Improving Analytical Efficiency and Reducing Cost of Operation

MELA and CWEA

Joint Technical Sessions

Craig Marvin

Global Environmental Industry Manager

Graham Robinett

Federal Account Manager – Linthicum

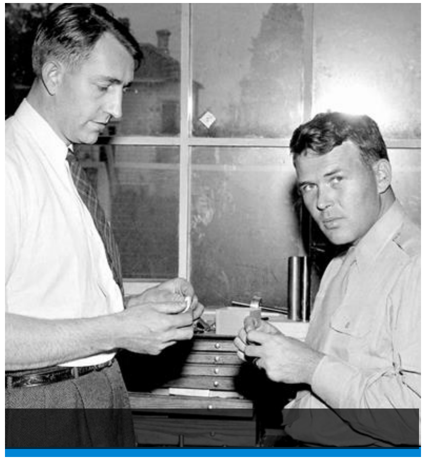
June 2017

Agilent

Trusted Answers

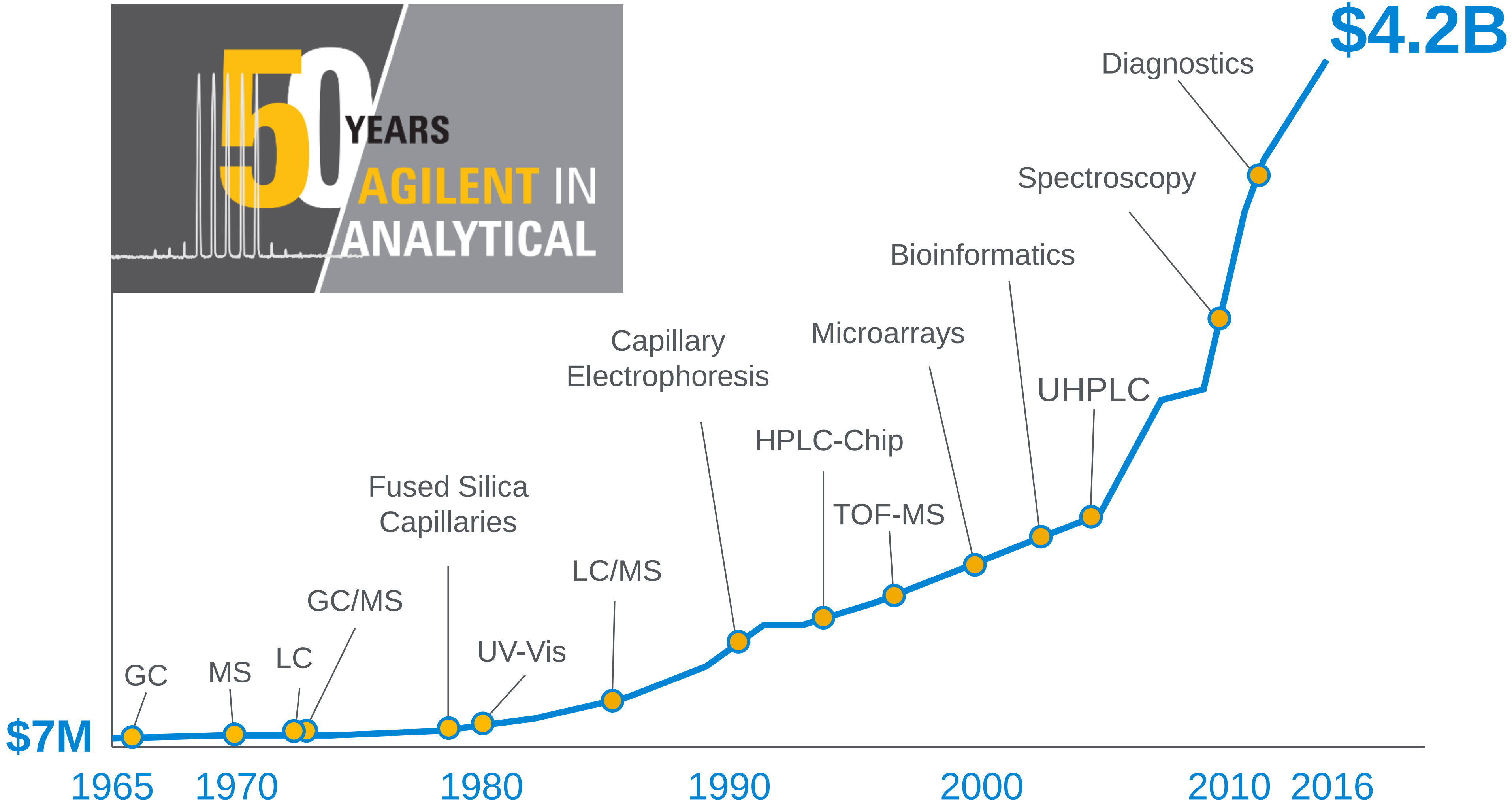
A Brief History of Agilent

1939–1998:	**The Hewlett-Packard years** 60-year heritage of leadership and innovation
1999:	**Agilent is born** Biggest IPO in Silicon Valley: $2.1 billion
2005:	**Agilent refines scope** Focus on measurement
2006–2010:	**Transformation** Acquisitions, divestitures and restructuring
2013:	**World's premier measurement company** $6.8 billion revenue
2013:	**Agilent announces spinoff of Electronic Measurement** Agilent to focus on Life Sciences, Diagnostics and Applied Chemical markets
2014:	**Agilent spins off Keysight Technologies** The spinoff is final Nov. 1, 2014, through a tax-free distribution of Keysight common stock



Agilent

Agilent
Leader in Analytical Applications for 50 Years

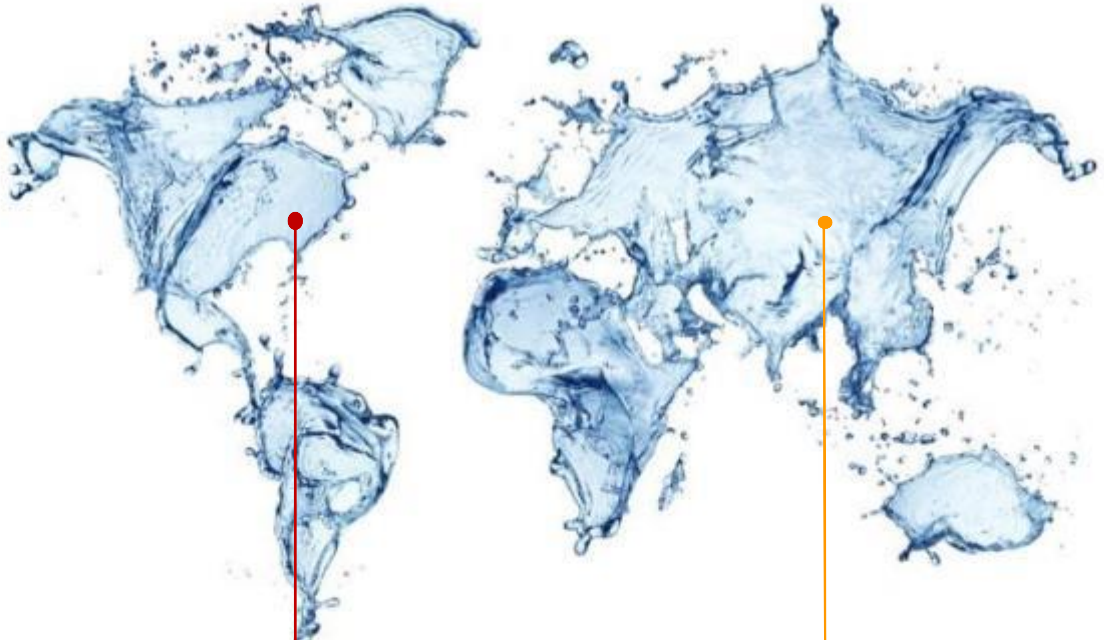


Environmental issues in the headlines

Water's importance?

Why Water?

- Population growth: **7.4 billion people** and counting
- Demand will increase **55% by 2050***
- Expects a **40% shortfall in water by 2030***
- Expected global population of **10.3 billion by 2050**
- More than **660 million people**+ live without a safe water supply close to home
- Clean water a lower priority than food/jobs/energy




More health news on NBCNEWS.com

Pharmaceuticals lurking in U.S. drinking water

AP probe found traces of meds in water supplies of 41 million Americans


c&en
CHEMICAL & ENGINEERING NEWS

Perfluorinated chemicals taint drinking water

Volume 94 Issue 20 | pp. 20-22
Issue Date: May 16, 2016

Opportunity

The demand for new applications is growing quickly – especially in the areas of **potable water** and **water reuse**

* United Nations
+ Environment Canada

Environmental Monitoring Applications

Current challenges and future requirements


VOCs and SVOCs


Glyphosate Herbicides


PPCPs and Hormones


Disinfection By-Products


Nanoparticles


PCBs, Dioxins, Furans


Indoor Air Quality


Pesticides Endocrine Disrupters


PFAS Residues PFOS/PFOA


Soil Contamination


Brominated Flame Retardants


Ambient Air Quality


Industrial contaminants (perchlorates)

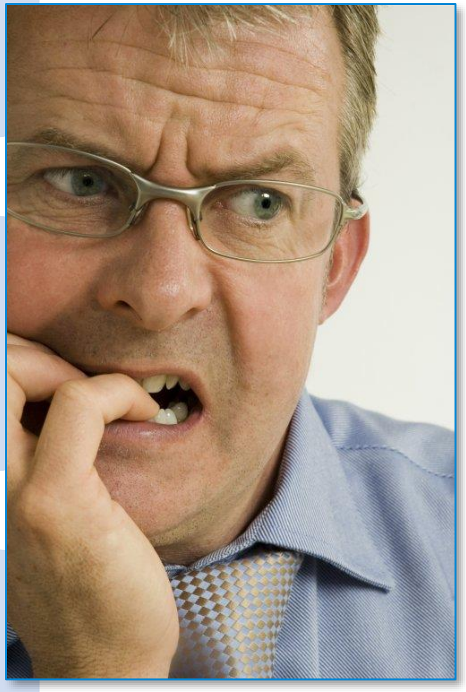

Algal Toxins and Odorants

Today's Challenges
Expecting More from Less

Business Challenges
- Increasing cost of ownership
- Demands for higher throughput

Resource Allocation
- Less time for method development
- Limited technical experience

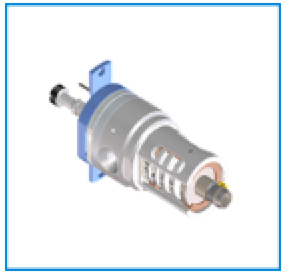
Optimizing Efficiency
- Trace analysis in complex matrices
- Quicker return on capital investment



Leveraging Innovation to Improve Efficiency

The challenge

Increase speed and sensitivity while decreasing cost



MS Source Redesign

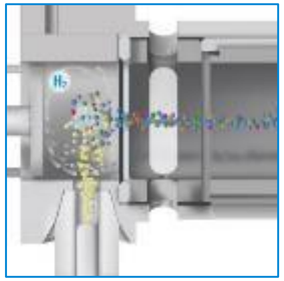
- Optimizing source efficiency
- High Efficiency Source, 20x Yield
- Dioxins, SVOCs, Nitrosamines

Multi-Mode Inlet

- Reduce solvent consumption
- Controlled, large volume, heated injection
- 95% reduction in usage

Oil Free Rough Pump

- Eliminates oil leaks
- Reduce maintenance cost, ~30%
- Reduce maintenance time, >50%
- For MS and MS/MS configurations



JetClean

- Self Cleaning Ion Source
- “Clean Only” or “Clean and Acquire” operation
- Extended operation, PAH ~ 2 yrs

