CEE 772: Instrumental Methods in Environmental Analysis

Lecture #8

Specialized Analyzers: Total Organic Carbon & Total Nitrogen
(Skoog, Chapt. 16C, 24D; pp.399-401, 632-636)

(Harris, Chapt. 16-6 & 17-4)
(pp.430, 457-461)

Literature on TOC

7. Water Research 34(14)3575  2000
What is TOC?

• **Total Organic Carbon**
• Organic contaminants (NOM’s, insecticides/herbicides, agricultural chemicals) – reach surface water via rainfall runoff
• Industrial organics due to spills
• Domestic/Industrial wastewater effluent

Fractionation & Nomenclature

![Fractionation Diagram]

- Total Carbon (TC)
  - Inorganic Carbon (IC)
    - Purgeable (Dissolved)
    - Non-Purgeable (Particulate)
  - Total Organic Carbon (TOC)
    - Purgeable Organic Carbon (POC)
    - Non-purgeable Organic Carbon (NPOC)
      - Particulate (PtOC)
      - Dissolved (DOC)
**TOC vs. TC & IC**

- **TOC** = Total Carbon (TC) – Inorganic Carbon (IC)
- **TOC** = all carbon atoms covalently bonded in organic molecules
- **TC** is a measure of all the carbon in the sample
- **IC** = carbonate, bicarbonate, and dissolved carbon dioxide
  - IC is often analyzed in liquid samples by acidifying with an inorganic acid to pH 2 or lower, then sparging for a few minutes with a stream of gas
- **POCs** (or VOC) = the fraction of TOC removed from an aqueous solution from gas stripping under specified conditions.
- **NPOC** = the fraction of TOC not removed by gas stripping
- **DOC** = the fraction of TOC that passes through a 0.45 μm-pore diameter filter
- **PtOC** (or “suspended org. carbon”) = the fraction of TOC retained by a 0.45 μm-pore diameter filter

**Distinguishing TOC from TIC**

- **Direct NVTOC measurement**
  - remove IC by acidification and purge
- **By difference: two channel**
  - Measure TC (high temp) and IC (low temp)
  - Subtract
- **By difference: gas & liquid**
  - Measure TC and PC (both high temp)
  - Subtract

- **Most common approach**
  - Can result in loss of OC due to precipitation at low pH
- **Used by old Beckman analyzers**
  - Separate channels
  - Two separate measurements
- **Some analyzers have a Purgeable carbon (PC) cycle**
  - Again requires 2 separate measurements
TOCs and Drinking Water

- Organic compounds may react with disinfectants to produce potentially toxic and carcinogenic compounds, or “disinfection by-products”
- Drinking water TOCs range from less than 100 µg/L to more than 25,000 µg/L
- Wastewater – TOC > 100 mg/L

Origins

- Humic substances (humic and fulvic acids)
  - Organic detritus modified by microbial degradation
  - lignin origin vs microbial
  - resistant to further biodegradation
  - “old” organics
- Non-humics & Structurally-defined groups
  - may be relatively “new”
  - includes many biochemicals and their immediate degradation products
  - generally more biodegradable
  - concentrations are highly variable with season
UV absorbance vs TOC: raw waters

Correlation Between TOC and UV absorbance for 53 samples of Grasse River Water (from Edzwald et al., 1985)

TOC in Large US WTPs

US Raw Drinking Waters

ICR Data
Methods of TOC Analysis

• High-Temperature Combustion Method
• Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method
• Wet-Oxidation Method (equipment for this method is no longer manufactured)

TOC Analyzer

• March 1963
• Required a Beckman L/B infrared analyzer
• Need to wait for development of a turnkey instrument (Beckman 915)
Great Recovery

