Comparison of the HydroInert and EI Source using US EPA Method 8260 with the Tekmar Atomx XYZ P&T and the Agilent 7890B GC and 5977B MS System with Hydrogen and Helium Carrier Gas

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Introduction

The United States Environmental Protection Agency (US EPA) last revised its 8260D method, revision 4, in February 2017, which differs from its 8260A-C methods with an updated Bromofluorobenzene (BFB) tune check acceptance criteria to help with interactions between the carrier gas and water vapor. This application is a demonstration of hydrogen carrier gas for the quantitation of volatile organic compounds (VOCs) with the method requirements of US EPA Method 8260D in conjunction with US EPA Method 5030 for the aqueous samples and US EPA Method 5035 for the solid waste samples.

The Agilent HydroInert source is a GC/MS ion source that improves chromatographic performance when using hydrogen as carrier gas. Its inertness minimizes hydrogenation and dechlorination reactions in the MS source, avoiding loss of sensitivity and spectral anomalies while offering a high-boiler peak shape. The Teledyne LABS Tekmar Atomx XYZ combined Purge and Trap (P&T) autosampler is compatible with hydrogen carrier gas and allows the use of nitrogen as purge gas, avoiding the need for a helium supply.

The Tekmar Atomx XYZ was paired with an Agilent 7890B GC and 5977B MS and the HydroInert ion source (Figure 1) to demonstrate the method requirements of 8260D: . This work also provides a comparison of the stated method requirements on the HydroInert source and the Electron Ionization (EI) source with hydrogen and helium carrier gas.

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	100 mL/min	Bake Flow	200 mL/min
Sparge Vessel Heater	Off	Bake Temp	270°C
Purge Mix Speed	Medium	MCS Bake Temp	180°C
Purge Time	11.00 min	Trap	9
Purge Flow	40 mL/min	Purge Gas	Nitrogen

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

Agilent 7890B GC Conditions		
	EI Source	HydroInert Source
Column	DB-624 Ultra Inert 20m x 0.18 mm, 1 µm Film Carrier gas (He or H2) 1.0 mL/min	DB-624 Ultra Inert 20m x 0.18 mm, 1 µm 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	220°C, 80:1 Split, 19.752 psi	200°C, 75:1 Split, 8.5032 psi
Agilent 5977A MSD Conditions		
	EI Source	HydroInert Source
Temp	Transfer Line 250°C; Source 250°C; Quad 150°C	Transfer Line 250°C; Source 230°C; Quad 150°C
Scan	Range 35 m/z to 270 m/z, Solvent Delay 0.75 min, Normal Scanning	Range 35 m/z to 270 m/z, Solvent Delay 0.50 min, Normal Scanning
Gain	Gain Factor 5.00, BFB Auto tune	Gain Factor 10.00, Auto tune

