# 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

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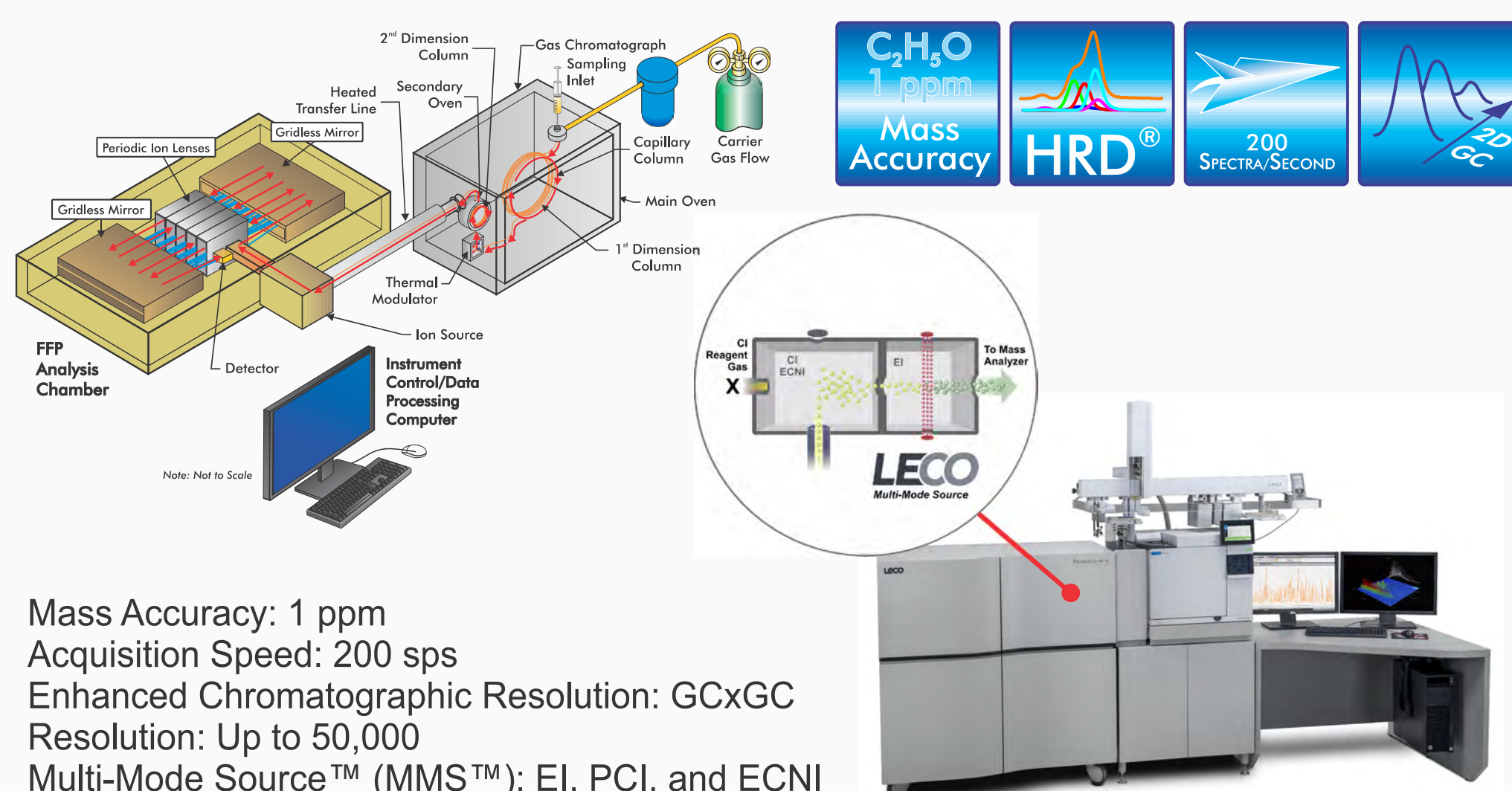


Mass Accuracy: 1 ppm
Acquisition Speed: 200 sps
Enhanced Chromatographic Resolution: GCxGC
Resolution: Up to 50,000
Multi-Mode Source™ (MMS™): EI, PCI, and ECNI

