Improving the Sensitivity, Ruggedness, and Accuracy of Pesticide Analysis

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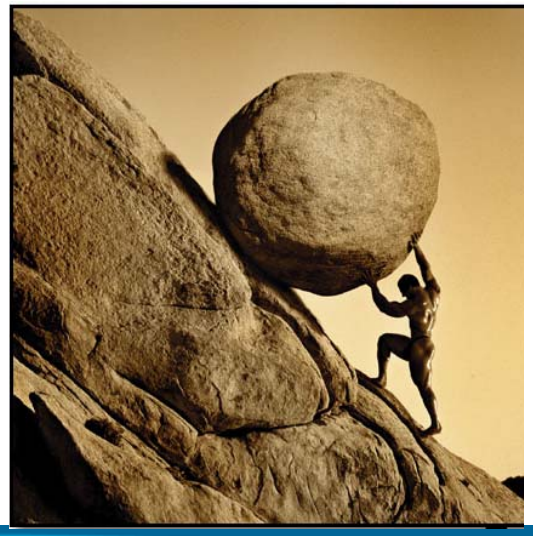
Pittcon, 2008
Paper 2180-4
Wednesday, 2:30 pm
Room 242

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 µL)
- SIM is more sensitive, but need scan for comprehensive method
- Food and environmental extracts are "dirty"
- 10 µL 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?

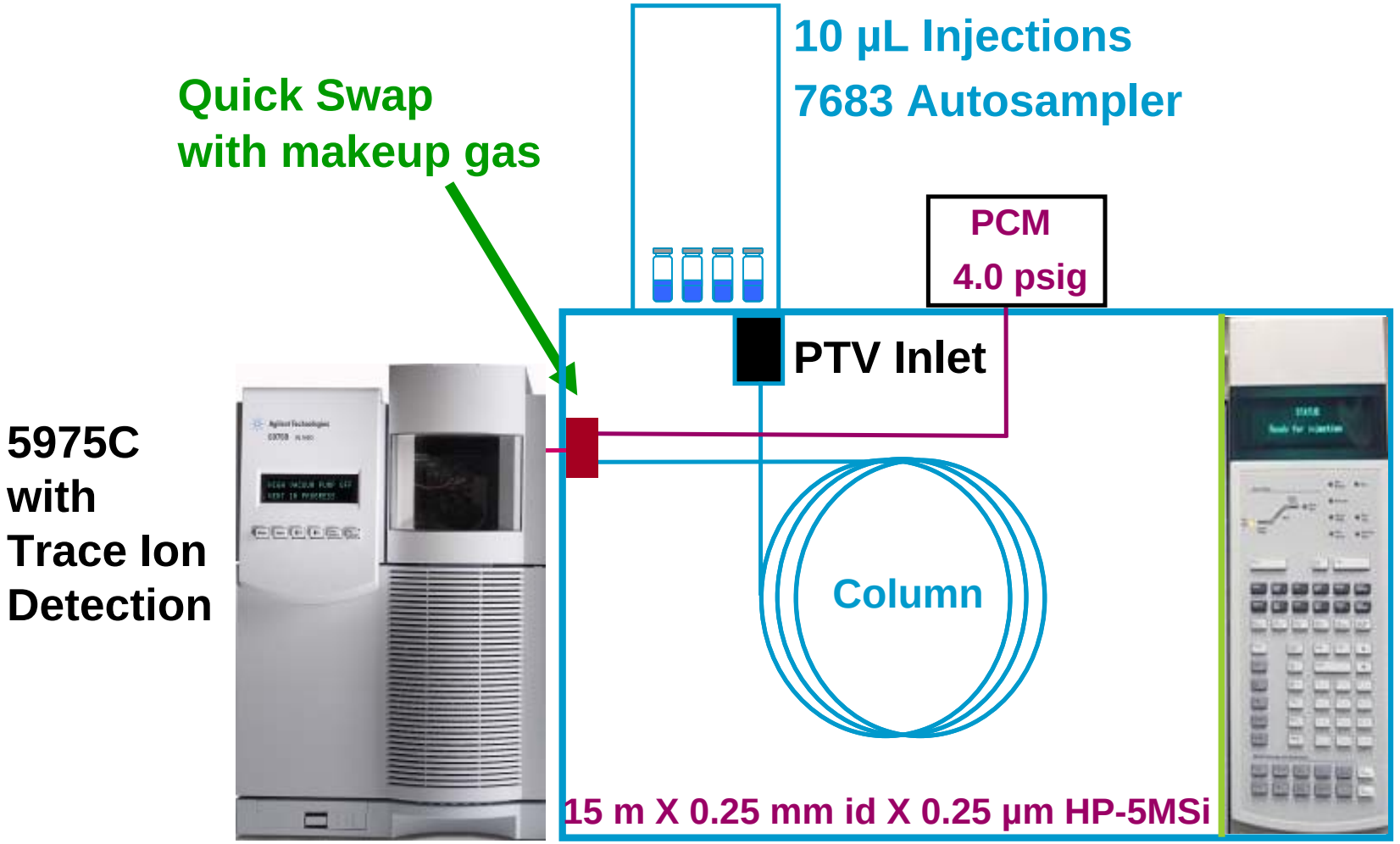


A Method to Screen for (and Quant Targets) Pesticides at <10 ppb in Food and Environmental Extracts

Keys to Success

- **Use GC/MS with Trace Ion Detection**
- **10 µL 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



