Total Organic Carbon (TOC) FUNdamentals

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Agenda

- TOC Basics
- Brief Overview of TOC Techniques
- TOC by NDIR Analysis Process
Basics of TOC
Purpose of TOC: Indirect Measurement of Water Purity or Cleanliness

- **Drinking water**
  - Tap water
  - Bottled water

- **Pharmaceutical**
  - Clean-in-place validation (batch processing)
  - Water for injections
  - Purified water

- **Other**
  - Brewing or food applications to prevent off tastes
  - Semiconductor manufacturing
Total Organic Carbon vs. Total Carbon

Total Organic Carbon (TOC)

Non-Purgeable Organic Carbon

Sparging Removes POC<1%

Total Carbon (TC)

Inorganic Carbon (IC)

Acid and Sparging removes IC

TOC = NPOC
Importance of TOC and Public Safety for Drinking Water

After collection of raw water:
- Starting purity to benchmark

After filtration but before disinfectant process:
- If TOC is high, it will form too many THMs and will need to filter again

After Disinfectant process:
- Measures effectiveness of purification process and sign of water cleanliness to report

Trihalomethanes (formed from the disinfectant process) are known to be carcinogenic.
Why choose TOC over other techniques for contamination readings?

<table>
<thead>
<tr>
<th>HPLC, GC, GC/MS:</th>
<th>TOC</th>
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</thead>
<tbody>
<tr>
<td>■ Expensive</td>
<td>■ Inexpensive</td>
</tr>
<tr>
<td>■ Highly technical</td>
<td>■ Ease of operation</td>
</tr>
<tr>
<td>■ Long method development process</td>
<td>■ Little to no method development</td>
</tr>
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<td>■ Selective</td>
<td>■ “Catch all”</td>
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HPLC, GC, GC/MS: 

- Expensive
- Highly technical
- Long method development process
- Selective
“Catch All” Includes in One Measurement…

Cleaning Agents → Bacteria → Solvents

Pollutants → Fertilizers → Pharmaceuticals

Pesticides → Organic matter (leaves, grass, crops, etc.) → More
Difference Between Organic Carbon and Inorganic Carbon

Organic Carbon: Carbon must be bonded to a hydrogen
Game: Organic or Inorganic carbon?

**Sodium Bicarbonate**
(Carbon bonded to Oxygen and Sodium)

**Inorganic**

**Dietary Fiber**
(Carbon bonded to carbon, hydrogen, oxygen, and nitrogen)

**Organic**
TOC Methods per EPA

- EPA 415.1-415.3: “Determination of Total Organic Carbon and Specific UV Absorbance at 254 nm in Source Water and Drinking Water”
- EPA 5310C: “For drinking waters in particular, organic compounds may react with disinfectants to produce potentially toxic and carcinogenic compounds”
TOC Techniques
<table>
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<tr>
<th>Type of Technique</th>
<th>UV/Persulfate - NDIR</th>
<th>Direct Conductivity</th>
<th>Membrane Conductivity</th>
<th>Catalytic Combustion - NDIR</th>
<th>High Temperature Combustion - NDIR</th>
<th>Colorimeter</th>
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<tr>
<td>How it works</td>
<td>UV Persulfate (UVP) system is where an aliquot of sparged sample is transferred to a UV reactor where the oxidation power comes from a combination of chemical oxidizer, usually sodium persulfate, and UV light to oxidize the specific carbon component in the sample into CO2 gas. This gas is swept through a detector that uses traditional NDIR technology. In this technique, the adsorption of the infrared light is measured over time as the CO2 is swept through the detector. The resulting measurement correlates to a peak, which can be integrated and correlated to a concentration.</td>
<td>Conductivity method measures the conductivity of the sample before and after oxidation where the difference yields the amount of TOC. The sample, in the oxidation phase, forms dissolved CO2 which acts as a weak acid which strengthens the conductivity of the sample which is propionate to the amount of TOC.</td>
<td>The use of membranes was used to improve the accuracy of conductivity. It employs the use of hydrophobic gas permeation membrane which allows for greater discrimination for dissolved CO2 over other chemical compounds.</td>
<td>Catalytic Combustion system is where the sample is injected into a catalyst packed tube. The catalyst tube is enclosed in a furnace which heats to 680˚C - 1000˚C. The combination of temperature, an oxygen rich environment from the carrier gas (generally Ultra Zero Air or Oxygen), and catalyst is used to oxidize the carbon in the sample to CO2. The CO2 is then swept to the Non-Dispersive, Infrared (NDIR) detector. At the CO2 absorption wavelength, 4.26um, the intensity of detected light is reduced in proportion to the concentration of CO2 in the optical path. The light intensity measured at the non-absorbing wavelength serves as a baseline for comparison. The degree of light absorption in the gas, indicated by the ratio of these two signals, is proportional to the gas concentration.</td>
<td>High Temperature Ceramic (HTC) system is where the sample is injected into a furnace up to 1800˚C with a stream of oxygen. There is no catalyst needed for this oxidation process since more heat is used. The CO2 is then swept to the Non-Dispersive, Infrared (NDIR) detector.</td>
<td>Colorimeter is built on digestion in a enclosed glass chamber. The carbon in the sample is oxidized to carbon dioxide by persulfate oxidation. The CO2 is then dispersed into a solution that is indicated which changes into carbonic acid. The color change is proportional to the concentration of carbon in the sample.</td>
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| Benefits          | • Great sensitivity, sub ppb level  
                   • Easy and quick sample pathway cleaning process  
                   • Accurate analytical results  
                   • Few interferences  
                   • Well documented method | • Great sensitivity  
                   • Provides a good system for online processing  
                   • Long –standing calibration | • Great sensitivity  
                   • Provides a good system for online processing  
                   • Long –standing calibration  
                   • Well documented method | • Robust and can handle a variety of sample matrixes: salts, particulates, oils, etc.  
                   • Handle large amounts of carbon  
                   • Solids Option  
                   • Large analytical range  
                   • Well documented method | • Robust and can handle a variety of sample matrixes: salts, particulates, oils, etc.  
                   • Handle large amounts of carbon  
                   • Solids Option  
                   • Large analytical range | • Inexpensive |
| Limitations       | • High level carbon samples >4000ppm  
                   • Particulates > 0.1mm  
                   • Salt > 0.5ppmC  
                   • UV lamps can fade overtime  
                   • More sample volume is needed for analysis  
                   • Must use nitrogen as a carrier gas | • Many molecules cause interference  
                   • Limited analytical range, cannot analyze > 50ppmC  
                   • Cannot handle salts, acids, particulates | • Membranes can clog and cleaning process takes hours  
                   • Amines can pass through membrane and give false high results  
                   • Ionic Contaminations  
                   • Limited analytical range, Cannot analyze > 50ppmC  
                   • Cannot handle Salts, acids, particulates | • Prone to leaks due to the heating and cooling of the furnace  
                   • Difficult to achieve quantifiable results < ~200ppb  
                   • Catalyst maintenance | • Prone to leaks due to the heating and cooling cycles of the furnace  
                   • Difficult to achieve quantifiable results <~2ppmC  
                   • New technology with limited competition and information | • Timely extraction process  
                   • Many interferences including but not limited to S, Cl, Mn, Ca, Mg, Cu, Fe  
                   • Limited analytical range ~0.3-20ppmC |
NDIR TOC Analysis
TOC Analysis Process