Inert Flow Path

- Ultra-inert or Ultimetal treatment of sample flow path components
- Inlet, columns, fittings, detector jets
- Gets trace analytes to detectors

VacShield

- Service capillary without venting
- Down time ~20 min vs 12 hr
- Ultivo, 6495B

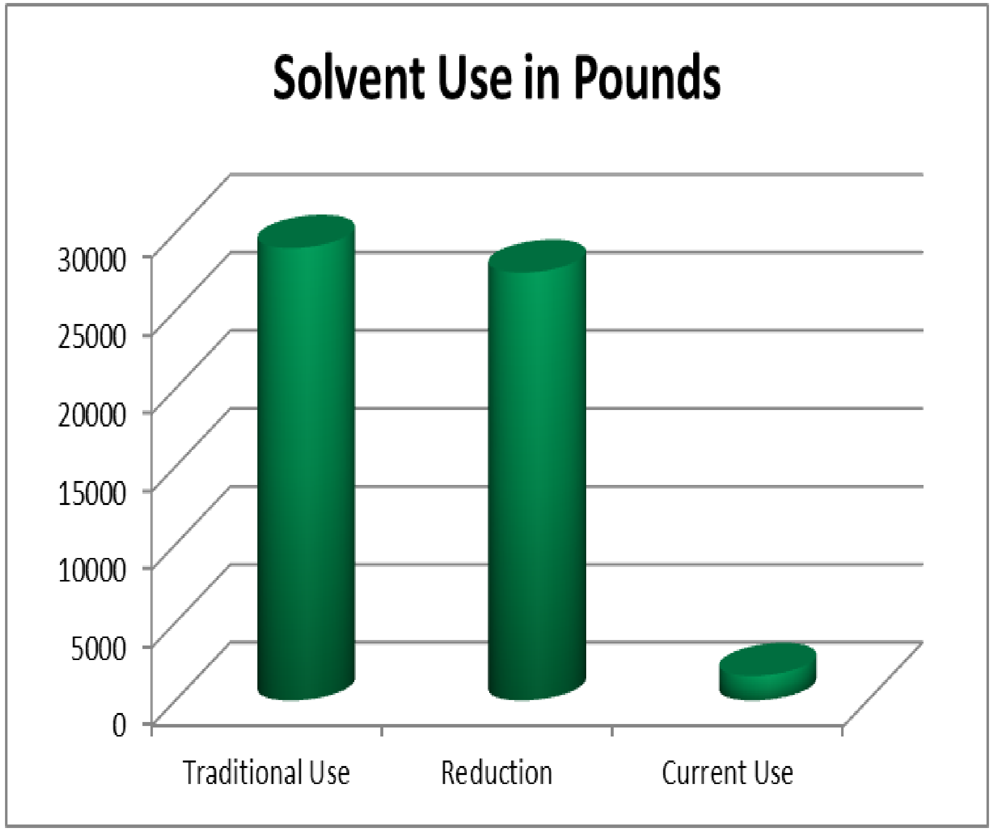
Reducing Emissions and Solvent Usage

Improvements Through Improved Technology

•Modification to Sample Prep

- **Large volume injection** helps optimize LOD performance
- LVI helps **reduce sample cleanup** requirements
  - **130mL** sample with **18mL** DMC extraction
  - Microwave Extraction with dilute to volume and direct injection
  - Validate recovery per method performance requirements

Chlorinated Solvent Reduction Profile
Improvements Through Technology



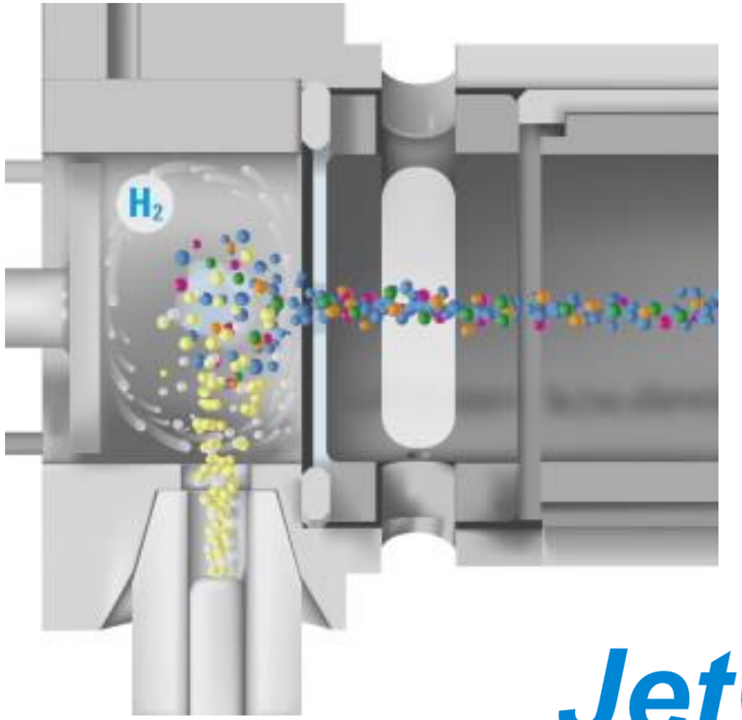
Laboratory Success

- **MMI** allowed for a reductions in Sample Volume
- Resulted in **REDUCED** chlorinated solvent usage from **30,000 lb** annually to only **1,600 lb**

Financial Benefit: **$200K** in the first twelve months!

GC/MS Quad Source that "Cleans Itself"

Continually Driving Technology Innovation



- ✓ "Clean Only" or "Clean and Acquire" operation
- ✓ Consistent response for extended period of time
- ✓ Reduces or eliminates downtime for manual source cleaning
- ✓ As Option or Upgrade for single and tandem quad GC/MS systems

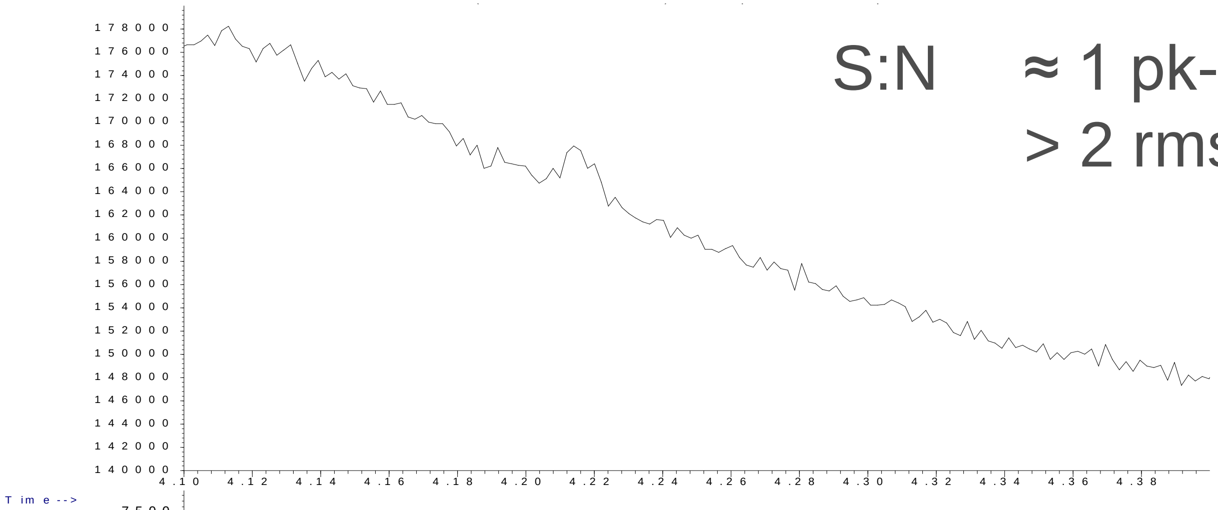
JetClean

Self-cleaning ion source

Cleaning Restores Analyte (OFN) Detection

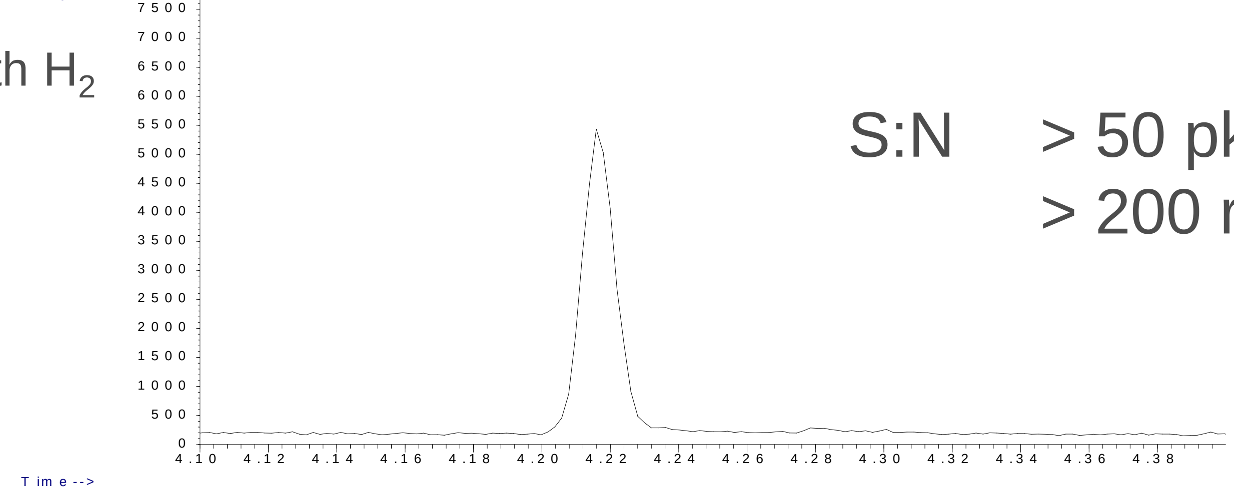
Comparable to manual cleaning

Very dirty source before cleaning



S:N ≈ 1 pk-pk
> 2 rms

After cleaning with H_2



S:N > 50 pk-pk
> 200 rms

Verified Performance PAH Analysis – Clean and Acquire

Journal of Chromatography A, 1419 (2015) 89–98

Contents lists available at ScienceDirect

Journal of Chromatography A

ELSEVIER

Modified ion source triple quad... ...s spectrometer gas chromatograph for polycyclic aromatic hydrocarbon analyses

CrossMark

Kim A. Anderson[a,*], Mi...
Peter D. Hoffman[a]

[a] Department of Environmental and Mo...
[b] Agilent Technologies, Wilmington, DE 19808, United States

62 PAHs, “archetypally difficult”

Range 1-10,000pg/µl, R^2>0.998

5% of true values, over many month

Mean limits of LODs 1.02 +/- 0.82pg/ µl

Now >2 years

Non-reactive, nonpolar compound classes are generating exceptional results in the Acquire & Clean operational mode

62 pol... ...ns (PAHs). Existing methods historically limited rigorous identifi- cation and q... ...small subset, such as the 16 PAHs the US EPA has defined as priority pollutants. Witho... ...critical source and extractor lens modifications, the off-the-shelf GC–EI/MS/MS system was unsuitable for complex PAH analysis. Separations were enhanced by increased gas flow, ...

values ... curve r^2 values were typically >0.998, exceptional for compounds which are ... With this method benzo[a]fluorene, benzo[b]fluorene, benzo[c]fluorene were fully separa... was benzo[b]fluor... Chrysene and triphenylene, were sufficien... of detection (LODs) across all PAHs were 1... lowest LOD at 0.26 pg µl^{-1} and only two ana... dibenzo[a,e]pyrene (6.44 pg µl^{-1}).

