Food Safety

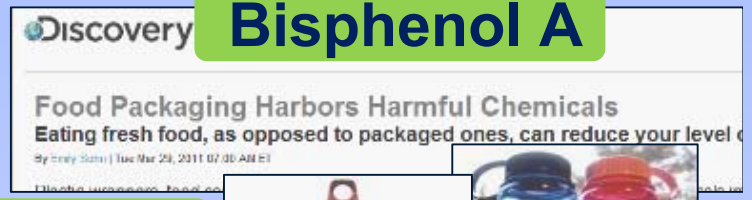
Sample Preparation

Products - 2011

Restek Corporation

Consumer Pressure

melamine



Bisphenol A

phthalates

acrylamide

mycotoxins

Vet drugs

pesticides

PAHs

Dioxins

4MEI

blog

Outline

- Customers – Who are they?
- Compounds and methods of interest
- The Restek Food Safety analysis arsenal
  - Sample preparation products (QuEChERS)
  - Reference standards (pesticides, melamine, etc.)
  - GC and LC columns and accessories
- Web tools, literature

Food Safety Customers

- Governmental organizations
  - FERA (UK), VWA (The Netherlands)
- Contract laboratories, research organizations
  - Eurofins, RIKILT (The Netherlands), Covance, Intertek, Silliker
- University research groups
  - Institute of Chemical Technology (Prague, CZ)
- Private food companies
  - Larger ones may do in-house testing

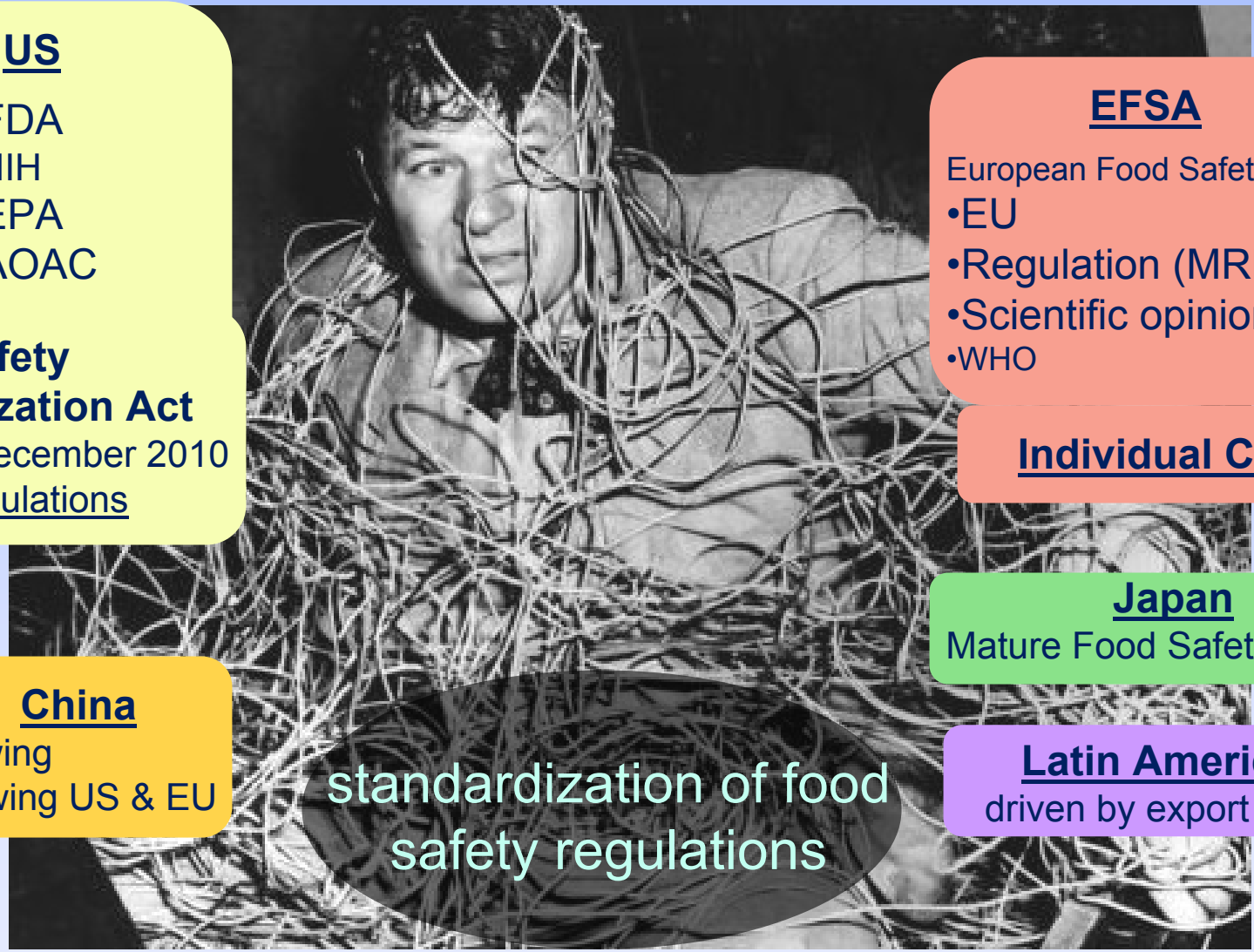
Food Safety Compounds

- Pesticides
  - Organochlorine/nitrogen/phosphorus, etc.
- Mycotoxins
- Veterinary drug residues
- Adulterants
  - Melamine, pesticides, other toxins
- PAHs, PBDEs, PCBs, dioxins, furans, etc.

Food Safety Methods

- Codex Alimentarus (Food Law)
  - United Nations Food and Agriculture Organization
  - World Health Organization
  - Methods are somewhat outdated
- Analytical Methods for Pesticide Residues in Foodstuffs
  - The Netherlands
  - Well-developed, multiresidue methods
  - Still used, but becoming outdated

Global Economy



US

- FDA
- NIH
- EPA
- AOAC

Food Safety Modernization Act
Passed December 2010
Import regulations

EFSA
European Food Safety Authority

- EU
- Regulation (MRLs)
- Scientific opinions
- WHO

Individual Country

Japan
Mature Food Safety system

Latin America
driven by export laws

China
Growing following US & EU

standardization of food safety regulations

Some statistics

•2008 = separations market accounted for more 20% of the laboratory analytical instrumentation demand in the food industry

•Growth driven by LC–MS and GC–MS systems

•U.S. food-safety testing market value
2010 = $3.4 billion
2015 = $4.7 billion in 2015

•Global food safety testing market
$11.4 billion by 2015

SDi's Market Analysis and Perspective report entitled, The Analytical Cornucopia: The Food, Beverage and Agriculture Market for Analytical Instruments.

What challenges arise for the chemist?

Trace analysis

many analytes

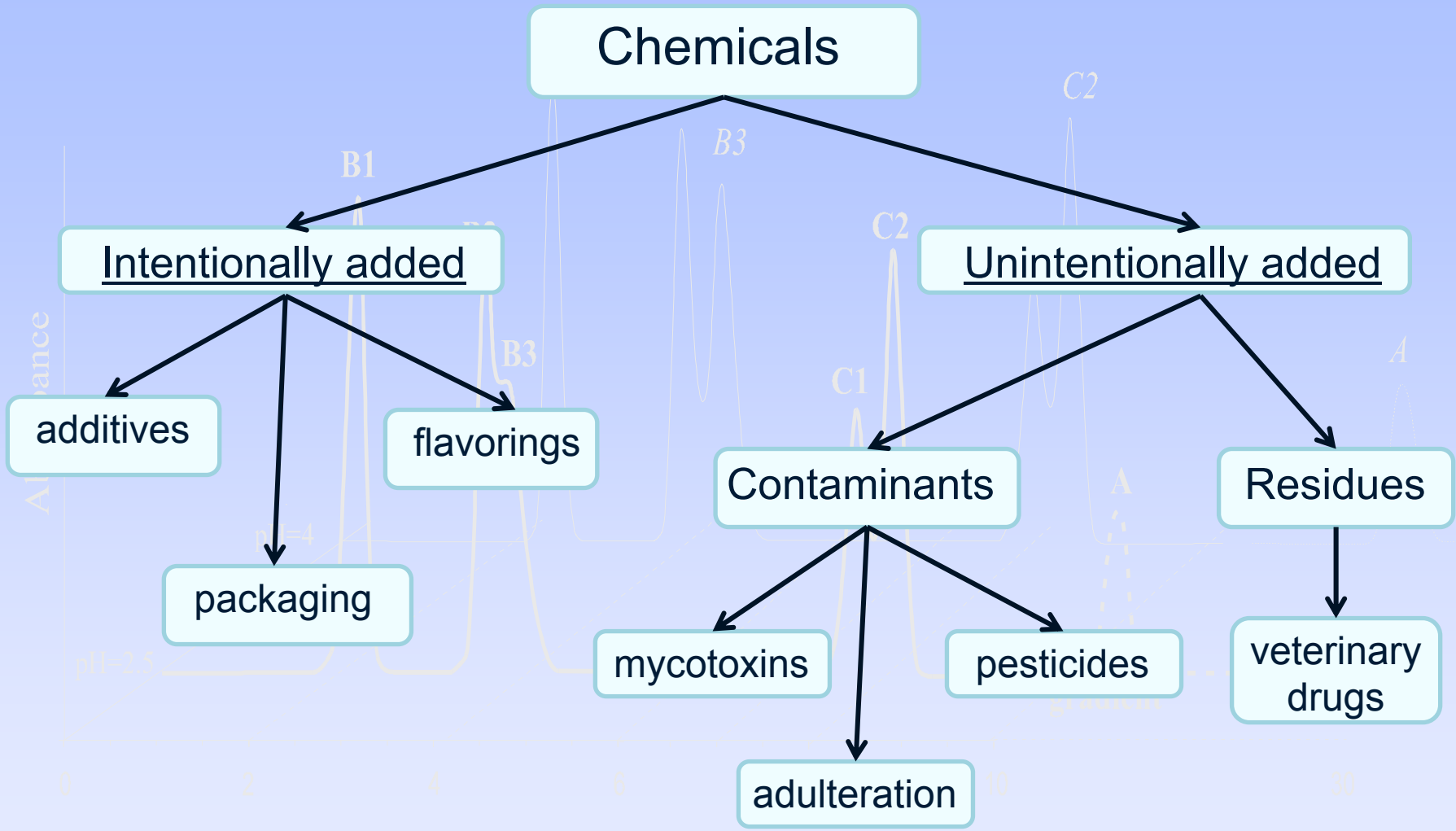
Diverse matrices

Sample matrix

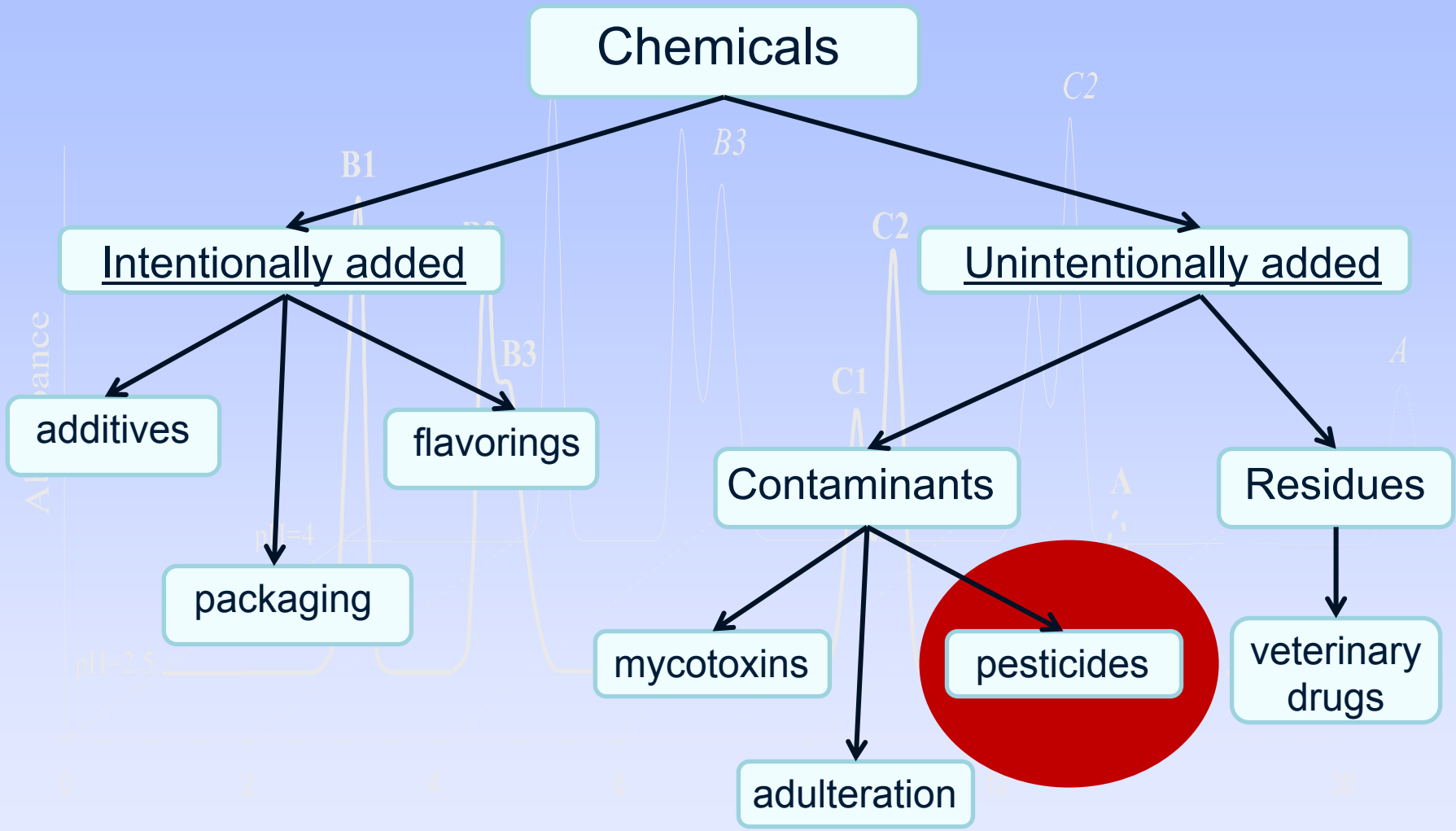
compound stability

sensitivity

Function or Chemical Class



Function or Chemical Class

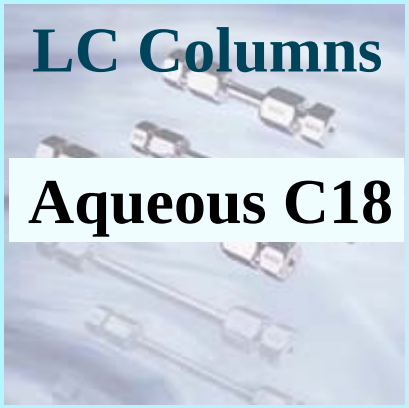


Pesticide Residues in Foods

- Techniques
  - Historically GC (ECD or MS)
  - Increasingly add LC-MS/MS
  - Comprehensive screening desirable
- Laboratory Needs
  - HIGH throughput
  - All-purpose phases
    - Ultra Aqueous C18
  - Application-specific columns
    - Target classes (e.g. Ultra Quat)

