Analysis of Trace Persistent Organic Pollutants (POPs) in Dust Using a Novel Multi-Mode Ionization Source and High Resolution Time-of-Flight Mass Spectrometry

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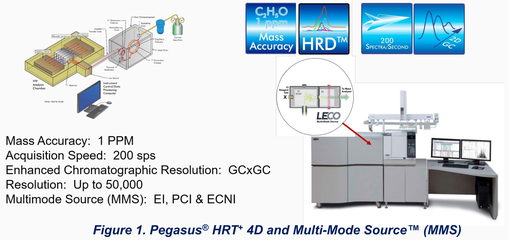
Introduction

- Household 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)
- Analysis of dust has primarily been conducted using targeted methods and different analytical instrumentation

Objectives

1) *To use a novel multi-mode source with high resolution time-of-flight mass spectrometry to analyze dust*
2) *To use enhanced chromatography and HRTOFMS to identify trace POPs in the complex samples*

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

Dust Sample Preparation

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

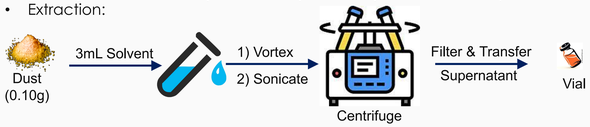


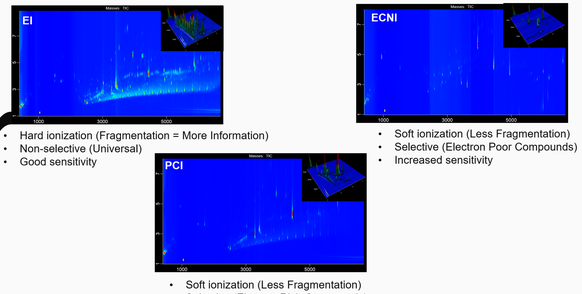
Figure 2. Dust General Extraction Procedure

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	70°C (1 min) to 140°CThen ramp 8°C/min to 300 °C, hold for 4 min Secondary oven maintained +40 °C relative to primary oven
Modulation Period	8.0 seconds
Transfer Line	300 °C
Mass Spectrometer	**LECO Pegasus® HRT⁺ 4D**
Ion Source Temperature	EI, 250ºC; PCI, ECNI, 165ºC
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

Table 1. Pegasus HRT⁺ 4D Instrument Acquisition Parameters

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 2585Data Collected using the Multi-Mode Source

Advantages of GCxGC-HRT⁺ 4D Data

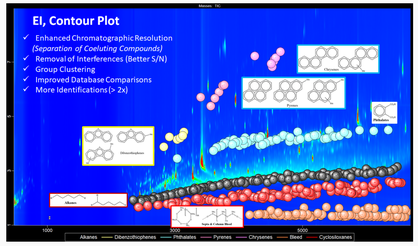


Figure 4. Contour Plot Displaying Some of the Major Compounds Compounds in NIST SRM 2585

