APPLICATION NOTE

Trace ion analysis

Water produced from Thermo Scientific Barnstead GenPure Pro UV water purification system

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Laboratory water produced by a Thermo Scientific™ Barnstead™ GenPure™ Pro UV water purification system was analyzed for trace ions, metals and dissolved silica.

Introduction

Advances in analytical instrumentation especially used in environmental, semiconductor, pharmaceutical and medical research have increased the sensitivity of detection for trace ions and metals. This can involve sensitivities in the sub-ppb (part per billion) or even ppt (part per trillion) range. With the ever increasing demands, it is important that the ultrapure water used in these applications does not introduce interference. Analytical testing often requires ultrapure water that meets and exceeds ASTM D1193-6 Type 1 specification of 18.0 Megohm-cm resistivity at 25 °C and <50 ppb total organic carbon[1].

Good laboratory practices (GLP) are necessary to achieve consistent and repeatable trace level analytical results. It is recommended that sampling and testing should be done in a clean, open air lab or clean room environment to prevent the possibility of airborne contamination. Attention must be given to possible contamination introduced during the process of collecting, storing and transporting the samples. 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, is also important. Before water collection, short flushes at the dispenser will help reduce the risk of contamination at point of use.

The GenPure Pro UV water system was designed to produce ultrapure water that exceeds ASTM Type 1 specifications. For lowest ion detection, ions attached to organic compounds need to be released so they can be removed by the system. Therefore, the system's first purification step utilizes a dual wavelength ultraviolet (UV) bulb to catalyze the breakdown of organic compounds. The by-products of the oxidation reactions are easily removed

in the next purification step by the high purity deionization (DI) cartridge. For units with TOC monitoring, the GenPure Pro UV system monitors the functional intensity of the UV bulb and alerts the user when the intensity falls below effective levels. This is designed to ensure the system is using the UV bulb to reduce organics and ions effectively and efficiently. In GenPure Pro UV systems without TOC monitoring, the system will monitor the use of the UV bulb and alert the researcher of any system problems. The high purity DI cartridge in the GenPure Pro UV systems utilizes high-quality, semiconductor grade resins specifically chosen for their strong attraction to even the weakest ionic impurities in the water. The final purification 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 bacteria.

The GenPure Pro UV system's product water was analyzed based on semi-conductor requirements, known for trace level testing. Analysis included: anions, cations, trace metals tested by either IC or IC/MS and dissolved silica tested by spectrophotometer.

Note, although testing for trace ions and metals was conducted on the GenPure Pro UV system, results found for the GenPure Pro UV system are expected to be similar in the family of GenPure systems which also includes the GenPure xCAD Plus UV and standard GenPure UV. 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. For this experiment, the feed water for the GenPure Pro system was supplied by a Thermo Scientific™ Barnstead™ Pacific TII™ 20 UV system which is designed to produce Type 2 water. To challenge the system, the GenPure Pro system was then fed with reverse osmosis water, which is less pure than the Type 2 water, to determine how the increased ionic load impacts the unit's ability to remove those impurities to below detection limits. Note, reverse osmosis (RO) feed water was used only as a challenge set of data and is not recommended feed water for the GenPure systems.

Methods

Sample Preparation

Clean techniques were used to reduce possible environmental contamination. The GenPure Pro UV water system was fed pretreated water (Type 2 water) from the Pacific TII 20 UV system with a 60 L Thermo Scientific reservoir. Both systems were set up according to the operational manuals, as shown in figure 1[2,3]. For consistent feed water quality, the Pacific TII UV system was programmed to continuously recirculate from the unit to the storage tank. Monitoring of the purity was observed by the resistivity displays on the Pacific TII and GenPure Pro systems. The Pacific TII tank was filled and drained twice times and the purity at sampling was displayed at 14.7 Megohm-cm resistivity. The GenPure Pro system was rinsed with 25 liters of Pacific TII water and was placed in nonstop recirculation mode until resistivity stabilized at 18.2 Megohm-cm resistivity at 25° C before taking samples. The GenPure Pro system was also set to continuously dispense during sample collection.

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

Pacific TII system | 60 L storage reservoir | GenPure Pro UV system

After a 0.2 L rinse, samples were collected from the GenPure Pro UV system cleaned and tested polypropylene using cleaned and tested polypropylene bottles supplied by Chemtrace, Fremont, CA, for specific ultrapure water semiconductor tests. Number of samples and volumes included: 1 x 125 mL for anions, 1 x 125 mL for cations, 2 x 250 mL for trace metals, and 1 x 250 mL for dissolved silica.

