Monitoring TOC in ultrapure laboratory water

The serious consequences of organic contamination of ultrapure water have resulted in the widespread use of Total Organic Carbon (TOC) monitoring in addition to resistivity as key indicators of water purity. For the first time, this article reviews the scope and limitations of such monitoring and the performance required from the TOC monitors to provide the information needed by the users.

TOC is a good indicator of general levels of organic contamination. On its own, it is not and never can be anything more. Because of the widely differing organic component levels that could correspond to a particular TOC value there is no benefit in highly accurate TOC monitoring. It is far more important that the TOC monitoring is truly continuous and does not miss any change in contamination level that could ruin an analysis or an experiment.

Monitoring of impurity levels

We need to be confident that the purified water we are using is pure enough, that we are not introducing an unknown variable into our work, and when we repeat the experiment or assay next week we will get the same result, or, at least, that any differences are not due to the water we used! In other words, we need to control the impurity levels in the water.

Ideally we would monitor for all potentially significant impurities but we probably don't know what all potential impurities could be and it would be impractical to routinely measure them all. To control the impurity levels in the water, we need to find parameters to monitor which

- are sensitive to a broad range of components,
- can be monitored very rapidly,
- can be monitored continuously and
- can be monitored with sufficient sensitivity and accuracy.

As shown in Table 1, ions can be monitored satisfactorily by measuring the electrical resistivity, which conforms to all the above criteria (except for measurements close to 18.2 Mohm.cm). For high purity water a built-in resistivity cell is always used.

Table 1: Control and monitoring of impurities

Type of impurity	Control and monitoring method
Ions	Use of RO & DI Built-in in-line resistivity monitor
Organics	Use of RO & DI, UV photo-oxidation & activated carbon Built-in in-line resistivity monitor
Particles	Use of absolute filter Occasional on-line testing if needed
Bacteria	Use of microfilter, UV & sanitization Off-line testing
Endotoxins	Use of ultrafilter & UV photo-oxidation Off-line testing
Bio-active species	Use of ultrafilter & UV photo-oxidation Off-line testing
Gases	Vacuum degassing at point-of-use Occasional on-line testing if needed

For most of the other types of impurity there are no suitable parameters and monitoring techniques available that give a rapid enough response at a sensible price. For particles, bacteria, endotoxins and other bio-active species, it is necessary to build-in sufficient purification technologies to minimize the risk of failure, to have a rigorous regime for cleaning and consumable replacement and to monitor at intervals, either off-line or on-line. Dissolved gases are not usually removed during water purification. Where required they are removed by degassing before use and dissolved oxygen levels can be checked periodically.

TECHNOLOGY NOTE 29

Organic impurities in mains water are common, can vary considerably in concentration and can have serious effects as illustrated in Table 2 for chromatographic applications. A number of techniques are used to reduce organic contaminants, principally reverse osmosis, activated carbon absorption and UV photo-oxidation. TOC (Total Organic Carbon) has become widely used as a key purity parameter, along with resistivity, for purified water. This role for TOC is based on the absence of any good alternative, rather than on the merits of TOC itself.

Table 2: Potential effects of organic contaminants in water.

Effects of Organic Contaminants	Consequences					
	Poor sensitivity		Poor reproducibility		Degraded chromatography	
Increased backgrounds	✓✓✓		✓✓		✓	
Spurious peaks	✓✓✓		✓✓		✓	
Chemical interferences	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓
Coating of surfaces		✓✓		✓		✓✓
Scattering effects	✓✓		✓✓		✓	
Fouling of media		✓✓		✓		✓✓✓
Aiding microbial growth		✓✓		✓✓		✓✓✓
Detector contamination	✓	✓✓✓	✓	✓✓✓		
Flow effects		✓		✓✓		✓✓

✓ – short-term ✓ – long-term.

Measuring the TOC concentration of water is the only currently available method to provide a general indication of the total concentration of organic substances present. They are generally very poorly detected by resistivity measurements. The primary roles of TOC are to categorise water within general purity bands e.g. less than 50 ppb TOC, less than 500 ppb TOC, as a trend indicator and to detect sudden changes in organic concentrations.

The actual level of different organic compounds equivalent to a particular TOC value will vary considerably depending on their carbon content and the organic compounds present will depend on the feed water and the purification techniques used. So any TOC range (set by a standard or otherwise) is an indication of water that is likely to be "fit for purpose", rather than having any precise technical significance.