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	696.2.084	890
Benzaldehyde	C_7H_6O	696.2.084	890
Acetophenone	C_8H_8O	528.2.140	942
Phenylethyl Alcohol	$C_8H_{10}O$	576.2.244	884
Octanoic acid	$C_8H_{16}O_2$	698.2.246	908
Oxacyclohexadecan-2-one	$C_{15}H_{28}O_2$	616.3.960	900
Benzophenone, 2-methoxy-	$C_{14}H_{12}O_2$	646.2.788	878
3-Dodecene, (Z)-	$C_{12}H_{24}$	648.1.893	917
Hexadecanoic acid, 14-dimethyl-	$C_{18}H_{36}O_2$	664.2.150	888
p-Acetyltoluene	$C_9H_{10}O$	672.2.678	937
Methyl salicylate	$C_8H_8O_3$	688.2.610	775
Naphthalene	$C_{10}H_8$	688.2.731	932
2-Undecanone, 6,9-dimethyl-	$C_{13}H_{26}O$	690.2.834	909
Benzothiazole	C_7H_5NS	732.3.504	928
Nonanoic acid	$C_9H_{18}O_2$	780.2.648	873
1-Decanol	$C_{10}H_{22}O$	1208.3.352	916
3H-Indol-3-one, 2,3-dihydro-	C_8H_7NO	894.4.076	835
Indole	C_8H_7N	880.4.418	878
N-Acetamethyl-7-fluoridehyde	$C_{11}H_{11}NO_2$	888.4.298	955
Tetradecanol	$C_{14}H_{30}O$	912.4.422	734
Benzamide	C_7H_7NO	968.4.027	854
Caprylic acid	$C_8H_{16}O_2$	1036.3.184	857
Capric acid	$C_{10}H_{20}O_2$	1036.3.344	898
Dodecanoic acid, 4-hydroxy-	$C_{12}H_{24}O_3$	1048.3.504	866
Tricosane	$C_{23}H_{48}$	1050.5.216	866
E-11,13-Tetradecadien-1-ol	$C_{14}H_{26}O$	1066.3.057	922
(CH3-Tricosene, dihydro-3-penta)	$C_{23}H_{46}O_2$	1066.4.352	928
2-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
5-Dodecanol	$C_{12}H_{26}O$	1504.4.008	954
Dihydrocuminaldehyde	$C_{10}H_{12}O$	1624.4.464	900
1-Dodecanamine, N,N-dimethyl-	$C_{14}H_{31}N$	1704.3.024	942
Tridecanal	$C_{13}H_{26}O$	1746.4.485	890
Levulic acid	$C_5H_8O_3$	1520.4.040	906
2,6-Dimethylpyridine	C_7H_9N	1048.3.960	907
2-Undecanone	$C_{11}H_{22}O$	1048.3.960	907
2-Tridecanone, 1-cyclopropyl-	$C_{16}H_{30}O$	1048.3.960	907
2-Tridecen-1-ol	$C_{13}H_{26}O$	1048.3.960	907
Ethyl salicylate	$C_9H_{10}O_3$	1048.3.960	907
Carvone	$C_{10}H_{14}O$	1048.3.960	907
2-Tetradecanone	$C_{14}H_{28}O$	1048.3.552	920
Epiestriol	$C_{18}H_{24}O_3$	1048.3.800	904
Diphenylamine	$C_{12}H_{11}N$	1048.3.530	896
Benzophenone	$C_{13}H_{10}O$	1060.3.647	937
Tributyl phosphate	$C_{12}H_{27}O_4P$	1060.3.744	912
Cinnamaldehyde, a-pentyl-	$C_{14}H_{18}O$	1068.3.520	953
9-Hydroxyfluorene	$C_{13}H_{10}O$	1068.3.960	902
Hexacosane	$C_{26}H_{54}$	1068.4.440	909
Methyl salicylate	$C_8H_8O_3$	1068.3.960	902
1-Hexacosanol, 2-hexyl-	$C_{32}H_{66}O$	1068.4.440	909
1-Pentacosanol, 2-hexyl-	$C_{31}H_{64}O$	1068.4.440	909
Tetradecanenitrile	$C_{14}H_{27}N$	1088.2.288	894
4-(1,1-Dimethylallyl)phenol	$C_{11}H_{14}O$	1092.3.536	895
Veramexa	$C_{18}H_{24}O_2$	1520.3.040	902
Diphenamid	$C_{16}H_{17}NO$	1092.3.830	902
Myristic acid	$C_{14}H_{28}O_2$	1036.3.480	892
Benzyl Benzoate	$C_{14}H_{12}O_2$	1040.3.360	926
Vanillyl Ester	$C_{18}H_{28}O_3$	2996.3.672	858
Tri-Decene, (Z)-	$C_{13}H_{26}$	2996.3.672	858
Benzene methanol, 3-phenoxy-	$C_{13}H_{12}O_2$	2985.3.680	840
Benzene, 1-methoxy-4-methyl-	$C_8H_{10}O$	2985.3.680	840
Vanillin	$C_8H_8O_3$	2985.2.888	872
Methyl palmitate	$C_{17}H_{34}O_2$	2996.3.491	795
Vanillin	$C_8H_8O_3$	3000.3.840	898
Phenylethyl salicylate	$C_{15}H_{14}O_3$	3040.3.920	854
Benzoguaiamine	$C_{10}H_{11}N_5O$	3076.3.960	825
2-(3H-Benzotriazol-2-yl)-5-methylphenol	$C_{13}H_{11}N_3O$	3272.4.584	845
Fluorenethene	$C_{15}H_{12}$	3272.3.208	930
3-Octadecanol	$C_{18}H_{38}O$	3280.3.808	945
Stearic acid	$C_{18}H_{36}O_2$	3304.3.512	882
Hexadecanamide	$C_{16}H_{33}NO$	3352.3.712	890
1-Triacontanol	$C_{30}H_{62}O$	3360.3.136	877
trans-13-Octadecenoylchloride	$C_{18}H_{35}ClO$	3696.3.136	877
2,6-Diphenylpyridine	$C_{17}H_{13}N$	3672.5.640	936
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	$C_{16}H_{22}O_4$	3672.5.640	936
Citronine	$C_{10}H_{16}$	2996.3.672	858
Tert-octylphenylamine	$C_{14}H_{23}N$	3776.4.472	768
Tributyl acetyl citrate	$C_{20}H_{34}O_8$	3712.3.592	870
Methyl dehydroabietate	$C_{21}H_{32}O_2$	3596.4.576	864
Octadecanamide	$C_{18}H_{37}NO$	4836.3.936	792
Benzo[g]chrysene	$C_{18}H_{12}$	4072.6.988	879
Triphenyl phosphate	$C_{18}H_{15}O_4P$	4656.4.432	870
Diphenyl 2-ethylhexyl phosphate	$C_{20}H_{27}O_4P$	4692.4.634	802
Isopropylphenyl diphenyl phosphate	$C_{21}H_{21}O_4P$	4692.5.304	835
Benzo[a]anthracene, 7-methyl-	$C_{19}H_{14}$	4608.7.512	848
Tri-o-cresyl phosphate	$C_{21}H_{21}O_4P$	4692.5.536	760
Tri-p-cresyl phosphate	$C_{21}H_{21}O_4P$	4692.5.536	760
Perylene	$C_{20}H_{12}$	5032.8.336	924
Cholestane	$C_{27}H_{48}$	5192.5.488	928
Cholesta-4,6-dien-3-ol, (3β)-	$C_{27}H_{44}O$	5272.4.784	861
Cholesta-1,5-dione	$C_{27}H_{42}O_2$	5328.4.288	910
Pipernine	$C_{17}H_{19}NO_3$	5344.8.344	921
1H-Pyrrole-2-carboxylic acid, 1-(2-furanylmethyl)-5-methyl-	$C_{11}H_{11}NO_3$	5184.4.944	865
Benzo[b]chrysene	$C_{18}H_{12}$	5436.7.592	790
Cholesta-4,6-dien-3-one	$C_{27}H_{42}O$	5272.4.784	861
Cholest-4-en-3-one	$C_{27}H_{46}O$	5328.4.288	910
Cholest-4-en-3-one, (3β)-(9CI)-Homolanopor	$C_{27}H_{46}O$	5328.4.288	910
Stigmastanol	$C_{29}H_{52}O$	5328.4.288	910
Cholesta-4,6-dien-3-one	$C_{27}H_{42}O$	5272.4.784	861
γ-Sitosterol	$C_{29}H_{50}O$	5520.4.480	919
Stigmasta-3,5-dien-7-one	$C_{29}H_{46}O$	5520.4.768	910
Cholesterol, T-sulv	$C_{27}H_{46}O$	5440.4.768	910

