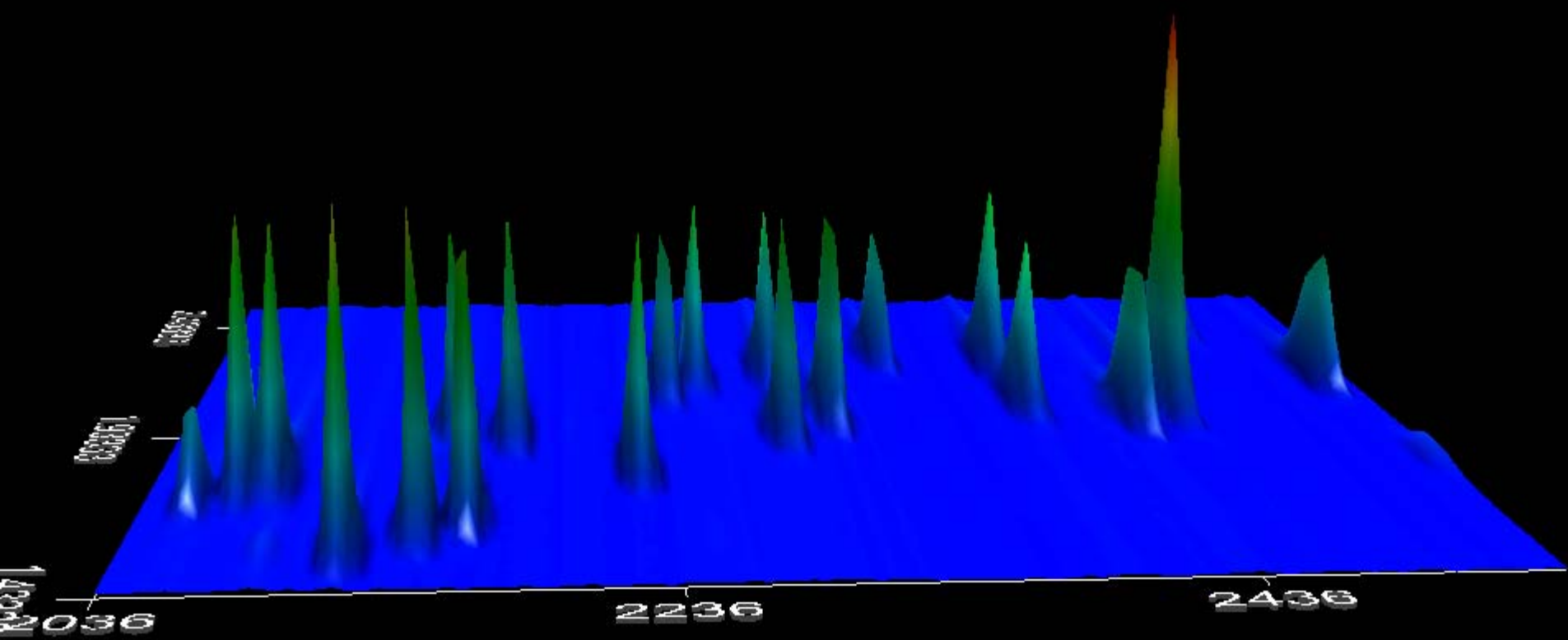
‘Fraction recombining’

