Sample Concentration for Volatile Organic Compounds (VOCs) Using Preparative USEPA Method 5030 and 5035 in Conjunction with Determinative Method 8260 Using Hydrogen Carries Gas with the Agilent HydroInert Source and Nitrogen Purge Gas with Teledyne Tekmar Atomx XYZ Purge and Trap

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Introduction

As helium supplies become scarcer and more expensive, laboratories have been seeking alternative carrier gases. Hydrogen is a low-cost, renewable gas suitable for several Gas Chromatograph/Mass Spectrometry (GC/MS) applications. The United States Environmental Protection Agency (US EPA) last revised its 8260D method, revision 4, in February 2017, which differs from its 8260A-C[2] methods with an updated Bromofluorobenzene (BFB) tune check acceptance criteria to help with interactions between the carrier gas and water vapor. This is a demonstration of hydrogen carrier gas for the quantitation of volatile organic compounds (VOCs) with the method requirements of US EPA Method 8260D[1] in conjunction with US EPA Method 5030[3] for the aqueous samples and US EPA Method 5035[4] for the solid waste samples. The Teledyne Labs Tekmar Atomx XYZ combined Purge and Trap (P&T) concentrator and autosampler was paired with an Agilent 7890B GC and 5977B MS and the HydroInert ion source to demonstrate the method requirements (Figure 1).

Experimental

Working 5, 50, and 250 parts per million (ppm) or milligram per liter (mg/L) calibration standards were prepared in methanol from the following commercially available standards: 8260B MegaMix, 8260B Acetate, California Oxygenates, VOA (Ketones), 502.2 Calibration Mix, 2-Chloroethyl Vinyl Ether, and Hexachloroethane. In total, the standards contained 97 compounds.

Nine-point average response factor (%RSD) calibration curves for both water and soil were prepared from 0.5 ppb to 200 parts per billion (ppb) for all compounds. The %RSD was calculated for each compound using four internal standards. Internal and surrogate standards were prepared in methanol from commercially available standards at a concentration of 25 ppm, after which 5 microliters (µL) was then mixed with each 5 milliliter (mL) sample for a resulting concentration of 25 ppb.

Seven 0.5 ppb water standards and seven 1 ppb soil standards were prepared to calculate the MDL calculations. Seven 20 ppb water and soil standards were also prepared for the accuracy and precision calculations of the mid-point calibration check.

All calibration, MDL, and mid-point calibration check standards were analyzed with the Tekmar Atomx XYZ conditions in Table I (water) and Table II (soil). GC-MS conditions are shown in Table III.

Experimental

Table I: Tekmar Atomx XYZ Water Method Conditions

Standby	Variable	Desorb	Variable
Valve Oven Temp	140°C	Methanol Needle Rinse	Off
Transfer Line Temp	140°C	Water Needle Rinse Vol	7.00 mL
Sample Mount Temp	90°C	Sweep Needle Time	0.25 min
Water Heater Temp	90°C	Desorb Preheat Temp	245°C
Sample Cup Temp	20°C	Desorb Temp	250°C
Soil Valve Temp	50°C	Desorb Time	2.00 min
Standby Flow	10 mL/min	Drain Flow	300 mL/min
Purge Ready Temp	40°C	GC Start Signal	Begin Desorb
Purge	**Variable**	**Bake**	**Variable**
Sample Equib Time	0.00 min	Methanol Glass Rinse	Off
Pre-sweep Time	0.25 min	Water Bake Rinses	1
Prime Sample Fill Vol	3.00 mL	Water Bake Rinse Vol	7.00 mL
Sample Volume	5.00 mL	Bake Rinse Sweep Time	0.25 min
Sweep Sample Time	0.25 min	Bake Rinse Sweep Flow	100 mL/min
Sweep Sample Flow	100 mL/min	Bake Rinse Drain Time	0.40 min
Sparge Vessel Heater	Off	Bake Time	2.00 min
Purge Time	11.00 min	Trap Bake Temp	270°C
Purge Flow	40 mL/min	MCS Bake Temp	180°C
Purge Temp	20°C	Bake Flow	200 mL/min
MCS Purge Temp	20°C		
Dry Purge Temp	20°C	Trap	9
Dry Purge Time	0.50 min	Chiller Tray	Off
Dry Purge Flow	100 mL/min	Purge Gas	Nitrogen