N-Nitrosamines in Drinking Water

GC-MS/MS with HES (all concentrations in ng/L)

Name	TS	RT	Avg. Conc.	Std. Dev.	MDL	LOQ	LOD	EPA MRLs	Noise	S/ N	Avg. Resp	Resp. RSD(%)
NDMA	1	7.15	1.62	0.0471	0.141	0.471	0.141	1.6	5	228	3275	3.9
NMEA	2	8.28	1.48	0.0287	0.086	0.287	0.086	1.5	3	258	2073	4.1
NDEA	3	9.13	1.43	0.0579	0.174	0.579	0.174	2.1	3	Inf.	1347	5.3
NDPA	4	11.08	1.29	0.1423	0.427	1.423	0.427	1.2	10	214	238	8.9
NMOR	5	11.47	1.19	0.0411	0.123	0.412	0.123		3	1912	2478	3.9
NPyr	5	11.64	1.32	0.124	0.372	1.240	0.372	1.4	1	1525	375	7.5
NPip	6	11.85	1.41	0.045	0.135	0.450	0.135	1.4	3	216	1206	3.5
NDBA	7	12.56	1.47	0.0595	0.178	0.595	0.178	1.4	8	Inf.	928	3.8

MDL/LOQ/LOD at 95% confidence level:
Calculated from 8 replicates at 1.25 ng/L using 0.5 µL injections

Performance

- Enhanced EI sensitivity meets, and exceeds, the requirements of EPA Method 521
  - Excellent alternative to the method specified PCI MS/MS Ion Trap systems.
- Excellent detection levels ranging from 0.08 – 0.4 ng/L
  - Well below the required levels **with only a 0.5 µL sample injection.**

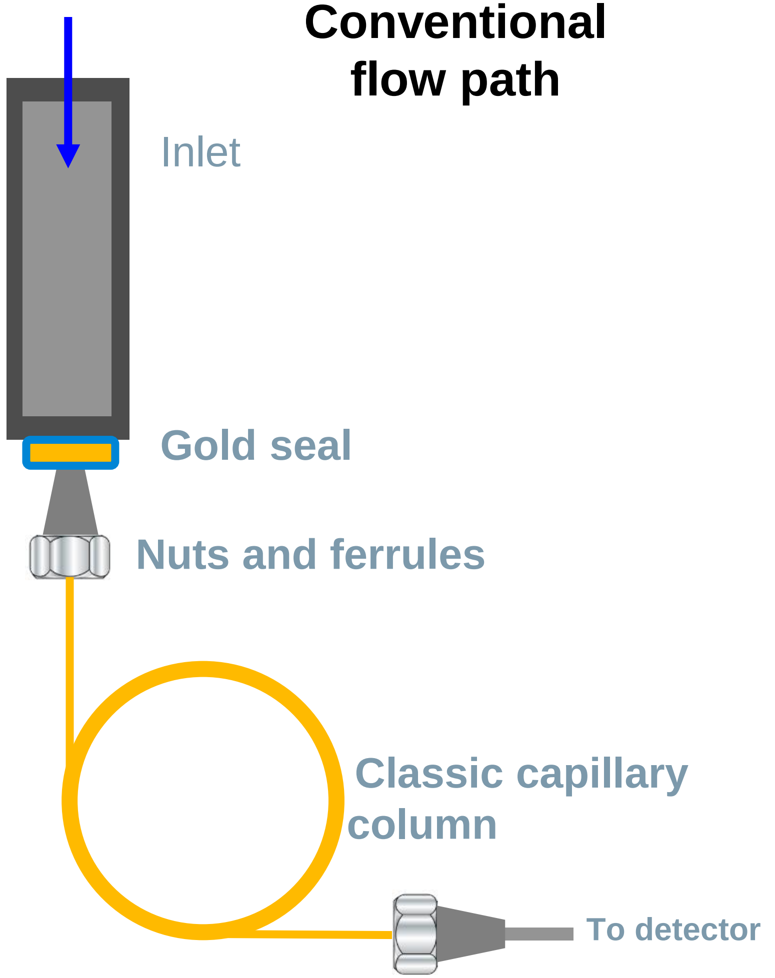
Smaller injection volume led to less sample on column, less matrix and longer time between system maintenance

LISTENING TO CUSTOMERS: THE SPARK FOR INNOVATION

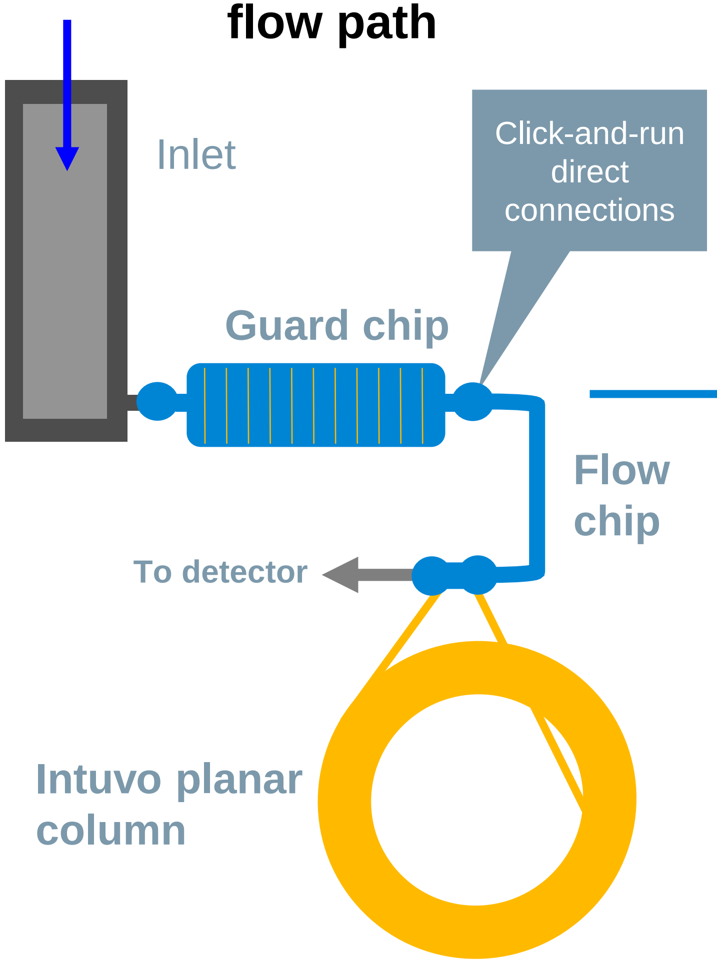
50 YEARS AGILENT IN ANALYTICAL

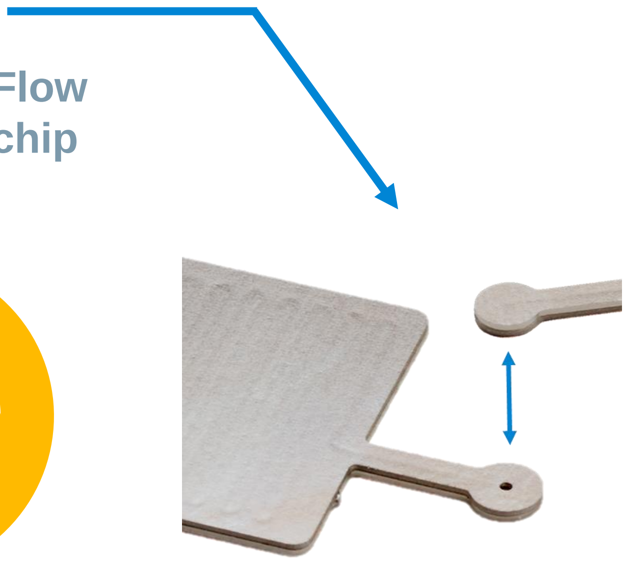
Innovating the GC Flow Path
Intuvo Model 9000 Gas Chromatograph

