Water Technologies & Solutions
application note

best operational practices for seawater TOC analysis with Sievers* InnovOx Laboratory TOC Analyzer

introduction

The analysis of seawater samples (3.5-5% chloride) for Total Organic Carbon (TOC) presents a unique challenge due to high total dissolved solid content and oxidizer scavenging characteristics of chloride. When run on conventional wet chemistry systems, brine samples show extremely low recoveries due to chloride interference. In comparison, combustion systems show good recoveries of TOC in seawater samples, but are subject to increased maintenance cycles/costs, signal drift, and frequent recalibration. The Sievers* InnovOx Laboratory TOC analyzer uses the patented Super Critical Water Oxidation (SCWO) method that eliminates chloride interference. This reduces expensive and time-consuming analyzer maintenance, while delivering best in class analytical performance, making it the perfect choice for TOC analysis of seawater samples.

The following document outlines how to correctly set up and configure the Sievers InnovOx Lab to achieve optimal results when analyzing seawater samples.

operating mode

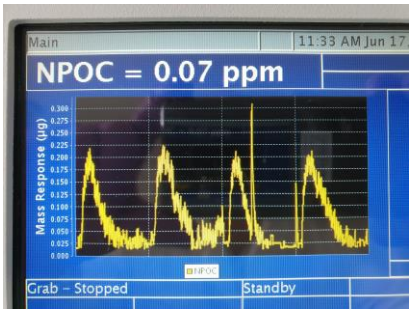
It is recommended that Non-Purgeable Organic Carbon (NPOC) mode be utilized over TOC mode for seawater analysis unless it is necessary to include purgeable/volatile organics in the measurement. In most seawater samples, purgeable/volatile organics are insignificant, and NPOC equates to TOC. Furthermore, NPOC mode is quicker and more accurate as results are not computed from two separate measurements (TOC = Total Carbon [TC] – Inorganic Carbon [IC]). Utilizing NPOC in place of TOC mode is common practice and is the standard operating mode of nearly all TOC analyzers on the market. TOC mode is typically only adopted when volatile compounds are present in a sample or if IC concentrations are of interest. If IC quantitation is required, it is recommended to perform a separate analysis in IC mode to obtain the most accurate results.

range and calibration

Seawater samples are expected to have lower TOC concentration, usually less than 1 ppm. Normally such samples would be run in the lowest Sievers InnovOx Lab range (0 to 100 ppm), however due to the challenging sample matrix, large variations in measurement may be observed if this range is used. For this reason, it is recommended that seawater samples be run in the 0 to 1,000 ppm range. The internal settings of the Sievers InnovOx Lab help compensate for matrix effects in the 0 to 1,000 ppm range better than in the 0 to 100 ppm range without a decrease in accuracy or precision. Therefore, it is best practice to use the 0 to 1,000 ppm range.

When using the 0 to 1,000 ppm range for low level sample analysis, it is not necessary to calibrate the analyzer to the top of the range. The calibration points used only need to cover the expected TOC concentration range of the samples. For example, if the highest expected results are around 1 ppm, the top standard of the calibration can be set to 5 ppm.

Before calibration, it is essential to flush the analyzer thoroughly. To do so, run high-quality deionized (DI) water (preferably 18MΩ-cm) until a stable carbon mass response of 0.45 µg or less is achieved (see figure).
During the flushing, pay attention only to the carbon mass response in the peak window, i.e., actual NPOC results should be disregarded. It may take several hours of continuous measurement to achieve this, depending on the instrument's condition and what samples had been analyzed before.



Acid: 3N HCl is recommended for all seawater analyses due to significant amounts of calcium and magnesium concentration typically seen in these samples. Chlorides from hydrochloric acid do not interfere with these compounds. If 6M H_3PO_4 is used, there is a high risk of forming insoluble phosphate salts of calcium and magnesium which can lead to destructive reactor clogging. For seawater analysis, the default acid addition of 5% is recommended.

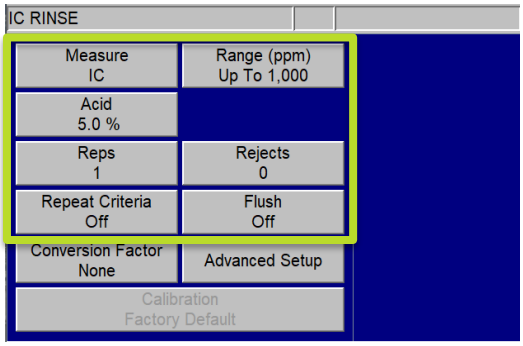
Oxidizer: 30% w/v sodium persulfate should be use for the oxidizing reagent. Do not use 15% w/v ammonium persulfate oxidizer from the M-series analyzers. At supercritical conditions, ammonium is oxidized to form nitrate, consuming some of the added oxidizer itself, thus reducing the overall oxidative potential of the reagent.

For seawater analysis, an oxidizer addition of 25% is recommended. Although the standard oxidizer setting for the 0 to 1,000 ppm range and higher is typically 15%, this is insufficient for seawater applications. During the heating phase, a portion of the chloride contents in the seawater is oxidized before the supercritical state is reached thus decreasing the strength of the oxidizer.

