

Semi-Volatiles Analysis with USEPA Method 525.2 using the GCMS-QP2010

Introduction

The USEPA Method 525.2 is the analytical method used to determine semi-volatile organic compounds (SVOCs) in drinking water, source water and finished drinking water under the guidance of the United States Environmental Protection Agency. The EPA method 525.2 requires numerous quality controls (QC).

This application shows that the GCMS-QP2010 with the EPA option software (accessory) satisfies these requirements of QC. Using the method file of the GCMS solution for the EPA 525.2, the analysis is simple and straightforward.

The method file of GCMS solution specialized EPA525.2 has been provided at no charge.



Experimental

Five calibration mixture samples from Supelco were mixed as stock standard sample. The analytical parameters for the GCMS-QP2010 are optimized according to technical guidance of EPA 525.2 method. (Table 1)

Table 1. Analytical Parameters of GCMS-QP2010

GC parameter

GC column	: RTX5ms (30m×0.25mm id, 0.25um)
Column oven temperature	: 45C (1min) → (45C/min)→ 130C → (12C/min) → 180C → (7C/min) → 240C → (12C/min) →320C(3min)
Injection mode	: Splitless
Injection temperature	: 230C
Flow control mode	: Linear velocity (33cm/sec)
Purge flow	: 4mL
Sampling time	: 1min

MS parameter

Ion source temperature	: 200C
Interface Temperature	: 250C
Detector voltage	: 0.9kV
Acquisition mode	: Scan
Acquisition range	: 45-450
Interval	: 0.5(sec)
Acquisition time	: 4-26min
Solvent cut time	: 3.5min

AOC-20i (Autosampler) parameter

Sample volume	: 1um
Viscosity comp. Temp	: 0.2sec
Number of rinse	
with solvent	: 2
Number of rinse	
with sample	: 1
Syringe injection speed	: high

Mass Tuning Check

The specific criteria for mass tuning is checked in order to provide continuity of analysis. Table 2 shows the ion abundance criteria of the EPA525.2 method. The GCMS solution software can automatically evaluate the measured mass spectrum of DFTPP(decafluorotriphenylphosphine) and print the result. (Fig.1 and 2) The report format can be easily modified.

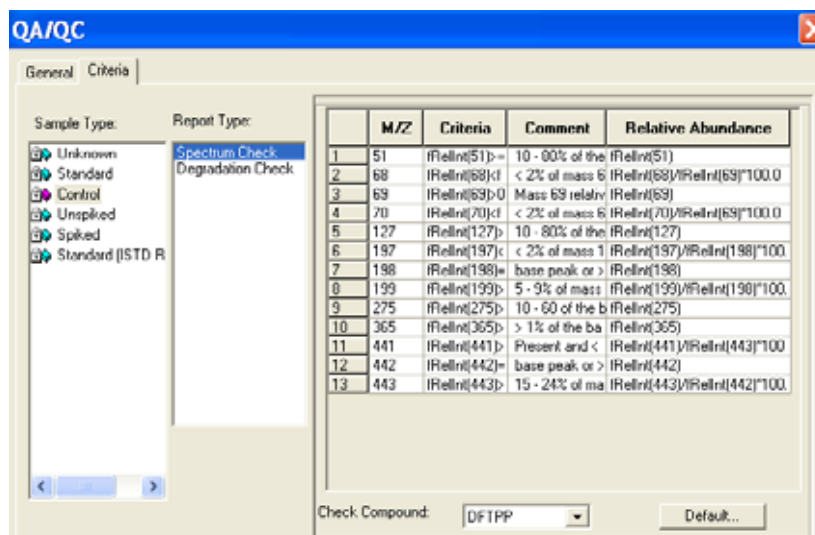


Figure 1. Ion Abundance Check macro

Table 2. Ion Abundance Criteria and it's Results

M/Z	Spectrum Check Criteria	Result
51	10 - 80% of the base peak	33.89
68	< 2% of mass 69	1.09
69	Mass 69 relative abundunce	29.68
70	< 2% of mass 69	0.31
127	10 - 80% of the base peak	34.89
197	< 2% of mass 198	0.15
198	base peak or > 50% of 442	78.43
199	5 - 9% of mass 198	6.47
275	10 - 60 of the base peak	19.35
365	> 1% of the base peak	1.66
441	Present and < mass 443	74.65
442	base peak or > 50% of mass 198	100.00
443	15 - 24% of mass 442	18.73

