

Application Note

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Introduction

As Standard Methods 5310 for Total Organic Carbon (TOC) Analysis states:

“Measurement of TOC is of vital importance to the operation of water treatment and waste treatment plants. Drinking water TOCs range from less than 100µg/L to more than 25,000 µg/L. Wastewater may contain very high levels of organic compounds (TOC > 100 mg/L). Some of these applications may include waters with substantial ionic impurities as well as organic matter....

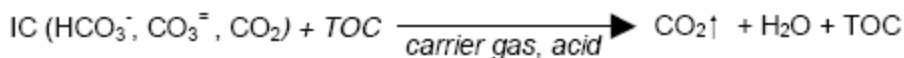
In most water samples, the inorganic carbon fraction is many times greater than the TOC fraction. Eliminating or compensating for inorganic carbon interferences requires determinations of both TC and inorganic carbon to measure TOC. Inorganic carbon interference can be eliminated by acidifying samples to pH 2 or less to convert inorganic carbon species to CO₂. Subsequent purging of the sample with a purified gas or vacuum degassing removes the CO₂ by volatilization. Sample purging also removes purgeable organic carbon so that the organic carbon measurement made after eliminating inorganic carbon interferences is actually a non-purgeable organic carbon determination: determine purgeable organic carbon to measure TOC. In many surface and ground waters the purgeable organic carbon contribution to TOC is negligible. Therefore, in practice, the non-purgeable organic carbon determination is substituted for TOC.” (1)

One potential problematic sample regarding TOC analysis is where the inorganic carbon (IC) is at a significantly high in concentration compared to the TOC value. If the IC is not removed fully by a TOC analyzer with normal operations, a false positive result may occur. The experimental design in this study was to simulate the potentially high levels of inorganic carbon in groundwater samples (as carbonate). As such, TOC standards ranging from ~2.0 – 100mg/L (as carbon) were prepared and spiked with varying levels of IC from ~2.0 – 400mg/L (as carbon). The TOC standards were prepared using potassium acid phthalate (KHC₈H₄O₄ or “KHP”), and the IC standards using sodium bicarbonate (NaHCO₃). Reference to “TOC” indicates carbon from KHP, and reference to “IC” indicates carbon from sodium bicarbonate. The intent was to quantify accurately TOC levels in the presence of the high levels of IC, detail any observable IC interference, and determine ranges of IC for which accurate TOC recovery could be expected. Particular attention was paid to the sequence of samples so that observances could be made in reference to calibration stability, instrument linearity, and the presence, if any, of sample carryover issues.

Instrumentation

A Teledyne Tekmar Fusion TOC Analyzer was used for this analysis. Results and findings obtained are presented in this paper. The Fusion TOC Analyzer uses an Ultraviolet (UV) persulfate oxidation process an overview of this process is shown in Figure 1. ⁽²⁾

Step 1: IC Removal



Step 2: TOC Oxidation and Detection

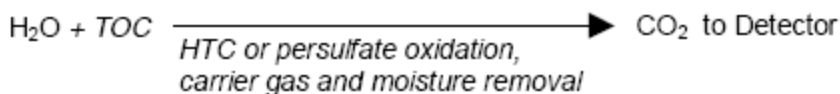


Figure 1: Two Step TOC Analysis Process

Method Parameters

Using a Tekmar Fusion TOC Analyzer, a common method was developed to accommodate all samples in the study without modification. It was expected that, for all TOC and IC ranges in question, the reagent volumes and sample sparge times would allow for accurate recoveries of TOC. Removing IC is a function of pH, as shown in Figure 2. Higher volumes of acid are required to liberate IC where high recovery levels of IC are expected. A volume of 3.0mL of acid, along with an increase in sparge time from 1 minute to 1.5 minutes, was used in order to liberate as much of the dissolved CO₂ as possible. It was expected that for all TOC and IC ranges in question, the reagent volumes and sample sparge times would eliminate interference from carbonate salts and allow for accurate recoveries of TOC. The optimal method parameters are provided in Table 1.

