

# Improving the Sensitivity, Ruggedness, and Accuracy of Pesticide Analysis

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**Agilent Technologies**

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Room 242



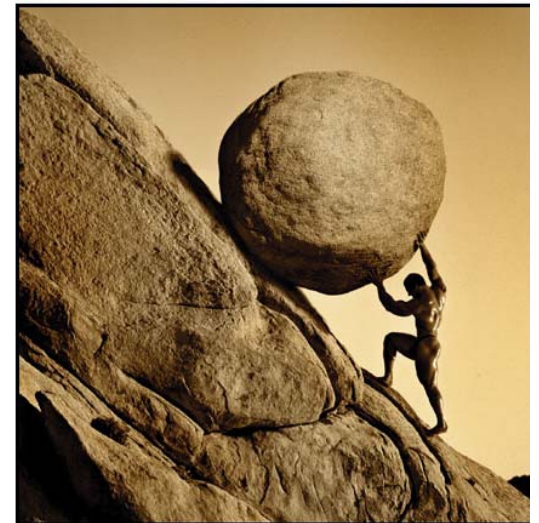
# Objectives

- 🍏 Create a multi-residue GC/MS method to detect large numbers of pesticides at <10 ppb
- 🍏 Screen for virtually all GC-able pesticides and endocrine disruptors in a single run
- 🍏 Quant target compounds while screening for “everything”
- 🍏 Shorten run times to <25 min
- 🍏 Reduce GC/MS maintenance
- 🍏 Obtain more accurate results



## Why it's Hard to Meet these Objectives

- 🍎 10 ppb detection limits in scan require large volume injection (~10  $\mu\text{L}$ )
- 🍎 SIM is more sensitive, but need scan for comprehensive method
- 🍎 Food and environmental extracts are “dirty”
- 🍎 10  $\mu\text{L}$  injections = 10 X more maintenance
  - Frequent source cleaning
  - Long bakeout times
  - Column gets dirty fast
- 🍎 How can we look for hundreds of pesticides in one run?



# A Method to Screen for (and Quant Targets) Pesticides at <10 ppb in Food and Environmental Extracts

## Keys to Success



**Use GC/MS with Trace Ion Detection**



**10  $\mu$ L injections using PTV inlet**



**Backflush column using QuickSwap**



**Use Deconvolution Reporting Software**

- Screen for 927 pesticides & endocrine disruptors in 1 run



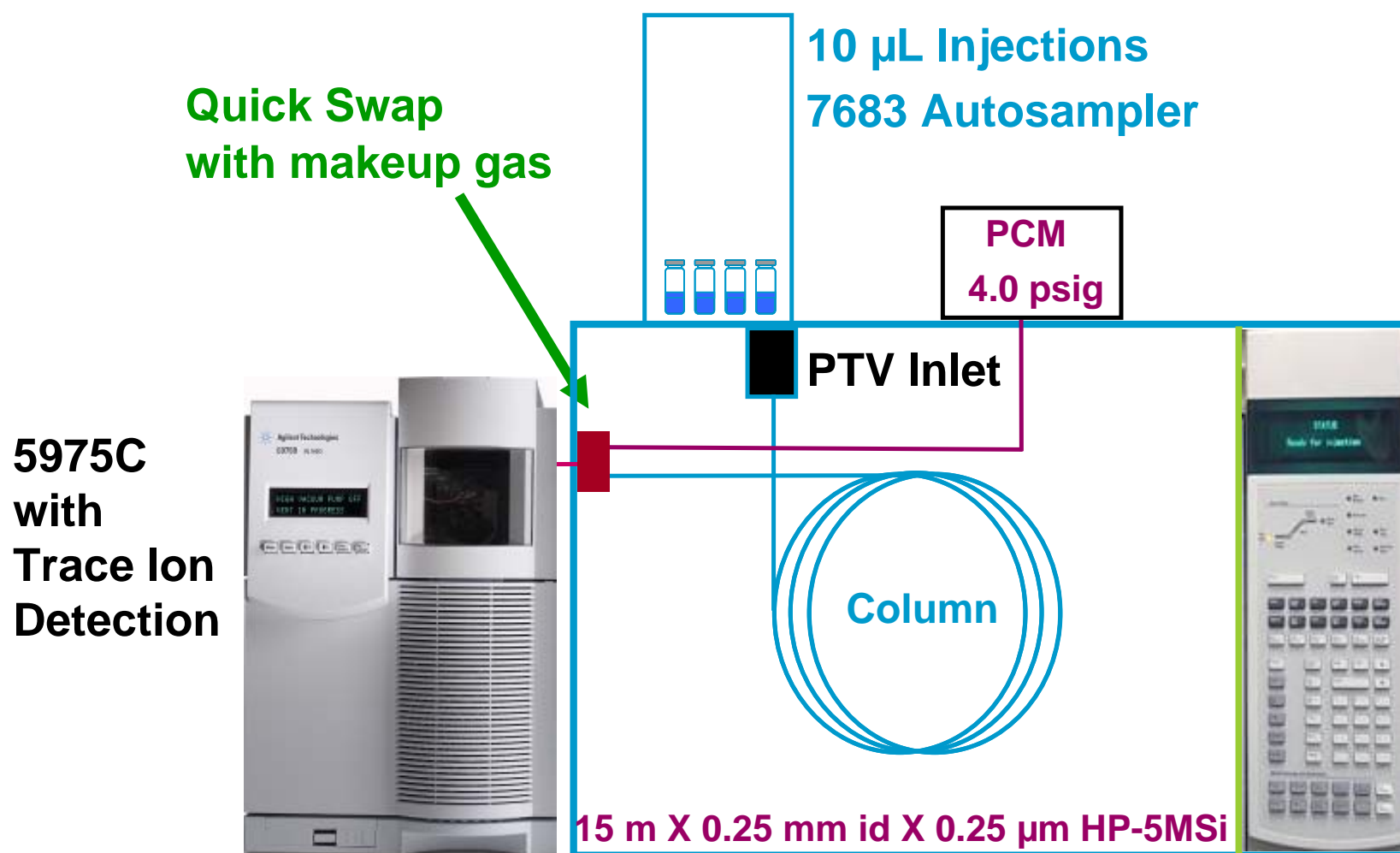
**Acquire data using Synchronous SIM/Scan**



**Quant targets using SIM, Scan, or deconvoluted scan peaks**



# Agilent 7890/5975 GC/MS System Configuration



# A Method to Screen for (and Quant Targets) Pesticides at <10 ppb in Food and Environmental Extracts

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**Backflush column using QuickSwap**



