
APLIKACIJSKI ČLANKI - APPLICATION ARTICLES

Total Organic Carbon - TOC in Water

Part II: Pharmaceutical and Semiconductor Applications

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1.0 A Brief History of TOC Analysis

TOC is the acronym for total oxidizable carbon, sometimes referred to as total organic carbon. Original TOC methods were developed to help correlate information obtained from chemical oxygen demand (COD) and biochemical oxygen demand (BOD) tests in drinking water and wastewater. The TOC methods were designed to be more efficient than the COD (requires hazardous agents) and BOD (requires 5 days to complete) tests. During the past decade, the importance of measuring TOC in drinking water and wastewater as well as the water used in the pharmaceutical, semiconductor, and power generation industries has increased dramatically. Today, new government regulations for TOC levels are demanding a more sensitive, flexible, and convenient method for TOC analysis.

Drinking water

The emphasis on drinking water and wastewater is increasing and government agencies, most notably the EPA (Environmental Protection Agency), are instituting rules to monitor municipal systems more closely. It is important to monitor the level of TOC, especially in drinking water, because of the potential for chlorine, the primary drinking water disinfectant, to react with the organics in the water and form halogenated hydrocarbons. These byproducts have been implicated to be carcinogenic.

Pharmaceutical applications

The pharmaceutical industry has maintained an oxidizable substances test for Purified Water (PW) and Water for Injection (WFI) in the United States Pharmacopeia (USP) for more than a century and has been sensitive to the advantages of TOC analysis for many years. As of November 15, 1996, the USP requires a TOC test or oxidizable substances test for PW and WFI. It is now being proposed that the oxidizable substances test be eliminated and replaced by the recently implemented TOC test. Measurement of TOC is a direct reflection on the quality of water being produced and can have a significant impact on the manufacturing process of drug products.

One of the new evolving pharmaceutical applications for TOC monitoring is cleaning validation. The FDA

expects companies to provide written procedures detailing the validation of cleaning process for various pieces of equipment (e.g. fermentation tanks). This validation includes testing for residual cleaning agents which can involve TOC analysis.

Semiconductor Applications

TOC in ultrapure water has been recognized as a contaminant and a major contributor to increased product defects in the semiconductor industry for more than 10 years. Today, device geometry reductions accompanied by increases in circuit densities are imposing challenging demands on the purity of water used in production. Semiconductor manufacturers must monitor TOC levels in all stages of the water purification, including at the point-of-use. Since even the slightest increase in TOC levels can effect production yield, the industry has incorporated on-line TOC monitoring to provide more information throughout the entire water purification process.

Power Generation Applications

The power generation industry recognizes TOC as a significant corrosion contributor. TOC found in water is a source of corrosive organic acids that can reduce the life of boilers, reactors, and turbine blades. High-purity water is necessary for continuous operation of power facilities, hence the importance of TOC monitoring.

2.0 Pharmaceutical applications

2.1 Introduction and Background

Since the late 1980's the Pharmaceutical Research and Manufacturers of America (PhRMA) (formally known as the Pharmaceutical Manufacturer's Association) Water Quality Committee (WQC) has investigated and studied new methods for testing the quality of USP PW and WFI. They determined that existing test methods were not ideal and that they should be updated to better reflect current analytical techniques. Table 1 shows the WQC's proposed changes for testing the quality of pharmaceutical water.

The committee proposed that (a) the calcium, sulfate, chloride, ammonia and carbon dioxide tests be re-

placed by single conductivity analysis, (b) heavy metals, total solids, and coliforms tests be deleted because they are irrelevant in any modern high-purity water system and (c) the oxidizable substance test be replaced by the non-selective and highly sensitive TOC method.

Table 1: List of old methodology and proposed new methodology

OLD METHODOLOGY	NEW METHODOLOGY
pH	Maintain
BET	Maintain
Calcium	Conductivity
Sulfate	
Chloride	
Ammonia	
Carbon dioxide	
Oxidizable Substances	Total Organic Carbon (TOC)
Heavy Metals	Delete
Total Solids	Delete
Coliforms	Delete
Microbial Count	Add (Information Chapter only)

The official methods for TOC and Conductivity were published in the USP 23 Fifth Supplement, November 15, 1996. Table 2 lists the acceptable limits of these methods and others for determining the quality of pharmaceutical water. Recommended microbial levels for PW and WFI water have been included in an information chapter.

Table 2: Acceptable limits for tests to meet the USP requirements for pharmaceutical waters

TOC	500 ppb maximum
Conductivity	limits of 4.7 μ S/cm (depending on pH)
Bacterial Counts	Purified water: 100 cfu/ml Water for Injection: 10 cfu/100 ml
Endotoxin (WFI water) only	0.25 EU per LAL test
pH	5-7

2.2 Calibration and System Suitability for USP TOC Analysis Using On-line Instrumentation

To ensure correct operation and accurate results the USP TOC method requires the instrument used for analysis be standardized or calibrated with 500 ppb sucrose solution and the suitability of the instrument be

tested by analyzing a solution containing 500 ppb 1,4-benzoquinone.

In order to perform the USP calibration and system suitability, methods needed to be developed that allowed solutions to be transported to the installed on-line instrument eliminating the need to remove the instrument and take it to the laboratory for testing. One method that has become quite popular for performing the USP calibration and system suitability was originally suggested by a large pharmaceutical company and is available commercially. Figure 1 shows how a stainless steel vessel can be cleaned with high purity water, filled with test solution, either sucrose or 1,4 benzoquinone, and the entire contents (typically 4 L) pressurized to approximately 25 psig (1.7 bar) through a series of three way valves. The vessel can then be transported to the installed on-line instrument, figure 2, and be connected to the inlet by another three way valve. The valve is then opened and the instrument can take as many as seven or eight measurements.

