Application Note # CA-270125

Evaluation of Tandem Mass Spectrometry for the Analysis of Environmental Samples

Introduction

U.S. Environmental Protection Agency (EPA) Method 525.2, "Determination of Organic Compounds in Drinking Water by Liquid – Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry", is a broad-spectrum method for the analysis of over 100 organic compounds in drinking water, source water, or drinking water in any treatment stage. Chemical classes included in this method are pesticides, herbicides, plasticizers, polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and other industrial chemicals [1].

Commercial, state, and federal laboratories use Method 525.2 for routine monitoring of public water supplies (PWS) that must comply with the Safe Drink Water Act (SDWA). The method employs gas chromatography coupled with full-scan mass spectrometry. In general, the method works well for clean finished tap water and most ground waters. However, some surface water sources contain high concentrations of fulvic/humic acids or other naturally occurring organic contaminants. This results in GC/MS chromatograms with highly elevated baselines that can potentially interfere with the identification of target analytes at low-levels using conventional full-scan or selected ion monitoring (SIM) mass spectrometry.

In this study, tandem MS/MS is compared to SIM in terms of: (a) method calibration, (b) precision and accuracy, and (c) quantitation; for over one hundred target compounds spiked into a challenging contaminated real-world drinking water extract using EPA method 525.2.

Instrumentation and materials

- Bruker 300-MS triple quadrupole mass spectrometer
- Bruker 450-GC gas chromatograph
- Bruker 1177 S/SL injector with Siltek frit insert
- CTC Analytics Combi PAL™ autosampler

Calibration solution and spiked sample

A series of seven calibration solutions in ethyl acetate were prepared, which contain the analytes of interest (except pentachlorophenol) at concentrations of 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, and 1 ng/µL; with a constant concentration of 2 ng/µL internal standards and surrogates in each calibration solution. Over one hundred compounds at 50 ng/mL (equivalent to 0.05 ng/µL or 0.05 ppb spiked into the original 1 L water sample before extraction) were spiked into: (a) a concentrated ground water extract provided by Underwriters Laboratories Inc., and (b) pure ethyl acetate solvent.

GC Conditions

Column	VF-5ms capillary column, 30m x 0.25 mm x 0.25 µm
Inlet Temperature	250 °C
Injection Volume	1 µL
Carrier Gas Flow	Helium at 1 mL/min
Injection Mode	Splitless
Oven Program	40 °C for 1 min, to 200 °C at 10 °C/min, to 270 °C at 5 °C/min, to 300 °C at 10 °C/min, and to 320 °C at 20 °C/min for 1 min, for a total run time of 36 min.
Pulse Pressure	40 psi
Pulse Duration	0.8 min

MS Conditions

Filament Delay	7 min
Manifold Temp.	40 °C
Transfer Line Temp.	280 °C
Ion Source Temp.	250 °C
Operation Mode	MS/MS or SIM

MS/MS and SIM parameters: see Table 1.

Table 1: MS/MS parameters for compounds in EPA Method 525.2.*

Name	Retention Time	Q1 (m/z)	Q3 (m/z)	Collision Energy (V)
o-Toluidine	8.34	106	77	18.0
Isophorone	9.14	138	82	12.0
Benzene, 1,3-dimethyl-2-nitro-	10.09	109	79	10.0
Dichlorvos	10.88	134	79	10.0
Quinoline	10.96	129	102	15.0
Hexachlorocyclopentadiene	12.16	237	143	30.0
EPTC	12.47	132	62	10.0
Mevinphos	13.40	146	90	10.0
Mevinphos	13.40	127	109	10.0
Butylate	13.40	128	57	10.0
Vernolate	13.65	128	86	11.0
Dimethyl	13.72	120	77	18.0
Dimethyl	13.72	149	121	15.0
Pebulate	13.83	156	57	10.0
2,4-dinitrotoluene	13.86	165	63	15.0
Acenaphthylene	13.91	152	150	30.0
Acenapthene-d10	14.25	164	160	30.0
2-Chlorobiphenyl	14.45	188	152	20.0
Chlorneb	14.45	206	191	15.0
Tebuthiuron	14.65	156	74	10.0
Benzene, 1-methyl-2,4-dinitro-	14.81	165	63	15.0
molinate	14.92	126	98	5.0
Diethyl Phthalate	15.42	149	121	15.0
Fluorene	15.57	166	164	36.0
Propachlor	15.67	163	77	20.0
Ethoprop	15.97	158	114	7.0
Cycloate	16.01	154	831	5.0
Chlorprophan	16.23	213	127	15.0
Triflualin	16.23	264	159	15.0
α-BHC	16.80	183	146	18.0
2,3-dichlorobiphenyl	16.82	222	152	18.0
Hexachlorobenzene	16.86	229	214	10.0
Hexachlorobenzene	16.86	284	214	30.0
Atraton	17.02	211	196	8.0
Prometon	17.15	225	168	11.0
Simazine	17.20	201	173	10.0
Atrazine	17.29	215	200	8.0
Propazine	17.37	54	39	5.0
β-BHC	17.37	183	146	18.0
Pentachlorophenol	17.39	266	202	13.0
Pentachlorophenol	17.39	266	133	25.0
γ-BHC	17.55	183	146	18.0
Terbufos	17.56	231	175	13.0
Propyzamide	17.65	173	145	18.0
Diazinone	17.67	179	137	15.0
Phenanthrene-d10	17.85	188	158	35.0
Phenanthrene	17.91	178	151	35.0
Disulfoton	17.97	88	60	7.0
Anthracene	18.05	178	151	35.0
δ-BHC	18.22	198	82	13.0
2,4,5-trichlorobiphenyl	18.51	256	186	20.0
Acetochlor	18.80	223	147	10.0
Acetochlor	18.80	202	147	6.0
Metribuzin	18.89	198	82	13.0
Alachlor	19.03	188	160	10.0
Simetryn	19.14	213	170	12.02
Simetryn	19.14	411	701	5.0
Ametryn	19.23	227	170	11.0