Table II: Tekmar Atomx XYZ Soil Method Conditions

Standby	Variable	Purge	Variable
Valve Oven Temp	140°C	Purge Temp	20°C
Transfer Line Temp	140°C	MCS Purge Temp	20°C
Sample Mount Temp	90°C	Dry Purge Time	2.00 min
Water Heater Temp	90°C	Dry Purge Flow	100 mL/min
Sample Cup Temp	40°C	Dry Purge Temp	20°C
Soil Valve Temp	100°C	Desorb	Variable
Standby Flow	10 mL/min	Methanol Needle Rinse	Off
Purge Ready Temp	40°C	Water Needle Rinse Vol	7.00 mL
Purge	**Variable**	Sweep Needle Time	0.25 min
Pre-purge Time	0.00 min	Desorb Preheat Temp	245°C
Pre-purge Flow	0 mL/min	Desorb Time	2.00 min
Pre-heat Mix Speed	Slow	Desorb Temp	250°C
Sample Pre-heat Time	0.00 min	Drain Flow	300 mL/min
Pre-sweep Time	0.25 min	GC Start Signal	Begin Desorb
Water Volume	10.00 mL	Bake	Variable
Sweep Water Time	0.25 min	Bake Time	2.00 min
Sweep Water Flow		Bake Flow	200 mL/min
Sparge Vessel Heater	100 mL/min	Bake Temp	270°C
Purge Mix Speed		MCS Bake Temp	180°C
Purge Time	Off	Trap	9
Purge Flow	Medium	Purge Gas	Nitrogen
	11.00 min		
	40 mL/min		

Table III: Agilent 7890B GC and 5977B MSD System Conditions

Agilent 7890B GC Conditions	
Column	DB-624 Ultra Inert, 30m x 0.25 mm, 1.4µm Film, Hydrogen carrier gas – 1.0 mL/min
Oven Profile	35 °C, hold 2 min, 15°C/min to 100°C, 30°C/min to 230°C, hold 1 min, Run Time 11.67 min
Inlet	200°C, 100:1 Split, 4.715 psi
Agilent 5977B MSD Conditions	
Temp	Transfer Line 250°C, Source 250°C, Quad 200°C
Scan	Range 35 m/z to 270 m/z, Solvent Delay 0.50 min, Normal Scanning
Gain	Gain Factor 1.00, Extractor tune

Results and Discussion

Average response factor calibration curves (%RSD) for both water and soil are shown in Table IV . For US EPA Method 8260D in conjunction with US EPA Method 5030 (water) three compounds used a quadratic regression with $r^2 \geq 0.99$. All compounds for this method passed the LLOQ recalculation of the true value, with three compounds using different calibration ranges, which are denoted at the bottom of Table IV. Moreover, all compounds passed MDL and mid-point calibration check criteria. For US EPA Method 8260D in conjunction with US EPA Method 5035 (soil) two compounds used a linear regression with $r^2 \geq 0.995$. All compounds for this method passed the LLOQ recalculation of the true value, MDL, mid-point calibration check criteria. Due to space constraints, please contact the authors for method detection limit and mid-point check data.

US EPA Method 8260D BFB tune criteria passed after the system performed an autotune (Atune). Although this data was performed with the extractor tune (Etune), future research will evaluate this analysis with the Atune. US EPA Method 8260C[2] has an extensive list of recommended minimum relative response factor criteria for initial and continuing calibration verification; while US EPA Method 8260D displays this table, it is noted that this criterion was developed using helium carrier gas and is not appropriate for hydrogen carrier gas due to reduced response of some analytes. Future research will evaluate the minimum relative response factors with the HydroInert source. Initial results show an increase in relative response factors in the HydroInert source compared to the electron impact (EI) ion source, as well as, lower %RSDs of the average response factors in the calibration curve (water).

Figure 2 displays an overlay of the calibration standards, with an inset demonstrating excellent peak shape and separation across all concentrations with minimal water interference for all target compounds.

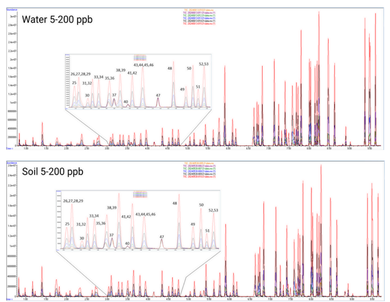

Figure 2: Overlaid TIC of calibration standards from 5-200 ppb in water and in soil

