

Portable Continuous TOC Monitoring in a Semiconductor Water System

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I. Introduction

The primary requirements of water systems are (or ought to be) driven by the required quality of the finished products. In the microelectronics industry, this often translates into “cleaner water for smaller linewidth devices”. While the most common on-line measurement in any semiconductor water system may be flow rate, the most common on-line measurement of the *quality* of the water is resistivity[1]. Throughout the 1980’s and early 1990’s, resistivity measurements have become effective early-warning detection systems for ionic contaminants[2]. The ability of resistivity instrumentation to measure low-level ionic impurities results in a water system specification with ionic impurity specifications. The effectiveness of resistivity measurements is due in part to its sensitivity at ppb levels[3], ability to operate on-line and in-line without harm to the water system, speed of response, and relatively low cost (\$900 to 1500) for a complete system.

A similar logic is now being applied to Total Organic Carbon (TOC) measurements. Organic residue left on a device can have the same devastating effect as an ionic impurity. Organic materials are usually non-ionic, i.e., non-charged, in water, though there are exceptions. While the number of simple ionic impurities is relatively finite and detectable by several means (AAS/AES, ion chromatography), the number of possible organic impurities is substantial due to the thousands of organic species that are present in raw water. While the common thread among all organic contaminants is the presence of carbon (this is the definition of “organic”), each carbon in each organic chemical is quite different in the following ways :

- the number of carbons in each chemical is different
- the chemical bonding is different
- the bond strength is different
- the oxidation potential is different
- the absorption strength of each organic contaminant in the UV and visible portions of the spectrum is different

While sodium exists only as a single type of hydrated ion at low concentrations, every carbon is very different. Despite this difference, it becomes practical to group all forms of carbon together and call it Total Organic Carbon. The only carbon-containing molecular species exempt from this definition are the bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions, and carbon dioxide (CO_2). These are considered Inorganic Carbon, though a more appropriate name would be “completely oxidized carbon”.

In this paper, we review the current TOC devices in terms of their oxidation and measurement technologies. Then, a new TOC analyzer technology is described. Finally, a few applications of advantages afforded by this new technology are presented. To address the need for rapid, on-line data processing, the discussion in this paper is constrained to on-line analyzers only.

II. Overview of Current TOC Measurement Technologies

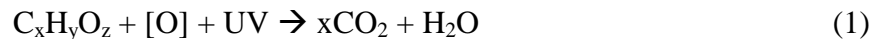
All of the common modern TOC analyzers are related in the following way :

- each contains a means to oxidize the organic contaminants
- each uses conductivity to detect the oxidized species at low TOC levels (high TOC levels are usually detected by IR absorption methods)

A. Oxidation

The primary means of oxidation is the use of ultraviolet (UV) radiation at 185 nm and 254 nm. At these wavelengths, light is conveniently and inexpensively produced by a mercury lamp. These lamps are similar in function to “TOC reduction lamps” found in water systems, but considerably smaller.

It is impossible to describe the detailed photo-oxidation mechanism of every possible organic oxidation reaction, and in many cases, it is not clearly known at the molecular level. The end result is usually a reaction which can be summarized in the following equation :



where $C_xH_yO_z$ is the organic contaminant and $[O]$ is an oxidation source, i.e., oxygen or persulfate in the case of two common technologies.

The oxidation of the organic carbon to carbon dioxide (CO_2) results in the formation of dissolved CO_2 in water. This leads to the formation of an unstable intermediate, carbonic acid (H_2CO_3), which is a weak acid and partially dissociates to ionic species.



The extent of the formation of ionic species is controlled by physical-chemical equilibria[4] and is described according to eq 3.

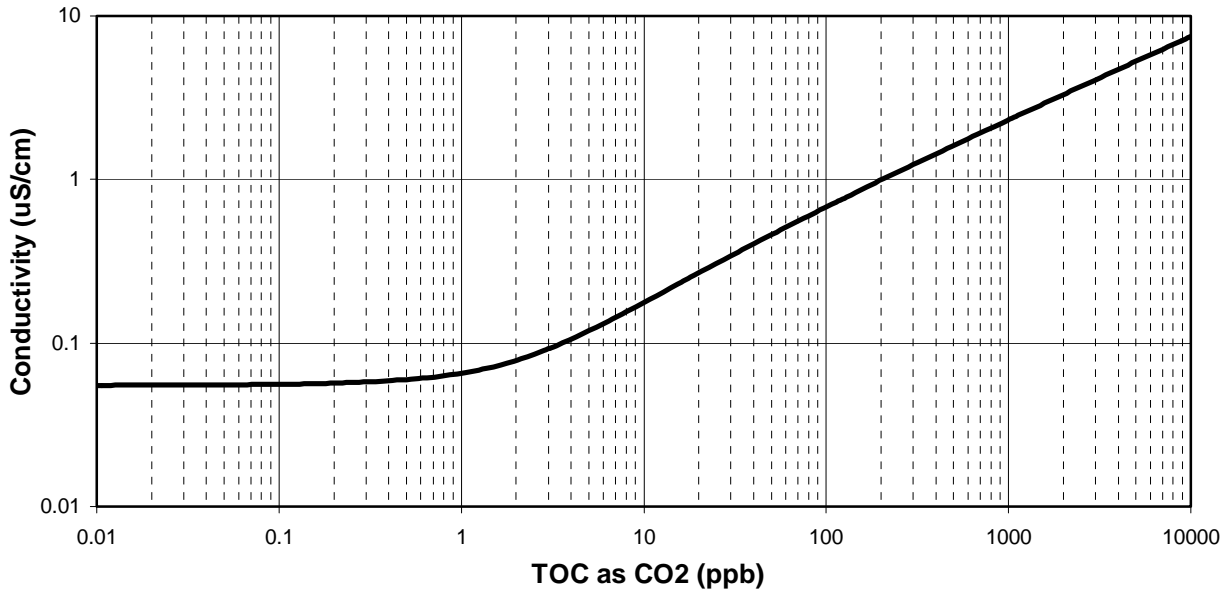
$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]_{aq}} = 4.45 \times 10^{-7} \text{ at } 25^\circ\text{C} \quad (3)$$

