

Comprehensive Screening of Pollutants in Household Dust Using High-Resolution Mass Spectrometry with Enhanced Chromatographic Resolution

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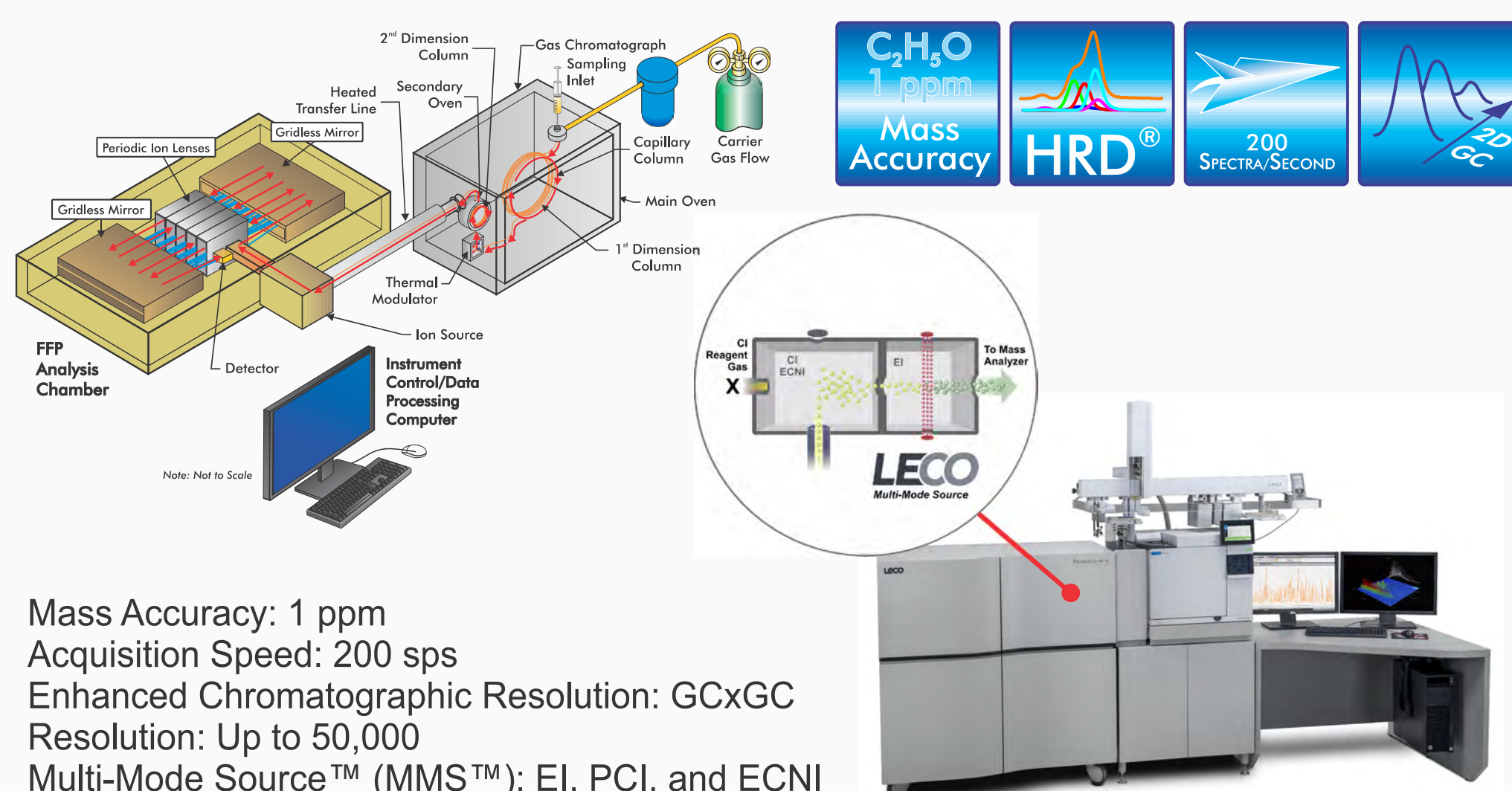


Introduction

- 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

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



Mass Accuracy: 1 ppm
Acquisition Speed: 200 sps
Enhanced Chromatographic Resolution: GCxGC
Resolution: Up to 50,000
Multi-Mode Source™ (MMS™): EI, PCI, and ECNI

Figure 1. Pegasus® HRT+ 4D and Multi-Mode Source (MMS)