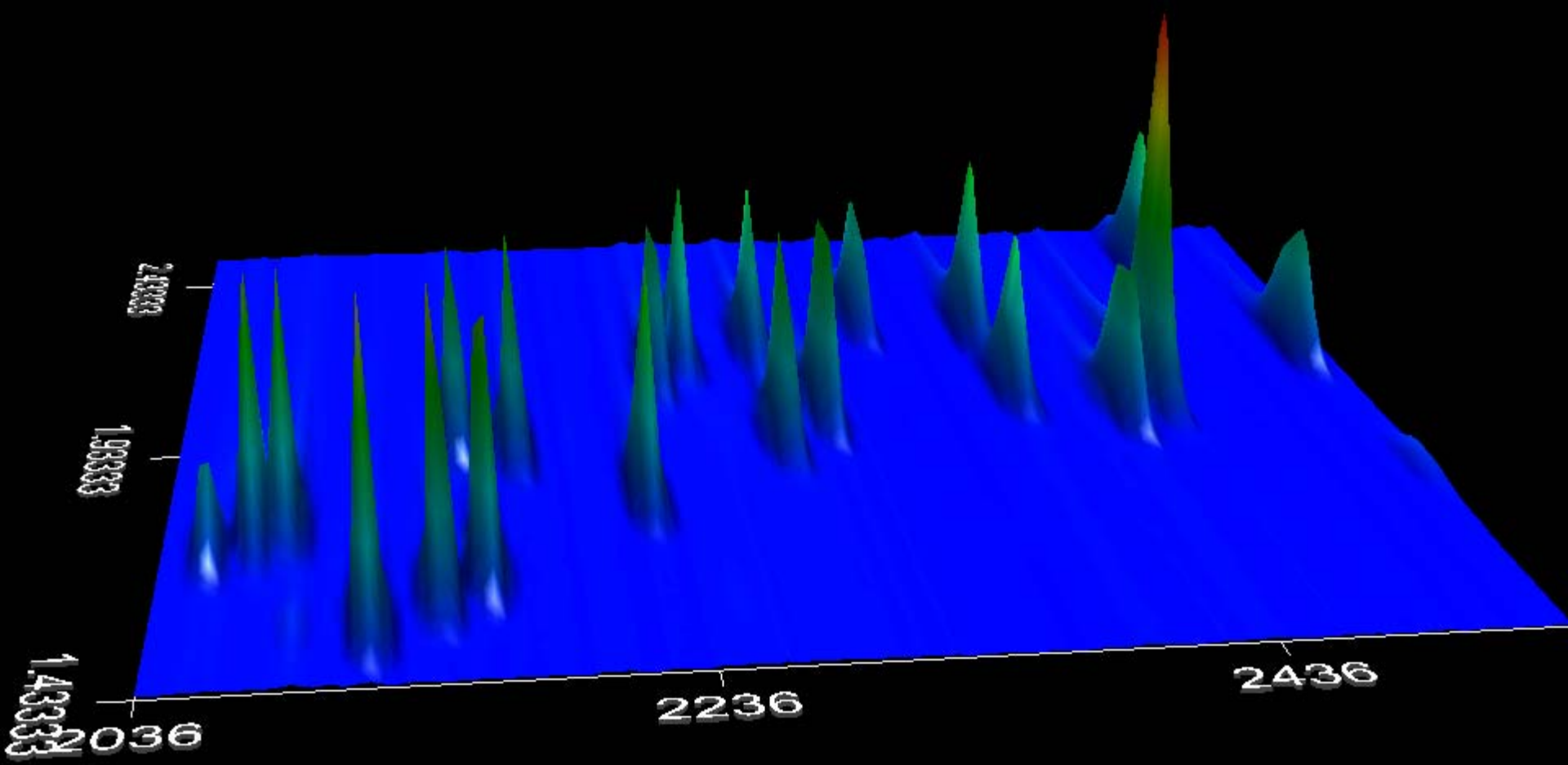
GCxGC-TOFMS

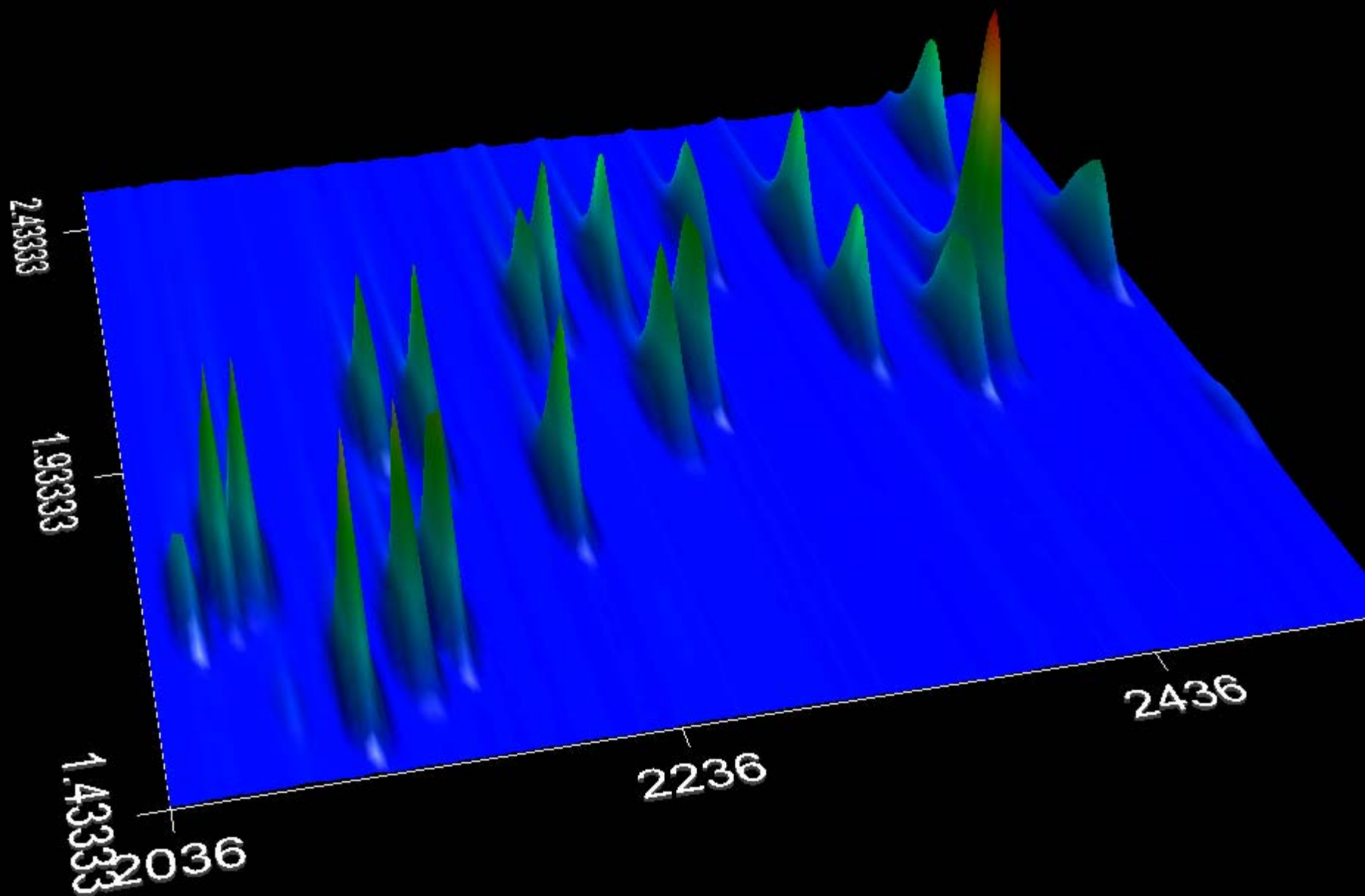
- ✓ **GC-QISTMSⁿ & GC-HRMS:** A separate injection is required for PCBs, BDEs, PCDD/Fs, ...
- ✓ **GCxGC-TOFMS:** The different fractions can be recombined and injected only once because of the improved peak capacity & TOF deconvolution capability