An alternate mechanism for delivering test solutions to on-line instruments that are installed is shown in figure 3. This method involves preparing the test solutions directly into 2 L volumetric flask and pumping the solution through the TOC analyzer. Because there is a potential for contamination due to exposure of the test solution to the outside air, this method should only be used for instruments that are installed in relatively clean environments.

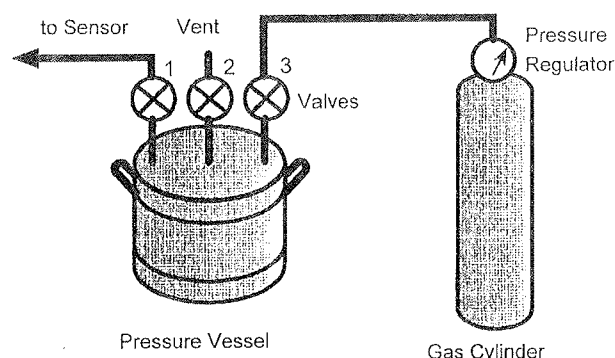


Figure 1: A stainless steel pressurized vessel system for transporting test solutions to an installed, on-line instrument

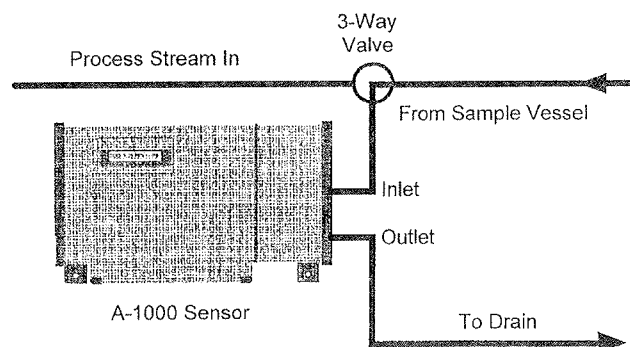


Figure 2: Connection of the stainless steel vessel to the installed on-line TOC sensor

Table 3: Data obtained with stainless steel pressurized vessels; values are an average of three measurements

Sucrose, Expected TOC Value (pppb)	Sucrose Measured TOC Value (ppb)	1,4-Benzoquinone, Expected TOC Value (ppb)	1,4-Benzoquinone, Measured TOC Value (ppb)	% Response Efficiency
500	540	500	470	87
500	547	500	507	93
500	524	500	496	95

Table 4: Data obtained with a volumetric flask and pump; values are an average of three measurements

Sucrose, Expected TOC Value (pppb)	Sucrose Measured TOC Value (ppb)	1,4-Benzoquinone, Expected TOC Value (ppb)	1,4-Benzoquinone, Measured TOC Value (ppb)	% Response Efficiency
500	525	500	531	101
500	553	500	549	99
500	534	500	545	102

Table 3 and 4 show the performance of test solutions delivered to installed on-line TOC instrumentation. The response efficiencies are all within the USP specified values of 85% to 115%.

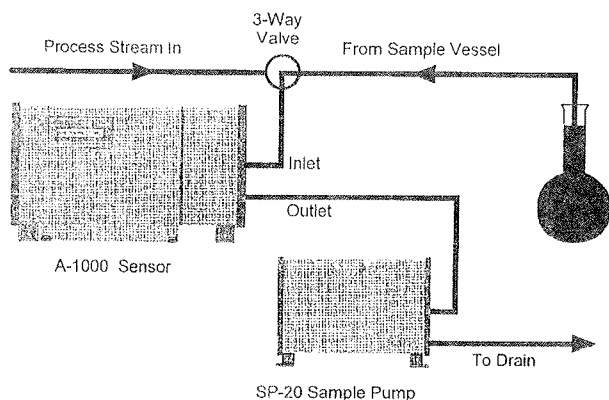


Figure 3: A one step preparation and delivery of test solutions to an installed, on-line instrument

2.3 USP Requirements for Measuring Conductivity

The USP conductivity test is comprised of three stages and meeting the requirements of any one of them is acceptable for pharmaceutical water manufacturers. Stage 1 consists of measuring the temperature and the conductivity of the water using a non-temperature-compensated conductivity probe. The measurement can be performed as a laboratory test, but optimally should be performed on-line. Since the conductivity of high-purity

water increases as a function of temperature, the USP has established a list of allowed conductivity values at temperatures ranging from 0°C to 100°C (table 5). These conductivity values are based upon the contributing conductivity of the maximum allowable limits for the chloride and ammonia ions previously specified in the USP (before the USP 23 Fifth Supplement, November 15, 1996).

If the conductivity of the water is higher than the stated table value for the corresponding temperature, then the water must be tested according to Stage 2. Stage 2 requires that the water be equilibrated with air at 25°C and that the conductivity of the water be less than 2.1 $\mu\text{S}/\text{cm}$. If the conductivity of the atmospheric, 25°C equilibrated water is greater than 2.1 $\mu\text{S}/\text{cm}$, then the pH of the water must be measured and the conductivity fall in the acceptable range as shown in figure 4.

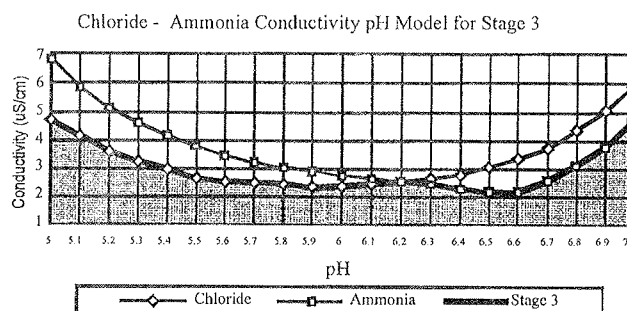


Figure 4: Stage 3 pH and conductivity requirements for the USP Conductivity Method <645>; the chloride and ammonia ions are the models used to determine the acceptable conductivity

Table 5: Temperature and conductivity requirements for USP Conductivity Method <645>, Stage 1: for non-temperature compensated conductivity measurements only.

