Application Brief

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Analysis of Semivolatile Organic Compounds in Drinking Water on the Agilent Intuvo and 5977 With Extended Calibration Range

Technology advantage:
Agilent Intuvo 9000 GC with MSD

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Introduction

Many government regulatory agencies throughout the world have established directives for monitoring organic contaminants in drinking water. Gas chromatography with mass spectrometry (GC/MS) is an essential technique for quantifying a wide range of these contaminants due to its sensitivity and selectivity[1]. In the Unites States, the Environmental Protection Agency (EPA) Method 525 details procedures for the extraction and analysis of over 100 organic compounds spanning a range of analyte classes[2,3]. These analytes include organochlorine pesticides, nitrogen and phosphorous pesticides, polycyclic aromatic hydrocarbons, selected polychlorinated biphenyls, and other semivolatile organic compounds. In addition, the method can be used for multicomponent analytes such as toxaphene, aroclors, and technical chlordane. Analysis of this wide range of compounds can be challenging due to the diversity of analyte polarity, volatility, and stability.

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 for full-scan analysis, respectively. Some state agencies have lowered the reporting limits, requiring laboratories to widen the calibration interval to include 0.02 ng/µL as a low-level standard[4]. Achieving linearity over a 0.02 to 5 ng/µL range can be difficult for some compounds, and calibration over a wider interval is not typically attempted. This may result in reanalysis of samples with concentration levels greater than the calibration range, particularly if the instrument is being used for the analysis of samples other than finished drinking water.

This study compared the effect of using a 9 mm draw-out plate in the inert EI source to the 3 and 6 mm plates over a calibration range of 0.02 to 15 ng/µL using the Agilent 5977 MSD and Agilent Intuvo 9000 GC. Results show that the linear range could be extended for all the compounds studied while maintaining sufficient sensitivity to allow for the detection of most low-level standards, and satisfy the calibration requirements specified in the method. The 9 mm draw-out plate provided more uniform response across the calibration range particularly for compounds that can be problematic due to their affinity for surface adsorption.

Sample preparation

Three 100 ng/µL multicomponent standards of semivolatiles (SVM-525), organochlorine pesticides (PPM-525E), and nitrogen/phosphorus pesticides (NPM-525C) were purchased from Ultra Scientific and combined to prepare a stock solution. Aliquots of the stock were diluted in ethyl acetate to prepare calibration standards of 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2.53, 5, 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 standard. It was assumed that the mixture was equimolar, providing concentrations close to those listed above. Pentachlorophenol was present at a 4-fold greater concentration in the semivolatiles mixture, yielding calibration standards 4-fold greater at each calibration level.

MGK-264 was present as a mixture of isomers, with a total concentration of 100 ng/µL in the nitrogen/phosphorus pesticide standard. Two predominant isomers were identified. Each was quantitated separately with an assumed concentration of half of the concentration levels listed above. Internal standards and surrogates (ISM-510) were added to each calibration standard to provide a concentration of 5 ng/µL at each level.

Experimental

Instrumentation

Parameter	Value
GC	Agilent Intuvo 9000 GC with simple MS flowpath
MS	Agilent 5977 MSD with Inert EI source
Draw-out plate	3, 6, and 9 mm (G2589-20100, G2589-20045, G3440-20022, respectively)
Column	Agilent DB-UI 8270D, 30 m × 0.25 mm, 0.25 µm (122-9732-INT)
Liner	Agilent Ultra Inert splitless single taper liner with glass wool (5190-2293)

Instrument conditions

Parameter	Value
Injection volume	1 µL
Inlet	Split/Splitless 280 °C Pulsed splitless 50 psi until 1 minute Purge 50 mL/min at 1 minute Septum purge switched flow mode 3 mL/min
Guard Chip	40 °C for 1 minute, 25 °C/min to 160 °C 3 minutes, 6 °C/min to 312 °C
Column temperature	40 °C for 1 minute, 25 °C/min to 160 °C 3 minutes, 6 °C/min to 312 °C
Bus temperature	245 °C
Flow	1.2 mL/min constant flow
Transfer line temperature	270 °C
Draw-out plates	Either 3, 6, or 9 mm
Ion source temperature	320 °C
Quadrupole temperature	200 °C

Results and discussion

Instrument performance verification

According to Method 525, the GC/MS must pass instrument suitability tests before samples can be analyzed. Included in the suitability test is the instrument performance check (IPC) standard, which contains DFTPP, endrin, and 4,4'-DDT as a validation of MSD tuning and flowpath inertness. Results of the IPC determination on the Intuvo and 5977 have been published elsewhere[5].

In Method 525.2, chromatographic resolution must be demonstrated for selected isomers. For anthracene and phenanthrene, baseline separation is required. For benz[a]anthracene and chrysene, a minimum resolution of less than 25 % is required. Resolution is measured as the ratio of valley height to the average of the two compound heights for a medium concentration solution. Figure 1A shows the separation achieved for all the target compounds at the intermediate concentration of 2.5 ng/µL, and internal standards and surrogates at 5 ng/µL. Figure 1B shows an extracted ion chromatogram (EIC) of anthracene and phenanthrene (*m/z* 178); Figure 1C shows an EIC of benz[a]anthracene and chrysene (*m/z* 228). For both isomer pairs, baseline separation was achieved.