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

## Dust Sample Preparation

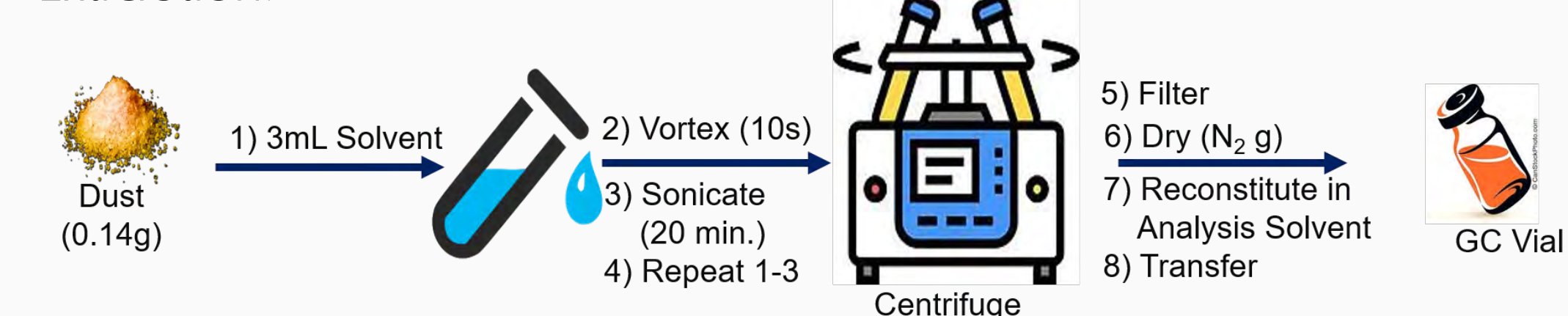- Dust: 1) NIST SRM 2585, 2) Office Sample, and 3) Household Sample
- Extraction:



Dust (0.14g) → 1) 3mL Solvent → 2) Vortex (10s) → 3) Sonicate (20 min.) → 4) Repeat 1-3 → Centrifuge → 5) Filter → 6) Dry (N₂ g) → 7) Reconstitute in Analysis Solvent → 8) Transfer → GC Vial

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 = CH₄) |
| 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
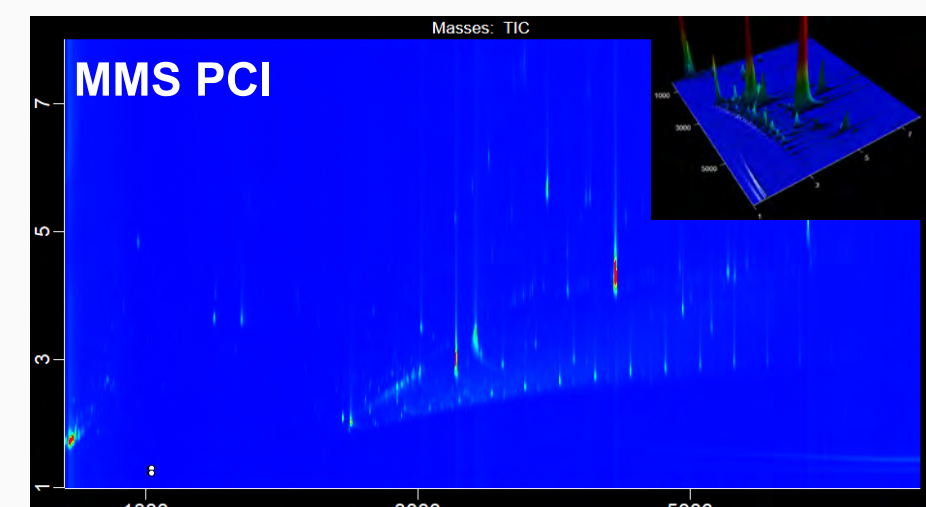
- **Soft ionization** (Less Fragmentation)
- Selective (Electron Rich Compounds)