Results and Discussion

Table IV: US EPA Method 8260D Calibration Data in Water and Soil, 0.5-100 ppb

Compound	HydroInert Source		EI Source, Helium		EI Source, Hydrogen		Compound	HydroInert Source		EI Source, Helium		EI Source, Hydrogen	
	Water	Soil	Water	Soil	Water	Soil		Water	Soil	Water	Soil	Water	Soil
	RRF (≤% RSD)	RRF (≤% RSD)	RRF (≤% RSD)	RRF (≤% RSD)	RRF (≤% RSD)	RRF (≤% RSD)		RRF (≤% RSD)	RRF (≤% RSD)	RRF (≤% RSD)	RRF (≤% RSD)	RRF (≤% RSD)	RRF (≤% RSD)
Pentafluorobenzene (IS 1)							**Propyl Acetate**	4.9	7.1	6.5	10.4	10.5	5.8
Dibromofluoromethane (SS 1)	8.5	7.1	2.2	1.8	10.3	3.3	**2-Nitropropane**	5.9	19.2	11.5	9.7	15.0	0.999[2]
Dichlorodifluoromethane	7.5	12.3	16.7	16.1	8.3	9.2	**2-Chloroethyl Vinyl Ether**	11.2	12.1	5.6	16.7	8.1	8.5
Chloromethane	8.9	8.3	8.0	10.5	9.2	5.1	**cis-1,3-Dichloropropene**	7.1	9.6	2.9	9.3	16.9	6.2
Vinyl Chloride	6.2	8.9	10.1	9.4	5.4	8.1	**4-Methyl-2-Pentanone**	13.3	12.3	4.6	7.7	11.3	14.2
Bromomethane	14.0	10.4	0.998[2]	0.995[2]	0.999[2]	13.4	**Toluene**	7.9	10.5	4.0	5.3	8.1	11.8
Chloroethane	11.5	9.2	9.4	7.9	7.0	9.5	**trans-1,3-Dichloropropene**	6.8	6.2	3.7	10.0	15.6	6.8
Trichlorofluoromethane	5.1	8.9	8.5	7.3	4.5	7.6	**Ethyl Methacrylate**	8.1	9.4	4.1	13.5	12.4	13.7
Diethyl Ether	8.9	3.7	6.3	5.9	3.6	10.3	**1,1,2-Trichloroethane**	8.3	5.5	4.5	6.5	9.2	6.4
1,1-Dichloroethene	6.8	8.8	7.1	8.1	5.3	11.2	**Tetrachloroethylene**	9.0	9.5	18.0	12.3	7.1	9.8
1,1,2-Trichlorotrifluoethane	6.4	10.7	7.2	10.2	4.5	6.7	**1,3-Dichloropropane**	5.0	9.4	2.7	6.6	5.3	8.0
Acetone	0.996[1]	0.999[2]	0.999[1]	0.998[1]	0.999[1]	0.998[1]	**2-Hexanone**	16.4	7.7	5.9	16.5	10.3	12.6
Iodomethane	17.2	11.7	0.999	20.0	0.999	0.999	**Dibromochloromethane**	8.5	8.3	4.8	7.6	14.2	6.3
Carbon Disulfide	11.2	0.999[1]	15.6	12.5	12.3	19.9	**Butyl Acetate**	8.0	3.7	2.9	8.2	6.5	5.4
Allyl Chloride	11.6	9.8	7.8	10.9	12.0	14.8	**1,2-Dibromoethane**	6.4	12.2	4.2	16.1	13.7	15.5
Methyl Acetate	5.6	10.1	9.8	14.0	7.3	9.3	**Chlorobenzene-d5 (IS 3)**						
Methylene Chloride	16.1	0.999[1]	15.7	0.999[1]	7.5	0.999[1]	**Toluene-d8 (SS 3)**	1.7	1.4	1.5	1.6	1.4	2.0
tert-Butyl alcohol	9.7	7.8	10.8	15.0	5.0	13.4	**Chlorobenzene**	5.4	7.0	6.2	6.1	7.5	5.3
trans-1,2-Dichloroethene	9.2	11.1	9.5	9.0	4.3	7.0	**1,1,1,2-Tetrachloroethane**	5.8	9.7	8.0	7.6	0.999[1]	9.3
Methyl tert-butyl ether	8.4	10.9	7.0	6.9	5.1	12.1	**Ethylbenzene**	7.6	11.3	5.3	6.3	11.4	6.9
Acetonitrile	10.5	10.9	8.6	10.2	5.1	7.7	**m, p-Xylene**	9.4	14.4	7.7	6.9	15.4	11.7
1,1-Dichloroethane	8.5	9.5	7.3	7.1	4.4	10.7	**o-Xylene**	10.2	12.8	8.0	6.3	14.4	9.7
Acrylonitrile	6.1	6.4	3.7	8.9	5.2	12.5	**Styrene**	6.1	13.3	8.7	9.0	9.4	13.7
Chloroprene	6.1	9.5	3.7	8.9	5.3	5.3	**Bromoform**	6.3	8.6	5.3	8.3	0.999[1]	5.8