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# QuickSwap MSD Interface

## Remove column w/o venting

- Air & H<sub>2</sub>O blocked

## Safe disconnection of column from inlet for inlet maintenance

- Reversed flow through column during inlet maintenance

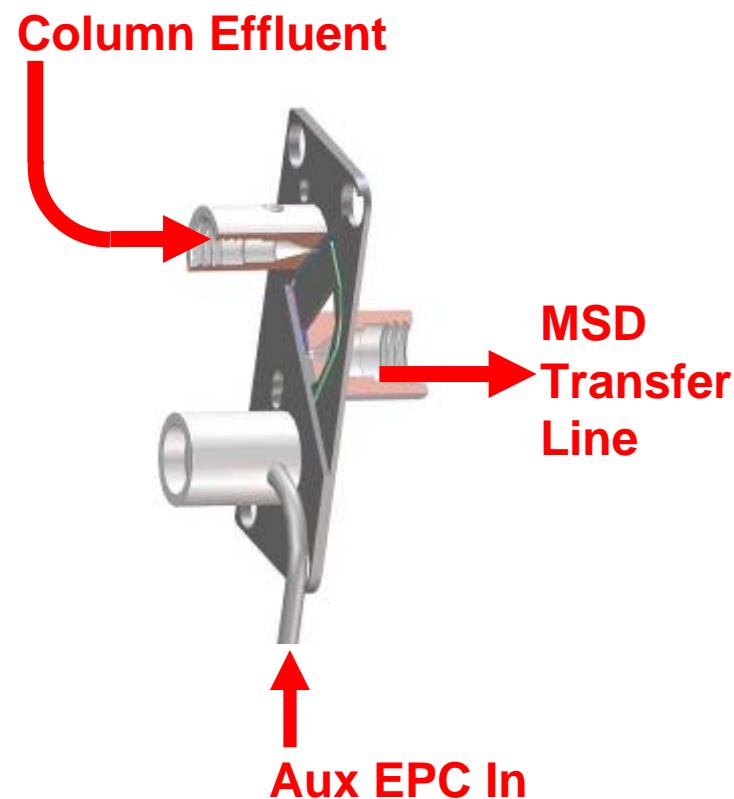
## Backflushing

- Removes heavies from column

## Maintain constant flow to MSD

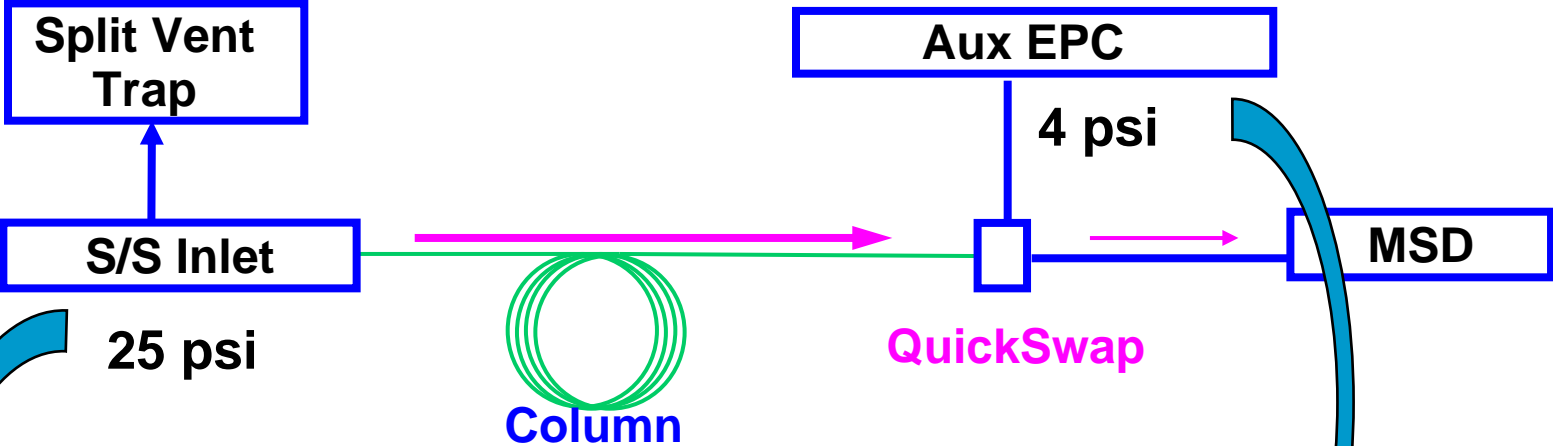
Compensate for loss of sensitivity by making 10  $\mu$ L injection