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
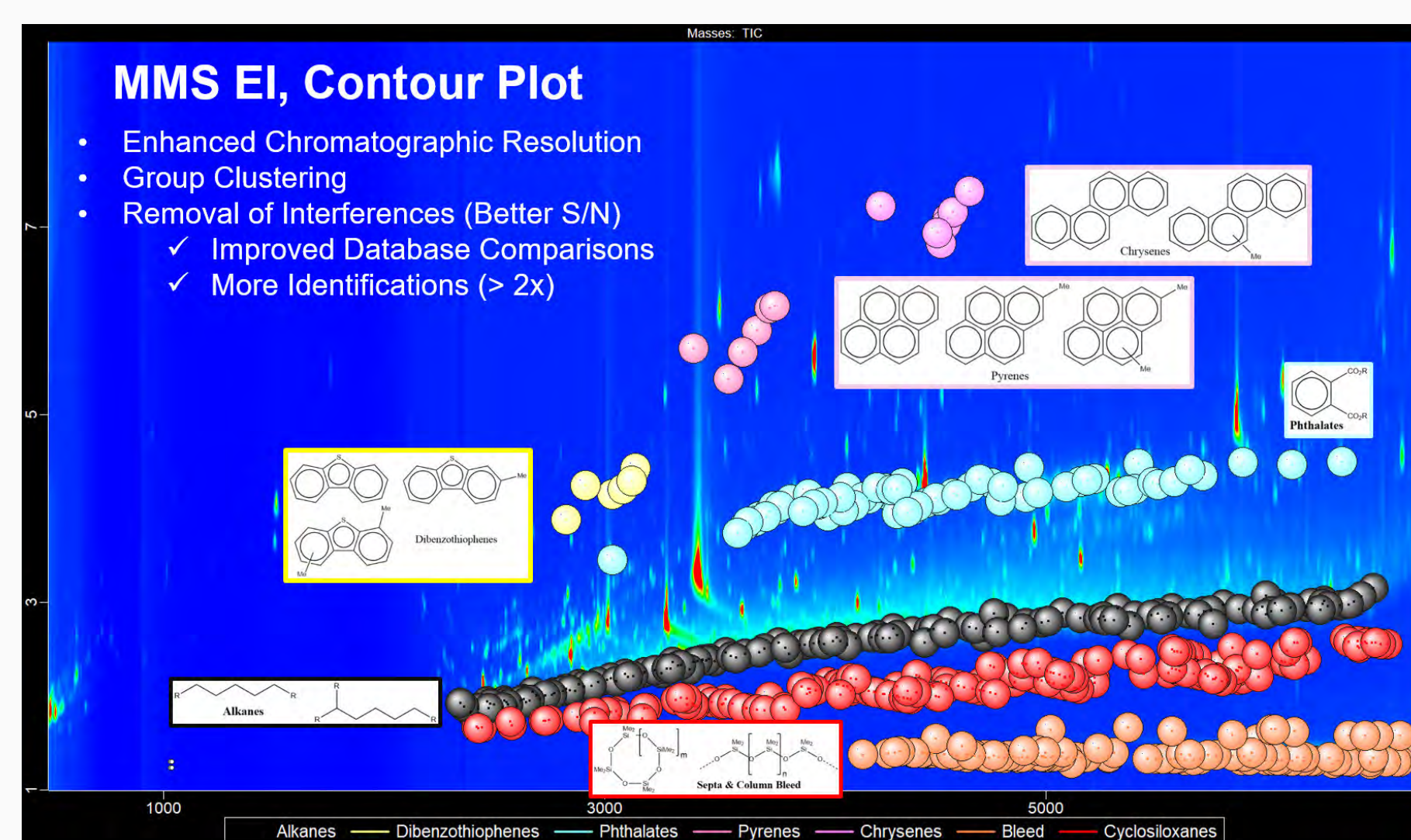


MMS EI, Contour Plot
- Enhanced Chromatographic Resolution
- Group Clustering
- Removal of Interferences (Better S/N)
  - ✓ Improved Database Comparisons
  - ✓ More Identifications (> 2x)

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

Table 2. Representative compounds in SRM 2585.