The main role of TOC is to detect deterioration in organic contamination levels. This can occur gradually, where TOC monitoring is serving as a trend indicator, or rapidly, where it is acting as an alarm. To achieve this role the TOC monitor must be able to provide a good indication of the TOC level in the water being dispensed and ensure that any breakthrough of organics is detected before the water is used.

To develop these arguments in more detail we will consider the nature of organics in water and their relationship to TOC itself, its removal and its measurement.

Organics in water

Ultrapure water is usually produced by the multi-stage treatment of a potable water supply. Organic compounds in the feed-water are both naturally occurring and man-made. 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 man-made compounds include industrial waste and domestic waste such as detergents, solvents and oils together with agro-chemicals such as fertilisers, herbicides and pesticides.

As the water is treated to make it suitable for domestic or industrial use many of the impurities are removed but others are introduced. These may include plasticizers from plastic pipes and tanks or compounds produced by reactions with treatment chemicals such as chlorine or ozone.

During the treatment of the feedwater to produce ultrapure water, the great majority of contaminants will be removed leaving small amounts of a very wide variety of impurities.

How does TOC relate to these impurities?

The key to understanding the value and limitations of TOC data lies in an awareness of the great potential variety of organic impurities in water and in the relationship between the TOC and the equivalent concentrations of various organic compounds potentially present in purified water. Some examples are given in Table 3.

Table 3: Examples of the relationship between TOC and concentration of some contaminants in purified water.

Compound	% carbon	ppb compound 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

Hardly surprisingly, and as is evident from Figure 3, the percentage of carbon in organic compounds found in water varies from about 10% to over 75%. Therefore, water with a certain TOC content could not only contain any combination of organic compounds but those compounds could also easily vary widely in concentration. Water with a TOC of 10 ppb could contain a mixture of 25 ppb urea and 50 ppb chloroform or it could contain, as easily, 6.6 ppb phenol and 9.6 ppb ethanol.

So is TOC measurement in purified water a waste of time?

TOC will give neither the exact composition of impurities in the water, nor the level of a particular impurity. But TOC is as close as we can get at present 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 given a sufficient concentration. A TOC value only provides a measure of confidence that organic contamination is within a certain range. If a TOC measurement shows 10 ppb we can only say, with confidence, from TOC measurement alone, that the total of the organic compounds present is between 15 and 100 ppb. Improving the accuracy in the TOC measurement will not help in defining the exact composition or levels of particular impurities. If a change in TOC could be due to virtually any combination of organic compounds with a possible eight-fold variation in concentration, do we need to know whether the TOC is 10 or 11 ppb? Clearly it would not give us any more useful information because the significance of any small change in TOC depends on what has caused the change and whether those compounds will interfere with the application of the water.

Therefore, TOC measurement is not a waste of time but only limited accuracy is needed.

So what do users of purified water actually need in terms of a TOC monitor?

Key factors in TOC measurement

1 Sensitivity

For trace level TOC measurements (i.e. less than 20 ppb) a detection limit of 1 ppb or lower is desirable. At this level, unacceptable risks of contamination will occur if such samples come into contact with ambient air and analysis must be carried out on-line.

2 Frequency of measurement

The frequency of TOC measurement required depends on the potential rate of change in organic content of the water and the significance of any change. Changes can arise from malfunction of the purifier, exhaustion of purification media but also from variations in the water supply. This can be in the original feedwater but is most likely to occur in the pre-treatment SDI (service deionization). This is inherently unpredictable and an on-line TOC monitor carrying out measurements regularly is the only way to provide the highest level of security.

3 Speed of response

Ideally TOC measurements should be sufficiently fast and continuous so as to avoid the risk of using contaminated water.

4 Accuracy

(i.e. freedom from likely interferences)

In view of the nature of TOC and its roles, very high accuracy is not required, say +/-10 to 15 % at 500 ppb and +/- 25% at trace levels.

5 Reproducibility

In view of its role in trend monitoring, good reproducibility (+/-2 to 5%) is desirable so that any changes can be detected reliably.

To meet the requirements set out above what is needed is a sensitive monitor with fast response preferably with low running costs and built-in to the water purifier for cost and convenience. To assess the suitability of current TOC monitors to meet these targets the alternatives available will be reviewed first.