Dust Sample Preparation

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

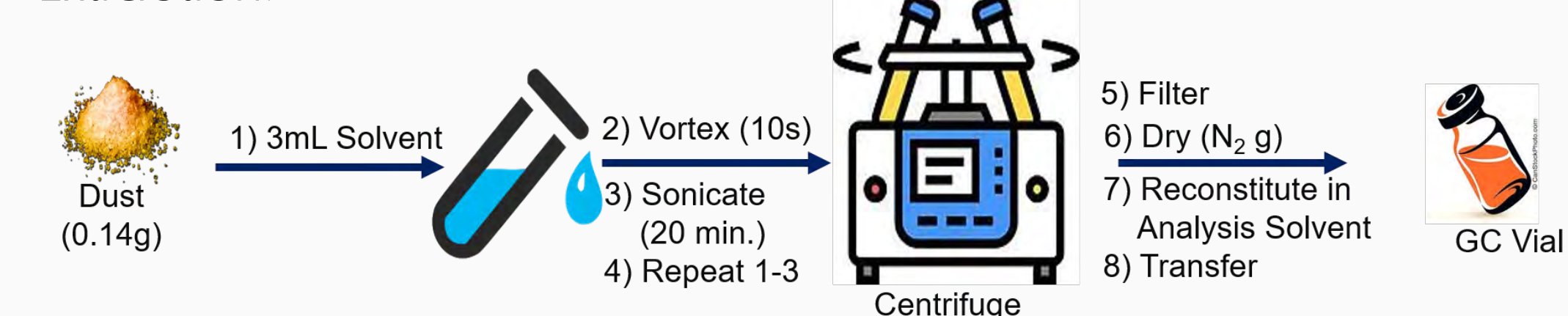


Figure 2. Dust general extraction procedure.

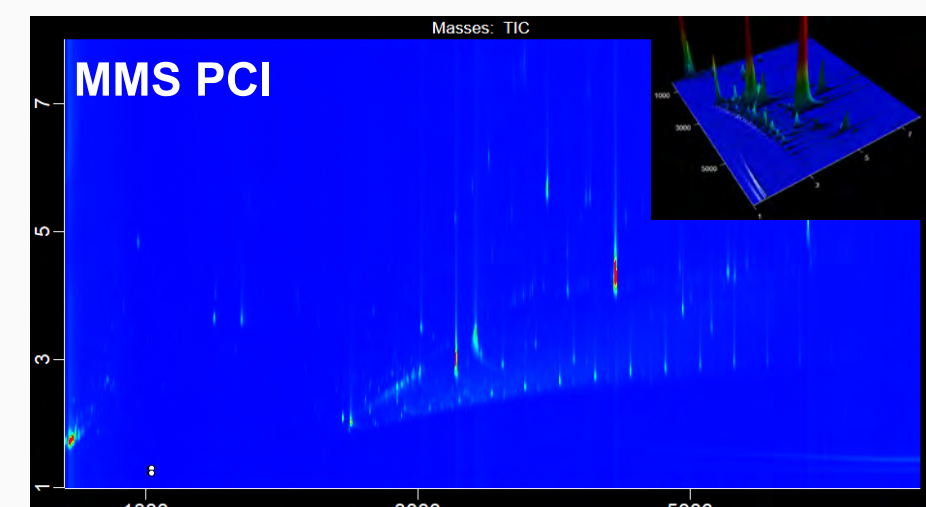
Table 1. HRT+ 4D instrument acquisition parameters.

Gas Chromatograph	Agilent 7890B with LECO Dual Stage QuadJet™ Modulator
Injection	2 µL 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 min), then ramp to 200 °C at 10 °C/min, and ramp 1.5 °C/min to 300 °C (Hold 5 min). Secondary oven maintained +5 °C relative to primary oven
Modulation Period	8.0 s; 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	125 sps

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



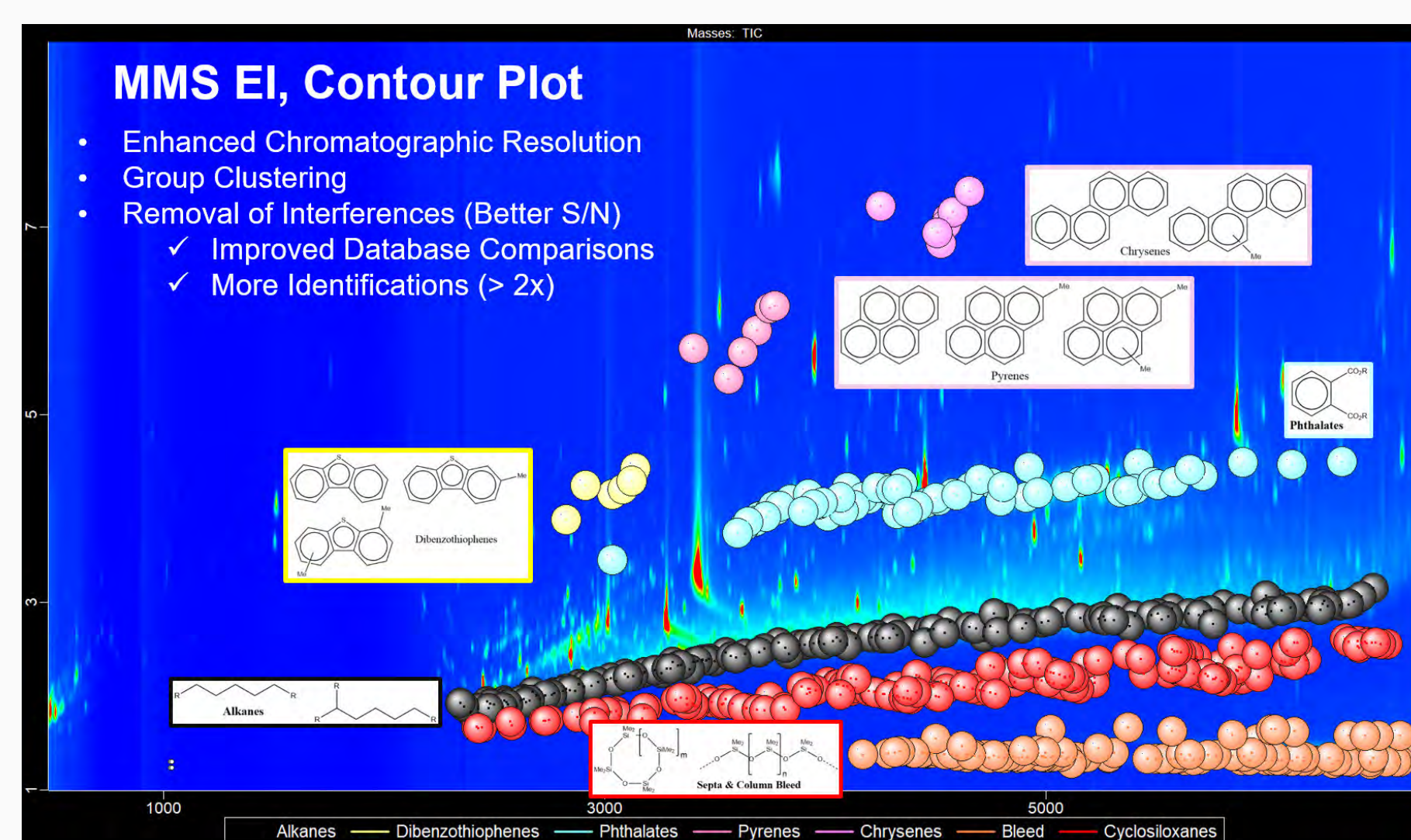
- Hard ionization** (Fragmentation = More Information)
- Non-selective (Universal)
- Good sensitivity
- Soft ionization** (Less Fragmentation)
- Selective (Electron Poor Compounds)
- Increased sensitivity



