



Ultrapure Water Monitoring Guidelines

Revision 2.0

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ANALYTICAL SERVICES



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These guidelines have been divided into sections with a focus on the needs of different users. Because some information pertains to more than one area, it may be appear in more than one section of this document, although not always in the exact same presentation.

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Introduction

The Balazs™ Philosophy

Balazs™ Analytical Services believes guidelines should be used as a starting point for setting water quality specifications. Our guidelines are compiled from real world data which is currently used successfully by our customers. Each customer site and process will need to develop a set of specifications based on their own specific internal requirements.

The original guidelines proposed several years ago by Balazs™ were adopted by SEMI in 1996 and are currently published in SEMI-F63¹. The continuing importance of maintaining up-to-date UPW guidelines/specifications is enforced by the knowledge the industry continues to gain from comparing actual water quality to contaminants found on wafers. This knowledge is identifying process yield problems based upon real conditions, which is driving changes both in water quality specifications and in what needs to be monitored.

Balazs™ Analytical Services, a division of Air Liquide Electronics, continues to be dedicated to the advancement of the UPW specifications through participation with UPW task forces sponsored by ASTM², SEMI and International Technology Roadmap for Semiconductors (ITRS)³. Balazs™ also works with industry leaders to resolve issues and form an industry consensus on UPW guidelines.

Our 2007 Edition of the Guideline Booklet is the second publication since Air Liquide acquired Balazs™ in 2001. It is an update based on current water quality studied from Fabs around the world. It reflects new industry information relating contaminants to yield, as well as further improvements in our ability to measure ultra pure water and the wafer environment.

Introduction – What's New

As geometries continue to shrink, much more focus is directed toward testing the wafer environment. In the “Increased Focus on Wafer Environment” section, we will discuss innovative ways to profile contaminant levels at the wafer Point-of-Process (POP,).

2007 ushers in new yield information from the International Technology Roadmap for Semiconductors regarding several analytical parameters. This brings both “good news” and “bad news” as some parameters have been relaxed while others have been tightened.

Balazs™ continues to be a company dedicated to helping both IC and component manufacturers with their understanding of ultra pure water systems and monitoring. We hope these Guidelines will continue to assist both facility and process engineers in setting specifications and monitoring the UPW they use on their products.

In Appendix I we discuss the relevance of data using detection limits vs. reporting limits, suggest a comprehensive monitoring program in Appendix II, review the history of guideline development in Appendix III, and offer the UPW system basic troubleshooting guide in Appendix IV. The intent is to have this serve as a reference when you go about the task of establishing or evaluating specifications specific to your operation and process.

Because state-of-the-art water systems consistently deliver high purity water from the point-of-delivery (POD), water quality requirements will now be presented by product type. Accordingly, the 2007 Guidelines have been revised to merge the Facilities Guidelines and the Product Type Guidelines into one section.

International Technology Roadmap for Semiconductors (ITRS)

The industry and ITRS continues to work towards a better understanding of water quality at the wafer point-of-use and how it impacts yield. In the past, water guidelines have focused on understanding water quality at the point of distribution while disregarding the wafer point of use. The shift to look at water quality at the tools has identified the need for the development of sampling techniques capable of obtaining useful samples at the POE (point of entry) and POP (point of process).

When testing the quality of UPW, consideration must be given to where that quality is required and where it is to be measured. First some definitions:

1. The Point of Delivery (POD) is the point in the system immediately after the last treatment step and before the distribution loop (formerly referred to as DI Supply). It is the standard location for the majority of analytical tests.
2. The Point of Entry (POE) is the location at the back of the tool, where ownership of the water generally transfers from the facilities staff to the tool owner or process engineer. This location is not commonly measured due to the ability of a well-designed distribution loop to maintain POD quality and to the cost of monitoring the large number of POE's.
3. The Point of Process (POP) is where the water contacts the wafer, either in a bath, spray, or some other configuration. Sampling water at this point represents a significant technical challenge and many of the parameters cannot be readily monitored by on-line methods at this location. An understanding of the potential changes to water quality between the POE and POP is critical to ensure that the water has retained its purity. *(Note: POP is the current ITRS nomenclature. This was formerly known as the POU or point-of-use.)*

ITRS

(Continued)

A consolidated effort by process and facilities engineers, analytical lab personnel, tool suppliers and manufacturers will be necessary to establish realistic guidelines at the wafer point of use.

Using what are now considered fairly routine methods, a competent trace laboratory can quickly produce accurate data at the low ppt level on a significant number of samples. The value of this testing is that it provides a sufficient number of data points in a timely manner which serve as indicators that the system is operating properly or that plant performance may be changing. A regular testing program enables facilities personnel to react to changes in the plant's performance early on allowing adjustments to be implemented quickly and efficiently. This routine monitoring data ties directly into the guidelines, which are geared towards the operational side of the process.

FACT: Many of the routine analytical and sampling methods will not provide the sensitivity required to meet the new ITRS specifications which are pushing sub ppt (ppq) levels of quantitation. For some parameters non-routine methods will be needed. In many cases these methods already exist, but they require an extended TAT and a higher cost, which translates into fewer samples.

Non-routine methods of testing and collection may also be required because the parameters of interest may not have been of importance before now. See the "Innovative New Test" section for a discussion of some of the parameters that are sparking interest.

Incorporating a balanced analytical monitoring program, which utilizes both routine and state-of-the-art water testing methods, will ensure facilities process control and safeguard product yields. It is hoped that this information can produce a cost of operation reduction, as individuals from both sides of the company better understand the quality of ultra pure water needed for processing their products. Sensible approaches to water system components, operation, and use of the

ITRS

(Continued)

analytical data from both the water and wafer points of view can result in quick actions that can reduce waste and yield loss.

