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Application News

No. GCMS-1502

Gas Chromatograph Mass Spectrometer

Shimadzu Guide to US EPA Methods 524.3 and 524.4 for Analysis of Volatile Organic Compounds in Drinking Water

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■ Abstract

Due to advances in analytical instrumentation the United States Environmental Protection Agency (US EPA) introduced a new drinking water method in June 2009. US EPA Method 524.3[1] allows laboratories to modify purge and trap and GCMS conditions in order to accommodate instrumental advances and shorten sample preparation time. The US EPA also investigated the option of using nitrogen as the purge gas in an additional drinking water method, US EPA Method 524.4[2]. This application note will compare analytical results when using helium and nitrogen purge gases.

■ Introduction

US EPA Method 524.3 allowed the ability to modify purge and trap parameters and take advantage of purge and trap improvements. However, the method still required helium for the purge gas. Since then, high-purity helium availability and price has changed making it harder to find and more expensive to buy. Due to this change in the helium market, the US EPA drafted Method 524.4, which allows the use of high-purity nitrogen for the purge gas.

Method 524.4 provides the same flexibility as Method 524.3, thus method parameters can be modified in order to optimize purge and trap cycle times. Although the new method allows for a shorter desorb time, moisture build up can still be a problem as the new preservation scheme causes effervescing in the sparge vessel. EST Analytical has two features that can aid in moisture control and the "foaming" caused by the effervescing. First, the Encon Evolution utilizes an 8-port valve instead of a 6-port valve. This unique engineering feature has the advantage of excluding the Moisture Reduction Trap (MoRT) from the desorb pathway during the desorb step, thus aiding in moisture control for the system. Secondly, EST Analytical has a foam sensor to detect any foaming. The foam sensor for the Encon Evolution has a unique placement above the bulb of the sparge vessel, thus allowing the bulb to control the effervescing bubbles and not sending a false positive signal to the software causing the sample sequence to be aborted. Furthermore, the Centurion WS (Water Soil) autosampler has the ability to remove samples from the vials without moving the vials. This eliminates opportunities for vial-movement errors that would negatively impact productivity.

For this study, helium and nitrogen purge gases were compared utilizing the same purge flow rate. Results from the linearity, precision, accuracy and overall compound response are compared for the two different purge gases.

■ Experimental

Instrumentation

The EST Analytical Encon Evolution purge and trap concentrator and Centurion WS autosampler were interfaced to a Shimadzu GCMS-QP2010 SE (Figure 1). The purge and trap concentrator was configured with a Vocarb 3000 (K) analytical trap. As required by the methods, a chiller unit capable of keeping the sample vials cooled below 10 °C was installed on the Centurion WS autosampler. The experimental parameters are listed in Tables 1 and 2.

Figure 1: Shimadzu GCMS-QP2010 SE

EST Analytical Encon Evolution purge and trap concentrator and Centurion WS autosampler

Table 1: Purge and Trap Parameters

Purge and Trap Concentrator	**EST Encon Evolution**
Trap Type	Vocarb 3000 (K Trap)
Valve Oven Temperature	150 °C
Transfer Line Temperature	150 °C
Trap Temperature	35 °C
Moisture Reduction Trap (MoRT) Temperature	39 °C
Purge Time	11 minutes
Purge Flow Rate	40 mL/minute
Dry Purge Temperature	Ambient
Dry Purge Flow Rate	50 mL/minute
Dry Purge Time	1 minute
Desorb Pressure Control	On
Desorb Pressure Control	5 psi
Desorb Preheat Delay	5 seconds
Desorb Time	1 minute
Desorb Temperature	260 °C
Moisture Reduction Trap (MoRT) Bake Temperature	230 °C
Bake Temperature	265 °C
Sparge Vessel Bake Temperature	120 °C
Bake Time	8 minutes
Bake Flow	40 mL/minute
Purge and Trap Autosampler	**EST Centurion WS**
Sample Size	5 mL
Internal Standard Volume	5 µL
Surrogate Volume	5 µL

Table 2: GC/MS Parameters

GC/MS	**GCMS-QP2010 SE**
Injection Mode	Split
Injection Temperature	200 °C
Flow Control mode	Constant Linear Velocity
Linear Velocity	34.3 cm/second
Column Flow Rate	0.9 mL/minute
Split Ratio	30:1
Purge Flow	1.0 mL/minute
Column	Rxi-624Sil MS 30 m x 0.25 mm I.D. 1.4 µm film thickness
Oven Temperature Program	45 °C, hold for 4.5 minutes 12 °C/minute to 100 °C, hold for 0.0 minute 25 °C/minute to 240 °C, hold for 1.32 minutes
Ion Source Temperature	185 °C
Interface Temperature	225 °C
Solvent Cut Time	0.0 minute
Scan Range	35-300 m/z
Event Time	0.30 second

Study Design

The GC column and standards were acquired from Restek. The linear range for both purge gases was established with a seven-point quadratic regression calibration from 0.5 ppb to 40 ppb. The internal standard and surrogate concentrations were held constant at 5 ppb. Figure 2 displays an overlay of the Total Ion Chromatograms (TIC) of the 20 ppb standard purged in helium (blue) and nitrogen (orange). Using the analytical conditions described in Tables 1 and 2, purge efficiency was nearly identical for the two gases, with helium providing slightly better purge efficiency for a few select compounds.

