Laboratory Monitoring of Total Organic Carbon in Ultrapure Water

by Paul Whitehead

The main reason scientists measure total organic carbon (TOC) in water in laboratory water purifiers is to be sure that the organic content of the water taken from the unit is low enough so as not to interfere with their application or to conform to a particular internal or external specification. For this to be so, the TOC monitor must be able to provide a good indication of the TOC level in the water actually being dispensed, and ensure that any breakthrough of organics is detected before the water is used. This application note summarizes the problems that can be caused by organic contaminants, as shown in *Table 1*, and considers the nature of organics in water and TOC and its removal and measurement.

Table 1 Potential effects of organic contaminants in water

Effects of organic contamination
Poor detection limits
Poor reproducibility
Increased blanks
Coating of reactive surfaces
Chemical interference
Scattering effects
Fouling of separation or purification media
Toxicity
Encouragement of microbial growth

Organics in water

Ultrapure water is usually produced by the multistage treatment of a potable water supply. Organic compounds in the feedwater are both naturally occurring and synthetic. The former are mainly a complex mixture of fulvic and humic acids and tannins derived from the decomposition of leaves and grasses or from peat or marsh areas. In addition, there are bacteria, other living creatures, and their by-products. Sources of synthetic compounds include industrial waste and domestic waste such as detergents, solvents, and oils, together with agrochemicals such as fertilizers, herbicides, and pesticides.

Since the water is treated to make it suitable for domestic or industrial use, many of the impurities are removed but others are introduced, for example, plasticizers from plastic pipes and tanks. Other compounds are generated by reactions with treatment chemicals such as chlorine and ozone.

During treatment of the feedwater to produce ultrapure water, organic compounds are removed by a combination of some or all of the following techniques: reverse osmosis, microfiltration, ion exchange, absorption, and UV photooxidation. These remove the majority of contaminants, leaving small amounts of a wide variety of impurities.

TOC

Total organic carbon is traditionally classified into various categories—particulate organic carbon (POC), dissolved organic carbon (DOC), and volatile organic carbon (VOC). These subdivisions are largely irrelevant to measurements in ultrapure water. The water has already been filtered during purification, and methods of detection used on-line do not distinguish between VOC and DOC.

Of more importance is the relationship between the TOC and the equivalent concentrations of various organic compounds potentially present in purified water. Some examples are given in *Table 2*.

Table 2 Examples of the relationship between TOC and concentration of contaminants in purified water

Compound	% Carbon	Compound (ppb) giving 10 ppb TOC
Ethanol	52.2	19.2
Urea	20.0	50.0
Chloroform	10.1	99.0
Phenol	76.5	13.1
Trichlorophenol	36.5	27.4
Diethyl phthalate	64.8	15.4

As is evident in the table, it is not surprising that the percentage of carbon in organic compounds found in water varies from about 10% to more than 75%. Therefore, water with a TOC content of, for example, 10 ppb can contain any combination of organic compounds, and these compounds can easily vary widely in concentration. Only using the compounds in Table 2, water with a TOC of 10 ppb may contain a mixture of 25 ppb urea and 50 ppb chloroform; on the other hand, it may contain 6.6 ppb phenol and 9.6 ppb ethanol.

The question, then, is: Is TOC measurement in purified water a waste of time? TOC provides neither the exact composition of impurities in the water nor the level of a particular impurity; at present, however, TOC comes closest to a universal indicator for the presence of organic impurities. Whether the impurity contains 10% carbon or 75% carbon, a TOC measurement will still detect it if it is present in sufficient concentration. Thus, a TOC value will provide a measure of confidence that organic contamination is below a certain level, but that is all it can offer. If a TOC measurement shows 10 ppb, it can only be said with confidence that the total of the organic compounds present is less than 100 ppb. The amount can be as low as 15 ppb, but this is not evident from TOC alone. Although this information is still very useful, it is not improved by accuracy of better than ±10% in the TOC measurement. If a change in TOC is due to virtually any combination of organic compounds with a possible eightfold variation in concentration, is it necessary to know whether the TOC is 10 or

11 ppb? Clearly, the answer would not provide additional, useful information because the significance of a small change in TOC depends on what has caused the change and whether those compounds will interfere with the application of the water.

Therefore, it can be concluded that, although TOC measurement is not a waste of time, highly accurate TOC measurement is unnecessary. What, then, do users of purified water actually need in terms of a TOC monitor? To meet the requirements discussed above, a sensitive monitor with fast response, preferably built into the water purifier and with low running costs, is needed. An assessment of the suitability of current TOC monitors to meet these targets is given below.

