Organophosphate Flame Retardants

Method Development for the Detection of OPFRs in House Dust and Consumer Products

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Key Points

Background Information

GCMS Method Development

- OPFR Chemical Structure
- GC-MSMS
- MRM Transitions

Dust

- SRM 2585 [Organic Contaminants in House Dust]
- Extraction Process
  - Sonication assisted solvent extraction
- Measured OPFRs in SRM 2585

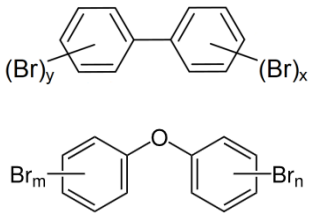
Foam

- Polyurethane Foam
- Extraction Process
- BEARHFTI

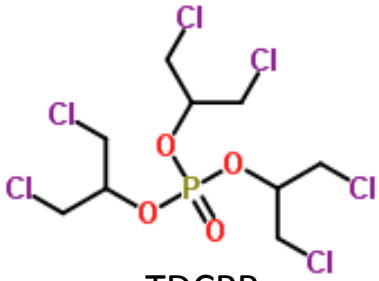
- Conclusion
  - Additional Work / Method Development / Application
  - References

Replacement Flame Retardants

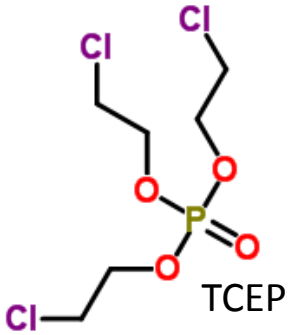
- Restrictions on the use of Polybrominated biphenyls (PBBs) & Polybrominated diphenyl ethers (PBDEs)
  - RoHS: Restriction of Hazardous Substances Directive (EU: PBBs & PBDE)[1, 5]
  - Stockholm Convention (POPs: octaBDE & pentaBDE)[2]
  - California Health and Safety Code Section 108922 (penta BDE)[12]
  - California Prop 65 (PBBs: cancer & development)[4]



- Organophosphate Flame Retardants (OPFRs)
  - California Prop 65[4]
  - Safer Consumer Products:
    - A Priority Product is a consumer product that contains one or more chemicals – known as Candidate Chemicals – that have a hazards trait that can harm people or the environment.[12]
      - Tris(1,3-dichloro-2-proply phosphate (TDCPP) → carcinogen
      - Tris(2-chloroethyl) phosphate (TCEP) → carcinogen
      - Tris(2,3-dibromopropyl) phosphate → carcinogen



TDCPP



TCEP

TDBPP

California LEGISLATIVE INFORMATION

Senate Bill No. 1019

Upholstered furniture: flame retardant chemicals

- Approved by Governor Brown September 30, 2014
  - Effective January 1, 2015

- bill requires labeling to indicate if the product contains flame retardant chemicals (>1000ppm or 0.1% wt/wt)[3]

  - Fine for Violation
  - Citation will be made available to public (www.bearhfti.ca.gov)

  ➢ consumers can make an informed decision

- DTSC to assist the BEARHFTI by testing for Flame Retardant Chemicals
  - When manufacture label indicates **No** added Flame Retardant Chemicals

NOTICE

THIS ARTICLE MEETS THE FLAMMABILITY REQUIREMENTS OF CALIFORNIA BUREAU OF ELECTRONIC AND APPLIANCE REPAIR, HOME FURNISHINGS AND THERMAL INSULATION TECHNICAL BULLETIN 117-2013. CARE SHOULD BE EXERCISED NEAR OPEN FLAME OR WITH BURNING CIGARETTES.

The upholstery materials in this product:
_____contain added flame retardant chemicals
_____contain NO added flame retardant chemicals
The State of California has updated the flammability standard and determined that the fire safety requirements for this product can be met without adding flame retardant chemicals. The State has identified many flame retardant chemicals as being known to, or strongly suspected of, adversely impacting human health or development.

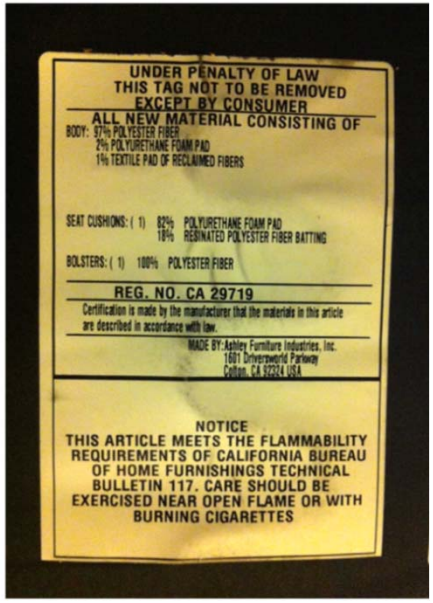
www.bearhfti.ca.gov

Label Requirement[13]

- Furniture manufacture date of January 1, 2015
- SB 1019 is not retroactive

Technical Bulletin 117

- Furniture (fill materials) to be able to withstand a small open flame for at least 12 seconds[13]
  - prevent combustion
  - delay spread of fire



TB 117 Furniture Label from Sofa Purchased in 2010

Compounds of Interest

AccuStandard® Spotlight Analytical Reference Standards

Phosphate Flame Retardants (PFRs)

Organophosphate compounds (OPs) are high production volume chemicals. They are utilized as flame retardants and plasticizers, antifoaming agents and additives not only in plastics, but in paints, lubricants and hydraulic fluids as well. The chlorinated OP compounds like tris(2-chloroethyl) phosphate and tris(1,3-dichloro-2-propyl) phosphate are flame retardants used in both flexible and rigid polyurethane foam (e.g. furniture foam, thermal insulation), rubber, textile coatings, and home electronics. OPs have been detected in indoor air and house dust, surface, ground, and even drinking water. Ongoing toxicological studies have shown several toxic effects of these compounds, prompting the recognition of potential ecological and human health concerns of neurotoxin and carcinogenic nature. AccuStandard is now providing a number of PFRs.

Trimethyl phosphate (TMP)

CAS 512-56-1 MF $C_3H_9O_4P$ MW 140.08

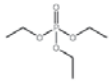
Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-016S	1 mL

Dimethyl phosphate

CAS 813-78-5 MF $C_2H_7O_4P$ MW 126.05

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-006S	1 mL

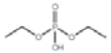
Triethyl phosphate (TEP)



CAS 78-40-0 MF $C_6H_{15}O_4P$ MW 182.16

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-012S	1 mL

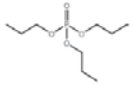
Diethyl phosphate (mono & di)



CAS 598-02-7 MF $C_4H_{11}O_4P$ MW 154.10

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-005S	1 mL

Tripropyl phosphate (TPrP)



CAS 513-08-6 MF $C_9H_{21}O_4P$ MW 224.23

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-021S	1 mL

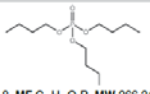
Additional PFRs on reverse side

Triisopropyl phosphate (TIPP, TiPrP)

CAS 513-02-0 MF $C_9H_{21}O_4P$ MW 224.23

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-013S	1 mL

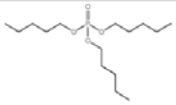
Tributyl phosphate (TBP)



CAS 126-73-8 MF $C_{12}H_{27}O_4P$ MW 266.31

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-009S	1 mL

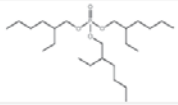
Tripentyl phosphate (TPeP)



CAS 2528-38-3 MF $C_{15}H_{33}O_4P$ MW 308.39

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-019S	1 mL

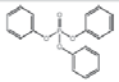
tris(2-Ethylhexyl) phosphate (TEHP)



CAS 78-42-2 MF $C_{24}H_{51}O_4P$ MW 434.63

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-028S	1 mL

Triphenyl phosphate (TPP, TPhP)

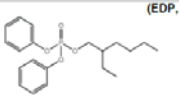


CAS 115-86-6 MF $C_{18}H_{15}O_4P$ MW 326.28

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-020S	1 mL

Ethylhexyl diphenyl phosphate

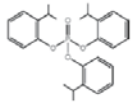
(EDP, DPEHP)



CAS 1241-94-7 MF $C_{20}H_{27}O_4P$ MW 362.40

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-007S	1 mL

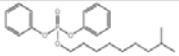
tris(2-Isopropylphenyl) phosphate



CAS 64532-95-2 MF $C_{27}H_{39}O_4P$ MW 452.52

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-014S	1 mL

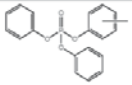
Isodecyl diphenyl phosphate



CAS 29761-21-5 MF $C_{22}H_{31}O_4P$ MW 390.45

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-008S	1 mL

Cresyl diphenyl phosphate (CDP)

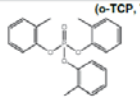


CAS 26444-49-5 MF $C_{19}H_{17}O_4P$ MW 340.31

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-004S	1 mL

Tri-o-cresyl phosphate

(o-TCP, TOCP, TOTP)



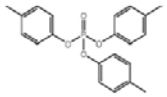
CAS 78-30-8 MF $C_{21}H_{21}O_4P$ MW 368.36

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-017S	1 mL

Phosphate Flame Retardants (PFRs)

Tri-p-cresyl phosphate

(p-TCP, TPCP, TPTP)

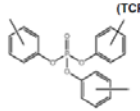


CAS 78-32-0 MF $C_{21}H_{21}O_4P$ MW 368.36

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-018S	1 mL

Tricresyl phosphate (mix of isomers)

(TCP, TCrP, TToP)

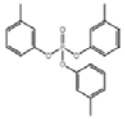


CAS 1330-78-5 MF $C_{21}H_{21}O_4P$ MW 368.36

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-011S	1 mL

Tri-m-cresyl phosphate

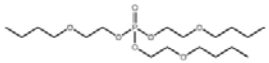
(m-TCP, TMTP)



CAS 563-04-2 MF $C_{21}H_{21}O_4P$ MW 368.36

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-015S	1 mL

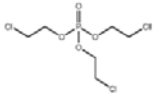
tris(2-Butoxyethyl) phosphate (TBEP)



CAS 78-51-3 MF $C_{18}H_{39}O_7P$ MW 398.47

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-022S	1 mL

tris(2-Chloroethyl) phosphate (TCEP)

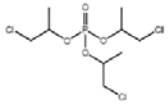


CAS 115-96-8 MF $C_6H_{12}Cl_3O_4P$ MW 285.49

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-024S	1 mL

tris(1-Chloro-2-propyl) phosphate

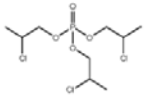
(TCPP)



CAS 13674-84-5 MF $C_9H_{18}Cl_3O_4P$ MW 327.57

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-025S	1 mL

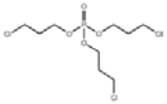
tris(2-Chloropropyl) phosphate



CAS 6145-73-9 MF $C_9H_{18}Cl_3O_4P$ MW 327.57

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-023S	1 mL

Tri(3-chloropropyl) phosphate (TCPP)

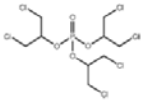


CAS 26248-87-3 MF $C_9H_{18}Cl_3O_4P$ MW 327.57

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-010S	1 mL

tris(1,3-Dichloro-2-propyl) phosphate

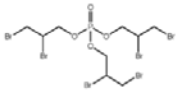
(TDCPP, TDCP)



CAS 13674-87-8 MF $C_9H_{15}Cl_6O_4P$ MW 430.98

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-027S	1 mL

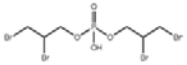
tris(2,3-Dibromopropyl) phosphate



CAS 126-72-7 MF $C_9H_{15}Br_6O_4P$ MW 697.61

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-026S	1 mL

bis(2,3-Dibromopropyl) phoshate

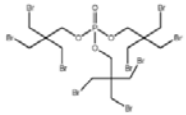


CAS 5412-25-9 MF $C_6H_{11}Br_4O_4P$ MW 497.74

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-002S	1 mL

tris(Tribromoneopentyl) phosphate

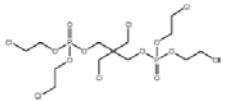
(TTBNP)



CAS 19186-97-1 MF $C_{15}H_{24}Br_9O_4P$ MW 1018.46

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-029S	1 mL

tetrakis(2-Chloroethyl)dichloro-isopentyl diphosphate (V6)

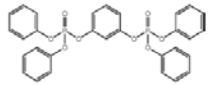


CAS 38051-10-4 MF $C_{13}H_{24}Cl_6O_8P_2$ MW 582.99

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-003S	1 mL

Resorcinol bis(diphenyl phosphate)

(RDP)

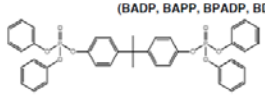


CAS 57583-54-7 MF $C_{30}H_{24}O_8P_2$ MW 574.45

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-030S	1 mL

Bisphenol A bis(diphenyl phosphate)

(BADP, BAPP, BPADP, BDP)



CAS 5945-33-5 MF $C_{36}H_{34}O_8P_2$ MW 692.63

Matrix	Cat. No.	Unit
100 µg/mL in Toluene	PFRS-001S	1 mL

www.accustandard.com/phosphate-flame-retardants/

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GC-MS/MS Settings	
Injection Volume	1 uL
GC Injector Temperature	250 C
GC Oven Program	Initial: 90 Hold 1 min Ramp 1: 15 C/min to 200C hold 3 min Ramp 2: 5 C/min to 250C Ramp 3: 15 C/min to 300C hold 6 min
GC Column	DB-5ms 30m x 250um x 0.25um
Transferline Temperature	280 C
MS Source	EI
Source Temperature	250 C
Collision Cell Gases	1.5 psi Nitrogen Collision & 2.25 Helium Quench
Quadrupole Temperature	150 C Q1 & 150 C Q2