Vinyl Acetate	5.5	7.5	12.6	7.5	11.4	6.1	**Amyl Acetate**	8.2	10.4	11.2	13.7	6.7	14.8
Diisopropyl ether	5.5	10.7	8.5	7.4	4.4	9.3	**Isopropylbenzene**	7.0	10.8	7.3	7.3	11.9	7.3
Ethyl tert-butyl ether	8.7	12.3	7.1	10.2	5.9	12.8	**cis-1,4-Dichloro-2-Butene**	7.1	10.3	10.9	14.2	14.1	9.8
2,2-Dichloropropane	8.2	8.5	5.5	7.7	4.6	8.2	**Bromobenzene**	7.8	11.6	8.4	7.4	5.5	7.8
cis-1,2-Dichloroethene	5.9	13.0	5.1	5.7	3.5	9.5	**1,1,2,2-Tetrachloroethane**	11.7	11.7	8.5	12.4	17.6	4.2
2-Butanone	11.1	8.0	10.1	7.5	9.3	10.7	**1,2,3-Trichloropropane**	6.3	9.5	7.2	10.1	7.6	4.1
Propionitrile	10.2	13.8	11.9	5.1	15.4	14.2	**Trans-1,4-dichloro-2-butene**	7.7	10.4	8.1	12.9	4.2	9.2
Ethyl Acetate	7.8	8.9	7.6	6.0	10.2	9.3	**n-Propylbenzene**	10.3	14.1	9.6	7.0	14.1	9.2
Methyl Acrylate	8.7	6.9	8.3	8.8	12.3	11.8	**2-Chlorotoluene**	7.8	11.0	9.0	6.6	12.2	8.9
Bromochloromethane	6.3	12.0	6.7	4.6	7.0	9.7	**1,3,5-Trimethylbenzene**	6.5	11.5	7.9	9.2	14.8	11.3
Methacrylonitrile	5.7	9.0	10.2	7.2	6.9	9.4	**4-Chlorotoluene**	7.1	10.2	12.4	7.9	14.8	10.7
Chloroform	4.2	7.3	7.4	5.2	3.8	7.2	**tert-Butylbenzene**	8.1	8.8	7.9	10.3	13.0	10.4
Tetrahydrofuran	10.5	11.7	10.5	9.6	11.3	16.9	**1,2,4-Trimethylbenzene**	7.3	9.5	7.6	8.6	14.3	11.8
1,1,1-Trichloroethane	5.5	5.7	4.4	4.9	5.7	5.8	**sec-Butylbenzene**	8.9	10.9	9.2	8.1	14.2	10.3
Trichloroethylene	6.5	12.7	6.9	7.0	2.7	7.2	**1,3-Dichlorobenzene**	8.8	14.3	16.5	13.2	11.3	11.9
Isobutyl alcohol	6.4	12.2	7.4	12.0	9.0	7.7	**p-Isopropyltoluene**	8.8	8.6	8.6	7.0	16.3	11.3
Isopropyl Acetate	6.4	9.4	7.4	11.8	10.7	6.8	**1,4-Dichlorobenzene-d4 (IS 4)**						
tert-Amyl methyl ether	8.7	8.6	7.1	12.0	7.9	13.1	**Bromofluorobenzene (SS 4)**	2.5	2.8	3.8	4.6	5.3	4.8
1,2-Dichloroethane	6.2	10.3	5.8	4.1	8.6	9.1	**1,4-Dichlorobenzene**	6.1	13.5	14.8	15.2	8.7	8.0
Benzene	4.3	3.8	2.6	3.5	7.9	5.8	**1,2-Dichlorobenzene**	4.6	8.8	8.7	12.3	6.5	6.1
1,1-Dichloropropene	8.5	10.2	2.7	6.1	4.9	8.8	**n-Butylbenzene**	6.9	8.3	8.3	11.4	11.3	6.1
Carbon Tetrachloride	4.1	6.2	4.9	7.5	9.4	4.6	**Hexachloroethane**	8.4	13.2	6.1	11.9	9.2	9.2
1,4-Difluorobenzene (IS 2)	6.9	7.3	4.0	10.9	12.2	10.0	**1,2-Dibromo-3-Chloropropane**						
1,2-Dichloroethane-d4 (SS 2)	3.7	5.2	1.7	1.6	3.7	9.6	**Nitrobenzene**	8.8	0.999[2]	16.7	0.999[2]	14.6	0.999[2]
Dibromomethane	6.5	7.4	7.7	9.0	8.6	13.7	**1,2,4-Trichlorobenzene**	4.7	12.8	14.1	16.7	4.5	5.9
1,2-Dichloropropane	9.8	12.4	4.8	5.4	3.9	9.6	**Hexachlorobutadiene**	7.4	8.4	14.9	11.8	0.999[1]	7.2
Methyl Methacrylate	5.9	7.4	6.0	8.8	13.6	9.3	**Naphthalene**	7.4	10.8	4.7	15.9	9.5	6.6
Bromodichloromethane	3.6	12.7	2.7	5.0	10.9	10.4	**1,2,3-Trichlorobenzene**	4.8	10.7	8.2	14.9	5.1	5.5