B. Detection

The strategic reason to form CO_2 is based not just on the relative ease to oxidize organic contaminants, but on its detectability and quantification by various analytical methods, especially conductivity. When ionic species are present in pure water, conductivity represents the most

sensitive real-time means of detection. The reaction products described in eq 2 are not only detectable by conductivity, but they are optimized for detection due to the formation of highly conductive H^+ . Figure 1 shows the relationship between conductivity and concentration of carbon (as CO_2) at $25^\circ C$.

Figure 1

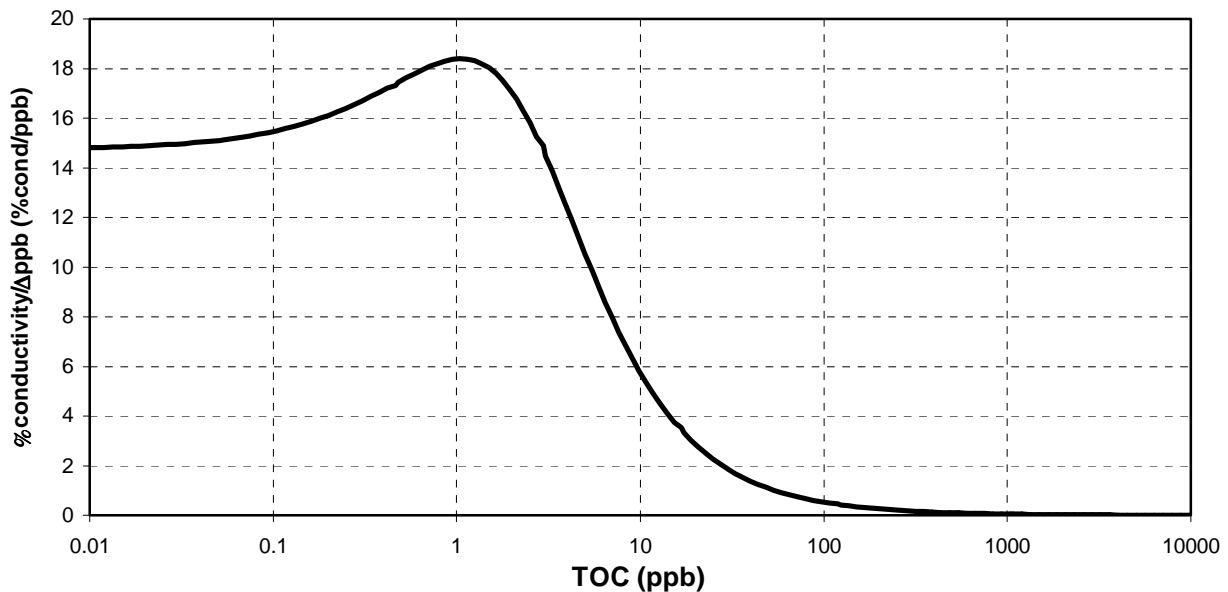


Based on eq 3, known chemical equations for conductivity, and the chemical equilibria for this system, the amount of carbon can be determined. This is usually expressed in “ppb” ($\mu g/L$), but it is implied that the concentration is “ppb (as CO_2)”.

For high concentrations of TOC, the conductivity due to CO_2 concentration does not increase linearly, though this is difficult to infer from the logarithmic scale in Figure 1. However, the reduced sensitivity at high concentrations of TOC is apparent in Figure 2. The sensitivity is defined as

$$S_{TOC} = 100 \times \left(\frac{\Delta cond}{\Delta TOC} \right) \tag{4}$$

The sensitivity of the conductivity signal is significant, $>1\%/ppb$ up to ~ 50 ppb, which demonstrates its usefulness as an analytical tool. Above, ~ 50 ppb, S_{TOC} is so low that other detection methods like FTIR become a practical and competitive means of detection. But for low TOC levels, no other detection method rivals conductivity. ***Consider the fact that at 1 ppb TOC, the conductivity increases at a rate of 18%/ppb TOC.***

Figure 2

While conductivity methods are very capable of measuring low ionic impurities, the large sensitivity is due entirely to the unique physical and chemical properties of dissolved CO_2 in H_2O . In a paper several years ago[4] detailing the fundamental relationship between conductivity and dissolved CO_2 in H_2O , no less than 20 equations were required to mathematically connect the measurement of conductivity to TOC concentration. While the details of these “connections” are proprietary, they are rooted in chemical principles, and a complete understanding of these principles is required to convert the measured conductivity into TOC.

