
Application Note

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Abstract

Water quality laboratories across the nation are faced with both a rising level of water quality awareness amongst the general public, as well as rising costs in water quality monitoring. As a result, laboratories are looking for more efficient ways to provide higher quality monitoring.

This study compares US EPA methods 524.2 and 524.3, as well as 8260B and 8260C, all on a single system. This study focuses on considerations for sample volume and purge parameters for the US EPA 524 methods, and considerations for quality control parameters for the US EPA 8260 methods.

Introduction

Water quality laboratories across the nation are faced with both a rising level of water quality awareness amongst the general public, as well as rising costs in water quality monitoring. As a result, laboratories are looking for more efficient ways to provide higher quality monitoring. One way of increasing the efficiency of analysis is reducing or eliminating down time between analyses.

In this study we have validated four of the most popular environmental analysis methods, utilizing two separate gas chromatograph/mass spectrometer (GC/MS) and purge and trap (P&T) methods. In an attempt to minimize down time between methods, no hardware changes were made, i.e. the same column, inlet liner and analytical trap was used for all four methods. By only making changes to purge and trap method parameters, analysts can seamlessly transition from one analysis to the next.

This study also discusses the considerations for sample volume and purge parameters for the US EPA 524 methods with special attention on dealing with moisture control. Finally, consideration is also given to the differing quality control (QC) requirements for the 8260 methods and how those differences affect calibration validation.

Experimental Conditions

Instrument Conditions

In this study the Teledyne Tekmar Atomx automated sample preparation system was utilized in conjunction with an Agilent 7890B GC coupled to a 5977A Mass Spectrometer (MS). Two purge and trap (P&T) methods were employed in this study. US EPA Methods 8260B, 8260C and 524.3 all utilized the Atomx's default water P&T method. In the case of the 524.2 analysis, a second P&T method was developed to optimize moisture control within the P&T system. The P&T parameters for each method are found in Table I. Those conditions that differed in the US EPA Method 524.2 method are reported in parentheses.

Two acquisition methods were developed for the 7890B/5977A. One method was used for the analysis of the 8260 methods as well as 524.3. A second method was developed specifically to overcome the water issue that is typical with EPA Method 524.2. The parameters for each method are found in Tables II and III.



Table I Atomx Purge and Trap Parameters			
Trap	#9 Trap	Dry Purge Time	0.5 min (2.00 min)
Sample Volume	5.0 mL (25 mL)	Dry Purge Flow	100 mL/min
Sparge Vessel Temp	Ambient [40 °C]	Desorb Time	2.00min (4.00 min)
Purge Gas	Helium	Desorb Temp	250 °C
Purge Time	11.00 min	Transfer Line Temp	140 °C
Purge Flow	40 mL/min	Sample Mount Temp	90 °C (40 °C)

Note: Differences in 524.2 analysis are reported in (), differences in 8260 analysis are reported in [].

Table II GC Parameters	
GC	Agilent 7890B
Column	Agilent DB-624 20 m x 0.18 mm x 1.0 µm
Oven Program	35 °C, for 4 min, 15 °C/min to 85 °C, 25 °C/min to 225 °C, hold for 2 min, run time 15 min
Split Ratio	100:1 (150:1)
Column Flow	0.80 mL/min
Gas	Helium
Split Flow	80.0 mL/min (120 mL/min)
Septum Purge Flow	0.5 mL/min

Table III MS Parameters	
MSD	Agilent 5977A
Source Temp	230 °C
Transfer Line Temp	225 °C
Quad Temp	150 °C
Scan Range	35-270 m/z
Scan Time	0.5 sec
Solvent Delay	none

Note: Differences in 524.2 analysis are reported in ().

Calibration

Seven point calibration curves were prepared in deionized (DI) water for method 524.2 and methods 8260B/C. The 524.2 calibration ranged from 0.5 to 50 ppb, while the 8260 calibration ranged from 0.5 to 200 ppb. An eight point calibration was prepared in Method 524.3 preserved DI water, ranging from 0.2 to 50 ppb. A mixed internal standard and surrogate standard solution was prepared in methanol and injected to a concentration of 12.5 ppb for the 524 methods and 25 ppb for the 8260 methods via the Atomx standard addition system. The preparation of standards was done according to the procedure detailed in the US EPA Methods 524.2¹, 524.3², and 8260C⁴. The US EPA methods 8260B and 8260C share a sample list and analysis conditions, so one calibration was prepared and analyzed for both. Each method's QC requirements were then applied to the data collected, and are reported on in the discussion section of this work.