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QuickSwap MSD Interface

Remove column w/o venting

- **Air & H_2O blocked**

Safe disconnection of column from inlet for inlet maintenance

- **Reversed flow through column during inlet maintenance**

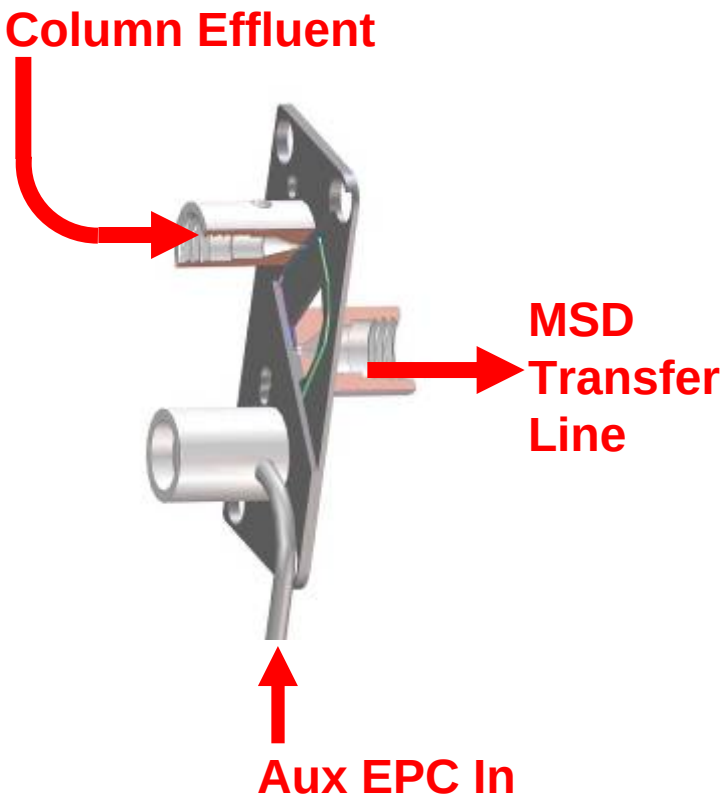
Backflushing

- **Removes heavies from column**

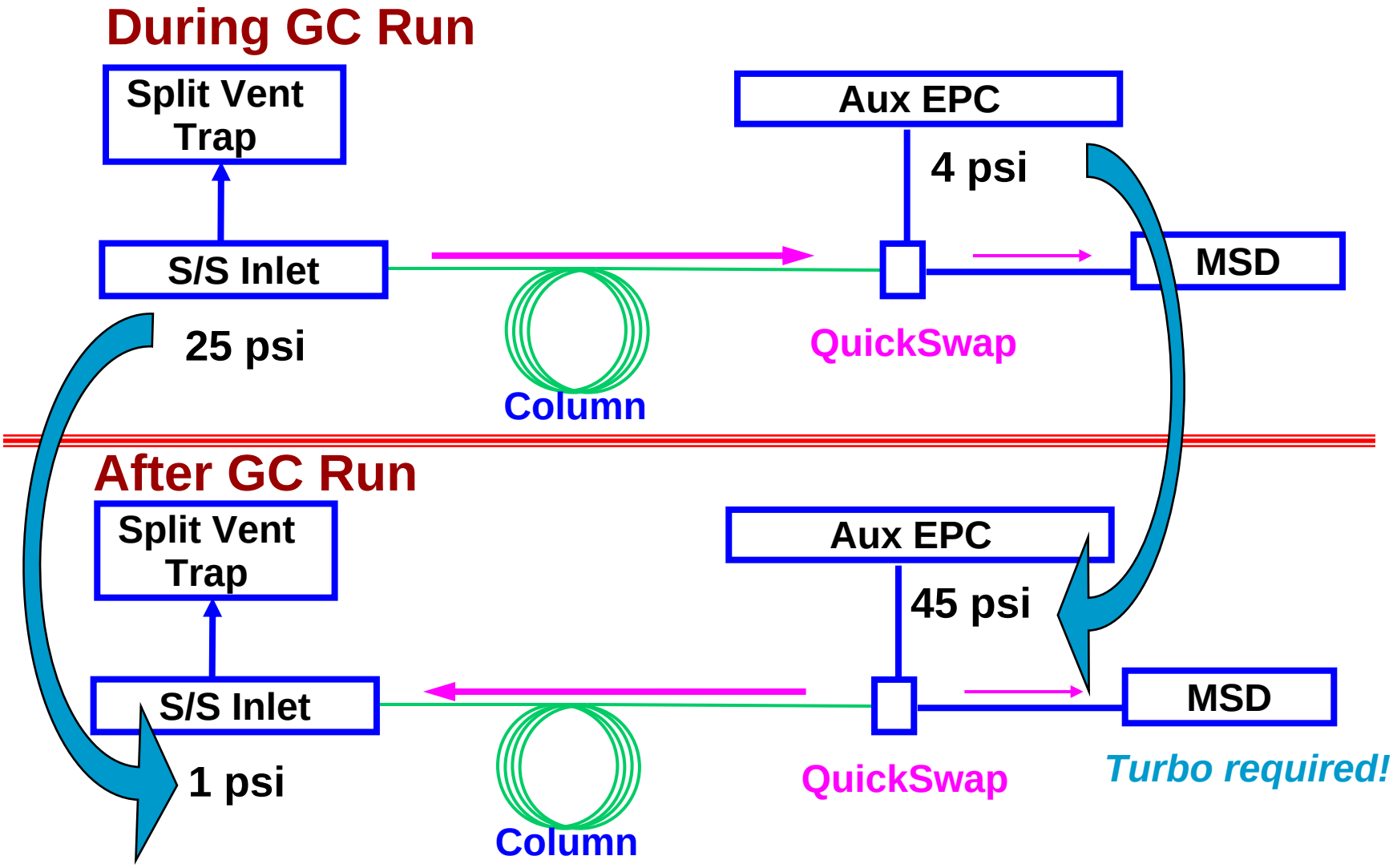
Maintain constant flow to MSD

Compensate for loss of sensitivity by making 10 µL injection

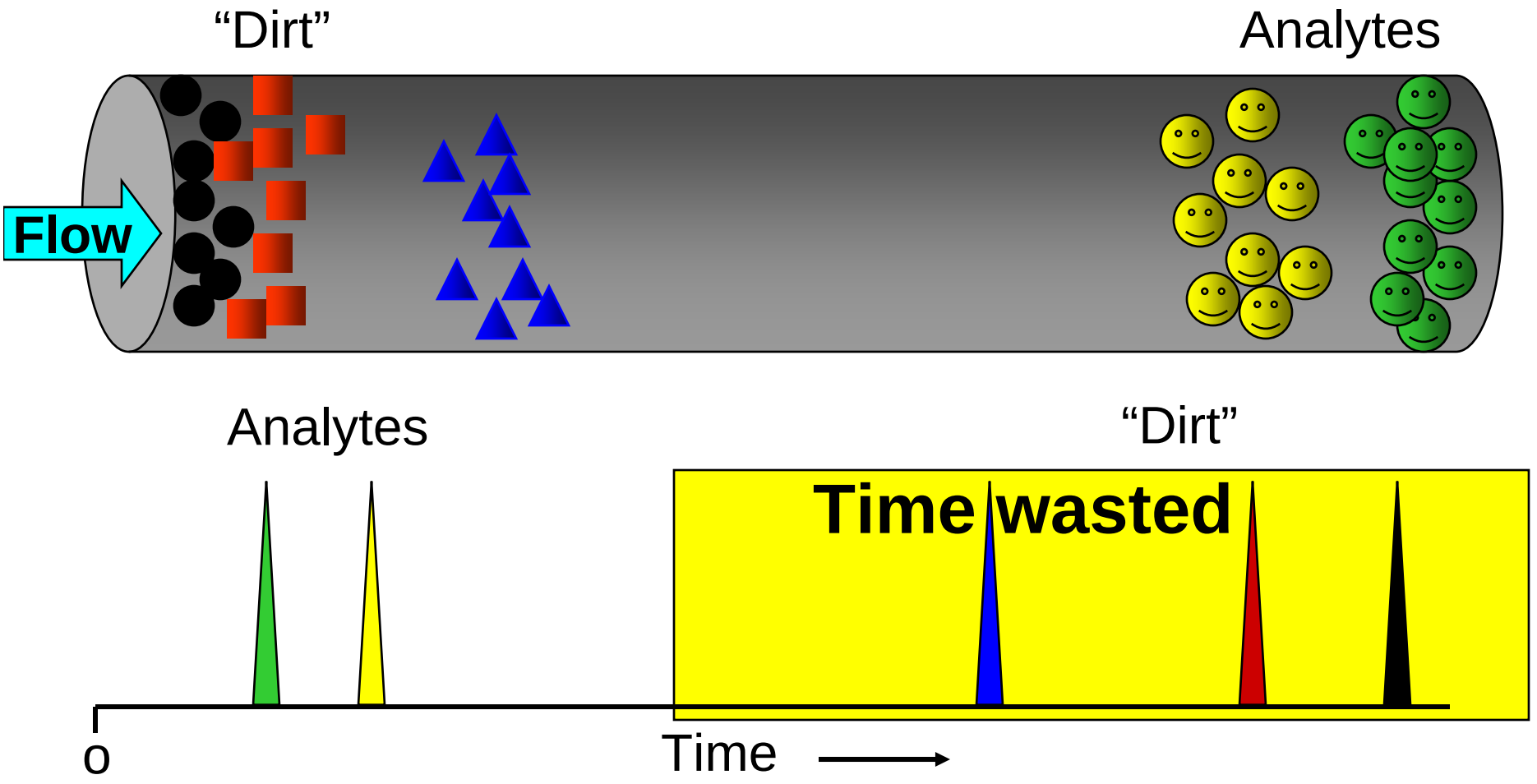
Turbo MSD required for backflushing