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

Ave. 880/1000

## NIST SRM 2585: Halogenated Organic Compounds



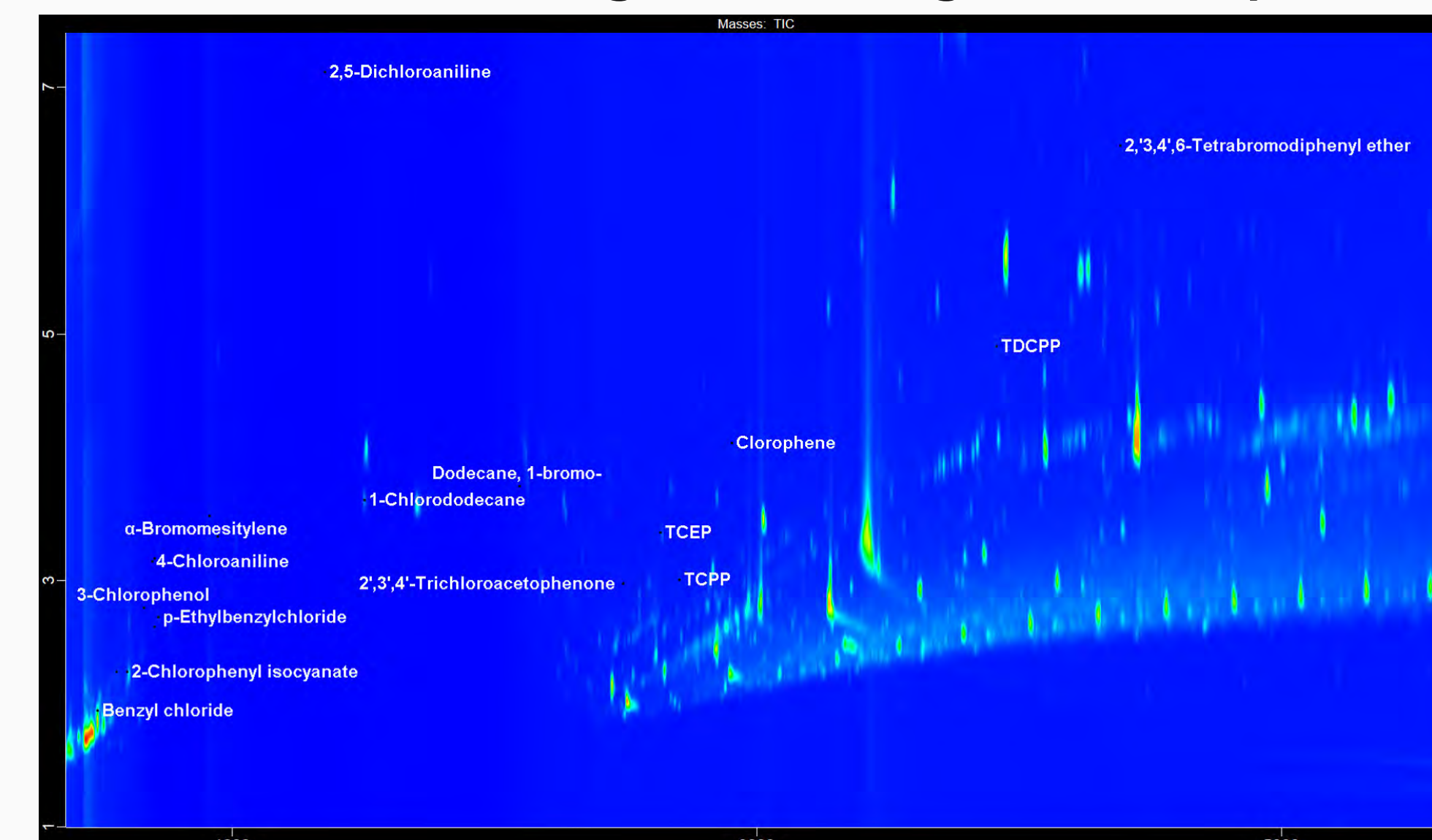Figure 5. EI plot displaying halogenated compounds in SRM 2585.

Table 3. SRM 2585 selected halogenated compounds.