Table 3 Requirements for a built-in TOC monitor for laboratory water purifiers

	Target	ELGA TOC monitor	Various TOC monitors
Purifier		PURELAB Ultra	Assorted
Type	Continuous	In-line, continuous	Side-stream, noncontinuous
Cost	Low	Low	Medium
Running cost	Minimal	Zero	High
Speed of response	Fast (<1 min)	Fast	Slow (up to 9 min)
Accuracy	Adequate (±2 ppb or ±10%)	±2 ppb at <10 ppb	±2 ppb
Measurement range	1–10 ppb essential; higher range optional	1–200 ppb	Typically 1–999 ppb
Water usage	As low as possible	None	Low
Sample volume	As large as possible	Whole water flow	Small (<1%)
"Dead-leg"	None	None	Yes
Traceable calibration	Yes	Yes	Yes
Outputs	Screen and printout	Screen and printout	Screen and printout

Types of TOC monitors

Relatively sophisticated and expensive TOC monitors have been available for many years to large industrial water purification plants. Their cost and size make them impractical as a permanent installation with each laboratory water purifier. They also possess other disadvantages for small-scale use.

Built-in monitors in laboratory water purifiers all rely on a similar effect. When water is exposed to UV light at a wavelength of 185 nm from a low-pressure mercury lamp, reactive species are generated that oxidize organic impurities in the water. The oxidation produces acids and other ions and, ultimately, the carbon present is converted to carbon dioxide. All of these species are electrically conductive and cause the conductivity of the water to rise. This conductivity change is measured and used to estimate the TOC content.

The TOC monitor in the ELGA PURELAB$^{®}$ (**USFilter,** Lowell, MA) Ultra differs from the TOC monitors in many other laboratory water purification systems. The latter are scaled-down versions of large-scale monitors that have lower performance specifications and robustness to reduce manufacturing costs. Unfortunately, they also retain many of the disadvantages of such systems. The TOC monitors are connected in a side-stream from the pure water recirculation loop near the dispense point. They are characterized by a measurement cycle in which water is first flushed through the reactor/cell for a fixed time; flow is then stopped to allow oxidation to proceed. In one system, measurements are made in the same cell and a final value is reported at the estimated end of oxidation. In other systems, a fixed oxidation time is used, followed by separate conductivity measurements. In both cases, there is a gap of at least several minutes between the time the sample is taken and the TOC value is displayed. Sampling and analysis are not continuous.

The TOC monitor in the PURELAB Ultra uses the 185-nm UV chamber, which is already built into the system, to reduce organic impurity concentrations. As described above, this UV light oxidizes most of the organics present to conducting species. The increase in conductivity is a function of the TOC level and is used to monitor the product water TOC by calibration against traceable monitors. The practical advantages of this approach are that the entire water stream is monitored and readings are continuous and almost instantaneous. Key features of alternate TOC monitors are summarized in *Table 3*.

TOC monitor response time

Unlike industrial plants that utilize large volumes of purified water, laboratory use is on a much smaller scale. TOC monitoring must reflect the immediate purity of the water that is about to be taken from the unit. This is easy with resistivity monitors that have a very rapid response, but is not the case for side-stream TOC monitors derived from industrial designs that require separate samples to process. As discussed above, these TOC monitors incorporate a series of steps—flushing (typically 1–3 min), oxidation (in which the sample is analyzed, also typically 3 min), and display of results. The overall time between a change of TOC level, however large, and its detection is a minimum of 3 min and may be up to 9 min. In addition to the delay in detecting a change in TOC levels, such TOC monitors are likely to miss entirely any transient organic contamination.

The PURELAB Ultra laboratory water purifier monitors TOC directly on-line with no processing delays (*Figure 1*). The examples below illustrate the benefits of the system.

Figure 1 PURELAB Ultra display showing TOC reading.

A TOC monitor, as fitted in a widely used laboratory water purifier, was connected just before the dispense in a modified PURELAB Ultra, and repeat injections of 3 mL of a 100-ppm solution of methylethylketone were added to the feedwater. The readings on the TOC monitors were logged and the TOC of the water dispensed was also measured. Injections were

Table 4 Detection of transient organic contaminants by ELGA TOC monitor and TOC monitor A

Test	Impurity injected Maximum value (ppb)	Detection delay Compared with dispense (sec)		Impurity found Maximum value (ppb)		Injection point in Monitor A cycle
		ELGA	A	ELGA	A	
1	25	<5	Not detected	20	Not detected	Start of oxidation
2	23	<5	320	20	5	Start of fill
3	24	<5	Not detected	20	Not detected	Mid-oxidation
4	25	<5	440	20	24	Mid-fill

carried out to coincide with different points in the other monitor's measurement cycle. The conditions and results are shown in *Table 4* and graphically in *Figure 2*.

