ULTRAPURE WATER:

The Evolution OF "Ultrapure"

A Trail Blazed by Instrumentation

By Chubb Michaud, CWS-V

Summary: *The pursuit of ultrapure water it would seem is driven less by initial need so much as the ability to detect increasingly tighter levels of purity and the instrumentation behind that. Still, absolute purity is as unachievable as absolute objectivity. Here is an attempt to objectively discuss the evolution from parts per million to parts per billion to parts per trillion in little more than two decades and its impact on water treatment, particularly for ultrapure water needs that include the semiconductor, microelectronics and pharmaceutical industries.*

It's been said, "necessity is the mother of invention," implying that the logical progression of process development is: 1, the expression of need, 2, the rush to supply, and 3, the ability to measure progress.

Progress is not always initiated by need, however. A case in point is high purity water. The need for water of higher and higher purity for industrial processes has never really been expressed until after the ability to measure it was developed. It can be safely said that instrumentation has been the driving force for high purity water development. Defining "ultimate" quality and perceiving its benefits is difficult until an accurate means of measuring an approach is developed.

There's a tendency among scientists to "peg the needle"—meaning that if a measuring device can detect room for improvement, one will demand realization of that improvement even though the need hasn't been established, nor the benefits of the improvement properly assessed. One wonders what would've happened to the development of the automobile and interstate highway system if all motor vehicles had speedometers that "pegged" at 60 mph.

Measure for measure

Water is one of the purest natural substances found on the planet. Even seawater is naturally 96.5 percent pure. Rivers and lakes are typically 99.95 percent pure—as is. In addition, no other strategic substance has availed itself to such high levels of purification and from such compact "refineries" as water. Today's technology can take city-supplied feed water from 99.95 percent to 99.999999 percent pure—that's double digit parts per billion, or ppb—in a matter of a few minutes. At that level of purity, a 20,000-gallon swimming pool evaporated to dryness would leave a residue of less that one gram—roughly the same amount of salts found in a single liter of some tap waters.

So what is "pure" water, and how far can we go towards achieving ultimate purity? "Pure," by definition, would be 100 percent. The practical interpretation of pure might describe 100 percent as containing non-detectable levels of contamination. Here we go—back to instrumentation! Obviously, different users of "pure" water will have varied definitions, according to their needs.

By any other name

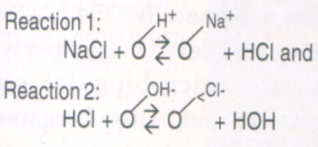
Water is defined chemically by the symbol H_2O. Yet the practical definition of water as we know it will always mean "an aqueous solution," containing various levels of dissolved or suspended contaminants. Seawater is water. Lakewater is water. High purity water is still water. There is no limit to the number of 9s we can place after the decimal point in describing purity and still be something less than 100 percent pure. In chemistry, Avagadro's number tells us that a single mole—about 18 cubic centimeters—of H_2O contains 6.02×10^{23} molecules of H_2O. One liter of water would contain about 55.6 moles, or 3.34×10^{25} molecules

(That's 10 followed by 25 zeroes!). The presence of a single molecule of salt as sodium chloride (NaCl) would still leave us shy of 100 percent pure by an infinitesimally small amount.

High purity H_2O has a marked ability to react with its own container and form a "salt" solution. It could be said that because of its excellent solvency, 100 percent H_2O, or "pure" water, does not, cannot and will not exist except as a single molecule. By this definition, 100 percent pure water is an impossibility.

The impossible dream

In high purity water production, the most complete salt removal technique remains ion exchange. In this process, positively charged cations are exchanged for hydrogen (H^+); and negatively charged anions are exchanged for hydroxyl (OH^-) ions, which then combine to form pure HOH or H_2O (water). However, these are equilibrium reactions that, by definition, are not 100 percent complete. As the driving force (the concentration of salts) approaches zero, the rate of reaction for ion exchange also approaches zero. In other words, the process slows down. The high purity of the water causes a degree of dissociation of the HOH and the water therefore ionizes to H^+ and OH^-. Since these ions are the regenerant ions for the ion exchange resin, there's some reversal. Hence, the reactions are always shown as:



Reaction 1:

$$NaCl + \overset{H^+}{O} \rightleftarrows \overset{Na^+}{O} + HCl \text{ and}$$

Reaction 2:

$$HCl + \overset{OH-}{O} \rightleftarrows \overset{Cl-}{O} + HOH$$

Table 1.
Evolution of Pure Water Specifications for Electronics

Test	1975	1980	1985	Attainable
Residue	0.5	0.3	< 0.3	0.1
TOC (ppb)	200	100	< 50	< 20
Particulates/L	4000	1000	<1000	<500
Bacteria/100 ml	20	20	<6	0
Silica (ppb)	5	3	<5	<3
Sodium (ppb)	—	—	0.2	0.05
Resistivity (megohm)	16.0	17.0	17.9	18.3