Agilent Technologies' Chemstation software was used for target compound calibration. All calibrations for all methods are reported in average response factor (Avg RF), unless otherwise noted. Those that did not meet the minimum requirements for Avg RF utilized a 1/x weighted quadratic calibration. The relative

standard deviation (%RSD) and Avg RF is reported for each target compound and surrogate standard in Tables IV to VI.

Initial Demonstration of Capability

Method detection limits (MDL) were determined for all four methods. Seven replicates spiked to a concentration of 0.5 ppb were used to determine the MDL of each target compound. One exception was the handling of the para and meta isomers of xylene, which were combined, and therefore analyzed at a concentration of 1 ppb. Additionally, accuracy and precision calculations were performed as described in methods 524.2 and 524.3. The results for these calculations are found in Tables IV to VI.

EPA method 8260B requires specific criteria to be met regarding the RFs of two groups of compounds, the System Performance Check Compounds (SPCC) and Calibration Check Compounds (CCC), which are found in Tables VII and VIII.

Table IV Method 524.2					
Compound	Calibration	Method Det. Limit		Accuracy and precision	
	%RSD	ppb	%RSD	Avg Conc	% Recovery
Dichlorodifluoromethane	4.0	0.10	6.1	0.55	109
Chloromethane	7.4	0.10	5.7	0.54	109
Vinyl chloride	6.6	0.13	8.1	0.50	101
Bromomethane	5.5	0.13	6.6	0.61	121
Chloroethane	3.0	0.13	8.4	0.51	101
Trichlorofluoromethane	8.4	0.21	13.6	0.49	99
Diethyl ether	4.5	0.24	14.3	0.53	107
1,1-dichloroethene	3.3	0.24	14.2	0.53	106
Acetone	12.1	0.21	14.6	0.46	91
Carbon disulfide	5.9	0.18	10.8	0.52	105
Iodomethane	0.999	0.23	6.2	1.19	238
Allyl chloride	5.6	0.13	8.1	0.53	105
Methylene chloride	10.3	0.11	6.9	0.50	101
trans-1,2-dichloroethene	3.9	0.17	10.1	0.55	109
D3-MTBE (Surr)	4.3				
MTBE	7.2	0.14	8.8	0.51	101
t-butyl alcohol	3.3	0.16	9.9	0.51	103
1,1-dichloroethane	2.5	0.21	12.8	0.52	103
t-butyl ethyl ether	6.9	0.14	9.5	0.47	94
2,2-dichloropropane	6.0	0.15	10.0	0.47	95
cis-1,2-dichloroethene	3.4	0.06	3.9	0.50	101
2-butanone	8.8	0.34	18.4	0.58	117
Propionitrile	13.0				Insufficient Data
Methyl acrylate	5.1	0.23	12.8	0.58	115
Bromochloromethane	12.9	0.19	12.2	0.50	101