Results and discussion

Over one hundred compounds were analyzed using both SIM and MS/MS acquisitions. Typical total ion chromatograms (TIC) of MS/MS and SIM acquisitions at 500 ng/mL are exhibited in Figure 2.

Calibration solutions of 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, and 1 ng/µL were used for all the analytes except pentachlorophenol, which is four times the other analytes. All compounds showed linear fit with excellent calibration coefficient and relative standard deviation in both SIM and MS/MS acquisitions (Table 2). The lowest concentration point of most compounds for this comparison was at 0.01 ng/µL, which is ten times lower than 0.1 ng/µL, as suggested in the EPA method. The average r^2, relative response factor (RRF) and relative standard deviation (RSD%) are 0.9987, 0.31 and 8.25 percent, respectively in MS/MS mode, while the average r^2, RRF and RSD% are 0.9997, 0.27 and 7.87%, respectively in SIM mode. Recovery studies were conducted by spiking over one hundred target compounds in EPA Method 525.2 into a concentrated ground water extract provided by Underwriters Laboratories Inc. (Figure 3) and compared to spikes in pure ethyl acetate.

Table 1 (cont.): MS/MS parameters for compounds in EPA Method 525.2.*

Heptachlor	19.27	272	236	15.0
Prometryne	19.29	241	184	10.0
Terbutryne	19.63	241	170	15.0
Dibutyl phthalate	19.76	149	121	20.0
2,2′,4,4′-tetrachlorobiphenyl	19.94	292	221	18.0
Metolachlor	20.01	238	162	11.0
Chlorpyrifos	20.05	314	258	15.0
DCPA (Dacthal)	20.19	301	222	20.0
Triadimefon	20.35	208	127	12.0
Diphenamid	20.70	167	152	20.0
Diphenamid	20.70	239	167	15.0
MGK-264	21.07	164	98	13.0
Heptachlor Epoxide	21.29	353	262	16.0
2,2′,3,4,6-pentachlorobiphenyl	21.36	326	255	16.0
2,2′,3,4,6-pentachlorobiphenyl	21.36	326	291	16.0
Captan	21.58	79	51	20.0
γ-Chlordane	21.96	373	266	15.0
Stirofos	22.04	329	109	25.0
Butachlor	22.09	176	147	20.0
pyrene	22.36	202	200	30.0
α-Chlordane	22.34	375	266	15.0
trans-nonachlor	22.41	409	301	17.0
Napropamide	22.53	128	72	15.0
Profenofos	22.84	339	269	12.0
p,p′-DDE	22.98	318	247	15.0
DEF (Tribufos)	23.01	169	57	10.0
Oxyfluorfen	23.11	252	196	20.0
2,2′,4,4′,5,6′-hexachlorobiphenyl	23.16	360	290	20.0
Carboxin	23.30	235	143	10.0
Nitrofen	23.76	283	202	12.0
Endrin	23.83	263	191	30.0
Chlorobenzilate	23.98	251	139	15.0
Endosulfan II	24.18	241	206	20.0
Ethion	24.23	231	175	12.0
p,p′-DDD	24.30	235	165	18.0
Endrin Aldehyde	24.64	345	244	12.0
Norflurazon	25.20	303	145	23.0
Benzyl butyl phthalate	25.31	149	121	18.0
Endosulfan sulfate	25.38	274	238	15.0
p,p′-DDT	25.49	235	165	18.0
Hexazinone	25.69	171	101	17.0
bis(2-ethylhexyl)adipate	25.82	129	101	7.0
Tebuconazole	25.93	250	125	18.0
Triphenyl phosphate	26.08	326	169	25.0
Heptachlorobiphenyl	27.07	396	324	20.0
Chrysene	27.18	228	226	30.0
Chrysene-d_{12}	27.22	240	236	30.0
Benzo[a]anthracene	27.32	228	226	30.0
Methoxychlor	27.33	227	169	25.0
bis(2-ethylhexyl)phthalate	27.92	149	121	18.0
cis-Permethrin	30.35	183	154	15.0
trans-Permethrin	30.60	183	168	15.0
Benzo[b]fluoranthene	31.55	252	250	30.0
Benzo[k]fluoranthene	31.65	252	250	30.0
Benzo[a]pyrene	32.63	252	250	30.0
Perylene-d12	32.82	264	260	30.0
Indeno[1,2,3-cd]pyrene	35.38	276	274	30.0
Dibenz[a,h]anthracene	35.46	278	276	30.0
Benzo[ghi]perylene	35.92	276	274	30.0