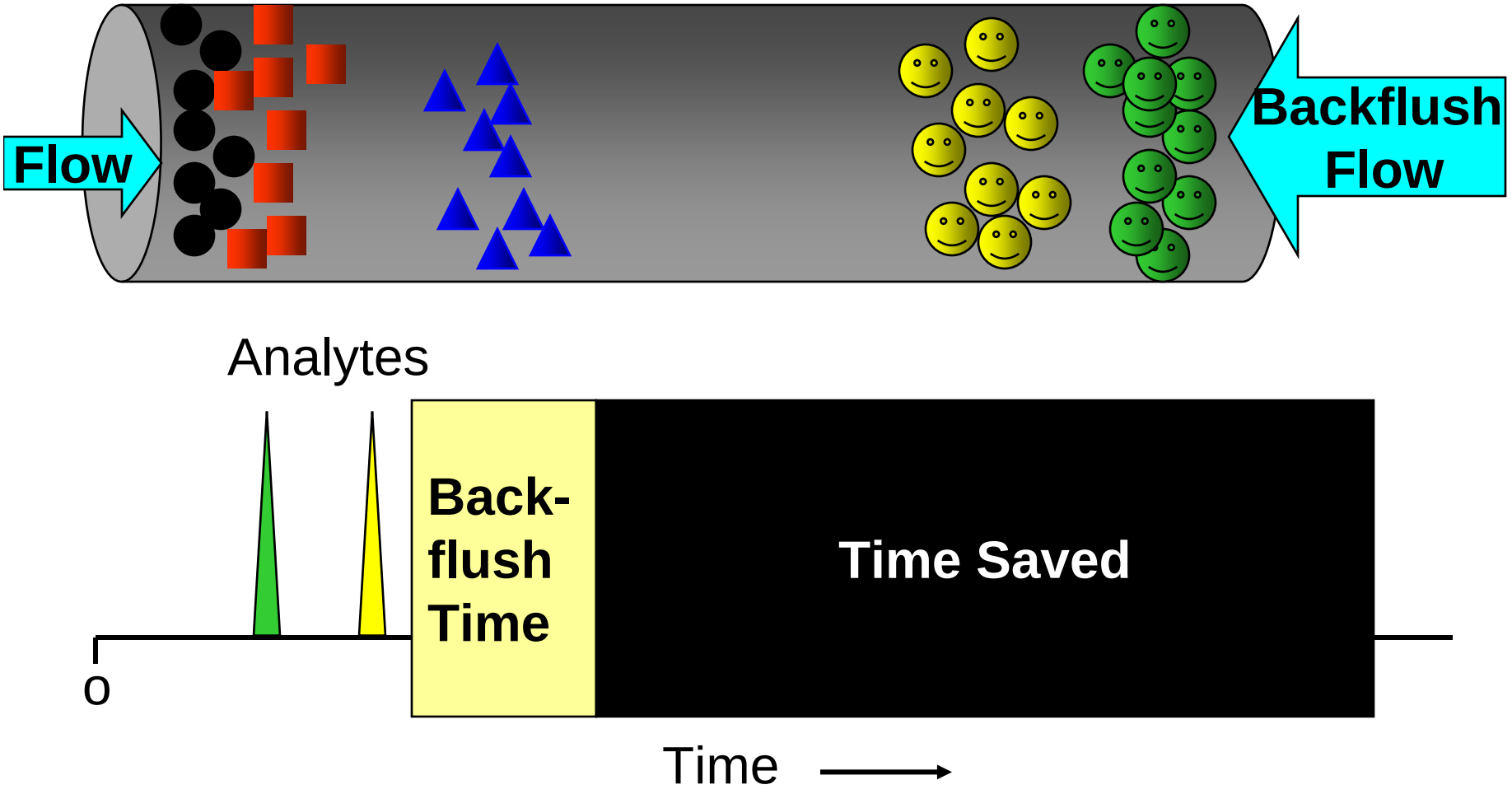
Backflush with QuickSwap



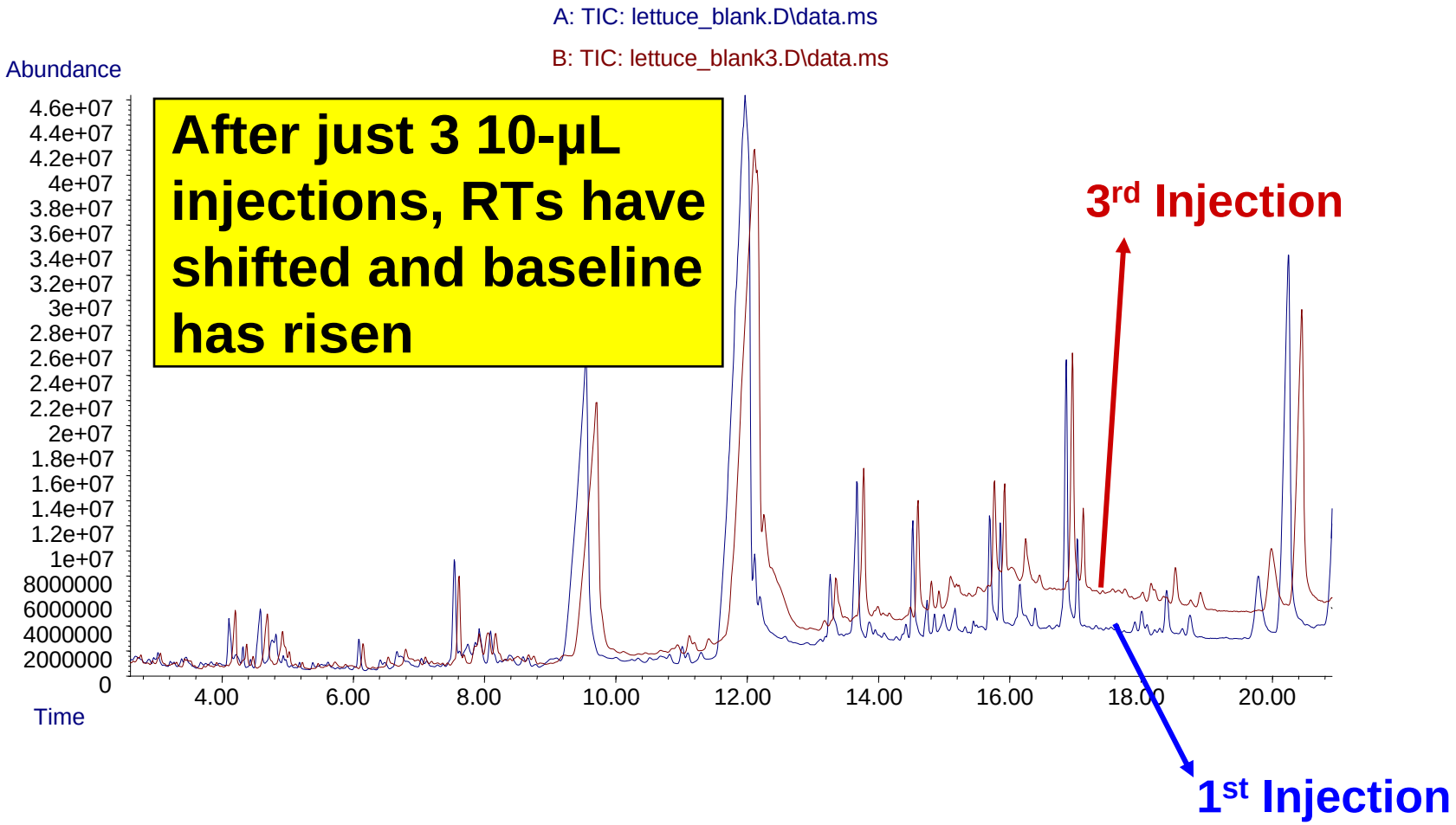
No Backflushing – Must Bake out the Column



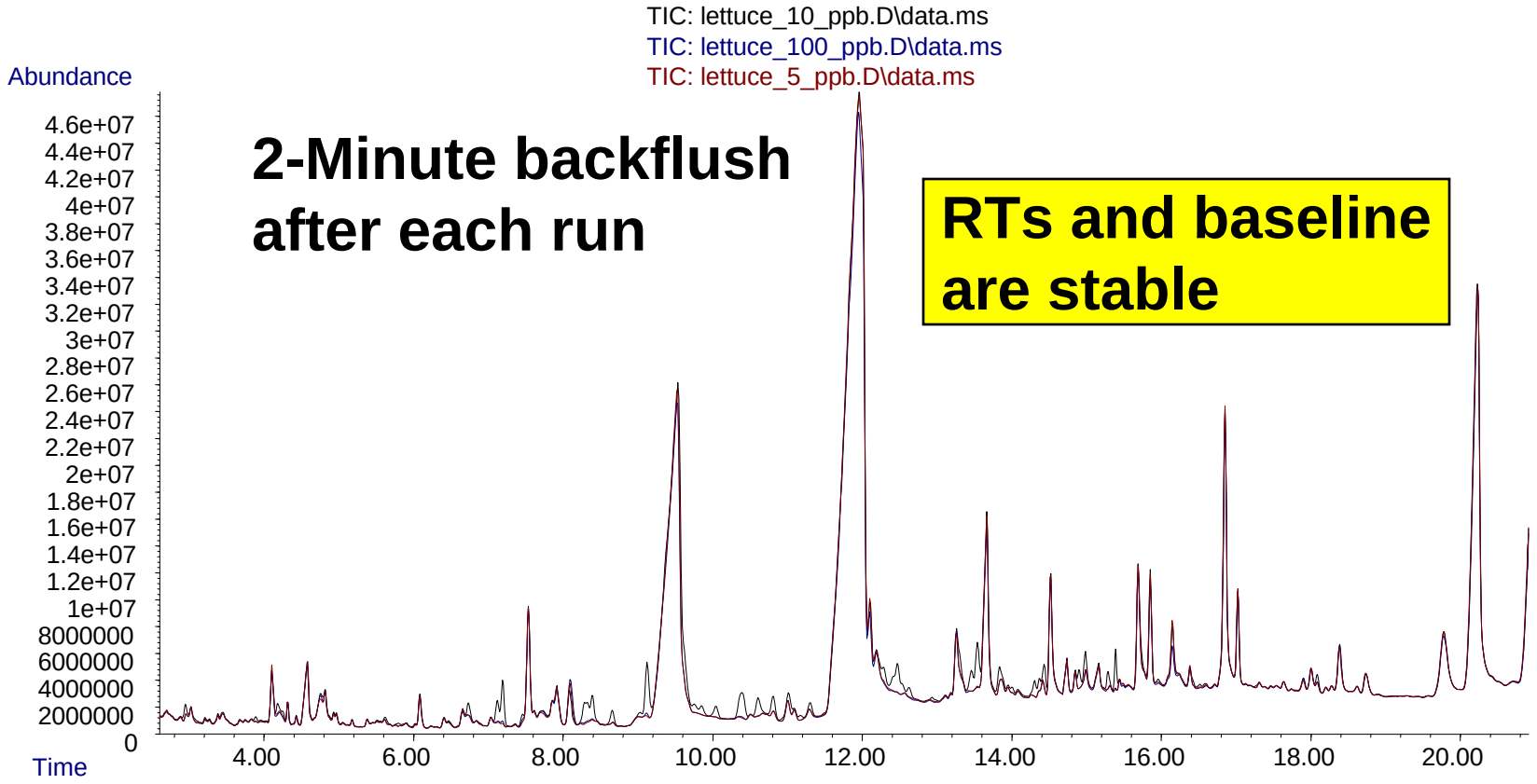
With Backflushing “Dirt” is Removed Through the Inlet’s Split Vent



