

## ABSTRACT

In June 2009, the United States Environmental Protection Agency (USEPA) promulgated a new drinking water method, 524.3. Due to advances in analytical instrumentation, Method 524.3 allows laboratories to modify purge and trap and GC/MS conditions. Currently the USEPA is investigating the option of using Nitrogen as the purge gas in a new drinking water method, 524.4. This poster will explore purge and trap conditions for both Helium and Nitrogen purge gases.

## DISCUSSION

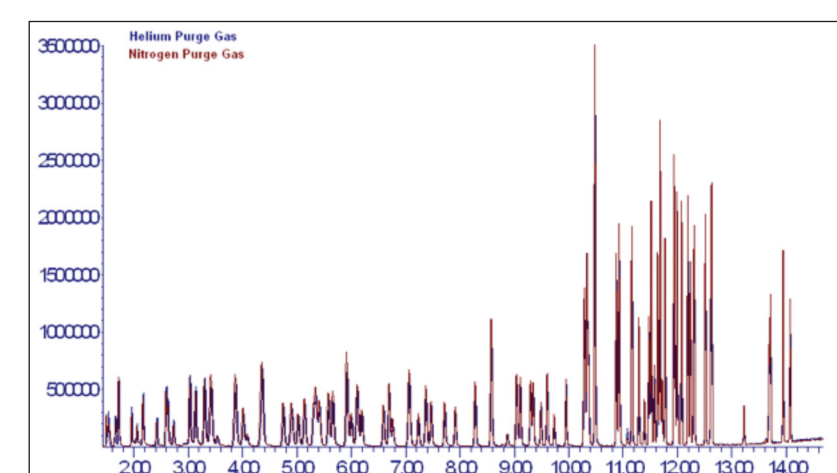
When the USEPA published Method 524.3, they allowed some method flexibility. However, the method still required Helium as the purge gas. Due to fluctuations in the price and availability of high purity Helium, the USEPA has drafted Method 524.4, which would allow for high purity Nitrogen to be used for 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 has two features that can aid in moisture control and the “foaming” caused by the effervescing. First, EST 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 send a false positive signal to the software, causing the sample sequence to be aborted. Secondly, 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. 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 two different purge volumes. The results from the different purge gases and volumes were compared for linearity, precision, accuracy and overall compound response.

## EXPERIMENTAL

The EST Analytical Encon Evolution purge and trap concentrator and Centurion WS Autosampler were interfaced to a GC/MSD. The purge and trap concentrator was configured with a Vocab 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**.



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

The GC column and standards were acquired from Restek. The linear range for both purge gases and purge volumes 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 and purge volumes 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**.

**Table 1. Purge and Trap Parameters**

Purge & Trap Concentrator	EST Encon Evolution
Trap Type	Vocab 3000 (K Trap)
Valve Oven Temp.	150°C
Transfer Line Temp.	150°C
Trap Temp.	35°C
MoRT Temp.	39°C
Purge Time	11 min. and 6.5 min.
Purge Flow	40ml/min and 60ml/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
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 2. GC/MS Parameters**

GC/MS	Agilent 7890/5975
Inlet	Split/Splitless
Inlet Temp.	220°C
Inlet Head Pressure	11.196 psi
Mode	Split
Split Ratio	30:1
Column	Rtx-VMS 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, ramp 25°C/min to 230°C, hold for 1.3min, 15.58 min run time
Column Flow Rate	0.9ml/min
Gas	Helium
Total Flow	30.9ml/min
Source Temp.	230°C
Quad Temp.	150°C
MS Transfer Line Temp.	180°C
Scan Range	m/z 47-265 (from 1min to 2.9 min); m/z 35-265 (from 2.9 min to end of run)
Scans	3.27 scans/sec (from 1min to 2.9 min); 3.12 scans/sec (from 2.9 min to end of run)
Solvent Delay	1.0 min.

## CONCLUSION

The Encon Evolution and Centurion WS performed very well using both the Helium and Nitrogen purge gases and the 440ml and 390ml purge volumes. The Nitrogen and the Helium purge gases met USEPA method 524.3 criteria. Furthermore, the 440ml purge volume and the 390ml purge volume 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

- Method 524.3, Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Version 1.0, June 2009.
- 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.