CAUTION: Pushing analytical data to the extreme levels of sensitivity required to hit some ITRS specifications puts a burden on the lab to ensure that they are producing both accurate and precise data. Additionally, the lab must understand and be able to communicate the uncertainty associated with the data reported. Only then can the user of the data act with confidence in making decisions related to their system or process.

Simply getting a lower detection limit is only a small part of the process involved in evaluating a system. It is incumbent upon the user of the data to fully understand how detection limits have been determined and what the confidence limits are. (*See Appendix I for more details.*)

ITRS Yield Information & Balazs™ Guidelines

Following are some of the key changes reflected in the current ITRS road map and how the Balazs™ Guideline addresses them.

1. Based on the most recent studies and research conducted by groups such as the ITRS, iron, calcium and nickel have each shown a negative impact on some wafer processes². As a result, ITRS water quality guidelines for critical metals were reduced from 10 ppt to 1 ppt. In 2008, levels will be further reduced to 0.5 ppt. However, ITRS also states that these levels pertain to only the most critical processes. The Balazs™ Guidelines will continue to reflect numbers which are currently working successfully for our customers.
2. ITRS found that anions and ammonium ions up to 50 ppt were not critical to processes and therefore the Balazs™ Guidelines will also relax recommendations to this level.
3. Dissolved silica and boron were considered operational parameters and removed from the ITRS list because they are not harmful to product at current levels (300 ppt and 50 ppt respectively). However, total silica remains a watched parameter. Balazs™ recommends monitoring both types of silica (dissolved & non-dissolved) in order to understand which is from ion exchange breakthrough (dissolved) and which is colloidal (non-dissolved).
4. The ITRS also increased particle levels in 2006 based on customer benchmarking information and instrument capabilities. These levels will slowly lower until 2010 where we begin to reach instrument detection limits. Balazs™ has revised its guideline to reflect the new values.
5. TOC levels will remain constant through the long term plan (through 2010).

Increased Focus on the Wafer Environment

The point-of-process (POP) is where water, chemicals and air meet the wafer. Ideally, this is the location we would prefer to have UPW quality Guidelines in place. Currently, our industry continues to focus on water quality supplied from the facilities point of distribution (POD).

There are several reasons why it is difficult to establish guidelines at the POP. First, a lack of high purity sampling methods makes it difficult to pull samples which are truly representative of the water at that point. This is especially true for spray processors and with online instrumentation.

Another issue is that there is not a reference data base for these sampling points. Only with time will there be a clear understanding of the actual water quality and its affect on the process.

This is a complex task as the water quality may be constantly changing at each POP. Residual contaminants from chemical rinsing or absorption of contaminants from the air above neighboring chemical baths can have a significant impact on water quality. Finally, when focusing on POP's, there are many locations throughout the FAB to monitor, which serves to compound the difficulty of data collection.

The industry is beginning to address these issues. The ITRS UPW task force is changing its focus on water quality to the tool's point-of-entry (POE). The task force is also beginning to address the need for accurate sampling methods. Guidelines are also being developed by SEMI for suppliers to ensure tool assemblies are rinsed to specified quality levels before installation. Balazs™ supports the efforts of these task forces by working to help develop new sampling and test methods to ensure that accurate data is collected.

Increased Focus on the Wafer Environment

(continued)

If POP water is contaminated by the environment of the wafer (chemicals, air or tool plumbing) demanding higher and higher water quality from facilities may simply be wasting dollars.

In today's technology, pure water constitutes a significant production cost. Studying water quality at the POP is paramount to the efficient and cost effective rinsing of wafers. As we continue to refine our understanding of water quality at the POP by developing new sampling methods and collecting data, it is believed that significant dollars spent on the production and use of ultra pure water can be reduced which would drop the per wafer costs.

As geometries shrink below 0.09 microns, discussions will continue to determine the best ways to meet wafer processing needs. With stable POD water quality the norm, it has become important to shift the focus of future guidelines from the POD to the wafer POP. Understanding water quality fluctuations originating from the semiconductor clean room environment, distribution lines, tool hardware, design and operation is the precursor to correlating data to process yields. In addition, with UPW production costs high and small improvements requiring large expenditures, facilities operational savings can also be realized with increased testing at the POP.

Innovative New Tests & Redeployment of Existing Tests

Following is a summary of some of the advances in testing methodologies that have been developed in response to the need for achieving lower sensitivity and/or to enable us to monitor parameters that until now have not been monitored on a regular basis. In some cases, existing methodologies have been modified or adapted to help address some of the emerging concerns as geometries shrink and focus shifts to the POP. Each of these tests are available at Air Liquide-Balazs™ Analytical Services. For more information or copies of papers visit our website at www.Balazs.com.

Part-per-Quadrillion (PPQ) Analysis of Ultrapure Water for Trace Metals

Analytical methodologies have been developed for the analysis of UPW to current ITRS specifications (1 ppt). However, the ITRS 2008 guidelines represent an additional challenge for analytical laboratories because they call for the detection of impurities below the capability of most analytical methods. Balazs™ has developed a method to not only detect whether the new specifications can be met, but also to quantitatively measure metallic impurities in a system to determine whether the system truly meets the new specifications.

