HRSD

Cleaning wastewater every day for a better Bay.

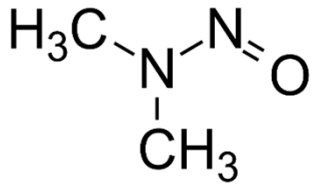
1,4-Dioxane, NDMA and Using GC/MS/MS for Environmental Analysis

Megan Pennington-Boggio, PhD

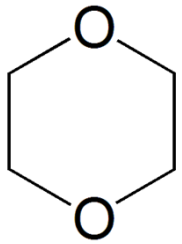
07/30/19

N-Nitrosodimethylamine (NDMA) and 1,4-Dioxane

NDMA (CCL3, UCMR2)



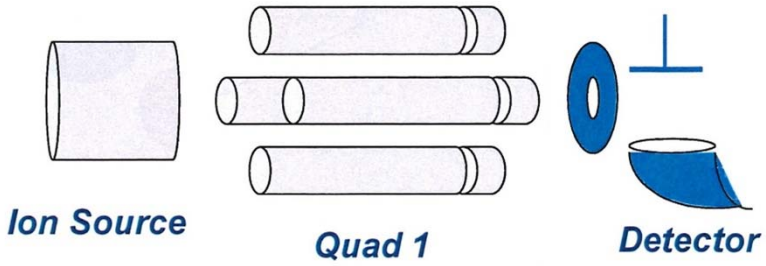
1,4-Dioxane (CCL4, UCMR3)



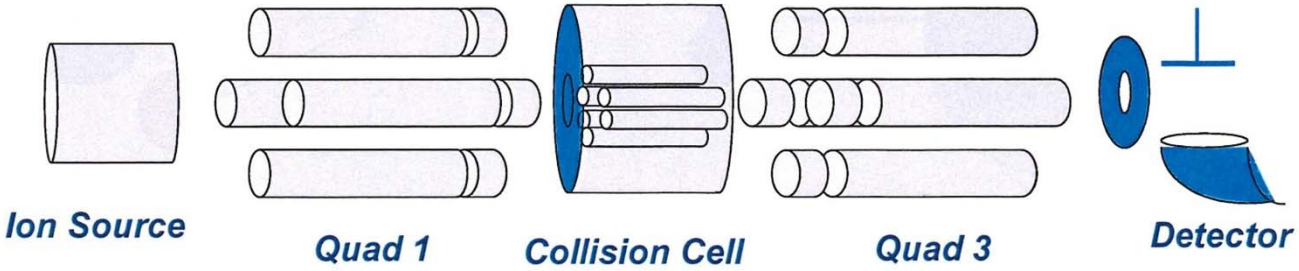
- Group B2, probable carcinogens
  - No MCL for drinking water set – yet
- Indirect Potable Reuse – SWIFT
  - Recharging the Potomac Aquifer
    - NDMA: 10 ng/L
    - 1,4-Dioxane: 1 µg/L

HRSD

- Single Quadrupole – Scan or SIM



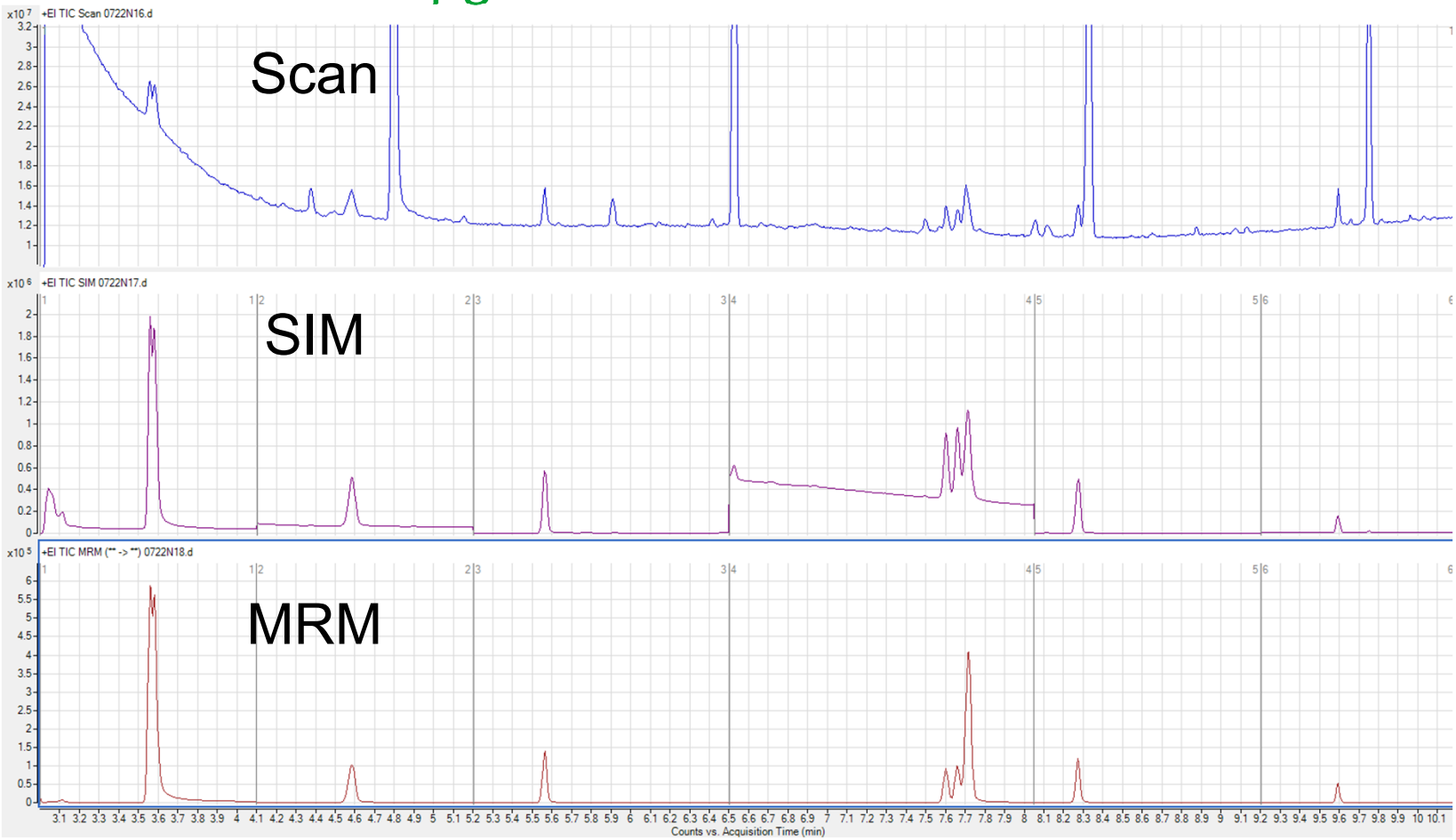
- "Triple" Quadrupole – MRM (multiple reaction monitoring)
  - Improved Sensitivity & Selectivity