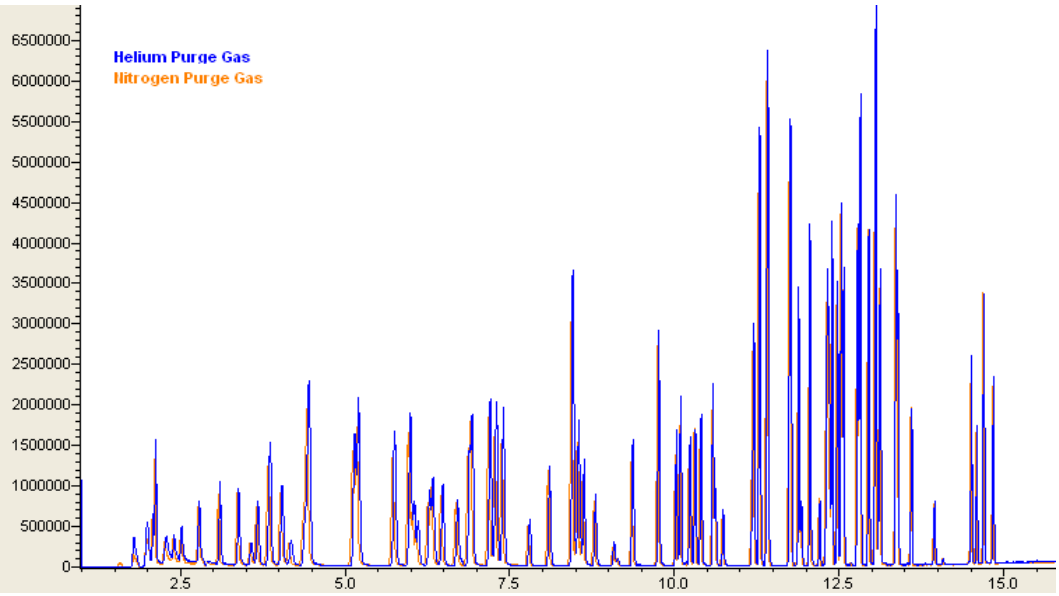

Figure 2: Overlay of 20ppb Standards Purged in Helium and Nitrogen

■ Results and Discussion

Calibration

The quadratic regression and average compound response of the respective purge gases are listed in Table 3.

Precision and Accuracy

Seven 0.5 ppb standards and seven 20 ppb calibration standards were analyzed in order to establish the precision and accuracy of the methods at both the low and the mid-range of the curves. These results are listed in Tables 4 and 5.

Minimum Reporting Level (MRL)

The Minimum Reporting Level (MRL) confirmation was conducted using the procedure outlined in section 9.2.4 of the method, and seven aliquots of the 0.5 ppb calibration standard. The Upper and Lower limits for the Prediction Interval of Results (PIR) are calculated and shown in Table 6.

Table 3: Quadratic Regression and Average Response Factors for 7-Point Calibration