Initial investigations into quantitative method development for the analysis of metallic impurities at the sub-ppt level revealed that special care must be taken during sampling collection, sample transport, and sample analysis steps. Sample collection, while generally considered as simple and routine, must be carefully assessed in each situation to eliminate the introduction of elemental contaminants from the sampling environment, sampling technique, and maintain sample integrity through sample transport. Sample analysis, even though completed within a clean room laboratory environment, must also be carefully scrutinized.

Innovative New Tests & Redeployment of Existing Tests

(continued)

TOC Speciation

Speciation of organics has become more of a concern. Historically, on-line monitors have been used to test for total oxidizable carbon (TOC), but this does not identify the specific compounds present. Unfortunately, due to the large number and types of potential organic compounds, there is no one test which covers all possibilities.

Following are examples of procedures which Balazs™ currently uses to assist system engineers to determine which organic compounds are present. We are continuing to develop new methods to further characterize the TOC in UPW systems.

TOC Speciation: Urea in Ultrapure Water

The presence of urea is concerning because typical fab systems cannot remove it from UPW or cleanroom air humidified with contaminated water. Each molecule of urea has the potential to travel to the wafer environment and generate two molecules of ammonia. The ammonia can then interfere with acid-catalyzed photoresist and cause T-topping and CD (critical dimension) shifts. Sourced in incoming city water, urea levels fluctuate over time due to many factors affecting agricultural run off, including agricultural usage, and rainfall patterns. Balazs™ uses Ion Chromatography – Mass Spectrometry for urea detection at the low ppb levels.

TOC Speciation: Resin Amines in UPW

As bases, resin amines have the capacity to interfere with acid-catalyzed photoresist. Anion exchange resin is the most significant source of resin amines, followed by tetramethylammonium hydroxide (TMAH) occurring in recycle water. Balazs™ utilizes ion chromatography to quantify and identify the amines present.

Innovative New Tests & Redeployment of Existing Tests

(continued)

TOC Speciation: Organic Acids in UPW

Speciation of TOC indicating increased levels of organic acids provides assurance that something more serious is not going on with a UPW system. Generally, processes can tolerate higher levels of TOC when organic acids are the source. Organic acids include acetate, formate, glycolate, lactate, propionate, pyruvate, butyrate, malate, tartrate, oxalate, and citrate. Potential sources include incoming city water, 185nm ultra-violet reduction of larger organic molecules, and recycle water.

TOC Speciation: Semi-Volatile Organics in Water

Organic contamination on wafer surfaces can seriously deteriorate wafer cleaning efficiency which can result in non-uniform etching. Balazs can test for semi-volatile organics in UPW at the ppb and sub-ppb levels. This technique utilizes TD-GC-MS and is capable of detecting a wide variety of organics such as plasticizers and siloxanes. This method can be a valuable resource to the process engineer looking for sources of contaminants.

There are many tests available to detect contamination on the wafer itself. Many of those used by IC chip manufacturers (such as optical and electrical) do not provide compositional information. Techniques such as VPD-ICP-MS, SARIS™ (laser ablation ICP-MS), SEM/EDS, FTIR, Raman, GC-MS, SIMS and TXRF are valuable tools used to identify contaminant composition at the elemental or compound level. All of these tests are recommended to assist the process engineer in determining the cause for yield loss or to improve yield. It is highly recommended that fabrication engineers use these tests not only when a problem is detected, but to gain baseline information for use in an evaluation as to what has changed when a problem is observed.

Innovative New Tests & Redeployment of Existing Tests

(continued)

Wafer Tests: Trace Elements on Wafers by VPD-ICP-MS

To confirm the efficacy of critical cleaning steps or to identify sources of metal contamination, it is often desirable to know the level of trace metals and their distribution across the wafer. For trace metal contamination, Vapor phase decomposition (VPD) coupled with inductively coupled plasma-mass spectrometry (ICP-MS) or TXRF is used to measure metals on full wafers.

Refined analytical methods such as radial VPD-ICP-MS and Quadrant VPD-ICP-MS allow the measurement of trace metal contamination in localized areas of the wafer. This also enables the comparison of trace metal levels on the outer edge of the wafer to those in the middle of the wafer. This analysis provides useful information about contamination distribution across the wafer surface. From this data, one can better identify the source of contamination and whether it is from resist removal processes, cleaning/rinsing processes, implanters, reactors, wafer handling, etc.

Wafer Tests: Organics on Wafers

A) GC-MS is a widely used technique employed to help identify organic contamination on wafers. With specialized techniques, Balazs™ is able to identify organics to sub monolayer levels. This is a very effective way to measure what “sticks” to the wafer.

B) FTIR is another approach used for the identification of organic contaminants through the identification of organic functional groups. It is a very useful tool when trying to determine if a part in a system (such as an o-ring) has failed.

Innovative New Tests & Redeployment of Existing Tests

(continued)

C) Raman Spectroscopy is used to identify closely related organic and inorganic materials. This technique can examine particles down to 0.7 μm in diameter and has the capability to map samples to show distribution of contaminants.

Balazs™ has a companion CD available which discusses AMC's in great detail. Please contact Balazs™ for a copy of this guideline.

Airborne Molecular Contaminants (AMC's)

In addition to the effects of water and cleaning processes on the wafer, cleanrooms, cleanroom air and the wafer environment are known to be potential source of contaminants. Airborne Molecular Contaminants (AMCs) diffuse to a surface faster than particles, leading to more rapid contamination. If adsorbed onto the wafer surface, it may react with the surface to etch, corrode or react with other AMCs, light or UV to form a deposit or haze. Therefore, on-going measurement of cleanrooms, air, gases and the wafer environment should be routinely conducted.