ION CRITERIA	REL 198%	REL 442%	STATUS
10-80% of the base peak	33.89338	78.43258	Pass
< 2% of mass 69	1.09250	1.088318	Pass
Mass 69 relative abundance	29.681266	29.681266	Pass
< 2% of mass 70	0.311343	0.309423	Pass
10-80% of the base peak	34.89794	34.89794	Pass
< 2% of mass 197	0.151108	0.145488	Pass
base peak or > 50% of 442	78.43118	78.43118	Pass
5-9% of mass 198	6.469361	6.469788	Pass
10-60 of the base peak	19.35123	19.348328	Pass
> 1% of the base peak	1.661111	1.661111	Pass
Present and < mass 443	74.65188	74.65188	Pass
base peak or > 50% of mass 198	100.00000	100.00000	Pass
15-24% of mass 442	18.73066	18.73066	Pass

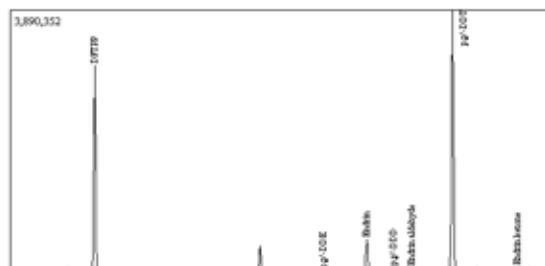
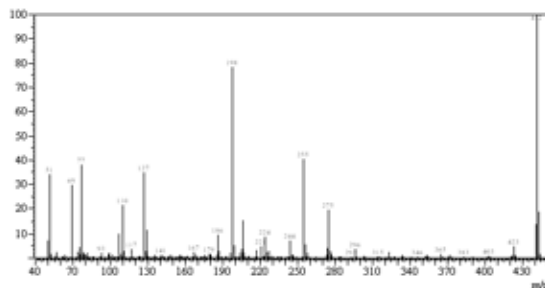


Figure 2. Report of Calibration of the Mass and Abundance

Degradation Check

4,4'-DDT and endrin are used for the degradation check. Fig.3 shows the total ion chromatogram of DFTPP, 4,4'-DDT and endrin at 5ng/uL. The degradation levels of 4,4'-DDT and endrin are shown in Table 3. These levels were less than 20% which is the maximum acceptable level.

Table 3. Degradation of 4,4'-DDT and endrin

Compound Name	Area	%Degradation
4,4'- DDT	7642500	1.39
4,4'- DDE	3681	
4,4'- DDD	104183	
endrin	1039250	11.79
endrin aldehyde	51504	
endrin ketone	87399	

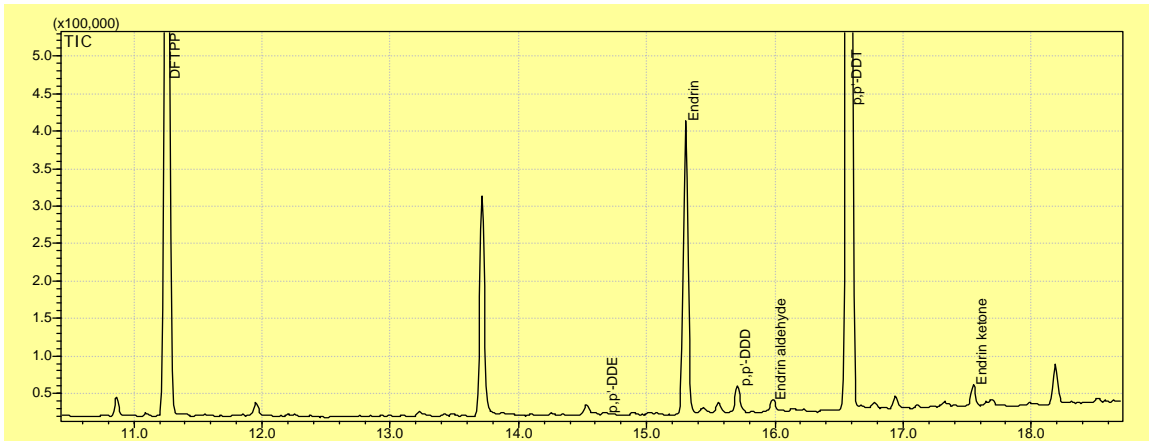


Figure 3. Total ion chromatogram of DFTPP and 4,4'-DDT and endrin

Calibration

The six calibration solutions were prepared at concentrations of 0.1, 0.5, 1,2, 5, 10 ng/ul except pentachloropnenol which was prepared at a four time higher. The concentration level for each internal standard and surrogate was set at 5 ng/ul. Fig.4 shows total ion chromatogram of the calibration solution at 1ppm. Fig.5 shows mass chromatograms of seven target compounds at 0.1 ng/ul. Also fig.5 shows calibration curves of six target compounds at concentrations from 0.1 to 10 ng/ul. For each analyte, the mean response factor (RF) and the relative standard deviation (RF %RSD) were calculated. (Table 4.) The RF%RSD for each analyte must be within 30% of the mean value. The RF %RSD of all compounds satisfied this criteria.