Pesticide Residues in Foods

Liquid Chromatography: LC/MS/MS



Aqueous C18 Advantages

•Highly base-deactivated

•Compatible with highly aqueous (up to 100%) mobile phases

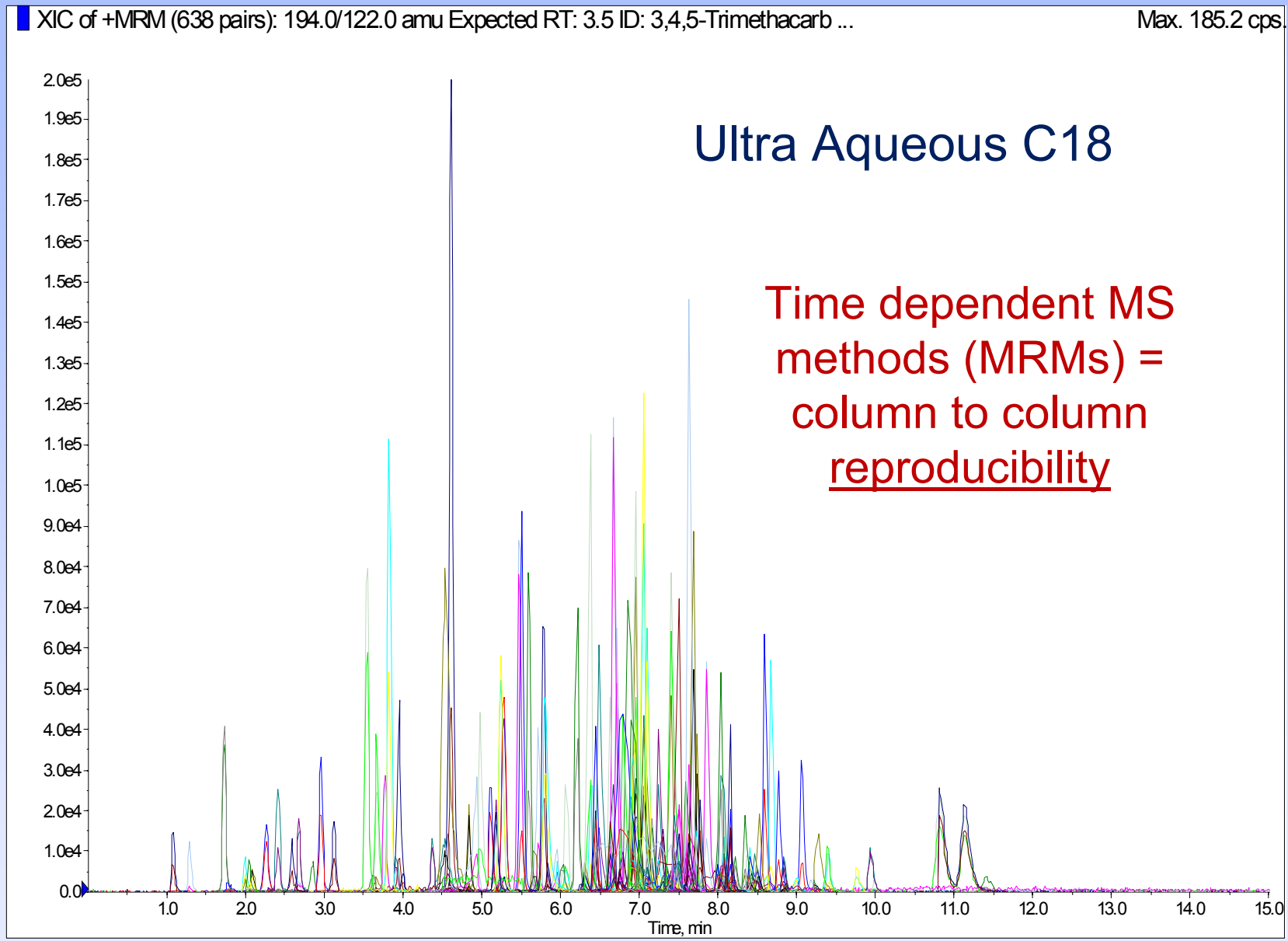
General purpose

Great for

•Multiresidue analysis

•Variety of pesticide classes

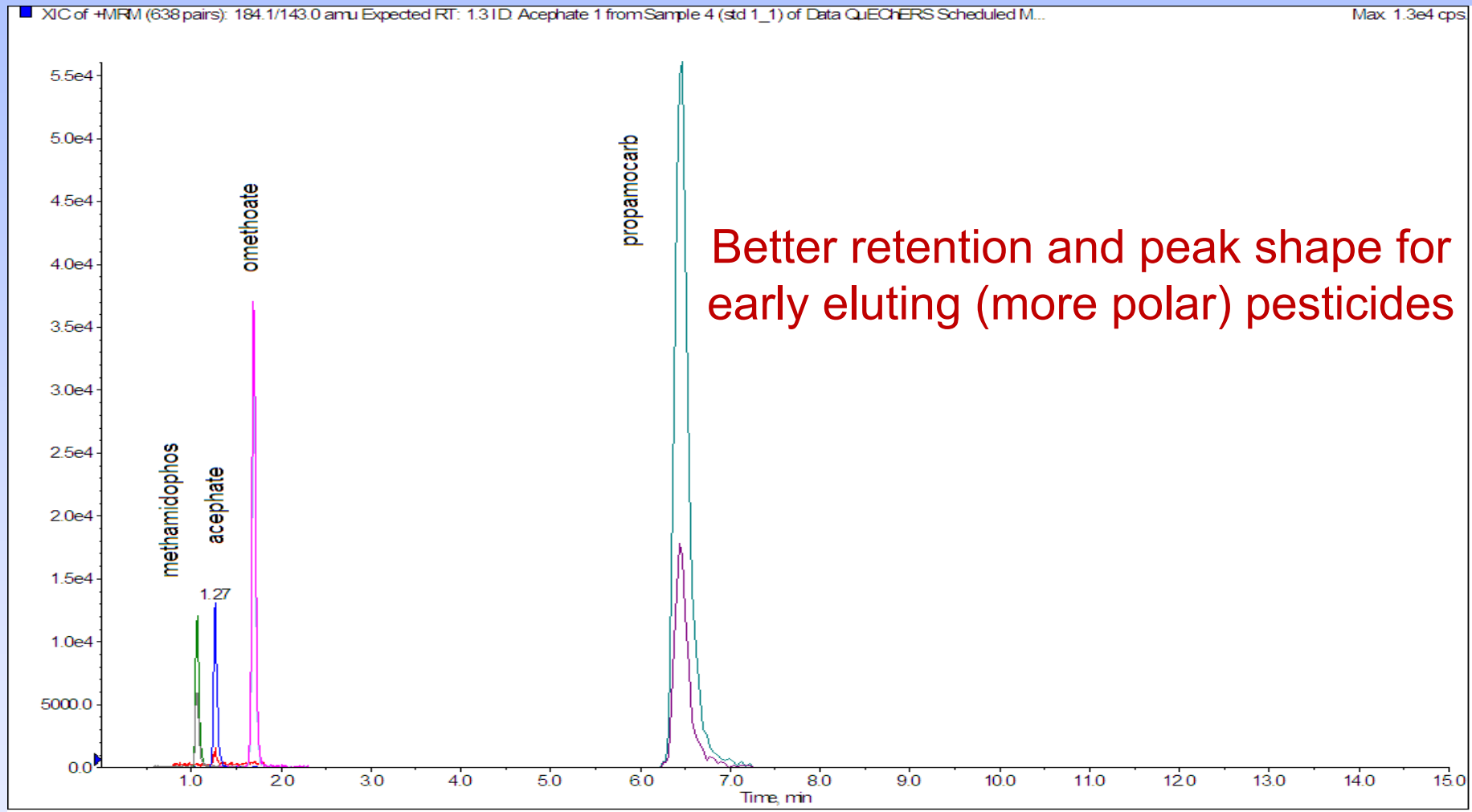
•Scalable on different silica families



Ultra Aqueous C18

Time dependent MS methods (MRMs) = column to column reproducibility

LC/MS/MS Pesticide Analysis: Ultra Aqueous C18
3µm, 100x2.1mm



Better retention and peak shape for early eluting (more polar) pesticides

Pesticide Residues in Foods

Gas Chromatography: GC-MS, GC-ECD and GC-NPD

Rxi technology

- Highest inertness
- Lowest bleed
- Exceptional reproducibility

General purpose

Great for

- Multiresidue analysis
- variety of pesticide classes

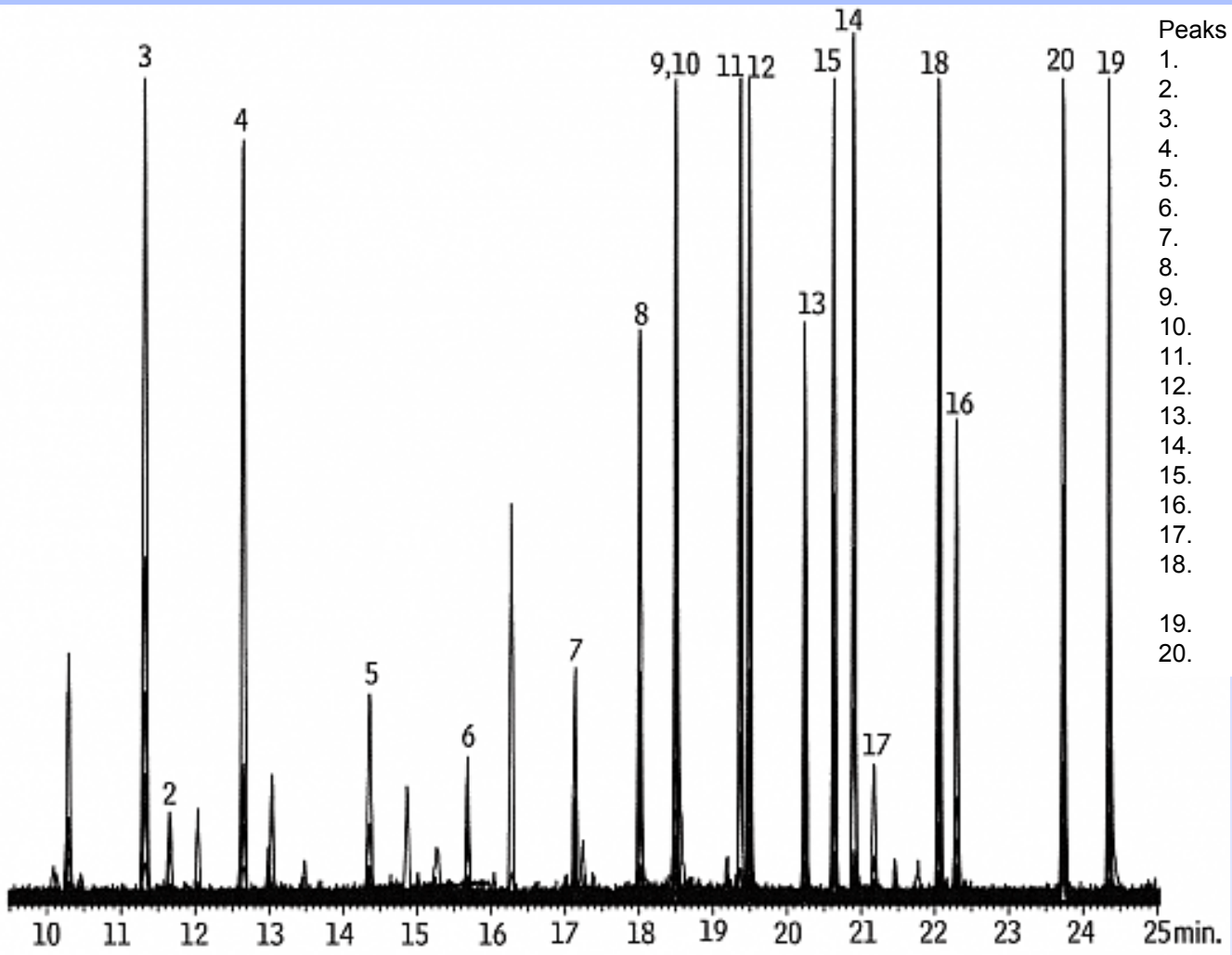
High sensitivity

- Ideal for applications requiring high sensitivity
- ppb detection limits

Retention Indices for Pesticides on “5” Columns

Compound	Type	DB-5MS	Rxi-5Sil MS	Difference
Methamidophos	OPP	1222.0	1221.8	0.2
Omethoate	OPP	1585.1	1583.2	1.9
Diazinon	OPP	1788.7	1788.3	0.4
Chlorothalonil	OCP	1789.8	1791.2	-1.4
Malathion	OPP	1959.7	1958.8	0.8
Myclobutanil	ONP	2186.4	2186.6	-0.2
4,4-DDT	OCP	2351.5	2353.7	-2.3
Propargite	OSP	2391.0	2391.1	-0.1
Bifenthrin	Pyr	2465.1	2466.2	-1.0
trans-Permethrin	Pyr	2712.2	2714.1	-1.9

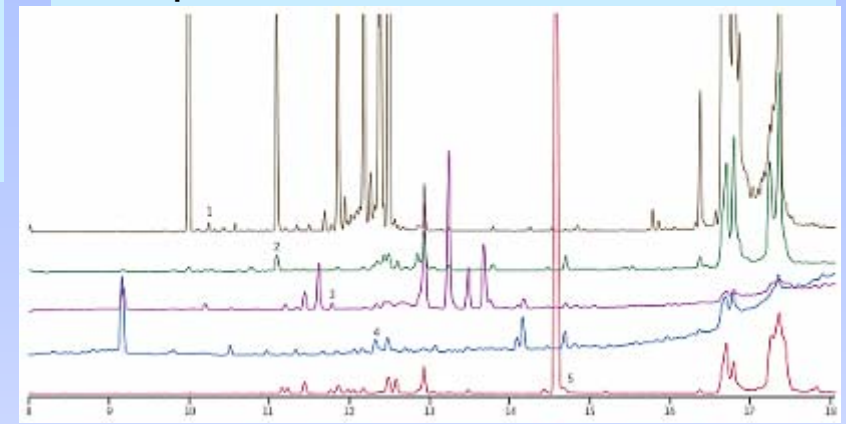
Chlorinated Pesticide Residues in Olive Oil Rxi®-5sil MS



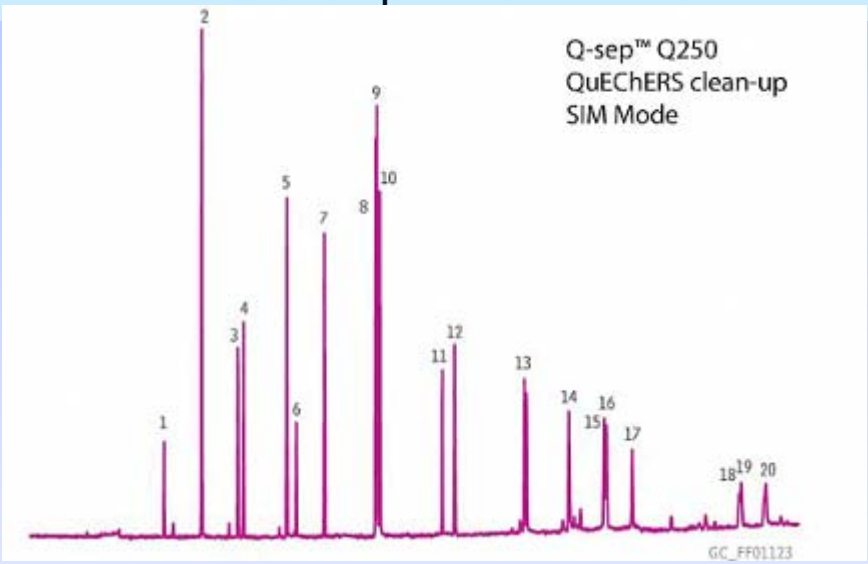
Peaks	Quant. ion	Qual. ion 1	Qual. i
1.	α-BHC*	219	181
2.	γ-BHC	219	181
3.	β-BHC	219	181
4.	δ-BHC	219	181
5.	Heptachlor	272	237
6.	Aldrin	263	293
7.	Heptachlor epoxide		263
8.	δ-chlordane	272	237
9.	α-Chlordane	272	237
10.	Endosulfan I	195	207
11.	4,4'-DDE	246	318
12.	Dieldrin	79	263
13.	Endrin	263	281
14.	4,4'-DDD	235	165
15.	Endosulfan II	195	207
16.	4,4'-DDT	235	165
17.	Endrin aldehyde	67	250
18.	Endosulfan sulfate	239	272
19.	Methoxychlor	227	274
20.	Endrin ketone	67	317

Rxi®-5Sil MS: versatile for other analyses

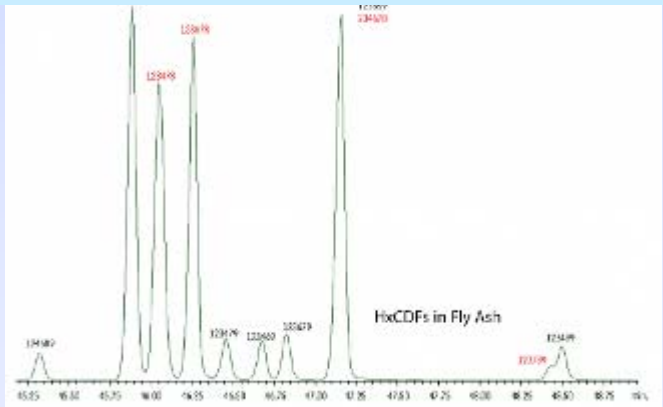
Analysis of Melamine and Related Compounds in Infant Formula



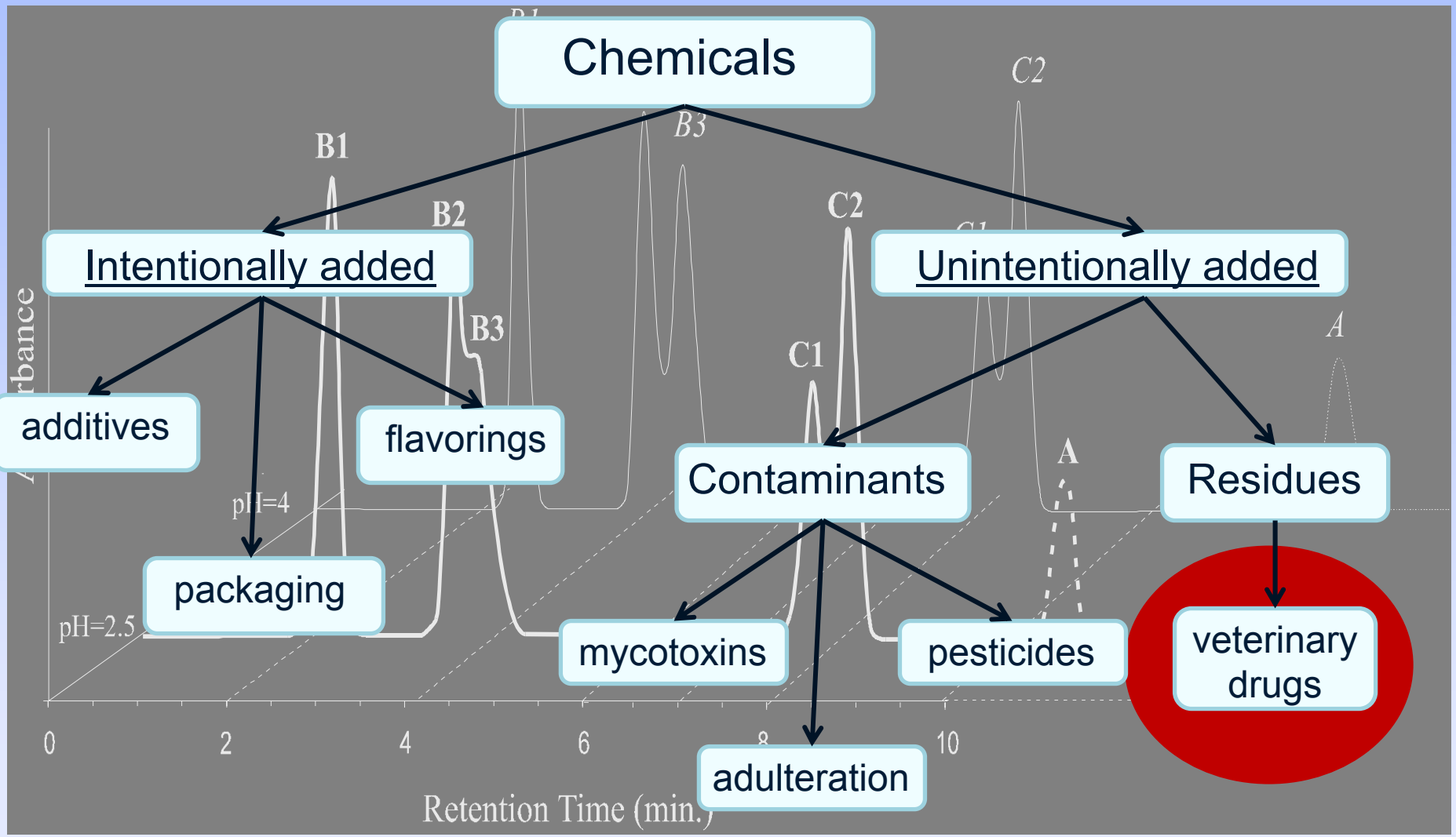
Polycyclic Aromatic Hydrocarbons Infant Formula with and without QuEChERS dSPE Clean-up on Rxi®-5Sil MS



Dioxins (HxCDFs) in Fly Ash on Rxi®-5Sil MS



Function or Chemical Class



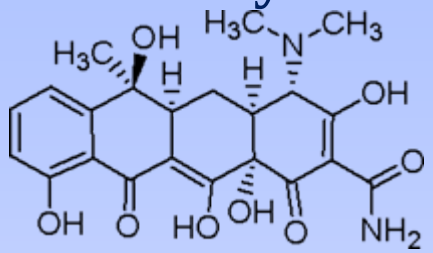
drugs in feed → drug residues remain → drug residues in food

- Prevent pathogen and disease
- Fear resistant strains

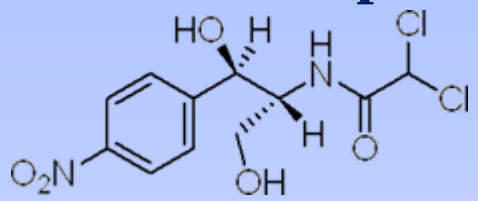
- Promote growth
- US, Canada, Australia