Challenge:

To challenge the system, the Pacific TII water system's high purity DI cartridge was bypassed allowing only RO water to fill the Pacific TII system 60 L storage reservoir. The 60 L reservoir was filled and drained three times to ensure all the water in the reservoir was replaced. The RO water was observed at 0.11 Megohm-cm resistivity at 25 °C. The GenPure Pro system was flushed several times with 5 L of water and allowed to recirculate. Samples were collected after a 0.2 L rinse from GenPure Pro UV system dispenser. Samples were collected from the GenPure Pro UV system as described above for ultrapure water semiconductor tests.

Ultrapure Water Semiconductor Tests

Testing was conducted by Chemtrace, Fremont, CA, on GenPure Pro UV system's product water. All sample preparation and instrument analyses were performed in either a Class 100 or Class 1000 clean room to minimize contamination of samples. Strict sample handling and clean room practices were followed at all times. The following methods were used for the specific impurities:

Cations: The ultrapure water (UPW) samples were analyzed on a Thermo Scientific™ Dionex™ DX-500 ion chromatography system equipped with an IP-20 isocratic pump and a CD20 conductivity detector. The sample was pre-concentrated on a concentration column, and then separated on an analytical column using isocratic sulfuric acid elution for cations. The unit was calibrated against NIST standards. The accuracy of each ion in the QC standard was within +10% of the nominal concentration after blank subtraction, or the data was QC-recovery corrected or repeated. Method detection limits were 5.0 - 20.0 ppt depending on the anion or cation.

Anions: The UPW samples were analyzed on a Dionex ICS 3000 ion chromatography system equipped with a gradient pump, eluent generator and a CD25 conductivity detector. The UPW sample was pre-concentrated on a concentration column, and then separated on an analytical column using potassium hydroxide gradient elution for anions. Unit was calibrated against NIST standards. The accuracy of each ion in the QC standard was within +10% of the nominal concentration after blank subtraction, or the data was QC-recovery corrected or repeated. Method detection limits were 5.0 - 20.0 ppt depending on the anion or cation.

Trace Metals by ICP-MS: The UPW samples were analyzed in duplicate on a Perkin Elmer® ELAN® 6100 DRC ICP-MS. The ICP-MS was calibrated with calibration standards made from NIST-traceable standards. A quality control standard was analyzed at the beginning and end of each set of samples. The accuracy of the quality control standard was within +10% of the nominal concentrations after blank subtraction, or the results were QC-recovery corrected or repeated. Method detection limits were 0.5 - 500 ppt depending on the element.

Dissolved Silica: The UPW samples were prepared for dissolved silica analysis by microwave pre-concentration, followed by addition of a molybdenum reagent and an amino acid reagent to form a heteropoly blue complexes. Samples were prepared in duplicate with duplicate blanks and spikes. The samples were analyzed on a Hach® DR/3900 spectrophotometer. The spectrophotometer was calibrated with calibration standards made from an NIST-traceable Si standard. Quality control standards, prepared from a second NIST-traceable source standard, were run with each set of samples to verify the accuracy of calibration daily. The accuracy of the quality control standard was within +15% of the nominal concentrations after blank subtraction, or the data were QC-recovery corrected or repeated. Method detection limit was 100 ppt for dissolved silica.

Results

Ultrapure water testing depends on many factors such as lab environment, feed water quality, rinse up time, and sampling technique, therefore, results may vary from lab to lab.

When fed with Type 2 water from the Pacific TII UV system, the GenPure Pro UV system was able to remove ions and metals below detection limits of the test method. When fed with RO water with purity of 0.11 Megohm-cm at 25C, trace levels of magnesium and sodium were present in the analysis.

Table 1: The Barnstead GenPure Pro UV water system's product water tested by IC for anions and cations. Results listed compare GenPure Pro product water when fed Type 2 feed water and challenged with RO feed water.

Anions		GenPure Pro UV System Water with Type 2 Feed Water (ppt)	GenPure Pro UV System with Challenge Feed Water (ppt)
Flouride	(F^-)	< 10	< 10
Chloride	(Cl^-)	< 5	< 5
Nitrite	(NO_2^-)	< 20	< 20
Bromide	(Br^-)	< 5	< 5
Nitrate	(NO_3^-)	< 20	< 20
Sulfate	(SO_4^-)	< 10	< 10
Phosphate	(PO_4^{3-})	< 10	< 10
Anions		**GenPure Pro UV System Water with Type 2 Feed Water (ppt)**	**GenPure Pro UV System with Challenge Feed Water (ppt)**
Lithium	(Li^+)	< 5	< 5
Sodium	(Na^+)	< 5	< 5
Potassium	(K^+)	< 5	< 5
Magnesium	(Mg^{2+})	< 10	< 10
Calcium	(Ca^{2+})	< 10	< 10

Results reported as < are below the limit of detection.