[1]Compound used a linear regression calibration curve fit, [2]Compound used a quadratic regression calibration curve fit

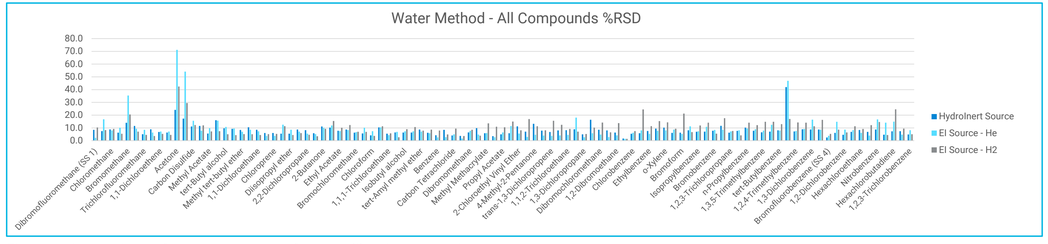

Figure 2. Comparison of average response factor calibration curves in water

Water Method Results

The method requirements for EPA 8260 are an average response factor (RF) calibration ≤20% RSD of RFs or r≥0.995, r≥0.99 for linear or quadratic regression respectively, lower standard (LLOQ) recalculation within ±50% of the true value and all other calibration levels within ±30% of true value, method detection limits (MDL), a mid-point calibration check with accuracy and precision. For US EPA Method 8260D in conjunction with US EPA Method 5030 (water) one compound, Acetone, used a linear regression calibration fit with r²≥0.995. All compounds for this method passed the LLOQ recalculation of the true value. Moreover, all compounds passed MDL and mid-point calibration check criteria. The HydroInert source utilized autotune (Atune) and passed BFB tune requirements.

Figure 2 shows a comparison of average response factor calibration curves (%RSD) for all compounds in water using the HydroInert source with hydrogen carrier gas, the EI source with helium carrier gas, and the EI source with hydrogen carrier gas.

Soil Method Results

US EPA Method 8260D in conjunction with US EPA Method 5035 (soil) with Atune analyzed by the HydroInert source is comparable or better than those analyzed by the EI source using both helium and hydrogen as the carrier gas. 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. All compounds for this method passed the LLOQ recalculation of the true value and the HydroInert source utilized Atune and passed BFB tune requirements.

Table IV shows a comparison of average response factor calibration curves (%RSD) for all compounds in water and soil. Due to space constraints, please contact the authors for further data including method detection limit and mid-point check data.

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

Conclusions

This study demonstrates the capability of the Tekmar Atomx XYZ system to process VOCs in water and solid 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.

A further study using the Teledyne LABS Tekmar Lumin Purge and Trap Concentrator with an Agilent 7890B GC and 5977A MS with the HydroInert source running the same application also demonstrated robustness and stability of the source over time when utilizing autotune.

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.

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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