Images adapted from Agilent Technologies training material

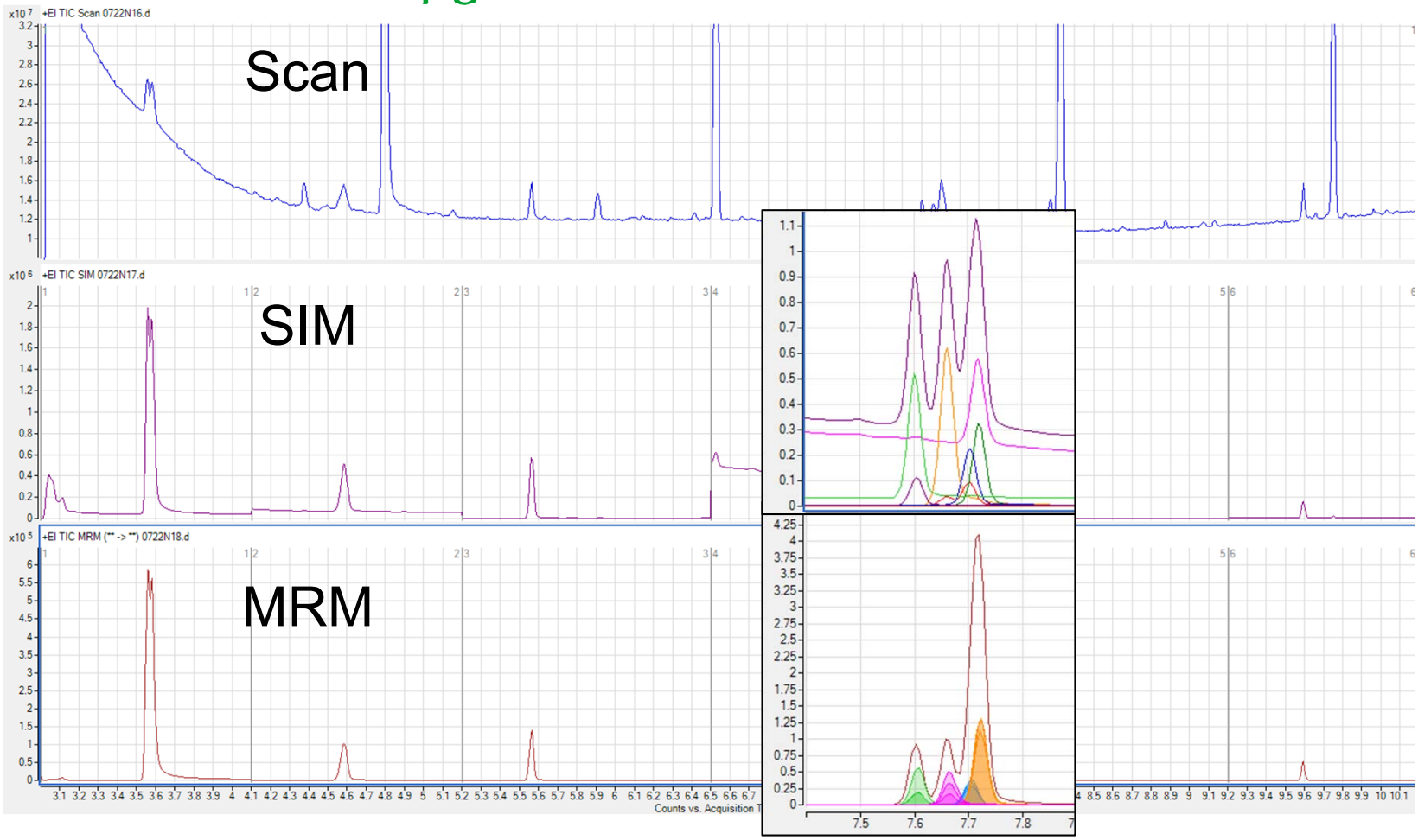
Scan vs. SIM vs. MRM - Standard

20 µg/L Nitrosamine Standard



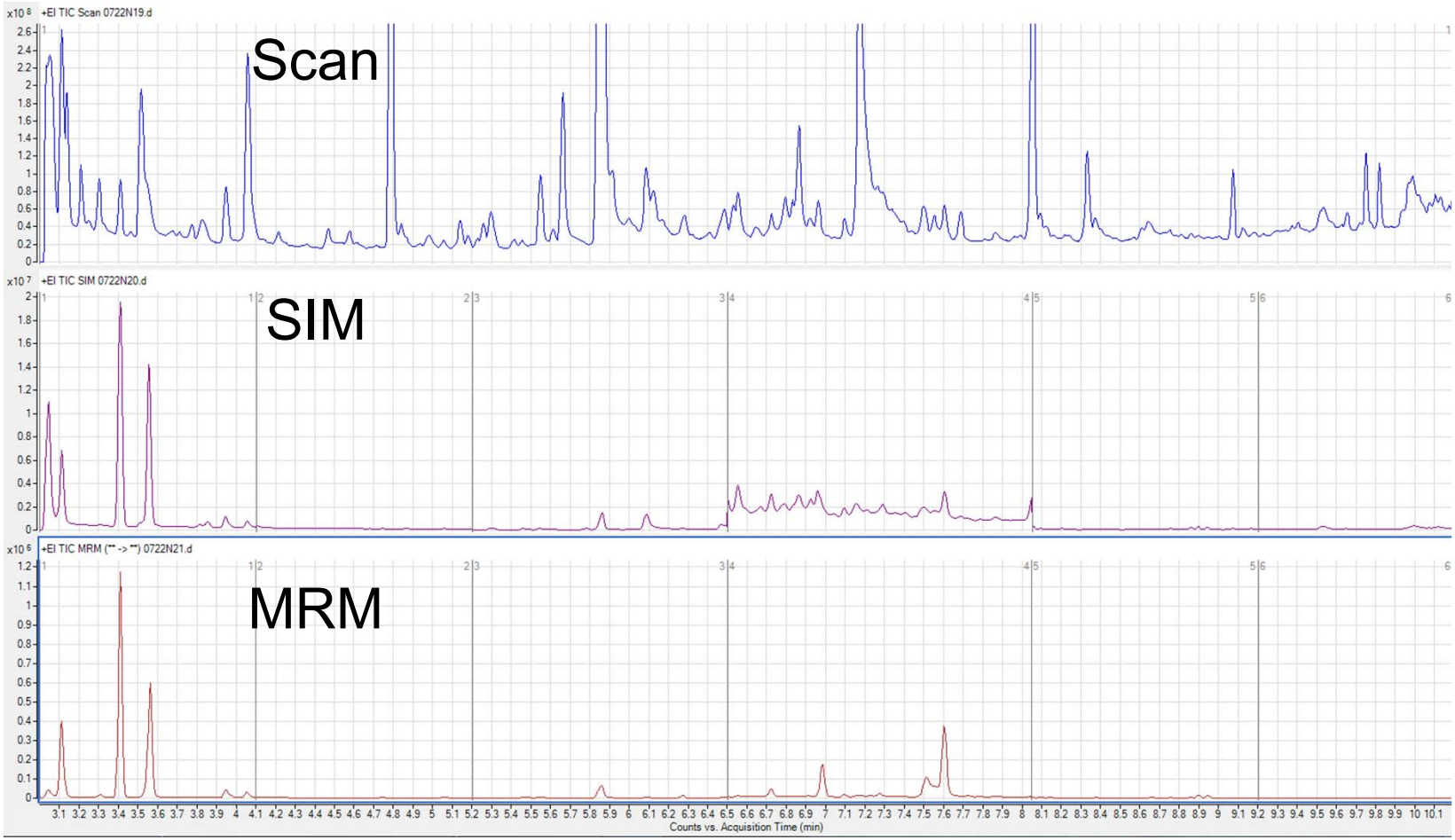
Scan vs. SIM vs. MRM - Standard

20 µg/L Nitrosamine Standard



Scan vs. SIM vs. MRM - Sample

Industrial Waste Sample



Scan vs. SIM vs. MRM - Sample

Industrial Waste Sample

Nitrosamines by GC/MS/MS

- EPA 521 uses chemical ionization, ion trap MS
  - Obsolete instrumentation
  - More maintenance than electron ionization
- ➡ Eurofins Eaton Analytical 521.1
  - Agilent 7010 or 7000 GC/MS/MS
  - No change to extraction