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

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

Advantages of GCxGC-HRT+ 4D Data



- Enhanced Chromatographic Resolution
- Group Clustering
- Removal of Interferences (Better S/N)
- Improved Database Comparisons
- More Identifications (> 2x)

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

Table 2. Representative compounds in SRM 2585.

Formula	R.T. (s)	Similarity	Formula	R.T. (s)	Similarity	Formula	R.T. (s)	Similarity
Benzyl chloride	C ₈ H ₉ Cl	488.1352	873	0.87	Benzyl chloride	C ₈ H ₉ Cl	488.1352	873
Benzyl bromide	C ₈ H ₉ Br	560.2263	866	0.54	Benzyl bromide	C ₈ H ₉ Br	560.2263	866
2-Chlorophenyl isocyanate	C ₈ H ₇ ClNO	600.2264	927	0.31	2-Chlorophenyl isocyanate	C ₈ H ₇ ClNO	600.2264	927
4-Chlorophenol	C ₆ H ₄ ClO	664.2274	896	1.32	4-Chlorophenol	C ₆ H ₄ ClO	664.2274	896
4-Chloroaniline	C ₆ H ₄ ClN	696.2169	933	1.52	4-Chloroaniline	C ₆ H ₄ ClN	696.2169	933
p-Ethylbenzyl chloride	C ₉ H ₉ Cl	704.2424	884	1.03	p-Ethylbenzyl chloride	C ₉ H ₉ Cl	704.2424	884
4-Chloroaniline	C ₆ H ₄ ClN	704.2424	884	1.13	4-Chloroaniline	C ₆ H ₄ ClN	704.2424	884
p-Ethylbenzyl chloride	C ₉ H ₉ Cl	720.2304	933	0.21	p-Ethylbenzyl chloride	C ₉ H ₉ Cl	720.2304	933
o-Bromophenylene	C ₆ H ₄ Br	812.2128	862	0.23	o-Bromophenylene	C ₆ H ₄ Br	812.2128	862
3,4-Dichlorophenyl isocyanate	C ₈ H ₅ Cl ₂ NO	844.3358	820	1.93	3,4-Dichlorophenyl isocyanate	C ₈ H ₅ Cl ₂ NO	844.3358	820
2,5-Dichloroaniline	C ₆ H ₃ Cl ₂ N	1352.7124	933	-0.25	2,5-Dichloroaniline	C ₆ H ₃ Cl ₂ N	1352.7124	933
1-Chloro-2-bromobenzene	C ₆ H ₄ BrCl	1594.3356	949	0.80	1-Chloro-2-bromobenzene	C ₆ H ₄ BrCl	1594.3356	949
Dodecane, 1-bromo-	C ₁₂ H ₂₅ Br	2096.3768	873	N/A	Dodecane, 1-bromo-	C ₁₂ H ₂₅ Br	2096.3768	873
2,2',4'-Trichloroacetophenone	C ₁₄ H ₉ Cl ₃ O	2488.2976	783	N/A	2,2',4'-Trichloroacetophenone	C ₁₄ H ₉ Cl ₃ O	2488.2976	783
TCEP	C ₁₂ H ₉ Cl ₃ O ₃ P	2832.3393	893	N/A	TCEP	C ₁₂ H ₉ Cl ₃ O ₃ P	2832.3393	893
TDCPP	C ₁₂ H ₉ Cl ₄ O ₃ P	2704.3308	938	N/A	TDCPP	C ₁₂ H ₉ Cl ₄ O ₃ P	2704.3308	938
TDCP	C ₁₂ H ₉ Cl ₃ O ₃ P	2728.1304	836	N/A	TDCP	C ₁₂ H ₉ Cl ₃ O ₃ P	2728.1304	836
Chlorophene	C ₁₂ H ₉ Cl ₃ O	2804.4124	824	1.22	Chlorophene	C ₁₂ H ₉ Cl ₃ O	2804.4124	824
TDCPP	C ₁₂ H ₉ Cl ₄ O ₃ P	2912.4304	902	N/A	TDCPP	C ₁₂ H ₉ Cl ₄ O ₃ P	2912.4304	902
2,3,4,6-Tetrabromodiphenyl ether	C ₁₂ H ₆ Br ₄ O	4384.6328	831	0.34	2,3,4,6-Tetrabromodiphenyl ether	C ₁₂ H ₆ Br ₄ O	4384.6328	831
2,2',4,4'-Tetrabromodiphenyl ether	C ₁₂ H ₆ Br ₄ O	5056.7296	892	-0.45	2,2',4,4'-Tetrabromodiphenyl ether	C ₁₂ H ₆ Br ₄ O	5056.7296	892

