Application Note

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Analysis of Semivolatile Organic Compounds in Drinking Water on the Agilent 8890 GC and 5977 GC/MSD with Extended Calibration Range

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Abstract

This Application Note coupled an Agilent 8890 GC with an Agilent 5977 MSD to analyze semivolatile organic compounds in drinking water sources according to United States Environmental Protection Agency (EPA) method 525. This workflow generated results that met method 525 calibration criteria, and demonstrated that this system is sufficiently sensitive to detect most of the low-level standards analyzed.

Introduction

Government agencies have developed directives for monitoring organic contaminants in drinking water. Gas chromatography with mass selective detection (GC/MSD) is a crucial technique for quantifying many of these contaminants due to its sensitivity and selectivity[1]. In the United States, the EPA method 525 (versions 525.2 and 525.3) details procedures for the extraction and analysis of over 100 organic compounds across a range of analyte types. These include polyaromatic hydrocarbons (PAHs), organochlorine pesticides, nitrogen and phosphorus pesticides, selected polychlorinated biphenyls, and other select semivolatile organic compounds[2,3]. The methods can also be applied to multicomponent analysis, such as toxaphene, arochlors, and technical chlordane. The compounds cited in the EPA methods exhibit a wide range of analyte polarity, volatility, and stability, and can be a challenge to analyze.

EPA method versions 525.2 and 525.3 specify calibration ranges from 0.1 to 10 ng/µL and 0.1 to 5 ng/µL, respectively. Some state agencies have lowered the reporting limits, and required laboratories to widen the calibration interval to include 0.02 ng/µL as a low-level standard[4]. The large dynamic range (0.02–15 ng/µL) can make it difficult for some compounds to achieve linearity, and calibration over a wider interval is not usually attempted. If samples have concentrations above the calibration range, they may require reanalysis, especially for systems being used for analysis of samples outside of finished drinking water. Previous work, completed on an Agilent Intuvo 9000 GC and an Agilent 5977 MSD, studied the effects of drawout plate diameter on the EPA 525 method compounds and the extended linear range[5].

This study tests the ability of the Agilent 8890 GC combined with a 5977 MSD to calibrate over a range of 0.02–15 ng/µL. Results exhibit that the linear range could be extended for all the compounds studied, while retaining sufficient sensitivity for detection of most low-level standards, and fulfilling the calibration requirements specified in the drinking water methods.

Experimental

Sample preparation

Three multicomponent standards of semivolatiles (SVM-525), organochlorine pesticides (PPM-525E), and nitrogen/phosphorus pesticides (NPM-525C) were purchased from Agilent, formerly Ultra Scientific, at 100 ng/µL concentrations, and combined to form a stock solution. Aliquots of the stock solution were diluted with ethyl acetate to prepare calibration standards at 0.02, 0.05, 0.10, 0.20, 0.50, 1.0, 2.53, 5.0, 10, and 15.3 ng/µL for most compounds (Appendix Table A1). The *cis* and *trans* permethrin isomers were present at a combined concentration of 200 ng/µL in the organochlorine pesticide standards. The mixture was assumed to be equimolar, which provides concentrations close to those listed previously. Pentachlorophenol was present at a four-fold higher concentration in the semivolatiles mixtures. MGK-264 was present as a mixture of isomers with a total concentration of 100 ng/µL in the nitrogen/phosphorus pesticide standard, and two predominant isomers were identified. Each was quantified separately with an assumed concentration of half of the concentration levels listed above. Alachlor and atrazine exist in two mixtures (organochlorine pesticides and nitrogen/phosphorus pesticides), resulting in calibration standards two-fold greater at each calibration level. To provide a concentration of 5 ng/µL at each calibration level, internal standards and surrogates (ISM-510) were added to each calibration standard.

Previous work on EPA 525 with an Intuvo 9000C GC/MSD tested different drawout plate sizes: 3, 6, and 9 mm. Studies indicated that a 9-mm drawout plate would be more ideal than the 3-mm plate, as the increased diameter correlated to better results across a larger dynamic range[5]. Based on the previous work, this study focused on using the 9-mm drawout plate.

Instrumentation

Table 1. GC and MSD instrumentation and consumables.