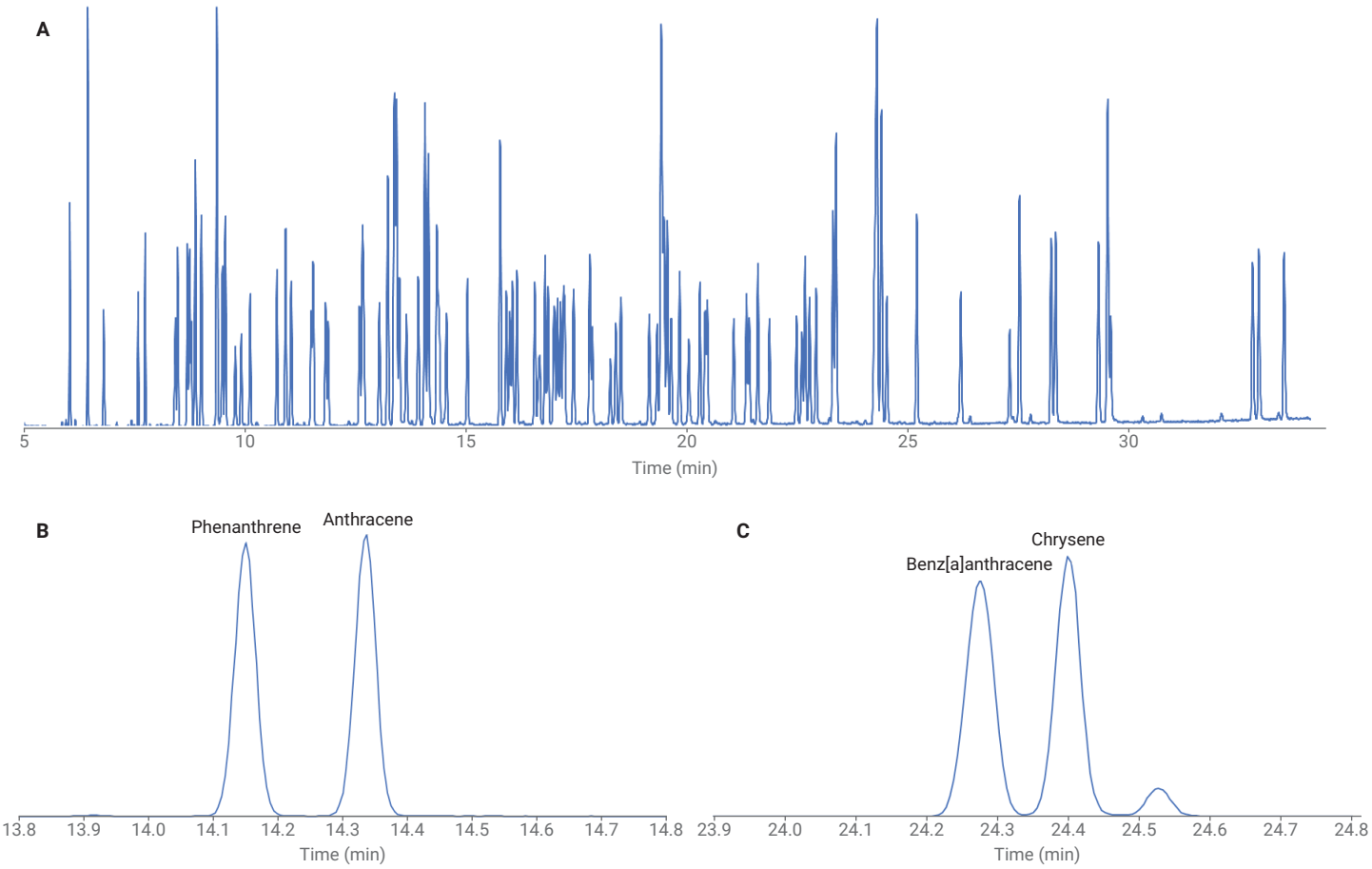

Figure 1. Total ion chromatogram showing separation of all target compounds, internal standards, and surrogates (A). Extracted ion chromatograms showing baseline resolution of phenanthrene and anthracene (B) and benz[a]anthracene and chrysene (C).

Comparison of EI draw-out plates

Response, linearity, and signal-to-noise ratio (S/N) were compared for the 3, 6, and 9 mm diameter draw-out plates in the inert EI source. The generalized performance differences can be illustrated by examining the results of three target compounds: 2,3-dichlorobiphenyl, *bis*(2-ethylhexyl) phthalate, and benzo[ghi]perylene. These compounds were selected because they have low-to-intermediate polarity, nonreactive, and nonlabile. However, the compounds vary in size, vapor pressure, boiling point, and polarizability (Table 1).

Figure 2 shows the relative response for each of the selected target compounds at each calibration level for the 3 and 6 mm plates normalized to the 9 mm plate (that is, extracted ion peak area ratio). The dashed lines in Figure 2 are the average normalized responses across the calibration range. As expected, the relative response was attenuated for the larger aperture plates. On average, the response decreased by about a factor of 1.5 going from the 3 to 6 mm lens, and by approximately a factor of 1.9 going from 6 to 9 mm. The plot also reveals variation in response related to the draw-out plate diameter and target compound. This was investigated in greater detail by looking at the effect of this variation on calibration.

According to Method 525, calibration by means of either regression or average response factor is acceptable as long as the acceptance criteria is achieved. For calibration using average response factor, the relative standard deviation (RSD) in response factors must be less than 30 %. For either method of calibration, the calculated concentration should be within 30 % of the actual concentration at each level. Table 2 lists the average response factor, standard deviation, and RSD for each selected target compound for each draw-out plate diameter over a calibration range from 0.02 to 15 ng/µL. Figure 3 shows the error in calculated concentration at each calibration level for each draw-out plate.