**Table 3. Quadratic Regression and Average Response Factors**

Compound	440ml Purge Vol. He		390ml Purge Vol. He		440ml Purge Vol. N2		390ml Purge Vol. N2	
	Curve Quadratic Regress	Curve RF	Curve Quadratic Regress	Curve RF	Curve Quadratic Regress	Curve RF	Curve Quadratic Regress	Curve RF
dichlorodifluoromethane	0.998	0.287	0.996	0.369	0.999	0.292	0.999	0.304
chlorodifluoromethane	0.995	0.555	1.000	0.564	0.999	0.441	0.999	0.478
chloromethane	1.000	0.490	1.000	0.569	0.997	0.452	0.998	0.470
vinyl chloride	1.000	0.412	1.000	0.454	0.997	0.326	0.999	0.351
1,3-butadiene	1.000	0.340	1.000	0.360	0.977	0.223	1.000	0.243
bromomethane	0.999	0.226	0.999	0.248	0.997	0.155	1.000	0.165
chloroethane	0.999	0.286	0.998	0.304	0.998	0.203	0.999	0.216
trichlorofluoromethane	0.999	0.621	1.000	0.623	0.998	0.457	0.998	0.502
diethyl ether	1.000	0.341	1.000	0.338	1.000	0.225	0.999	0.224
1,1-dichloroethane	1.000	0.321	1.000	0.306	0.997	0.206	1.000	0.223
carbon disulfide	1.000	0.970	1.000	1.025	0.998	0.652	1.000	0.706
methyl iodide	0.999	0.360	0.999	0.353	0.998	0.221	0.999	0.215
allyl chloride	0.999	0.206	1.000	0.217	0.998	0.141	0.999	0.153
methylene chloride	1.000	0.383	1.000	0.387	0.999	0.244	1.000	0.253
trans-1,2-dichloroethane	1.000	0.330	1.000	0.304	0.998	0.265	1.000	0.280
methyl acetate	1.000	0.348	0.999	0.305	0.999	0.276	1.000	0.295
methyl-t-butyl ether (MtBE)	1.000	1.067	1.000	1.063	1.000	0.768	1.000	0.734
t-butyl alcohol (TBA)	1.000	0.026	1.000	0.028	0.999	0.020	0.999	0.020
diisopropyl ether (DIPE)	1.000	1.211	1.000	1.244	1.000	0.915	0.999	0.889
1,1-dichloroethane	1.000	0.634	1.000	0.661	0.998	0.536	0.999	0.574
t-butyl ethyl ether (ETBE)	1.000	1.060	0.999	1.070	0.999	0.764	0.999	0.742
cis-1,2-dichloroethane	1.000	0.318	0.999	0.338	0.997	0.258	0.999	0.259
bromochloromethane	0.999	0.157	0.999	0.159	0.998	0.131	0.999	0.140
chloroform	1.000	0.691	1.000	0.672	1.000	0.526	1.000	0.551
carbon tetrachloride	1.000	0.453	1.000	0.478	0.998	0.351	0.999	0.395
tetrahydrofuran	0.999	0.069	0.998	0.063	0.999	0.046	1.000	0.043
1,1,1-trichloroethane	1.000	0.533	0.999	0.562	0.999	0.419	0.999	0.469
1,1-dichloropropane	0.999	0.331	1.000	0.339	0.998	0.251	0.999	0.273
1-chlorobutane	1.000	0.723	1.000	0.717	0.999	0.546	1.000	0.567
benzene	1.000	1.386	1.000	1.389	0.999	1.055	0.999	1.064
t-amyl methyl ether (TAME)	1.000	0.921	0.999	0.876	0.999	0.605	0.999	0.605
1,2-dichloroethane	1.000	0.520	1.000	0.542	1.000	0.378	1.000	0.420
trichloroethane	1.000	0.322	1.000	0.322	0.999	0.243	0.999	0.257
t-amyl ethyl ether (TAEE)	1.000	0.790	1.000	0.763	1.000	0.512	0.999	0.532
diisobutylene	1.000	0.206	1.000	0.208	1.000	0.163	0.999	0.166
1,2-dichloropropane	1.000	0.352	1.000	0.356	0.999	0.283	0.999	0.281
bromodichloromethane	1.000	0.471	0.999	0.483	0.999	0.361	0.999	0.376
cis-1,3-dichloropropene	1.000	0.535	1.000	0.519	1.000	0.389	0.999	0.399
toluene	1.000	0.799	1.000	0.732	1.000	0.601	0.999	0.614
tetrachloroethane	0.999	0.335	0.999	0.317	1.000	0.254	0.999	0.289
trans-1,3-dichloropropene	1.000	0.500	1.000	0.479	1.000	0.392	0.999	0.369
ethyl methacrylate	1.000	0.418	1.000	0.359	0.999	0.302	0.998	0.273
1,1,2-trichloroethane	0.999	0.259	0.999	0.236	1.000	0.208	1.000	0.202
1,2-dibromochloromethane	1.000	0.325	0.999	0.305	0.999	0.256	1.000	0.258
1,3-dichloropropane	1.000	0.521	1.000	0.497	0.999	0.418	1.000	0.417
1,2-dibromomethane	1.000	0.290	1.000	0.266	0.999	0.228	0.998	0.217
chlorobenzene	1.000	0.874	1.000	0.832	0.999	0.702	1.000	0.727
ethylbenzene	1.000	1.548	1.000	1.481	1.000	1.226	0.999	1.280
1,1,1,2-tetrachloroethane	1.000	0.317	1.000	0.319	0.999	0.252	0.999	0.258
xylylene (m+p)	1.000	0.588	0.999	0.539	1.000	0.458	0.999	0.476
xylylene (o)	0.999	0.541	0.999	0.502	0.999	0.435	0.998	0.465
styrene	1.000	0.894	1.000	0.848	0.999	0.694	0.999	0.718
bromoform	1.000	0.220	0.998	0.195	1.000	0.168	0.998	0.163
isopropylbenzene	1.000	1.536	1.000	1.429	1.000	1.172	0.999	1.249
bromobenzene	0.999	0.584	1.000	0.565	0.999	0.484	0.999	0.468
n-propylbenzene	1.000	2.993	0.999	2.835	1.000	2.458	0.999	2.523
1,1,2,2-tetrachloroethane	1.000	0.668	0.999	0.616	1.000	0.592	0.999	0.510
2-chlorotoluene	1.000	0.554	0.999	0.529	1.000	0.460	0.998	0.469
1,3,5-trimethylbenzene	1.000	2.034	0.999	1.895	1.000	1.660	0.998	1.665
1,2,3-trichloropropane	1.000	0.214	0.998	0.185	0.999	0.175	0.998	0.163
4-chlorotoluene	1.000	0.813	1.000	0.559	1.000	0.477	1.000	0.500
t-butylbenzene	1.000	0.478	1.000	0.440	1.000	0.379	0.998	0.386
pentachloroethane	1.000	0.396	0.999	0.390	0.998	0.326	0.998	0.302
1,2,4-trimethylbenzene	1.000	2.142	1.000	1.994	1.000	1.716	0.999	1.712
sec-butylbenzene	1.000	2.612	0.999	2.382	0.999	2.065	0.999	2.152
4-isopropyltoluene	1.000	2.160	1.000	1.966	1.000	1.701	0.998	1.723
1,3-dichlorobenzene	1.000	1.165	0.999	1.129	0.999	0.954	0.998	0.996
1,4-dichlorobenzene	1.000	1.169	1.000	1.125	0.999	0.986	0.999	0.991
n-butylbenzene	1.000	0.556	0.999	0.514	1.000	0.450	0.998	0.441
hexachloroethane	1.000	0.326	0.999	0.324	0.998	0.259	0.999	0.262
1,2-dichlorobenzene	1.000	1.113	1.000	1.092	1.000	0.939	0.999	0.951
1,2-dibromo-3-chloropropane	1.000	0.139	0.999	0.129	0.999	0.129	0.997	0.111
hexachlorobutadiene	0.999	0.310	1.000	0.289	0.996	0.238	0.999	0.256
1,2,4-trichlorobenzene	1.000	0.687	1.000	0.684	0.999	0.581	0.998	0.575
naphthalene	1.000	2.000	0.999	1.684	0.999	1.708	0.999	1.552
1,2,3-trichlorobenzene	1.000	0.631	0.999	0.598	1.000	0.539	0.998	0.543
Average	1.000	0.704	1.000	0.681	0.999	0.560	0.999	0.568

