Comprehensive Characterization of Household Dust Samples Using a Multi-Mode Source, Enhanced Chromatographic Resolution, and High Resolution Mass Spectrometry

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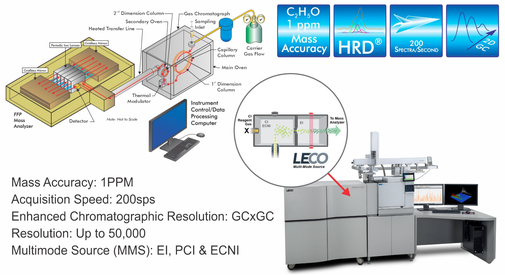
Introduction

- Humans spend most of their lifetimes indoors and are regularly exposed to harmful substances in dust
- Harmful chemicals include persistent organic pollutants, pesticides, polyaromatic hydrocarbons, and flame retardants
- In the past, dust analysis has primarily been conducted using targeted methods

Objective

To use enhanced chromatographic resolution, a novel multi-mode source, and high-resolution time-of-flight mass spectrometry for the comprehensive analysis of dust.

Analytical Platform



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

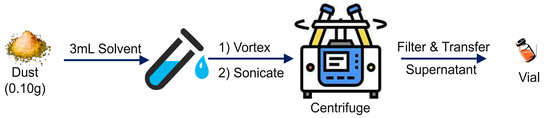
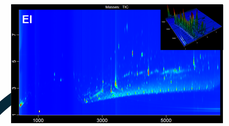


Figure 2. Dust General Extraction Procedure

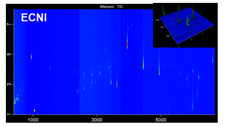
Table 1. Pegasus HRT⁺ 4D Instrument Acquisition Parameters

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 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	55EI3 200 sps; MMS 125 sps

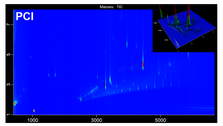
NIST SRM: EI, ECNI and PCI-HRT⁺ 4D Data



- 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 NIST SRM 2585 Data Collected using the Multi-Mode Source

Advantages of GCxGC-HRT⁺ 4D Data

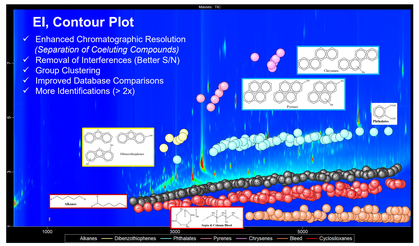


Figure 4. Contour Plot Displaying Some of the Major Compounds in NIST SRM 2585

Table 2. Representative Compounds in NIST SRM 2585

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

Name	Formula	R.T. (s)	Similarity
Benzyl alcohol	C_7H_8O	496.2,0[illegible]	896
p-Cresol	C_7H_8O	520.2,1[illegible]	826
Acetophenone	C_8H_8O	528.2,1[illegible]	942
Phenylethyl Alcohol	$C_8H_{10}O$	576.2,1[illegible]	884
Octanoic acid	$C_8H_{16}O_2$	606.2,1[illegible]	908
Oxacyclohb-2-one	$C_6H_8NO_2$	616.3,1[illegible]	950
Benzonitrile, 2-methoxy-	C_8H_7NO	646.2,1[illegible]	908
3-Dodecene, (Z)-	$C_{12}H_{24}$	646.3,1[illegible]	932
Benzenemethanol, α-dimethyl-	$C_9H_{12}O$	652.2,1[illegible]	910
p-Acetylphenol	$C_8H_8O_2$	672.2,1[illegible]	932
Methyl salicylate	$C_8H_8O_3$	688.2,632	775
Naphthalene	$C_{10}H_8$	686.2,7[illegible]	952
Ethanol, 2-phenoxy-	$C_8H_{10}O_2$	720.3,064	809
Benzothiazole	C_7H_5NS	732.3,104	906
Nonanoic acid	$C_9H_{18}O_2$	760.2,646	873
5-Decanol	$C_{10}H_{22}O$	792.2,4[illegible]	920
1H-Indole-3-one, 2,3-dihydro-	C_8H_7NO	804.4,076	815
Indole	C_8H_7N	888.4,438	835
5-Acetoxymethyl-2-furaldehyde	$C_8H_8O_4$	896.4,200	915
Decanal	$C_{10}H_{20}O$	904.2,4[illegible]	910
Benzamide	C_7H_6NO	968.3,657	934
Capric acid	$C_{10}H_{20}O_2$	1008.3,184	897
Caprin acid	$C_{10}H_{20}O_2$	1016.3,344	898
Benzaldehyde, 4-hydroxy-	$C_7H_6O_2$	1024.5,384	915
Cinpedin	$C_{15}H_{24}O$	1032.5,1[illegible]	864
E-11,13-Tetradecadien-1-ol	$C_{14}H_{26}O$	1064.3,057	922
2(3H)-Furanone, dihydro-5-pentyl-	$C_9H_{16}O_2$	1064.4,352	874
1-Tetradecene	$C_{14}H_{28}$	1120.2,600	944
Dodecanal	$C_{12}H_{24}O$	1208.3,352	934
Acetophenone	C_8H_8O	1408.3,363	905
2-Undecanethiolane	$C_{15}H_{30}S$	1432.3,[illegible]	915
1-Dodecanol	$C_{12}H_{26}O$	1464.3,[illegible]	910
Diisobutyl maleate	$C_{12}H_{20}O_4$	1624.4,464	900
1-Dodecanamine, N,N-dimethyl-	$C_{14}H_{31}N$	1704.3,152	942
1-Iodo-octad	$C_{18}H_{37}I$	1744.4,461	890
Lauric acid	$C_{12}H_{24}O_2$	2120.4,046	906

