Trace Analysis of Volatile and Semi-volatile Organic Compounds in Water Produced from a Thermo Scientific Barnstead Genpure Pro UV Water Purification System

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Application Note

Key Words

Ultrapure Water, Thermo Scientific Barnstead, GenPure, ASTM Type 1, volatile organic compounds, VOC, semi-volatile compounds, S-VOC, TOC, Total Organic Carbon

Abstract

Laboratory water produced by a Thermo Scientific™ Barnstead™ GenPure™ Pro UV water purification system was analyzed for volatile organic compounds (VOC) and semi-volatile compounds (S-VOC).

Introduction

Volatile and semi-volatile organic compounds are a group of organic contaminates found in drinking water supplies as well as waste water. These compounds can come from agricultural run off, plastic food containers and piping as well as medical and pharmaceutical by-products. Phthalates, a type of semi-volatile organic, are especially of interest because of their potential endocrine disruption capabilities and potential harm during human development.[1] Fortunately, technological advances in analytical instrumentation have increased the detection sensitivity of organic compounds to trace levels in the ppt (part per trillion) range. With the ever increasing demands, it is important that the ultrapure water used in trace organics testing do not introduce baseline interference. To help reduce this risk, it is important to use reagent grade water from an ultrapure water system designed to produce high purity water with ultralow VOC and SVOC levels.

Good techniques and lab practices need to be employed to help achieve consistent trace level results. It is recommended that sampling and testing should be done in a clean, open air laboratory or clean room to prevent possible airborne or other environmental contamination. Contamination could also be possible during the process of collecting, storing and transporting the samples. Also important is the proper maintenance of the ultrapure water system, including regular cartridge and filter replacements, disinfection as well as consistent recirculation of the water within the system to stabilize purity. Before sample collection, short flushes at the dispenser will help reduce the risk of contamination at point of use. Even with adherence to these details, results may vary from lab to lab.

The ultrapure water used in sensitive organic analysis should exceed the ASTM D1193-06 Type 1 specification of 18.0 Megohm-cm resistivity and <50 ppb total organic carbon (TOC)[2]. Customer demands often require TOC levels to be < 5 ppb. To achieve this ultralow level, the GenPure Pro UV system uses a dual wavelength ultraviolet (UV) light with 185/254 nm wavelength to catalyze the breakdown of organic compounds, and 254 nm wavelength to also destroy microorganisms. The by-products of the oxidation reactions are CO_2 and H_2O. The CO_2 is easily removed by the high purity DI cartridge in the next step of the purification process. This cartridge utilizes high quality, semiconductor grade resins to attract even the weakest ionic impurities from the water and any that were released from the UV oxidation process. This resin was specifically chosen for maximum purity and low TOC[2]. This process will reduce the TOC level of the ultrapure water to 1-5 ppb. Due to the importance of a properly working UV lamp, the GenPure Pro UV water system is engineered to continuously monitor the use of the UV bulb and will alert the user if it needs to be replaced. The final step of the system is a 0.2 micron absolute point of use final filter. This provides an effective means to protect product water from any particulate impurities or microorganisms. Every material in the water system that comes into contact with the water was carefully selected to protect the purity of the water. The wetted parts in a GenPure water purification system were selected to prevent leaching of even trace amounts of organics into the ultrapure water.

Testing for trace VOC and S-VOC was conducted on the GenPure Pro UV system. Results found for GenPure Pro UV system would be expected to be similar in the

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entire family of GenPure systems, which also includes the GenPure xCAD Plus UV and standard GenPure UV systems. All of these systems have the same feed water requirements, basic flow path, UV lamp, high purity DI cartridge and dispense water through a 0.2 micron final filter. The GenPure systems require a pretreated water supply of < 2 µS/cm conductivity and maximum of 50 ppb TOC. Testing was conducted using Thermo Scientific™ Pacific™ TII 20 UV Type 2 water system to supply feed water. To challenge the system, the GenPure Pro UV system was connected to reverse osmosis (RO) water, to determine how the change in feed water impacts the unit's ability to remove organics to below detection limits.

The U.S. Environmental Protection Agency (EPA) established the methods 524.2 and 525.2 for monitoring organic compounds, VOC and S-VOC, in drinking water supplies. The GenPure Pro UV system was tested based on these EPA methods in controlled conditions.