Methacrylonitrile	17.7	0.41	24.9	0.53	106
Chloroform	8.1	0.14	10.0	0.46	91
Carbon tetrachloride	9.0	0.21	16.4	0.42	83
Tetrahydrofuran (1-50)	6.1	0.11	6.7	0.50	101
1,1,1-trichloroethane	3.0	0.11	6.9	0.50	100
1,1-dichloropropane	2.6	0.17	9.9	0.55	110
1-chlorobutane	2.7	0.10	6.7	0.50	99
Benzene	3.2	0.07	4.7	0.49	97
t-amyl methyl ether	3.5	0.14	9.5	0.48	96
1,2-dichloroethane	3.0	0.20	12.4	0.51	102
Trichloroethene	2.6	0.12	7.1	0.53	105
t-amyl ethyl ether	6.9	0.14	9.5	0.47	94
Dibromomethane	5.4	0.21	12.8	0.53	106
1,2-dichloropropane	3.9	0.08	5.0	0.52	104
Methylmethacrylate	5.7	0.31	17.3	0.58	116
Bromodichloromethane	6.3	0.13	9.3	0.46	92
cis-1,3-dichloropropene	9.5	0.09	6.1	0.46	92
4-methyl-2-pentanone	13.1	0.20	14.0	0.46	92
Toluene	5.2	0.14	9.1	0.48	96
Tetrachloroethene	4.1	0.11	6.6	0.52	105
trans-1,3-dichloropropene	13.8	0.16	10.6	0.47	93
Ethyl methacrylate	13.9	0.13	8.6	0.49	99
1,1,2-trichloroethane	2.8	0.10	6.2	0.53	106
Dibromochloromethane	8.6	0.65	35.2	0.59	119
1,3-dichloropropane	4.2	0.13	8.3	0.51	101
2-hexanone	10.7	0.30	19.9	0.48	95
1,2-dibromoethane	4.1	0.11	7.0	0.50	101
Chlorobenzene	4.0	0.11	7.3	0.48	96
Ethylbenzene	6.4	0.12	8.1	0.47	93
1,1,1,2-tetrachloroethane	6.6	0.10	6.3	0.48	97
m,p-xylene	8.3	0.11	7.7	0.46	92
o-xylene	7.5	0.12	8.3	0.47	94
Styrene	8.1	0.11	7.8	0.47	93
Bromoform	9.7	0.11	7.8	0.46	91
Isopropylbenzene	6.5	0.14	9.4	0.46	93
4-bromofluorobenzene (Surr)	3.5				
Bromobenzene	3.1	0.14	8.8	0.50	101
trans-1,4-dichloro-2-butene	16.3	0.67	35.1	0.61	121
n-propylbenzene	2.5	0.13	8.5	0.48	96
1,1,2,2-tetrachloroethane	3.4	0.18	10.3	0.54	109
2-chlorotoluene	4.1	0.16	9.9	0.51	102

1,3,5-trimethylbenzene	4.9	0.12	7.9	0.48	95
1,2,3-trichloropropane	9.7	0.23	12.6	0.59	119
4-chlorotoluene	3.9	0.09	5.6	0.49	98
t-butylbenzene	2.6	0.13	8.7	0.49	99
Pentachloroethane	10.9	0.17	11.3	0.48	96
1,2,4-trimethylbenzene	4.8	0.12	7.9	0.47	94
sec-butylbenzene	3.1	0.14	9.3	0.49	98
4-isopropyltoluene	3.3	0.12	8.1	0.48	95
1,3-dichlorobenzene	2.8	0.11	7.3	0.50	100
1,4-dichlorobenzene	4.6	0.12	7.5	0.51	103
n-butylbenzene	4.4	0.18	12.3	0.47	94
Hexachloroethane	4.3	0.21	11.6	0.57	113
1,2-dichlorobenzene-d4 (Surr)	2.7				
1,2-dichlorobenzene	4.4	0.08	5.4	0.50	99
1,2-dibromo-3-chloropropane	4.5	0.25	14.6	0.54	107
Hexachlorobutadiene	2.2	0.11	6.6	0.52	104
1,2,4-trichlorobenzene	2.3	0.12	7.5	0.49	98
Napthalene	7.1	0.10	6.7	0.49	98
1,2,3-trichlorobenzene	5.8	0.17	10.6	0.51	103

Table V 524.3						
Compound	Calibration	MDL			Midpoint	
	%RSD	LPIR	UPPIR	ppb	%RSD	% Recovery
Dichlorodifluoromethane	7.3	83	120	0.07	3.1	94
Chlorodifluoromethane	5.7	85	135	0.10	3.4	100
Chloromethane	7.2	89	113	0.05	2.9	93
Vinyl chloride	11.8	66	139	0.15	3.4	95
1,3-butadiene	9.9	70	129	0.12	3.3	96
Bromomethane	7.2	84	144	0.12	1.7	91
Trichlorofluoromethane	3.9	57	141	0.17	2.1	98
Diethyl ether	4.8	75	149	0.15	2.2	96
1,1-dichloroethene	7.0	78	127	0.10	2.8	94
Carbon disulfide	3.4	91	122	0.06	0.6	99
Iodomethane	7.6	61	136	0.15	3.3	105
Allyl chloride	10.1	59	145	0.17	1.7	93
Methyl acetate	9.1	73	124	0.10	3.0	95
Methylene chloride	11.5	69	130	0.12	1.7	94
trans-1,2-dichloroethene	8.8	92	122	0.06	3.6	96
D3-MTBE (Surr)	2.1					