Veterinary Drugs

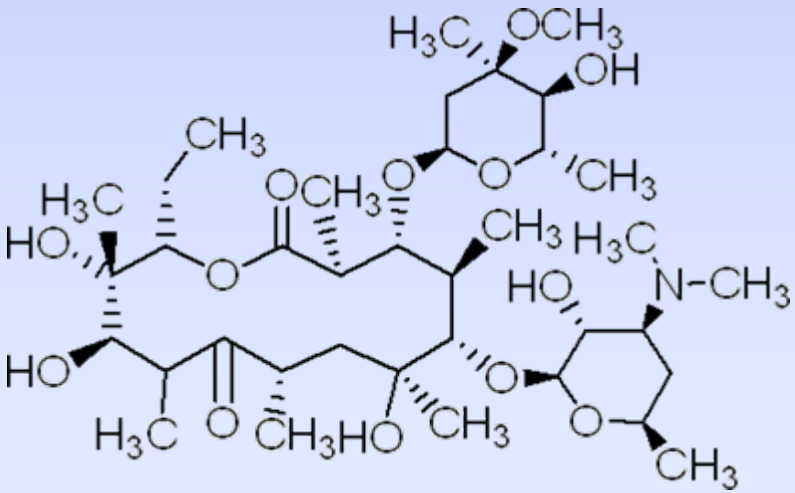
Tetracyclines



Chloramphenicol

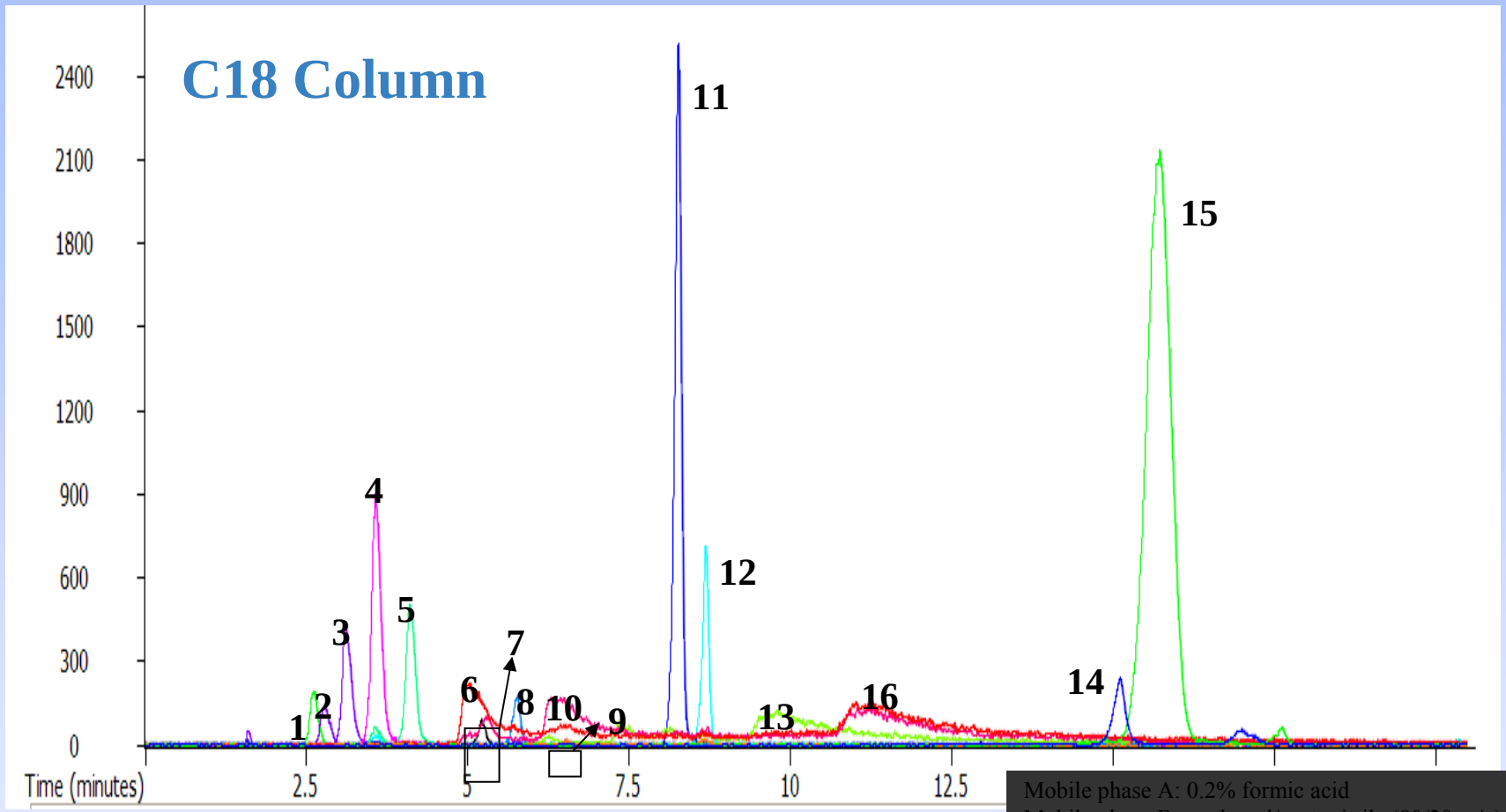


erythromycin



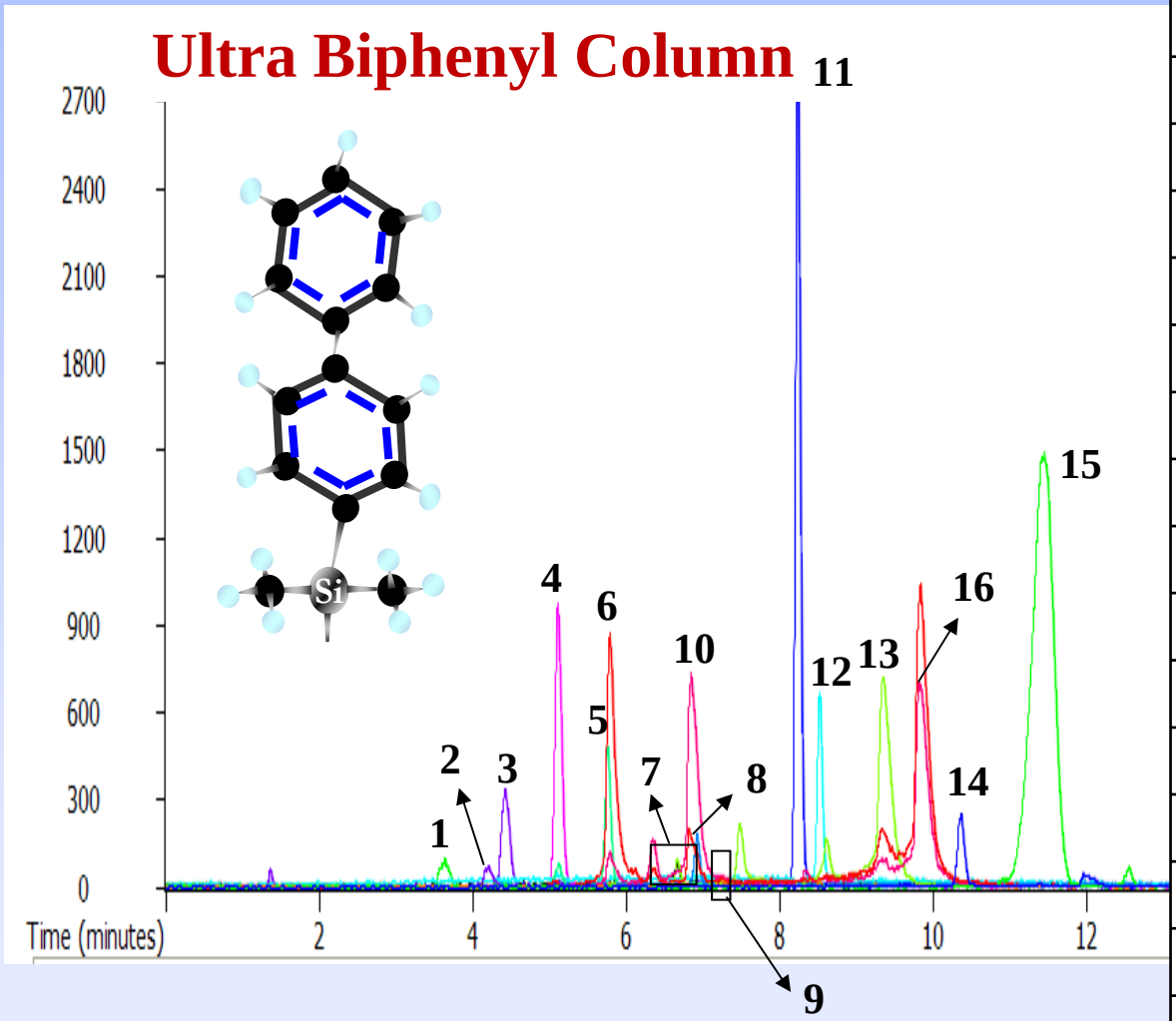
Class	Compound
sulfonamides	sulfachloropyridazine
sulfonamides	sulfadiazine
sulfonamides	sulfadimethoxine
sulfonamides	sulfamerazine
sulfonamides	sulfamethazine
sulfonamides	sulfaquinoxaline
sulfonamides	sulfathiazole
sulfonamides	sulfamethoxypyridazine
sulfonamides	sulfamethoxazole
tetracyclines	chlortetracycline
tetracyclines	doxycycline
tetracyclines	oxytetracycline
tetracyclines	tetracycline
nitrobenzenes	chloramphenicol
macrolides	tylosin
macrolides	erythromycin

Veterinary Drug Residues



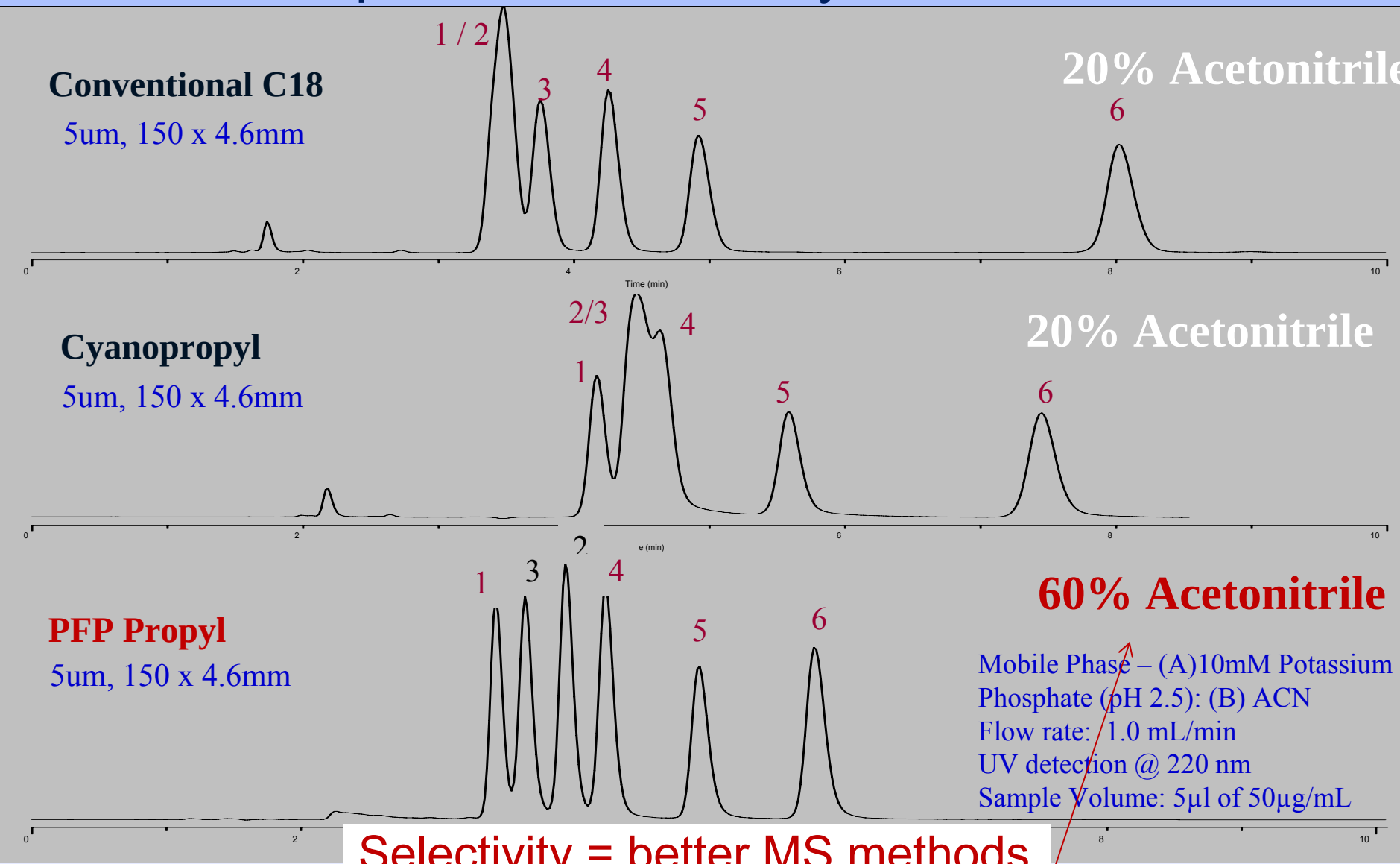
Mobile phase A: 0.2% formic acid
Mobile phase B: methanol/acetonitrile (80/20, v/v) with 0.2% formic acid
Flow: 1 mL/min with pre-injection split delivering 0.2 mL/min to column
Temp: ambient
Injection volume: 10 µL

Veterinary Drug Residues



1	sulfadiazine
2	sulfathiazole
3	sulfamerazine
4	sulfamethazine
5	sulfamethoxypyridazine
6	oxytetracycline
7	sulfachloropyridazine
8	sulfamethoxazole
9	chloramphenicol
10	tetracycline
11	sulfadimethoxine
12	sulfaquinoxaline
13	chlortetracycline
14	erythromycin
15	tylosin
16	doxycycline

Fluoroquinolone Stationary Phase Selection



Summary

Rxi®-5Sil MS

required resolution
Isobaric compounds

Application Specific Phases

Ultra Aqueous C18

required resolution and more
amenable to LCMS interface

Think about…

- Focused or multi-method user = general or specific column

- MS or MS/MS user =
  - column bleed
  - specific problems
    (isobaric compounds and isobaric interferences)
  - LC interface
  - reproducibility

- Low levels= optimize chromatography strategies (S/N)

QuECh-ing for Beginners

3 Easy Steps

What is QuEChERS?

- Simplified shake extraction of fruits and vegetables for multi-pesticide residue analysis
- Acetonitrile solvent and partition/buffering salts
- Centrifugation
- Dispersive solid phase extraction cleanup
- Extract produced for GC and LC analysis!
- Quick – Easy – Cheap – Effective – Rugged – Safe

Fast and Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning and "Dispersive Solid-Phase Extraction" for the Determination of Pesticide Residues in Produce

Author(s): Michelangelo Anastassiades [1] | Steven J. Lehotay [2] | Darinka Štajnbaher [3] | Frank J. Schenck [4]

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Journal of AOAC INTERNATIONAL

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Page(s): 412-431

Abstract

A simple, fast, and inexpensive method for the determination of pesticide residues in fruits and vegetables is introduced. The procedure involves initial single-phase extraction of 10 g sample with 10 mL acetonitrile, followed by liquid–liquid partitioning formed by addition of 4 g anhydrous $MgSO_4$ plus 1 g NaCl. Removal of residual water and cleanup are performed simultaneously by using a rapid procedure called dispersive solid-phase extraction (dispersive-SPE), in which 150 mg anhydrous $MgSO_4$ and 25 mg primary secondary amine (PSA) sorbent are simply mixed with 1 mL acetonitrile extract. The dispersive-SPE with PSA effectively removes many polar matrix components, such as organic acids, certain polar pigments, and sugars, to some extent from the food extracts. Gas chromatography/mass spectrometry (GC/MS) is then used for quantitative and confirmatory analysis of GC-amenable pesticides. Recoveries between 85 and 101% (mostly >95%) and repeatabilities typically <5% have been achieved for a wide range of fortified pesticides, including very polar and basic compounds such as methamidophos, acephate, omethoate, imazalil, and thiabendazole. Using this method, a single chemist can prepare a batch of 6 previously chopped samples in <30 min with approximately $1 (U.S.) of materials per sample.

1. Blend

Add H_2O to Leaves

Blend!

2. Extraction

10g sample + 10mL acetonitrile

Shake (1 min)

Add buffering salts to extraction sample

Shake (1 min)

Centrifuge (5 min)

3. Cleanup

Transfer supernatant to cleanup tube

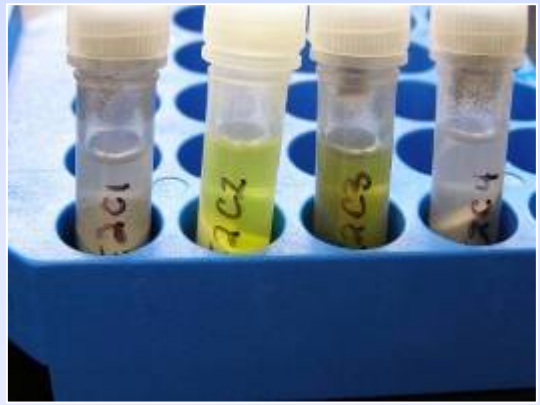
Shake (30 sec)

Centrifuge (5 min)

Guide to Sorbents

Sorbent	Removes
Primary secondary amine (PSA)	Sugars and fatty acids
Octadecyl (C18)	Lipids
Graphitized carbon black (GCB)	Pigments and sterols

Transfer cleaned extract to an autosampler vial for analysis



Analyzing QuEChERS Samples

- Rxi-5Sil MS
  - Gas chromatography
- Equivalent to popular DB-5MS
  - Selectivity
  - Rxi-5Sil MS is more inert and has lower bleed
- 30m x 0.25mm x 0.25µm suggested
  - Has capacity, is rugged towards “dirt”, inert
- Ultra Aqueous C18
  - HPLC
- Excellent peak shapes for early eluting, polar pesticides!
  - Methamidophos, acephate
- 100mm x 2.1mm, 3µm suggested
  - FDA and AB Sciex SRM and retention time data
    - >280 pesticides
  - Restek FFFF1185.pdf

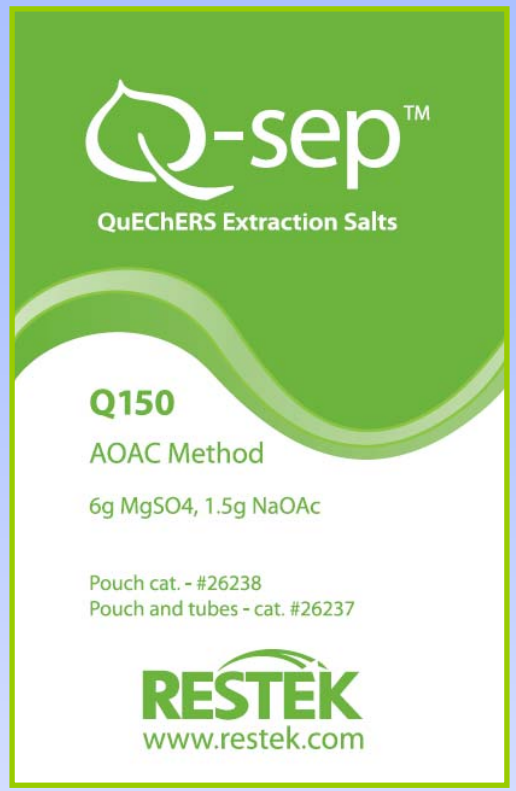
QuEChERS

- What is the problem?
  - Most competitors package the extraction salts in 50mL centrifuge tubes.
  - This results in an extra salt transfer step
  - And a wasted tube
- How can we:
  - Make it easier to follow the EN, AOAC, and original unbuffered methods…
  - …while we reduce waste?

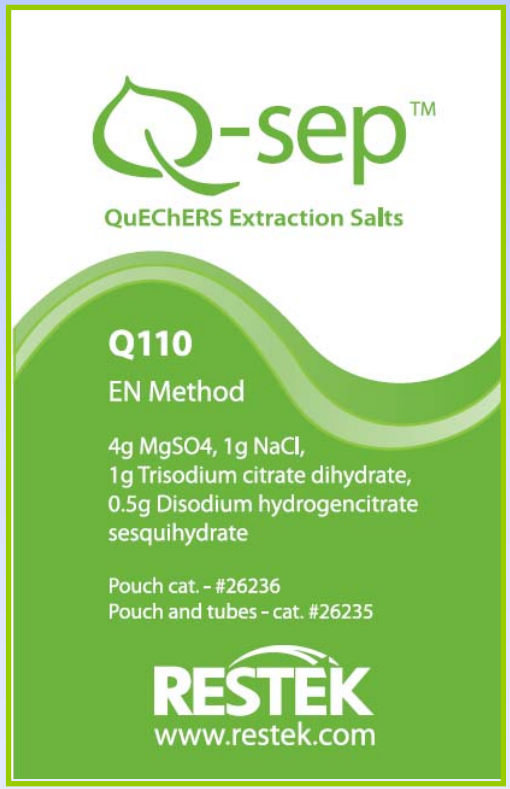
One tube, not two = “Greener” solution

“Packet” only packaging allows PTFE or FEP tube use

Vapor and moisture barrier protection



Salts do not clump in packets (problem for Agilent packets)



Q-sep Extraction Salt Packets

- Salts are poured from the packet into the tube.
- No wasted tube
- Packets can be purchased by themselves to be used with reusable tubes
- This has also allowed us to dramatically improve our price

Look how happy and productive these lab workers are!

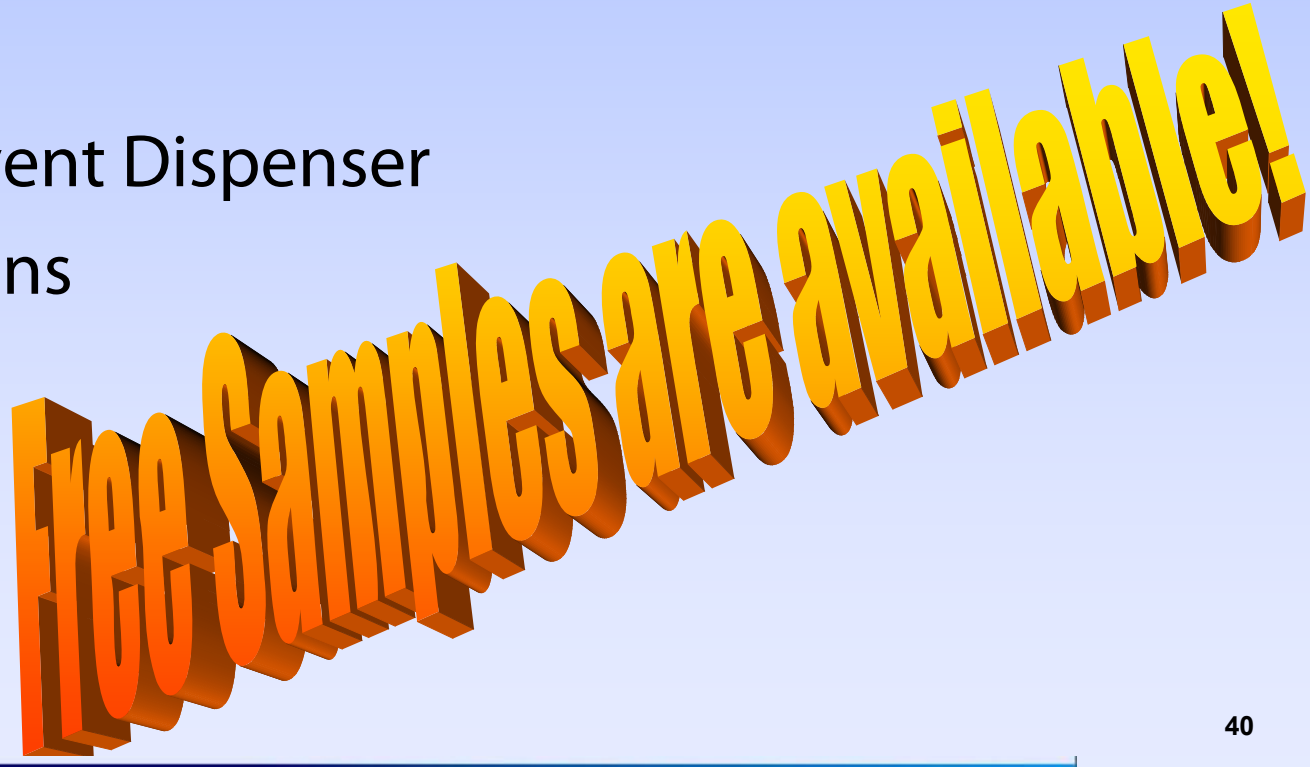
Product Offering

- EN and AOAC packets introduced in 2010
- Re-usable FEP tubes in January 2011
- Original unbuffered packets in May 2011

- Current Promotion - Buy one package of reusable FEP tubes, and ***get one box of salt packets free***.