Compound	Helium		Nitrogen		Compound	Helium		Nitrogen	
	Quadratic Regression	Avg RF	Quadratic Regression	Avg RF		Quadratic Regression	Avg RF	Quadratic Regression	Avg RF
dichlorodifluoromethane	1.000	0.202	0.995	0.179	tetrachloroethene	0.999	0.244	0.999	0.246
chlorodifluoromethane	1.000	0.053	0.999	0.057	trans-1,3-dichloropropene	1.000	0.433	0.999	0.365
chloromethane	1.000	0.537	0.999	0.534	ethyl methacrylate	1.000	0.460	0.999	0.391
vinyl chloride	1.000	0.406	0.999	0.411	1,1,2-trichloroethane	1.000	0.222	0.999	0.202
1,3-butadiene	1.000	0.442	0.999	0.420	dibromochloromethane	1.000	0.237	0.999	0.231
bromomethane	1.000	0.178	0.999	0.176	1,3-dichloropropane	1.000	0.501	0.999	0.444
chloroethane	1.000	0.265	0.999	0.265	1,2-dibromomethane	1.000	0.260	0.999	0.240
trichlorofluoromethane	1.000	0.403	0.998	0.446	chlorobenzene	1.000	0.803	0.999	0.749
diethyl ether	1.000	0.275	1.000	0.271	ethylbenzene	1.000	1.359	0.999	1.301
1,1-dichloroethene	1.000	0.220	1.000	0.250	1,1,1,2-tetrachloroethane	1.000	0.258	0.999	0.244
carbon disulfide	1.000	0.810	0.999	0.845	xylene (m+p)	1.000	1.138	0.999	1.101
methyl iodide	1.000	0.213	0.999	0.199	xylene (o)	1.000	1.138	0.999	1.097
allyl chloride	1.000	0.423	0.999	0.422	styrene	1.000	0.942	0.999	0.852
methylene chloride	1.000	0.489	0.999	0.469	bromoform	1.000	0.161	0.999	0.167
trans-1,2-dichloroethene	1.000	0.395	1.000	0.416	isopropylbenzene	1.000	1.342	0.999	1.259
methyl acetate	1.000	0.382	0.999	0.402	bromobenzene	0.999	1.252	1.000	1.045
methyl-t-butyl ether (MtBE)	1.000	0.903	1.000	0.416	n-propylbenzene	0.999	2.638	1.000	2.428
t-butyl alcohol (TBA)	1.000	0.047	0.999	0.057	1,1,2,2-tetrachloroethane	0.999	0.627	0.999	0.574
diisopropyl ether (DIPE)	1.000	1.354	1.000	1.238	2-chlorotoluene	0.999	0.560	1.000	0.514
1,1-dichloroethane	1.000	0.507	1.000	0.557	1,3,5-trimethylbenzene	0.999	1.980	1.000	1.751
t-butyl ethyl ether (ETBE)	1.000	0.946	0.999	0.862	1,2,3-trichloropropane	0.999	0.200	1.000	0.184
cis-1,2-dichloroethene	0.999	0.454	1.000	0.453	4-chlorotoluene	0.999	0.584	1.000	0.535
bromochloromethane	1.000	0.151	1.000	0.169	t-butylbenzene	0.999	1.615	1.000	1.466
chloroform	1.000	0.460	1.000	0.486	pentachloroethane	0.999	0.314	0.999	0.288
carbon tetrachloride	1.000	0.263	0.999	0.286	1,2,4-trimethylbenzene	0.999	2.087	1.000	1.799
tetrahydrofuran	1.000	0.257	1.000	0.280	sec-butylbenzene	0.999	2.346	1.000	2.097
1,1,1-trichloroethane	1.000	0.361	1.000	0.385	4-isopropyltoluene	0.999	1.907	0.999	1.740
1,1-dichloropropene	1.000	0.126	1.000	0.132	1,3-dichlorobenzene	1.000	1.129	1.000	1.012
1-chlorobutane	1.000	0.632	0.999	0.640	1,4-dichlorobenzene	0.999	1.149	0.999	1.052
benzene	1.000	1.135	1.000	1.129	n-butylbenzene	0.999	1.681	1.000	1.528
t-amyl methyl ether (TAME)	1.000	0.847	1.000	0.708	hexachloroethane	0.999	0.194	1.000	0.183
1,2-dichloroethane	1.000	0.391	1.000	0.380	1,2-dichlorobenzene	0.999	1.062	0.999	0.970
trichloroethene	1.000	0.248	1.000	0.287	1,2-dibromo-3-chloropropane	0.999	0.134	1.000	0.137
t-amyl ethyl ether (TAEE)	1.000	0.718	1.000	0.648	hexachlorobutadiene	0.999	0.289	1.000	0.279
dibromomethane	1.000	0.152	0.999	0.170	1,2,4-trichlorobenzene	0.999	0.628	1.000	0.585
1,2-dichloropropane	1.000	0.289	0.999	0.310	napthalene	0.999	1.860	0.999	1.807
bromodichloromethane	1.000	0.324	1.000	0.325	1,2,3-trichlorobenzene	1.000	0.565	0.999	0.537
cis-1,3-dichloropropene	1.000	0.430	0.999	0.408	Average	1.000	0.687	0.999	0.640
toluene	1.000	1.214	0.999	1.151					

Table 4: Precision and Accuracy at 0.5 ppb (n=7)