MTBE	7.7	69	137	0.13	1.8	98
t-butyl alcohol	2.8	64	138	0.15	2.0	100
Diisopropyl ether	3.8	68	130	0.12	1.9	101
1,1-dichloroethane	3.7	81	119	0.08	3.7	96
t-butyl ethyl ether	4.2	89	105	0.03	2.6	102
cis-1,2-dichloroethene	8.2	103	116	0.03	2.1	97
Bromochloromethane	3.4	93	131	0.08	2.5	99
Chloroform	9.4	84	111	0.05	2.1	96
Carbon tetrachloride	9.6	69	140	0.14	2.3	107
Tetrahydrofuran	15.3	70	142	0.14	4.7	94
1,1,1-trichloroethane	3.1	81	131	0.10	1.9	100
1,1-dichloropropane	13.6	76	127	0.10	3.3	95
1-chlorobutane	6.7	83	116	0.06	2.2	97
Benzene	2.5	78	128	0.10	1.9	102
t-amyl methyl ether	4.6	74	127	0.10	2.1	103
1,2-dichloroethane	5.6	63	138	0.15	1.2	100
Trichloroethene	9.0	81	124	0.09	2.7	98
t-amyl ethyl ether	4.2	89	105	0.03	2.6	102
Dibromomethane	6.1	85	111	0.05	1.5	96
1,2-dichloropropane	5.3	83	123	0.08	1.8	99
Bromodichloromethane	6.3	79	135	0.11	1.2	102
cis-1,3-dichloropropene	7.8	81	120	0.08	1.3	104
Toluene	8.2	78	122	0.09	1.9	103
Tetrachloroethene	5.6	72	143	0.14	1.8	99
trans-1,3-dichloropropene	9.1	83	124	0.08	2.4	106
Ethyl methacrylate	14.3	63	136	0.14	2.3	109
1,1,2-trichloroethane	7.5	89	123	0.07	2.5	97
Dibromochloromethane	6.6	68	122	0.11	2.5	103
1,3-dichloropropane	6.5	65	140	0.15	1.8	102
1,2-dibromoethane	5.0	77	132	0.11	2.7	101
Chlorobenzene	6.4	67	132	0.13	1.7	101
Ethylbenzene	9.0	80	114	0.07	1.9	105
1,1,1,2-tetrachloroethane	8.3	65	143	0.16	2.3	103
m,p-xylene	9.0	68	119	0.10	2.2	108
O-xylene	8.9	74	128	0.11	3.0	108
Styrene	9.8	70	112	0.08	1.3	110
Bromoform	9.9	49	129	0.16	1.9	108
Isopropylbenzene	8.3	71	114	0.09	2.1	108
4-bromofluorobenzene (Surr)	1.5					
Bromobenzene	3.1	83	137	0.11	2.3	103
n-propylbenzene	6.3	85	114	0.06	1.3	107

