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Validation of USEPA Method 524.2 Using a Stratum PTC and the New AQUATek 100 Autosampler

Application Note

Abstract

Automation is the key to increasing laboratory productivity and minimizing costs. It is equally important to prove that the changes in technology to achieve these results may be done without sacrificing sample integrity or data quality. The AQUATek 100 is a new vial autosampler which features many new benefits to help increase productivity, minimize carryover, and provide more flexibility to the end user in terms of maintaining sample integrity and servicing the unit. The data presented in this application note was provided by a large drinking water facility and validates USEPA Method 524.2[1] with regard to reproducibility, Surrogate percent recovery, and Method Detection Limits (MDLs) using a Stratum Purge and Trap Concentrator (PTC) and the new AQUATek 100 Vial Autosampler interfaced to an Agilent 7890A GC and a 5975C Triple Axis Detector.

Figure 1: AQUATek 100

Introduction

The AQUATek 100 is a liquid autosampler that interfaces to a purge and trap concentrator for measuring Volatile Organic Compounds (VOCs) in drinking water, groundwater and surface water. It includes a 100-sample position carousel for standard 40mL vials and is removable from the drive assembly for easy vial loading. It also includes a water reservoir to provide auto-blanking which frees up vial space in the carousel increasing sample throughput. It comes standard with a vial chiller tray which allows for sample cooling to 10°C which is now a requirement for the new USEPA Method 524.3[2] for preserving sample integrity.

In today's environment, many analysts are being required to troubleshoot and service their own instruments. The system has a Plumbing Access Compartment (PAC) which is a pullout drawer for easy access to the sample loop, plumbing, tubing, valves, electronic boards, and other hardware components.

In this study, a linear calibration was performed and the percent Relative Standard Deviation (%RSD) and Method Detection Limits (MDLs) were determined for a target list of analytes. A 25mL purge volume was used and the requirements, conditions and specifications according to EPA Method 524.2[1] were all met.

Experimental-Instrument Conditions

The Stratum PTC and AQUATek 100 were configured with an Agilent 7890A GC and a 5975C Triple Axis Detector for this study. The column used was an HP-VOC 30m x 0.20mm x 1.12µm (Agilent Technologies P/N 19091R-303). The columns were configured with an ultra large (6mm) inert draw-out lens (Agilent Technologies P/N G2589-20045). A larger draw-out plate was chosen due to better performance for use with Purge and Trap as found in a previous application note. A 1.0mm ID Restek 1mm split 20973-214.5 inlet liner was also employed for this study. The analytical trap used was a Vocarb 3000 adsorbent trap. The column flow was 0.47mL/min and all analyses were performed using a 30:1 split ratio and a septum purge of 3mL/min. Tables 1 and 2 display the GC/MS parameters while Table 3 displays the Stratum PTC and AQUATek 100 conditions.

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GC Parameters	
GC:	Agilent 7890A
Column:	HP-VOC 30m x 0.200mm x1.12um
Oven Program:	35°C for 4 min,8°C/min to 220°C for 0 min, 27.125 min runtime
Inlet:	220°C
Column Flow	0.47054mL/min
Gas:	Helium
Split	30:1
Pressure:	8.75 psi
Inlet:	Split/Splitless

MSD Parameters	
MSD:	5975C Triple Axis Detector
Source:	230°C
Quad:	150°C
Solvent Delay:	2.34 min
Scan Range:	m/z 35-260
Scans:	5.98 scans/sec
Threshold:	500
MS Transfer Line Temp.:	220°C

