Exploring the US EPA 524 Purge and Trap Variables

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Abstract

Since 1983, the US EPA has provided water laboratories with convenient methods to test for potentially toxic Volatile Organic Compounds (VOC) in water. US EPA Method 524 has provided purge and trap parameters for these laboratories. Through the years since its initial release, this method has progressed through numerous revisions to allow laboratories to match improvements in purge and trap instruments and mass spectrometry detectors.

It has also revised the VOC list to remain current with the ever-changing toxic compounds that might be found in water. This poster will provide insight into how modifications to purge and trap parameters can affect VOC detection limits and sample concentration ranges for US EPA Methods 524.2[1], 524.3[2], and 524.4[3]. These parameters will also allow laboratories to successfully meet the requirements for all three methods, while maximizing the number of samples they can process in a given calibration cycle.

Introduction

Purge and trap concentrators have been used extensively for the analysis of VOCs in water since the mid 1970's. An issue with the technique is while the purge gas strips VOCs from water, it also transfers water vapor to the trap. This water negatively affects the GC/MS system used for quantitation of VOCs.

This poster will demonstrate the significant water reduction of the Lumin Purge and Trap Concentrator (PTC) Moisture Control System (MCS). The dry purge time, the sparge vessel size and the trap desorb time will be investigated. US EPA Method 524 was used to demonstrate the water reduction between moisture control systems. A Vocarb® 3000 (K trap) was used. Finally, the purge parameters were varied following US EPA Method 524.3. The time savings possible to a high volume Volatile Organic Analysis (VOA) laboratory will be discussed.

Moisture Control System (MCS)

The Lumin MCS eliminates the need for dry purging by removing more water from the purge flow path than other moisture control designs.

Figure 1 compares the water vapor transferred by both the Stratum PTC and Lumin PTC with a 1 min dry purge time. Figure 2 compares the amount of water transferred between the Stratum and the Lumin with varying dry purge times. Table 1 provides the % water reduction.

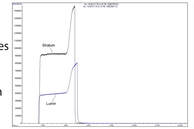

Figure 1: Comparison of the specific ion chromatogram of water (m/z 18) transferred to the GC/MS between the Stratum and the Lumin.

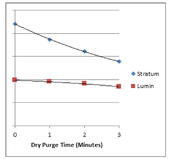

Figure 2: Comparison of the amount of water transferred to the GC/MS between the Stratum and the Lumin with various dry purge times.

Dry Purge Time	% Water Reduction
0	55
1	49
2	44
3	93

Table 1: % Water Reduction from the Stratum by the Lumin for various Dry Purge Times.

Sparge Vessel Size

USEPA Method 524 allows a 25 mL or 5 mL sparge vessel depending on which method is followed. The amount of water transferred to a GC/MS system was compared for both vessels.

Figure 3 is the comparison of this amount between the two sample volumes in their respective sparge vessels. This indicates that for the same purge volume of gas, the same amount of water is transferred to the GC/MS instrument.

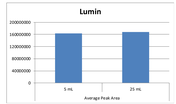

Figure 3: Comparison of the amount of water transferred to a GC/MS for various sparge vessel size with 440 mL of dry helium.

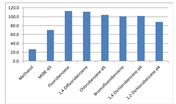

Figure 4: % of the 5 mL Sparge Vessel for the Various Internal Standards and Surrogate Standards, by Peak Area.

An equal amount of internal and surrogate standards were added to each sparge vessel. Figure 4 compares the amount of these standards transferred from a 25 mL sparge vessel versus the amount transferred from a 5 mL sparge vessel. Methyl tert butyl ether, a polar compound, had a significantly lower amount transferred from a 25 mL sparge vessel.

Trap Desorb Time

The desorb time is another variable that can be modified under US EPA Methods 524.3 and 524.4. The amount of water transferred with a desorb time from 0.5 to 4 minutes was tested.

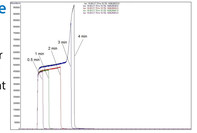

Figure 5: Comparison of the specific ion chromatogram of water (m/z 18) transferred to the GC/MS between the Stratum and the Lumin.

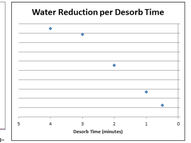

Figure 6: Graph of the Peak Area of the Water Transferred to the GC/MS per Trap Desorb Time.

Figure 5 compares the water mass ion chromatogram for the 5 different trap desorb times. Table 2 compares the amount of water transferred as a percent of the water amount at 4 minutes. Figure 6 graphs this amount of water.