Types of TOC monitors

There is a wide range of off-line laboratory TOC analyzers that provide TOC analysis of purified water. These analyzers have advantages of easy calibration and can be used to analyze other types of samples, however due to sample contamination problems they are not suitable for trace TOC monitoring. On-line measurements can be made using dedicated instruments that are coupled directly to the purified water stream. They are the preferred technology for TOC levels of <50 ppb and are essential when TOC levels of <30 ppb are to be monitored.

Relatively sophisticated and expensive on-line TOC monitors have been available for many years for large industrial water purification applications. Their cost and size as well as a number of other disadvantages for small-scale use make them impractical as a permanent installation with each laboratory water purifier.

ELGA launched the first TOC monitor to be built in to a laboratory water purifier in 1994. Other suppliers have followed later with different designs.

Figure 4: ELGA PURELAB Chorus 1 with Halo Dispense display showing TOC reading

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

The ELGA TOC monitor differs basically from the TOC monitors in all other laboratory water purification systems. The TOC monitors in these other systems are scaled-down versions of industrial monitors but with lower performance specifications and robustness in order to reduce manufacturing costs. Unfortunately, they also retain many of the disadvantages of such systems.

The TOC monitors in other laboratory water purifiers are connected in a side-stream from the pure water recirculation loop before the dispense point. They are characterised by a measurement cycle in which water is first flushed through the reactor/cell for a fixed time before being 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 sample being taken and the TOC value being displayed. The sampling and analysis are **not** continuous.

The ELGA TOC uses the 185nm UV chamber, which is already fitted in the PURELAB Chorus 1 to reduce organic impurity concentrations. As described above, this UV light oxidises most of the organics present to conducting species. The resulting increase in conductivity is used to estimate the product water TOC. The great practical advantages of this approach are that the whole water stream is monitored and that the readings are continuous and almost instantaneous. The key features of the alternative TOC monitor types are summarised in Table 5:

Table 5: Requirements for a built-in TOC monitor for laboratory water purifiers

	Target	**ELGA TOC**	**Other TOC monitors**
Purifier		**PURELAB Chorus 1**	**Other brands**
Type	Continuous	In-line, continuous	Side-stream, non-continuous
Cost	Low	Low	Medium
Running cost	Minimal	Nil	High
Speed of response	Fast (<1 minute)	Fast (<1 minute)	Slow (up to 9 minutes)
Accuracy	Adequate (+/- 2 ppb or +/-20%)	+/- 2 ppb at <10 ppb	+/- 2 ppb
Measurement range	1 to 10 ppb essential, higher range optional	1 to 200 ppb	Typically 1 to 999 ppt
Water usage	As low as possible	Nil	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 print-out	Screen and print-out	Screen and print-out

TOC monitor response time

Unlike industrial plant using large volumes of purified water, laboratory use is on a much smaller scale. TOC monitoring has to 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 take separate samples to process. As discussed, these TOC monitors incorporate a series of steps – flushing (typically 1 to 3 minutes), oxidation (in which the sample is analyzed, also typically 3 minutes) and result display. The overall time between a change of TOC level, however large, and its detection will be a minimum of 3 minutes and could be up to 9 minutes. A further drawback of such TOC monitors is that they are likely to miss entirely any transient organic contamination. These problems are all avoided with the ELGA PURELAB Chorus 1 laboratory water purifier that monitors TOC directly on-line with no processing delays. Some examples below will illustrate the advantages offered by the ELGA system.