Ave. Similarity: 876/1000

NIST SRM 2585: Halogenated Organic Compounds

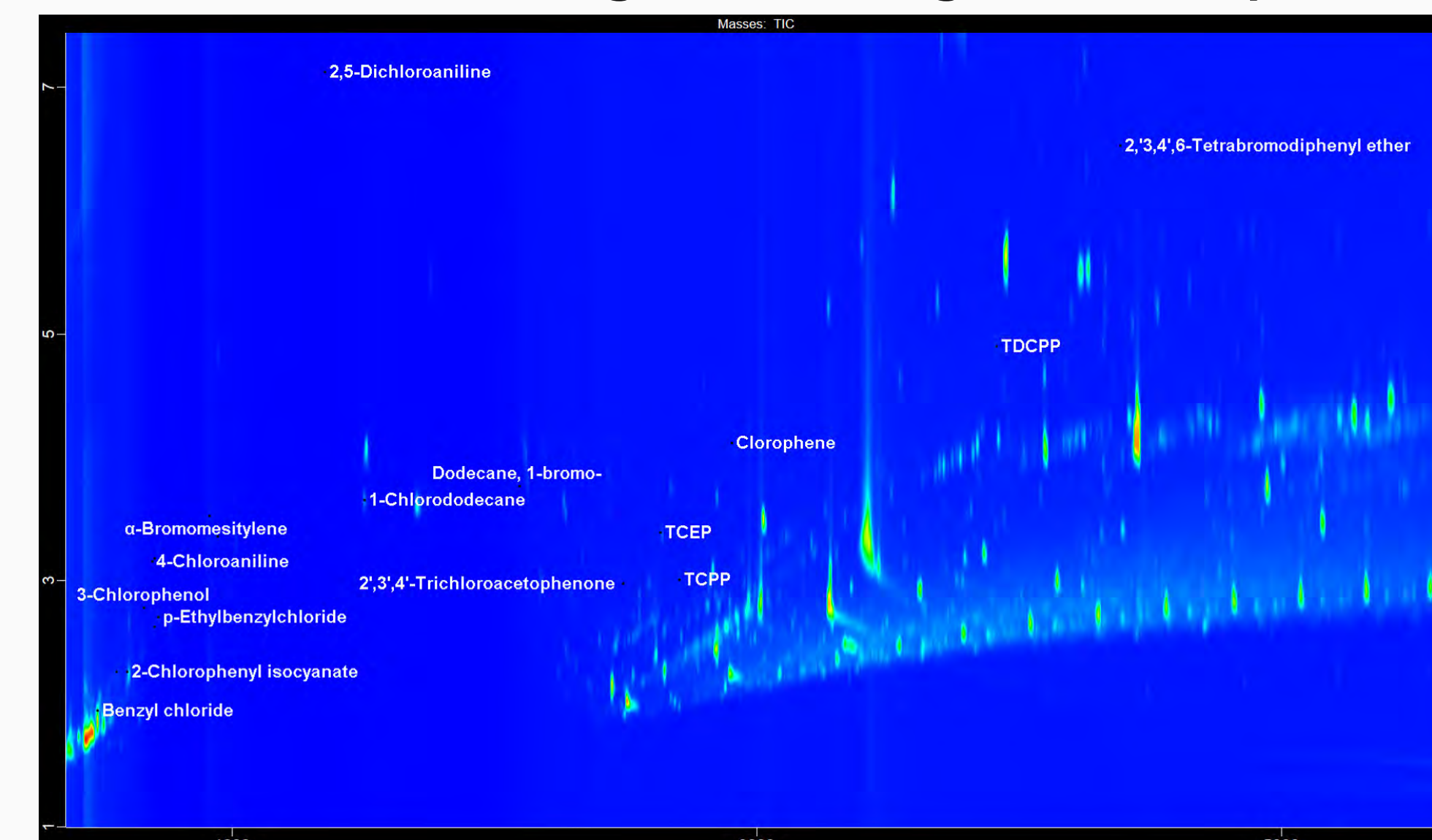


Figure 5. EI plot displaying halogenated compounds in SRM 2585.

Table 3. SRM 2585 selected halogenated compounds.