Compound	Helium		Nitrogen		Compound	Helium		Nitrogen	
	Precision as %RSD (n=7)	Accuracy as % Recy. (n=7)	Precision as %RSD (n=7)	Accuracy as % Recy. (n=7)		Precision as %RSD (n=7)	Accuracy as % Recy. (n=7)	Precision as %RSD (n=7)	Accuracy as % Recy. (n=7)
dichlorodifluoromethane	4.89	85.34	5.81	66.29	tetrachloroethene	4.27	91.74	4.08	98.00
chlorodifluoromethane	9.42	100.03	10.81	96.34	trans-1,3-dichloropropene	3.01	99.23	3.80	100.66
chloromethane	7.04	99.63	7.41	76.11	ethyl methacrylate	3.74	109.60	3.30	102.77
vinyl chloride	7.03	102.89	5.96	80.77	1,1,2-trichloroethane	6.41	94.31	6.61	105.83
1,3-butadiene	8.98	95.17	8.53	75.57	dibromochloromethane	4.98	100.51	2.15	103.71
bromomethane	11.95	99.89	9.35	94.31	1,3-dichloropropane	2.44	101.94	2.74	99.43
chloroethane	8.78	95.74	8.33	92.57	1,2-dibromomethane	4.99	98.14	5.22	98.11
trichlorofluoromethane	7.78	100.06	8.38	77.94	chlorobenzene	3.15	98.14	2.87	100.14
diethyl ether	6.33	107.49	5.37	85.17	ethylbenzene	3.96	103.43	5.56	100.09
1,1-dichloroethene	7.85	103.31	9.85	86.77	1,1,1,2-tetrachloroethane	3.62	102.14	4.61	103.80
carbon disulfide	6.54	106.11	9.00	78.66	xylene (m+p)	4.37	102.66	4.58	98.70
methyl iodide	7.04	112.63	4.70	108.17	xylene (o)	3.82	103.97	4.12	96.77
allyl chloride	3.87	101.34	9.56	87.74	styrene	1.53	97.17	4.12	101.11
methylene chloride	5.36	103.54	5.07	94.17	bromoform	5.47	107.60	6.17	105.26
trans-1,2-dichloroethene	5.03	109.63	8.02	88.34	isopropylbenzene	3.93	100.37	5.17	100.51
methyl acetate	10.60	103.89	6.79	96.63	bromobenzene	6.12	96.66	7.31	18.90
methyl-t-butyl ether (MtBE)	3.75	98.14	3.96	92.09	n-propylbenzene	3.80	97.54	6.27	86.20
t-butyl alcohol (TBA)	5.16	124.15	10.12	95.26	1,1,2,2-tetrachloroethane	8.38	106.97	5.10	102.91
diisopropyl ether (DIPE)	3.69	105.20	3.69	96.26	2-chlorotoluene	5.59	102.94	5.21	91.54
1,1-dichloroethane	3.56	119.00	7.77	92.11	1,3,5-trimethylbenzene	3.37	100.57	6.58	91.63
t-butyl ethyl ether (ETBE)	1.96	100.34	4.79	92.94	1,2,3-trichloropropane	4.81	114.43	6.22	93.06
cis-1,2-dichloroethene	3.00	98.94	7.00	92.11	4-chlorotoluene	4.02	102.91	8.78	95.23
bromochloromethane	4.56	95.80	8.69	93.69	t-butylbenzene	2.21	101.89	7.41	96.11
chloroform	4.45	110.89	10.03	88.26	pentachloroethane	4.16	102.97	5.59	99.46
carbon tetrachloride	6.46	92.37	5.83	88.49	1,2,4-trimethylbenzene	3.01	96.74	4.06	94.80
tetrahydrofuran	9.34	104.66	9.07	88.69	sec-butylbenzene	3.65	98.40	7.08	88.54
1,1,1-trichloroethane	5.14	100.74	7.91	89.69	4-isopropyltoluene	3.39	98.86	7.14	96.80
1,1-dichloropropene	6.58	101.17	9.76	89.14	1,3-dichlorobenzene	2.46	100.06	5.00	97.54
1-chlorobutane	4.01	103.69	5.95	85.57	1,4-dichlorobenzene	2.19	93.20	6.23	88.69
benzene	2.81	96.54	8.24	98.66	n-butylbenzene	4.01	96.89	7.27	92.71
t-amyl methyl ether (TAME)	2.16	100.49	1.72	100.03	hexachloroethane	8.31	94.77	8.51	94.00
1,2-dichloroethane	3.43	105.06	4.86	87.57	1,2-dichlorobenzene	2.69	101.37	4.20	95.23
trichloroethene	4.62	115.83	8.55	91.97	1,2-dibromo-3-chloropropane	4.38	120.20	6.24	92.06
t-amyl ethyl ether (TAEE)	3.19	99.23	5.02	98.94	hexachlorobutadiene	11.07	93.46	4.43	75.97
dibromomethane	3.69	101.40	4.06	95.46	1,2,4-trichlorobenzene	5.86	90.91	6.58	89.00
1,2-dichloropropane	3.16	109.83	5.47	94.37	napthalene	3.43	101.31	2.25	98.74
bromodichloromethane	4.34	101.51	10.40	99.77	1,2,3-trichlorobenzene	4.20	105.00	2.43	93.97
cis-1,3-dichloropropene	3.81	102.43	6.70	99.97	Average	4.95	101.91	6.20	92.46
toluene	3.72	102.09	4.99	98.57					

Table 5: Precision and Accuracy at 20 ppb (n=7)