Methods

Testing for volatile and semi-volatile organic compounds from the GenPure Pro UV system using pre-treated feed water

Clean techniques were used to reduce the chance of environmental contamination. A Pacific TII 20 UV system with a Thermo Scientific 60L reservoir was used to pre-treat the feed water for the GenPure UV Pro system. Both systems were set up according to the operational manuals, as shown in Figure 1[5, 6]. A Sievers™ 900 TOC analyzer was used to verified TOC levels before sampling. The entire system was put into operation and the first fill of the 60 L reservoir was discarded. For consistent TOC levels in the Pacific TII UV product water, the system was programmed to continuously recirculate from the unit to the storage tank. The Pacific TII tank was filled and drained two more times after which the displayed purity was 16.2 Megohm-cm resistivity and tested at 46 ppb TOC. The GenPure unit rinsed with one 60 L tank of Pacific TII water and was placed in nonstop recirculation mode until system's resistivity was stabilized at 18.2 Megohm-cm resistivity at 25°C and TOC was recorded at 6.42 ppm before taking samples and several liters of water were dispensed through the final filter. The GenPure Pro UV system was set to dispense continuously for hands free sampling.

Bottles used to collect the samples were supplied by TestAmerica™, Inc., Savannah, GA as described below. After a 0.2 L rinse from GenPure Pro UV dispenser, VOC samples were collected in three 46 mL VOA glass bottles that supplied with HCl. S-VOC samples were collected in two 1 amber L bottles. Each S-VOC sample bottle included a small vial of HCL which was added to the sample and mixed. Bottles were refrigerated at 4 °C then shipped overnight in a cooler to TestAmerica labs per their standard procedures. VOC tests were conducted per EPA method 524.2 using GC-MS; S-VOC samples were tested per EPA method 525.2 using GC-MS.

Challenge:

The GenPure Pro UV system was challenged with RO feed water. The Pacific TII system tank was drained and the high purity DI cartridge was bypassed so only RO water would collect in the storage tank. The tank was then filled and drained three times. To ensure the RO water was completely fed through the GenPure Pro UV, the system was flushed three times followed by a 5 L dispense and two-hour recirculation. Before sampling, the system was flushed twice followed by 0.2 L dispense. The RO water quality was recorded at 0.11 Megohm-cm on the display. TOC was recorded at 110 ppb as tested with Sievers 800 TOC Analyzer by Chemtrace, Fremont, CA.

Figure 1. Diagram of a Pacific TII 20 UV system with a 60 L storage reservoir feeding a GenPure Pro UV water system.

Table 1: Analysis of VOC compounds sampled from GenPure Pro UV system's product water tested per EPA Method 524.2 using GC-MS with Type 2 feed water and challenged with RO feed water. Results reported as < are below the limit of detection.

VOC Compounds	Method Detection Limit (ppb)	GenPure Pro UV System with Type 2 Feed Water (ppb)	GenPure Pro UV System with Challenge Feed Water (ppb)
1,1,1,2- Tetrachloroethane	<0.076	<0.076	<0.076
1,1,1-Trichloroethane	<0.058	<0.058	<0.058
1,1,2,2- Tetrachloroethane	<0.079	<0.079	<0.079
1,1,2-Trichloroethane	<0.10	<0.10	<0.10
1,1-Dichloroethane	<0.054	<0.054	<0.054
1,1-Dichloroethene	<0.058	<0.058	<0.058
1,1-Dichloropropene	<0.057	<0.057	<0.057
1,2,3-Trichloropropane	<0.086	<0.086	<0.086
1,2,4-Trichlorobenzene	<0.059	<0.059	<0.059
1,2-Dichlorobenzene	<0.052	<0.052	<0.052
1,2-Dichloroethane	<0.063	<0.063	<0.063
1,2-Dichloropropane	<0.028	<0.028	<0.028
1,3-Dichlorobenzene	<0.051	<0.051	<0.051
1,3-Dichloropropane	<0.10	<0.10	<0.10
1,4-Dichlorobenzene	<0.043	<0.043	<0.043
2,2-Dichloropropane	<0.066	<0.066	<0.066
2-Chlorotoluene	<0.049	<0.049	<0.049
4-Chlorotoluene	<0.073	<0.073	<0.073
Benzene	<0.051	<0.051	<0.051
Bromobenzene	<0.082	<0.082	<0.082
Bromoform	<0.057	<0.057	<0.057
Bromomethane	<0.083	<0.083	<0.083
Carbon tetrachloride	<0.081	<0.081	<0.081
Chlorobenzene	<0.072	<0.072	<0.072
Chlorodibromomethane	<0.068	<0.068	<0.068
Chloroethane	<0.10	<0.10	<0.10
Chloroform	<0.056	<0.056	0.12
Chloromethane	<0.084	<0.084	<0.084
cis-1,2-Dichloroethene	<0.051	<0.051	<0.051
cis-1,3-Dichloropropene	<0.10	<0.10	<0.10
Dibromomethane	<0.095	<0.095	<0.095
Dichlorobromomethane	<0.052	<0.052	<0.052
Ethylbenzene	<0.051	<0.051	<0.051
Methyl tert-butyl ether	<0.079	<0.079	<0.079
Methylene Chloride	<0.068	<0.068	<0.068
m-Xylene & p-Xylene	<0.099	<0.099	<0.099
o-Xylene	<0.051	<0.051	<0.051
Styrene	<0.052	<0.052	<0.052
Tetrachloroethene	<0.065	<0.065	<0.065
trans-1,2-Dichloroethene	<0.071	<0.071	<0.071
trans-1,3-Dichloropropene	<0.17	<0.17	<0.17
Trichloroethene	<0.055	<0.055	<0.055
Vinyl chloride	<0.051	<0.051	<0.051

