

Abstract:

Due to advances in analytical instrumentation the United States Environmental Protection Agency (USEPA) introduced a new drinking water method. USEPA Method 524.3 allows laboratories to modify purge and trap and GCMS conditions in order to accommodate instrumental advances and shorten sample preparation time. Currently, the USEPA is investigating the option of using Nitrogen as the purge gas in an additional drinking water method, USEPA Method 524.4. This application note will compare Helium and Nitrogen purge gases.

Discussion:

USEPA 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. Recently, 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 USEPA 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 has the advantage of excluding the Moisture Reduction Trap (MoRT) from the desorb pathway thus aiding in moisture control for the system. Secondly, EST Analytical has a foam sensor to detect any issues with 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



has the ability of taking samples from the vials without moving the samples. 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 then comparing results the linearity, precision, accuracy and overall compound response for the different purge gases.

Experimental:

The EST Analytical Encon Evolution purge and trap concentrator and Centurion WS autosampler were interfaced to a Shimadzu QP2010 SE GCMSD. The purge and trap concentrator was configured with a Vocarb 3000 (K) analytical trap. 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.

Purge and Trap Concentrator	EST Encon Evolution
Trap Type	Vocarb 3000 (K Trap)
Valve Oven Temp.	150°C
Transfer Line Temp.	150°C
Trap Temp.	35°C
Moisture Reduction Trap (MoRT) Temp.	39°C
Purge Time	11 min.
Purge Flow	40ml/min
Dry Purge Temp.	ambient
Dry Purge Flow	50ml/min
Dry Purge Time	1 min.
Desorb Pressure Control	On
Desorb Pressure Control	5psi
Desorb Preheat Delay	5 sec.
Desorb Time	1 min
Desorb Temp.	260°C
Moisture Reduction Trap (MoRT) Bake Temp.	230°C
Bake Temp.	265°C
Sparge Vessel Bake Temp.	120°C
Bake Time	8 min.
Bake Flow	40ml/min
Purge and Trap Autosampler	EST Centurion WS
Sample Size	5ml
Internal Standard Volume	5µl
Surrogate Volume	5µl

Table 1: Purge and Trap Parameters

GC/MS	Shimadzu QP 2010SE
Injection Mode	Split
Injection Temp.	200°C
Flow Control mode	Linear Velocity
Linear Velocity	34.3 cm/sec
Column Flow	0.9 ml/min
Split Ratio	30:1
Purge Flow	1.0 ml/min
Column	Rxi-624Sil MS 30m x 0.25mm I.D. 1.4µm film thickness
Oven Temp. Program	45°C hold for 4.5 min, ramp 12°C/min to 100°C, hold for 0.0min, ramp 25°C/min to 240°C, hold for 1.32min,
Ion Source Temp.	185°C
Interface Temp.	225°C
Solvent Cut Time	0.0 min
Scan Range	35-300 m/z
Event Time	0.30 sec

Table 2: GC/MS Parameters

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 0.5ppb to 40ppb. The internal standard and surrogate concentrations were held constant at 5ppb. Figure 1 displays an overlay of the 20ppb standard purged in Helium (blue) and in Nitrogen (orange). The quadratic regression and average compound response of the respective purge gases are listed in Table 3. Finally, seven 0.5ppb standards and seven 20ppb calibration standards were run in order to establish passing Minimum Reporting Limits (MRLs) for each of the analytes and also 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.

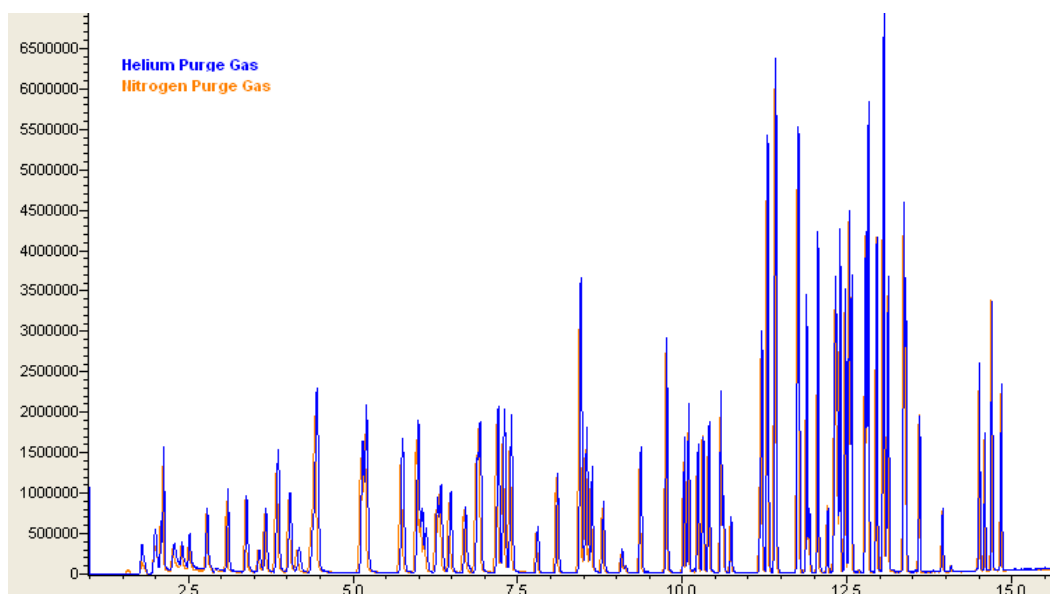


Figure 1: Overlay of 20ppb Standards Purged in Helium and Nitrogen

Compound	Helium		Nitrogen		Compound	Helium		Nitrogen	
	Curve Quadratic Regress	Curve RF	Curve Quadratic Regress	Curve RF		Curve Quadratic Regress	Curve RF	Curve Quadratic Regress	Curve 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	1,1,1,2-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	naphthalene	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 3: Quadratic Regression and Average Response Factors

Compound	Helium		Nitrogen		Compound	Helium		Nitrogen	
	0.5ppb Precision	0.5ppb Accuracy (%Recovery)	0.5ppb Precision	0.5ppb Accuracy (%Recovery)		0.5ppb Precision	0.5ppb Accuracy (%Recovery)	0.5ppb Precision	0.5ppb Accuracy (%Recovery)
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	naphthalene	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 4: 0.5ppb Precision and Accuracy

Compound	Helium		Nitrogen		Compound	Helium		Nitrogen	
	20ppb Precision	20ppb Accuracy (%Recovery)	20ppb Precision	20ppb Accuracy (%Recovery)		20ppb Precision	20ppb Accuracy (%Recovery)	20ppb Precision	20ppb Accuracy (%Recovery)
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	1,1,1,2-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	naphthalene	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 5: 20ppb Precision and Accuracy

Conclusion:

The Encon Evolution and Centurion WS in conjunction with the Shimadzu QP2010 SE GCMS performed very well using both the Helium and Nitrogen purge gases. The Nitrogen and the Helium purge gases met USEPA 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.

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 (Draft), Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry (Using Nitrogen Purge Gas), Version 1, September 2011.