Temperature, °C	Conductivity, $\mu\text{S}/\text{cm}$
0	0.60
5	0.8
10	0.9
15	1.0
20	1.1
25	1.3
30	1.4
35	1.5
40	1.7
45	1.8
50	1.9
55	2.1
60	2.2
65	2.4
70	2.5
75	2.7
80	2.7
85	2.7
90	2.7
95	2.9
100	3.1

2.4 USP Calibration Requirements for Conductivity Measurements

The USP conductivity method requires the cell constant of the instrument to be determined within $\pm 2\%$ of a known reference. Procedures can include measuring a solution of known concentration such as the conductivity standard used in American Society of Testing and Materials (ASTM) method D1125, or by comparing the instruments readings to values from a known certified probe. Of the two methods the latter is preferable because electrolyte solutions can be very difficult to prepare and measure consistently, and commercially available solutions are higher in conductivity than the USP limits. Figure 5 shows a comparison between an on-line TOC sensor and a NIST traceable Thorton[®] conductivity probe that has a known cell constant. A homogenous atmosphere equilibrated water sample was allowed to flow simultaneously, in parallel, to both instruments using a "tee" in the sample line. The results demonstrate excellent agreement between the two instruments, well within the USP requirement of $\pm 2\%$.

The USP conductivity method also requires that the instrument or meter accuracy be $0.1 \mu\text{S}/\text{cm}$ excluding cell constant. A well designed on-line conductivity instrument or meter will contain metal film precision resistors that are accurate to within $\pm 0.01\%$ of the stated value. These resistors verify the measuring electronic circuitry prior to each conductivity measurement to ensure that the instrument's accuracy is within $\pm 0.1 \mu\text{S}/\text{cm}$.

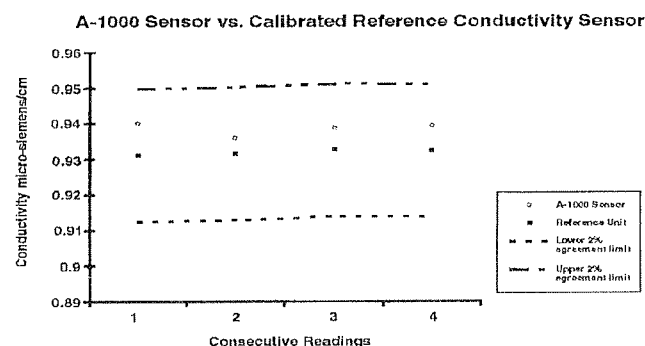


Figure 5: Conductivity measurements comparing the performance of an on-line conductivity sensor to a calibrated, NIST traceable conductivity probe

2.5 Pretreatment Strategies for TOC Reduction in WFI and USP PW

TOC by its nature is nonionic; therefore, deionization (DI) resins have little effect on TOC reduction. For deionization to work properly, TOC must be deionized. The ionization of TOC can be accomplished by oxidation, whether complete or partial, with $\text{HO}\cdot$. These free-radical hydroxyls help in the formation of by-products, including organic acids. Organic acids are compounds with anion valences. In these organic acid forms, the anion resin beads can produce excellent results. Figure 6 represents various pretreatment schemes for identical water systems. All readings were generated from an A-100 TOC analyzer (Anatel, Boulder, Colorado). The top set of readings shows TOC measurements between 1000 and 1300 ppb using deionizing resin beads in a mixed-bed configuration. There was no pretreatment of the water other than rough particle filters at $10 \mu\text{m}$ and $1 \mu\text{m}$. The raw water was municipally treated water, which complies with the Federal Safe Drinking Water Act (42 USC 300 g-1).

The middle set of TOC readings in figure 6 was taken after the addition of granulated activated carbon (GAC) module. GACs are regularly used for pretreatment in water purification systems to reduce or eliminate chlorine and help reduce TOC loading, especially of volatile compounds. The addition of GAC module with the existing DI system reduced the TOC loading in the water system by almost half. The system maintained 600 ppb of TOC, rather than the 1200 range. Although the reduc-

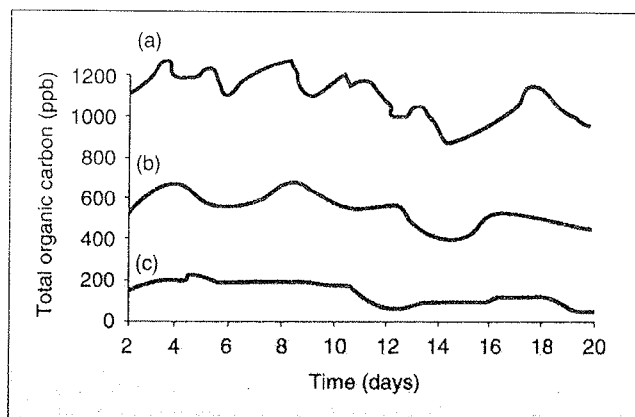


Figure 6: TOC measurements after various water pre-treatment schemes using
 a) deionization resin beads only
 b) deionization beads and granulated activated carbon
 c) reverse osmosis and deionization

tion was significant, it was above the 500 ppb proposed specification limit. GAC reduction efficiency is diminished over a short period of time and may require frequent backflushing and steam regeneration. Diminished GAC beds will cause leakage of bacteria and TOC over time.

The lower set of TOC readings shows the value of combining reverse osmosis (RO) and DI. The values were consistently reduced below 200 ppb, with the system approaching 50 ppb.

RO membranes have a typical molecular cutoff range of 300-400 daltons. TOC can range in molecular weight from <100 to >1 million daltons. TOC in organic chains can be removed effectively with RO. Although RO is not 100% efficient, all RO membranes will reduce TOC, some with greater efficacy than others.