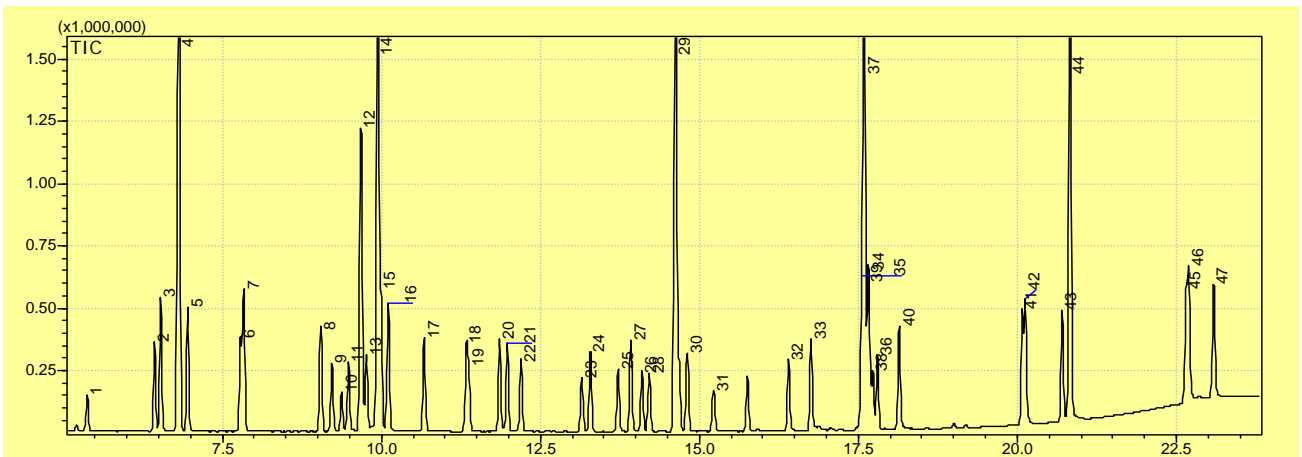


Figure 4. Total ion chromatogram of 1ppm standard solution

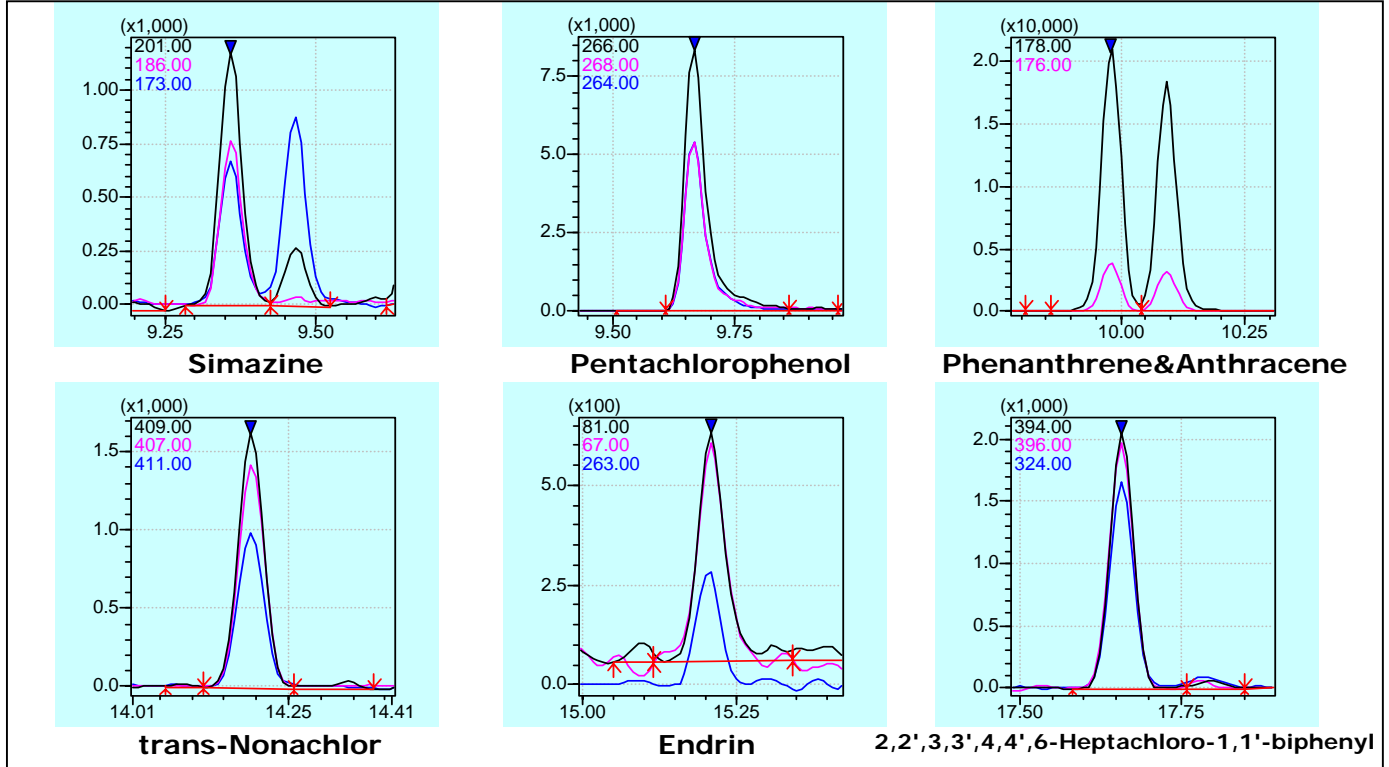


Figure.5 7 compounds Mass chromatogram of 0.1ppm Standard except for pentachlorophenol (Pentachlorophenol was analyzed at 0.4ppm)

