RELIABILITY OF TOC RESULTS IN ULTRAPURE WATER ANALYSIS

The intent of this technical note is to discuss current methods of TOC (Total Organic Carbon) analysis, including their advantages and limitations in the analysis of ultrapure water. For purposes of this paper, "ultrapure" water is defined as that water in the 500 ppb (parts-per -billion) range of TOC and lower.

The two basic components of any TOC analyzer defining accuracy and precision of analysis are:

1. **The Oxidation Reactor**, which converts the organic carbon in the water to CO_2 gas, usually either by thermal, chemical or ultraviolet radiation. Oxidation efficiency, assuring complete conversion of the organic carbon to CO_2, is critical.

AND

2. **The CO_2 Detector**, which measures the concentration of the CO_2 gas generated in the oxidation chamber. This component is critical for precise analytical results, since it directly correlates to the organic carbon content of the analyzed water.

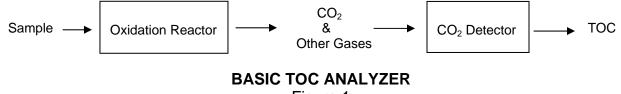Figure 1 presents the basic analytical method for TOC analysis.

Sample $\longrightarrow$ | Oxidation Reactor | $\longrightarrow$ CO$_2$ & Other Gases $\longrightarrow$ | CO$_2$ Detector | $\longrightarrow$ TOC

BASIC TOC ANALYZER
Figure 1

The Oxidation Reactor

For ultra-pure water analysis, three techniques are in common use:

High Temperature Catalytic Oxidation

UV Oxidation, with the addition of chemical reagents

UV Oxidation only

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The High Temperature Oxidation method may be useful in those applications where difficult to oxidize compounds are present and speed of response is critical. Limitations of this method in ultrapure water analysis include requiring a special catalyst of relatively short lifetime. These analyzers generally exhibit low sensitivity and require high maintenance of its high temperature components. The major limitation of this method, however, is its inability to maintain the required stable baseline to reliably achieve accurate low level TOC analysis. This is due to the accumulation of nonvolatile residues in the high temperature reactor, adding false and continuously changing "TOC" background levels to the current TOC analysis, resulting in unreliable data.[1]

The UV/Chemical Oxidation method offers a relatively low maintenance, high sensitivity method but must demonstrate its efficiency to fully oxidize the organic carbon to CO_2 in the particular application. To compensate for oxidation limitations of some UV Reactors, the addition of an oxidizing reagent (usually a persulfate) aids in the conversion of the organic carbon to CO_2 gas. Limitations of this method include the inaccuracies associated with the addition of any foreign substance into the analyte. "Blanking" of chemical additions help but will still contribute error to the analysis in levels below 200 ppb TOC.

The UV Oxidation method offers the most reliable, low maintenance method of analyzing TOC in ultrapure waters but the efficiency of its oxidation technique is critical and should be guaranteed to perform satisfactorily in the chosen application.

The CO_2 Detector

By far, this component is the most critical for accurate TOC analysis. Two basic methods are in common use:

CONDUCTIVITY

AND

NON-DISPERSIVE INFRARED (NDIR)

THE CONDUCTIVITY method measures the conductivity of the sample before and after it is oxidized, attributing this differential measurement to the TOC of the sample. During the sample oxidization phase, CO_2 (directly related to the TOC in the sample) and other gases are formed. The dissolved CO_2 forms a weak acid, thereby changing the conductivity of the original sample proportionately to the TOC in the sample. In this technique, it is assumed that only CO_2 is present and, if true, the TOC of the sample may be validly calculated by this differential measurement. Depending on the chemical species present in the sample and their individual products of oxidation, they may present either a positive or a negative interference to the actual TOC value, resulting in commensurate analytical error.

While this method offers the simplest, most compact TOC analyzer available, potential users of this method should be aware of its instrumental limitations when used in ultrapure water analysis. They are:

Over 50 ppb TOC, conductivity measurements are not uniformly proportional to the TOC of the sample and widely vary with the specific carbon-containing species present, thus contributing significant error.[2]

Conductivity compensation errors involving temperature and TOC concentration are little known but are of significant importance. Because it is often not practical to ascertain all the chemical constituents of an analyte and measure their effects, it is equally unlikely to be able to derive a valid algorithm to compensate for both TOC "concentration" conductivity error and error deriving from "temperature" effects, since conductivity temperature effects are also dependent on chemical and TOC concentrations. [3] These errors could be of major importance in critical applications.

Thus, conductivity measurements are beset by many interferences, such as changing sample composition or when there are non-fully oxidized organics or residual inorganic impurities left over from the oxidation process. Certain amines will pass through membranes and add conductivity to water loops. Urea hydrolysis and ammonia can cause both questionable results and contamination. Small changes in pH and temperature fluctuations are also well known contributors to inaccuracy. Certain manufacturers of these TOC analyzers have taken measures to ameliorate these deficiencies but they, themselves, could have serious limitations and must be considered in their use.

Simple temperature and pH corrections are insufficient to completely eliminate their effects, as they introduce errors of their own as discussed above. The interference of the non-fully oxidized organics would remain, presenting both the error of incomplete oxidation and the consequent CO_2 detection interference.