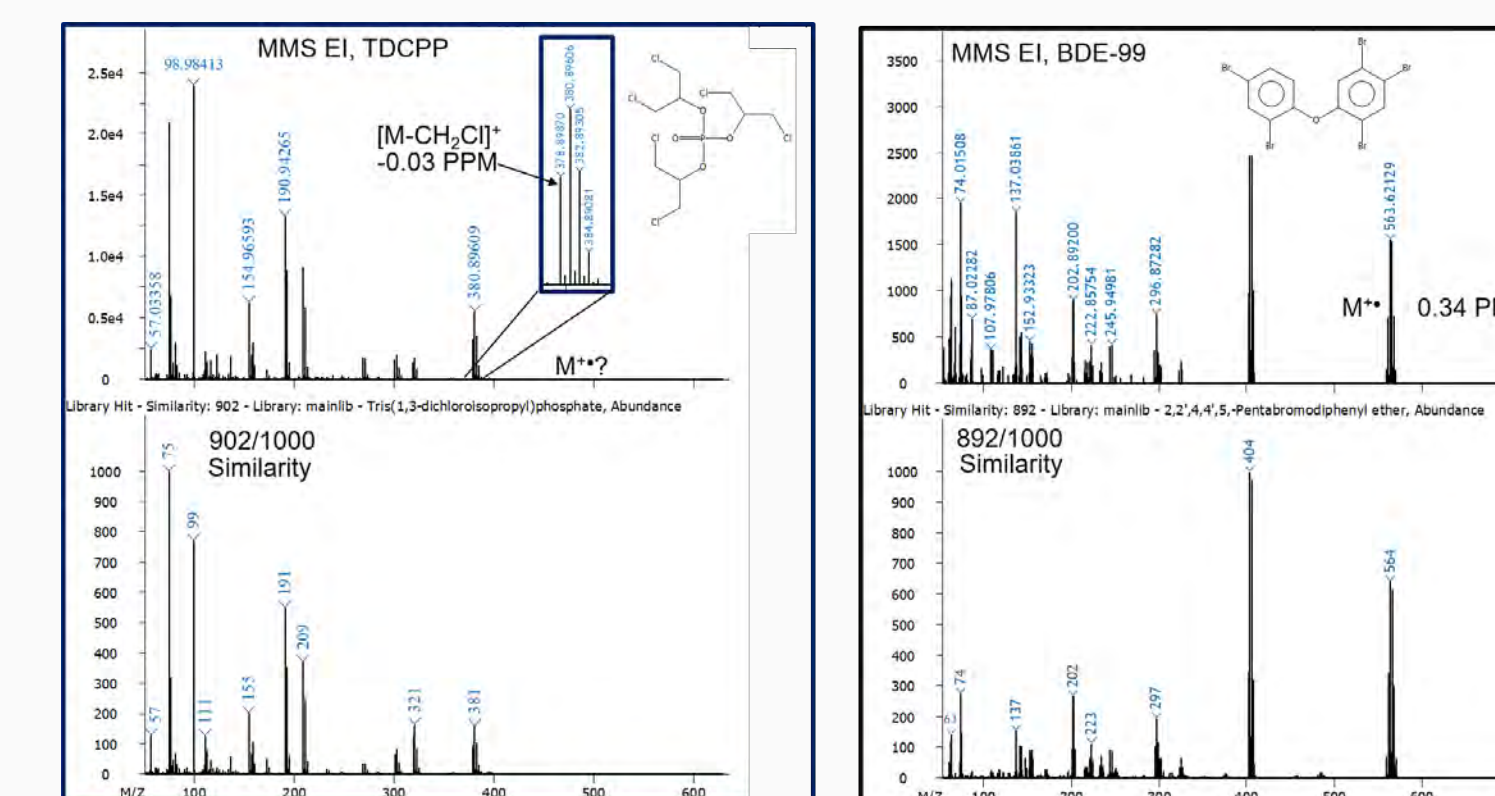Ave. Similarity: 876/1000



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

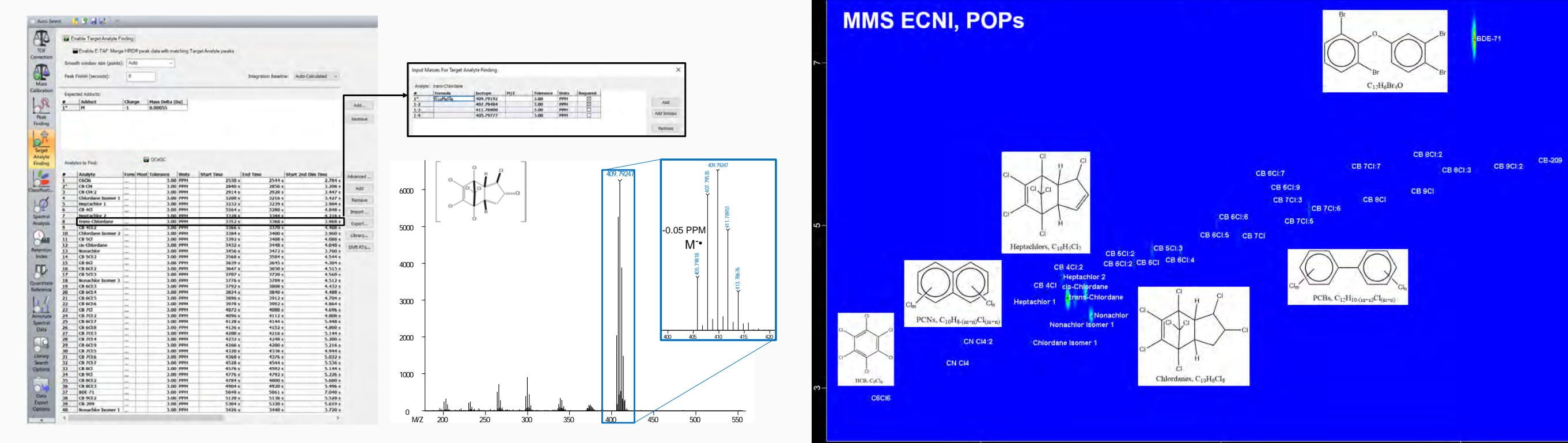## ECNI: Locating Trace POPs in NIST, Office and House Dust