Additional Tests and Services

Dynamic/Static Leach Tests (Tool Component Tests)

Balazs™ routinely conducts leaching studies which can help to determine rinse down profiles or contamination contribution through ruggedness testing. SEMI has developed a guideline requiring rinsing and testing for all assembly units installed in process equipment before shipment of these

Innovative New Tests & Redeployment of Existing Tests

(continued)

units to tool manufacturers or to the fab (SEMI E49.2)⁴. This procedure tests potential impacts to water quality between the POE and POP. Challenges for SEMI E49.2 include possible redesign of assemblies to allow samples to be pulled, the potential need for specialized sampling techniques, and in some cases multiple sampling points within a tool.

SARIS™ Laser Ablation ICP-MS

This is a powerful technique which can assist the engineer in performing detailed materials evaluation and contamination identification to help trace back contaminants to a potential source be it a system component, powder or residue. SARIS™ provides quantitative analytical results and serves as an excellent compliment to other techniques such as SEM-EDS and SIMS. SARIS™ is capable of detecting all elements with the exception of He, H, F, N, Ar and O.

Product Type vs. UPW Guideline

The following tables are included as a Guideline for the quality of water that the Process Engineer can expect from Facilities at the Point of Delivery (POD). It is not meant to represent all of the parameters that the facility engineer must monitor to ensure that the UPW system is operating appropriately. Other parameters that need to be watched such as pressure drop across filters, make-up operational parameters, rejection rates on the reverse osmosis (RO) units, total production volume, etc., have not been included in this guide. These measurements are also very important and must be followed to insure maximum production and quality while reducing cost.

In addition to the POD, many supporting locations are also monitored within the purification system to ensure quality compliance. Monitoring the incoming water, major water system components and the return water to the plant is equally important to detect quality changes before they negatively impact the POD. See the Comprehensive Monitoring Guide (Appendix II) for more information.

To make the best decisions from this data, it is critical that the users of laboratory results fully understand how a lab generates its data and how that data is manipulated to arrive at the final reported number. Please see Appendix 1 for important information.

Product Type vs. UPW Guideline Tables

(General Paramters)

Memory Size	16M	16-64 M	16-256 M	64M-1G	256M-1G	1-4 G	1-4 G		
Geometry Design Rule (nm)	500	350	250	180	130	90	65	57	50
Resistivity @ 25° C	18	18.1	18.2	18.2	18.2	18.2	18.2	18.2	18.2
% of time	90	95	99	100	100	100	100	100	100
TOC (ppb)									
Batch	10	10	10	--	--	--	--	--	--
On-Line	2	2	2	2	1	1	1	1	1
Particles cts/L μm									
SEM									
0.05 - 0.1	3000	1500	1000	1000	1000	1000	900	800	400
0.1 - 0.2	1000	700	350	250	100	100	100	100	100
0.2 - 0.5	500	400	200	100	50	50	50	50	50
0.5 - 1.0	100	50	30	30	10	10	10	10	10
>1.0	50	30	20	20	10	10	10	10	10
On-Line									
0.05 - 0.1	--	1000	1000	1000	1000	1000	900	800	400
0.1 - 0.2	1000	350	250	100	100	100	100	100	100
0.2 - 0.5	500	100	30	10	10	10	10	10	10
0.5 - 1.0	200	50	10	5	5	5	5	5	5
>1.0	100	20	5	1	1	1	1	1	1
Oxygen (ppb)	--	10	10	10	10	10	10	10	10
Bacteria (cfu/vol)									
100mL	5	3	1	--	--	--	--	--	--
1 Liter	50	30	10	1	1	1	1	1	1
Silica (ppb)									
Total	--	5.0	3.0	2.0	1.0	0.5	0.5	0.5	0.5
Dissolved	3.0	1.0	0.3	0.3	0.3	0.3	0.3	0.3	0.3

Product Type vs. UPW Guideline Tables

(Metals & Other Elements)

Memory Size	16M	16-64 M	16-256 M	64M-1G	256M-1G	1-4 G	1-4 G		
Geometry Design Rule (nm)	500	350	250	180	130	90	65	57	50
Trace Elements by ICP/MS (ppt)									
Aluminum	20	10	10	5	3	3	3/1 ^{Note 2}	3/0.5	3/0.5
Antimony	10	5	5	3	2	2	2	2	2
Arsenic	20	10	5	2	2	2	2/1	2/0.5	2/0.5
Barium	10	5	3	1	1	1	1/1	1/0.5	1/0.5
Bismuth	10	5	3	3	2	2	2	2	2
Boron ^{Note 1}	--	30/1000	20/500	10/300	10/100	10/100	10/100	10/100	10/100
Calcium	20	20	15	5	3	3	3/1	3/0.5	3/0.5
Cadmium	10	10	5	3	3	3	3	3	3
Cobalt	10	10	5	3	2	2	2/1	2/0.5	2/0.5
Chromium	20	10	5	3	2	2	2/1	2/0.5	2/0.5
Copper	20	10	5	3	2	2	2/1	2/0.5	2/0.5
Gallium	10	8	5	3	2	2	2	2	2
Germanium	20	20	10	10	5	2	2	2	2
Iron	30	20	20	10	2	2	2/1	2/0.5	2/0.5
Lead	20	20	10	5	2	2	2/1	2/0.5	2/0.5
Lithium	20	10	10	5	2	2	2/1	2/0.5	2/0.5
Magnesium	20	10	5	3	3	3	3/1	3/0.5	3/0.5
Manganese	20	10	10	5	3	3	3/1	3/0.5	3/0.5
Molybdenum	20	10	5	3	3	3	3	3	3
Nickel	20	10	10	5	3	1	1/1	1/0.5	1/0.5
Potassium	20	20	20	10	2	2	2/1	2/0.5	2/0.5
Sodium	30	20	20	10	2	2	2/1	2/0.5	2/0.5
Strontium	10	5	5	2	1	1	1	1	1
Tin	20	10	10	5	2	2	2/1	2/0.5	2/0.5
Titanium	30	10	10	5	3	3	3/1	3/0.5	3/0.5
Tungsten	20	10	5	5	1	1	1	1	1
Vanadium	20	20	10	5	2	2	2	2	2
Zinc	20	20	10	5	5	3	3/1	3/0.5	3/0.5

