Non-targeted analysis of contaminants in dust using multidimensional chromatography, high-resolution mass spectrometry and advanced software tools

David E. Alonso and Joseph E. Binkley; LECO Corporation, Saint Joseph, Michigan, USA

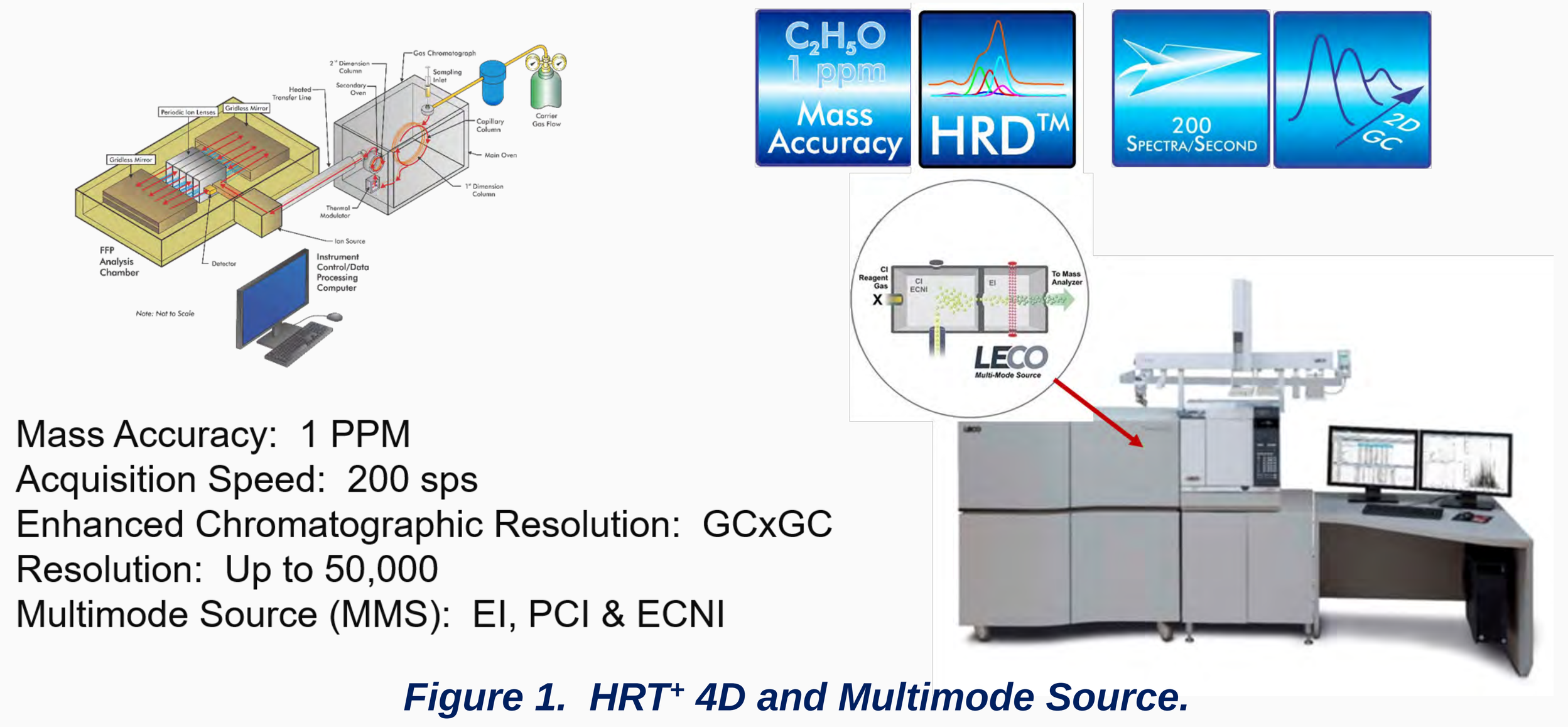
Introduction

- Dust is complex: Numerous, chemically diverse constituents in a wide concentration range
- Dust can be used to estimate human exposure to contaminants (e.g., Pesticides, PAHs, flame retardants)
- Analysis of dust has primarily been conducted using targeted methods and a variety of instrumental techniques

Objectives

1) Untargeted characterization of dust extracts using GCxGC and a novel multimode source with high resolution time-of-flight mass spectrometry
2) To perform quantitative analysis of Polychlorinated Paraffins (PCPs) in dust

Analytical Platform



Mass Accuracy: 1 PPM
Acquisition Speed: 200 sps
Enhanced Chromatographic Resolution: GCxGC
Resolution: Up to 50,000
Multimode Source (MMS): EI, PCI & ECNI

Figure 1. HRT⁺ 4D and Multimode Source.

Dust Sample Preparation

- Dust: 1) NIST SRM 2585, 2) Office Sample, and 3) Household Sample
- Extraction:

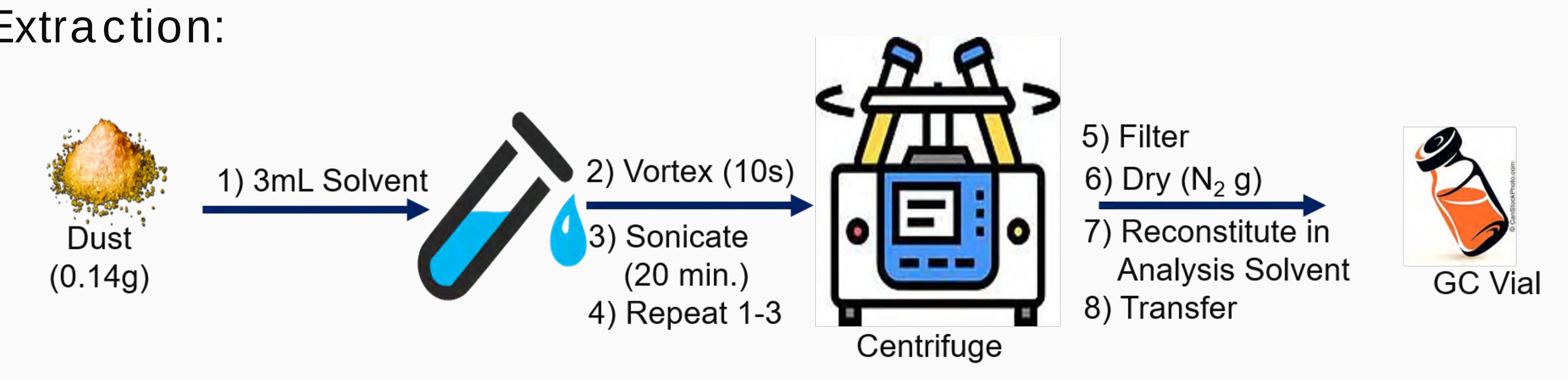


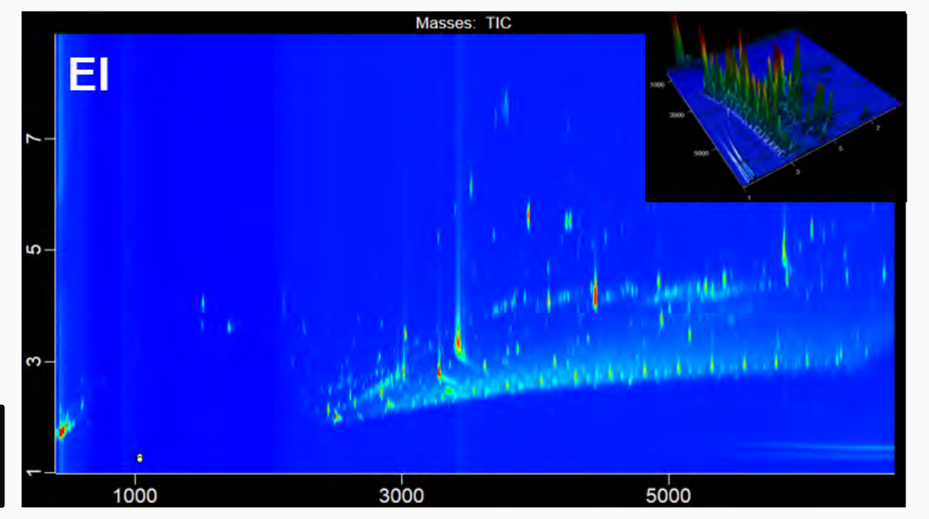
Figure 2. Dust general extraction procedure.