Overlapped chromatograms of a Lettuce Extract: 1st & 3rd Injections made *without* Backflushing



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



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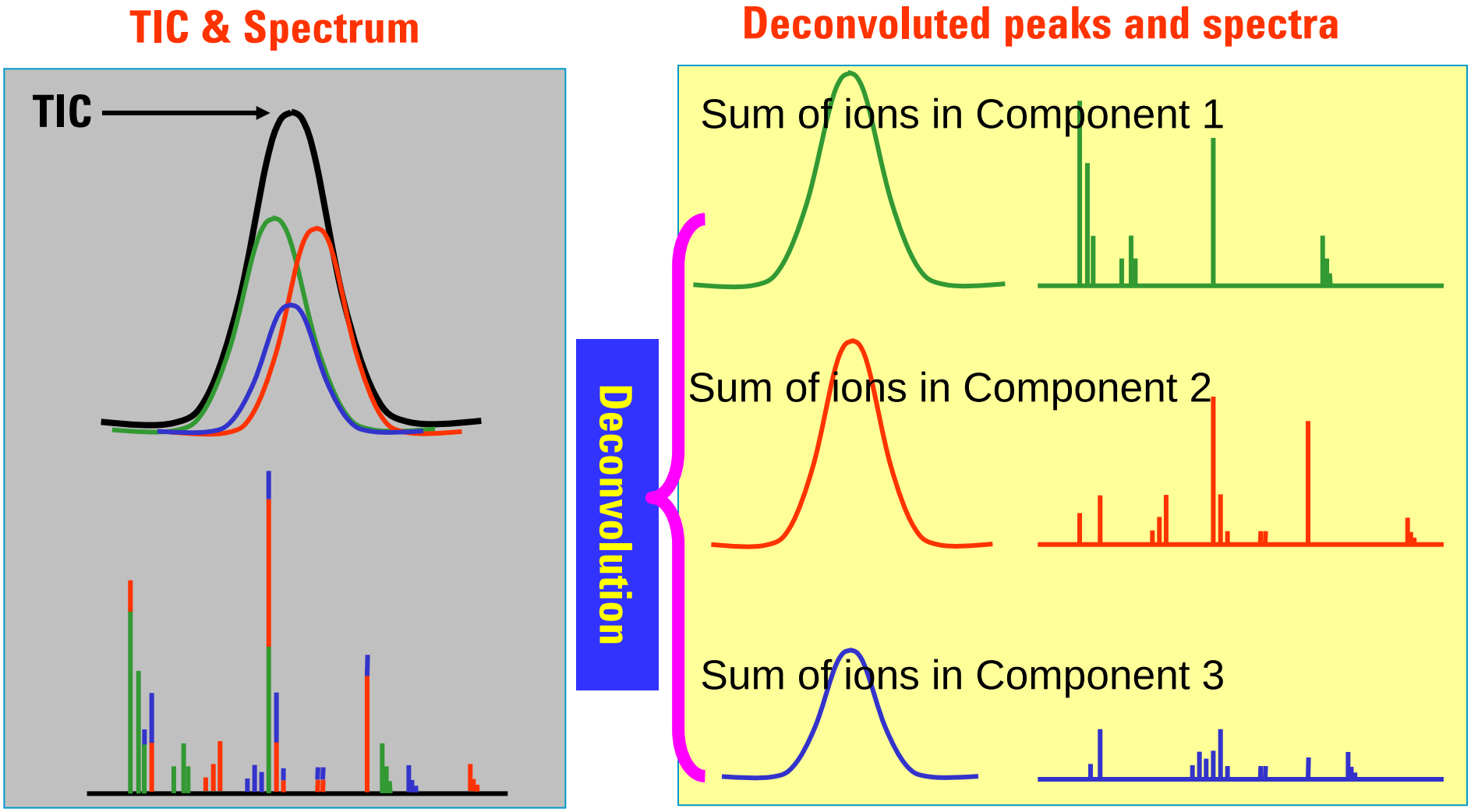
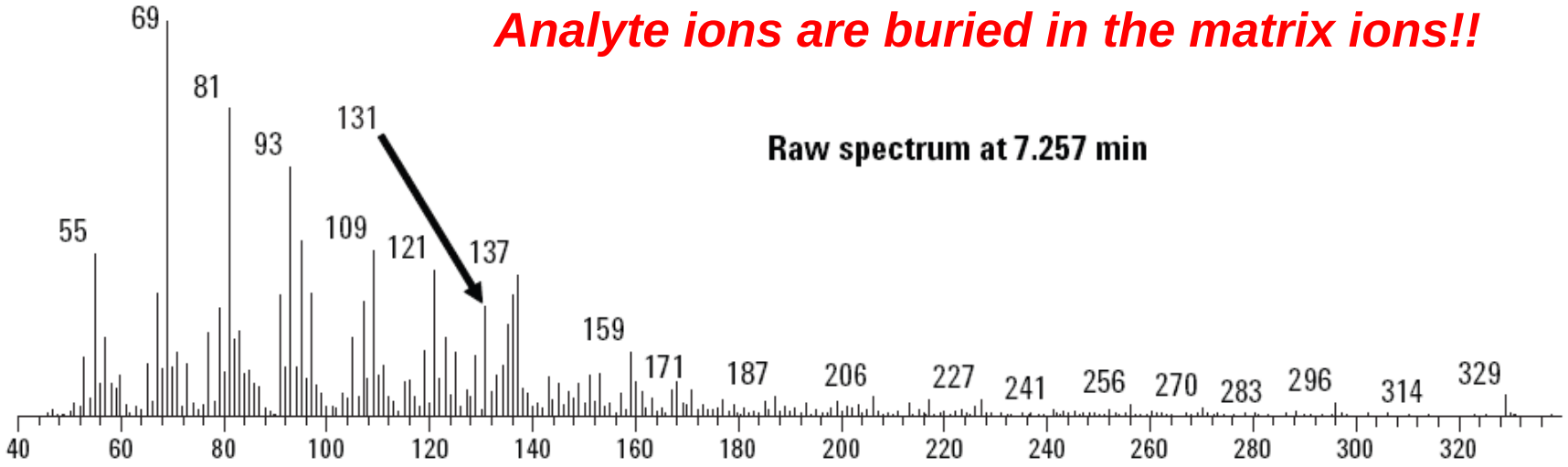
AMDIS Deconvolution Pulls Out Individual Components and their Spectra