Agilent 7000 Triple Quadrupole GC-MS System

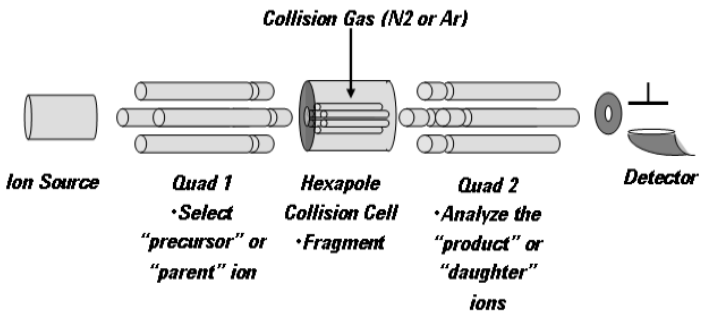
- Dust and Foam Sample analysis by both GC-MS & GC-MS/MS

GC-MS MRM Transitions Table

			Quantifier			Qualifier		
Compound Abbreviation	**Compound Name**	**RT**	**Precursor**	**Product**	**CE**	**Precursor**	**Product**	**CE**
dTnPP	Tri-propyl phosphate-d_{21}	5.994	151.1	103.1	5	199.2	103.1	5
TnPP	Tri-propyl phosphate	6.145	141.1	99	5	183.2	99	5
dTnBP	Tri-n-butyl phosphate-d_{27}	8.200	167.4	103	5	231.4	103	10
TnBP	Tri-n-butyl phosphate	8.340	155.3	99	5	211.4	99	5
dTCEP	Tris(2-chloroethyl) phosphate-d_{12}	9.235	261.3	196.1	5	261.3	131	10
TCEP	Tris(2-chloroethyl) phosphate	9.340	249.3	124.9	10	249.3	186.9	5
dTCPP	Tris(2-chloroisopropyl) phosphate-d_{18}	9.536	293.3	131	10	295.3	131.1	10
TCPP	Tris(1-chloro-2-propyl) phosphate	9.675	277.4	124.9	5	279.4	125	5
dTDCPP	Tris(1,3-dichloro-2-propyl) phosphate-d_{15}	17.430	394.3	164.1	15	396.3	164.1	15
TDCPP	Tris(1,3-dichloro-2-propyl) phosphate	17.691	381.2	159	15	383.2	159	15
dTPhP	Triphenyl phosphate-d_{15}	18.792	341.5	223.1	30	341.5	178.1	35
TPhP	Triphenyl phosphate	18.930	326.4	215	25	326.4	169	30
TBEP	Tris(2-butoxyethyl) phosphate	19.160	199	101.1	5	299.2	199.1	5
TEHP	Tris(2-ethylhexyl) phosphate	19.998	210.9	98.9	5	323.2	98.9	5
o-TCP	Tri-o-cresyl-phosphate	21.724	368.2	181.1	10	368.2	165.1	25
m-TCP	Tri-m-cresyl-phosphate	22.597	368.2	165.1	25	368.2	261.1	10
p-TCP	Tri-p-cresyl-phosphate	23.513	368.2	198.1	15	368.2	261.1	10
PCB209L	PCB209L	24.515	509.8	437.8	40	509.8	439.6	40
TDBPP	Tris(2,3-dibromopropyl) phosphate	25.896	216.8	137	5	218.8	137	5

MRM Transitions

- Standards
- MS1 Scan →Retention Time & Precursor Ion
- MS2 →Product Ion Scan
- MSMS → CE Optimization
    - 6 Labelled Compounds
    - 12 Native



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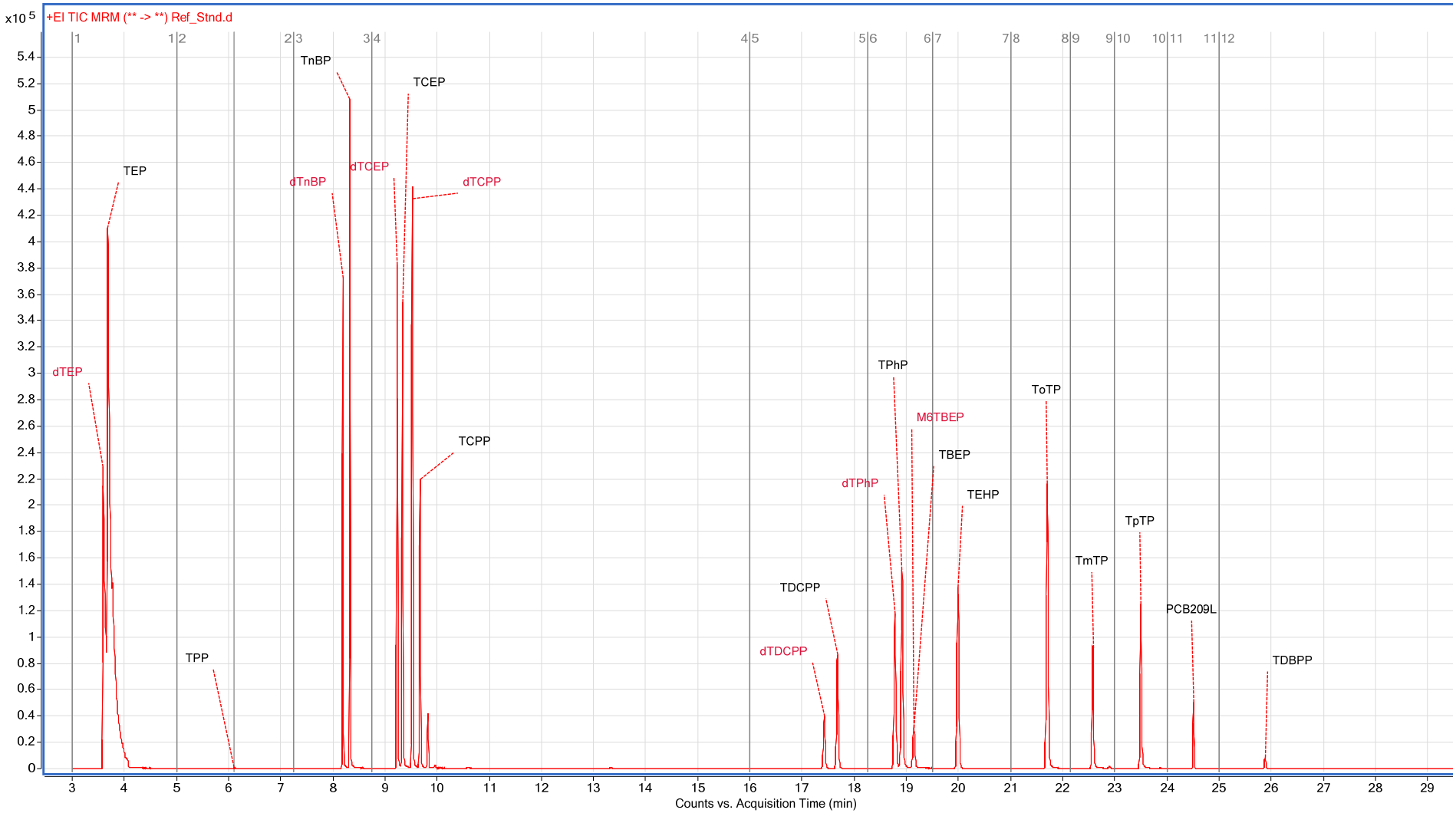
Reference Standard



- 250 pg/uL alkyl, 500 pg/uL chlorinated, 1000 pg/uL TBEP & TDBPP, 2000 pg/uL TEHP
  - TPP not included in initial standards
- TBEP, TDBPP and TEHP
  - Insource fragmentation w/high number of MS1 Fragments → lower abundance per fragment
  - Inlet breakdown w/multiple breakdown products, tris & bis(2-ethylhexyl) phosphate & cyclic /alkyl products

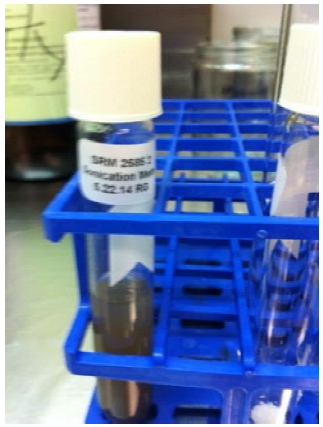
DUST SRM 2585

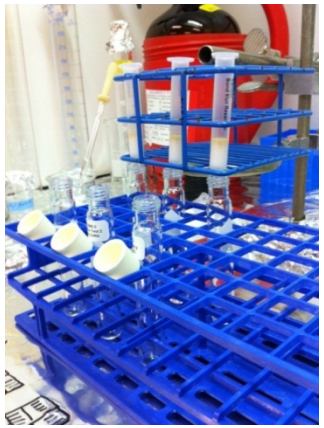
- Investigate the feasibility of OPFR analysis by Sonication Assisted Solvent Extraction followed by GC-MSMS

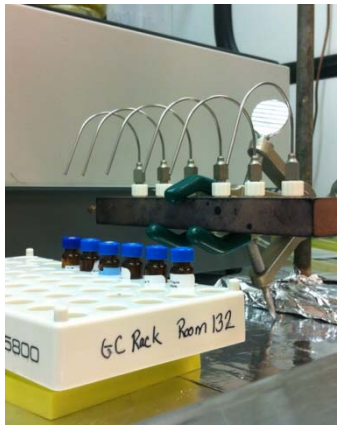
- SRM 2585 Organic Contaminants in House Dust[11]
  - Dust collected from homes and commercial sources (cleaning services, motels & hotels)
    - Vacuum cleaner Bags
    - North Carolina, Maryland, Ohio, New Jersey, Montana & Wisconsin (1993-94)
  - Certified Concentration Values:
    - 33 polycyclic aromatic hydrocarbons (PAHs)
    - 30 polychlorinated biphenyls congeners (PCB)
    - 4 chlorinated pesticides
    - 15 polybrominated diphenyl ether congeners (PBDE)
      - 3 – 5000 ug/Kg (ppb) certified analyte conc. range
      - Additional 58 reference conc. values + 9 information conc.. Values

- No certification for OPFRs

SRM 2585 - Primary & Secondary Extraction





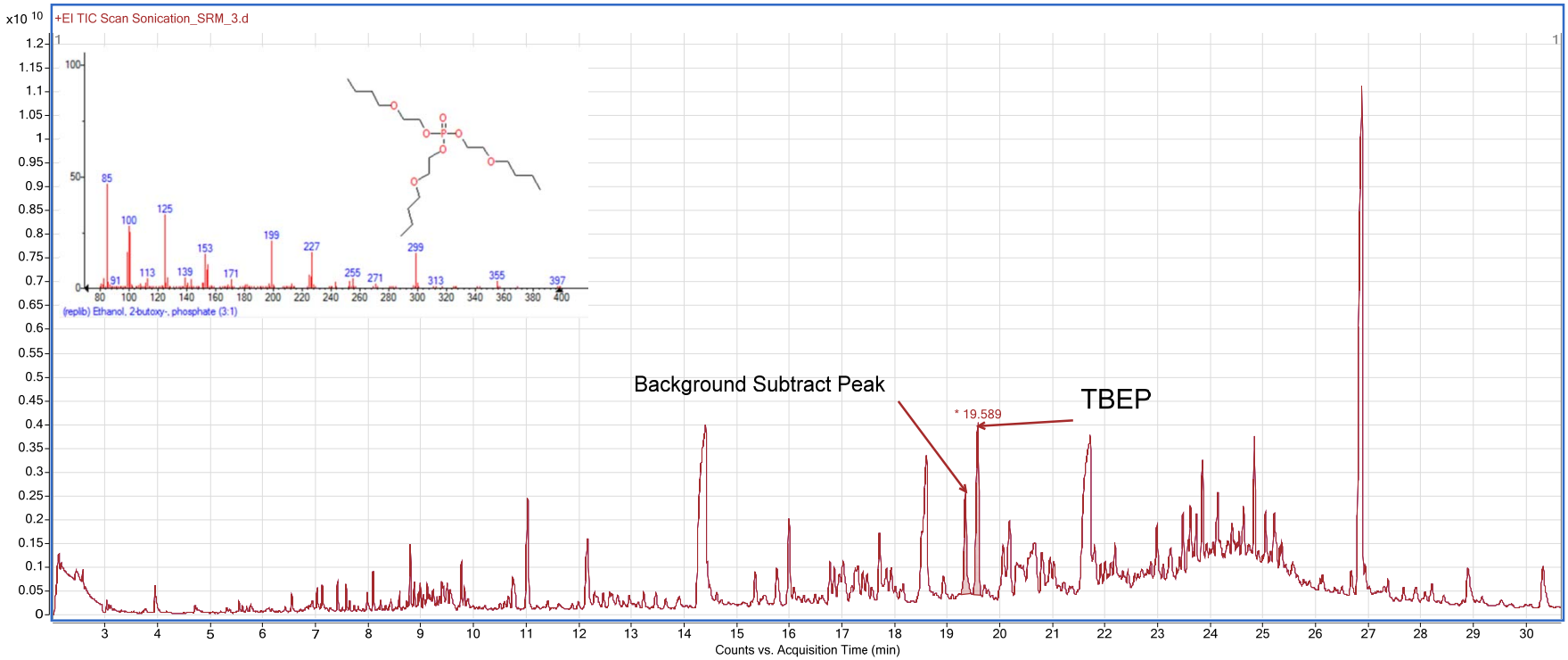


50 mg SRM → Vortex/Sonication/Centrifuge → Evaporation → Florisil Column → Evaporation → QqQ