Dry Purge Time	% Water Reduction	% Reduction
4	100	0
3	93	7
2	58	71
1	28	251
0.5	13	658

Table 2: Calculated Values of Water Reduction Based on the 4 minutes Trap Desorb Time.

A group of five 10 ppb standards were tested at each desorb time. The standard included 95 of the compounds typically in all 524 Methods, including internal and surrogate standards. Their peak areas were averaged and compared as a percent of the 0.5 minute desorb time.

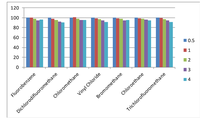

Figure 7: Comparison of the Peak Area of the Quantitation Ions for the First Six Gases and Fluorobenzene as a Percent of the 0.5 minute Trap Desorb Time.

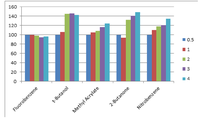

Figure 8: Comparison of the Peak Area of the Quantitation Ions for Four Polar Compounds and Fluorobenzene as a Percent of the 0.5 minute Trap Desorb Time.

All but four of the compounds fell within 20% of the 0.5 minute desorb time. These four are polar compounds that typically have poor purge efficiency. Figure 7 compares this percent of the first six gases to fluorobenzene to demonstrate the majority of the 96 compound. Figure 8 compares the four that had greater than 20% of the 0.5 minute desorb time.

Response Factor (RF) %RSD and MDL Values with Three Different Purge Parameters

The purge time and purge flow were varied and compared to the typical 524.2 Method parameters for a calibration curve from 0.5 ppb to 50 ppb. The calibration standard included compounds from Restek® Drinking Water VOA MegaMix, Oxygenates, Ketones and 502.2 Mixes.

The ketones mix compounds were present at 2.5 times the concentration of other compounds in the mix. The oxygenate compound, t-butanol, was 5 times the concentration of other compounds in the mix. The relative Response Factor (RF) for each VOC was calculated using the three 524.3 internal standards.

Seven of each 0.5 ppb and 5 ppb standards were prepared to calculate the Method Detection Limit (MDL). The Lumin PTC conditions that were varied are shown in Table 3 and the GC/MS conditions in Table 4.

The Relative Standard Deviation (RSD) of the Response Factor (RF), and MDL for the three different purge volumes are shown in Table 5.

Experimental Instrument Conditions

Standby	Low Volume	524.2	High Volume
Total Purge Volume	360 mL	440 mL	520 mL
Purge Time	4.5 min	11 min	5.2 min
Purge Flow	80 mL/min	40 mL/min	100 mL/min
Total Purge Time	4.5 min	11 min	5.2 min
Dry Purge Time	0 min	0 min	0 min
Desorb Time	1 min	4 min	1 min
Total Time	5.5 min	15 min	6.2 min

Table 3: Lumin and AQUATek 100 Conditions

Agilent 7890A Conditions	
Column	Rtx-VMS, 20 m x 0.18 mm, 1 µm Film, Helium – 0.8 mL/min
Oven Profile	35 °C, 2 min, 10 °C/min to 85 °C, 25 °C/min to 220 °C, 2 min hold
Inlet	150 °C, 10:01 Split, helium saver 20 mL/min after 4 min
Agilent 5975C Conditions	
Temp	Transfer Line 225 °C; Source 230 °C; Quad 150 °C
Scan	Range 35 to 300, Delay 0.6 min, Gain Factor 4

Table 4: Agilent 7890A GC / 5975C MS

Compound	Response Factor % RSD			MDL		
	360 mL	440 mL	520 mL	360 mL	440 mL	520 mL
Dichlorodifluoromethane	10.0	6.1	8.9	0.09	0.04	0.06
Chloromethane	18.1	12.4	13.0	0.08	0.09	0.08
Vinyl Chloride	4.0	2.7	6.6	0.11	0.13	0.07
Bromomethane	11.6	7.3	11.9	0.12	0.15	0.10
Chloroethane	5.1	3.4	5.3	0.14	0.17	0.17
Trichlorofluoromethane	6.0	3.9	5.0	0.07	0.08	0.06
Diethyl Ether	6.6	8.1	6.9	0.13	0.12	0.15
1,1-Dichloroethene	10.8	3.5	6.2	0.20	0.13	0.08
Carbon disulfide	6.4	4.8	6.7	0.08	0.09	0.04
Iodomethane	5.8	10.8	4.4	0.08	0.09	0.11
Allyl chloride	3.3	5.6	6.1	0.12	0.12	0.21
Methylene Chloride[1]	1.0000	0.9993	0.9998	0.25	0.28	0.17
Acetone[1,2]	0.9990	0.9997	0.9995	1.31	0.73	0.74
trans-1,2-Dichloroethene	4.3	5.9	4.0	0.08	0.10	0.10
MTBE-d3 (Surr)[3]	3.8	1.9	3.7	0.28	0.53	0.65
Methyl tert Butyl Ether	4.8	5.4	1.8	0.05	0.05	0.09
t-Butanol[4]	14.3	6.5	9.4	1.17	0.75	1.09
Diisopropyl ether	5.9	5.3	5.3	0.12	0.11	0.12
1,1-Dichloroethane	6.7	3.2	4.3	0.11	0.12	0.10
Acrylonitrile	15.3	12.0	7.5	0.18	0.28	0.21