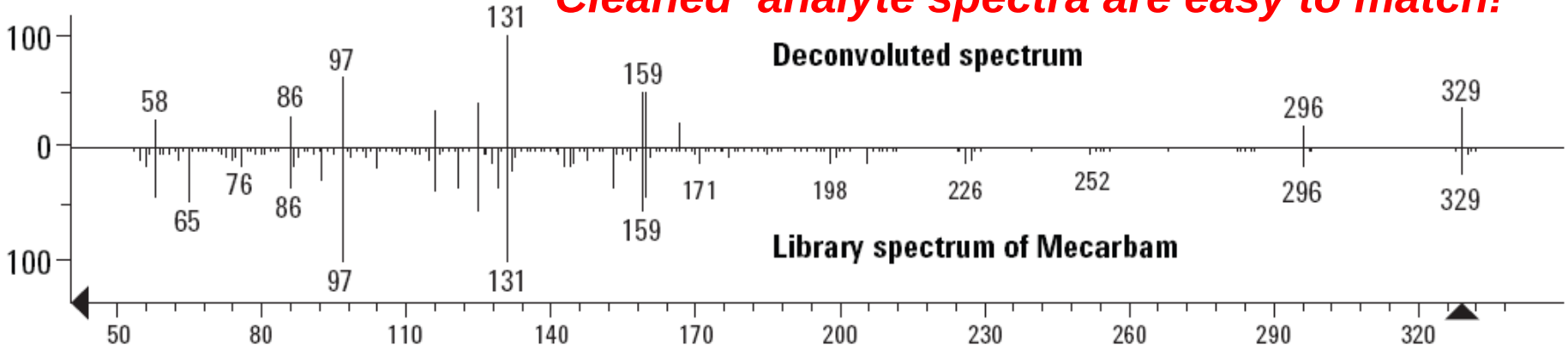


AMDIS: Pulling a Useable Spectrum Out of a Mess

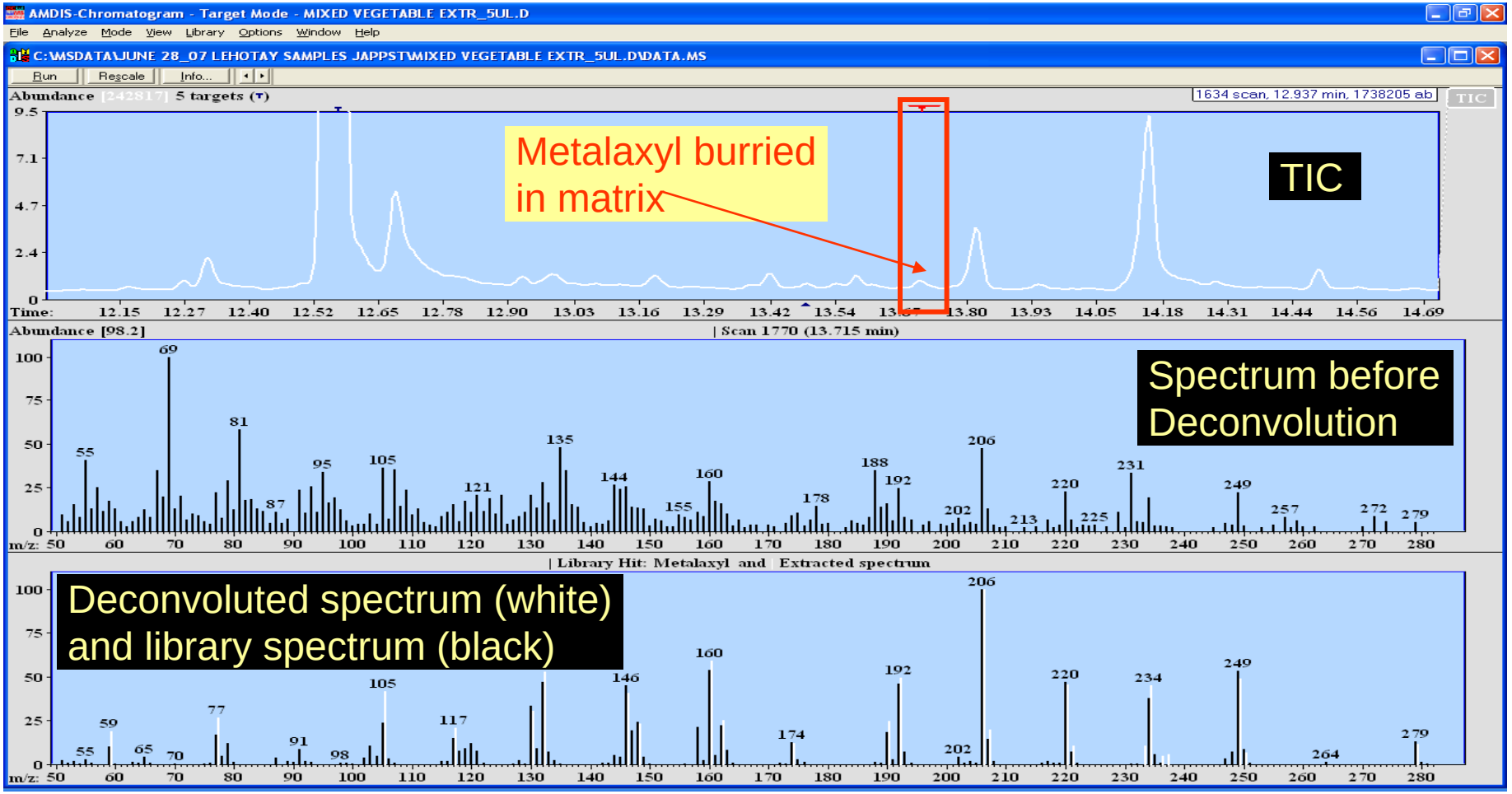
Analyte ions are buried in the matrix ions!!