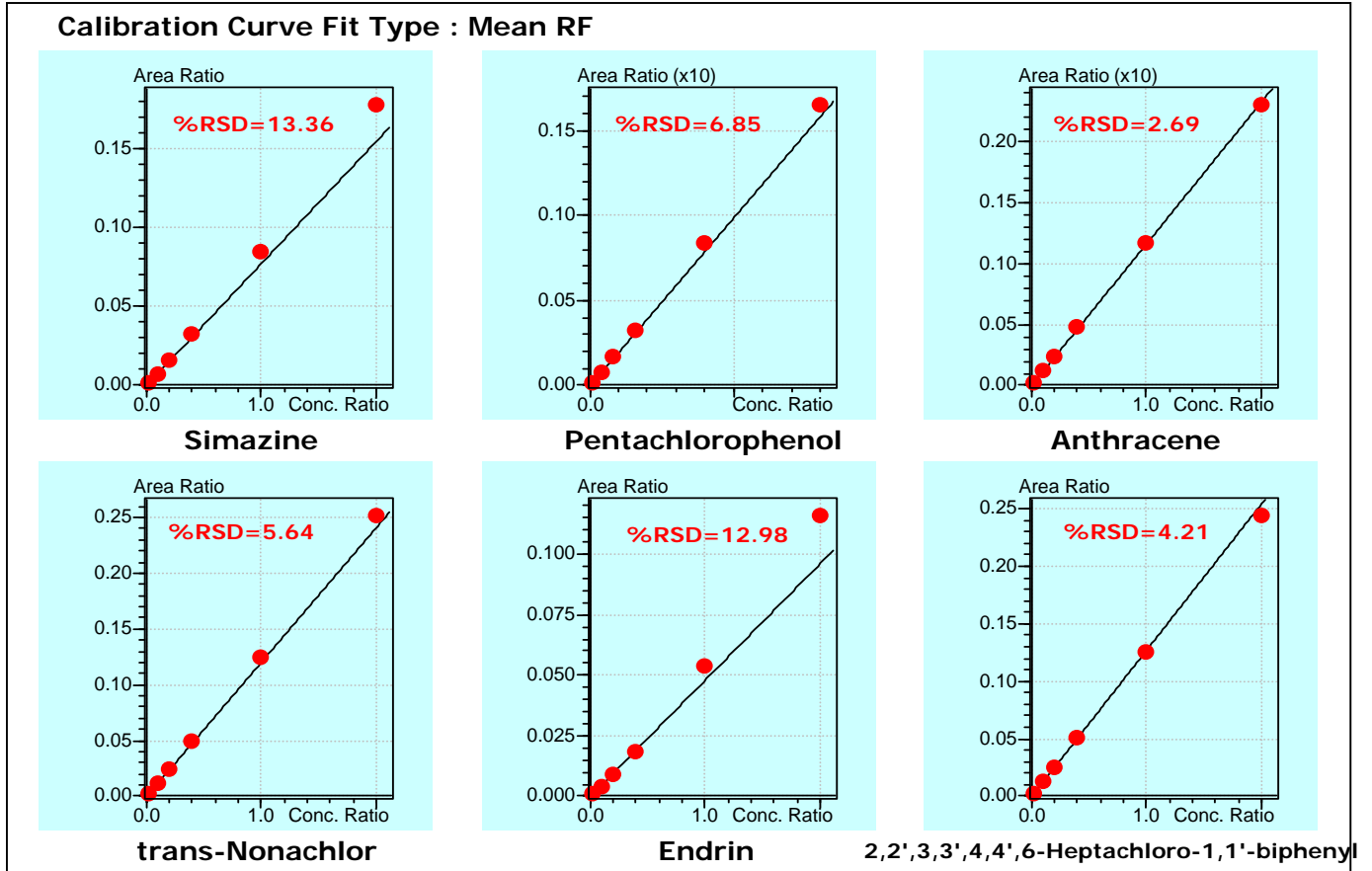


Figure.6 Calibration curve of 6 target compounds

Table 4. Target compound list with calibration QA/QC

ID	Compound Name	Retention time	Quantitation ion	IS Reference	Mean RF	RF %RSD
1	Hexachlorocyclopentadiene	5.370	237	1	0.145	16.25
2	Dimethyl phthalate	6.427	163	1	1.082	1.76
3	Acenaphthylene	6.528	152	1	1.802	3.62
4	Acenaphthene-d10 (IS1)	6.807	164	1	ISTD	ISTD
5	2-Chlorobiphenyl	6.951	188	1	0.782	4.35
6	Diethyl Phthalate	7.781	149	1	1.064	1.91
7	Fluorene	7.828	166	1	1.260	2.23
8	2,3-Dichlorobiphenyl	9.040	222	1	0.484	3.18
9	Hexachlorobenzene	9.220	284	1	0.288	4.98
10	Simazine	9.382	201	2	0.077	13.36
11	Atrazine	9.485	215	2	0.096	6.29
12	Pentachlorophenol	9.680	266	2	0.198	6.85
13	Lindane	9.763	181	2	0.121	2.68
14	Phenanthrene-D10 (IS2)	9.939	188	2	ISTD	ISTD
15	Phenanthrene	9.994	178	2	1.185	3.63
16	Anthracene	10.103	178	2	1.165	2.69
17	2,4,5-Trichlorobiphenyl	10.667	256	2	0.275	1.99
18	Alachlor	11.331	160	2	0.209	11.85
19	Heptachlor	11.369	100	2	0.152	10.69
20	di-n-Butyl phthalate	11.854	149	2	1.337	5.31
21	2,2',4,4'-Tetrachlorobiphenyl	11.971	290	2	0.163	3.53
22	Aldrin	12.190	66	2	0.200	2.47
23	Heptachlor epoxide	13.150	81	2	0.110	1.28