*For SIM acquisition, only Q1 ions are used.

As shown in Table 3, some compounds showed very similar results in both solvent and matrix using both MS/MS and SIM modes. The average recoveries of these compounds in matrix using SIM and MS/MS acquisition modes are 126% and 118%, respectively, with average RSD%'s of 5.69 and 3.69%. The average recoveries of these compounds spiked in pure solvent are 112% and 109% with average RSD%'s of 2.58 and 3.22% using SIM and MS/MS acquisition modes, respectively.

The compounds listed in Table 4 showed high biased results in the matrix in SIM mode, while results are consistent in both matrix and pure solvent using MS/MS mode.

As indicated in Figure 4A, δ-BHC can be analyzed in the solvent accurately using SIM acquisition without any interference. However, significant matrix interference prevented accurate quantitation in SIM mode. On the other hand, MS/MS acquisition gave accurate results in both solvent and matrix samples (Figure 4B). Similarly, triadimefon (Figure 5) and other compounds listed in Table 4 showed high biased results in the matrix using SIM acquisition, but consistent results are yielded again in both solvent and matrix from the MS/MS acquisition.

	MS/MS			SIM		
Compound Name	**Correlation Coefficient (r^2)**	**Average RRF**	**RSD %**	**Correlation Coefficient (r^2)**	**Average RRF**	**RSD %**
o-Toluidine	0.9997	0.67	8.67	0.9982	0.78	10.82
Isophorone	0.9997	0.32	5.49	0.9999	0.13	13.24
1,3-dimethyl-2-nitrobenzene (SS)						
Dichlorvos	0.9989	0.48	16.86	0.9996	0.60	21.62
Quinoline	0.9993	1.18	20.26	0.9999	0.98	24.44
Hexachlorocyclopentadiene	0.9996	0.03	8.36	0.9997	0.15	16.21
EPTC	0.9999	0.04	5.7	0.9999	0.11	5.14
Mevinphos	0.9985	0.32	8.45	1.0000	0.30	3.13
Butylate	0.9990	0.45	5.34	1.0000	0.26	4.40
Vernolate	0.9995	0.04	11.69	1.0000	0.48	3.17
Dimethyl phthalate	0.9997	1.29	5.34	0.9999	0.93	6.35
Pebulate	0.9996	0.44	5.23	1.0000	0.45	4.74
2,4-dinitrotoluene	0.9966	0.09	8.58	0.9994	0.16	6.80
Acenaphthylene	0.9998	0.47	5.18	1.0000	1.29	4.60
Acenapthene-d10 (IS)						
Chlorneb	0.9998	0.28	3.37	0.9997	0.09	4.99
2-Chlorobiphenyl	1.0000	1.09	2.54	0.9997	0.38	3.73
Tebuthiuron	0.9976	0.09	18.94	1.0000	0.14	27.56
Benzene, 1-methyl-2,4-dinitro-	0.9945	0.04	18.06	0.9982	0.08	21.76
Molinate	0.9992	0.22	3.29	0.9999	0.28	2.25
Diethyl Phthalate	0.9997	0.32	4.69	0.9999	0.47	5.91
Fluorene	0.9999	0.3	5.15	0.9999	0.48	2.45
Propachlor	0.9977	0.53	7.52	0.9992	0.27	8.07
Ethoprop	0.9990	0.16	8.08	0.9999	0.09	7.61
Cycloate	1.0000	0.21	2.57	0.9999	0.20	1.17
Chlorprophan	0.9999	0.11	5.09	0.9998	0.05	7.99
Triflualin	0.9986	0.05	6.12	0.9993	0.10	5.52
Alpha-BHC	0.9999	0.17	4.36	0.9993	0.09	4.01
2,3-dichlorobiphenyl	0.9999	1.31	1.87	0.9998	0.24	2.30
Hexachlorobenzene	0.9999	0.24	3.06	0.9998	0.15	3.28
Atraton	0.9995	0.05	13.35	0.9997	0.06	24.13
Prometon	0.9987	0.09	7.84	0.9998	0.06	9.07
Simazine	0.9996	0.06	9.96	0.9999	0.06	12.91
Atrazine	0.9997	0.17	3.01	0.9999	0.10	7.67
Propazine	0.9995	0.31	6.05	0.9995	0.17	8.03
Beta-BHC	0.9999	0.12	4.91	0.9999	0.07	2.19
Gamma-BHC	0.9998	0.14	5.78	0.9999	0.08	5.32
Terbufos	0.9987	0.14	7.04	0.9999	0.13	5.18
Propyzamide	0.9997	0.72	7.64	0.9999	0.20	3.23
Diazinone	0.9968	0.08	13.77	0.9997	0.10	4.38
Phenanthrene-d10 (IS)						
Phenanthrene	1.0000	0.73	1.85	0.9998	0.68	5.15
Disulfoton	0.9987	1.48	11.46	0.9998	0.38	3.83
Anthracene	0.9999	0.62	2.18	0.9998	0.64	2.49
Delta-BHC	1.0000	0.13	4.29	0.9999	0.07	4.35
2,4,5-trichlorobiphenyl	0.9998	0.98	2.2	0.9998	0.20	2.37
Acetochlor	0.9984	0.05	9.44	0.9995	0.03	8.18
Metribuzin	0.9996	0.08	10.12	0.9998	0.07	11.43
Alachlor	0.9955	0.39	12.91	0.9996	0.17	4.99
Simetryn	0.9993	0.12	9.65	0.9999	0.15	11.40
Ametryn	0.9997	0.12	5.36	0.9997	0.12	5.79
Heptachlor	0.9995	0.12	4.02	0.9999	0.06	2.92
Prometryn	0.9988	0.17	6.92	0.9999	0.12	4.50
Terbutryn	0.9994	0.15	6.43	1.0000	0.05	4.78