Parameter	Value
GC	8890 GC
MS	5977 GC/MSD with Inert EI source
Drawout plate	9 mm (p/n G3870-20449)
Column	Agilent DB-8270D Ultra Inert, 30 m × 0.25 mm × 0.25 µm (p/n 122-9732)
Liner	Agilent Ultra Inert splitless single-taper liner with glass wool (p/n 5190-2293)
Inlet septum	Agilent Advanced Green, nonstick 11 mm septum (p/n 5183-4759 for 50 pack)
Autosampler	Agilent 7650A automatic liquid sampler
Vials	Agilent A-Line certified amber (screw top) vials; 100/pk (p/n 5190-9590)
Vial inserts	Agilent deactivated vial inserts; 100/pk (p/n 5181-8872)
Vial screw caps	Agilent screw caps, PTFE/silicone/PTFE septa, cap size: 12 mm; 500/pk (p/n 5185-5862)

Results and discussion

Instrument performance verification

According to EPA method 525, the GC/MS must pass instrument suitability tests before samples can be analyzed. Included in this gambit of tests is the instrument performance check (IPC) standard, which contains DFTPP, endrin, and 4,4`-DDT to validate the MSD tune and system flowpath inertness. Versions 525.2 and 525.3 require DFTPP to pass a tuning check, and for 4,4`-DDT breakdown to be lower than 20 %. Method 525.2 also states that endrin breakdown should be lower than 20 % for the system to be declared suitable[2,3]. Results of the IPC determination on the 8890 GC and 5977 MSD have been published elsewhere[6].

Figure 1 illustrates the separation of target compounds, surrogates, and ISTDs for the 35-minute method. In EPA method 525.2, chromatographic resolution must be shown for two sets of isomers, specifically anthracene and phenanthrene, and benz[a]anthrachene and chrysene as the respective pairs. Anthracene and phenanthrene are required to have baseline separation, while benz[a]anthracene and chrysene require a minimum resolution of 25 %. Resolution is measured as the ratio of valley height of the average of two compound heights for a medium concentration level. Figure 1 illustrates the separation of all target compounds at the intermediate concentration of 2.5 ng/µL, and internal standards and surrogates at 5 ng/µL. Figure 2A shows an extracted ion chromatogram (EIC) for phenanthrene and anthracene (*m/z* 178). Figure 2B displays the EIC for the benz[a]anthracene and chrysene pair (*m/z* 228) at 1.0 ng/µL. The phenanthrene and anthracene isomer set shows baseline resolution, while the benz[a]anthracene and chrysene isomers are very nearly baseline separated; both isomer sets pass the method criteria.

Instrument conditions

Table 2. GC and MSD instrument conditions.

Parameter	Value
Injection volume	1 µL
Inlet	Split/splitless 250 °C, Pulsed splitless 50 psi until one minute, Purge 50 mL/min at one minute, Switched septum purge
Column temperature program	40 °C (hold for one minute), 25 °C/min to 160 °C (hold three minutes), 6 °C/min to 312 °C
Carrier gas and flow rate	Helium at 1.2 mL/min, constant flow
Transfer line temperature	270 °C
Ion source temperature	320 °C
Quadrupole temperature	200 °C

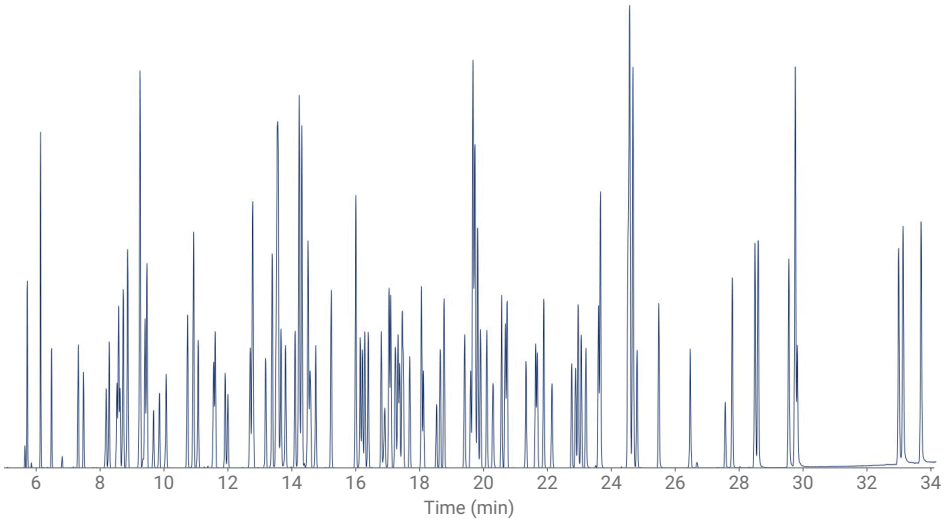

Figure 1. Total ion chromatogram (TIC) showing separation of the target compounds (2.5 ng/µL), internal standards, and surrogates (5 ng/µL for internal standards and surrogates). The actual concentration levels for certain target compounds were different from 2.5 ng/µL, which were noted in the sample preparation section.