Product Type vs. UPW Guideline Tables (Metals & Other Elements Continued)

Notes For Metals Tables:

- 1) Tolerable boron concentrations are product dependant. However, there is evidence that even higher levels can be tolerated by some fabs. Our ultimate recommendation is that fabs establish their own boron specifications.
- 2) Specifications for the ITRS critical elements are indicated in **RED**. The corresponding Balazs™ Guidelines (indicated in **BLACK**) continue to reflect numbers which are currently working successfully for our customers and are achievable using routine (non-research) procedures. *NOTE: Detection limits at or below both specifications are available.*

Product Type vs. UPW Guideline Tables (Anions/Cations)

Memory Size	16M	16-64 M	16-256 M	64M-1G	256M-1G	1-4 G	1-4 G		
Geometry Design Rule (nm)	500	350	250	180	130	90	65	57	50
Cations by IC (ppb)									
Sodium	0.05	0.05	0.05	Note 1	Note 1	Note 1	Note 1	Note 1	Note 1
Potassium	0.05	0.05	0.05	Note 1	Note 1	Note 1	Note 1	Note 1	Note 1
Ammonium	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Calcium	0.05	0.05	0.05	Note 1	Note 1	Note 1	Note 1	Note 1	Note 1
Magnesium	0.05	0.05	0.05	Note 1	Note 1	Note 1	Note 1	Note 1	Note 1
Anions by IC (ppb)									
Fluoride	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Chloride	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Bromide	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Nitrate	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Nitrite	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Phosphate	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Sulfate	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05

Note 1: See the “Metals” summary table for guidelines.

Appendix I: How to Use the Data

Detection Limits vs. Reporting Limits

The analysis of UPW in the ppq (sub ppt) to low ppt range presents some challenging issues for the fab, facilities and laboratory. Pushing analytical data to the extreme levels of sensitivity required to satisfy some ITRS specifications puts a burden on the lab to ensure that they are producing both accurate and precise data. Once results are reported, fab personnel must then use the data to make decisions. Very often these are go/no go decisions. Obviously the reliability of the data is crucial and the end user must have full confidence that the result is accurate and representative of the material analyzed.

All labs have published "detection" limits. The important question, which has a direct impact on the usefulness of the data, is how are these limits defined and determined? Often results can be reported which look impressive but in actuality are at best minimally useful since they may be deep in the noise and uncertainty of the method.

At Balazs™, we are very careful to distinguish between method detection limits (MDL), instrument detection limits (IDL) and reporting limits (RL or quantitation limits) so that those using the data understand that the result has a certain degree of confidence and that the uncertainty of the measurement is understood.

The fact is that results can be provided which are lower than our published reporting limits, but the user must be aware that this practice increases the uncertainty associated with those numbers and reduces the usefulness of the information.

Appendix I: How to Use the Data DLs vs. RLs

(continued)

Balazs™ determines the IDL and MDL. The IDL is a measure of the performance of the analytical tool under optimum conditions with no impact from sample handling or matrix effect. In contrast, the MDL incorporates sample preparation and matrix issues (just as would be the case with a sample) into the determination. The IDL is always less than or equal to the MDL.

Unfortunately, because both IDLs and MDLs are statistically-based, they may not be achievable on a daily basis. The signal to noise ratio may not even be sufficient for detection. Statistics are set to limit chances of a false positive, not a false negative. Generally, neither one takes impacts from sample collection into account. Data reported at the IDL or MDL look impressive, but the uncertainty of the data may be quite high (>200%). This data is not reliable for making operational decisions.

In most cases, Balazs™ takes the MDL and sets a reporting limit (RL) 2 to 5 times higher. This means that the reported result has a much greater degree of certainty associated with it and the user can have more confidence that the number has significance. It is possible, however, for results at the RL to still have an uncertainty of 50% or more.

Additionally, the laboratory's reliability checks and routine QC procedures must be clearly stated. Only by understanding how a lab defines its data and monitors itself will the user of the data be in a position to make effective go/no go decisions.

When determining detection and reporting limits, Balazs™ looks at four critical areas including the background equivalent concentration (BEC), data precision, data accuracy and the confidence limits at the reporting limit (not the detection limit). The trace levels at which we are all working make it imperative that all four areas be fully investigated and understood by the

Appendix I: How to Use the Data DLs vs. RLs

(continued)

laboratory. This is the only way that a lab can ensure that the results reported are both precise and accurate.

Table II contains data contrasting the confidence intervals of statistically derived MDLs with RLs. The main difference between the MDL and the RL is that the RL was reproducibly measured at the analytical tool using actual low level spikes whereas the MDL is simply a calculated value.