Tables 1 & 2: GC and MSD Parameters for the DB-624 Column

Stratum PTC and AQUATek 100 Parameters Water Parameters			
Variable	**Value**	**Variable**	**Value**
Pressurize Time	0.95 min	Preheat Time	1.00 min
Sample Transfer Time	1.25 min	Preheat Temp	40°C
Rinse Loop Time	0.85 min	Purge Time	11.00
Sweep Needle Time	0.35 min	Purge Temp	0°C
Bake Rinse	On	Purge Flow	40mL/min
Number of Bake Rinses	1	Dry Purge Time	2.00 min
Bake Rinse Drain Time	0.60 min	Dry Purge Temp	30°C
Presweep Time	0.35 min	Dry Purge Flow	100mL/min
Valve Oven Temp	150°C	GC Start	Start of Desorb
Transfer Line Temp	150°C	Desorb Preheat Temp	245°C
Sample Mount Temp	45°C	Desorb Time	2.00 min
Purge ready Temp	40°C	Desorb Temp	250°C
Condenser Ready Temp	35°C	Drain Flow	200mL/min
Condenser Purge Temp	35°C	Bake Time	7.00 min
Standby Flow	10mL/min	Bake Temp	270°C
Sparge Vessel Heater	OFF	Condenser Bake Temp	200°C
Pre-Purge Time	0.50 min	Bake Flow	250mL/min
Pre-Purge Flow	40mL/min		

Table 3: Stratum PTC and AQUATek 100 Parameters

Stratum PTC Parameters are in Blue

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Calibration

To evaluate the system's linearity, a 5-point calibration curve was performed at 0.5ppb, 1.0ppb, 2.0ppb, 5.0ppb, and 10ppb. A target list of analytes from EPA Method 524.2 in addition to the oxygenate gasoline additives were evaluated. Due to the poor purge efficiency of 4 specific compounds, a higher calibration range was used and is listed in Table 4.

The AQUATek 100 stores the Internal Standards and Surrogates in two- 15mL amber glass vessels to prevent transmission of UV radiation. The vessels are sealed with a PEEK™ cap to prevent adsorption and contamination of the standard solution. Each standard vessel can deliver volumes of 1, 2, 5, 10, or 20µL to each sample and delivers the exact amount minimizing waste and reducing overall costs for standards. The vessels are under constant pressure which may extend the life of the standard for 2-3 months.

For this study, the required Internal Standard (IS) and Surrogates (SS) were prepared in methanol at a concentration of 62.5ppm. This was then transferred to the standard vessel on the AQUATek 100 and a 2µL aliquot was added to each sample for a final concentration of 2.5ppb.

Compounds	Calibration Range
Tert-Butyl Alcohol	2.5-50ppb
Methyl Ethyl Ketone	5.0-100ppb
Tetrahydrofuran	5.0-100ppb
4-Methyl-2-Pentanone	5.0-100ppb
All Other Compounds	0.5-10ppb

Table 4: Calibration Range for Target Analytes

The calibration data was processed using Agilent Chemstation software. The relative response factors were evaluated for linearity and %RSD, and the calibration results for all compounds are listed in Table 5. Three calibration curves were run over several weeks and the average %RSD for each curve was 6.48%, 7.06%, and 6.82% respectively. Over 600 samples were run and after cleaning the source, another calibration curve was processed and all analytes were <10%RSD. A chromatogram of the 5ppb calibration standard is shown in Figure 1.