C. Differential and Membrane-Based Detection

A common means of signal enhancement is to make a differential measurement. Differential measurements have the advantage of effectively removing the “zero background”, or in this case, the conductivity of the water before oxidation. This is a critical fact in the ability to measure sub-ppb TOC in ultrapure water, effectively eliminating the background signal of $0.055 \mu\text{S}/\text{cm}$ so that small increases in conductivity can be detected.

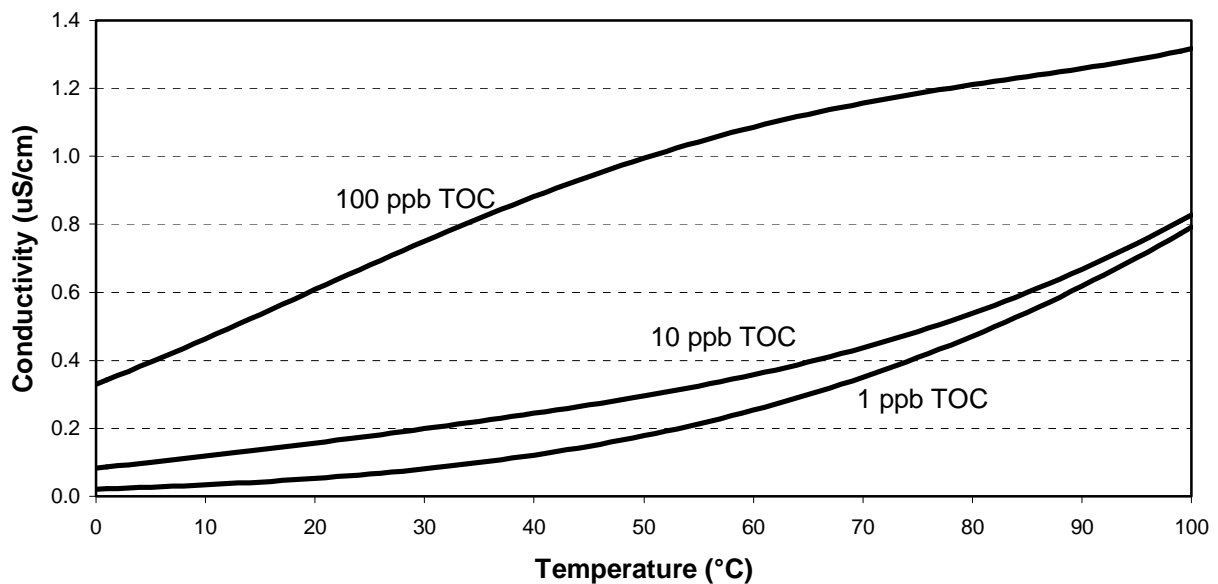
But the genesis of the differential conductivity measurements is based not on need for low TOC detection, but for the need to subtract off the conductivity of the incoming (pre-oxidized) water. This is required to account for any ionic impurities in the water prior to oxidation. This permits the sampling and measurement of waters exposed to air and other impurities, though the limit of detection increases as the background conductivity increases. Each of the prevalent on-line low level TOC technologies employs a differential conductivity measurement.

With the addition of more hardware, even the effects of an increased background signal can be reduced by the actuation of a proprietary gas-permeable membrane-based separation[5] just prior to conductivity detection. This has the advantage of reducing the huge background signal and lowering the limit of detection for high conductivity waters.

D. Temperature Compensation

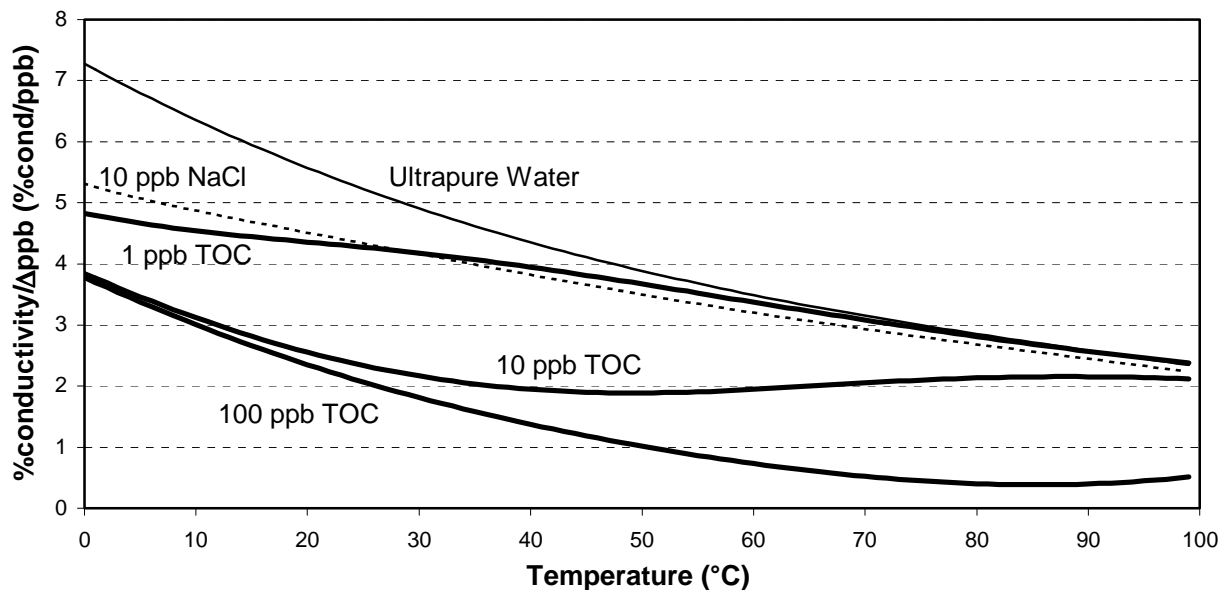
If the uncompensated conductivity increases, this could be the result of a temperature increase, an increase in impurity, or some combination of the two. The purpose of temperature-compensation is to allow the conductivity analyzer the opportunity to distinguish between a temperature disruption and a purity disruption. The same holds true for a TOC measurement. Not only is the relationship between conductivity and TOC complex, but it also has a temperature, chemical, and concentration dependence that is quite unique and complicated. The increase in conductivity as a function of temperature for three different solutions of varying TOC (but 18 M Ω -cm) is shown in Figure 3. It is evident from the figure that the increase in TOC vs. temperature is not constant across these temperatures and for these concentrations.

