MONITORING

MINIMIZING CONTAMINATION FOR STATE-OF-THE-ART SAMPLE ANALYSIS

Semiconductor geometries continue to shrink and ultrapure water (UPW*) guidelines continue to push quality requirements and analytical methods to lower levels in order to meet fab processing needs.

Sampling is the fundamental step of high-purity water testing and an appropriate, representative sample is critical for accurate results. Extremely low levels are only achieved by continually refining and improving our basic knowledge and understanding of sample collection. Sample valve design and set-up can be a significant hindrance to obtaining clean samples. At times, data is reported with a note indicating potentially false high hits due to suspected sampling contamination. False high data generates confusion for facilities operations personnel where port or environmental artifacts must be explained or rechecked to show the UPW system is or is not in compliance. It also wastes time and money due to resampling. Eliminating or minimizing false high hits is possible by investigating proper sample valve designs, set-up and preparation techniques.

Several sample valve types and configurations are available for high-purity application. This article will compare the most commonly used valves, and also discuss their proper installation and preparation. Selected case studies from the semiconductor industry will be reviewed. In addition to sampling at the point-of-distribution (POD), this article will also discuss field experience regarding the challenges of sampling high-purity water at the wafer point-of-entry (POE), and point-of-process (POP).

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Sample Valve Designs

General recommendations. There are several recommendations for design optimization. The most important factors (especially for obtaining clean bacteria samples) are a low dead volume, a smooth surface, and the ability to sanitize the port surfaces.

Ultraclean materials, such as polyvinylidene fluoride (PVDF), perfluoroalkoxy (PFA), and electropolished 316 SS are necessary to minimize contamination from the materials of construction. Polyvinyl chloride (PVC) is known to release total organic carbon (TOC), and chloride ions when new. PVC also has a porous/rough surface that encourages bacteria growth over time.

The port location should also be a strong consideration to eliminate or minimize contamination from the environment. Placement of the port indoors, away from walls and floors will reduce potential interference from calcium, and other environmental ions. Installation far away from processes with volatile contaminants, such as acid waste neutralization is also essential. Finally, the port should be accessible for ease of sampling and the location should be representative of the UPW being sampled. These considerations will be discussed in more detail later.

Recommended valves.

PVDF needle valves are appropriate valves for UPW sampling due to their low dead volumes, low extractables, and smooth surface. The low dead volume and smooth surface minimizes bacteria growth. The valves are also easy to sterilize and flush when needed to reduce biological buildup. It should be noted that PVDF valves will wear over time and occasionally need replacing. Several manufacturers are available.

One manual needle valve is a multi-turn with a rising stem made of all PVDF construction except for the stem seal of polytetrafluoroethylene (PTFE) (no O-ring seals). The design allows for precise metering and no lubricants are used. Only the body and needle materials, along with PTFE seal, contact the fluid. It can be disassembled for inspection or cleaning and the high-purity design ensures no "dead" areas. The PTFE seal is located below the thread, isolating the thread and top works from the fluid media. The valve is available in both globe and angle patterns, and can operate up to 200 pounds per square inch gauge (psig) at 73°F.

Figure 1 shows a picture of a spindle needle valve IR welded onto an instrumentation fitting. The IR weld may offer higher purity when compared to conventional socket-welded versions.

316L electropolished SS sanitary sampling valves are an appropriate choice for bacteria sampling in UPW (Figure 2). This valve's design advantages allow sampling from mid stream. The sampler can inject isopropyl alcohol (IPA), or hydrogen peroxide inside to sterilize and can attach bacteria monitors directly for large sample volumes.

The sanitary sampling valve is recommended if very low bacteria levels are specified. The valve can be sanitized effectively and easily in place to eliminate

Figure 1. Spindle needle valve.

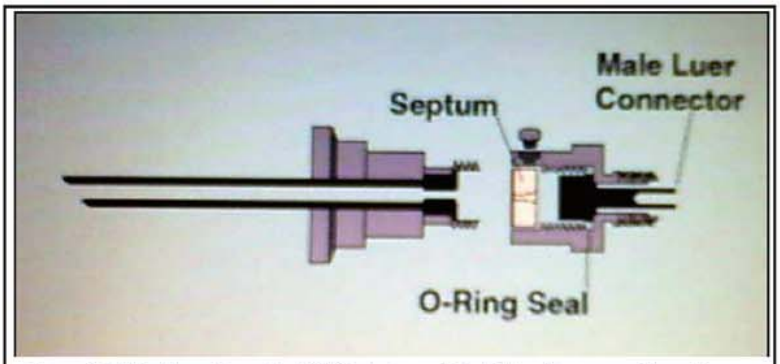

Figure 2. Side view schematic of 316L electropolished SS sanitary sampling valves.