Name	Formula	R.T. (s)	Similarity
22-Cholestanolide	$C_{27}H_{46}O_2$	2168.1,810	897
α-Tridecan-1-ol	$C_{13}H_{28}O$	2184.2,908	970
Ethyl salicylate	$C_9H_{10}O_3$	2192.3,600	940
Cotinine	$C_{10}H_{12}N_2O$	2248.2,240	934
2-Undecanone	$C_{11}H_{22}O$	2264.3,512	930
Epicotinine	$C_{10}H_{12}N_2O$	2328.2,800	904
Octadecanamine	$C_{18}H_{39}N$	2352.3,600	906
Benzophenone	$C_{13}H_{10}O$	2360.3,047	910
Tributyl phosphate	$C_{12}H_{27}O_4P$	2400.2,304	917
2-Ethyl-1-hexanol, (R-(R*,R*))-	$C_8H_{18}O_2$	2408.3,[illegible]	913
β-Hepbalanone	$C_{13}H_{26}O$	2464.3,592	919
n-Hexyl salicylate	$C_{13}H_{18}O_3$	2464.3,840	929
Triamcinolonolone	$C_{21}H_{30}O_5$	2472.3,040	882
3-Phenoxy-4-fluorobenzaldehyde	$C_{13}H_9FO_2$	2472.3,064	888
Tetradecanamide	$C_{14}H_{29}NO$	2488.2,288	884
9(11),5-Dimethylheptylfulvene	$C_{14}H_{20}$	2512.2,528	995
Veratrone	$C_{11}H_{14}O_3$	2520.3,040	902
Cholesterol	$C_{27}H_{46}O$	2544.3,488	910
Myristic acid	$C_{14}H_{28}O_2$	2616.3,400	902
Benzyl Benzoate	$C_{14}H_{12}O_2$	2640.3,360	926
Vanillylidene	$C_8H_8O_3$	2656.3,672	904
9-Octanone, (E)-	$C_{18}H_{34}O$	2672.3,032	901
Benzenecarboxamide, 3-phenoxy-	$C_{13}H_{11}NO_2$	2680.3,680	882
1H-Indole-3-carboxaldehyde	C_9H_7NO	2720.3,024	920
Vanillin	$C_8H_8O_3$	2840.3,888	872
Methyl palmitate	$C_{17}H_{34}O_2$	2936.3,400	795
Isomitis acid	$C_{18}H_{32}O_2$	3024.3,848	898
Phenylethyl salicylate	$C_{15}H_{14}O_3$	3040.3,920	854
Methyl dehydroabietate	$C_{21}H_{30}O_2$	3048.4,[illegible]	910
9,12H-Benzanthrone	$C_{17}H_{10}O$	3072.4,584	845
p-Terphenyl	$C_{18}H_{14}$	3080.5,592	822
trans-3,5-Dimethoxystilbene	$C_{16}H_{16}O_2$	3656.5,136	877