- TOC

<table>
<thead>
<tr>
<th>Compound</th>
<th>Carbon, p.p.m.</th>
<th>Std. dev. (±)</th>
<th>Av. % recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Caled.</td>
<td>Max.</td>
<td>Min.</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>68.8</td>
<td>69.0</td>
<td>67.4</td>
</tr>
<tr>
<td>Phenol</td>
<td>76.6</td>
<td>77.2</td>
<td>76.5</td>
</tr>
<tr>
<td>Sucrose</td>
<td>104.8</td>
<td>105.1</td>
<td>104.3</td>
</tr>
<tr>
<td>Glycine</td>
<td>100.7</td>
<td>101.2</td>
<td>99.5</td>
</tr>
<tr>
<td>Pyridine</td>
<td>100.6</td>
<td>104.4</td>
<td>103.6</td>
</tr>
<tr>
<td>Urea</td>
<td>100.0</td>
<td>100.9</td>
<td>99.1</td>
</tr>
<tr>
<td>Sodium cyanide</td>
<td>122.5</td>
<td>122.1</td>
<td>119.5</td>
</tr>
<tr>
<td>Aetanolide</td>
<td>75.4</td>
<td>76.0</td>
<td>75.0</td>
</tr>
<tr>
<td>p-Nitroaniline</td>
<td>106.2</td>
<td>105.8</td>
<td>104.9</td>
</tr>
<tr>
<td>4-Aminoantipyrine</td>
<td>111.5</td>
<td>110.6</td>
<td>108.9</td>
</tr>
<tr>
<td>Sulfanilic acid</td>
<td>59.3</td>
<td>90.5</td>
<td>58.6</td>
</tr>
<tr>
<td>Diphenylamine sulfonate, 3H salt</td>
<td>87.8</td>
<td>87.0</td>
<td>85.8</td>
</tr>
<tr>
<td>dl-Methionine</td>
<td>105.0</td>
<td>102.7</td>
<td>101.8</td>
</tr>
<tr>
<td>2,4,6-Trichlorophenol</td>
<td>75.4</td>
<td>76.0</td>
<td>74.0</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>99.5</td>
<td>100.0</td>
<td>99.2</td>
</tr>
<tr>
<td>Acetic acid in 20% NaCl</td>
<td>100.0</td>
<td>101.0</td>
<td>99.0</td>
</tr>
<tr>
<td>Acetic acid in 20% CaCl₂</td>
<td>100.0</td>
<td>100.0</td>
<td>98.1</td>
</tr>
</tbody>
</table>

* All results based on 4 determinations. Calibrations made with standard solutions of acetic acid in water.

UMass TOC Instrumentation

- High Temperature Pyrolysis
  - Beckman Corp., Model 915 (the first!)
  - Shimadzu Model 4000 (308 Elab II)
  - Shimadzu Model 5000 (201 & 308 Elab II)

- UV-Persulfate
  - Dohrmann Model DC-80 (Marston 24)

- Wet Chemical Oxidation
  - OI Corp., Model 700 with persulfate digestion (Environmental Institute)
High-Temperature Combustion Method

- **Advantages:**
  - Oxidizes particulates and solids
  - Rapid
  - Relatively interference-free
- **Disadvantages**
  - Low sensitivity (min. detectable conc. = 1 mg C/L or less depending on instrument)
  - Highest maintenance (particularly in high temp. components)
  - Prone to lose CO₂ in stream condensation phase
  - Problem recovering certain aromatics
  - Low salt tolerance
  - Difficult to obtain reliable system blanks
  - Can accumulate nonvolatile residues in the analyzer

Pyrolysis TOC Unit

High temperature, in oxygen, with a cobalt catalyst
Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method

- **Advantages:**
  - High sensitivity (< 1 mg C/L samples)
  - Good recovery in most applications
  - Good precision
  - Low maintenance
  - Nonvolatile residuals are drained from the analyzer

- **Disadvantages:**
  - Potential interference with halide samples at CO₂ detection phase in oxygen-rich atmosphere

![UV-Persulfate TOC Unit](image)

\[
S_2O_8^{2-} \xrightarrow{hν} 2SO_4^{-} + e^{-}
\]
\[
H_2O \xrightarrow{hν} H^* + OH
\]
\[
SO_4^{2-} + H_2O \rightarrow SO_4^{2-} + H^* + OH
\]
Non-Dispersive Infrared Analysis (NDIR)