Table 1. Physical properties of selected target compounds.

Target compound	Molecular formula	Boiling point (°C)	Vapor pressure (Torr) [9]	Polarizability (cm^3) [10]	Cross-section surface area ($Å^2$) [11]
2,3-Dichlorbiphenyl	$C_{12}H_8Cl_2$	172 [6]	1.29×10^{-3}	24×10^{-24}	227.13
Benzo[ghi]perylene	$C_{22}H_{12}$	550 [7]	1.12×10^{-9}	40×10^{-24}	276.58
bis(2-Ethylhexyl) phthalate	$C_{24}H_{38}O$	386 [8]	3.95×10^{-6}	45×10^{-24}	484.54

Table 2. Average response factors and deviations for selected targets.

	2,3-Dichlorobiphenyl			Benzo[ghi]perylene			*bis*(2-Ethylhexyl) phthalate		
	3 mm	6 mm	9 mm	3 mm	6 mm	9 mm	3 mm	6 mm	9 mm
Average RF	0.804	0.756	0.730	0.830	0.946	0.974	0.531	0.806	0.962
Standard deviation	0.033	0.038	0.035	0.162	0.103	0.051	0.202	0.090	0.063
%RSD	4.13	4.99	4.84	19.53	10.90	5.20	38.13	11.14	6.54

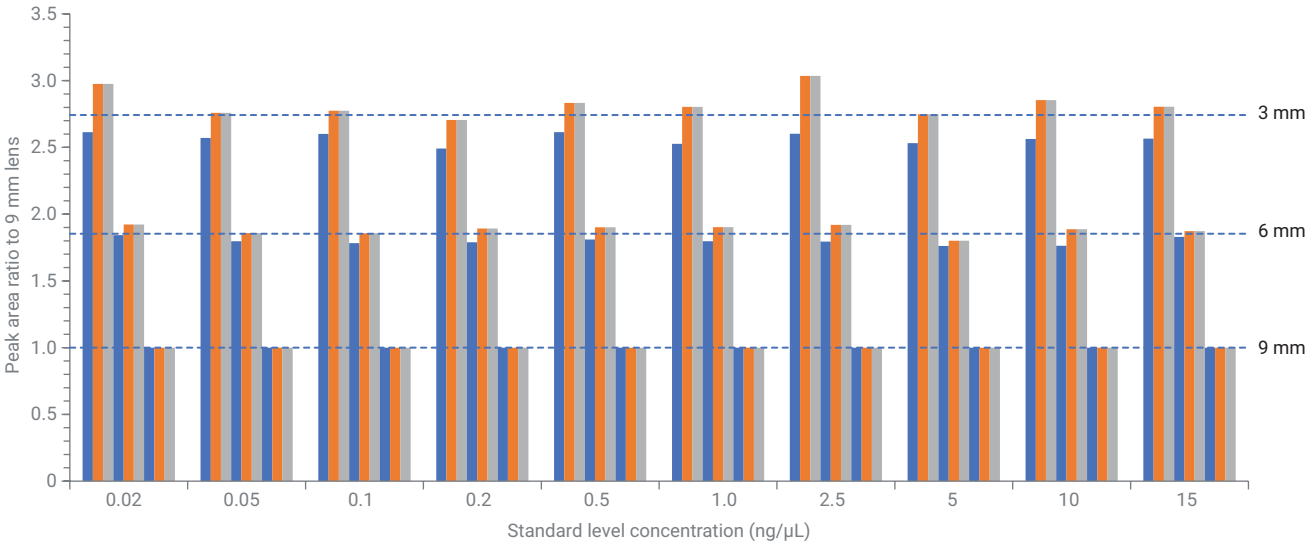

Figure 2. Response comparison for selected target compounds 2,3-dichlorobiphenyl (blue), benzo[ghi]perylene (orange), and *bis*(2-ethylhexyl) phthalate (gray). Average normalized response across all the compounds and concentration for each plate diameter are shown as dashed lines.

Several effects are apparent in these calibration results. For 2,3-dichlorobiphenyl, the average response factors (Table 2) decreased slightly going from the 3 to 9 mm plate, but are still within two standard deviations. This indicates that the difference in mean is likely not significant. More importantly, for each draw-out plate, the calibrations passed the average response factor RSD and calculated error criteria (Figure 3A). Essentially, no difference in calibration performance was observed regardless of draw-out plate diameter. For benzo[ghi]perylene, results were quite different. This compound was the last eluter in the target list, with a relatively high boiling point and low vapor pressure (Table 1). As noted in Table 2 and Figure 3B, there was a considerable difference in calibration results based upon the selection of draw-out plate diameter. The RSD in average response factor and calculated errors at each calibration level decreased going from the 3 to 9 mm plate. A similar trend but amplified effect was observed for *bis*(2-ethylhexyl) phthalate. This compound failed both RSD and calculated concentration criteria with the 3 mm draw-out plate. Interestingly, *bis*(2-ethylhexyl) phthalate has a lower boiling point and higher vapor pressure than benzo[ghi]perylene, but has a greater polarizability and larger cross-sectional surface area (Table 1). This suggests that the observed nonlinearity is not strictly related to volatility, but is also dependent upon the propensity of interaction between the analyte and the draw-out plate surface.