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Compound	%RSD	Compound	%RSD
fluorobenzene (IS)	N/A	toluene	4.24
chlorodifluoromethane	6.00	trans-1,3-dichloropropene	12.52
dichlorodifluoromethane	4.57	1,1,2-trichloroethane	2.16
chloromethane	5.06	1,3-dichloropropane	5.12
vinyl chloride	15.08	dibromochloromethane	9.28
bromomethane	6.09	tetrachloroethene	3.75
chloroethane	4.91	chlorobenzene	4.96
trichlorofluoromethane	3.24	1,1,1,2-tetrachloroethane	6.80
1,1-dichloroethene	4.70	ethyl benzene	8.61
1,1,2-Trichlorotrifluoromethane	3.64	m,p-xylene	8.40
tert-butyl-alcohol (TBA)	15.33	styrene	13.74
methylene chloride	3.27	o-xylene	7.29
methyl-tert-butyl-ether (MTBE)	3.30	bromoform	9.17
trans-1,2-dichloroethene	2.60	1,1,2,2-tetrachloroethane	7.08
1,1-dichloroethane	2.37	4-bromofluorobenzene (surr)	3.07
di-isopropyl ether (DIPE)	4.82	isopropylbenzene	9.43
methylethylketone (MEK)	6.85	1,2,3-trichloropropane	6.29
cis-1,2-dichloroethene	2.64	bromobenzene	5.55
2,2-dichloropropane	6.91	n-propylbenzene	8.22
ethyl-tert-butyl-ether (ETBE)	5.32	2-chlorotoluene	4.46
chloroform	2.48	4-chlorotoluene	7.87
bromochloromethane	5.65	1,3,5-trimethylbenzene	12.32
tetrahydrofuran (THF)	5.28	tert-butylbenzene	10.30
1,1,1-trichloroethane	4.18	1,2,4-trimethylbenzene	14.31
1,2-dichloroethane	2.42	sec-butylbenzene	11.27
1,1-dichloropropene	5.29	1,3-dichlorobenzene	7.66
carbon tetrachloride	5.48	4-isopropyltoluene	14.08
benzene	3.08	1,4-dichlorobenzene	8.03
tert-amyl-methyl-ether (TAME)	4.86	1,2-dichlorobenzene-d4 (surr)	3.64
trichloroethene	3.78	1,2-dichlorobenzene	6.75
1,2-dichloropropane	3.65	n-butylbenzene	12.22
dibromomethane	2.53	1,2,4-trichlorobenzene	9.71
bromodichloromethane	5.27	naphthalene	16.09
4-methyl-2-pentanone	7.82	hexachlorobutadiene	15.56
cis-1,3-dichloropropene	9.37	1,2,3-trichlorobenzene	9.72

Table 5: %RSDs from Calibration Curve

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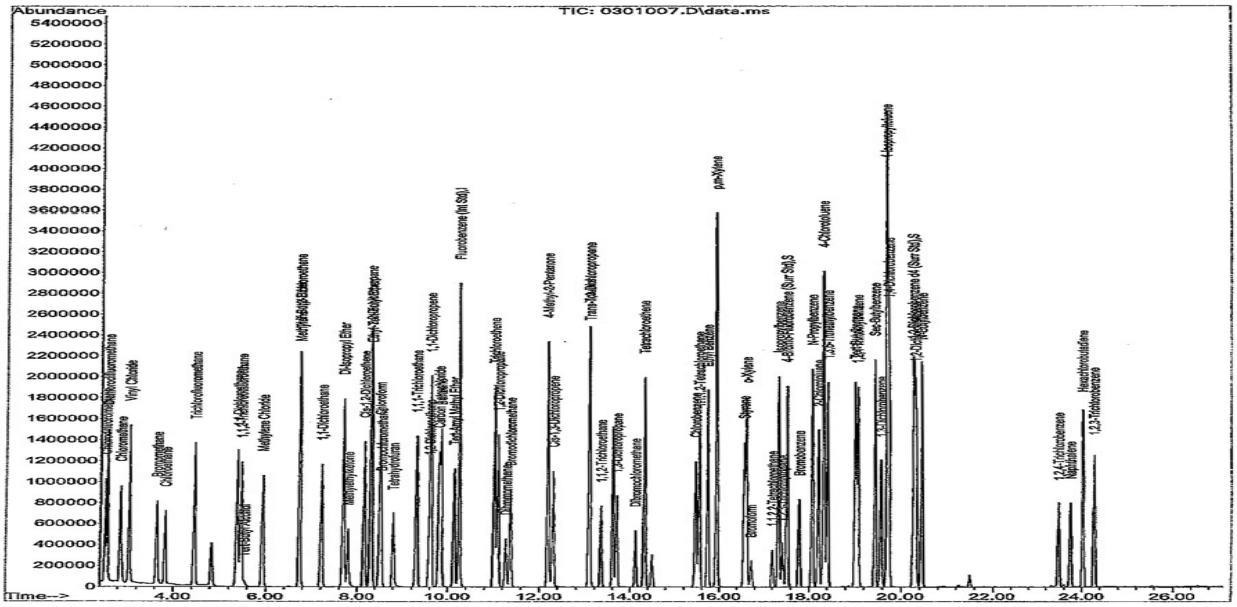

Figure 1: Total Ion Chromatogram of a USEPA Method 524.2 5ppb Calibration Standard

Minimum Detection Limits

MDLs and %recovery were evaluated over a period of 8 days by running seven replicates at the lowest concentration level for individual compounds (Table 6). This data was calculated using a 99% confidence level and is shown in Table 7.