Table 2: Comparison of calibration results of compounds analyzed based on EPA Method 525.2 in both MS/MS and SIM modes.

Typical TIC and SIM data

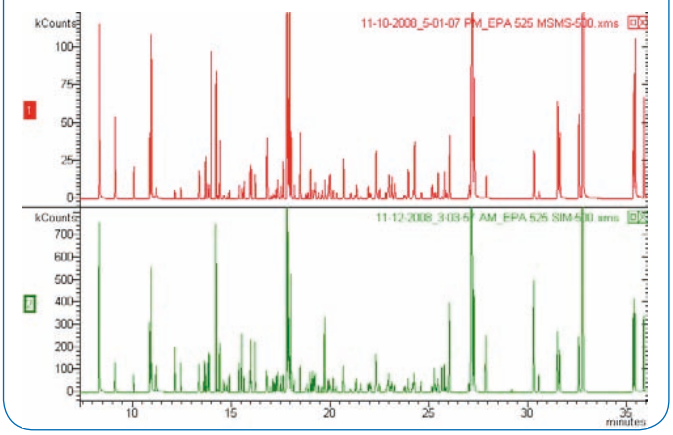

Figure 2: TIC of over 100 compounds in EPA 525.2 in MS/MS (A) and SIM (B) acquisition modes at concentration of 500 ng/mL in a pure solvent.

Ground water recovery study

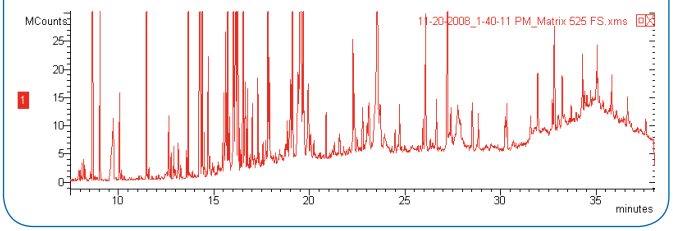

Figure 3: Full scan TIC of ground water extract spiked at 50 ng/mL provided by Underwriters Laboratories, Inc. Note the highly elevated baseline and total ion counts, indicating a large amount of co-extracted matrix interference.

