

## Análisis del TOC en agua de mar mediante un Analizador basado en combustión de alta temperatura y detección bajo presión estática.

### Aplicación 015

#### Resumen

La determinación del parámetro TOC en agua de mar puede resultar costoso y difícil. Se precisa por ello métodos de análisis más productivos y eficientes en esta matriz. El efecto que la matriz puede tener en los analizadores de TOC puede significar un rápido deterioro del fungible con la consecuencia de los costes en mantenimiento y reparación. La presente aplicación se ha desarrollado para maximizar la productividad frente al mantenimiento.

#### Introduction

The concentration of organic carbon in seawater is of considerable interest. Teledyne Tekmar's high temperature TOC analyzer, the Torch, has been designed for straight forward analysis of such waters, with special features to avoid some of the problems associated with saltwater samples.

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 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 to an intolerable extent. Further, the chloride ion is oxidized to chlorine, which can damage the instrument's detector. Therefore, the low temperature UV-persulfate oxidation TOC analyzers are not advised for these saltwater applications. In the Torch high temperature combustion analyzer chloride ions do not affect the reaction rate and chlorine gas is not formed in such a high concentration, which makes it ideal for this application.

Sodium and other cations can interfere with low temperature oxidations. Also, sodium ion has a devitrifying effect on quartz glassware, which worsens with increasing temperature. Sodium chloride also fuses onto catalyst at high temperatures, impairing oxidation efficiency, and is difficult to remove. These observations were also made on this set of analyses. However, using a different catalyst these effects were reduced allowing for acceptable analysis employing a slightly modified version of the standard TOC



drinking water method. The Torch was set up using 8.5g of a special catalyst (part number: 511-914). For best results, fresh catalyst should be conditioned by running 10 saltwater samples at three reps each

Torch Saltwater Analysis Apps note.docx; 10-Jan-12

prior to running the calibration curve. The method was found to allow for 75 to 100 samples of seawater to be run at three replicates each without performing maintenance.

To detect and quantify CO<sub>2</sub> the Torch uses static pressure concentration (SPC) detection technology in conjunction with non-dispersive infrared (NDIR) detection. SPC technology is a process by which a single measurement of the CO<sub>2</sub> 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 CO<sub>2</sub> inside the detector to a predetermined pressure set-point. Once the pressure setting has been achieved, a single CO<sub>2</sub> measurement is taken. The amount of CO<sub>2</sub> detected correlates to the amount of carbon in the sample<sup>1</sup>.

### **Instrument Conditions**

The method parameters used for analysis of saltwater samples are that of the standard drinking water method with one modification: The default sample volume was changed from 0.5ml to 0.3ml. A 0.3mL sample volume is ideal for saltwater sample analysis, providing ample carbon mass to be deposited onto the catalyst and a small volume allowing for multiple replicates. The default 1.0mL water chase volume is used to flush the sample pathway after the injection to clean it of particulates and salts. The following is the exact method parameters used in this set of analyses:

<b>Methods</b>			
<b>Name: TOC Drinking Water (TOC)</b>			
Version:	8	Operator:	Torch (Torch)
Ver Creation:	2011/09/19 08:25		
Comment:			
Parameter	Value	Advanced Parameter	Value
SampleVolume	0.3mL	SpargelInVialEnable	Off Optional sparge kit must be installed
WaterChaseVolume	1.00mL	NeedleRinseVolume	2.5mL
Dilution	1:1	VialPrimeVolume	2.0mL
NumberOfInjectionLineRinses	1	ICSamplePrimeVolume	2.0mL
InjectionLineRinse	On		

		BaselineStabilizeTime	0.25 min
InjectionLineRinseVolume	0.50mL	DetectorPressureFlow	175mL/min
AcidVolume	1.0mL	SyringeSpeedWaste	10
ICSpurgeFlow	300mL/min	SyringeSpeedAcid	7
CarrierGasDelayTime	0.40 min	SyringeSpeedDIWater	7
ICSpurgeTime	1.00 min	NDIRPressurization	50psig
DetectorSweepFlow	500mL/min		
FurnaceSweepTime	1.00 min	SyringeSpeedSampleDispense	7
SystemFlow	200mL/min	SyringeSpeedSampleAspirate	7
		SyringeSpeedICDispense	7
		SyringeSpeedICAspirate	5
		NDIRPressureStabilize	0.60 min
		SyringeSpeedFurnaceDispense	3
		SyringeSpeedFurnaceAspirate	5
		FurnaceTemp	750°C

Table 1: Method Parameters

### **Calibration**

A calibration curve was generated by auto-dilution from a 50mg/L carbon (C) potassium hydrogen phthalate (KHP) stock standard with calibration points of 1.0, 5.0, 10, 25, and 50mg/L C. Each calibration point was analyzed in triplicate with the calibration data found in figure 1.