- All EPA approved methods for organic carbon analysis require NDIR method
- Measures infrared light absorbed by carbon dioxide as it passes through an absorption cell
- $\text{CO}_2$ Property $\rightarrow$ Absorbance $= 4.26 \, \mu\text{m} \, (\text{IR range})$
- TSI Monitor – $[\text{CO}_2]$ determined when the instrument is calibrated using pure nitrogen (0 ppm $\text{CO}_2$) and a known concentration of $\text{CO}_2$ such as 1000 or 5000 ppm

NDIR (con’t)

- “Nondispersive” – no monochromator and infrared sources are broadband emitters
- Detector cells are pressure-sensitive: affected only by wavelengths absorbed by $\text{CO}_2$
- Interference caused by gases that have overlapping infrared absorption bands – like water vapor
  - Therefore, water vapor removed by condensation before getting to the detector
Beer’s Law

- \( A = a \cdot b \cdot c \)
  - \( A \) = Absorbance
  - \( a \) = absorptivity coefficient
  - \( b \) = path length
  - \( c \) = analyte (CO₂) concentration

OR

- \( I = I_o e^{kp} \)
  - \( I \) = intensity of light striking the IR detector
  - \( I_o \) = measured signal with 0 ppm CO₂
  - \( k \) = a system dependant constant
  - \( P = [CO_2] \)

CO₂ Analyzer

- Non-dispersive Infrared Analyzer (seen above)
- Electrolytic Conductivity Detection (interference from other ionic species)
- Coulometric Titration
- Reduction to CH₄, then FID (flame ionization detection) – longer testing times
Instrument Specs.
Shimadzu 5000

- Analyte = TC, IC, TOC (TC-IC), NPOC
- Method – Combustion (680° C)/NDIR gas analysis
- Measuring Range = 4 ppb to 4000 ppb
- Avg. Analysis Time = 2 – 3 min. for both TC and IC
- Shimadzu ASI-5000 – Automatic Sample Injector
  - 78 vial or 16 vial turntables available
  - Rinsing between samples minimizes sample “carry-over”

Shimadzu 5000 TOC Analyzer (schematic)
- Schematic diagram showing the coupled Shimadzu TOC 5000A HTCO–Sievers NCD 255 nitrogen chemiluminescence detector, and associated hardware.

- Mitsubishi Unit
• Chemiluminescent detection

\[2 \text{NO} + 2 \text{O}_3 \rightarrow 2 \text{NO}_2^* + 2 \text{O}_2\]

\[\text{NO}_2^* \rightarrow \text{NO}_2 + h\]

• Rapid decay of the \(\text{NO}_2^*\) produces light in the 590-2,900 nanometer range. This light is detected and amplified by a photomultiplier tube.

Table 3. Recovery of N from commonly cited N compounds dissolved in ultrapure water using the coupled HTCO TOC–NCD method in our laboratory (recovery in relation to potassium phthalate/glycine standard), and literature results.
<table>
<thead>
<tr>
<th>Model</th>
<th>TOC-VCSH</th>
<th>TOC-VCSN</th>
<th>TOC-VCPS</th>
<th>TOC-VCPSN</th>
<th>TOC-VE</th>
<th>TOC-VWS</th>
<th>TOC-VWP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement method</td>
<td>680 degC combustion catalytic oxidation/NDIR method</td>
<td>wet oxidation/NDIR</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operation method</td>
<td>standalone</td>
<td>PC-controlled</td>
<td>standalone</td>
<td>PC-controlled</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Measured items</td>
<td>TC, IC, TOC, NPOC (optional POC, TN)</td>
<td>TC, IC, TOC, NPOC (optional TN)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Applicable samples</td>
<td>aqueous sample (optional solid/gas samples)</td>
<td>aqueous sample</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Measurement range (mg/L)</td>
<td>TC: 0 to 25000, IC: 0 to 30000</td>
<td>TC: 0 to 25000, IC: 0 to 30000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Detection limit</td>
<td>4μg/L</td>
<td>50μg/L</td>
<td>50μg/L</td>
<td>50μg/L</td>
<td>---</td>
<td>0.5μg/L</td>
<td></td>
</tr>
</tbody>
</table>
### Comparison of TOC levels