Name	Formula	R.T. (s)	Similarity	Mass Accuracy (ppm)
Benzyl chloride	C ₈ H ₉ Cl	488.1352	873	0.87
Benzyl bromide	C ₈ H ₉ Br	560.2263	866	0.54
2-Chlorophenyl isocyanate	C ₈ H ₇ ClNO	600.2264	927	0.31
4-Chlorophenol	C ₆ H ₄ ClO	664.2274	896	1.32
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p-Ethylbenzyl chloride	C ₉ H ₉ Cl	704.2424	884	1.03
4-Chloroaniline	C ₆ H ₄ ClN	704.2424	884	1.13
p-Ethylbenzyl chloride	C ₉ H ₉ Cl	720.2304	933	0.21
o-Bromophenylene	C ₆ H ₄ Br	812.2128	862	0.23
3,4-Dichlorophenyl isocyanate	C ₈ H ₅ Cl ₂ NO	844.3358	820	1.93
2,5-Dichloroaniline	C ₆ H ₃ Cl ₂ N	1352.7124	933	-0.25
1-Chloro-2-bromobenzene	C ₆ H ₄ BrCl	1594.3356	949	0.80
Dodecane, 1-bromo-	C ₁₂ H ₂₅ Br	2096.3768	873	N/A
2,2',4'-Trichloroacetophenone	C ₁₄ H ₉ Cl ₃ O	2488.2976	783	N/A
TCEP	C ₁₂ H ₉ Cl ₃ O ₃ P	2832.3393	893	N/A
TDCPP	C ₁₂ H ₉ Cl ₄ O ₃ P	2704.3308	938	N/A
TDCP	C ₁₂ H ₉ Cl ₃ O ₃ P	2728.1304	836	N/A
Chlorophene	C ₁₂ H ₉ Cl ₃ O	2804.4124	824	1.22
TDCPP	C ₁₂ H ₉ Cl ₄ O ₃ P	2912.4304	902	N/A
2,3,4,6-Tetrabromodiphenyl ether	C ₁₂ H ₆ Br ₄ O	4384.6328	831	0.34
2,2',4,4'-Tetrabromodiphenyl ether	C ₁₂ H ₆ Br ₄ O	5056.7296	892	-0.45