1,1,2,2-tetrachloroethane	6.0	61	145	0.16	2.5	103
2-chlorotoluene	4.1	75	137	0.12	1.0	101
1,3,5-trimethylbenzene	8.0	65	125	0.12	1.5	109
1,2,3-trichloropropane	9.7	72	139	0.13	3.1	92
4-chlorotoluene	3.9	87	113	0.05	1.4	106
t-butylbenzene	5.1	89	127	0.08	2.9	104
Pentachloroethane	13.0	71	134	0.12	2.5	109
1,2,4-trimethylbenzene	9.3	78	111	0.06	1.0	110
sec-butylbenzene	8.6	84	104	0.04	1.5	109
4-isopropyltoluene	8.4	76	113	0.07	1.5	108
1,3-dichlorobenzene	5.3	77	135	0.11	1.6	101
1,4-dichlorobenzene	5.8	79	131	0.10	1.7	103
n-butylbenzene	9.3	90	129	0.08	2.0	104
Hexachloroethane	5.2	38	152	0.23	2.7	96
1,2-dichlorobenzene-d4 (Surr)	2.6					
1,2-dichlorobenzene	2.2	79	136	0.11	2.0	101
1,2-dibromo-3-chloropropane	8.9	60	133	0.15	3.9	96
Hexachlorobutadiene	5.9	57	144	0.17	2.3	101
1,2,4-trichlorobenzene	8.0	74	142	0.13	1.9	103
Napthalene	7.1	81	114	0.06	2.3	107
1,2,3-trichlorobenzene	6.9	66	131	0.13	2.5	108

Table VI Method 8260 b/c				
Compounds	Calibration		MDL	
	%RSD	Avg RF	(ppb)	%RSD
Dichlorodifluoromethane	10.7	0.29	0.33	16.9
Chloromethane	5.9	0.27	0.25	11.6
Vinyl chloride	9.4	0.29	0.23	11.6
Bromomethane	10.3	0.19	0.43	14.6
Chloroethane	8.2	0.17	0.30	14.5
Trichlorofluoromethane	8.7	0.47	0.22	11.5
Diethyl ether	5.6	0.17	0.13	6.9
1,1-dichloroethene	7.5	0.23	0.40	19.5
Carbon disulfide	11.7	0.63	0.19	7.9
Iodomethane	6.6	0.46	0.11	8.7
Acetone	6.2	0.11	0.19	11.7
Allyl chloride	10.5	0.14	0.40	20.5
Acetonitrile	7.0	0.29	0.32	15.5
Methylene chloride	6.6	0.26	0.29	14.6

MTBE	9.6	0.73	0.14	8.8
trans-1,2-dichloroethene	5.3	0.25	0.44	23.0
Acrylonitrile	12.6	0.14	0.27	16.4
1,1-dichloroethane	5.9	0.38	0.31	17.6
Chloroprene	7.9	0.27	0.16	9.1
Vinyl acetate	13.2	0.46	0.27	15.2
Ethyl-tert-butyl ether	9.5	0.60	0.12	6.5
2,2-dichloropropane	10.2	0.29	0.24	12.8
cis-1,2-dichloroethene	9.6	0.27	0.23	13.0
2-butanone	15.3	0.21	0.23	16.3
Methyl acrylate	14.5	0.34	0.31	19.1
Propionitrile	13.5	0.07	0.1	6.8
Bromochloromethane	7.9	0.20	0.23	11.7
Chloroform	6.8	0.42	0.15	7.3
Methacrylonitrile	13.8	0.19	0.30	18.6
1,1,1-trichloroethane	5.8	0.37	0.22	12.4
Dibromofluoromethane (Surr)	5.9	0.59		
Carbon tetrachloride	7.9	0.34	0.14	7.7
1,1-dichloropropane	8.2	0.28	0.24	11.6
Benzene	4.1	0.88	0.25	13.3
1,2-dichloroethane	5.3	0.31	0.24	12.7
t-amyl methyl ether	13.5	0.63	0.22	12.2
Trichloroethene	6.5	0.19	0.19	10.7
1,2-dichloropropane	10.0	0.14	0.15	9.3
Dibromomethane	10.3	0.12	0.16	9.1
Methyl methacrylate	11.1	0.15	0.17	11.4
n-propyl acetate	12.2	0.29	0.16	10.7
Bromodichloromethane	4.3	0.21	0.14	8.4
cis-1,3-dichloropropene	13.6	0.22	0.15	10.1
Toluene-D8 (Surr)	5.1	1.20		
4-methyl-2-pentanone	10.6	0.24	0.14	9.5
Toluene	6.4	0.61	0.04	2.5
trans-1,3-dichloropropene	12.7	0.21	0.15	10.5
Ethyl methacrylate	15.1	0.22	0.11	7.9
Tetrachloroethene	9.0	0.22	0.16	8.7
1,1,2-trichloroethane	5.8	0.14	0.14	8.4
1,3-dichloropropane	6.5	0.26	0.07	4.3
2-hexanone	14.2	0.18	0.19	12.9
Dibromochloromethane	5.6	0.20	0.15	10.0
Butyl acetate	12.3	0.28	0.09	7.0
1,2-dibromoethane	4.4	0.19	0.12	7.6