Complete Line of QuEChERS Products

- Extraction Salts
- Empty Polypropylene and FEP Tubes
- 2mL and 15mL dSPE Tubes
- Tube Racks
- Bottle Top Solvent Dispenser
- GC & LC Columns
- Centrifuge
- Standards



Introducing NEW Q-sep™3000 Centrifuge for QuEChERS

- Meets AOAC and EU QuEChERS method requirements.
- Supports 50, 15, and 2 mL tubes.
- Small, bench-top footprint.
- Extremely price competitive.

Q-sep™ QuEChERS Pr

Featured Products

Q-sep™ 3000 Centrifuge

- First centrifuge specifically designed for QuEChERS methodolo
- Compact, quiet, yet powerful unit spins at 3000g force require the European method.

Products

QuEChERS Internal Standards and Quality Control Standards

- Single and multiple component standards as specified in EN Method 15662.
- Support for GC and HPLC with MS, MS/MS, and selective detectors.
- Ready to use for QuEChERS extractions—no dilutions necessary.

Products

QuEChERS Standards & Products

More Information About Restek Q-sep™ QuEChERS Products
Q-sep™ 3000 Centrifuge for QuEChERS
Q-sep™ QuEChERS Tubes for Pesticide Residue Analysis
QuEChERS Internal Standard Mix for GC/ECD Analysis
QuEChERS Internal Standard Mix for GC/MS Analysis
QuEChERS Internal Standard Mix for GC/NPD and LC/MS/MS Analysis
QuEChERS Internal Standard Mix for LC/MS/MS Analysis (nicarbazin)
QuEChERS Quality Control Standards for GC/MS Analysis
QuEChERS Single-Component Reference Standards

Complete reference materials support for European Standard 15662 QuEChERS method!

RESTEK Chromatography Products

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Please note: Restek will be closing at 3:30pm on May 20, while our employee-owners attend the ESOP shareholders meeting. Orders placed after 2:00pm will be processed Friday, May 21.

< Food, Flavor, and Fragrance Reference Standards < QuEChERS Standards & Products

QuEChERS Internal Standard Mix for GC/MS Analysis

Pesticide analysis is fast and simple using QuEChERS methods. Use these cost-effective QuEChERS standards for even greater lab efficiency. Standards are compatible with all major methods, including mini-multiresidue, AOAC, and European procedures. Save time with convenient mixes or make your own blend using our full line of single component solutions.

- Ready to use for QuEChERS extractions--no dilutions necessary.
- Support for GC and HPLC with MS, MS/MS, and selective detectors.

PCB 18 50µg/mL
PCB 28 50
PCB 52 50
triphenyl phosphate 20
tris-(1,3-dichloroisopropyl)phosphate 50
triphenylmethane 10

Chromatogram Datapack

Description	Conc. in Solvent/Volume	qty.	Cat.#	Price	Wish list	Cart
QuEChERS Internal Standard Mix for GC/MS Analysis	In acetonitrile, 5mL/ampul	ea.	33267	$30.00	☐	

Restek is currently only supplier.
Snap-and-shoot standard additions.

New QuEChERS Products in Development

- More dSPE products
- Vials
- Shaker
- More standards

Other Applications for QuEChERS

- Antibiotics in honey
- Pesticides in olives and olive oil
- Acrylamide in food
- Flukicides and anthelmintics in meat and milk
- Veterinary drugs in meat
- Pharmaceuticals in whole blood
- Pesticides in marijuana

Applications

- New Blog content regularly
- Restek.com/quechers
- Dietary Supplements
- Tylenol
- Cannabanoids
- Shellfish

Restek ChromaBLOGraphy

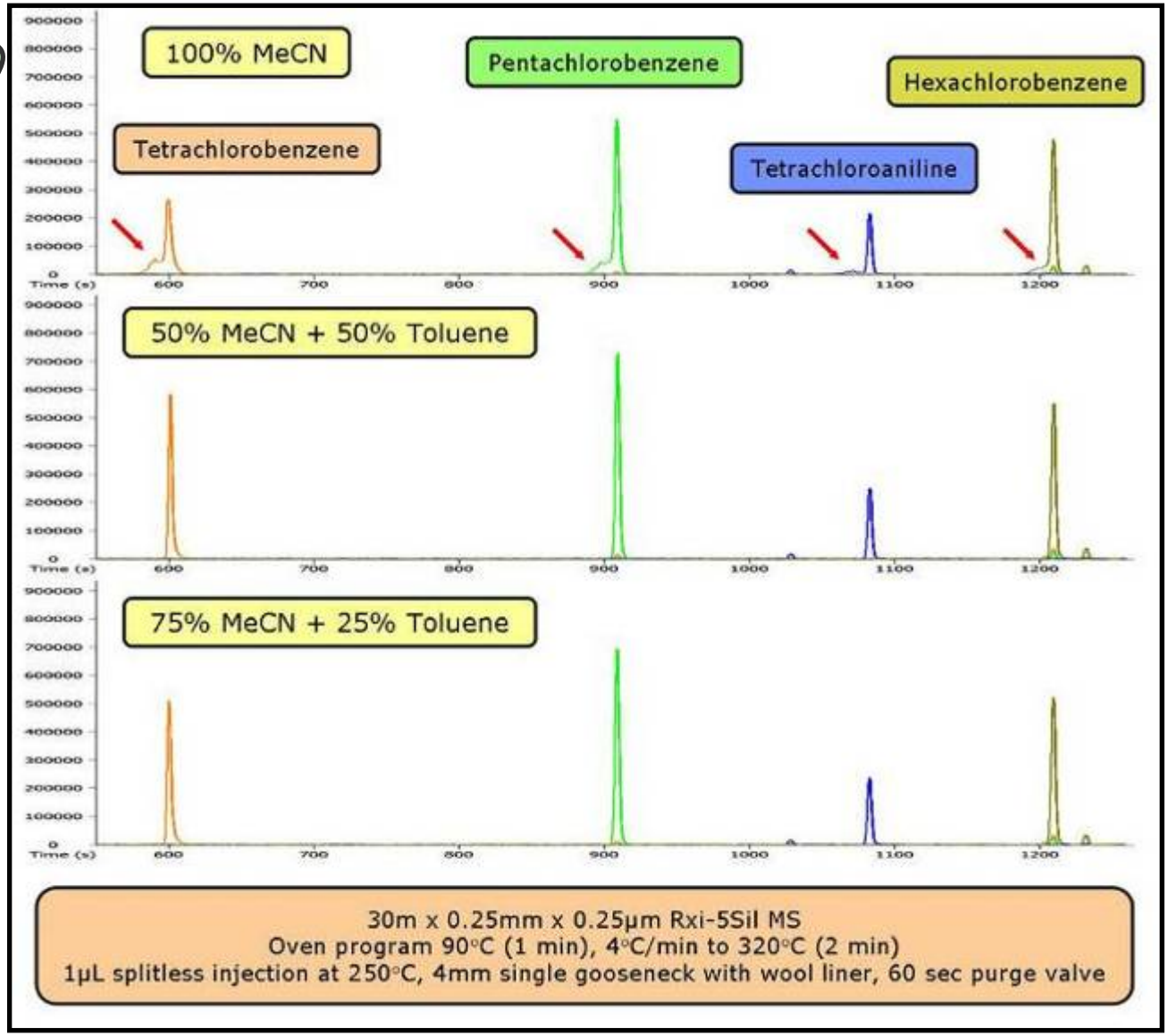
- Developed by Kent Rauch
  - Restek webmaster extraordinaire
- Posts from Restek Innovations staff
- Often contains pertinent (but unreleased) technical info
- Heavily food safety oriented
  - QuEChERS, pesticides, injection techniques
- Restek exclusive!

Information

not

available

elsewhere



RESTEK
Chromatography Products

Fast Screening of Recalled Tylenol® for Tribromoanisole and Related Adulterants

Using QuEChERS and GC-TOFMS

- Rapid sample preparation with QuEChERS improves turnaround time for emergency response analysis situations.
- Prepackaged QuEChERS extraction salts and snap-and-shoot standards reduce human error and save time.
- Rugged, inert, thermally stable Rxi®-5Sil MS column extends applicability to acids, bases, and higher molecular weight adulterants.

Introduction

The recent recall of Tylenol® pain reliever and other related products highlights the need for simple, quick sample preparation and a comprehensive analytical method for adulterants in consumer products. The rush to examine a multitude of samples in a short period of time is a common scenario for potential recalls, especially when a contaminant is found in a given product and rapid determinations need to be made to assess how widespread the problem may be.

The QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) sample preparation approach, originally developed to prepare fruit and vegetable samples for pesticide residue analysis, is being adopted for other applications and may be useful when rapid screening methods are required. QuEChERS employs a simple solvent shake and centrifugation step, with an optional dispersive solid phase extraction (dSPE) cleanup. In addition to being quick and easy, the use of acetonitrile in QuEChERS allows compounds containing a wide variety of chemical functionalities to be extracted, which is very important when trying to isolate an unknown adulterant. The resulting extract is appropriate for both GC/MS and LC/MS work.

The utility of the QuEChERS method is illustrated here using the aforementioned Tylenol® example, showing the applicability to this problem and, by extension, to others like it. This particular recall was due to the presence of 2,4,6-tribromoanisole (TBA) causing a musty smell in the product and, in some cases, nausea in the consumer [1]. TBA is a known breakdown product of 2,4,6-tribromophenol (TBP), which is a fumigant used on shipping pallets; TBA production occurs through a process actuated by a fungus, *Paecilomyces variotii* [2]. TBA is a common and undesirable odorant in the winemaking industry where

QuEChERS and Cartridge SPE Cleanup for Pesticides in Dietary Supplements

Michelle Misselwitz, Julie Kowalski, Jack Cochran, Jason Thomas, Rick Lake

Restek Corporation, Bellefonte, Pennsylvania

Sample Preparation of Cannabinoids in Urine Using the QuEChERS Method

Jack Cochran, Amanda Rigdon, Kristi Sellers

Restek Corporation, Bellefonte, Pennsylvania

American Academy of Forensic Sciences Annual Scientific Meeting 2009

Foods, Flavors & Fragrances

Comprehensive Pesticide Residue Analysis by LC/MS/MS

Using an Ultra Aqueous C18 Column

By Becky Wittig, Ph.D., Global HPLC Specialist, and Andrè Schreiber, Ph.D., Applied Biosystems/MDS Analytical Technologies

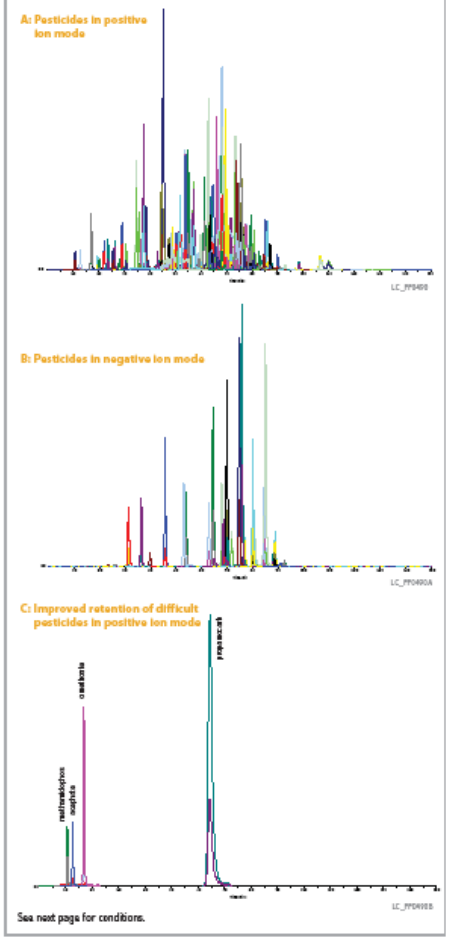
- Easily resolve and quantify more than 280 pesticide species.
- Use LC/MS/MS to reliably monitor difficult polar and/or thermally unstable species.
- Aqueous C18 phase offers optimal selectivity and retention.

Food safety is a topic of great interest globally. With recent contamination issues in a wide range of commodities, ensuring the quality of our food supply is becoming increasingly important. Pesticide residue content is one area of concern. While pesticides have typically been monitored by gas chromatography, polar and/or thermally unstable pesticides are difficult or impossible to monitor using this approach. Thus, traditional HPLC techniques are used for select pesticide classes, such as the carbamate and phenylurea pesticides.

With recent advances in LC/MS/MS instrumentation, this technique is quickly gaining acceptance for pesticide residue testing. LC/MS/MS can be used to simultaneously monitor hundreds of potential contaminants—including those difficult to detect by GC. Using both LC/MS/MS and GC approaches allows for a faster, more complete picture of pesticide residues. MS/MS technology also permits identification of the target pesticides through the selection of specific MRM transitions for each compound. For example, aldicarb, a carbamate pesticide, uses two MRM transitions of 208.2→89.1amu and 208.2→116.1amu.

While the MS/MS detector allows for specific, sensitive detection of the pesticide species, the LC separation is still important to ensure the highest quality data. Conventional C18 stationary phases are typically used for pesticide monitoring, but the selectivity and retention is poor for more polar species. In contrast, Ultra Aqueous C18 columns are ideal for multi-pesticide residue monitoring methods. In Figure 1, the analysis of more than 280 pesticides using the 3µm Ultra Aqueous C18 is shown. Optimized stationary phase selectivity

Figure 1 More than 280 pesticide residues—including difficult polar species—show excellent peak shape and retention on a 3µm Ultra Aqueous C18 column.



See next page for conditions.

Conditions for Figure 1 (previous page):

Sample:	multicomponent pesticide standard
Inj.:	10µL
Conc.:	1ppb each pesticide
Sample diluent:	acetonitrile
Column:	Ultra Aqueous C18
Cat. #:	917831Z:
Dimensions:	100mm x 2.1mm
Particle size:	3µm
Pore size:	100Å
Conditions:	
Instrument:	Shimadzu Prominence® UFLCxr
Mobile phase:	A: 10 mM NH_4OAc in water B: 10 mM NH_4OAc in methanol

Time (min.)	%B
0.0	20
8.0	90
12.0	100
14.8	100
14.9	20

Flow:	500µL/min
Temp.:	25°C
Det.:	Applied Biosystems 4000 QTRAP® LC/MS/MS system
Ion Source:	TurboIonSpray® A & C: ESI+ B: ESI-
IonSpray Voltage:	5kV (ESI+), -4.2kV (ESI-)
Gas 1:	50psi
Gas 2:	60psi
Source Temp.:	600°C

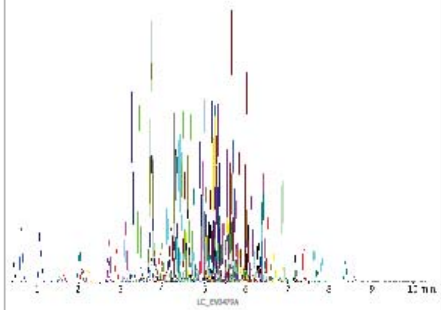
Table I Peak list for pesticides in negative ion mode.

Compound ID	Retention Time (min)	Transition 1	Transition 2
Acrinathrin	9.09	540 → 372	540 → 372
Chlorfluazuron	9.24	539.9 → 356.8	539.9 → 356.8
Clothianidin	3.63	249.9 → 58	247.9 → 59
Diflubenzuron	7.68	309 → 156.1	310 → 288.9
Diuron	6.78	230.9 → 185.8	230.9 → 149.8
Fluazuron	7.99	462.5 → 435.8	462.5 → 397.9
Fludioxonil	6.93	246.9 → 179.9	246.9 → 125.9
Forchlorfenuron	6.44	246 → 126.9	246 → 91.2
Hexaflumuron	8.45	459 → 438.8	459 → 174.9
Imibenconazol	8.82	409 → 250.9	411 → 253
Lufenuron	8.87	509 → 325.9	509 → 175
Metaflumizon	8.5	505.1 → 303.9	505.1 → 340.9
Metamitron	3.97	203 → 184.8	203 → 116.9
Methoxyfenozid	6.98	366.9 → 104.9	366.9 → 148.9
Nitenpyram	2.59	269.2 → 223.6	269.2 → 100.8
Novaluron	8.42	491.1 → 470.7	493.1 → 472.7
Profoxydim	7.57	464.3 → 277.9	464.3 → 126.8
Propoxycarbazon	3.09	396.9 → 156	396.9 → 112.9
Prothioconazol	7.16	342 → 100.1	343.9 → 99.9
Tebufenozid	7.46	350.9 → 149	350.9 → 105
Teflubenzuron	8.85	378.6 → 338.8	378.6 → 195.9
Topralcopdim	4.57	340 → 248	340 → 220.1
Torbacil	5.38	214.9 → 158.9	216.9 → 160.9
Trallcopdim	6.28	328.1 → 253.8	328.1 → 283.8
Triadimefon	7.01	292 → 67.9	292 → 234.9
Triflumuron	8	356.9 → 153.8	358.9 → 155.9

allows for an even distribution of the compounds throughout the retention time window (Tables I and II). As well, retention of more polar pesticides is greatly improved, as demonstrated in Figure 1C. The Ultra Aqueous C18 column, in a 100 x 2.1mm, 3µm configuration is the column of choice for LC/MS/MS pesticide monitoring methods.

Ultra-high pressure LC (UHPLC) can also be used with MS/MS detection for monitoring pesticide residues. UHPLC allows for higher sample throughput when used in conjunction with a highly efficient <2µm particle size column. The 1.9µm Pinnacle® DB Aqueous C18, in a 50 x 2.1mm configuration, is ideally suited for this application, as shown in Figure 2.

Figure 2 Higher sample throughput can be achieved using UHPLC and MS/MS with a 1.9µm Pinnacle® DB Aqueous C18 column.



Compounds analyzed are a subset of those in Figure 1; data are shown for a qualitative overall run time comparison only.