Figure 3. Close-up of sample lines under a Plexiglas cover.

residual viable contaminants and prevent additional contaminant growth. These valves also require periodic maintenance for O-ring change out, but not complete valve replacement.

The construction of the sanitary sampling valve allows a mid-stream sample to be collected. This also helps prevent build up of bacteria inside the sampling probe. The Luer-slip valve outlet is designed for the direct attachment of a bacteriological monitor or for directing liquid flow into any type of bottle. The sampling valve comes with two, 18-gauge blunt-end syringe needles (for sanitizing the unit), a spare O-ring, a plug seal, and two plastic caps to cover the outlet Luer-slip after sanitization.

A recent improvement to the valve is the option to use additional fittings to make an extra-secure sample connection. This allows the use of a Galtek® retaining nut and ¼-inch (in) diameter PFA Teflon® tubing to securely attach water quality monitoring equipment.

The 316L electropolished SS has very low extractables, however, trace chromium, iron, and nickel have been detected when using the ultra sensitive metal analysis with preconcentration DRC-ICP/MS (Table A). Table A compares SS valves at the POD with PVDF gooseneck at the POU over a few days.

Challenging valves.

Ball valves present the biggest challenge for obtaining clean bacteria samples. Because they have large dead volumes, bacteria growth can be substantial. They are also difficult to sanitize because there are pockets behind the ball that are not accessible to sterilizing agents. Many ball valves are made of schedule 80 PVC, and this material of construction has a porous and rough surface area that can also harbor more places for bacteria to grow. Schedule 80 PVC also adds a source for organic and inorganic extractable contaminants when they are new. Over time, these extractables will rinse to a satisfactory level for most UPW parameters.

Diaphragm valves sometimes make it difficult to control sample flow. They can also vibrate and/or pulse at low flows. Therefore, obtaining clean samples for bacteria or particles can be difficult because of pipe shake.

SS valves that are not 316L and electropolished will contribute higher level metal contaminants such as chromium, nickel, and iron.

Sample Valve Installation

Physical location. For optimum results, all sample ports should be tapped into the process line with minimal distance between the port outlet and the sampling point. Sample ports should not employ tees, pressure gauges, or manifolds, among other items as they may contribute contamination. The ideal location for a UPW sample valve is directly on the main pipe at the point-of-distribution (POD). The valve should not be located near any walls, tees, or flanges, and it should be upstream of any pressure gauges or flowmeters.

The primary drawback to this location is difficulty in maintaining, or replacing the sample valve unless the main water system is shutdown. Work arounds include installing extra sample valves on the main line to use until a shut down is scheduled or building a sample manifold to bypass the main line. Manifolds should be designed carefully to avoid adding false high contamination. When possible, sample manifolds with many valves, connectors and meters, and gauges should be avoided.

Ports should be located indoors, when possible, to minimize effects from environmental contamination. Sample valve accessibility is another important safety concern. Standing height is preferred to far overhead or just above the floor.

Other helpful considerations include having the valve face forward rather than behind pipes, be at a 90° for needle valves and 45° downward for SS sanitary valves. A drain or conduit to drain should be nearby and there should be enough room around the port to allow access of 500 milliliter (mL) sample bottles. A low traffic area is preferred, especially for on-line or long-term SEM particle counting samples.

Sample Valve Preparation

Cleaning/flushing procedures. Sample valve and line preparation is critical to obtaining contaminant free samples. Sample lines should flow continuously for best results. The unused water can be recycled back into the water system through the return line if desired for conservation. If bacteria samples are to be taken, the sampling port must first be rinsed with IPA, or 3% to 10% hydrogen peroxide (H_2O_2). However, if TOC samples are also to be taken, they must be collected before rinsing with IPA, as this chemical will cause a positive interference. Before opening the valve, rinse all interior sampling surfaces with IPA or H_2O_2. This process may be repeated several times. The port should be allowed to air dry before beginning sample collection.