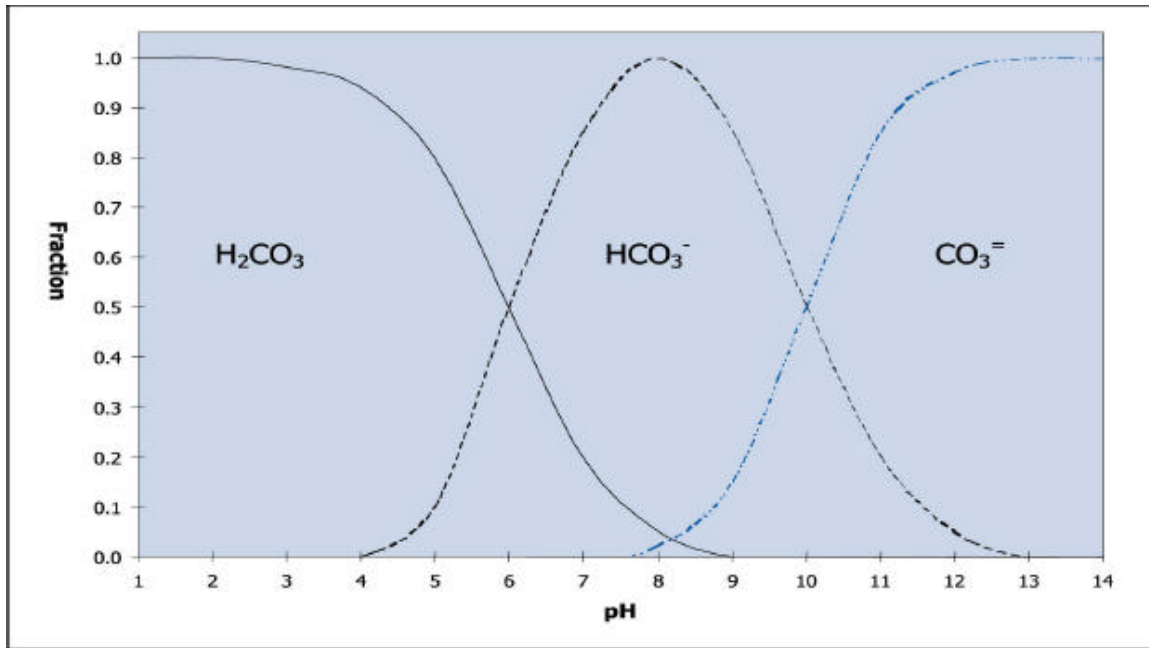


Figure 2: CO₂ Distribution in Water versus pH

Parameter	Value	Advanced Parameter	Value
Sample Volume	4.0 mL	Needle Rinse Volume	5.0 ml
Dilution	1:1	Vial Prime Volume	2.0 ml
Acid Volume	3.0 ml	IC Sample Prime Volume	2.0 ml
Reagent Volume	1.0 ml	IC Sparge Rinse Volume	5.0 ml
UV Reactor Prerinse	On	Baseline Stabilize Time	0.70 min
UV Reactor Prerinse Volume	5.0	Detector Pressure Flow	300 ml/min
Number Of UV Reactor Prerinses	1	Syringe Speed Waste	10
IC Sparge Time	1.50 min	Syringe Speed Acid	7
Detector Sweep Flow	500 ml/min	Syringe Speed Reagent	7
Pre-Sparge Time	0.00 min	Syringe Speed DI Water	7
System Flow	200 ml/min	NDIR Pressurization	50 psig

Table 1: Fusion TOC Analyzer User Adjustable Method Parameters

Syringe Speed Sample Dispense	7
Syringe Speed Sample Aspirate	4
Syringe Speed UV Dispense	7
Syringe Speed UV Aspirate	5
Syringe Speed IC Dispense	7
Syringe Speed IC Aspirate	5
NDIR Pressure Stabilize	0.50 min
Sample Mixing	Off
Sample Mixing Cycles	1
Sample Mixing Volume	10.0
Low Level Filter NDIR	Off

Calibration Curve

The calibration curve was performed with the intention of being able to utilize one calibration range for the analysis of all samples in question. A multipoint curve was obtained as follows (Table 2, Fig 3):