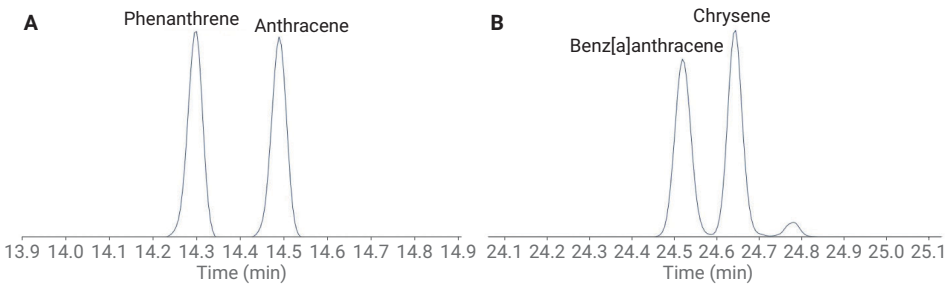

Figure 2. EICs illustrating the baseline resolution of phenanthrene and anthracene (A) and almost baseline resolution of benz[a]anthracene and chrysene (B).

Extended linear calibration range

An extended calibration range from 0.02 to 15 ng/µL was compared to calibrations from 0.1 to 10 ng/µL, specified in EPA method 525.2, and from 0.1 to 5 ng/µL, as specified in EPA method 525.3 for all 102 target compounds. The calibration curve calculations followed the method requirements and typical approach of environmental laboratories. Initially, calibration was attempted using all 10 calibration levels based on an average response factor. According to method 525.2, calibration by an average response factor or regression is acceptable, if the acceptance criteria is achieved.

- If a standard deviation of less than 30 % RSD in average response factor was realized, the calculated concentration at each level was verified to be within 30 % of the true value.
- If the calculated concentration failed the 30 % threshold or % RSD criteria, the lower end calibration levels were dropped until the requirements were passed.
- If the minimum number of five calibration points could not be achieved by removing levels, then weighted linear regression was used. Both methods of calibration, linear regression or average response factors, require the calculated concentration to be within 30 % of the actual concentration at each calibration level.

Figure 3 displays the comparison of RSDs for each of the three calibration ranges for all target compounds, based on average response factor. Exceptions are chlorothalonil, endosulfan I, and endosulfan sulfate. Each of these compounds required weighted linear regression only for the extended calibration range (0.02–15 ng/µL), Appendix Table A2. When the EPA 525.2 and 525.3 calibration ranges were tested, all compounds had average response factor %RSDs under 30 % RSD, and the calculated concentrations were within 30 % of the actual concentrations for all target compounds. Table 3 tabulates the average and standard deviations in RSDs for target compounds for each of the calibration ranges. The distribution of RSDs for the calibrations from 0.1 ng/µL to 5 and 10 ng/µL are nearly identical, while the extended calibration range, which includes two lower concentrations and one higher concentration than the EPA 525.2 range, showed an increase in the average RSD. Response factors for surrogate compounds, which were held at 5 ng/µL throughout the 10 concentration levels of the target compounds, were also monitored, and are listed in Appendix Table A3. These response factors were not included in the calculations shown in Table 3. The increase for the extended range is understandable with its wider dynamic range and low concentrations for a single quad MSD. In all three calibration range cases, calibration was successfully achieved based on method criteria (response factors for all targets listed in Appendix Table A1).