Sample:	multicomponent pesticide standard
Inj.:	5µL
Conc.:	33.3ppb each pesticide
Sample diluent:	acetonitrile
Column:	Pinnacle® DB Aqueous C18
Cat. #:	9412252:
Dimensions:	50mm x 2.1mm
Particle size:	1.9µm
Pore size:	140Å

Conditions:	
Mobile phase:	A: 10mM NH_4OAc in water B: 10mM NH_4OAc in methanol

Time (min.)	%B
0.0	10
1.0	10
8.0	90
10.0	90
11.0	10

Flow:	600µL/min.
Temp.:	35°C
Instrument:	Shimadzu Prominence® UFLCxr
Det.:	Applied Biosystems 4000 QTRAP® LC/MS/MS system
	Ion Source: TurboIonSpray®, ESI+
	IonSpray Voltage, ESI voltage: 5kV (ESI+)
	Gas 1: 40psi
	Gas 2: 60psi
	Source Temp.: 500°C; max pressure ~7,200psi

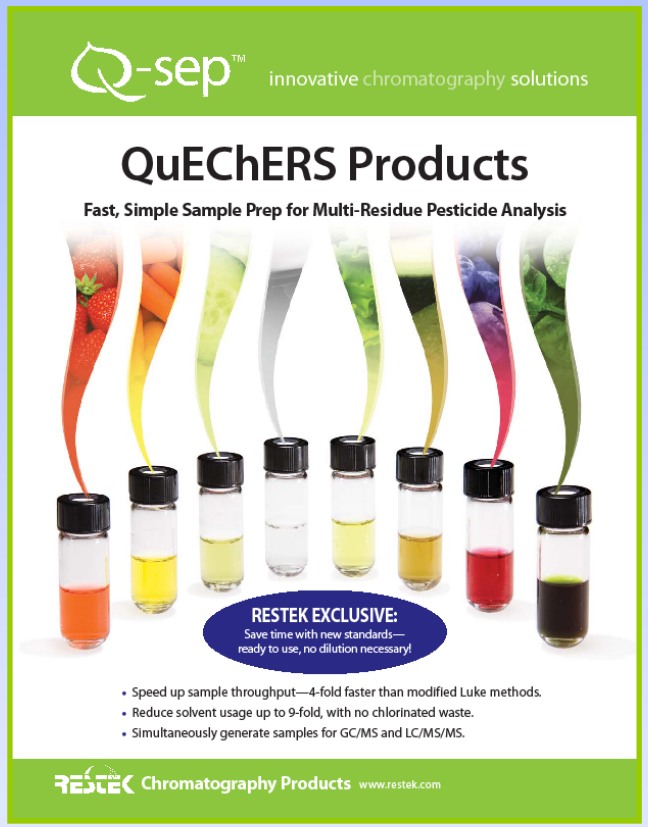
Using LC/MS/MS technology and Aqueous C18 columns, in combination with gas chromatography, results in the most comprehensive monitoring of pesticide residues. Labs interested in more complete multi-residue analysis of pesticides in food matrices, including difficult polar or thermally unstable compounds, should consider adding LC/MS/MS and Aqueous C18 columns to routine testing procedures. The Aqueous C18 phase is also available on 1.9µm Pinnacle® DB silica for UHPLC platforms.

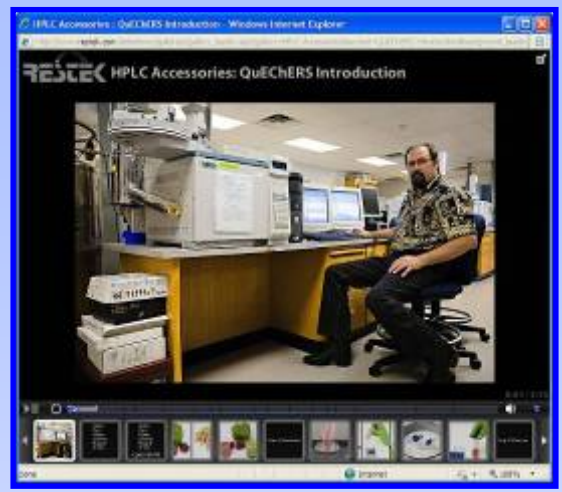
Acknowledgements

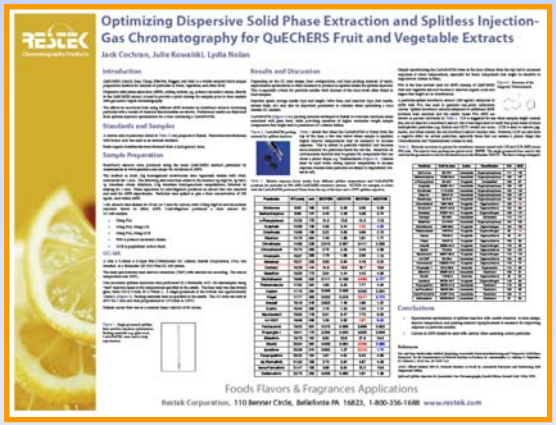
The authors wish to thank the US FDA for their collaboration and recognize the participation of multiple FDA labs in this work.

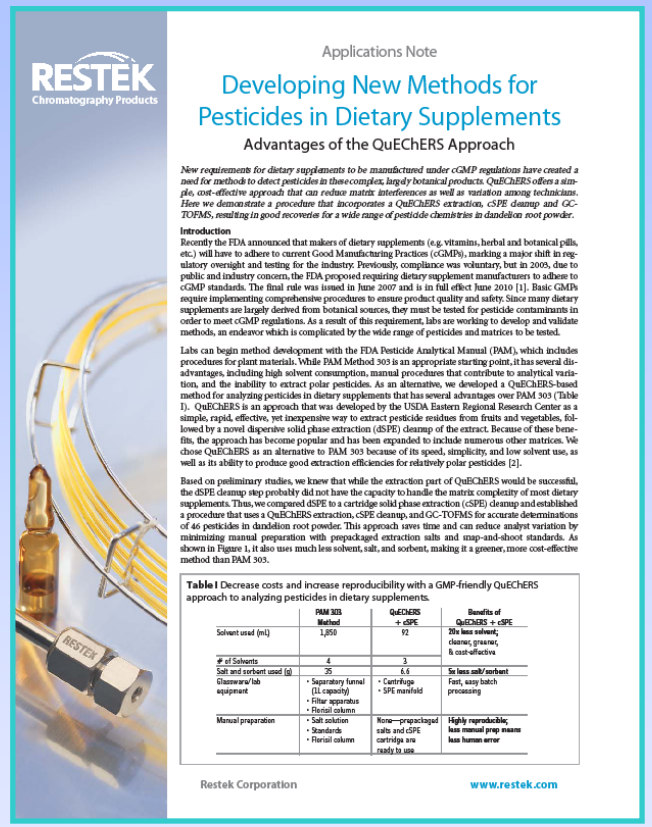
Restek.com/quechers

Restek Technical Information Available at restek.com
Food, Flavors, and Fragrances





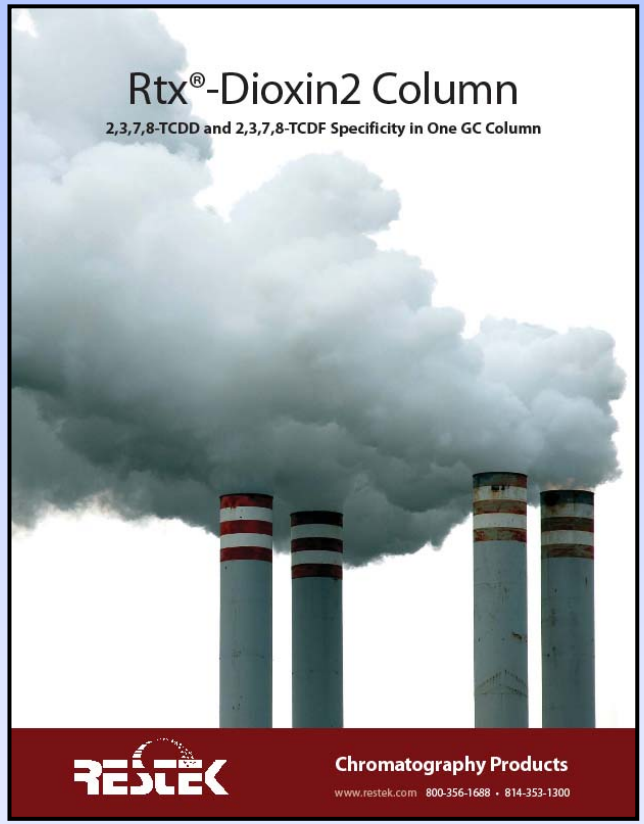




Application notes, chromatograms, flyers, mini-catalogs, tear sheets, technical guides, audio slideshows, bibliographies, web links, instruction sheets, presentations

Chlorinated Dioxins and Furans in Food
Restek GC Selectivity Solutions

- Determine 2378- TCDD and TCDF in one GC run
  - Rxi-5Sil MS (60m x 0.25mm x 0.25µm)
    - Primary column
    - Also does 12378 penta dioxin (very toxic)
  - Rtx-Dioxin2 (60m x 0.25mm x 0.25µm)
    - Secondary column for TCDF confirmation
- Customer already using DB-5MS
  - Selectivity equivalent to Rxi-5Sil MS
  - Rxi-5Sil MS is more inert, lower-bleed
- Rtx-Dioxin2 is a Restek exclusive!
  - Fully characterized for all 136 Cl_4 to Cl_8 chlorinated dioxins and furans



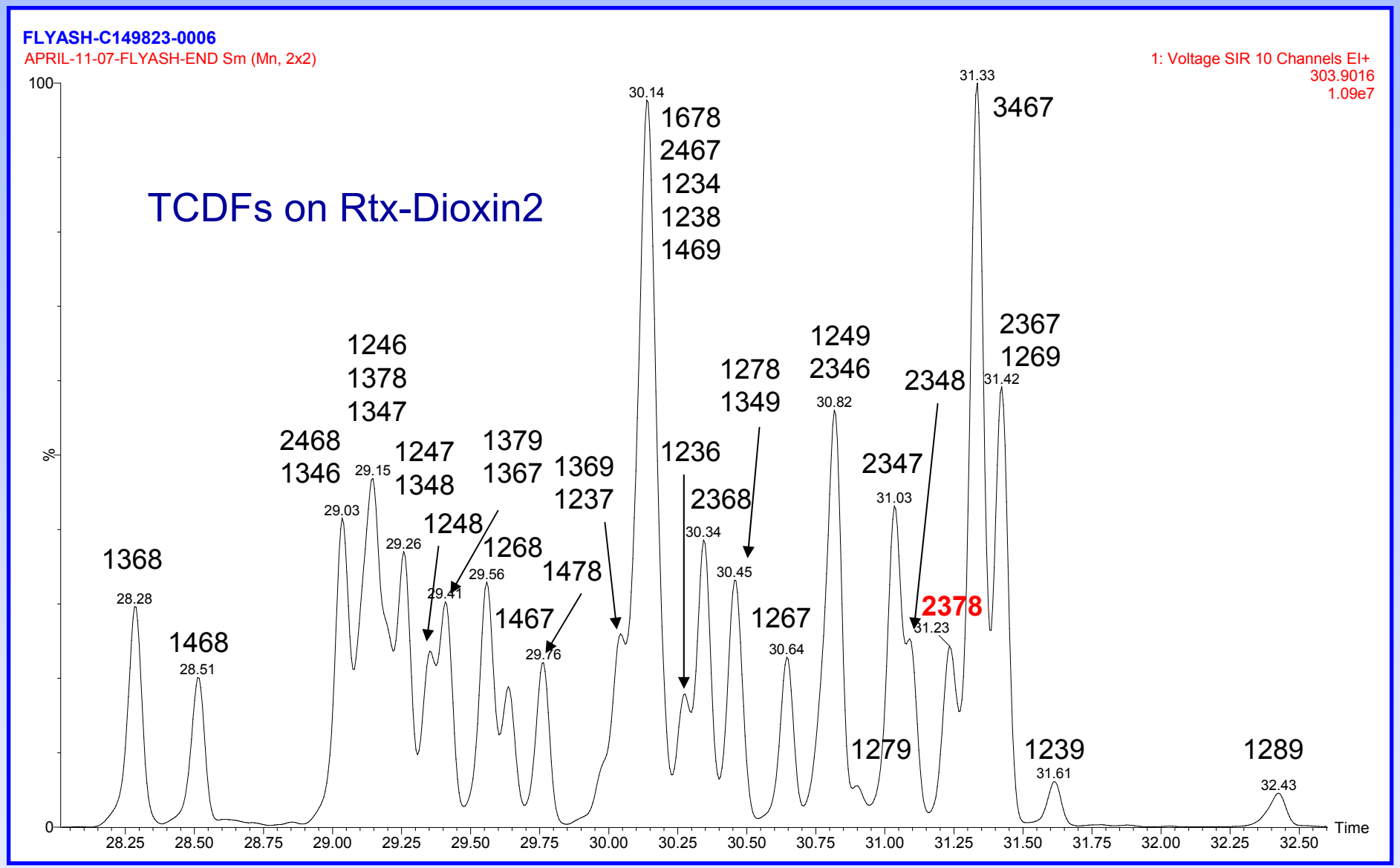
USPs for Restek Rxi-5Sil MS GC Column for Chlorinated Dioxins and Furans

- Replacement for DB-5
  - Specified in EPA Methods 1613 and 8290a
  - Primary column, but coelution on 2378 TCDF
- Rxi-5Sil MS separates 2378 TCDD and TCDF
- Rxi-5Sil MS separates 12378 PnCDD
- Rxi-5Sil MS is more inert and has lower bleed than DB-5

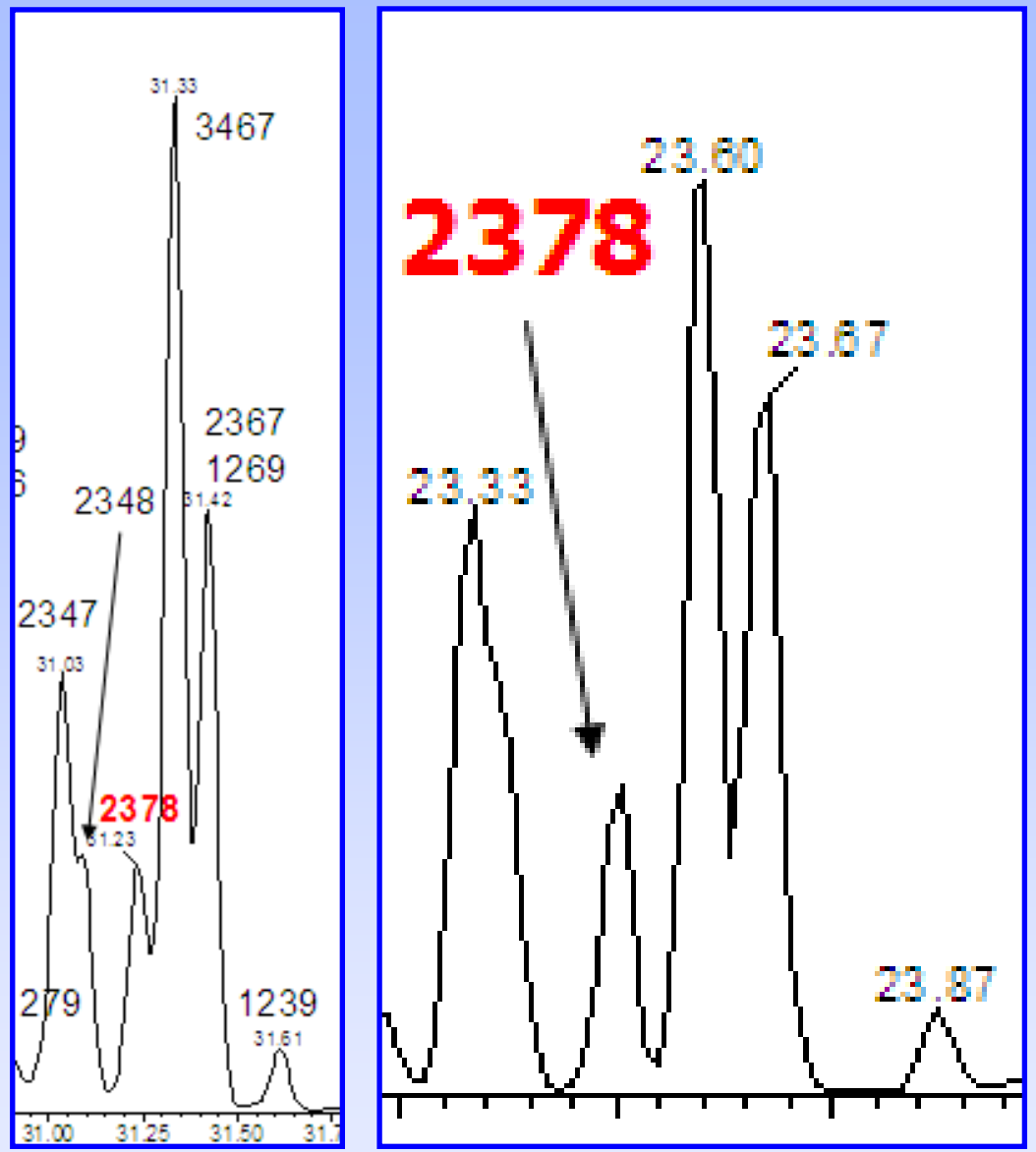
Rxi-5Sil MS has equivalent selectivity to DB-5MS and other “5” silphenylene columns.

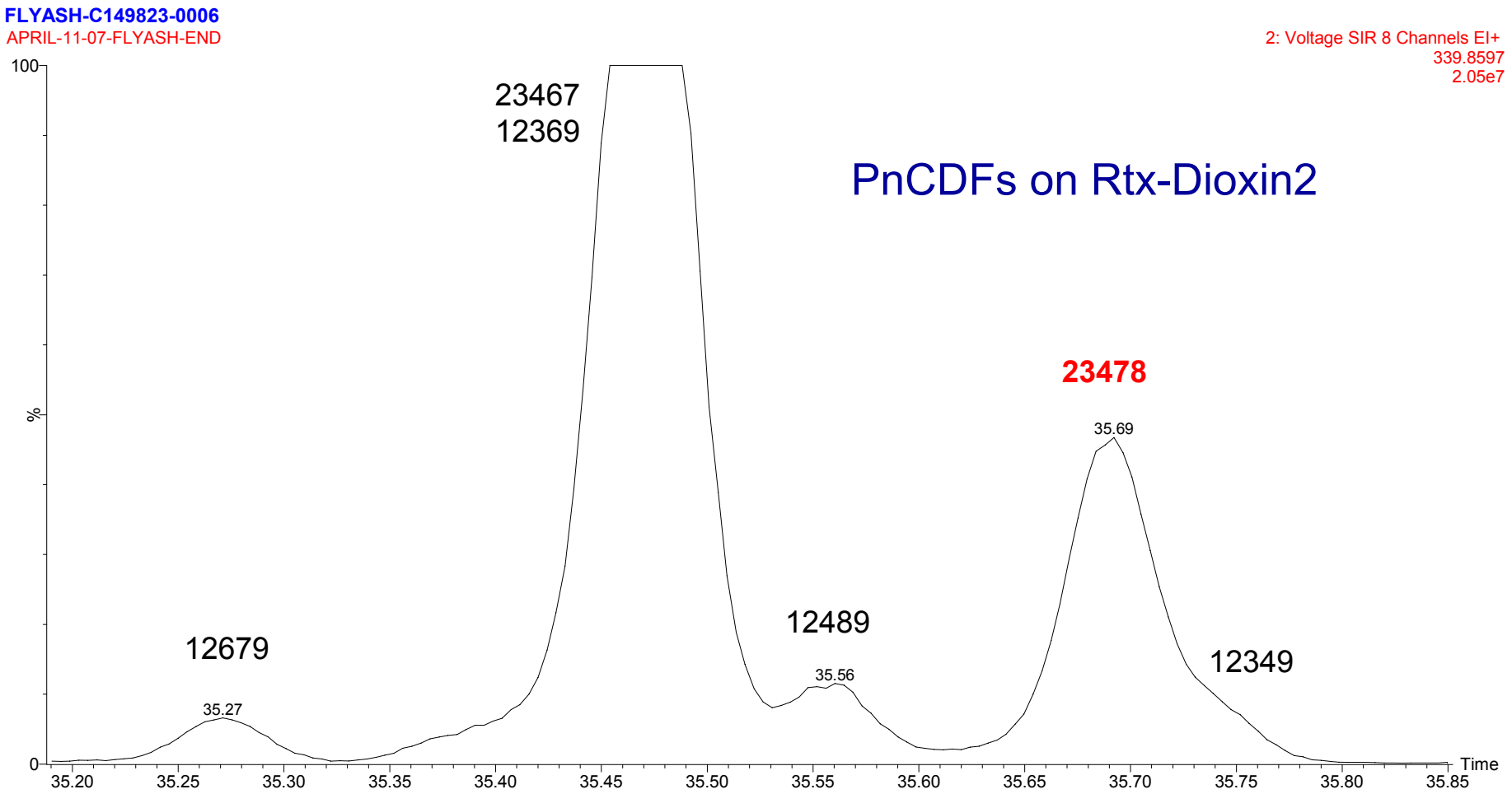
USPs for Restek Rtx-Dioxin2 GC Column

- Replacement for DB-225, SP-2330/2331
  - Used for 2378 TCDF confirmation
  - High cyano content puts max temps at 220-270
- Rtx-Dioxin2 separates 2378 TCDF
- Rtx-Dioxin2 has high max temp of 340°C
- Rtx-Dioxin2 partially separates 23478 PnCDF
  - Sometimes an important congener
- Rtx-Dioxin2 is a Restek exclusive



- 2378 TCDF in fly ash on Rtx-Dioxin2 under different GC conditions
- Flow and temperature program optimization can improve separations





Dioxin contamination scandal hits Belgium

1999

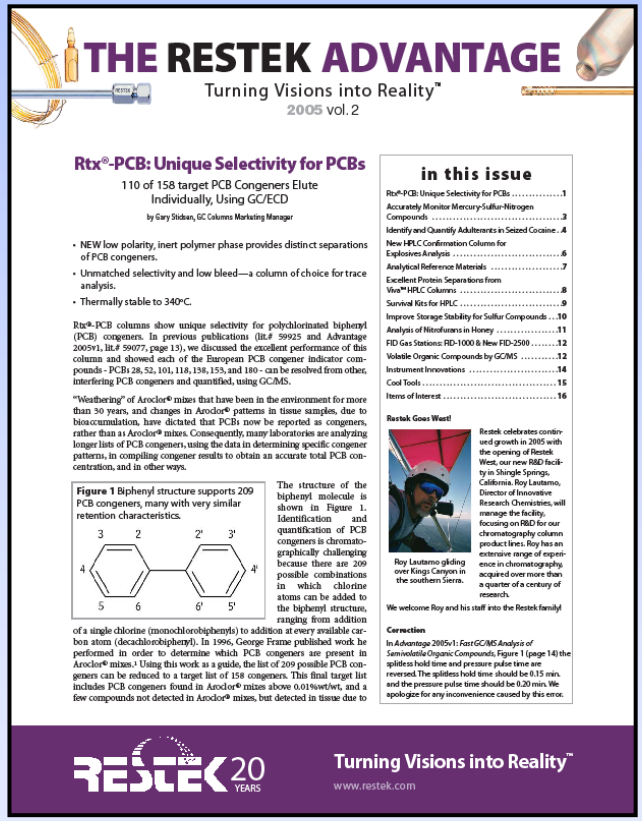
Effects spread through European Union and beyond

By Richard Tyler
8 June 1999

Farms in Belgium have been ordered to destroy livestock that were given animal feeds believed to be contaminated with dioxin, a serious carcinogen. The European Union has ordered a complete ban on Belgian agricultural exports of eggs, chickens, pork and beef. All chickens and eggs exported after January 15 have been ordered destroyed and this may be widened to include pigs, cattle and other foods containing possibly tainted ingredients.