25: Ethyl tert-butyl ether 26: 2,2-Dichloropropane 27: cis-1,2-Dichloroethene 28: 2-Butanone 29: Propionitrile 30: Methyl Acrylate 31: Methacrylonitrile 32: Bromochloromethane 33: Tetrahydrofuran 34: Chloroform 35: Dibromofluoromethane (SS) 36: 1,1,1-Trichloroethane 37: Pentafluorobenzene (IS) 38: 1,1-Dichloropropene 39: Carbon Tetrachloride 40: 1,2-Dichloroethane-d4 (SS) 41: Benzene 42: 1,2-Dichloroethane 43: Isobutyl alcohol 44: Propyl Acetate 45: Ethyl Acetate 46: tert-Amyl methyl ether 47: 1,4-Difluorobenzene (IS) 48: Trichloroethylene 49: 1,2-Dichloropropane 50: Dibromomethane 51: Methyl Methacrylate 52: Isopropyl Acetate 53: Bromodichloromethane

Table IV: US EPA Method 8260D Calibration Data in Water and Soil

Compound	Water Calibration (0.5-200 ppb) RT	Ion	RRF ≤% RSD	Avg. RRF	Soil Calibration (0.5-200 ppb) RT	Ion	RRF ≤% RSD	Avg. RRF
Dichlorodifluoromethane	0.828	85	9.1	0.291	0.828	85	9.4	0.310
Chloromethane	0.929	50	10.7	0.055	0.935	50	6.7	0.060
Vinyl Chloride	0.984	62	9.6	0.128	0.984	62	8.0	0.140
Bromomethane	1.17	94	12.6	0.194	1.17	94	7.7	0.187
Chloroethane	1.23	64	8.3	0.081	1.23	64	9.0	0.077
Trichlorofluoromethane	1.40	101	7.7	0.725	1.40	101	6.2	0.616
Diethyl Ether	1.60	59	5.7	0.049	1.59	59	7.0	0.056
1,1-Dichloroethene	1.74	61	13.2	0.046	1.73	61	6.9	0.096
1,1,2-Trichlorotrifluoroethane	1.76	101	10.2	0.118	1.74	101	6.1	0.157
Acetone[13]	1.77	43	1.0	0.070	1.77	43	0.998	0.082
Iodomethane	1.83	142	15.7	0.083	1.83	142	13.1	0.189
Carbon Disulfide	2.01	76	11.7	0.035	1.88	76	14.7	0.046
Allyl Chloride	2.01	41	11.1	0.029	1.99	41	7.3	0.041
Methyl Acetate	2.05	43	6.0	0.059	2.04	43	10.2	0.028
Methylene Chloride[13]	2.11	49	1.0	0.060	2.08	49	0.998	0.117
Acetonitrile	2.26	41	8.3	0.017	2.23	59	10.4	0.073
tert-Butyl alcohol	2.26	59	6.9	0.147	2.26	41	14.9	0.009
Acrylonitrile	2.30	53	9.5	0.045	2.26	53	8.5	0.022
trans-1,2-Dichloroethene	2.34	61	9.1	0.038	2.31	61	5.3	0.084
Methyl tert-butyl ether	2.37	73	4.1	0.670	2.34	73	4.3	0.307
1,1-Dichloroethane	2.68	63	10.3	0.167	2.63	63	5.4	0.126
Vinyl Acetate	2.75	43	13.7	0.103	2.70	43	6.3	0.066
Chloroprene	2.76	53	12.7	0.086	2.72	53	7.9	0.09
Diisopropyl ether	2.80	45	5.4	0.234	2.74	45	5.5	0.128
Ethyl tert-butyl ether	3.08	59	3.2	0.271	3.04	59	4.9	0.223
2,2-Dichloropropane	3.14	77	6.7	0.195	3.10	77	8.4	0.222
cis-1,2-Dichloroethene	3.14	61	9.8	0.098	3.10	61	5.1	0.159
2-Butanone	3.17	43	9.6	0.032	3.12	43	7.9	0.018
Propionitrile	3.18	54	11.6	0.017	3.14	54	8.5	0.011
Methyl Acrylate	3.26	55	9.0	0.057	3.22	55	4.6	0.049
Methacrylonitrile	3.31	41	13.6	0.040	3.27	41	7.5	0.026
Bromochloromethane	3.32	49	11.3	0.033	3.28	49	6.4	0.113
Tetrahydrofuran	3.38	42	10.0	0.014	3.34	42	14.6	0.011
Chloroform	3.40	83	8.9	0.308	3.36	83	7.3	0.281
Dibromofluoromethane (SS)	3.52	113	4.9	0.284	3.48	113	1.1	0.241
1,1,1-Trichloroethane	3.54	97	9.9	0.285	3.50	97	8.0	0.311
Pentafluorobenzene (IS)	3.60	168			3.56	168		
1,1-Dichloropropene	3.67	75	9.9	0.054	3.64	75	4.7	0.101
Carbon Tetrachloride	3.68	117	5.4	0.241	3.65	117	6.9	0.310
1,2-Dichloroethane-d4 (SS)	3.78	65	2.3	0.196	3.74	65	1.1	0.17
Benzene	3.83	78	8.5	0.292	3.80	78	7.2	0.408
1,2-Dichloroethane	3.84	62	8.5	0.163	3.84	62	6.9	0.136
Isobutyl alcohol	3.94	43	6.8	0.234	3.93	43	5.5	0.143
Propyl Acetate	3.95	43	6.8	0.207	3.94	43	5.1	0.144
Ethyl Acetate	3.96	43	6.8	0.234	3.95	43	5.5	0.158
tert-Amyl methyl ether	3.97	73	4.8	0.420	3.95	73	3.9	0.292
1,4-Difluorobenzene (IS)	4.17	114			4.14	114		
Trichloroethylene	4.37	130			4.34	130		
1,2-Dichloropropane	4.53	63	13.3	0.354	4.51	63	6.6	0.166
Dibromomethane	4.62	93	7.8	0.075	4.60	93	5.7	0.087
Methyl Methacrylate	4.68	41	6.6	0.095	4.66	41	7.1	0.096
Isopropyl Acetate	4.75	43	4.9	0.048	4.73	43	4.6	0.072
Bromodichloromethane	4.77	83	8.4	0.105	4.75	83	9.0	0.024
			2.9	0.24			5.4	0.228