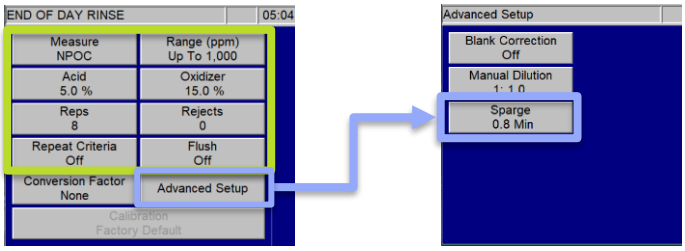
Insufficient oxidizer dosing or the use of outdated/depleted oxidizer can lead to a ruptured reactor tube, particularly if the analyzer is still equipped with the older style titanium reactor tube (Sievers InnovOx Lab before 2020). The reactor tube material used in the current Sievers InnovOx Lab, tantalum, mitigates this risk of rupture, however, insufficient oxidizer dosing will still lead to poor organics recovery.

Sparge time: Seawater can contain a significant amount of IC. The default IC sparge time of 0.8 min may be insufficient to remove the majority of IC present in the samples. As IC levels can be several times higher than the TOC level in seawater samples, any remaining IC may have a significant impact on the NPOC result. To address this, it is recommended that the IC sparge time be increased to 2.0 min. In addition to complete IC removal, the longer sparge time also provides better mixing of sample and reagents. The sparge time during calibration can be left at 0.8 min since only KHP/sucrose standards are analyzed.

Flushing: To help minimize sample carryover and prevent crystallization at gas/liquid interfaces, a DI water flush is recommended after every sample. The most efficient way to accomplish this is to program an IC measurement of a DI water sample. Program only 1 repetition.



At the end of a working day, the analyzer should be thoroughly flushed to clean/remove any sample remaining within the system. To perform this flush, use a 40mL vial filled with DI water and run the following rinse protocol:



Carrier gas supply: Most Sievers InnovOx Lab Analyzers are equipped with an internal air pump and an air filter to produce and provide CO_2-free carrier gas. This setup is designed to obtain accurate results for all ranges. If low-level TOC measurements are required, i.e. near the limit of quantitation of the analyzer, connecting the analyzer to a high-grade nitrogen gas source is recommended.

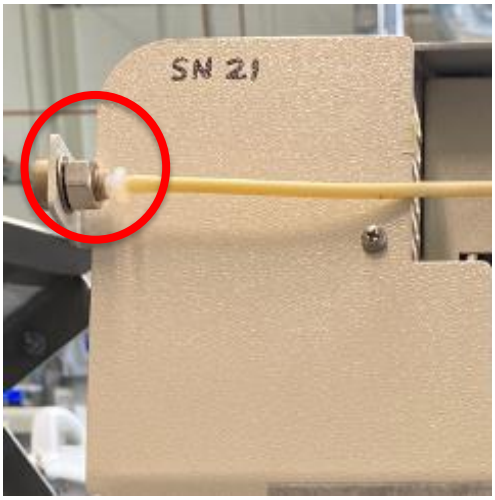
Sampling: For seawater analysis, an external sipper tube or the Sievers InnovOx Autosampler with optional rinse station are recommended for optimal sampling. The vial port should not be used as thorough cleaning is difficult to achieve, and sample residues can lead to corrosion.

If seawater samples are pre-acidified in the vial with HCl, replacement of the stainless-steel sample port and autosampler line connections with the plastic equivalent is highly recommended (see figure below).

The following parts are needed to complete this replacement:

HTF 68003-01 Bulkhead (PEEK)	**HTF 68115-01** 1/8" Tube OD Nut (PEEK)	**HTF 68114-01** 1/8" Tube OD Ferrule (PP)	**HTF 68041-01** 1/4" - 28 - 1/8" ID Barb Fitting (ETFE)
QTY 1	QTY 1	QTY 1	QTY 2
			

Note: These parts are not included in the standard accessory kit and must be purchased separately.



Analyzer Location & Waste Handling

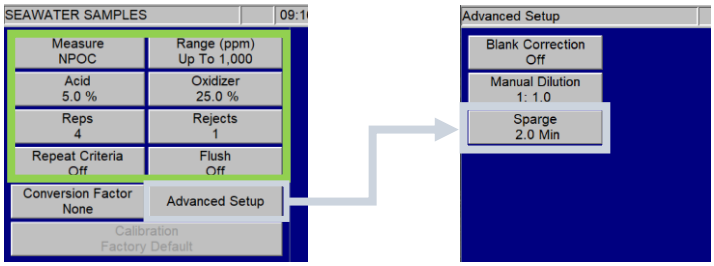
During seawater analysis, trace amounts of halogen gas can be created in both the waste container as well as the analyzer itself. To mitigate the risk of exposure it is recommended that the analyzer, reagents and waste container be placed in a fume hood. If a fume hood is not available, the analyzer should be placed on a work surface in a well-ventilated space with the waste container located below it on the floor. To assist in ventilation, it is also suggested that the fluidics cover of the analyzer be removed when running seawater samples.

To prevent the formation of halogen gas in the waste container, add a generous amount of solid sodium or potassium hydroxide pills waste solution prior to starting analysis. This will neutralize any unreacted sample/reagents and prevent the formation of halogen gas.

DO NOT USE bicarbonate or carbonate salts to neutralize the waste container as this will produce CO_2 gas and disperse any halogen gas created into the surrounding environment. Ensure that the waste container is emptied at the end of the working day and refilled with neutralizing agent before staring analysis the next day.

Method Summary for Seawater Analysis

Below are the recommended analytical method settings for seawater analysis with the Sievers InnovOx Laboratory TOC Analyzer.



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