Turbo MSD required for backflushing

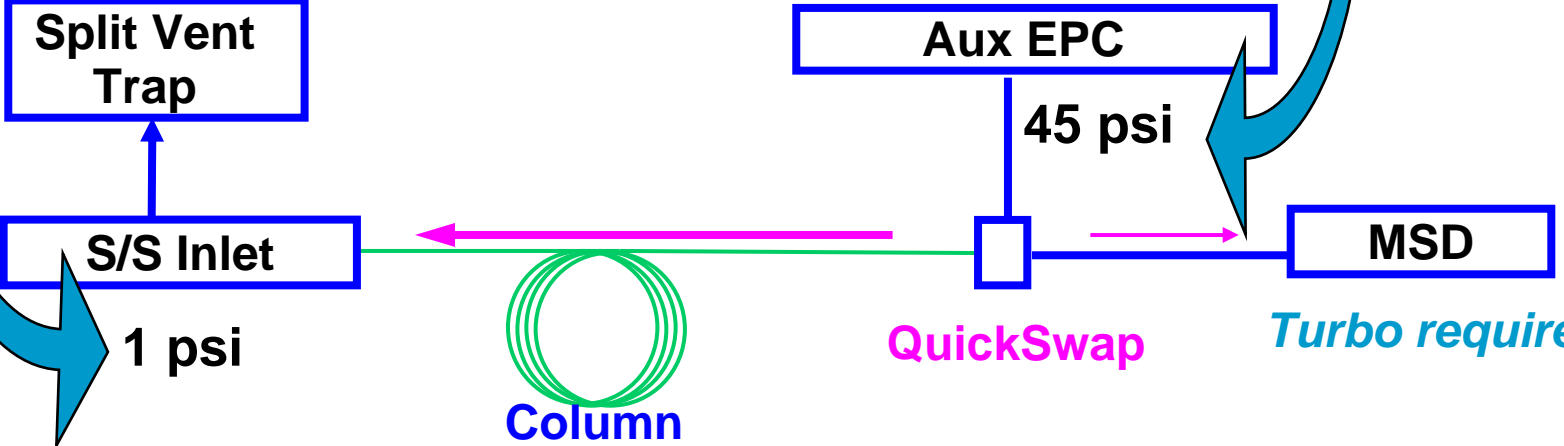


# Backflush with QuickSwap

## During GC Run

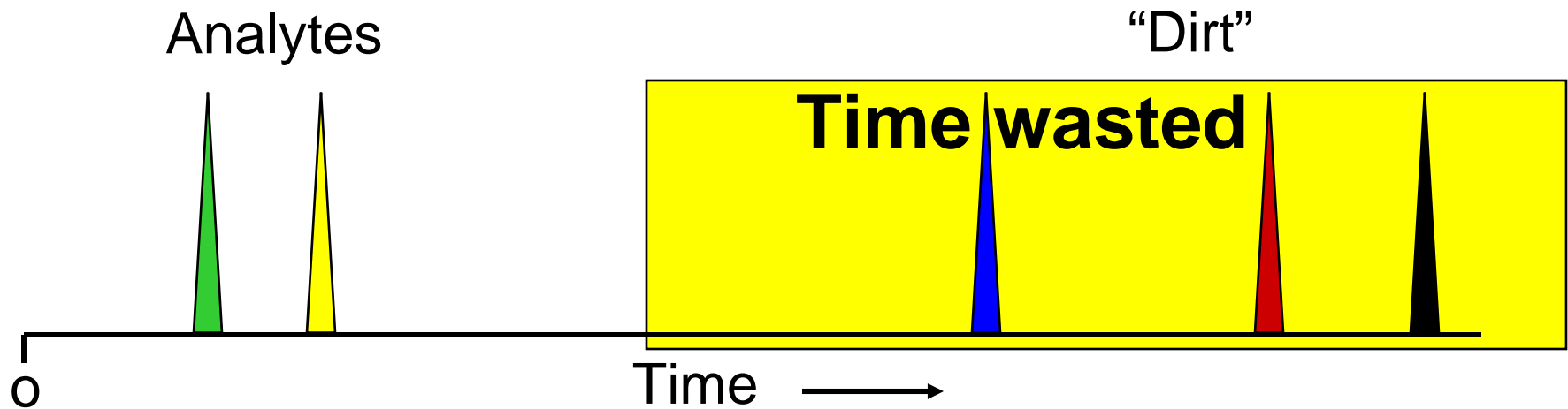
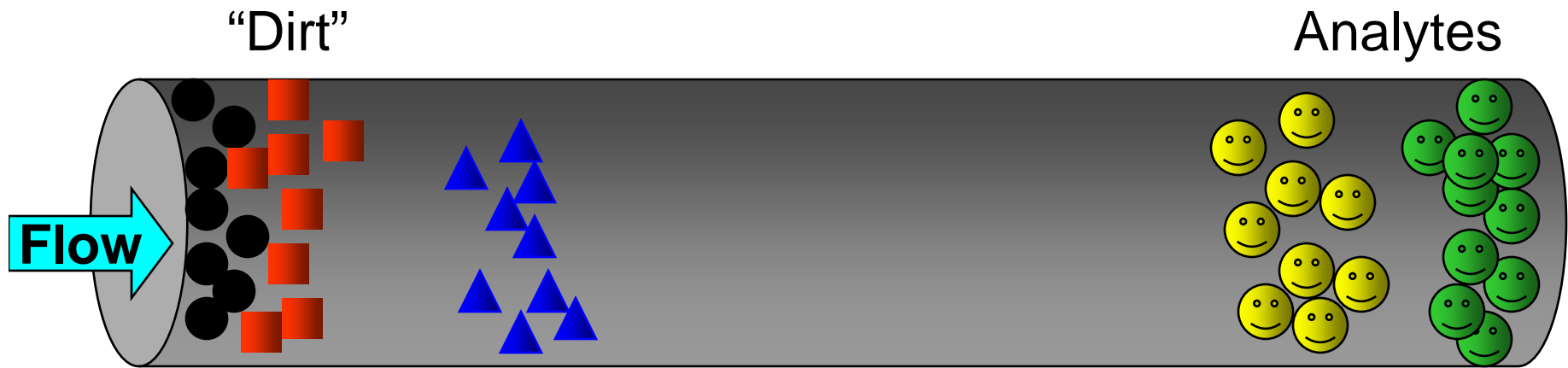


## After GC Run

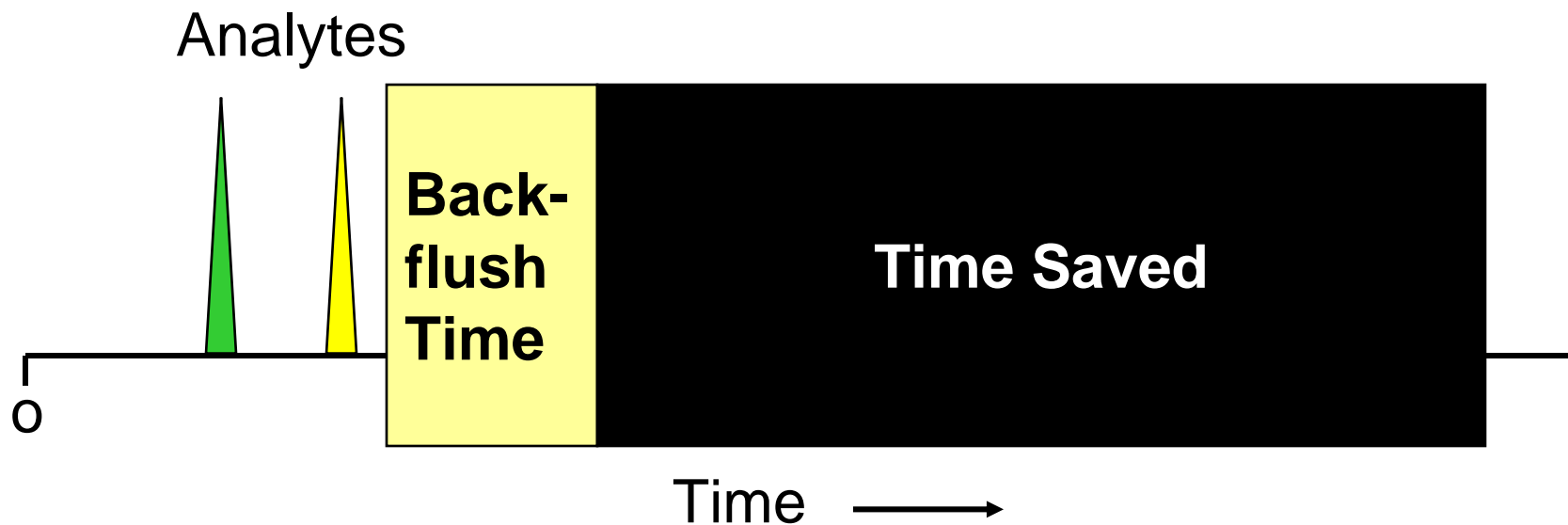
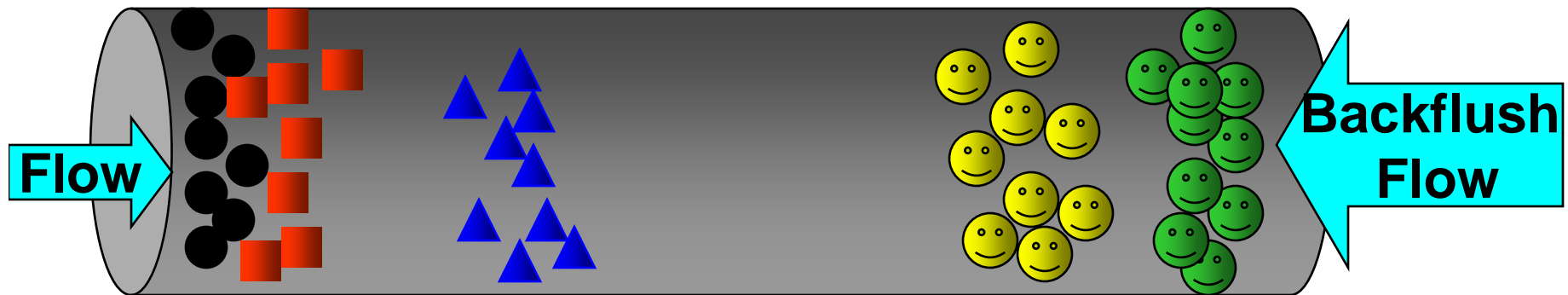