Figure 3



A well-designed TOC analyzer will adjust each conductivity measurement for its temperature, resulting in a temperature-compensated conductivity. But it is equally critical to use a compensation algorithm intended for solutions containing weak acids like CO₂, and the compensation algorithm should also be smart enough to include concentration correction.

We have been collecting conductivity measurement data over the last several years on UPW and UPW with known impurities. As a result, we have been generating a database of conductivity vs. temperature vs. concentration for a number of “impurities”. While it may be convenient to use a single linear compensation factor to temperature compensate a measurement, the type of impurity and the temperature dictate otherwise[6]. Our data shown in Figure 4 demonstrates the need for sophisticated compensation algorithms, yet they should always remain transparent to the user. *The ability to distinguish between an increase in the temperature and an increase in the TOC is just as important in TOC measurements as it is for conductivity/resistivity measurements.*

Figure 4

III. Advantages and Limitations of On-Line TOC Analyzers

While there are advantages and limitations to all TOC analyzers, the greatest triumph has been the ability to collect data in several minutes. The advantages of on-line TOC testing have been exploited while serving semiconductor, pharmaceutical and other pure water systems for several years. A summary of the advantages are :

- Real-time TOC, resistivity, and temperature process information.
- Immediate alarms and control options.
- Data logging capability to provide a history.
- Easier and cost-effective.
- Elimination of sample collection and transportation errors.

The advantages require no further elucidation. *However, the single limitation that is common to the traditional TOC measurement technologies is the requirement to sample in “batches”.* Batch sampling is necessary with these traditional oxidation/measurement technologies in order to generate sufficient oxidation products with the current available hardware. In the two dominant on-line technologies, an aliquot of water is allowed into the analyzer, the water is oxidized, and the analyzer requires anywhere from 5 to 30 minutes to report a result for that sample of water. This water is expelled to drain and the next aliquot of water is allowed into the analyzer for the next analysis.

Considering that older TOC measurement technologies were usually done as often as 1-2 times/day and as infrequently as 1 time/week or less, a static measurement every several minutes represents a huge improvement. Despite this improvement in measurement frequency, there is more to be gained if the measurement is made continuously.

The increased cycling time would allow the user to make full use of the advantages afforded by on-line sampling to a greater extent. Sudden system upsets, which can be detected immediately by pressure, flow, and resistivity sensors, could also be detected immediately by TOC analyzers. The availability of such a technology is critical to the development of sophisticated reclaim and recycle water systems[7]. Reclaim/recycle water would require smaller (or no) holding tanks, thereby reducing storage requirements as well as reducing the water intake and sewer discharge. Furthermore, the water that is commonly discharged, often the product of the second, third, or more rinses, is usually cleaner than the municipal feed. This lowers the UPW production costs by extending regeneration cycle time, RO maintenance, and other purification steps.

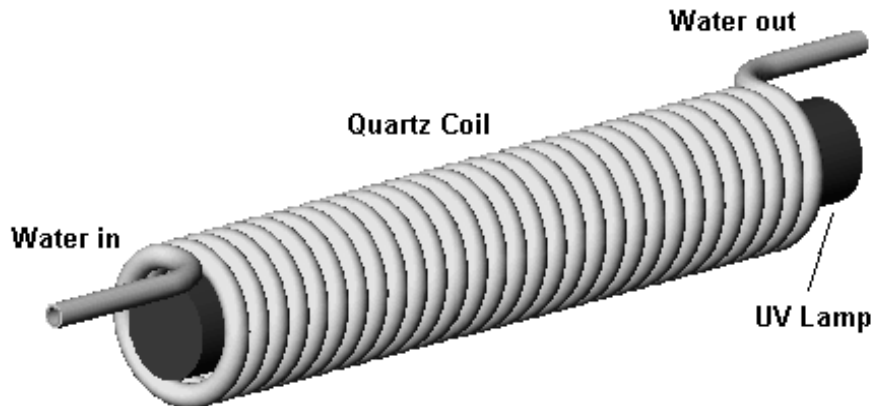
A second benefit to all users would be the added data from the increase sampling frequency. The ability to sample continuously would give water system personnel the luxury to see real-time data, not data from 5 or 10 or 20 minutes ago. Further, a continuous stream of data would permit the user to see what is happening during those intervals. This is already available today for ionic impurities in the form of resistivity instrumentation, and similar TOC instrumentation would offer complementary purity information.