  - Improved sensitivity
  - Added NMOR
  - Run time decreased from 40 min to 15 min
- EPA approved method equivalency

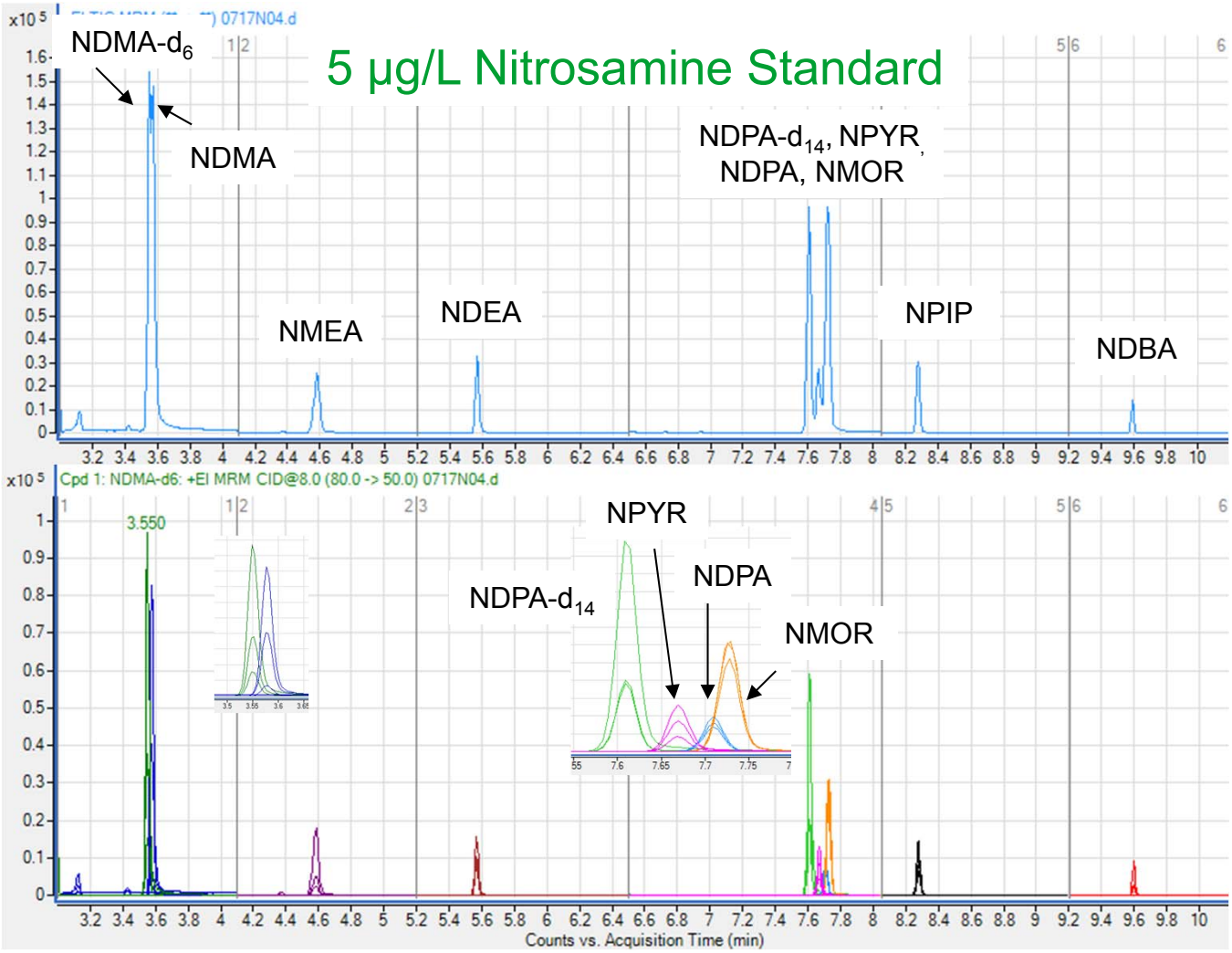
HRSD

Nitrosamine Analysis in Our Lab: GC Conditions

Column	RXI-5SilMS; 30 m, 0.25 mm ID, 0.5 µm film	
Injection Volume	1.5 µL	4 mm Single Taper w/wool
Pulsed Splitless	260 ºC; 35 psi until 0.5 min Purge flow: 100 mL/min at 0.5 min	
Oven Program	35 ºC for 1 min 35 ºC/min to 80 ºC, for 2 min 20 ºC/min to 135 ºC, for 0.9 min 35 ºC/min to 200 ºC 50 ºC/min to 220 ºC 3 min post-run, 300 ºC	10 min run + 3 min post
Carrier	Helium; 1.2 mL/min constant flow 2 mL/min for post-run	