# No Backflushing – Must Bake out the Column



# With Backflushing “Dirt” is Removed Through the Inlet’s Split Vent



# Overlapped chromatograms of a Lettuce Extract: 1<sup>st</sup> & 3<sup>rd</sup> Injections made without Backflushing

A: TIC: lettuce\_blank.D\data.ms

B: TIC: lettuce\_blank3.D\data.ms

Abundance

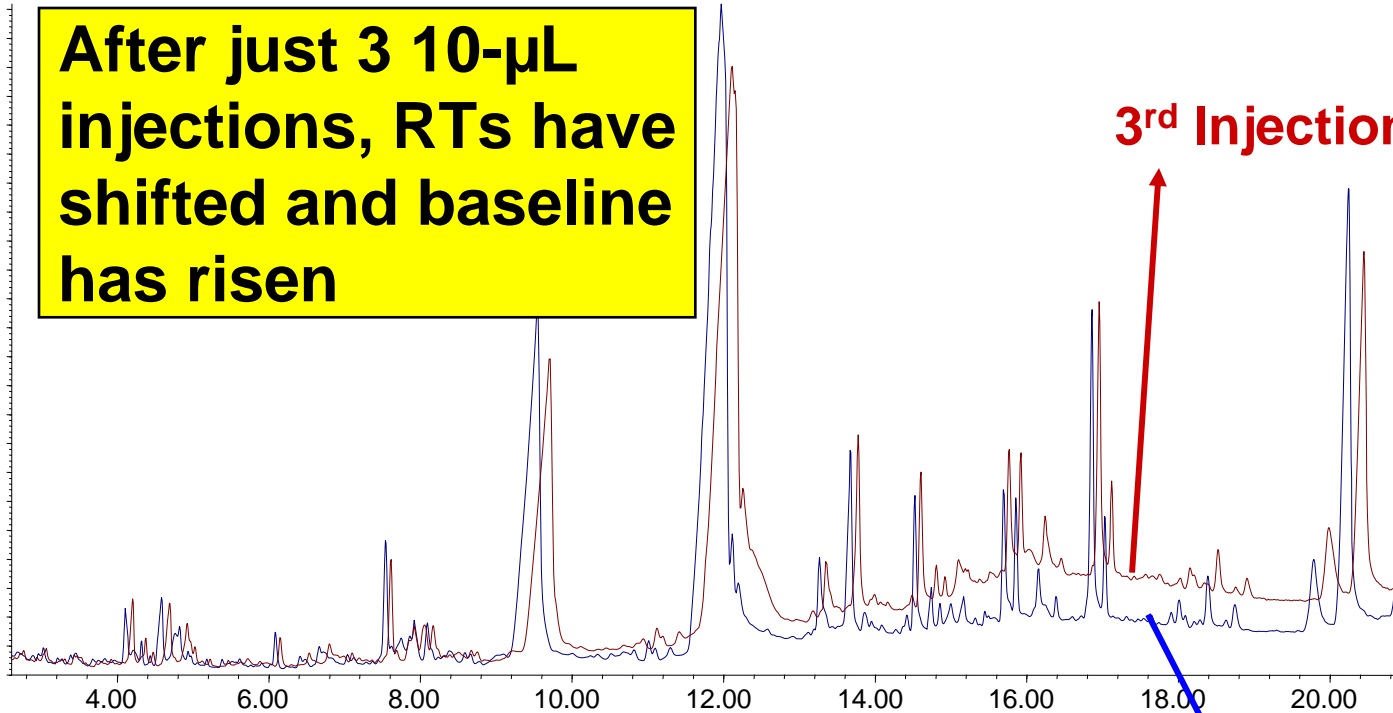
4.6e+07  
4.4e+07  
4.2e+07  
4e+07  
3.8e+07  
3.6e+07  
3.4e+07  
3.2e+07  
3e+07  
2.8e+07  
2.6e+07  
2.4e+07  
2.2e+07  
2e+07  
1.8e+07  
1.6e+07  
1.4e+07  
1.2e+07  
1e+07  
8000000  
6000000  
4000000  
2000000  
0