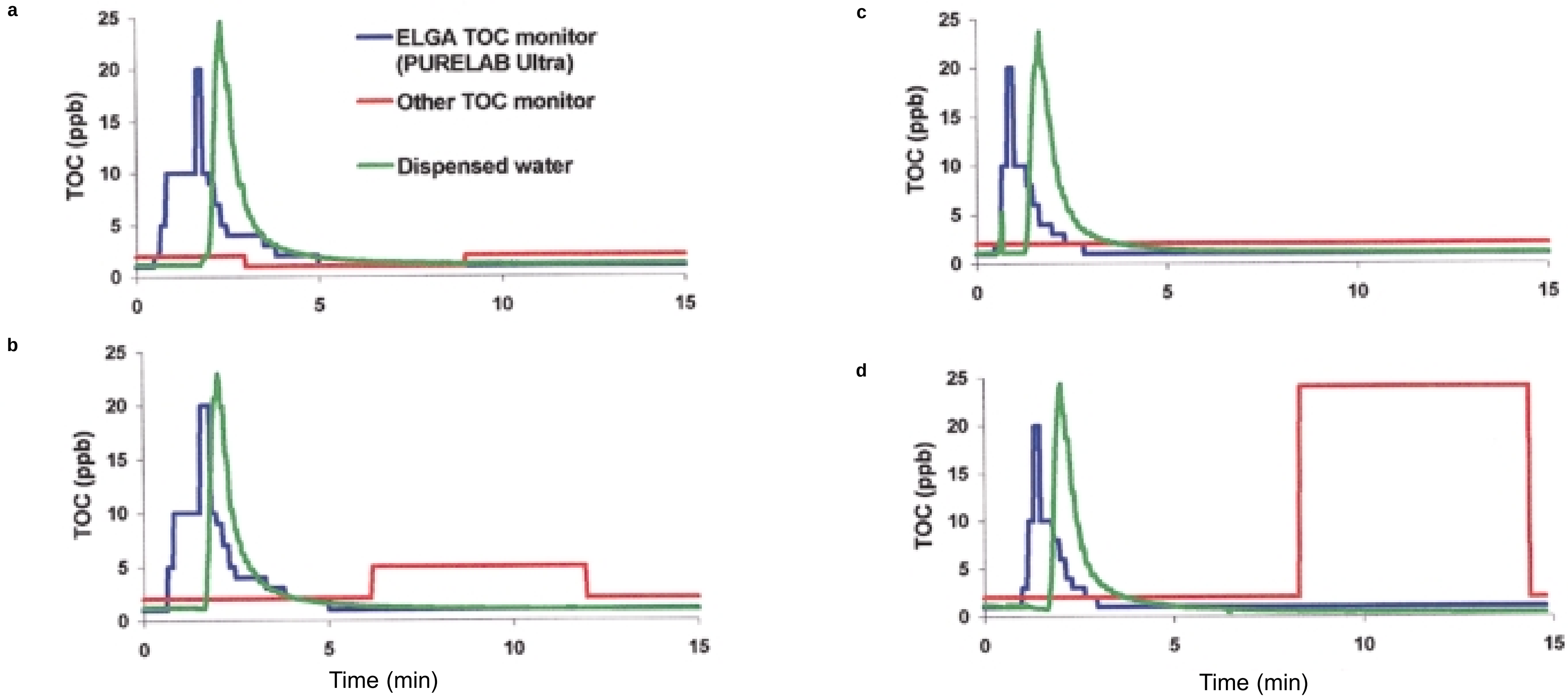

Figure 2 Detection of transient organic contaminants by ELGA TOC monitor and by TOC monitor A.

The TOC was injected into the feedwater at time 0. As water is dispensed from the unit, this contamination is drawn in. The green trace shows the TOC actually present in water dispensed from the unit. After about 2 min, the TOC in the water increases sharply. Any water taken at this point would be contaminated. The blue traces show the response of the TOC monitor in the PURELAB Ultra, while the red traces are that of the other TOC monitor (A). The graphs shown in Figure 2*a–d* correspond to different injection times relative to the cycle of TOC monitor A.

The difference in performance between the two types of monitors is striking. The TOC monitor built into the PURELAB Ultra consistently and rapidly detects the impurity incursion. In order for TOC monitor A to detect the impurity, it has to be in the water flowing through the measuring cell when the flow is stopped, i.e., at the end of the fill period. If it is not, as in Figure 2*a* and *b*, it will not be detected. This is true no matter how severe the contamination. In Figure 2*c*, the contaminant is partly detected. In Figure 2*d*, it is well detected, but even in these cases, TOC monitor A only picks up the change at least 6 min after the contamination occurred and 4 min after contaminated water was taken from the unit.

Many TOC monitors suffer from similar limitations when faced with a sudden permanent change in the organic content of the purified water. There is a delay of typically more than 5 min before it is detected. Only the TOC monitor in the PURELAB Ultra detects organic breakthrough as it occurs.

Because the organic contamination of ultrapure water has potentially serious consequences, built-in TOC monitoring is now expected in top-of-the-line laboratory water purifiers. However, until recently there has been no attempt to consider the scope and limitations of such monitoring and the performance required from the TOC monitors to provide the information needed by users.

Due to the widely differing organic component levels that can correspond to a particular TOC value, there is no benefit in highly accurate TOC monitoring. TOC is an excellent indicator of general levels of organic contamination. On its own, it is not and never can be anything more.

It is far more important that TOC monitoring be truly continuous and not overlook any change in contamination level, which can potentially ruin an analysis or experiment. Previous TOC monitors missed transient contamination entirely and detected changes in TOC only after water was taken from the water purifier. The TOC monitor in the PURELAB Ultra can fulfill this essential need.

Dr. Whitehead is R&D Laboratory Manager, ELGA LabWater, the global laboratory brand name of ***USFilter,*** *Lowell, MA, U.S.A.. He can be reached at +44 149 488 7795 or via e-mail at paulwhitehead@elgalabwater.com.*