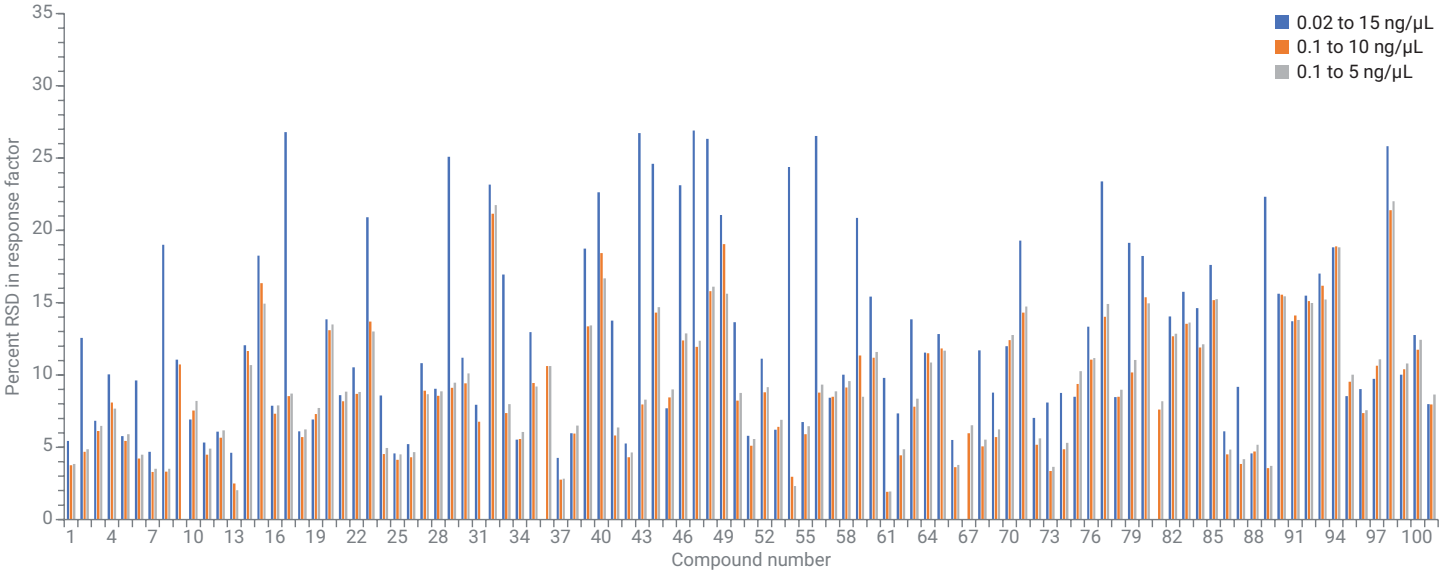

Figure 3. Comparison of percent RSDs for calibration ranges of the target analytes from 0.02 to 15 ng/µL (blue), 0.1 to 10 ng/µL (orange), and 0.1 to 5 ng/µL (gray). Compound identifications are shown in Appendix Table A1.

Table 3. Statistical characteristics for three calibration ranges of target analytes.

Calibration range (ng/µL)	Average RSD in RFs	Standard deviations in average RSD RFs	Targets requiring linear regression
0.02–15	12.71	6.60	Chlorothalonil, endosulfan I, endosulfan sulfate
0.1–10	8.97	4.46	
0.1–5	8.96	4.45	

Conclusions

The calibration requirements for the analysis of semivolatiles in drinking water following EPA method 525 can be achieved with the 8890 GC and 5977 MSD. For many of the 102 target analytes, calibration can be accomplished across an extended range of 0.02–15 ng/µL, following the EPA method guidelines for establishing a calibration curve. In agreement with the previous work using an Intuvo 9000 GC and 5977 MSD, a 9-mm drawout lens helps with compound detection and linearity for the extended calibration range.

References

1. Padilla-Sánchez, J.A.; Plaza-Bolaños, P.; Frenich, A.G. Applications and Strategies based on Gas Chromatograph-Low-Resolution Mass Spectrometry (GC-LRMS) for the Determination of Residues and Organic Contaminants in Environmental Samples. In *Comprehensive Analytical Chemistry*; Cappiello, A.; Palma, P., Eds.; Advanced Techniques in Gas Chromatography-Mass Spectrometry (GC-MS-MS and GC-TOF-MS) for Environmental Chemistry, Volume 61; Ferrer, I.; Thurman, E., Eds; Elsevier, Oxford, 2013, 181-202.
2. Munch, J. W. Method 525.2: Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/ Mass Spectrometry. *United States Environmental Protection Agency*, Department of Water, **1995**.
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5. Giardina, M. Analysis of Semivolatile Organic Compounds in Drinking Water on the Agilent Intuvo and 5977 with Extended Calibration Range, *Agilent Technologies Application Note*, publication number 5994-0013EN, **2018**.
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Appendix A

Table A1. Retention times, response factors, average response factor, and % RSD for target compounds from 0.02 to 15 ng/µL.