IV. A New Technology for Continuous, Dynamic Sampling

The Thornton 502P TOC Analyzer utilizes a technology that overcomes the batch-sampling limitations of traditional TOC analyzers. This analyzer also utilizes a differential conductivity measurement, but the measurement is performed on a continuously flowing sample. Water flows into the analyzer from the process pipe via PFA tubing. The water flows through a conductivity sensor, through a spiral-wound quartz tube, through another conductivity sensor, and then to drain. The pressure and flow rate are regulated by the analyzer.

Inside the spiral-wound quartz tube is a mercury lamp (Figure 5) that is designed to optimize the oxidation rate by :

- Increasing the output of the 185 nm wavelength light.
- Using high optical grade of fused silica to reduce absorption losses and improve transmission of UV light to the water.
- Orienting the tube with respect to the radiation source to provide good coupling of the light to the water.
- Irradiating a low volume of water.
- Transporting the water slowly through the tube.

Figure 5. Geometry for Effective Coupling of UV light into Water

By improving the oxidation rate by these optical and mechanical designs, two critical performance parameters are achieved. First, oxidation of organic components to organic acids and CO₂ is thorough. Second, the total transport time through the tube is 15 seconds. This permits the use of sensitive conductivity methods to continuously measure the inlet and outlet conductivity and convert that to TOC. Furthermore, not only is the measurement continuous, but it is rapid. This obviates any need for large holding tanks. It also allows water system personnel to directly correlate TOC measurements (just like resistivity measurements) to “upsets” or other events right down to the second.

Though the analyzer is designed with pure water systems in mind (PFA tubing and passivated 316L SS conductivity sensors, for example), all locations downstream from the 1st RO unit are measurable by this analyzer. No reagents or gases are needed for its installation, operation, maintenance, or calibration. All that is required is your water for analysis. Installation requires a sidestream with the ability to connect to ¼” tubing which is supplied. Like other TOC analyzers, this technology can be calibrated on- or off-site, depending upon the desired extent of calibration. No “regeneration” of the hardware is necessary. The only maintenance that is required is a semi-annual replacement of the lamp which requires approximately ~10 minutes.

This technology does not screen out the effects of high THMs in the water. Thus it exhibits enhanced sensitivity to these impurities, if they have not been removed already by GAC or similar purification methods. Like other on-line technologies, high concentration of particulates may be difficult to oxidize, but those types of problems would be atypical in UPW water systems.

The analyzer possesses other user-related features that are similar to existing on-line TOC technologies. The instrument reports TOC, inlet resistivity/conductivity (compensated and uncompensated), and temperature of the inlet water. Alarms for any measured parameter and for lamp lifetime are provided. Relay, analog, and RS-232 signal outputs are also standard features. Water temperatures up to 90°C are acceptable.

V. Applications

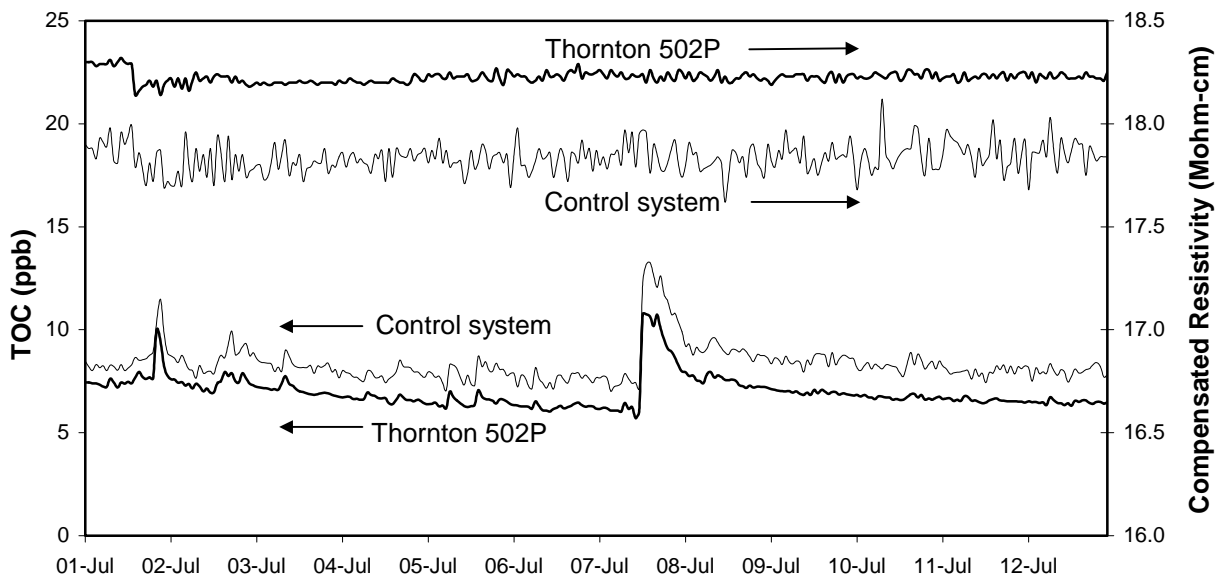
Using the TOC technology described above, three different and unique applications and locations are discussed below. First, two TOC analyzers were installed in the UPW loop of a large semiconductor fabricator, and the performance of the water system was monitored for two weeks. Second, the effect of brief, intermittent upsets was explored in order to determine the instrument's ability to respond rapidly relative to other analyzers. Third, the flexibility of this TOC technology is demonstrated as it is used as diagnostic tool in all portions of a water system of another semiconductor fabricator.