The data illustrates that there is a significant degree of uncertainty associated with each of the MDL values. In practice the uncertainty associated with results reported at the MDL can easily be 100% to 200% or more. Although the confidence of values at the RL is tighter than at the MDL, the data also demonstrates that the degree of uncertainty varies from element to element. This factor must be considered when using the data and in setting guidelines.

Table II: Example Statistical Summary

Element	MDL ¹ (PPT)	Confidence Interval ²	RSD ³ %	RL ⁴ (PPT)	Confidence Interval ²	RSD ³ %
Calcium	0.9	± 0.46	43.3	2	± 0.21	7.0
Iron	0.8	± 0.34	22.4	2	± 0.19	5.9
Nickel	0.8	± 0.65	76.8	2	± 0.45	13.7

Notes:

- 1) Statistically determined method detection limit (parts per trillion).
- 2) 95% Confidence interval.
- 3) Percent relative standard deviation of results obtained using several different low-level standards.
- 4) Reporting limit verified by reading actual low level standards (parts per trillion).

Appendix I: How to Use the Data DLs vs. RLs

(continued)

Understanding the uncertainty associated with the data will allow the user of the data to act with confidence in making decisions related to their system or process. Inevitably, the likelihood of a water system “failing” will increase if specs continue to be set at the MDL of an analytical method. It is recommended to set a spec limit of 10 times the RL for the parameter when possible. Unless one has confidence in and an understanding of the laboratory’s practices, decisions should not be made on the basis of the data reported.

Appendix II: Comprehensive Monitoring Program

Water quality guidelines for the microelectronics industry have historically aimed towards best achievable and best-measurable levels of water quality at the point of distribution (POD). With stable, high quality water in place at the POD, the industry is shifting its focus to study water quality closer to the wafer point of use.

Monitoring the POD location assures the customer that the water plant is operating correctly and high purity water is consistently discharged. However, in addition to the POD, many supporting locations are also monitored within the purification system to ensure quality compliance.

Monitoring the incoming water, major water system components and the return water to the plant is important to detect quality changes before they negatively impact the POD. Unfortunately, many companies only monitor water quality at the POD; therefore “normal” levels from the city through the water plant are unknown. By focusing only at the POD, a problem is not discovered until it is too late. Establishing a comprehensive baseline from the incoming water to the POD can be a great aid in troubleshooting during crisis times.

Profiling each major component would be ideal, however, this is usually time and cost prohibitive. Key areas to profile would be the incoming city water (before any treatment), Pre RO (after all makeup system components), Post RO, Post Primary Ion Exchange Beds, Post Polish Ion Exchange Beds, POD, and Fab Return. Important parameters to consider are Ions, TOC, Silica, Metals and Bacteria.

Collecting all samples on the same day produces a water quality “snapshot” of the entire water system. Because a water system is dynamic, a database should be collected to understand “normal” system variances over time.

Appendix II: Comprehensive Monitoring Program

(continued)

Parameter	Incoming City Feed ¹	Pre RO ²	Post RO	Post Primary IE ³	POD ⁴	Return Loop	POE/POU Tools ⁵
Resistivity	On-Line	On-Line	On-Line	On-Line	On-Line	On-Line	Note 6
TOC ⁷	On-Line or Monthly	On-Line or Monthly	On-Line or Monthly	On-Line or Monthly	On-Line	On-Line	TBD
Particles on-line	Turbidity or Silt Density	Turbidity or Silt Density	-	-	On-Line	-	TBD
Particle SEM	-	-	-	-	Monthly	-	Monthly (POC)
Dissolved Oxygen	-	-	-	-	On-Line		TBD
Bacteria	-	-	-	-	Weekly	Weekly	Weekly
Silica Total	Monthly	Monthly	Monthly	Monthly	Monthly	-	-
Silica Dissolved	Monthly	Monthly	Monthly	On-Line	On-Line	-	-
Anions	Monthly	Monthly	Quarterly	Monthly	Monthly	Monthly	Monthly
Trace Metals ⁸ (Incl Na & B)	Monthly	Monthly	Monthly	Monthly	Monthly	Monthly	Monthly
Sodium	-	-	-	-	On-Line	On-Line	-

Note: This table represents a general guideline to sample method, location and frequency. Site specific monitoring packages can be designed for cost savings.

- 1) Incoming feed before any pre-treatment.
- 2) Pre RO is Post any RO prefilters.
- 3) Post primary ion exchange.
- 4) Post final filter.

- 5) On-line to be developed.
- 6) Applicability of test & ability to measure is limited.
- 7) On-line vs. batch dependant on spec. On-line required if spec is <10ppb.
- 8) Includes Na & B. These may be measured at post primary IE & POD.



Appendix III: Guidelines History

In 1976, Balazs™ Analytical Laboratory recognized a need for more extensive measurements than resistivity to measure the quality of ultra pure water. Consequently, after conducting numerous measurements of the water used to produce products with satisfactory yields, we introduced our first pure water specifications which included six basic tests required to measure water quality. This started the focus on pure water measurements in more extensive and practical ways that allowed correlation of water quality to product yield.

As systems improved and operations became more efficient, the quality of the ultra pure water improved. In 1980, Balazs™ issued a new expanded specification with lower allowable contaminant levels. Another expansion and reduction was issued in 1985. It was at this time that the SEMI chemical committee, after a task force study, adopted the Balazs™ Pure Water Specifications and included them in their BOSS¹ book as Pure Water Guideline. The term "guidelines" was used instead of "specifications" due to the inability to have a UPW Standard that all could use.

