Wait – You Can Do That With a GC Triple Quad?

ASMS 2018 San Diego, CA

Thomas P. (Tom) Doherty, Ph.D.
GC/TQ Product Manager
June 5, 2018

Agilent
Trusted Answers

Outline

- A little history
- Wait – I can retire my mag sector?
- Wait – that's not how you use a triple quad. Or is it?
- Wait – I can replace my ion trap?
- Wait – I can do volatiles?
- Wait – it's not just for MS/MS?

Agilent's Revolutionary 7000A Triple Quadrupole GC/MS Introduced at ASMS 2008

- First modern GC/TQ purpose-built for GC/MS
- Based on the #1 and most trusted single quad, the Agilent 5975
- Was #1 in the market within 5 months, and has been ever since
- Perfectly timed to:
  - Ride the wave of the globalization of the food market and the increased concern over food safety
  - Lead the transition from multi-detector, multi-method GC-only pesticide residue methods to comprehensive GC/MS methods
  - Enable the use of QuEChERS and other simplified sample prep techniques

Food safety is the #1 market for GC/TQ, and the one that evolved at the same time the technology did – much like environmental and the single quad

What Does 10 Years of Evolution Look Like?

Agilent 7010B with Intuvo 9000 GC

Anal Bioanal Chem
https://doi.org/10.1007/s00216-017-0723-x

RESEARCH PAPER

Further improvements in pesticide residue analysis in food by applying gas chromatography triple quadrupole mass spectrometry (GC-QqQ-MS/MS) technologies

Elena Hakme[1] · Ana Lozano[1] · Samanta Uclés[1] · Amadeo R. Fernández-Alba[1]

In this work, the feasibility of decreasing the run time to 12.4 min by modifying the oven temperature program, for a multiresidue method covering 203 pesticides, was evaluated. Satisfactory sensitivity results were achieved by reaching a limit of quantitation of 2 μg kg^{-1} for a great variety of fruits and vegetables. The validated method based on updated GC-QqQ-MS/MS has confirmed the abovementioned challenges with adequate robustness by its application to routine analyses for 69 real samples.

✉ Amadeo R. Fernández-Alba
amadeo@ual.es

[1] Agrifood Campus of International Excellence (CeiA3), European Union Reference Laboratory for Pesticide Residues in Fruit and Vegetables, Department of Chemistry and Physics, University of Almería, 04120 Almería, Spain

Wait – I can retire my mag sector?

Dethroning the King
GC Triple Quad OK'd For Confirmation of Dioxins in Food in the EU

European Market for Dioxin analysis in [Animal] Feed and Foodstuffs

Commission Regulation (EU) No 589/2014 (of 2 June 2014)
laying down methods of sampling and analysis for the control of levels of dioxins, dioxin-like PCBs and non-dioxin-like PCBs in certain foodstuffs and repealing Regulation (EU) No 252/2012

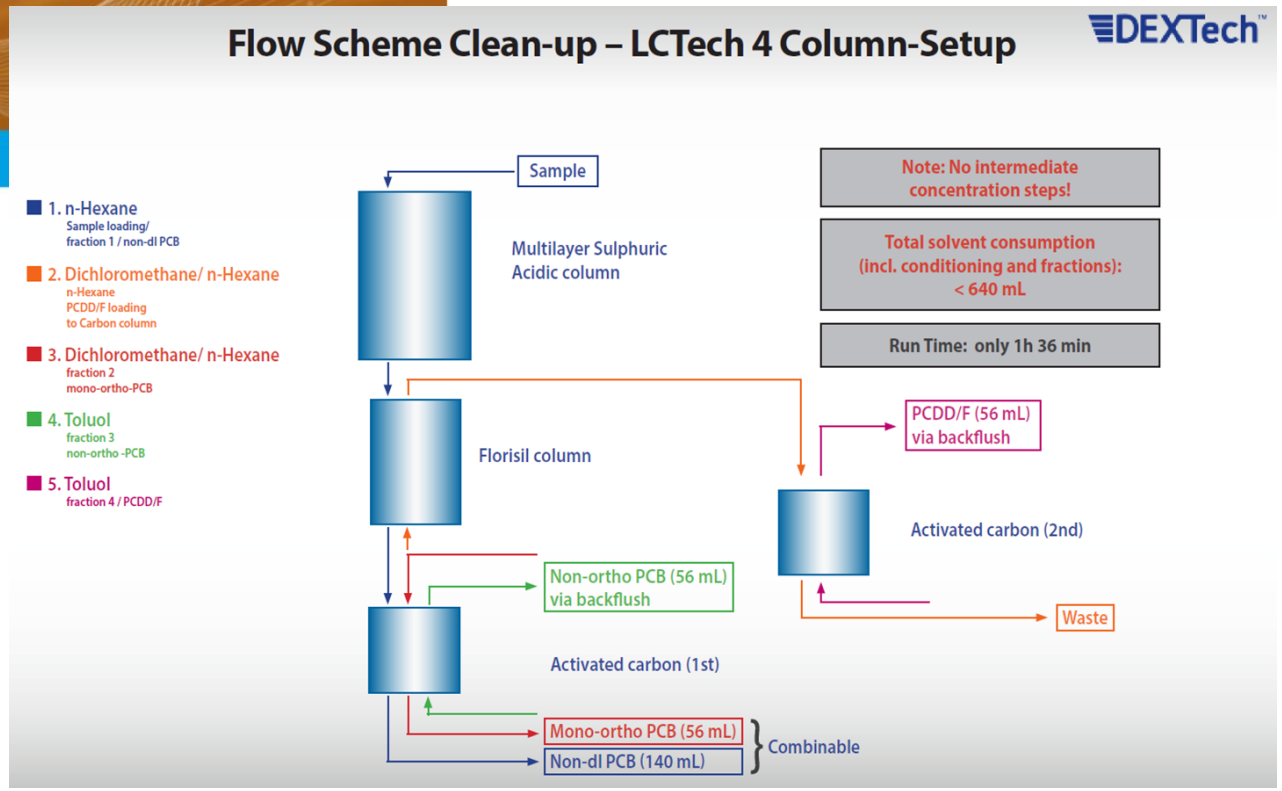
Commission Regulation (EU) No 709/2014 (of 20 June 2014)
amending Regulation (EC) No 152/2009 as regards the determination of the levels of dioxins and polychlorinated biphenyls in feed

Except from EU No 589/2014

(9) In addition to the gas chromatography/high resolution mass spectrometry (GC-HRMS), technical progress and developments have shown that also gas chromatography/tandem mass spectrometry (GC-MS/MS) can be used as a confirmatory method for checking compliance with the maximum level (ML). Regulation (EU) No 252/2012 should therefore be replaced by a new Regulation providing for the use of gas chromatography/tandem mass spectrometry (GC-MS/MS) as an appropriate confirmatory method for checking compliance with the maximum level.

In force as of June 20th 2014

Agilent's Dioxins in Feed and Food Analyzer



Dioxin Analyzer GC and MS Conditions

GC Conditions			
Column	DB 5MSUI 60 m x 0.25 mmID x 0.25 µm		
Injection port liner	2mm id dimpled splitless liner, UI		
Injection mode	Cold-splitless (compressed air/CO_2 cooled MMI)		
Injection volume	1 µL		
Column Flow	1 mL/min *(Retention Time Locked to PCB 105 @ 14.520 min)*		
Inlet temperature program		60 °C	0.31 min
	600 °C/min	330 °C	5 min
Carrier gas	He, constant flow 0.700 mL/min		
Oven program		60 °C	1 min
	30 °C/min	270 °C	1 min
	2 °C/min	310 °C	0 min
	5 °C/min	350 °C	0.5 min
MS transfer line temperature	350 °C		

MS set points	
Electron Energy	70 eV
Tune	eihs.tune.xml
EM gain	10
MS1 resolution	Unit
MS2 resolution	Unit
Collision Cell	1.5 mL/min N_2 4 mL/min He
Quant/Qual transitions	Fraction Specific
Dwell times	Fraction Specific
Collision energies	Optimized
Source temperature	350 °C
Quad temperatures	150 °C

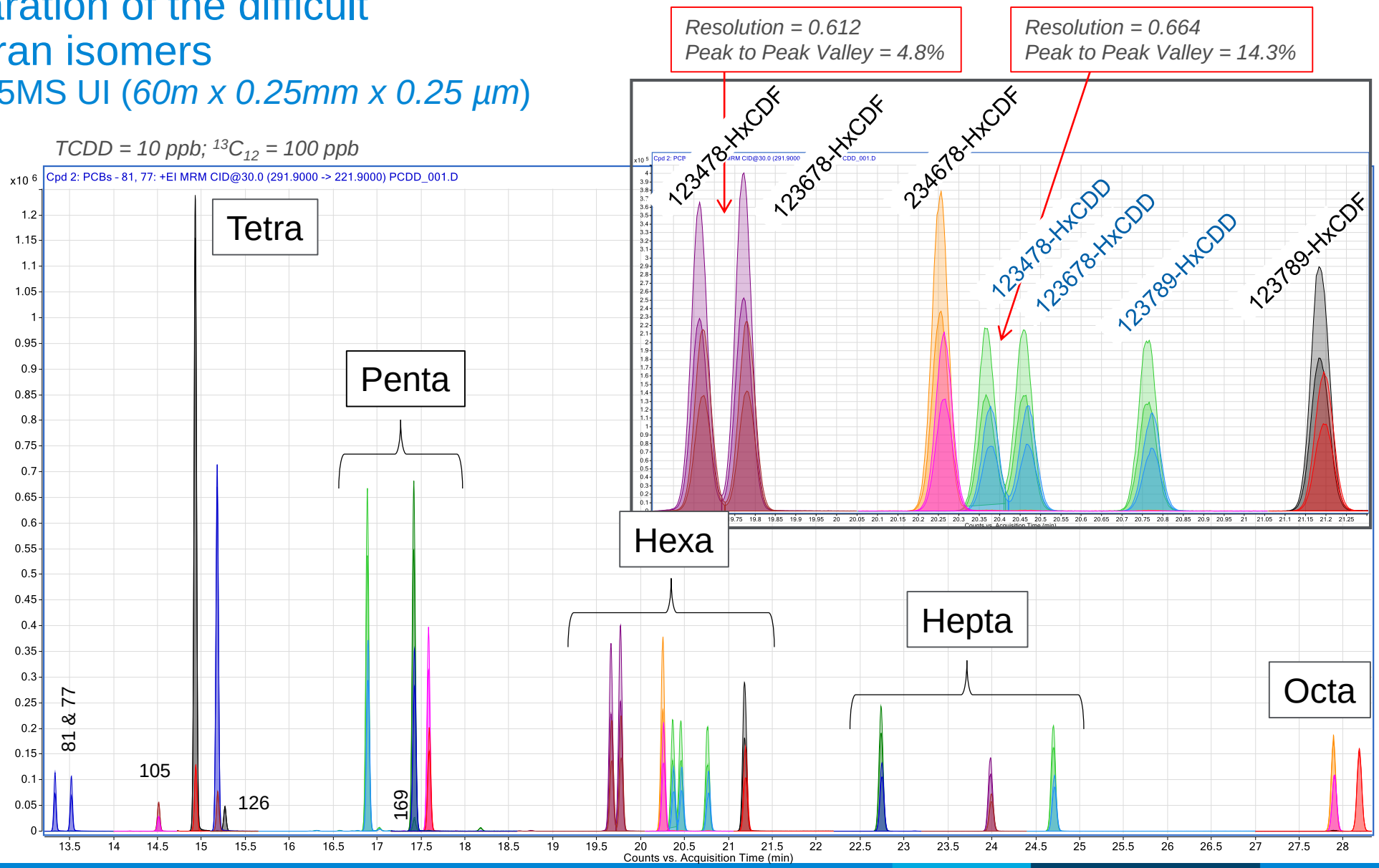
GC Conditions same for both fractions!

Developed by Jef Focant
CART Liege Belgium

Dioxins/Furans – Chromatogram

Excellent separation of the difficult *hexa*-dioxin/furan isomers

GC Column – DB5MS UI (*60m x 0.25mm x 0.25 µm*)

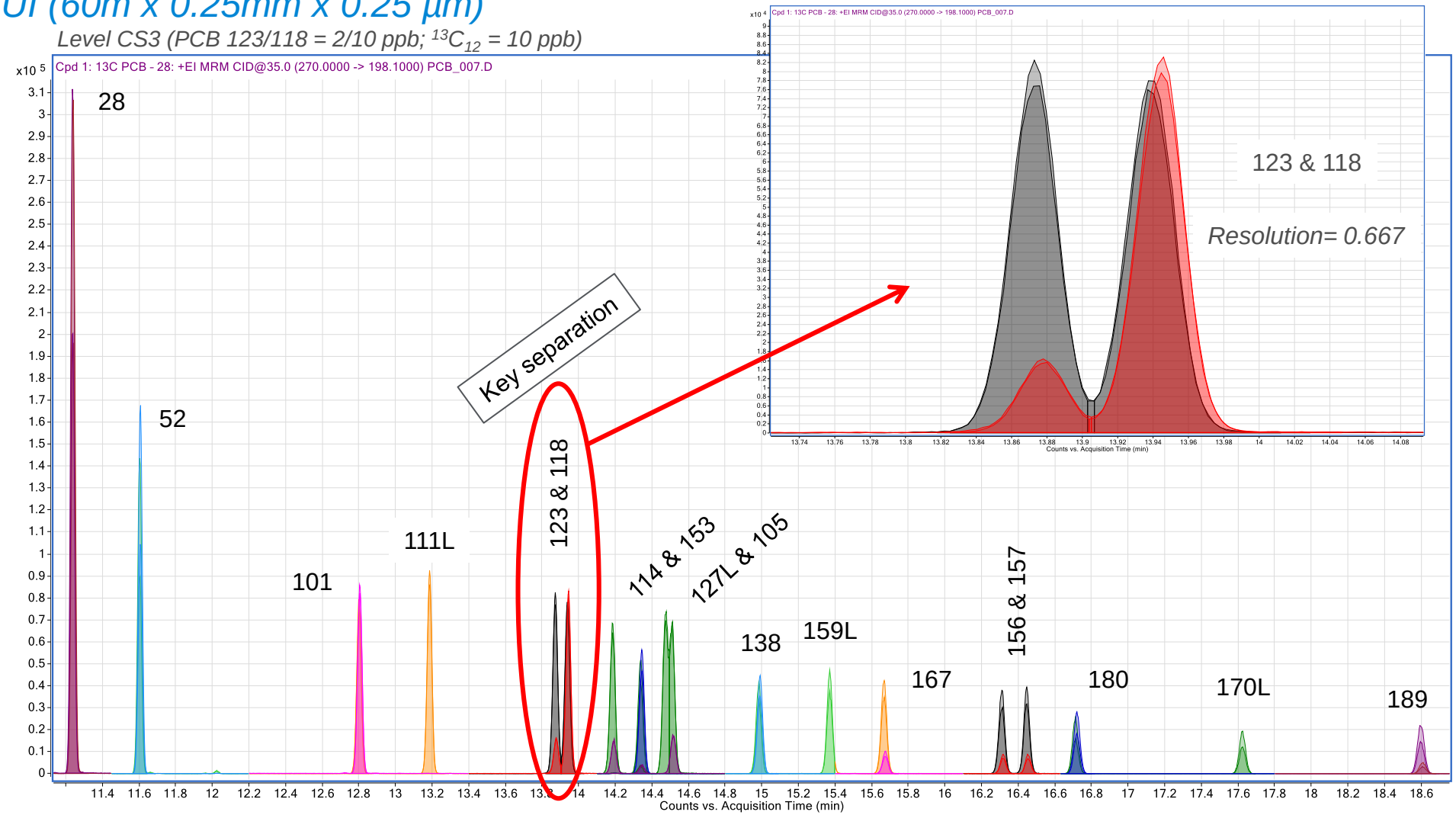


PCBs – Chromatogram

Key separation between the difficult mono-ortho substituted PCBs 123 & 118 is achieved on same method parameters as the dioxin method

GC Column – DB 5MS UI (60m x 0.25mm x 0.25 µm)

Level CS3 (PCB 123/118 = 2/10 ppb; $^{13}C_{12}$ = 10 ppb)



7010 MS/MS Instrument Detection Limit (IDL_{RSD}) in ***fg***

$$IDL_{RSD} = \frac{t_{\alpha,n-1} \times RSD \times c}{100}$$

$t_{\alpha,n-1}$ = t value (coefficient) at the level of α with the sample size of n-1

c = concentration of the std sample injected

CMPD	RRF	10 reps (CS1)	
		%RSD	IDL_{RSD} (fg)
2378-TCDF	1.180	4.92	6.8
2378-TCDD	1.258	4.28	**5.9**
12378-PeCDF	1.206	2.39	16.5
23478-PeCDF	0.961	2.98	20.6
12378-PeCDD	1.080	3.91	27.0
123478-HxCDF	1.278	3.33	23.0
123678-HxCDF	1.194	2.58	17.8
234678-HxCDF	1.171	2.71	18.7
123478-HxCDD	1.184	4.83	33.4
123678-HxCDD	1.183	4.40	30.4
123789-HxCDD	1.178	4.92	34.0
123789-HxCDF	1.906	2.24	15.5
1234678-HpCDF	1.183	2.54	17.6
1234678-HpCDD	1.171	3.37	23.3
1234789-HpCDF	0.875	5.44	37.6
OCDD	1.391	3.69	51.0
OCDF	1.963	3.04	42.0

CMPD	RRF	10 reps (CS1)	
		%RSD	IDL_{RSD} (fg)
PCB – 28	1.077	2.40	33.9
PCB – 52	1.465	1.91	26.9
PCB – 101	1.276	1.57	22.1
PCB – 81	1.040	1.41	4.0
PCB – 77	1.024	1.71	4.8
PCB – 123	2.854	16.11	45.5
PCB – 118	0.620	1.43	4.0
PCB – 114	3.316	9.89	27.9
PCB – 153	0.883	1.97	27.8
PCB – 105	0.671	19.44	54.8
PCB – 138	1.402	1.17	16.5
PCB – 126	1.061	5.43	15.3
PCB – 167	1.168	2.11	6.0
PCB – 156	1.053	4.24	12.0
PCB – 157	1.025	3.49	9.8
PCB – 180	0.930	1.24	17.5
PCB – 169	1.228	2.12	6.0
PCB – 189	1.095	3.13	8.8

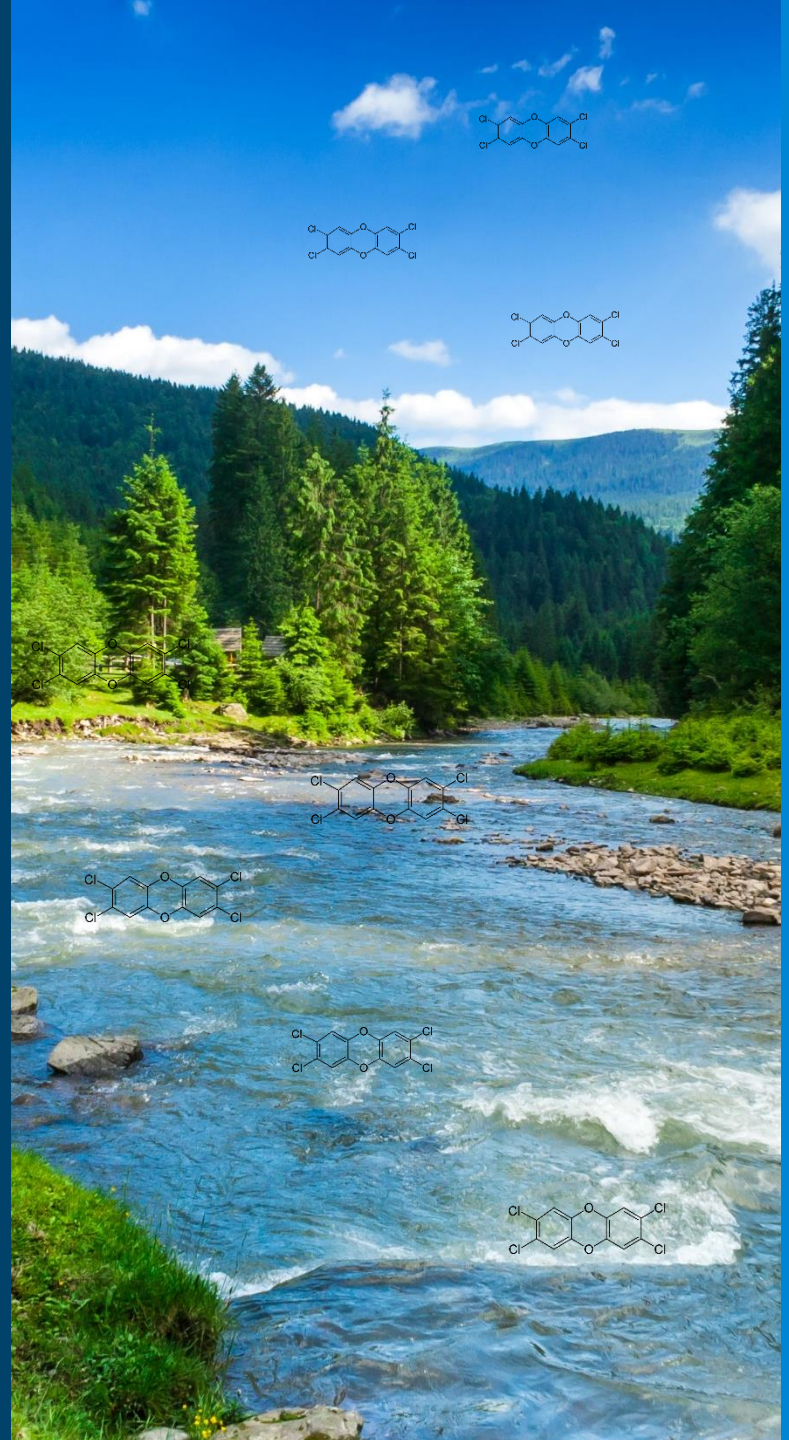
STDs in solvent

Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution GC/MS/MS

Following EPA Method 1613

Hui Lin[1], Diana Wong[2], Dale Walker[2], Tarun Anumol[2], Craig Marvin[2]

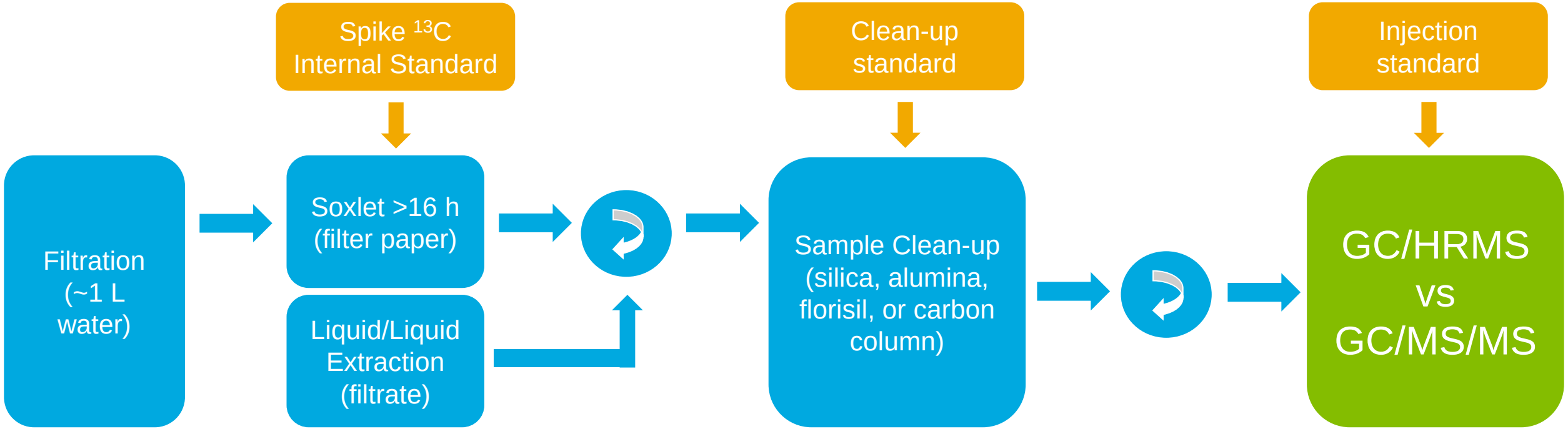
[1]The DOW Chemical Company
[2]Agilent Technologies



Agilent
Trusted Answers

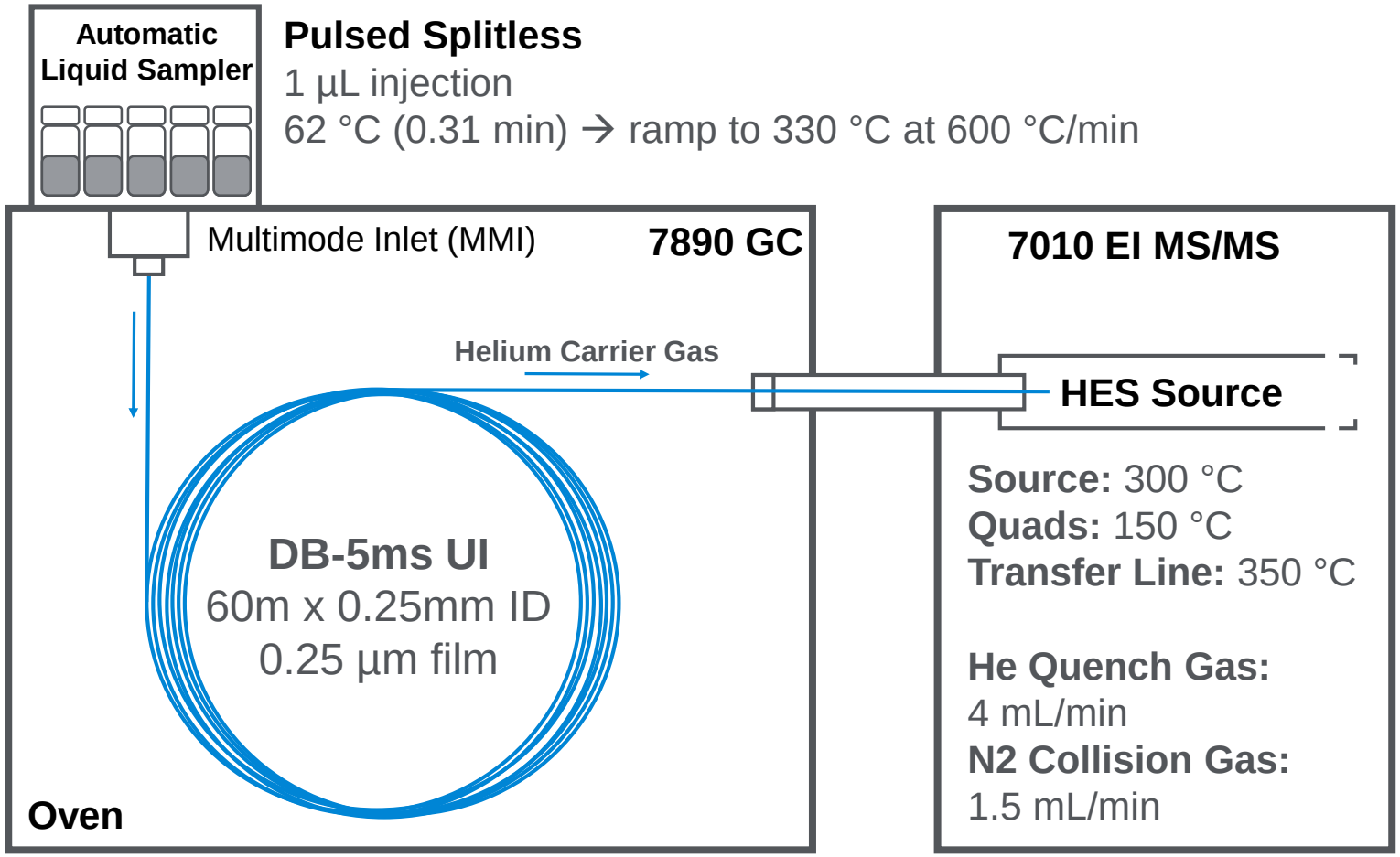
EPA Method 1613B Sample preparation

No changes to sample preparation



EPA 1613B is a performance based method

GC/MS/MS System Parameters



Inlet liner
2mm Dimpled, splitless, UI

GC Parameters
MMI Inlet → MSD
Constant Flow
Flow 1.1 mL/min

Oven program:
100 °C (2 min)
30 °C/min to 220 °C (16 min)
2 °C/min to 240 °C (5 min)
5 °C/min to 270 °C (4 min)
15 °C/min to 330 °C (6 min)

MRM Parameters and Collision Energy

Toxic TetraCDD/TetraCDF (Segment 1)

Analyte	Precursor Ion	Product Ion	CE
13C-TCDD	333.9	269.9	26
13C-TCDD	331.9	267.9	26
TCDD	321.9	258.9	26
TCDD	319.9	256.9	26
13C-TCDF	317.9	253.9	40
13C-TCDF	315.9	251.9	40
TCDF	305.9	242.9	40
TCDF	303.9	240.9	40

PentaCDD/PentaCDF (Segment 3)

Analyte	Precursor Ion	Product Ion	CE
13C-PeCDD	367.9	302.9	26
13C-PeCDD	365.9	301.9	26
PeCDD	355.9	292.9	26
PeCDD	353.9	290.9	26
13C-PeCDF	351.9	287.9	40
13C-PeCDF	349.9	285.9	40
PeCDF	339.9	276.9	40
PeCDF	337.9	274.9	40

HeptaCDD/HeptaCDF (Segment 5)

Analyte	Precursor Ion	Product Ion	CE
13C-HpCDD	437.8	373.8	24
13C-HpCDD	435.8	371.8	24
HpCDD	425.8	362.8	24
HpCDD	423.8	360.8	24
13C-HpCDF	421.8	357.8	40
13C-HpCDF	419.8	355.8	40
HpCDF	409.8	346.8	40
HpCDF	407.8	344.8	40

Non-Toxic last eluted TCDD/TCDF and first eluted non-toxic PeCDF (Segment 2)

Analyte	Precursor Ion	Product Ion	CE
13C-PeCDF	351.9	287.9	40
13C-PeCDF	349.9	285.9	40
PeCDF	339.9	276.9	40
PeCDF	337.9	274.9	40
13C-TCDD	333.9	269.9	26
13C-TCDD	331.9	267.9	26
TCDD	321.9	258.9	26
TCDD	319.9	256.9	26
13C-TCDF	317.9	253.9	40
13C-TCDF	315.9	251.9	40
TCDF	305.9	242.9	40
TCDF	303.9	240.9	40

HexaCDD/HexaCDF (Segment 4)

Analyte	Precursor Ion	Product Ion	CE
13C-HxCDD	403.9	339.9	25
13C-HxCDD	401.9	337.9	25
HxCDD	391.8	328.8	25
HxCDD	389.8	326.8	25
13C-HxCDF	387.9	323.9	40
13C-HxCDF	385.9	321.9	40
HxCDF	375.8	312.8	40
HxCDF	373.8	310.8	40

OctaCDD/OctaCDF (Segment 6)

Analyte	Precursor Ion	Product Ion	CE
13C-OCDD	471.8	407.8	24
13C-OCDD	469.8	405.8	24
OCDD	459.7	396.7	24
OCDD	457.7	394.7	24
13C-OCDF	455.8	391.8	40
13C-OCDF	453.8	389.8	40
OCDF	443.7	380.7	40
OCDF	441.7	378.7	40