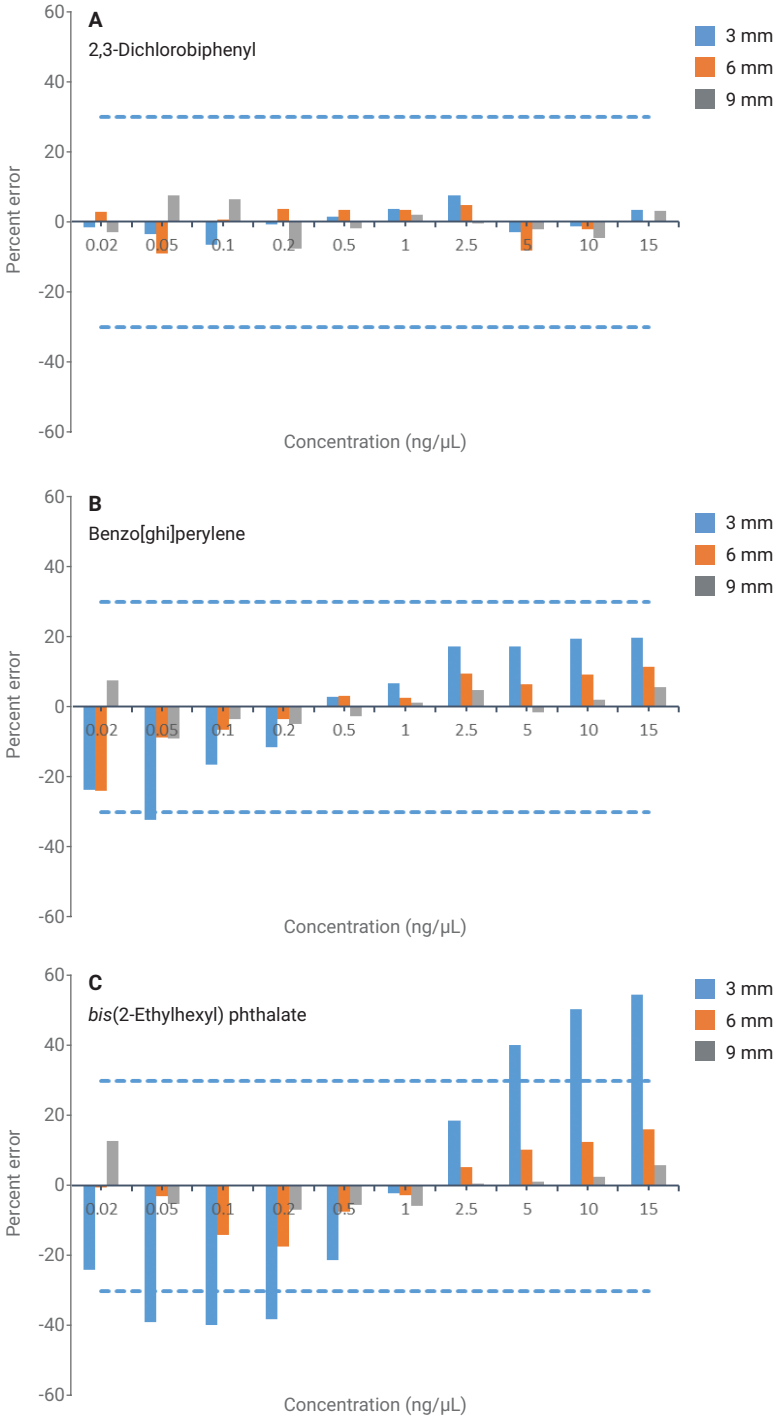

Figure 3. Errors in calculated concentrations based on average response factors at each calibration level for 2,3-dichlorobiphenyl (A), Benzo[ghi]perylene (B), and *bis*(2-ethylhexyl) phthalate (C) for the 3 mm (blue), 6 mm (orange) and 9 mm (gray) draw-out plate diameters.

The peak-to-peak S/N was calculated for each target compound at 0.02 ng/µL for the three apertures (Table 3). Only the 2,3-dichlorobiphenyl shows a clear trend of decreased S/N with increased draw-out aperture. It is possible that the adsorptive effect is obscuring a clear trend in S/N for benzo[ghi]perylene and *bis*(2-ethylhexyl) phthalate.

Extended linear range calibration (9 mm draw-out plate)

With the 9 mm draw-out plate installed, an extended calibration range from 0.02 to 15 ng/µL was compared to calibrations from 0.1 to 10 ng/µL (as specified in Method 525.2) and from 0.1 to 5 ng/µL (as specified in Method 525.3) for all 101 target compounds. The calibration scheme followed the method requirements and the typical approach used in environmental laboratories. In the first pass, calibration was attempted using all 10 calibration levels based on average response factor. If a standard deviation of less than 30 % RSD in average response factor was achieved, 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 30 % RSD criteria, then lower-end calibration levels were removed 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. The calculated concentration of all levels must be within 30 % of the true value.

Figure 4 shows a comparison of RSDs for each of the three calibration ranges for all the target compounds based upon average response factor, except for endrin and endosulfan sulfate. Endrin required weighted linear regression for each of the three calibration ranges, and endosulfan sulfate required weighted linear regression for the 0.02 to 15 ng/µL range (Appendix Table A2). Table 4 lists the average and standard deviations in RSDs for each of the calibration ranges. The distribution of RSDs for the calibrations up to 5 and 10 ng/µL appeared indistinguishable, while the calibration up to 15 ng/µL revealed a slight increase in average RSD. In all three cases, calibration was successfully achieved based upon the method criteria. (Response factors for all targets are listed in Appendix Table A1.)

Table 3. S/N of selected targets.