A. Data from a Semiconductor Water System

There are few ways to independently verify the performance of a new TOC analyzer in an in-line industrial environment. A common method is to use an existing TOC analyzer that has been independently accepted by industry. Ultimately, this leads to side-by-side comparisons – but that is not the intent of this test. We wanted to know if the continuous measurement technology is capable of responding to natural excursions found in a semiconductor water system under live conditions, i.e., real TOC, resistivity, and temperature fluctuations.

Ultrapure water was prepared from a combination of mixed-bed ion-exchange, a set of UV lamps (254 nm), and 0.1 μ filters to produce low TOC, >18 M Ω -cm quality water. For two weeks, the TOC and the resistivity were monitored using the Thornton 502P and a leading TOC analyzer to serve as the control measurement. Both analyzers were calibrated prior to use. Data was recorded at hour intervals and the results of each analyzer are shown in Figure 6.

Figure 6. TOC and Resistivity Data from a Semiconductor Facility



The TOC response of the new analyzer gave a virtually identical response to the control instrument, including the disruptions late on July 1 and July 2, and midday July 7. Each analyzer responded with an equal amplitude increase and an equal decay. The root cause of these 3 events

was not thoroughly investigated, but the ongoing maintenance during that period was the likely culprit.

The two primary distinctions between the two TOC measurements are :

- The control system showed a 1 to 1.5 ppb TOC nominal offset relative to the new technology.
- The TOC signal from the new technology was less noisy. This is evident over the last two days of testing when the TOC level was stable (see Table 1). The fluctuation in the TOC signal of the control unit (~3%) was nearly double that of the new TOC technology (~1.6%)

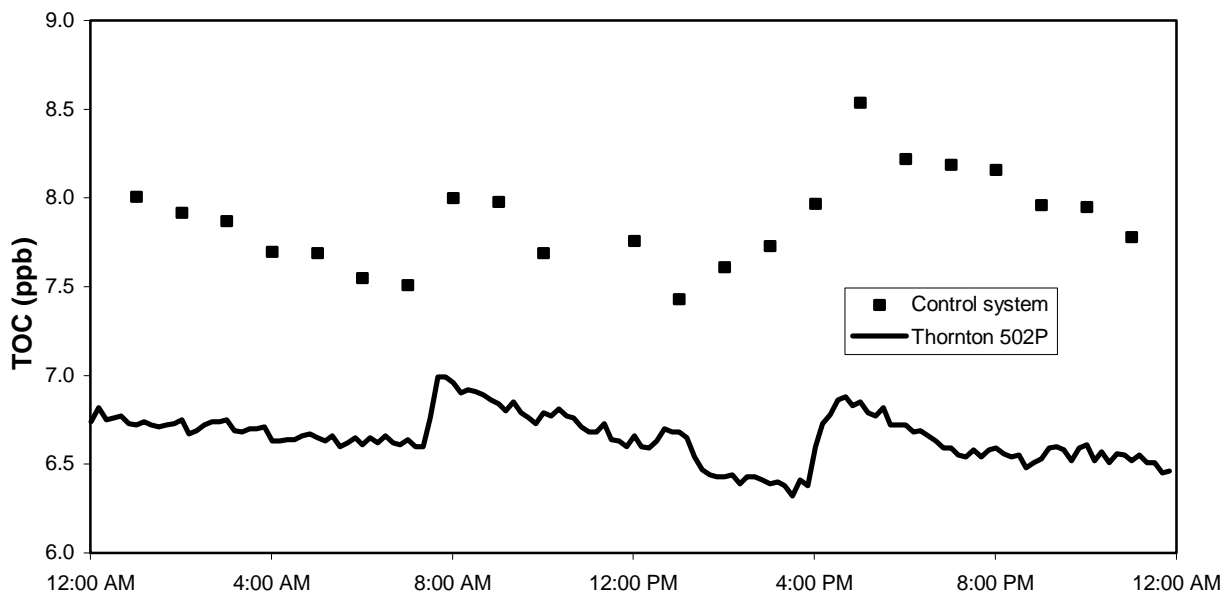
The results are similar for the resistivity measurement. Both systems gave even, unchanging responses for this water system, albeit at a different resistivity and noise level. Like above, the resistivity measurements were more than 3 times less noisy for the new technology.