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Table 2. Representative Compounds in NIST SRM 2585

NIST SRM 2585: Halogenated Organic Compounds

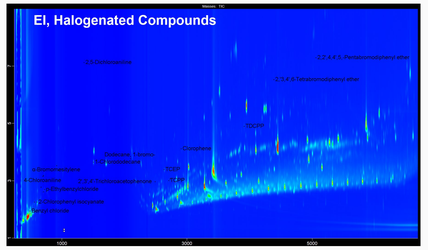

Figure 5. Selected Halogenated Compounds In SRM 2585

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-Chlorocaniline	C_6H_6ClN	704.3.184	816	1.13
p-Ethylbenzylchloride	$C_9H_{11}Cl$	720.2.704	931	0.23
α-Bromomcstylene	C_9H_9Br	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',4,5-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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Table 3. SRM 2585 Halogenated Compounds

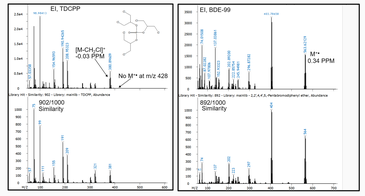

Figure 6. Peak True and Library EI Mass Spectra for TDCPP And BDE-99 in SRM 2585

NIST SRM 2585: EI, Pesticides

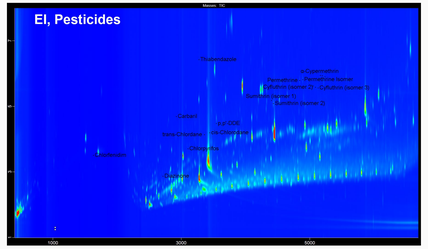

Figure 7. Pesticides in SRM 2585

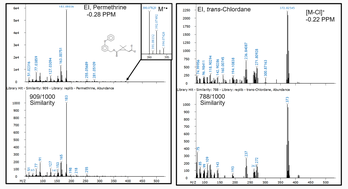

Figure 8. Peak True and Library EI Mass Spectra for Permethrine and trans-Chlordane in SRM 2585