Dibutyl phthalate	0.9994	0.41	22.47	0.9999	1.42	26.95
2,2′,4,4′-tetrachlorobiphenyl	1	0.27	3.35	0.9999	0.14	2.17
Metolachlor	0.9954	0.57	10.6	0.9999	0.12	6.34
Chlorpyrifos	0.9989	0.2	7.56	0.9998	0.04	5.57
DCPA (Dacthal)	0.9995	0.16	5.07	0.9999	0.14	2.26
Triadimefon	0.9994	0.11	12.36	0.9997	0.08	7.25
Diphenamid	0.9991	0.77	4.7	0.9997	0.31	3.12
MGK-264	0.9996	0.12	3.99	1.0000	0.05	3.50
Heptachlor Epoxide	0.9996	0.07	13.1	0.9999	0.05	2.62
2,2′,3,4,6-pentachlorobiphenyl	0.9999	0.21	3.65	0.9999	0.10	1.63
Captan	0.9968	0.06	11.93	0.9990	0.12	23.26
gama-Chlordane	0.9999	0.2	5.39	1.0000	0.08	1.53
Stirofos	0.9972	0.12	18.15	0.9998	0.09	19.15
Butachlor	0.997	0.1	11.31	0.9998	0.12	6.17
Alpha-Chlordane	0.9999	0.18	4.34	1.0000	0.07	2.25
Pyrene	0.9999	0.54	4.27	0.9996	0.78	1.78
trans-nonachlor	0.9996	0.09	4.29	1.0000	0.08	2.85
Napropamide	0.999	0.25	5.69	0.9999	0.16	5.99
profenofos	0.996	0.1	13.73	0.9997	0.03	16.16
p,p′-DDE	0.9997	0.16	6.39	1.0000	0.09	1.58
DEF (Tribufos)	0.9893	0.16	18	0.9989	0.13	8.83
Oxyfluorfen	0.9971	0.03	7.58	0.9968	0.06	11.47
2,2′,4,4′,5,6′-hexachlorobiphenyl	0.9999	0.41	2.67	1.0000	0.11	2.42
Carboxin	0.99	0.28	5.86	0.9997	0.07	17.61
Nitrofen	0.9924	0.06	9.84	0.9966	0.04	25.43
Endrin	0.9996	0.01	8.24	0.9992	0.03	2.70
Chlorobenzilate	0.9961	0.24	9.12	0.9996	0.17	5.60
Endosulfan II	0.9993	0.01	7.83	0.9999	0.02	3.13
Ethion	0.9975	0.06	11.1	0.9988	0.12	7.95
p,p′-DDD	0.9992	0.46	5.17	0.9997	0.26	3.99
Endrin Aldehyde	0.9994	0.01	15.53	0.9997	0.02	5.83
Norflurazon	0.9981	0.12	10.64	0.9996	0.07	25.75
Benzyl butyl phthalate	0.9979	0.05	6.73	0.9998	0.33	3.30
Endosulfan sulfate	0.9993	0.04	3.62	0.9999	0.04	3.78
p,p′-DDT	0.9981	0.22	7.33	0.9988	0.19	5.03
Hexazinone	0.9993	0.02	24.17	0.9999	0.33	21.21
bis(2-ethylhexyl)adipate	0.9971	0.21	13.31	0.9996	0.36	6.85
Tebuconazole	0.997	0.04	21.99	0.9990	0.06	25.34
Triphenyl phosphate (SS)						
Heptachlorobiphenyl	1	0.09	2.18	0.9996	0.08	3.73
Chrysene	0.9997	0.7	13.96	0.9999	0.73	24.03
Chrysene-$d1_2$ (IS)						
Benzo[a]anthracene	0.9992	1.84	8.14	0.9996	1.25	6.18
Methoxychlor	0.9981	0.09	10.37	0.9994	0.41	5.94
bis(2-ethylhexyl)phthalate	0.9957	0.33	13.62	0.9996	0.93	7.73
cis-Permethrin	0.9971	0.17	8.61	0.9996	0.62	4.66
trans-Permethrin	0.9986	0.03	13.44	0.9996	0.09	3.40
Benzo[b]fluoranthene	0.9989	0.67	5.74	1.0000	0.68	2.68
Benzo[a]fluoranthene	0.9994	0.5	4.69	1.0000	0.52	1.38
Benzo[a]pyrene	0.9993	0.57	4.54	1.0000	0.61	2.06
Perylene-d_{12} (SS)						
Indeno[1,2,3-cd]pyrene	0.9995	0.55	5.99	1.0000	0.66	3.83
Dibenz[a,h]anthracene	0.9988	0.7	5.83	1.0000	0.65	4.59
Benzo[ghi]perylene	0.9996	0.59	4.57	1.0000	0.71	1.44
Average	0.9987	0.31	8.25	0.9997	0.27	7.87

*Pentachlorophenyl was not included for this comparison.

Table 2 (cont.): Comparison of calibration results of compounds analyzed based on EPA Method 525.2 in both MS/MS and SIM modes.