Table 1

TOC* (ppb)	Thornton 502P	Control System
Average	6.53	7.99
Standard Deviation, σ	0.104	0.237
Relative σ	1.59%	2.97%
Resistivity (M Ω -cm)	Thornton 502P	Control System
Average	18.22	17.83
Standard Deviation, σ	0.022	0.069
Relative σ	0.12%	0.39%

* for July 13-14

Figure 7. TOC data from July 4, 1998



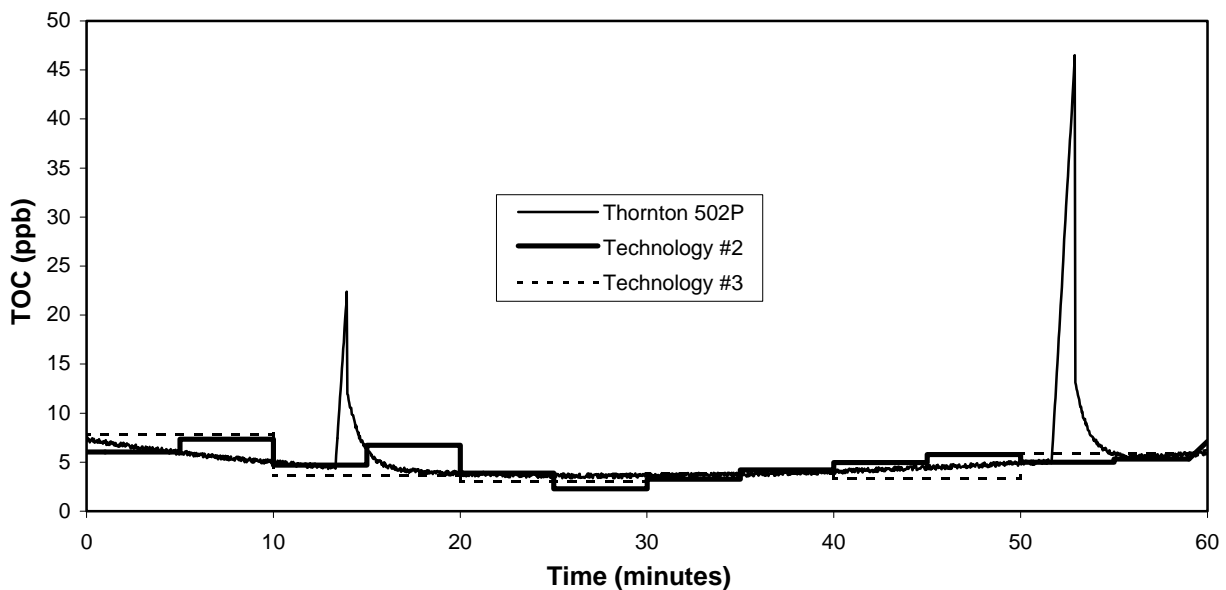
On July 4, data was collected more frequently on the Thornton 502P to determine if the fluctuations in the TOC signal were due to noise or to real fluctuations of the water quality. The very small, abrupt increases at ~8AM and 4PM are determined to be real events, as proven by their natural decay to baseline conditions as the water purity returns to normal.

B. Detection of Instantaneous Upsets

A closed-loop recirculating water system was utilized for these tests. The primary component of the water system was a laboratory-grade 4-stage mixed-bed deionization unit that typically produced <10 ppb TOC water at >18 MΩ-cm. This purification unit fed the “continuous measurement” technology TOC measurement system, and the output (or the bypass) of each TOC measurement system was returned to an overflow tank. The overflow tank provided gravity feed to the purification unit. A tee was inserted between the purification unit and different TOC monitoring systems in order to inject controlled quantities of organic impurities. A microsyringe injection system was used to deliver the impurities at a pre-programmed rate.

At different times during that testing, the injection system was started for a couple seconds and then immediately stopped. In each case, the disruption to the water system was virtually instantaneous. Typical results for the “continuous measurement” technology are shown in Figure 8. The impurity spikes from the injection system were immediately detected by this technology, and within seconds the TOC signal dissipated. For both disruptions, the entire impurity was captured by the analyzer.

Figure 8. Response of TOC Measurement Technologies to Brief Upsets



To the contrary, the response of the “batch measurement” TOC technologies greatly depends on the duration of the impurity, and the cycle time and timing of the measurement method. If fortuitous timing is achieved, then the brief impurity can be detected by the batch measurement. However, if the system upset occurs while these TOC measurement technologies are in the middle of an oxidation/measurement cycle, then these TOC excursions will not be detected. As an example, the response of the “batch measurement” TOC technology with a 5 and 10 minute

cycle time is simulated in Figure 8. For the shorter cycle time, the two upsets are virtually undetected, with only the tail end of the first upset being barely observed. For the 10 minute cycle time, both upsets are missed entirely in this example. In all cases, the “batch measurement” method missed the impurity entirely because they were busy oxidizing the previous water sample. The advantages of the continuous monitoring with minimum response time results in the ability to catch all excursions, regardless of its duration.