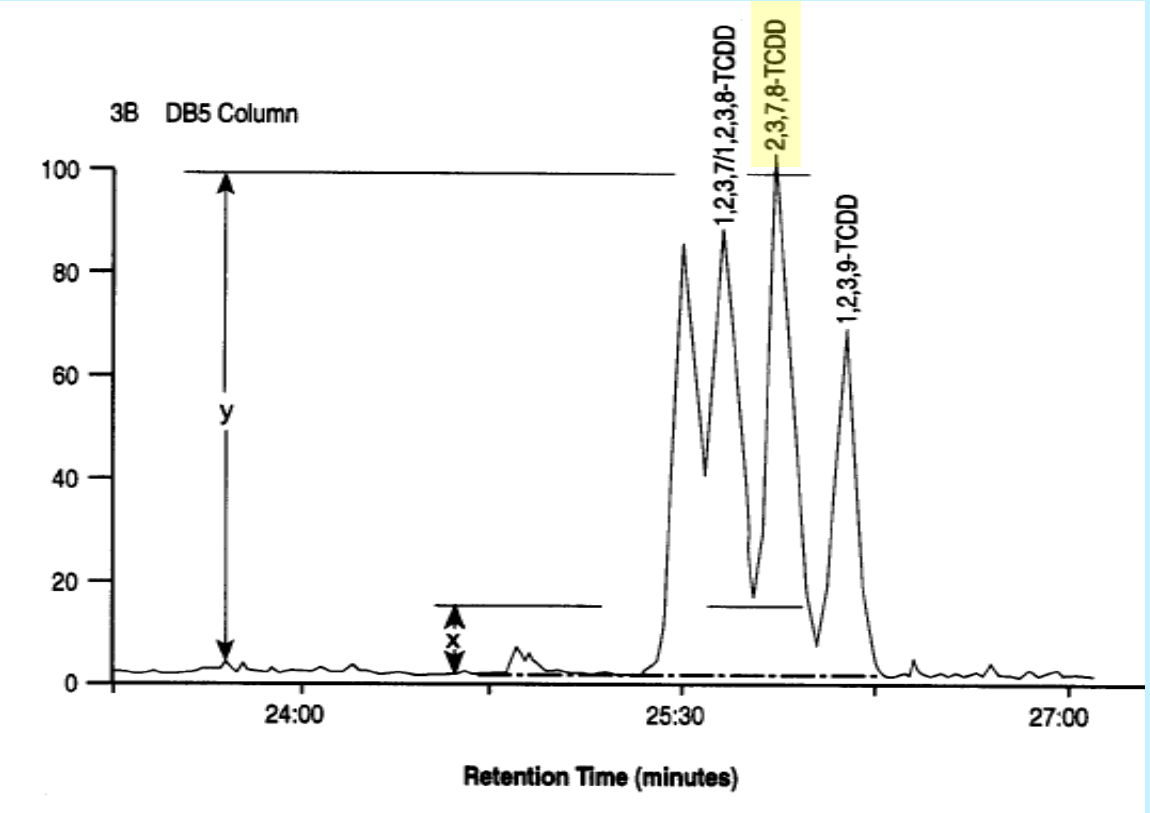
Unit resolution for precursor and product ions

Isomer Specificity

EPA Method 1613B Requirements

Percent Valley

Percent valley must be less than 25% between the toxic 2378-TCDD and the closest eluted isomers



Order of Isomer Specificity

DB-5 column TCDD specificity Test Standard	DB-5MS column TCDD specificity Test Standard
1,2,3,7/1,2,3,9-TCDD	1,2,3,7/1,2,3,9-TCDD
2378-TCDD	1239-TCDD
1239-TCDD	2378-TCDD
EPA Method 1613B	Current Study

- The order of specificity standards of TCDD isomers are slightly different on a DB-5MS column (used in current study) compared to the DB-5 column (recommended in EPA 1613b)
- Peer review journals by **The DOW Chemical Company** published elution order of EPA Method 1613B dioxins using the DB-5MS UI (Fishman et al., 2004 and 2011; Wilken et al., 2008)

(EPA Method 1613B, 1994)

GC Retention Time Window Defining Solution

EPA Method 1613B Requirements

TABLE 5. GC RETENTION TIME WINDOW DEFINING SOLUTION AND ISOMER SPECIFICITY TEST STANDARD (SECTION 7.15)

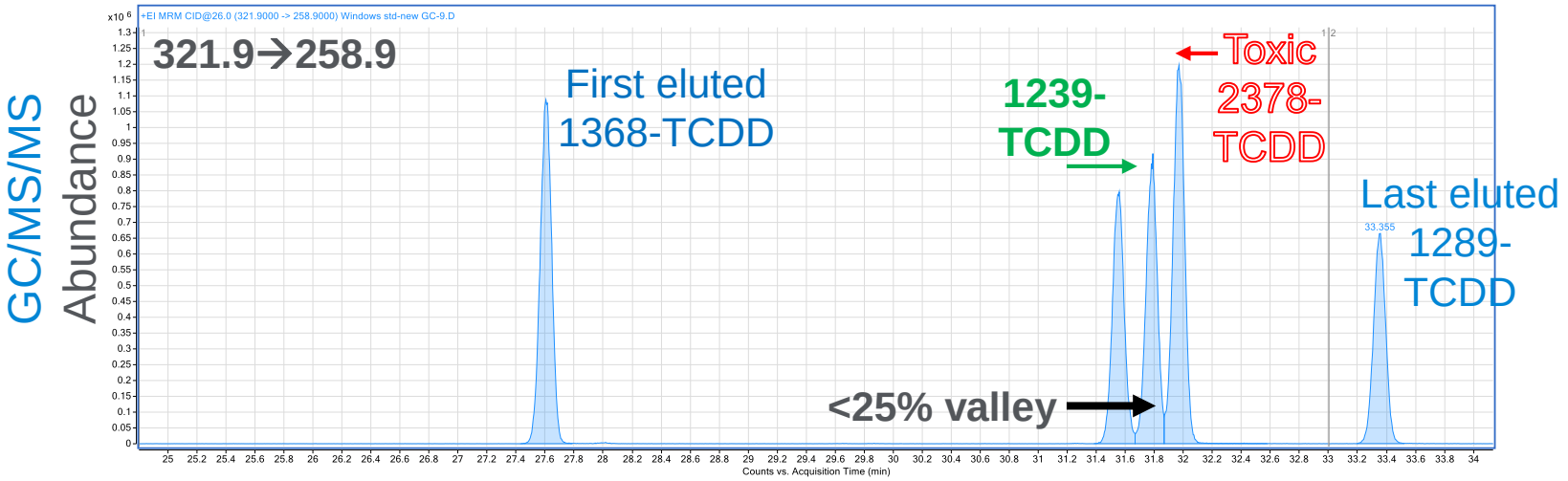
DB-5 Column GC Retention-Time Window Defining Solution		
CDD/CDF	First Eluted	Last Eluted
TCDF	1,3,6,8-	1,2,8,9-
TCDD	1,3,6,8-	1,2,8,9-
PeCDF	1,3,4,6,8-	1,2,3,8,9-
PeCDD	1,2,4,7,9-	1,2,3,8,9-
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-
HxCDD	1,2,4,6,7,9-	1,2,3,4,6,7-
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-

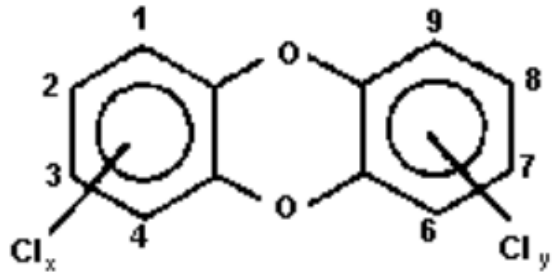
→ 1,2,3,7,8,9 -

EPA Method 1613B (1994): Window Defining Solution defines the beginning (first eluted) and ending (last eluted) retention times for dioxin and furan isomers to demonstrate isomer specificity. Standards must contain compounds listed in this order

Tetrachlorinated dibenzodioxins (TCDD)

Peaks match between GCMS/MS vs High Resolution GC/MS

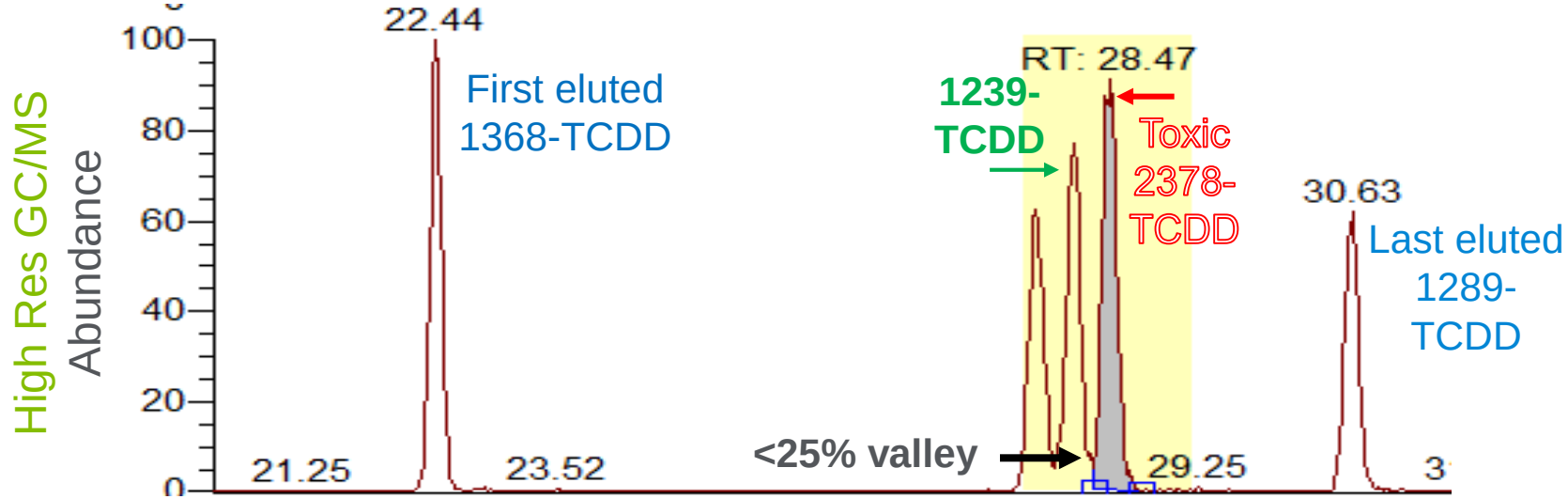




$x + y = 4$

22 isomers

1 toxic



Calibration and Linear Range

Response Factor, Signal-to-noise, and Relative Retention Time all meet the 1613B criteria

Cal. Sample Name	Level
200 ppt Cal Std.	L1
500 ppt Cal Std.	L2
1000 ppt Cal Std.	L3
4000 ppt Cal Std.	L4
10000 ppt Cal Std.	L5
50000 ppt Cal Std.	L6
250000 ppt Cal Std.	L7
1000000 ppt Cal Std.	L8
2500000 ppt Cal Std.	L9

Calibration Standard 1 (CS1) for EPA 1613B

Name	Avg. RF	Avg. RF RSD	CS1 RF	Difference	CS1 S/N	CS1 RRT	1613b RRT criteria	Pass/Fail
2378-TCDD	1.123	6	1.004	-11%	*25*	1.002	0.999-1.002	*Pass*
2378-TCDF	0.97	2.9	0.943	-3%	*50*	1.001	0.999-1.003	*Pass*
12378-PeCDD	0.985	3.5	0.994	1%	*42*	1.001	0.999-1.002	*Pass*
12378-PeCDF	0.991	2.8	1.025	3%	*54*	1.001	0.999-1.002	*Pass*
23478-PeCDF	1.007	2.1	0.997	-1%	*63*	1.000	0.999-1.002	*Pass*
123478-HxCDD	0.991	4.2	0.999	1%	*21*	1.001	0.999-1.001	*Pass*
123478-HxCDF	0.924	4.4	0.921	0%	*33*	1.001	0.998-1.004	*Pass*
123678-HxCDD	0.929	3.6	0.917	-1%	*25*	1.000	1.000-1.019	*Pass*
123678-HxCDF	0.908	4.5	0.877	-3%	*43*	1.000	0.999-1.001	*Pass*
123789-HxCDD	1.027	5.3	1.000	-3%	*42*	1.000	0.997-1.005	*Pass*
123789-HxCDF	0.912	5.2	0.902	-1%	*38*	1.000	0.999-1.001	*Pass*
234678-HxCDF	0.983	4.1	0.999	2%	*48*	1.000	0.999-1.001	*Pass*
1234678-HpCDD	1.008	4	1.033	2%	*83*	1.000	0.999-1.001	*Pass*
1234678-HpCDF	0.912	3.5	0.943	3%	*92*	1.000	0.999-1.001	*Pass*
1234789-HpCDF	0.902	4.2	0.948	5%	*90*	1.000	0.999-1.001	*Pass*
OCDD	1.056	2.4	1.040	-1%	*150*	1.000	0.999-1.001	*Pass*
OCDF	0.913	3.5	0.940	3%	*148*	1.000	0.999-1.008	*Pass*

Example of RF calculation for 2378-TCDD

$$RF = \frac{A_{2,3,7,8-TCDD,Std}}{A_{13C,Std}} \times \frac{M_{13C,Std}\ (ng)}{M_{2,3,7,8-TCDD,Std}\ (ng)}$$

1613B Criteria: Avg RSD < 10%; Difference (CS1 RF and Average RF) < 15%; S/N (CS1) > 10; Relative Retention Time (CS1) must meet criteria

Verification Standard Recoveries

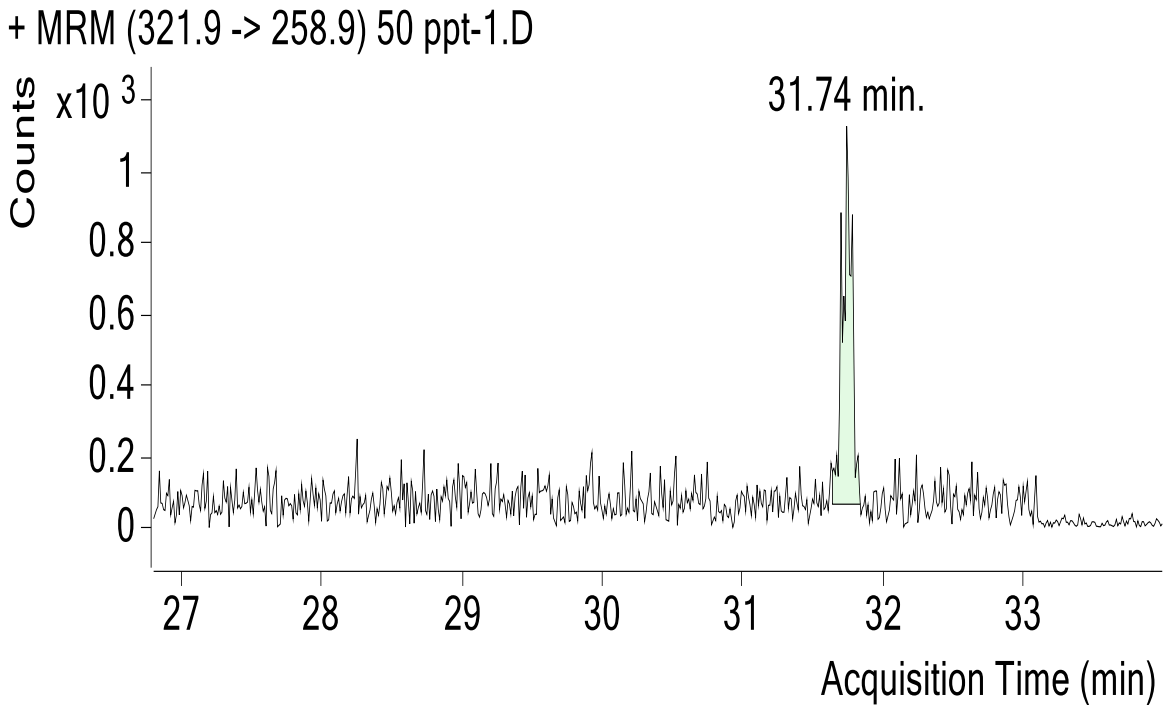
Calibration is verified and passed the 1613B criteria

Comp. Name	Chemstation Amt (ng)	Theoretical Amt (ng)	% Recovery	1613b criteria	Pass/Fail
2378-TCDF	1.815	2	91%	84-120%	**Pass**
2378-TCDD	1.833	2	92%	78-129%	**Pass**
12378-PCDF	4.790	5	96%	82-120%	**Pass**
23478-PCDF	4.705	5	94%	82-122%	**Pass**
12378-PCDD	4.742	5	95%	78-130%	**Pass**
123478-HxCDF	4.642	5	93%	90-112%	**Pass**
123678-HxCDF	4.629	5	93%	88-114%	**Pass**
234678-HxCDF	4.600	5	92%	88-114%	**Pass**
123789-HxCDF	4.701	5	94%	90-112%	**Pass**
123478-HxCDD	4.342	5	87%	78-128%	**Pass**
123678-HxCDD	4.385	5	88%	78-128%	**Pass**
123789-HxCDD	4.422	5	88%	82-122%	**Pass**
1234678-HpCDF	4.823	5	96%	90-110%	**Pass**
1234789-HpCDF	5.097	5	102%	86-116%	**Pass**
1234678-HpCDD	4.840	5	97%	86-116%	**Pass**
OCDF	9.221	10	92%	63-159%	**Pass**
OCDD	9.175	10	92%	79-126%	**Pass**

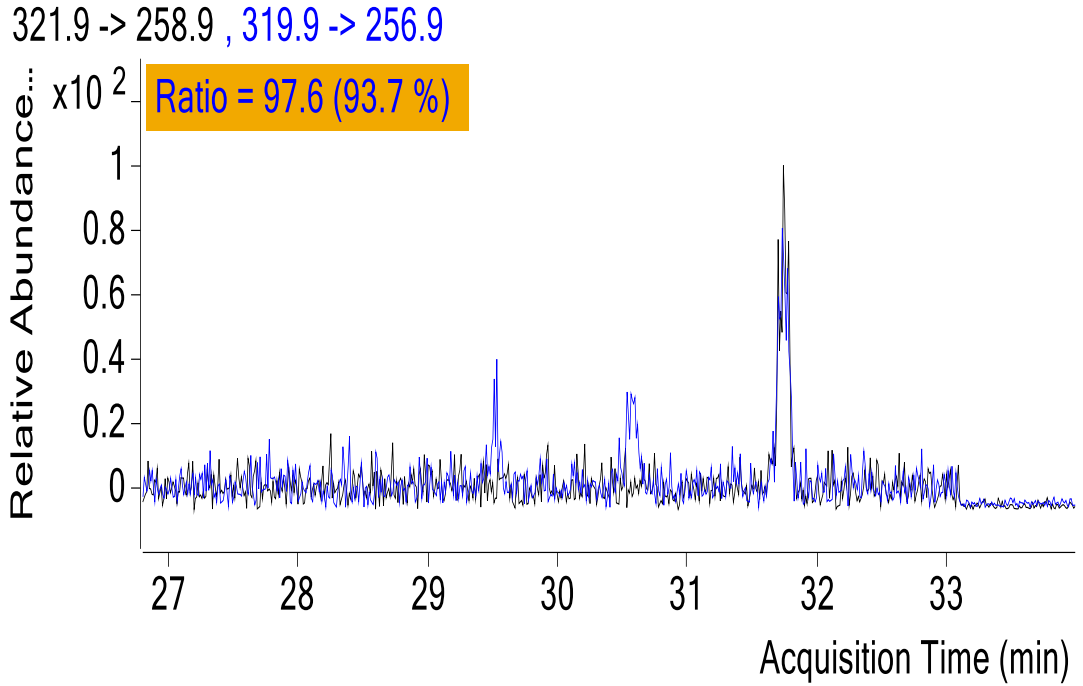
Low working range and sensitivity

50 femtogram of 2378-TCDD can be detected by GC/MS/MS

Primary Native 2378-TCDD S/N = 5.8



Secondary Native 2378-TCDD S/N = 4.6

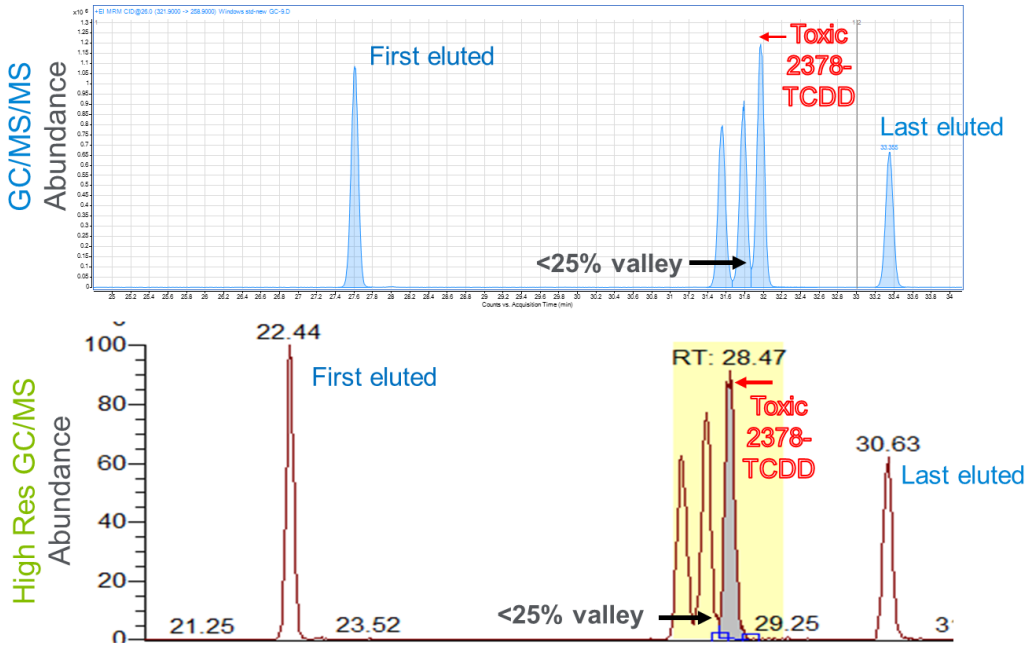


Method 1613 Criteria

- > 2.5 signal to noise ratio
- The relative ion intensities is within 15% difference to the calibration average

Conclusion

EPA Method 1613B Criteria are met using GC/MS/MS



- <25% valley between toxic 2378-TCDD and the closest isomer
- Isomer specificity observed for all CDDs and CDFs
- All analytes elute within the defined time window (between first and last eluted in the window defining solution)
- CDDs/CDFs calibration using isotope dilution: RSD, Cal Standard 1 RF, S/N, Relative RT, and recovery meet the 1613B criteria
- Low femtogram level of CDD/CDF can be detected by GC/MS/MS

Wait – that's not how you use a triple quad. Or is it?

Determination of polycyclic aromatic hydrocarbons in surface water using a simplified liquid-liquid micro-extraction and pseudo-MRM GC/MS/MS

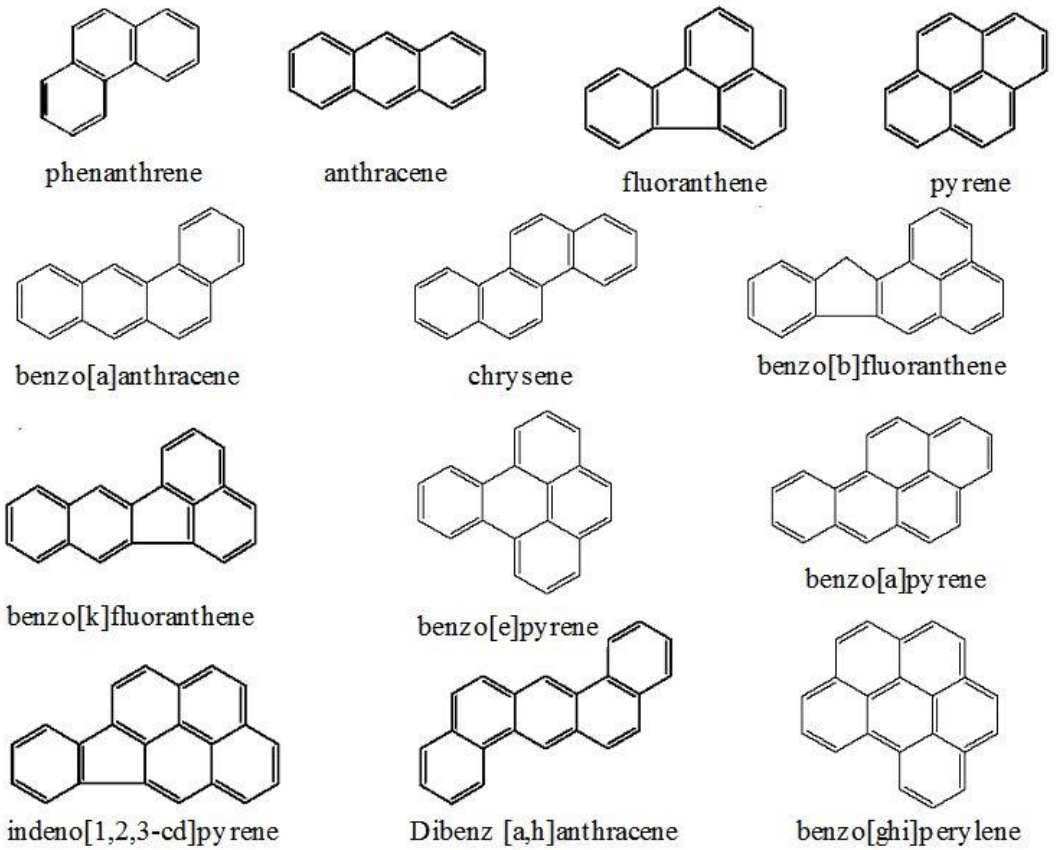
Marcus Kim, Ph.D.

Agilent Technologies

marcus.kim@agilent.com

GCMSMS@twitter.com

Polycyclic Aromatic Hydrocarbons



- Ubiquitous pyrogenic compounds created by incomplete combustion
- Mostly of anthropogenic sources
- Heavier PAHs (more than four rings) tend to adsorb to particulate matter, while lighter PAHs (less than four rings) tend to remain gaseous until removed via precipitation
- PAH's have low solubility in water, but can be absorbed by plants and concentrate in soil
- PAH's leach into water
- PAH levels in soils near refineries have been measured to be 200,000 μg/kg (200 ppm)

Hydrocarbon/PAH analyses is one of most common services offered in contract labs

- Extraction out of soil or water requires multi-steps; large volumes of solvent; silica or florisil gel clean ups
- Analysis is typically performed on a single quadrupole GCMS and GC-FID

CCME

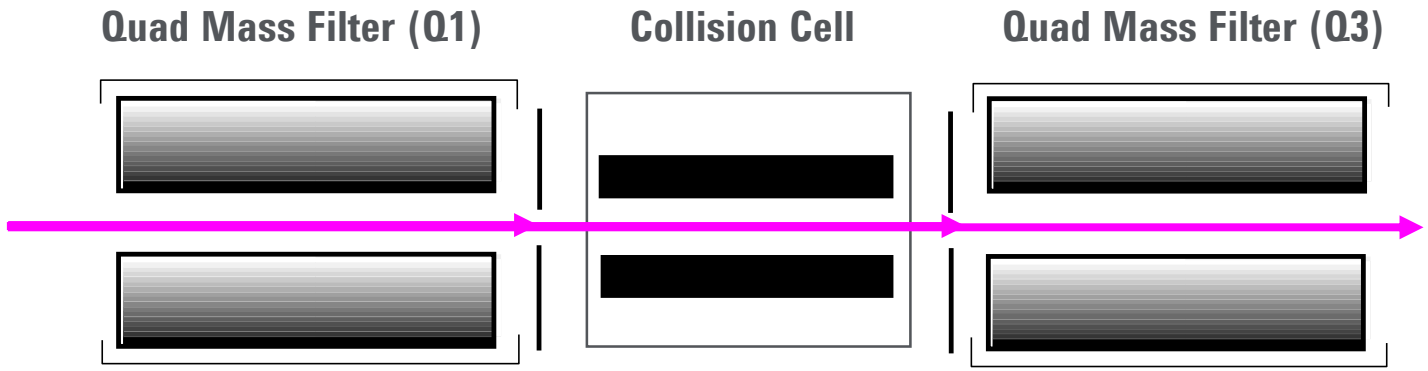
Canadian Council of Ministers of the Environment | Le Conseil canadien des ministres de l'environnement

Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method

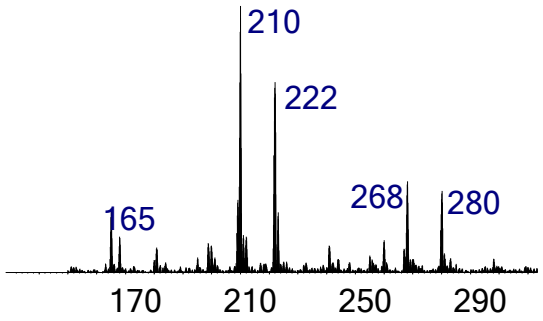
The CCME Tier 1 method

- F1, i.e., n-C_6 to n-C_{10}, as defined by this method, from which the results of a BTEX analysis have been subtracted, described as F1-BTEX
- F2, i.e., n-C_{10} to n-C_{16}, as defined by this method from which naphthalene has been subtracted, described as F2-napth
- F3, i.e., n-C_{16} to n-C_{34}, as defined by this method, less the PAHs phenanthrene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, fluoranthene, dibenz(a,h)anthracene, indeno(1,2,3-c,d)pyrene and pyrene, if analyzed. This is described as F3-PAH
- F4, either as n-C_{34} to n-C_{50} obtained by gas chromatography from analysis of extractable hydrocarbons as defined by this method, or F4G, gravimetric heavy hydrocarbons, whichever is the greater result.

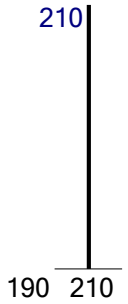
Multiple Reaction Monitoring (MRM)



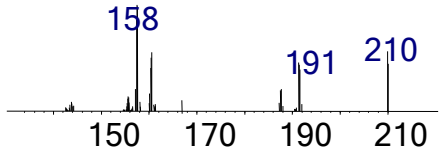
Spectrum with background ions (from EI)



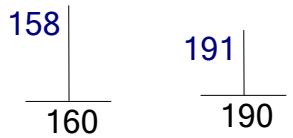
Q1 lets **only** target ion 210 pass through



Collision cell breaks ion 210 apart

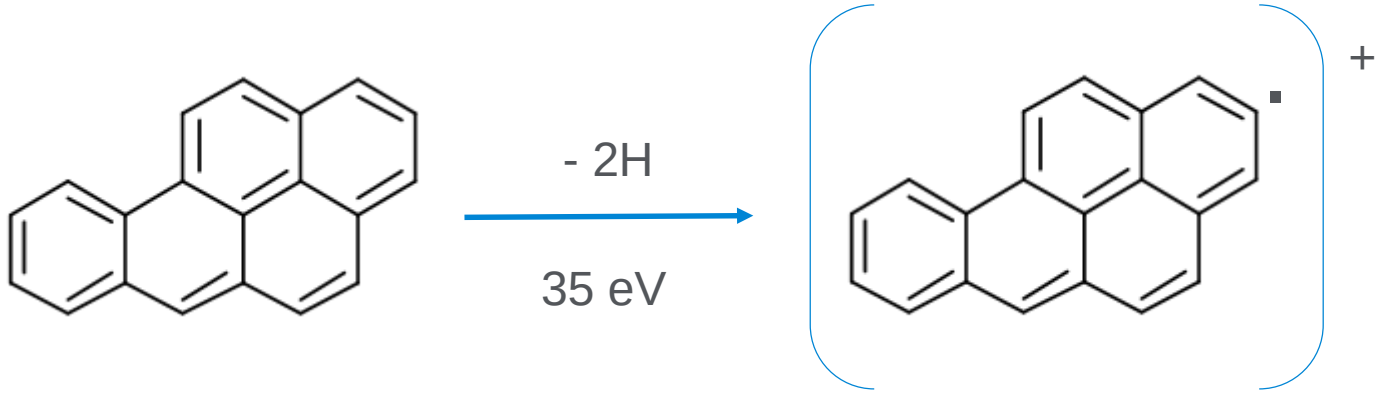


Q3 monitors **only** characteristic fragments 158 and 191 from ion 210 for quant and qual.