Instrument Acquisition Parameters

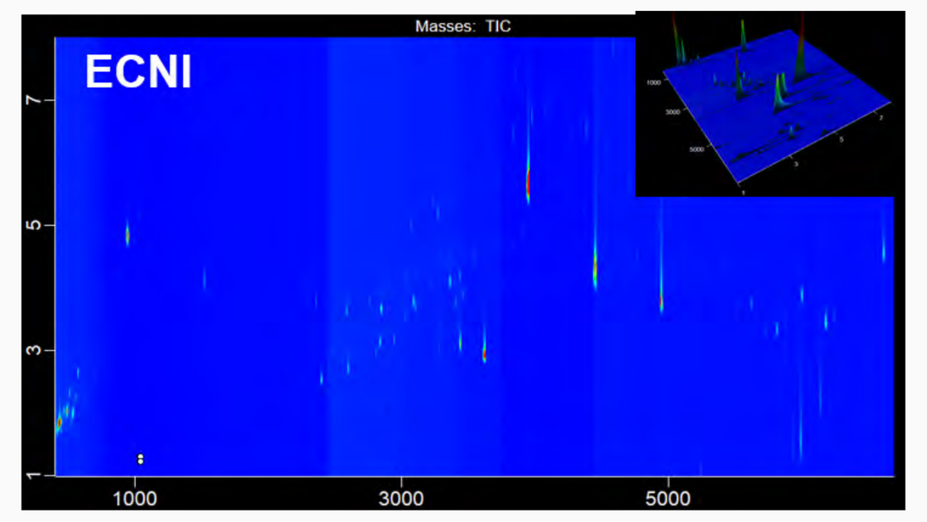
Gas Chromatograph	Agilent 7890B with LECO Dual Stage Quad Jet Modulator
Injection	2µL liquid injection, Splitless, 70°C to 300°C at 500°C/min
Carrier Gas	He @ 1.0 mL/min, Corrected Constant Flow
Primary Column	HP-5MS UI, 30 m x 0.25 mm i.d. x 0.25 µm
Secondary Column	BPX-50, 0.60 m x 0.10 mm x 0.10 µm
Temperature Program	80°C (1 min) ramp 20°C/min to 140°C (Hold 30 mins), then ramp to 200°C at 10°C/min, and ramp 1.5°C/min to 300°C (Hold 5 mins). Secondary oven maintained +5 °C relative to primary oven
Modulation Period	8.0 seconds; modulator maintained +15 °C relative to secondary oven
Transfer Line	300 °C
Mass Spectrometer	**LECO Pegasus® HRT⁺ 4D**
Source Temperature	EI, 250°C; PCI, ECNI, 165°C
Acquisition Mode	High Resolution, R ≥ 25,000 for m/z 219, Mass Accuracy ≤ 1 ppm
Ionization	EI, PCI/ECNI (Reagent Gas = CH_4)
Mass Range (m/z)	EI 50-1000; PCI 60-1000; ECNI 30-1000
Acquisition Rate	MMS 125 sps

Table 1. HRT⁺ 4D instrument acquisition parameters.

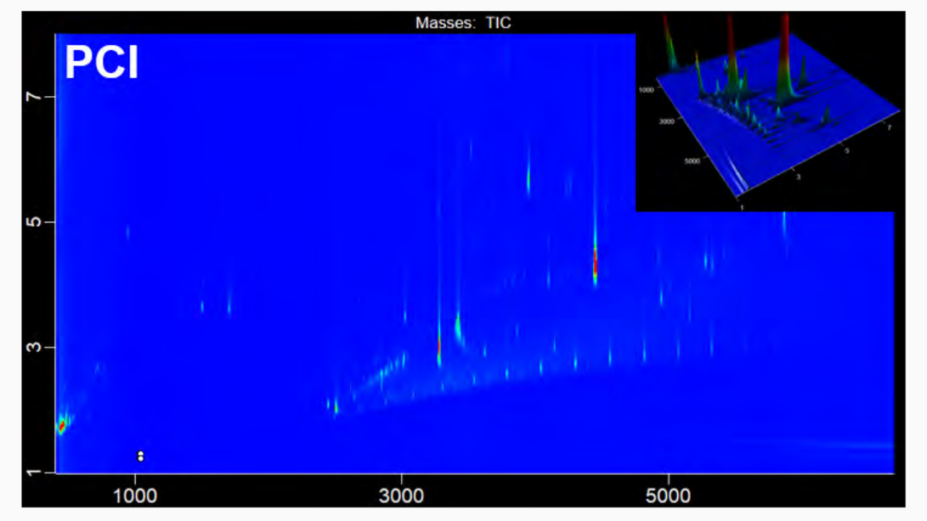
NIST SRM: EI, ECNI & PCI-HRT⁺ 4D Data



- Hard ionization (Fragmentation = More Information)
- Non-selective (Universal)
- Good sensitivity



- Soft ionization (Less Fragmentation)
- Selective (Electron Poor Compounds)
- Increased sensitivity



- Soft ionization (Less Fragmentation)
- Selective (Electron Rich Compounds)

Figure 3. EI, ECNI, and PCI contour plot displaying NIST SRM 2585 data collected using the Multimode Source and GCxGC-TOFMS.