Compounds	MDL True Concentration
Tert-Butyl Alcohol	2.5ppb
Methyl Ethyl Ketone	5.0ppb
Tetrahydrofuran	5.0ppb
4-Methyl-2-Pentanone	5.0ppb
Benzenes/Toluene	0.25ppb
All Other Compounds	0.5-10ppb

Table 6: MDL Concentration for Target Analytes

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Analyte	True Conc. µg/L	Mean Conc. µg/L	% Recovery	Standard Deviation SD µg/L	MDL µg/L
chlorodifluoromethane	0.50	0.49	97	0.034	0.11
dichlorodifluoromethane	0.50	0.50	99	0.045	0.14
chloromethane	0.50	0.48	96	0.041	0.13
vinyl chloride	0.50	0.46	92	0.037	0.12
bromomethane	0.50	0.49	98	0.035	0.11
Chloroethane	0.50	0.51	102	0.032	0.10
trichlorofluoromethane	0.50	0.53	106	0.041	0.13
1,1-dichloroethene	0.50	0.52	104	0.029	0.09
1,1,2-Trichlorotrifluoromethane	0.50	0.54	109	0.046	0.14
tert-butyl-alcohol (TBA)	2.50	2.78	111	0.224	0.70
methylene chloride	0.50	0.55	109	0.040	0.12
methyl-tert-butyl-ether (MTBE)	0.50	0.49	99	0.040	0.13
trans-1,2-dichloroethene	0.50	0.52	103	0.043	0.13
1,1-dichloroethane	0.50	0.52	105	0.035	0.11
di-isopropyl ether (DIPE)	0.50	0.50	99	0.043	0.13
methylethylketone (MEK)	5.00	4.93	99	0.339	1.06
cis-1,2-dichloroethene	0.50	0.52	105	0.049	0.15
2,2-dichloropropane	0.50	0.52	103	0.036	0.11
ethyl-tert-butyl-ether (ETBE)	0.50	0.49	99	0.034	0.11
chloroform	0.50	0.53	106	0.043	0.13
bromochloromethane	0.50	0.53	106	0.044	0.14
tetrahydrofuran (THF)	0.50	4.79	96	0.301	0.95
1,1,1-trichloroethane	0.50	0.53	105	0.036	0.11
1,2-dichloroethane	0.50	0.54	108	0.037	0.12
1,1-dichloropropene	0.50	0.50	100	0.034	0.11
carbon tetrachloride	0.50	0.52	103	0.036	0.11
benzene	0.25	0.26	105	0.021	0.07
tert-amyl-methyl-ether (TAME)	0.50	0.50	99	0.042	0.13
trichloroethene	0.50	0.52	105	0.040	0.12
1,2-dichloropropane	0.50	0.52	104	0.043	0.14
dibromomethane	0.50	0.53	105	0.044	0.14
bromodichloromethane	0.50	0.52	104	0.040	0.13
4-methyl-2-pentanone	5.00	4.71	94	0.356	1.12
cis-1,3-dichloropropene	0.50	0.49	99	0.032	0.10
toluene	0.25	0.25	100	0.016	0.05
trans-1,3-dichloropropene	0.50	0.48	95	0.035	0.11
1,1,2-trichloroethane	0.50	0.53	106	0.053	0.17