Compound	Water Calibration (0.5-200 ppb) RT	Ion	RRF ≤% RSD	Avg. RRF	Soil Calibration (0.5-200 ppb) RT	Ion	RRF ≤% RSD	Avg. RRF
2-Nitropropane	4.95	43	10.0	0.039	4.93	43	10.8	0.026
2-Chloroethyl Vinyl Ether	5.05	63	15.6	0.089	5.04	63	9.9	0.055
cis-1,3-Dichloropropene	5.15	75	6.3	0.083	5.13	75	8.3	0.035
4-Methyl-2-Pentanone	5.30	43	10.0	0.756	5.37	43	10.4	1.03
Toluene-d8 (SS)	5.38	98	1.4	0.574	5.37	98	0.8	0.77
Toluene	5.43	91	9.2	0.233	5.42	91	11.0	0.205
trans-1,3-Dichloropropene	5.63	75	6.7	0.177	5.61	75	6.3	0.134
Ethyl Methacrylate	5.76	69	6.9	0.239	5.74	69	5.0	0.117
1,1,2-Trichloroethane	5.77	97	6.2	0.974	5.76	97	7.3	0.551
Tetrachloroethylene	5.91	166	8.7	0.231	5.90	166	9.1	0.200
1,3-Dichloropropane	5.92	76	2.9	0.06	5.90	76	12.4	0.042
2-Hexanone	6.03	43	10.3	0.409	6.00	43	6.3	0.326
Dibromochloromethane	6.10	129	5.4	0.107	6.09	129	3.8	0.078
Butyl Acetate	6.18	43	6.9	0.267	6.17	43	6.1	0.164
1,2-Dibromoethane	6.18	107	5.0		6.18	107	8.2	
Chlorobenzene-d5 (IS)	6.61	117			6.60	117		
Chlorobenzene	6.63	112			6.63	112		
1,1,1,2-Tetrachloroethane	6.71	131	8.2	0.584	6.70	131	7.0	0.857
Ethylbenzene	6.74	91	4.9	0.308	6.74	91	5.5	0.385
m, p-Xylene	6.84	91	10.9	0.707	6.84	91	12.6	1.14
o-Xylene	7.13	91	11.2	0.549	7.13	91	13.2	0.864
Styrene	7.14	104	10.4	0.631	7.13	104	13.2	0.921
Bromoform	7.24	173	10.8	0.685	7.24	173	11.8	0.922
Amyl Acetate	7.32	43	4.7	0.360	7.32	43	6.6	0.388
Isopropylbenzene	7.40	105	12.1	0.087	7.40	105	7.5	0.101
cis-1,4-Dichloro-2-Butene	7.44	75	11.0	1.04	7.49	75	10.5	1.43
Bromofluorobenzene (SS)	7.49	95	5.3	0.057	7.49	95	9.4	0.059
Bromobenzene	7.58	77	4.9	0.421	7.49	95	3.2	0.449
1,1,2,2-Tetrachloroethane	7.59	83	11.2	0.241	7.49	75	8.8	0.144
1,2,3-Trichloropropane	7.61	75	14.7	0.126	7.58	77	10.0	0.598
trans-1,4-dichloro-2-butene	7.63	75	6.3	0.150	7.59	83	6.9	0.184
n-Propylbenzene	7.68	91	13.1	0.069	7.63	75	9.4	0.037
2-Chlorotoluene	7.72	91	11.8	0.990	7.68	91	11.2	1.37
4-Chlorotoluene	7.79	91	11.1	0.591	7.72	91	10.0	0.773
1,3,5-Trimethylbenzene	7.80	105	10.1	0.727	7.79	91	12.3	0.946
Pentachloroethane	8.00	117	11.0	0.942	7.80	105	14.2	1.27
tert-Butylbenzene	8.01	119	19.5	0.055	8.00	167	6.3	0.211
1,2,4-Trimethylbenzene	8.03	105	9.8	1.04	8.00	119	11.6	1.45
sec-Butylbenzene	8.14	105	12.1	1.02	8.03	105	14.6	1.32
1,3-Dichlorobenzene	8.19	146	11.5	1.22	8.14	105	13.0	1.65
1,4-Dichlorobenzene-d4 (IS)	8.23	152	12.9	0.938	8.19	146	12.8	1.13
p-Isopropyltoluene	8.24	119	12.8	1.29	8.23	152		
1,4-Dichlorobenzene	8.25	146	14.1	1.07	8.23	119	13.0	1.67
1,2-Dichlorobenzene	8.47	146	11.2	1.07	8.25	146	10.2	1.56
n-Butylbenzene	8.48	91	10.9	0.896	8.47	146	8.9	1.46
Hexachloroethane[13]	8.63	117	1.0	0.201	8.48	91	10.5	1.48
1,2-Dibromo-3-Chloropropane	8.91	157	7.9	0.156	8.63	117	8.4	0.691
Nitrobenzene	9.02	77	11.2	0.029	8.90	157	12.5	0.063
1,2,4-Trichlorobenzene	9.38	180	11.5	1.08	9.02	77	11.8	0.037
Hexachlorobutadiene	9.49	225	8.5	0.55	9.38	180	7.4	1.34
Naphthalene	9.51	128	12.2	1.97	9.49	225	9.4	0.954
1,2,3-Trichlorobenzene	9.64	180	9.0	1.06	9.50	128	17.0	2.30
					9.64	180	7.8	1.27