Conventional flow path

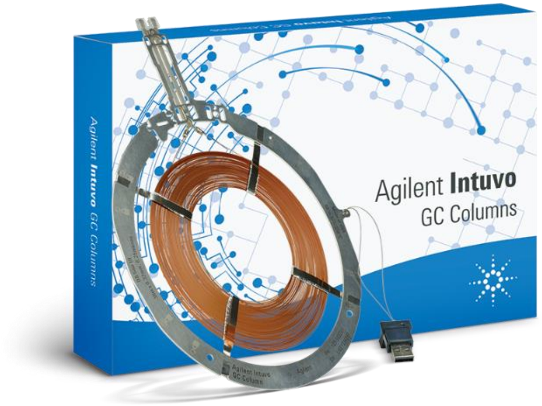


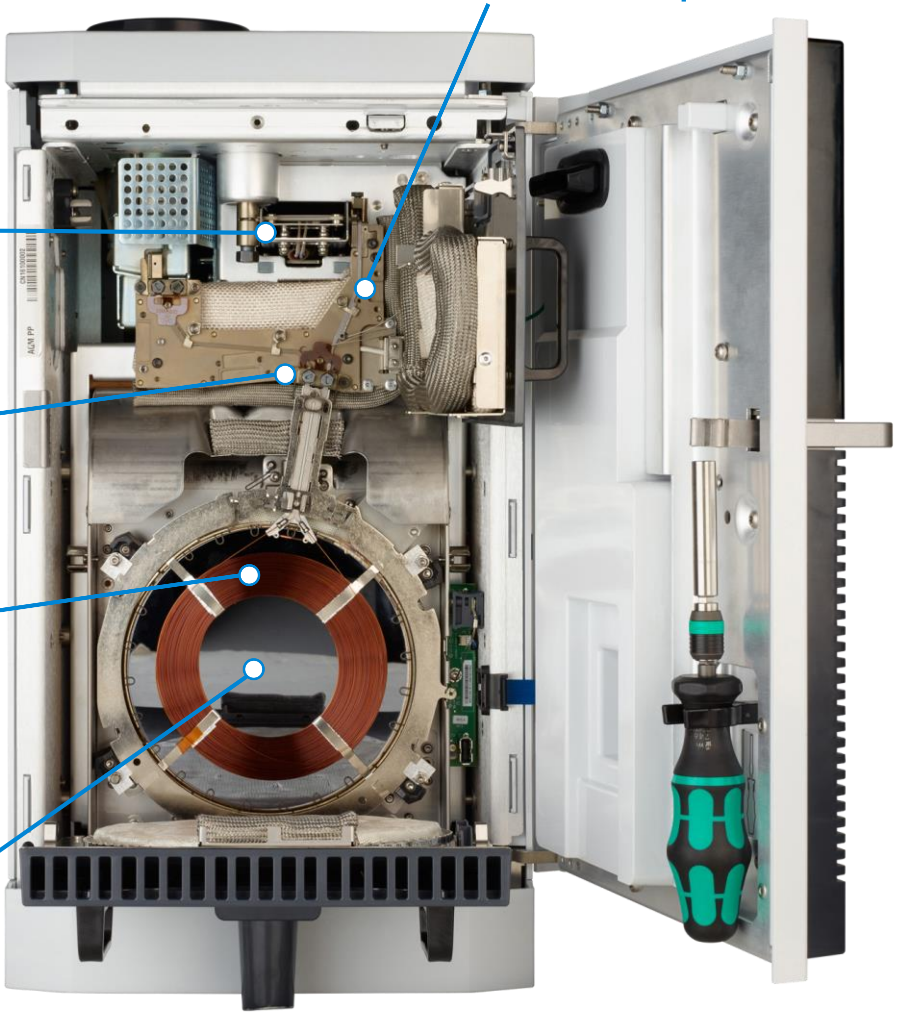
Intuvo flow path





Innovating a New Path to GC Productivity
A new approach to GC

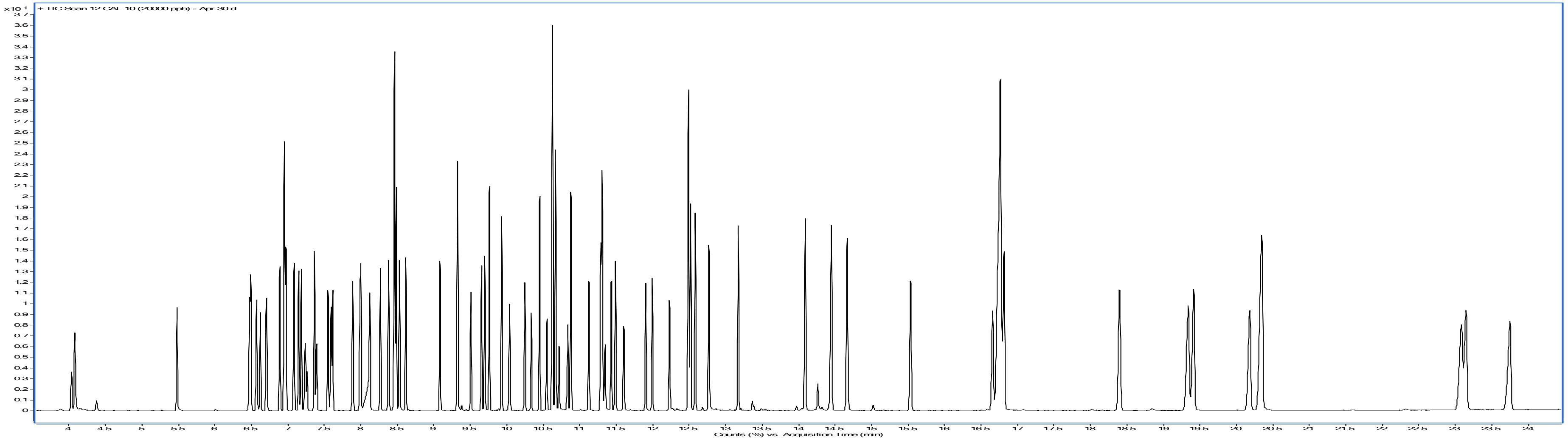


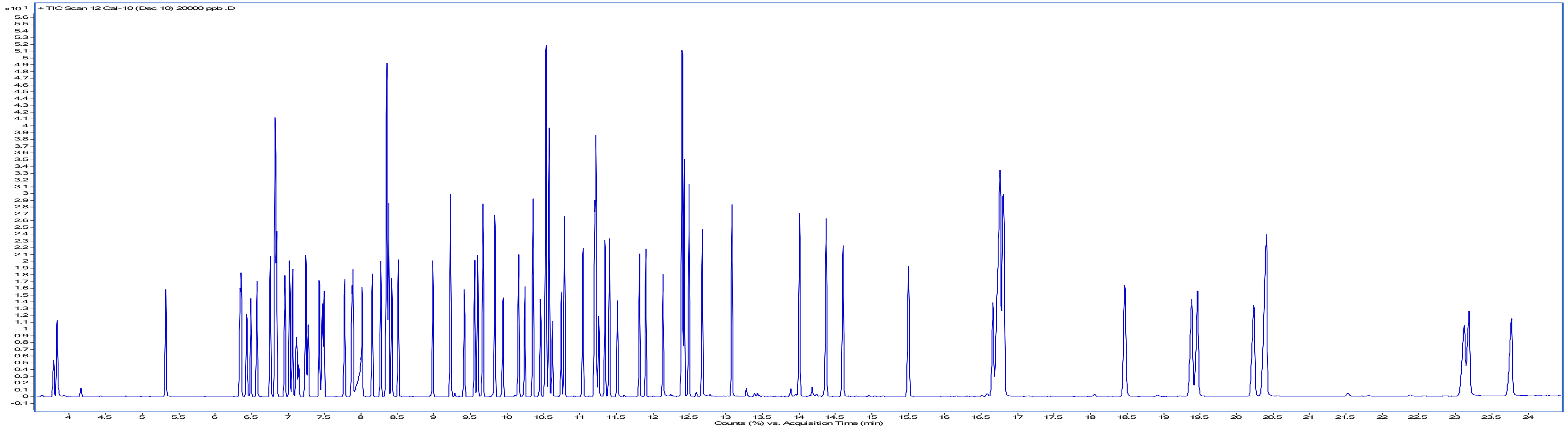


Seamless Method Migration to Intuvo

Preserving method and SOP investments

83 SVOC by US EPA 8270





Next Generation of LC/TQ
"Fit for Purpose"

SMALL IS BIG AGAIN!

Expectations for LC/TQ performance

- Bench space requirements
- Robust, reliable and accurate measurements, day in – day out
- Minimal downtime for maintenance
- Intuitive and user-friendly
- Quickly achieve ROI

Ultivo LC/TQ

Ultivo
"Fit for Purpose" LC/TQ

Diagnostics – Provide "real-time" information concerning stability/usability of the system

Reliability – Overall (mean time to service), sample throughput, consumable components (TMP, ion injector)

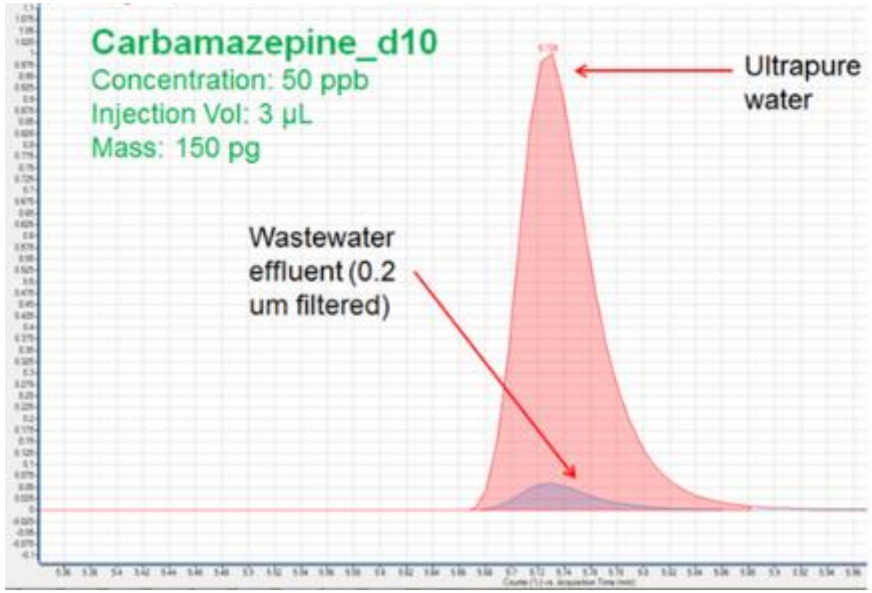
Performance – Sensitivity, selectivity, positive/ negative switching, mass range / resolution, matrix

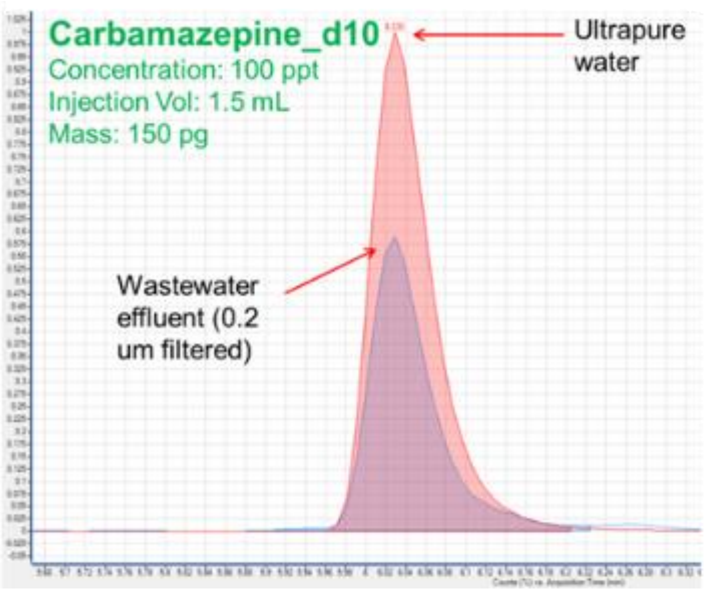
Form Factor – Size/ Footprint, stackability, external appearance

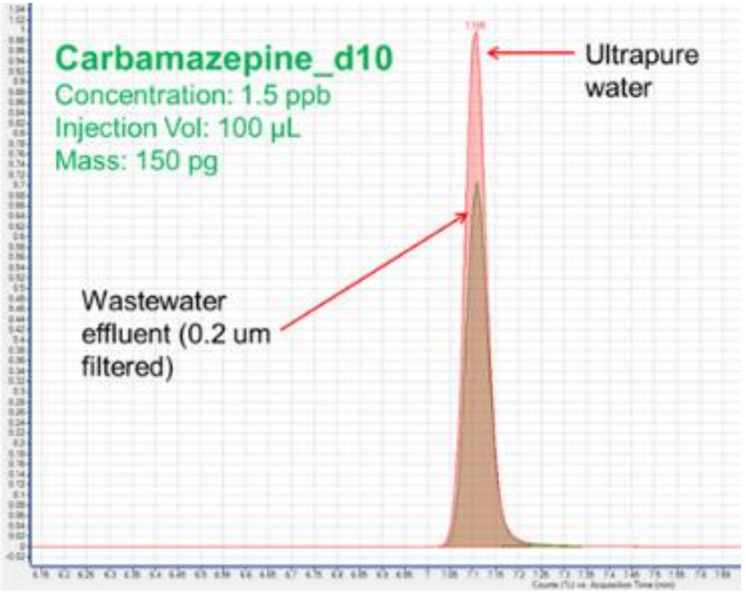
Ease-of-Use - Initial set-up / post-sales support (e.g. method development), training, fit into workflow

Total Cost of Ownership – Initial cost, reduced maintenance cost, gas usage, noise reduction, training

Analysis of Trace Organic Contaminants
Ion Suppression Comparison by Sample Prep Method