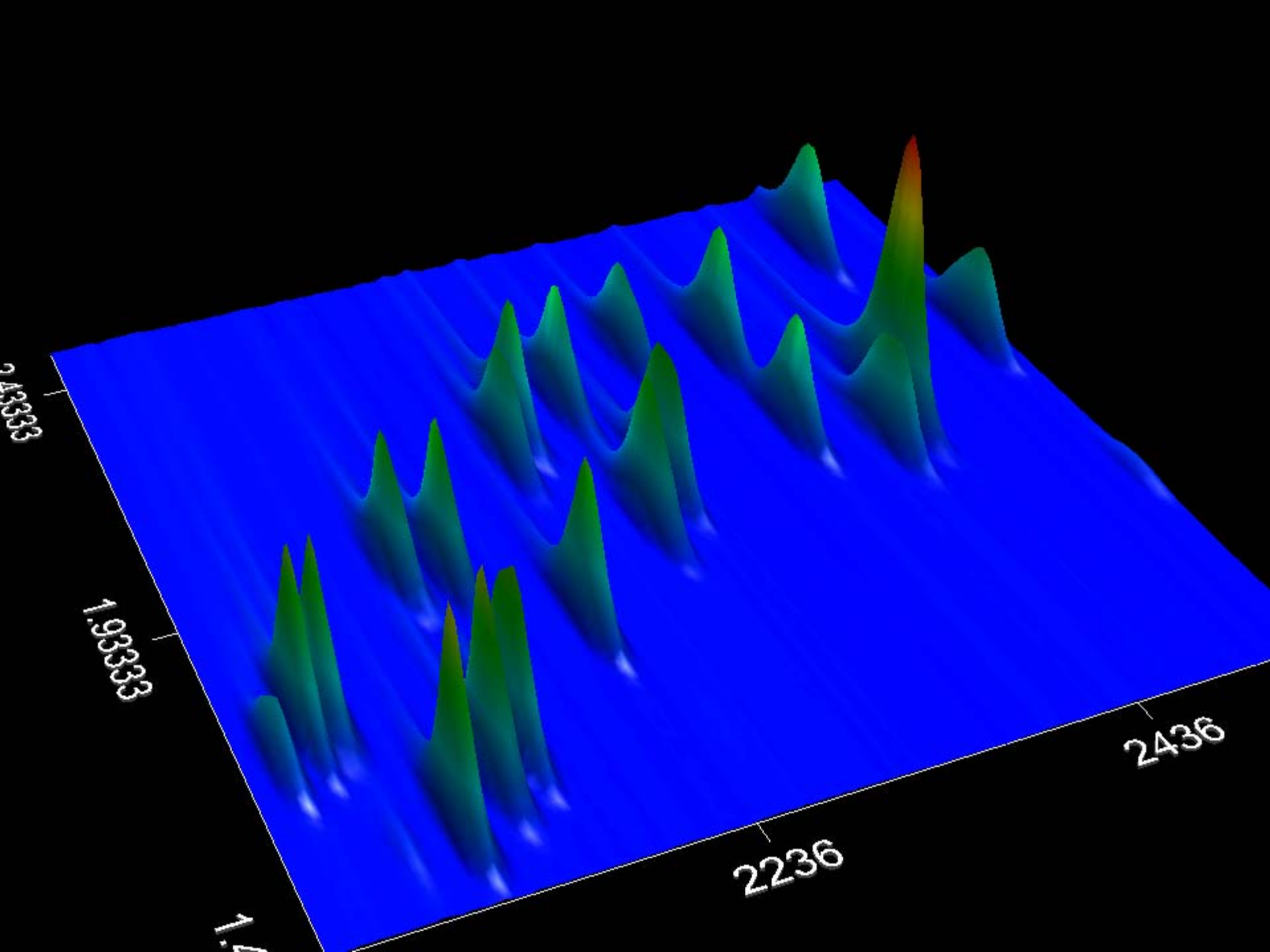


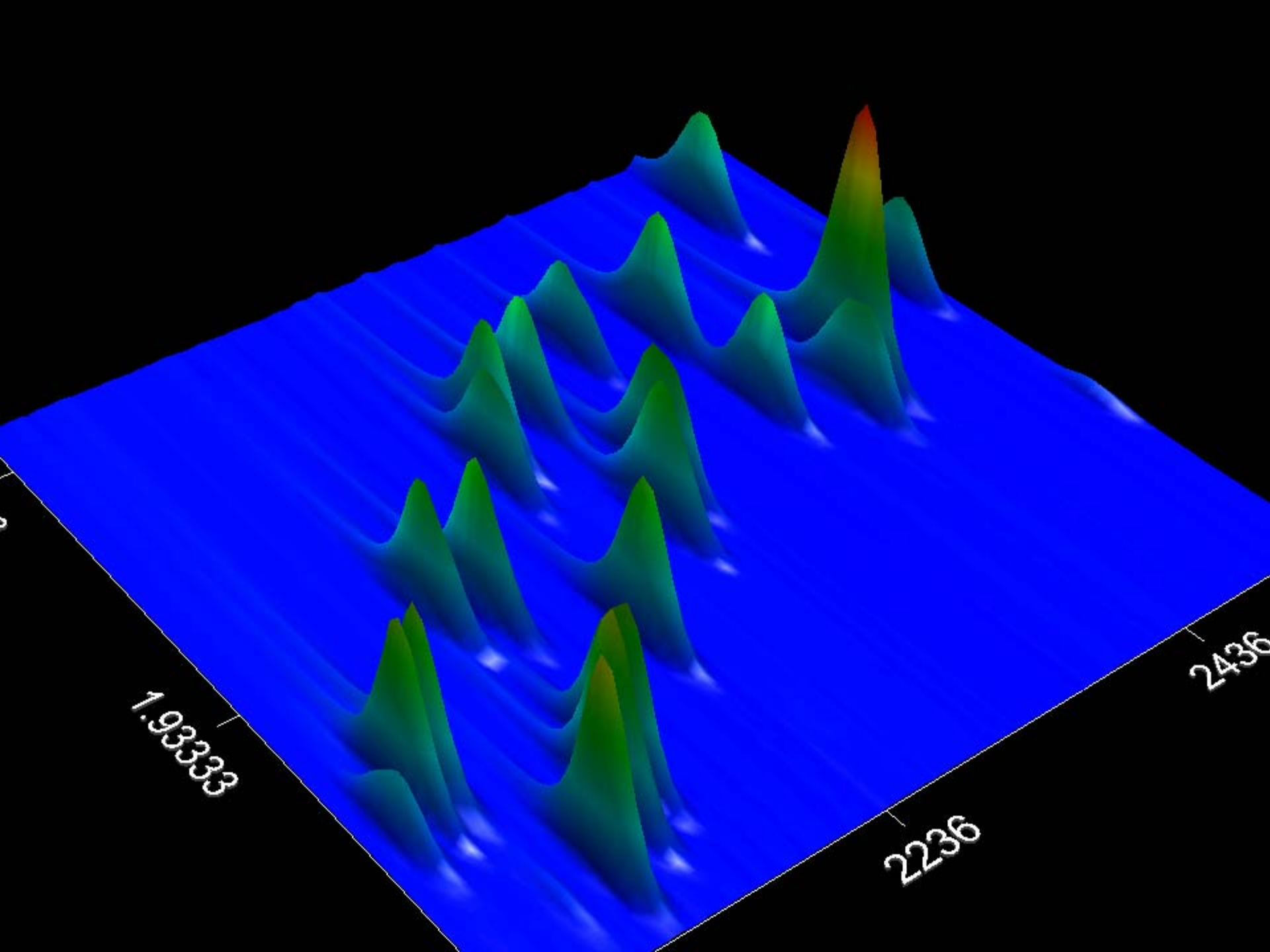


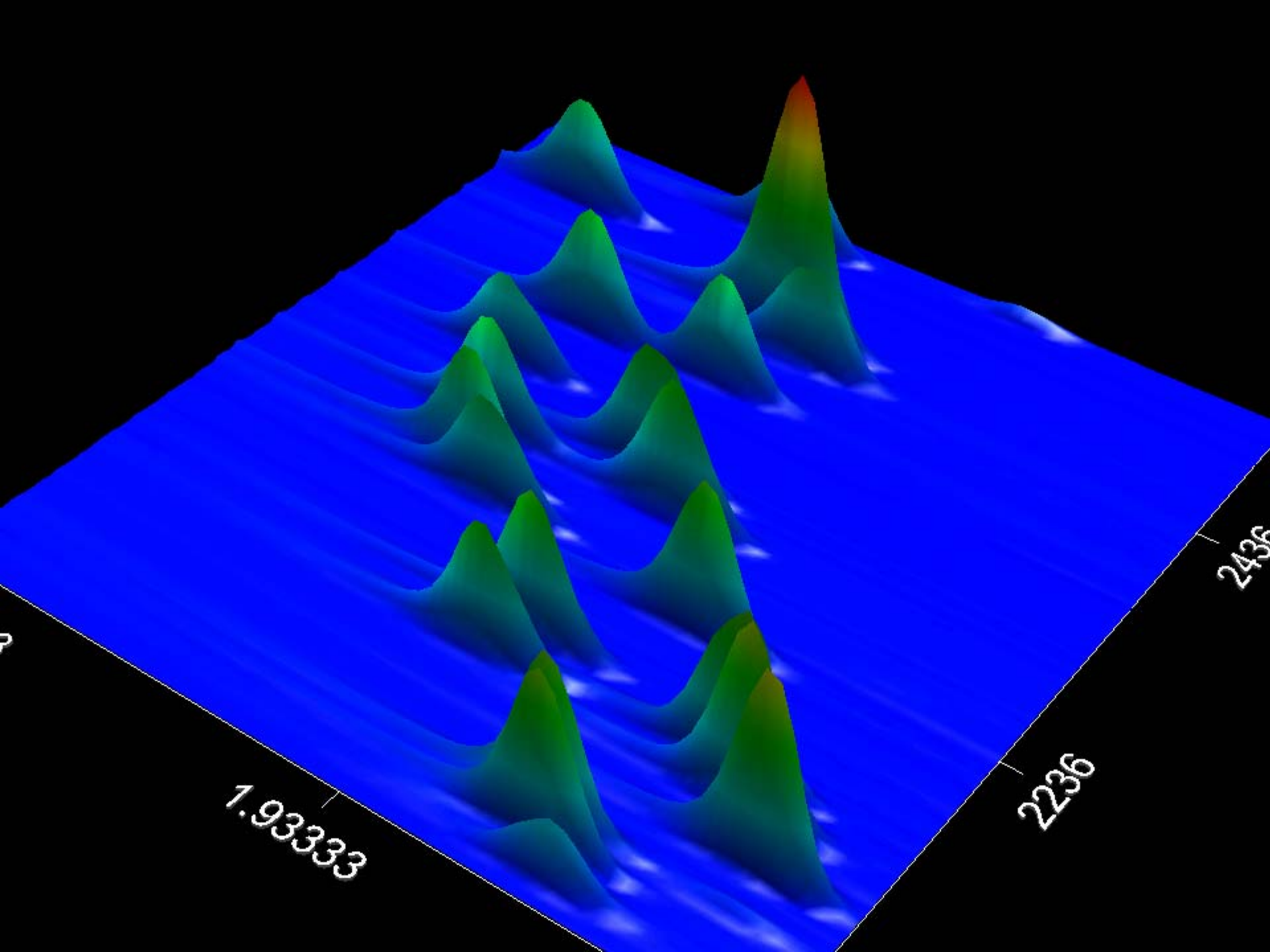


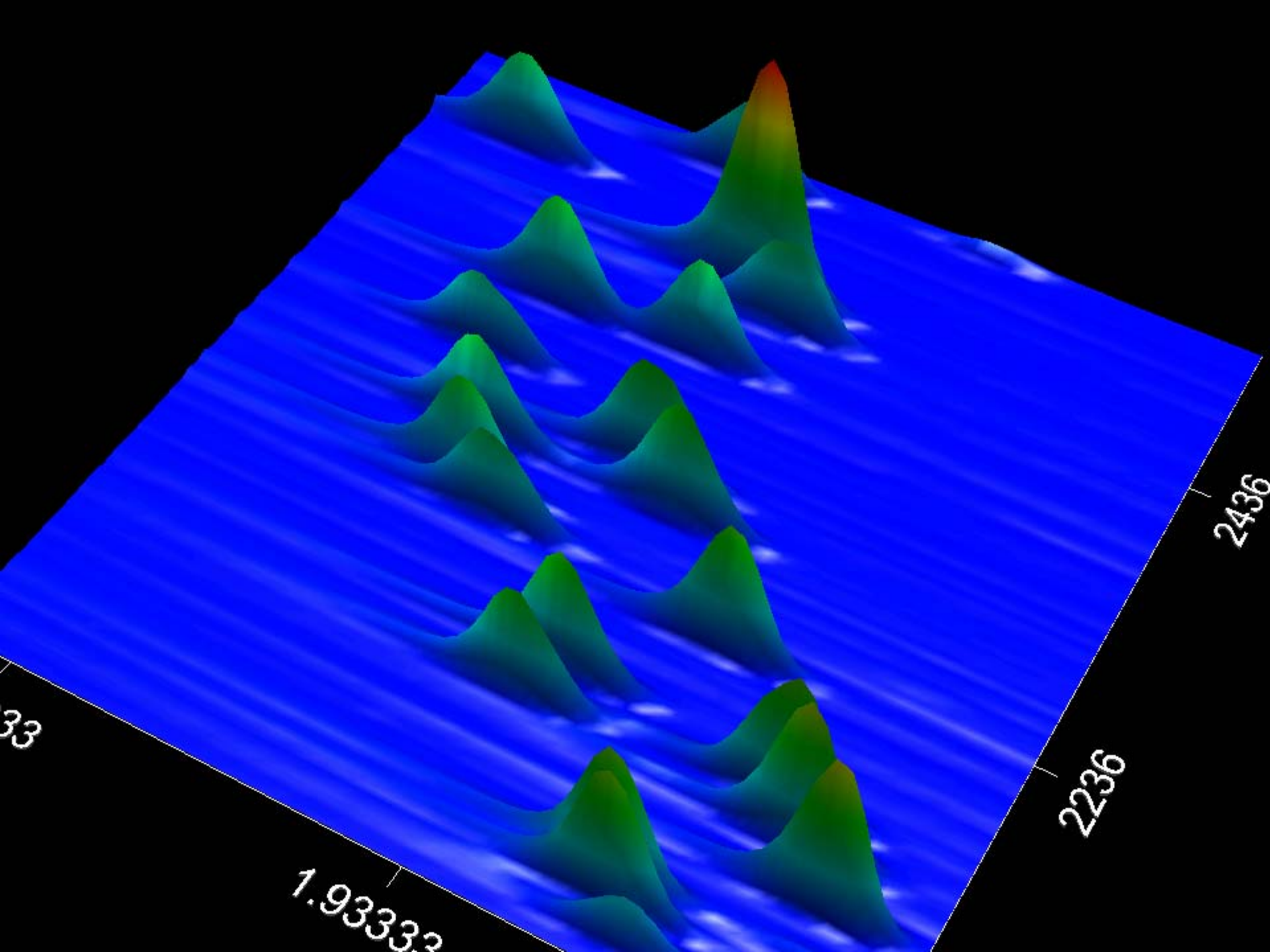


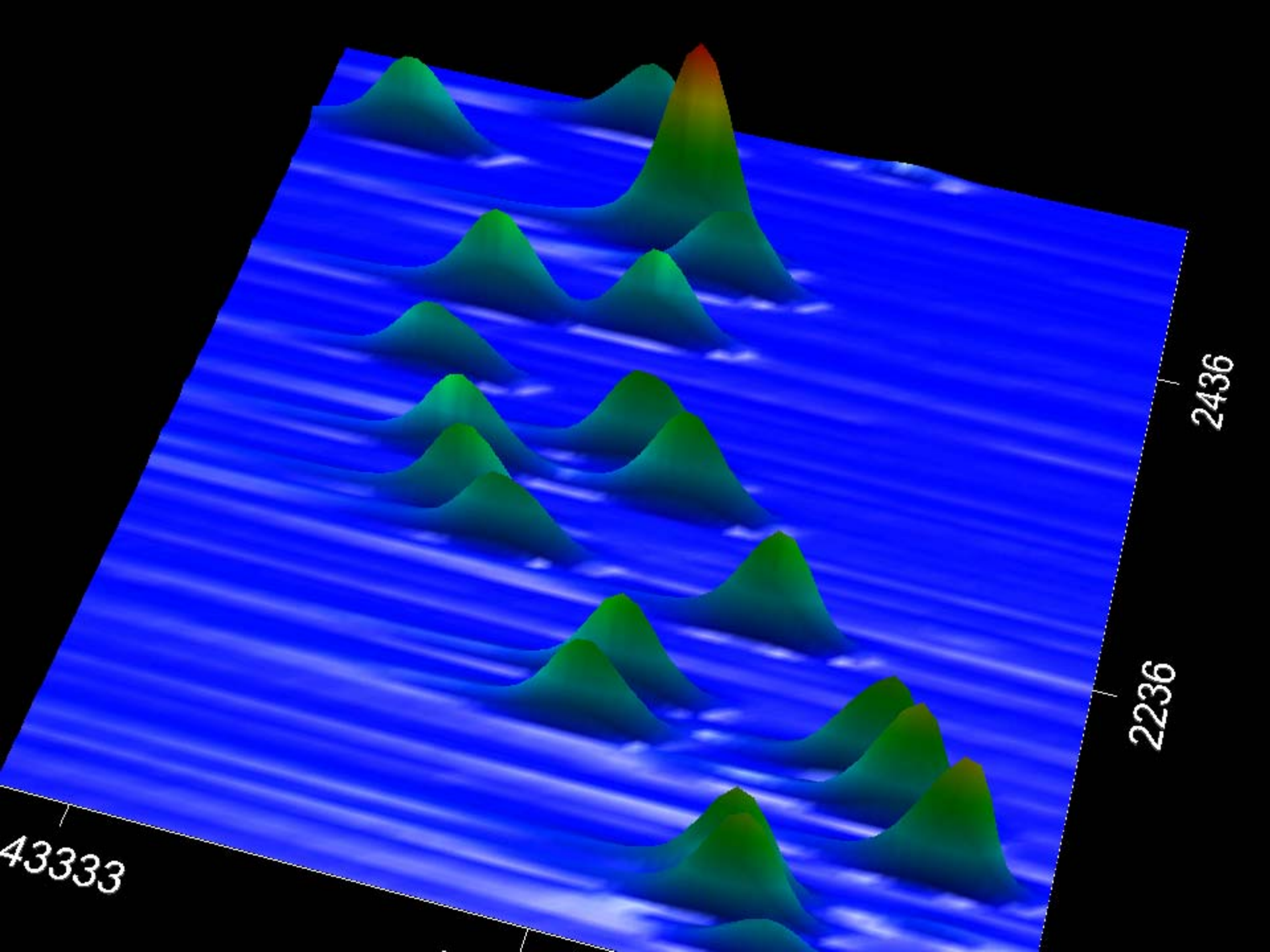


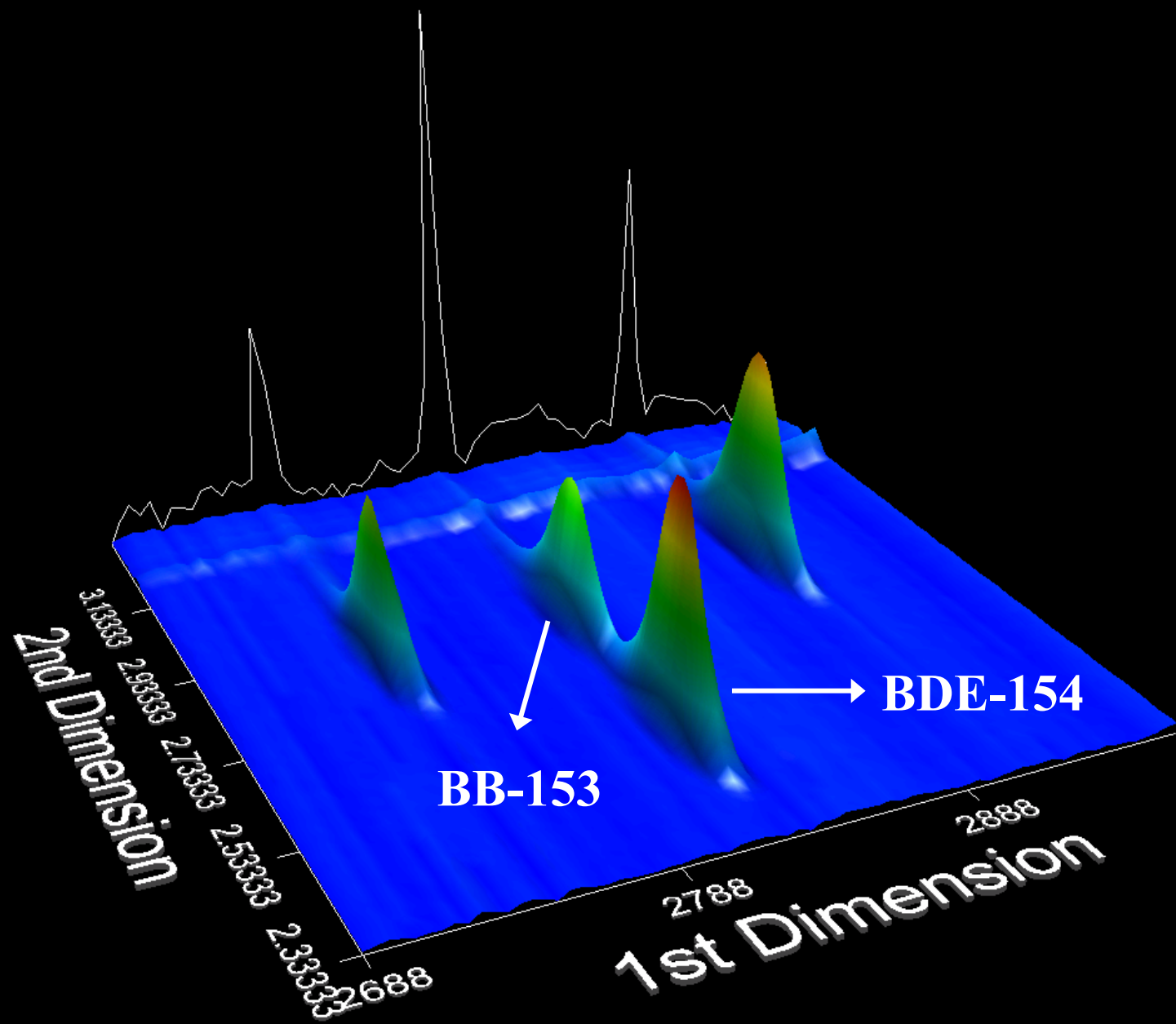












**Integrated
sample prep.**

**GCxGC/MS
Analysis**

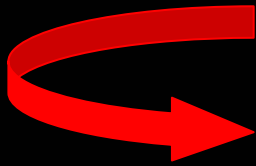
2D

3D

Comprehensive Multidimensionality

Extraction/clean-up/GCxGC/IDTOFMS

5D System for POPs Monitoring



Take Home Message #2