Draw-out plate id (mm)	2,3-Dichlorobiphenyl	Benzo[ghi]perylene	*bis*(2-Ethylhexyl) phthalate
3	23.7	43.4	18.7
6	20.7	26.4	36.2
9	13.4	26.0	22.8

Table 4. Characteristics for three calibration ranges.

Calibration range (ng/µL)	Average RSD in RFs	Standard deviations in average RSD RFs	Targets requiring weighted linear regression
0.02–15	8.38	3.51	Endrin, endosulfan sulfate
0.1–10	6.69	3.42	Endrin
0.1–5	6.64	3.30	Endrin

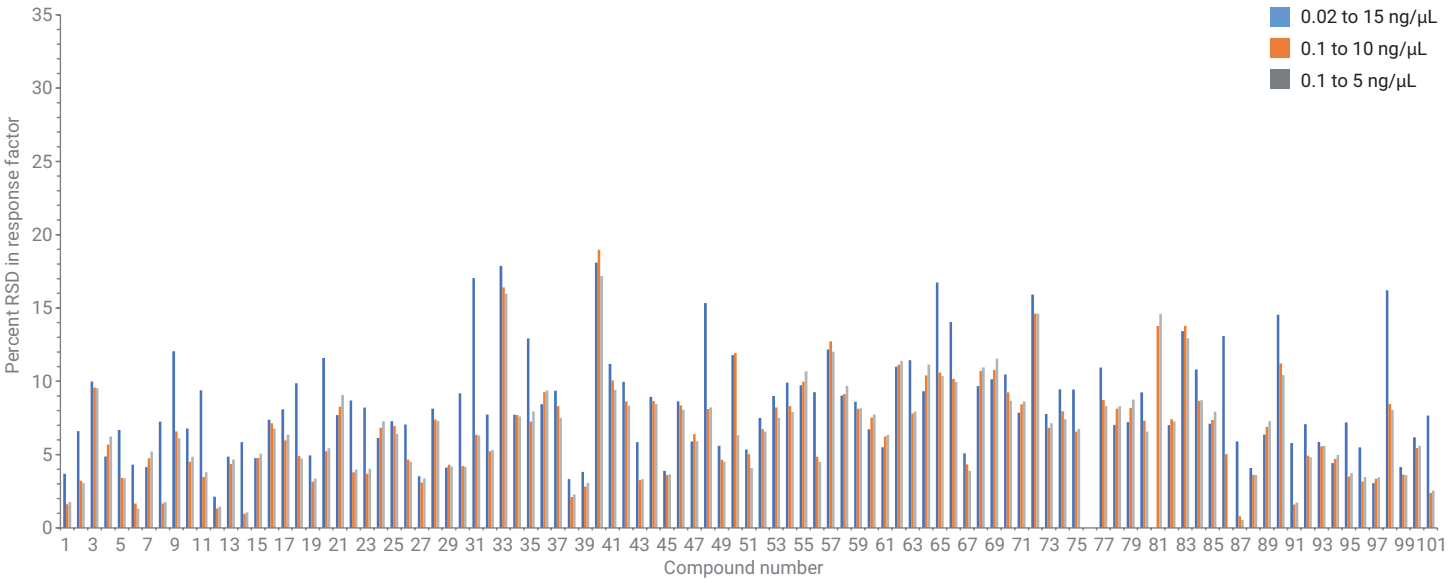

Figure 4. Comparison of percent RSDs for calibration ranges from 0.02 to 15 ng/µL (blue), 0.1 to 10 ng/µL (orange), and 0.1 to 5 ng/µL (gray). (Compound identifications are listed in Appendix Table A1).

Conclusions

The calibration requirements for the analysis of semivolatile organic compounds in drinking water following EPA Method 525 could be achieved using the Intuvo and 5977. Increasing the diameter of the draw-out plate in the EI source from 3 to 9 mm increased the quantitative dynamic range allowing calibration from 0.02 to 15 ng/µL for most compounds.

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; pp 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**.
3. Munch, J. W.; *et al.* Method 525.3: Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Ga Chromatography/ Mass Spectrometry. United States Environmental Protection Agency, **2012**.
4. Title 18. Environmental Quality, Chapter 11. Department of Environmental Quality – Water Quality Standard, Arizona Department of State, Phoenix, AZ, **2016**.
5. Endrin and DDT Stability Study for Drinking Water Method EPA 525.2 on the Intuvo, *Agilent Technologies Application Note*, publication number 5991-9277EN, **2018**.
6. de Crauw, Th. Recueil des Travaux Chimiques des Pays-Bas et de la Belgique. **1931**, *50(9)*, 753-855.
7. Katsoyiannis, *A. Environ. Sci. Technol.* **2011**, *45(20)*, 8897-8906.
8. Gartner, S. J. *Agric. Food Chem.* **2009**, *57(22)*, 10675-10681.
9. Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02.
10. ChemSpider. http://www.chemspider.com/ (accessed April 18, **2018**).
11. Spartan '16, Version 2.0.7, 64-bit for Windows and Linux, Wavefunction, Inc. Irvine, CA, August 1, **2017**.