Conventional SPE
Mass on Column :150 pg

Online SPE
Mass on Column :150 pg

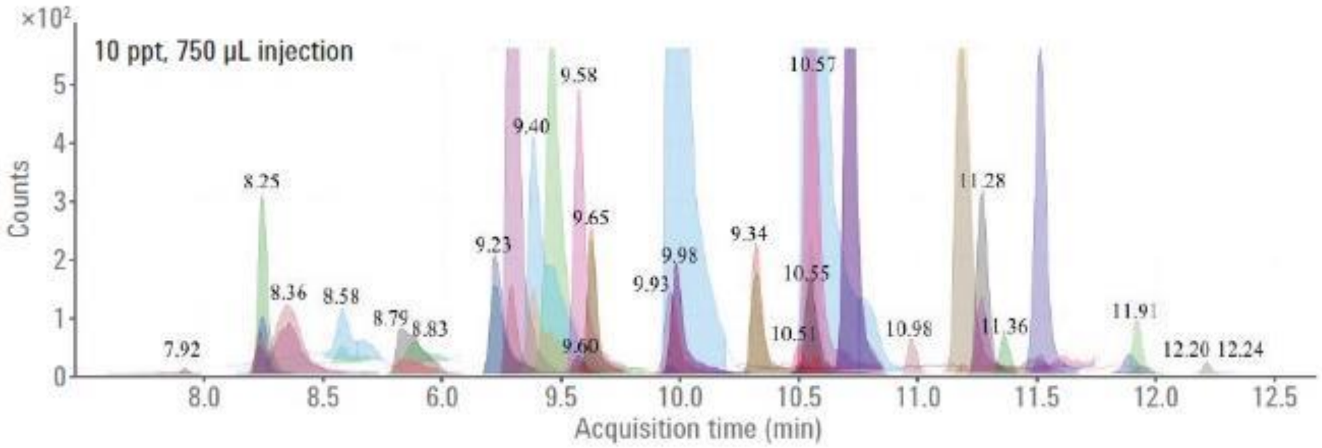
Direct Injection
Mass on Column :150 pg

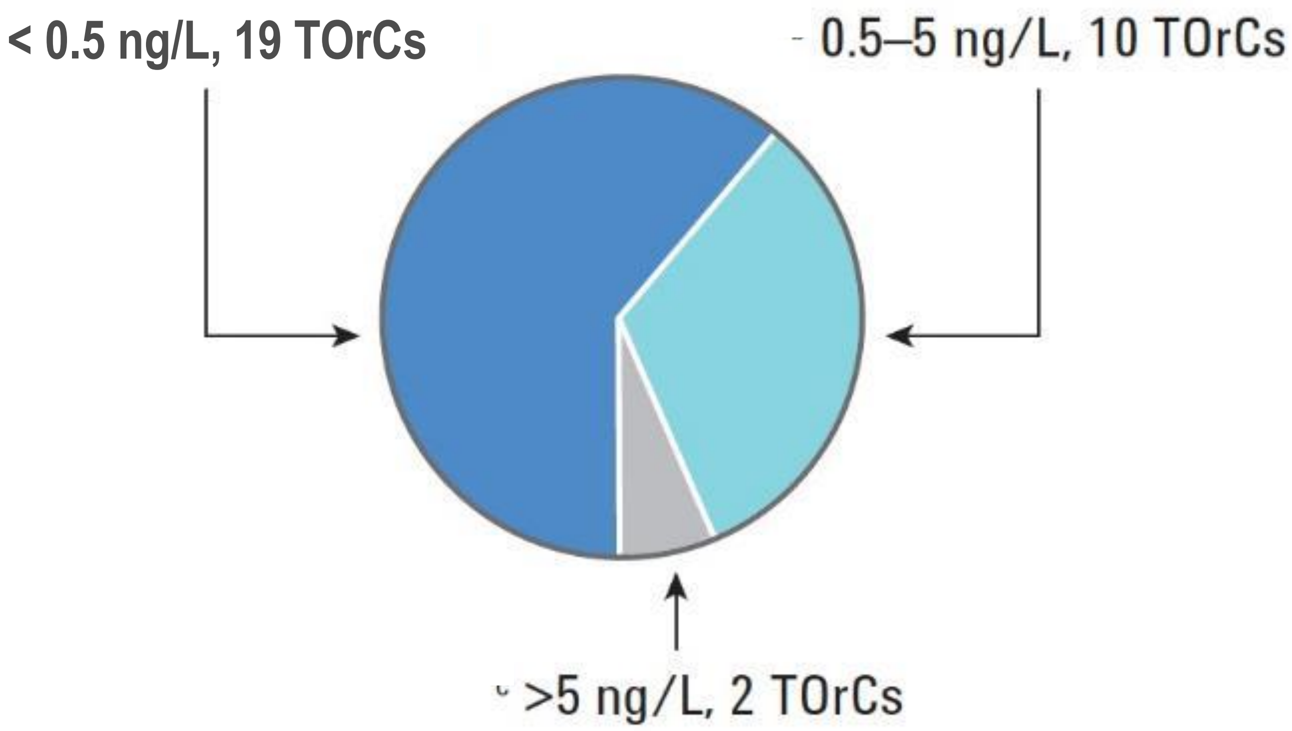
Dr. Shane Snyder
University of Arizona

Analysis of Trace Organic Contaminants in Drinking Water

FlexCube Online SPE + 1290 II LC + Ultivo Triple Quad LC/MS

- 750 µL injection onto Flexcube
- <20 min cycle time
- $R^2 > 0.99$ for range 0.5 – 200 ng/L



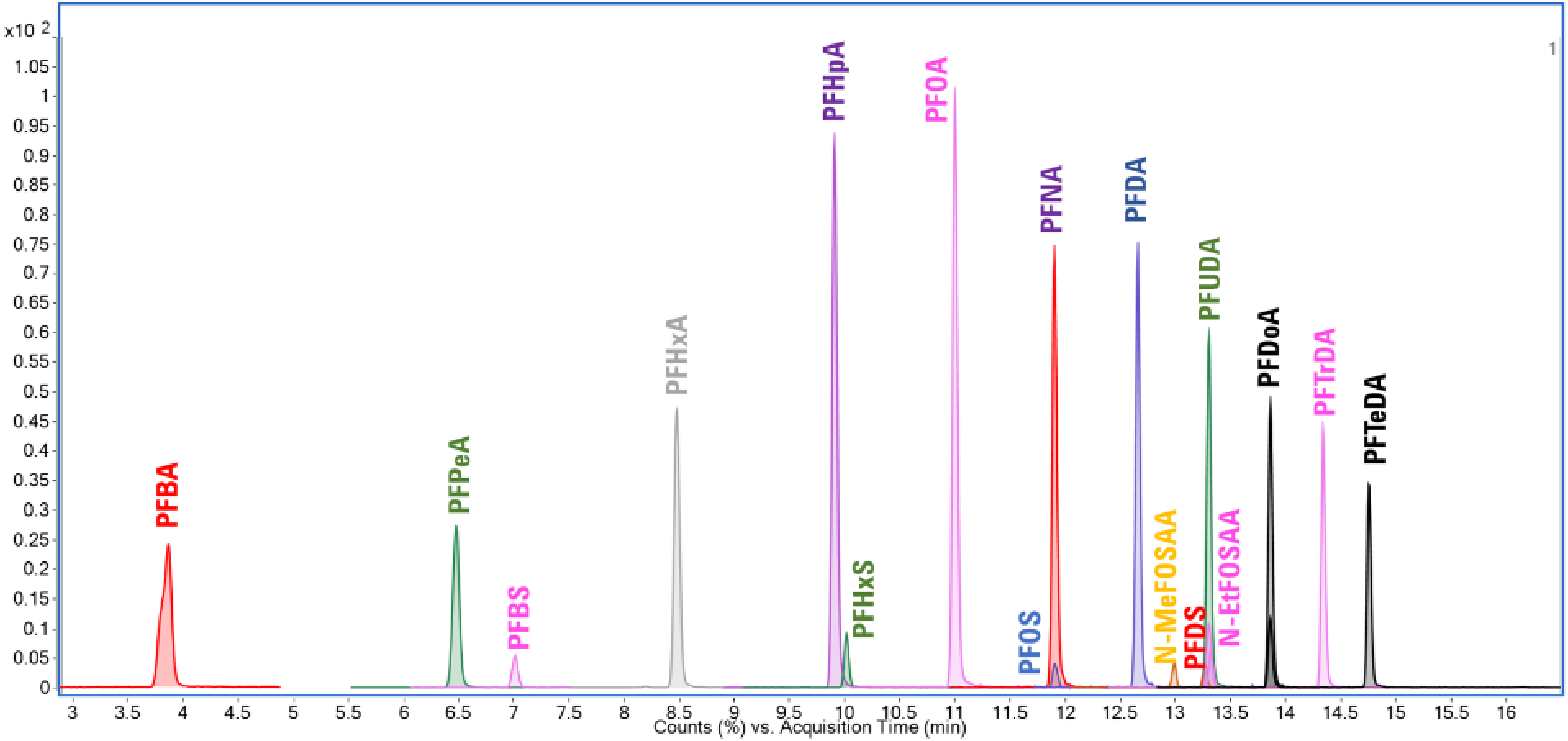


Distribution of the limits of detection for 31 common TOrCs found in water

Analysis of PFAS in Drinking Water with Ultivo

EPA Method 537

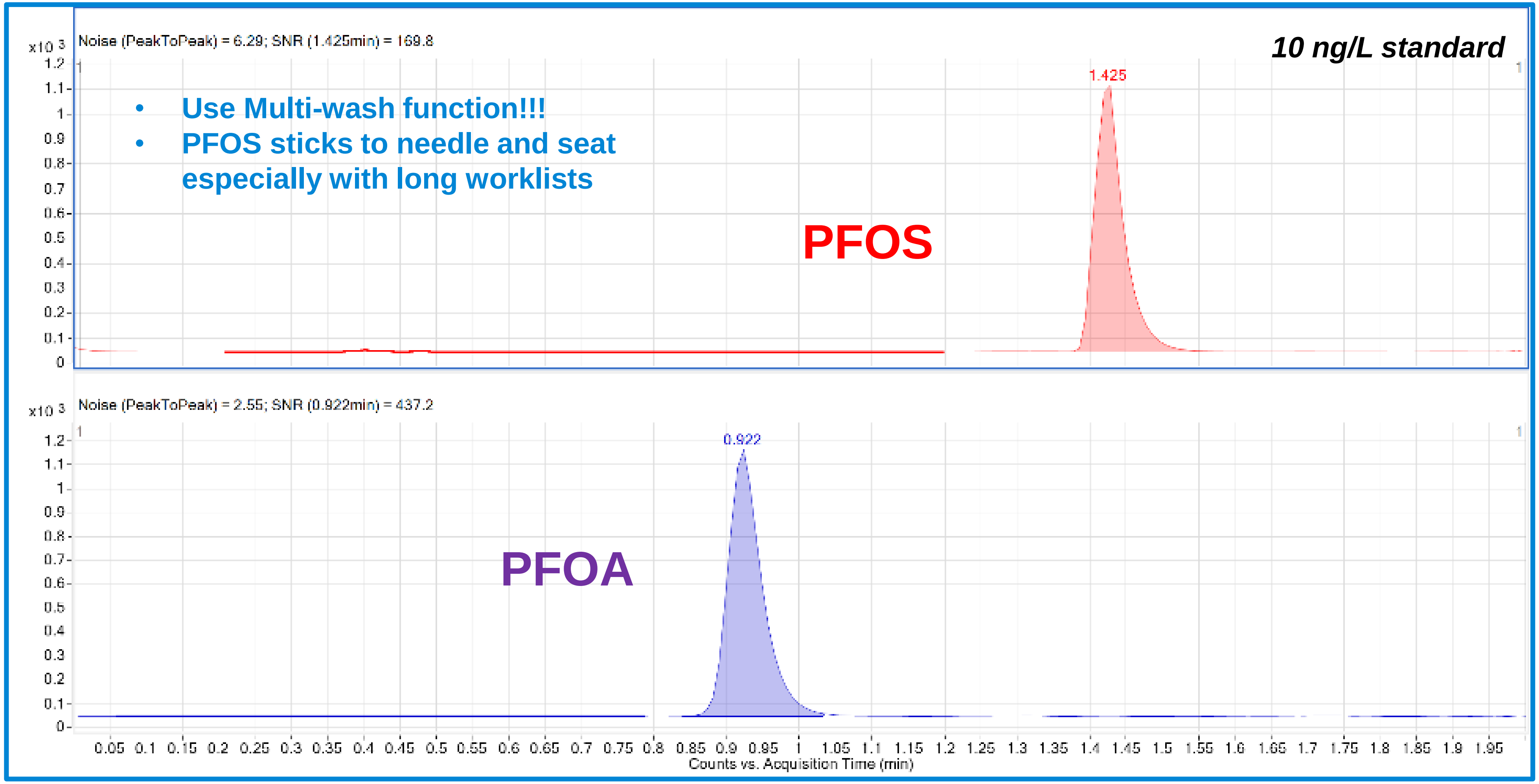
Analysis of 17 PFASs in drinking water with <0.1 ng/mL DLs in extract (includes all 14 compounds in EPA 537)