In 1987, Balazs™ Analytical Laboratory made a complete study of pure water quality throughout the U.S. covering 80 IC manufacturing sites, which produced numerous devices of varying complexity. This six-month study resulted in our 1988 Pure Water Specifications and Guidelines, which focused on purity as it related to product complexity. Again, the tests were expanded and allowable contaminant levels lowered. SEMI adopted these specifications as their SEMI Guidelines in 1992. They first appeared in the 1993 BOSS book.

From 1988-1992 Water Systems continued to improve through system component evaluation, and new analytical methods, which allowed the semiconductor industry to use UPW in new ways when processing wafers. Improvements in many areas once again allowed for higher quality of water and far more sensitive measurements of ultra pure water. The studies again related water quality to product yields at manufacturing sites all over the U.S. and was completed in 1992. At that time we published our 1993 Water Specifications and Guidelines booklet, which also included a "Trouble Shooting" section.

From 1993-2000, the process of testing, trouble shooting, consulting on the design of ultra pure water systems, and relating water quality to yields continued. After numerous requests, a detailed study was performed again in 1999. The result of this study led to our 2000 Ultrapure Water Monitoring Guidelines Booklet.

Our 2007 Edition of the Guideline Booklet is the second publication since Air Liquide acquired Balazs™ in 2001. It is an update based on current water quality studied from Fabs around the world. It reflects new industry information relating contaminants to yield, as well as further improvements in our ability to measure ultra pure water and the wafer environment.

Appendix IV: UPW System Basic Trouble Shooting Tables

All is well, then suddenly something changes and an ultrapure water parameter is out of spec. Now, the source of the contaminant must be found and quickly. The first questions usually asked are what changed and where? This is always a difficult situation.

In an effort to help individuals responsible for pure water production, a troubleshooting guide has been included. It is not meant to be all-inclusive or to be considered adequate support for untrained personnel. An experienced operator who understands UPW components, who can interpret analytical data and who is able to maximize efficiency is an absolute requirement for all companies who use UPW today.

A water system is dynamic. There are untold ways contaminant levels can increase. Some areas to consider when troubleshooting are: Analytical instrument problems, operational activities, city water feed changes, and Fab activities. Usually, the first step in tracking a contaminant is to verify that the reading is real. The reading can either be supported by other instruments within the water system or by placing a known “good” instrument in its place. If the reading is real, tracking the source can begin. Have there been any recent operational activities within the water system? This could be routine maintenance like backwashing multimedia beds, cleaning RO membranes, regenerating ion exchange beds. Have any new components been installed or removed? Any new filters added, old carbon beds replaced, or new ion exchange resins installed? Sometimes small activities can be overlooked yet be the source of the problem. A plant with detailed log books can speed troubleshooting. Pre-qualifying new components to spec before they are installed can help avoid problems altogether.

If no operational activities can be identified, then a look at the city water is in order. This is usually a difficult location to identify problems, as not much on-line monitoring is done. Changes in city water quality can be “voluntary” such as a change in distribution locations, or water sources or “involuntary” changes from variations due to droughts, floods, or seasons. It is important to

Appendix IV: UPW System Basic Trouble Shooting

(continued)

monitor as many parameters as often as possible at the city water location. It is helpful to establish alarms which will alert operations to any changes in the feed water. Establishing a relationship with your city water provider and/or other local users can help provide additional information about current source water quality. Some companies build much redundancy into the make up system to minimize or eliminate any upsets from the city water. Containing an upset may not be possible without additional resources available to assist with contaminant removal.

Another important area to monitor closely is the return water from the fab. On-line instrumentation is usually in place to identify any contaminant spikes from fab activities. In addition to resistivity, ions are usually sampled off-line to understand which contaminants are “normal” so that if a change occurs, the type of ion can help determine it’s source i.e. chloride or sulfate from an acid, or ammonium from a base.

Isolating and identifying contaminants in an ultrapure water system can be difficult at best. Establishing a comprehensive monitoring program through the system during “normal” times, can aid tracking the source of an upset condition when something changes. Please call our lab at 510-624-4000 for further assistance.

Appendix IV: UPW System Basic Trouble Shooting

(continued)

Situation I: Resistivity Drops Below 18.2 megohm-cm

Possible Cause	What to Do
Resistivity Meter Failure	a) Check Meter Calibration. b) Check and Clean Sensor c) Check water temperature for drastic changes which can affect readings.
Depleted Ion Exchange	Have resistivity, silica and IC samples taken (cations/anions) post polishers. ^{Note 1}
Organic Contamination	a) Turn UV off. If resistivity goes up, test for THMs (Trihalomethanes) or UV active materials. b) Check TOC monitor and note total carbon, P1, P2, P3 if using an Anatel on-line meter. If P2 or P3 quantity increases significantly get a more in-depth organic analysis. Call Balazs™ at 510-624-4000 c) Check for Purgeable organics or organic acids. d) Add an organic scavenger such as carbon or anion resin.

Note 1: If sufficient silica is not stripped from the primary mixed beds after regeneration, they will not rinse-up properly and short service runs can result.

Appendix IV: UPW System Basic Trouble Shooting

(continued)

Situation II: Trihalomethane (THM) Concentration Increasing

Possible Cause	What to Do
High THM's in Source Water.	Test for THM's on source water. If high, call source water supplier to determine if they are seeing larger quantities of THM's or have increased chlorination. If so, increase UV before primary mixed beds.
Producing More THM's With System Chlorine Injection.	Check chlorine concentration and analyze pre and post chlorine injection for THM's. If chlorination is causing high THM's, reduce chlorine injection.