Compound	Helium		Nitrogen		Compound	Helium		Nitrogen	
	Precision as %RSD (n=7)	Accuracy as % Recy. (n=7)	Precision as %RSD (n=7)	Accuracy as % Recy. (n=7)		Precision as %RSD (n=7)	Accuracy as % Recy. (n=7)	Precision as %RSD (n=7)	Accuracy as % Recy. (n=7)
dichlorodifluoromethane	6.97	93.44	11.57	97.36	tetrachloroethene	5.98	96.59	5.99	93.89
chlorodifluoromethane	8.31	100.82	8.06	81.39	trans-1,3-dichloropropene	2.19	98.14	2.04	95.91
chloromethane	6.39	99.28	7.17	93.91	ethyl methacrylate	2.02	99.92	1.60	97.88
vinyl chloride	7.46	97.60	8.13	94.70	1,1,2-trichloroethane	2.03	98.62	2.33	95.10
1,3-butadiene	8.21	97.05	7.51	93.50	dibromochloromethane	2.44	100.51	2.82	96.13
bromomethane	5.73	100.55	6.74	101.72	1,3-dichloropropane	2.15	98.61	2.61	95.75
chloroethane	6.54	97.21	8.16	94.04	1,2-dibromomethane	2.18	98.67	1.71	96.80
trichlorofluoromethane	8.42	97.56	8.15	95.92	chlorobenzene	3.44	98.67	3.67	96.35
diethyl ether	3.45	97.91	3.67	95.47	ethylbenzene	5.04	99.83	4.70	95.79
1,1-dichloroethene	7.69	98.80	5.99	94.20	1,1,1,2-tetrachloroethane	3.06	99.04	3.08	95.42
carbon disulfide	7.41	100.70	5.42	96.18	xylene (m+p)	5.02	99.99	4.46	95.89
methyl iodide	5.10	99.10	6.58	96.72	xylene (o)	4.40	99.76	3.95	96.59
allyl chloride	5.62	100.23	5.19	94.84	styrene	3.57	99.15	3.57	95.84
methylene chloride	3.87	98.09	3.39	94.47	bromoform	3.35	97.44	2.60	96.49
trans-1,2-dichloroethene	6.32	101.36	5.43	96.58	isopropylbenzene	5.39	99.19	4.71	95.69
methyl acetate	3.61	103.36	2.19	92.30	bromobenzene	2.54	99.26	1.67	95.88
methyl-t-butyl ether (MtBE)	2.37	98.32	1.75	94.93	n-propylbenzene	5.08	101.74	4.06	95.81
t-butyl alcohol (TBA)	6.60	102.59	2.91	89.37	1,1,2,2-tetrachloroethane	2.67	101.46	1.27	97.58
diisopropyl ether (DIPE)	3.63	100.89	2.35	95.67	2-chlorotoluene	4.24	100.69	3.54	95.57
1,1-dichloroethane	5.60	100.50	4.40	95.94	1,3,5-trimethylbenzene	4.83	99.99	3.71	96.08
t-butyl ethyl ether (ETBE)	2.99	99.41	2.21	96.65	1,2,3-trichloropropane	2.69	99.30	1.73	94.36
cis-1,2-dichloroethene	6.92	101.61	4.86	96.32	4-chlorotoluene	5.21	99.12	3.43	95.11
bromochloromethane	3.88	101.11	2.99	95.06	t-butylbenzene	5.35	97.70	5.56	99.30
chloroform	4.99	99.68	3.92	94.97	pentachloroethane	2.88	99.97	3.20	96.44
carbon tetrachloride	7.68	99.90	6.77	94.30	1,2,4-trimethylbenzene	4.49	99.99	2.98	95.26
tetrahydrofuran	4.80	104.87	2.18	95.96	sec-butylbenzene	5.80	99.96	5.57	94.54
1,1,1-trichloroethane	7.14	100.09	4.97	94.89	4-isopropyltoluene	5.06	100.51	4.12	96.08
1,1-dichloropropene	8.01	98.49	5.23	96.67	1,3-dichlorobenzene	4.64	99.29	3.45	95.41
1-chlorobutane	6.51	98.99	5.49	96.46	1,4-dichlorobenzene	3.42	99.58	2.78	95.07
benzene	5.59	100.09	4.30	96.36	n-butylbenzene	5.89	101.79	4.30	95.70
t-amyl methyl ether (TAME)	3.33	98.37	2.06	96.11	hexachloroethane	5.46	98.87	5.31	92.15
1,2-dichloroethane	3.40	100.29	2.55	97.24	1,2-dichlorobenzene	3.47	99.14	2.52	95.68
trichloroethene	6.63	100.76	4.62	95.99	1,2-dibromo-3-chloropropane	3.84	101.90	1.83	95.85
t-amyl ethyl ether (TAEE)	4.07	99.97	2.77	98.02	hexachlorobutadiene	5.75	102.24	4.99	94.87
dibromomethane	3.60	101.41	3.65	95.69	1,2,4-trichlorobenzene	4.31	99.87	2.07	95.63
1,2-dichloropropane	4.89	101.74	3.51	95.85	napthalene	3.58	101.17	0.99	97.94
bromodichloromethane	4.53	100.80	2.83	96.90	1,2,3-trichlorobenzene	4.74	98.74	2.22	96.56
cis-1,3-dichloropropene	4.26	99.41	2.35	96.60	Average	4.69	99.85	3.96	95.71
toluene	4.54	99.88	4.04	96.35					

Table 6: MRL and calculated PIR Upper and Lower limits at 0.5 ppb, using helium purge gas (40 mL/minute for 11 minutes)