Downstream components can add TOC to a water system. Pump seals, valves, plastic components, resin beads, and resin-composed vessels are examples of water system components made from organic material that can elute TOC into a water system. In extremely low TOC waters, elution of TOC from the water system's components can be the greatest contamination source. The elastomers used in a high purity water system can be minimized if careful consideration to materials is designed in the water system.

Ozonation and 185 nm UV lights can be excellent TOC reduction methods. First used in France in 1897, ozonation is commonly used in European drinking water as the main sanitizing agent. Ozon produces free-radical hydroxyls, which oxidize the TOC to organic acids and CO_2 . Compatibility of elastomers, resins, and piping is extremely important because ozone is a very aggressive compound. A 185 nm UV lamp cleaves a water molecule, yielding the free radicals $\text{H}\cdot$ and $\text{HO}\cdot$. The hydroxyls oxidize the TOC to organic acids and CO_2 . Once the TOC has been partially or completely oxidized, it can be removed from the water by ion-exchange resins and

degasification. Figure 7 demonstrates the reduction of TOC from >100 ppb to <10 ppb. Installation of a 185 nm UV lamp system on a multipass polishing loop can help maintain low TOC levels.

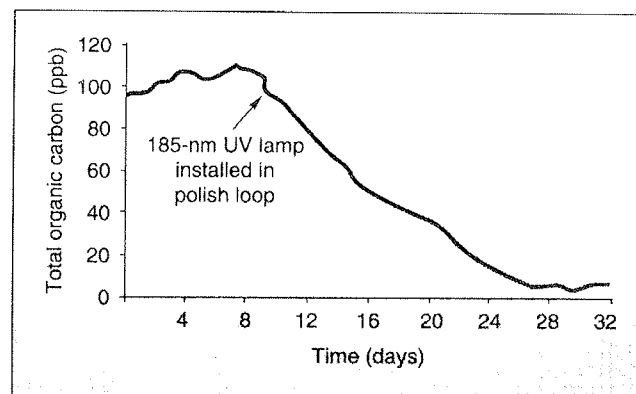


Figure 7: TOC reduction using multipass 185 nm UV lamp

In the pharmaceutical industry, most WFI water systems are composed of stainless steel. The use of stainless steel piping will retard the elution of TOC. However, many of the seals, gaskets, and diaphragm valves can contribute to the overall TOC condition. WFI systems that use distillation to deliver microprobe-free and endotoxin-reduced waters often carry over TOC, especially volatilized organics, into the production water.

It has been shown that high-pressure and high-temperature systems can produce organic acids as by-products of complex organics. High organic loading can result in the development of acidic species levels that corrode stainless steel piping, turbines, and condensation units.

TOC analyzers offer greater data compilation and interpretation than just the replacement of the oxidizable substances test. TOC, resistivity, temperature, and a profile of the organics can readily help the facility's engineer, pharmaceutical engineer, and QC or QA personnel determine the exact operating state of a water system. The delivery of consistent and stable WFI or USP water to the production facility is crucial to the repeatability and quality of the product. In many cases, the water is blamed as a major contributing factor in the loss of a product or a batch. Specific water parameters need to be identified and isolated as contributing or noncontributing factors to the loss of product or batch. On-line measurements of TOC, resistivity, and temperature and profiling of the organics can help in determining the causes of product or batch failure.

Well designed water systems offer the best hedge against TOC upsets. Many components exist in USP PW and WFI systems. Almost exclusively, distillation units are used for WFI. After decades of usage in pharmaceutical industry, distillation units have shown durability and efficacy in microbial reduction, endotoxin reduction, and maintaining high-quality water production.