24	2,2',3,4,6-Pentachlorobiphenyl	13.279	326	2	0.156	2.52
25	r-Chlordane	13.718	373	2	0.105	2.53
26	a-Chlordane	14.090	375	3	0.099	7.99
27	Pyrene	13.919	202	3	1.005	3.52
28	trans-Nonachlor	14.201	409	3	0.121	5.64
29	Terphenyl-D14 (Fortification Standard)	14.615	244	3	0.888	1.50
30	2,2',4,4',5,6'-Hexachlorobiphenyl	14.803	360	3	0.176	1.08
31	Endrin	15.219	81	3	0.048	12.98
32	Butyl benzyl phthalate	16.400	149	3	0.501	19.55
33	2-ethylhexyladipate	16.753	129	3	0.468	20.85
34	2,2',3,3',4,4',6-Heptachloro-1,1'-biphenyl	17.667	394	3	0.128	4.21
35	Benzo[a]anthracene	17.547	228	3	1.055	1.79
36	2,2',3,3',4,5',6,6'-Octachlorobiphenyl	17.796	430	3	0.151	2.47
37	Chrysene-D12 (IS3)	17.589	240	3	ISTD	ISTD
38	Methoxychlor	17.724	227	3	0.459	23.40
39	Chrysene	17.653	228	3	1.023	5.62
40	2-ethylhexylphthalate	18.136	149	3	0.799	8.71
41	Benzo[b]fluoranthene	20.082	252	3	1.041	4.66
42	Benzo[k]fluoranthene	20.128	252	3	1.126	3.10
43	Benzo[a]pyrene	20.706	252	3	1.006	6.65
44	Perylene-D12 (Surrogate)	20.822	264	3	0.940	2.07
45	Indeno[1,2,3-cd]pyrene	22.655	276	3	1.331	4.46
46	Dibenz[a,h]anthracene	22.696	278	3	1.163	3.84
47	Benzo[ghi]perylene	23.091	276	3	1.167	2.35