No.	Compound	RT (min)	Concentration level (ng/µL)										Average RF	%RSD
			1 (0.02)	2 (0.05)	3 (0.1)	4 (0.2)	5 (0.5)	6 (1.0)	7 (2.53)	8 (5.0)	9 (10)	10 (15.3)		
1	Isophorone	5.671	1.106	1.039	0.979	1.010	1.035	1.067	1.088	1.102	1.066	0.983	1.048	4.42
2	Dichlorvos	6.426	0.636	0.695	0.737	0.678	0.714	0.742	0.750	0.748	0.754	0.693	0.715	5.44
3	Hexachlorocyclopentadiene	7.249	NA	0.349	0.338	0.324	0.342	0.345	0.364	0.370	0.362	0.333	0.347	4.37
4	EPTC	7.412	0.437	0.391	0.408	0.443	0.431	0.459	0.482	0.482	0.472	0.434	0.444	6.82
5	Mevinphos	8.109	0.641	0.809	0.758	0.740	0.812	0.815	0.883	0.893	0.910	0.843	0.811	10.04
6	Butylate	8.203	0.496	0.432	0.427	0.442	0.462	0.479	0.490	0.496	0.476	0.442	0.464	5.77
7	Vernolate	8.434	0.401	0.420	0.499	0.479	0.512	0.512	0.535	0.542	0.528	0.485	0.491	9.63
8	Dimethyl phthalate	8.486	1.456	1.328	1.330	1.307	1.335	1.389	1.417	1.417	1.340	1.241	1.356	4.68
9	Etridiazole	8.528	NA	0.169	0.186	0.191	0.183	0.182	0.198	0.196	0.194	0.181	0.187	4.92
10	2,6-Dinitrotoluene	8.628	0.212	0.222	0.220	0.220	0.242	0.249	0.267	0.282	0.285	0.263	0.246	11.06
11	Pebulate	8.633	0.565	0.617	0.542	0.543	0.606	0.635	0.645	0.650	0.620	0.565	0.599	6.93
12	Acenaphthylene	8.769	1.868	1.893	1.954	1.912	1.984	2.083	2.134	2.152	2.045	1.887	1.991	5.32
13	Chloroneb	9.309	0.424	0.471	0.422	0.438	0.489	0.466	0.491	0.484	0.460	0.422	0.457	6.09
14	2-Chlorobiphenyl (BZ #1)	9.367	1.100	1.125	1.114	1.049	1.085	1.094	1.090	1.101	1.041	0.955	1.075	4.61
15	Tebuthiuron	9.561	0.376	0.343	0.387	0.345	0.398	0.412	0.451	0.465	0.484	0.447	0.411	12.07
16	2,4-Dinitrotoluene	9.755	0.220	0.274	0.267	0.266	0.275	0.300	0.346	0.374	0.387	0.360	0.307	18.26
17	Molinate	9.959	0.552	0.579	0.550	0.610	0.616	0.656	0.680	0.677	0.657	0.601	0.618	7.88
18	Diethyl phthalate	10.625	NA	NA	1.721	1.516	1.395	1.387	1.422	1.415	1.365	1.250	1.434	9.57
19	Fluorene	10.814	1.208	1.336	1.268	1.237	1.358	1.381	1.432	1.443	1.370	1.266	1.330	6.11
20	Propachlor	10.95	0.614	0.678	0.669	0.599	0.652	0.694	0.732	0.738	0.718	0.663	0.676	6.93
21	Ethoprophos	11.438	0.203	0.218	0.209	0.222	0.240	0.265	0.288	0.289	0.287	0.266	0.249	13.86
22	Cycloate	11.49	0.721	0.719	0.711	0.764	0.780	0.845	0.883	0.892	0.847	0.779	0.794	8.60
23	Chlorpropham	11.81	0.288	0.368	0.337	0.343	0.351	0.384	0.403	0.414	0.407	0.373	0.367	10.54
24	Trifluralin	11.894	NA	0.155	0.214	0.188	0.184	0.210	0.242	0.253	0.259	0.239	0.216	16.38
25	*alpha*-Lindane	12.575	0.179	0.223	0.217	0.225	0.237	0.233	0.244	0.248	0.235	0.217	0.226	8.59
26	2,3-Dichlorobiphenyl (BZ #5)	12.649	0.663	0.679	0.670	0.682	0.689	0.728	0.731	0.750	0.705	0.657	0.695	4.57
27	Hexachlorobenzene	12.67	0.474	0.427	0.434	0.447	0.457	0.476	0.476	0.492	0.456	0.421	0.456	5.21
28	Atraton	13.047	0.176	0.132	0.151	0.163	0.164	0.169	0.188	0.188	0.190	0.176	0.170	10.83
29	Prometon	13.246	0.133	0.137	0.142	0.137	0.146	0.153	0.170	0.168	0.165	0.154	0.150	9.04
30	Simazine	13.246	NA	0.103	0.114	0.102	0.112	0.122	0.131	0.130	0.129	0.118	0.118	9.35
31	Atrazine*	13.403	0.196	0.210	0.227	0.208	0.241	0.255	0.270	0.269	0.259	0.240	0.237	11.19
32	*beta*-Lindane	13.388	0.129	0.115	0.131	0.125	0.130	0.138	0.150	0.148	0.140	0.130	0.134	7.94
33	Pentachlorophenol†	13.445	NA	0.092	0.094	0.100	0.124	0.136	0.159	0.160	0.160	0.149	0.130	22.10
34	Propazine	13.529	NA	0.163	0.173	0.158	0.181	0.184	0.195	0.196	0.187	0.165	0.178	7.90
35	*gamma*-Lindane	13.676	0.122	0.131	0.113	0.126	0.127	0.126	0.135	0.131	0.124	0.116	0.125	5.53
36	Pronamide	13.975	0.229	0.310	0.297	0.300	0.302	0.326	0.355	0.366	0.364	0.340	0.319	12.96