- ✓ The automated system has come a long way
- ✓ Fractionation allows multi-group measurements from a single sample extract
- ✓ ‘Tunability’ to accommodate various analyte and matrix types
- ✓ Additional developments under going
- ✓ Might fit with a global multi-dimensional approach for POPs analysis (one step closer to the ‘Magic Box’...)

Related papers (i)

- J.-F. Focant, C. Pirard, G. Eppe, E. DePauw, Fast Clean-up for polychlorinated dibenzo-*p*-dioxins, dibenzofurans and coplanar polychlorinated biphenyls analysis of high fat content biological samples. *J. Chromatogr. A* 925 (2001) 207-221.
- J.-F. Focant, E. DePauw, Fast automated extraction and clean-up of biological fluids for polychlorinated dibenzo-*p*-dioxins, dibenzofurans and coplanar polychlorinated biphenyls analysis. *J. Chromatogr. B* 776 (2002) 199-212.
- J.-F. Focant, H. Shirkhan, E. DePauw, On-line automated pPLE and multi-column clean-up system for PCDD/F and PCB analysis in foodstuffs. *Organohalogen Compds* 55 (2002) 33-36.
- C. Pirard, J.-F. Focant, E. DePauw, An improved clean-up strategy for simultaneous analysis of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) in fatty food samples. *Anal. Bioanal. Chem.* 372 (2002) 373-381.

Related papers (ii)

- C. Pirard, E. DePauw, J.-F. Focant, A new strategy for comprehensive analysis of polybromodiphenylethers (PBDEs), polychlorodibenzo-*p*-dioxins (PCDDs), polychlorodibenzofurans (PCDFs) and polychlorobiphenyls (PCBs) by gas chromatography coupled with mass spectrometry (GC/MS). *J. Chromatogr. A* 998 (2003) 169-181.
- J.-F. Focant, A. Sjödin, D.G. Patterson Jr., Qualitative evaluation of thermal desorption-programmable temperature vaporization-comprehensive multi-dimensional gas chromatography-time-of-flight mass spectrometry for the analysis of selected halogenated contaminants. *J. Chromatogr. A* 1019 (2003) 143-156.
- J.-F. Focant, C. Pirard, E. DePauw, Automated sample preparation-fractionation for the measurement of dioxins and related compounds in biological matrices: A review. *Talanta* (2004) in press.