↓ 2nd Extraction SRM & Na_2SO_4

Vortex/Sonication/Centrifuge → Evaporation → Florisil Column → Evaporation → QqQ

Full Scan SRM 2585



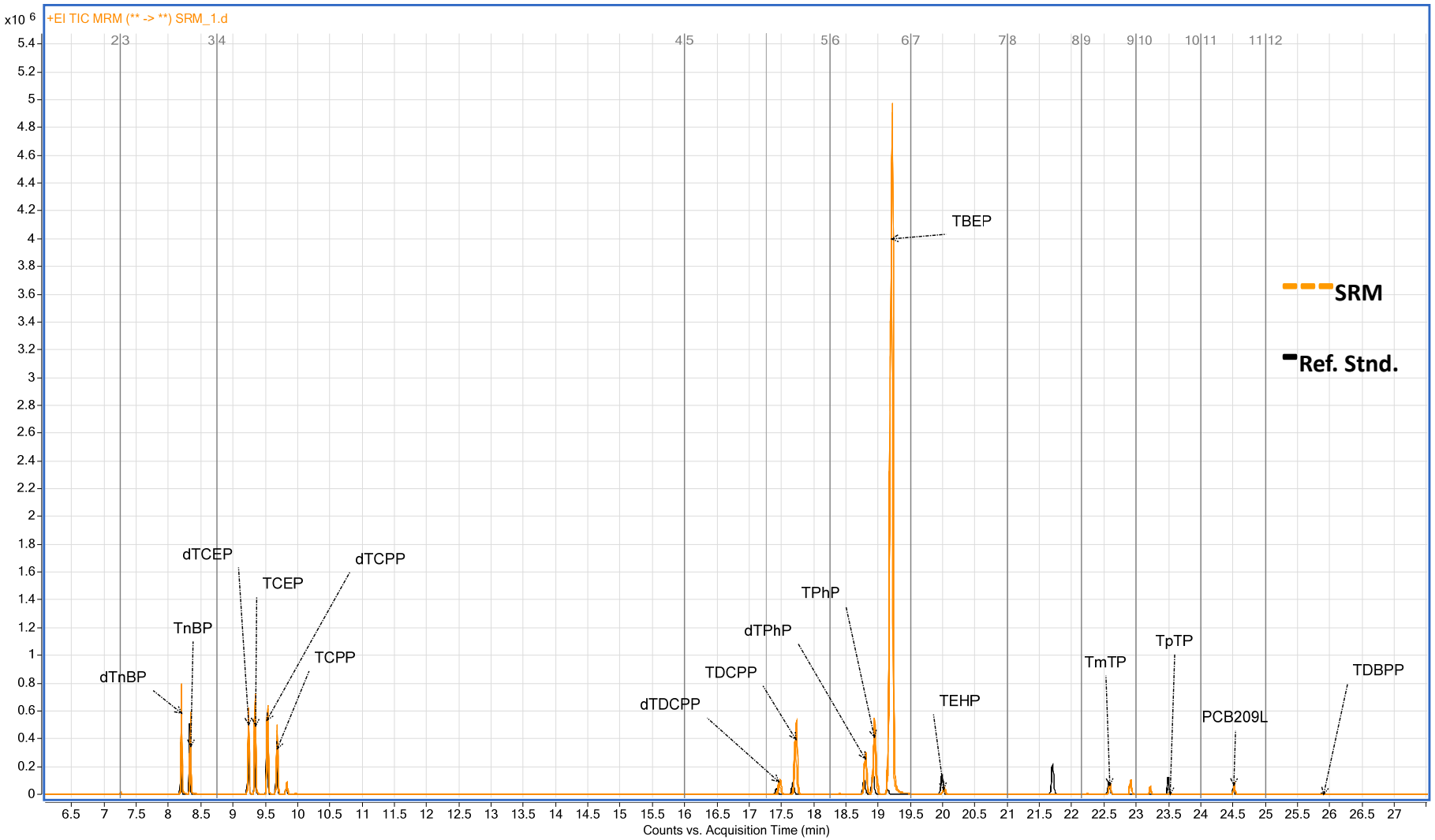
#	Lib	Match	R Match	Prob. (%)	Name
1	R	652	729	82.4	Ethanol, 2-butoxy-, phosphate (3:1)
2	R	646	722	82.4	Ethanol, 2-butoxy-, phosphate (3:1)
3	R	618	752	82.4	Ethanol, 2-butoxy-, phosphate (3:1)
4	M	609	688	82.4	Ethanol, 2-butoxy-, phosphate (3:1)
5	M	562	576	7.04	Morphinan-3-ol-6-one, 4,5-epoxy-N-formyl-, (5α)-
6	M	529	545	1.84	Ruthenium, 1,3-butadiene-1,4-dicarboxylic acid, diethyl ester-tricarbony
7	M	514	537	1.11	Morphinan-6-one, N-formyl-4-methoxy-
8	M	507	595	0.85	3-Cyclopentene-1,2-dicarboxylic acid, 4-trimethylsilyloxy-, diethyl ester,
9	M	504	519	0.75	Metopon
10	R	503	518	0.75	Metopon
11	R	489	506	0.45	Hydrocodone
12	M	484	494	0.36	(5Alpha)-7,8-didehydro-4,5-epoxy-3-methoxy-17-methylmorphinan-14-ol
13	M	481	570	0.32	6-Methyl-2-oxo-4-(3-trifluoromethyl-phenyl)-1,2,3,4-tetrahydro-pyrimidine
14	M	480	493	0.31	Morphinan-6-one, 4,5-epoxy-2-methoxy-N-methyl-, (5α-
15	M	478	542	0.28	Pyridine-3-carbonitrile, 1,2-dihydro-4-(4,5,6,7-tetrahydro-benzothien-2-yl

- 50 mg SRM 2585
- MS1 Scan (80-550) of SRM 2585

- Tris (2-butoxyethyl) phosphate (TBEP) – detected in Sonication SRM dust sample
  - Retention Time 19.5
  - NIST Library probability ~ 82.4% with background subtraction

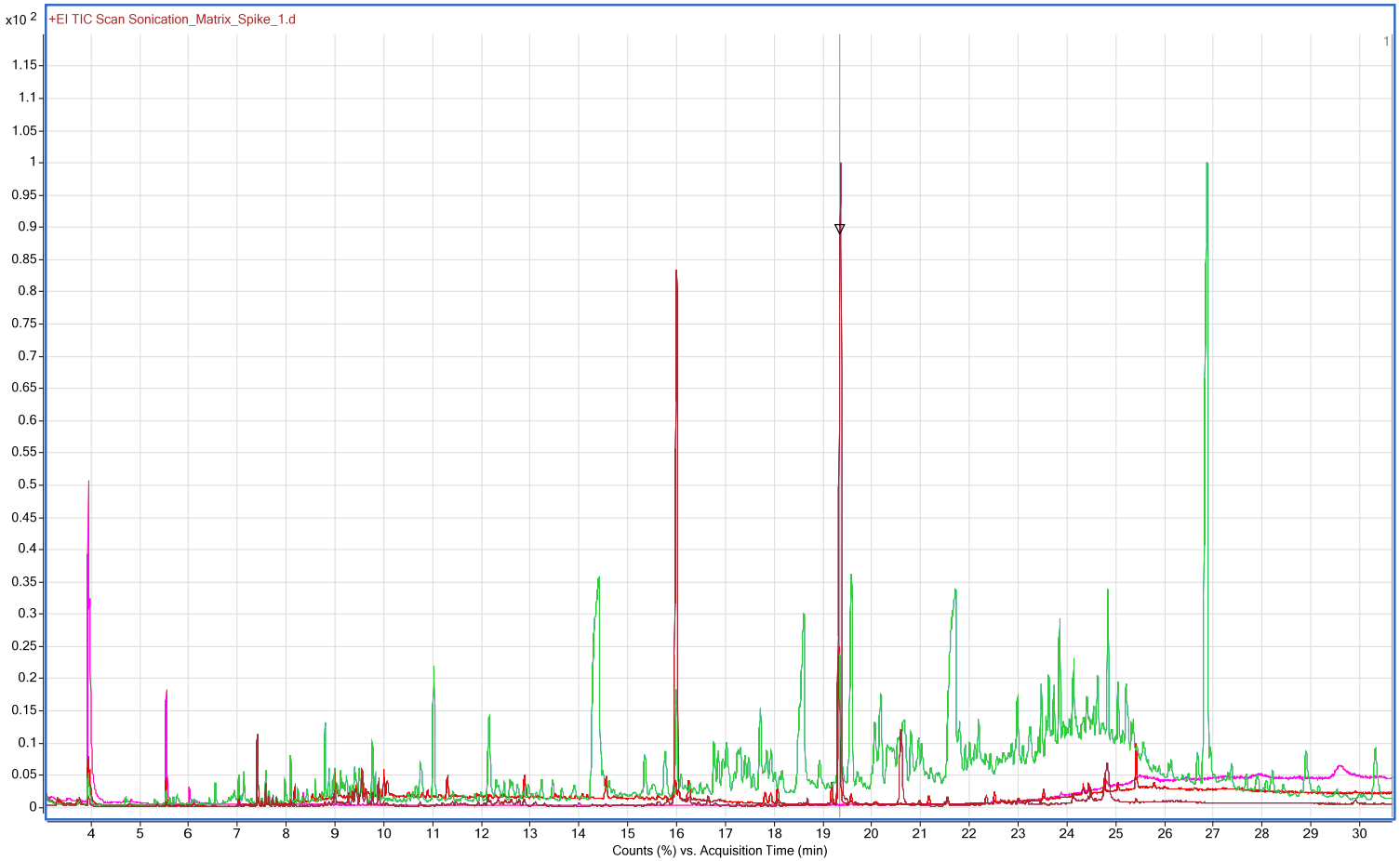
- Other analytes are difficult to detect with Scan
  - Use MRM method

GC-MS/MS SRM 2585



- SRM 2585 matrix background is reduced
  - Native analytes and Standards detected
    - TBP, TCEP TCPP, TDCPP, TPhP, TBEP & TEHP