Time

After just 3 10- $\mu$ L injections, RTs have shifted and baseline has risen

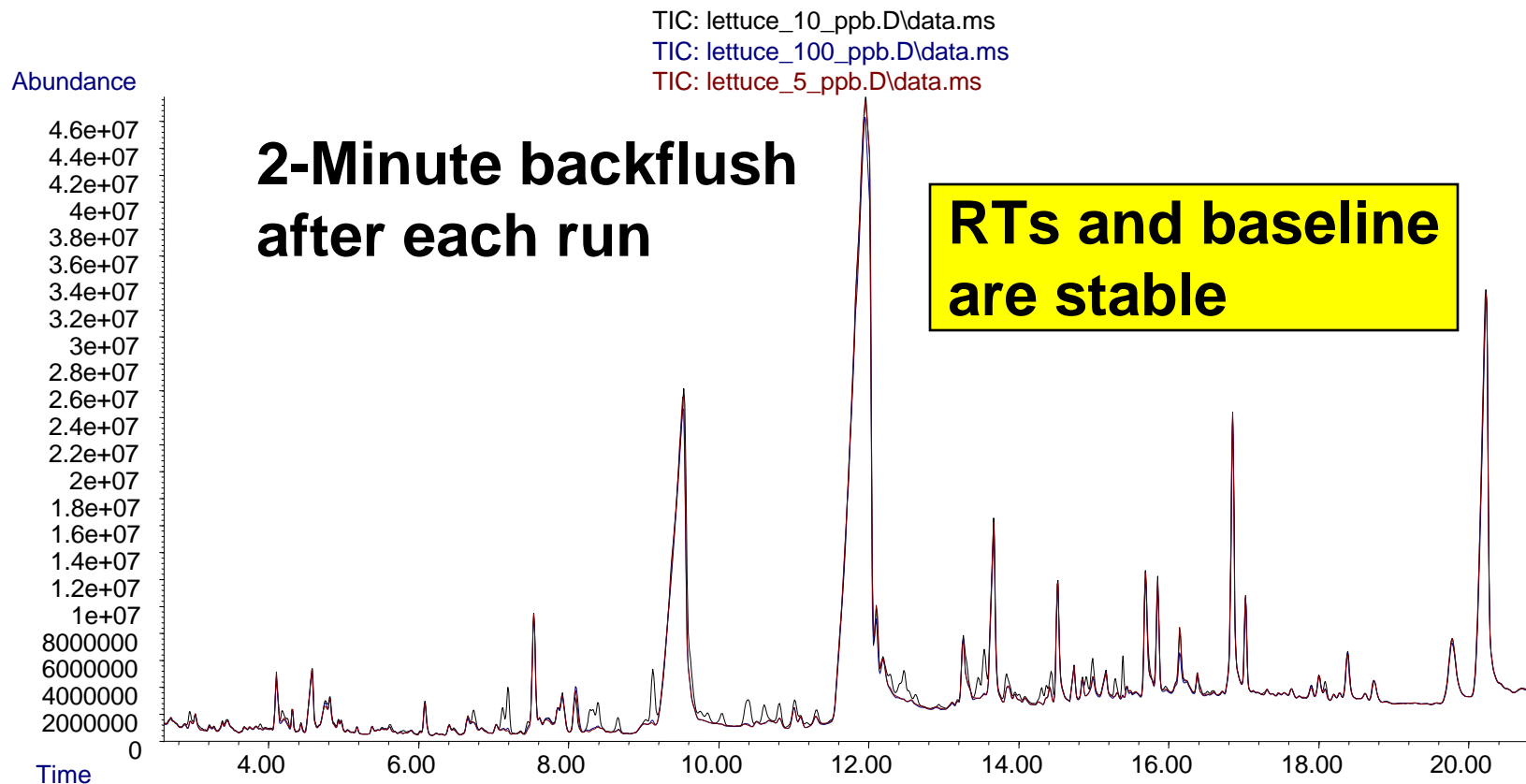
3<sup>rd</sup> Injection

1<sup>st</sup> Injection



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# Overlapped chromatograms of a Lettuce Extract: 3 Injections made with Backflushing