Accurate results using MS/MS acquisition

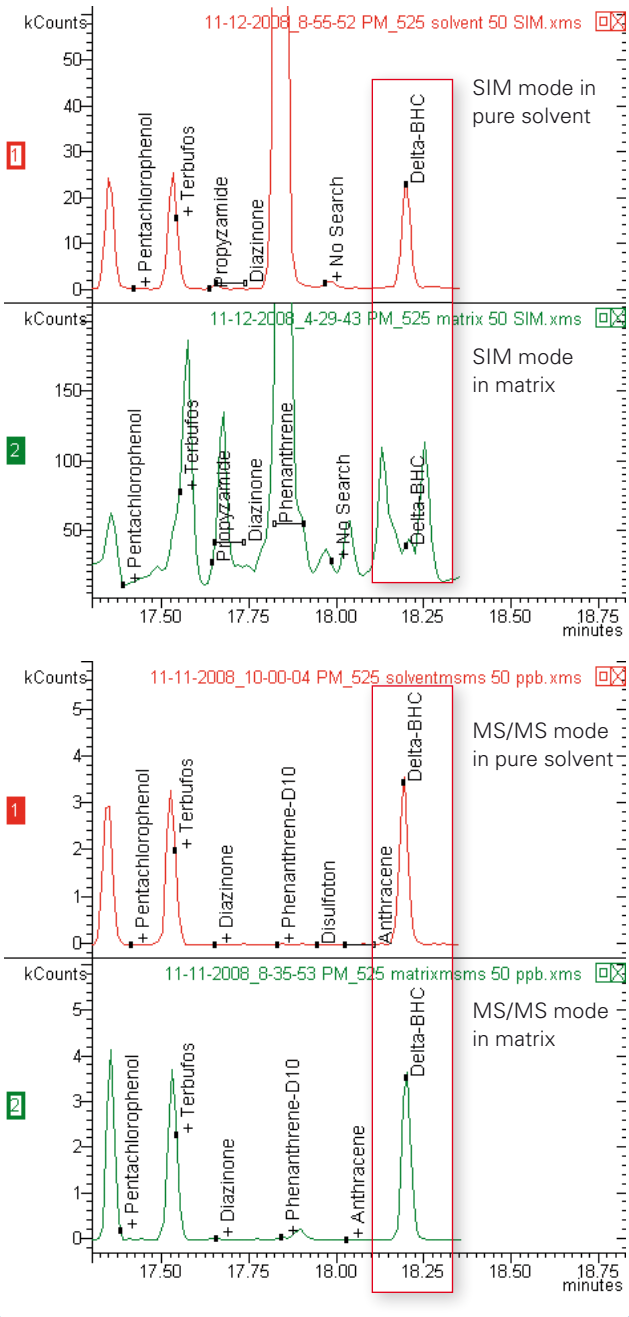

Figure 4A: SIM mode showing delta-BHC (δ-BHC) in pure solvent and matrix.

Figure 4B: Chromatograms showing delta-BHC (δ-BHC) in both solvent and concentrated water matrix in MS/MS.

Table 3: Precision and accuracy comparison of compounds in EPA 525.2 in both matrix and solvent using both MS/MS and SIM modes. Spiked concentration was 50 ng/mL (n=5).