Advantages of GCxGC-HRT⁺ 4D Data

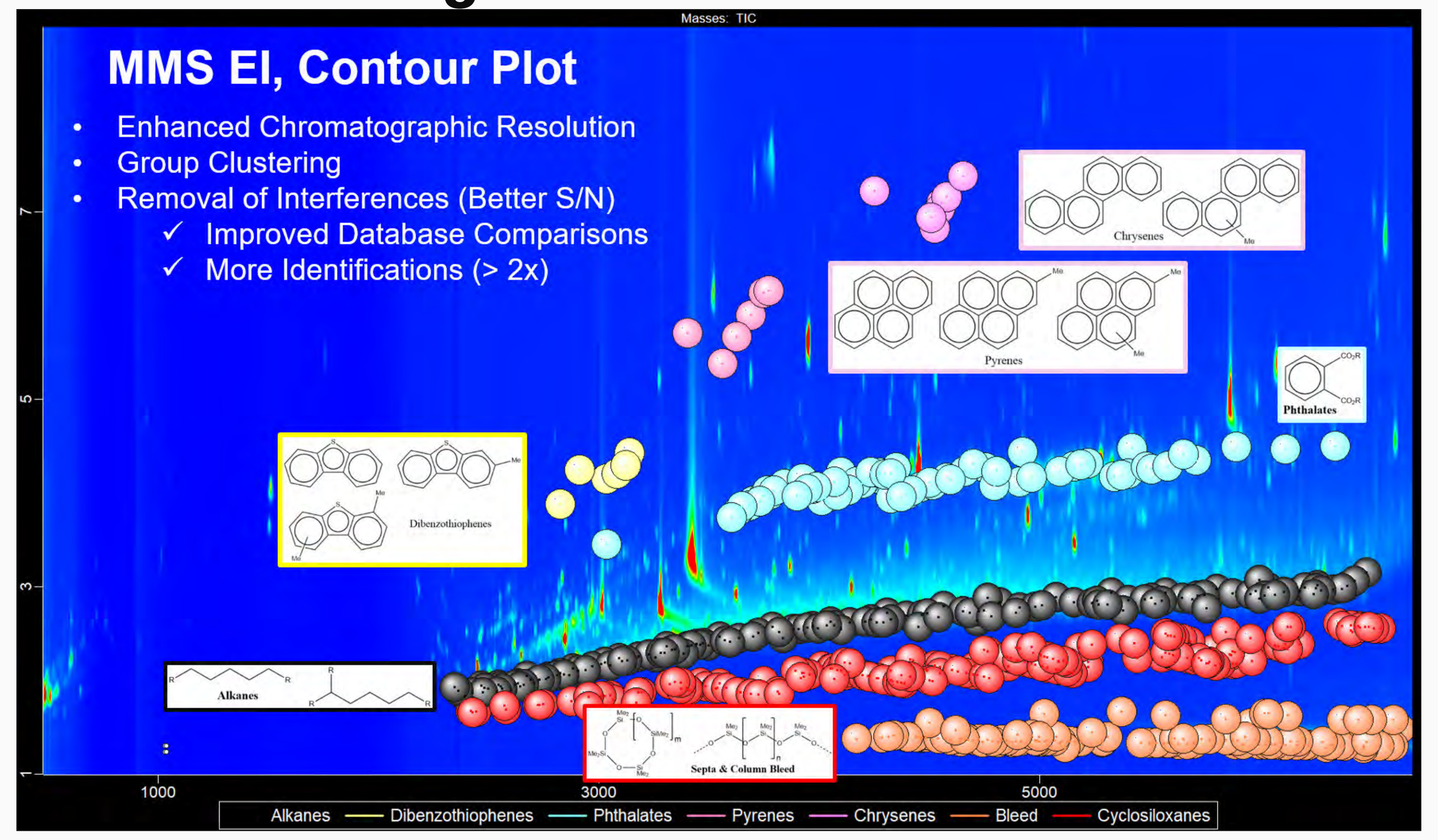


Figure 4. EI Plot displaying some of the major compounds in SRM 2585.

NIST SRM 2585: Representative Compounds

- ✓ Hydrocarbons
- ✓ Acids
- ✓ Aromatics
- ✓ Amines
- ✓ Alcohols
- ✓ Aldehydes
- ✓ Ketones
- ✓ Phenols
- ✓ Fatty Acids
- ✓ Sterols
- ✓ Phosphates
- ✓ More…

Name	Formula	R.T. (s)	Similarity
Benzyl alcohol	C_7H_8O	496, 2.064	890
p-Cresol	C_7H_8O	520, 2.112	826
Acetophenone	C_8H_8O	528, 2.143	942
Phenylethyl Alcohol	$C_8H_{10}O$	576, 2.344	884
Octanoic acid	$C_8H_{16}O_2$	608, 2.240	908
Oxazolidin-2-one	$C_3H_5NO_2$	616, 3.967	950
Benzenamine, 2-methoxy-	C_7H_9NO	640, 2.768	839
3-Dodecene, (Z)-	$C_{12}H_{24}$	648, 1.893	917
Benzaldehyde, 3,4-dimethyl-	$C_9H_{10}O$	664, 2.592	888
p-Acetyltoluene	$C_9H_{10}O$	672, 2.678	937
Methyl salicylate	$C_8H_8O_3$	688, 2.632	771
Naphthalene	$C_{10}H_8$	688, 2.755	952
Ethanol, 2-phenoxy-	$C_8H_{10}O_2$	720, 3.064	809
Benzothiazole	C_7H_5NS	752, 3.504	909
Nonanoic acid	$C_9H_{18}O_2$	760, 2.648	873
1-Decanol	$C_{10}H_{22}O$	792, 2.456	920
1H-Inden-1-one, 2,3-dihydro-	C_9H_8O	864, 4.076	815
Indole	C_8H_7N	880, 4.418	870
5-Acetoxymethyl-2-furaldehyde	$C_8H_8O_4$	888, 4.200	915
Sesamol	$C_7H_6O_3$	912, 4.422	754
Benzamide	C_7H_7NO	968, 6.027	854
Capric acid	$C_{10}H_{20}O_2$	1008, 3.184	897
Capric acid	$C_{10}H_{20}O_2$	1016, 3.344	898
Benzaldehyde, 4-hydroxy-	$C_7H_6O_2$	1024, 5.384	935
Tropeolin	C_8H_7NS	1032, 5.216	864
E-11,13-Tetradecadien-1-ol	$C_{14}H_{26}O$	1064, 3.037	922
2(3H)-Furanone, dihydro-5-pentyl-	$C_9H_{16}O_2$	1064, 4.352	874
1-Tetradecene	$C_{14}H_{28}$	1128, 2.600	944
Dodecanal	$C_{12}H_{24}O$	1208, 3.352	916
Coumarin	$C_9H_6O_2$	1408, 8.263	901
Acenaphthylene	$C_{12}H_8$	1472, 6.872	925
1-Dodecanol	$C_{12}H_{26}O$	1504, 4.008	954
Diisobutyl maleate	$C_{12}H_{20}O_4$	1624, 4.464	900
1-Dodecanamine, N,N-dimethyl-	$C_{14}H_{31}N$	1704, 3.616	942
Tridecanal	$C_{13}H_{26}O$	1744, 4.485	890
Lauric acid	$C_{12}H_{24}O_2$	2120, 4.040	906

