operation, calibration and autozero guidance for TOC monitoring in microelectronics UPW applications

This document provides guidance and best practices for optimizing online Total Organic Carbon (TOC) analysis for operation in microelectronics UPW applications where it is common for the water system to be operating at low and sub-ppb levels. Analyzers from SUEZ and other vendors have limits of detection between 0.02 and 0.03 ppb. Typical UPW system TOC levels can be in the range of 0.2 to 0.4 ppb, or one order of magnitude higher than the detection limit. Optimizing instrument performance when operating so closely to the detection limits is possible but requires a calibration strategy that differs from those employed in higher TOC applications.

hardware selection

SUEZ offers two TOC analyzers designed specifically for microelectronic applications—the Sievers* M9^{e} and 500 RL^{e}. While they share similar low-end performance specifications, the Sievers M9^{e} uses acid and oxidizer reagents that enable it to measure TOC values in excess of 2.5 ppm (the upper limit of the Sievers 500 RL^{e}), handle high IC levels, or measure water where the pH is not neutral. The use of these reagents may contribute trace amounts of organics to the sample. A blank procedure that compensates for this contribution is described later in this document, however, it is recommended to use the Sievers 500 RL^{e} in all applications where the use of reagents is not essential for the reasons stated above.

The Sievers 500 RL^{e} is available in two configurations–with an Integrated On-line Sampler (iOS) or with a Stainless Steel Sample Block. The iOS allows a unit to be operated online while providing a simple means to introduce a grab sample or reference standard to the unit without having to break sample connections. The iOS device is particularly useful for calibrating and verifying calibration.

For reasons described below, traditional calibration of TOC instruments operating at low- and sub-ppb levels is of limited benefit. Therefore, the recommended instrument configuration for low- and sub-ppb applications is a Sievers 500 RL^{e} with Stainless Steel Sample Block. Not only does this reduce instrument cost, the sample block provides a closed sampling system that is more appropriate for low- and sub-ppb applications.

calibration and autozero

There are two factors that affect the calibration of any analytical instrument–gain and offset. The gain impacts the slope of a calibration curve; the offset impacts where the calibration curve passes through a zero point. The role each plays in the analytical performance of an instrument depends on the concentration of TOC in the UPW system relative to the analytical range of the instrument. The closer that UPW TOC concentrations are to the instrument's detection limits–or to zero–the more important the role of the autozero in optimizing instrument performance, and calibration becomes less impactful (see **Figure 1**).

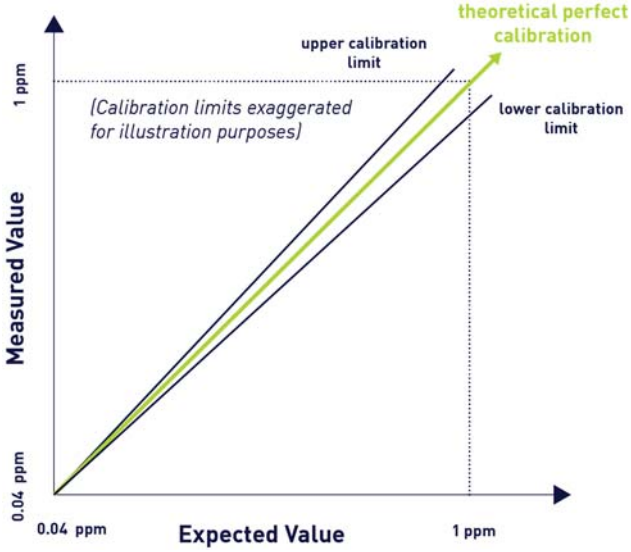

Figure 1. TOC Calibration

Can a low or sub-ppb TOC calibration standard be used to calibrate in the range of interest? The most scrupulously clean vials used in the preparation of calibration standards are certified to have less than 10 ppb of TOC. Therefore, it is not possible to create a sub-ppb calibration standard. Furthermore, given the contribution of error from the vial and the preparation of a calibration solution–typically several ppb TOC–calibration standards only become practical starting in the hundreds of ppb range where errors of weights and measures become negligible. Adjusting the calibration (gain) at these concentrations (e.g., 1 ppm calibration) can have a positive impact on accuracy of reported results when an instrument is operating near the calibration point but has very little impact on results when an instrument is operating at concentrations that are orders of magnitude lower (closer to zero).

As can be seen in **Figure 1**, moving the calibration curve to the worst-case upper or lower calibration limit has no impact on the response of the instrument at the sub-ppb level.

TOC autozero

At these low concentrations, changing the zero point or "offset" is what most impacts instrument performance, ensures reliable results, and facilitates instrument-to-instrument agreement (see **Figure 2**).