Compound	Run 1 ppb	Run 2 ppb	Run 3 ppb	Run 4 ppb	Run 5 ppb	Run 6 ppb	Run 7 ppb	Avg. ppb	Std. Dev. ppb	Upper PIR	Lower PIR	Upper PIR Pass/Fail	Lower PIR Pass/Fail
Dichlorofluoromethane	0.42	0.40	0.44	0.41	0.46	0.45	0.42	0.43	0.02	101.88	68.81	pass	pass
Chlorodifluoromethane	0.42	0.50	0.57	0.51	0.55	0.51	0.46	0.50	0.05	137.39	62.67	pass	pass
Chloromethane	0.48	0.45	0.53	0.52	0.47	0.55	0.49	0.50	0.04	127.44	71.82	pass	pass
1,3-Butadiene	0.47	0.41	0.50	0.46	0.49	0.56	0.45	0.48	0.04	129.06	61.29	pass	pass
Vinyl Chloride	0.50	0.46	0.49	0.53	0.54	0.58	0.51	0.51	0.04	131.56	74.21	pass	pass
Bromomethane	0.58	0.43	0.46	0.43	0.53	0.58	0.49	0.50	0.06	147.18	52.59	pass	pass
Chloroethane	0.43	0.42	0.46	0.54	0.51	0.52	0.47	0.48	0.04	129.06	62.42	pass	pass
Trichlorofluoromethane	0.50	0.44	0.54	0.49	0.50	0.57	0.47	0.50	0.04	130.91	69.21	pass	pass
Diethyl Ether	0.56	0.49	0.53	0.60	0.56	0.53	0.51	0.54	0.03	134.45	80.52	pass	pass
1,1-Dichloroethene	0.51	0.43	0.52	0.54	0.52	0.58	0.53	0.52	0.04	135.46	71.16	pass	pass
Iodomethane	0.54	0.51	0.51	0.60	0.59	0.62	0.57	0.56	0.04	144.06	81.19	pass	pass
Carbon Disulfide	0.54	0.51	0.54	0.51	0.49	0.61	0.51	0.53	0.03	133.64	78.59	pass	pass
Allyl Chloride	0.51	0.46	0.51	0.52	0.52	0.51	0.52	0.51	0.02	116.87	85.82	pass	pass
Methylene Chloride	0.49	0.48	0.53	0.54	0.54	0.56	0.48	0.52	0.03	125.54	81.55	pass	pass
MTBE	0.48	0.48	0.52	0.50	0.49	0.51	0.46	0.49	0.02	112.71	83.57	pass	pass
trans-1,2-dichoroethene	0.55	0.52	0.54	0.53	0.55	0.61	0.55	0.55	0.03	131.50	87.76	pass	pass
methyl acetate	0.51	0.44	0.51	0.62	0.54	0.56	0.46	0.52	0.06	147.53	60.24	pass	pass
TBA	2.82	3.20	3.34	3.23	3.12	3.02	3.01	3.10	0.16	149.55	98.75	pass	pass
diisopropyl ether	0.53	0.52	0.52	0.54	0.53	0.55	0.48	0.53	0.02	120.59	89.81	pass	pass
1,1-Dichloroethane	0.59	0.55	0.61	0.60	0.61	0.63	0.58	0.60	0.02	135.77	102.23	pass	pass
t-butyl ethyl ether (ETBE)	0.49	0.49	0.51	0.51	0.51	0.51	0.50	0.50	0.01	108.15	92.53	pass	pass
cis-1,2-dichloroethene	0.50	0.49	0.49	0.49	0.50	0.53	0.47	0.49	0.01	110.70	87.19	pass	pass
Bromochloromethane	0.46	0.50	0.50	0.49	0.44	0.50	0.47	0.48	0.02	113.12	78.48	pass	pass
Chloroform	0.53	0.52	0.55	0.58	0.55	0.60	0.56	0.55	0.02	130.43	91.34	pass	pass
Carbon Tetrachloride	0.46	0.43	0.49	0.48	0.41	0.49	0.48	0.46	0.03	116.03	68.71	pass	pass
THF	0.53	0.53	0.45	0.57	0.50	0.61	0.48	0.52	0.05	143.39	65.93	pass	pass
1,1,1-trichloroethane	0.50	0.45	0.50	0.51	0.53	0.54	0.50	0.50	0.03	121.25	80.23	pass	pass
1,1-dichloropropene	0.51	0.47	0.54	0.47	0.56	0.47	0.52	0.51	0.03	127.54	74.80	pass	pass
1-chlorobutane	0.48	0.50	0.52	0.52	0.54	0.54	0.52	0.52	0.02	120.15	87.22	pass	pass
Benzene	0.49	0.45	0.48	0.50	0.49	0.49	0.48	0.48	0.01	107.29	85.79	pass	pass
t-amyl methyl ether (TAME)	0.50	0.50	0.49	0.51	0.48	0.52	0.51	0.50	0.01	109.10	91.87	pass	pass
1,2-Dichloroethane	0.52	0.51	0.51	0.56	0.52	0.54	0.52	0.53	0.02	119.32	90.79	pass	pass