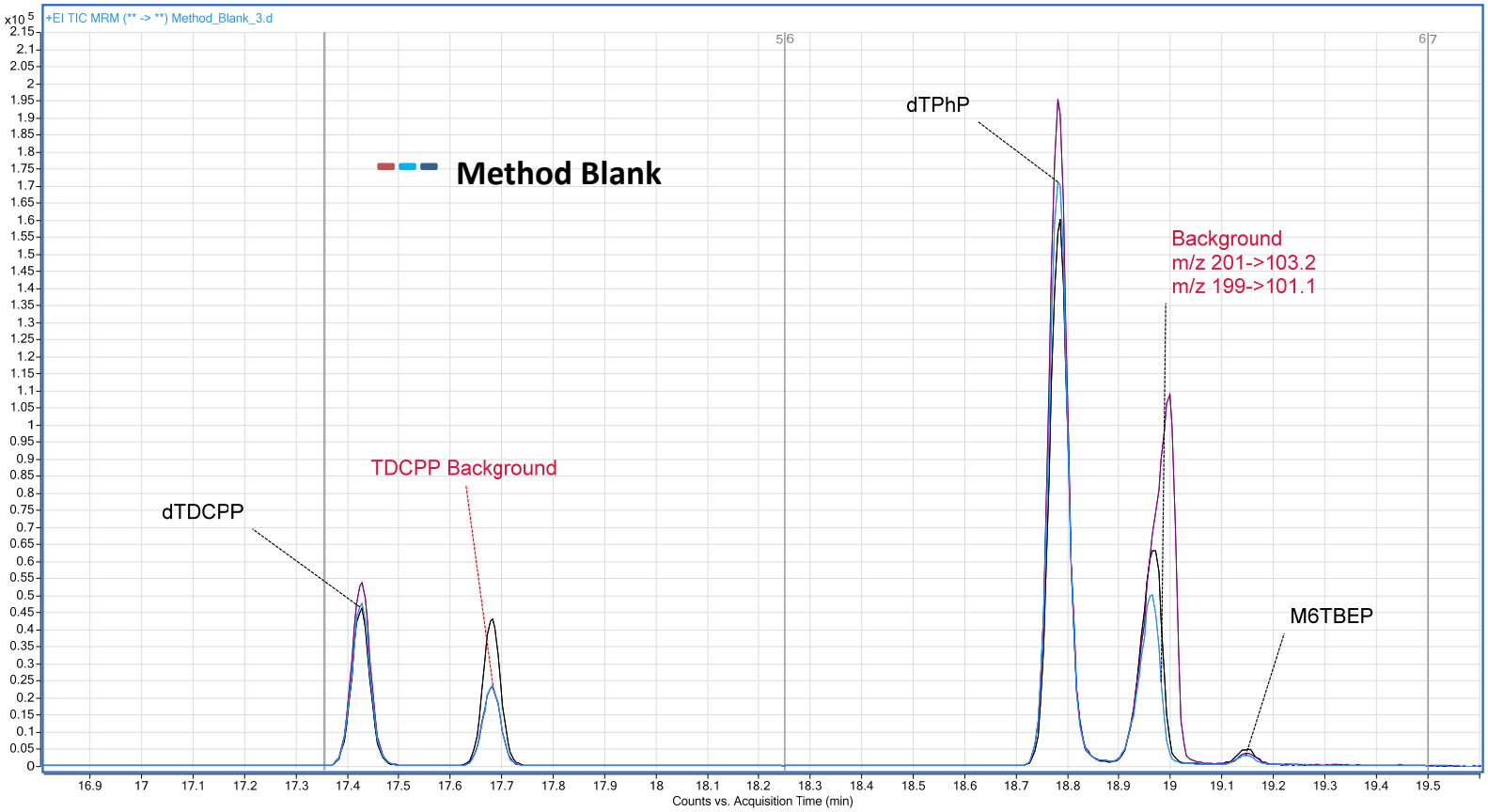
Other Background Sources



- SRM
- Matrix Spike
- Ref. Stnd.
- Isooctane

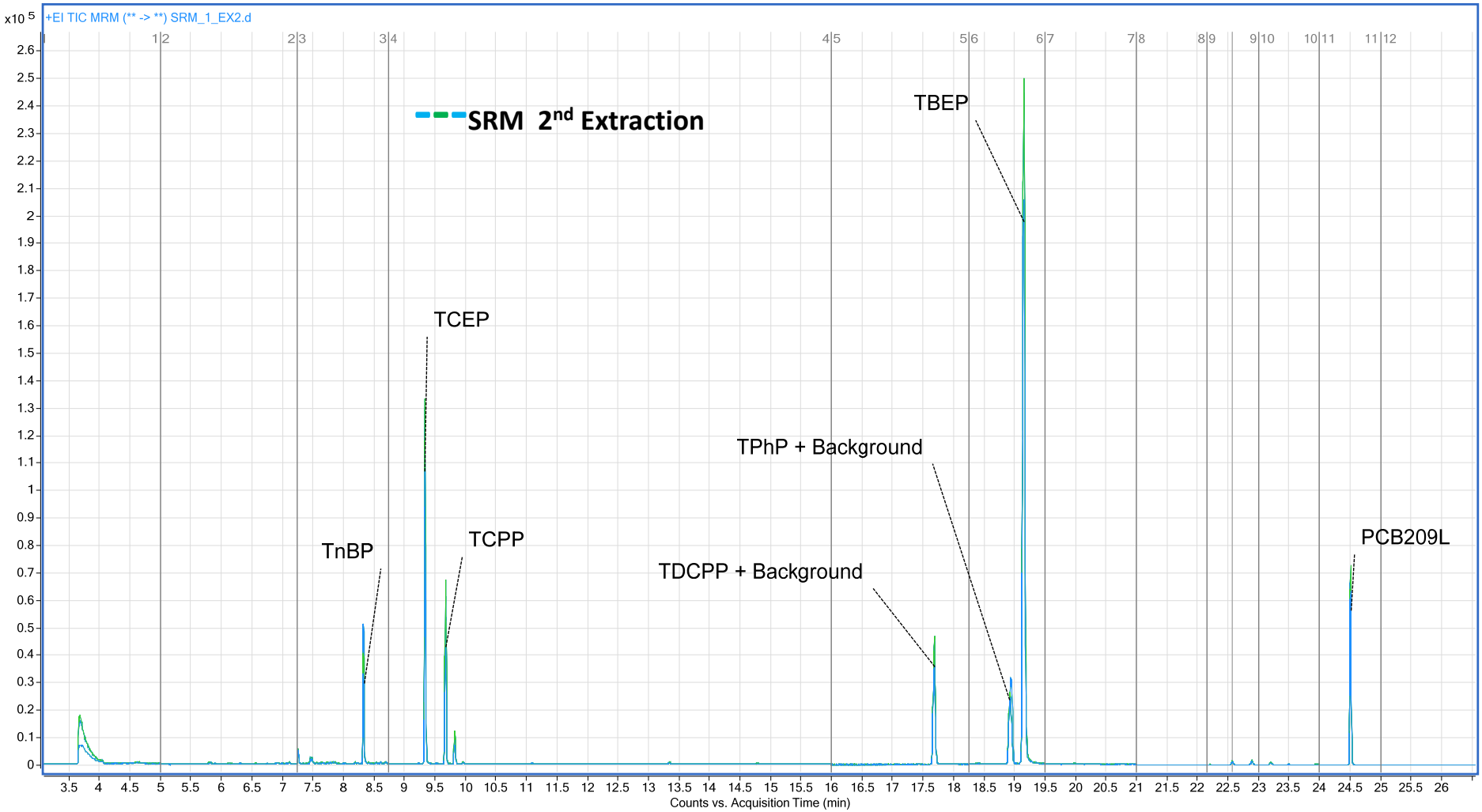
- Matrix – Dust Primary Contributor
  - Instrumentation - Extraction Secondary Contribution
  - Peaks at 16 and 19.5 minutes from Florisil
    - **Wash Florisil with Hexane:Acetone and Bake at 500C, store at 150C**

Background Contributions



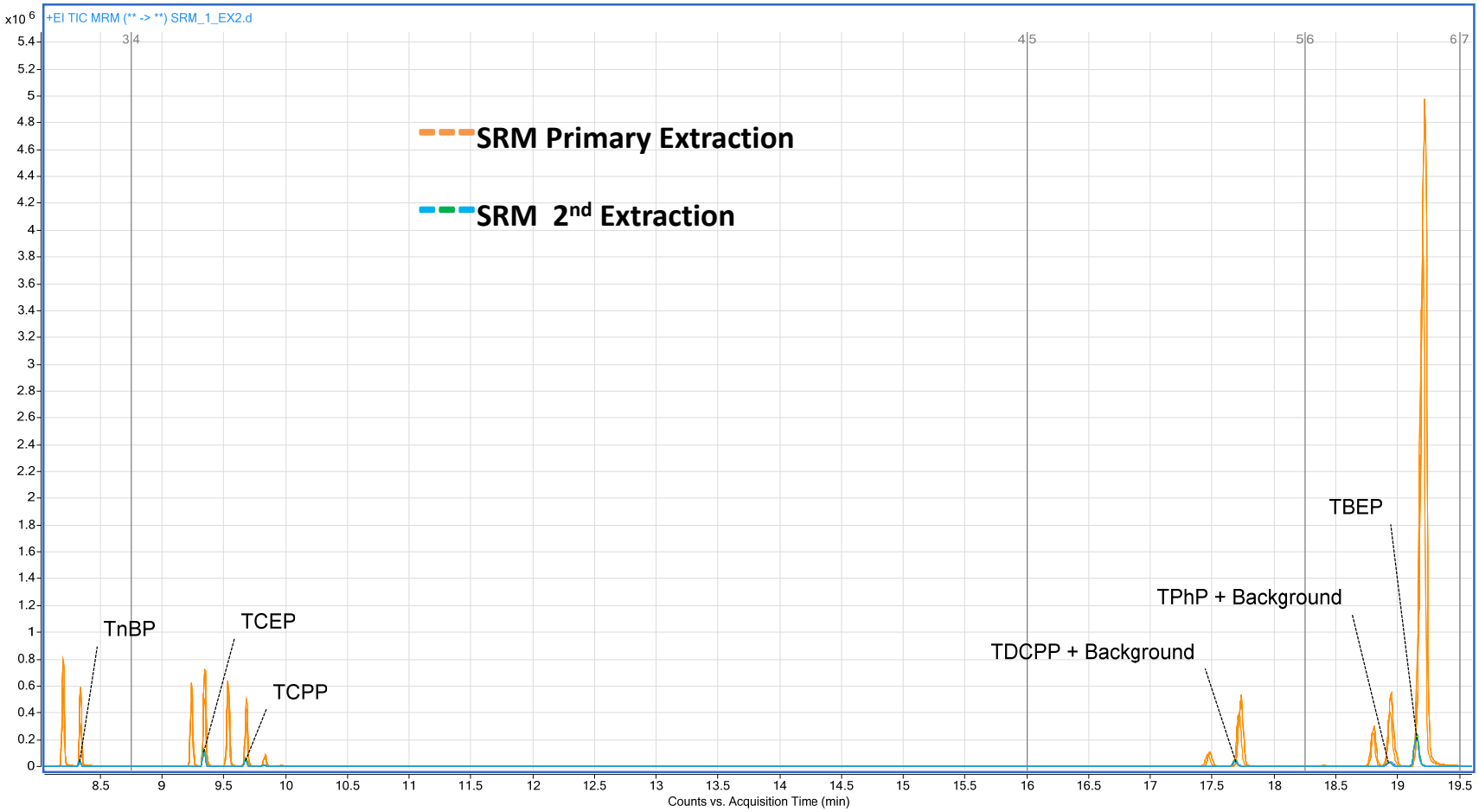
- TDCPP - Lab background / equipment, difficult to eliminate
  - Blank correct final results
- Florisil background at 18.95 min (TBEP RT 19.16) and matching transition
  - Wash Florisil with Hexane:Acetone / bake at 500C before use → Background is reduced
    - Retention time window is different (post solvent rinse overlap is eliminated)
    - Ion Qual/Quant ratio to authenticate
      - » Post solvent wash contaminate < 8% abundance of TBEP dust
    - Method Blanks

Second Extraction Cycle SRM



- 2nd Extraction Cycle for SRM
  - **Note that all compounds not Extracted are Native** → indicating some level of binding/mass transfer process
  - Surrogate (labelled compounds) are completely transferred in primary Extraction → indicating limited/no binding/mass transfer process

2nd Extraction Cycle SRM



Analyte	2nd Extraction Relative average Abund./Total Relative Abund. (%)
TBP	9.7
TCEP	17.5
TCPP	14.5
TDCPP	9.3
TPhP	3.8
TBEP	5.8

Additional Method Development Experiments

- ASE Comparison
- Florisil Background
    - 500C bake, solvent rinse & MF
- Extraction Tubes
    - 500C bake, solvent rinse & MF
- Solvent miscibility of standards
- Test for Extraction Efficiency based on 3 cycles
  - Increase sonication time/additional cycle
- Recovery of low boilers
  - Eliminate evaporation to dryness steps
    - High volatility of low boilers (TBP, TPP, TCEP, TCPP)
- Test for loss of analytes during fractionation
    - Hexane fraction was tested and no lose of analytes observed
- Retention of analytes on Florisil
    - Additional ethyl acetate eluent added to Florisil column, showed no retention
- Investigation of low responding compounds
    - TDBPP for break down (single RT & multiple fragments in MS1 scan)
    - TEHP for break down (multiple RT (cyclization of alkyl groups, BEHP & TEHP and multiple fragments in MS1 scan)
    - TBEP for break down (single RT and multiple fragments in MS1 scan)
      - Checked different Transitions pairs for increased detection

Surrogate Recovery

Compound	Method Blank Average % Surrogate Recovery	MB Standard Deviation	Matrix Spike Average % Surrogate Recover	MS Standard Deviation	SRM (DUST) Average % Surrogate Recovery	SRM Standard Deviation
dTBP	**34.99**	5.81	**40.2**	16.1	**106.7**	18.04
dTCEP	**50.78**	5.26	**59.4**	10.3	**92.6**	3.65
dTCPP	**54.80**	13.24	**68.0**	11.7	**92.3**	5.52
dTDCPP	**89.52**	1.23	**100.4**	7.0	**152.6**	16.96
dTPhP	**107.47**	0.99	**116.6**	2.0	**149.0**	6.92

- Higher recovery for SRM
- Lower Recovery for Na_2SO_4 Spiked MB and MS
  - SRM acts as keeper
  - Evaporation to 100uL rather than dryness
    - **Showed 30-40% increase in recovery**

%recovery = [(MB/PCB209L)/(Ref.Stnd./PCB209L)]*100
%average recovery is over three replicates for each of MB, MS and SRM

Mean value (Standard Deviation) of OPFRs Measured in Matrix Spike

Compound	Average Matrix Spike ng/g Na_2SO_4	Calculated Value ng/g Na_2SO_4	Accuracy
TEP	610 (77)	492	124
TBP	457 (9)	492	93
TCEP	880 (11)	984	89
TCPP	973 (50)	984	99
TDCPP	1125 (50)	984	114
TPhP	599 (54)	984	61
TBEP	1858 (83)	1969	94
TEHP	4608 (504)	3937	117
o-TCP	782 (15)	984	79
m-TCP	1129 (40)	984	115
p-TCP	1022 (97)	984	104
TDBPP	1104 (97)	1969	56

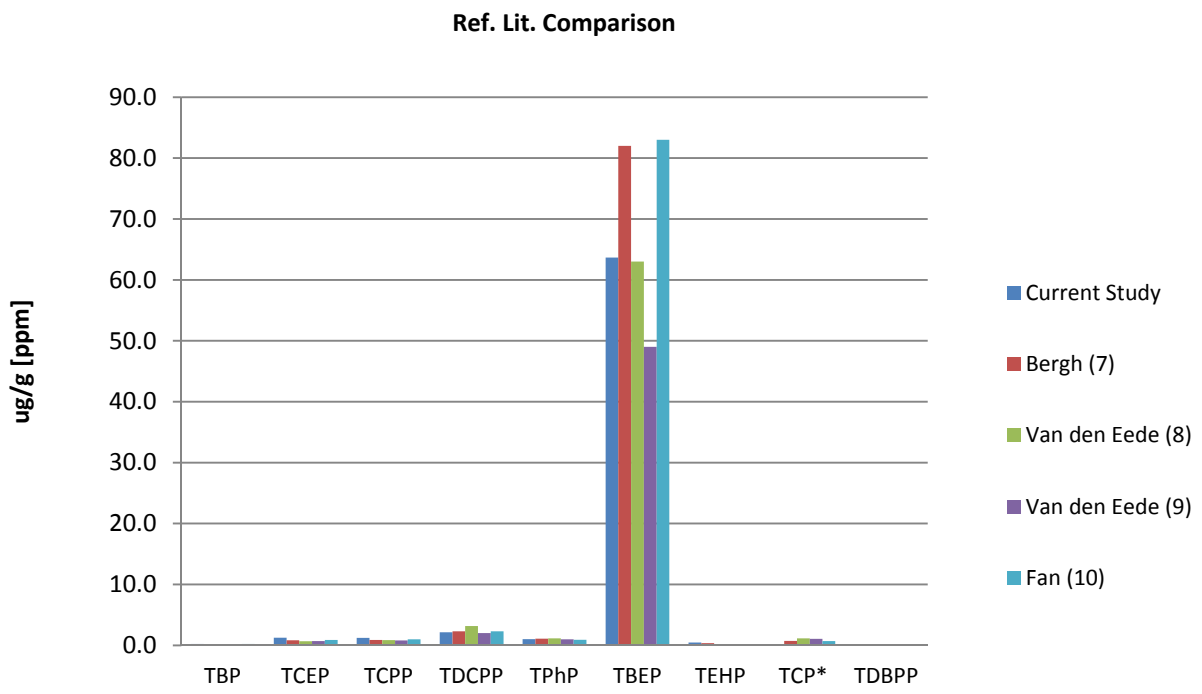
$$\frac{\frac{TPhP_{RefSd}}{dTPhP_{RefSd}}}{[Conc._{TPhP\ RefSd}]} = \frac{\frac{TPhP_{SRM}}{dTPhP_{SRM}}}{[\boldsymbol{Conc._{TPhP\ SRM}}]}$$

$$\frac{\frac{TEHP_{RefSd}}{dTPhP_{RefSd}}}{[Conc._{TEHP\ RefSd}]} = \frac{\frac{TEHP_{SRM}}{dTPhP_{SRM}}}{[\boldsymbol{Conc._{TEHPSRM}}]}$$