Source: High Purity Water Preparation, pg 24

Table 2.
***Requirements for Electronic-Grade Water**

	Type E-I	Type E-II	Type E-III	Type E-IV
Resistivity *(megohm at 25ºc)*	>18 for 95% of time Not <17.0	>17.5 for 90% of time Not <16.0	12.0	0.5
Silica	5 ppb	10 ppb	50 ppb	1 ppm
Particle/mL	1	3	10	100
Particle Size	<.10µm	<.5µm	<1.0µm	<10µm
Viable Bacteria	<1/1,000 ml	<10/1,000 ml	<10/ml	<100/ml
Sodium	**0.5 pp**	**1 ppb**	**5 ppb**	**1 ppm**
TOC	<25 ppb	< 50 ppb	<300 ppb	<1 ppm
Endotoxins	0.03 eu	0.25 eu	N/A	N/A

Source: High Purity Water Preparation, pg 17

eu = Endotoxin Unit
**Table is incomplete - certain trace metals are not included.*

Determining purity

As the soluble ionic content (or salts) level in water is reduced, many of the contaminants of water become too low to measure by selective ion analysis. We must, therefore, rely on other means of determining purity. Salts ionize, making water conduct electricity—hence the warning on hair dryers and other electrically powered devices stating not to use them around running water or in the shower. The more salts, the higher the conductivity of the water. So it follows then that the lower the salts, the lower the conductivity or conversely, the higher the resistivity.

Resistivity is measured in ohms. Conductivity is the reciprocal or opposite of resistivity, and is measured in mhos (ohm spelled backwards). One ohm is also written as 1 Ω (using the Greek letter omega). One million ohms is equal to 1 megohm ("mega" meaning 1 million). Converting this to conductivity units, 1 megohm (or meg) is equal to 1 micromho (written as µmho using the Greek letter "mu" (µ) to signify 1/1,000,000). This is also called a micro-siemen (written as 1 µS). Therefore, 1 µmho = 1 µS = 1 meg Ω.

High purity water—often referred to as 18 meg water—is approximately 0.06 µS and contains a salt level of 0.03 ppm or 30 ppb. The purest water produced will read 18.3 meg (0.05 µS) and even water containing ppt (parts per trillion) levels of salt (in the swimming pool above, for example, this would equate to less than a milligram of residue) will not measure much better than that. However, instrumentation that can readily determine ppt levels of sodium now exist—that's 1/1,000,000,000,000 or one millionth of a millionth of a part. The highest purity water specifications need not use resistivity as a defining quality because instrumentation now allows us to measure even higher purity via sodium levels. If it meets the sodium level, it automatically "pegs" the resistivity meter.

Pure evolution

The connection between higher purity water and higher acceptance yields from semiconductor manufacturers has always been known but not fully appreciated (see *Table 1*). Sixteen megohm water specs were pretty typical in the '70s; bacteria and particle counts were low, but not zero. The ability to produce "holy" water was limited in part by equipment and experience as well as instrumentation. There was little drive to go full speed ahead because the cost of doing so, as well as the potential return, were both unknowns.

As the circuitry in modern electronics shrinks, the need for higher purity water is beginning to outpace both the ability to measure and the ability to produce it. Since the '70s, we have progressed in both these areas of concern as well as gaining a better understanding of the potential benefits for electronics manufacturing (see *Table 2*).

Circuits can now be produced with dimensions measured in fractions of a micron, with spaces in between that are even smaller. A single bacterium, dead or alive, can lay across the "wires" and short out the system. The need must now be answered.

ASTM D-5127 defines the requirements for "electronic"-grade water as seen in Table 2:[2]

High purity water must not only be low in dissolved (ionic) solids, but with particulate (suspended) solids as well. Ultrafiltration is able to remove particles down to below the size of even the smallest virus (.004 µm).[4]

The smallest animals

Many bacteria seem to find a source of nutrients and multiply—even in the purest of water. A single molecule of NaCl contains only two atoms. By contrast, a single bacterium may contain 10 billion atoms. Bacteria have a composition that is very similar to other animals including humans, less the skeletal components (see *Table 3*).