Polychlorinated Biphenyls in Food

- Do you need to do congener-specific PCB analyses in fish or other animal tissues?
- Do you need European indicator congener separations?
  - 31/28, 153/132, 163/138
- Rtx-PCB is a Restek exclusive!
  - Separates difficult congeners
  - Elution orders for all 209 PCBs
  - Excellent when combined with MS



THE RESTEK ADVANTAGE

Turning Visions into Reality™

2005 vol. 2

Rtx®-PCB: Unique Selectivity for PCBs

110 of 158 target PCB Congeners Elute Individually, Using GC/ECD

by Gary Stidsen, GC Columns Marketing Manager

- NEW low polarity, inert polymer phase provides distinct separations of PCB congeners.
- Unmatched selectivity and low bleed—a column of choice for trace analysis.
- Thermally stable to 340°C.

Rtx®-PCB columns show unique selectivity for polychlorinated biphenyl (PCB) congeners. In previous publications (lit.# 59925 and Advantage 2005v1, lit.# 59077, page 13), we discussed the excellent performance of this column and showed each of the European PCB congener indicator compounds - PCBs 28, 52, 101, 118, 138, 153, and 180 - can be resolved from other, interfering PCB congeners and quantified, using GC/MS.

"Weathering" of Aroclor® mixes that have been in the environment for more than 50 years, and changes in Aroclor® patterns in tissue samples, due to bioaccumulation, have dictated that PCBs now be reported as congeners, rather than as Aroclor® mixes. Consequently, many laboratories are analyzing longer lists of PCB congeners, using the data in determining specific congener patterns, in compiling congener results to obtain an accurate total PCB concentration, and in other ways.

Figure 1 Biphenyl structure supports 209 PCB congeners, many with very similar retention characteristics.

The structure of the biphenyl molecule is shown in Figure 1. Identification and quantification of PCB congeners is chromatographically challenging because there are 209 possible combinations in which chlorine atoms can be added to the biphenyl structure, ranging from addition of a single chlorine (monochlorobiphenyls) to addition at every available carbon atom (decachlorobiphenyl). In 1996, George Frame published work he performed in order to determine which PCB congeners are present in Aroclor® mixes.[1] Using this work as a guide, the list of 209 possible PCB congeners can be reduced to a target list of 158 congeners. This final target list includes PCB congeners found in Aroclor® mixes above 0.01%wt/wt, and a few compounds not detected in Aroclor® mixes, but detected in tissue due to

in this issue

Restek Goes West!

Roy Lautamo gliding over Kings Canyon in the southern Sierra.

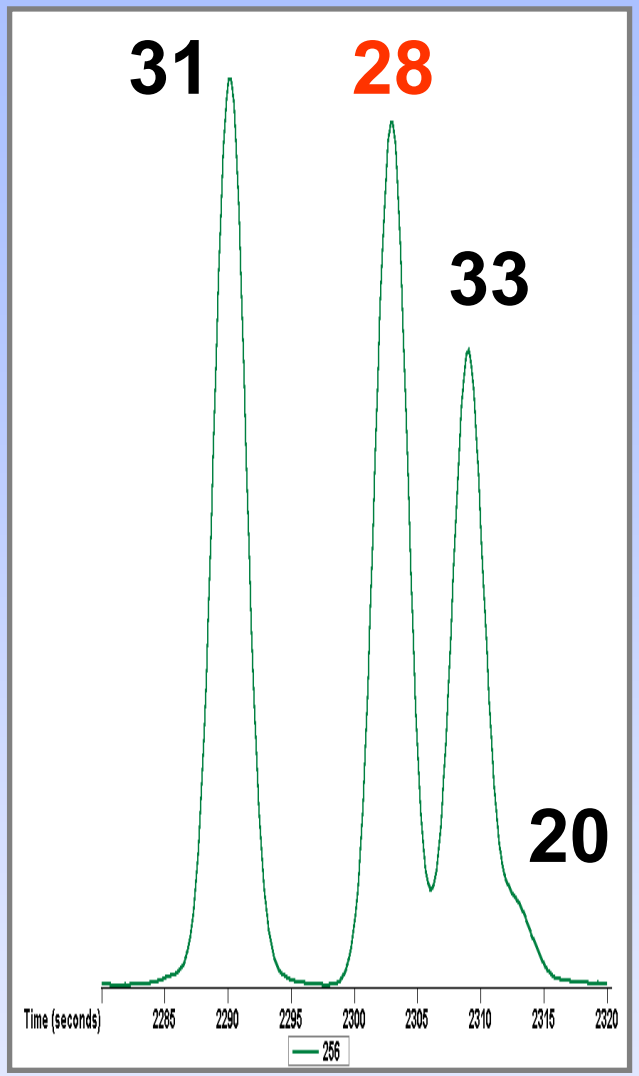
Restek celebrates continued growth in 2005 with the opening of Restek West, our new R&D facility in Shingle Springs, California. Roy Lautamo, Director of Innovative Research Chemistries, will manage the facility, focusing on R&D for our chromatography column product lines. Roy has an extensive range of experience in chromatography, acquired over more than a quarter of a century of research.

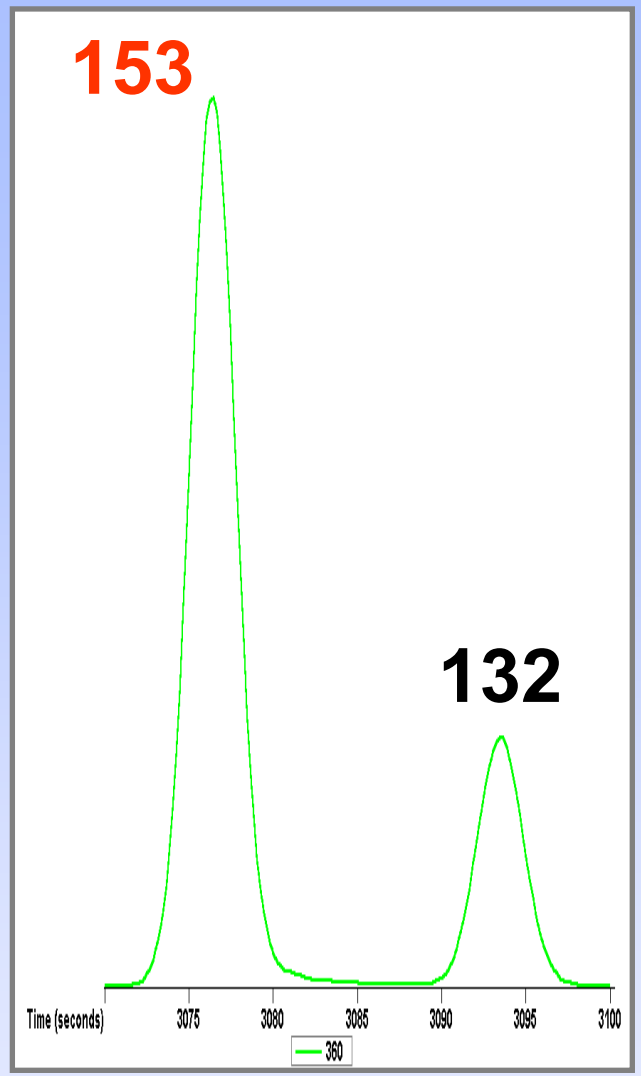
We welcome Roy and his staff into the Restek family!

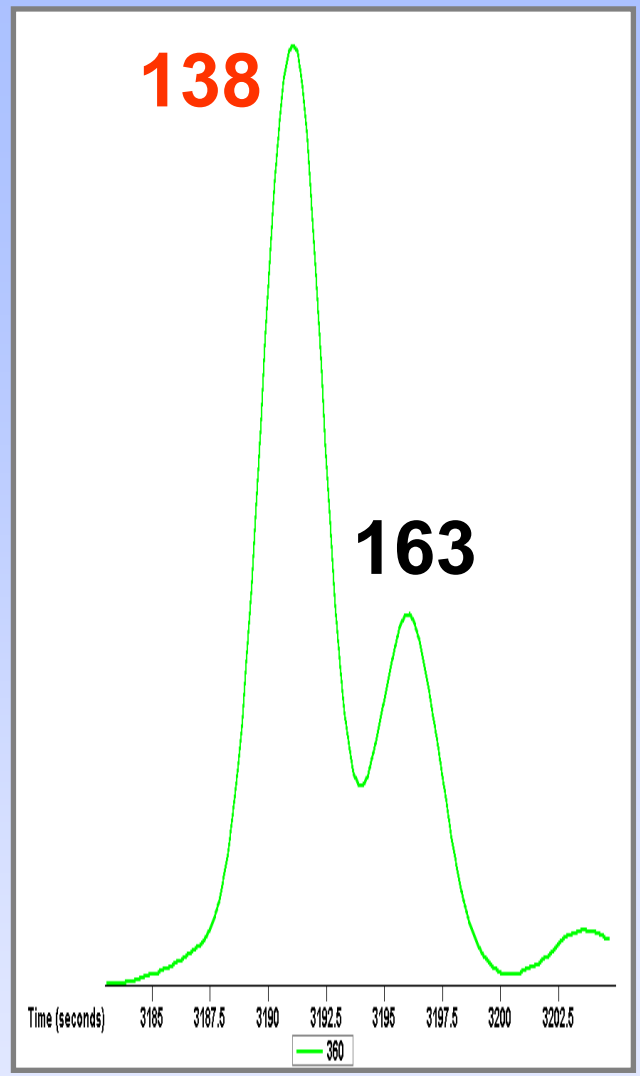
Correction

In *Advantage* 2005v1: *Fast GC/MS Analysis of Semivolatile Organic Compounds*, Figure 1 (page 14) the splitless hold time and pressure pulse time are reversed. The splitless hold time should be 0.15 min. and the pressure pulse time should be 0.20 min. We apologize for any inconvenience caused by this error.

RESTEK 20 YEARS Turning Visions into Reality™ www.restek.com







European Indicator PCB Congeners Separated on Rtx-PCB

USPs for Restek Rtx-PCB GC Column

- Replacement for 5 and 5Sil columns, etc.
  - Do not separate European congeners
  - Especially 31/28, 153/132, and 163/138
- Rtx-PCB separates EU indicator PCBs
  - When used with MS
- Rtx-PCB is a Restek exclusive
- Watch for SGE HT8 and J&W DB-XLB
  - Restek has Rxi-XLB

European Food Safety Authority

The EFSA Journal (2008) 724, 1-114

Polycyclic Aromatic Hydrocarbons in Food[1]

Scientific Opinion of the Panel on Contaminants in the Food Chain

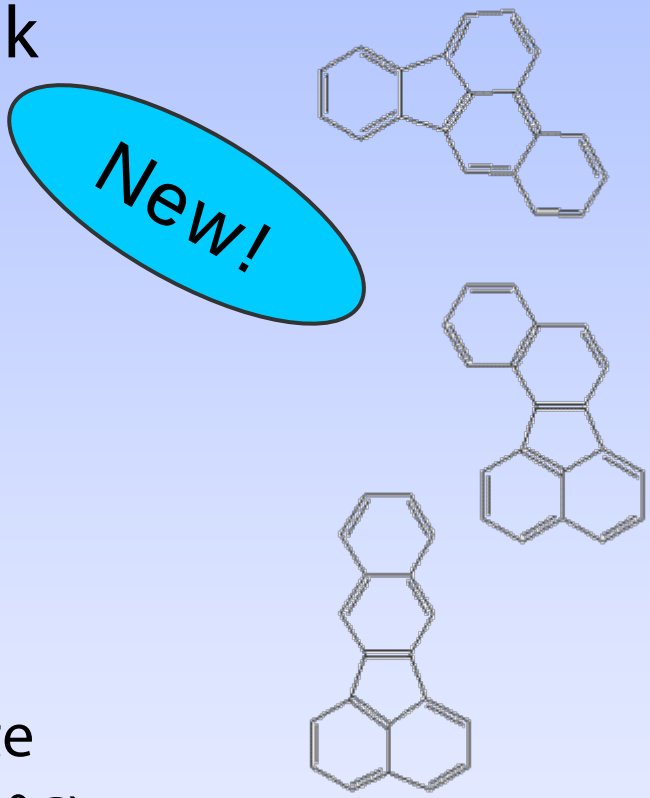
(Question N° EFSA-Q-2007-136)

Adopted on 9 June 2008

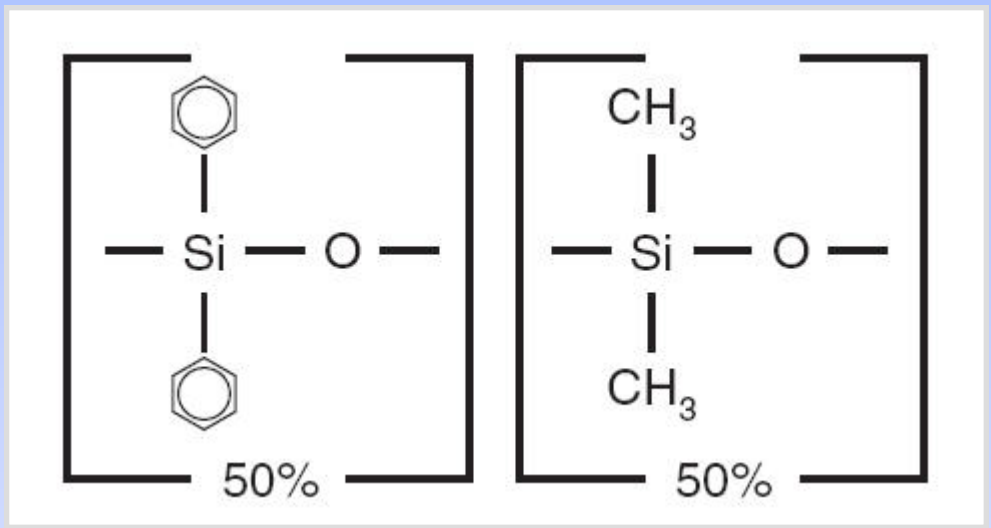
benzo(a)anthracene; benzo(b)fluoranthene; benzo(j)fluoranthene; benzo(k)fluoranthene; benzo(ghi)perylene; benzo(a)pyrene; chrysene; dibenz(a,h)anthracene; dibenzo(a,e)pyrene; dibenzo(a,h)pyrene; dibenzo(a,f)pyrene; dibenzo(a,l)pyrene; 5-methylchrysene

GC Selectivity Questions Polycyclic Aromatic Hydrocarbons

- Need to separate benzo b, j, and k fluoranthenes?
  - Rxi-17Sil MS (50% diphenyl type)
- Need to separate chrysene and triphenylene?
  - Rxi-XLB (close elution though)
- Rt-PAH? (liquid crystal)
  - Separates chrysene, triphenylene
  - Benzo b and j fluoranthenes coelute
  - Narrow temperature range (80-285°C)