Tables 5: Method 524.2

Compound	Response Factor % RSD			MDL		
	360 mL	440 mL	520 mL	360 mL	440 mL	520 mL
t-Butyl Ethyl Ether (ETBE)	7.4	6.1	6.7	0.07	0.07	0.09
cis-1,2-Dichloroethene	2.8	2.2	4.6	0.11	0.09	0.08
2,2-Dichloropropane	3.5	2.6	5.8	0.08	0.12	0.08
Bromochloromethane	8.7	2.7	6.6	0.22	0.14	0.11
Chloroform	7.7	2.2	5.7	0.09	0.06	0.05
Carbon Tetrachloride	4.3	2.2	6.1	0.06	0.11	0.09
Methyl Acrylate	19.7	6.7	12.5	0.28	0.09	0.19
Tetrahydrofuran	8.9	10.6	17.7	0.57	0.74	0.28
1,1,1-Trichloroethane	3.3	5.8	1.6	0.08	0.06	0.08
1,1-Dichloropropene	8.5	7.1	7.9	0.08	0.09	0.10
2-Butanone[2]	10.4	4.2	13.3	0.48	0.54	0.36
1-Chlorobutane	6.6	3.6	5.1	0.07	0.10	0.09
Benzene	2.9	3.4	2.6	0.04	0.05	0.06
Propionitrile[2]	16.1	8.7	9.7	1.04	0.93	1.10
Methacrylonitrile	8.1	5.5	6.8	0.18	0.22	0.16
t-Amyl Methyl Ether (TAME)	8.9	6.1	8.7	0.08	0.12	0.07
1,2-Dichloroethane	8.3	3.9	3.5	0.10	0.07	0.05
Trichloroethylene	7.4	7.8	8.7	0.09	0.17	0.08
Fluorobenzene (Surr)[3]	0.8	2.0	2.3			
t-Amyl Ethyl Ether (TAEE)	8.5	5.8	7.8	0.07	0.05	0.11
Dibromomethane	7.7	7.8	8.3	0.12	0.15	0.19
1,2-Dichloropropane	3.1	5.5	3.0	0.14	0.12	0.08
Bromodichloromethane	2.0	4.5	3.3	0.08	0.13	0.07
Methylmethacrylate	12.3	5.4	9.8	0.19	0.18	0.12
cis-1,3-Dichloropropene	8.4	4.9	6.6	0.17	0.13	0.12
Toluene	13.5	7.4	8.6	0.09	0.07	0.09
Chloroacetonitrile[6]	13.4	5.7	9.2	1.62	2.61	1.08
2-Nitropropane	19.5	11.6	13.4	0.75	0.62	0.38
1,1-Dichloro-2-propanone[2]	6.8	5.8	8.0	0.61	0.26	0.33
Tetrachloroethylene	5.3	7.1	1.9	0.06	0.07	0.10
Methyl Isobutyl Ketone[2]	10.9	7.1	11.5	0.46	0.24	0.33
trans-1,3-Dichloropropene	12.9	7.6	11.0	0.11	0.14	0.07
1,1,2-Trichloroethane	8.0	7.6	4.8	0.13	0.20	0.12
Ethyl Methacrylate	18.8	11.4	13.5	0.10	0.22	0.13
Dibromochloromethane	6.0	4.8	1.9	0.08	0.07	0.11
1,3-Dichloropropane	6.3	8.2	3.5	0.11	0.10	0.11
1,2-Dibromoethane	4.9	8.8	1.4	0.10	0.10	0.05
2-Hexanone[2]	13.3	8.9	13.5	0.35	0.57	0.17
Chlorobenzene	4.6	2.0	5.9	0.04	0.11	0.05
Ethylbenzene	15.3	7.4	11.8	0.06	0.17	0.08
1,1,1,2-Tetrachloroethane	4.7	5.3	2.3	0.07	0.16	0.10
m-, p-Xylene	17.5	11.5	16.1	0.08	0.31	0.09
o-Xylene	14.9	7.6	12.6	0.10	0.16	0.10
Styrene	22.1	11.7	20.2	0.04	0.13	0.09
Bromoform	3.1	8.6	4.5	0.13	0.14	0.08
Isopropylbenzene	17.3	9.1	15.1	0.05	0.15	0.02
Bromofluorobenzene (Surr)[3]	2.8	7.4	1.8			
Bromobenzene	6.5	6.1	4.0	0.07	0.13	0.05
n-Propylbenzene	12.9	8.5	9.7	0.04	0.13	0.06
1,1,2,2-Tetrachloroethane	11.8	5.7	8.3	0.07	0.07	0.05
2-Chlorotoluene	10.1	10.8	5.7	0.06	0.18	0.05
1,2,3-Trichloropropane	8.6	2.9	6.5	0.15	0.17	0.06
1,3,5-Trimethylbenzene	18.4	8.1	14.5	0.04	0.11	0.02
trans-1,4-Dichloro-2-butene	6.7	5.5	3.7	0.27	0.20	0.10
4-Chlorotoluene	12.9	7.3	9.0	0.04	0.12	0.03
tert-Butylbenzene	11.3	6.4	8.2	0.04	0.12	0.04
Pentachloroethane	8.4	4.7	7.5	0.08	0.17	0.08
1,2,4-Trimethylbenzene	19.7	9.3	17.2	0.05	0.14	0.05
sec-Butylbenzene	16.8	8.4	13.4	0.04	0.12	0.05
4-Isopropyltoluene	20.0	8.9	17.1	0.05	0.11	0.06
1,3-Dichlorobenzene	1.9	3.1	2.3	0.07	0.10	0.06
1,4-Dichlorobenzene	2.3	2.7	2.7	0.05	0.11	0.04
n-Butylbenzene	16.7	8.6	14.2	0.04	0.07	0.06
Hexachloroethane	11.7	7.9	9.3	0.10	0.14	0.09
1,2-Dichlorobenzene-d4 (Surr)[3]	4.7	1.3	3.4			
1,2-Dichlorobenzene	3.6	2.6	3.1	0.06	0.06	0.08
1,2-Dibromo-3-chloropropane	13.2	4.9	9.2	0.19	0.08	0.12