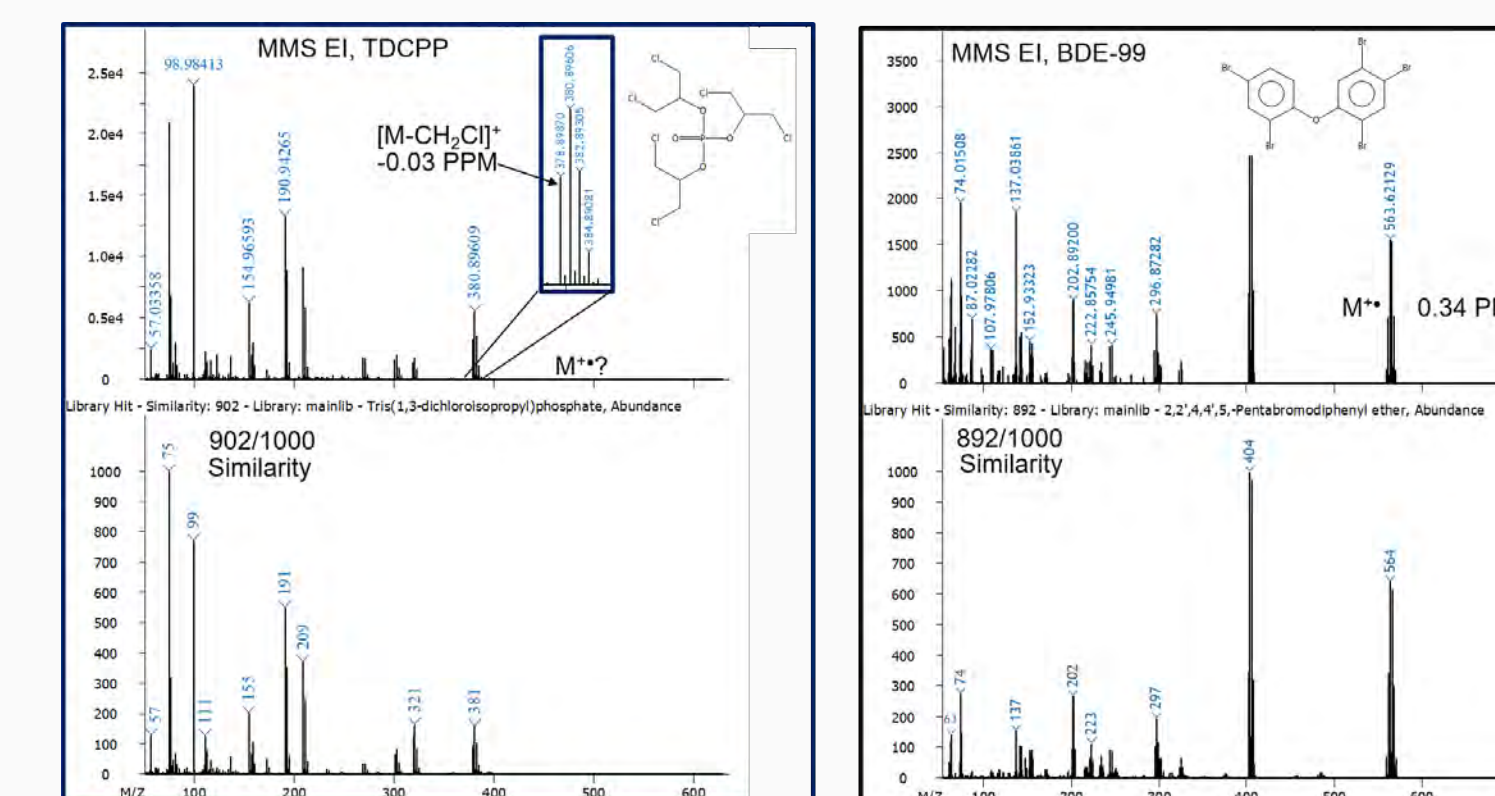


Figure 6. Peak True and library EI mass spectra for TDCPP and BDE-99 in SRM 2585.

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

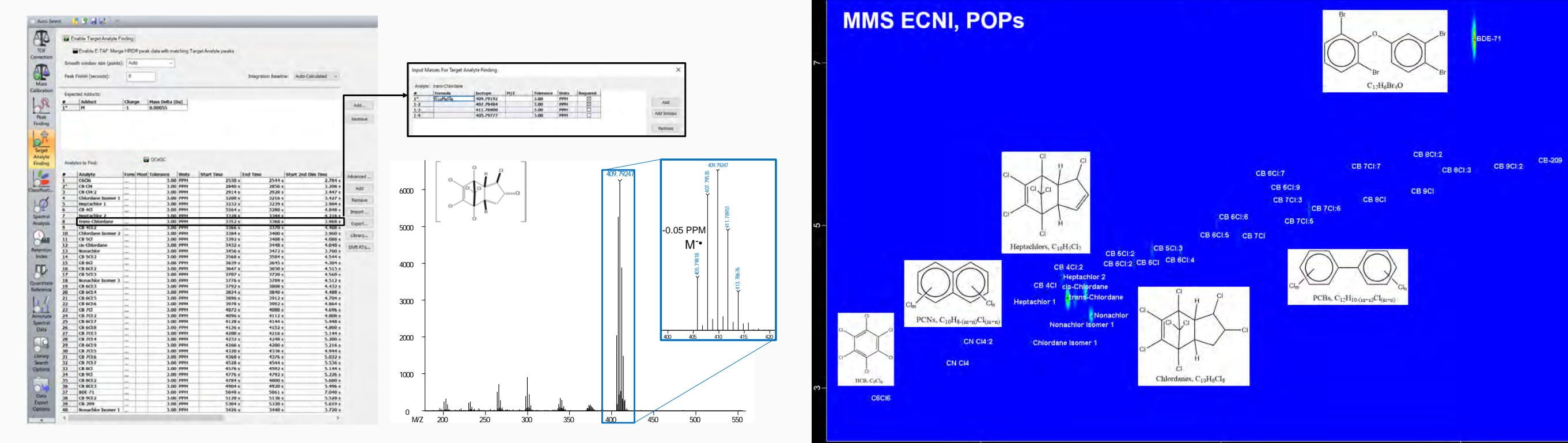


Figure 7. Target Analyte Finding (TAF) method for POPs in dust samples.

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

Target POP	R.T. (s)	NIST (area)	Office (area)	House (area)
CaCl ₂	2536.2872	66777	10364	485688
CN Cl4	2840.3304	13710		
CN Cl-2	2920.3568	143301		
Chloridane Isomer 1	3208.3552	62129		
Heptachlor 1	3272.4128	15887		
CB 4Cl	3400.4224	21645	8827	
Heptachlor 2	3336.4360	215913		
trans-Chloridane	3460.4112	1738979	3025	11470
CB 4Cl-2	3368.4552	10321	1454	
Chloridane Isomer 2	3392.4096	266412		
CB 5Cl	3400.4224	54160	50338	
Nonachlor Isomer 1	3432.3848	9577		
cis-Chloridane	3440.4176	62489		
Nonachlor	3460.4388	596540		
CB 5Cl-2	3584.4720	44766	55571	
CB 6Cl	3640.4536	23649	33324	
CB 6Cl-2	3648.4520	23937		
CB 5Cl-3	3712.4712	304119	305058	
Nonachlor Isomer 3	3784.4656	98500		
CB 6Cl-3	3800.4576	44400	46349	