HRSD

Nitrosamine Analysis in Our Lab: Chromatogram



Nitrosamine Extraction

- Automated Solid Phase Extraction (SPE)
  - Biotage Horizon SmartPrepII
- EPA 521 extraction procedure
  - Sodium Sulfate drying column
  - Concentration to 1 mL
- Initial recoveries were poor
  - Average 60% recovery for NDMA
  - 30-40% lost in drying and concentration steps

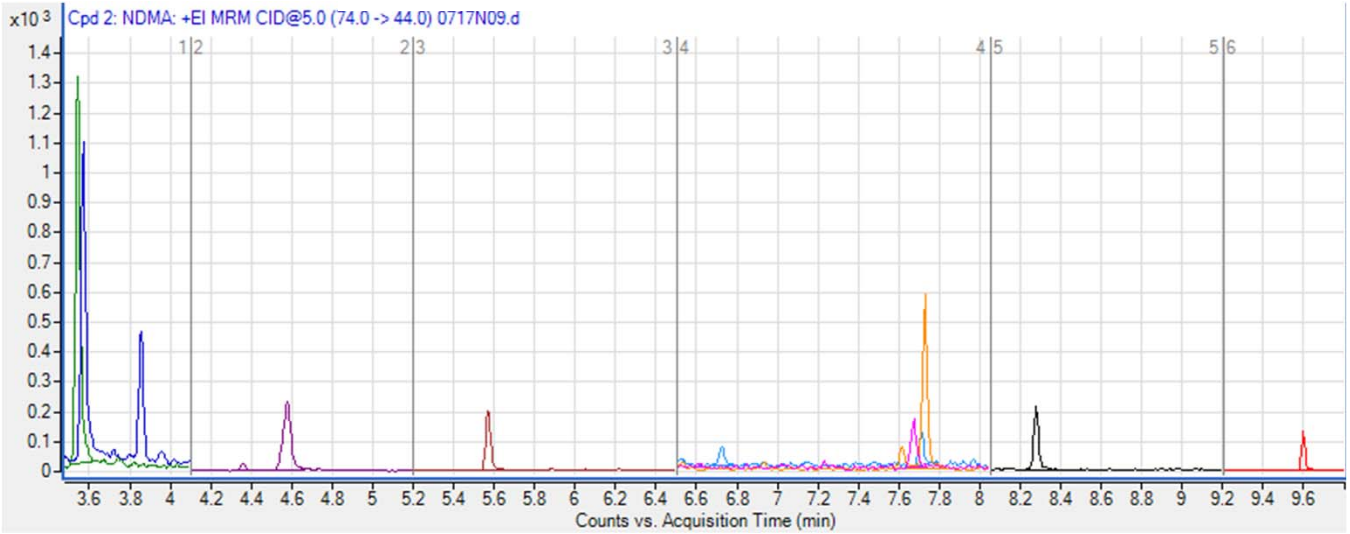
HRSD

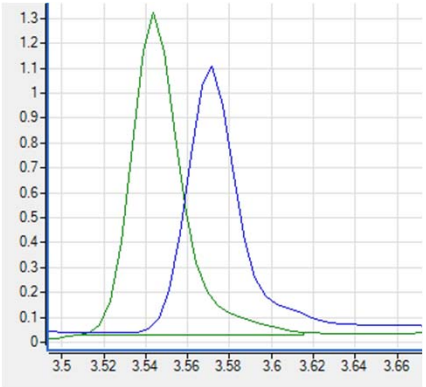
Can We Avoid Drying Columns?

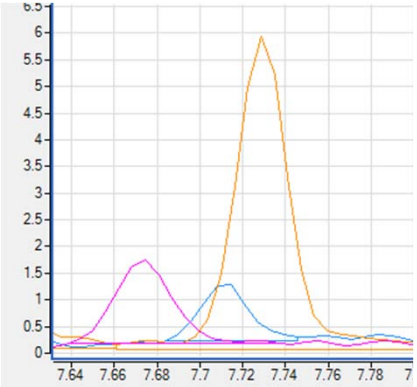
- Let the instrument do the work!
  - Agilent HES provides increased sensitivity
- Decreased calibration concentrations by 10x
  - Lowest standard: 100 ng/L
    - Quantitation limit for 500 mL sample = 2.0 ng/L
    - NDMA Area ≈ 2000 counts, S/N ≈ 60:1
- Final volume of 10 mL

Low Level Nitrosamine Calibration

0.1 µg/L Nitrosamine Standard







Current EPA Method- EPA 522

- GC/MS with SIM
- Requires Purge & Trap grade MeOH
- 18 min run time
- SPE extraction
  - 10 mL final volume, dry in situ

Not terrible, but we already have a GC/MS/MS…

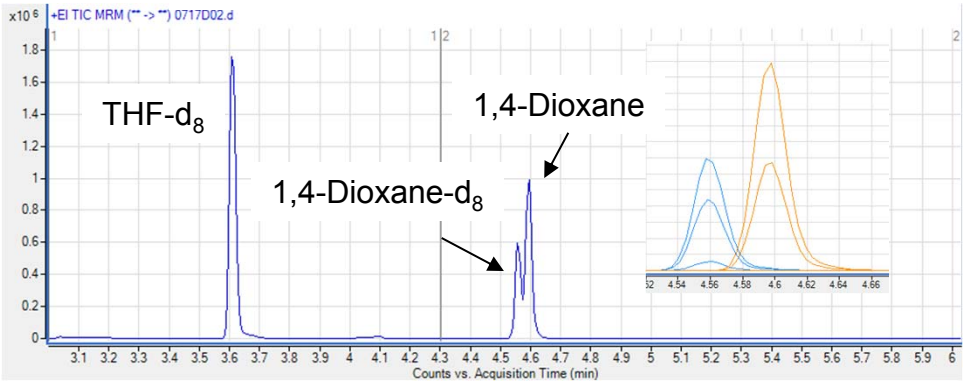
1,4-Dioxane Analysis in Our Lab: GC Conditions