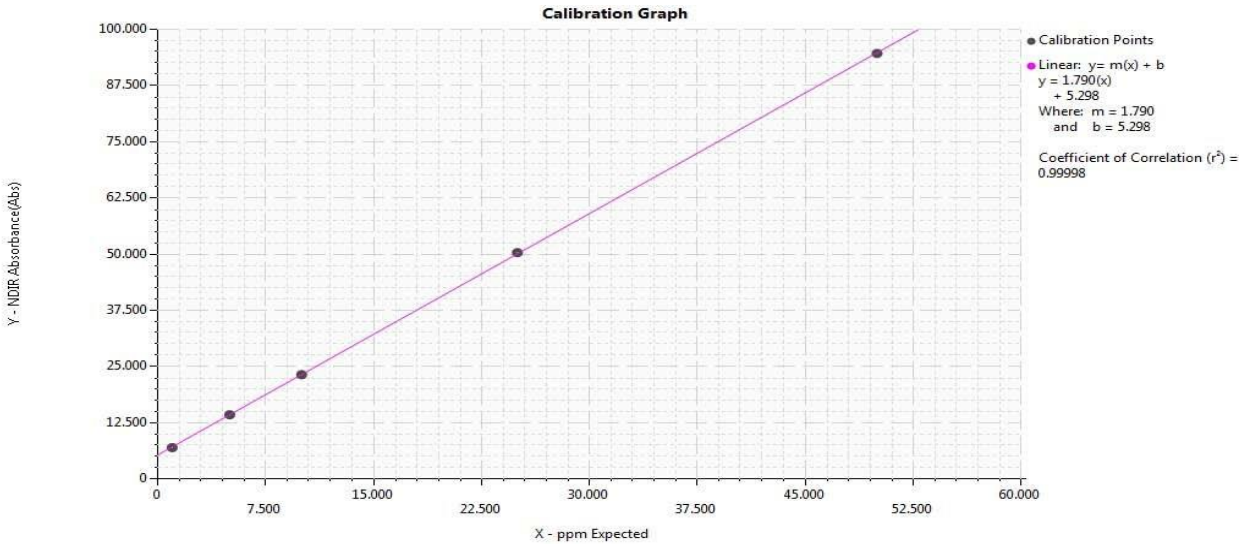


Figure 1: Linear calibration data generated on the Torch TOC analyzer (ABS vs. mg/L C),  $r^2 = 0.99975$

## Results & Discussion

Samples used for this application were drawn from Myrtle Beach, SC which has a salinity of about 3.5%<sup>2</sup>. All analyses were performed in the TOC mode, where acid is added to the sample, followed by purging to remove inorganic carbon.

The sample volume of 0.3mL and water chase volume of 1.0mL were used to ensure adequate sample mass reached the detector and to lessen the amount of salt build up within the sample pathway. The normal detector pressure setting of 50psig and a furnace temperature of 750°C was employed for the samples containing salts.

The following table shows the results obtained after analyzing 107 Myrtle Beach seawater samples at three reps each with a calibration check performed after each set of five samples:

Sample ID	Number of samples	TOC value (mean) (mg/L C)	Mean %RSD
Myrtle Beach Sea Water	107	2.0123	8.7531
10ppm KHP Cal. Check	22	10.294	1.6031

Table 2: Analysis Results

The %RSD for the sample is elevated due to the low concentration of organic carbon and matrix effects from the seawater samples.

Seawater samples were spiked with KHP at 1ppm, 5ppm, and 10ppm. The results obtained are as follows:

Sample	TOC Value (mg/L C)	TOC less SW TOC
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Seawater (SW)	2.8725	
SW + 1 ppm C/KHP	4.0370	1.1645
SW + 5 ppm C/KHP	7.8159	4.9434
SW + 10 ppm C/KHP	12.3731	9.5006

The TOC of the seawater measured 2.87mg/L C. Subtracting the seawater value from the spiked seawaters yielded, 1.16mg/L C, 4.94mg/L C and 9.50mg/L C. The deposition of salts onto the catalyst will eventually cause a reduction in the response to organics and erroneous sample results<sup>3</sup>. Once this occurs the combustion tube can be cooled, rinsed with DI water while still fully packed and dried in a 150°C oven for one hour. When properly maintained, the life of the combustion tube will be prolonged.

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. The Torch TOC analyzer is well suited for the rigors of saltwater analysis.

### **References**

1. TOC Torch Manual
2. Rhode Island Sea Grant Fact Sheet <http://seagrant.gso.uri.edu/factsheets/salt.html>
3. Booth, R.A, "Measuring Carbon in Salty Waters" Application note, Tekmar, Mason, OH