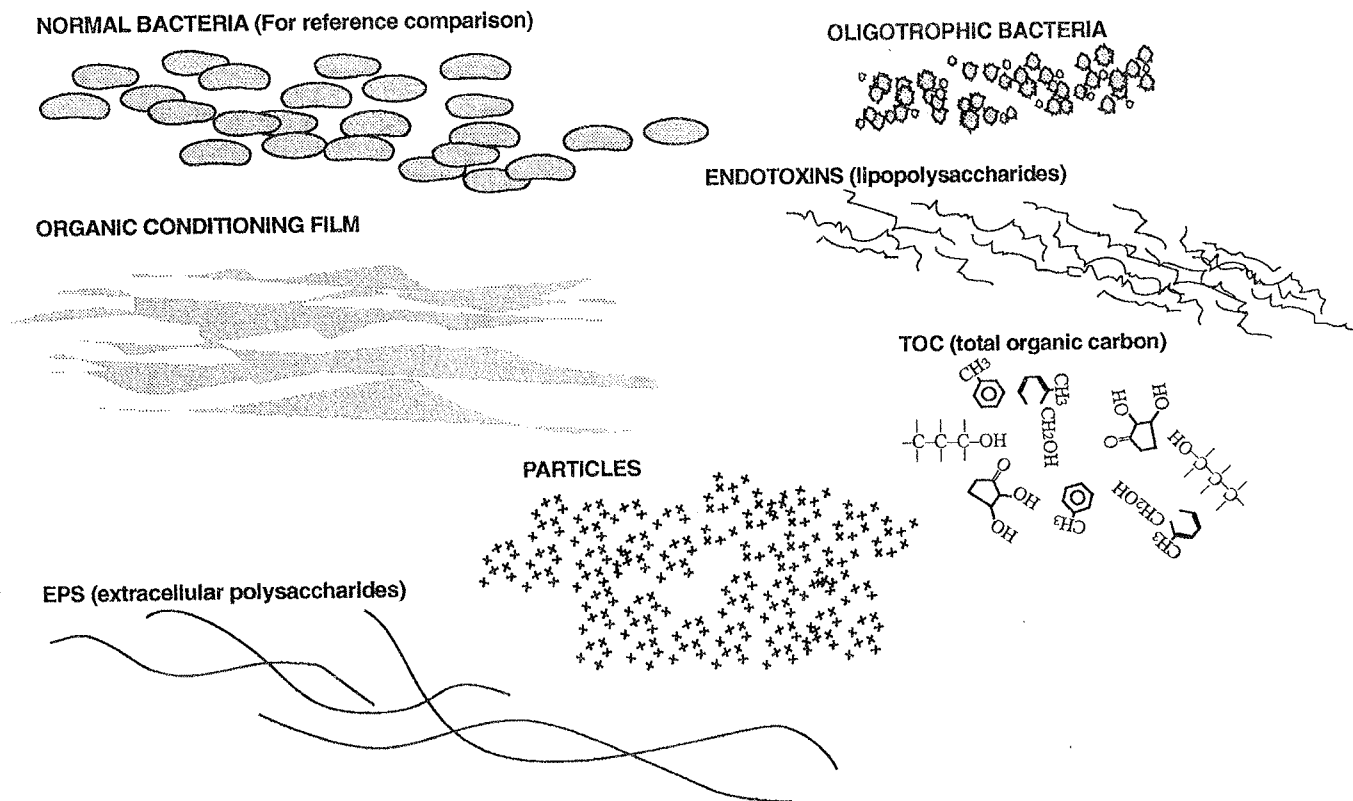


Figure 8: Micro-components of a Low Nutrient Water Environment

2.6 Relationship among TOC, bacterial cells, and endotoxins, /4 /

Although the increasingly efficient high purity water (HPW) systems being installed in the pharmaceutical industry produce a product with less and less contaminants present, closer examination shows the presence of numerous materials associated with living and dynamic biofilms.

The purification process does reduce the inorganic and organic constituents normally found in water to extremely low levels. For example, oxidizable carbon which serves as nutrient source for bacteria is often reduced to less than 100 ppb concentration. To cope with this low nutrient environment, the bacteria, which normally enter the system through a number of means, generally from the feed water, assume a starved or oligotrophic character. They typically become smaller, their metabolism changes and they can, under certain conditions, become stressed both in appearance and physiology.

The gram negative bacteria produce endotoxins or lipopolysaccharides as their cell membranes break down. These oligotrophic bacteria also produce extracellular polysaccharides which form a glycocalyx and organic conditioning film. This glycocalyx can easily capture particles which become part of the biofilm.

Biofilms in high purity water systems are formed through a complex and not so sequential, dynamic sequence that begins with organic compounds loosely binding to pipe walls, bacteria attaching themselves to these walls in search of nutrients that the organics provide, cell adaptation to an oligotrophic form to survive in the hostile low-nutrient environment, and finally the forming of the lipopolysaccharide glycocalyx. Particles are also trapped and the biofilm becomes a living environment that allows the bacteria to survive.

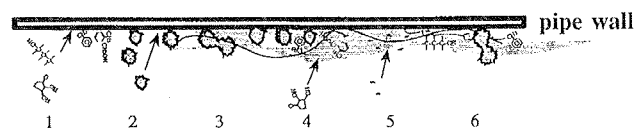


Figure 9: Theoretical development of biofilms:

- 1) Organic compounds including nutrients chemically bond to the surface material (organic conditioning film)
- 2) Planctonic bacteria seeking nutrients attach to the pipe walls
- 3) Bacteria form biofilms with EPS glycocalyx
- 4) More nutrients are captured
- 5) Particles are also captured
- 6) Biofilm becomes a living environment

Table 6: Summary table of effect of TOC changes on total cells, viable cells and endotoxins
Epi = total bacteria count by epifluorescence microscopy,
CFU = ColonyForming Unit of viable oligotrophic bacteria,
LAL = bacterial endotoxin concentration by LAL method

Elapsed time (days)	Site	Δ TOC ppb	Δ Epi %	Δ CFU %	Δ Ebdotoxin by LAL %
77.2-77.7	RO Prod	2.2	63	/	300
80-81	RO Prod	4	4300	/	/
77-77.7	2nd MB	2.5	62	/	200
80-80.6	2ns MB	3	330	185	400
78.4-79	970POD	2	/	138	5000
78-79	Skid 2 Ain	4	367	/	1800
77.6-78.6	UV out	3.5	271	/	636
80-80.4	UV out	4	223	/	/
80.4-81.4	UV out	4	/	/	83
81-81.6	UV out	3	123	183	200
78.2	UF out	0.4	235	/	667
80-80.6	UF out	0.3	2400	/	267
81-81.6	UF out	0.6	2720	/	310

The increase in total cells and endotoxins, which are associated with the lipopolysaccharide cell membrane structure of gram negative bacteria, as a function of small increases in TOC levels is based on the theory that includes the formation of biofilms in any water system that is not sterilized regularly.

The biofilm includes living bacteria, dead cells, a glycocalyx of extracellular polysaccharides, cell fragments,

endotoxins, and particles. The biofilm is a dynamic entity, even in this hostile starved environment. "Pieces" of biofilm shed from the cell wall and planctonic (free floating in the water stream) bacteria find their way into the biofilm to seek nutrients and a more comfortable environment. The hypothesis even suggests that breakdown materials from dead and fragmented cells can serve as food for other living cells. Reproduction is very slow.