Appendix A

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

	Compound	Retention time (min)	Concentration level (ng/µL)										Average	% RSD
			1 (0.02)	2 (0.05)	3 (0.1)	4 (0.2)	5 (0.5)	6 (1)	7 (2.53)	8 (5)	9 (10)	10 (15.3)		
1	Isophorone	6.026	1.415	1.229	1.399	1.370	1.352	1.331	1.342	1.365	1.353	1.347	1.350	3.69
2	Dichlorvos	6.791	0.924	0.720	0.787	0.773	0.832	0.803	0.817	0.835	0.843	0.853	0.819	6.61
3	Hexachlorocyclopentadiene	7.572	0.308	0.335	0.287	0.345	0.353	0.357	0.372	0.382	0.390	0.396	0.352	9.99
4	EPTC	7.732	0.438	0.454	0.507	0.420	0.445	0.454	0.459	0.460	0.458	0.458	0.455	4.87
5	Mevinphos	8.417	0.829	0.674	0.851	0.778	0.822	0.792	0.830	0.836	0.850	0.850	0.811	6.68
6	Butylate	8.470	NA	0.750	0.680	0.676	0.666	0.684	0.661	0.666	0.652	0.657	0.677	4.32
7	Vernolate	8.690	NA	0.516	0.570	0.495	0.497	0.529	0.525	0.524	0.527	0.524	0.523	4.15
8	Dimethyl phthalate	8.738	1.670	1.580	1.420	1.427	1.373	1.373	1.379	1.382	1.375	1.374	1.435	7.25
9	Etridiazole	8.775	0.259	0.214	0.170	0.199	0.180	0.189	0.188	0.201	0.206	0.209	0.202	12.05
10	2,6-Dinitrotoluene	8.861	0.320	0.330	0.306	0.265	0.278	0.283	0.292	0.280	0.291	0.302	0.295	6.78
11	Pebulate	8.872	0.641	0.512	0.491	0.531	0.474	0.495	0.490	0.496	0.494	0.490	0.511	9.39
12	Acenaphthylene	9.005	1.999	1.850	1.952	1.933	1.879	1.951	1.923	1.948	1.928	1.932	1.930	2.13
13	Chloroneb	9.481	0.473	0.474	0.528	0.554	0.513	0.506	0.483	0.505	0.503	0.502	0.504	4.86
14	2-Chlorobiphenyl (BZ #1)	9.546	1.299	1.116	1.117	1.084	1.093	1.092	1.088	1.093	1.094	1.083	1.116	5.86
15	Tebuthiuron	9.776	0.492	0.474	0.531	0.454	0.499	0.496	0.511	0.493	0.515	0.531	0.499	4.76
16	2,4-Dinitrotoluene	9.909	0.313	0.353	0.301	0.328	0.342	0.345	0.357	0.367	0.374	0.379	0.346	7.38
17	Molinate	10.107	0.813	0.671	0.765	0.667	0.643	0.662	0.670	0.667	0.656	0.656	0.687	8.09
18	Diethyl phthalate	10.717	1.771	1.466	1.465	1.492	1.367	1.370	1.359	1.325	1.314	1.295	1.423	9.87
19	Fluorene	10.915	1.471	1.507	1.419	1.407	1.367	1.298	1.335	1.341	1.336	1.326	1.381	4.94
20	Propachlor	11.038	0.946	0.774	0.766	0.667	0.737	0.688	0.681	0.687	0.676	0.687	0.731	11.59
21	Ethoprophos	11.492	NA	NA	0.214	0.270	0.212	0.229	0.233	0.235	0.233	0.239	0.233	7.70
22	Cycloate	11.535	1.043	1.288	1.105	1.006	0.998	0.999	1.020	1.017	0.996	1.000	1.047	8.69
23	Chlorpropham	11.819	0.499	0.445	0.390	0.430	0.383	0.398	0.400	0.407	0.402	0.414	0.417	8.21
24	Trifluralin	11.878	NA	0.257	0.291	0.248	0.237	0.250	0.251	0.256	0.268	0.271	0.259	6.13
25	*alpha*-BHC	12.584	0.252	0.251	0.313	0.276	0.281	0.279	0.265	0.263	0.253	0.251	0.268	7.28
26	2,3-Dichlorobiphenyl (BZ #5)	12.653	0.864	0.956	0.883	0.852	0.819	0.800	0.794	0.790	0.777	0.769	0.830	7.05
27	Hexachlorobenzene	12.680	0.413	0.405	0.436	0.436	0.450	0.415	0.441	0.413	0.429	0.414	0.425	3.53
28	Atraton	13.038	NA	0.239	0.191	0.191	0.203	0.200	0.227	0.220	0.224	0.227	0.214	8.14
29	Simazine	13.231	0.147	0.153	0.146	0.138	0.143	0.136	0.150	0.150	0.152	0.153	0.147	4.12
30	Prometon	13.231	0.159	0.207	0.216	0.206	0.205	0.201	0.218	0.223	0.222	0.224	0.208	9.18
31	*beta*-BHC	13.364	0.193	0.121	0.131	0.113	0.117	0.120	0.129	0.131	0.133	0.131	0.132	17.04
32	Atrazine	13.381	0.270	0.223	0.219	0.209	0.209	0.221	0.237	0.233	0.233	0.237	0.229	7.73
33	Pentachlorophenol†	13.423	0.104	0.105	0.103	0.108	0.121	0.126	0.150	0.150	0.155	0.157	0.128	17.86
34	Propazine	13.493	0.214	0.182	0.187	0.187	0.196	0.196	0.218	0.222	0.220	0.217	0.204	7.72
35	*gamma*-BHC	13.648	0.181	0.159	0.153	0.125	0.129	0.127	0.128	0.137	0.134	0.133	0.141	12.92
36	Pronamide	13.915	0.379	0.341	0.299	0.342	0.348	0.350	0.387	0.388	0.388	0.392	0.361	8.43
37	Chlorothalonil	14.140	0.247	0.223	0.255	0.235	0.239	0.258	0.279	0.282	0.292	0.290	0.260	9.35