The sample lines should only be PFA. Many other plastic materials contaminate because of plasticizers or ionic contaminants. It is preferred that no other tubes, connections, or other devices should be attached to the valve outlet for sampling purposes. The valve is exercised slowly by opening (full throttle) and closing the valve 5 times, then opened full throttle for at least 2 minutes. Longer times may be required for "problem" valves, or if there are long tubing runs or complicated setups.

The flowrate should be adjusted to allow the bottle to be filled quickly but minimize any splashing while introducing and removing the bottle from the stream. The water should flow at this rate for at least 5 minutes before collecting samples. It is very important that the sample valve not be adjusted again until testing is completed—moving the valve generates contaminants, especially when testing for particles and bacteria.

Figure 4. Second sampling valve added at the end of an existing sample line.

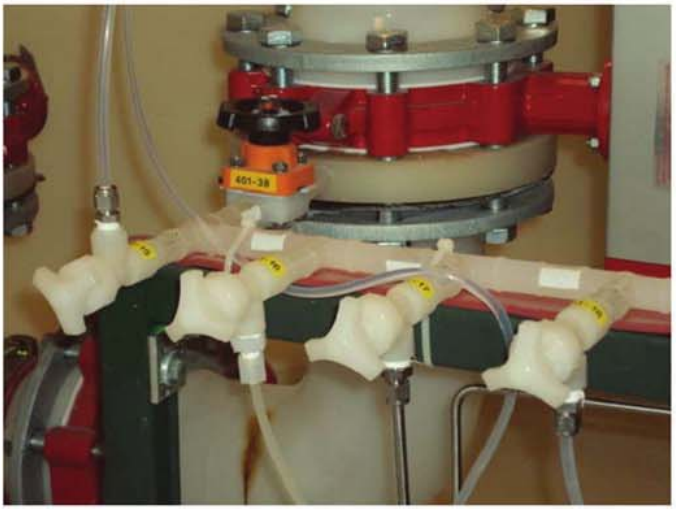

Figure 5. Sampling valves placed next to each other on a manifold.

Persistent bacteria issues. If bacteria triplicate, results are non reproducible, or counts are seen at the POD and not in the return loop; these are an indication of false high hits. The sample valve may need to be disassembled and sterilized if the problem persists after extended flushing periods. Last resorts are to modify the sampling port set up, or move the valve to a cleaner location.

Selected Case Studies of Sampling Configurations

We have discussed "ideal" sampling valve design and set up for optimum sample collection. Now we will look at a few facilities' "real world" operations that have devised creative variations to collect UPW samples at the POD. We will review the accomplishments, and discuss areas for enhancement for each set up. Although these are complicated setups, it should be noted that good analytical results are obtained when using proper flushing and sampling techniques. Specific protocols will need to be developed for individual sampling sites. Please note that in these case studies, bacteria samples are 100 mL, unless specifically noted as 1 liter (L) or greater.

Site #1. This is a very convenient set up and provides much protection from the outdoor elements with the Plexiglas cover (Figure 3). The sample lines run continuously which helps maintain water purity. Bacteria samples less than 1 colony forming units per liter (cfu/L) are routinely achieved. On/off valves at each sample collection point allow ease of replacement and occasional stronger line flushing if needed. An occasional line or valve becomes contaminated and must be replaced at approximately 18-month intervals. Due to this site's outdoor sampling location and close proximity of sample lines, sample collection during occasional heavy rains is avoided (Figure 3).

Site #2. This example shows a needle valve attached to a piece of SS inserted into the pipe (Figure 4). There are also resistivity probes, flowmeters, pressure gauges, and ball valves in close proximity to the valve. False high bacteria data hits of approximately 20 cfu/100 mL have been detected at this location. The sample port does not run continuously and must be flushed into a bucket before sampling. To achieve non-detect bacteria counts, approximately 8 gallons are flushed at full speed, and then flow is slowed and allowed to equilibrate for several minutes before sampling. There are also physical constraints with this port due to box storage.

To stop a drip from the initial sample valve, a second sampling valve (blue) was added to the end of the existing sample line (Figure 4). This creates an additional area to add false contamination to the UPW sample, and should be avoided when possible. Still, non-detect bacteria counts have been achieved with this set up.

Site #3. This is an example of several valves placed next to each other on a manifold with the manifold feed originating from a flange (Figure 5). An improvement would have the sample line originating from the main pipe rather than the flange.