Name	Formula	R.T. (s)	Similarity
β-Calacorene	$C_{15}H_{20}$	2168, 3.810	807
n-Tridecan-1-ol	$C_{13}H_{28}O$	2184, 2.968	935
Amyl salicylate	$C_{12}H_{16}O_3$	2192, 3.600	940
Cetene	$C_{16}H_{32}$	2248, 2.240	934
2-Tetradecanone	$C_{14}H_{28}O$	2264, 2.512	920
Epicedrol	$C_{15}H_{26}O$	2304, 2.800	904
Diphenylamine	$C_{12}H_{11}N$	2344, 3.330	886
Benzophenone	$C_{13}H_{10}O$	2360, 3.247	937
Tributyl phosphate	$C_{12}H_{27}O_4P$	2400, 2.304	917
Cinnamaldehyde, α-pentyl-	$C_{14}H_{18}O$	2400, 2.520	913
8-Heptadecene	$C_{17}H_{34}$	2464, 1.950	919
n-Hexyl salicylate	$C_{13}H_{18}O_3$	2464, 2.448	929
Triaminotriazine	$C_3H_6N_6$	2472, 3.040	882
3-Phenoxy-4-fluorobenzaldehyde	$C_{13}H_9FO_2$	2472, 3.064	886
Tetradecanenitrile	$C_{14}H_{27}N$	2488, 2.288	884
4-(1,1-Dimethylheptyl)phenol	$C_{15}H_{24}O$	2512, 2.528	895
Veramoss	$C_{10}H_{12}O_4$	2520, 3.040	902
Oplopanone	$C_{15}H_{26}O_2$	2592, 2.816	803
Myristic acid	$C_{14}H_{28}O_2$	2616, 2.400	892
Benzyl Benzoate	$C_{14}H_{12}O_2$	2640, 3.360	926
Vertofix Coeur	$C_{17}H_{26}O$	2656, 2.672	856
9-Eicosene, (E)-	$C_{20}H_{40}$	2672, 2.053	903
Benzenemethanol, 3-phenoxy-	$C_{13}H_{12}O_2$	2680, 3.688	842
1H-Indole-3-carboxaldehyde	C_9H_7NO	2720, 5.016	920
Versalide	$C_{18}H_{26}O$	2840, 2.888	872
Methyl palmitate	$C_{17}H_{34}O_2$	2936, 2.455	795
Palmitic acid	$C_{16}H_{32}O_2$	3016, 2.848	898
Phenylethyl salicylate	$C_{15}H_{14}O_3$	3040, 3.920	854
Benzoguanamine	$C_9H_9N_5$	3176, 5.963	825
2-(2H-Benzotriazol-2-yl)-5-methylphenol	$C_{13}H_{11}N_3O$	3272, 4.584	845
Fluoranthene	$C_{16}H_{10}$	3272, 5.208	933
1-Octadecanol	$C_{18}H_{38}O$	3280, 2.808	945
Stearic acid	$C_{18}H_{36}O_2$	3464, 3.112	800
Hexadecanamide	$C_{16}H_{33}NO$	3512, 3.712	890
p-Terphenyl	$C_{18}H_{14}$	3560, 5.192	822
trans-3,5-Dimethoxystilbene	$C_{16}H_{16}O_2$	3656, 5.136	877

Name	Formula	R.T. (s)	Similarity
2,6-Diphenylpyridine	$C_{17}H_{13}N$	3672, 5.640	795
1,8-Diazacyclotetradecane-2,7-dione	$C_{12}H_{22}N_2O_2$	3704, 7.416	874
Tributyl acetylcitrate	$C_{20}H_{34}O_8$	3712, 3.592	874
Tert-octyldiphenylamine	$C_{20}H_{27}N$	3776, 4.472	768
N-Methyl-N-benzyltetradecanamine	$C_{22}H_{39}N$	3864, 3.228	850
Methyl dehydroabietate	$C_{21}H_{30}O_2$	3936, 4.576	864
Octadecanamide	$C_{18}H_{37}NO$	4016, 4.016	790
Benzo[ghi]fluoranthene	$C_{18}H_{10}$	4072, 6.888	879
Triphenyl phosphate	$C_{18}H_{15}O_4P$	4080, 6.432	878
Diphenyl 2-ethylhexyl phosphate	$C_{20}H_{27}O_4P$	4152, 4.824	802
Isopropylphenyl diphenyl phosphate	$C_{21}H_{21}O_4P$	4432, 6.004	815
Benz[a]anthracene, 7-methyl-	$C_{19}H_{14}$	4608, 7.312	865
Tri-m-tolylphosphate	$C_{21}H_{21}O_4P$	4800, 6.536	847
Tri-p-cresyl phosphate	$C_{21}H_{21}O_4P$	4880, 6.568	761
Perylene	$C_{20}H_{12}$	5032, 8.200	924
Squalene	$C_{30}H_{50}$	5152, 3.480	924
Cholesta-4,6-dien-3-ol, (3β)-	$C_{27}H_{44}O$	5272, 4.364	861
Cholesta-3,5-diene	$C_{27}H_{44}$	5328, 4.288	910
Piperine	$C_{17}H_{19}NO_3$	5344, 8.344	921
17αH-Trisnorhopane	$C_{27}H_{46}$	5384, 4.864	805
Benzo[b]chrysene	$C_{22}H_{14}$	5416, 7.983	790
p,p'-Dioctyldiphenylamine	$C_{28}H_{43}N$	5456, 4.752	909
28-Nor-17α(H)-hopane	$C_{29}H_{50}$	5712, 4.632	900
Cholesterol	$C_{27}H_{46}O$	5848, 4.848	895
α-Tocopheryl acetate	$C_{31}H_{52}O_3$	6040, 4.160	904
Cholesta-3,5-dien-7-one	$C_{27}H_{42}O$	6072, 5.394	922
Campesterol	$C_{28}H_{48}O$	6112, 4.872	844
Cholest-4-en-3-one	$C_{27}H_{44}O$	6160, 5.232	936
17α(H),21β(H)-Homohopane	$C_{31}H_{54}$	6168, 4.648	846
Stigmasterol	$C_{29}H_{48}O$	6184, 4.824	808
Cholesta-4,6-dien-3-one	$C_{27}H_{42}O$	6224, 5.416	876
γ-Sitosterol	$C_{29}H_{50}O$	6320, 4.880	919
Stigmasta-3,5-dien-7-one	$C_{29}H_{46}O$	6528, 5.765	825
Cholesterol, 7-oxo-	$C_{27}H_{44}O_2$	6568, 6.768	913

Ave. 880/1000

Table 2. Representative compounds in SRM 2585.