# A Method to Screen for (and Quant Targets) Pesticides at <10 ppb in Food and Environmental Extracts

## Keys to Success



Use GC/MS with Trace Ion Detection



10  $\mu$ L injections using PTV inlet



Backflush column using QuickSwap



**Use Deconvolution Reporting Software**

**- Screen for 927 pesticides & endocrine disruptors in 1 run**



Acquire data using Synchronous SIM/Scan

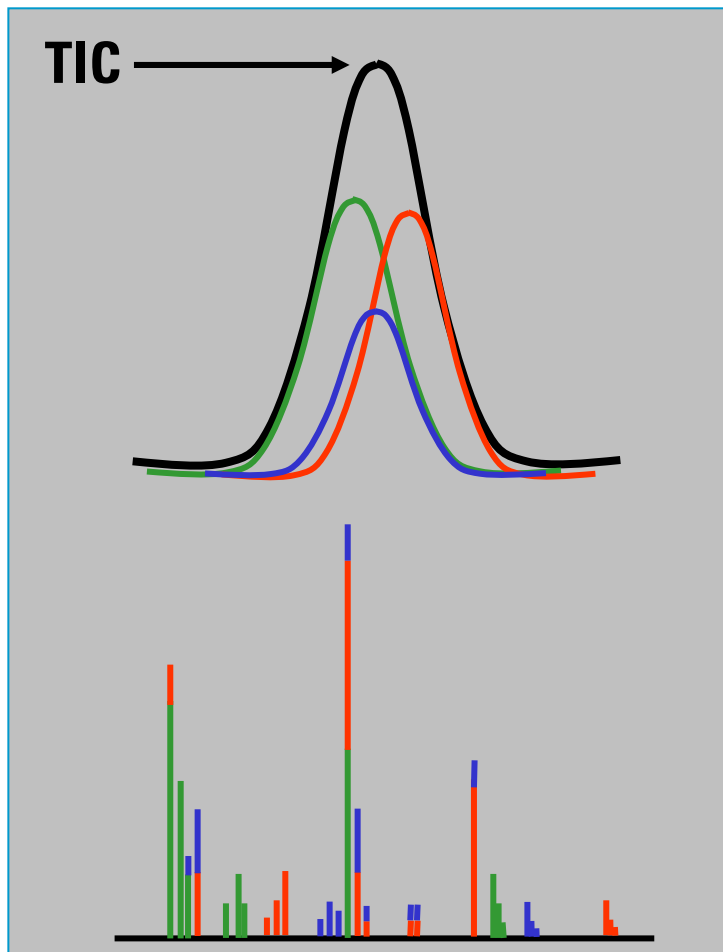


Quant targets using SIM, Scan, or deconvoluted scan peaks

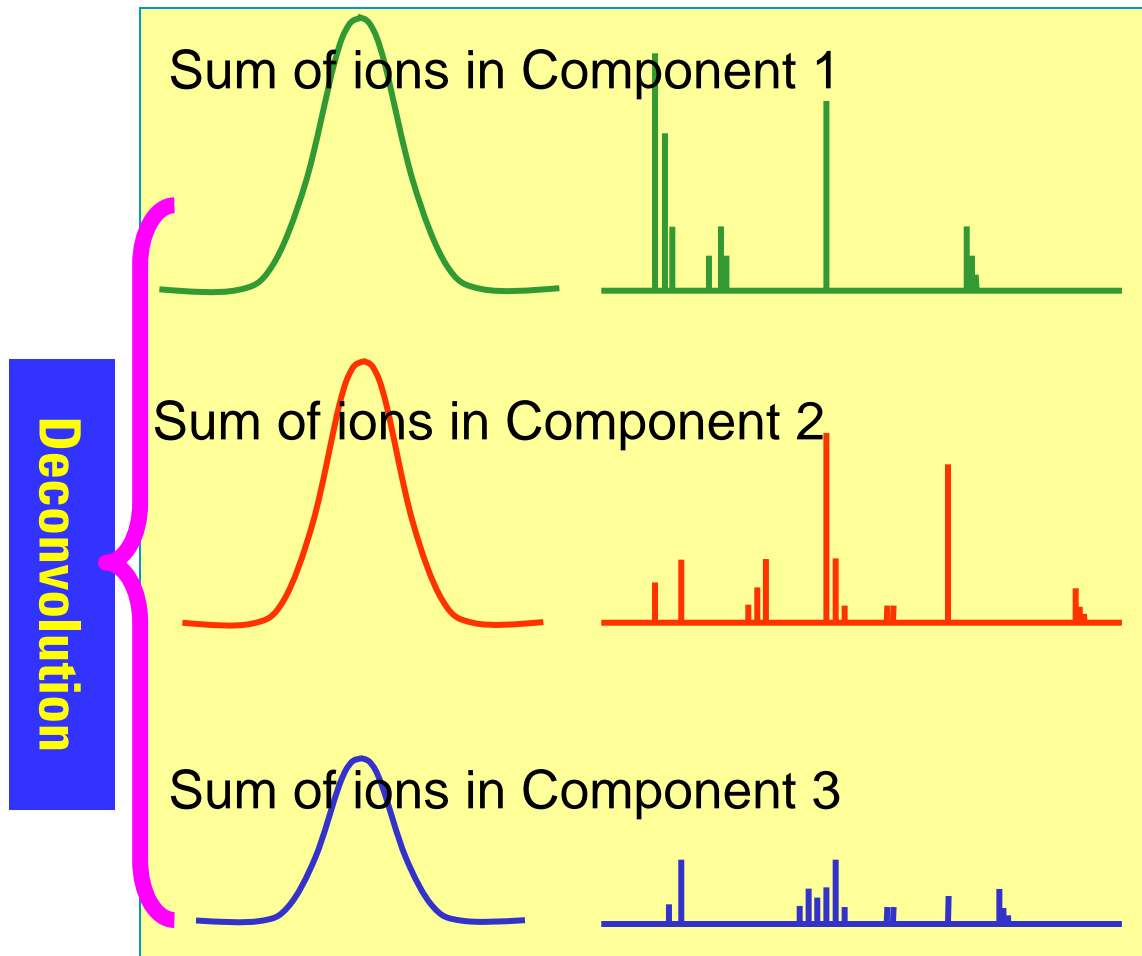


# AMDIS Deconvolution Pulls Out Individual Components and their Spectra

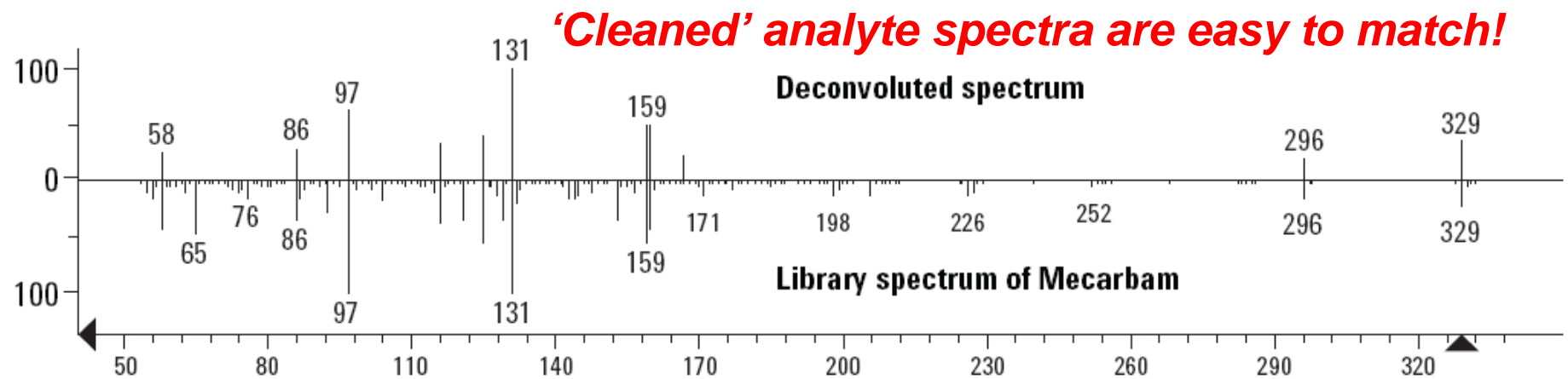
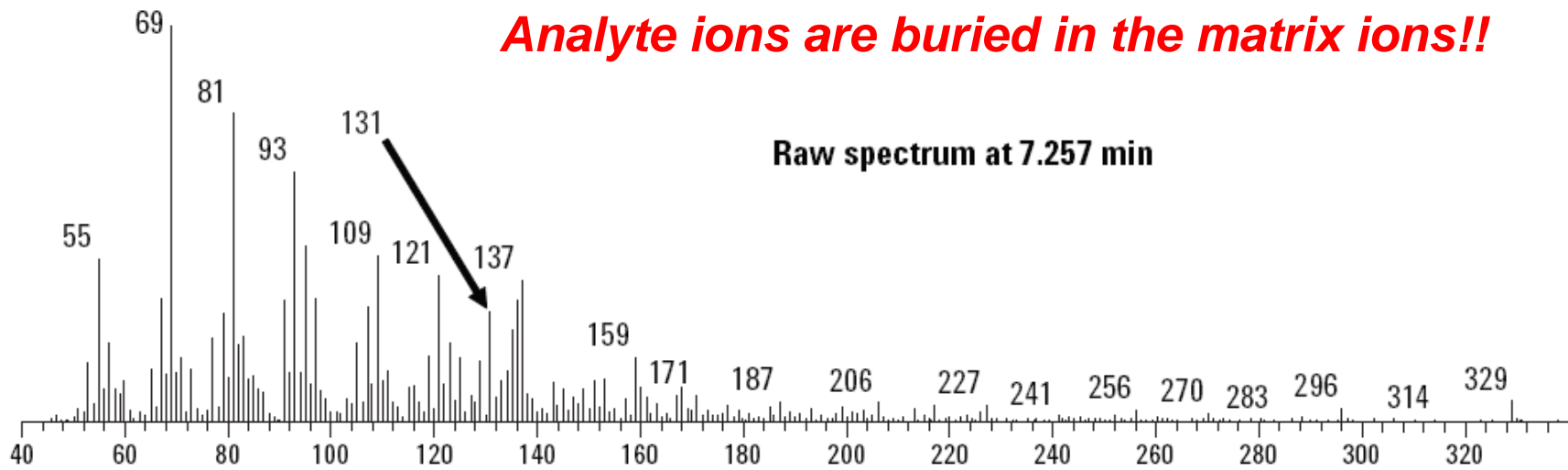
## TIC & Spectrum



