

Abstract

As coastal areas are acutely vulnerable to climate variability and change, concerns over rising sea levels and land loss have increased due to implications for water resources. According to the US Geological Survey, sea levels have risen along most of the U.S. coast and around the world¹. The increase in sea levels has a direct impact on the salinity of both surface and ground waters through saltwater intrusion. This paper focuses on the use of a High Temperature Combustion analyzer to effectively analyze saltwater intrusion samples.

Introduction

The presence of the chloride ion in waters being analyzed for carbon presents problems when the method uses low temperature oxidation of carbon to carbon dioxide. Such instruments typically use persulfate ion with or without ultraviolet radiation. The chloride ion scavenges the free radicals that are the principal agents of oxidation, markedly reducing oxidation efficiency and prolonging oxidation time. The complexation of chlorine with the mercury (II) ion reduces this effect, but presents disposal problems.

Further problems arise as the chloride ion is oxidized to chlorine. Chlorine is produced in sufficient quantities, with the use of low temperature UV-persulfate oxidation, which may damage the instrument's detector. In High Temperature Combustion (HTC) analyzers the chloride ion does not affect the catalyzed reaction rate and chlorine gas is not formed in such a high concentration making it the method of choice for this application.

One advantage using low temperature carbon oxidation methods is that they are not affected by the interference caused by sodium and other cations. In contrast, when using HTC the sodium ion does have a devitrifying effect on the quartz glassware. Another problem analyzing brines using HTC is that sodium chloride impairs the catalyst oxidation efficiency. At high temperatures sodium chloride fuses onto the catalyst and is difficult to remove.

Detection

To detect and quantify CO₂ the Total Organic Carbon (TOC) Torch uses Static Pressure Concentration (SPC) detection technology in conjunction with NDIR detection. SPC technology is a process by which a single measurement of the CO₂ inside a pressurized NDIR detector is taken. The oxidation of the carbon is performed through catalytic high temperature combustion. The detector outlet is sealed capturing the CO₂ inside the detector to a predetermined pressure set-point. Once the pressure setting has been

achieved a single CO₂ measurement is taken. The amount of CO₂ detected correlates to the amount of carbon in the sample ².

Instrument Conditions

The method parameters for analysis of ground water samples are shown below in Table 1. The use of a 0.5mL sample volume is ideal for ground water sample analysis, providing ample sample carbon mass to be deposited onto the detector and sample volume for multiple replicates.

A 2.0mL Water Chase Volume is used to flush the sample pathway after the injection of samples containing particulates and those with salts

General Parameter	Value
Sample Volume	0.5mL
Water Chase Volume	2.0mL
Dilution	1:1
Number Of Injection Line Rinses	1
Injection Line Rinse	On
Injection Line Rinses Volume	0.5mL
Acid Volume	1.0mL
IC Sparge Flow	300mL/min
Carrier Gas Delay Time	0.0 min
IC Sparge Time	1.0 min
Detector Sweep Flow	500mL/min
Furnace Sweep Time	1.0 min
System Flow	400mL/min

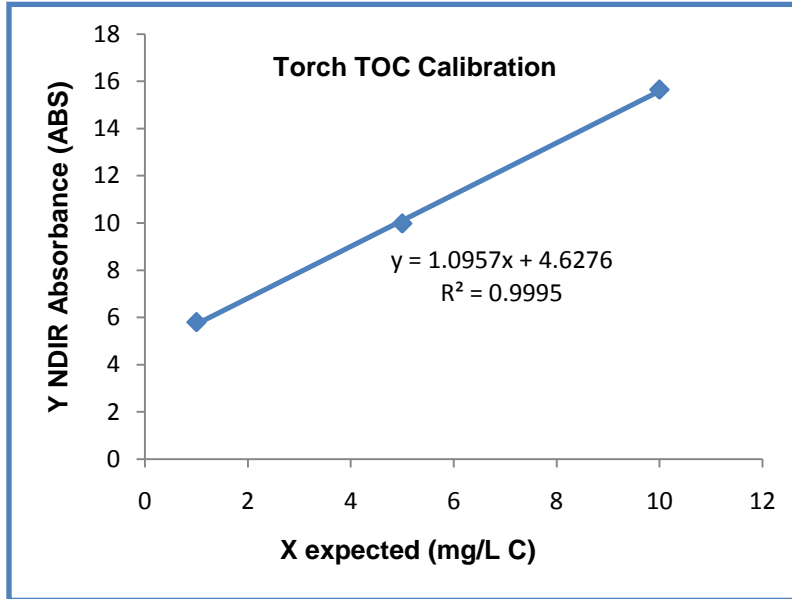
Table 1: The method parameters for analysis of ground water samples