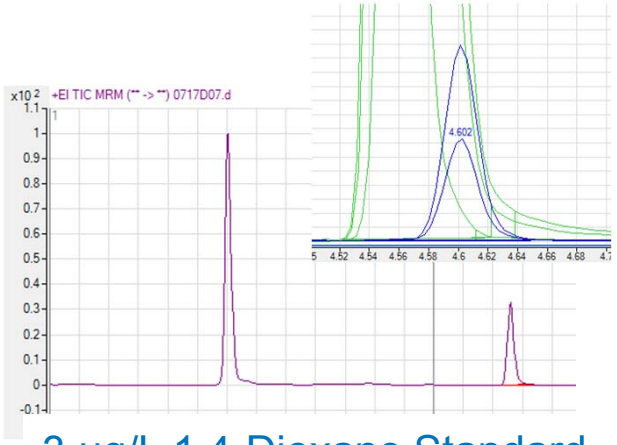
Column	RXI-5SilMS; 30 m, 0.25 mm ID, 0.5 µm film	
Injection Volume	1.0 µL	4 mm Single Taper w/wool
Pulsed Splitless	150 ºC; 35 psi until 0.5 min Purge flow: 100 mL/min at 0.5 min	
Oven Program	30 ºC for 1.5 min 10 ºC/min to 50 ºC 30 ºC/min to 90 ºC 50 ºC/min to 150 ºC 5 min post-run, 300 ºC	6 min run + 5 min post
Carrier	Helium; 1.2 mL/min constant flow 2 mL/min for post-run	

GC/MS/MS Analysis of 1,4-Dioxane

- P&T grade MeOH not required
- Lowest standard: 3 µg/L
  - Quantitation limit for 500 mL sample = 0.06 µg/L
    - Area ≈ 5600 counts
    - S/N ≈ 280:1

500 µg/L 1,4-Dioxane Standard





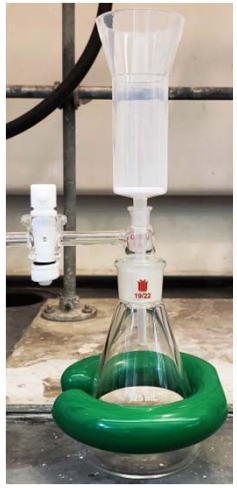
3 µg/L 1,4-Dioxane Standard

What About Wastewater?

- Established Non-Potable Methods
  - 1,4-Dioxane:
    - 8260: Purge & Trap, MS
    - 8015: Direct injection, FID
    - 8270: Liquid-Liquid Extraction, MS
  - NDMA:
    - 625, 8270: Liquid-Liquid Extraction, MS
- RLs 100-1000 times higher

Dirty matrices acceptable, with modification:

- Prefiltration
  - Raw influent, industrial waste
    - Surrogate added before filtration
- Dilution of extract
  - Raw influent
    - NDMA: RL= 4 ng/L
- Extraction of smaller volume
  - Industrial waste
    - 1,4-Dioxane: RL= 0.30 µg/L
    - NDMA: RL= 20 ng/L



HRSD

These Extractions Seem Redundant

- Extraction procedure nearly identical
  - Only preservation differs
- Extracting 50-70 samples each week
  - Can we save time and resources?

Combined Determination of 1,4-Dioxane and Nitrosamine Contaminants in Drinking Water

Using a Single SPE Cartridge and Concurrent Solvent Recondensation–Large Volume Splitless Injection (CSR-LVSI) With EI GC-MS

By Chris Rattray and Jack Cochran

RESTEK

HRSD

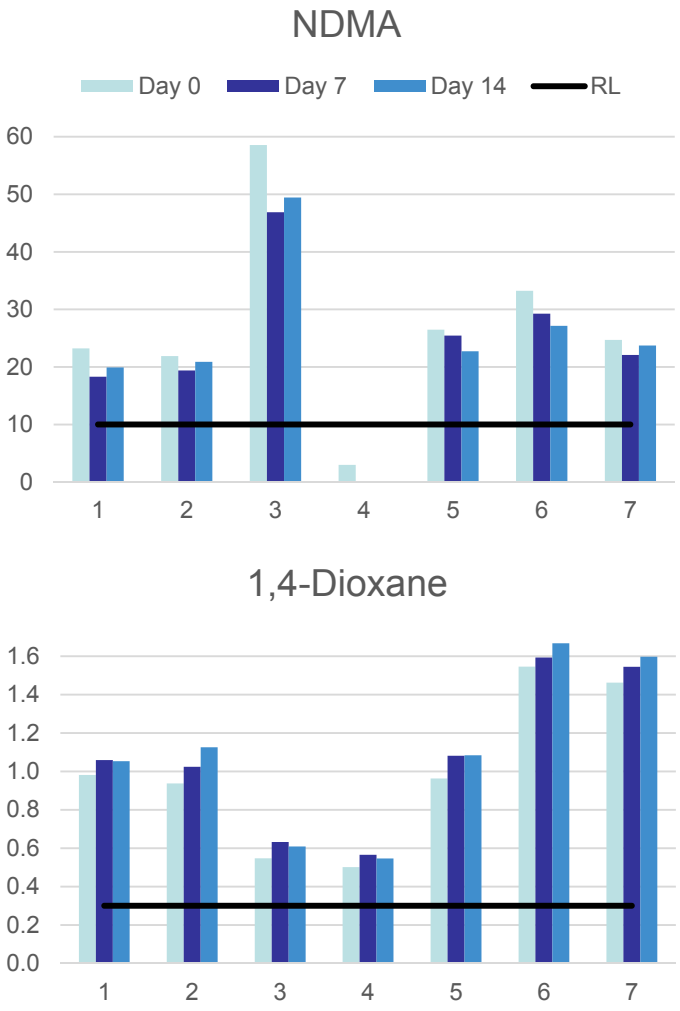
Combined Extraction of Nitrosamine and 1,4-Dioxane

- Restek paper did not address preservation
  - EPA 522 samples are pH <4
    - 25 mg Sodium Sulfite
    - 500 mg Sodium Bisulfate
  - EPA 521 samples are not pH adjusted
    - 50 mg Sodium Thiosulfate

	521 Preservation		522 Preservation	
Conc.	NDMA	1,4-Dioxane	NDMA	1,4-Dioxane
Low	121%	102%	133%	106%
Medium	107%	107%	100%	99%
High	98%	108%	86%	85%

HRSD

What about Holding Time?