**Table 4. 0.5ppb Precision and Accuracy**

Compound	440ml Purge Vol. He		390ml Purge Vol. He		440ml Purge Vol. N2		390ml Purge Vol. N2	
	0.5ppb Precision	0.5ppb Accuracy	0.5ppb Precision	0.5ppb Accuracy	0.5ppb Precision	0.5ppb Accuracy	0.5ppb Precision	0.5ppb Accuracy
dichlorodifluoromethane	2.294	129.429	4.251	124.286	5.735	106.857	6.533	94.000
chlorodifluoromethane	6.837	69.429	7.900	78.571	5.286	117.429	8.040	75.714
chloromethane	4.527	126.857	7.744	72.857	11.008	90.286	7.344	90.571
vinyl chloride	5.262	112.857	8.520	98.571	7.448	87.143	7.832	76.000
1,3-butadiene	5.323	116.857	7.345	80.286	7.517	71.714	4.877	62.000
bromomethane	6.484	118.571	6.974	114.429	8.956	106.571	9.926	90.571
chloroethane	5.788	115.143	9.413	88.286	11.458	100.857	6.298	73.429
trichlorofluoromethane	2.691	134.286	8.852	82.286	4.337	124.286	6.783	76.286
diethyl ether	5.255	114.571	10.164	88.000	6.168	82.857	7.582	85.429
1,1-dichloroethane	7.523	113.429	5.865	109.143	6.774	72.000	11.237	96.286
carbon disulfide	3.909	127.429	6.181	99.14				