NIST SRM 2585: Halogenated Organic Compounds

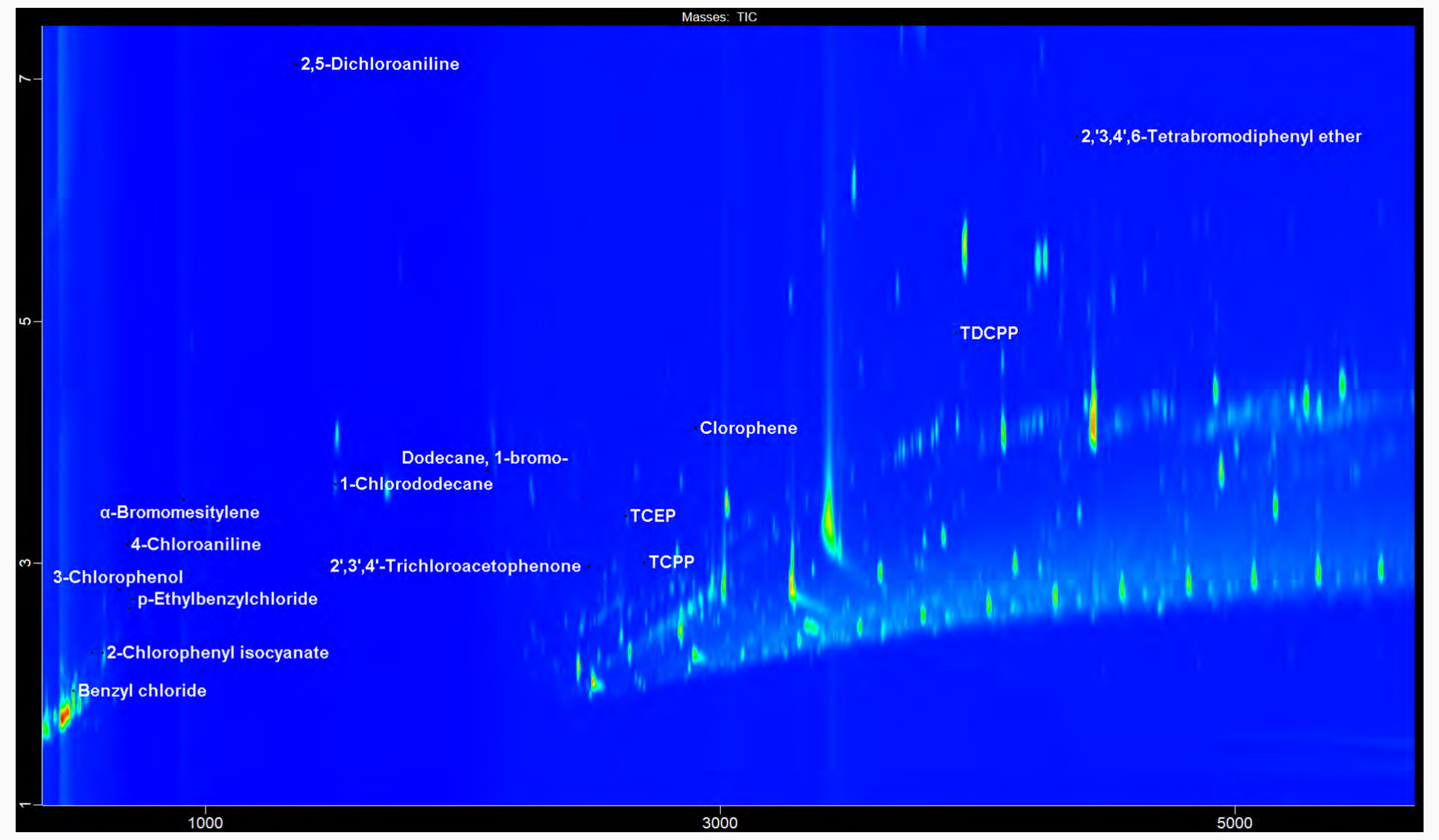


Figure 5. EI plot displaying halogenated compounds In SRM 2585.

Name	Formula	R.T. (s)	Similarity	Mass Accuracy (ppm)
Benzyl chloride	C_7H_7Cl	488, 1.952	873	0.87
Benzyl bromide	C_7H_7Br	560, 2.263	866	0.54
2-Chlorophenyl isocyanate	C_7H_4ClNO	600, 2.264	927	0.31
3-Chlorophenol	C_6H_5ClO	664, 2.784	896	1.32
4-Chloroaniline	C_6H_6ClN	696, 3.160	913	1.52
p-Ethylbenzyl chloride	$C_9H_{11}Cl$	704, 2.624	884	0.10
4-Chloroaniline	C_6H_6ClN	704, 3.184	816	1.13
p-Ethylbenzylchloride	$C_9H_{11}Cl$	720, 2.704	931	0.21
α-Bromomesitylene	$C_9H_{11}Br$	912, 3.528	861	-0.23
3,4-Dichlorophenyl isocyanate	$C_7H_3Cl_2NO$	944, 3.358	820	1.93
2,5-Dichloroaniline	$C_6H_5Cl_2N$	1352, 7.124	933	-0.25
1-Chlorododecane	$C_{12}H_{25}Cl$	1504, 3.656	949	-0.80
Dodecane, 1-bromo-	$C_{12}H_{25}Br$	2096, 3.768	873	N/A
2',3',4'-Trichloroacetophenone	$C_8H_5Cl_3O$	2488, 2.976	781	N/A
TCEP	$C_6H_{12}Cl_3O_4P$	2632, 3.392	893	N/A
TCPP	$C_9H_{18}Cl_3O_4P$	2704, 3.008	918	N/A
TCPP	$C_9H_{18}Cl_3O_4P$	2728, 3.064	816	N/A
Clorophene	$C_{13}H_{11}ClO$	2904, 4.120	824	1.22
TDCPP	$C_9H_{15}Cl_6O_4P$	3912, 4.904	902	N/A
2,'3,4',6-Tetrabromodiphenyl ether	$C_{12}H_6Br_4O$	4384, 6.528	831	0.34
2,2',4,4',5,-Pentabromodiphenyl ether	$C_{12}H_5Br_5O$	5056, 7.296	892	-0.45

Ave. Similarity: 876/1000

Table 3. SRM 2585 selected halogenated compounds.

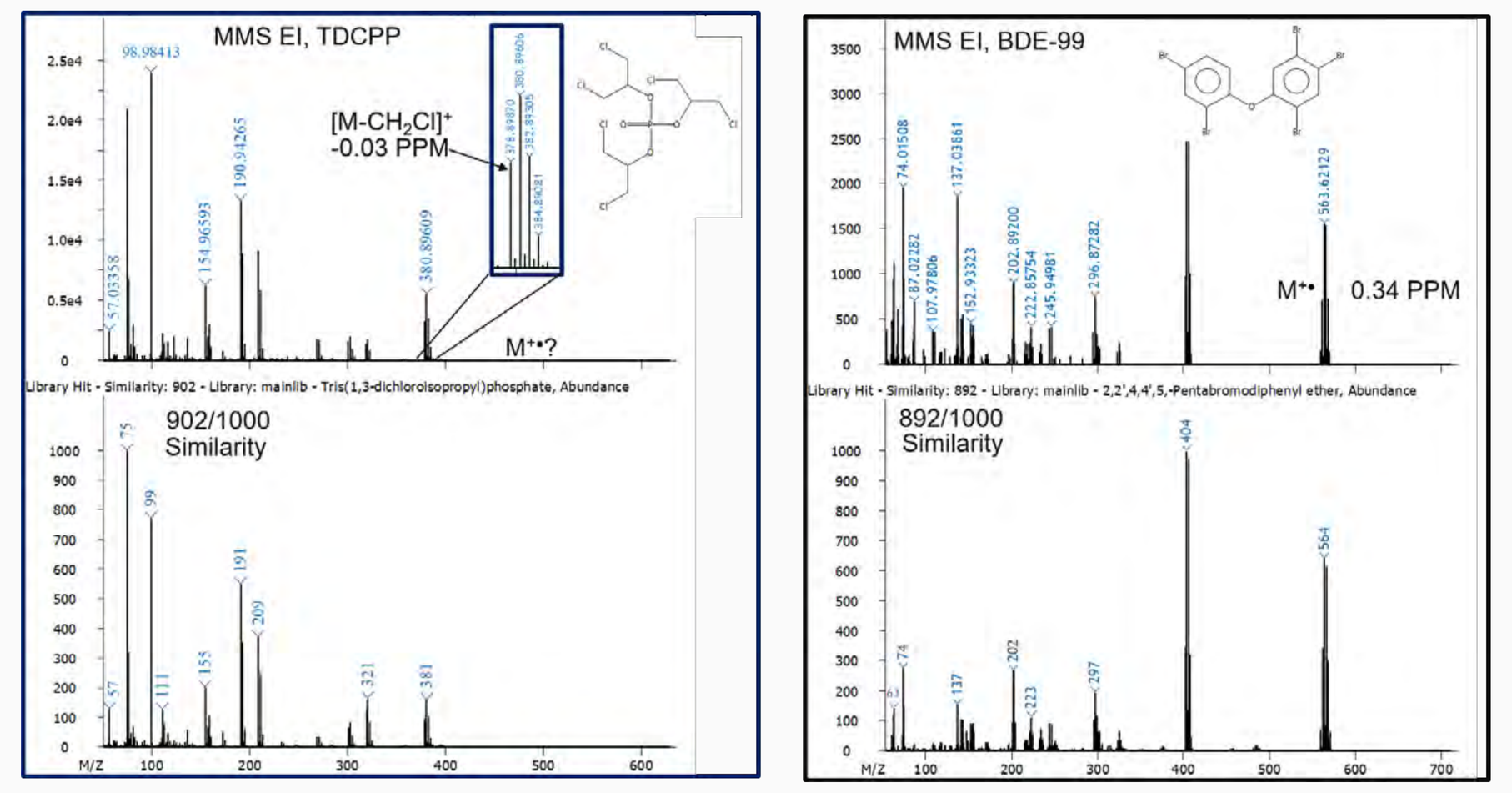


Figure 6. Peak True & library EI mass spectra for TDCPP and BDE-99 in SRM 2585.