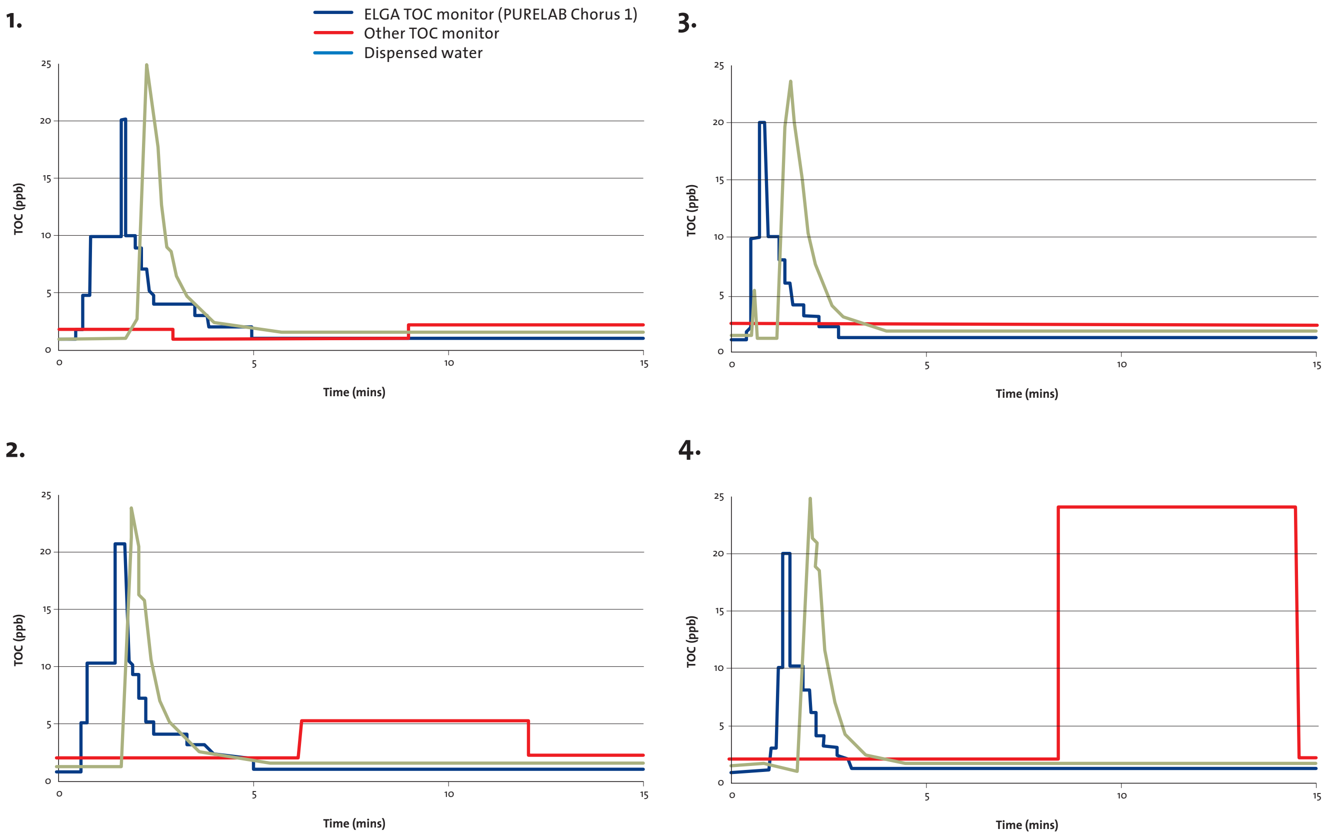
A TOC monitor, as fitted in another widely used laboratory water purifier, was connected just before the dispense in a modified PURELAB Chorus 1 and repeat injections of 3 ml of a 100 ppm solution of methyl ethyl ketone were made into the feed water. The readings on the TOC monitors were logged while the TOC of the water dispensed was measured continuously. Injections were carried out to coincide with different points in the other monitor's measurement cycle. The conditions and results are shown in Table 6 and graphically in Figure 7.

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 minutes TOC in this water increases sharply. If users were taking water at this time it would be contaminated. The blue traces show the response of the ELGA TOC monitor in the PURELAB Chorus 1 and the red traces that of the other TOC monitor. The different graphs correspond to different injection times relative to the cycle of the other TOC monitor

Table 6: Detection of transient organic contaminants by the ELGA TOC monitor and by the other type of TOC monitor. The ELGA TOC monitor reliably detects the impurity while the water is being dispensed. The other monitor's response is late and unreliable.

Test	Impurity injected maximum value (ppb)	Detection delay compared with dispense (seconds)		Impurity found maximum value (ppb)		Injection point In other monitor cycle
		ELGA	Other	ELGA	Other	
1	25	<5	not detected	20	not detected	Start of oxidation
2	24	<5	320	20	5	Start of Fill
3	23	<5	not detected	20	not detected	Mid oxidation
4	25	<5	440	20	24	Mid fill

Figure 7: Detection of transient organic contaminants by the ELGA TOC monitor and by the other type of TOC monitor. The TOC was injected into the feedwater at time 0. As water is dispensed from the unit this contamination is drawn in. The green traces show the TOC actually present in water dispensed from the unit. After about 2 minutes the TOC level in this water increases sharply. If users were taking water at this time it would be contaminated. It is essential that the TOC monitor detects this problem at the time. The blue traces show the response of the ELGA PURELAB Ultra TOC monitor and the red traces that of the other monitor. The different graphs correspond to different injection times relative to the cycle of the other TOC monitor – see Table 5.