Sample ID	Y Raw Value	X Expected
DI Water	1.2700	0.0000
DI Water	1.0867	0.0000
1.000 mg/L	27.6267	1.0000
5.000 mg/L	142.6267	5.0000
20.000 mg/L	561.0233	20.0000

Table 2: TOC Calibration Data from the Tekmar Fusion TOC Analyzer

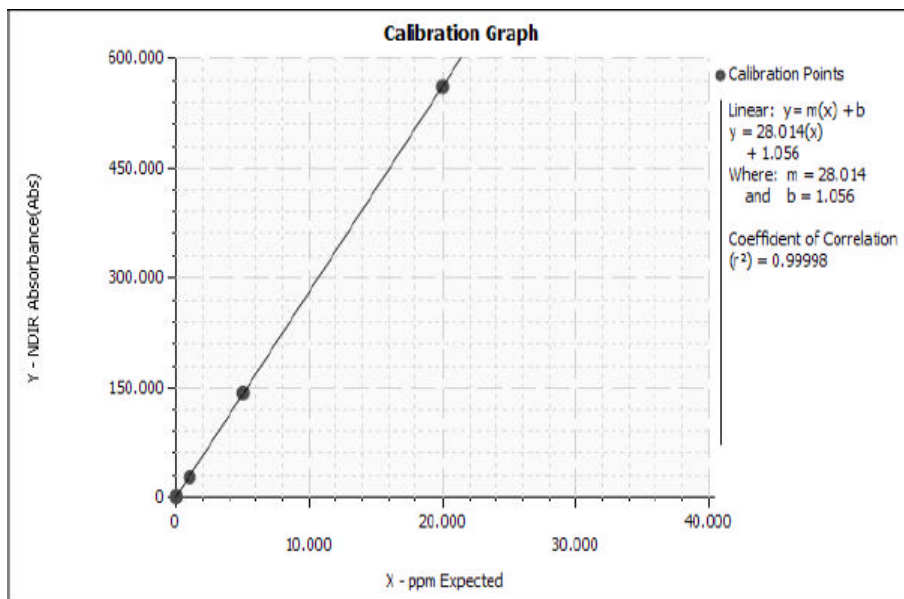


Figure 3: TOC Calibration Curve from the Tekmar Fusion TOC Analyzer

Preparation of Stock Solutions

Potassium Hydrogen Phthalate (KHP) ($\text{KHC}_8\text{H}_4\text{O}_4$)

All KHP solutions were diluted from a certified 1000mg/L C KHP standard.

Sodium Bicarbonate (NaHCO_3)

$\text{NaHCO}_3 = 84.00687 \text{ g/mol}$

Carbon = 12.01 g/mol

$$= 12.01/84.00687 = 14.30 \% \text{ C}$$

4000 mg/L stock solution

$$wt \text{ of } \text{NaHCO}_3 = \frac{4000 \text{ ppm} \cdot 1.0 \text{ L}}{0.1430} \cdot \frac{1 \text{ g}}{1000 \text{ mg}} = 27.9720 \text{ g}$$

Actual weight = 27.9797 g

Expected [C] = 4001.1 mg/L

Sample	TOC (mg/L)	IC (mg/L)
1	1	0
2	100	0
3	200	0
4	2	40
5	2	100
6	2	200
7	2	2
8	10	10
9	25	25
10	50	50
11	100	100

Table 3: Sample Overview *

*Stock solutions were diluted appropriately to make the following sample concentrations:

- Sample 1: Manual dilution (1:1000) from the 1000mg/L C KHP standard
- Sample 2: Instrument Auto-dilution method from the 200mg/L C KHP solution
- Sample 3: Manual dilution (1:20) was from the 1000mg/L C KHP standard.
- Samples 4 – 6: Manual dilutions were created separately by diluting from the 1000mg/L C KHP standard and the 4000mg/L NaHCO_3 IC stock standard.
- Samples 7 – 10: Prepared and analyzed via an instrument auto-dilution method using sample 11 with the Fusion TOC Analyzer.
- Sample 11: Manual dilution of the 1000mg/L C KHP and 4000mg/L NaHCO_3 standards