ECNI: Locating Trace POPs in NIST, Office & House Dust

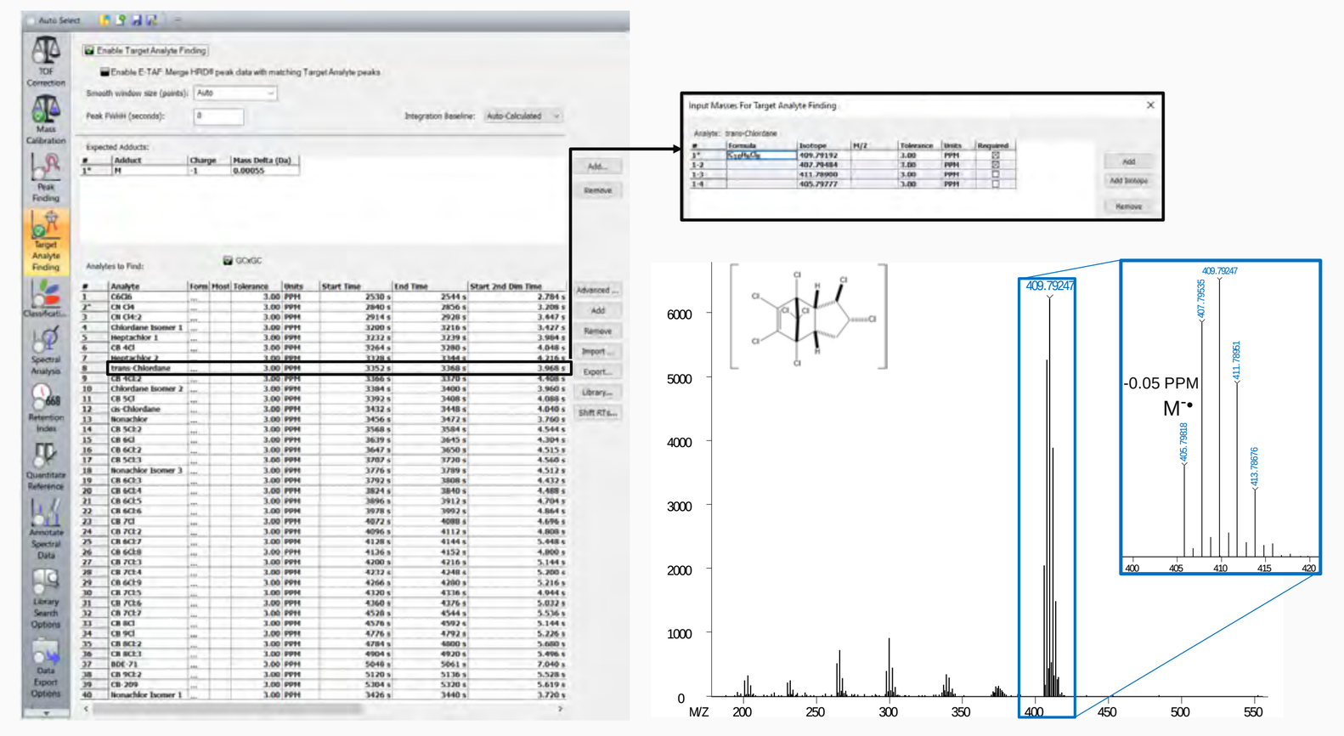


Figure 7. Target Analyte Finding (TAF) method for POPs in dust samples.

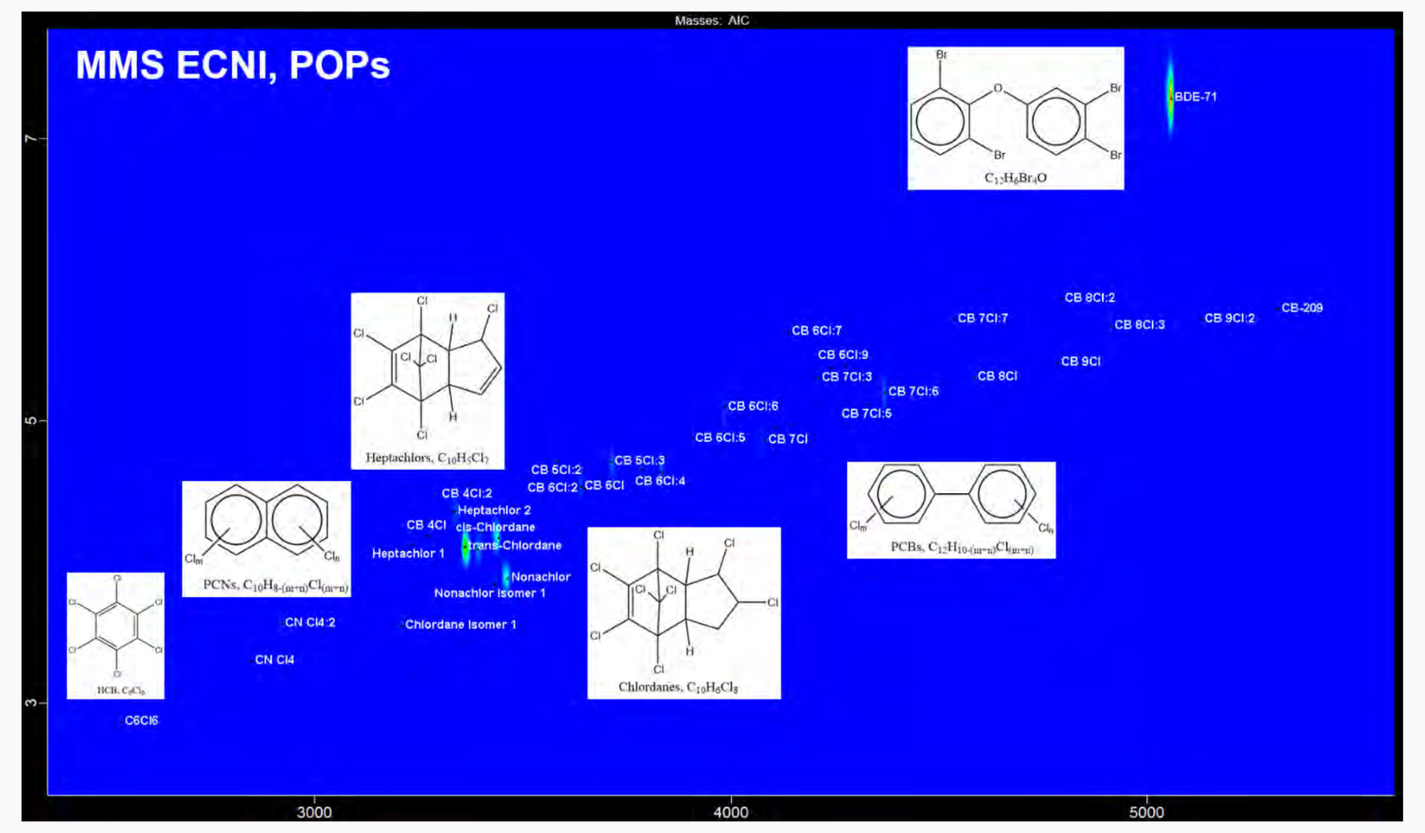


Figure 8. ECNI plot displaying POPs in SRM 2585.