Tables 5: Method 524.2 cont'd

Compound	Response Factor % RSD			MDL		
	360 mL	440 mL	520 mL	360 mL	440 mL	520 mL
Nitrobenzene[2]	24.9	22.2	20.9	1.32	1.63	1.92
1,2,4-Trichlorobenzene	8.3	3.7	7.3	0.07	0.05	0.08
Hexachlorobutadiene	7.7	6.3	5.6	0.13	0.12	0.15
Naphthalene	14.4	8.3	12.2	0.06	0.04	0.09
1,2,3-Trichlorobenzene	7.6	7.6	7.3	0.11	0.08	0.09

Tables 5: Method 524.2 cont'd

1 – Laboratory Background, Linear Curve used
2 – Ketone Mix Compound, Calibration Curve from 1.25 ppb to 125 ppb
3 – Surrogate/Internal Standard at 12.5 ppb
4 – Calibration Curve from 2.5 ppb to 250 ppb
5 – Peak not detected below 1 ppb for 360 mL Purge Curve, MDL calculated from 5 ppb standard
6 – Peak not detected below 5 ppb for 360 mL curve, or 2 ppb for 440 mL and 520 mL curve, MDL calculated from 5 ppb standard
7 – Peak not detected below 2 ppb for all 3 Calibration Curves, MDL calculated from 5 ppb standard

Conclusion

The Lumin MCS reduces the amount of water vapor transferred to a GC/MS system by at least 50% over current moisture control designs when no dry purge is used. This effectively reduces the purge and trap cycle time by at least 1 minute.

The calibration data for response factor %RSD for a calibration curve from 0.5 ppb to 50 ppb indicates similar values for all compounds studied. The MDL for all compounds were also similar. By varying the purge flow rate and volume, the purge portion of the purge and trap cycle time can be cut in half. Consequently more samples can be processed during a typical calibration cycle.

References

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3. Munch, D.J.; Wendelken, S.C. PhD. US EPA Method 524.4 - Measurement of Purgeable Organic Compounds in Water by Gas Chromatography/Mass Spectrometry Using Nitrogen Purge Gas, Revision 4.1; U.S. Environmental Protection Agency - Office of Water: Cincinnati, Oh, 2013

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