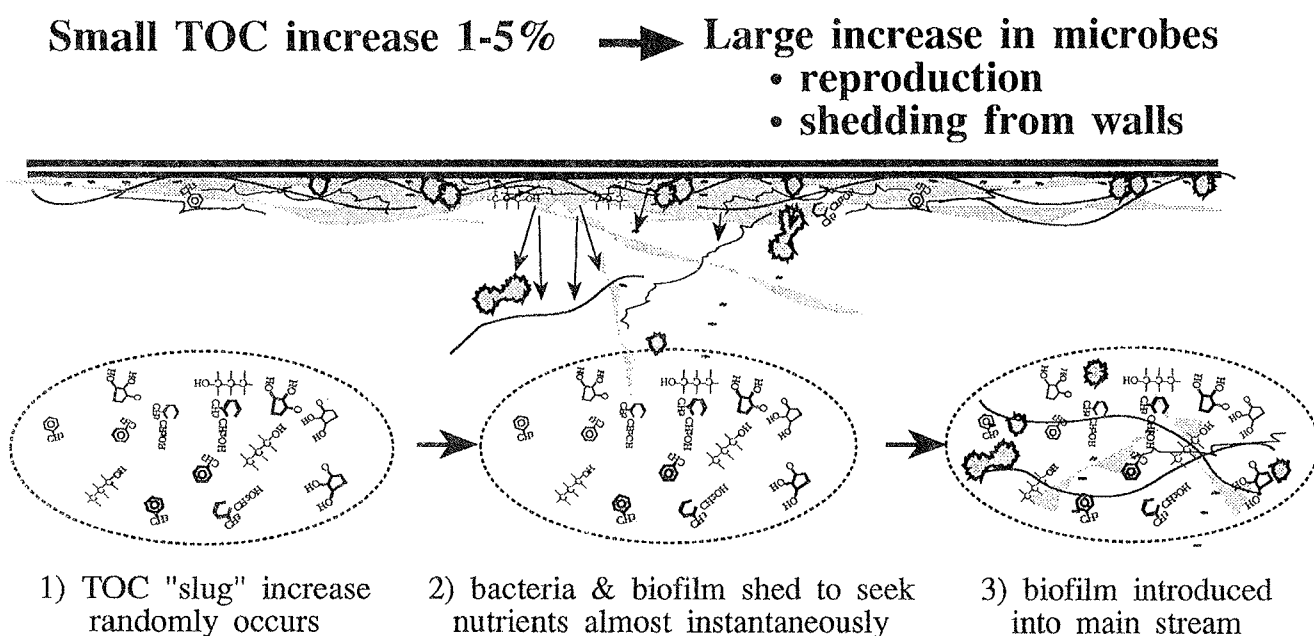


Figure 10: interpretation of data in table 6: small TOC increase of 1-5% lead to large increase in microbes

When a small increase in TOC occurs, the fragile equilibrium of biofilm and sessile (attached to the surface) cells and what occurs in the free flowing stream is upset. The sessile cells sense the increased nutrient in the flowing water and shed from the surface to seek this extra food. Since relatively large sections of the biofilm can shed under these conditions, they break down, in the turbulence and release dead cells, viable cells, endotoxins, and extraneous extracellular material. As a result, the increase of total cells and endotoxins in the flowing water is quite dramatic.

The summary table 6 shows how small increase in TOC values within the water system are rapidly followed by increase in the total cell count, viable cells, and endotoxin levels. Inconclusive results were omitted for clarity.

2.7 Conclusion

The new USP TOC and conductivity methods each require their own calibration procedure to verify the accuracy and correct operation of the chosen instrument. How frequent these calibration procedures need to be performed is not specified, but is dependent on the manufacturing application and degree of use. On-line instrumentation offers significant advantages over laboratory testing, but requires special handling when performing the USP test methods. Whether the instrument is operated on-line or in the laboratory, the instrument manufacturer should provide complete installation and operation guidelines as well as complete standard operation procedures (SOP's) to ensure that the instrument complies with all the USP requirements.

Contemporary UPW and PW systems are both complex and dynamic, yet are required to consistently produce very high purity product water. The concentrations of bacteria, metabolites like endotoxin, and particulate contaminants present in high purity waters must be adequately measured and regulated for process to remain within control limits. However, current stages rely upon off-line analyses which are inherently retrospective and thereby unsuited to feedback control in real time.

The high purity water industry has not yet developed instantaneous measurements of biofilm levels to determine its response to changing system parameters. Nor have analytical methods been developed, for real time on-line measurements of water phase bacteria or endotoxin concentrations in these systems.

Endotoxin measurements reported are approximately three logs more sensitive than conventional methods that do not employ concentration by ultrafiltration. This modification makes LAL method suitable for endotoxin measurements in high purity water systems for trending purposes.

Continuous TOC measurements at multiple system points may offer a gateway measurement to predict bacterial, endotoxin and particle variations. Transient elevations in TOC, observed to occur in high performan-

ce high purity systems, even when of modest magnitude, may produce significant variations in bacteria and endotoxin concentrations. Aggressive control of TOC may be required to consistently control bacterial and endotoxin quality of high purity water systems.

3.0 Semiconductor Applications

3.1 Background

The quest for ultrapurity in the semiconductor fabricating (FAB) environment and in the materials which are specific to the fabricating process continues to warrant investigation. As the industry goes towards deep sub-micron range for volume production, contamination looms as the obstacle to maintaining acceptable yields.

Primary areas where purity is mandatory are:

- process water
- process chemicals
- process gases
- fabrication equipment
- fabrication environment

It has been well established that the purity of water used in fabrication of ICs has a direct and significant effect on the level of yield. That's why monitoring of water purity is of the utmost importance.

Water is so important because it is the media that wafers come into contact most frequently with during the process. Water is used for washing and rinsing silicon wafers after etching or cleaning operations and for making steam for oxidation of wafers. A CMOS fabrication process may have about 20 separate wafer rinse steps which means that a single IC may require up to 600 L of high purity water for complete processing.

Besides water resistivity, bacterial count and volume particle content, TOC is one of the most important water parameters that need to be monitored. In figure 11 a typical semiconductor pure-water system is depicted and in table 7, typical TOC levels at several points in a properly functioning semiconductor pure-water system are shown.