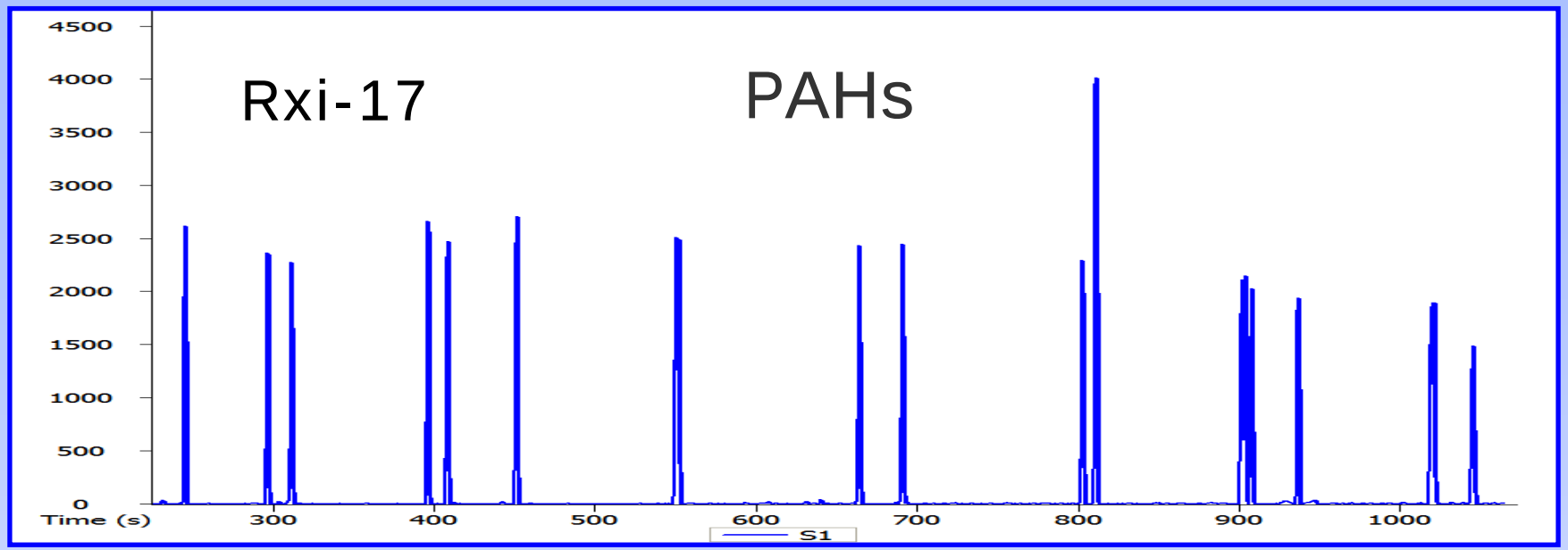


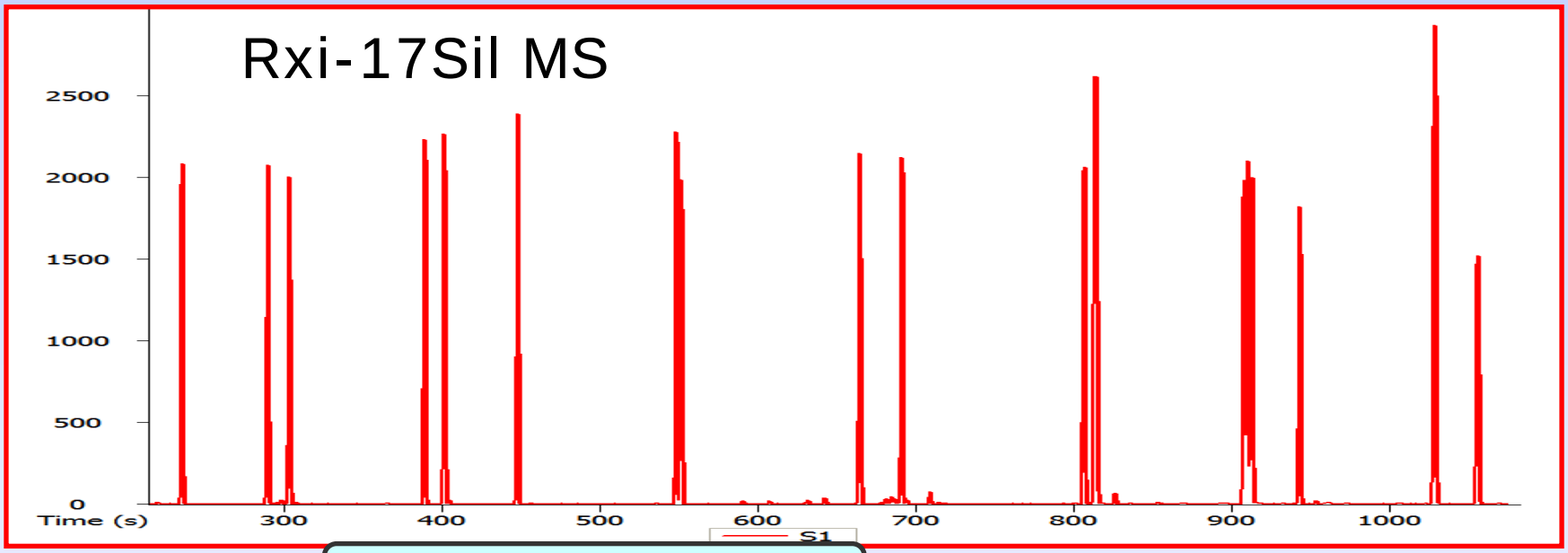
Rxi-17

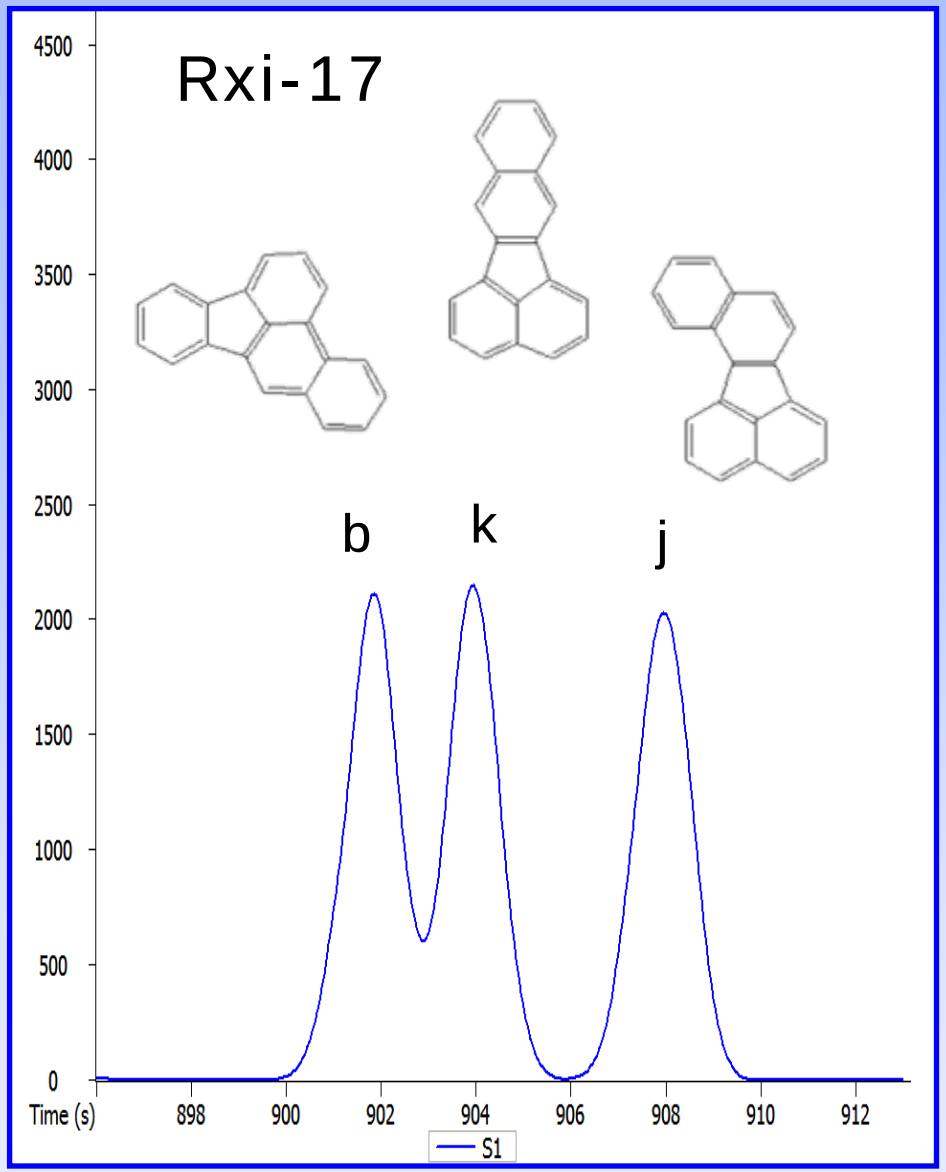


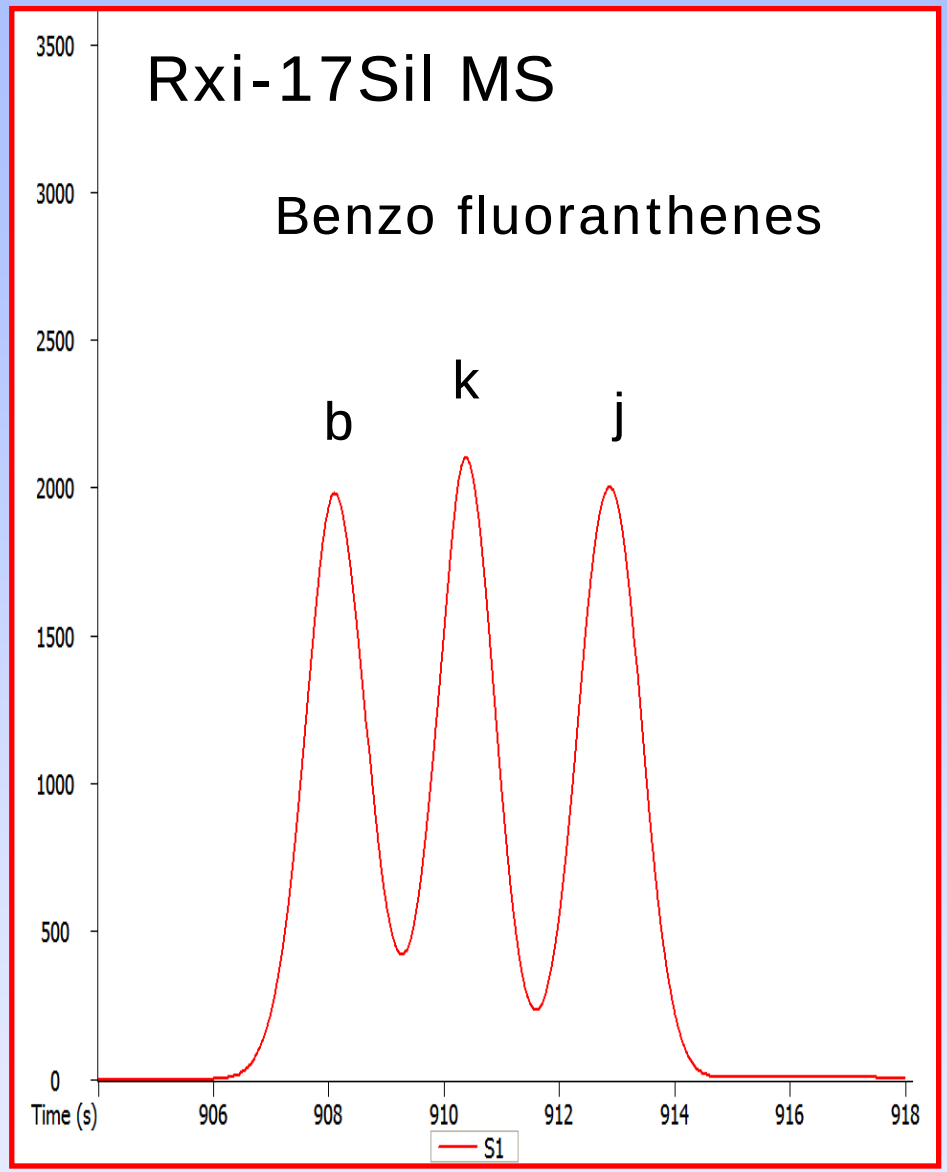
Structure not shown

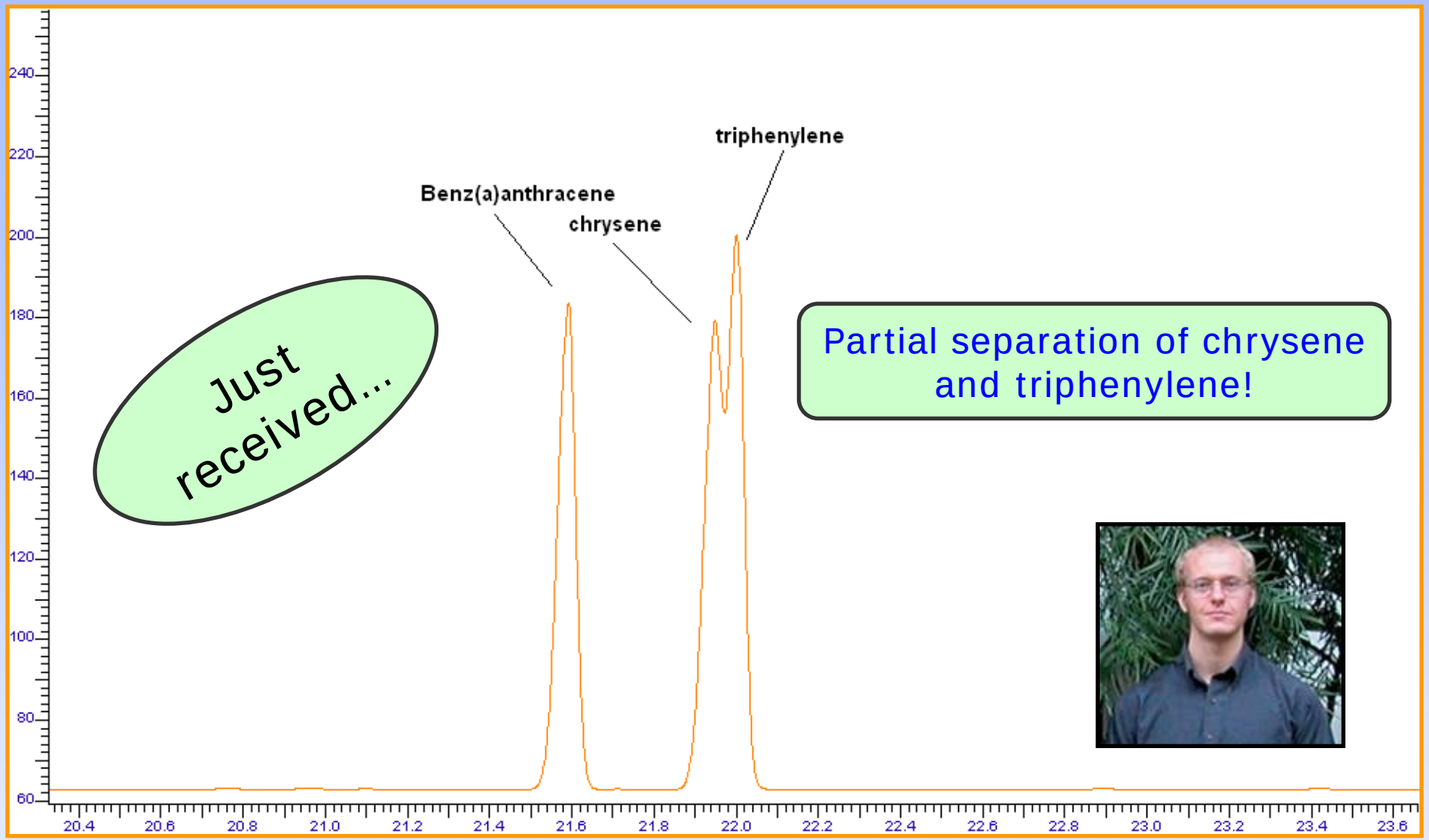
Rxi-17Sil MS: an arylene-based polymer with 50% diphenyl selectivity



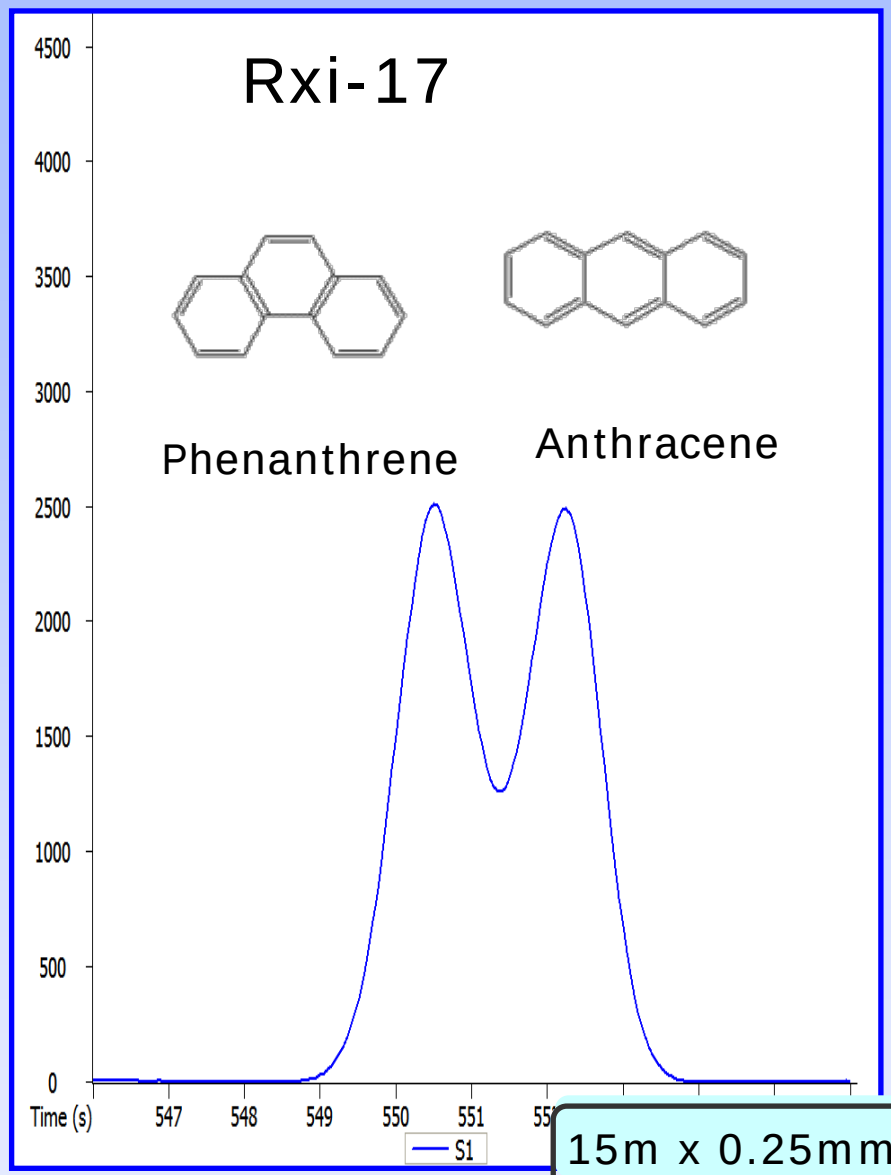


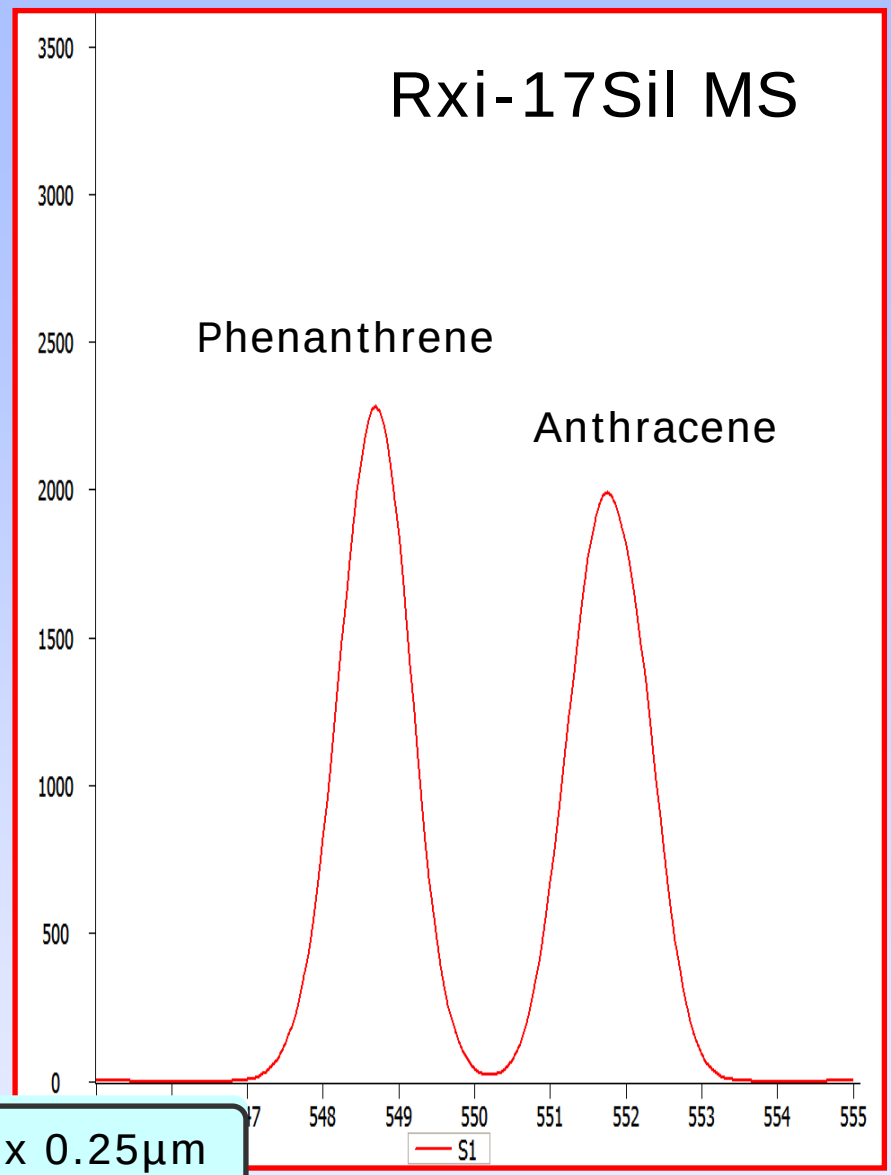






30m x 0.25mm x 0.25µm Rxi-17Sil MS





15m x 0.25mm x 0.25µm

USPs for Restek Rxi-17Sil MS GC Column

- Rxi-17Sil MS is a low-bleed analog of Rxi-17
  - Maximum operating temperature of 360°C
  - Similar, but not exact, selectivity to Rxi-17
- Rxi-17Sil MS separates benzo b,k, and j fluoranthenes
- Rxi-17Sil MS partially separates chrysene and triphenylene
- Watch for Agilent DB-EUPAH and Varian Select PAH

HPLC of PAHs

Peak List:	Retention Time
1. naphthalene	6.19
2. acenaphthylene	7.16
3. 1-methylnaphthalene	7.78
4. 2-methylnaphthalene	8.17
5. acenaphthene	8.46
6. fluorene	8.82
7. phenanthrene	9.64
8. anthracene	10.39
9. fluoranthene	11.22
10. pyrene	11.75
11. benzo(a)anthracene	13.55
12. chrysene	13.91
13. benzo(j)fluoranthene	14.92
14. benzo(b)fluoranthene	15.27
15. benzo(k)fluoranthene	15.82
16. benzo(a)pyrene	16.35
17. dibenzo(a,h)anthracene	17.10
18. benzo(ghi)perylene	17.67
19. indeno(1,2,3-cd)pyrene	17.99