Table 2: Analysis of S-VOC compounds sampled from GenPure Pro UV system's product water tested per EPA Method 525 using GC-MS with Type 2 feed water and challenged with RO feed water. Results shown in parentheses were for second set of tests if tested levels were different from first run. Results reported as < are below the limit of detection.

S-VOC Compounds	Method Detection Limit (ppb)	GenPure Pro UV System with Type 2 Feed Water (ppb)	GenPure Pro UV System with Challenge Feed Water (ppb)
2,2',3',4,6- Pentachlorobiphenyl	<0.050	<0.050	<0.050
2,2',4,4'- Tetrachlorobiphenyl	<0.027	<0.027	<0.027
2,3-Dichlorobiphenyl	<0.019	<0.019	<0.019
2,4,5-Trichlorobiphenyl	<0.033	<0.033	<0.033
2,4-Dinitrotoluene	<0.053	<0.053	<0.053
2,6-Dinitrotoluene	<0.041	<0.041	<0.041
2-Chlorobiphenyl	<0.039	<0.039	<0.039
4,4'-DDD	<0.030	<0.030	<0.030
4,4'-DDE	<0.019	<0.019	<0.019
Acenaphthene	<0.039	<0.039	<0.039
Acenaphthylene	<0.019	<0.019	<0.019
Acetochlor	<0.041	<0.041	<0.041
Alachlor	<0.032	<0.032	<0.032
Aldrin	<0.037	<0.037	<0.037
alpha-BHC	<0.039	<0.039	<0.039
alpha-Chlordane	<0.040	<0.040	<0.040
Anthracene	<0.022	<0.022	<0.022
Atrazine	<0.021	<0.021	<0.021
Benzo[a]anthracene	<0.019	<0.019	<0.019
Benzo[a]pyrene	<0.028	<0.028	<0.028
Benzo[b]fluoranthene	<0.021	<0.021	<0.021
Benzo[g,h,i]perylene	<0.044	<0.044	<0.044
Benzo[k]fluoranthene	<0.034	<0.034	<0.034
Bis(2-ethylhexyl) phthalate	<0.58	<0.58	<0.58
Bromacil	<0.024	<0.024	<0.024
Butachlor	<0.031	<0.031	<0.031
Butyl benzyl phthalate	<0.043	<0.043	0.1*
Butylate	<0.032	<0.032	<0.032
Chlorobenzilate	<2.8	<2.8	<2.8
Chloroneb	<0.029	<0.029	<0.029
Chlorothalonil	<0.019	<0.019	<0.019
Chlorpropham	<0.036	<0.036	<0.036
Chlorpyrifos	<0.044	<0.044	<0.044
Chrysene	<0.019	<0.019	<0.019
cis-Permethrin	<0.024	<0.024	<0.024
Cycloate	<0.021	<0.021	<0.021
DCPA	<0.028	<0.028	<0.028
delta-BHC	<0.035	<0.035	<0.035
Di(2-ethylhexyl)adipate	<0.58	<0.58	<0.58
Dibenz(a,h)anthracene	<0.060	<0.060	<0.060
Dichlorvos	<0.058	<0.058	<0.058
Dieldrin	<0.044	<0.044	<0.044
Diethyl phthalate	<0.019	<0.019	0.02*

Table continues on next page.

* Compound was found in Trip Blank and sample and values were estimated.

Table 2 CONTINUED: Analysis of S-VOC compounds sampled from GenPure Pro UV product water tested per EPA Method 525 using GC-MS with Type 2 feed water and challenged with RO feed water. Data in the column for GenPure Pro UV system with Type 2 feed water are shown once if results for the two sample sets were identical. Results reported as < are below the limit of detection.