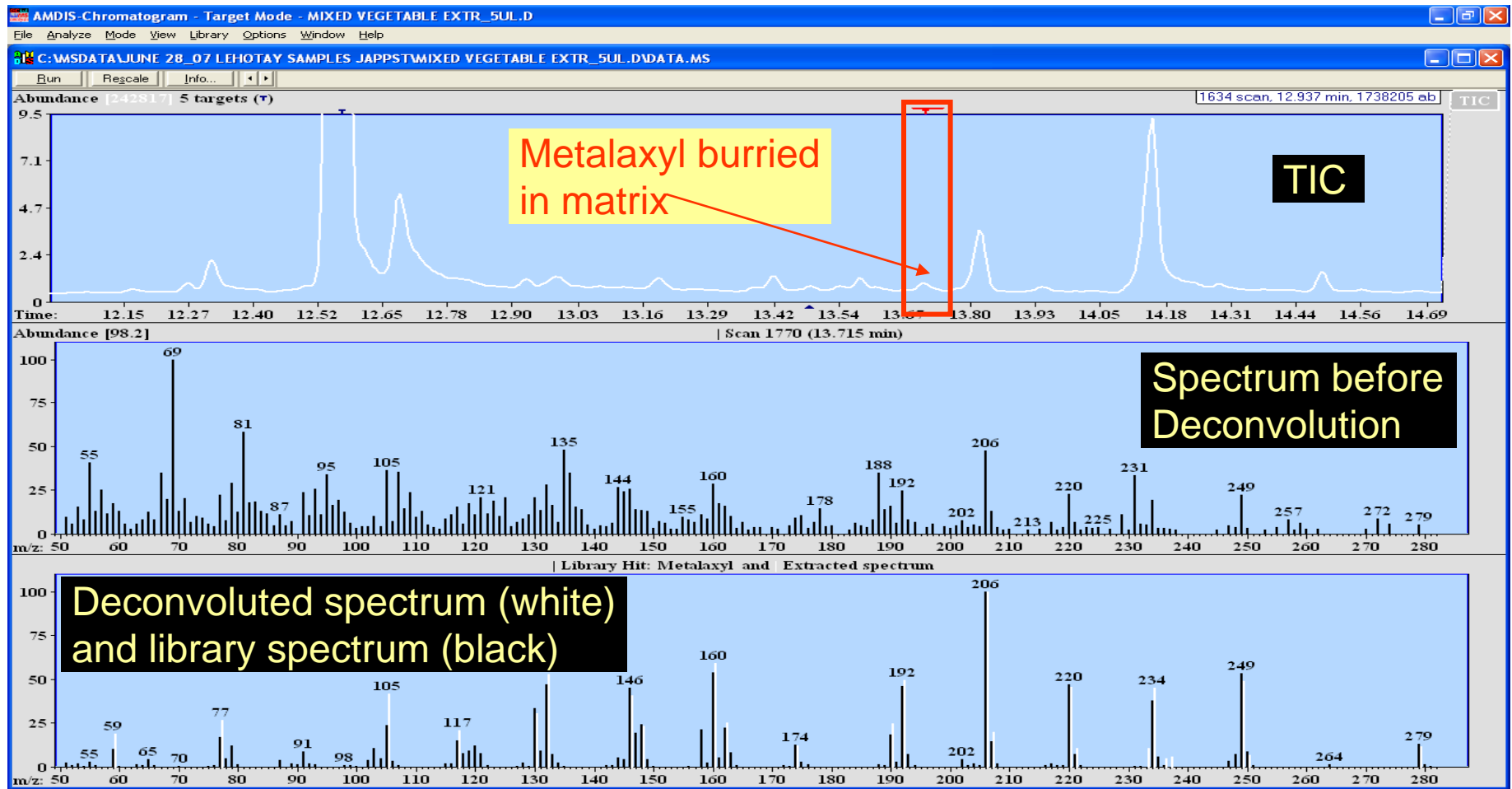
## Deconvoluted peaks and spectra



# AMDIS: Pulling a Useable Spectrum Out of a Mess



# Metalaxyl Identified by DRS in Mixed Vegetable (QuEChERS) Extract (AMDIS View)





# What is Agilent DRS?

**MSD Deconvolution Report**  
Sample Name: + 400 ppb ISTDs, 25 µL PTV  
Data File: C:\MSDCHEM\1\DATA\SPINACH.D  
Date/Time: 11:17:02 AM Tuesday, Apr 27 2006

The NIST library was searched for the component.

R.T.	Cas #	Compound Name	Agilent	AMDIS		NIST	
			ChemStation Amount (ng)	Match	R.T. Diff sec.	Reverse Match	Hit Num.
18.445	84742	Di-n-butylphthalate	7.08	86	1.3	92	1
23.966	80057	Bisphenol A		93	7.9	91	1
24.066	72559	p,p'-DDE		79	2.5	77	1
27.928	51036	Piperonyl butoxide	37.83	91	2.2	94	1
29.672	117817	Bis(2-ethylhexyl)phthalate		91	1.9	86	3
31.420	52645531	Permethrin I		67	3.7	74	5
31.616	52645531	Permethrin II		88	4.6	91	3
13.718		Phenanthrene-d10	10				

D - RT

# Two Pesticide Databases Available for use with Deconvolution Reporting Software

## “RTL Pest3”

927 Compounds

Almost all GCable pesticides

Many metabolites

More endocrine disruptors

Important PCBs & PAHs

Some dyes (e.g., Sudan Red)

Synthetic musk compounds

Some OP fire retardants

Locked RTs + Mass Spectra

Uses Agilent’s constant flow GC/MS method

## “Japanese Positive List Pesticide Database”

430 Compounds

Contains **all** GC-amenable pesticides discussed in the Japanese Positive List System or in Quarantine Station publications

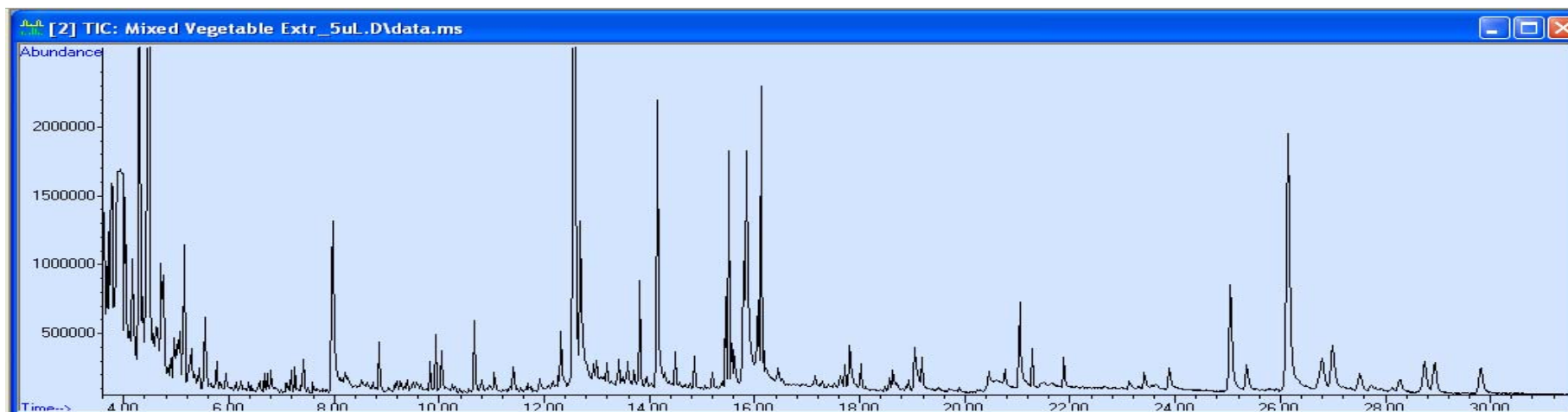
Nearly all are Pesticides

No other endocrine disruptors

Locked RTs + Mass Spectra

Uses Japanese Ministry of Health Labour & Welfare constant flow GC/MS method

# QuEChERS Extract of a Mixed Vegetable Sample: DRS Report (Sample was **not** spiked)



R.T.	Cas #	Compound Name	Agilent	AMDIS		NIST	
			ChemStation Amount (ng)	Match	R.T. Diff sec.	Reverse Match	Hit Num.
6.5630	10265926	Methamidophos		68	8.0	77	1
8.5817	30560191	Acephate		66	-2.3	69	1
10.7634	122394	Diphenylamine		69	-1.4	67	1
12.5722	1517222	Phenanthrene-d10		98	-0.7	84	2
13.7143	57837191	Metalaxyl		85	-0.8	79	2
12.571		Phenanthrene-d10	10				