No.	Compound	RT (min)	Concentration level (ng/µL)										Average RF	%RSD
			1 (0.02)	2 (0.05)	3 (0.1)	4 (0.2)	5 (0.5)	6 (1.0)	7 (2.53)	8 (5.0)	9 (10)	10 (15.3)		
37	Chlorothalonil	14.179	Linear regression											
38	Phenanthrene	14.184	1.134	1.253	1.218	1.175	1.225	1.221	1.278	1.252	1.197	1.119	1.207	4.28
39	Anthracene	14.373	1.105	1.103	1.108	1.105	1.160	1.208	1.286	1.264	1.210	1.128	1.168	5.97
40	Terbacil	14.436	NA	0.169	0.218	0.177	0.201	0.215	0.249	0.255	0.254	0.240	0.220	14.80
41	Methyl paraoxon	14.441	0.133	0.135	0.166	0.155	0.172	0.185	0.222	0.232	0.247	0.233	0.188	22.64
42	*delta*-Lindane	14.62	NA	0.119	0.109	0.105	0.122	0.116	0.122	0.121	0.116	0.109	0.115	5.55
43	2,4,5-Trichlorobiphenyl (BZ #29)	15.107	0.308	0.322	0.328	0.319	0.338	0.345	0.361	0.354	0.335	0.314	0.333	5.26
44	Alachlor*	15.867	NA	0.183	0.190	0.178	0.181	0.197	0.216	0.215	0.210	0.197	0.196	7.40
45	Simetryn	16.009	NA	0.188	0.216	0.211	0.238	0.257	0.293	0.296	0.291	0.274	0.252	15.96
46	Heptachlor	16.072	0.148	0.160	0.153	0.142	0.159	0.170	0.177	0.179	0.173	0.165	0.163	7.70
47	Ametryn	16.156	NA	0.147	0.164	0.189	0.178	0.198	0.226	0.225	0.220	0.207	0.195	14.41
48	Prometryn	16.26	NA	0.118	0.156	0.156	0.168	0.183	0.204	0.204	0.200	0.187	0.175	16.33
49	Terbutryn	16.669	NA	0.129	0.145	0.164	0.187	0.195	0.220	0.221	0.223	0.207	0.188	18.47
50	Bromacil	16.737	0.133	0.181	0.157	0.159	0.189	0.194	0.221	0.227	0.263	0.244	0.197	21.07
51	Dibutyl phthalate	16.916	1.879	1.609	1.249	1.221	1.295	1.367	1.492	1.491	1.431	1.344	1.438	13.66
52	2,2`,4,4`Tetrachlorobiphenyl (BZ #47)	16.968	0.223	0.238	0.230	0.236	0.250	0.261	0.261	0.262	0.252	0.236	0.245	5.79
53	Metolachlor	17.104	0.441	0.534	0.531	0.522	0.551	0.587	0.643	0.639	0.626	0.590	0.566	11.12
54	Chlorpyrifos	17.194	0.154	0.138	0.143	0.141	0.148	0.155	0.167	0.163	0.158	0.148	0.152	6.22
55	Aldrin	17.235	NA	0.131	0.103	0.102	0.106	0.103	0.109	0.104	0.099	0.093	0.099	24.39
56	DCPA	17.324	0.234	0.249	0.243	0.250	0.275	0.270	0.286	0.282	0.271	0.252	0.261	6.74
57	Cyanazine	17.351	NA	0.030	0.066	0.061	0.067	0.070	0.078	0.077	0.074	0.069	0.063	26.53
58	Triadimefon	17.56	0.369	0.302	0.316	0.308	0.321	0.344	0.374	0.377	0.365	0.343	0.342	8.42
59	Diphenamid	17.922	0.499	0.509	0.533	0.519	0.573	0.584	0.650	0.650	0.631	0.589	0.574	10.01
60	MGK-264a‡	17.99	NA	0.252	0.329	0.316	0.330	0.360	0.381	0.387	0.432	0.404	0.339	20.86
61	MGK-264b‡	18.404	0.138	0.132	0.157	0.161	0.171	0.190	0.202	0.206	0.201	0.189	0.175	15.42
62	Heptachlor epoxide	18.499	0.078	0.112	0.092	0.090	0.088	0.091	0.093	0.091	0.089	0.083	0.091	9.79
63	2,2`,3`,4,6-Pentachlorobiphenyl (BZ #98)	18.64	0.151	0.178	0.180	0.173	0.185	0.192	0.196	0.194	0.185	0.174	0.181	7.34
64	*gamma*-Chlordane	19.28	0.094	0.112	0.130	0.126	0.129	0.143	0.151	0.152	0.146	0.136	0.132	13.86
65	Tetrachlorvinphos	19.463	0.287	0.217	0.231	0.219	0.226	0.245	0.277	0.282	0.288	0.267	0.254	11.55
66	Butachlor	19.589	0.195	0.188	0.196	0.206	0.219	0.224	0.257	0.261	0.262	0.243	0.225	12.83
67	Pyrene	19.6	1.396	1.449	1.384	1.252	1.304	1.305	1.374	1.350	1.291	1.205	1.331	5.51
68	Endosulfan I	19.683	Linear regression											
69	*alpha*-Chlordane	19.689	0.087	0.104	0.117	0.116	0.123	0.129	0.132	0.129	0.126	0.117	0.118	11.71
70	*trans*-Nonachlor	19.767	0.133	0.145	0.153	0.159	0.159	0.168	0.179	0.177	0.168	0.158	0.160	8.79
71	Napropamide	19.972	0.362	0.368	0.370	0.357	0.377	0.424	0.472	0.476	0.467	0.435	0.411	11.99
72	Tricyclazole	20.181	0.163	0.164	0.213	0.192	0.218	0.241	0.273	0.278	0.272	0.253	0.227	19.30
73	*p,p'*-DDE	20.433	0.242	0.198	0.218	0.229	0.233	0.239	0.253	0.250	0.242	0.225	0.233	7.03
74	Dieldrin	20.538	0.270	0.215	0.215	0.213	0.217	0.225	0.234	0.227	0.220	0.205	0.224	8.10
75	2,2`,4,4`,5,6`-Hexachlorobiphenyl (BZ #154)	20.601	0.210	0.160	0.194	0.197	0.207	0.211	0.222	0.216	0.206	0.193	0.202	8.76