Polychlorinated Paraffins: Cloud Quant

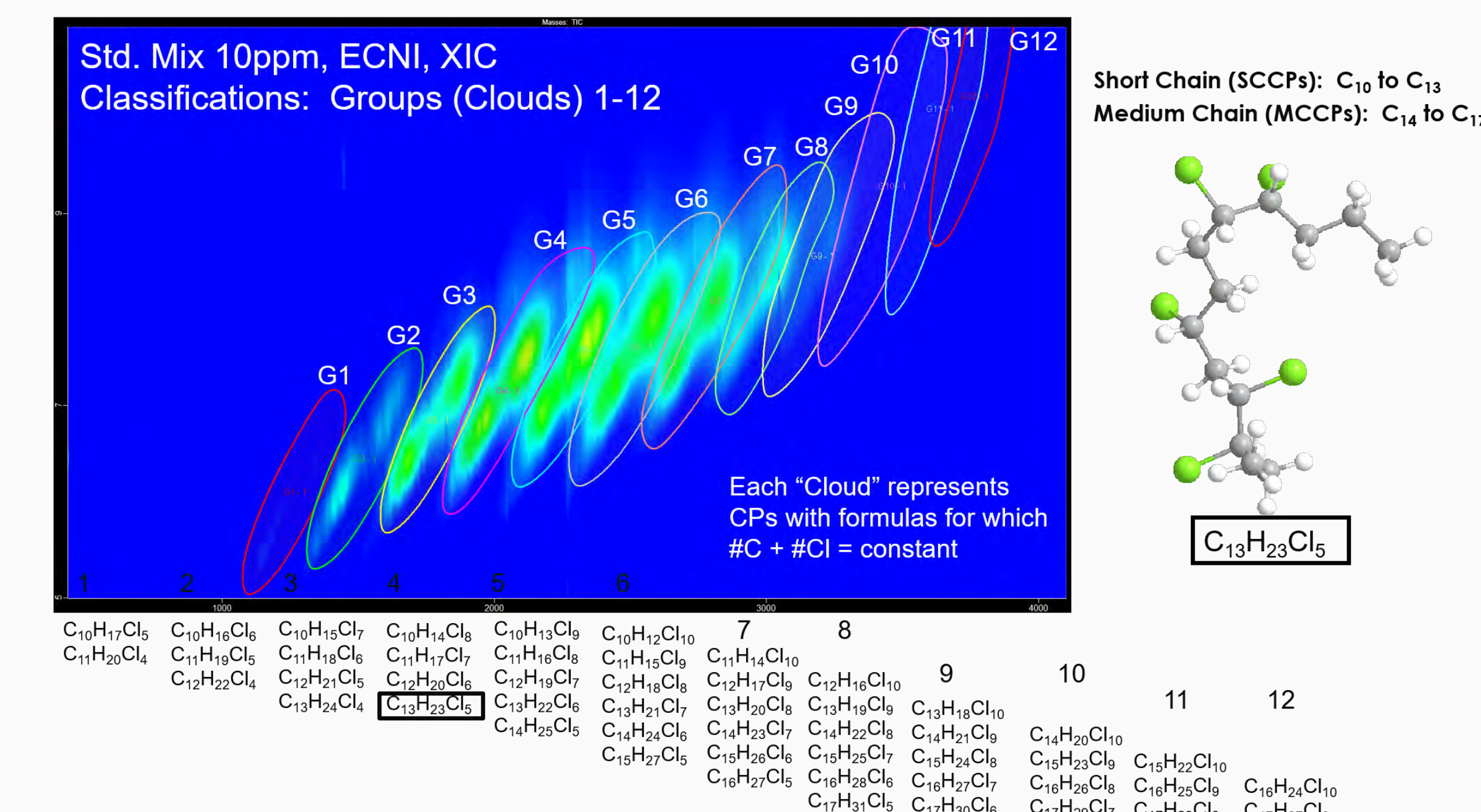


Figure 9. ECNI plot for PCPs in a calibration standard mix. Each group (cloud) region represents PCPs for which the number of carbon + chlorine atoms is constant.