		Spiked in Matrix under SIM		Spiked in Matrix under MS/MS		Spiked in Solvent under SIM		Spiked in Solvent under MS/MS	
Peak Name	**Retention Time (min)**	**Measured**	**RSD%**	**Measured**	**RSD%**	**Measured**	**RSD%**	**Measured**	**RSD%**
Isophorone	9.12	67.39	7.78	50.79	8.44	57.36	2.62	45.07	2.55
Dichlorvos	10.87	71.33	6.66	59.73	5.30	63.33	2.86	53.50	3.21
Quinoline	10.97	57.26	10.56	50.81	6.42	57.46	2.15	50.48	3.32
Hexachlorocyclopentadiene	12.15	72.95	2.26	77.56	1.55	62.30	1.98	69.56	2.77
EPTC	12.45	50.10	14.58	45.93	10.10	51.52	2.24	43.35	7.95
Mevinphos	13.39	56.23	6.17	46.92	6.04	51.23	1.78	43.64	4.11
Butylate	13.39	58.62	7.84	48.32	8.34	50.14	2.31	42.45	4.58
Vernolate	13.63	54.55	8.13	42.22	10.88	50.54	2.94	37.29	4.06
Dimethyl phthalate	13.71	68.73	6.16	50.30	5.13	53.12	2.34	48.03	2.31
Pebulate	13.82	55.51	6.99	47.76	7.47	50.53	3.02	44.39	4.23
2-Chlorobiphenyl	14.43	58.52	4.88	44.13	5.63	51.96	1.96	44.91	2.81
Chlorneb	14.43	57.41	6.01	47.70	1.69	52.35	3.51	42.60	4.06
molinate	14.90	60.57	5.90	54.78	4.24	52.52	1.83	50.03	4.92
Diethyl Phthalate	15.40	69.36	4.79	53.17	2.67	54.73	2.00	43.95	6.02
Propachlor	15.65	63.33	4.44	62.68	5.91	58.90	2.64	58.36	2.44
Ethoprop	15.95	94.92	5.49	74.84	1.37	56.87	2.32	67.06	2.56
2,3-dichlorobiphenyl	16.81	60.28	4.59	50.62	1.35	53.55	2.11	47.39	2.01
Hexachlorobenzene	16.85	55.77	4.18	48.18	2.50	51.40	2.93	46.90	2.18
Atraton	17.02	73.54	4.16	74.21	3.70	62.17	4.11	64.50	1.76
Prometon	17.14	62.06	6.38	67.13	5.04	58.01	3.64	62.55	2.04
Simazine	17.17	52.62	4.47	64.76	6.09	58.62	2.39	59.46	3.00
Atrazine	17.27	65.55	3.64	61.20	1.94	59.47	2.14	59.59	2.48
Propazine	17.35	58.29	5.30	58.32	6.74	51.38	0.88	50.41	3.17
Propyzamide	17.64	64.60	4.14	60.39	3.09	56.10	1.96	54.50	2.60
Disulfoton	17.95	58.41	4.14	62.96	0.69	54.76	1.89	59.36	1.75
2,4,5-trichlorobiphenyl	18.50	59.55	5.63	49.58	1.95	54.69	2.03	47.29	1.10
Alachlor	19.01	69.43	5.06	75.38	1.79	58.01	1.30	67.35	2.24
Ametryn	19.22	57.82	4.65	64.43	4.75	57.19	2.20	59.98	4.03
Heptachlor	19.25	62.77	3.80	74.27	1.80	56.91	2.37	71.40	2.33
Prometryn	19.27	60.88	4.39	65.99	2.53	57.48	2.38	62.85	2.16
Terbutryn	19.61	64.10	10.83	66.15	2.88	58.09	2.12	63.85	4.35
Dibutyl phthalate	19.75	73.16	8.29	71.32	6.70	60.01	3.55	53.75	2.64
2,2',4,4'-tetrachlorobiphenyl	19.92	58.44	6.54	49.03	3.76	54.70	2.27	45.85	3.08
Chlorpyrifos	20.03	66.24	4.02	62.19	0.94	60.79	2.59	59.19	1.62
DCPA (Dacthal)	20.18	62.00	4.27	54.02	2.63	57.65	2.99	52.38	4.00
Diphenamid	20.68	61.67	7.73	58.64	3.64	52.08	2.21	51.34	2.10
Heptachlor Epoxide	21.27	58.51	6.42	60.04	3.81	54.46	3.21	55.44	7.78
2,2',3,4,6-pentachlorobiphenyl	21.34	61.59	5.34	47.25	2.20	55.74	3.04	46.36	1.99
gama-Chlordane	21.95	60.67	6.30	51.58	3.79	56.12	2.75	48.85	3.22
Alpha-Chlordane	22.33	58.98	5.83	51.39	2.79	54.89	2.04	48.70	5.29
trans-nonachlor	22.39	60.37	4.43	53.49	2.96	55.85	1.92	50.23	4.93
Napropamide	22.51	68.43	6.30	61.59	4.31	54.23	3.83	54.56	3.08
p,p'-DDE	22.97	61.20	5.41	51.69	3.31	57.44	1.72	49.38	4.32
2,2',4,4',5,6'-hexachlorobiphenyl	23.15	59.71	5.47	50.87	1.59	55.56	1.85	49.50	2.44
Carboxin	23.28	54.23	2.83	64.99	2.64	58.39	3.94	60.17	2.58
p,p'-DDD	24.28	63.50	5.21	63.95	1.77	58.24	1.81	60.19	2.32
Endrin Aldehyde	24.62	66.54	7.03	66.25	2.78	55.91	3.67	65.25	3.92
Norflurazon	25.18	70.40	2.48	69.30	1.88	63.15	4.89	63.17	3.62
Endosulfan sulfate	25.37	72.72	8.08	63.66	4.05	55.63	3.23	60.65	4.03
Hexazinone	25.67	69.21	4.82	68.92	3.13	58.37	3.63	66.15	6.75
Heptachlorobiphenyl	27.05	60.74	5.96	53.79	2.25	56.83	1.67	53.61	1.84
Benzo[e]pyrene	32.61	67.85	5.08	68.99	1.73	57.16	2.86	62.61	1.29
Indeno[1,2,3-cd]pyrene	35.37	64.54	3.80	66.81	0.46	57.13	3.14	64.13	1.53
Dibenz[a,h]anthracene	35.44	61.40	2.48	66.64	0.88	57.97	3.30	66.39	1.43
Benzo[ghi]perylene	35.90	62.21	4.88	63.34	1.14	55.39	3.06	60.08	1.92
Average		63.03	5.69	58.93	3.69	56.12	2.58	54.73	3.22

Table 4: Compounds with high biases using SIM acquisition and accurate results in MS/MS acquisition in the matrix (spiked concentration is 50 ng/mL, n=5).