No.	Compound	RT (min)	Concentration level (ng/µL)										Average RF	%RSD
			1 (0.02)	2 (0.05)	3 (0.1)	4 (0.2)	5 (0.5)	6 (1.0)	7 (2.53)	8 (5.0)	9 (10)	10 (15.3)		
76	Endrin	21.193	0.059	0.060	0.062	0.047	0.055	0.051	0.060	0.057	0.056	0.053	0.056	8.50
77	Chlorobenzilate	21.492	0.259	0.280	0.303	0.289	0.316	0.341	0.375	0.377	0.376	0.354	0.327	13.34
78	Endosulfan II	21.544	NA	0.023	0.023	0.024	0.029	0.030	0.033	0.033	0.032	0.030	0.029	14.44
79	4,4`-DDD	21.749	0.366	0.341	0.353	0.355	0.377	0.394	0.432	0.431	0.416	0.390	0.386	8.46
80	Endrin aldehyde	22	0.108	0.055	0.080	0.062	0.065	0.077	0.079	0.079	0.077	0.072	0.076	19.13
81	Norflurazon	22.614	NA	0.203	0.189	0.197	0.204	0.226	0.259	0.269	0.272	0.251	0.230	14.38
82	Endosulfan sulfate	22.734	Linear regression											
83	Benzyl butyl phthalate	22.818	0.416	0.438	0.453	0.448	0.499	0.536	0.597	0.599	0.597	0.555	0.514	14.06
84	*p,p'*-DDT	22.918	0.248	0.239	0.264	0.267	0.292	0.321	0.353	0.362	0.360	0.336	0.304	15.75
85	Hexazinone	23.054	0.403	0.472	0.484	0.488	0.522	0.563	0.621	0.642	0.626	0.584	0.541	14.63
86	*bis*(2-Ethylhexyl) adipate	23.452	0.455	0.371	0.420	0.497	0.485	0.534	0.611	0.635	0.629	0.588	0.523	17.61
87	2,2`,3,3`,4,4`,6-Heptachlorobiphenyl (BZ #171)	24.375	0.145	0.156	0.163	0.159	0.160	0.168	0.178	0.176	0.172	0.160	0.164	6.10
88	Benz[a]anthracene	24.401	1.510	1.301	1.219	1.146	1.125	1.184	1.238	1.246	1.212	1.127	1.231	9.19
89	Chrysene	24.522	1.162	1.218	1.181	1.094	1.139	1.200	1.249	1.249	1.189	1.106	1.179	4.59
90	2,2`,3,3`,4,5`,6,6`-Octachlorobiphenyl (BZ #200)	24.538	NA	0.243	0.236	0.258	0.239	0.252	0.257	0.254	0.243	0.225	0.245	4.47
91	Methoxychlor	24.658	0.537	0.535	0.525	0.528	0.610	0.655	0.727	0.757	0.760	0.706	0.634	15.63
92	*bis*(2-Ethylhexyl) phthalate	25.334	1.035	0.817	0.706	0.697	0.732	0.817	0.910	0.959	0.955	0.890	0.852	13.71
93	Fenarimol	26.309	0.159	0.154	0.166	0.153	0.172	0.189	0.212	0.225	0.222	0.208	0.186	15.50
94	*cis*-Permethrin	27.405	0.278	0.242	0.269	0.267	0.286	0.312	0.360	0.379	0.389	0.361	0.314	17.01
95	*trans*-Permethrin	27.625	0.606	0.593	0.562	0.599	0.678	0.756	0.855	0.901	0.904	0.840	0.729	18.84
96	Benzo[b]fluoranthene	28.322	1.138	1.080	1.032	1.095	1.121	1.210	1.301	1.327	1.276	1.198	1.178	8.55
97	Benzo[k]fluoranthene	28.422	0.986	1.110	1.135	1.089	1.178	1.262	1.339	1.243	1.296	1.208	1.185	9.04
98	Benzo[a]pyrene	29.376	1.009	1.055	0.932	1.031	1.096	1.156	1.224	1.263	1.227	1.157	1.115	9.73
99	Fluridone	29.643	NA	0.451	0.554	0.490	0.582	0.661	0.794	0.861	0.819	0.745	0.662	22.69
100	Indeno[1,2,3-cd]pyrene	32.799	1.126	1.060	1.142	1.035	1.146	1.239	1.331	1.386	1.334	1.233	1.203	10.02
101	Dibenz[a,h]anthracene	32.935	0.993	1.078	1.041	1.119	1.189	1.299	1.375	1.442	1.362	1.262	1.216	12.76
102	Benzo[ghi]perylene	33.496	1.226	1.197	1.249	1.208	1.253	1.363	1.432	1.497	1.381	1.253	1.306	7.98