Table 2: Trace Metals tested by ICP-MS of the GenPure Pro UV system's product water. Results listed compare GenPure Pro product water when fed Type 2 feed water and challenged with RO feed water.

Elements		GenPure Pro UV System Water with Type 2 Feed Water (ppt)	GenPure Pro UV with Challenge Feed Water (ppt)
Aluminum	(Al)	<3	<3
Antimony	(Sb)	<2	<2
Arsenic	(As)	<0.5	<0.5
Barium	(Ba)	<0.5	<0.5
Beryllium	(Be)	<3	<3
Bismuth	(Bi)	<1	<1
Boron	(B)	<20	<20
Cadmium	(Cd)	<2	<2
Calcium	(Ca)	<20	<20
Cerium	(Ce)	<1	<1
Cesium	(Cs)	<1	<1
Chromium	(Cr)	<3	<3
Cobalt	(Co)	<1	<1
Copper	(Cu)	<3	<3
Dysprosium	(Dy)	<1	<1
Erbium	(Er)	<1	<1
Europium	(Eu)	<1	<1
Gadolinium	(Gd)	<1	<1
Gallium	(Ga)	<0.5	<0.5
Germanium	(Ge)	<3	<3
Gold	(Au)	<5	<5
Hafnium	(Hf)	<1	<1
Holmium	(Ho)	<1	<1
Indium	(In)	<1	<1

Elements		GenPure Pro UV System Water with Type 2 Feed Water (ppt)	GenPure Pro UV with Challenge Feed Water (ppt)
Iridium	(Ir)	<2	<2
Iron	(Fe)	<20	<20
Lanthanum	(La)	<1	<1
Lead	(Pb)	<2	<2
Lithium	(Li)	<2	<2
Lutetium	(Lu)	<1	<1
Magnesium	(Mg)	<2	3.0
Manganese	(Mn)	<2	<2
Mercury	(Hg)	<5	<5
Molybdenum	(Mo)	<2	<2
Neodymium	(Nd)	<1	<1
Nickel	(Ni)	<3	<3
Niobium	(Nb)	<1	<1
Osmium	(Os)	<2	<2
Palladium	(Pd)	<2	<2
Platinum	(Pt)	<5	<5
Potassium	(K)	<20	<20
Praseodymium	(Pr)	<1	<1
Rhenium	(Re)	<3	<3
Rhodium	(Rh)	<1	<1
Rubidium	(Rb)	<1	<1
Rthenium	(Ru)	<2	<2
Samarium	(Sm)	<2	<2
Scandium	(Sc)	<5	<5
Selenium	(Se)	<500	<500
Silicon	(Si)	<500	<500
Silver	(Ag)	<1	<1
Sodium	(Na)	<5	7.0
Strontium	(Sr)	<0.5	<0.5
Tantalum	(Ta)	<3	<3
Tellurium	(Te)	<1	<1
Terbium	(Tb)	<1	<1
Thallium	(Tl)	<1	<1
Thorium	(Th)	<1	<1
Thulium	(Tm)	<0.5	<0.5
Tin	(Sn)	<3	<3
Titanium	(Ti)	<2	<2
Tungsten	(W)	<2	<2
Uranium	(U)	<2	<2
Vanadium	(V)	<1	<1
Ytterbium	(Yb)	<1	<1
Yttrium	(Y)	<1	<1
Zinc	(Zn)	<5	<5
Zirconium	(Zr)	<5	<5

Results reported as < are below the limit of detection.

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Table 3: Dissolved silica of the GenPure Pro UV system's product water tested with a spectrophotometer. Results compare GenPure Pro product water when fed Type 2 feed water and challenged with RO feed water.

Silica	GenPure Pro UV System Water with Type 2 Feed Water (ppt)	GenPure Pro UV with Challenge Feed Water (ppt)
Dissolved silica	<100	<100

Results reported as < are below the limit of detection.

Conclusion

Ultrapure water produced by a GenPure Pro UV water purification system was analyzed for trace ions and metals and were determined to be below the sensitive ppt detection limits for IC and IC-MS.

References

1. ASTM D 1193 – 06. Standard Specification for Reagent Water.
2. Operational Instructions for the Thermo Scientific Barnstead Pacific TII water purification system. Thermo Fisher Scientific, Niederelbert, Germany.
3. Operational Instructions for the Thermo Scientific Barnstead GenPure Pro water purification system. Thermo Fisher Scientific, Niederelbert, Germany.

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