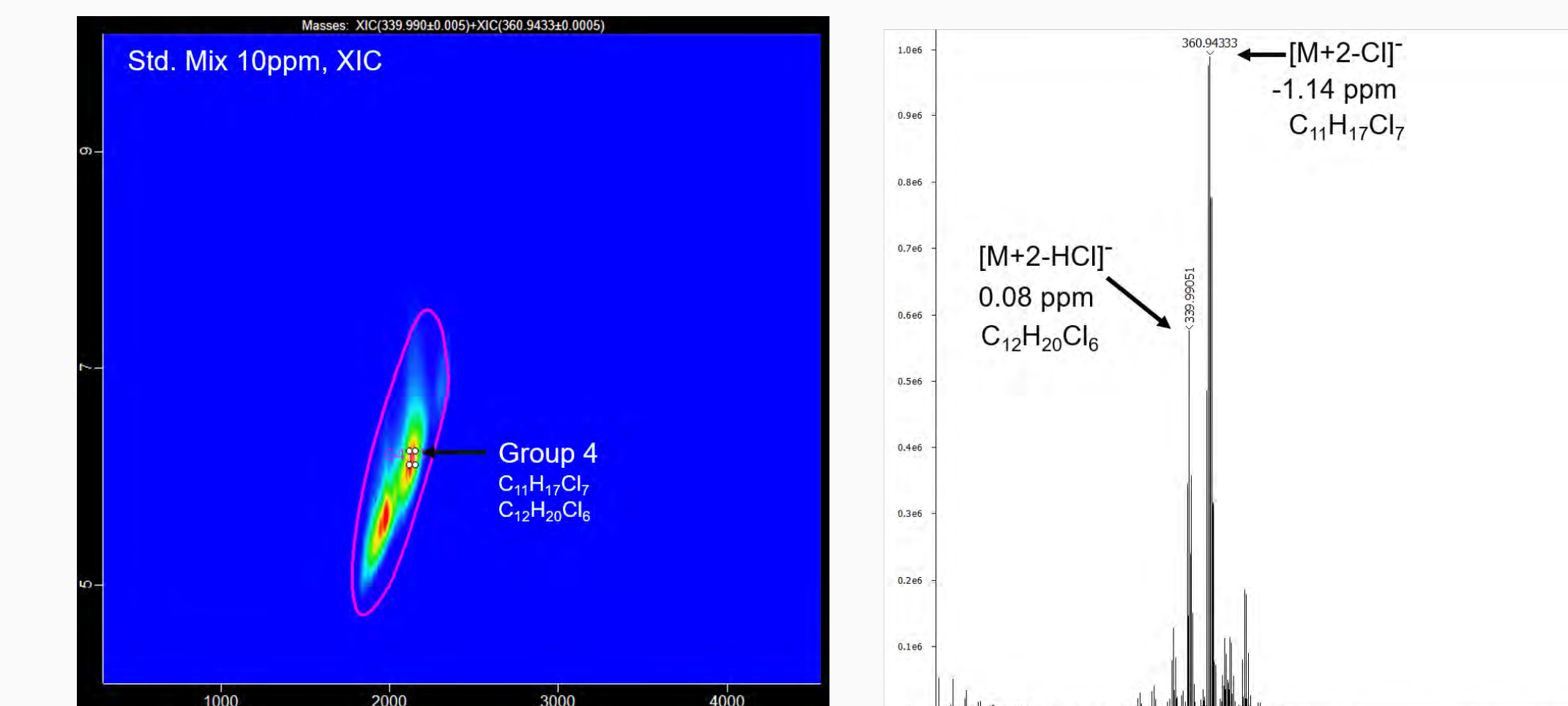


Figure 10. ECNI Plot for Group 4 PCPs with formulas C₁₁H₁₇Cl₇ and C₁₂H₂₀Cl₆. Mass accuracy values for the most abundant isotope in each cluster was -1.14 and 0.08 ppm respectively.

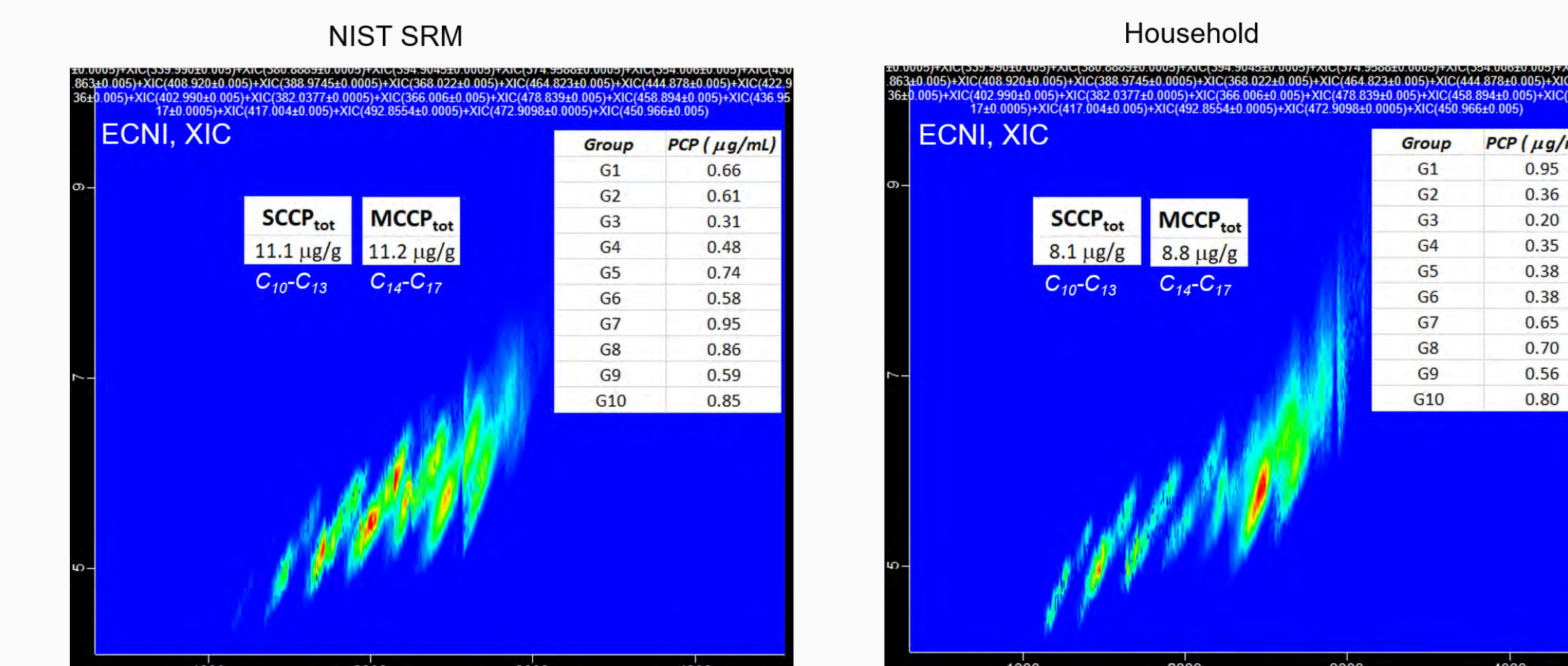


Figure 11. ECNI Plot for SCCPs and MCCPs in the NIST SRM and a household dust sample.

Summary

- HRT and 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