Target POP	R.T. (s)	NIST (area)	Office (area)	House (area)
C_6Cl_6	2536, 2.872	66777	10364	485688
CN Cl4	2848, 3.304	13710		
CN Cl4:2	2920, 3.568	143301		
Chlordane Isomer 1	3208, 3.552	62129		
Heptachlor 1	3232, 4.128	15887		
CB 4Cl	3272, 4.192	21645	8827	
Heptachlor 2	3336, 4.360	215913		
trans-Chlordane	3360, 4.112	1730979	3025	11470
CB 4Cl:2	3368, 4.552	10321	1454	
Chlordane Isomer 2	3392, 4.096	266412		
CB 5Cl	3400, 4.224	54160	50338	
Nonachlor Isomer 1	3432, 3.848	9577		
cis-Chlordane	3440, 4.176	624489		
Nonachlor	3464, 3.888	596640		3023
CB 5Cl:2	3584, 4.720	44766	55571	
CB 6Cl	3640, 4.536	23649	33324	
CB 6Cl:2	3648, 4.520	23937		
CB 5Cl:3	3712, 4.712	304119	305058	
Nonachlor Isomer 3	3784, 4.656	98500		
CB 6Cl:3	3800, 4.576	44400	46349	

Target POP	R.T. (s)	NIST (area)	Office (area)	House (area)
CB 6Cl:4	3832, 4.640	285099	324443	
CB 6Cl:5	3904, 4.872	85405	83716	
CB 6Cl:6	3984, 5.096	280450	328292	
CB 7Cl	4080, 4.864	149348	108803	
CB 7Cl:2	4104, 4.952	68723	50837	
CB 6Cl:7	4136, 5.632	39203	47433	
CB 6Cl:8	4144, 4.976	27026	22346	
CB 7Cl:3	4208, 5.304	92038	91365	
CB 7Cl:4	4240, 5.376	38110	38962	
CB 6Cl:9	4272, 5.392	67431	66771	
CB 7Cl:5	4328, 5.120	26105	19932	
CB 7Cl:6	4368, 5.200	397534	369028	
CB 7Cl:7	4536, 5.720	86694	109695	
CB 8Cl	4584, 5.312	119235	53370	
CB 9Cl	4784, 5.416	13906		
CB 8Cl:2	4792, 5.864	27430	15635	
CB 8Cl:3	4912, 5.672	94752	58564	
BDE-71	5056, 7.288	5480469	433778	663837
CB 9Cl:2	5128, 5.720	51490	10114	
CB-209	5312, 5.792	9879		

Table 4. TAF Processing results for POPs in SRM 2585, office, and household dust.

Polychlorinated Paraffins: Cloud Quant

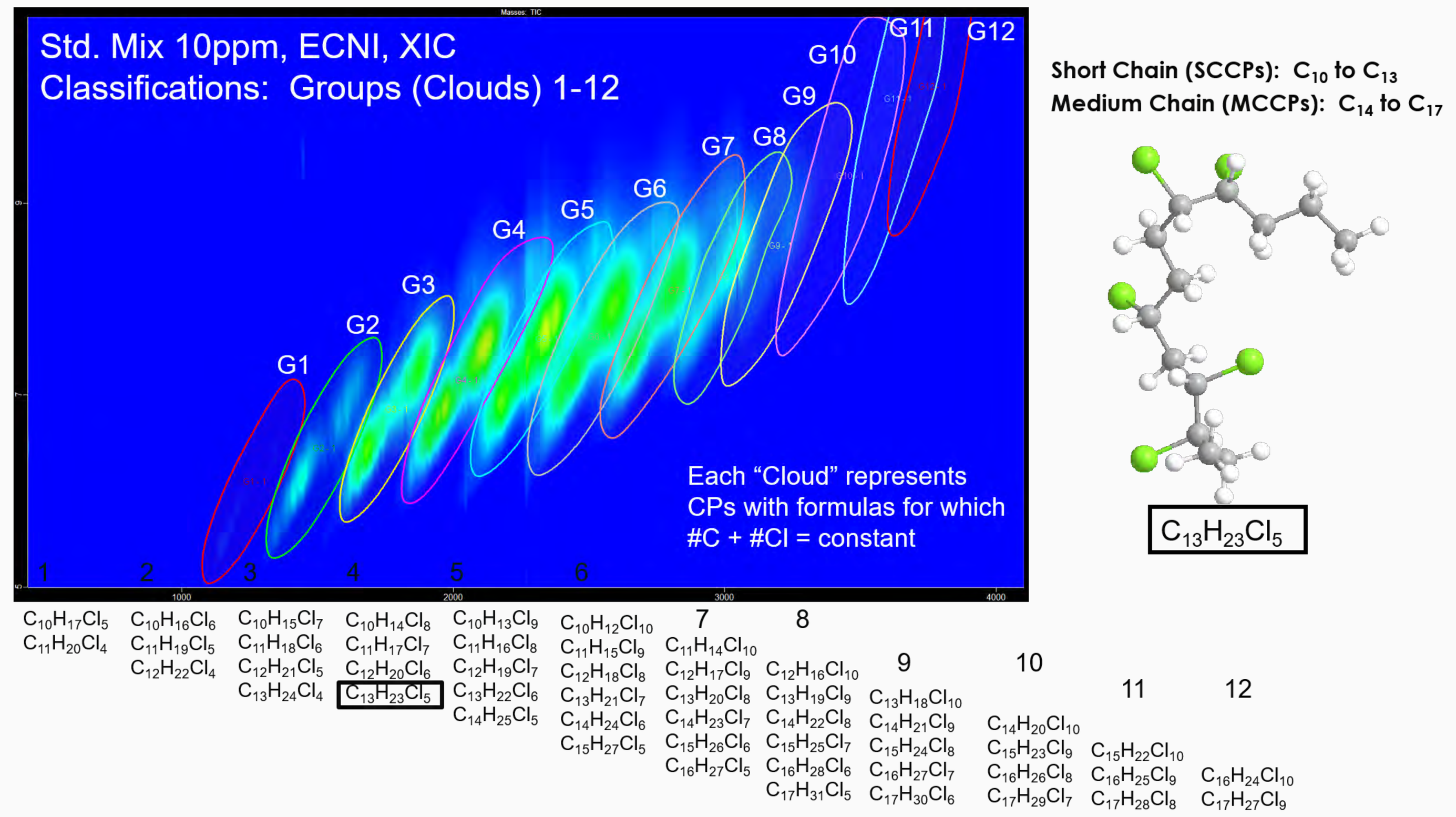


Figure 9. ECNI plot for PCPs in a calibration standard mix. Each group (cloud) region represents PCPs for which the number of carbon + chlorine atoms is constant.