Table 7: MDLs and % Recovery for Target Analytes

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Analyte	True Conc. µg/L	Mean Conc. µg/L	% Recovery	Standard Deviation SD µg/L	MDL µg/L
1,3-dichloropropane	0.50	0.51	101	0.042	0.13
dibromochloromethane	0.50	0.51	101	0.029	0.09
tetrachloroethene	0.50	0.53	107	0.035	0.11
chlorobenzene	0.25	0.25	102	0.020	0.06
1,1,1,2-tetrachloroethane	0.50	0.51	101	0.044	0.14
ethyl benzene	0.25	0.23	93	0.011	0.03
m,p-xylene	0.50	0.44	87	0.025	0.08
styrene	0.25	0.22	87	0.022	0.07
o-xylene	0.25	0.22	89	0.014	0.04
bromoform	0.50	0.50	101	0.046	0.14
1,1,2,2-tetrachloroethane	0.50	0.53	107	0.045	0.14
isopropylbenzene	0.25	0.22	89	0.015	0.05
1,2,3-trichloropropane	0.50	0.50	100	0.025	0.08
bromobenzene	0.25	0.25	101	0.017	0.05
n-propylbenzene	0.25	0.22	90	0.014	0.04
2-chlorotoluene	0.25	0.23	93	0.016	0.05
4-chlorotoluene	0.50	0.46	91	0.026	0.08
1,3,5-trimethylbenzene	0.25	0.22	90	0.011	0.04
tert-butylbenzene	0.25	0.22	88	0.008	0.03
1,2,4-trimethylbenzene	0.25	0.21	85	0.014	0.04
sec-butylbenzene	0.25	0.22	87	0.011	0.03
1,3-dichlorobenzene	0.25	0.24	95	0.013	0.04
4-isopropyltoluene	0.50	0.43	86	0.028	0.09
1,4-dichlorobenzene	0.50	0.47	95	0.027	0.08
1,2-dichlorobenzene	0.50	0.49	99	0.035	0.11
n-butylbenzene	0.25	0.23	91	0.012	0.04
1,2,4-trichlorobenzene	0.25	0.23	91	0.021	0.07
naphthalene	0.50	0.42	85	0.048	0.15
hexachlorobutadiene	0.50	0.47	93	0.027	0.08
1,2,3-trichlorobenzene	0.50	0.47	93	0.044	0.14

Table 7: MDLs and % Recovery for Target Analytes (cont.)

Surrogate Percent Recovery

The %recovery for all surrogates must be maintained at ±30% over a period of time according to Section 9.4 of EPA Method 524.2. The 4-bromofluorobenzene and 1,4-dichlorobenzene-d4 were evaluated over a period of 10 days and 224 samples showing an average consistent recovery of 93.25% and 92.97% respectively. This indicates that the AQUATek 100 is very accurate in the amount of standard delivered to each sample and reproducible over time.

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Optional pH Module

A pH sensing probe option will enable the purge and trap system to measure and record pH values for all samples in the schedule (Figure 2).

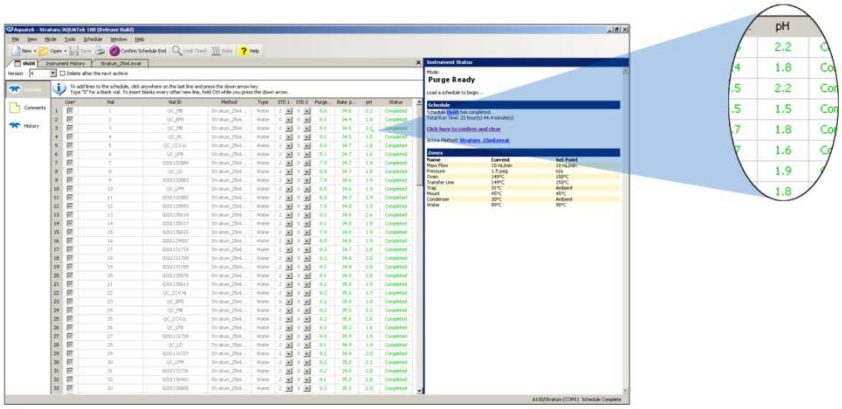

Figure 2: Schedule with pH Values Shown

Figure 3: pH Probe

Conclusions

The AQUATek 100 provides many enhancements to improving laboratory productivity while maintaining sample integrity and high quality data. Analytically, the AQUATek 100 meets or exceeds the cleanliness, reproducibility, and accuracy specifications required in a vial autosampler.

References

1. USEPA Method 524.2, Measurement of Purgeable Organic Compounds in Water By Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS), Revision 4.1, 1995.
2. USEPA Method 524.3, Measurement of Purgeable Organic Compounds in Water By Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS), Version 1.0, June 2009.

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