* Atrazine and alachlor concentration levels: 0.04, 0.1, 0.2, 0.4, 1.0, 2.0, 5.07, 10, 20, and 30.67 ng/µL.

† Pentachlorophenol concentration levels: 0.08, 0.2, 0.4, 0.8 2.0, 4.0, 10, 20, 40, and 60 ng/µL.

‡ MGK-264a and b estimated concentration levels: 0.01, 0.03, 0.05, 0.1, 0.25, 0.5, 1.27, 2.5, 5.0, and 7.67 ng/µL.

Table A2. Retention times and calculated concentrations for targets using linear regression.

No.	Compound	RT (min)	Concentration level (ng/µL)									
			1 (0.02)	2 (0.05)	3 (0.1)	4 (0.2)	5 (0.5)	6 (1.0)	7 (2.53)	8 (5.0)	9 (10)	10 (15.3)
37	Chlorothalonil	14.179	NA	0.039	0.117	0.193	0.495	1.017	2.710	4.948	10.513	14.648
		$y = 0.053290x - 0.001789$; weighting 1/x; $R^2 = 0.9978$										
68	Endosulfan I	19.683	NA	0.054	0.106	0.193	0.537	1.066	2.747	5.250	10.149	14.584
		$y = 0.007419x - 7.778928 \times 10^{-5}$; weighting 1/x; $R^2 = 0.9977$										
82	Endosulfan sulfate	22.734	0.022	0.037	0.110	0.186	0.518	1.035	2.661	5.258	10.254	14.621
		$y = 0.013198x - 2.280692 \times 10^{-4}$; weighting 1/x; $R^2 = 0.9981$										

Table A3. Retention times, response factors, average response factor, and % RSD for surrogate compounds, whose concentrations were held at 5 ng/µL, while target compounds ranged from 0.02 to 15 ng/µL.

No.	Surrogates	RT (min)	Concentration level (ng/µL)										Average RF	%RSD
			1 (5)	2 (5)	3 (5)	4 (5)	5 (5)	6 (5)	7 (5)	8 (5)	9 (5)	10 (5)		
S1	1,3-Dimethyl-2-nitrobenzene	6.086	0.291	0.300	0.289	0.294	0.292	0.291	0.301	0.294	0.299	0.293	0.294	1.47
S2	Pyrene-d_{10}	19.537	1.106	1.112	1.115	1.101	1.107	1.113	1.111	1.113	1.109	1.120	1.111	0.49
S3	Triphenyl phosphate	23.515	0.258	0.251	0.246	0.242	0.271	0.266	0.263	0.247	0.269	0.271	0.258	4.29
S4	Perylene-d_{12}	29.586	1.024	1.029	1.002	1.021	1.022	1.069	1.039	1.050	1.068	1.077	1.040	2.39

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