Report  
in 90  
seconds



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# New DRS V.04: Qual (Spectra) + Quant (Peak Area)

The screenshot displays the Quick Qedit software interface with several key components:

- Top Left:** A chromatogram showing the overlay of target ions (blue, green, red) and deconvoluted ion plots (black). Peaks are labeled at retention times 27.010 and 27.013.
- Top Right:** Two zoomed-in chromatograms. The left one is labeled 'Target ion plot' with a peak at 27.010. The right one is labeled 'Deconvoluted ion plot' with a peak at 27.013.
- Center:** A list of compounds with their retention times and AMDIS results. The list includes:
 

#	Compound Name
1	x 13.718 *Phenanthrene-d10
2	5.792 Dichlorvos
3	7.565 Mevinphos
4	7.762 Vernolate
5	11.182 Dibrom (naled)
6	11.272 Ethalfuralin
7	11.632 Trifluralin
8	13.028 Prometon
9	13.184 Atrazine
10	13.233 b-BHC
11	13.432 Lindane
12	13.583 Aminocarb
13	14.790 Chlorothalonil
14	16.618 Methyl parathion
15	16.618 Chlorpyrifos Methyl
16	16.769 Heptachlor
17	18.508 Bromacil
18	xA 18.444 Di-n-butylphthalate
19	18.832 Malathion
20	19.250 Chlorpyrifos
21	19.538 Carbetamide
22	xA 23.978 Bisphenol A
23	23.864 Dieldrin
24	A 24.039 p,p'-DDE
25	A 25.686 p,p'-DDD
26	A 26.982 p,p'-DDT
27	A 27.007 Butyl benzyl phthalate
28	27.424 Hexazinone
29	27.745 Propargite
30	xA 27.927 Piperonyl butoxide
31	A 29.649 Bis(2-ethylhexyl)phthalate
32	29.649 Bis(2-ethylhexyl)phthalate
33	
34	A
35	
36	
37	
- Bottom Left:** A spectral review window showing the 'AMDIS Extracted Spectrum' (top) and 'AMDIS Library Spectrum' (bottom) for comparison. Peaks are labeled at m/z 36.0, 91.0, 149.0, 206.0, 235.0, 299.1, and 388.0.
- Bottom Right:** A table of hits with their retention times, expected percentages, and actual percentages.
 

Ion	Exp%	Act%
149.00	100	100
91.00	60.00	125.86#
206.00	25.40	14.53#
104.00	16.20	33.38#

# 54 Pesticides at 10 ppb in Lettuce Extract – Identified in ~2 min

MSD Deconvolution Report  
 Sample Name: lechuga\_10\_ppb  
 Data File: C:\DOCUME~1\LFS-WY~1\MYDOCU~1\COLLAB~1\ALMERI~1\DATAAN~1\JAN09\_~1\DATA\_F~1\LETTUC~1.D  
 Date/Time: 04:26 PM Wednesday, Feb 27 2008

Adjacent Peak Subtraction = 1  
 Resolution = High  
 Sensitivity = High  
 Shape Requirements = Medium

The NIST library was searched for the components that were found in the AMDIS target library.

R.T.	Cas #	Compound Name	Amount (ppb)		AMDIS		NIST	
			Chem station	AMDIS	Match	R.T. Diff sec.	Reverse Match	Hit Num.
2.9335	10265926	Methamidophos			87	12.7	85	1
2.9491	62737	Dichlorvos			94	4.0	76	1
3.2439	3228033	Promecarb artifact [5-isopropyl-3-methylphenol]			71	8.6		
3.2439	1450722	Ethanone, 1-(2-hydroxy-5-methylphenyl)-					86	1
3.4364	97530	Eugenol			82	4.6	82	1
3.8936	30560191	Acephate			76	5.8	88	1
4.1809	27813214	Tetrahydrophthalimide, cis-1,2,3,6-			87	6.0	90	3
4.3176	33704619	Cashmeran			74	0.9	71	21
4.9708	84662	Diethyl phthalate			96	-1.0	90	1
5.4542	126738	Tributyl phosphate			66	-0.6	71	2
5.6359	4710172	Dichlofluanid metabolite (DMSA)			95	7.0	88	1
5.8632	3689245	Sulfotep			88	-6.0	80	1
6.7323	58899	Lindane			91	0.2	83	4

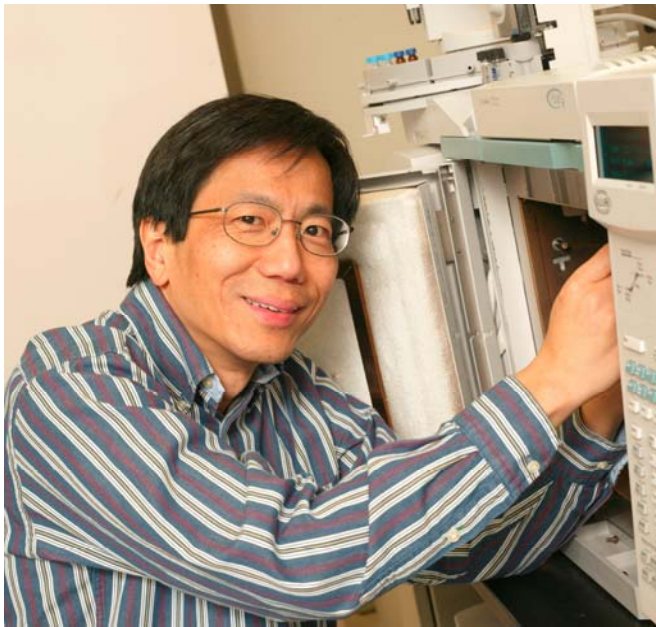


## Summary

- 10  $\mu$ L injection with Trace Ion Detection allow <10 ppb pesticide detection
- Backflushing with QuickSwap keeps column & MSD clean
- DRS used to screen for 927 pesticides & endocrine disruptors in one 23-minute GC/MS run
- Quant using scan, SIM, or Deconvoluted scan ions
- Rugged, Sensitive, Quantitative, and Accurate



**Thanks to Dr. Kai Meng and to Prof. Amadeo Fernancez-Alba,  
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Analysis Group at the University of Almeria, Spain**



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