Chlorobenzene	2.5	0.46	0.06	3.8
1,1,1,2-tetrachloroethane	4.3	0.17	0.05	3.5
Ethylbenzene	4.0	0.66	0.07	4.8
m,p-xylene	5.5	0.54	0.07	4.8
O-xylene	6.6	0.52	0.08	5.7
Styrene	7.6	0.45	0.11	7.8
Bromoform	7.3	0.18	0.12	7.6
Isopropylbenzene	8.0	0.68	0.08	5.7
cis-1,4-dichloro-2-butene	15.9	0.09	0.15	11.7
4-bromofluorobenzene (Surr)	2.5	0.46		
Bromobenzene	4.8	0.22	0.08	5.1
n-propylbenzene	4.9	0.79	0.07	4.6
1,1,2,2-tetrachloroethane	4.5	0.46	0.09	5.5
1,2,3-trichloropropane	10.0	0.06	0.47	19.6
trans-1,4-dichloro-2-butene	3.2	0.13	0.27	13.6
2-chlorotoluene	1.6	0.75	0.11	7.0
1,3,5-trimethylbenzene	6.8	0.90	0.08	5.5
4-chlorotoluene	1.9	0.89	0.09	5.9
t-butylbenzene	7.1	1.00	0.10	6.9
1,2,4-trimethylbenzene	5.7	0.95	0.09	6.5
sec-butylbenzene	5.8	1.17	0.11	7.1
1,3-dichlorobenzene	4.3	0.67	0.12	7.1
p-isopropyltoluene	8.7	1.02	0.13	8.6
1,4-dichlorobenzene	8.0	0.70	0.10	6.0
n-butylbenzene	6.3	0.92	0.08	5.2
1,2-dichlorobenzene	3.2	0.68	0.06	3.9
1,2-dibromo-3-chloropropane	7.9	0.12	0.36	20.5
Nitrobenzene	16.6	0.03	0.36	20.5
1,2,4-trichlorobenzene	4.7	0.54	0.11	6.8
Hexachlorobutadiene	7.0	0.27	0.15	8.4
Napthalene	12.0	1.46	0.03	2.0
1,2,3-trichlorobenzene	4.7	0.54	0.11	6.8
Dichlorodifluoromethane	10.7	0.29	0.33	16.9

Note: Green and red flagged average RF reflect minimum RF for those compounds as recommended in 8260C

Table VII Method 8260B SPCC RF Requirement Data		
SPCC	Avg RF	Minimum RF
Chloromethane	0.27	0.10
1,1-dichloroethane	0.23	0.10
Chlorobenzene	0.46	0.30
Bromoform	0.18	0.10
1,1,2,2-tetrachloroethane	0.46	0.30

Table VIII Method 8260B CCC Requirement Data	
CCC	%RSD
Vinyl chloride	9.4
1,1-dichloroethene	7.5
Chloroform	6.8
1,2-dichloropropane	10.0
Toluene	6.4
Ethylbenzene	4.0

Discussion

Method 524 Sample Volume and Purge Parameters

EPA Methods 524.2 and 524.3 differ most significantly in two areas: sample volume and desorb time. Whereas 524.2 recommends a 25 mL sample volume and requires a 4 minute desorb time, 524.3 recommends a 5 mL sample volume and allows a variable desorb time, with a 2 minute recommendation². The primary issue that analysts face with 524.2 is water management. Water vapor can cause several analytical issues, including retention time shifting, reduced sensitivity in low concentration samples, poor peak shape and vacuum issues within the MS. The combination of a 25 mL sample and 4 minute desorb results in significantly more water to the MS than with a smaller sample and shorter desorb.