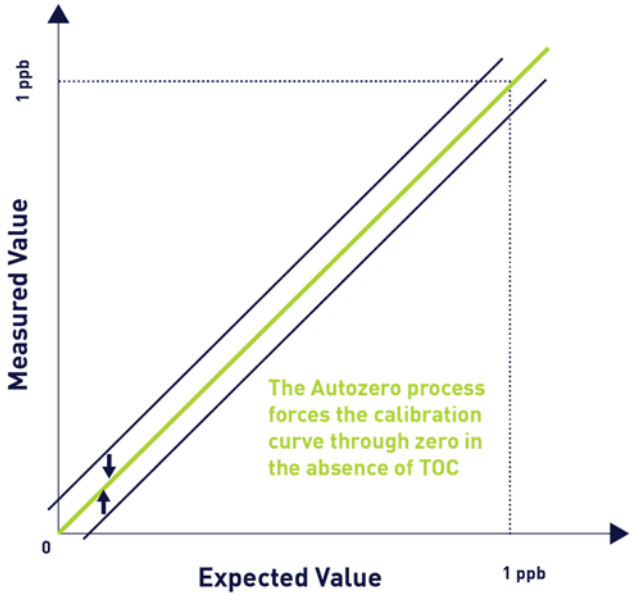

Figure 2. TOC Autozero

The Sievers M9[e] and 500 RL[e] use an auto-zero process that ensures that the instrument reports zero in the absence of TOC. This process is described in the instrument manual. This is a valuable process that helps optimize the instrument for low-level TOC measurement and facilitates optimal instrument to instrument agreement.

TOC autozero strategy for Sievers M9[e] and 500 RL[e]

An instrument's zero point is impacted during new instrument rinse-down or by major maintenance. It can also be influenced to a lesser extent by water system characteristics such as inorganic carbon levels. Therefore, the following autozero process is recommended for establishing optimal instrument performance:

- Upon installation of a new instrument, the autozero process should be run on a daily basis for approximately a week while the instrument rinses down. After the first week, the autozero can be run weekly for the remainder of the first month. After the first month, the autozero can be run monthly and remain at this periodicity as it is not expected to change significantly.
- Following routine maintenance (change out of lamp, tubing, DI resin cartridge, etc.), the instrument should be allowed to rinse down for a day and an autozero should be performed. Calibration need not be performed for the reasons described above. Calibration can be performed–there is no harm–but it has little benefit and may extend post-PM rinse down as the system recovers from exposure to PPM level calibration standards. After the initial post-PM autozero, the autozero procedure can be repeated a week later, and then the typical monthly routine can be resumed.
- If an instrument is moved to a new location, an autozero should be performed after the Analyzer readings have stabilized. As with routine maintenance, the autozero can be run again a week later, and then the typical monthly routine can be resumed.
- If major repair maintenance is performed–major component replacement–a post-repair calibration is appropriate to demonstrate basic analyzer performance. For units with a Stainless Steel Sample Block, an iOS can be temporarily installed to support calibration. Sievers repair technicians are equipped and trained to perform this service.

conductivity autozero for Sievers M9^{e} and 500 RL^{e} Analyzers

The Sievers M9^{e} and 500 RL^{e} also use a conductivity autozero feature. The temperature and conductivity cells for the TC and IC channels are only exposed to deionized water containing small amount of CO_2 and therefore should not require calibration of the conductivity gain. Over time, the offset of these cells may drift as ionic contaminants leach from the cells. The conductivity autozero calibration protocol allows for adjustment of the offset for the TC and IC cells.

The conductivity autozero, unlike the TOC autozero, is not a commonly run process. It is typically recommended when troubleshooting negative TOC values. It should only be run if recommended by Technical Support or a Field Service Engineer.

Sievers M9^{e} TOC Analyzer reagent blank

The reagentless Sievers 500 RL^{e} is the TOC analyzer specifically designed for, and most often used for, sub-ppb TOC measurement. The Sievers M9^{e} is designed for use in higher level TOC applications where addition of oxidizer reagent is required to measure ppm level TOC, or in systems with high levels of inorganic carbon where acidification and IC removal may be necessary. However, there are applications where there is very low TOC but with high conductivity or high IC where the Sievers M9^{e} features are required for optimal TOC measurement.

Oxidizer is not needed for these ultrapure applications; therefore, this procedure applies only to the acid reagent. The Sievers M9^{e} utilizes electronics grade acid reagent. However, there can still be trace organics contribution from the acid which may have a small but measurable impact on low-level readings. The Sievers M9^{e} (firmware version 1.06 and later) offers an automated acid reagent blank procedure that measures the actual organics contribution from the acid, and applies an offset, based on the selected flow rate, that subtracts out this contribution from the reported TOC values.

The amount of trace organics contributed by the acid can vary slightly from one acid cartridge to the next. Therefore, the reagent blank procedure needs to be performed each time a new acid cartridge is installed.