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

Figure 8. ECNI plot displaying POPs in SRM 2585.

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



## Polychlorinated Paraffins: Cloud Quant



Std. Mix 10ppm, ECNI, XIC
Classifications: Groups (Clouds) 1-12

Short Chain (SCCPs): $C_{10}$ to $C_{13}$
Medium Chain (MCCPs): $C_{14}$ to $C_{17}$

Each "Cloud" represents CPs with formulas for which #C + #Cl = constant
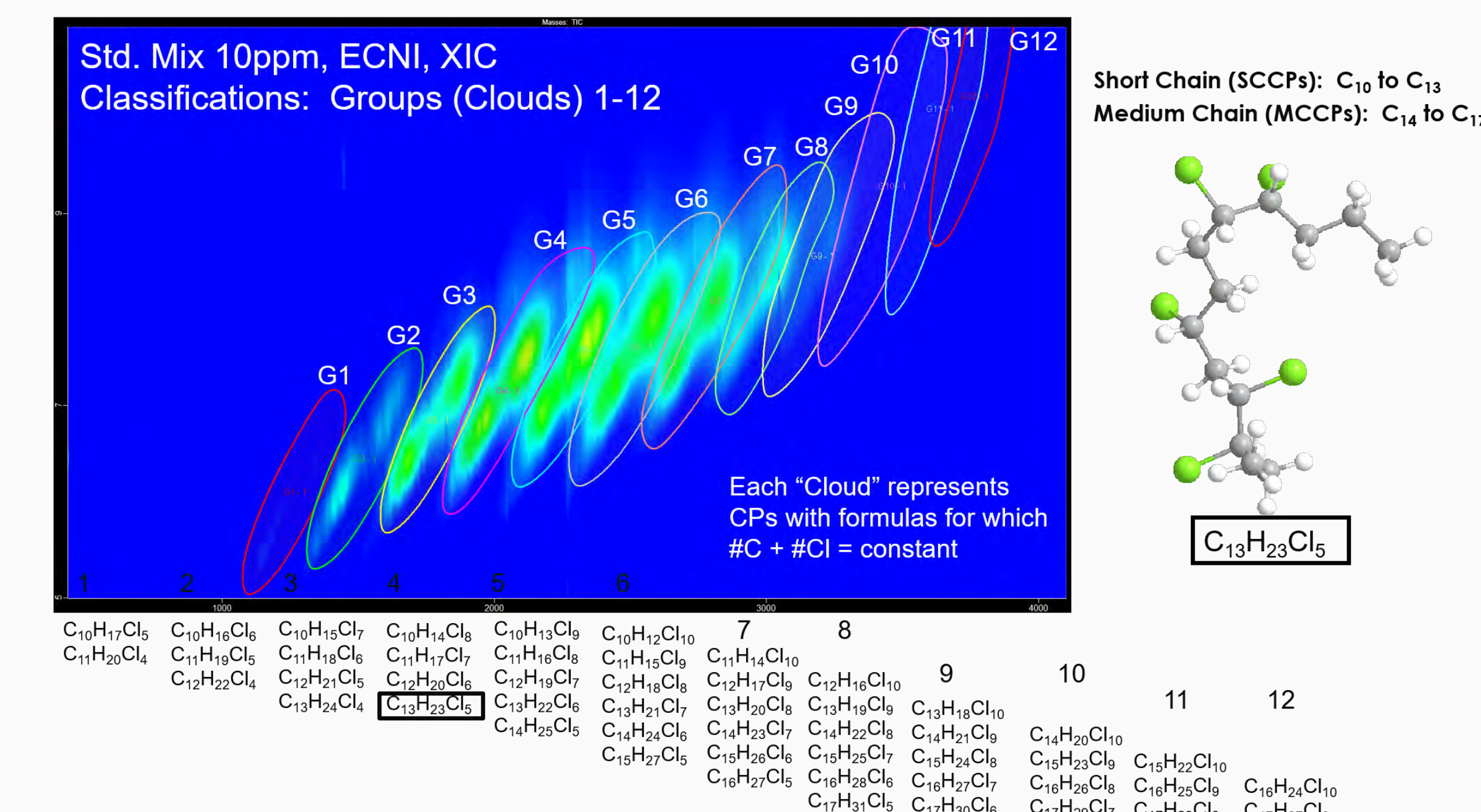
$C_{13}H_{23}Cl_5$