Sample → Acidification → Removes IC → Oxidation → CO₂ Detection → TOC Results
Acidification: IC Sparger

\[ \text{HCO}_3^- + \text{CO}_3^{2-} + \text{CO}_2 + \text{POC}-> \text{CO}_2 + \text{POC} \]

1.) Add Sample
2.) Add Acid

3.) Carrier gas moves through a porous frit on bottom to form bubbles

4.) CO\textsubscript{2} from IC is removed
Types of Oxidation

- **Acidification**: Removes IC

- **Oxidation**
  - CO$_2$ Detection

- **Combustion**
  - Furnace (heat)
  - Gas supply of oxygen
  - Catalyst

- **UV/Persulfate**
  - Sodium Persulfate
  - UV Light

**Sample**

**TOC Results**
Clean Up

Sample gas

Acidification → Removes IC → Oxidation → CO₂ Detection

CLEAN UP Sample gas Before detection

Remove moisture and halogens

TOC Results
TOC Analysis Process

- Acidification
- Removes IC
- Oxidation
- CO₂ Detection

Sample

TOC Results
CO$_2$ Detection: NDIR
Teledyne Tekmar - TOC Product Portfolio

Lotix
Oxidation: Combustion
Detector: NDIR

Torch
Oxidation: Combustion
Detector: NDIR

Fusion
Oxidation: UV/Persulfate
Detector: NDIR
# Fusion: EPA 415.3 Results

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Success</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Demonstration of Low System Background</td>
<td>$\leq 0.35 \text{ ppmOC}$</td>
<td>0.0680 ppmOC</td>
</tr>
<tr>
<td>Initial Instrument Calibration Verification</td>
<td>$\pm 20%$ of true value (2.0-3.0 ppmOC)</td>
<td>2.6363 ppmOC, 5.45% of true value</td>
</tr>
<tr>
<td>Initial OC Flow Injection Memory</td>
<td>$\leq 0.35 \text{ ppmOC}$</td>
<td>0.1276 ppmOC</td>
</tr>
<tr>
<td>Inorganic Carbon Removal Sparging Efficiency Test</td>
<td>$\leq 0.35 \text{ ppmOC}$</td>
<td>0.2450 ppmOC</td>
</tr>
<tr>
<td>Initial Demonstration of Accuracy (n=5)</td>
<td>$\pm 20%$ of true value (2.0-3.0 ppmOC)</td>
<td>2.6029 ppmOC, 5.17% of true value</td>
</tr>
<tr>
<td>Initial Demonstration of Precision (n=5)</td>
<td>$\leq 20% \text{ RSD}$</td>
<td>0.44% RSD</td>
</tr>
<tr>
<td>Organic Carbon Detection Limit Determination (n=7 over 3 days)</td>
<td>$&lt; 0.35 \text{ ppmOC}$</td>
<td>0.034 ppmOC</td>
</tr>
</tbody>
</table>
TOC Key Takeaways

TOC is a great “catch all” method to determine water cleanliness

Most states require TOC in drinking water quality report

TOC is important to public safety due to its ability to prevent THM formation which are known to be carcinogenic

TOC can be measured by a simple and quick oxidation of carbon followed by infrared detection
Questions?

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- https://www.facebook.com/pages/Teledyne-Tekmar/147905135273052
- @TeledyneTekmar
- https://www.linkedin.com/company/teledyne-tekmar
- http://blog.teledynetekmar.com/

Webinar coming up on Bottled Water with the Fusion May 22nd

Please feel free to email me at joy.osborne@teledyne.com

Feel free to stop by our booth