EPA 521 Preservation

- 1: Spiked HPW
- 3: Sample
- 5: Spiked Sample

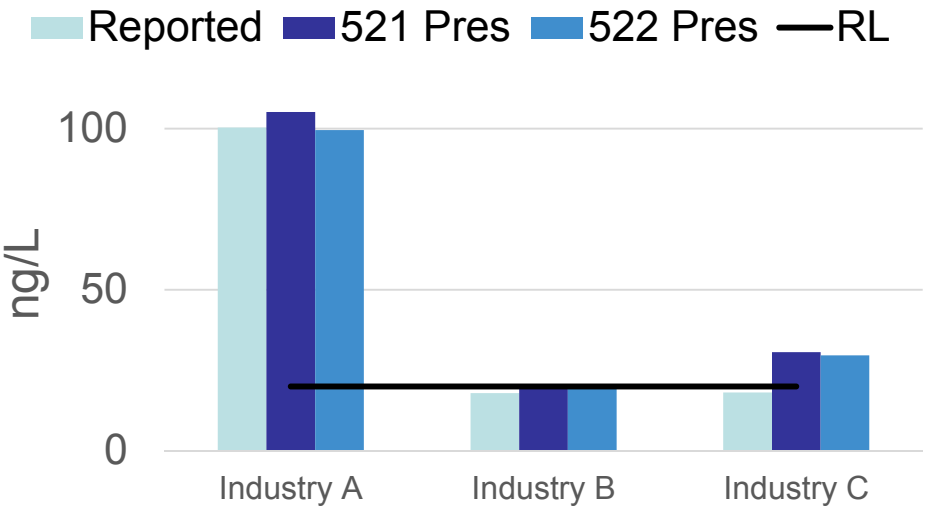
EPA 522 Preservation

- 2: Spiked HPW
- 4: Sample
- 6: Spiked Sample

No Preservation

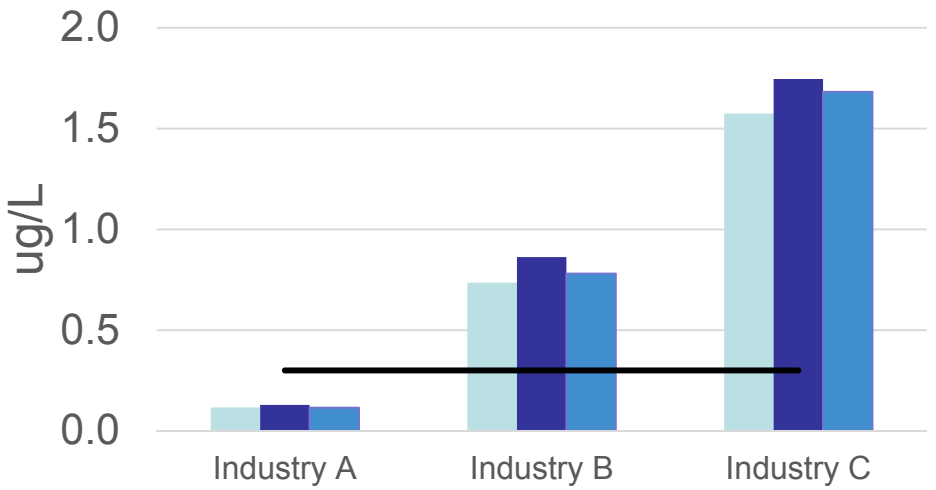
- 7: Spiked Sample

Does it work for Complex Matrices?



NDMA

1,4-Dioxane



Combined Extraction Summary

- EPA 521 extraction conditions
  - Add both surrogates and internal standards
  - 10 mL final volume
- EPA 522 preservation
- Analyzed by both instrument methods
- Used for research samples

Decreased our workload by ~30 samples/week

HRSD

What's Next?

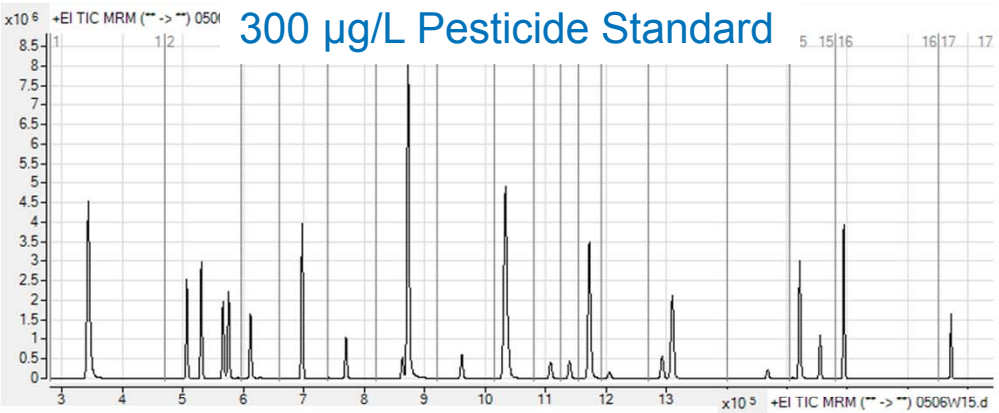
- Add Tetrahydrofuran (THF)
- Develop single instrument method
  - 8 Nitrosamines, 1,4-Dioxane, THF

HRSD

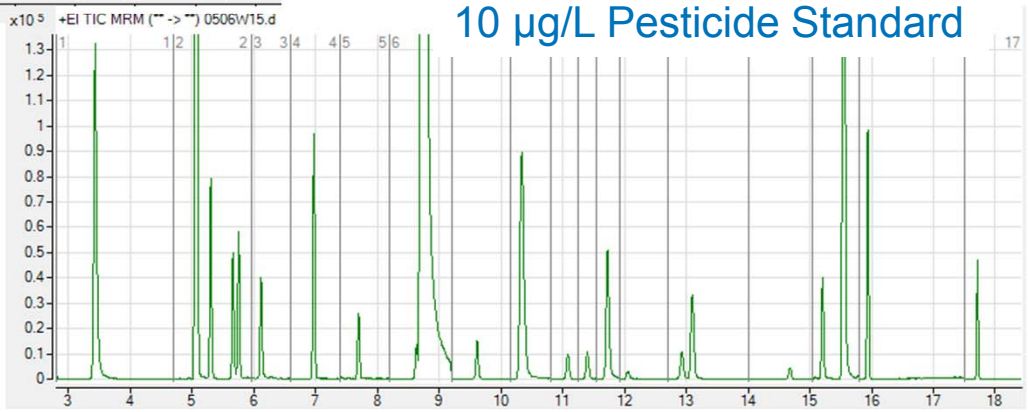
What Else Can GC/MS/MS Do?