Analysis of PFOA/PFOS

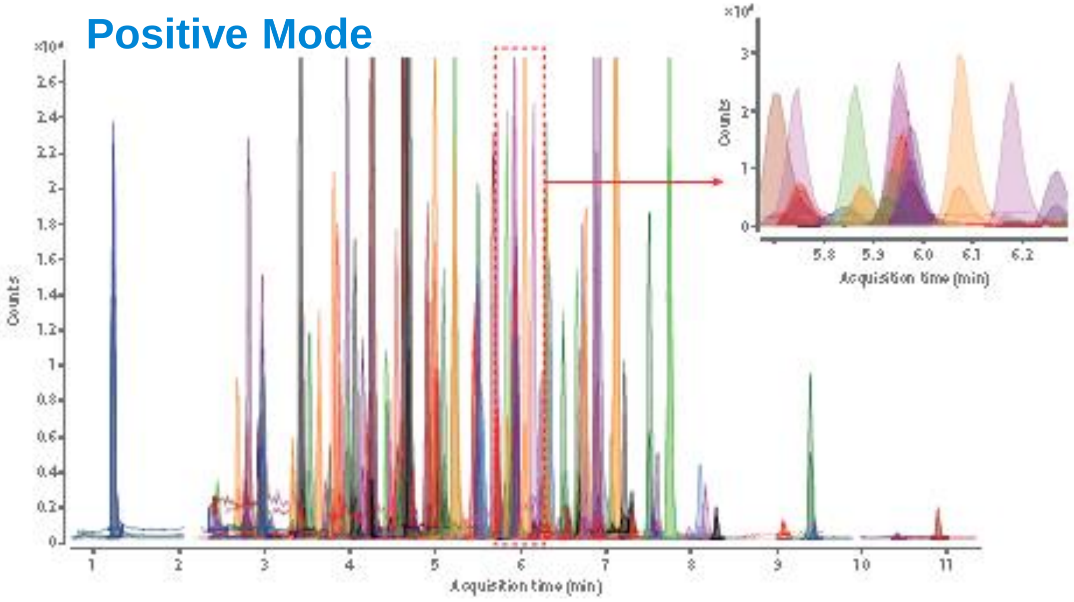
Direct Injection; Rapid Analysis (1290 II UHPLC + 6495 LC-MS/MS)

Liquid Chromatograph	Agilent 1290 Infinity II Binary Pump
Mass Spectrometer	Agilent 6495 triple quadrupole LC-MS
Analytical Column	Agilent Poroshell 120 EC-C18; 3.0 x 50mm; 2.7um
Delay Column	Agilent Eclipse Plus C18, 4.6 x 50mm; 3.5um
Mobile Phase	A: Water+5mM Amm. Acetate B: Acetonitrile
Run Time	2 min
Injection Volume	80 uL (Water)

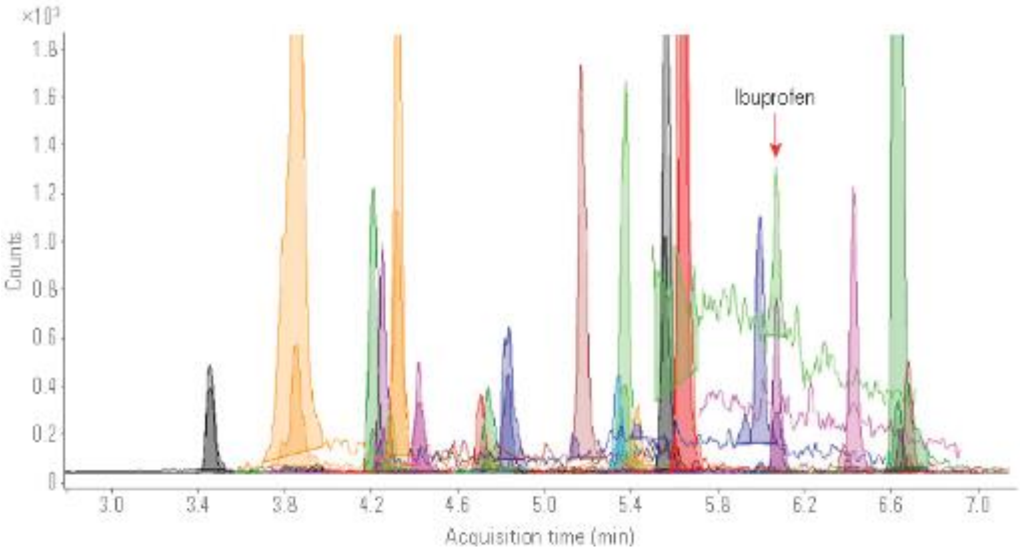


Key Application for LC/TQ
Low Level Detection of PPCPs using Model 6495

Positive Mode



Negative Mode



Performance

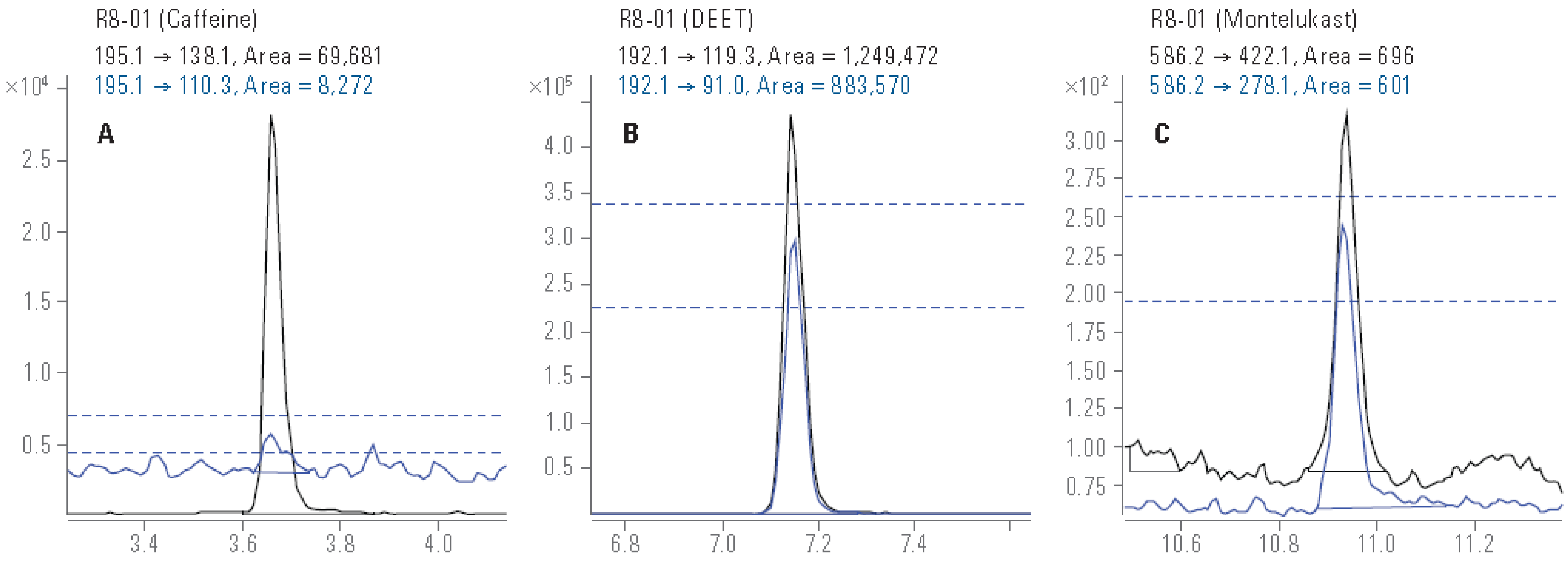
Detection at concentration <10 ppt without sample enrichment.

Calibration range from 2 to 1,000 ppt (R^2 >0.995 for most compounds)

Accuracy 80–120%

PPCPs Identified Positive Ion Mode
Remote Source Water (>10ppt)

Name	Injection 1 (ppt)	Injection 2 (ppt)	Average (ppt)
Montelukast	12.1	11.9	12.0
Caffeine	27.0	14.5	20.7
DEET	107.4	118.6	113.0



PPCPs Identified
Urban Source Water (>10ppt)

Name	Injection 1 (ppt)	Injection 2 (ppt)	Average (ppt)
10,11-dihydro-10-hydroxycarbamazepine	903	861	882
Amitriptyline metabolite	30	30	30
Amitriptyline	29	29	29
Atenolol	2,599	2,212	2,405
Atorvastatin	40	37	39
Atrazine	43	41	42
Benzoylecgonine	221	206	214
Bupropion	169	154	162
Caffeine	1,473	1,241	1,357
Carbamazepine 10,11 epoxide	38	36	37
Carbamazepine	214	229	221
Carisoprodol	27	28	28
Clopidogrel carboxylic acid	223	204	214
Cocaine	37	35	36
Codeine	67	67	67
Cotinine	98	90	94
DEET	503	570	536
Desmethylcitalopram	107	88	97
Desmethylvenlafaxine	744	827	786
Dextromethorphan	31	42	36
Diltiazem	55	61	58
Diphenhydramine	205	205	205
Ecgonine methyl ester	39	39	39
EDDP	102	100	101
Erythromycin	44	44	44
Erythromycin-anhydro	38	31	34
Escitalopram	192	179	186
Fluoxetine	30	28	29
Gabapentin	>>1,000	>>1,000	>>1,000
Hydrocodone	28	24	26
Hydroxybupropion	260	253	257
Ketoprofen	17	15	16
Lamotrigine	868	1,013	940
Levorphanol	213	205	209
Lidocaine	360	325	343

Positive Ion Mode

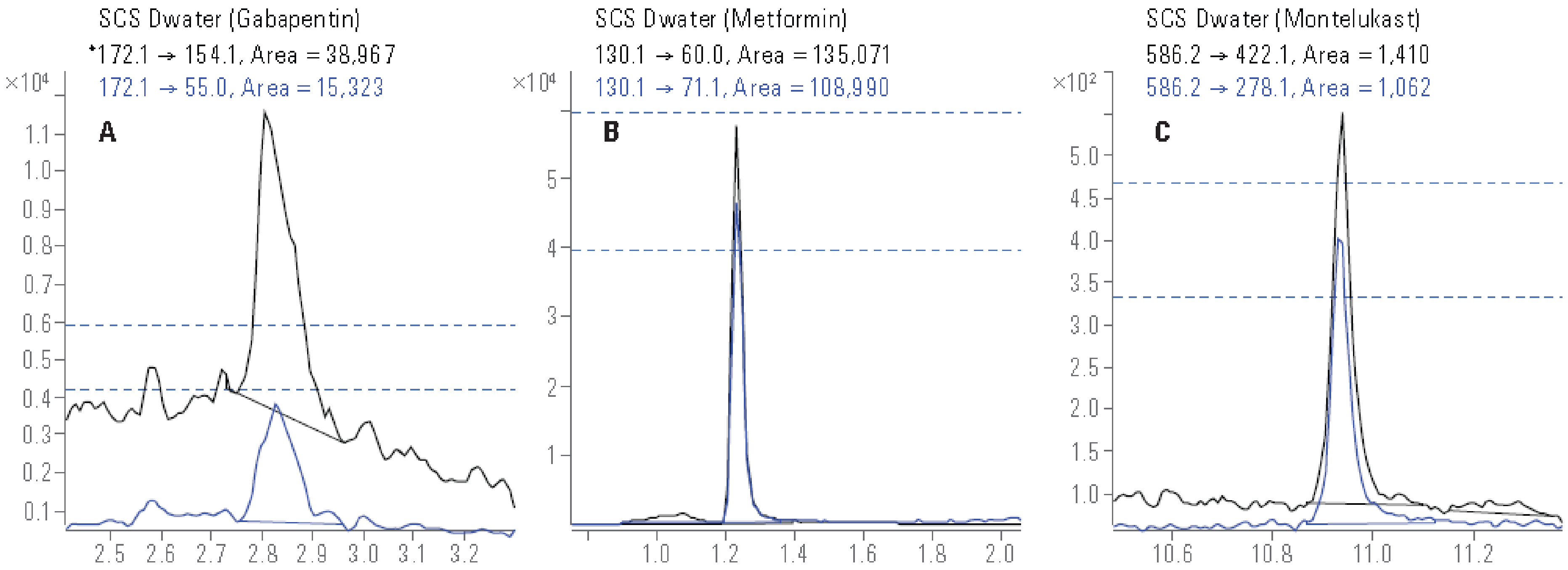
Name	Injection 1 (ppt)	Injection 2 (ppt)	Average (ppt)
Loratadine	10	10	10
Lorazepam	137	143	140
Meprobamate	160	147	154
Metformin	3,956	3,956	3,956
Methadone	58	39	49
Methamphetamine	259	315	287
Metoprolol	295	334	315
Modafinil	16	14	15
Monoethylglycinexylidide	28	31	30
Montelukast	12	12	12
Norquetiapine	32	25	28
Norsertraline	32	24	28
Oxazepam	29	27	28
Oxcarbazepine	45	42	44
Oxycodone	95	83	89
Oxymorphone	17	14	15
Phentermine	117	117	117
Pregabalin	440	445	442
Primidone	77	58	68
Propranolol	70	71	70
Pseudoephedrine	211	236	223
Ritalinic acid	111	127	119
Sertraline	47	44	46
Sotalol	68	72	70
Sulfamethazine	10	13	11
Temazepam	89	83	86
Thiabendazole	37	43	40
Tramadol	708	727	717
Trazadone	35	30	33
Triamterene	100	111	106
Trimethoprim	277	321	299
Tylosin	13	10	11
Valsartan	475	517	496
Venlafaxine	446	384	415
Verapamil	11	10	11
Zolpidem phenyl-4-carboxylic acid	46	47	47