A different approach to improving the accuracy of TOC analysis using conductivity has incorporated the use of hydrophobic gas permeation membranes to allow a more "selective" passage of the dissolved CO_2 gas to the "zero" water for subsequent conductivity analysis. While this has solved certain problems, membranes have their own particular limitations, such as with true selectivity, clogging and, more undetectably, they provide secondary sites for other chemical reactions, which are prone to display "false negatives," a condition far more severe than "false positives" in critical applications. Micro leaks, flow problems, dead spots, microbial growth (blockage) are also potential problems. Most disconcerting is the inability of membrane methods to recover to operational performance after an overload or "spill" condition arises to overrange the instrument, often taking hours before it can be returned to reliable service and recalibration, just when accuracy of TOC analysis is most critical to operators for quality control.

Some Examples of Conductivity Interference

For purposes of clarity, the other well known factors which have significant effect on accuracy of conductivity measurements will not be covered. These factors include:

> Temperature
> PH
> Differential Measurement Errors
> Calibration
> Membranes (if used)

In general, for reasons described in subsequent paragraphs, conductivity cannot be reliably used if the following species are present in the sample <u>OR FORMED BY THE OXIDATION PROCESS:</u>

Interfering Species

Acid Gases	Iodine
Organic Acids	Hypochlorous Acids
Halogenated Organics	Nitrite Ions
Sulfide Ions	Other Ions with Dissolved Gas Phases

Example #1 - Organic Acids

A sample contains 1,250 parts-per-billion per liter (ppb/l) of acetic acid ($CH_3 COOH$) or 500 ppb/l of TOC. The original unoxidized acetic acid is generally ionized and this sample would have an equivalent conductivity of 4.8 µS/cm (at 25⁰C).

When acetic acid is oxidized to CO_2 and water, the equivalent conductivity is 1.71µS/cm. Thus the output of the conductivity detector is -3.09 µS/cm (1.71 µS/cm - 4.8), which is obviously a gross instrumental error. Most manufacturers of this approach default all negative readings to "Zero", which could have serious future harmful consequences to equipment or processes. Hidden false negatives are more pernicious than false positives, such as in the next example.

Example #2 - Halogenated Organics

A sample contains 990 ppb of chloroform ($CHCl_3$) equivalent to 100 ppb of organic carbon. Chloroform is oxidized to CO_2 and hydrochloric acid (HCl), which dissociates to H^+ and Cl^- ions. The oxidized chloroform sample conductivity is approximately 10 µS/cm. This is a significant error of about 900%, as the CO_2 contribution should only contribute about 1 µS/cm.

<u>THE NON-DISPERSIVE INFRARED ANALYSIS (NDIR)</u> method offers the only practical interference-free method for detecting CO_2 in TOC analysis. It is required to fully comply with approved EPA Standards for TOC analysis. The principal advantage of using NDIR is that it directly and specifically measures the CO_2 generated by oxidation of the organic carbon in the Oxidation Reactor, rather than relying on a measurement of a secondary, corrected effect, such as used in conductivity measurements.

Unfortunately, many analyzers using NDIR have previously lacked the sensitivity required for ultrapure water analysis. Auto-zeroing and auto-calibration prior to each measurement cycle is easy to incorporate into NDIRs and have been used effectively for many years in higher level TOC analysis. While improving performance, these techniques did not completely solve lower detection limit shortcomings. Current computer technology and algorithms now allow considerable improvement of older NDIR methods in obtaining the desired ultra low ppb ranges. Caution should be exercised in the selection of adequate NDIR sensitivity for the chosen application.

CALIBRATION

A serious limitation for verification of the accuracy of TOC results is the ability for the user to perform on-demand analyzer verification and calibration and to periodically check reliable analyzer performance. "Factory-Set" calibrations at levels beyond operational ones are questionable. When using a chemical calibration standard solution significantly greater than the operating range and relying on a manufacturer's mathematical factor to produce reliable results, frequent instrument validations must be performed at the operating levels, unless the instrument sensors are self-calibrating, using properly referenced techniques.

The practical problem of preparing a stable standard solution at low levels requires great care.

Below are recommendations to obtain a reliable **"zero"** and **"span"** of the analyzer:

a) "Zero": The following methods are recommended in order of the most desirable:

1. Use of oxygen or CO_2-free air flowing through the reactor to the CO_2 sensor (only practical with NDIR).
2. Use of fully-oxidized, triple-distilled, deionized water while still in the oxidation chamber
3. Use of a fully oxidized previous sample while still in the oxidation chamber.
4. Use of fully-oxidized, triple distilled, deionized water captured from the oxidation chamber after being oxidized
5. Use of triple-distilled, deionized water.

b) "Span": Depending on the availability of the "ZERO" water, listed by preference, above:

1. Prepare a stock solution, using "zero" water and dried anhydrous potassium hydrogen phthalate. Dissolve in a 100 mL flask, and then perform standard volumetric dilutions to obtain the TOC value of interest.
2. Be sure to "blank" the "ZERO" water used, then immediately span the analyzer on the solution prepared.
3. If reagents are required, they must be blanked accordingly after being prepared with "ZERO" water.

CONCLUSION

For reliable ultrapure water monitoring, TOC analysis is required and is a beneficial control parameter if its limitations are recognized and accounted for, but could be very misleading if "blind faith" in the manufacturer is relied upon, without user verifiable performance and detailed knowledge of sample composition.

References

1. "Standard Method 5310"
2. "The Conductivity of Low Concentrations of CO_2 Dissolved in Ultrapure Water From 0-100ºC", T. S. Light, B. Kingman, A.C. Bevilacqua, **209th American Chemical Society National Meeting,** Anaheim, CA, April 2-6, 1995
3. "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, CA, March 3-6, 1997.

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