- Analysis of Organochlorine Pesticides & PCBs

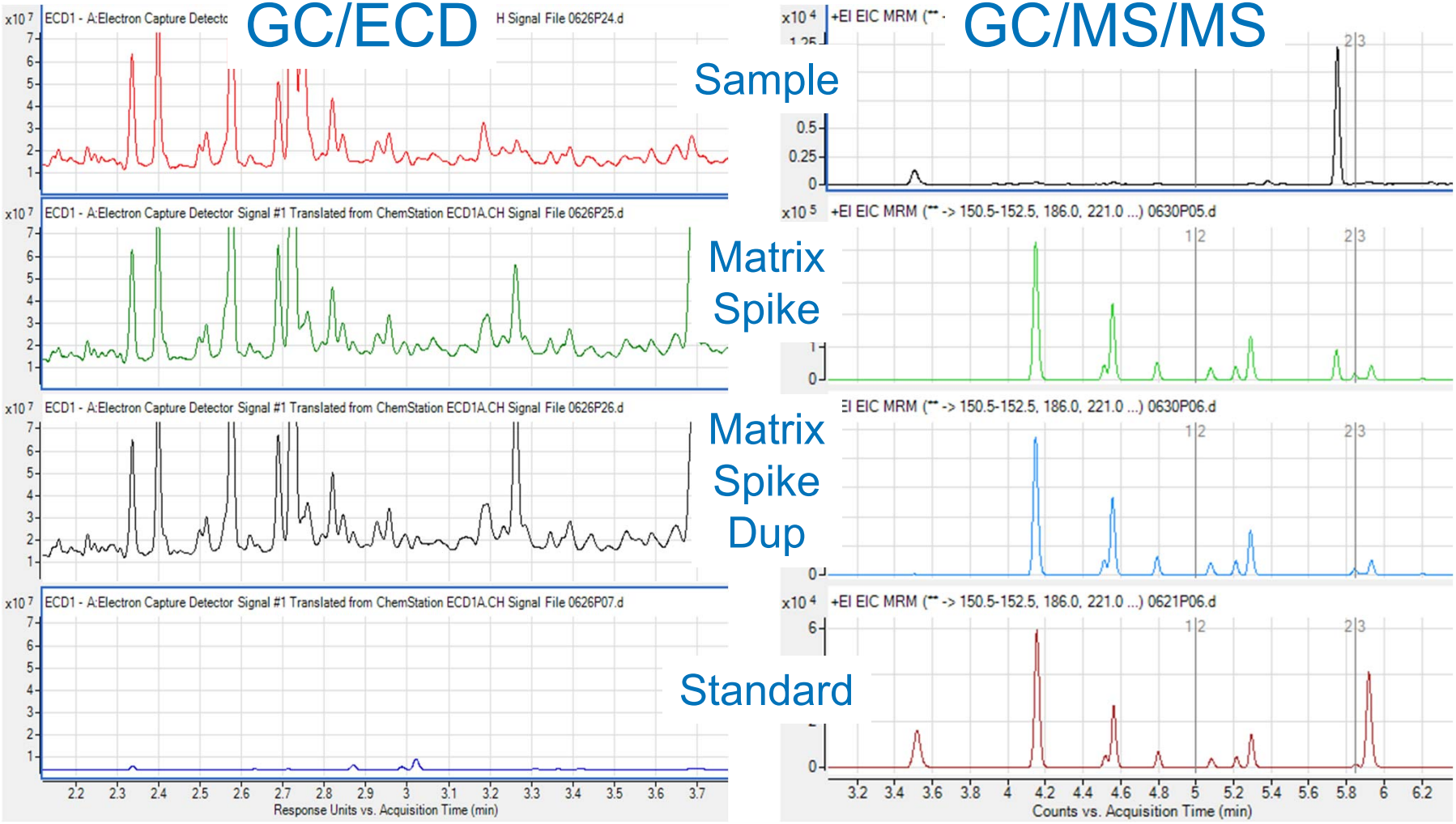
300 µg/L Pesticide Standard



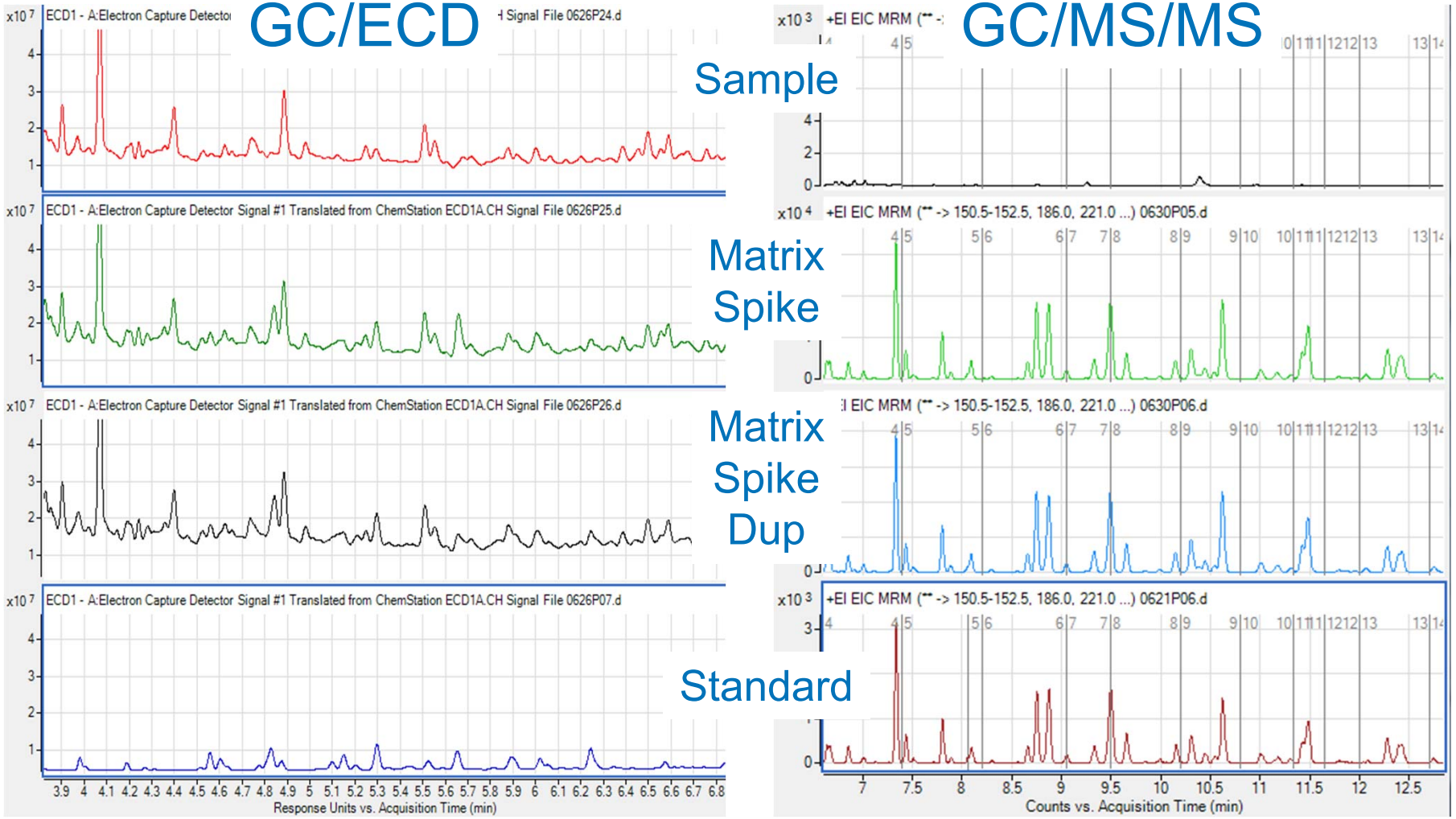
10 µg/L Pesticide Standard



Fingerprinting by GC/MS/MS – AR1221



Fingerprinting by GC/MS/MS – AR1254



Questions?

Contact:
757-460-4286
mboggio@hrsd.com

N-Nitrosodimethylamine (NDMA)

- Formerly, used in the production of:
  - Rocket fuel
  - Antioxidants and
  - Softeners for copolymers
- Currently, primarily a disinfection byproduct
- Classified as Group B2, probable carcinogen
  - No MCL for drinking water set – yet
  - On CCL3 and UCMR2 lists
- Treatment options:
  - UV irradiation
  - Removal of precursors before Chloramination

HRSD

1,4-Dioxane

- Formerly, widely used as a solvent stabilizer
- Present as a byproduct in a variety of goods
- Present in waste from manufacture of:
  - Pharmaceuticals
  - PET plastic, Textiles
- Classified as Group B2, probable carcinogen
  - No MCL for drinking water set – yet
  - On CCL4 and UCMR3 lists
- Treatment options:
  - Oxidation by H_2O_2 and UV or Ozone

HRSD

Nitrosamine Analysis in Our Lab: MS Parameters

Transfer Line Temperature	280 ºC
Ionization Mode	EI; using HES source
Source Temperature	230 ºC
Quadrupole Temperature	150 ºC
Collision gas Quench Gas	1.5 mL/min 4.0 mL/min
Emission	100 µA

Nitrosamine Analysis in Our Lab: Transitions

Compound	Transition	CE		Compound	Transition	CE
NDMA-d6	**80 → 50**	8		NPYR	100 → 70	5
	80 → 48	14			100 → 68	14
	80 → 46	24			**100 → 55**	8
NDMA	**74 → 44**	5		NDPA	**130 → 113**	2
	74 → 42	22			130 → 43	10
	74 → 30	14			101 → 70	2