Name	Injection 1 (ppt)	Injection 2 (ppt)	Average (ppt)
Celecoxib	45	41	43
Chloramphenicol	12	12	12
Diclofenac 4-hydroxy	41	45	43
Diclofenac	237	292	265
Furosemide	400	387	393
Gemfibrozil	309	337	323
Hydrochlorothiazide	503	487	495
Ibuprofen	140	139	139
Modafinil acid	118	114	116
Naproxen	354	347	350
Phenobarbital	55	53	54
Phenytoin	126	121	123
Pravastatin	57	52	54
Sulfamethoxazole	573	582	577
Triclocarban	40	39	39
Triclosan	242	268	255

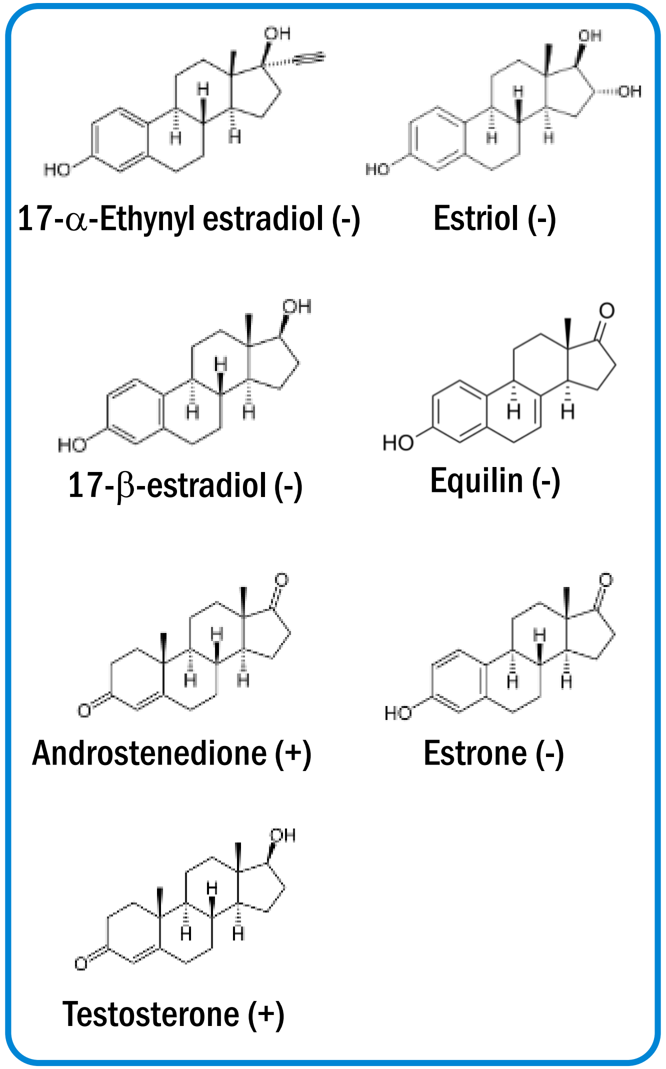
Positive Ion Mode

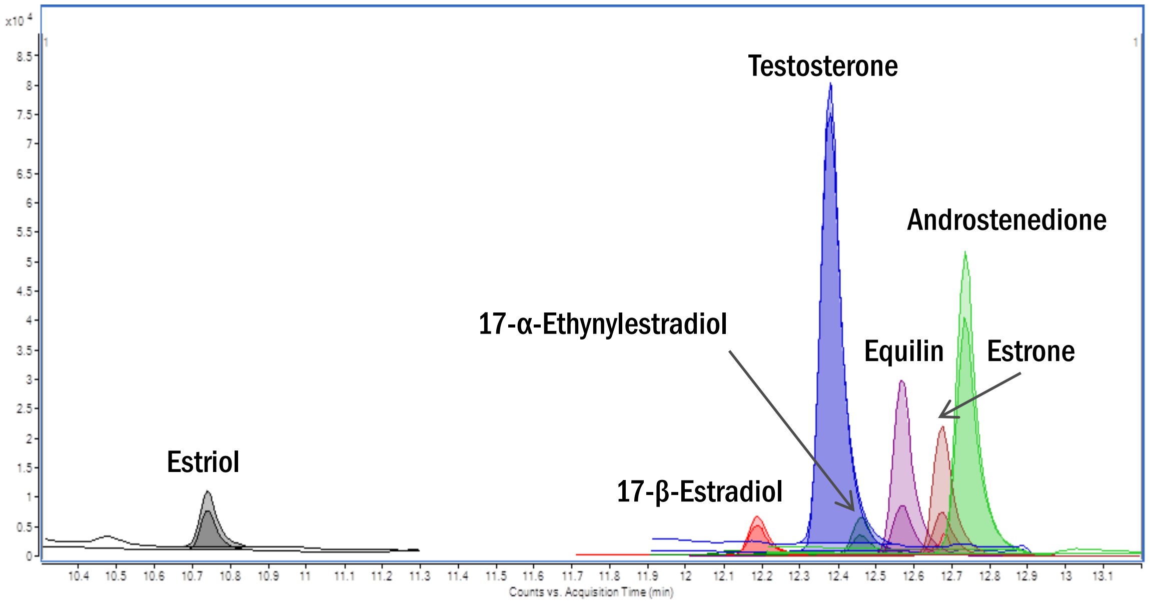
PPCPs Identified Positive Ion Mode
Local Tap Water (>10ppt)

Name	Injection 1 (ppt)	Injection 2 (ppt)	Average (ppt)
Gabapentin	20.7	19.6	20.2
Metformin	31.2	30.1	30.6
Montelukast	12.7	12.3	12.5



Analysis of Hormones in Drinking Water
5 ng/L (testosterone) to 17.5 ng/L (EE)



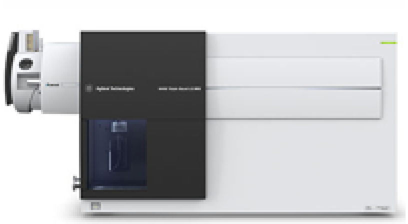


Compounds	LLOQ (ng/L)	IDL (ng/L)	R^2	Precision (%RSD, n = 8)	%Accuracy
Estriol		0.168	0.997	0.81 – 10.6	93.6 – 113.6
17β-Estradiol	< 0.5	0.202	0.996	0.73 – 13.7	87.5 – 120.3
Testosterone	< 0.1	0.031	0.994	2.09 – 10.3	88.8 – 114.5
17α-Ethynylestradiol	1.75	0.78	0.996	2.50 – 16.5	95.3 – 107.2
Equilin	< 0.2	0.022	0.997	3.00 – 5.21	88.9 – 115.1
Estrone	< 0.2	0.043	0.996	2.57 – 9.41	91.2 – 115.1
Androstenedione	< 0.1	0.026	0.995	1.48 – 9.07	89.2 – 107.2

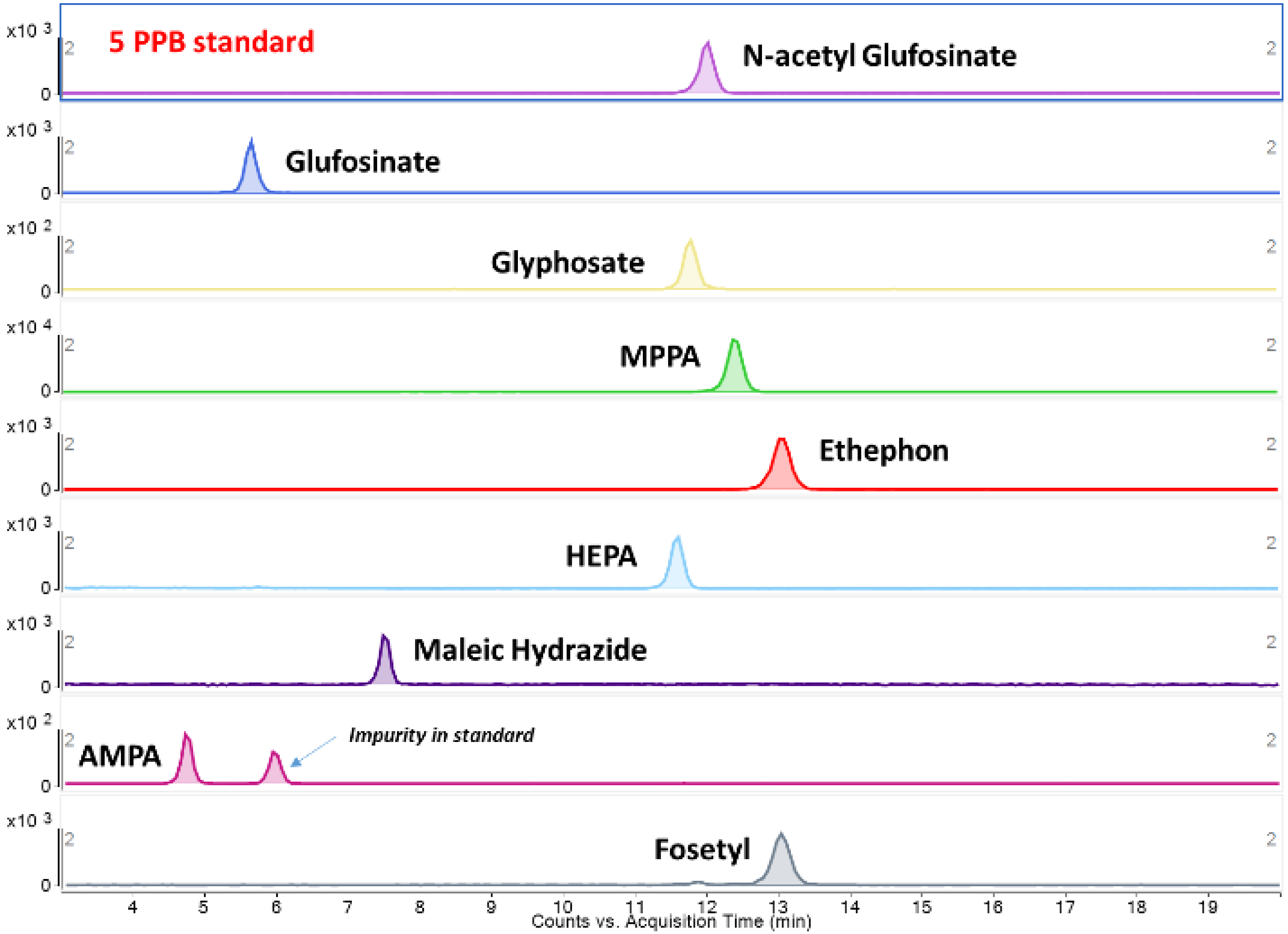
Analysis of 9 Polar Pesticides in Water - Glyphosate