Situation III: Dissolved Silica Level High

Possible Cause	What to Do
Polisher Anion Resin Depleted	Regenerate or replace resin.
Improper Ratio or Insufficient Regeneration of Anion Resin in Polishers.	<p>a) Check anion resin after regeneration. If necessary, regenerate anion resin at 175 deg F using sodium hydroxide.</p> <p>b) Check ratio of anion to cation. Have resins analyzed by manufacturer for % regeneration, integrity, fouling, etc</p>
RO Malfunction	Check overall RO rejection for silica and TDS.
Makeup Mixed Bed or Anion Resin Failure.	Check ratio of anion to cation. Have resins analyzed by manufacturer for % regeneration, integrity, fouling, etc

Appendix IV: UPW System Basic Trouble Shooting

(continued)

Situation IV: TOC Out of Spec

Possible Cause	What to Do
Failed TOC Analyzer	a) Check against another analyzer. b) Check against off-line TOC (batch) results from commercial laboratory. c) Have analyzer checked and recalibrated from the manufacturer.
RO Malfunction	Determine TOC rejection by measuring carbon content in source vs. permeate water. If low, check individual pressure vessels for an outlier.
D.I. Failure Due to Carbon Overload on Anion Resin.	Check silica and TOC level polishing resins. If high, regenerate anion resin at 175 deg F using sodium hydroxide.
Source Water has Changed.	Call the local municipal water supplier and ask if source water supply has changed. If yes, add organic resin scavenger. Replace carbon media. Add more 185 UV. Increase Ozone levels in storage tank.
Operational Activities	New components added (resins, filters etc.)
Change in Make-up System Chemical Additives	New coagulants, biocides or antiscalants
185nm UV Lamp Deteriorating	Replace bulbs and/or quartz sleeves as recommended by manufacturer.

Appendix IV: UPW System Basic Trouble Shooting

(continued)

Situation V: Bacteria Level Constantly Higher Than Spec

Possible Cause	What to Do
Sample Port Contaminated.	<ul style="list-style-type: none">a) Clean sample port by flushing with IPA and then thoroughly flushing with UPW, by exercising the valve, before resampling.b) Replace valve if bacteria persists at that valve, but not elsewhere in the line.c) Be sure valve is not a deadleg. It must not be more than three (3) pipe diameters from the line being tested.d) Remove and replace any ball valves.
Deadleg	Check both pre and post sampling port for deadlets, unused valves or meters, slow flowing lines.
254 nm UV Lamp Deteriorating	<ul style="list-style-type: none">a) Check lamp intensity. If lamp is over 6-9 months old, replace.b) Sample for bacteria level before and after UV.
Lines or Filter Housing Contaminated.	<ul style="list-style-type: none">a) Sample for bacteria levels on individual filters.b) Perform system sanitization and replace filters.

Appendix IV: UPW System Basic Trouble Shooting (continued)

Situation VI: Particles Out of Spec by Size or Quantity

Possible Cause	What to Do
Analyzer Malfunctioning	<ul style="list-style-type: none"> a) Check instrument for calibration and setup parameters. b) Check sample valve and feed tubing to instrument for cracks, leaks, vibrations c) Use different test method, i.e., SEM/DCM
Sampling Procedure or Port.	<ul style="list-style-type: none"> a). Replace sampling valve with high quality type for UPW sampling, minimize use of Teflon tape. b). Although not recommended, if batch sampling is used, install protected atmosphere (HEPA or Nitrogen) over sampling valve especially if valve is in high traffic area.
Bubbles	<ul style="list-style-type: none"> a) Check flowrate and back pressure valves. b) Test with method that does not detect bubbles such as SEM/EDS with additional testing by FTIR/Raman for organics as indicated.
Filters are Sloughing	<ul style="list-style-type: none"> a). Check final filter housing for un-seated filter visually or by using filter integrity test. b). If new filters, take back off line and slush for 24 hrs. c). Determine particle composition by SEM/EDS analysis.
RO Failure	Check overall system rejection for TDS. If low, check individual pressure vessels for an outlier.
Deadleg	Track system very carefully to look for deadlegs, unused valves, especially post final filter and pre test port. <i>Note: Valves on filter housing can serve as a particle source especially if in standby mode.</i>
Resin Bed Deteriorating	Have resin analyzed, by mfg especially for bead integrity.
O-Ring or Elastomer Shedding	<ul style="list-style-type: none"> a). If using Ozone, make sure complete decomposition. b). Wrong type of product being used. Replace part. c). Poor quality valve deteriorating. Replace valve.

Appendix IV: UPW System Basic Trouble Shooting

(continued)

Situation VII: Residue Found

Possible Cause	What to Do
RO Bypass	Check TDS and TOC rejection by measuring content in source vs. permeate water. If low, check each pressure vessel.
Degenerated D.I. Beds	<ul style="list-style-type: none"> a) Have resin analyzed, by mfg especially for bead integrity. b) Regenerate and retest. c) If using ozone, check for ppb levels before resins.
Filters Not Functioning Properly	<ul style="list-style-type: none"> a) Check particle count post filter b) Identify residue. Use SEM/EDS test.

Situation VIII: Anions, Cations or Metals Above Spec

Possible Cause	What to Do
Possible Sample Port or Bottle Contamination.	Retest
Resins Depleted	<ul style="list-style-type: none"> a) Check resin performance pre and post polishers. b) Check ratio of anion to cation resin. c) Check resin condition d) Recalculate expected resin capacity vs. usage e) If using ozone, be sure complete decomposition.
Stainless Steel Degradation	Test after Teflon coated components to detect deterioration.

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