C. Unique Applications of TOC and Resistivity

During the evaluation of the new TOC measurement technology at a West Coast Semiconductor Facility, two unique problems were identified by the new TOC measurement technology in the water purification system. In each case, unexplained and borderline TOC levels increased mysteriously. While these were not the first time these problems arose, the problems were determined not to be typical failure modes either, i.e., exhausted carbon beds or filters or the like.

Normally, without the use of multiple TOC units, the sporadic nature of the increased TOC was considered too difficult to find the root cause. It was the opportunity to move the TOC analyzer throughout the facility with no startup or installation time that allowed the user to sample many points throughout the facility rapidly. A description of each problem is provided.

First, a large source of organic impurity was detected at a point-of-use. The 502P, which requires only a sample port to connect to its ¼” inlet tubing, was carried around the DI loop and installed in numerous locations, seeking the source of the increased TOC signals. The normal course of investigation revealed that the impurity was not from any failed purification components in the DI loop. Eventually, the trace of the TOC signal brought the user back to the pre-purification area at the second-stage RO system, and specifically the pumps. In this case, there was a significant increase in the TOC from the suction (inlet) side to the discharge (outlet) of the pump. In general, an increase of anything more than 1% should warn the user that the pump seals require some attention. In this case, the culprit was propylene glycol that is used as an antifreeze to protect the pump during shipment.

The second unusual upset was the repeated and sporadic rise and fall of TOC and resistivity levels in storage tanks for systems that are intended to be maintained at >18 MΩ-cm. The unusual part was that the TOC and resistivity signal would rise together and fall together. Usually, as water is purified, the resistivity increases and the TOC decreases. In this tank, as the water became cleaner ionically, it was getting dirty organically and vice versa. An ozone tank is used as the source to keep TOC levels in the tank low. The ozone tank uses air to generate ozone, with particulates being removed by a HEPA[®] filter.

The source of the TOC and resistivity fluctuations was eventually correlated to tank level, and the following was determined. As the tank level lowered, more air was drawn into the water system, and this had two predominant effects. The increased oxygen intake increased the amount of ozone produced, and this lowered the TOC because of its excellent oxidation capabilities. Furthermore, the increased air intake also meant increased CO₂ intake, and therefore a lowered resistivity (see eq 2). Conversely, the rising water tank level caused less ozone and less CO₂ to

be injected into the tank, thereby increasing TOC and lowering resistivity. The “breathing” of the tank was the source of the purity oscillations.

VI. Conclusions

An alternative technology has been developed that measures low level TOC rapidly and continuously. The new technology employs similar oxidation and measurement methods that have been proven to be very effective and successful for TOC measurement. Yet these methods have been further developed in order to provide an instantaneous response, while offering ease of installation, portability, and no reagents. All that is required is a continuous sample stream of water to analyze. The new technology has been demonstrated in live water systems to be accurate and effective in reporting upsets, in real time, before they are allowed to impact downstream processes and eventually products.

VII. Acknowledgements

Our appreciation is extended to William Bornak of Aqueous Solutions for his effort to collect the thousands of data points that were generated in the semiconductor water system. Also, we acknowledge the assistance of the personnel at all of the semiconductor facilities (unnamed at their discretion) for allowing us the opportunity to conduct these tests.

VIII. References

1. Conductivity and resistivity are identical measurements, differing only in the units of expression. Those involved in the production of semiconductor grade high-purity water use resistivity terms, i.e., 18.2 M Ω -cm. Chemists tend to prefer conductivity terms such as 0.055 μ S/cm. Neither terminology is exclusive. The remainder of the paper will utilize both terms depending on the application, but both terms are always applicable.
2. K.R. Morash, R.D. Thornton, C.H. Saunders, A.C. Bevilacqua, and T.S. Light, "Measurement of the Resistivity of High-Purity Water at Elevated Temperatures", *Ultrapure Water*, December, 1994.
3. "Ultrapure Water - The Standard for Resistivity Measurements of Ultrapure Water", A.C. Bevilacqua, *17th Annual Semiconductor Pure Water and Chemicals Conference*, Santa Clara, California, March 2-5, 1998.
4. T.S. Light, B. Kingman, A.C. Bevilacqua, "The Conductivity of Low Concentrations of CO₂ Dissolved in Ultrapure Water from 0-100°C", *209th American Chemical Society National Meeting*, Anaheim, CA, April 2-6, 1995.
5. R.G. Godec, K. O'Neill, and R. Hutte, "New Technology for TOC analysis in water", *Ultrapure Water*, December, 1994.
6. "The Effect of Temperature, Temperature Error, and Impurities on Compensated Conductivity Measurements", A.C. Bevilacqua, *16th Annual Semiconductor Pure Water and Chemicals Conference*, Santa Clara, California, March 3-6, 1997.
7. The definitions of reclaim and recycle water are often misused or interchanged, and they are the subject of some debate. For this paper, we categorize them together because the speed of response is critical to each type of re-used water, whether it is for a cooling tower or for re-purification.

IX. Biography

Dr. Anthony C. Bevilacqua is the Research and Sensor Development Manager at Thornton Inc., a manufacturer of sensors and instrumentation for all parameters relating to water systems and quality, including resistivity/conductivity, TOC, flow, pH, temperature, and pressure. He has 13 years of instrumentation and sensor development experience, the last five relating to high purity water systems. He holds a B.S., M.S., and Ph.D. in Chemistry.

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