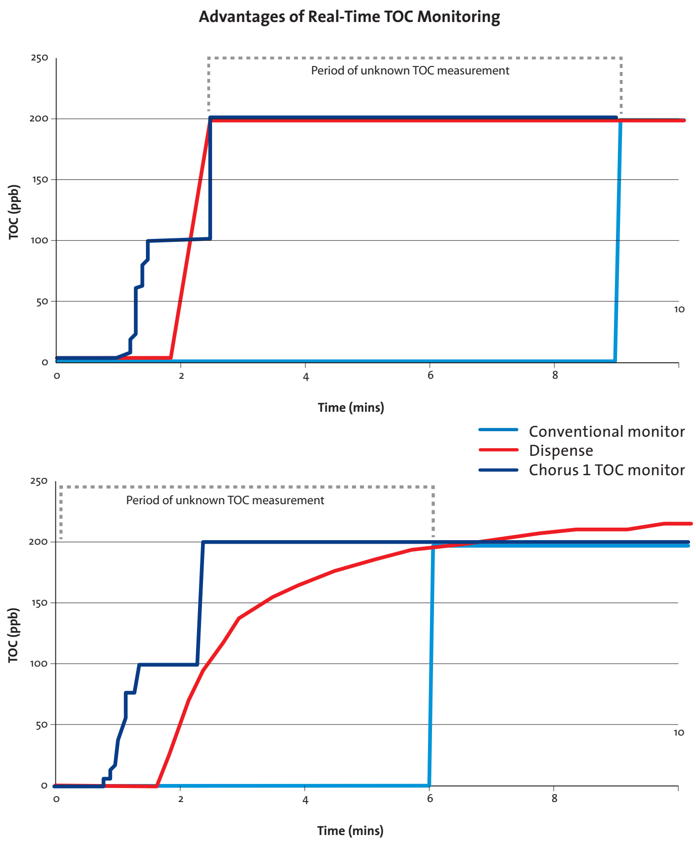


TECHNOLOGY NOTE 29

The difference in performance between the two types of TOC monitor is striking. The ELGA TOC monitor built into the PURELAB Chorus 1 always, consistently and rapidly detects the impurity incursion. The other TOC monitor can only detect the impurity if it is in the measuring cell when the flow is stopped i.e. at the end of the fill period. If it is not, as in examples 1 and 3, it will not be detected. This is true however severe the contamination. In example 2 the contaminant is partly detected and in example 4 it is well detected but even in these cases the other TOC monitor only picks up the change at least 6 minutes after the contamination occurred and 4 minutes after contaminated water has been taken from the unit.

All the other TOC monitors suffer from similar limitations when faced with a sudden change in organic content of the purified water. As shown in Figure 8, there will be a delay of typically over 5 minutes before it is detected. Only the ELGA TOC monitor will detect any organic breakthrough as it occurs.

Figure 8: detection of a sudden charge in TOC level



Conclusion

Organic contamination of ultra-pure water has potentially serious consequences and built-in TOC monitoring is now expected in top-of-the-range laboratory water purifiers. However, until now, 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 the users.

Because of the widely differing organic component levels that could correspond to a particular TOC value there is no benefit in highly accurate TOC monitoring. TOC is a good 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 the TOC monitoring is truly continuous and does not miss any change in contamination level that could ruin an analysis or an experiment. All other TOC monitors will usually miss any transient contamination altogether and will only detect changes in TOC well after water is taken from the water purifier.

Scientists monitor the TOC in the water in their laboratory water purifier to be sure that the organic content of the water they take from the unit is low enough either not to interfere with their application or to conform to a particular internal or external specification. The only built-in TOC monitor available at present that consistently provides users with this information is the ELGA TOC monitor in the PURELAB Chorus 1. The TOC monitors in all other laboratory water purifiers fail to do so. Only the ELGA TOC monitor in the PURELAB Chorus 1 can provide this essential security.

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