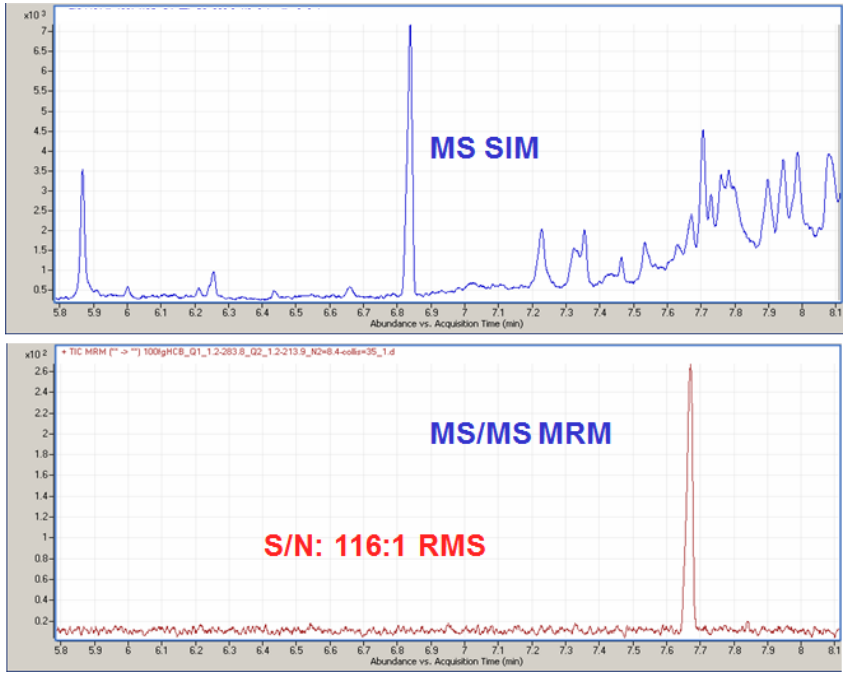


no chemical background

PAH's are inherently stable



+

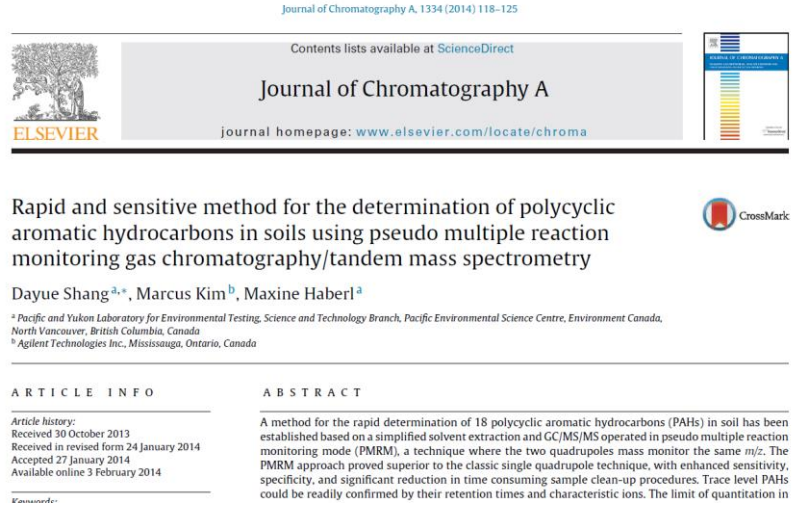


Product ion is typically 1/10th intensity of precursor ion

Pseudo-MRM approach is to tune collision energy to fragment isobaric co-eluters and monitor precursor to precursor transitions

252 m/z → 252 m/z

10 eV



Journal of Chromatography A, 1334 (2014) 118–125

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

ELSEVIER

Rapid and sensitive method for the determination of polycyclic aromatic hydrocarbons in soils using pseudo multiple reaction monitoring gas chromatography/tandem mass spectrometry

CrossMark

Dayue Shang[a,*], Marcus Kim[b], Maxine Haberl[a]

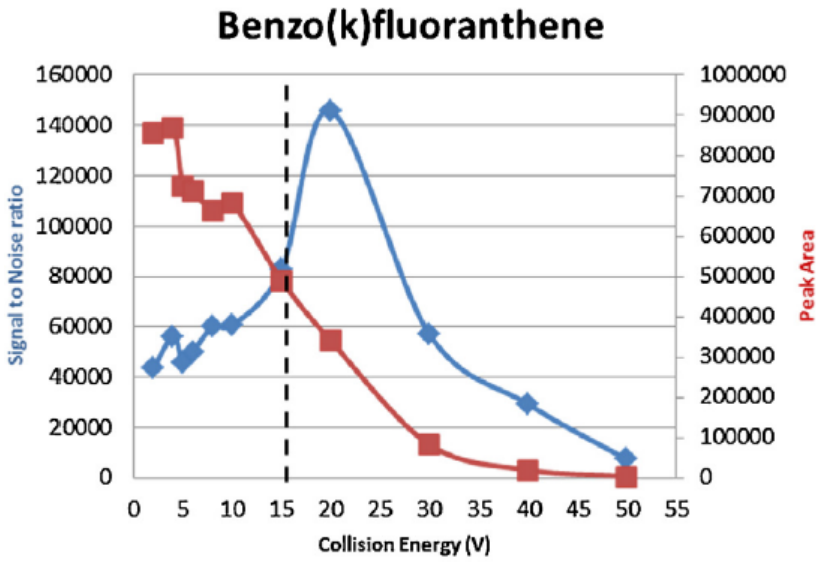
[a] Pacific and Yukon Laboratory for Environmental Testing, Science and Technology Branch, Pacific Environmental Science Centre, Environment Canada, North Vancouver, British Columbia, Canada
[b] Agilent Technologies Inc., Mississauga, Ontario, Canada

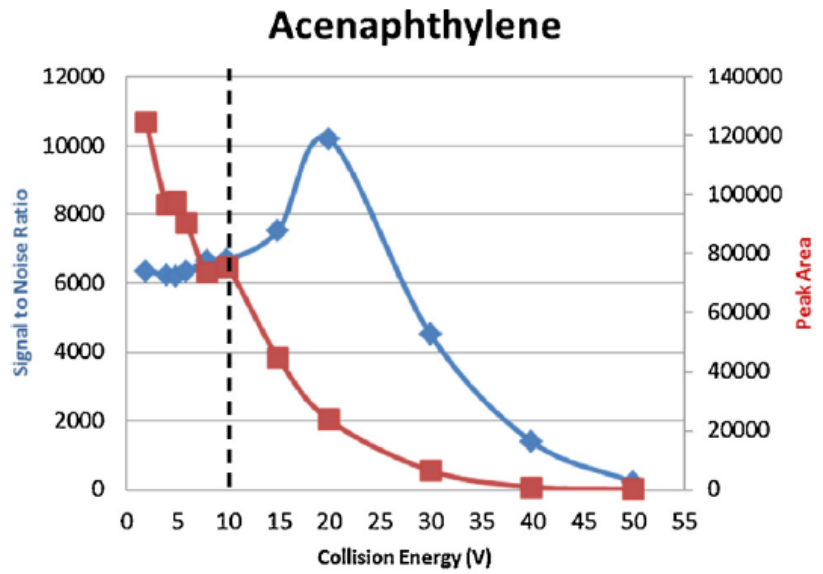
ARTICLE INFO

Article history:
Received 30 October 2013
Received in revised form 24 January 2014
Accepted 27 January 2014
Available online 3 February 2014

ABSTRACT

A method for the rapid determination of 18 polycyclic aromatic hydrocarbons (PAHs) in soil has been established based on a simplified solvent extraction and GC/MS/MS operated in pseudo multiple reaction monitoring mode (PMRM), a technique where the two quadrupoles mass monitor the same *m/z*. The PMRM approach proved superior to the classic single quadrupole technique, with enhanced sensitivity, specificity, and significant reduction in time consuming sample clean-up procedures. Trace level PAHs could be readily confirmed by their retention times and characteristic ions. The limit of quantitation in

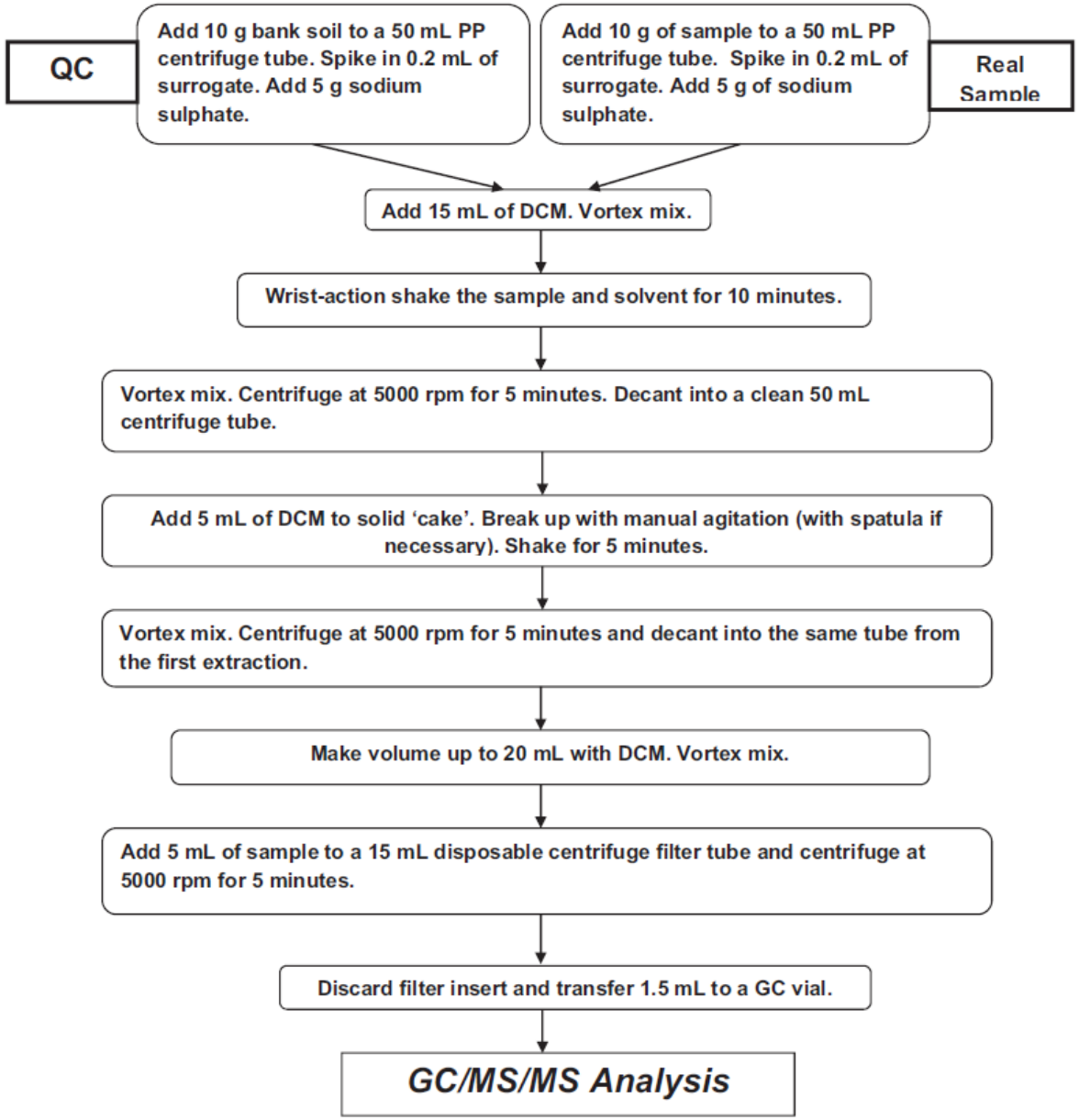




- Collision energy was tuned to find optimum of peak area and signal/noise
- Maximize peak area for maximum sensitivity
- At high collision energies, precursor ion is gone but product ion intensity is also low

Pseudo-MRM for PAH but it is true MRM for isobaric, co-eluting interferences

Agilent 7890B GC & 7000C MS/MS



- Due to selective nature of pMRM, the sample extraction was performed with 20mL of DCM; wrist shaking and centrifugation
- Sample extraction procedure ~30 minutes
- No silica gel clean up step

Comparison of pMRM technique vs. conventional SQ

	Agilent 7000 triple quadrupole			Agilent 5975 single quadrupole		
Compound	**2 ppb**	**10 ppb**	**20 ppb**	**2 ppb**	**10 ppb**	**20 ppb**
Napthalene	999	3909	8121	ND	29	57
Acenaphthylene	537	2619	5758	ND	25	45
Acenaphthene	343	1190	2877	ND	33	33
Fluorene	ND	1551	2790	ND	22	42
Phenanthrene	1372	4810	6462	ND	ND	ND
Anthracene	930	2046	4213	ND	ND	ND
Fluoranthene	1325	3659	7925	ND	46	86
Pyrene	1641	4056	9323	ND	46	94
Benzo(a)anthracene	ND	955	2521	ND	ND	ND
Chrysene	1029	2791	6306	ND	ND	ND
Benzo(b)fluoranthene	ND	1859	4778	ND	35	70
Benzo(k)fluoranthene	ND	652	1411	ND	35	85
Benzo(e) pyrene	405	1841	3922	ND	42	85
Benzo(a) pyrene	355	1159	3230	ND	33	74
Perylene	813	1976	4363	ND	49	102
Indeno(1,2,3-cd) pyrene	202	587	2237	ND	17	47
Benzo(g,h,i)perylene	455	1531	3963	ND	29	63
Dibenz(a,h)anthracene	ND	804	2293	ND	0	45

*ND = Not detected.

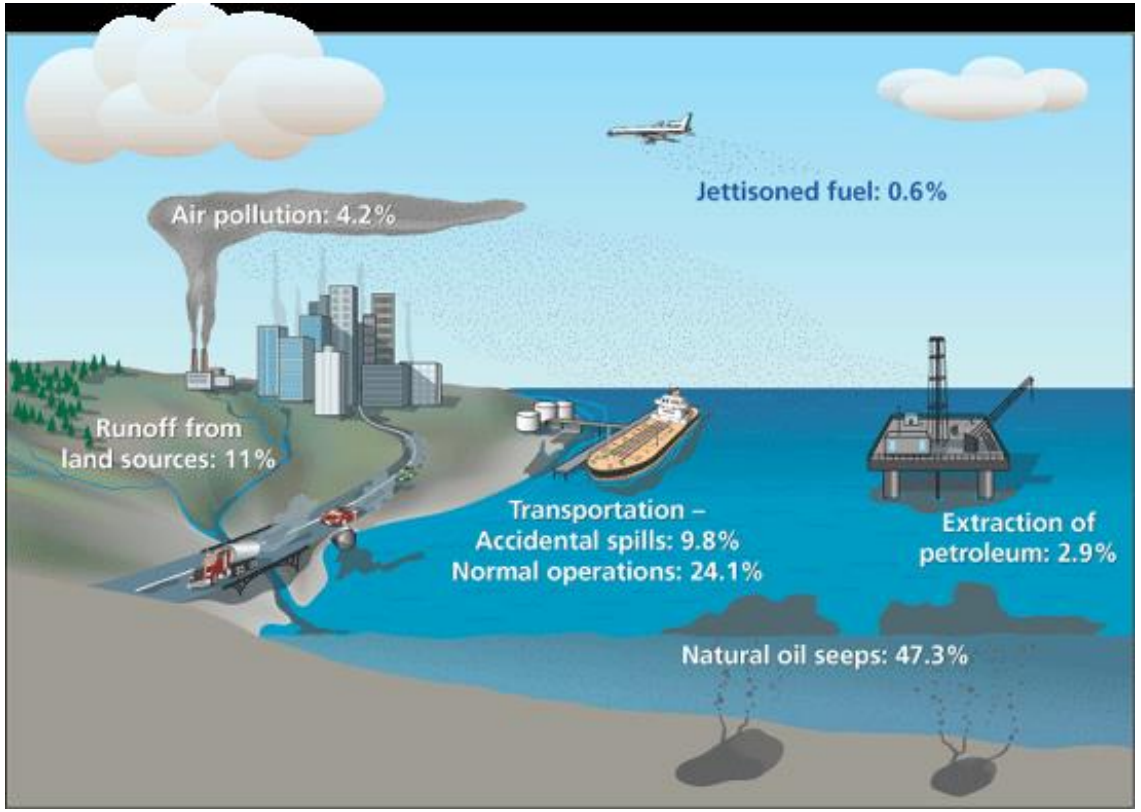
- 12 of the 18 PAH's were improved with pMRM
- CALA proficiency testing showed this technique to be accurate for most PAHs

CALA Proficiency testing sample C-18-04: measured vs. assigned concentrations.

Compound	Sample	Actual concentration (p p b)	Calculated concentration (p p b)	Accuracy (%)
Acenaphthene	C-18-04	1119	1161	104
Acenaphthylene	C-18-04	1343	1501	112
Anthracene	C-18-04	1224	1543	126
Benzo (a) anthracene	C-18-04	6076	5363	88
Benzo (a) pyrene	C-18-04	4007	3222	80
Benzo (b) fluoranthene	C-18-04	7869	5198	66
Benzo (g,h,i) perylene	C-18-04	4452	3843	86
Benzo (k) fluoranthene	C-18-04	4119	4127	100
Chrysene	C-18-04	6784	5947	88
Dibenzo (a,h) anthracene	C-18-04	1029	1202	117
Fluoranthene	C-18-04	19517	14658	75
Fluorene	C-18-04	1322	1095	83
Indeno (1,2,3 - cd) pyrene	C-18-04	5045	4400	87
Naphthalene	C-18-04	36372	33325	92
Phenanthrene	C-18-04	16835	13059	78
Pyrene	C-18-04	13368	14165	106

Measured concentrations vs. assigned concentrations in CALA PT-C-18-04.

Extractable Petroleum Hydrocarbons



About 1.4B litres (9M barrels or 380M gallons) of oil enter the world's oceans and coastal waterways each year (natural and human sources)

From Woods Hole Oceanographic Institute

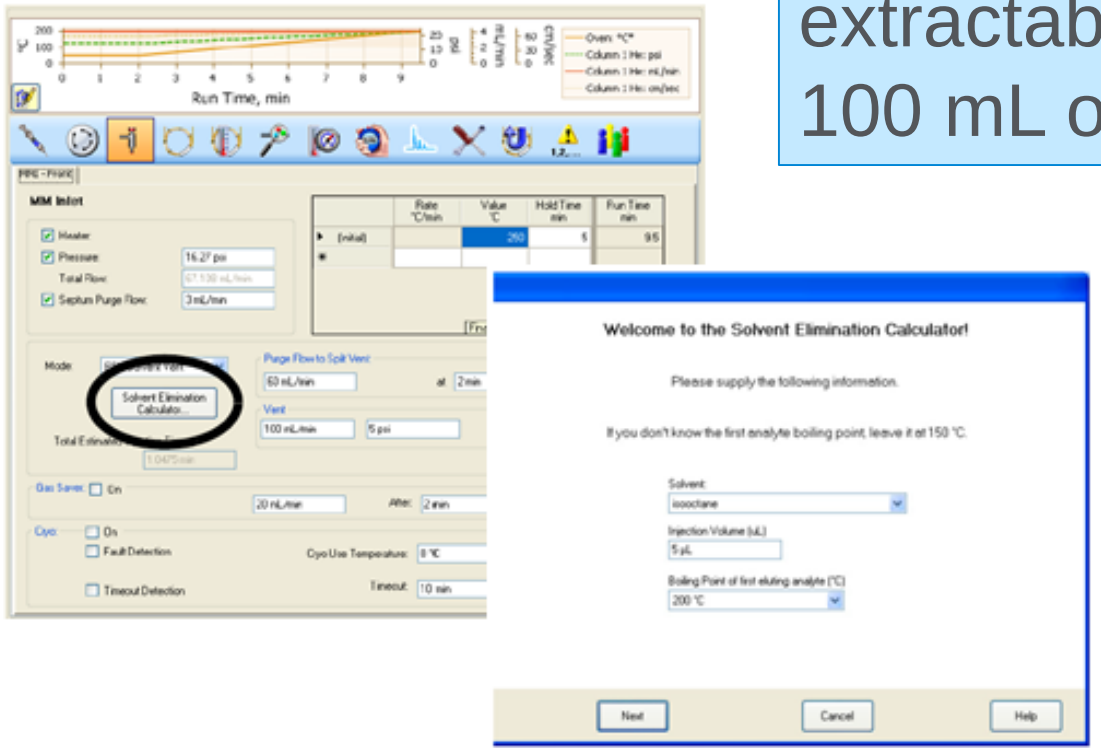
Significant pain points for Extractable Petroleum Hydrocarbons

- Sampling volumes of **1L** (EPA methods 610 and 3510c)
- Significant costs associated with transport
- Samples break during transit
- Significant usage of solvents for extraction (cost and disposal)
- Extensive sample cleanup with columns

Can we apply technique of pMRM to reduce sampling volume?

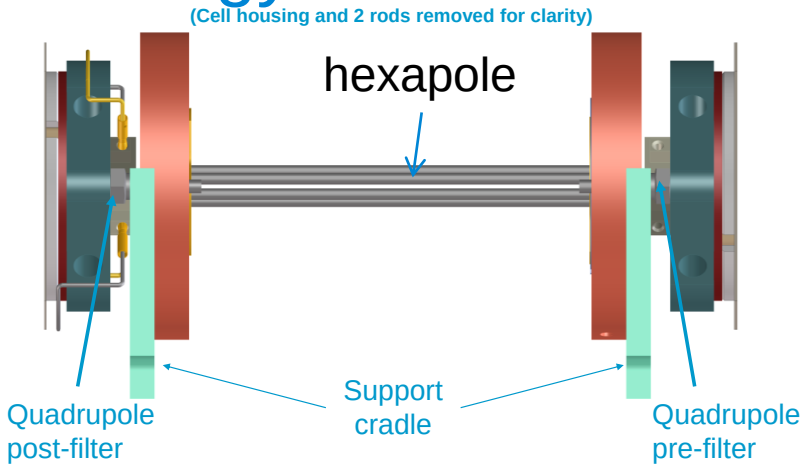
Agilent's Programmable Inlet – MultiMode Inlet (MMI)

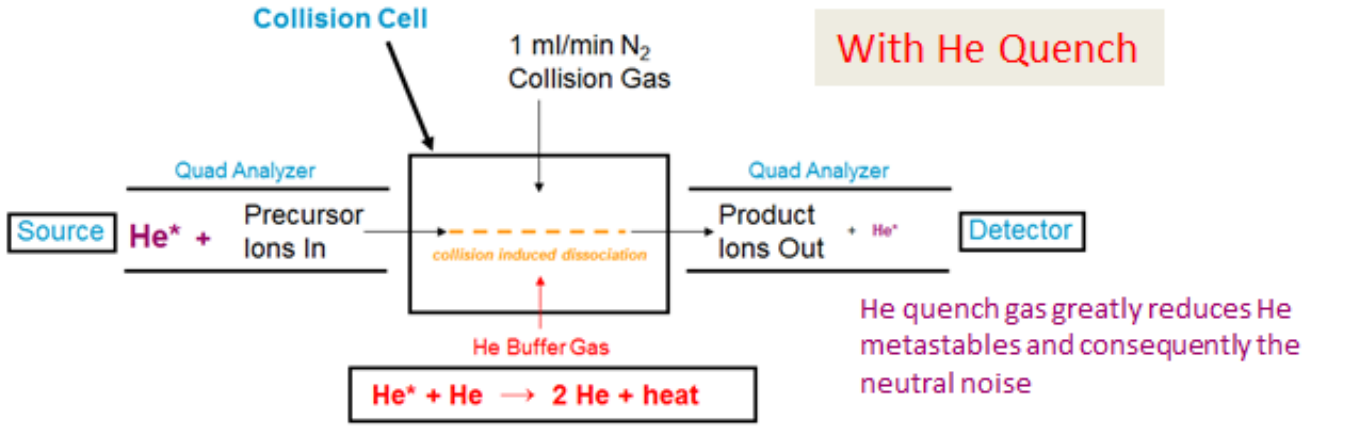
Temperature range of -160C to 450C
Heating @ 15C/sec (900C/min)

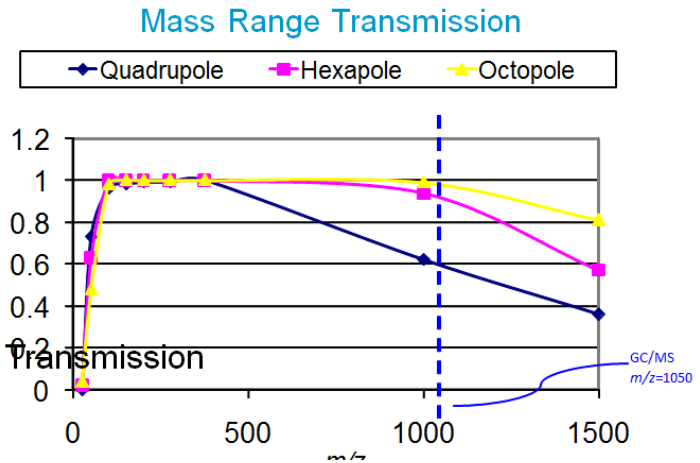


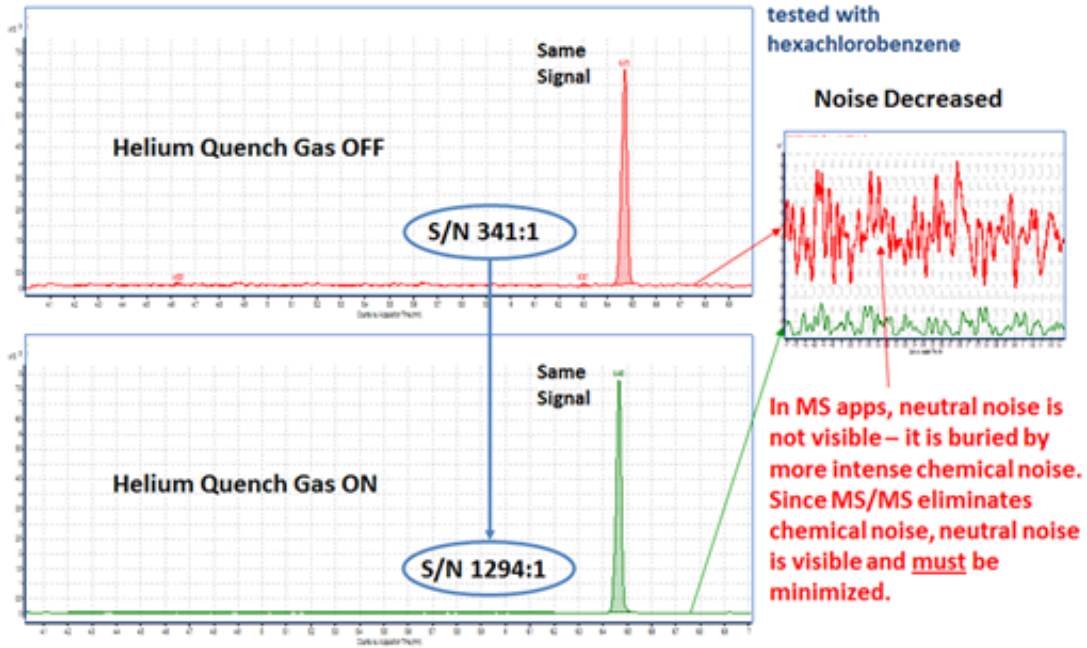
Able to reduce extractable volumes to 100 mL of water

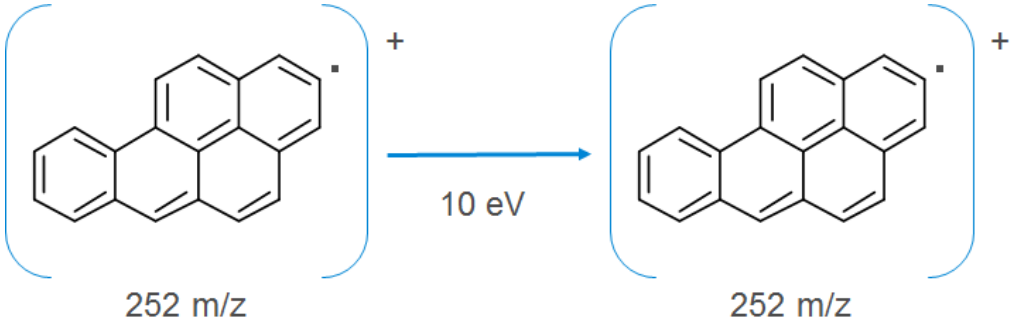
Agilent Hexapole Collision Cell with Quench Gas Technology







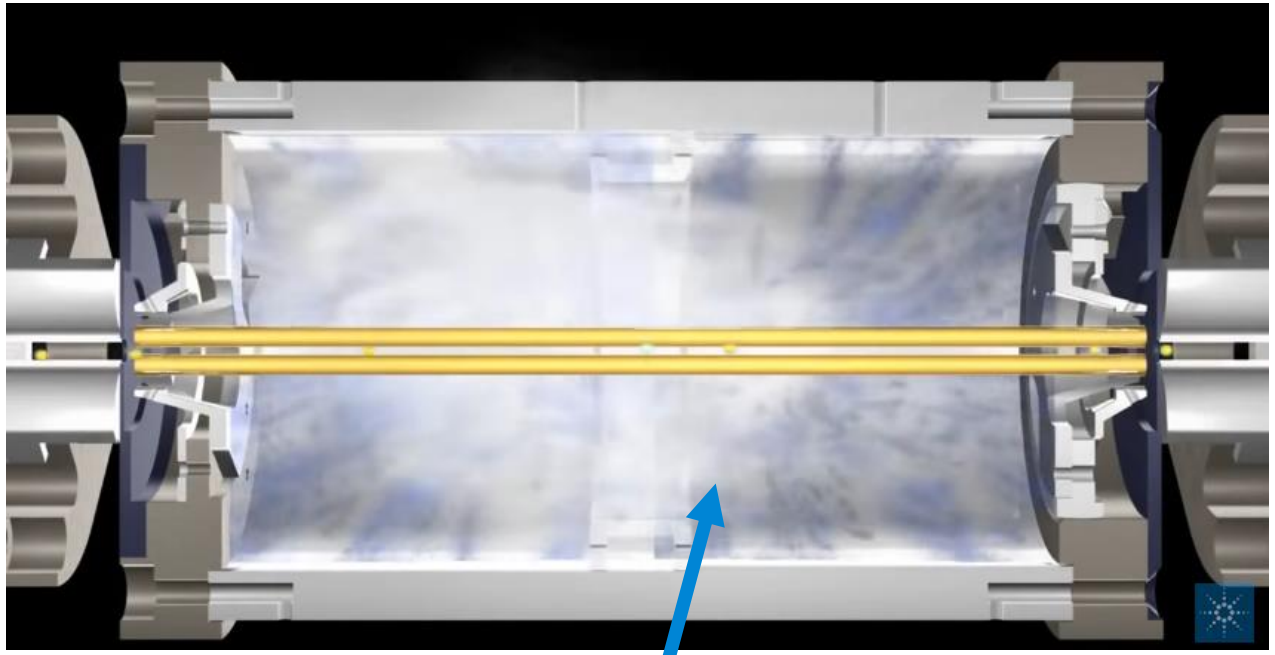




Interference
252 m/z

10 eV

Not detected



- Higher transmission of ions through collision cell
- Collision cooling and focusing of ions

Helium only as collision gas

Determination of polycyclic aromatic hydrocarbons in surface water using a simplified liquid-liquid micro-extraction and pseudo-MRM GC/MS/MS

Jeffrey Yan, Dayue Shang, Marcus Kim, Maxine Haberl, Honoria Kwok, Pamela Brunswick, Ceara MacInnis, Graham van Aggelen

- Extraction of 50mL of water with 2.2 mL of DCM
- Detection down to 2 ppt

Analytical Methods

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Anal. Methods*, 2018, 10, 405

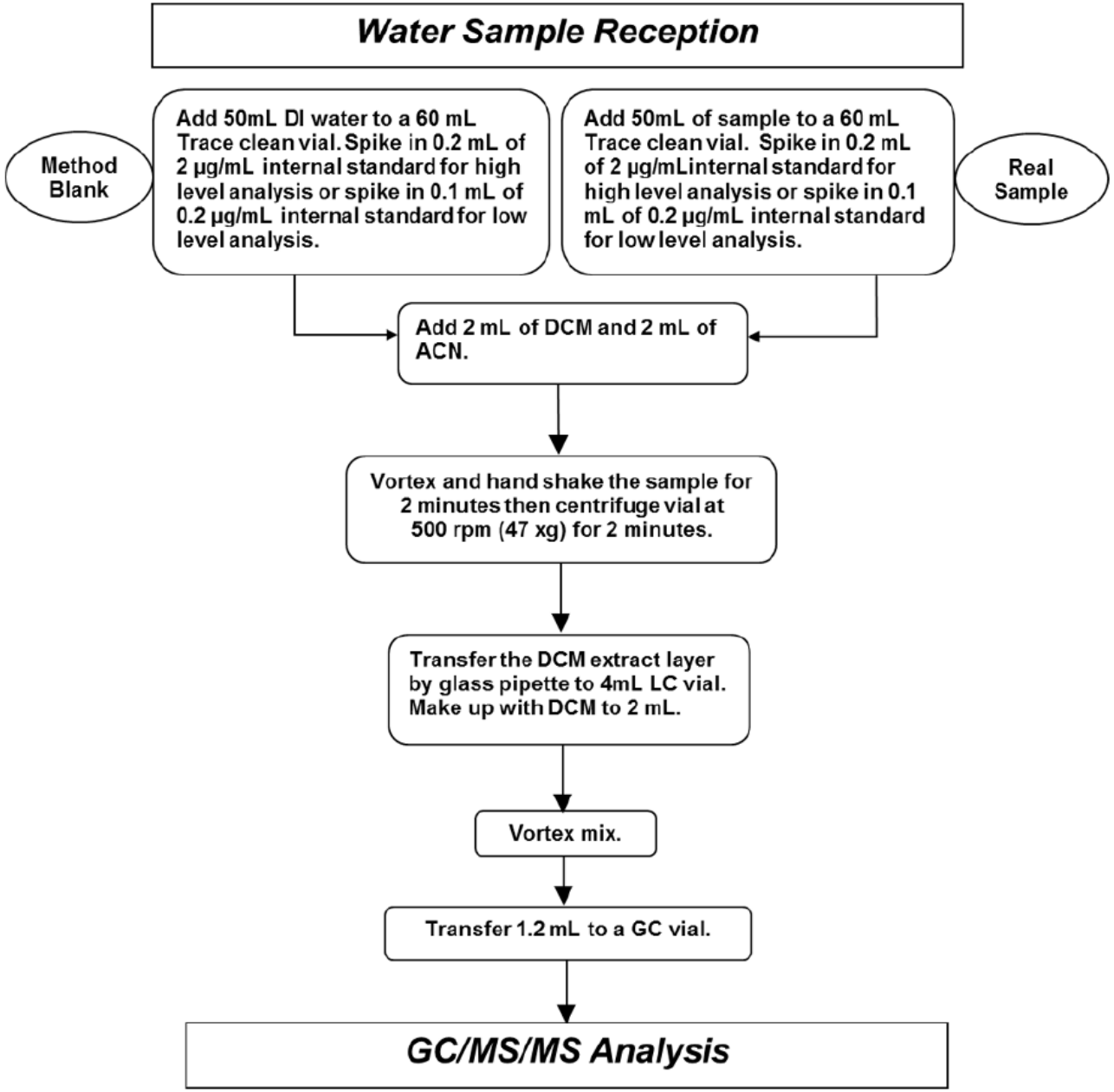
Determination of polycyclic aromatic hydrocarbons in surface water using simplified liquid–liquid micro-extraction and pseudo-MRM GC/MS/MS†