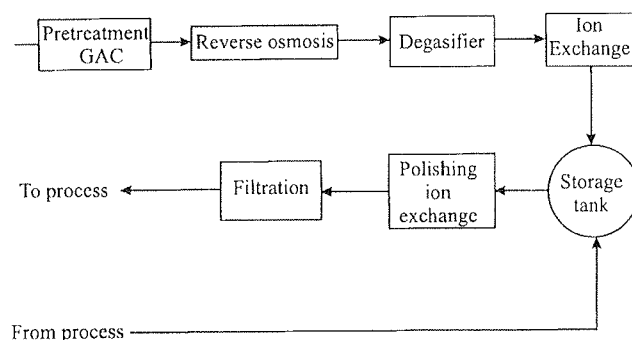


Figure 11: A typical semiconductor pure-water system

Table 7: Typical TOC levels at several points in a properly functioning semiconductor pure-water system

Measuring point	TOC in ppb	
	Mean	Range
City input water	3200	2500-6200
GAC	2950	2400-4200
Reverse osmosis unit	275	150-500
Primary ion exchange	75	<50-200
Final filter	<20	<20-150
Return line	<50	<50-225

Main sources and reasons for high TOC levels in pure water are

- raw incoming water which must be properly treated to reduce TOC levels to acceptable values
- improperly chosen materials DI water comes into contact with (piping, fittings, filter housings, storage tanks)
- large surface areas of materials DI water comes into contact with
- improper flow dynamics in the entire system
- high downtime of makeup and reclaim systems

This means that design and construction criteria are critical to the attainment of a state of the art DI water system. These criteria involve the piping size and layout, flow and pressure characteristics, the make up and storage capacity, and installation procedures.

The choices of construction materials are important to ensure a contamination free system. PVDF is chosen as a piping material for its ability to meet present and contemplated requirements.

Levels of less than 10 ppb TOC can be obtained through the organic removal capability of 185 nm UV irradiation.

3.2 Effects of TOC on CMOS Fabrication Processes

In table 8, typical effects of high TOC values on CMOS fabrication processes are shown.

A certain CMOS FAB reported problems in growing consistently acceptable gate oxides in the thickness range 10 - 20 nm. The nonuniformity manifested itself as areas of increased oxide thickness on individual wafers. After eliminating furnace tubes and process gas contamination as causative factors, the wafer cleaning process was investigated. The major source of particles was found to be contaminated DI water. Analysis of the water found high levels of TOC (750 ppb range) and

particles, figure 12. Wafers rinsed in such DI water showed pronounced level of hazing on wafer surface, as well as their surface appeared to be hydrophilic after prolonged DI water rinse.

Table 8: Typical TOC impact on fabrication processes

PROCESS STEP		Observed TOC impact
LAYERING	Oxidation	High particle counts
	Chemical Vapour Deposition	Uneven oxide growth
		Large CV drifts
		High leakage currents
		Low breakdown voltages
	Evaporation	Uneven deposition
PHOTO-MASKING	Sputtering	Poor film adhesion
		Pin-hole defects
	Resist	Poor film adhesion
	Exposure	Mask defects
DOPING	Etch	Pin-hole defects
	Diffusion	High leakage currents
	Ion implantation	Improper doping levels
		Carbon nucleation sites

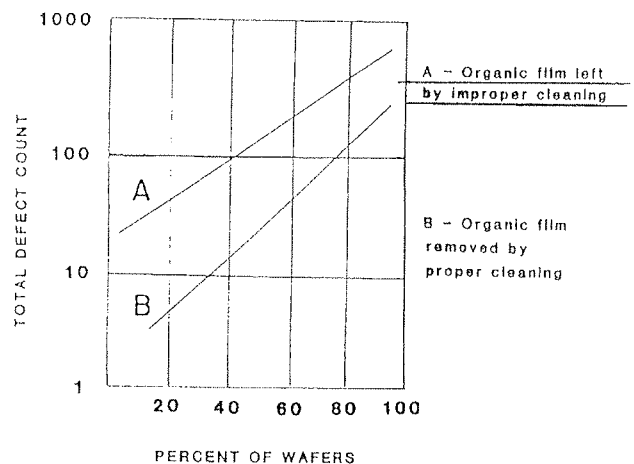


Figure 12: Defect counts by laser scatter on silicon wafers after pre-clean

Modification of the DI water system was initiated. Gate oxide defect densities, threshold voltage shifts and background doping level contamination were monitored throughout the modification of the water system. Figure 13 clearly shows the level of direct TOC impact on gate oxide relative defect density. Each defect data point reflects the relative number of electrical defects per square centimeter in the gate oxide as measured by breakdown voltage test.

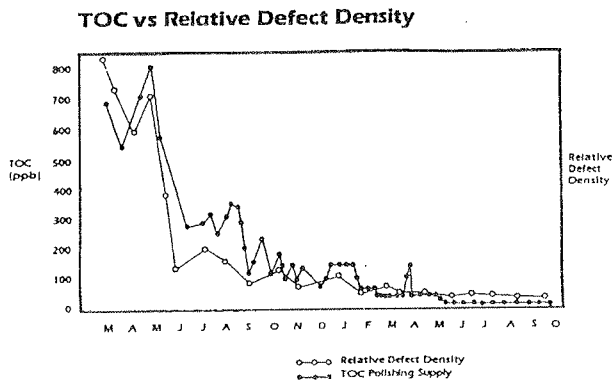


Figure 13: TOC vs relative defect density, gate oxide, 20 nm

Oxide uniformity on wafer also improved with decreased TOC values. It has been proposed that organics on the wafer's surface decomposed to form water vapour and other byproducts. The water vapour served to increase the local oxidation rate, resulting in increase in oxide thickness of as much as 6 nm.