NMEA	88 → 73	5		NMOR	**116 → 86**	2
	88 → 71	3			116 → 56	15
	88 → 57	9			86 → 56	8
NDEA	**102 → 85**	5		NPIP	114 → 97	8
	102 → 56	15			**114 → 84**	8
	102 → 44	14			114 → 55	22
NDPA-d14	144 → 126	1		NDBA	158 → 141	2
	144 → 50	14			158 → 99	10
	78 → 46	14			**116 → 99**	2

HRSD

1,4-Dioxane Analysis in Our Lab: MS Parameters

Transfer Line Temperature	280 ºC
Ionization Mode	EI; using HES source
Source Temperature	230 ºC
Quadrupole Temperature	150 ºC
Collision gas Quench Gas	1.5 mL/min 2.25 mL/min
Emission	100 µA

1,4-Dioxane Analysis in Our Lab: Transitions

Compound	Transition	CE
THF-d8	**80 → 78**	5
	80 → 48	12
	80 → 46	24
1,4-Dioxane-d8	96 → 64	7
	96 → 62	10
	96 → 46	38
1,4-Dioxane	88 → 58	7
	88 → 57	10

DFTPP and Endrin Degradation, Too!

- It is possible to pass a DFTPP tune check
- Endrin/DDT Degradation, too!

Target Mass	Rel. To Mass	Lower Limit%	Upper Limit%	Rel. Abn%	Raw Abn	Pass/Fail
68	69	0	2	0.9	26678	Pass
69	198	0	100	16.0	2895046	Pass
70	69	0	2	1.6	46534	Pass
197	198	0	2	0.1	12597	Pass
198	198	1	100	100.0	18081142	Pass
199	198	5	9	8.3	1508332	Pass
365	198	1	100	1.9	342149	Pass
441	443	0	150	80.1	2964987	Pass
442	198	1	200	88.9	16071824	Pass
443	442	15	24	23.0	3702286	Pass

Compound Name	Expected RT	Observed RT	TIC Area	Breakdown %	Pass/Fail
4,4'-DDT	9.220	9.121	301587439	1.7	Pass
4,4'-DDD	8.900	8.816	2114473		
4,4'-DDE	8.550	8.459	3192897		
Endrin	8.820	8.725	123522176	0.0	Pass
Endrin Aldehyde	9.050	0.000	0		
Endrin Ketone	9.650	0.000	0		

Expanding GC/MS/MS Analysis – DFTPP Tune Check

- Requires custom tune parameters
- Concentration of DFTPP, Pentachlorophenol and Benzidine important