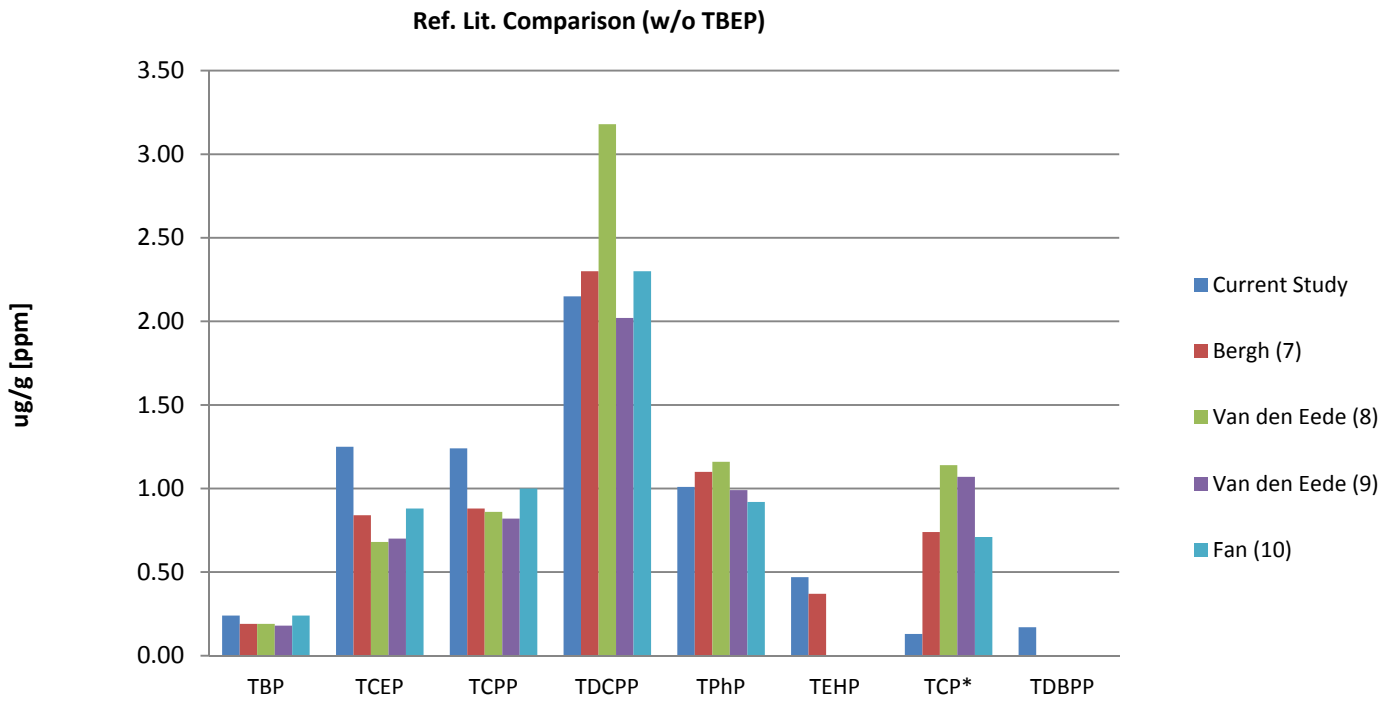
Mean value (Stdev) of OPFRs Measured in SRM 2585
Comparison to Reference Literature

	This Study		Bergh et al.[7]		Van den Eede et al.[8]		Van den Eede et al.[9]		Fan et al. [10]	
Analyte	Avg (ug/g)	Stdev (ug/g)	Avg (ug/g)	Stdev (ug/g)	Avg (ug/g)	Stdev (ug/g)	Avg (ug/g)	Stdev (ug/g)	Avg (ug/g)	Stdev (ug/g)
TBP	0.24	0.04	0.19	0.02	0.19	0.01	0.18	0.02	0.24	0.04
TCEP	1.25	0.02	0.84	0.06	0.68	0.06	0.70	0.17	0.88	0.12
TCPP	1.24	0.07	0.88	0.14	0.86	0.07	0.82	0.10	1.00	0.15
TDCPP	2.15	0.06	2.30	0.28	3.18	0.07	2.02	0.26	2.30	0.16
TPhP	1.01	0.07	1.10	0.10	1.16	0.14	0.99	0.07	0.92	0.13
TBEP	63.66	0.40	82.00	6.50	63.00	0.20	49.00	9.60	83.00	6.90
TEHP	0.47	0.02	0.37	0.04	-	-	-	-	-	-
TCP*	0.13	0.01	0.74	0.11	1.140	0.030	1.070	0.110	0.710	0.080
TDBPP	0.17	0.08	-		-	-	-	-	-	-

*Includes Ortho, Para and Meta Isomers



Mean value (Stdev) of OPFRs Measured in SRM 2585 Comparison to Reference Literature



TCEP & TCPP are higher than Ref. Lit. values
TCP is lower than Ref. Lit. values

- Method Changes tighten up results

- Five Samples from (BEARHFTI)
  - Visual inspection for color, adhesive, mixture of different types of foam (homogeneity)
- Sample Screening
  - Extract 50 mg foam with 10 mL DCM
  - Vortex 1 minute & Sonication for 10 minutes
    - Remove liquid layer with pasteur pipette
  - Add 100 uL of DCM Foam Extract to 9.9 mL DCM and vortex
    - **100x dilution**
      - **Further dilutions maybe needed if high concentration is found**
      - **No dilution of extract (if 100x shows no Flame Retardant)**
  - Transfer 80 uL of 100x Dilution to GC vial
      - (aliquot 80 uL 100x Extract, add 10 uL IS Surrogate and 10uL PCB209L)
    - Analyze on GCMS
      - Scan & MRM

Physical Appearance

Sample A

Sample B

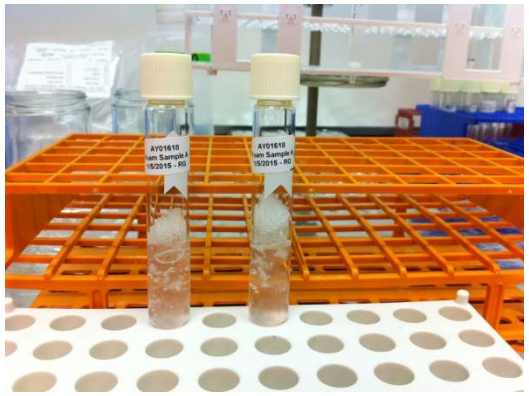
Sample C

Sample D

Sample E

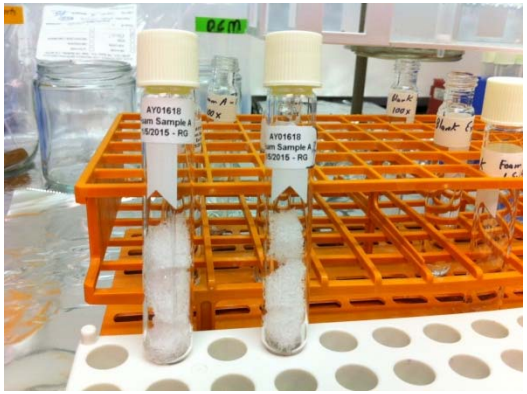
Sample Screening

Sample A

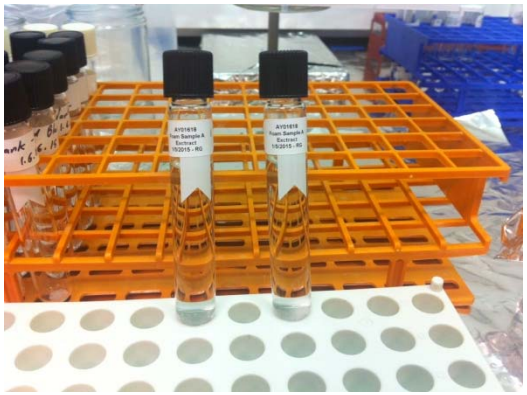


Extract 50 mg foam with 10 mL DCM

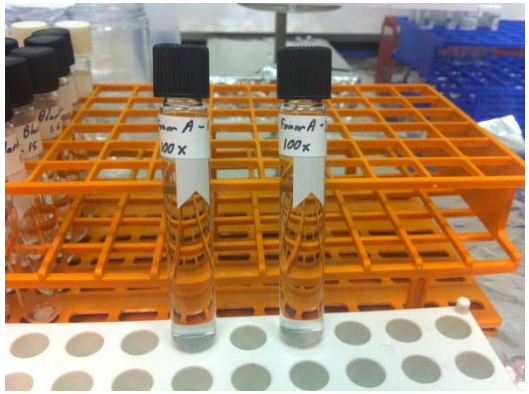
- Vortex/Sonication
- Further Testing Required to Test Extraction Efficiency



Remove liquid phase with pasteur pipette



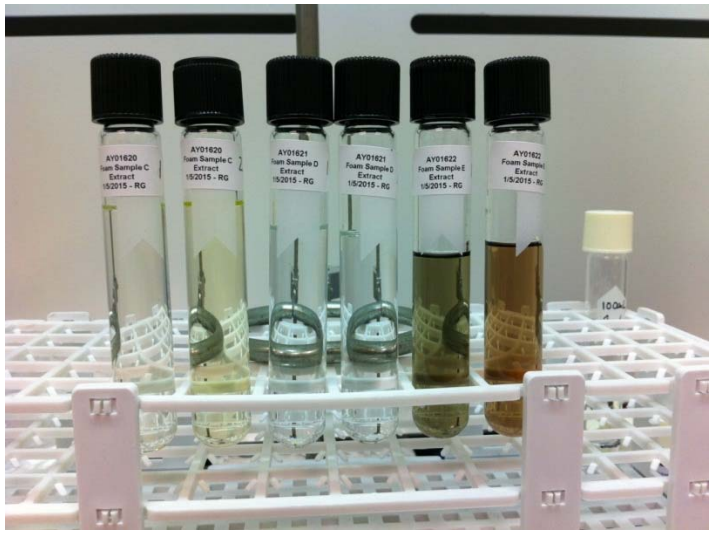
100 uL of DCM Foam Extract to 9.9 mL DCM (100x)



80 uL 100x Extract + 10 uL IS Surrogate + 10uL PCB209L

Final GC Vial Dilution 125x

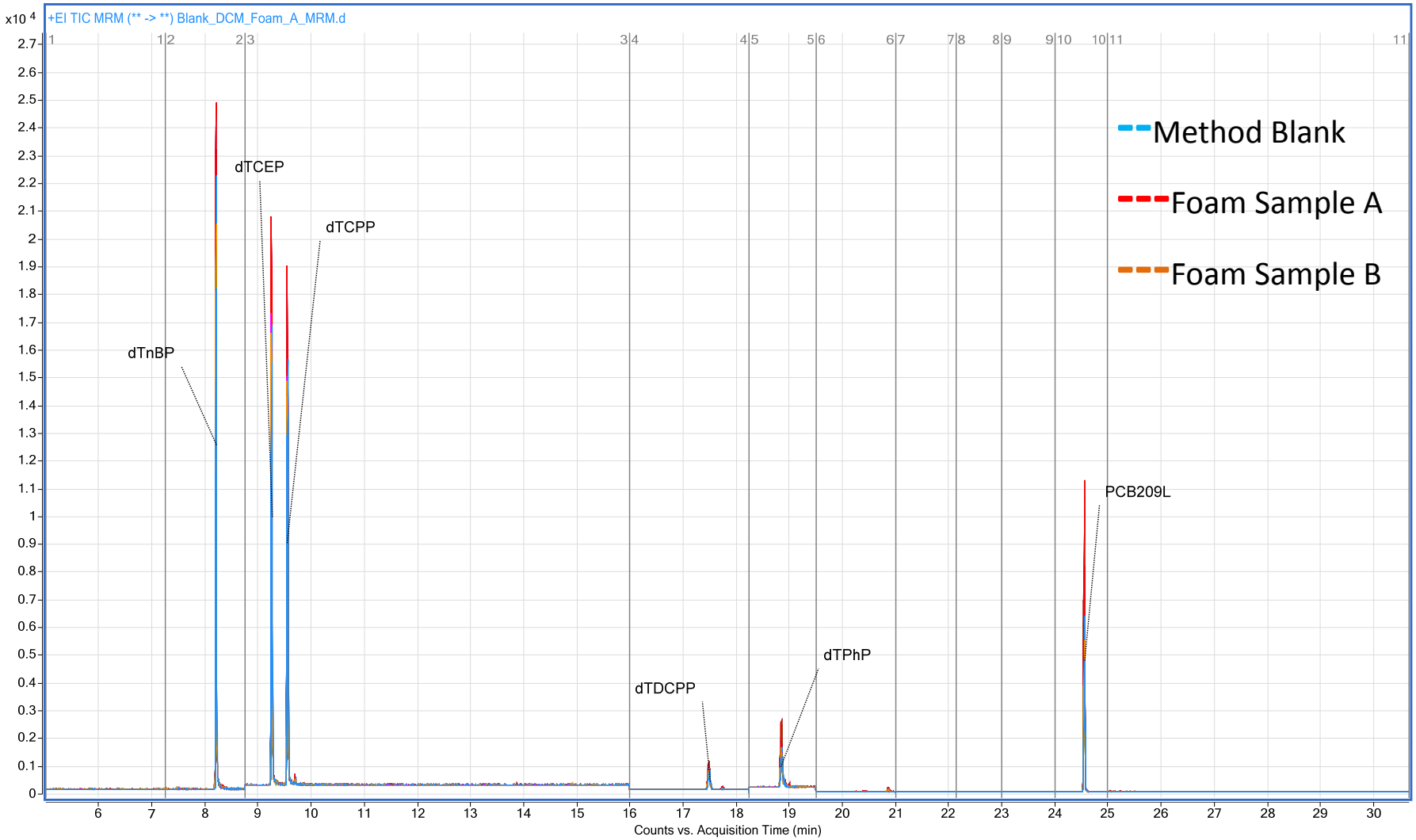
Sample C, D, & E Duplicate Extracts



Sample E

- multi component foam/compressed together or adhesive?
  - Cloth, Fibers, plastic mesh, different color foam
    - Possibly recycled material
- Difficulty in sampling heterogeneous foam sample
  - Extract for Sample and Duplicate have different color
  - Increased sample size to 200 mg
    - increasing sample size may decrease sample variability