Advanced Parameter	Value
Sparge IN Vial Enable	Off
Needle Rinse Volume	2.5mL
Vial Prime Volume	2.0mL
IC Sample Prime Volume	2.0 L
Baseline Stabilize Time	0.50 min
Detector Pressure Flow	175mL/min
Syringe Speed Waste	8
Syringe Speed Acid	7
Syringe Speed DI Water	7
NDIR Pressurization	20 psig
Syringe Speed Sample Dispense	7
Syringe Speed Sample Aspirate	7
Syringe Speed IC Dispense	7
Syringe Speed IC Aspirate	5
NDIR Pressure Stabilize	0.60 min
Syringe Speed Furnace Dispense	3
Syringe Speed Furnace Aspirate	5
Furnace Temperature	680°C

Calibration

A calibration curve was generated by auto-dilution from a 10 mg/L carbon (C) potassium hydrogen phthalate (KHP) working source standard with standard points of 1.0, 5.0, and 10mg/L C. Each calibration point was analyzed in triplicate. (Figure 1)

Figure 1: Linear Calibration data generated on the Torch TOC Analyzer (ABS vs. mg/L C)



Results & Discussion

Sample	TOC Value (mg/L C)	TOC less SW TOC	TOC After 30 0.5mL SW Injections
DI water	0.017 ± 0.029		
DI / 5 ppm C	4.95 ± 0.041		
Seawater (SW)	2.13 ± 0.131		
SW + 1 ppm C/KHP	3.23 ± 0.213	1.10	1.33
SW + 5 ppm C/KHP	7.14 ± 0.098	5.01	5.40
SW + 10 ppm C/KHP	11.23 ± 0.062	9.10	9.73
DI / 5 ppm C	5.12 ± 0.205		

Table 2: Seawater Analysis

The samples used for this poster were drawn from an eastern coastal sound of the Atlantic Ocean, which has a salinity of 3.2% – 3.5%³. All analyses were performed in the TOC mode where acid is added to the sample followed by sparging to remove inorganic carbon. Since seawater contains high amounts of inorganic carbon as compared to the organic carbon, increased amounts of acid, IC sparge flow and IC sparge time were used.

The sample volume of 0.5mL and 2.0mL water chase volume were used to ensure enough sample mass reached the detector and to lessen the amount of salt build up within the sample pathway. The normal detector pressure settings of 45psig – 60psig were lowered to 20psig in order to lessen the effects of the salt on the combustion tube. Normal pressure settings can be used with samples containing lower concentrations of salt or lower injection volumes. A furnace temperature of 680°C is standard for samples containing salts.

The TOC of the seawater measured 2.13mg/L C ± 0.131. The TOC value of the seawater was an average of twenty replicate analyses. Subtracting the seawater value from the spiked seawaters yielded, 1.10mg/L C, 5.01mg/L C and 9.10mg/L C. The TOC values in Table 2 were not evaluated for accuracy but for the possible changes in TOC response to the standards after a large amount of salt has been injected onto the catalyst. A series of 100 injections of 0.5 mL water and KHP aliquots were deposited onto the catalyst followed by ten samples of 0.5mL seawater aliquots analyzed in triplicate with alternating reagent water vials interspersed among them. The deposition of salts onto the catalyst will eventually cause a reduction in the response to organics and erroneous sample results⁴.

The Torch TOC analyzer has been designed for easy sample analysis. The combustion tube is housed in a furnace that permits effortless access even during sample analysis. The halogen scrubber and other routine maintenance items can be easily reached through front or side access panels. A shorter, thicker furnace injection needle was incorporated specifically to withstand the harsh conditions of salinity and high temperature. The Torch TOC analyzer is well suited for the rigors of salt water analysis.

References

1. US Geological Survey, <http://pubs.usgs.gov/fs/fs095-02/fs095-02.html>, February 24, 2011
2. TOC Torch Manual
3. Center for Environmental Sciences and Engineering, University of Connecticut
4. Booth, R.A, "Measuring Carbon in Salty Waters" Application note, Tekmar, Mason, OH