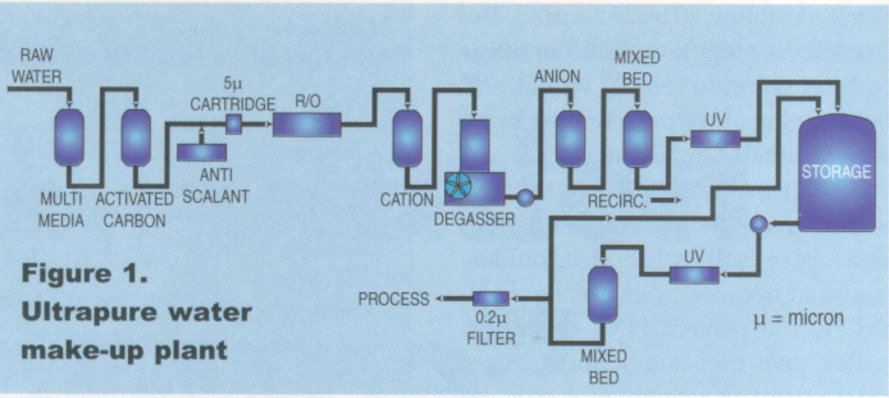


Figure 1. Ultrapure water make-up plant

Table 3. Composition of Bacteria

Element	*Content*
Carbon	50%
Oxygen	20
Nitrogen	14
Hydrogen	8
Phosphorous	3
Sulfur	1
Potassium	1
Sodium	1
Calcium	.5
Magnesium	.5
Chloride	.5
Iron	.2
Other	.3

Source: High Purity Water Preparation, pg. 58

Studies made in Japan in the early '80s reiterated the need for electronic-grade waters to be microbially pure as well.[1] Advances in ultrafiltration followed.

Avoiding clichés

"Pure as the driven snow" is just a cliché! All natural waters, including rainwater, will contain all of the following:

- Ionic contaminants,
- Organic contaminants,
- Particulate contaminants,
- Microbial contaminants, and
- Gaseous contaminants.

No one single filter or unit operation will remove all contaminants. Ionic contamination can be reduced by reverse osmosis (RO), EDR (electrodialysis reversal), EDI (electrodeionization), distillation and ion exchange. Adsorbents such as granulated activated carbon (GAC) RO and ion exchange can reduce organics. Near-complete removal usually requires some form of oxidation such as ozone or ultraviolet (UV) radiation, which characteristically involves an ozone residual, followed by ion exchange to polish out the ionic constituents formed from the oxidation—usually carbon dioxide (CO_2), and other mineral acids. Gaseous components such as CO_2 can be reduced by degassing towers, membrane scrubbers or ion exchange. Oxygen removal requires degassing, destruction via bi-sulfite reducing agents or adsorption by GAC.

Particulates such as colloids, dirt or microbes must be filtered out. Even sterile water, often considered "bacteria free," still contains the dead bodies of bacteria and billions of atoms. Further steps to destroy the carcasses and remove debris with ozone, UV, membrane filters and ion exchange are still necessary. In general, a combination of several or all of the monitored operations may be employed.

A typical ultrapure water production system will generally have "roughing" demineralizers with pre-treatment, followed by a polishing loop to maintain quality. Depending on the quality of the feedwater, pre-treatment can be rather extensive and may even include complete softening prior to an RO unit as part of the initial demineralization. An oxidation process—ozone or UV—will generally be employed to inactivate microbials prior to storage. Generally, 254 UV wavelength is considered the proper wavelength for microbiocidal effect. Whereas, 185 nm is the "organic destruct" wavelength.

Polishing loops generally consist of an organic destruct UV followed by a polishing mixed-bed deionization (DI) followed by particulate filtration. Special care is given to the preparation of these mixed bed resins. They must be treated with high purity chemicals and ultrapure water from their ion manufacturing plant, so that no traces of total organic carbon (TOC), silica, metals and sodium can stem from the resins themselves. They're frequently not returned to the polishing loop once regeneration is required. New resins are used and the regenerated ones move down the line to less critical applications. A typical ultrapure water plant is shown in Figure 1.

Conclusion

New advancements in analytical instrumentation have enabled us to measure ultrapure water more consistently, leading to better production control. Parts per trillion (ppt) levels of sodium are now not only measurable, but also achievable. Upgrading old clean water systems to newer ultrapure specifications probably remains not "do-able" because older-type systems are actually generators of particles and organics. Ultrapure water production is not an "off the shelf" design. Each system is carefully engineered by experts in the field to accommodate individual raw water supplies and end-user needs.❑

References

1. Meltzer, T.H., *High Purity Water Preparation*, Tall Oaks Publishing, Littleton, Colo., 1993.

2. Michaud, C.F., "Water and Nutrition from A-Z," *WC&P*, January 1998.

3. Michaud, C.F., "Catching Up with the Metric System," *WC&P*, March 1996.

4. *WQA Glossary of Terms*, 3rd Edition, Water Quality Association, Lisle, Ill., 1997.

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