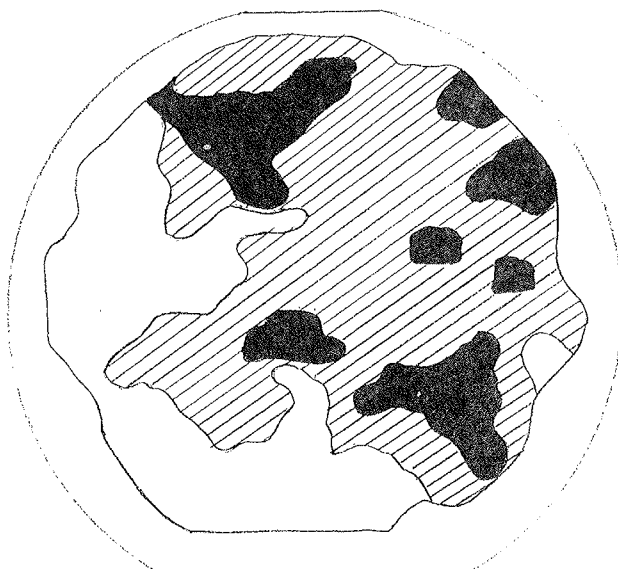


Figure 14: 100 mm wafer MAP of background concentration after gate oxidation; wafer was pre-cleaned in TOC contaminated DI water

- N_D 2.5 - 4.5 $E15 /cm^3$
- ▨ N_D 4.6 - 6.5 $E15 /cm^3$
- N_D 6.6 - 8.5 $E15 /cm^3$

Some FABs, [7], reported large MOS transistor threshold voltage shifts and increased background wafer dopant concentrations after the wafers were exposed to TOC contaminated DI water during gate oxide pre-clean. In figure 14 a typical wafer MAP of average dopant concentration is presented. Wafer average concentration was measured after gate oxidation with C-V technique. Typical dopant concentration should be below $4.5E15/cm^3$, while more than 50% of the wafer area shows increased phosphorous type contamination.

The above described type contamination has a disastrous effect on MOS transistor threshold voltages. In figure 15 a direct connection between PMOS transistor threshold voltage and TOC is depicted. Clearly, allowable TOC limit for successful gate oxide pre-clean must be below 20 ppb.

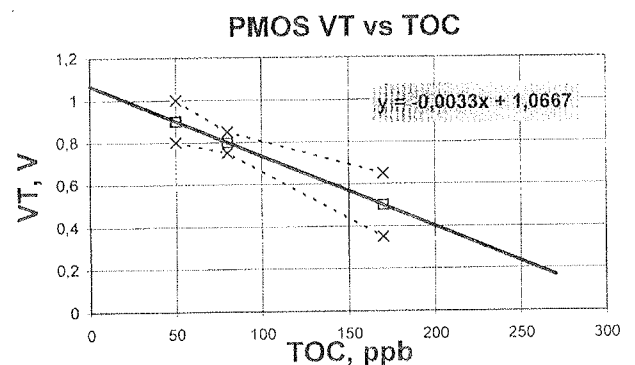


Figure 15: PMOS transistor (5 μm gate length) threshold vs TOC concentration

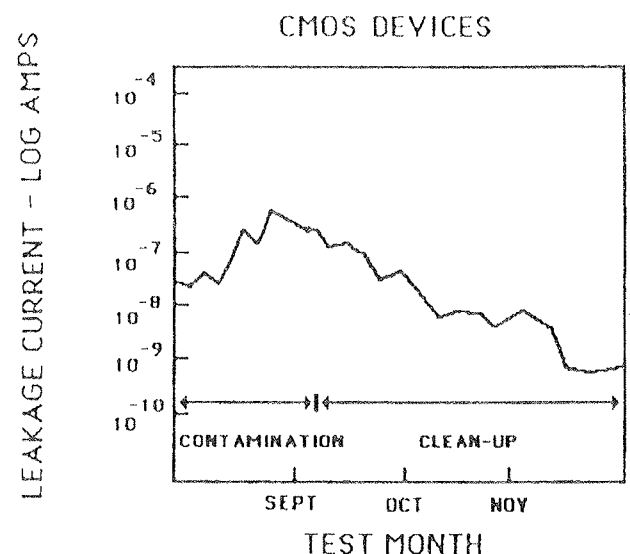


Figure 16: Effect of TOC contamination on IC leakage current: >400 ppb TOC contamination levels in water caused three orders of magnitude higher leakage currents compared to normal <50 ppb TOC levels

Further on carbon atoms as part of TOC can act as nucleation sites and attract boron, phosphorous or arsenic atoms during diffusion which alters the junction depth and hence device electrical characteristics.

Organic contaminants can carry mobile ions (e.g. Na). Once on the surface, these ions can diffuse into the wafer during high temperature steps and can migrate to an active junction and cause high leakage currents, figure 16.

For GaAs devices the group IV compounds (including C) can act as dopant species and unwanted carbon contamination can affect junction electrical parameters. In fact, TOC levels >200 ppb in pre-clean DI water have been traced to low device reliability problems.

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SODOBNA
ELEKTRONIKA

44. SEJEM SODOBNA ELEKTRONIKA THE 44th MODERN ELECTRONICS FAIR

Ljubljana, 6. - 10. oktober 1997

Tradicionalna sejemska prireditev s področja elektronike bo letos potekala v času od 6. do 10. oktobra na Gospodarskem razstavišču v Ljubljani.

O pomenu sejma prepričljivo govorijo naslednji podatki. V letu 1996 se je na njem predstavilo 540 podjetij iz 29 držav, od tega več kot polovica tujih, obiskalo pa ga je okoli 34.000 obiskovalcev iz 25 držav. Poleg slovenskega trga omogoča nastop na sejmu zato vse bolj tudi poslovne stike s sosednjimi trgi srednje in jugovzhodne Evrope.

Sejem obsega predvsem programske sklope komponent, avtomatizacije z merilno elektroniko, telekomunikacij in profesionalne audio/video opreme z radiodifuzijo.

Traditional modern electronics fair will be held this year in Ljubljana fair from October 6 till October 10.

We feel sure the following data themselves prove that this fair is very significant. In 1996, 540 companies from 29 countries introduced themselves, of which more than a half came from abroad. The fair was visited by around 34.000 visitors from 25 countries. Besides inland business contacts the participation in this fair enables also more numerous business contacts with other markets of the Central and South-western Europe.

The exhibition programmes comprise electronic components, automation with measuring electronics, telecommunications and professional audio/video equipment including broadcasting.