Trichloroethene	0.56	0.56	0.59	0.58	0.56	0.64	0.57	0.58	0.03	137.04	94.62	pass	pass
t-amyl ethyl ether (TAEE)	0.51	0.47	0.49	0.51	0.49	0.52	0.49	0.50	0.02	111.79	86.67	pass	pass
Dibromomethane	0.52	0.52	0.49	0.54	0.49	0.52	0.48	0.51	0.02	116.22	86.58	pass	pass
1,2-Dichloropropane	0.52	0.55	0.56	0.57	0.54	0.55	0.57	0.55	0.02	123.58	96.08	pass	pass
Bromodichloromethane	0.48	0.50	0.49	0.50	0.52	0.55	0.52	0.51	0.02	118.96	84.07	pass	pass
cis-1,3-Dichloropropene	0.49	0.50	0.48	0.54	0.52	0.53	0.53	0.51	0.02	117.88	86.98	pass	pass
Toluene	0.52	0.49	0.51	0.49	0.50	0.55	0.51	0.51	0.02	117.15	87.02	pass	pass
Tetrachloroethane	0.45	0.44	0.43	0.49	0.48	0.46	0.47	0.46	0.02	107.25	76.24	pass	pass
trans-1,3-Dichloropropene	0.51	0.50	0.47	0.50	0.50	0.51	0.48	0.50	0.01	111.07	87.39	pass	pass
ethyl methacrylate	0.57	0.52	0.55	0.56	0.53	0.57	0.52	0.55	0.02	125.85	93.35	pass	pass
1,1,2-Trichloroethane	0.50	0.47	0.47	0.50	0.44	0.50	0.43	0.47	0.03	117.27	71.36	pass	pass
Dibromochloromethane	0.51	0.53	0.46	0.48	0.51	0.53	0.49	0.50	0.03	120.34	80.69	pass	pass
1,3-dichloropropane	0.51	0.51	0.50	0.54	0.50	0.52	0.51	0.51	0.01	111.79	92.10	pass	pass
1,2-Dibromoethane	0.52	0.49	0.48	0.46	0.52	0.51	0.46	0.49	0.02	117.53	78.75	pass	pass
Chlorobenzene	0.48	0.49	0.46	0.48	0.51	0.51	0.50	0.49	0.02	110.41	85.88	pass	pass
1,1,1,2-Tetrachloroethane	0.51	0.48	0.49	0.52	0.54	0.53	0.52	0.51	0.02	116.79	87.49	pass	pass
Ethylbenzene	0.51	0.50	0.50	0.50	0.53	0.55	0.54	0.52	0.02	119.64	87.22	pass	pass
Xylene (p&m)	1.00	1.03	1.03	0.99	1.01	1.13	1.00	1.03	0.04	120.43	84.89	pass	pass
Styrene	0.48	0.49	0.47	0.48	0.49	0.50	0.49	0.49	0.01	103.06	91.28	pass	pass
Xylene (o)	0.51	0.52	0.52	0.51	0.53	0.56	0.49	0.52	0.02	119.71	88.24	pass	pass
Bromoform	0.57	0.53	0.53	0.50	0.53	0.59	0.51	0.54	0.03	130.92	84.28	pass	pass
Isopropylbenzene	0.49	0.48	0.50	0.48	0.52	0.54	0.50	0.50	0.02	115.99	84.75	pass	pass
Bromobenzene	0.50	0.51	0.49	0.49	0.45	0.51	0.43	0.48	0.03	120.11	73.21	pass	pass
1,1,2,2-Tetrachloroethane	0.56	0.52	0.52	0.53	0.59	0.58	0.45	0.53	0.04	142.52	71.43	pass	pass
n-Propylbenzene	0.48	0.48	0.47	0.48	0.50	0.53	0.48	0.49	0.02	112.24	82.85	pass	pass
2-Chlorotoluene	0.53	0.46	0.54	0.49	0.51	0.56	0.52	0.51	0.03	125.76	80.13	pass	pass
4-Chlorotoluene	0.53	0.52	0.48	0.53	0.50	0.54	0.50	0.51	0.02	119.32	86.51	pass	pass
1,3,5-Trimethylbenzene	0.48	0.49	0.49	0.51	0.50	0.54	0.50	0.50	0.02	113.99	87.16	pass	pass
1,2,3-trichloropropane	0.53	0.56	0.57	0.59	0.59	0.61	0.54	0.57	0.03	136.22	92.64	pass	pass
tert-Butylbenzene	0.50	0.49	0.50	0.52	0.53	0.51	0.51	0.51	0.01	110.80	92.97	pass	pass
pentachloroethane	0.50	0.48	0.53	0.52	0.54	0.54	0.50	0.51	0.02	119.95	86.00	pass	pass
sec-Butylbenzene	0.49	0.47	0.49	0.50	0.50	0.53	0.47	0.49	0.02	112.64	84.16	pass	pass
1,2,4-Trimethylbenzene	0.49	0.47	0.49	0.48	0.48	0.51	0.47	0.48	0.01	108.29	85.20	pass	pass