Jeffrey Yan,[a] Marcus Kim,[b] Maxine Haberl,[a] Honoria Kwok,[a] Pamela Brunswick,[a] Ceara MacInnis,[a] Graham van Aggelen[a] and Dayue Shang *[a]

A simplified liquid–liquid micro-extraction (LLME) GC/MS/MS method was developed for the determination of 18 polycyclic aromatic hydrocarbons (PAHs) in surface water. This method utilizes a pseudo multiple

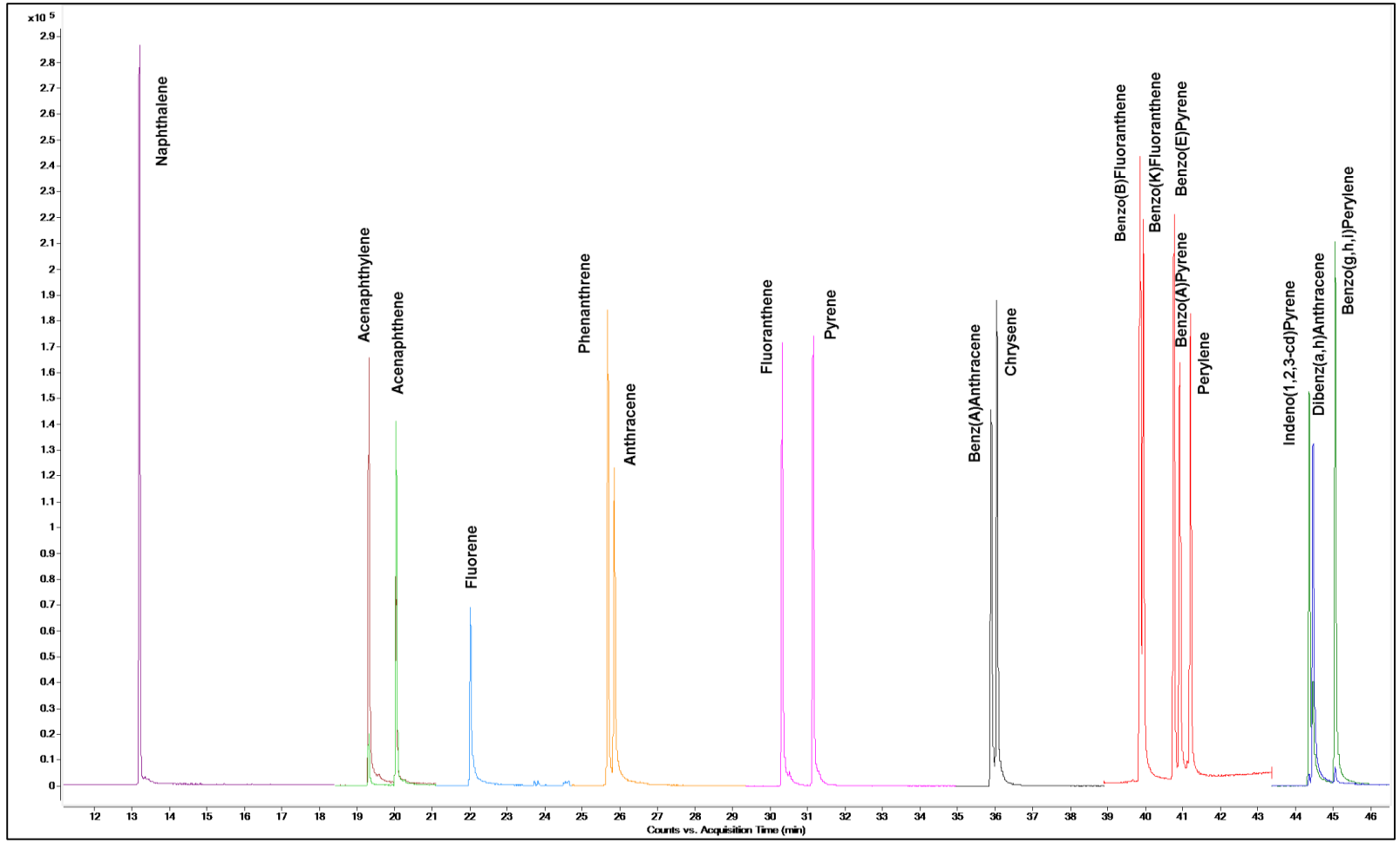
Compound	Detected Total Concentration (ng/L)								Average % Recovery	Mean (ng/L)	Std. Dev. (ng/L)	% Rel. Std. Dev.
	S1	S2	S3	S4	S5	S6	S7	S8				
Acenapthene	10.2	9.3	9.2	9.4	10.3	9.6	10.4	9.6	98	9.8	0.470	4.8
Acenaphthylene	9.3	9.4	9.7	9.2	9.0	9.5	8.8	9.5	93	9.3	0.286	3.1
Anthracene	9.1	9.1	8.9	9.3	9.3	9.0	10.2	8.9	92	9.2	0.431	4.7
Benzo(a)anthracene	10.4	10.3	9.5	10.1	9.5	9.8	9.4	9.6	98	9.8	0.391	4.0
Benzo(a)pyrene	9.3	9.7	9.1	9.1	9.7	10.2	9.7	9.3	95	9.5	0.378	4.0
Benzo(e)pyrene	11.1	11.0	10.7	10.5	10.6	10.9	10.4	11.1	108	10.8	0.263	2.4
Benzo(b)fluoranthene	11.5	11.4	11.4	11.9	11.8	11.1	10.5	11.8	114	11.4	0.443	3.9
Benzo(g,h,i)Perylene	9.3	9.5	9.7	10.5	10.1	9.6	9.9	9.6	98	9.8	0.370	3.8
Benzo(k)fluoranthene	10.0	9.8	9.9	9.9	9.8	10.2	9.9	10.1	100	10.0	0.142	1.4
Chrysene	10.0	9.7	9.7	9.9	9.4	9.5	9.9	9.7	97	9.7	0.202	2.1
Dibenz(a,h)anthracene	8.3	8.3	7.9	8.6	8.2	8.1	8.4	8.3	83	8.3	0.217	2.6
Fluoranthene	10.4	10.4	10.0	10.6	10.5	10.7	10.4	10.0	104	10.4	0.252	2.4
Fluorene	9.2	9.5	8.8	9.4	10.0	9.6	9.9	9.0	94	9.4	0.411	4.4
Indeno(1,2,3-cd)pyrene	8.9	8.4	8.8	8.2	8.4	8.7	8.0	8.3	85	8.5	0.297	3.5
Naphthalene	8.3	8.3	8.8	8.4	8.3	9.1	8.3	8.6	85	8.5	0.284	3.3
Perylene	9.6	9.6	9.1	9.7	10.1	9.9	9.4	9.8	96	9.6	0.319	3.3
Phenanthrene	8.3	8.2	7.9	8.2	7.9	7.7	8.3	7.7	80	8.0	0.259	3.2
Pyrene	10.2	10.3	10.4	10.1	9.8	10.4	9.6	9.9	101	10.1	0.297	2.9

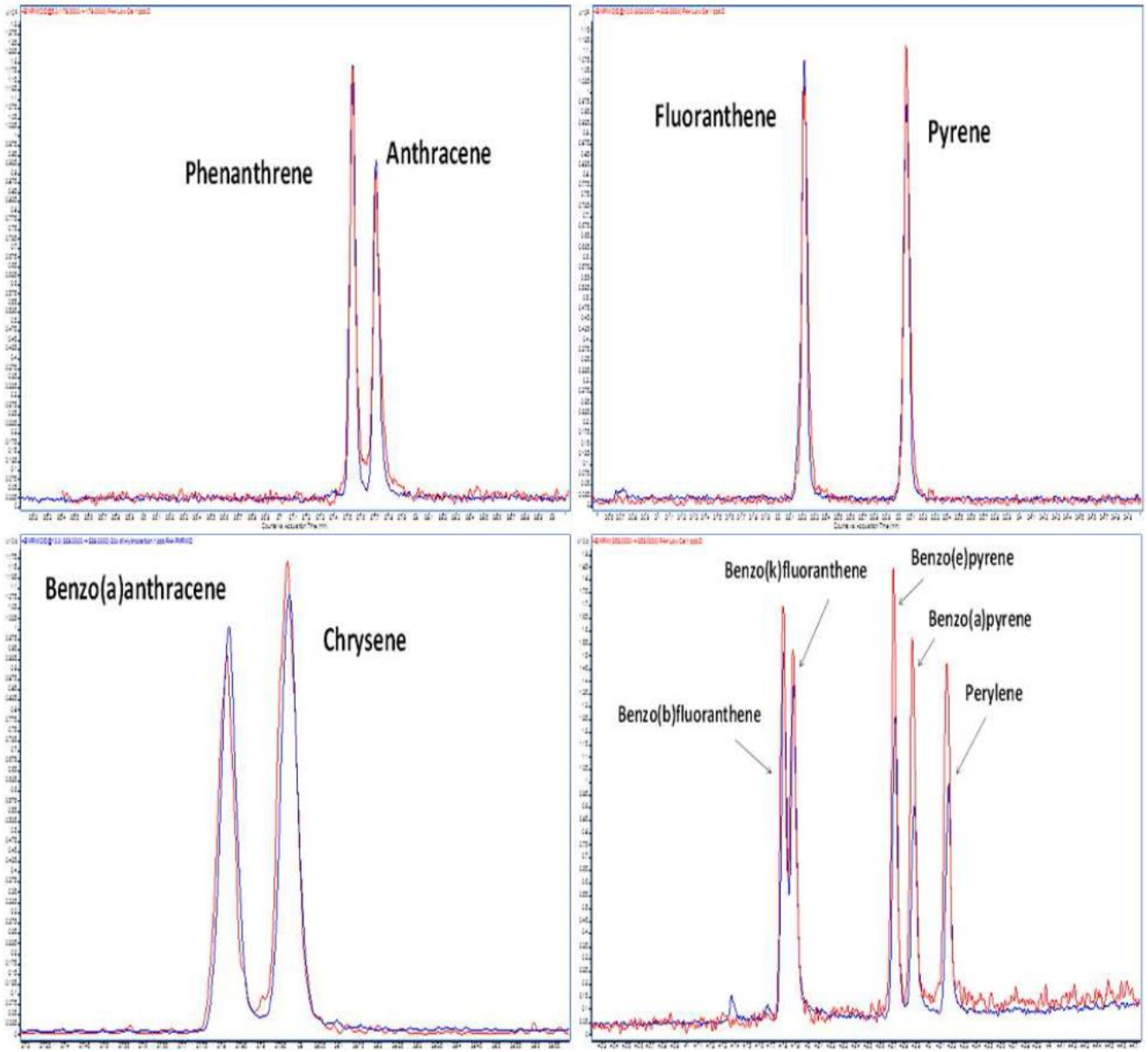
Table 2) Method Validation: Limit of Quantitation Replicates at PAH Concentration of 10 ng/L in Water.



Sample prep is similar to the soil example shown earlier, but even simpler. Starts with 50 mL, and involves only 6 steps. Takes less than 10 minutes!

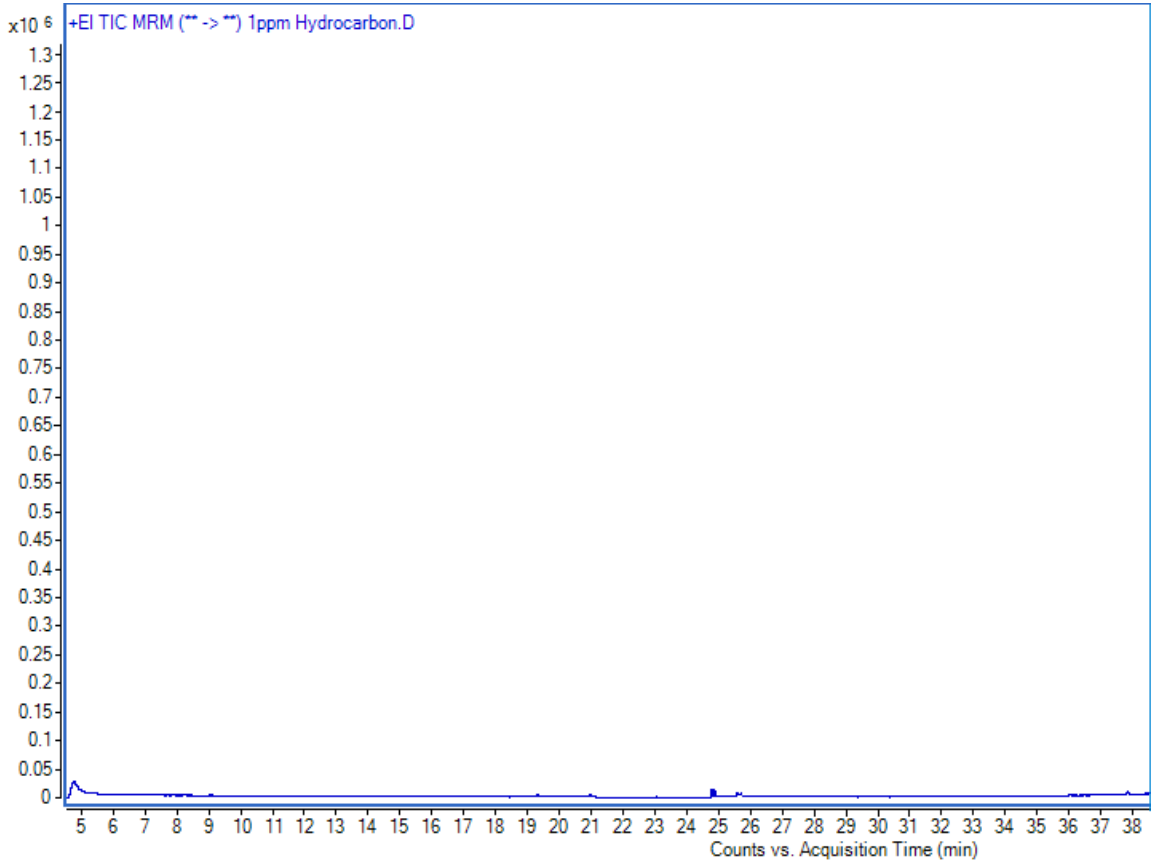
Extracted Ion Chromatogram of 18 PAHs at 0.8 µg/L (0.8 ppb) in Water



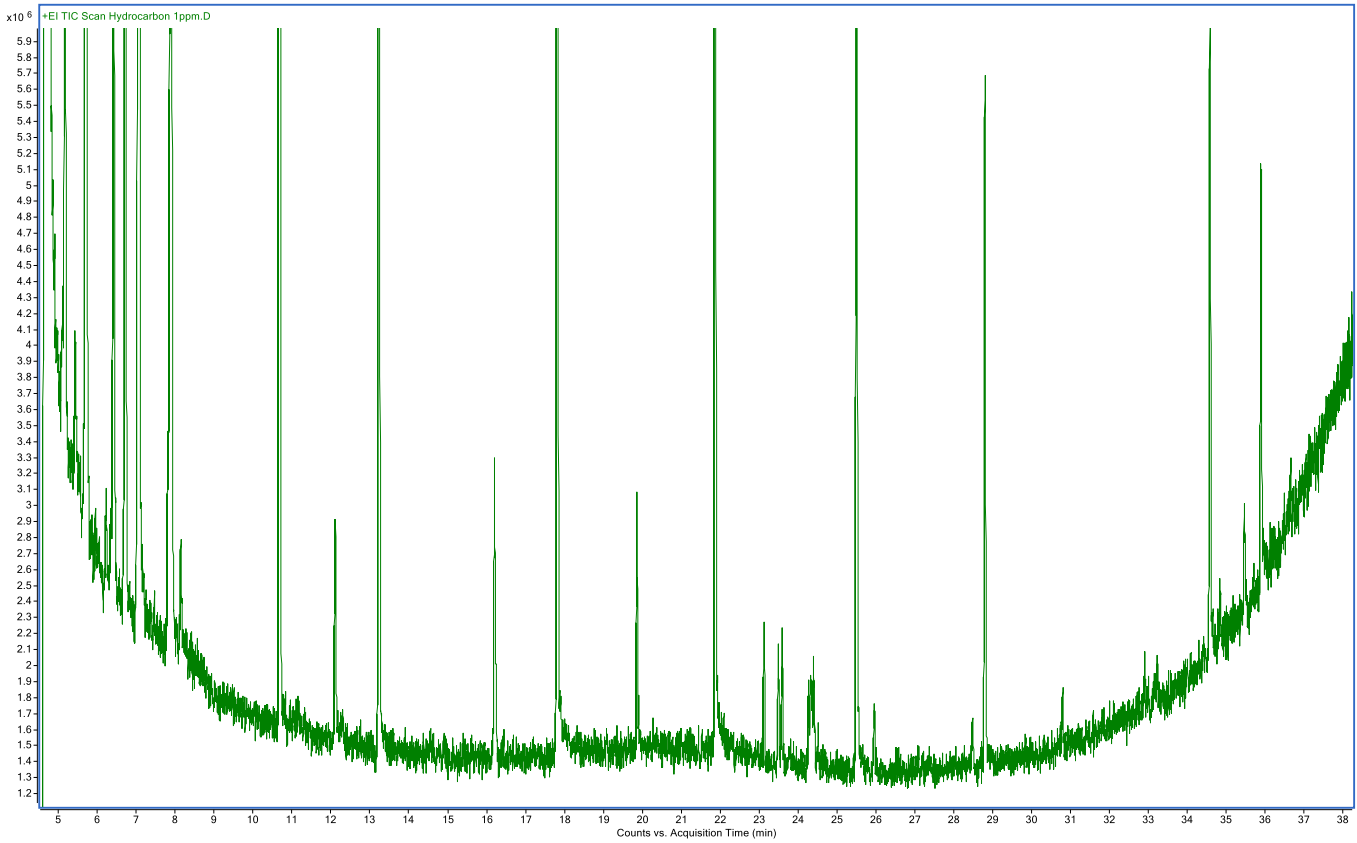


Example chromatograms of 1 µg/L target PAHs spiked in hydrocarbon standard (shown in blue) and neat DCM (shown in red).

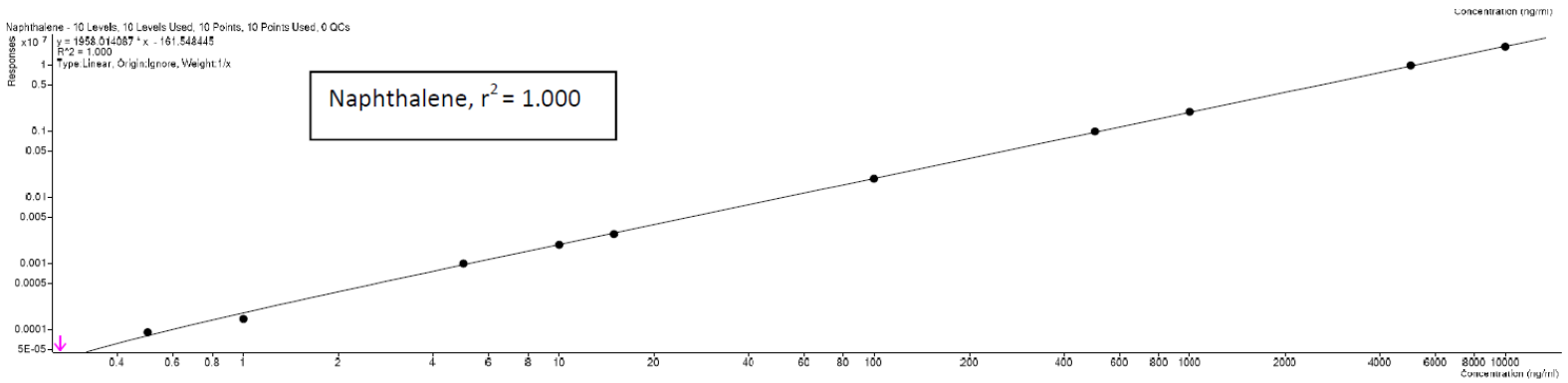
1ppm hydrocarbon with He pMRM

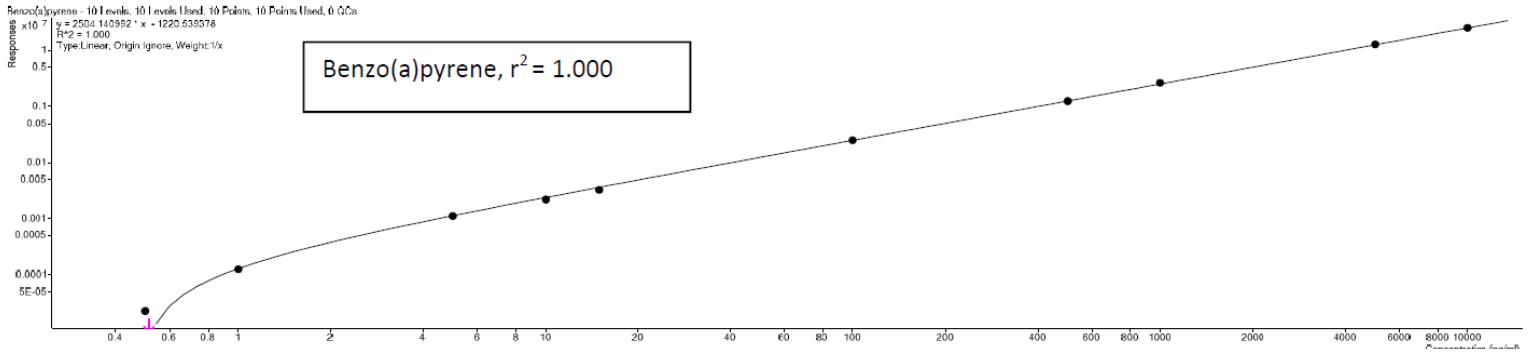


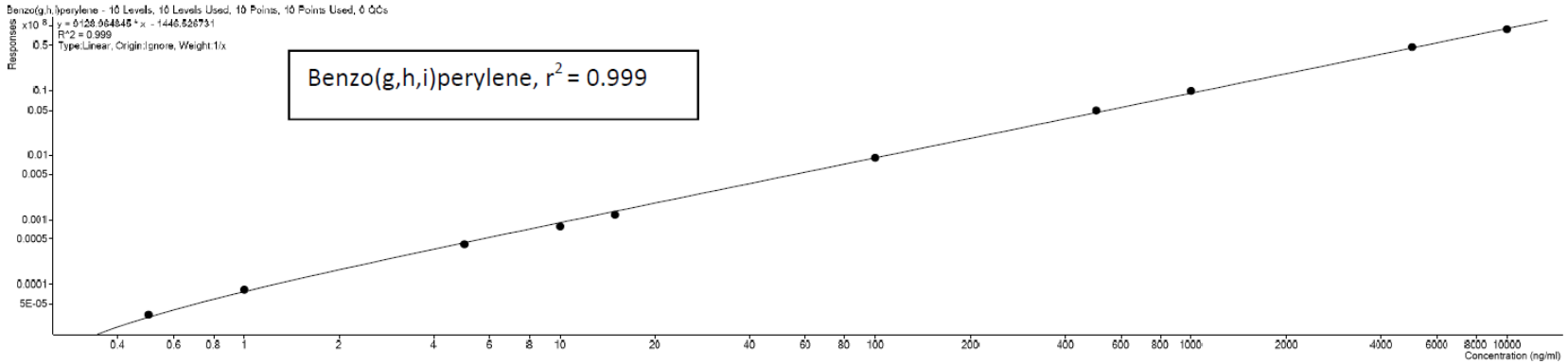
1ppm hydrocarbon in EI scan



Representative curves (10 point calibration from 0.1 µg/L to 2000 µg/L)







All curves at 0.999 or 1

Conclusion

- pMRM with He is an extremely efficient method for low level detection of PAHs in hydrocarbon matrix
- The He pMRM has been subjected to 8 separate proficiency tests (PT) from 3 different organizations (*Phenova of Phenomenex, Environment and Climate Change Canada, and The Canadian Association for Laboratory Accreditation Inc. (CALA*)) and has been extremely successful
    - 6 separate CALA Proficiency Tests between 2015-2017 with scores of 84-96 out of 100
- The validated He pMRM method has been (and continues to be) used routinely to analyze PAH concentrations in over 500 surface water samples from the Athabasca oil sands region, oil spill cases, and other environmental monitoring projects
- Method is fast, inexpensive, green and easy to switch between classic MRM and He pMRM

Acknowledgements

Dr. Dayue Shang – Environment Canada, North Vancouver
Maxine Haberl
Jeffrey Yan
Honoria Kwok
Dr. Pamela Brunswick
Ceara MacInnis

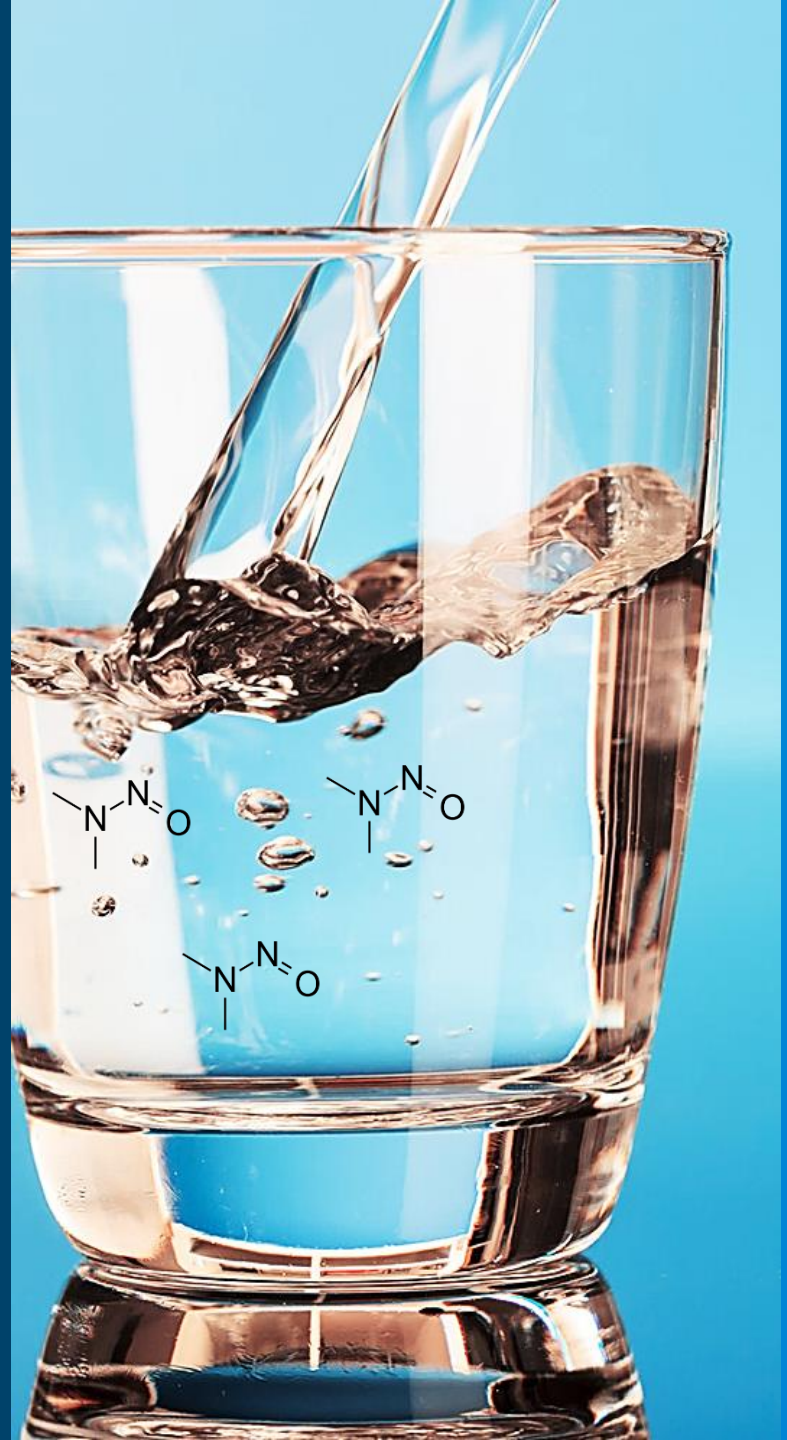
Wait – I can replace my ion trap?