		SIM Mode in Matrix		MS/MS Mode in Matrix		SIM Mode in Solvent		MS/MS Mode in Solvent	
Peak Name	Retention Time (min)	Measured	RSD%	Measured	RSD%	Measured	RSD%	Measured	RSD%
Chlorprophan	16.26	1199.17	6.24	64.51	1.35	57.62	2.67	59.96	1.03
Triflualin	16.22	92.04	3.00	77.63	1.49	61.70	2.70	67.35	3.66
α-BHC	16.76	1014.07	6.52	44.38	7.45	47.29	4.46	38.45	3.14
β-BHC	17.35	135.83	7.35	46.74	5.94	51.73	2.33	41.03	6.05
γ-BHC	17.56	313.12	5.30	45.19	4.09	50.25	1.94	39.20	6.86
δ-BHC	18.20	ND	ND	45.11	3.88	51.45	1.75	40.80	3.96
Metribuzin	18.76	366.28	5.69	66.27	1.81	58.64	4.45	66.71	5.95
Simetryn	19.12	309.58	6.58	68.75	0.97	57.93	2.81	64.48	3.76
Triadimefon	20.30	297.47	12.78	69.67	3.47	60.83	2.36	63.90	4.31
MGK-264	21.06	75.82	6.50	54.76	4.96	55.36	3.31	51.98	4.03
Endosulfan II	24.16	104.43	17.74	51.34	6.37	55.11	1.88	46.27	9.08
Average		365.09	7.45	59.50	3.84	55.87	2.72	54.25	4.53

MS/MS acquisition: Accurate and consistent results

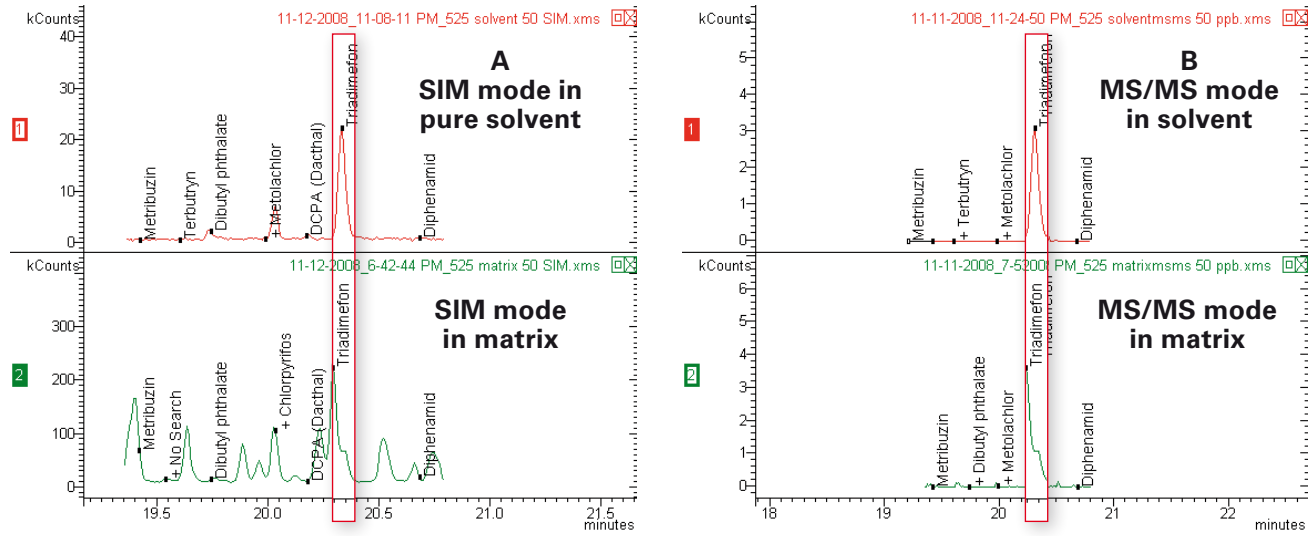

Figure 5: Chromatograms of triadimefon in both solvent and concentrated water matrix under SIM (A) and MS/MS (B) acquisitions.

Conclusion

The Bruker 300-MS triple quadrupole mass spectrometer has excellent sensitivity and linearity for the analysis of over one hundred compounds in U.S. EPA Method 525.2, including pesticides, herbicides, plasticizers, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and other industrial chemicals in both SIM and MS/MS acquisition modes. Further investigation showed that high biased results are observed for some target compounds in a representative concentrated groundwater extract using SIM. This can potentially lead to false positive results that may exceed a regulatory limit or trigger a threshold response, resulting in increased monitoring and cost to public water supplies. Consistent and accurate results for all compounds were obtained in both solvent and matrix in MS/MS acquisition mode. The MS/MS mode provided an additional filtering step to significantly reduce the matrix effects, providing greater confidence in identifying and quantifying these components at low concentrations in drinking source waters.

References

[1] Munch, J.W., EPA method 525.2: Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/ Mass Spectrometry, Revision 2, 1995; Microbiological and Chemical Exposure Assessment Research Division (MCEARD), Cincinnati, OH 45268-0001, [formerly the Environmental Monitoring Systems Laboratory (EMSL), Cincinnati, OH].

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