38	Phenanthrene	14.151	1.183	1.220	1.165	1.137	1.130	1.094	1.108	1.146	1.120	1.117	1.142	3.33
39	Anthracene	14.338	1.257	1.121	1.220	1.162	1.134	1.124	1.133	1.162	1.147	1.143	1.160	3.82
40	Methyl paraoxon	14.370	0.186	0.191	0.150	0.169	0.178	0.184	0.221	0.236	0.250	0.258	0.202	18.10
41	Terbacil	14.397	0.092	0.077	0.089	0.085	0.089	0.082	0.100	0.103	0.105	0.107	0.093	11.18
42	*delta*-BHC	14.557	0.136	0.103	0.104	0.113	0.126	0.118	0.127	0.131	0.134	0.133	0.122	9.97
43	2,4,5-trichlorobiphenyl	15.028	0.367	0.337	0.304	0.325	0.300	0.311	0.318	0.324	0.324	0.323	0.323	5.85
44	Alachlor	15.771	0.304	0.253	0.281	0.238	0.270	0.266	0.299	0.301	0.307	0.312	0.283	8.95
45	Simetryn	15.910	NA	0.303	0.324	0.308	0.308	0.309	0.329	0.333	0.330	0.333	0.320	3.88
46	Heptachlor	15.985	0.185	0.158	0.135	0.170	0.149	0.164	0.158	0.164	0.174	0.174	0.163	8.64
47	Ametryn	16.050	NA	0.245	0.236	0.221	0.236	0.235	0.258	0.257	0.263	0.259	0.246	5.90
48	Prometryn	16.151	0.278	0.297	0.186	0.189	0.216	0.212	0.223	0.225	0.227	0.227	0.228	15.34
49	Terbutryn	16.558	0.280	0.238	0.260	0.253	0.250	0.240	0.264	0.273	0.272	0.271	0.260	5.60
50	Bromacil	16.670	0.266	0.256	0.212	0.223	0.225	0.219	0.247	0.245	0.295	0.290	0.248	11.79
51	Dibutyl phthalate	16.788	1.445	1.298	1.318	1.310	1.297	1.268	1.389	1.407	1.454	1.452	1.364	5.35
52	2,2′,4,4′-tetrachlorobiphenyl (BZ #47)	16.857	0.197	0.180	0.190	0.194	0.196	0.202	0.222	0.218	0.221	0.221	0.204	7.51
53	Metolachlor	16.996	0.568	0.493	0.520	0.523	0.545	0.549	0.593	0.627	0.631	0.636	0.568	8.99
54	Chlorpyrifos	17.071	0.196	0.158	0.161	0.139	0.155	0.148	0.168	0.173	0.176	0.177	0.165	9.91
55	Aldrin	17.135	NA	0.158	0.212	0.194	0.181	0.160	0.167	0.172	0.173	0.173	0.177	9.72
56	DCPA	17.205	0.210	0.181	0.234	0.220	0.229	0.220	0.241	0.244	0.248	0.249	0.228	9.25
57	Cyanazine	17.237	0.064	0.054	0.044	0.052	0.048	0.049	0.060	0.058	0.061	0.060	0.055	12.17
58	Triadimefon	17.435	0.187	0.176	0.176	0.135	0.151	0.157	0.166	0.174	0.171	0.173	0.167	9.02
59	Diphenamid	17.804	0.828	0.670	0.685	0.656	0.688	0.705	0.793	0.794	0.788	0.783	0.739	8.61
60	MGK-264a‡	17.857	NA	0.311	0.303	0.260	0.287	0.292	0.319	0.323	0.320	0.316	0.303	6.73
61	MGK-264b‡	18.264	NA	0.232	0.210	0.240	0.229	0.216	0.241	0.246	0.245	0.240	0.233	5.50
62	Heptachlor epoxide	18.392	NA	0.059	0.055	0.062	0.066	0.064	0.076	0.072	0.074	0.073	0.067	10.99
63	2,2′,3′,4,6-pentachlorobiphenyl (BZ #98)	18.510	0.143	0.105	0.131	0.138	0.141	0.132	0.156	0.157	0.155	0.156	0.141	11.44
64	*gamma*-Chlordane	19.152	0.096	0.099	0.085	0.113	0.096	0.099	0.114	0.109	0.110	0.111	0.103	9.32
65	Tetrachlorvinphos	19.323	0.366	0.199	0.242	0.254	0.258	0.259	0.307	0.306	0.308	0.304	0.280	16.74
66	Butachlor	19.441	0.361	0.314	0.256	0.224	0.243	0.252	0.287	0.291	0.293	0.291	0.281	14.05
67	Pyrene	19.483	1.412	1.232	1.249	1.297	1.242	1.244	1.337	1.355	1.374	1.373	1.311	5.09
68	*alpha*-Chlordane	19.553	NA	0.083	0.069	0.075	0.086	0.076	0.090	0.090	0.090	0.090	0.083	9.67
69	Endosulfan	19.558	NA	NA	0.049	0.037	0.042	0.037	0.047	0.046	0.046	0.046	0.044	10.15
70	*trans*-Nonachlor	19.644	NA	0.088	0.091	0.096	0.100	0.097	0.112	0.112	0.115	0.116	0.103	10.47
71	Napropamide	19.836	0.538	0.529	0.537	0.496	0.546	0.542	0.622	0.611	0.608	0.609	0.564	7.86
72	Tricyclazole	20.045	0.180	0.227	0.213	0.194	0.235	0.238	0.279	0.282	0.284	0.278	0.241	15.91
73	4,4′-DDE	20.291	0.283	0.227	0.258	0.225	0.250	0.236	0.264	0.273	0.266	0.268	0.255	7.77
74	Dieldrin	20.409	NA	0.180	0.197	0.190	0.207	0.209	0.226	0.230	0.234	0.234	0.212	9.45
75	2,2′,4,4′,5,6′-hexachlorobiphenyl (BZ #154)	20.462	0.185	0.138	0.131	0.154	0.148	0.148	0.158	0.157	0.159	0.156	0.153	9.45
76	Endrin	21.061	**Linear regression**											
77	Chlorobenzilate	21.350	0.275	0.260	0.279	0.317	0.307	0.287	0.340	0.340	0.349	0.352	0.310	10.94
78	4,4′-DDD	21.607	0.438	0.450	0.397	0.432	0.436	0.454	0.497	0.488	0.489	0.481	0.456	7.03
79	Endrin aldehyde	21.869	NA	0.143	0.127	0.153	0.128	0.127	0.147	0.147	0.146	0.146	0.140	7.22
80	Norflurazon	22.484	0.271	0.214	0.250	0.248	0.238	0.258	0.276	0.282	0.289	0.288	0.261	9.25