The issue of increased water vapor seen in 524.2 is typically overcome by increasing dry purge time and GC inlet split ratio. However, by increasing these two parameters, some sensitivity can be lost at lower concentrations and, in the case of dry purge, the loss of more highly volatile compounds from the analytical trap. By the careful selection of these parameters and others, including sample mount temperature, we were able to manage water sufficiently enough to achieve results comparable to those seen in the 524.3 section of this study. As Table IV shows, most compounds show single digit RSDs with only one compound (Iodomethane) requiring a quadratic calibration.

As a demonstration of the flexibility of the Atomx, all method parameters for 524.3 were also met in this study, as Table V shows. As in the 524.2 results, all compounds were calibrated using average response factors, with fewer than 10% of compounds having double digit RSD values. A larger dynamic range of calibration, including higher sensitivity at the low end, was possible thanks to the broader range of purge parameters allowed in 524.3. By optimizing these parameters, not only was more sensitivity achieved, but also lower MDLs (Tables IV and V).

Method 8260 Quality Control Parameters

The primary difference between methods 8260B and 8260C lies in calibration acceptance criteria. Method 8260B requires the RSD of the response factors to be 15% or less in order to calibrate via RF. If the 15% is not met, then the method does allow calibration by other means, such as quadratic or linear regression³. Method 8260C on the other hand, increases the range of RSD to 20%, but also limits the number of compounds failing the RSD requirement to fewer than 10%⁴.

In this study, both calibration criteria were easily met. All 90 compounds included in this study met the 20% requirement under 8260C and 86 compounds met the 15% requirement under 8260B. Additionally, the MDL data shows excellent low end sensitivity despite the dynamic range of the calibration (0.5 to 200 ppb).

The second change this study addresses is the removal of system performance check compound and calibration check compound requirements. In 8260B, the average RF of the SPCCs must meet or exceed a minimum value (listed in Table VII), and the CCCs must have RSDs of 30% or better (Table VIII). In 8260C, SPCC and CCC requirements are dropped in favor of minimum RF values for 49 of the most popular method compounds (Table VI, highlighted values). In this case, the minimum RF values for the 49 most popular compounds may be seen as a tighter restriction than the requirements set forth for the SPCC and CCC compounds under 8260C. However, the method does concede that minimum RF values are dependent on numerous analytical factors, and therefore are only offered as recommendations. It is suggested, however, that if a system struggles to meet these minimums, it may suggest performance issues.

Here we have demonstrated excellent results for the SPCC and CCC requirements under 8260B. All compounds for both criteria were met with no failures, with all SPCC compounds reporting response factors above the minimum required, and all CCC compounds having relative standard deviations below 10% (Tables VII and VIII).

Of the 44 compounds reported here with recommended minimum RF values for 8260C, only two failed to meet the minimum, a failure rate of less than 5%. These failures are due, in part, to poor compound recovery. While the compounds in question seem to show robust calibrations, and represent a minor subset of the total list, there appears to be room for method optimization. However, an attempt to improve upon these compounds in particular would likely come at the expense of other compounds. For this reason, the method states that emphasis should be placed on those compounds of immediate interest to the analyst, with less attention given to those that are unlikely to be seen in unknown samples⁴.

Conclusion

In this study we demonstrated the effectiveness of the Agilent 7890B/5977A GC/MS in performing multiple EPA methods using one analytical method (8260B/C and 524.3). We were also successful in overcoming the sensitivity issues typically seen with EPA Method 524.2 by carefully selecting the appropriate P&T and GC parameters. Excellent sensitivity was obtained for the target analytes listed for each method, with only two compounds falling outside of recommended RF values for calibration.

Furthermore, we demonstrated the ability to meet the QC requirements for both EPA Method 8260B and 8260C, thus demonstrating the sensitivity of the 7890B/5977A across both a dynamic range of compounds as well as concentrations.

References

1. US EPA Method 524.2 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Revision 4.1, 1995.
2. US EPA Method 524.3 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Revision 1.0, June, 2009.
3. US EPA Method 8260B Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) Revision 2, December 1996.
4. US EPA Method 8260C Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) Revision 3, August 2006.