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.
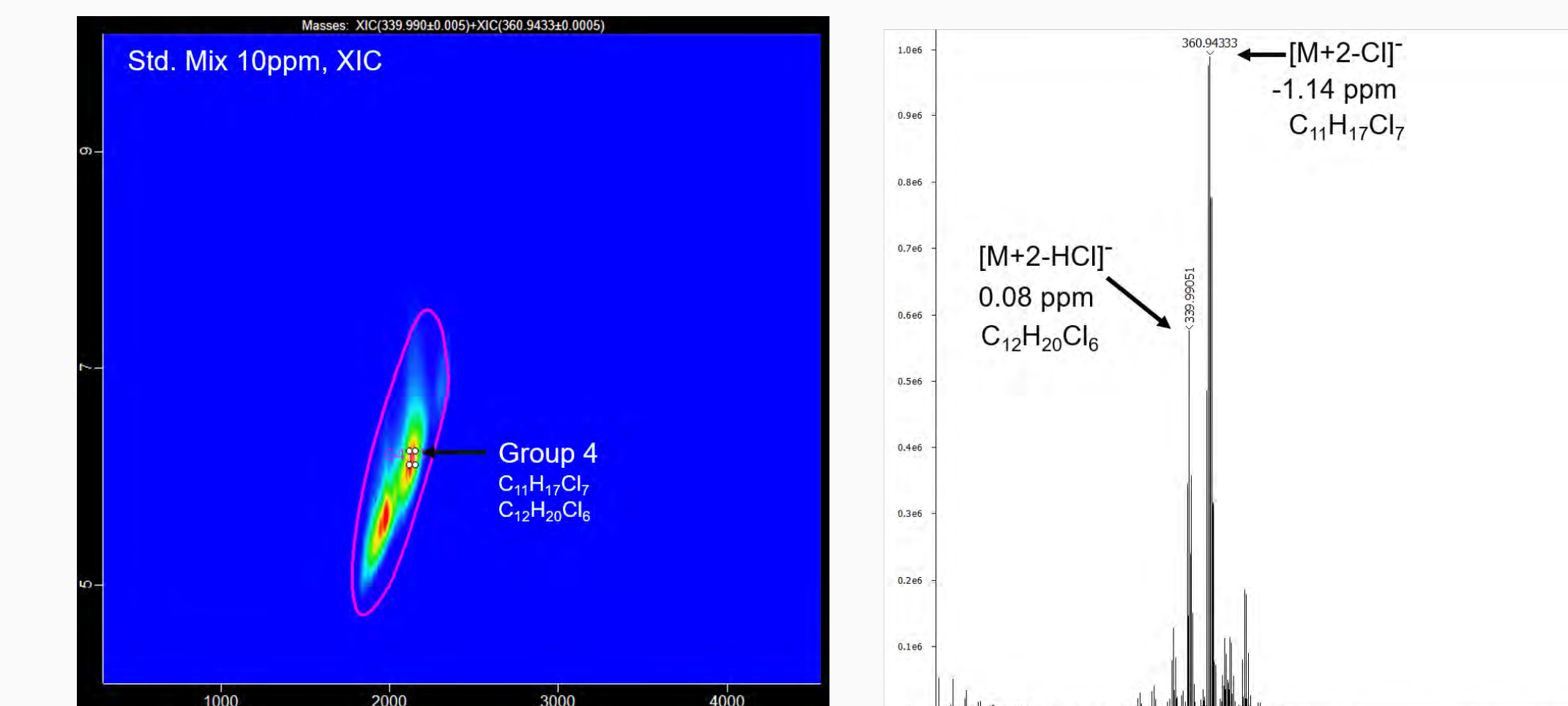