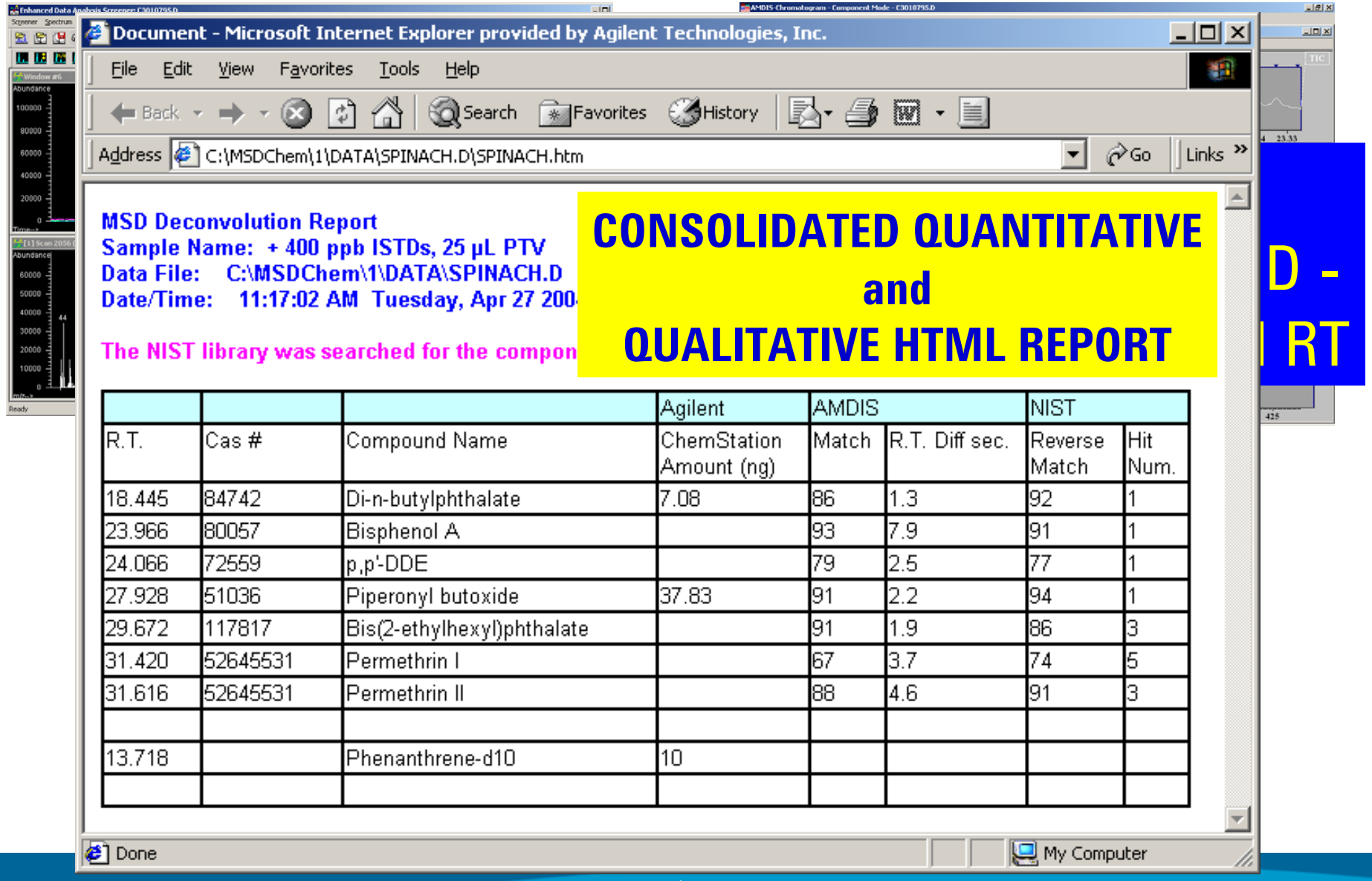
'Cleaned' analyte spectra are easy to match!



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



What is Agilent DRS?