Name	Formula	R.T. (s)	Similarity	Mass Accuracy (ppm)
Chlorfenidim	$C_9H_{11}ClN_2O$	1632.3.512	811	N/A
Diazinone	$C_{12}H_{21}N_2O_3PS$	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	$C_{10}H_6Cl_8$	3360.4.136	788	N/A
cis-Chlordane	$C_{10}H_6Cl_8$	3440.4.200	772	N/A
p,p'-DDE	$C_{14}H_8Cl_4$	3544.4.480	855	-0.62
Sumithrin (isomer 1)	$C_{23}H_{26}O_3$	4400.5.184	871	-0.21
Sumithrin (isomer 2)	$C_{23}H_{26}O_3$	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
Cyflluthrin	$C_{22}H_{18}Cl_2FNO_3$	5048.5.624	751	N/A
Cyflluthrin (isomer 2)	$C_{22}H_{18}Cl_2FNO_3$	5088.5.584	805	N/A
Cyflluthrin (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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Table 4. SRM 2585 Pesticides

NIST SRM: PCI and ECNI, Pesticides

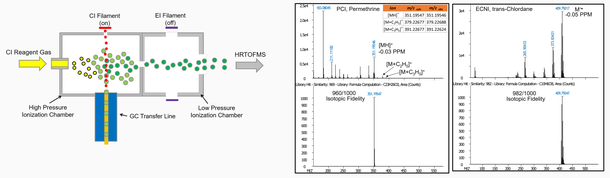

Figure 9. MMS Operating in CI Mode (Left). Peak True Mass Spectra and Isotopic Fidelity for Permethrine (PCI) and trans-Chlordane (ECNI) in SRM 2585

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

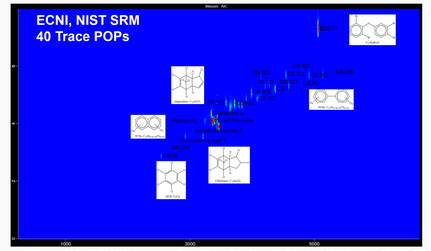

Figure 10. ECNI Contour Plot Displaying Selected POPs in SRM 2585

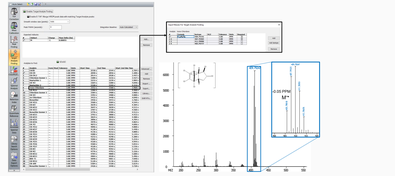

Figure 11. Processing Method Used to Locate Selected POPs in Dust

Target POP	R.T. (s)	NIST (area)	Office (area)	House (area)
C_6Cl_6	2536.2.872	66777	55364	485688
CN CH	2848.3.304	13710		
CN CH-2	2920.3.568	543301		
Chlordane Isomer 1	3208.3.552	62129		
Heptachlor 1	3232.4.128	15887		
CB 4CI	3272.4.192	21645	8827	
Heptachlor 2	3336.4.360	215913		
trans-Chlordane	3360.4.112	1730979	3025	11470
CB 4CI-2	3368.4.552	10321	1454	
Chlordane Isomer 2	3392.4.096	266412		
CB 5CI	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 5CI-2	3584.4.720	44766	55571	
CB 6CI	3640.4.536	23649	33324	
CB 6CI-2	3648.4.520	23937		
CB 5CI-3	3712.4.712	304119	305058	
Nonachlor Isomer 3	3784.4.656	98500		
CB 6CI-3	3800.4.576	44400	46349	

Target POP	R.T. (s)	NIST (area)	Office (area)	House (area)
CB 6CI-4	3832.4.640	285099	324443	
CB 6CI-5	3904.4.872	85405	83716	
CB 6CI-6	3984.5.096	280450	328292	
CB 7CI	4080.4.864	149348	108803	
CB 7CI-2	4104.4.952	68723	50837	
CB 6CI-7	4136.5.632	39203	47433	
CB 6CI-8	4144.4.976	27026	22346	
CB 7CI-3	4208.5.304	92038	91365	
CB 7CI-4	4240.5.376	38110	38962	
CB 6CI-9	4272.5.592	67431	66771	
CB 7CI-5	4328.5.120	26105	19932	
CB 7CI-6	4384.5.200	397534	369028	
CB 7CI-7	4536.5.720	86694	109695	
CB 8CI	4584.5.312	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		

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

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