Results and Discussion

Referring to Table 3, the first set of samples was intended to demonstrate the general instrument accuracy, precision, and linearity. The second set was intended to demonstrate the ability to recover accurately 2.0mg/L C TOC in the presence of increasing levels of IC. The third set is intended to demonstrate the ability to recover

accurately TOC in the presence of increasing, but equivalent levels of IC. The samples cover the extremes of analysis in the presence of IC and provide a sufficient picture of the performance of the Fusion TOC Analyzer's capabilities under similar situations.

The calibration, depicted in Figure 4, demonstrates the exceptional linearity of the method chosen for these samples. The Fusion TOC Analyzer demonstrates excellent accuracy and linearity as well as its ability to remove excessive amounts of IC (Table 4). Percent errors ranging from 0.23 – 6.11 are reasonable when considering all the possible sources of error, especially sample preparation and handling. Instrument linearity over the range of TOC from 1 – 200mg/L was excellent, with a curve slope of approximately 1 and a y-intercept in the range of DI water blanks (Fig 4). The r^2 value of 0.9986 confirms that the use of our calibration curve is appropriate for the TOC concentrations of interest in this study. Carryover was not observed between samples of higher and lower concentrations. Perhaps the most important note is that all of samples were analyzed using a single calibration curve. Percent error could likely be decreased substantially by using two methods/calibration curves and applied to two TOC ranges (low and high).

Sample	Actual IC (mg/L)	Actual TOC (mg/L)	Measured TOC (mg/L)	Accuracy (% Error)
1	0	1	1.03	3.31 %
2	0	100	102.51	2.51 %
3	0	200	192.50	3.75 %
4	40	2	2.01	0.54 %
5	100	2	2.02	1.23 %
6	200	2	2.12	6.11 %
7	2	2	2.05	2.53 %
8	10	10	9.95	0.48 %
9	25	25	25.88	3.51 %
10	50	50	50.11	0.23 %
11	100	100	101.18	1.18 %

Table 4: Summary of TOC Results at various concentrations with varying amounts of IC interference

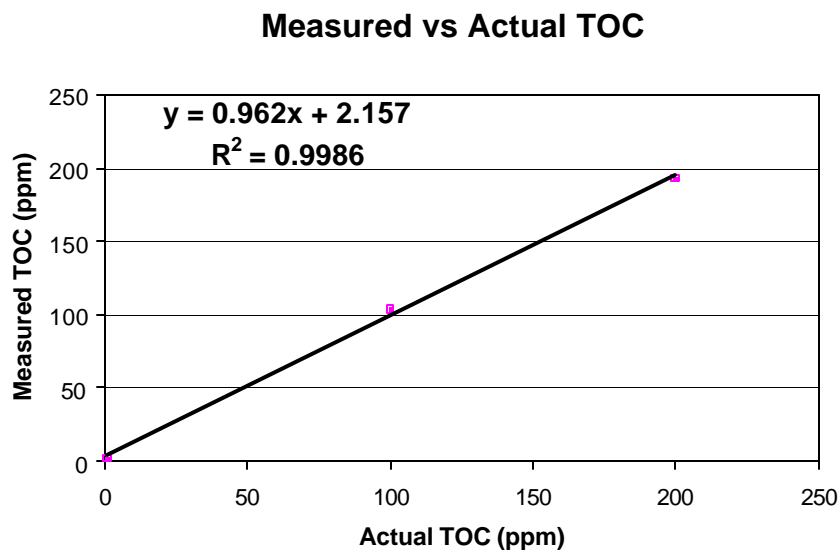


Figure 4: Performance Linearity comparing Measured to Actual TOC Concentration

References

1. *Standard Methods for the Examination of Water and Wastewater*, ed. A.D.Eaton, L.S. Clesceri and A.E.Greenberg., APHA/AWWA/WEF, Washington, DC, 19th edn. Method 5310.
2. Fusion User Manual, Teledyne Tekmar pp 1-5 – 1-7