- Pinnacle II PAH
  - Restek exclusive!
  - Shape selective

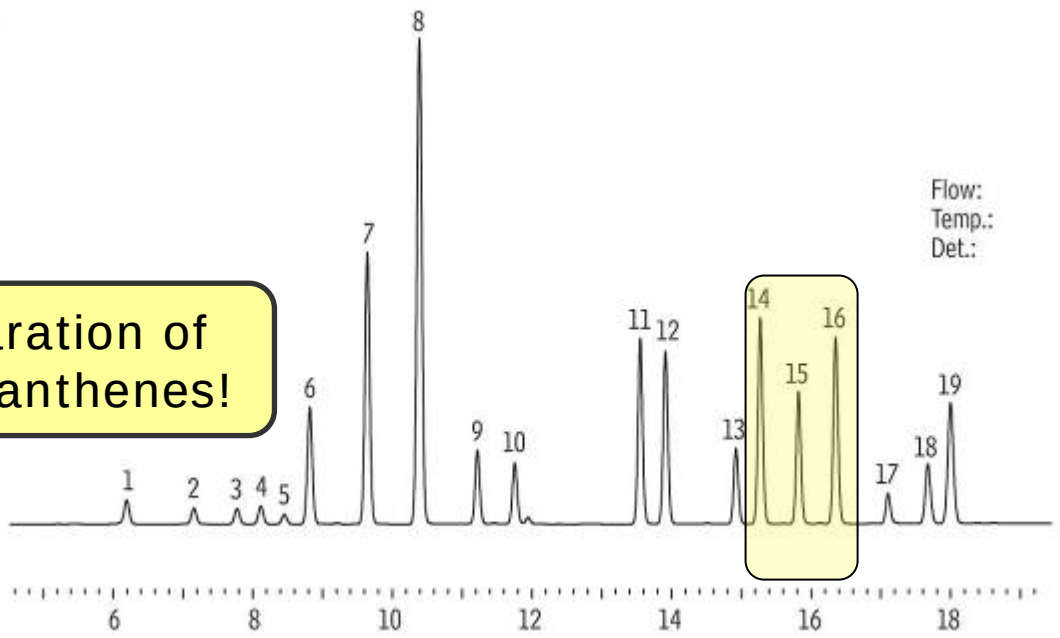
Sample:
Inj.: 10µL
Conc.: 20µg/mL each component
Sample diluent: acetonitrile

Column: Pinnacle® II PAH
Cat.#: 9219463
Dimensions: 150mm x 3.2mm
Particle size: 4µm
Pore size: 110Å

Conditions:
Instrument: Shimadzu Prominence HPLC
Mobile phase: A: purified water
B: acetonitrile

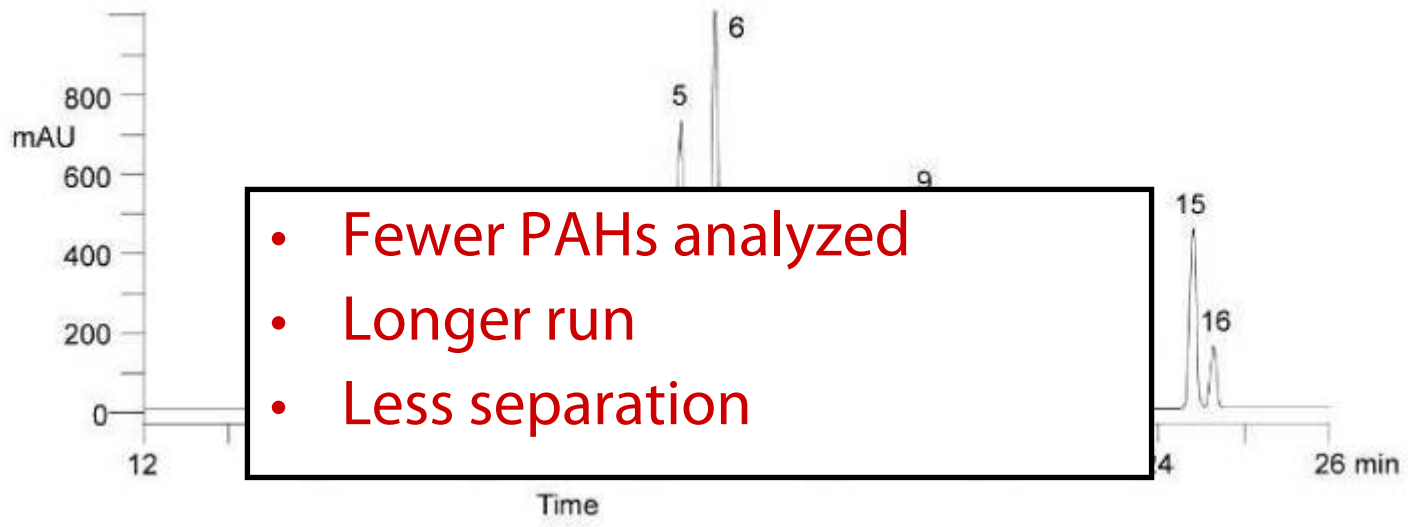
Time (min.)	%B
0	40
7	60
16	100
18.9	100
19	40

Flow: 1.2mL/min.
Temp.: 30°C
Det.: UV @ 254nm



Good separation of benzo fluoranthenes!

Competitor HPLC of PAHs



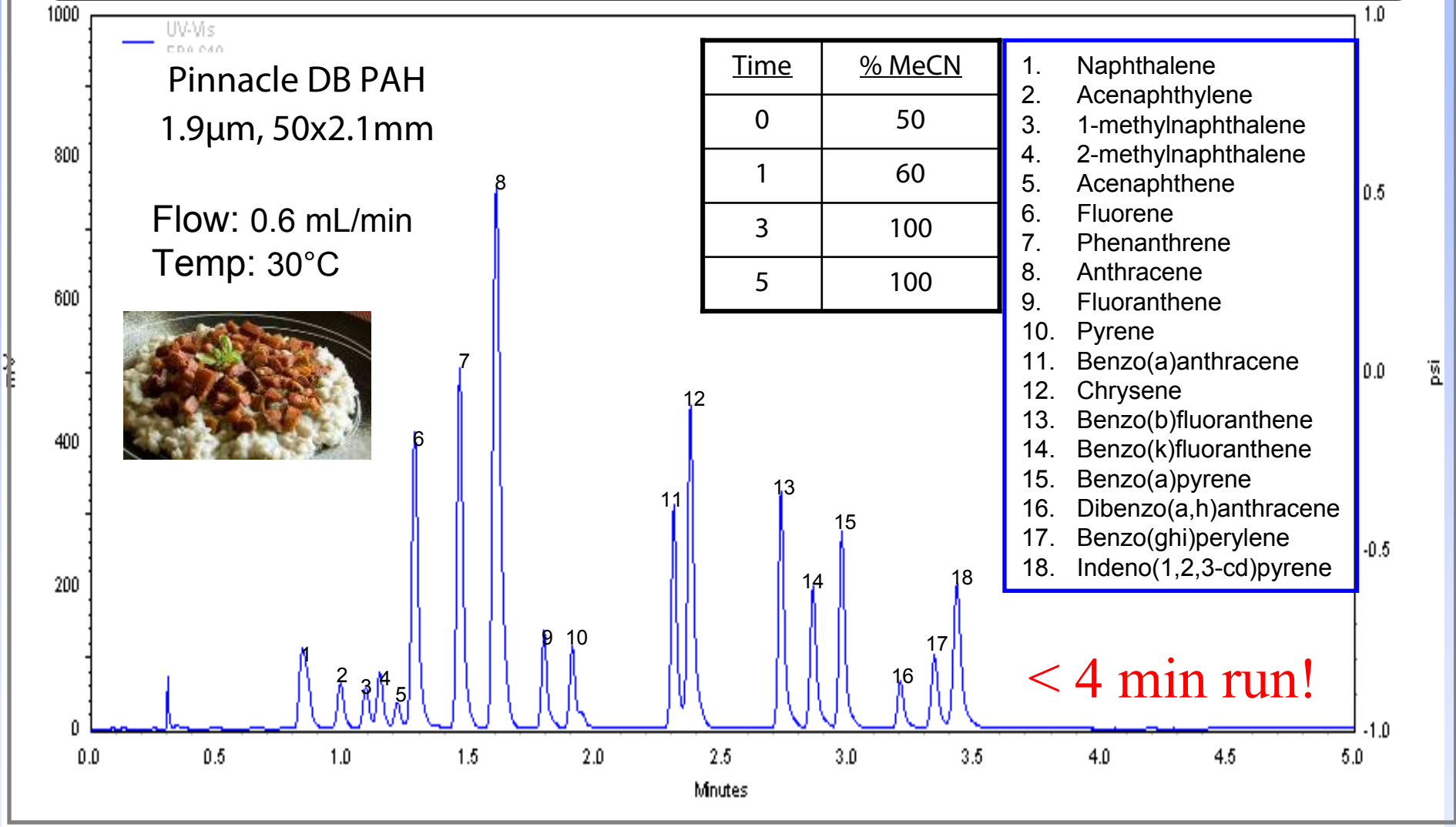
- Fewer PAHs analyzed
- Longer run
- Less separation

ANALYTES:

1 naphthalene
2 acenaphthylene
3 acenaphthene
4 fluorene
5 phenanthrene
6 anthracene
7 fluoranthene
8 pyrene
9 benzo (a) anthracene
10 chrysene
11 benzo (b) fluoranthene
12 benzo (k) fluoranthene
13 benzo (a) pyrene
14 dibenzo (a,h) anthracene
15 benzo (g,h,i) perylene
16 indeno (1,2,3-cd) pyrene

Phenomenex Synergi Max-RP
4µm, 250x4.6mm, 80Å

Restek UHPLC of PAHs – Very Fast Run



Time	% MeCN
0	50
1	60
3	100
5	100

1. Naphthalene
2. Acenaphthylene
3. 1-methylnaphthalene
4. 2-methylnaphthalene
5. Acenaphthene
6. Fluorene
7. Phenanthrene
8. Anthracene
9. Fluoranthene
10. Pyrene
11. Benzo(a)anthracene
12. Chrysene
13. Benzo(b)fluoranthene
14. Benzo(k)fluoranthene
15. Benzo(a)pyrene
16. Dibenzo(a,h)anthracene
17. Benzo(ghi)perylene
18. Indeno(1,2,3-cd)pyrene

Summary of Food Safety

- Years of personnel experience at Restek
  - Best food safety technical support
- Wide range of QuEChERS products
  - Rapidly growing food safety sample preparation method
- GC and HPLC columns for food safety
  - Inert, selective, tested, adopted
- Total solution offerings
  - Sample preparation, standards, GC/LC columns/consumables
- Innovative new products
  - QuEChERS, Rxi-17Sil MS, 5mm GC inlet liner
- Technical information support
  - Web, literature, presentations, ChromaBLOGraphy, etc.

Appendix

- Extra slides for distributors to review
- Additional topics and/or applications

Other Topics for Food Safety

- PBDEs in food
  - Rtx-1614 column (Restek exclusive!)
    - Fast runs and minimal BDE 209 breakdown
    - www.restek.com/aoi_env_A035.asp
- Melamine in infant formula
  - Rxi-5Sil MS, standards, derivatization reagents
    - www.restek.com/restek/images/external/FFAN1137.pdf
- Veterinary drug residues
  - Biphenyl HPLC columns (Restek exclusive!)
    - Julie Kowalski (Florida Pesticide Residue Workshop)

Other Topics for Food Safety

- Dietary supplements
  - Restek publishes first QuEChERS method
    - www.restek.com/restek/images/external/PHAN1242.pdf
- Food authentication and origin
  - Not really food safety, but hot food topic
    - Lots of GCxGC work being done
- GCxGC for food safety and food applications
  - Restek has two GCxGC systems
    - LECO Pegasus 4D GCxGC-TOFMS, GCxGC-ECD/FID
  - Full line of 0.10, 0.15, 0.18mm columns for GCxGC

Jaap de Zeeuw
International
GC Specialist

Fast GC Using 0.10mm and 0.18mm ID Capillary Columns and Comprehensive GC

- Significantly reduces analysis time without sacrificing resolution.
- Highest column efficiencies, great for GC/MS.
- Excellent for comprehensive GC (GCxGC) as second dimension column.

Narrow bore (0.18mm ID) columns are attractive alternatives to conventional-diameter capillary columns because they provide faster analysis times and higher resolving power. As column ID decreases, column efficiency (plates/meter) greatly increases. For instance, a 0.18mm ID column (5,150 plates/meter) is 32% more efficient than a 0.25mm ID column (3,900 plates/meter). Therefore, resolution can be achieved with a shorter column, which decreases the analysis time. When switching from a 0.25mm ID column to a 0.10mm ID column (8,500 plates/meter) the column efficiency is improved dramatically (118%).

Typically, 0.18mm ID columns are used for fast GC analysis, and methods are easily converted. The 0.10mm ID columns require more research to switch methods to the smaller ID due to higher back pressures and lower column capacity.

The outer diameter of the 0.10mm ans 0.18mm ID tubing is the same as 0.25mm ID tubing, which makes connections less complicated.

tech tip

Operating considerations for 0.10mm ID columns

The small degree of extra care involved in using 0.10mm ID columns will be more than repaid by faster analyses and higher column efficiencies. 0.10mm ID columns require higher operating pressures (>40psig), which can result in more ferrule leaks, septum leaks, and sample flashback through leaking syringe plungers. Connections must be monitored and leak-checked more often. Operating a 0.10mm ID column below optimum pressure will cause poor resolution and other poor performance. Sample capacity also is reduced, relative to wider-bore columns. Take care to not overload the column, and make sure you inject fast when using split injection.

Rxi®-1ms Columns (fused silica)
(Crossbond® 100% dimethyl polysiloxane)

ID	df (µm)	temp. limits	10-Meter	20-Meter
0.10mm	0.10	-60 to 330/350°C	13301	
0.18mm	0.18	-60 to 330/350°C		13302

Rxi®-5ms Columns (fused silica)
(Crossbond® 5% diphenyl/95% dimethyl polysiloxane)

ID	df (µm)	temp. limits	10-Meter	20-Meter
0.10mm	0.10	-60 to 330/350°C	13401	
0.18mm	0.18	-60 to 330/350°C		13402
	0.30	-60 to 330/350°C		13409
	0.36	-60 to 330/350°C		13411

Rxi®-5Sil MS Columns (fused silica)
(Crossbond®, selectivity similar to 5% diphenyl/95% dimethyl polysiloxane)

ID	df (µm)	temp. limits	10-Meter	20-Meter
0.10mm	0.10	-60 to 330/350°C	43601	
0.18mm	0.18	-60 to 330/350°C		43602
	0.36	-60 to 330/350°C		43604

Rxi®-17 Columns (fused silica)
(Crossbond® 50% diphenyl/50% dimethyl polysiloxane)

ID	df (µm)	temp. limits	10-Meter
0.10mm	0.10	40 to 280/320°C	13501

Rtx®-Wax Columns (fused silica)
(Crossbond® Carbowax® polyethylene glycol)

ID	df (µm)	temp. limits	10-Meter	20-Meter
0.10mm	0.10	20 to 250°C	41601	41602
	0.20	20 to 240/250°C	41603	41604

Rt™-LC50 Columns (fused silica)

ID	df (µm)	temp. limits	10-Meter
0.10mm	0.10	100°C to 270°C	19736
0.18mm	0.10	100°C to 270°C	19735

Rtx®-CLPesticides (fused silica)

ID	df (µm)	temp. limits	10-Meter	20-Meter
0.10mm	0.10	-60 to 310/330°C	43101	
0.18mm	0.18	-60 to 310/330°C	42101	42102

Rtx®-CLPesticides2 (fused silica)

ID	df (µm)	temp. limits	10-Meter	20-Meter
0.10mm	0.10	-60 to 310/330°C	43301	43302
0.18mm	0.14	-60 to 310/330°C	42301	42302

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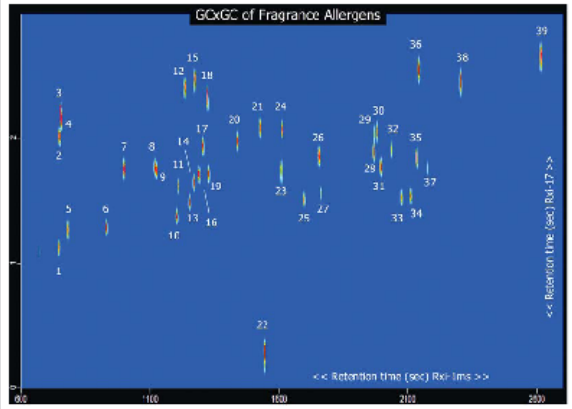
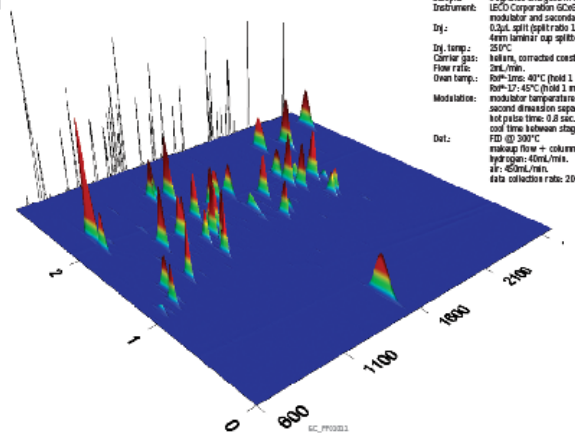
Fragrance Allergens
Rxi®-1ms & Rxi®-17 (GC x GC)



1. limonene
2. 1-fluoronaphthalene
3. benzyl alcohol
4. phenyl acetaldehyde
5. eucalyptol
6. linalool
7. camphor
8. methyl-2-octynoate
9. estragole
10. citronellol
11. citral 1
12. trans-cinnamaldehyde
13. geraniol
14. citral 2
15. anise alcohol
16. hydroxycitronellol
17. safrole
18. cinnamyl alcohol
19. methyl-2-nonynoate
20. eugenol
21. methyl eugenol
22. coumarin
23. hydroxycitronellol contaminant
24. isoeugenol
25. α-isomethyl ionone 1
26. lilial
27. α-isomethyl ionone 2
28. amyl cinnamal
29. lyral 1
30. lyral 2
31. amylcinnamyl alcohol 1
32. amylcinnamyl alcohol 2
33. tarragol 1
34. tarragol 2
35. hexyl cinnamal 1
36. benzyl benzoate
37. hexyl cinnamal 2
38. benzyl salicylate
39. benzyl cinnamate



Columns: Rxi®-1ms, 30m, 0.25mm ID, 0.25µm (cat.# 13323)
Rxi®-17, 1m, 0.10mm ID, 0.10µm (cat.# 13501)
Sample: fragrance allergens in MTBE
Instrument: LECO Corporation GCxGC/FID with quad-jet, dual-stage modulator and secondary oven
Inj.: 0.2µL split (split ratio 1:200), 4mm laminar cup splitter (cat.# 20801)
Inj. temp.: 250°C
Carrier gas: helium, corrected constant flow via pressure ramps
Flow rate: 2mL/min.
Oven temp.: Rxi®-1ms: 40°C (hold 1 min.) to 240°C @ 4°C/min.
Rxi®-17: 45°C (hold 1 min.) to 245°C @ 4°C/min.
Modulation: modulator temperature offset 20°C
second dimension separation time: 3 sec.
hot pulse time: 0.8 sec.
cool time between stages: 0.7 sec.
Det.: FID @ 300°C
makeup flow + column flow: 50mL/min.
hydrogen: 40mL/min.
air: 450mL/min.
data collection rate: 200 Hz

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Columns for Comprehensive GC (GCxGC)

GCxGC Selectivity Kit A

The selectivity kit contains four columns of different selectivity for method development. Includes one each of the following:

- Rxi®-17, 1.1m (±3cm), 0.10mm ID, 0.10µm, 50% diphenyl dimethylpolysiloxane
- Rtx®-CLPesticides, 1.1m (±3cm), 0.10mm ID, 0.10µm, trifluoropropyl containing polymer
- Stabilwax®, 1.1m (±3cm), 0.10mm ID, 0.10µm, polar polyethylene glycol
- Rt®-LC350, 1.1m (±3cm), 0.15mm ID, 0.10µm, liquid crystalline phase selective for aromatic compounds

Description	Length	qty.	Cat.#	Price	Wish list	Cart
GCxGC Selectivity Kit A		kit	15105		☐	
0.15mm ID						
0.10µm df						
Rt-LC350	1.1m (±3cm)	ea.	15101		☐	
0.10mm ID						
0.10µm df						
Stabilwax	1.1m (±3cm)	ea.	15102		☐	
Rtx-CLPesticides	1.1m (±3cm)	ea.	15103		☐	
Rxi-17	1.1m (±3cm)	ea.	15104		☐	