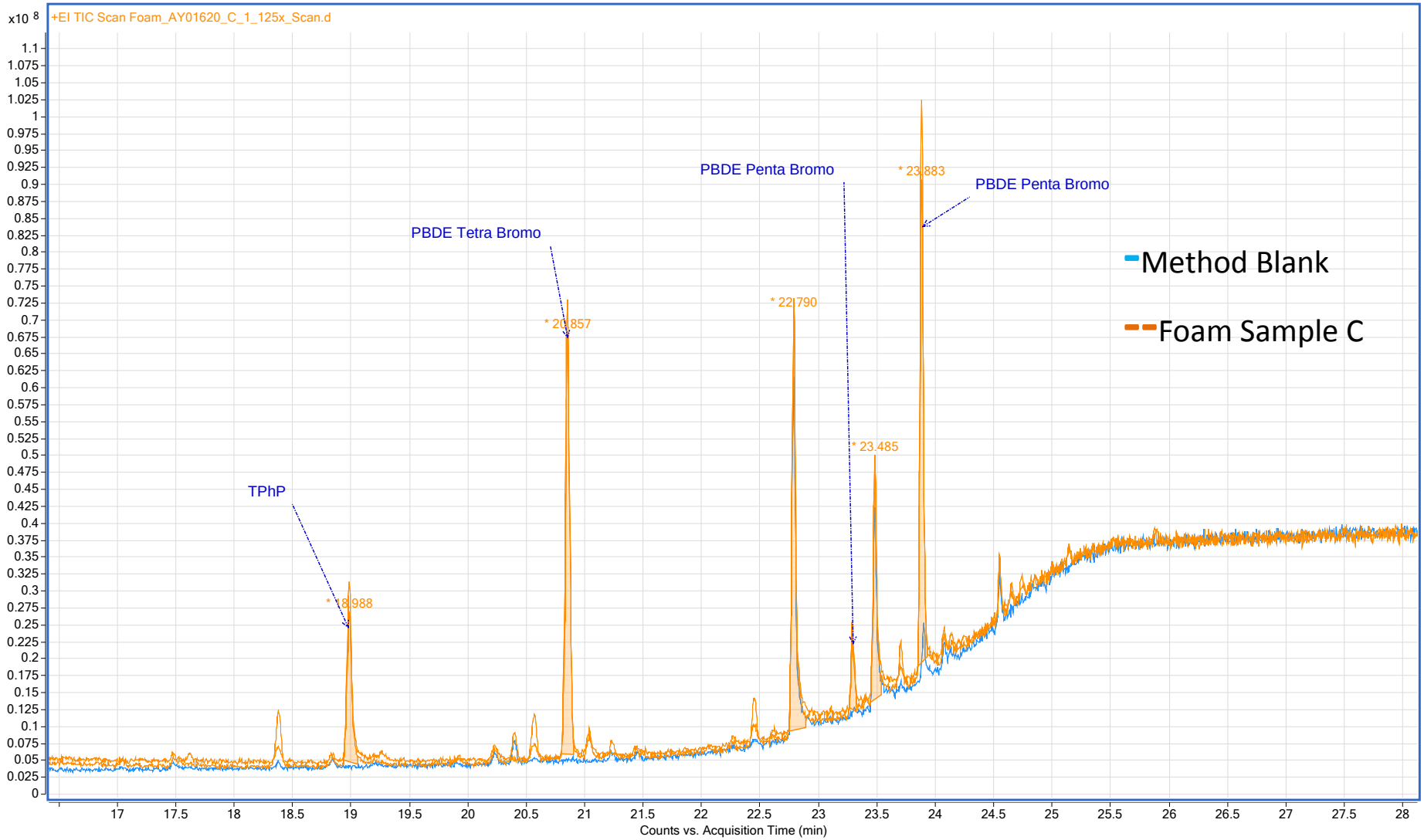
MRM - Foam Samples A & B



MRM & Scan of Foam Samples A & B show no evidence for select OPFRs

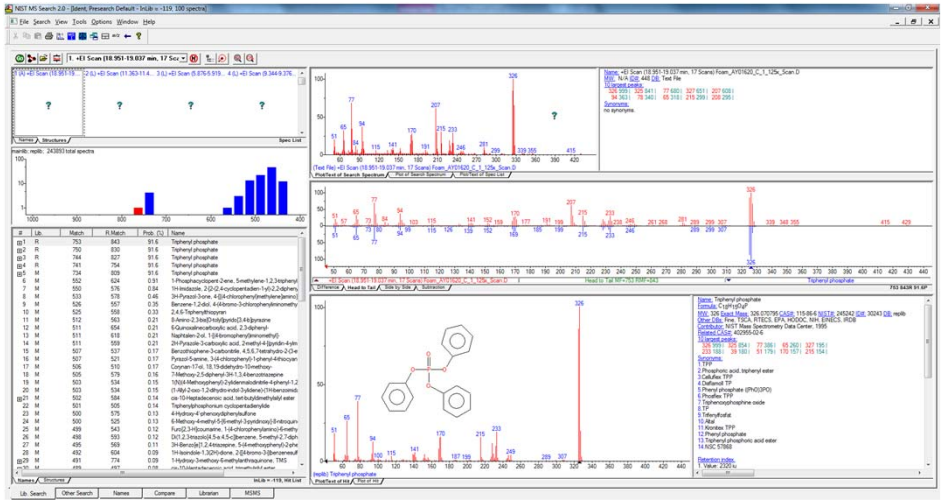
- 125x (n=2), 1.25x (n=1)
- Overlaid with Na_2SO_4 method blank (n=2)

Foam Sample C – unknown analysis

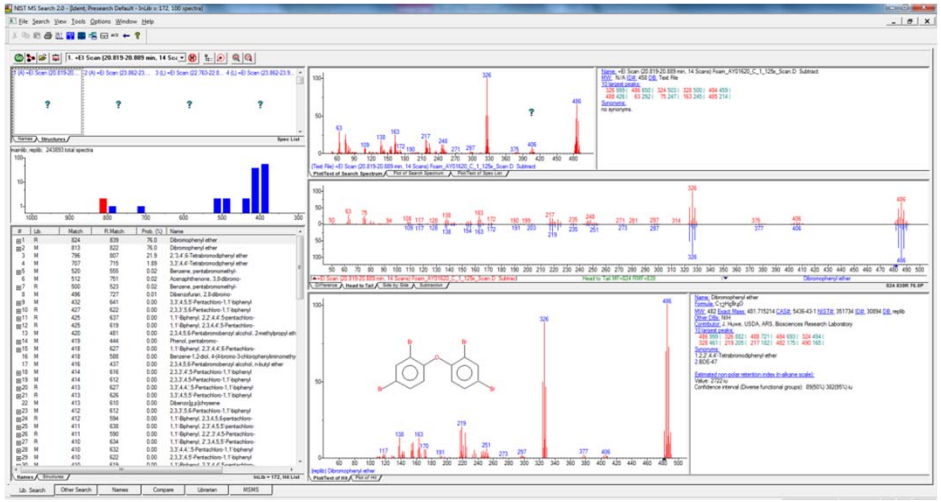


- TPhP Full Scan NIST Library - TPhP 91.6% Probability
- PBDE (Tetra and Penta also detected, NIST Probability)
    - 76.0% PBDE (Tetra Bromo), 54.4% & 66.7% PBDE (Penta Bromo)

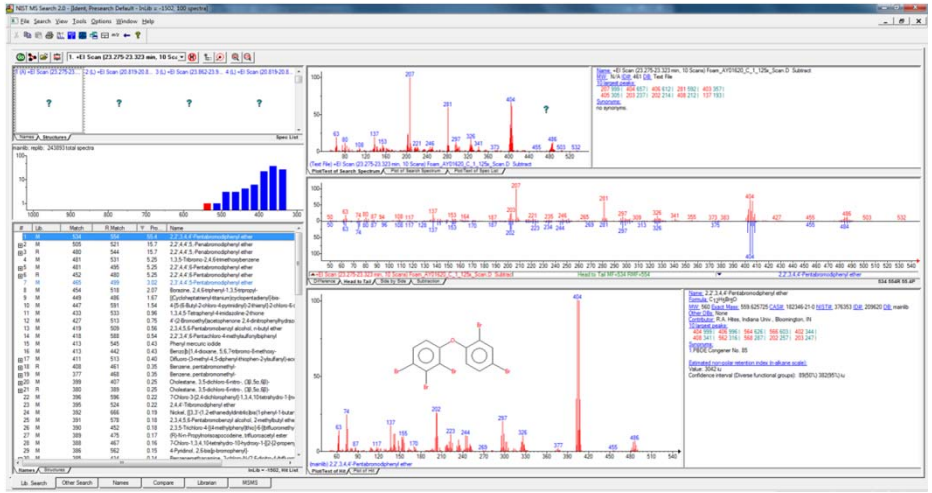
Sample C – Unknown NIST Data



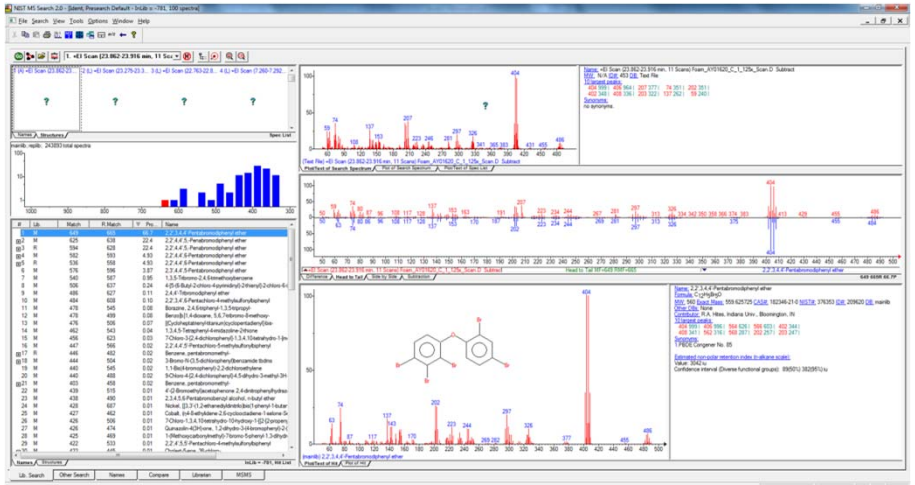
- 91.6% TPhP



- 76.0% PBDE (Tetra Bromo)