Std. Mix 10ppm, XIC

$[M+2-Cl]^-$
−1.14 ppm
$C_{11}H_{17}Cl_7$

$[M+2-HCl]^-$
0.08 ppm
$C_{12}H_{20}Cl_6$

Group 4
$C_{11}H_{17}Cl_7$
$C_{12}H_{20}Cl_6$

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 and 0.08 ppm respectively.
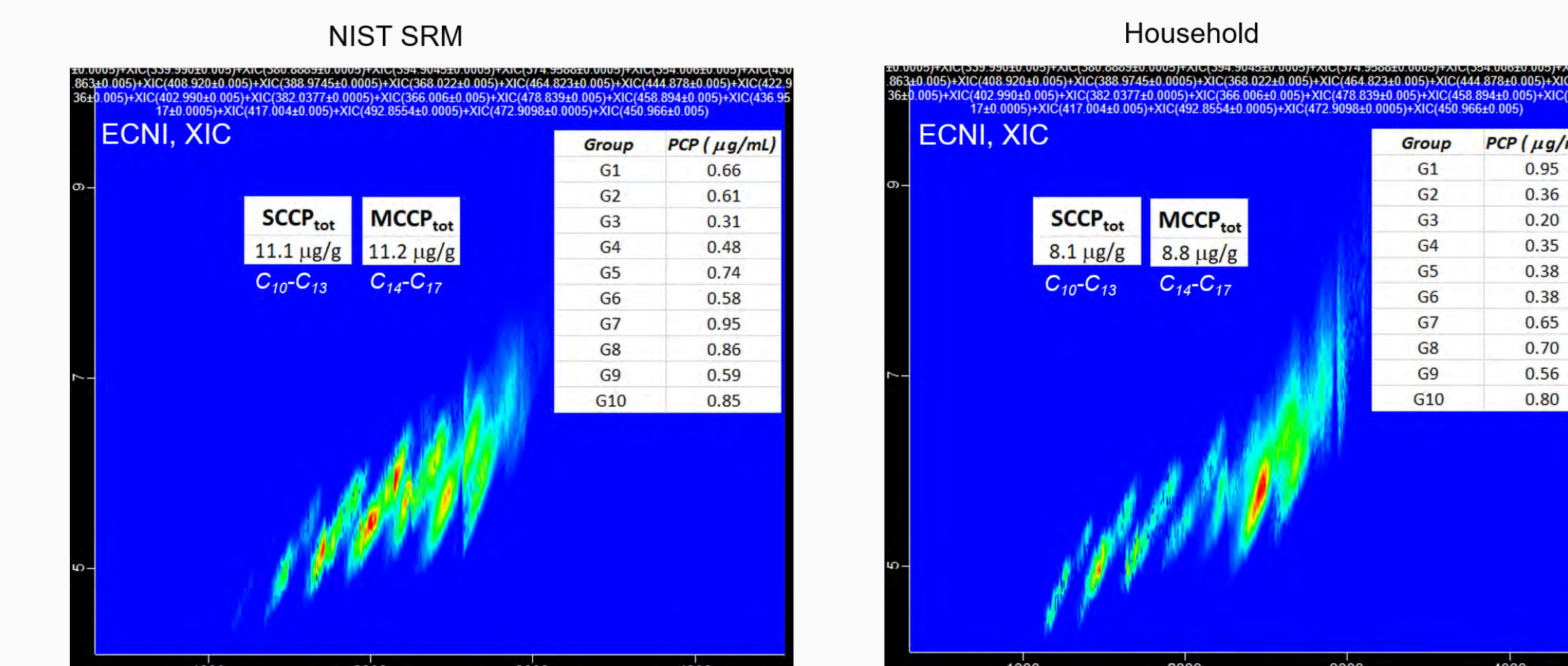


Figure 11. ECNI Plot for SCCPs and MCCPs in the NIST SRM and a household dust sample.

## 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