81	Endosulfan sulfate	22.607	Linear regression											
82	Butyl benzyl phthalate	22.677	0.560	0.553	0.530	0.555	0.552	0.550	0.624	0.627	0.626	0.632	0.581	7.00
83	4,4′-DDT	22.778	0.302	0.344	0.293	0.290	0.311	0.320	0.373	0.392	0.399	0.408	0.343	13.43
84	Hexazinone	22.928	0.480	0.658	0.536	0.546	0.591	0.593	0.651	0.662	0.656	0.663	0.604	10.81
85	*bis*(2-Ethylhexyl) adipate	23.308	0.510	0.478	0.445	0.529	0.549	0.548	0.551	0.550	0.550	0.552	0.526	7.11
86	2,2′,3,3′,4,4′,6-heptachlorobiphenyl (BZ #171)	24.238	0.081	0.070	0.096	0.105	0.097	0.104	0.111	0.105	0.105	0.105	0.098	13.08
87	Benz[a]anthracene	24.276	NA	1.395	1.189	1.194	1.190	1.181	1.182	1.177	1.166	1.180	1.206	5.90
88	Chrysene	24.399	1.217	1.251	1.243	1.175	1.183	1.125	1.150	1.139	1.124	1.135	1.174	4.08
89	2,2′,3,3′,4,5′,6,6′-octachlorobiphenyl (BZ #200)	24.410	NA	0.120	0.144	0.117	0.131	0.125	0.131	0.124	0.123	0.124	0.126	6.37
90	Methoxychlor	24.527	0.508	0.571	0.570	0.570	0.657	0.672	0.706	0.731	0.762	0.789	0.654	14.54
91	*bis*(2-Ethylhexyl) phthalate	25.207	NA	1.013	0.866	0.840	0.875	0.848	0.875	0.870	0.868	0.886	0.882	5.79
92	Fenarimol	26.201	NA	0.204	0.160	0.165	0.170	0.179	0.177	0.181	0.183	0.182	0.178	7.07
93	*cis*-Permethrin	27.309	0.425	0.456	0.369	0.402	0.427	0.396	0.419	0.428	0.432	0.438	0.419	5.87
94	*trans*-Permethrin	27.533	0.933	0.902	0.843	0.924	0.959	0.946	0.965	0.961	0.965	0.988	0.938	4.42
95	Benzo[b]fluoranthene	28.250	0.909	1.024	1.045	1.099	1.137	1.109	1.165	1.137	1.141	1.148	1.091	7.19
96	Benzo[k]fluoranthene	28.352	1.336	1.166	1.084	1.199	1.149	1.142	1.184	1.160	1.153	1.163	1.174	5.49
97	Benzo[a]pyrene	29.320	1.069	1.113	1.014	1.085	1.047	1.081	1.114	1.101	1.107	1.112	1.084	3.06
98	Fluridone	29.598	0.365	0.345	0.441	0.488	0.473	0.496	0.539	0.547	0.556	0.570	0.482	16.21
99	Indeno[1,2,3-cd]pyrene	32.812	0.897	0.973	0.923	0.959	0.939	0.954	1.006	1.006	1.004	1.013	0.967	4.15
100	Dibenz[a,h]anthracene	32.951	0.866	0.949	0.885	0.931	0.967	0.984	1.025	1.023	1.020	1.031	0.968	6.18
101	Benzo[ghi]perylene	33.524	0.833	0.911	1.075	1.075	1.009	1.025	1.053	1.043	1.033	1.033	1.009	7.67

† Pentachlorophenol concentration levels: 0.08, 0.2, 0.4, 0.8, 2, 4, 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, and 7.67 ng/µL

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

	Compound	Retention time (min)	Concentration level (ng/µL)									
			0.02	0.05	0.1	0.2	0.5	1	2.53	5	10	15.3
76	Endrin	21.061	NA	NA	0.11	0.24	0.43	0.87	2.32	4.93	9.86	15.89
	$y = 0.011191x - 6.052770 \times 10^{-4}$; weighting 1/x; $R^2 = 0.9976$											
81	Endosulfan sulfate	22.607	NA	0.05	0.11	0.16	0.52	0.92	2.59	5.06	10.06	15.23
	$y = 0.013896x - 3.895983 \times 10^{-4}$; weighting 1/x; $R^2 = 0.9994$											

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