S-VOC Compounds	Method Detection Limit (ppb)	GenPure Pro UV System with Type 2 Feed Water (ppb)	GenPure Pro UV System with Challenge Feed Water (ppb)
Dimethyl phthalate	<0.021	<0.021	<0.021
Di-n-butyl phthalate	<0.039	0.047*	0.05*
Diphenamid	<0.023	<0.023	<0.023
Endosulfan I	<0.085	<0.085	<0.085
Endosulfan II	<0.083	<0.083	<0.083
Endosulfan sulfate	<0.049	<0.049	<0.049
Endrin	<0.070	<0.070	<0.070
Endrin aldehyde	<0.14	<0.14	<0.14
EPTC	<0.024	<0.024	<0.024
Ethoprop	<0.030	<0.030	<0.030
Etridiazole	<0.054	<0.054	<0.054
Fenarimol	<1.9	<1.9	<1.9
Fluoranthene	<0.019	<0.019	<0.019
Fluorene	<0.019	<0.019	<0.019
Fluridone	<0.060	<0.060	<0.060
gamma-BHC (Lindane)	<0.079	<0.079	<0.079
gamma-Chlordane	<0.044	<0.044	<0.044
Heptachlor	<0.053	<0.053	<0.053
Heptachlor epoxide	<0.18	<0.18	<0.18
Hexachlorobenzene	<0.040	<0.040	<0.040
Hexachlorocyclopentadiene	<0.041	<0.041	<0.041
Hexazinone	<0.022	<0.022	<0.022
Indeno[1,2,3-cd]pyrene	<0.034	<0.034	<0.034
Isophorone	<0.061	<0.061	<0.061
Methoxychlor	<0.042	<0.042	<0.042
Methyl paraoxon	<0.038	<0.038	<0.038
Metolachlor	<0.019	<0.019	<0.019
Metribuzin	<0.021	<0.021	<0.021
Mevinphos	<0.026	<0.026	<0.026
MGK 264 - isomer a	<0.055	<0.055	<0.055
MGK 264 - isomer b	<0.054	<0.054	<0.054
Molinate	<0.037	<0.037	<0.037
Naphthalene	<0.019	<0.019	<0.019
Napropamide	<0.019	<0.019	<0.019
Norflurazon	<0.029	<0.029	<0.029
PCB-154	<0.041	<0.041	<0.041
PCB-171	<0.078	<0.078	<0.078
PCB-201	<0.050	<0.050	<0.050
Pebulate	<0.043	<0.043	<0.043
Phenanthrene	<0.019	<0.019	<0.019
Pronamide	<0.025	<0.025	<0.025
Propachlor	<0.024	<0.024	<0.024
Propazine	<0.039	<0.039	<0.039

* Compound was found in Trip Blank and sample and values were estimated.

Table 2 CONTINUED: Analysis of S-VOC compounds sampled from GenPure Pro UV system's product water tested per EPA Method 525 using GC-MS with Type II feed water and challenged with RO feed water. Results shown in parentheses were for second set of tests if tested levels were different from first run. Results reported as < are below the limit of detection.

S-VOC Compounds	Method Detection Limit (ppb)	GenPure Pro UV System with Type 2 Feed Water (ppb)	GenPure Pro UV System with Challenge Feed Water (ppb)
Pyrene	<0.019	<0.019	<0.019
Simazine	<0.034	<0.034	<0.034
Terbacil	<0.048	<0.048	<0.048
Tetrachlorvinphos (Stirophos)	<0.22	<0.22	<0.22
trans-Nonachlor	<0.060	<0.060	<0.060
trans-Permethrin	<0.027	<0.027	<0.027
Triadimefon	<0.16	<0.16	<0.16
Tricyclazole	<0.046	<0.046	<0.046
Trifluralin	<0.041	<0.041	<0.041

* Compound was found in Trip Blank and sample and values were estimated.

Results

Tables 1 and 2 list analysis of VOCs and S-VOCs tested in the GenPure Pro UV system product water being fed with Pacific TII system water and RO challenge water. TestAmerica, Inc. laboratory provided a trip blank sample to test in parallel with GenPure Pro samples. In some cases, the trip blank had measureable levels of specific contaminant. Therefore, the values listed for the GenPure Pro system should be considered to be an estimate and were flagged with an * in Tables 1 and 2. The GenPure Pro UV system demonstrated an ability to remove VOCs and S-VOCs below the GC-MS system's detection limits when fed with Type II feed water.

Conclusion

Ultrapure water produced by a GenPure Pro UV water purification system was analyzed for VOCs and S-VOCs and were determined to be below the sensitive detection limits of the GC-MS.

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