Although water continually flows through the manifold, the sample valve does not flush continuously. The short piping runs to the valve can create dead leg areas, harboring bacteria. There is also a resistivity probe on the right end of the sample line that can also cause a slow-flow area. Occasional bacteria counts of approximately 10 cfu/100 mL were detected until a proper flushing technique was implemented.

Clean bacteria samples are collected by flushing the valve and sample line with IPA and a vigorous line flush before sample collection. To achieve counts of <1 cfu/100mL about 10 gallons of UPW are flushed at full speed then slowed to a sampling flow of approximately 200 mL/min for several minutes.

Note that the orange diaphragm valve does not cause pulsing in this application as it is used wide open; not to regulate the flow of the sampling line.

Site #4A. This is an example of a challenging sampling location (Figure 6).

Figure 6. Example of a more difficult place to get UPW samples.

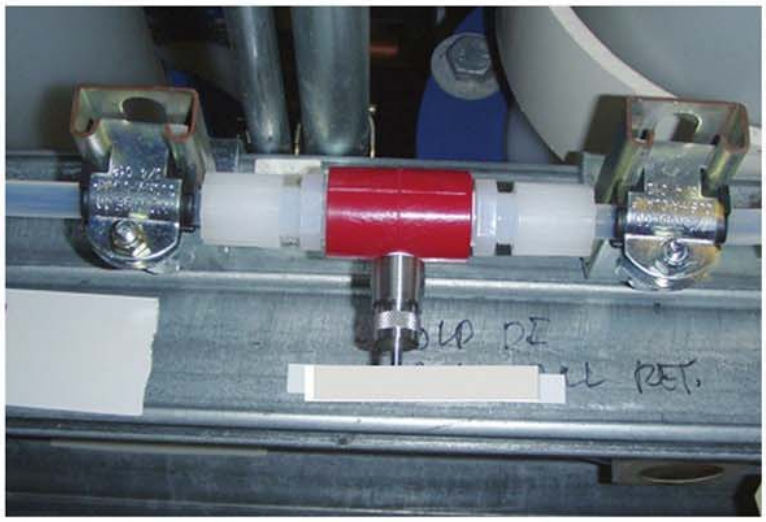

Figure 7. A sanitary valve using PFA tubing and unions to allow accessible sampling.

In addition, 2-L bacteria samples are collected at this site, making the data much more sensitive to false high hits. The valve is in a tight area, located overhead and in a flange. The original port location was in the bottom of the flange, making it very difficult to achieve accurate bacteria data on a consistent basis. Many times, even after strenuous

Figure 8. A sample box not large enough to accommodate a sample bottle without touching the bottle neck to the end of the port.

Figure 9. Example of all sample lines running into a common sink in a plant's control room.

port preparation, counts >500 cfu/2 L would be detected. The port was subsequently relocated to the top of the flange; yielding much better results. However, extensive line flushing is still required to achieve non-detectable results. This sample valve is purged wide open for 1 hour (h) before slowing to sampling rate of ~200 mL/min. It is allowed to flush at this rate for 2 to 3 h before sample collection begins.

Site #4B. Figure 7 shows a creative installation of a sanitary valve. The sanitary valve was installed using PFA tubing and unions rather than directly into the piping to allow accessible sampling at the return. The set up is held in place with metal struts.

Site #5. Another creative design is to place a sanitary valve in a location other than a pipe (Figure 8). The positive aspects with this set up are that it runs continuously and is located at a convenient height. Limitations are that the sample line is very long, and the sample box is not quite large enough to accommodate the sample bottle without touching the neck of the bottle to the end of the port. Therefore, in this instance a 6-foot long ¼-in PFA tube must be attached to the port at the time of sample collection.

The tubing is not used to collect bacteria samples to reduce chances of bacterial contamination from the tubing and because there is sufficient space for 100-mL cups. Great care is used to avoid splashing from the walls or floor of the box when collecting the bacteria samples. To minimize splashing, only one port at a time is on during the sample collection process.

The sampling box is also located in fairly tight physical quarters, with instrumentation cabinets located on both sides.

Because of the very long tubing runs, the sample lines must be periodically disconnected from the main pipe and sanitized. The main sample valves are located very high overhead but only require sterilization once or twice a year, based on reproducible count increases in analytical data. Lines are sterilized when approximately 10 cfu/100mL are detected and confirmed by resample.