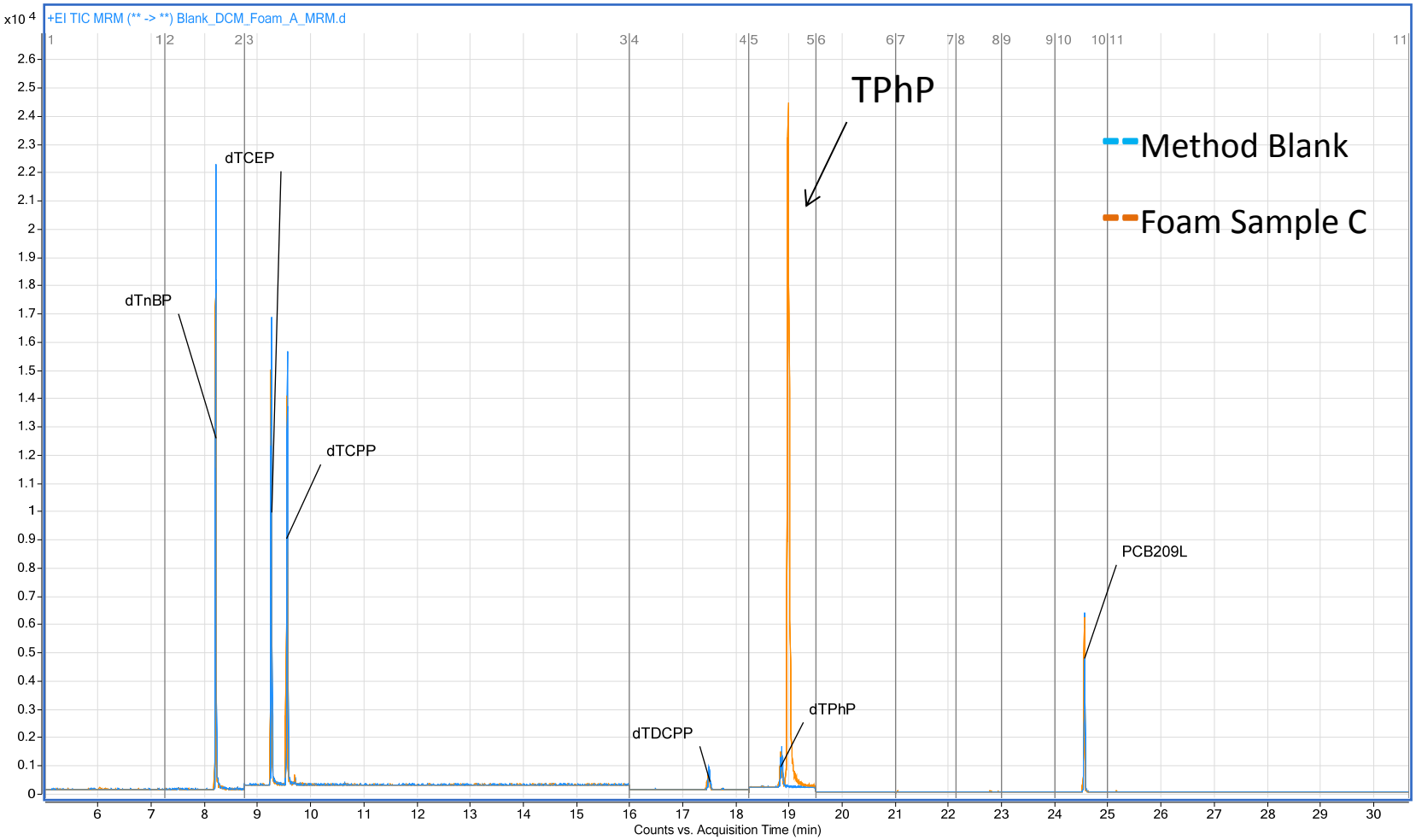


- 55% PBDE (Penta Bromo)



- 66.7% PBDE (Penta Bromo)

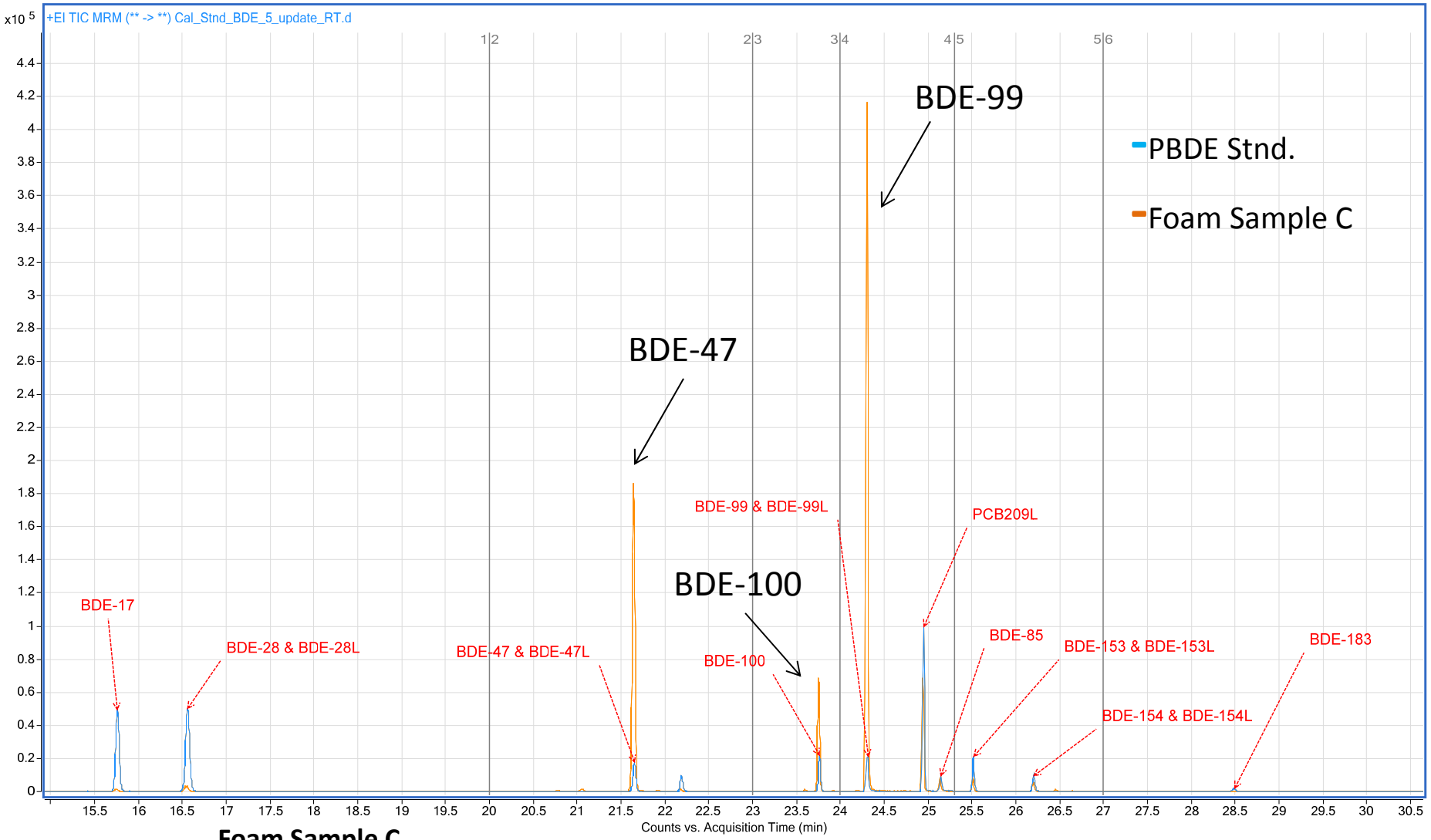
Foam Sample C



Foam Sample C

- TPhP detected
- MRM - 125x dilution of Foam DCM Extract (n=2)
  - 10965 ug/g foam (1.1% TPhP)

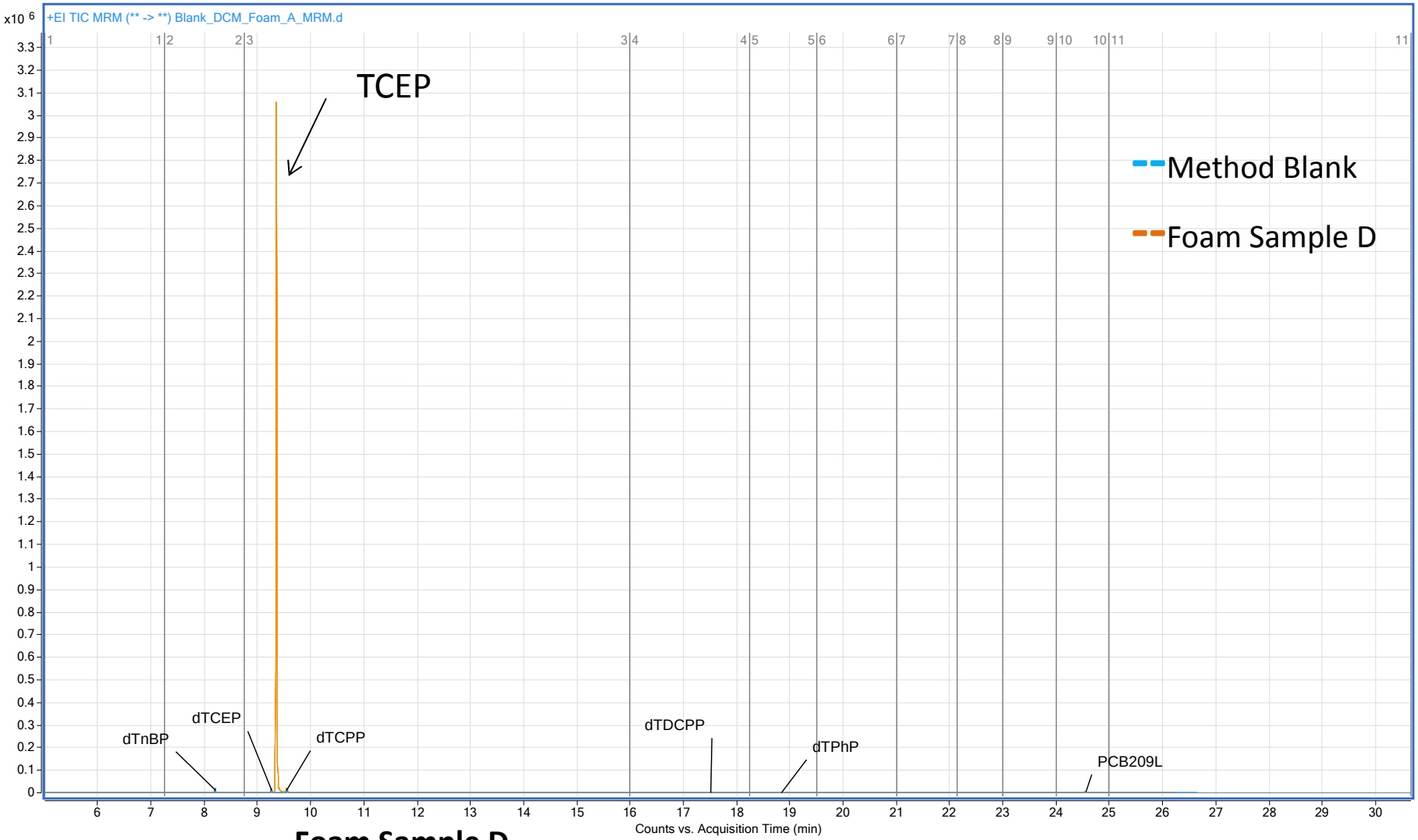
POPs QqQ PBDE Method – Sample C



Foam Sample C

- BDE-47, BDE-100 BDE-99
  - Compares well with composition of commercial technical mixture
- **PBDE MRM Method** - 125x dilution of Foam DCM Extract
  - 67705 ug/g foam (6.7% PBDE)

Foam Sample D



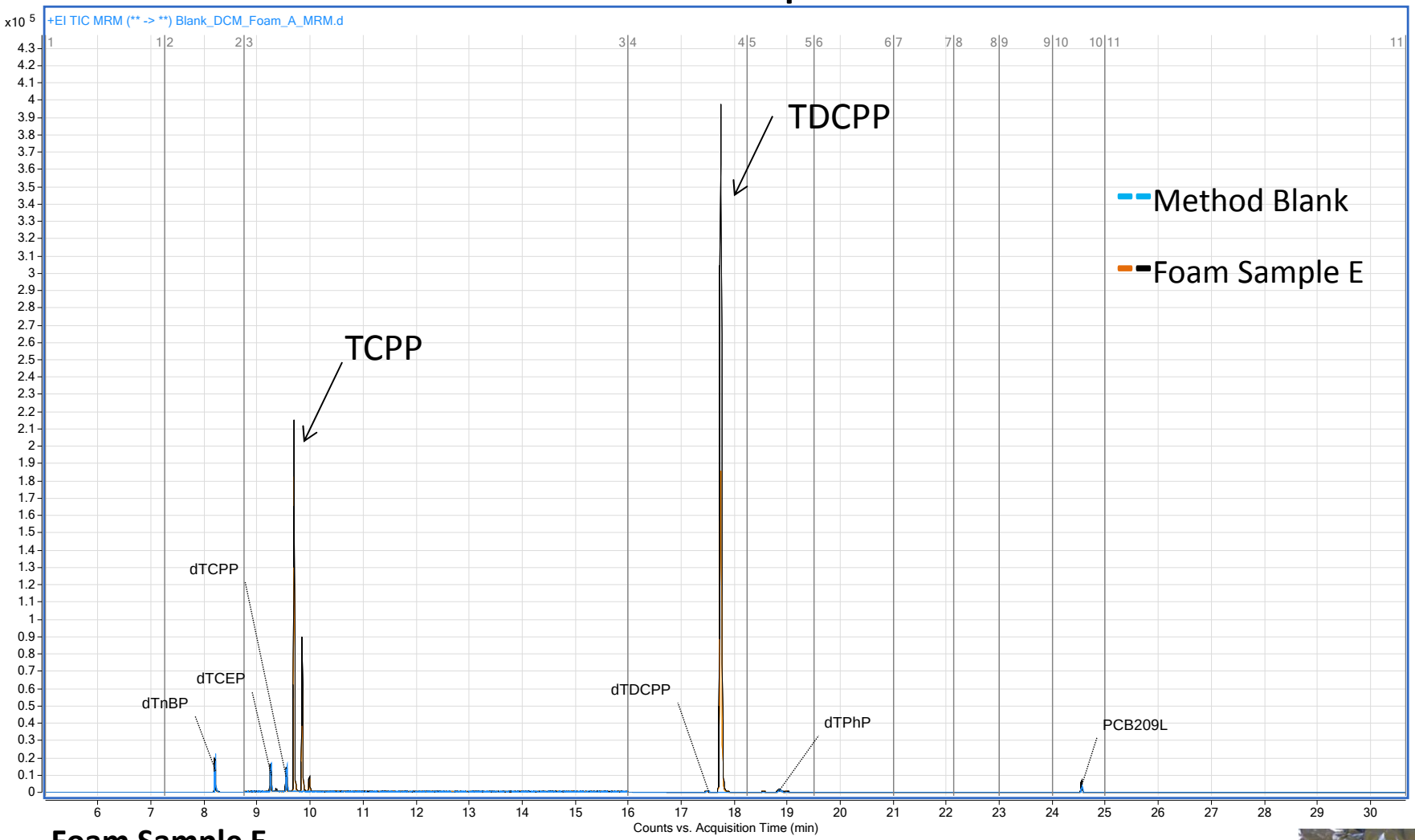
Foam Sample D

- TCEP detected (dwarfs IS peaks)
  - Full Scan NIST Library Match 90.1 %
- MRM - 125x dilution of Foam DCM Extract
  →500x Dilution 81054 ug/g foam (8.1 % TCEP)