			Agilent	AMDIS		NIST	
R.T.	Cas #	Compound Name	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				

Two Pesticide Databases Available for use with Deconvolution Reporting Software

"RTLPest3"

927 Compounds

- Almost all GCable pesticides
- Many metabolites
- More endocrine disrupters
- 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"

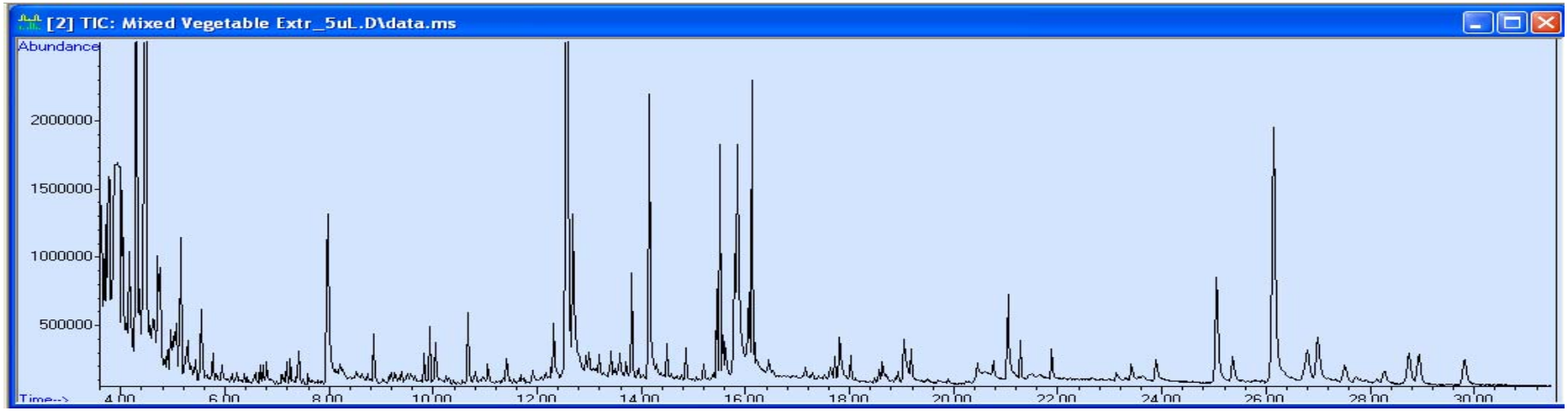
430 Compounds

- 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

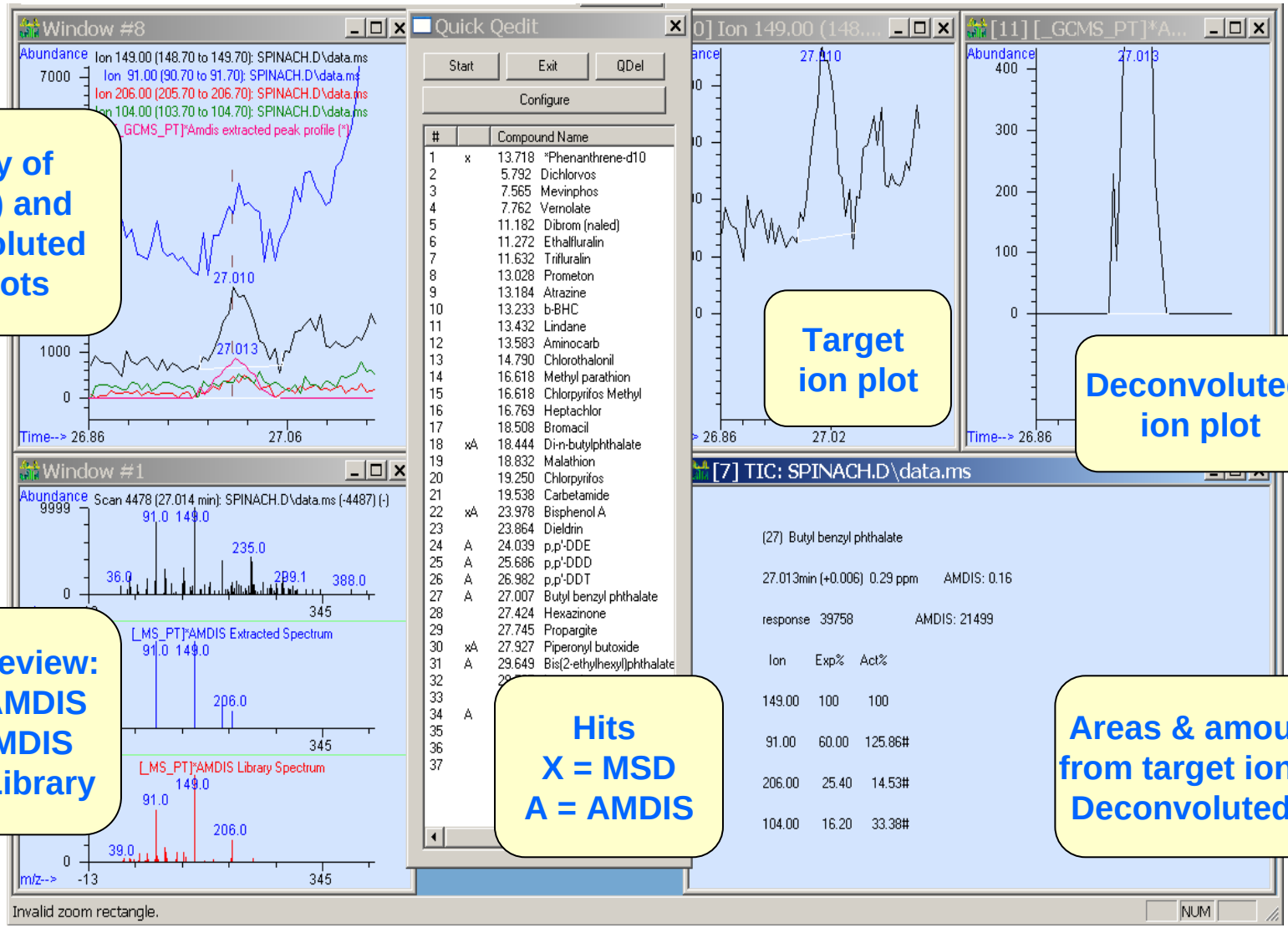
QuEChERS Extract of a Mixed Vegetable Sample: DRS Report (Sample was **not** spiked)



			Agilent	AMDIS		NIST	
R.T.	Cas #	Compound Name	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

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



Overlay of target(s) and Deconvoluted ion plots

Target ion plot

Deconvoluted ion plot

Spectral review: Before AMDIS After AMDIS AMDIS Library

Hits X = MSD A = AMDIS

Areas & amounts from target ion and Deconvoluted ion

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.

			Amount (ppb)		AMDIS		NIST	
R.T.	Cas #	Compound Name	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 µL 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, Dr. Ana Aguera, Dr. Milagros Mezcua & the Pesticide Analysis Group at the University of Almeria, Spain