Nitrosamine Analysis in Drinking Water using GC-MS/MS

Meeting Equivalence to EPA Method 521

Andy Eaton[1], Charles Grady[1], Konjit Tadigo[1]
Yongtao Li[2], William Davis[2] Ralph Hindle[3]
Diana Wong[4], Ron Honnold[4], Craig Marvin[4]

[1]Eurofins Eaton Analytical (EEA) – Monrovia, CA
[2]Eurofins Eaton Analytical (EEA) – South Bend, IN
[3]Vogon Labs – Cochrane, AB, Canada
[4]Agilent Technologies

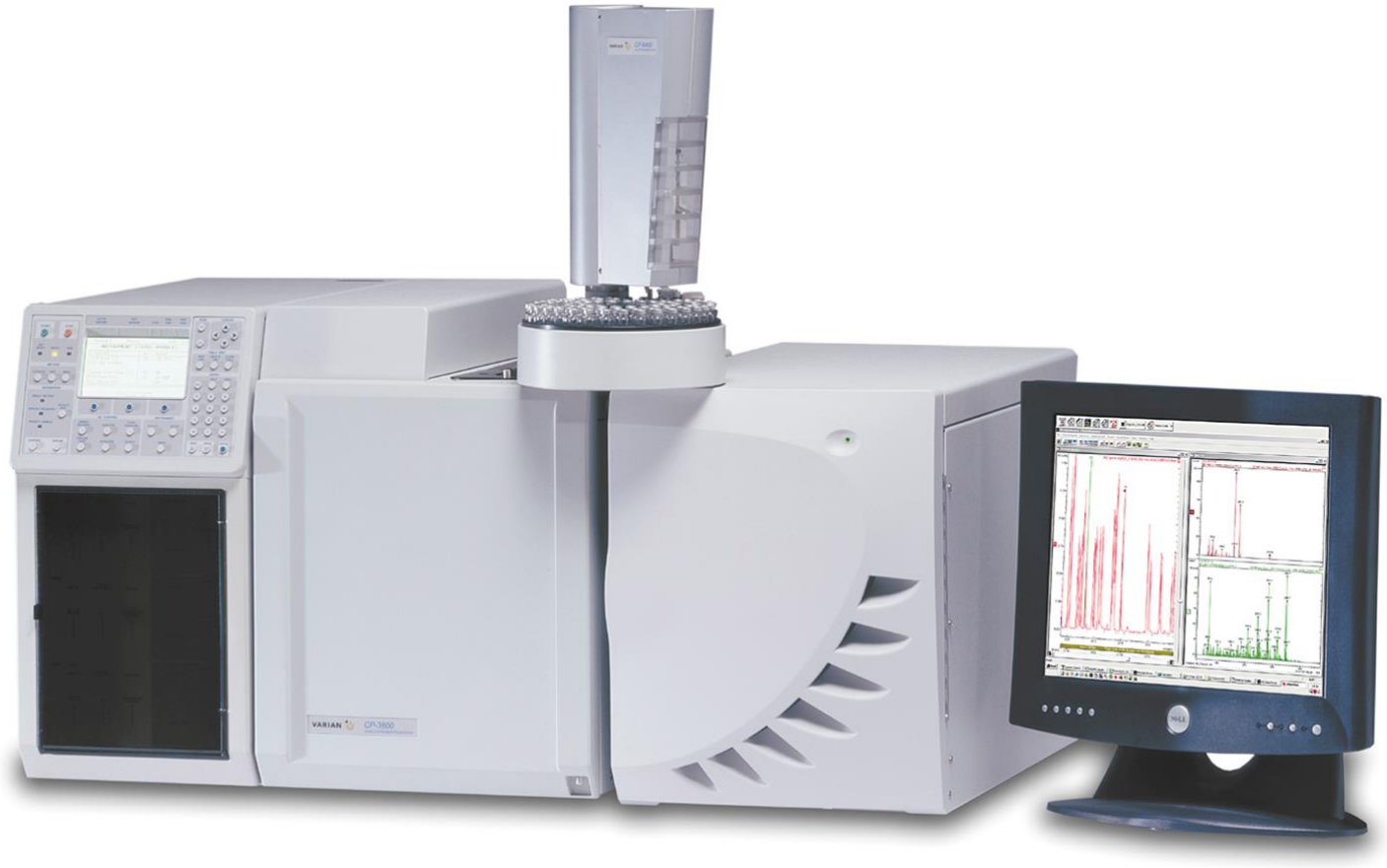


Agilent
Trusted Answers

Background and Purpose of Project

- EPA Method 521 (2004): “Determination of nitrosamines in drinking water by **solid phase extraction** and capillary column **gas chromatography** with **large volume injection** and **chemical ionization tandem mass spectrometry**”
- Ion Trap GC/MS is the approved instrumentation for Method 521 but it is being obsoleted
- EPA might regulate nitrosamines due to the occurrence in drinking water and wastewater (particular NDMA)
- EPA Office of Ground Water/Drinking water (OGWDW) considers alternate detection techniques without changing the guidelines for sample preparation
- Purpose of the project is to directly compare Triple Quadrupole GC/MS (GC-MS/MS) and the currently used Ion Trap GC/MS (GC-IT) method using split samples set
- Phase I: Varian 4000 GC-IT vs Agilent 7010 GC-MS/MS
- Phase II: Three Lab Validation Studies of GC-MS/MS Method

Varian 4000 GC/MS Ion Trap System

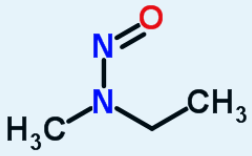


Nitrosamines Investigated

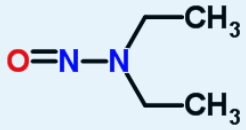
NMOR were evaluated in addition to all nitrosamines in Method 521

Analytes in EPA Method 521

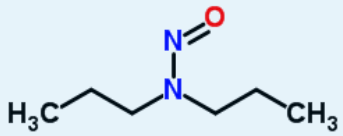
NDMA
N-Nitrosodimethylamine



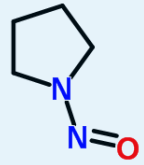
NMEA
N-Nitrosomethylethylamine



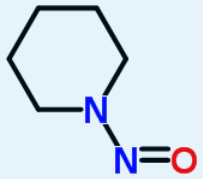
NDEA
N-Nitrosodiethylamine



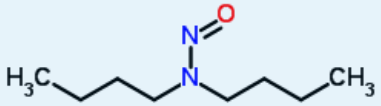
NDPA
N-Nitrosodi-n-propylamine



NPYR
N-Nitrosopyrrolidine

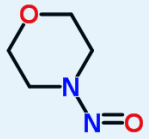


NPIP
N-Nitrosopiperidine



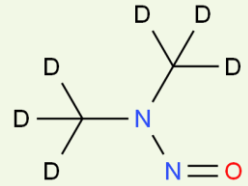
NDBA
N-Nitrosodi-n-butylamine

Addition



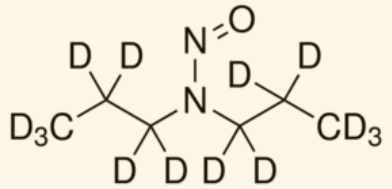
NMOR
N-Nitrosomorpholine

Surrogate



NDMA-d6
N-Nitrosodimethylamine-d6

Internal Standard



NDPA-d14
N-Nitrosodipropylamine-d14

Note: Method 521 (2004) evaluated NMOR but was not included in the method due to contamination problems

Drinking Water Extraction

All water samples were extracted manually. No changes made to Method 521 sample preparation

SPE Procedure

Condition Cartridge

Methylene Chloride
Methanol
Reagent water

Extract Sample

500-mL water sample

Elute Cartridge

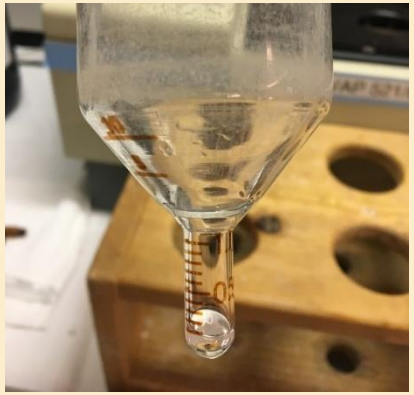
Methylene chloride
Soak
Collect

Concentration

Remove residual water

Sodium Sulfate
(anhydrous)

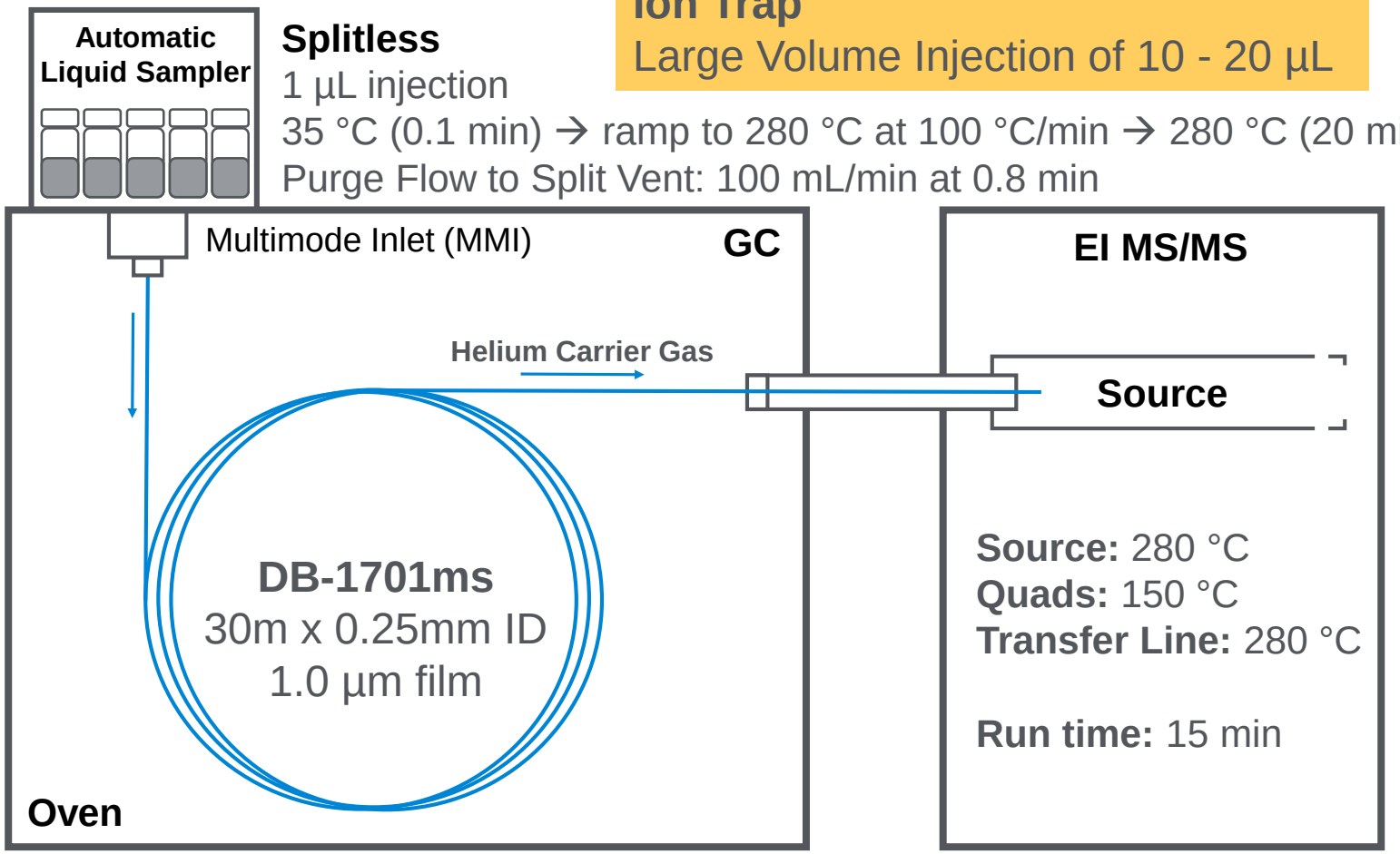
Concentration



Water Bath
1mL sample

GC-MS/MS System Parameters

Ion Trap
Large Volume Injection of 10 - 20 µL



Ion Trap
Similar Oven Parameters

Ion Trap
Chemical Ionization
Run time = 40 min

Inlet liner
4mm double-tapered, UI

GC Parameters
MMI Inlet → MSD
Constant Flow
Flow 1.2 mL/min

Column
DB-1701ms UI
14% cyanopropylphenyl
86% dimethylpolysiloxane

Oven program:
33 °C (1min)
35 °C/min to 80 °C (2 min)
10 °C/min to 140 °C (0 min)
50 °C/min to 280 °C (2 min)

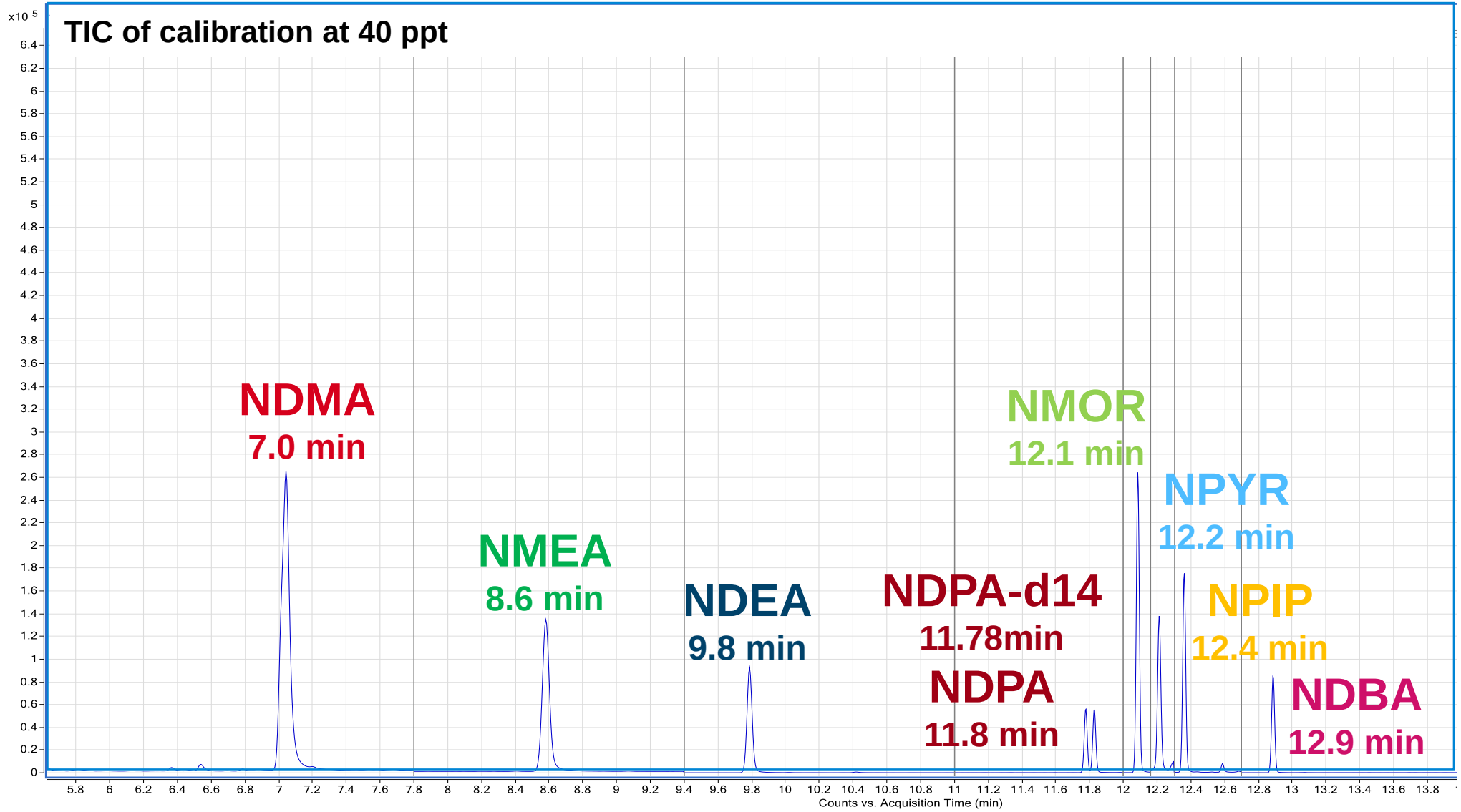
MRM Transitions using GC-MS/MS

Optimized using MS1 Scan, Product Ion Scan, and Multiple Reaction Monitoring (MRM)

Analyte	Retention time (min)	Precursor ion (m/z)	Product ion (m/z)	Collision Energy
NDMA-d6 (SUR)	7.02	80	50	8
		80	46	25
NDMA	7.05	74	44	6
		74	42	22
NMEA	8.58	88	71	4
		88	42	23
NDEA	9.79	102	85	4
		102	44	12
NDPA-d14 (IS)	11.78	144	126	10
		144	50	20
NDPA	11.83	130	43	10
		101	70	10
NMOR	12.09	116	86	2
		116	56	15
NPYR	12.3	100	55	7
		100	70	7
		100	43	10
NPIP	12.59	114	84	7
		114	55	25
NDBA	12.89	158	141	10
		158	99	10
		116	99	10

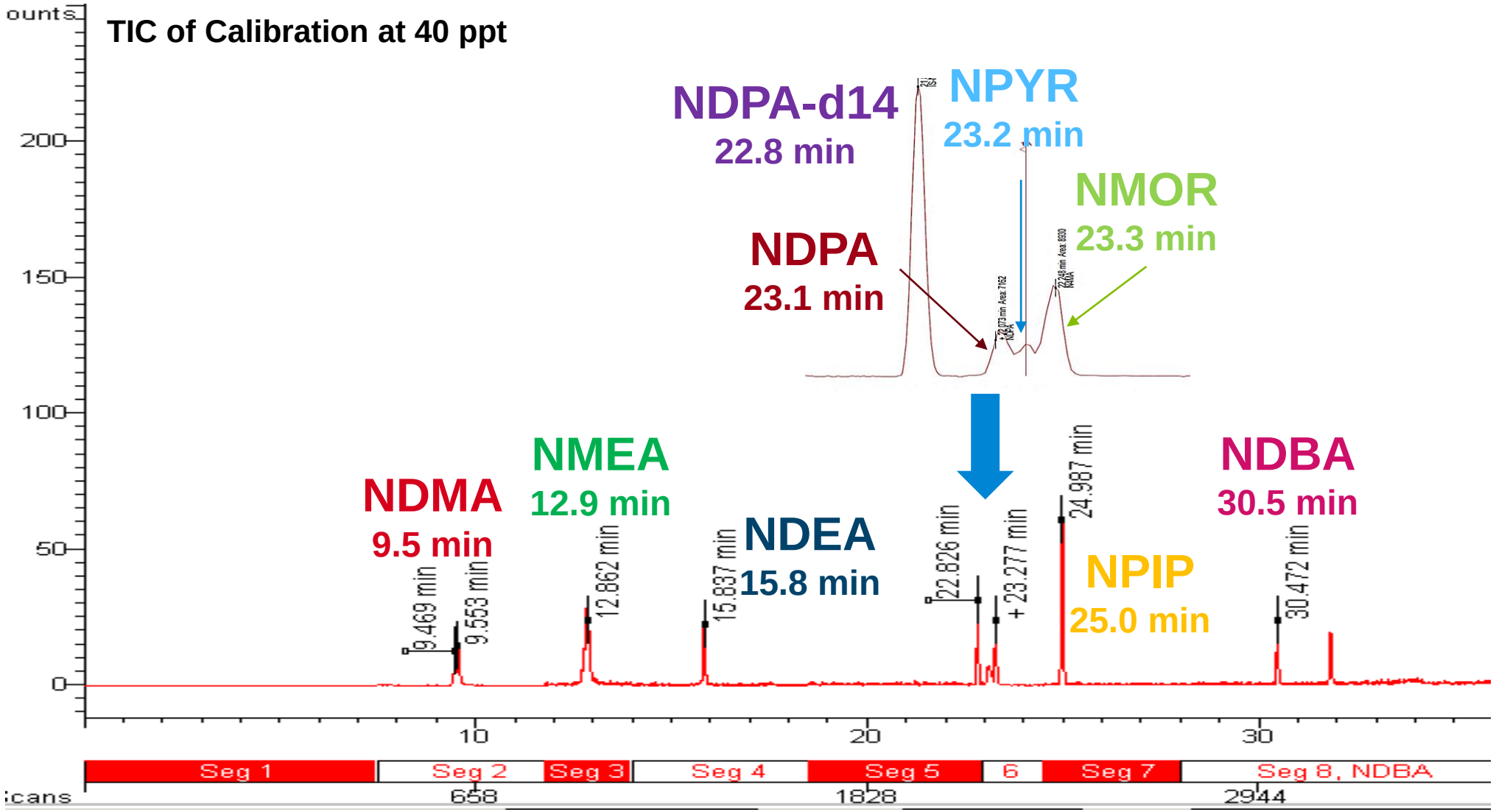
Nitrosamines analysis using GC-MS/MS

Triple Quad Run Time is 15 min, Baseline separation observed for NDPA, NPYR, and NMOR



Nitrosamine analysis using GC-IT

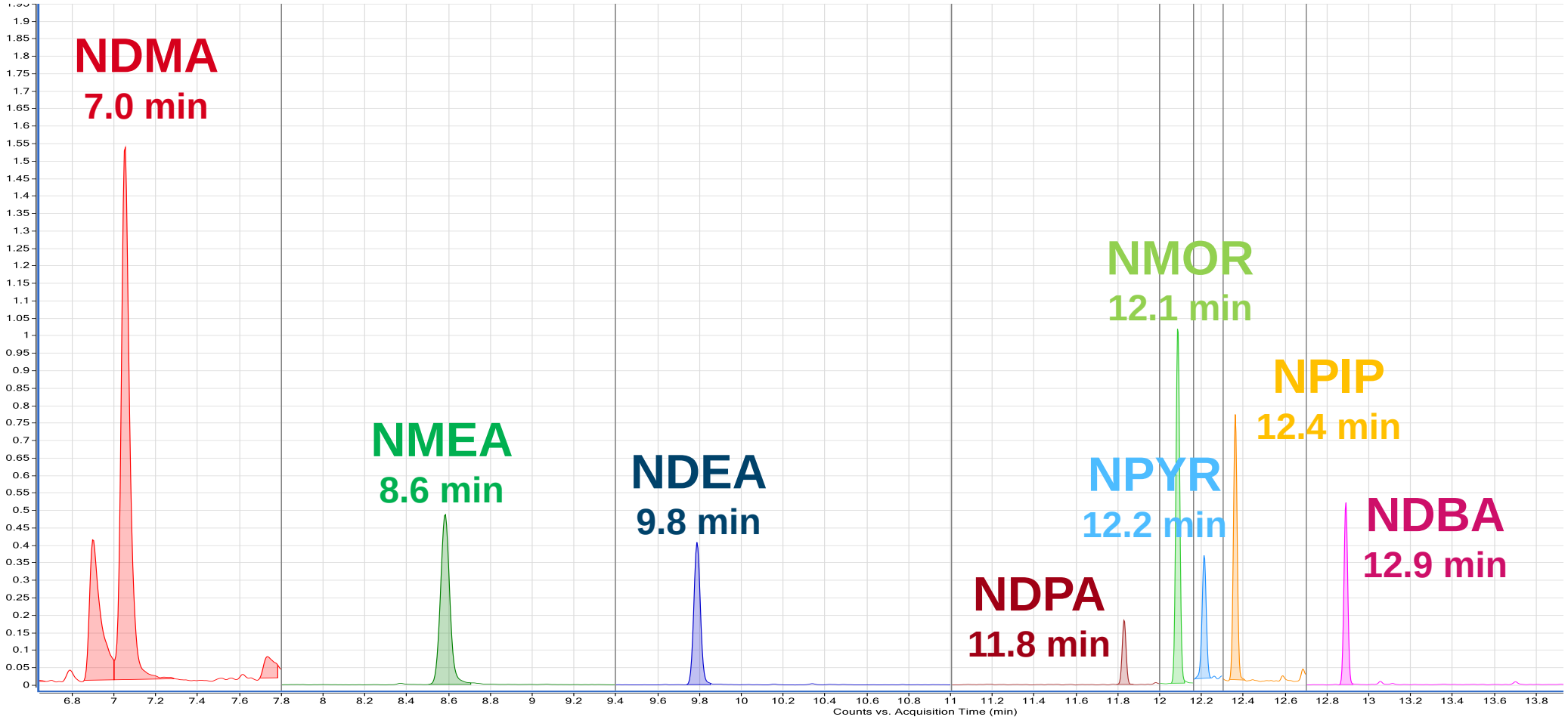
40 min run-time, Poor baseline separation for NDPA, NPYR, and NMOR



Nitrosamine Analysis in Sample Water Extracts using GC-MS/MS

0.5 ppt nitrosamines in Sample Water Extract

Quantifier ion

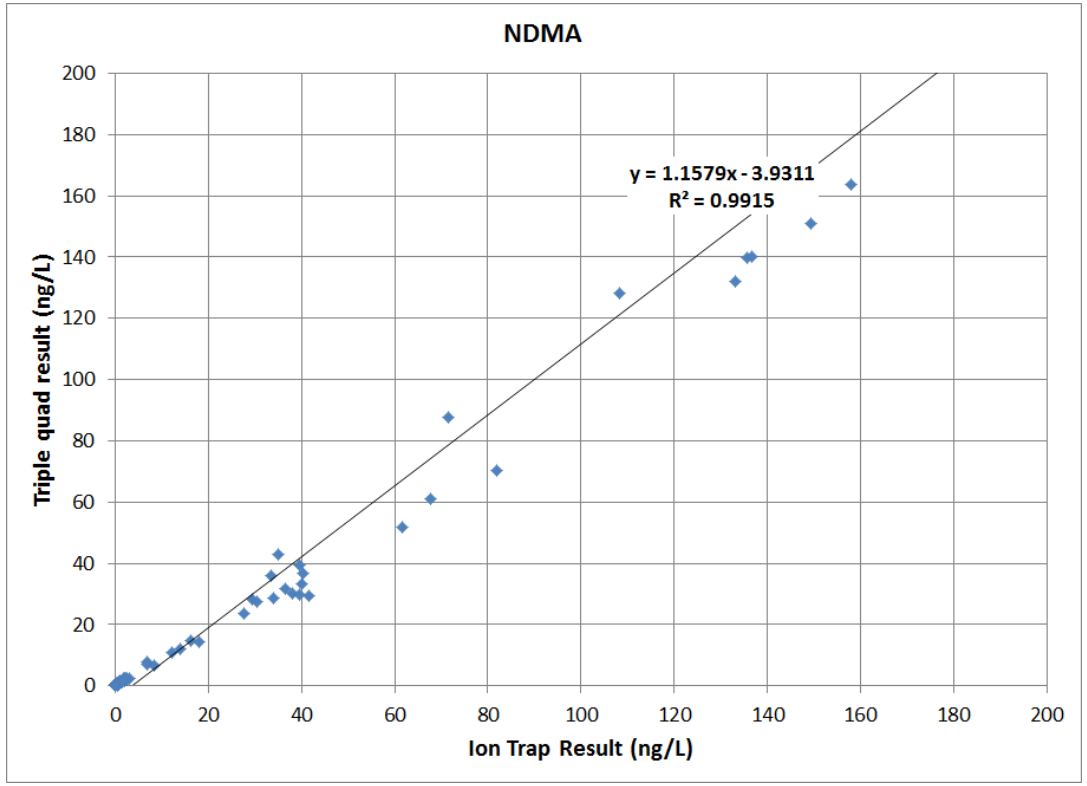


Internal standard is not plotted as 20 ppt overwhelms TIC when plotted with 0.5ppt analytes in extract.

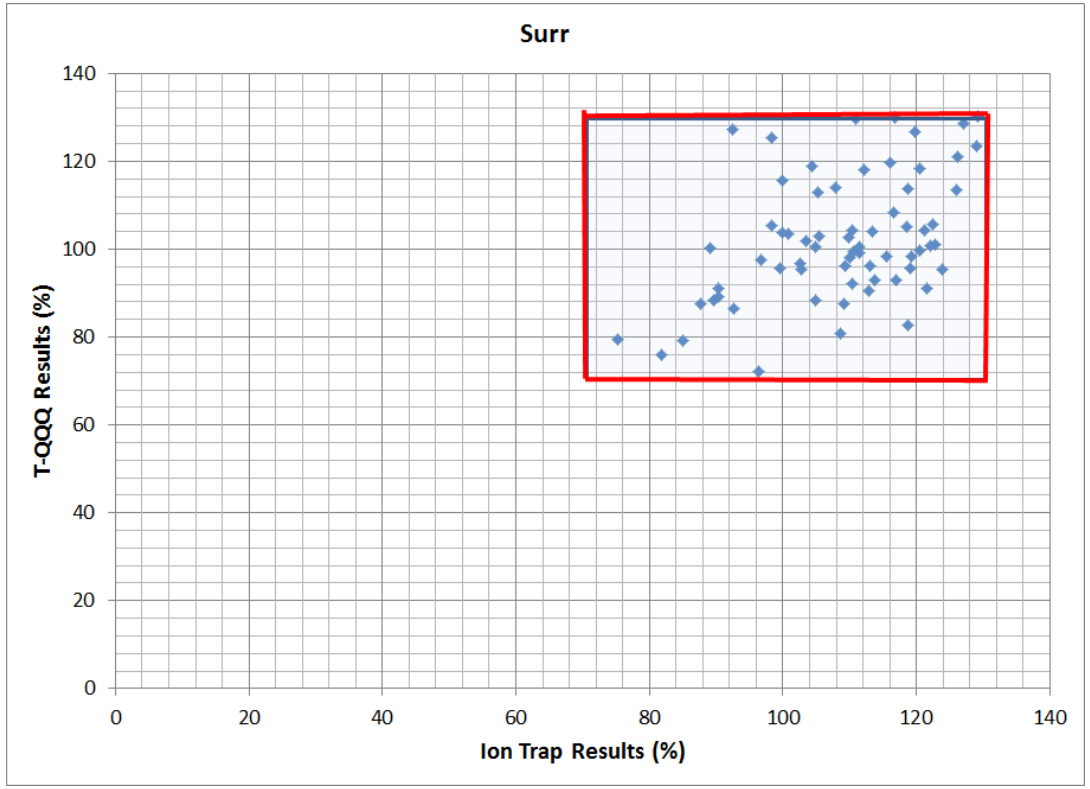
Field Sample Comparison (GC-IT vs GC-MS/MS)

Correlation observed in samples and surrogates

Real Extracted Water Samples



Surrogate recoveries are within limits

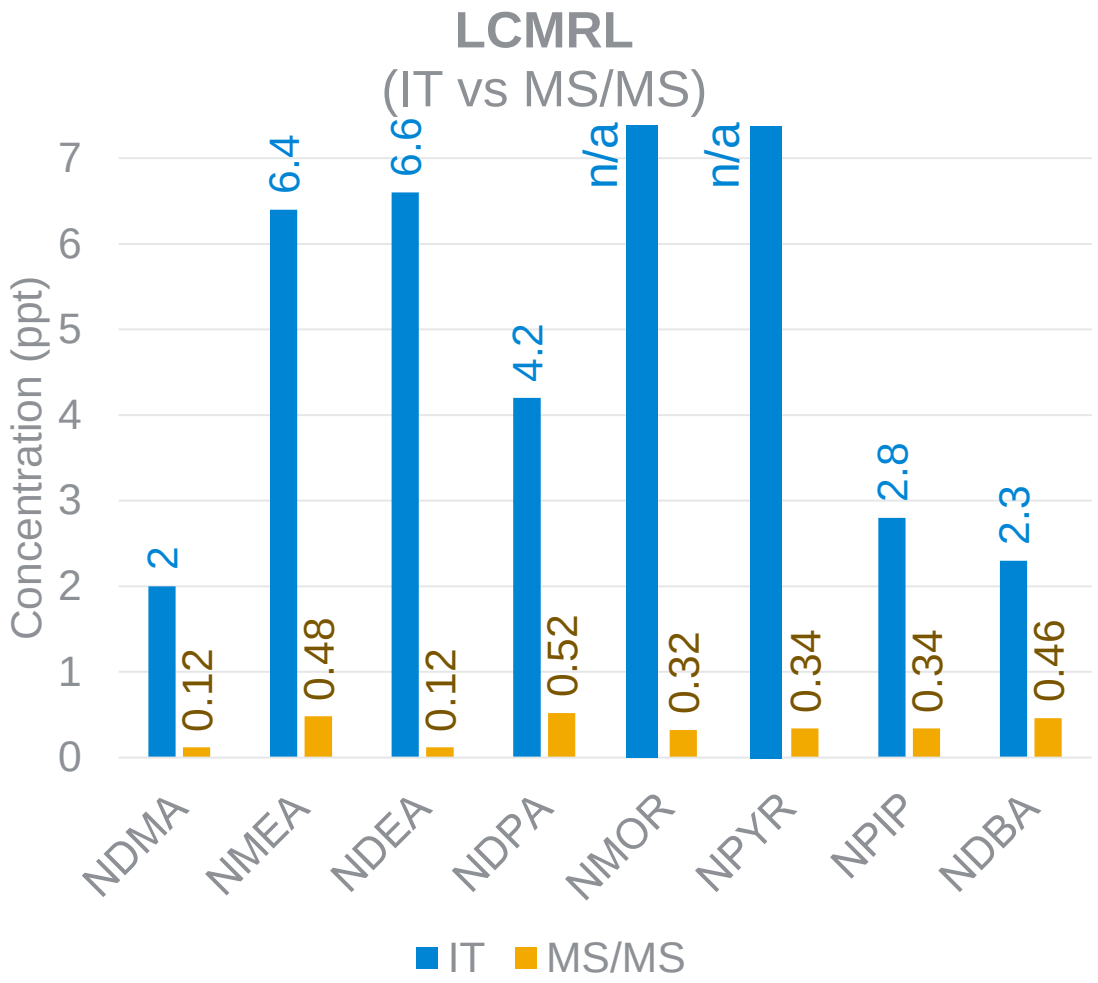


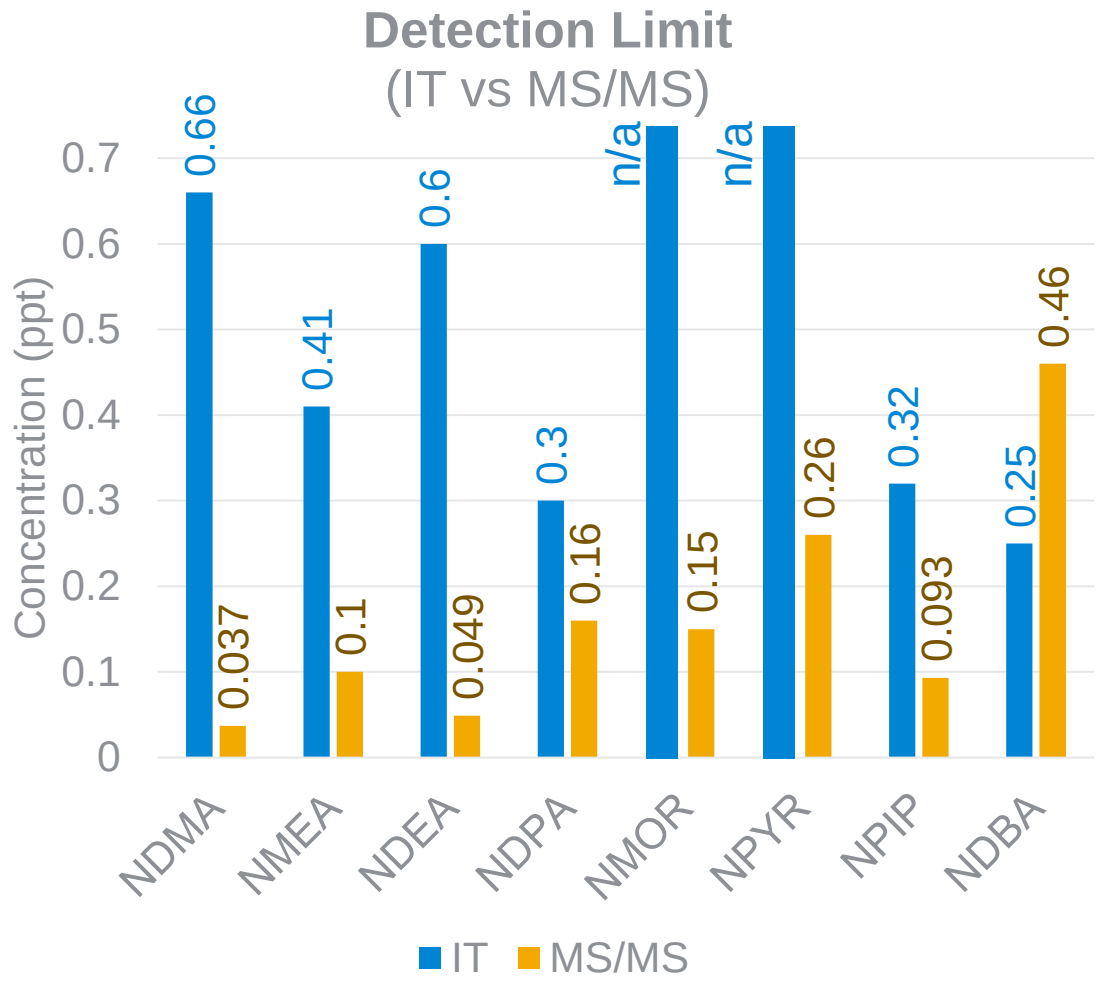
Note:

- Real Extracted Samples were analyzed using GC-IT and GC-QQQ
- Same holding time, standards, extraction process, mixes

LCMRL and DL of water extract (GC-MS/MS vs GC-IT)

GC-MS/MS achieves lower DL and LCMRL



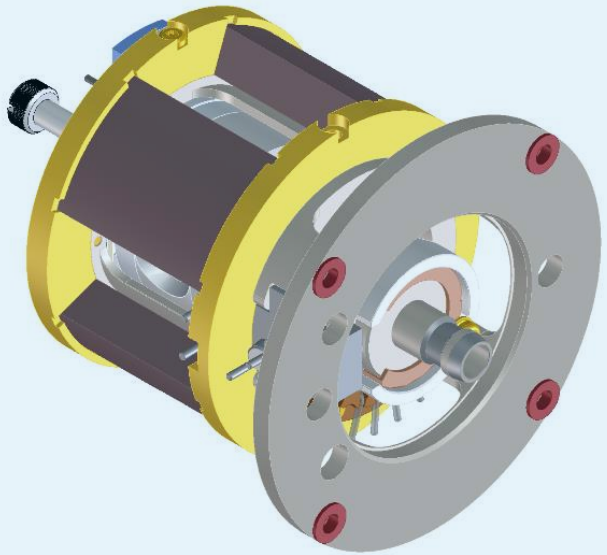


Note: n/a LCMRL and DL on GC-IT is above the highest spiking level or spiking level exceeds working range for NMOR and NPYR. Spiking levels Range 0.1 to 10 ppt

GC-MS/MS used in Interlaboratory Validation Study

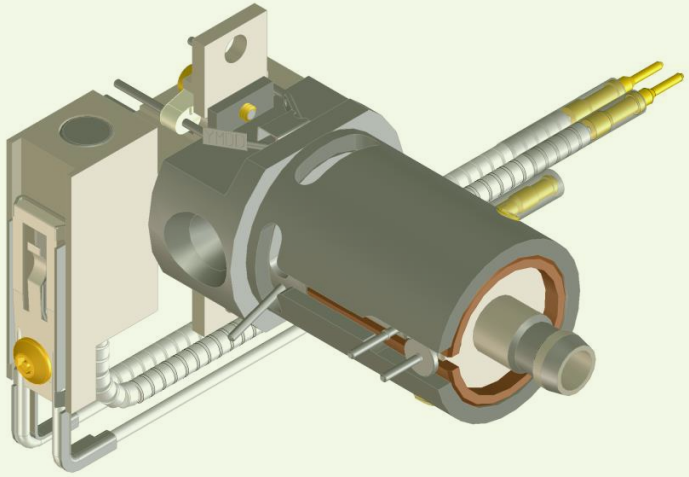
LAB A and LAB B

7010 GC-MS/MS
High Efficiency Source



LAB C

7000 GC-MS/MS
Extractor Source



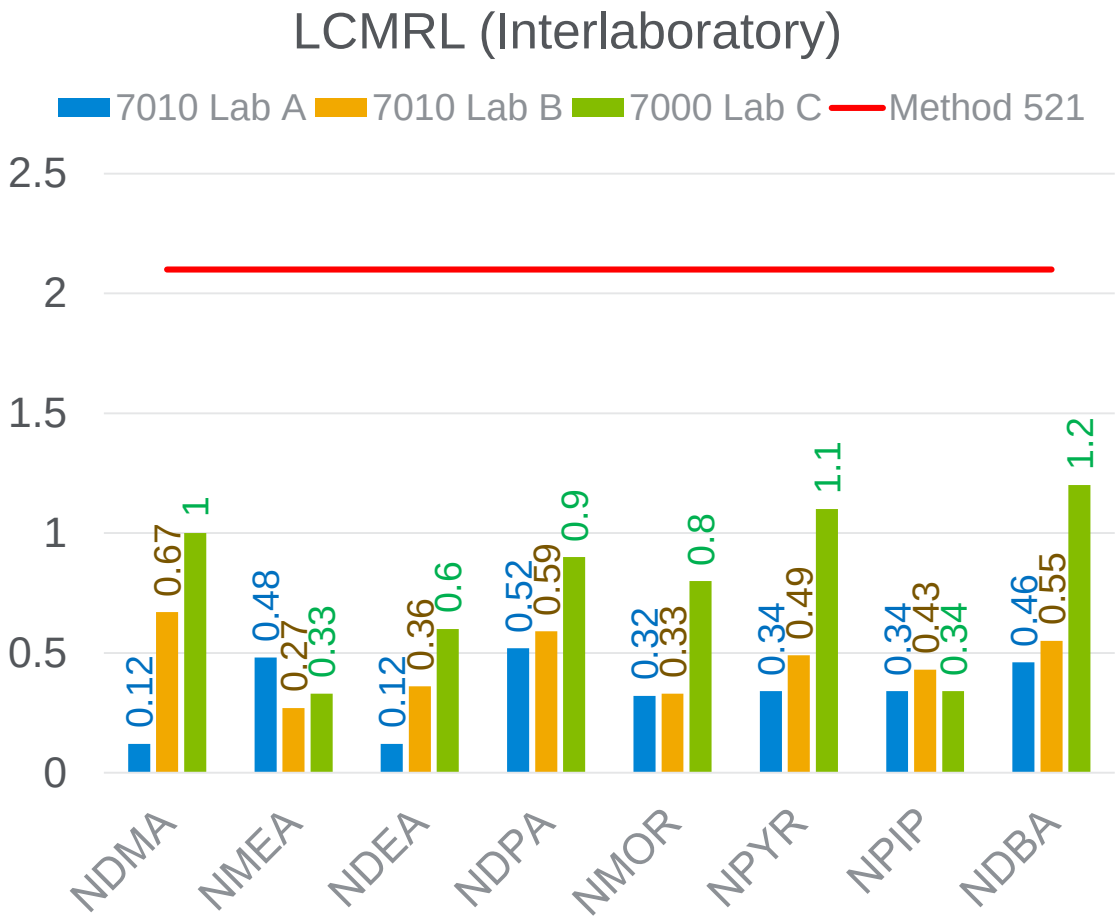
Complete Source Redesign
on the 7010 GC-MS/MS

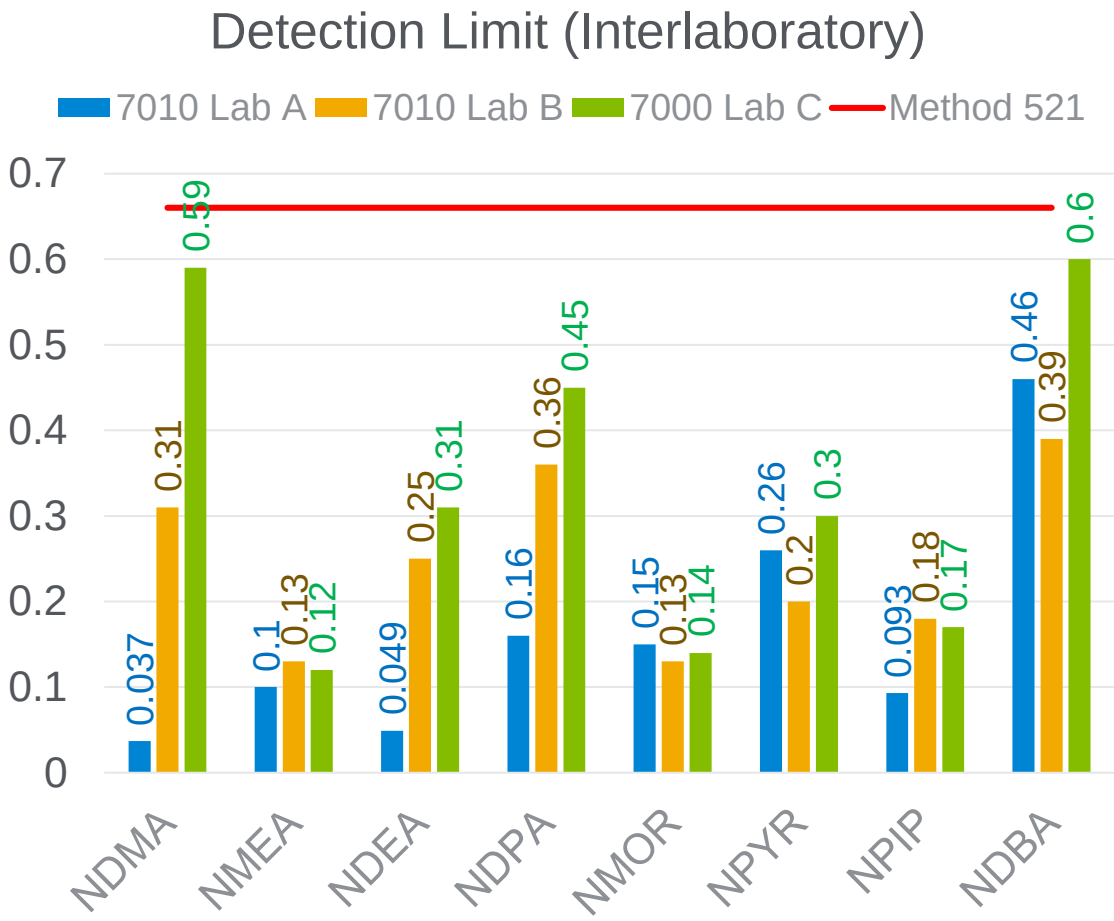
20x more ions

Is the
High Efficiency Source
required to meet the
LCMRL?

LCMRL Results from Interlaboratory Validation Study

Both GC-MS/MS systems achieved lower LCMRL and DL than Method 521 (2004)





Four replicates at 0.1, 0.25, 0.50, 1.0, 2.0, 3.0, 4.0, 5.0, 8.0, and 10.0 ppt
*Lab C NMDA at 1.0, 2.0, 3.0, 4.0, 5.0, 8.0, and 10.0 ppt

Method 521 are limits from EPA 521 with exception of NMOR

Calibration Curve of ILS

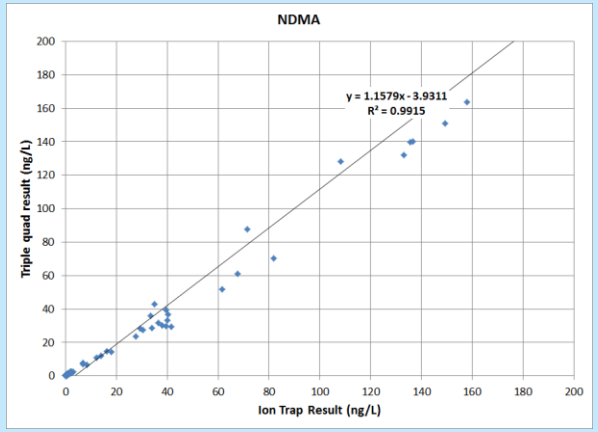
$R^2 \geq 0.99$ for both 7000 and 7010 GC-MS/MS

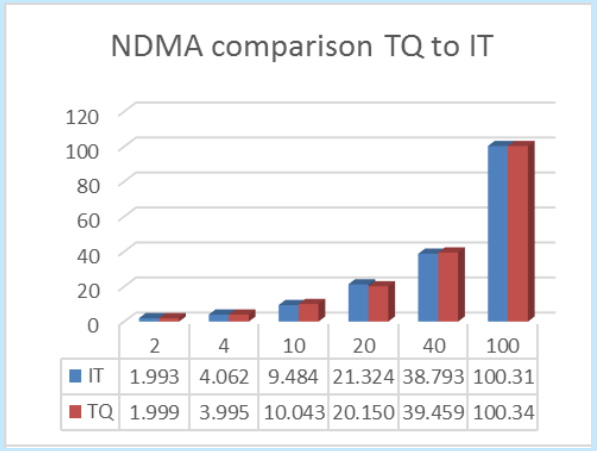
Analyte	7010 Lab A	7010 Lab B	7000 Lab C
NDMA	0.9999	0.9979	0.9935
NMEA	0.9999	0.9983	0.9988
NDEA	0.9999	0.9993	0.9986
NDPA	0.9998	0.9987	0.9965
NMOR	1.0000	0.9993	0.9992
NPYR	0.9981	0.9994	0.9976
NPIP	0.9999	0.9993	0.9979
NDBA	0.9996	0.9990	0.9985

Linear, 1/x weight, 11 calibration points (0.0625,0.125,0.25,0.5,1.0,2.0,4.0,10,20,40,100 ppt)

Phase I Summary – GC-MS/MS Advantages

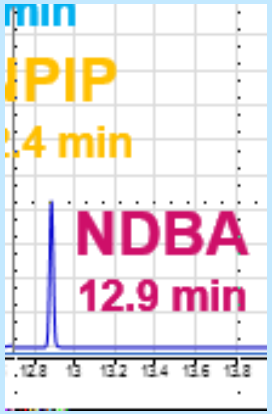
Good Correlation



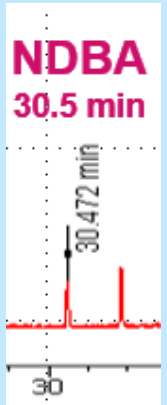


Shorter Run Time

GC-MS/MS

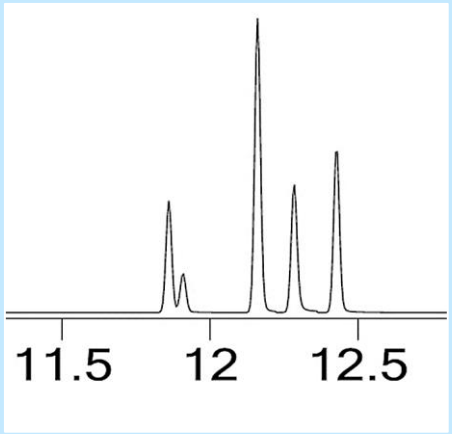


GC-IT

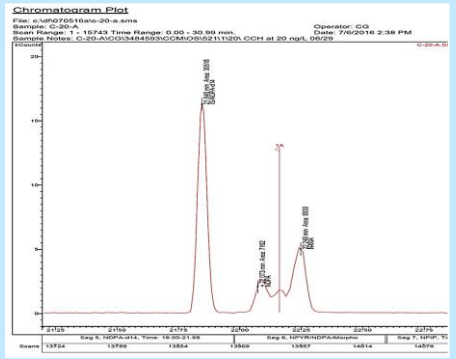


Better Separation (NDPA, NPYR, NMOR)

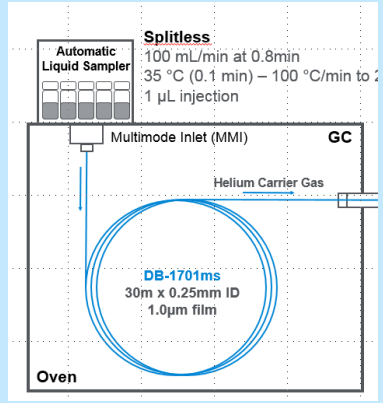
GC-MS/MS



GC-IT



Lower injection volume



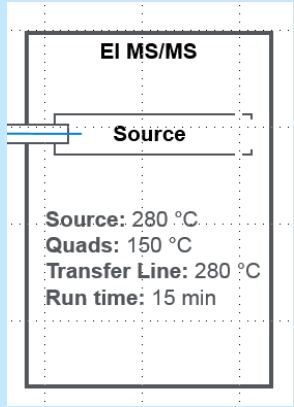
1 µL (GC-MS/MS)
vs
10-20 µL (GC-IT)

10-20X
Lower Volume

EI vs CI mode

Easier Operation

Increase Reliability

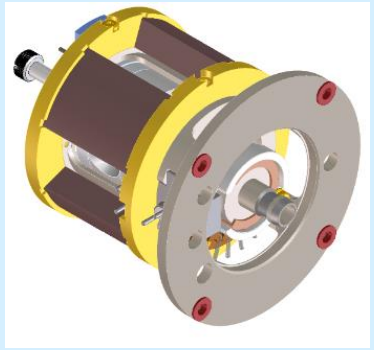


Phase II Summary – Interlaboratory Validation

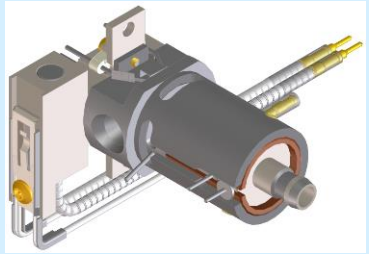
Method Compliance

Both Systems Work!

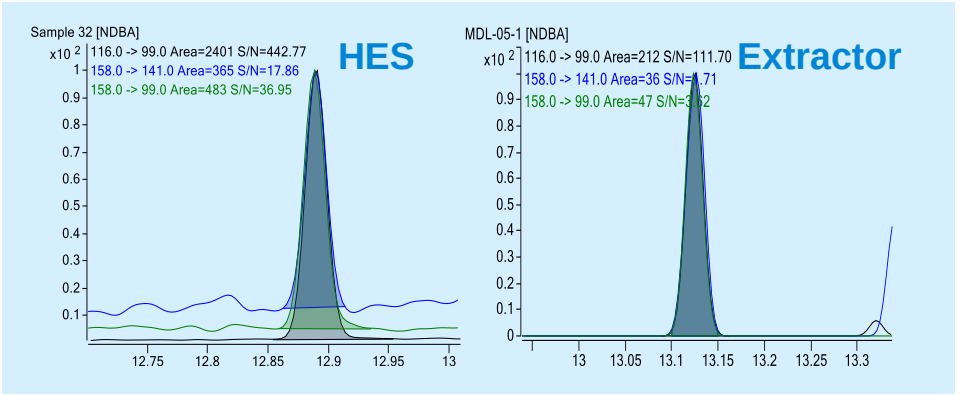
7010 GC-MS/MS
High Efficiency Source



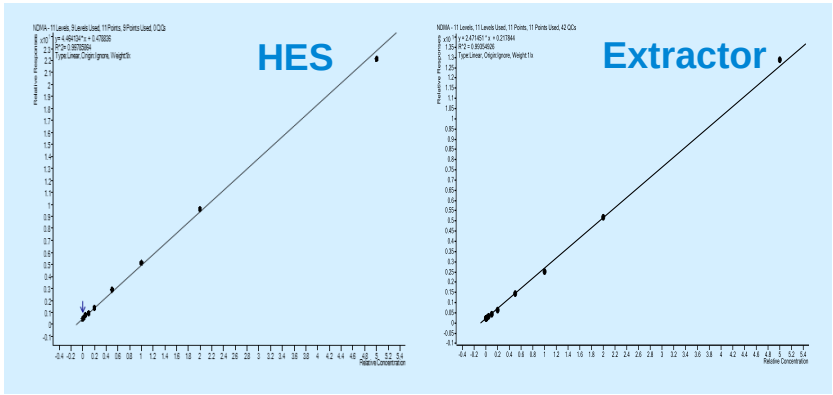
7000 GC-MS/MS
Extractor Source



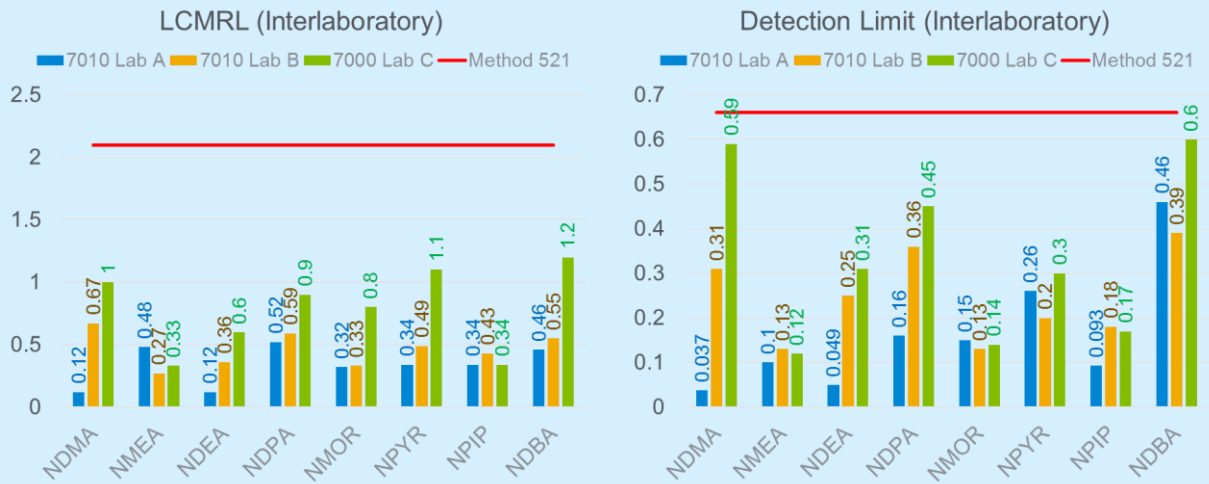
Baseline Separation and Sensitivity



$R^2 > 0.99$

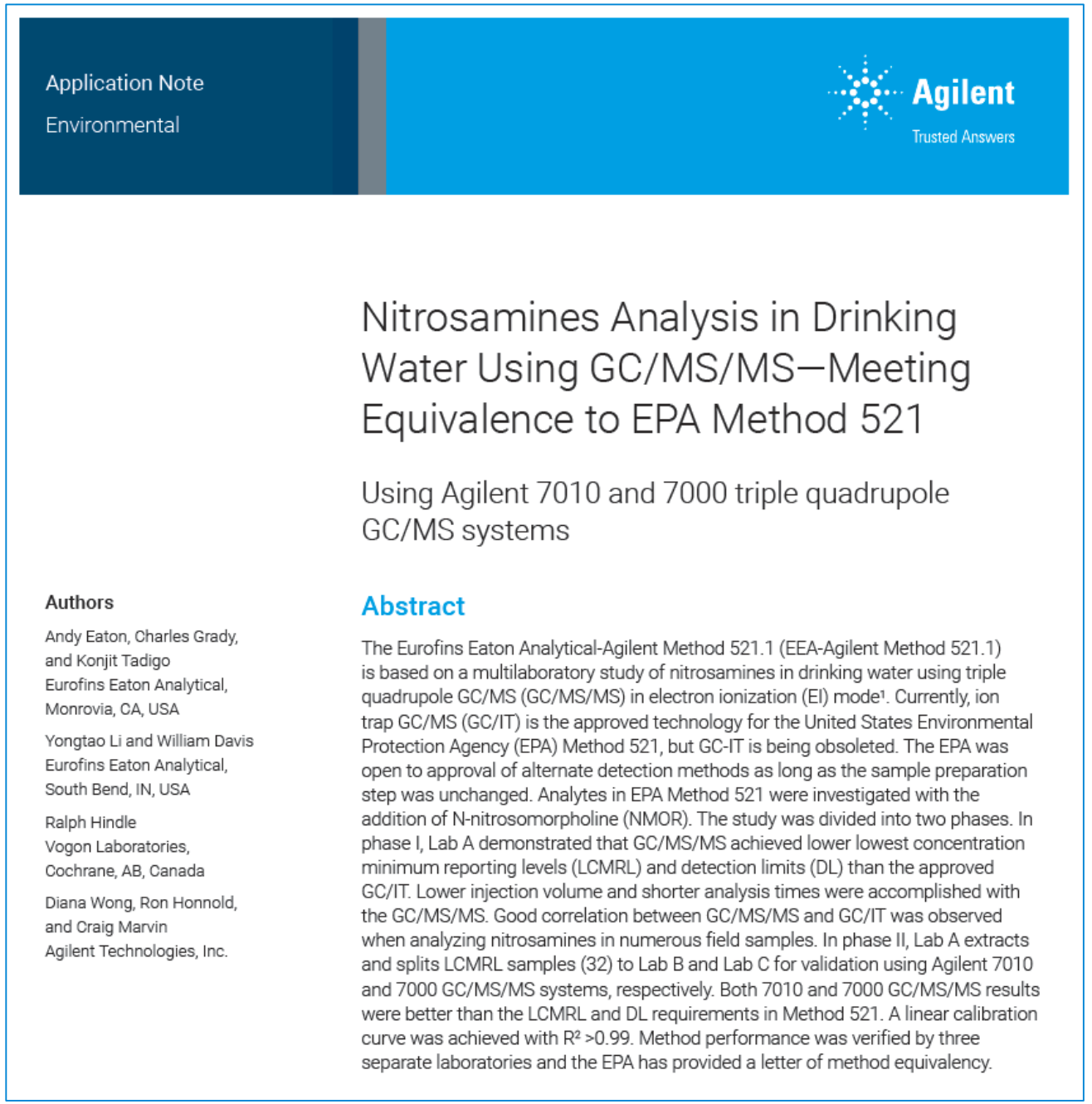


LCMRL and Detection Levels



Current Status

- Method performance was verified by three separate laboratories
- EPA has provided a letter of method equivalency
- Application Note: 5991-9224EN



Application Note

Environmental

Agilent

Trusted Answers

Nitrosamines Analysis in Drinking Water Using GC/MS/MS—Meeting Equivalence to EPA Method 521

Using Agilent 7010 and 7000 triple quadrupole GC/MS systems

Authors

Andy Eaton, Charles Grady, and Konjit Tadigo
Eurofins Eaton Analytical, Monrovia, CA, USA

Yongtao Li and William Davis
Eurofins Eaton Analytical, South Bend, IN, USA

Ralph Hindle
Vogon Laboratories, Cochrane, AB, Canada

Diana Wong, Ron Honnold, and Craig Marvin
Agilent Technologies, Inc.

Abstract

The Eurofins Eaton Analytical-Agilent Method 521.1 (EEA-Agilent Method 521.1) is based on a multilaboratory study of nitrosamines in drinking water using triple quadrupole GC/MS (GC/MS/MS) in electron ionization (EI) mode[1]. Currently, ion trap GC/MS (GC/IT) is the approved technology for the United States Environmental Protection Agency (EPA) Method 521, but GC-IT is being obsoleted. The EPA was open to approval of alternate detection methods as long as the sample preparation step was unchanged. Analytes in EPA Method 521 were investigated with the addition of N-nitrosomorpholine (NMOR). The study was divided into two phases. In phase I, Lab A demonstrated that GC/MS/MS achieved lower lowest concentration minimum reporting levels (LCMRL) and detection limits (DL) than the approved GC/IT. Lower injection volume and shorter analysis times were accomplished with the GC/MS/MS. Good correlation between GC/MS/MS and GC/IT was observed when analyzing nitrosamines in numerous field samples. In phase II, Lab A extracts and splits LCMRL samples (32) to Lab B and Lab C for validation using Agilent 7010 and 7000 GC/MS/MS systems, respectively. Both 7010 and 7000 GC/MS/MS results were better than the LCMRL and DL requirements in Method 521. A linear calibration curve was achieved with R^2 >0.99. Method performance was verified by three separate laboratories and the EPA has provided a letter of method equivalency.

Acknowledgements – Interlaboratory Validation Study

Eurofins Eaton Analytical
Monrovia, California (USA)

Andy Eaton
Chuck Grady
Konjit Tadigo

Eurofins Eaton Analytical
South Bend, Indiana (USA)

Bruce Li
Bill Davis

Vogon Laboratories
Cochrane, Alberta (Canada)

Ralph Hindle

Wait – I can do volatiles?