Direct Aqueous Injection with LC-MS/MS

1260 Bioinert LC
Metrohm Asupp IX column
100 µL inj.
20 min RT



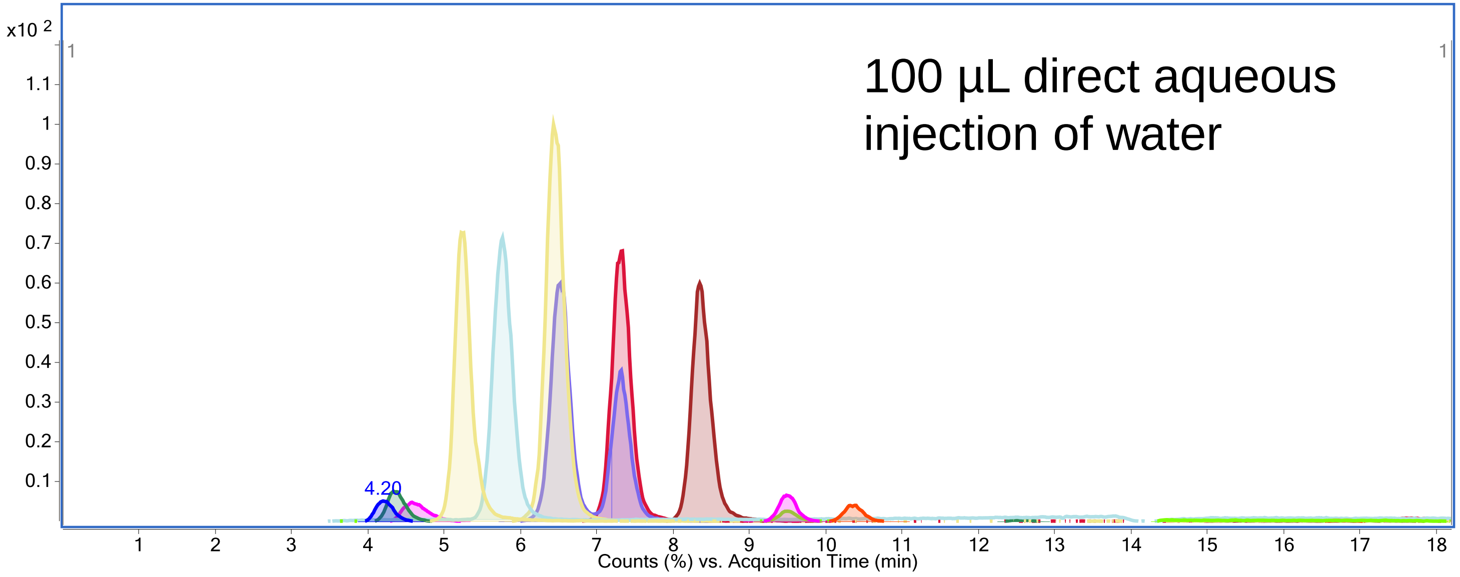
6495 Triple Quad LC/MS
ESI Negative
LOD: 0.2 ppb for Glyphosate; lower for



Agilent Technologies

Haloacetic Acids and Bromate in Water by IC-MS/MS

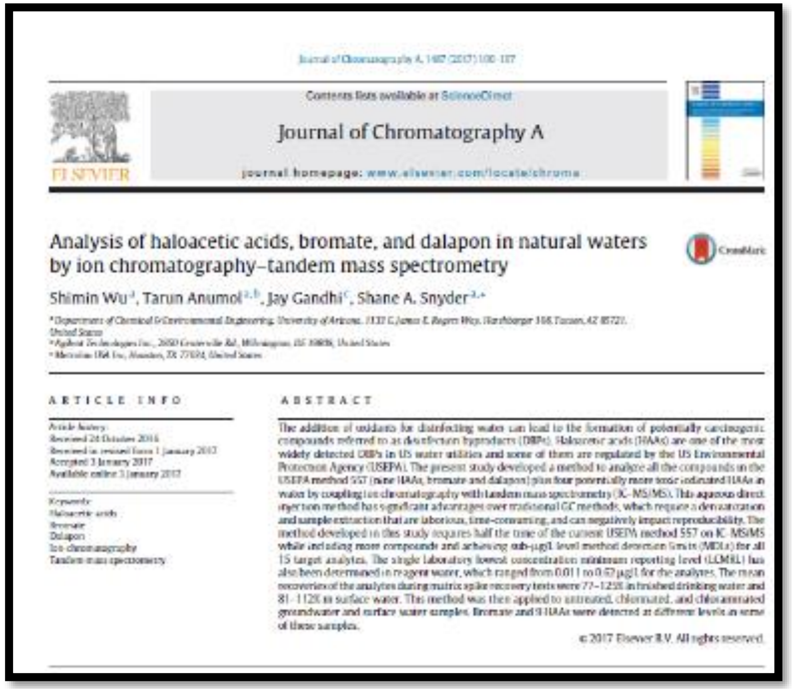
EPA method 557 (Metrohm 950 IC + Agilent 6490 Triple Quad LC/MS)



Analyte	MDL (µg/L)	MDL (µg/L) in USEPA Method 557
BrO_3^-	0.0051	0.020
MCAA	0.041	0.20
MBAA	0.014	0.064
MIAA	0.14	–
DCAA	0.010	0.055
BCAA	0.037	0.11
DAL	0.44	0.038
DBAA	0.060	0.015
CIAA	0.024	–
BIAA	0.013	–
DIAA	0.010	–
TCAA	0.030	0.090
BDCAA	0.11	0.050
CDBAA	0.10	0.041
TBAA	0.10	0.067

Advantages:

- **Method runtime (20 min) is a third of EPA method**
- **MDLs are better in most cases than EPA method**
- **Includes 4 Iodo-HAAs not in EPA method**



Journal of Chromatography A, 1487 (2017) 100–107
Contents lists available at ScienceDirect
Journal of Chromatography A
journal homepage: www.elsevier.com/locate/chroma

Analysis of haloacetic acids, bromate, and dalapon in natural waters by ion chromatography–tandem mass spectrometry

Shimin Wu[a], Tarun Anumol[a,b], Jay Gandhi[c], Shane A. Snyder[a,*]

ARTICLE INFO

ABSTRACT

The addition of oxidants for disinfecting water can lead to the formation of potentially carcinogenic compounds referred to as disinfection byproducts (DBPs). Haloacetic acids (HAAs) are one of the most widely detected DBPs in US water utilities and some of them are regulated by the US Environmental Protection Agency (USEPA). The present study developed a method to analyze all the compounds in the USEPA method 557 (nine HAAs, bromate and dalapon) plus four potentially more toxic iodinated HAAs in water by coupling ion chromatography with tandem mass spectrometry (IC-MS/MS). This aqueous direct injection method has significant advantages over traditional GC methods, which require a derivatization and sample extraction that are laborious, time-consuming, and can negatively impact reproducibility. The method developed in this study requires half the time of the current USEPA method 557 on IC-MS/MS while including more compounds and achieving sub-µg/L level method detection limits (MDLs) for all 15 target analytes. The single laboratory lowest concentration minimum reporting level (LCMRL) has also been determined in reagent water, which ranged from 0.011 to 0.62 µg/L for the analytes. The mean recoveries of the analytes during matrix spike recovery tests were 77–125% in finished drinking water and 81–112% in surface water. This method was then applied to untreated, chlorinated, and chloraminated groundwater and surface water samples. Bromate and 9 HAAs were detected at different levels in some of these samples.

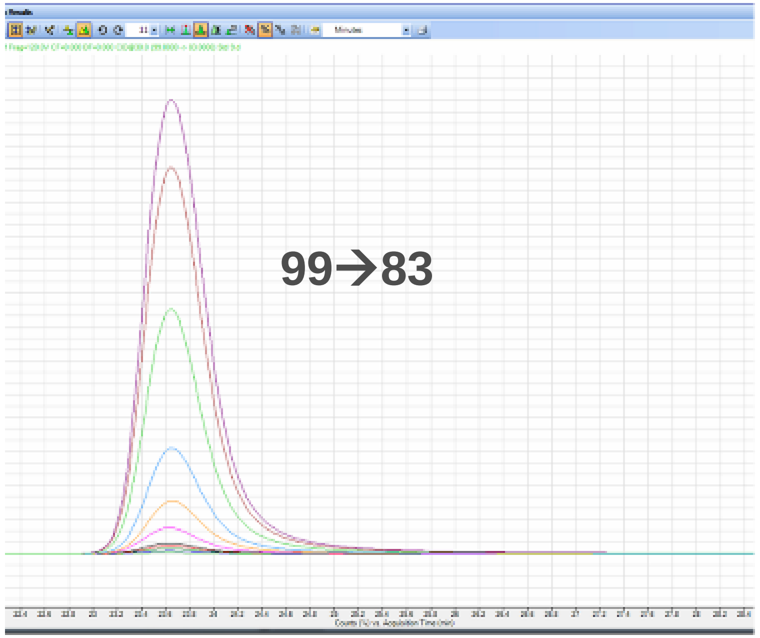
Wu et al. (2017), "Analysis of haloacetic acids, bromate and dalapon in natural waters by ion chromatography-tandem mass spectrometry", J Chrom A, 100-107

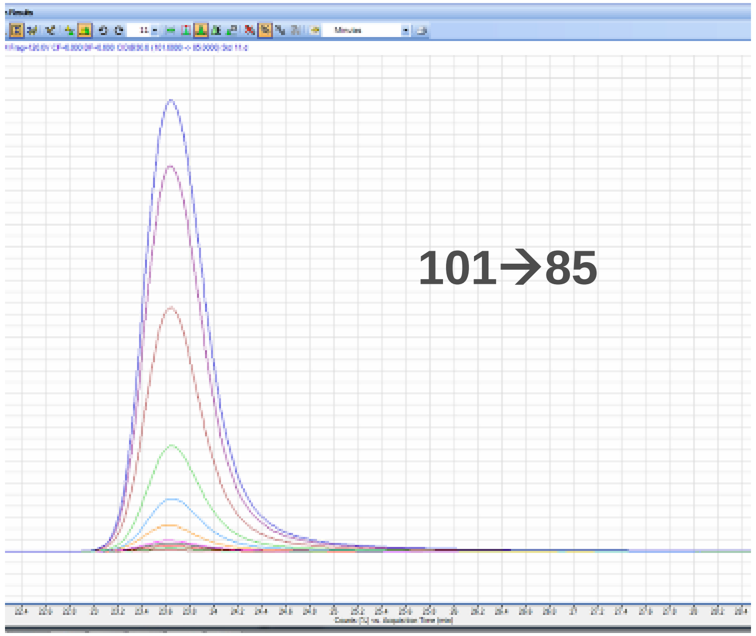
Analysis of Perchlorate by IC-MS/MS in Potable Water

EPA method 332.0 (Metrohm 950 IC + Agilent 6470 LC-MS)

Direct aqueous injection with 100 µL water sample
Isocratic elution with 10.6 mM sodium carbonate and 25% ACN
MRL: 0.1 ppb in drinking water (Round Robin Challenge Matrix)

MS/MS allows for elimination of sulfate interference that occurs with MSD or conductivity detector





Thank you

Let's Continue the Conversation