Detection limit

In order to prove the instrument stability, the detection limit for each compound was determined by analyzing 7 replicates at 0.1 ng/ul. The results of these replicates are shown in Table 5. These DL's range from 0.0039 ng/ul for acenaphthylene to 0.0530 ng/ul for 2-ethylhexylphthalate.

Table 5. Detection limit for the GCMS-QP2010

ID	Compound Name	SD	%RSD	DL (ng/ul)
1	Hexachlorocyclopentadiene	0.0022	2.6332	0.0082
2	Dimethyl phthalate	0.0020	2.0682	0.0075
3	Acenaphthylene	0.0011	1.1227	0.0039
4	Acenaphthene-d10	I.S (%RSD=2.0250)		
5	2-Chlorobiphenyl	0.0015	1.4282	0.0055
6	Diethyl Phthalate	0.0024	2.4812	0.0088
7	Fluorene	0.0010	0.9756	0.0036
8	2,3-Dichlorobiphenyl	0.0032	3.1130	0.0119
9	Hexachlorobenzene	0.0023	2.2760	0.0086
10	Simazine	0.0029	3.3787	0.0106
11	Atrazine	0.0025	2.9496	0.0094
12	Pentachlorophenol	0.0093	3.2189	0.0344
13	Lindane	0.0046	4.7156	0.0171
14	Phenanthrene-D10	I.S (%RSD=1.8833)		
15	Phenanthrene	0.0014	1.3075	0.0051
16	Anthracene	0.0014	1.5310	0.0054
17	2,4,5-Trichlorobiphenyl	0.0025	2.4135	0.0093
18	Alachlor	0.0024	2.9118	0.0088
19	Heptachlor	0.0021	2.4859	0.0079
20	di-n-Butyl phthalate	0.0031	2.8519	0.0116
21	2,2',4,4'-Tetrachlorobiphenyl	0.0033	2.9831	0.0121
22	Aldrin	0.0025	2.6384	0.0094
23	Heptachlor epoxide	0.0032	3.1527	0.0118
24	2,2',3,4,6-Pentachlorobiphenyl	0.0029	2.7243	0.0107
25	r-Chlordane	0.0048	4.9758	0.0178
26	a-Chlordane	0.0020	2.0934	0.0075
27	Pyrene	0.0021	2.1657	0.0076
28	trans-Nonachlor	0.0031	3.3448	0.0113
29	Terphenyl-D14	F.S (%RSD=0.6141)		
30	2,2',4,4',5,6'-Hexachlorobiphenyl	0.0027	2.5278	0.0099
31	Endrin	0.0090	8.8427	0.0332
32	Butyl benzyl phthalate	0.0022	3.0292	0.0082
33	2-ethylhexyladipate	0.0022	3.1014	0.0081
34	2,2',3,3',4,4',6-Heptachloro-1,1'-biphenyl	0.0050	4.9510	0.0187
35	Benzo[a]anthracene	0.0016	1.6834	0.0059
36	2,2',3,3',4,5',6,6'-Octachlorobiphenyl	0.0042	3.9497	0.0155
37	Chrysene-D12	I.S (%RSD=2.3188)		
38	Methoxychlor	0.0031	4.4922	0.0114
39	Chrysene	0.0016	1.4116	0.0059
40	2-ethylhexylphthalate	0.0143	12.8762	0.0530
41	Benzo[b]fluoranthene	0.0039	4.0434	0.0144
42	Benzo[k]fluoranthene	0.0028	2.8167	0.0104
43	Benzo[a]pyrene	0.0035	3.8825	0.0128
44	Perylene-D12	Surrogate (%RSD=1.0587)		
45	Indeno[1,2,3-cd]pyrene	0.0021	2.2415	0.0076
46	Dibenz[a,h]anthracene	0.0024	2.5060	0.0088
47	Benzo[ghi]perylene	0.0027	2.7303	0.0098

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