Dr. Detlef Knappe
Professor of Civil, Construction and Environmental Engineering
North Carolina State University
knappe@ncsu.edu

Combined CVOC and 1,4-Dioxane Analytical Method Overview

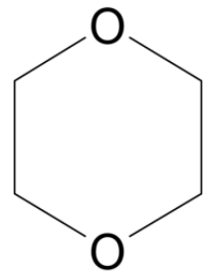
EPA Methods 522
"Determination of 1,4-dioxane in Drinking Water by Solid Phase Extraction (SPE) and Gas Chromatography/ Mass Spectrometry (GC/MS) with Selected Ion Monitoring (SIM)"

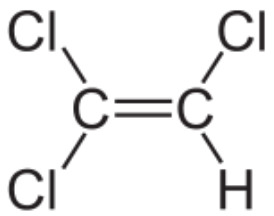
EPA Method 524.3
"U.S. EPA Method 524.3 for Analysis of Volatile Organic Compounds (VOCs) in Finished Drinking Water"

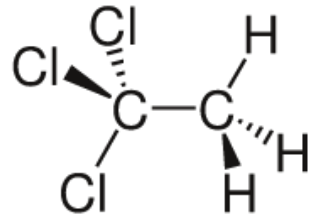
Combined method for VOCs and 1,4-dioxane

1,4-Dioxane and VOC Challenges

- Co-occurrence of 1,4-dioxane and chlorinated solvents is common in contaminated groundwater
  - 1,4-dioxane was a stabilizer for 1,1,1-trichloroethane (1,1,1-TCA)
  - Trichloroethene (TCE) use often preceded 1,1,1-trichloroethane use
- Separate analytical methods
  - EPA Method 522 for 1,4-dioxane
  - EPA Method 524.3 for VOCs
- Recent CA database evaluation (Adamson et al. 2014 ES&T Letters 1: 254-258)
  - 95% of 1,4-dioxane sites contained other chlorinated solvents
  - 76% of 1,4-dioxane sites contained 1,1,1-TCA
  - No 1,4-dioxane analyses were conducted at 67% of sites containing 1,1,1-TCA







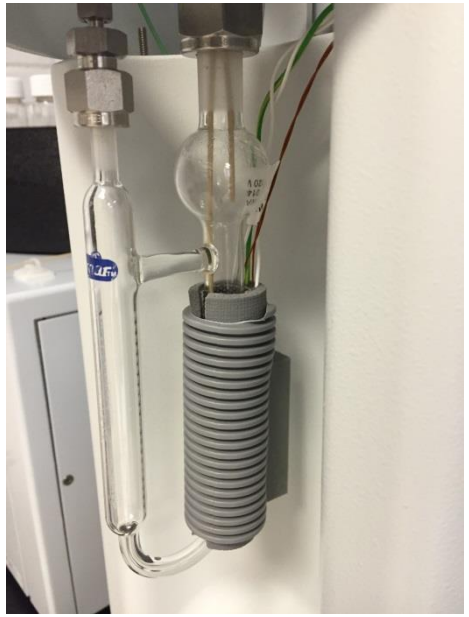
Methods and Materials

- Analytes
  - 52 VOCs from method 524.3
  - Vinyl Chloride, 1,3-butadiene
  - Tert-butyl alcohol, 1,4-dioxane, 1,3-dioxane, 1,3-dioxolane
- Internal standards
  - 1,4-difluorobenzene
  - 1,4-dioxane-d8
  - chlorobenzene-d5
  - 1,2,3-trichloropropane d5 for low concentration method

Analytical Instrumentation

- Purge and Trap
  - 5 mL sample volume
  - Heated at 60°C
  - #9 trap

Mass spectrometer
Agilent 7010
Selected-ion monitoring
Most compounds
Triple quadrupole with MRM
1,4D, 1,2,3-TCP, DBM



- Gas chromatograph
  - Agilent 7890B
  - Column: DB-624 Ultra Inert (Agilent 121-1324UI)
  - Temperature program:

Temperature Rate	Temperature	Hold	End Time
	35 °C	4 minutes	4 minutes
15 °C per minute	240 °C	0 minutes	17.667 minutes

Trip[le Quadrupole GC/MS System

71

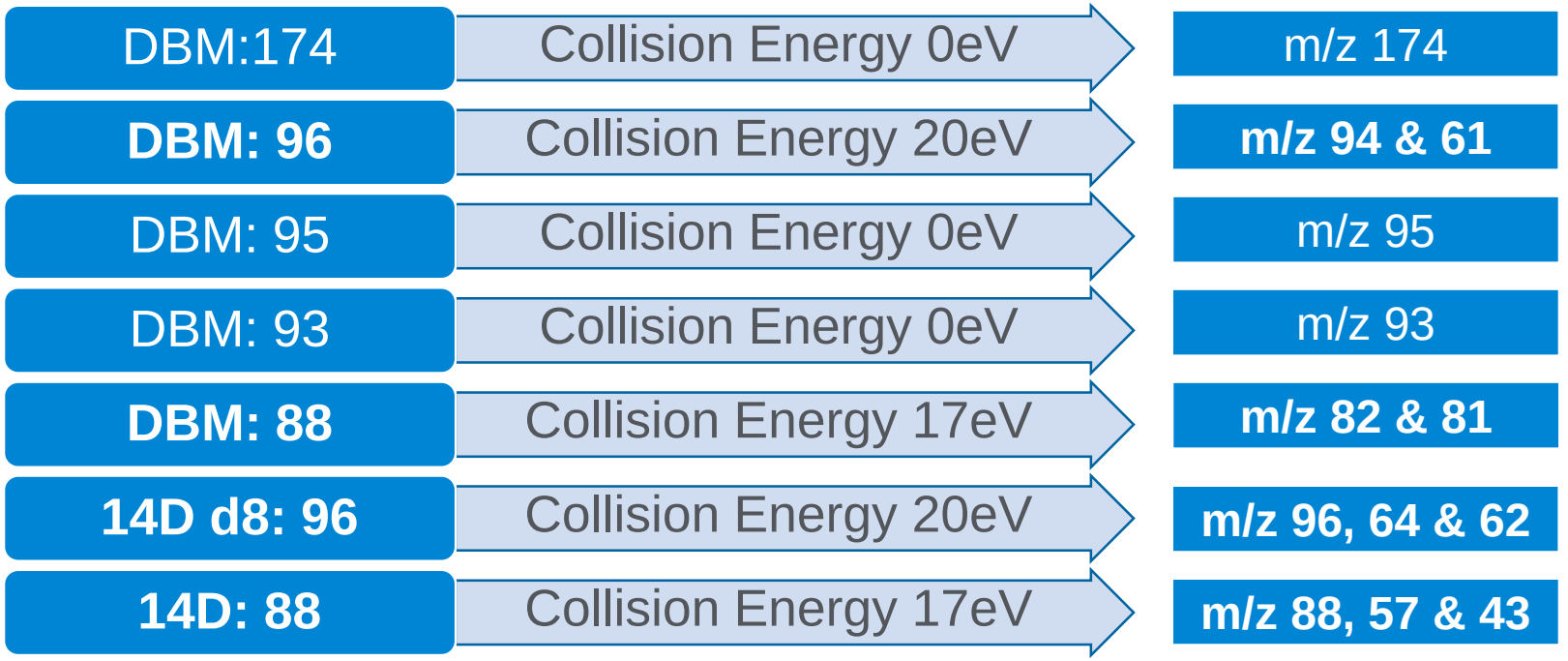
MMI Inlet and MS Settings

Parameter	High Concetnration Setting	Low Concentration Setting
Temperature	200°C	200°C
Pressure	14.125 psi	14.125 psi
Total Flow	215.7 mL/min	215.7 mL/min
Septum Purge Flow	5 mL/min	5 mL/min
Mode	Split	Split
Split Ratio	300 to1	30 to1
Split Flow	210 mL/min	21 mL/min

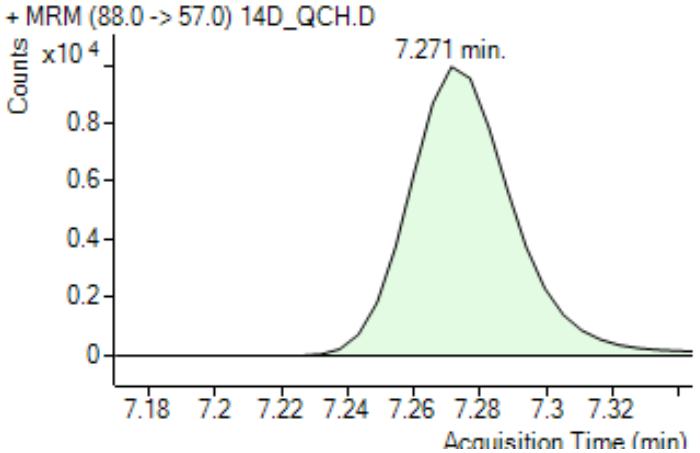
Transfer Line Temperature	250°C
Tune File	atunes.eihs.tune.xml
Ion Source	Electron Impact
Source Temperature	270°C
Electron Energy	Tune setting, 70 eV
Detector Setting	Gain, EM Saver, Limit 1E+09
Solvent Delay	1.05 min
Time Filtering	On, Time = 0 min, Peak width = 0.8 sec
Miscellaneous	Automatically subtract baseline

MRM Used to Resolve Coeluting DBM and 1,4-Dioxane d8

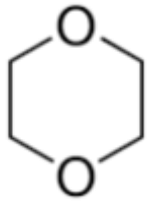
- 1,4-Doxane d8 (internal standard for 1,4-dioxane)
- Dibromomethane (quantification ion 174, qualifier ions 95/93)
  - Interferes with m/z 96, 64, 62
  - MRM allows 1,4-dioxane d8 to be separated from dibromomethane



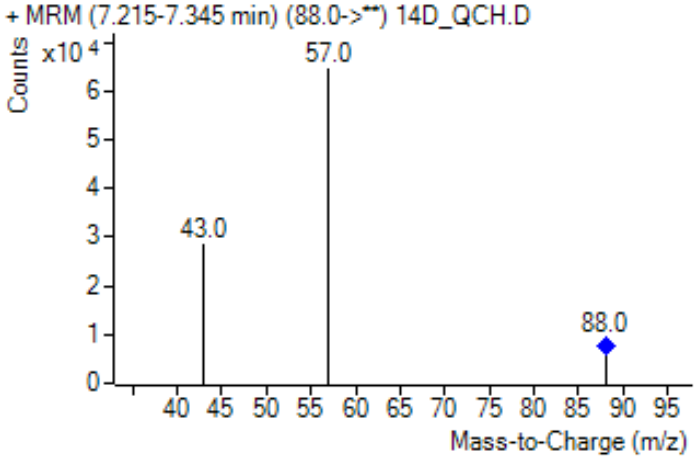
1,4-Dioxane

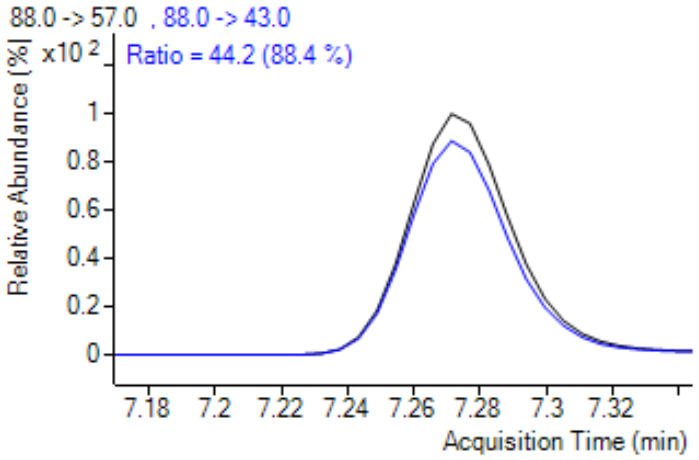


Ion chromatogram:
Precursor Ion m/z 88

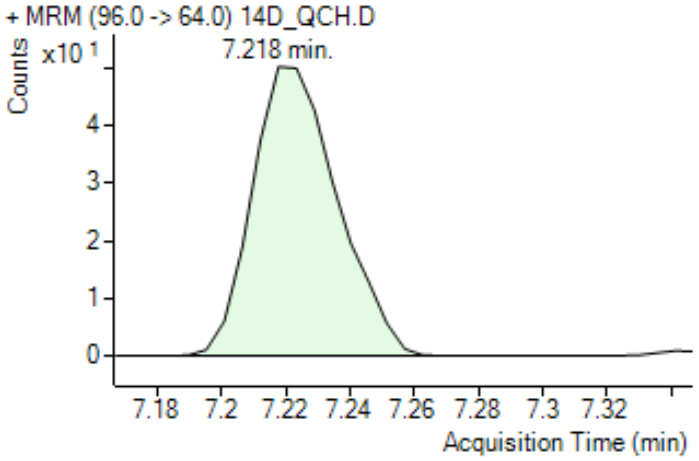


Product Ions Used:
m/z 57 / m/z 43

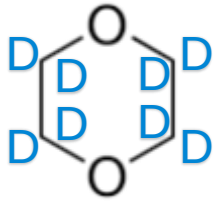




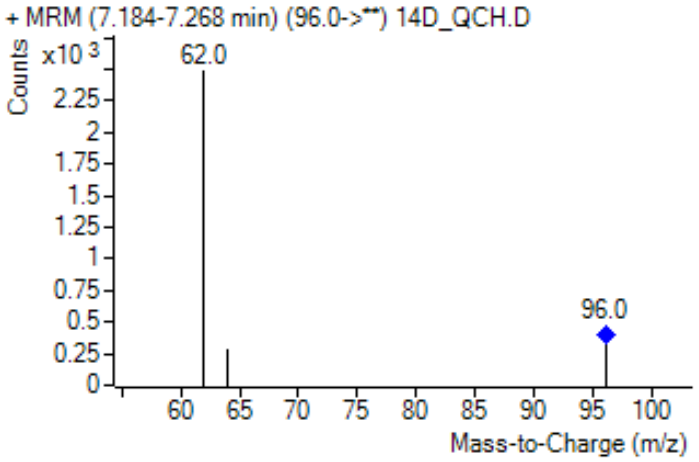
1,4-Dioxane d8

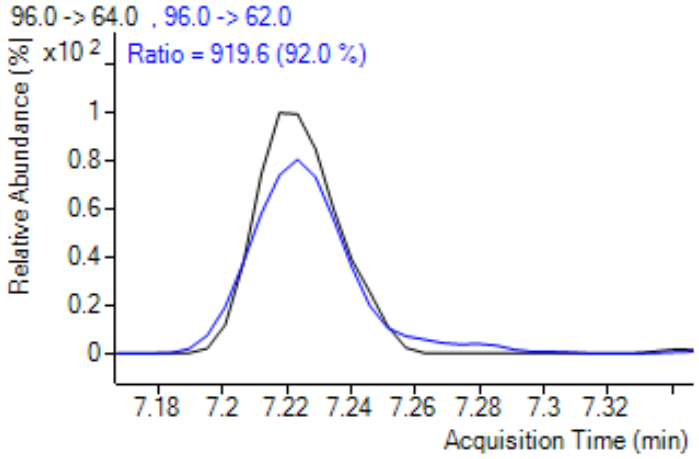


Ion chromatogram:
Precursor Ion m/z 96



Product Ions Used:
m/z 64 / m/z 62

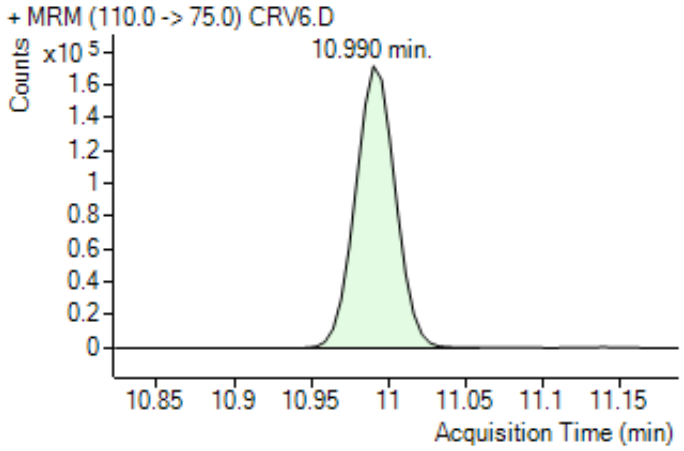




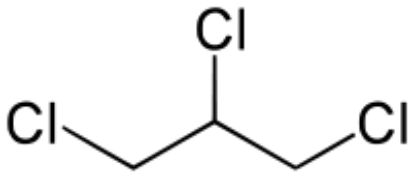
MRM Used for Low Concentrations

- 1,2,3-Trichloropropane d5 desired as internal standard for low concentration TCP analyses
- Interference from Bromobenzene with 1,2,3-Trichloropropane d5
  - With MRM 1,2,3-Trichloropropane-d5 yields stable response in the presence of bromobenzene
- MRM also reduces background noise
  - Expected to result in lower quantification limit

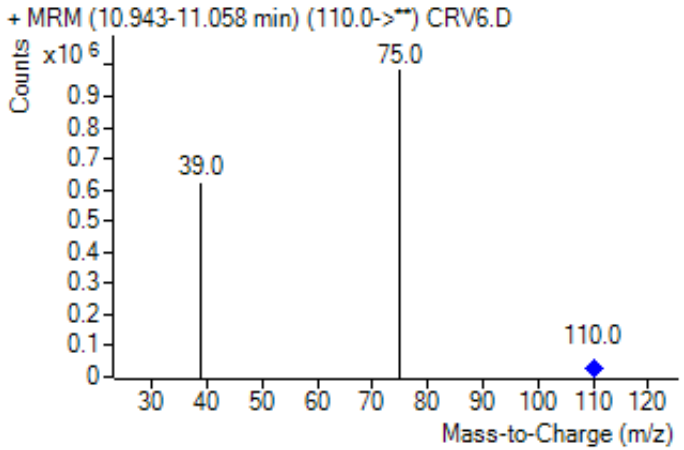
1,2,3-Trichloropropane

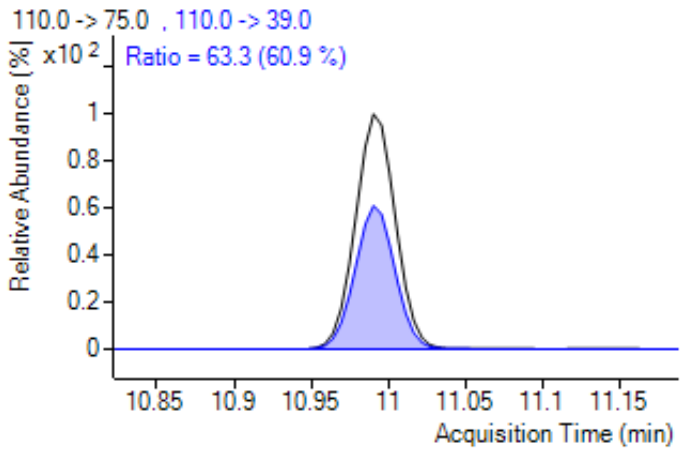


Ion chromatogram:
Precursor Ion m/z 110

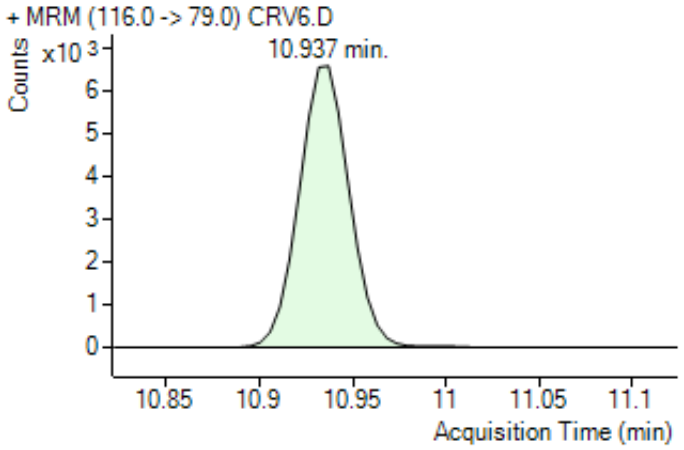


Product Ions Used:
m/z 75 / m/z 39

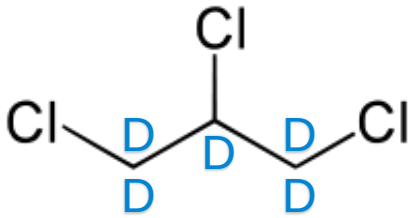




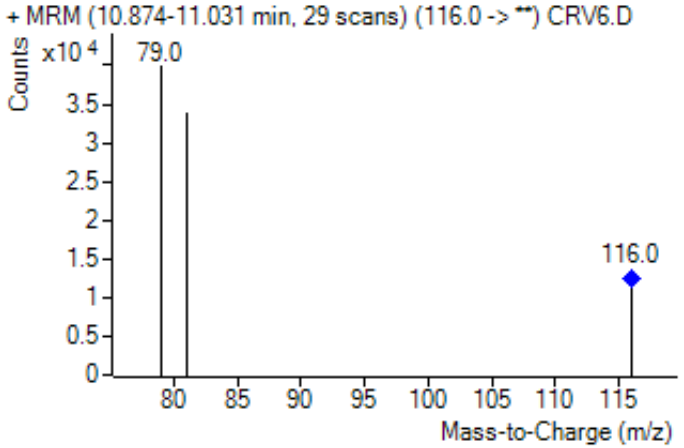
1,2,3-Trichloropropane d5

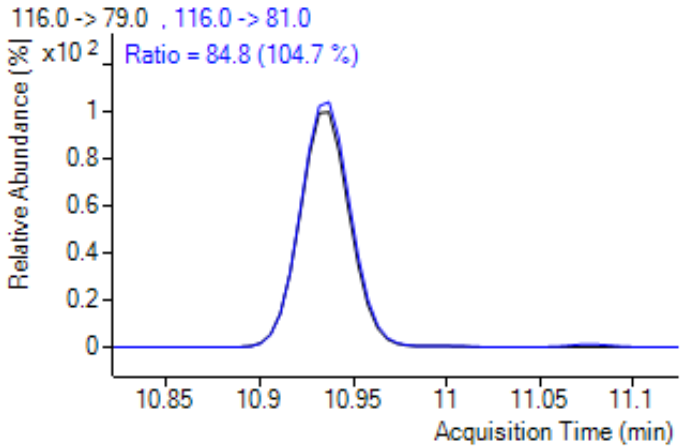


Ion chromatogram:
Precursor Ion m/z 116

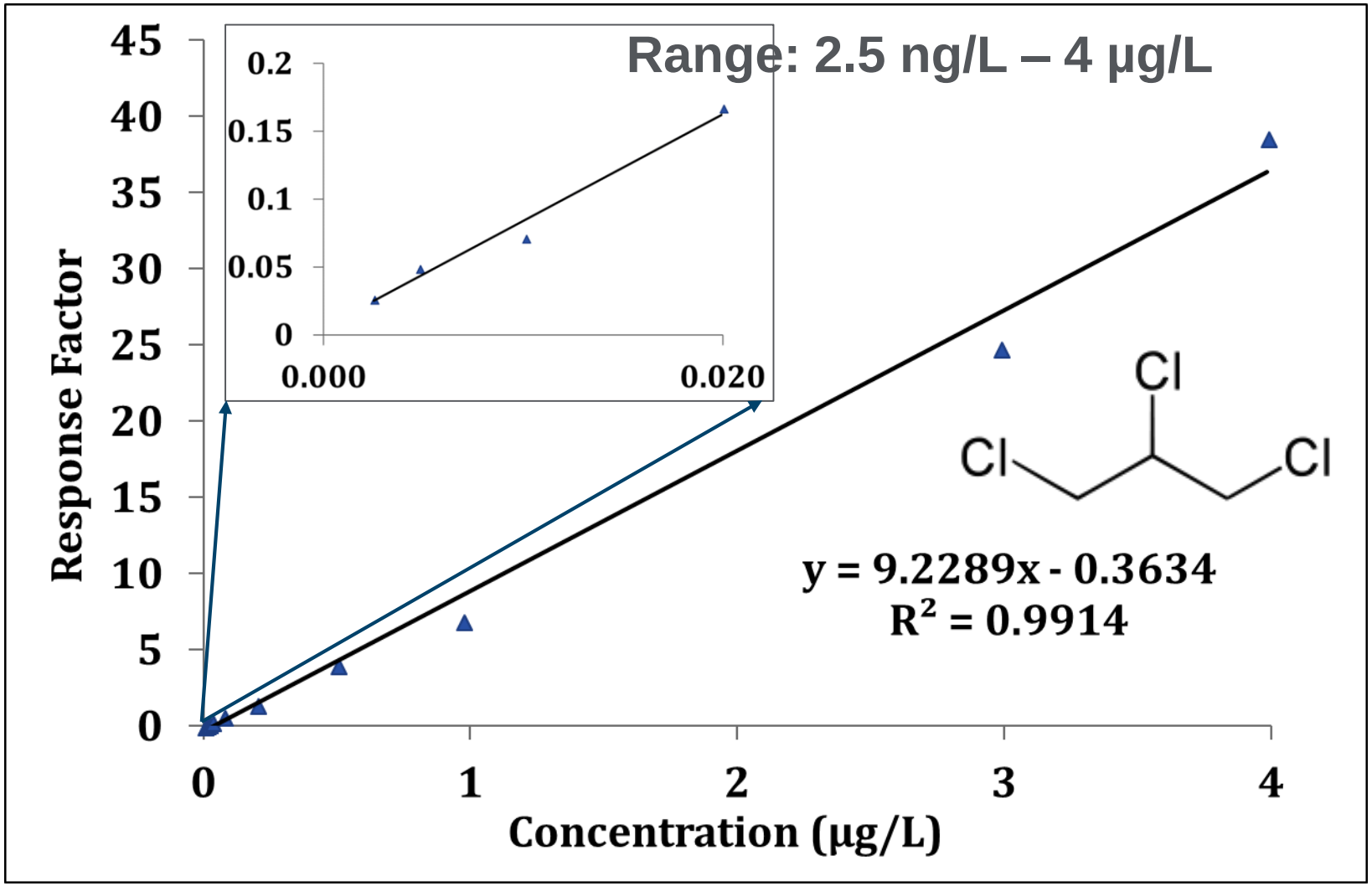


Product Ions Used:
m/z 79 / m/z 81



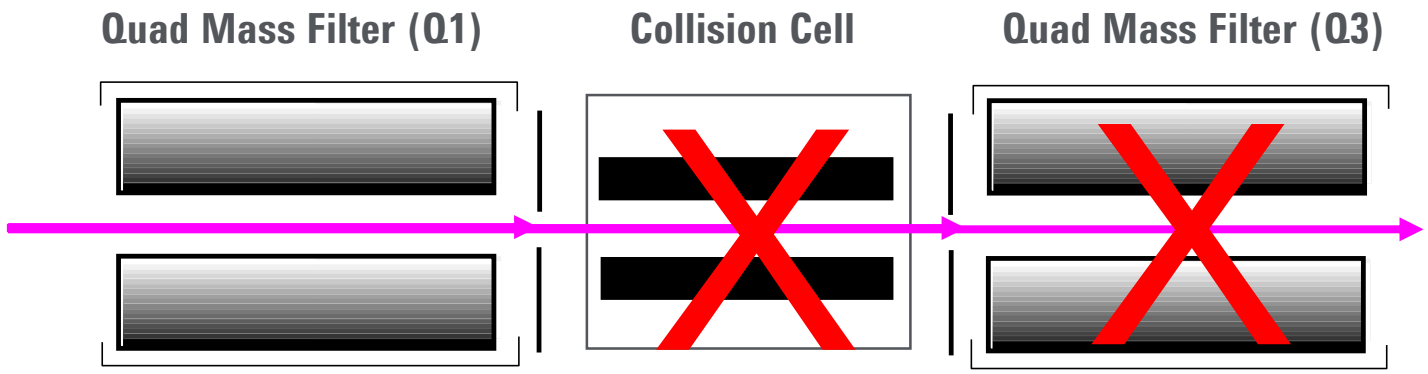


Low Concentration Curve: 1,2,3-Trichloropropane



Wait – it's not just for MS/MS?

Scanning on a Triple Quad



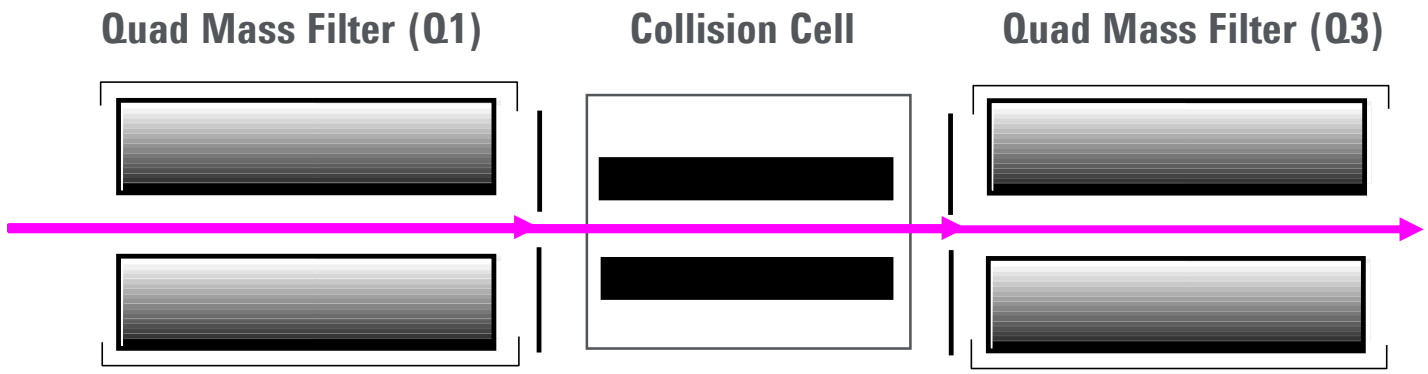
So far, just like a single quad…

…transmission <100% and possible fragmentation…

…transmission <100%

Maybe scanning in a triple quad is not a good idea. But wait…

Scanning on a Triple Quad



So far, just like a single quad…

Operate Q1 in all-pass mode…

…transmission <100% and possible fragmentation…

…collisional cooling and focusing…

…transmission <100%

…scan Q3 to produce low noise, high quality scan data

Triple Quad Scan Data Used in a Series of Tea Aroma Studies

Food Research International 108 (2018) 413–422

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Study of the aroma formation and transformation during the manufacturing process of oolong tea by solid-phase micro-extraction and gas chromatography–mass spectrometry combined with chemometrics

Chengying Ma[a], Junxing Li[b,*], Wei Chen[a], Wenwen Wang[c], Dandan Qi[a], Shi Pang[a], Aiqing Miao[a,*]

[a] Guangdong Provincial Key Laboratory of Tea Plant Resources Innovation & Utilization, Tea Research Institute, Guangdong Academy of Agricultural Sciences, Guangzhou 510640, China
[b] Vegetable Research Institute, Guangdong Academy of Agricultural Sciences, Guangzhou 510640, China
[c] Agilent Technologies (China) Co. Ltd., Beijing 100102, China

Food Chemistry 265 (2018) 189–199

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Study on the effects of rapid aging technology on the aroma quality of white tea using GC–MS combined with chemometrics: In comparison with natural aged and fresh white tea

Dandan Qi[a,1], Aiqing Miao[a,1], Junxi Cao[a], Wenwen Wang[c], Wei Chen[a], Shi Pang[a], Xiugu He[b], Chengying Ma[a,*]

[a] Tea Research Institute, Guangdong Academy of Agricultural Sciences/Guangdong Provincial Key Laboratory of Tea Plant Resources Innovation & Utilization, Guangzhou 510640, China
[b] Guangdong Academy of Agricultural Sciences, Guangzhou 510640, China
[c] Agilent Technologies (China) Co. Ltd., Beijing 100102, China

Chemometric Methods for the Analysis of Graftage-Related Black Tea Aroma Variation by Solid Phase Mirco-Extraction and Gas Chromatography-Mass Spectrometry

Application Note

Authors

Wei Chen, Chengying Ma, Aiqing Miao, Shi Pang, and Dandan Qi
Tea Research Institute,
Guangdong Academy of Agricultural Sciences,
Guangdong, China

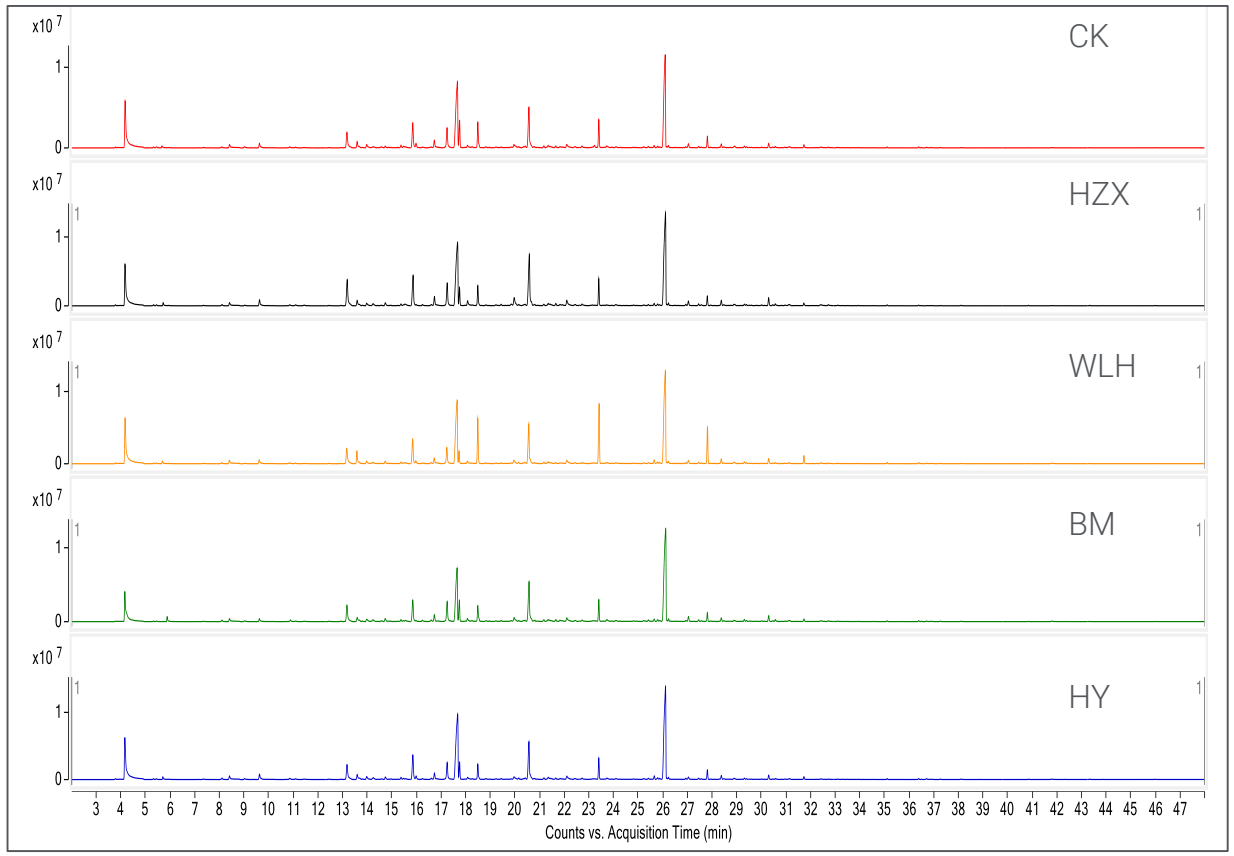
Wenwen Wang
Agilent Technologies, Inc.
Beijing, China

Abstract

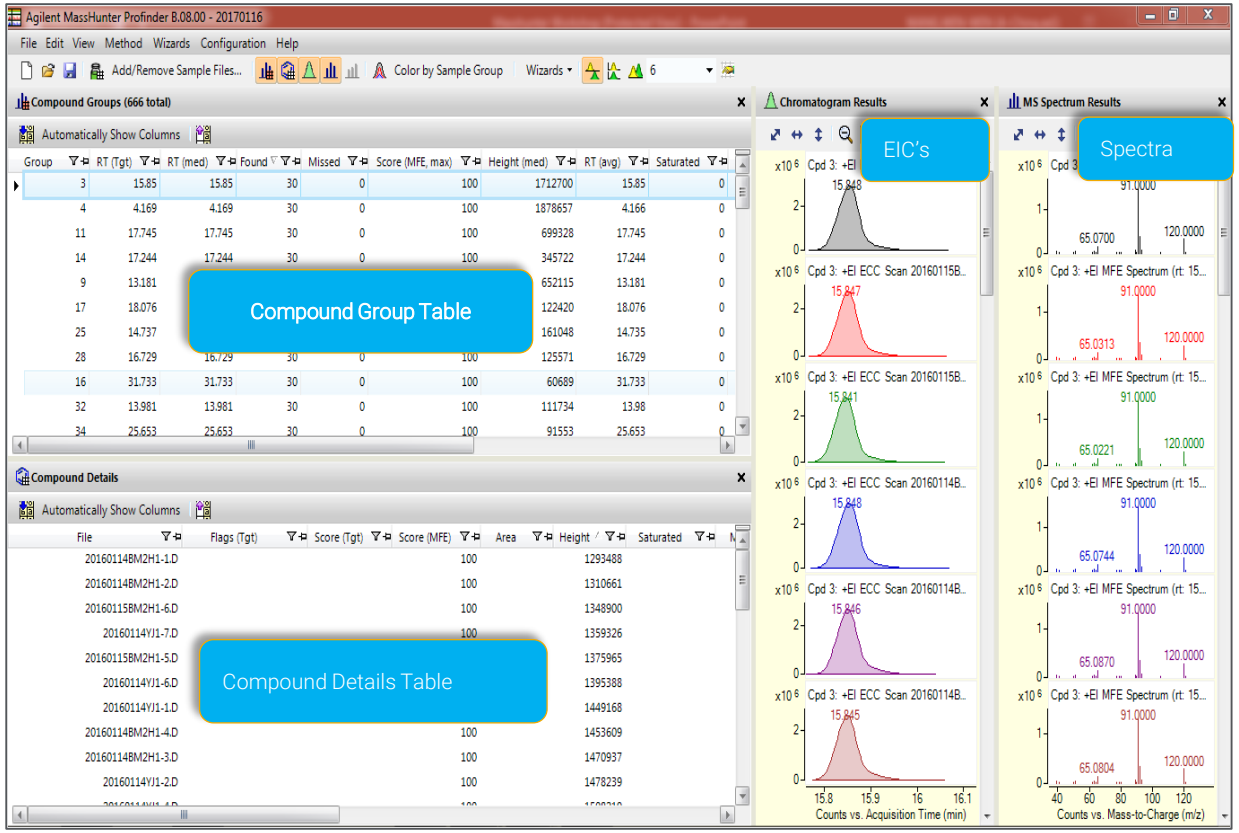
A solid-phase micro-extraction (SPME) and gas chromatography/triple quadrupole mass spectrometry (GC/MS/MS) method was developed to analyze graftage-related black tea samples. Data extraction and statistical analysis were performed using Agilent MassHunter Profinder and Agilent Mass Profiler Professional (MPP) software. The characteristic volatile compounds, which were identified or tentatively identified, were subjected to principle component analysis and hierarchical clustering analysis to reveal the differences among tea samples.