Name	Formula	R.T. (s)	Similarity
2,8-Diphenylpyridine	$C_{23}H_{15}N$	3672.5,640	795
1,8-Dioxacyclotetradecane-2,7-dione	$C_{12}H_{20}O_4$	3704.7,416	874
Tributyl acetylcitrate	$C_{20}H_{34}O_8$	3712.5,592	874
Tert-octylphenylperoxe	$C_{14}H_{22}O_2$	3776.4,672	768
N-Methyl-N-benzylstearoylacetamide	$C_{28}H_{55}N$	3864.5,216	850
Methyl dehydroabietate	$C_{21}H_{32}O_2$	3936.4,576	894
Octadecanamide	$C_{18}H_{37}NO$	4056.4,016	790
Benzoylfluoranthene	$C_{23}H_{12}O$	4072.4,680	879
Benzo[ghi]perylene	$C_{22}H_{12}$	4080.4,696	879
2-Ethyl-2-ethylhexyl phosphate	$C_{16}H_{35}O_4P$	4072.4,824	902
Isopropylphenyl diphenyl phosphate	$C_{21}H_{21}O_4P$	4832.6,024	815
Benzo[pqr]tetraphene, 7-methyl-	$C_{23}H_{14}$	4888.7,112	885
Tri-m-tolylphosphate	$C_{21}H_{21}O_4P$	4896.6,536	847
Tri-p-cresyl phosphate	$C_{21}H_{21}O_4P$	4896.6,568	792
Perylene	$C_{20}H_{12}$	5032.9,200	924
Squalene	$C_{30}H_{50}$	5192.1,440	924
Cholesta 4,6-dien-3-ol, (3β)	$C_{27}H_{44}O$	5272.4,504	881
Cholesta 3,5-diene	$C_{27}H_{46}$	5336.4,248	910
Pyrene	$C_{16}H_{10}$	5368.4,344	901
Methyl tricosahexaene	$C_{24}H_{42}O_2$	5432.4,680	790
Benzo[j]fluoranthene	$C_{20}H_{12}$	5456.9,736	790
p,p'-Dioctylphenylamine	$C_{28}H_{43}N$	5496.4,752	909
28-Nor-17β(H)-hopane	$C_{29}H_{52}$	5552.4,632	900
Cholesterol	$C_{27}H_{46}O$	5648.4,648	895
α-Tocopheryl acetate	$C_{31}H_{52}O_3$	5680.4,160	908
Cholesta 3,5-dien-7-one	$C_{27}H_{42}O$	5872.5,184	922
Campesterol	$C_{28}H_{48}O$	6112.4,872	944
Cholest-4-en-3-one	$C_{27}H_{44}O$	6160.5,172	936
(7bβ,9β)(H)-Hemihopane	$C_{30}H_{54}$	6168.4,648	846
Stigmastanol	$C_{29}H_{52}O$	6184.4,424	936
Stigmasta-4,6-dien-3-one	$C_{29}H_{46}O$	6208.5,616	876
γ-Sitosterol	$C_{29}H_{50}O$	6232.4,880	910
Stigmasta-3,5-dien-7-one	$C_{29}H_{48}O$	6536.5,760	835
Cholestanol, 7-one	$C_{27}H_{48}O$	6560.5,704	912

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NIST SRM 2585: Halogenated Organic Compounds

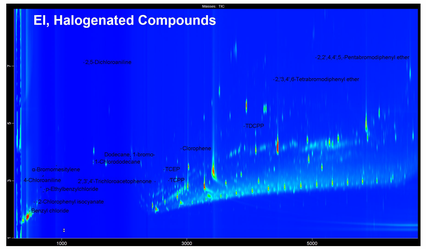

Figure 5. Selected Halogenated Compounds In SRM 2585

Table 3. SRM 2585 Halogenated Compounds

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-Chlorosaline	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',2',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
TDCPP	$C_9H_{15}Cl_6O_4P$	2728.3,064	816	N/A
Clorophene	$C_{13}H_{11}ClO_2$	2904.4,120	824	1.22
TDCPP	$C_9H_{15}Cl_6O_4P$	3912.4,904	902	N/A
2,2',6,6'-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

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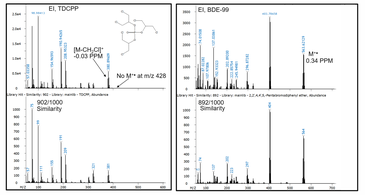

Figure 6. Peak True and Library EI Mass Spectra for TDCPP And BDE-99 in SRM 2585

NIST SRM 2585: EI, Pesticides

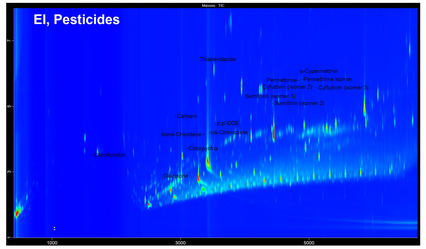

Figure 7. Pesticides in SRM 2585

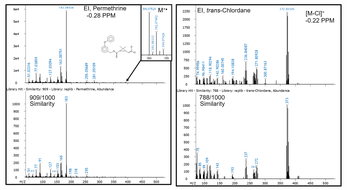

Figure 8. Peak True and Library EI Mass Spectra for Permethrine and trans-Chlordane in SRM 2585