Site #6. This is another convenient sampling set-up with all sample lines running into a common sink in the facilities control room (Figure 9). There are long SS lines that run continuously. The fittings leak so a paper towel is wrapped around the line at sampling time to prevent any contaminating drips from entering the sample bottle. Clean samples are collected here because the lines run continuously and are flushed under high flow before sampling. It should be noted that sub-parts-per-trillion (ppt) levels (parts per quadrillion [PPQ]) of metals have not been tested here, and metallic contamination may be detected at those very low levels due to the very long SS lines.

At the time of writing, the facilities' city water sample port was out of service at this site. As an alternative, the bathroom sink was used as a successful work around for collecting incoming city water samples.

Site #7. A photo was not allowed at this site. The initial sample valve was a large diaphragm valve located at the bottom of a 3-foot pipe extension deadleg. Bacteria counts were >500 cfu/100 mL. The site was retested along with a small sample ball valve located directly on the distribution pipe and upstream of the diaphragm valve. The diaphragm valve counts

remained elevated at >500 cfu/100 mL, while the ball valve tested non detect (<1 cfu/100mL) for bacteria.

Additional Monitoring Locations

UPW system. In addition to POD, installing ports on the incoming feedwater line and common effluent from each of the major processing components allows the entire water system to be monitored effectively. By monitoring each area proactively, negative water quality changes can be detected before reaching the final supply water to the customer.

Additional sample valves placed on the individual components provide a comprehensive system for monitoring and troubleshooting if needed.

Tool POE. Sample valves located at the POE are convenient for isolating contamination detected at the tool. Testing water at POE provides information about the water quality from the POD through the distribution system up to the tool inlet. Many times, standard UPW valves can be used at this location because the water is still on a pressurized line from the main distribution system.

Tool POP. This is the most challenging location to sample because of the many different configurations. There are nozzles that spray directly on the wafer, spray nozzles used for filling quick-dump rinsers, and hand-held sprayers. Gooseneck faucets are also found at the POP, and may or may not be on a recirculating line. Lines within the tool may harbor contamination due to the many valves, deadlegs, or slow flow areas. Sampling is usually developed on a case-by-case basis, and can be a challenge due to slow flows and low pressures in the tool.

Implementing sample valves into the tool design would greatly increase access for troubleshooting and minimize false contamination from sample collection.

As UPW quality can fluctuate rapidly at the POP, building an analytical database to understand the normal range of variation is recommended. It is especially important to verify outlier data points before making any major operational changes.

Summary

Accurate sample collection is the key to obtaining accurate analytical data. This is especially true as semiconductor geometries continue to shrink and UPW guidelines continue to push quality requirements and analytical methods to lower levels. The goal is to minimize contamination introduced during sample collection, and to ensure accurate analytical data is obtained.

Sub-ppt analytical analysis is only achievable by continually refining and improving our basic knowledge and understanding of sample collection.

Sample valve type, design, installation, and technique each play a critical role in proper sample collection. By designing specific sampling protocols at each site, many hindrances to obtaining clean samples will be eliminated. Improved productivity and cost savings will be realized as analytical data will not have to be questioned or resampled.

Expanding the number of sampling ports and monitoring locations throughout the water system, distribution system, and point of use (POU), will allow water quality changes to be detected before they are out of compliance. Troubleshooting will also be much quicker and more comprehensive. Any outlier data points should always be verified by resample before major operational changes are made.

TABLE A
ppt Level Metals Analysis at POD and POU

		1	*2*	*3*	*4*	*Avg.*
Chromium	**POD**	**1.52**	**1.82**	**1.11**	**1.27**	**1.43**
	POU	<0.50	<0.50	<0.50	<0.50	<0.50
Iron	**POD**	**2.53**	**2.36**	**1.61**	**2.28**	**2.20**
	POU	<0.50	<0.50	<0.50	<0.50	<0.50
Nickel	**POD**	**0.73**	**0.74**	**0.59**	**0.76**	**0.71**
	POU	<0.50	<0.50	<0.50	<0.50	<0.50
Manganese	**POD**	**<0.50**	**<0.50**	**<0.50**	**<0.50**	**<0.50**
	POU	<0.50	<0.50	<0.50	<0.50	<0.50

Endnote

*In the text, the term UPW refers to semiconductor-grade water produced in microelectronics facilities. Its quality parameters are defined under the International Technology Roadmap for Semiconductors (ITRS).❑

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