Conclusions

This study demonstrates the capability of the Tekmar Atomx XYZ system to process VOCs in soil waste matrices following the US EPA Method 8260D in conjunction with US EPA Method 5030 and 5035 with detection by an Agilent 7890B GC/5977B MS with the HydroInert source. Utilizing the Tekmar Atomx XYZ's ability to purge with nitrogen, along with using Hydrogen as the GC/MS carrier gas with the HydroInert source, helps to conserve resources without sacrificing system performance.

The average response factor (%RSD) calibration curves from 0.5 ppb to 200 ppb passed method requirements. Furthermore, the LLOQ recalculation for both calibration curves passed method requirements. Average MDL for all compounds was 0.15 ppb with a 7.0%RSD (water) and 0.21 ppb with a 6.2%RSD (soil). Seven 20 ppb mid-point calibration check standards averaged a 105% recovery with a 4.2%RSD (water) and 96% recovery with a 3.3%RSD (soil).

Future research will evaluate US EPA Method 8260D with the 6 mm draw out lens on the HydroInert source compared to the 9 mm that was used in this analysis, along with tune choice. The J&W DB-624 Ultra Inert 20 m, 0.18 mm, 1 µm column will be evaluated as well. Additionally, more testing will need to be completed on trapping materials and inert tubing choices, for robustness in a hydrogenous environment over the long term.

Figure 1. Teledyne Labs Tekmar Atomx XYZ combined P&T concentrator and autosampler (left), Agilent 7890B GC with 5977B MS (right)

References

[1]USEPA Method 8260D, "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)," Revision 4, February 2017.

[2]Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); US EPA, Office of Solid Waste, SW-846 Method 8260C, Revision 3, August 2006.

[3]Purge and Trap for Aqueous Samples; US EPA, Office of Solid Waste, SW-846 Method 5030B, Revision 2, December 1996.

[4]Purge and Trap for Aqueous Samples; US EPA, Office of Solid Waste, SW-846 Method 5030C, Revision 3, May 2003.

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