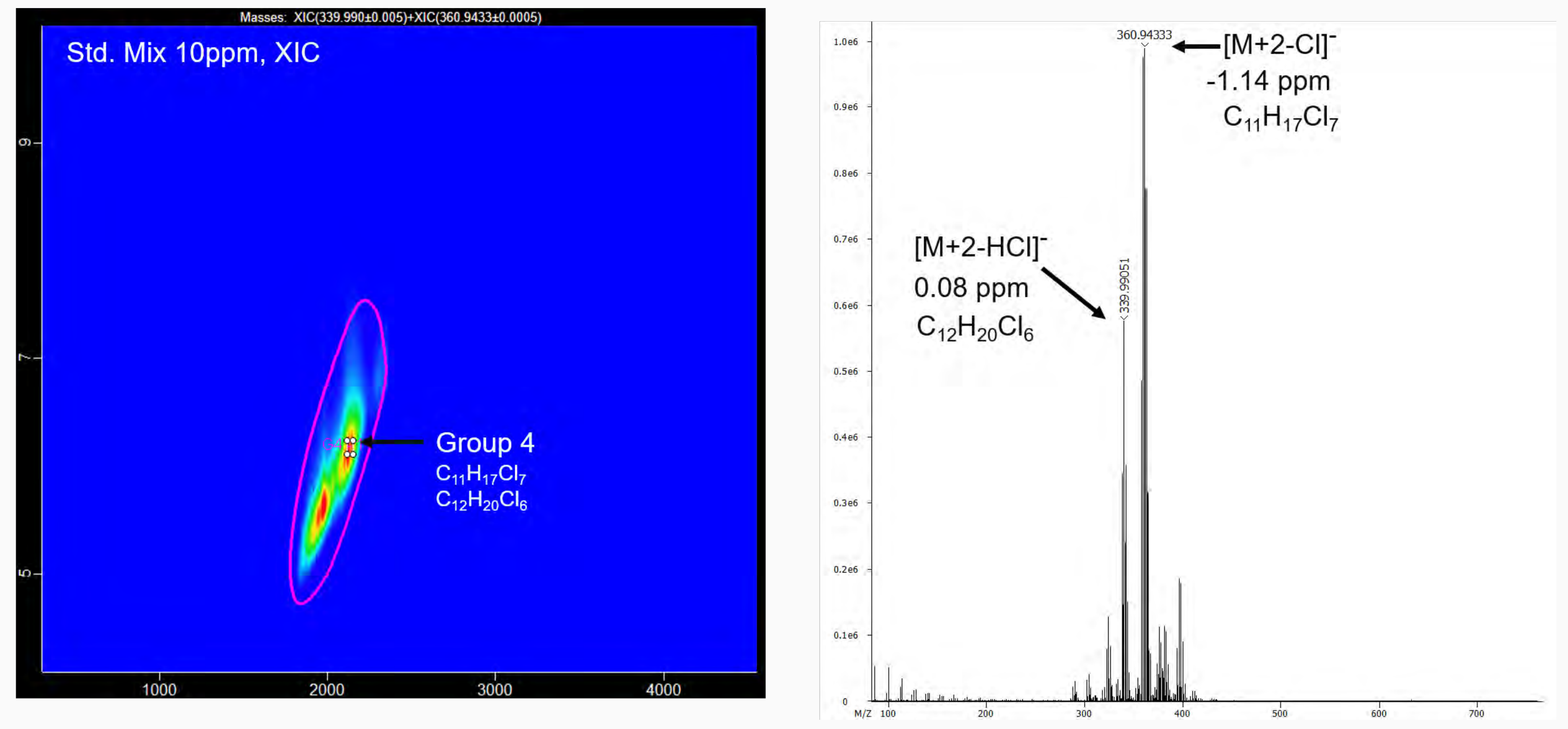


Figure 10. ECNI Plot for Group 4 PCPs with formulas $C_{11}H_{17}Cl_7$ and $C_{12}H_{20}Cl_6$. Mass accuracy values for the most abundant isotope in each cluster was -1.14 & 0.08 ppm respectively.

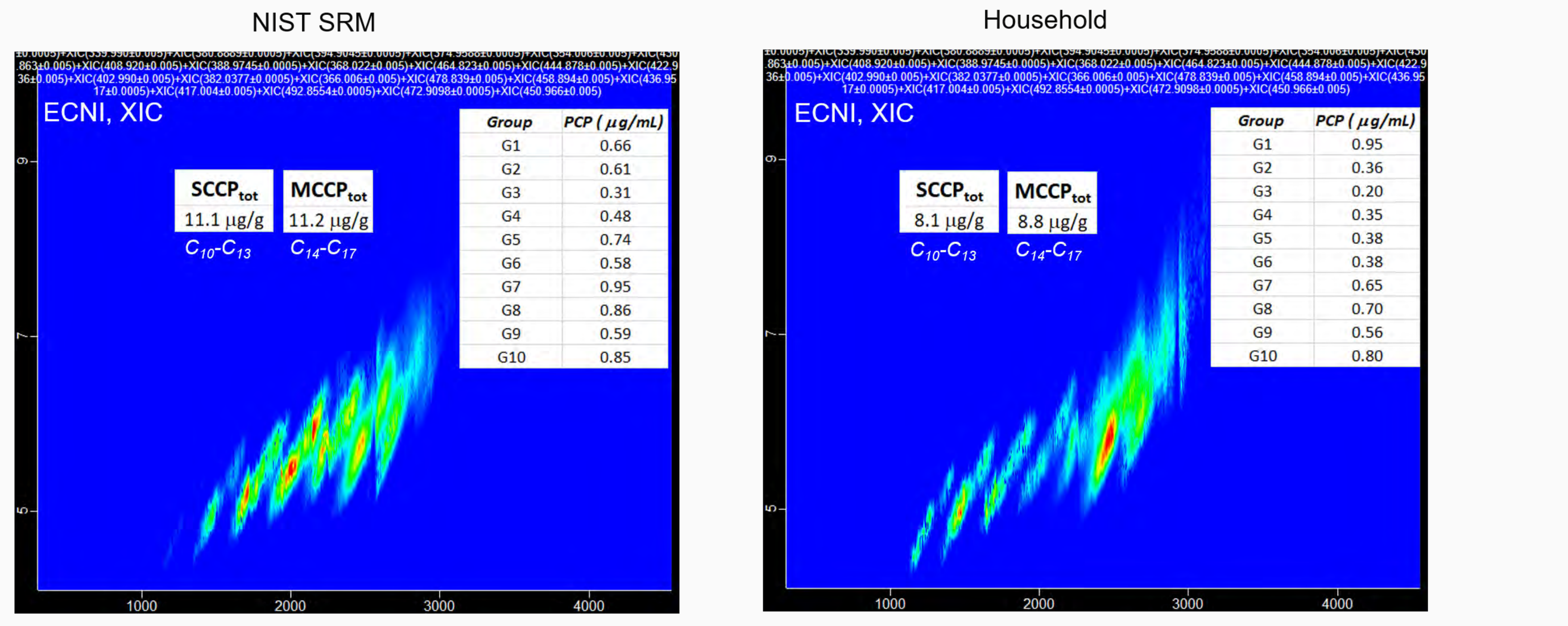


Figure 11. ECNI Plot for SCCPs and MCCPs in the NIST SRM and a household dust sample.

Summary

- ✓ HRT & MMS technology are valuable tools for the analysis of complex samples
- ✓ The highly ordered, comprehensive contour plots can be used to target trace POPs in dust with pinpoint accuracy
- ✓ POPs in Dust: SRM 2585 >> Office Dust > Household Samples
- ✓ Quantitative analysis of PCPs in dust samples was conducted using GCxGC-ECNI-TOFMS