Table 6 cont.

Compound	Run 1 ppb	Run 2 ppb	Run 3 ppb	Run 4 ppb	Run 5 ppb	Run 6 ppb	Run 7 ppb	Avg. ppb	Std. Dev. ppb	Upper PIR	Lower PIR	Upper PIR Pass/Fail	Lower PIR Pass/Fail
1,3-Dichlorobenzene	0.51	0.50	0.51	0.49	0.50	0.52	0.48	0.50	0.01	109.81	90.31	pass	pass
1,4-Dichlorobenzene	0.46	0.46	0.46	0.46	0.46	0.48	0.48	0.47	0.01	101.27	85.13	pass	pass
Isopropyltoluene	0.49	0.48	0.49	0.49	0.50	0.53	0.48	0.49	0.02	112.15	85.56	pass	pass
1,2-Dichlorobenzene	0.51	0.50	0.52	0.52	0.49	0.52	0.49	0.51	0.01	112.18	90.57	pass	pass
n-Butylbenzene	0.49	0.47	0.51	0.48	0.45	0.50	0.49	0.48	0.02	112.29	81.48	pass	pass
Hexachloroethane	0.42	0.48	0.45	0.47	0.54	0.52	0.45	0.47	0.04	126.00	63.55	pass	pass
1,2-Dibromo-3-chloropropane	0.60	0.56	0.59	0.65	0.60	0.60	0.63	0.60	0.03	141.07	99.33	pass	pass
1,2,4-Trichlorobenzene	0.48	0.47	0.49	0.45	0.44	0.45	0.40	0.45	0.03	112.03	69.80	pass	pass
Naphthalene	0.52	0.50	0.54	0.48	0.50	0.51	0.49	0.51	0.02	115.09	87.54	pass	pass
Hexachlorobutadiene	0.41	0.45	0.46	0.40	0.50	0.57	0.48	0.47	0.05	134.46	52.45	pass	pass
1,2,3-Trichlorobenzene	0.52	0.55	0.54	0.51	0.54	0.54	0.48	0.53	0.02	122.48	87.52	pass	pass

■ Conclusion

The Encon Evolution and Centurion WS autosampler in conjunction with the Shimadzu GCMS-QP2010 SE performed very well using both the helium and nitrogen purge gases. The nitrogen and the helium purge gases met US EPA method 524.3 criteria and produced comparable results.

Overall, the principal difference between the two purge gases was exhibited in the compound response. When examining the overall compound response factors over the curve range, it is evident that the analytes' responses are slightly lower with the nitrogen purge gas as opposed to the helium purge gas due to slight differences in purge efficiency with the two gases.

■ References

1. Method 524.3, Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Version 1.0, June 2009.
2. Method 524.4, Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry (Using Nitrogen Purge Gas), Version 1, September 2011.
3. This application note was originally published by EST Analytical as "Drinking Water Analysis Conditions for US EPA Methods 524.3 and 524.4" in 2010. It is republished here with their permission.

■ Ordering Information for Replacement Consumables

The consumables used in this application note are shown in the table below. To order any of these items please contact Customer Service at Shimadzu Scientific Instruments at 1-800-477-1227, or visit our web store at http://store.shimadzu.com.

Part Number	Item Name	Photo	Item Description
221-75962-30	Capillary Column		SH-RXI-624 SIL MS, 30 m x 0.25 mm x 1.40 µm
220-90784-10	Inlet Liner		Low-volume Liner, 1.0 mm ID, Straight, 5/Pkg (Restek)
220-94775-10	VOA Tuning Compound		1-Bromo-4-fluorobenzene (BFB), 5,000 µg/mL in P&T MeOH, 1 mL/ampule, CAS #: 460-00-4 (Restek)
Restek PN 30013	524.3 VOA Mega Mix		2,000 µg/mL each in P&T MeOH, 1 mL/ampule (Restek)
Restek PN 30015	524.3 Internal Standard Mix		2,000 µg/mL each in P&T MeOH, 1 mL/ampule (Restek)
Restek PN 30016	524.3 Surrogate Mix		2,000 µg/mL each in P&T MeOH, 1 mL/ampule (Restek)
Restek PN 30014	524.3 Gas Calibration Mix		2,000 µg/mL each in P&T MeOH, 1 mL/ampule (Restek)
220-94775-00	n-Alkane Mix		AART Standard for determination of Retention Index (RI) and Retention Times (RT)
220-94594-00	Electronic Flow Meter		ProFLOW 6000 Electronic Flow Meter (Restek)
220-94594-01	Electronic Leak Detector		Electronic Leak Detector With Hard-Sided Carrying Case and Universal Charger Set (Restek)

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