Sample D – NIST Match

TCEP Full Scan NIST Library Match 90.1 %

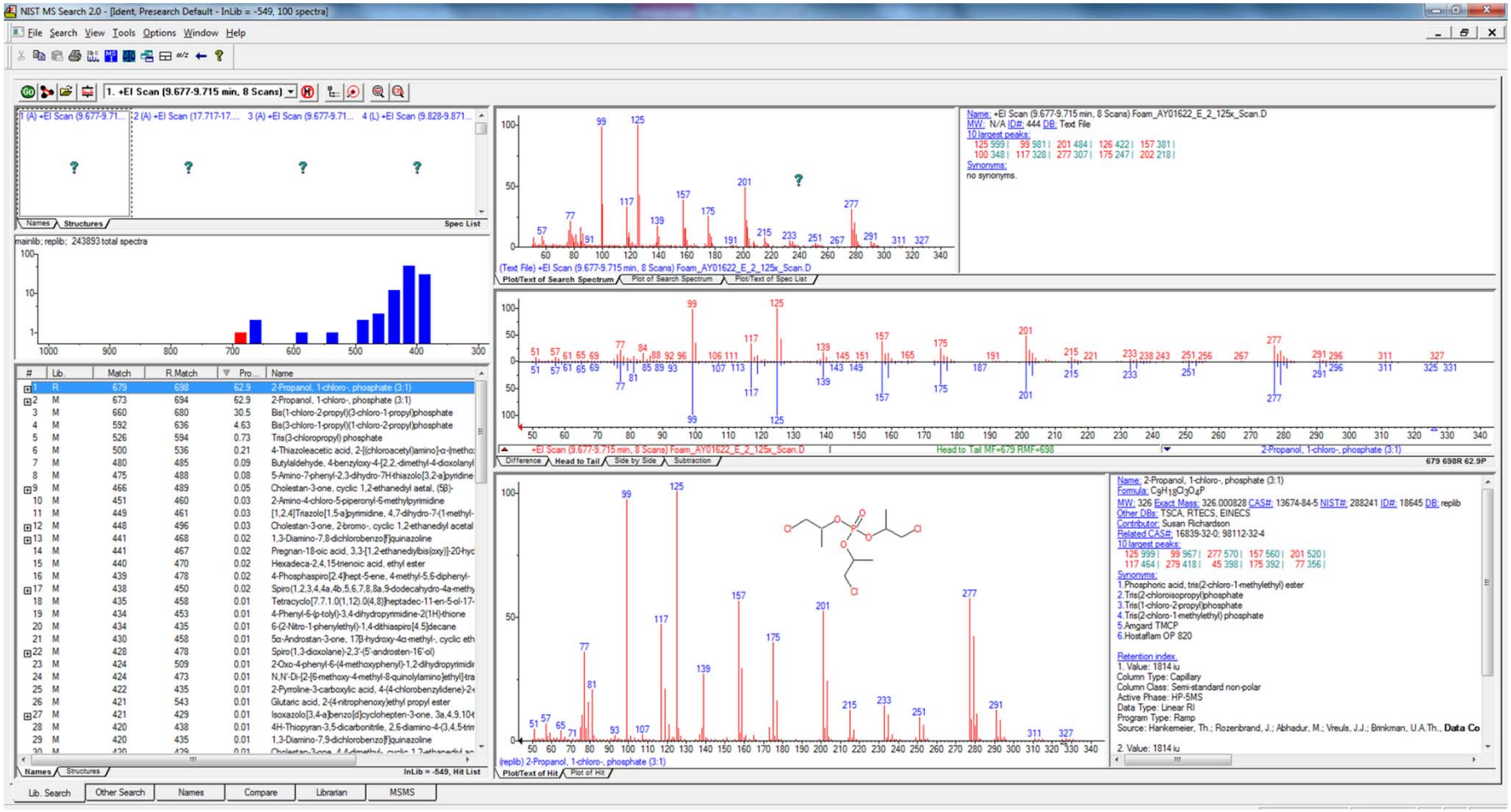
Foam Sample E



Foam Sample E

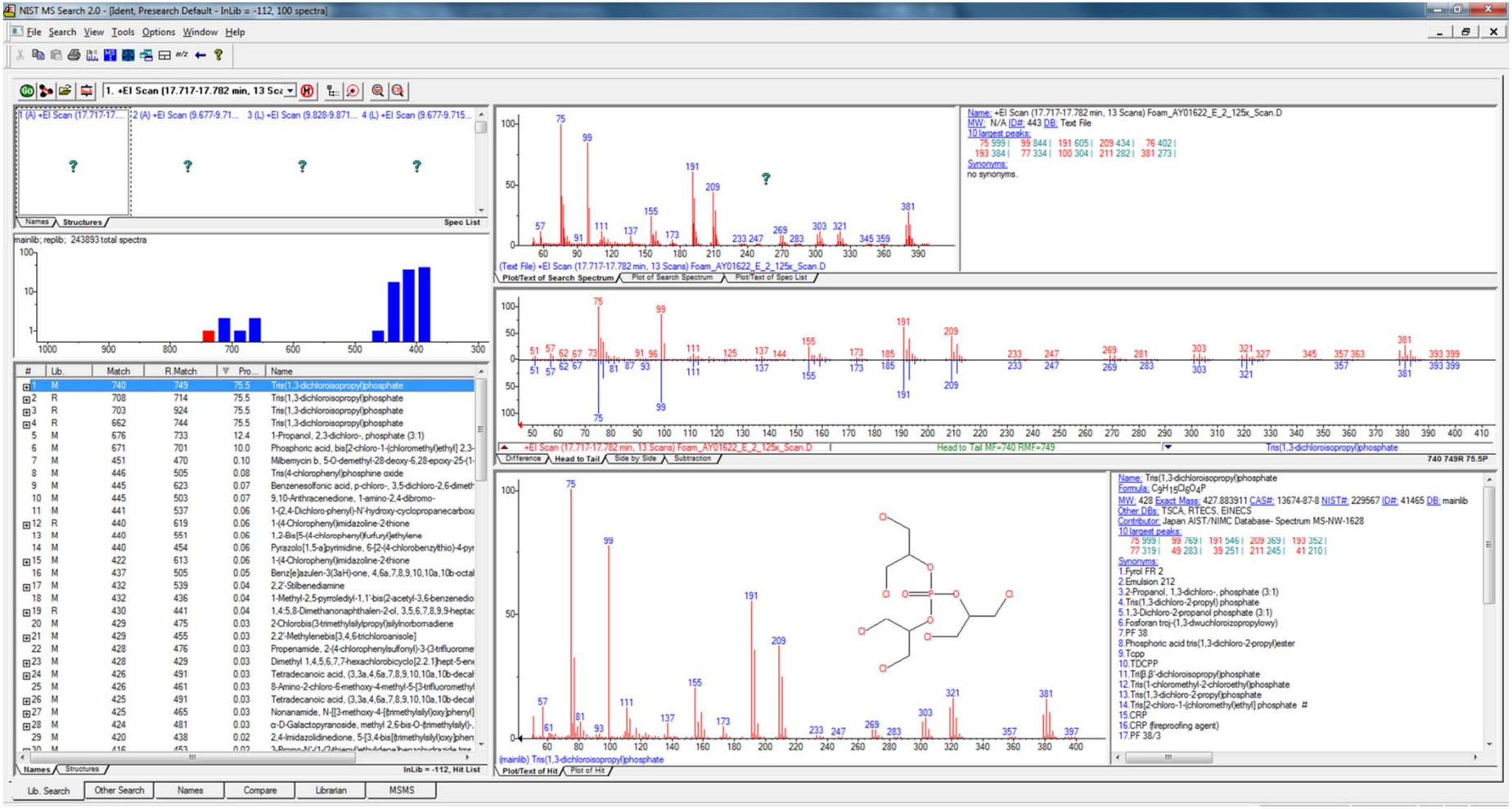
- TPhP & TCPP detected, Full Scan Library Match TCPP 62.9% & TDCPP 75.5%
- MRM - 125x dilution of Foam DCM Extract
  →500x dilution 23481 ug/g foam & 31545 ug/g foam (E1 2.35 % & E2 3.16%)
  - 200 mg Foam Sample to decrease sample variability

Sample E – NIST Library Match TCPP



Full Scan NIST Library Match TCPP 62.9%

Sample E – NIST Library Match TDCPP



Full Scan NIST Library Match TDCPP 75.5%

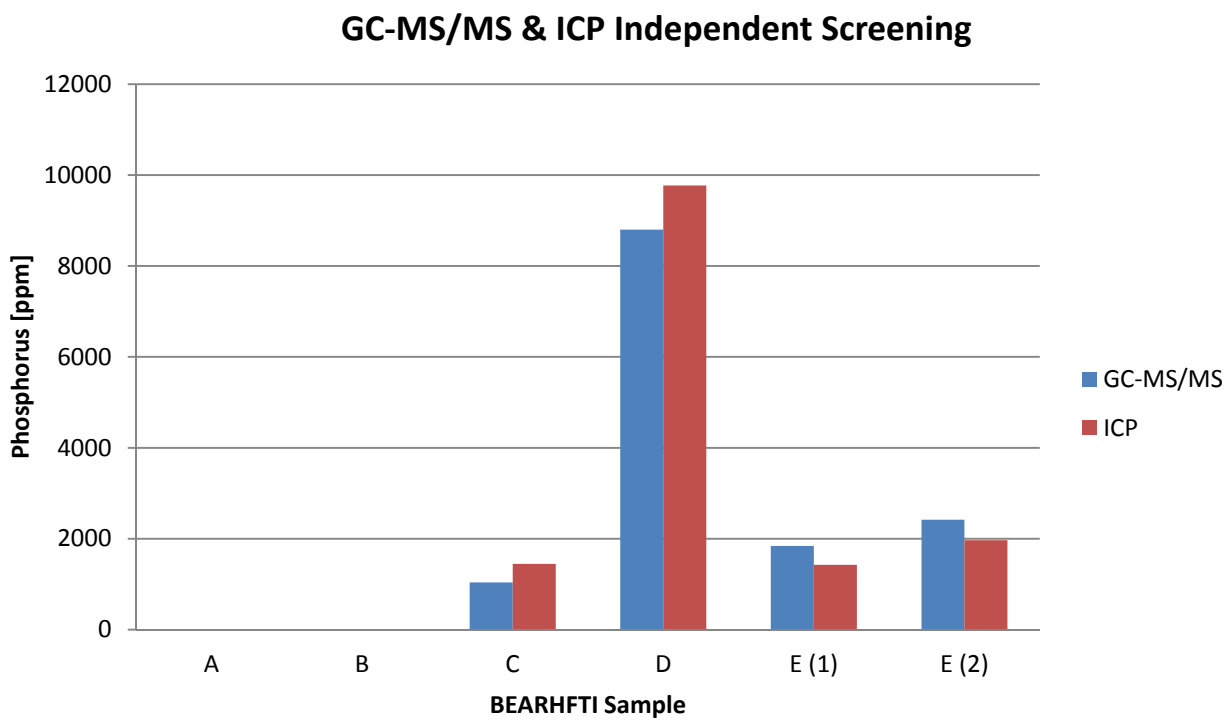
% Flame Retardant in BEARHFTI Foam Samples

BEARHFTI	% OPFR (wt/wt)	% PBDE (wt/wt)	% Phosphorus (wt/wt)	ppm (mg P/kg Foam)	**XRF**
A - AY01618 - 1	-	-	- [-]	- [-]	-
B - AY01619 - 1	-	-	- [-]	- [-]	-
C - AY01620 - 1	1.1 % (TPhP)	6.74 %[2.8 % BDE-47 + 0.54 % BDE-100 + 3.4 % BDE-99]	0.104 [0.15]	1040 [1446]	Phosphorus Bromine
D - AY01621 - 1	8.1 % (TCEP)	-	0.88 [0.98]	8800 [9772]	Phosphorus Chlorine
E - AY01622 - 1	2.36 % [0.66 % (TCPP) + 1.7 % (TDCPP)]	-	0.184 [0.14]	1840 [1426]	Phosphorus Chlorine
E - AY01622 - 2	3.16 % [0.66 % (TCPP) + 2.5 % (TDCPP)]	-	0.242 [0.20]	2420 [1969]	Phosphorus Chlorine

XRF Results Agree

- Screening for the presences of Phosphorus, Chlorine & Bromine

GCMS & ICP [P] Screening Results Agree



Additional Work

- Test Multiple Sampling Locations for Variability
  - Homogenous and Heterogeneous Samples
- Standard Blank Foam and SRM Foam
- Extraction Efficiency
  - Add additional extraction steps to increase extraction efficiency

Additional Method Development

- Foam - Further Development of Method QC
  - Foam Blank & Foam SRM
  - Test extraction efficiency & Sample Variability
  - Integrate additional OPFRs & PBDEs

- Dust – Finalize Method Changes

- Method Application Goals
  - Fire Fighter Occupational Exposure
  - California Residential Dust
  - Consumer Products
    - SB 1019
      - Screening Method
      - OPFRs & PBDEs

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Questions

Questions Asked

- Foam
  - Year, Density, Source (furniture), does it correspond with expected use?
  - Does foam dissolve in DCM?
  - Any additional compounds detected in the foam samples?
  - Is the plan to add additional OPFRs and PBDEs to method?
  - Why were standards added at end of process.

- Dust
  - Comparison with most recent studies, how is it compare?
  - Evaporation to dryness and loss of low boilers.