Graftage-related Tea Aroma Variation

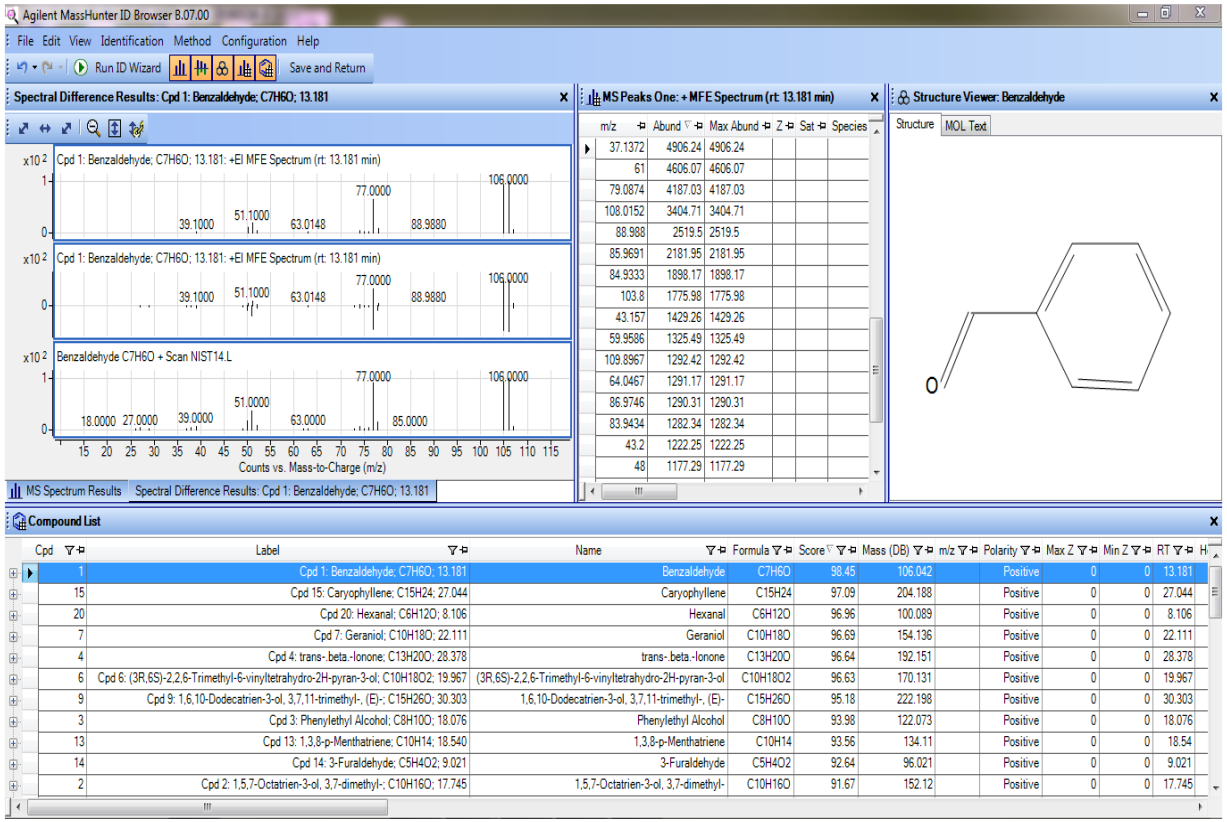
For 5 replicates of each graftage type:
Tea infused with boiling water, then held in a water bath for 4 min at 60 °C.
Extracted at 60 °C for 40 min with a DVB/CAR/PDMS-50/30µm SPME fiber.
SPME fiber desorbed for 4.5 min at 270 °C.
7890B/7000D operated in scan mode



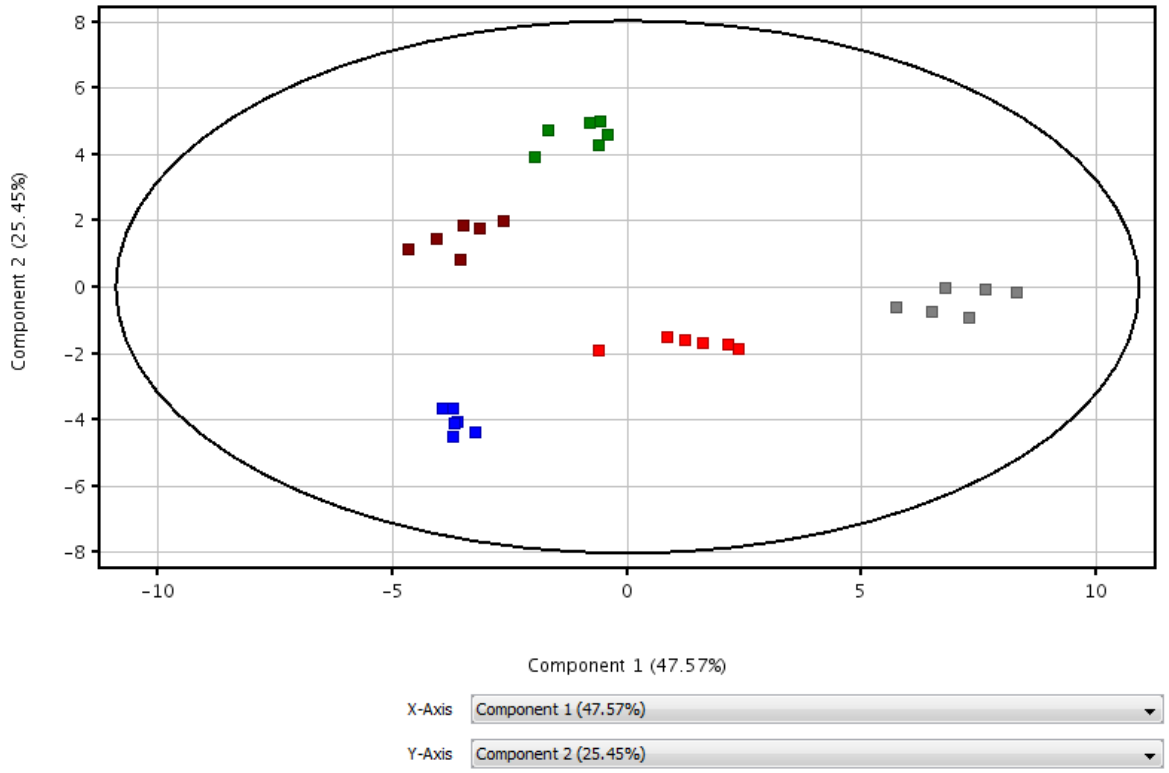
Components Identifed and Examined Across Multiple Samples ProFinder and Mass Profiler Professional with ID Browser

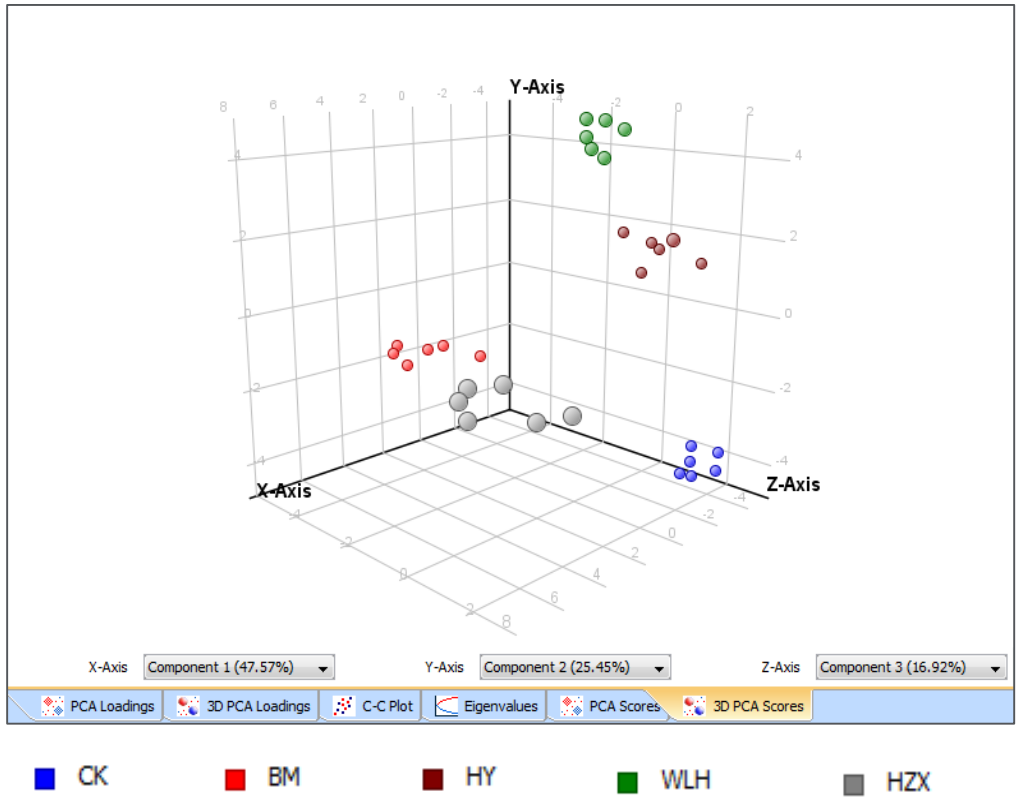


44 components found to be significant by one-way ANOVA
34 identified by ID Browser in NIST 14
Most were alcohols, ketones, aldehydes, esters, organic acids

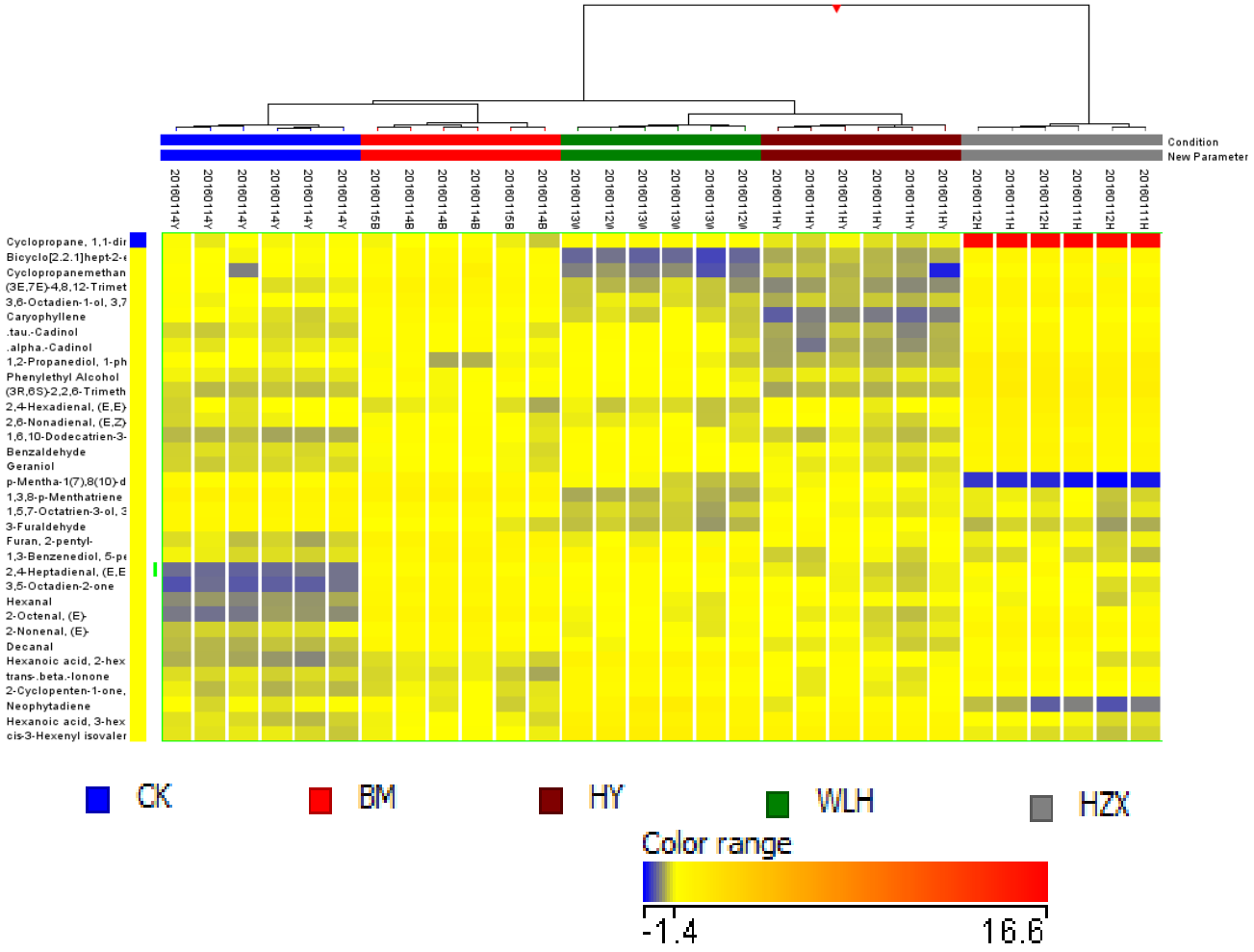


Results of Principal Components Analysis
Visualizations of the Two (2D) and 3 (3D) Most Significant Components





Dendrogram from Hierarchical Cluster Analysis



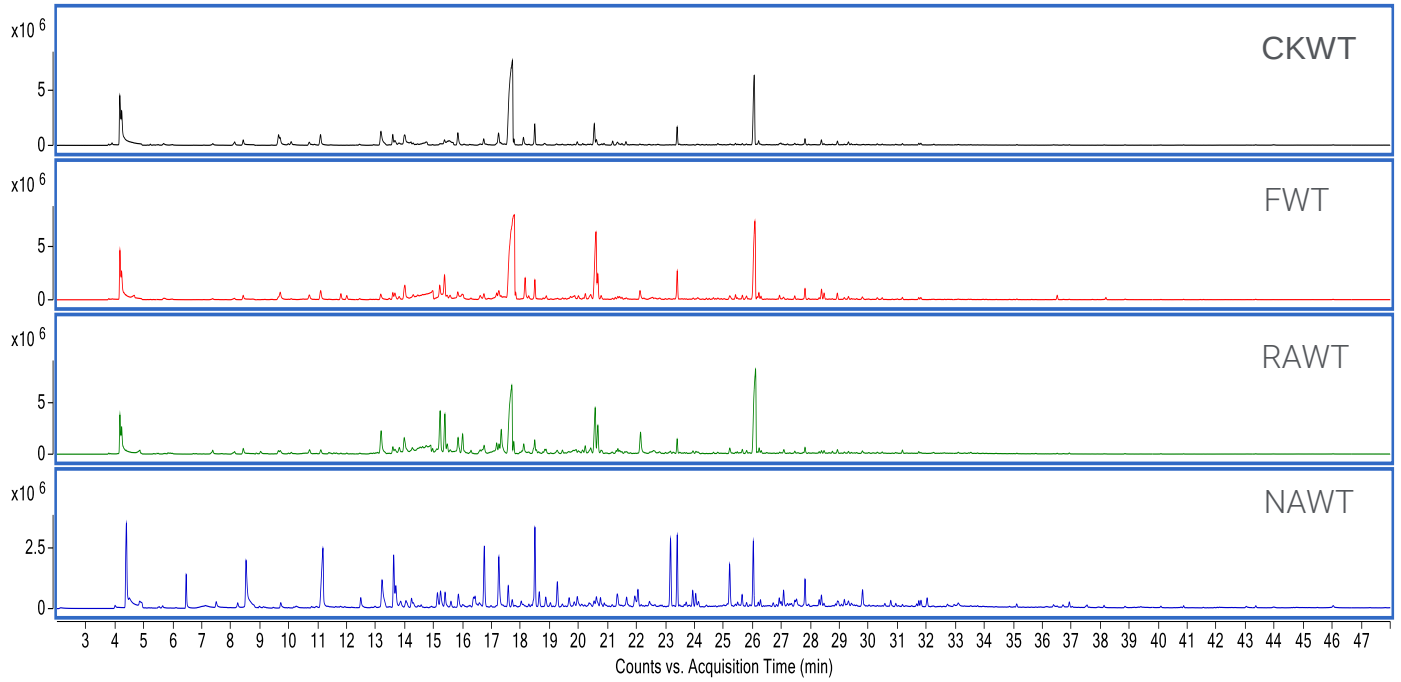
Conclusions:

- Profile of BM stock very similar to CK (non-grafted)
- HZX stock profile different from all the rest (CK and every other graft)

Effect of Rapid Aging Process on Aroma-Influencing Components

(180 days @ -20 °C)

(12 years)



For 3 replicates of each aging type:
Tea infused with boiling water, then held in a water bath for 5 min at 60 °C. Extracted at 60 °C for 40 min with a DVB/CAR/PDMS-50/30µm SPME fiber. SPME fiber desorbed for 4.5 min at 270 °C.
7890B/7000D operated in scan mode

TP157 at ASMS 2018

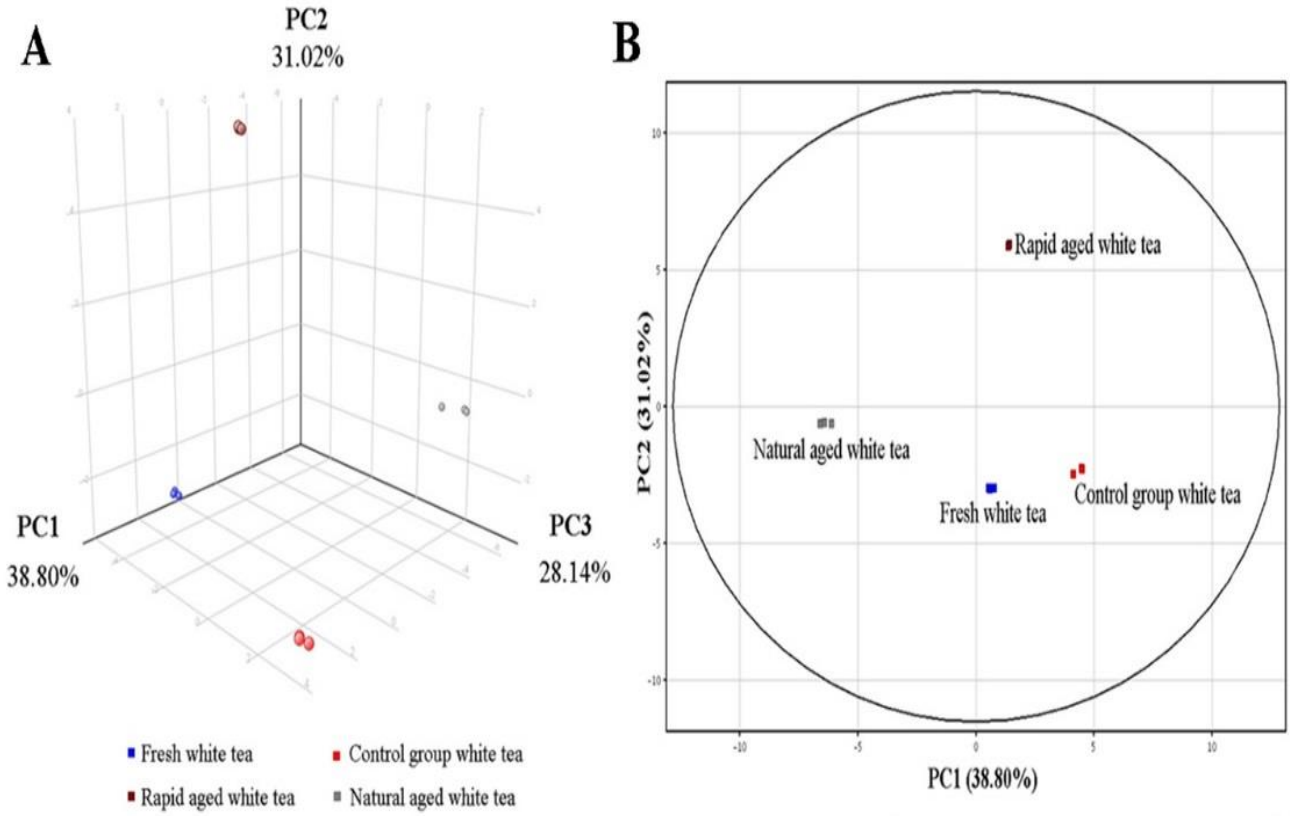
Principal Components Visualization

Frequency (>60%) and Coefficient of Variation (<25%) filters applied

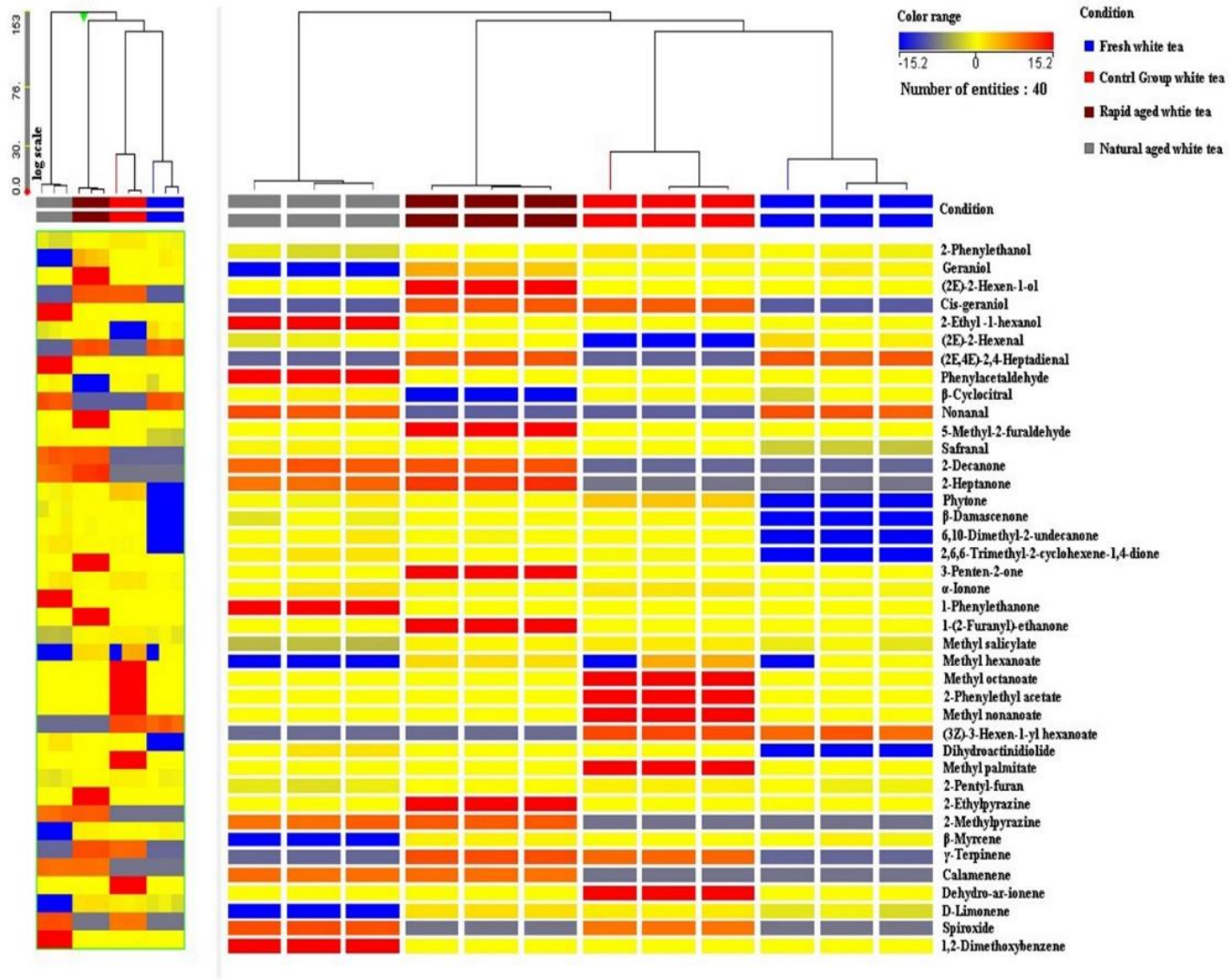
164 components found to be significant by one-way ANOVA ($p<0.05$, Fold-change >2x)

40 identified by ID Browser in NIST 14

Most were alcohols, ketones, aldehydes, esters, heterocyclics, alkanes



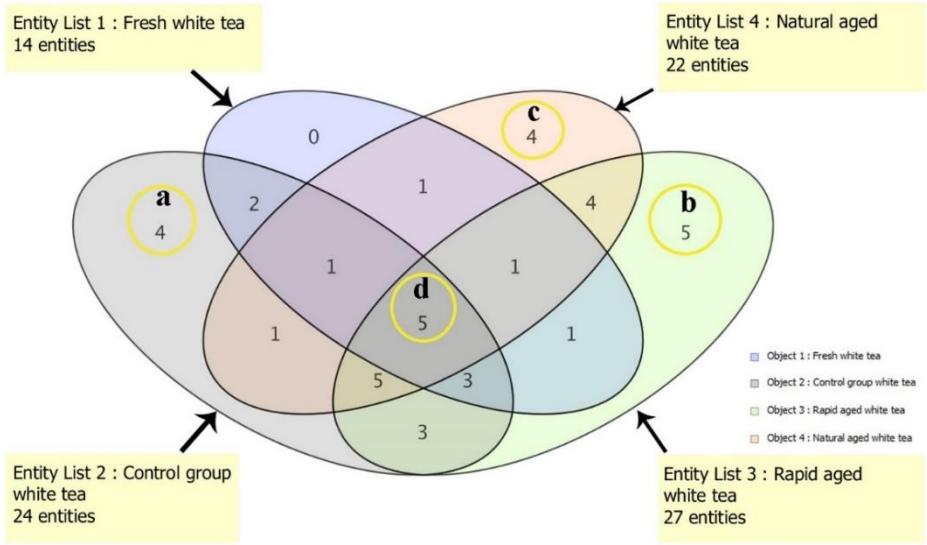
HCA of the Differently-Aged Teas



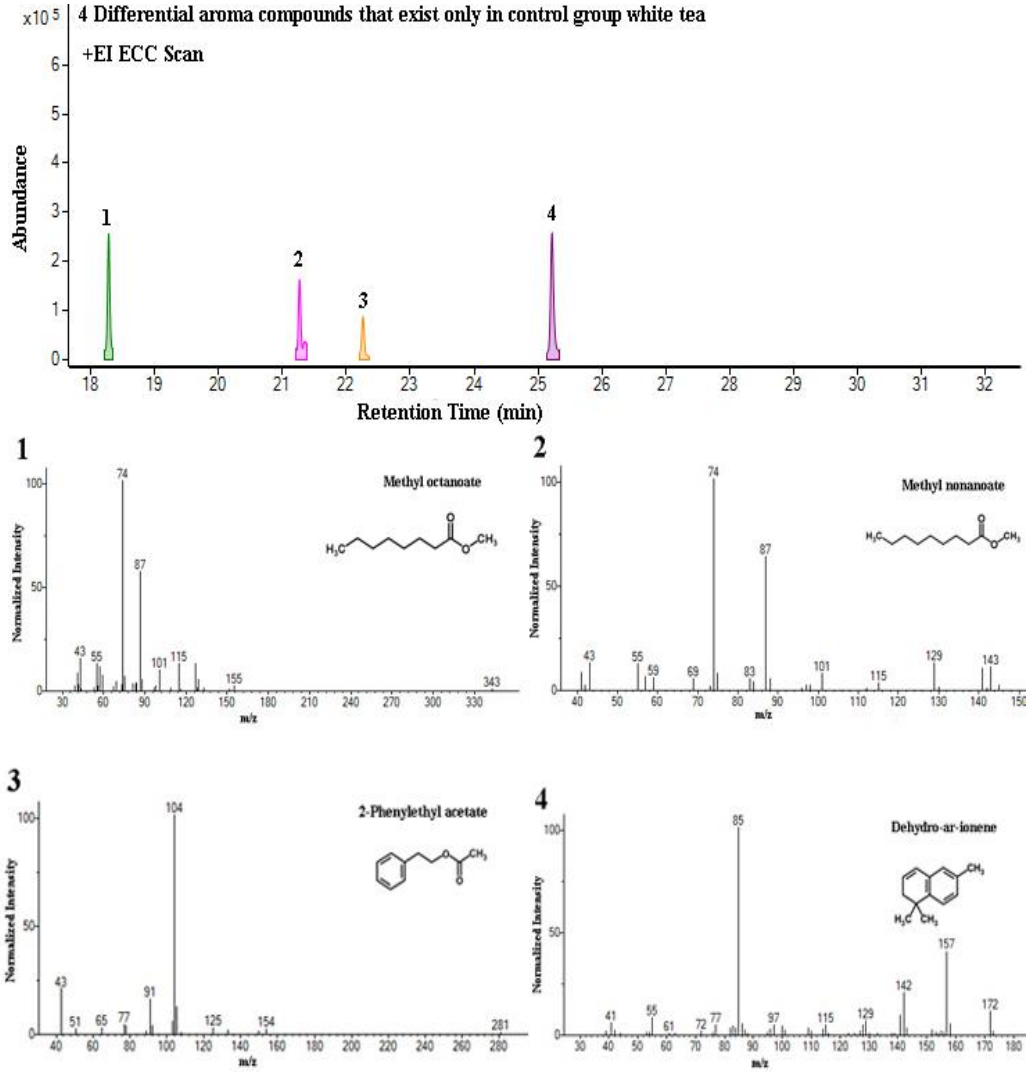
Conclusions:

- Fresh and control teas most (but not very) similar
- Rapid aged tea significantly different than that unaged group
- Natural aged tea even more different
- Rapid aged tea distinguishable (in this analysis) from natural aged tea

Venn Diagram Provides a Global View
Shows Number of Components in Common and Unique



Circle “a” shows that there are 4 components found only in the control group tea. At right is a chromatogram showing only those components, along with their spectra



Yes – You Can Do That With a GC Triple Quad!

- You can move up from 1D chromatography detection to:
  - Combine multiple classical methods into one
  - Reach lower limits of detection
  - Simplify your sample prep to:
    - Save time
    - Save money
    - Minimize waste
    - Eliminate sources of variability

- You can move over from other MS techniques (HR sector, ion trap) to
  - Achieve business continuity
  - Streamline the # of different platforms/skills/training required
  - Increase the flexibility to distribute your workload

- You can obtain exquisite selectivity in unconventional ways

- You can enhance already-effective single quad methods in ways that save time, improve results and lead to greater insights

- You can do every step of a differential analysis (for product optimization, enviro/tox studies, metabolomics, etc.) on a single platform by taking advantage of the scan capabilities of a triple quad

Thanks for coming, and enjoy the rest of ASMS 2018!

tom_doherty@agilent.com