Table 4. SRM 2585 Pesticides

Name	Formula	R.T. (s)	Similarity	Mass Accuracy (ppm)
Chlorfenidim	$C_9H_{11}ClN_2O$	1632.3,512	811	N/A
Diazinone	$C_{12}H_{21}N_2O_4PS$	2712.2,872	818	-0.84
Carbaril	$C_{12}H_{11}NO_2$	2920.4,696	818	N/A
Chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	3104.3,712	827	N/A
Thiabendazole	$C_{10}H_7N_3S$	3272.6,424	929	0.66
trans-Chlordane	$C_{10}H_5Cl_8$	3360.4,136	788	N/A
cis-Chlorodane	$C_{10}H_5Cl_8$	3440.4,200	772	N/A
p,p'-DDE	$C_{15}H_8Cl_4$	3544.4,480	855	-0.62
Sumithrin (isomer 1)	$C_{19}H_{26}O_3$	4400.5,184	871	-0.21
Sumithrin (isomer 2)	$C_{19}H_{26}O_3$	4432.5,084	935	0.2
Permethrine	$C_{21}H_{20}Cl_2O_3$	4840.5,792	909	-0.28
Permethrine Isomer	$C_{21}H_{20}Cl_2O_3$	4888.5,816	914	-0.55
Cyfluthrin	$C_{22}H_{18}Cl_2FNO_3$	5048.5,624	751	N/A
Cyfluthrin (isomer 2)	$C_{22}H_{18}Cl_2FNO_3$	5088.5,584	805	N/A
Cyfluthrin (isomer 3)	$C_{22}H_{18}Cl_2FNO_3$	5128.5,560	817	N/A
α-Cypermethrin	$C_{22}H_{19}Cl_2NO_3$	5160.5,944	844	N/A
β-Cypermethrin	$C_{22}H_{19}Cl_2NO_3$	5192.5,936	883	N/A
Cypermethrin (isomer 3)	$C_{22}H_{19}Cl_2NO_3$	5232.5,904	869	N/A

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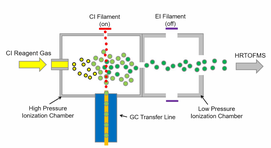
NIST SRM: PCI and ECNI, Pesticides



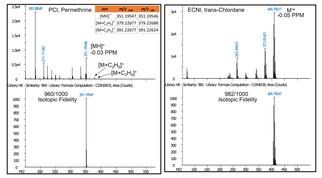


Figure 9. MMS Operating in CI Mode (Left). Peak True Mass Spectra and Isotopic Fidelity for Permethrine (PCI) and trans-Chlordane (ECNI) in SRM 2585

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

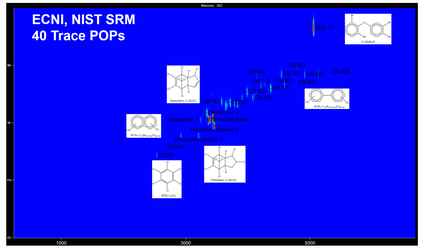


Figure 10. ECNI Contour Plot Displaying Selected POPs in SRM 2585

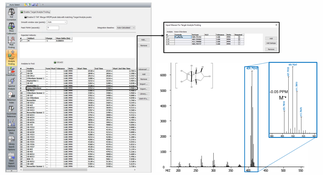


Figure 11. Processing Method Used to Locate Selected POPs in Dust

Table 5. Processing Results Listing POPs in SRM 2585, Office, and Household Dust

Target POP	R.T. (s)	NIST (area)	Office (area)	House (area)
$C_{14}F_8$	2536.2,872	66777	10364	
CN CIII	2848.3,304	13710		
CN CIII-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-6CL2	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-5CL2	3584.4,720	44766	55571	
CB-6CL	3640.4,536	23649	33324	
CB-6CL2	3648.4,520	23937		
CB-5CL3	3712.4,712	304119	305058	
Nonachlor Isomer 3	3784.4,656	98500		
CB-6CL3	3800.4,576	44400	46349	

Target POP	R.T. (s)	NIST (area)	Office (area)	House (area)
CB-8CL4	3832.4,640	20509	34443	
CB-6CL5	3904.4,872	85405	83716	
CB-6CL6	3984.5,096	280450	328292	
CB-7CI	4080.4,864	149348	108803	
CB-7CI-2	4104.4,952	68723	50837	
CB-6CL7	4136.5,632	39203	27433	
CB-6CL8	4144.4,976	27026	22346	
CB-7CI-3	4208.5,304	92038	91365	
CB-7CI-4	4240.5,376	38110	38962	
CB-6CL9	4272.5,392	66771	66771	
CB-7CI-5	4328.5,120	26105	19932	
CB-7CI-6	4368.5,200	397534	369028	
CB-7CI-7	4536.5,720	86694	109695	
CB-8CI	4584.5,332	119235	53370	
CB-9CI	4784.5,416	13906		
CB-8CI-2	4792.5,864	27430	15635	
CB-8CI-3	4912.5,672	94752	58564	
BDE-71	5056.7,288	5480469	433778	663837
CB-9CI-2	5128.5,720	51490	10114	
CB-209	5312.5,792	9879		

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