- **Sample 1** – Bridgeport Hydraulic Company (BHC) potable water
  - Private water supply company in Connecticut
- **Sample 2** – water taken from water fountain in Marcus Building on the UMass campus
- **Sample 3** – water taken from Campus Pond to simulate raw water sample
TOC Analytical Accuracy and QA

- Fukushima et al – November 1996
- Used Shimadzu 5000
- Believed the differential method was more user friendly than the purging method, but both gave good results

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TOC Analytical Accuracy and QA

- Kaplan – January 1992
- Compared Shimadzu 5000 to O.I. Model 700 (persulfate oxidation method)
- Determined that Pt-catalyzed persulfate oxidation at 100°C with an O.I. 700 underestimates DOC concentrations in freshwaters by ~5% when compared to the Shimadzu 5000, but considers that a “small source of error”.

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Comparison of methods

- From: Tekmar application document
- TOC Analysis of Difficult Compounds

### UV/Perisulfate Analysis

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>ppm</th>
<th>RSD %</th>
<th>Percent Recovery</th>
<th>RSD %</th>
<th>Percent Recovery</th>
<th>RSD %</th>
<th>Percent Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium Hydrogen Phthalate (KHP)</td>
<td>1.02</td>
<td>102.0%</td>
<td>1.27 %</td>
<td>99.4%</td>
<td>0.72 %</td>
<td>101.0%</td>
<td></td>
</tr>
<tr>
<td>1,4-Benzoquinone</td>
<td>1.07</td>
<td>99.0%</td>
<td>1.17 %</td>
<td>10.2%</td>
<td>0.70 %</td>
<td>99.3%</td>
<td></td>
</tr>
<tr>
<td>Citric Acid</td>
<td>0.60</td>
<td>93.0%</td>
<td>0.83 %</td>
<td>37.8%</td>
<td>1.41 %</td>
<td>91.5%</td>
<td></td>
</tr>
<tr>
<td>Isocitric Acid</td>
<td>0.62</td>
<td>103.0%</td>
<td>1.14 %</td>
<td>10.3%</td>
<td>2.36 %</td>
<td>90.2%</td>
<td></td>
</tr>
<tr>
<td>L-glutamate</td>
<td>0.62</td>
<td>104.0%</td>
<td>0.87 %</td>
<td>37.8%</td>
<td>2.54 %</td>
<td>101.0%</td>
<td></td>
</tr>
<tr>
<td>Na-Naphthalene-1-Sulfonate</td>
<td>0.55</td>
<td>96.0%</td>
<td>0.60 %</td>
<td>92.6%</td>
<td>1.50 %</td>
<td>95.8%</td>
<td></td>
</tr>
<tr>
<td>Triphenylphosphine</td>
<td>0.60</td>
<td>103.0%</td>
<td>0.82</td>
<td>95.2%</td>
<td>1.46</td>
<td>90.2%</td>
<td></td>
</tr>
<tr>
<td>Lignosulfonic Acid</td>
<td>0.72</td>
<td>96.0%</td>
<td>1.32 %</td>
<td>95.4%</td>
<td>2.62 %</td>
<td>96.2%</td>
<td></td>
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<tr>
<td>Terephthalic Acid</td>
<td>0.03</td>
<td>35.0%</td>
<td>0.43 %</td>
<td>35.0%</td>
<td>2.05 %</td>
<td>97.0%</td>
<td></td>
</tr>
</tbody>
</table>

### Combustion Analysis

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>ppm</th>
<th>RSD %</th>
<th>Percent Recovery</th>
<th>RSD %</th>
<th>Percent Recovery</th>
<th>RSD %</th>
<th>Percent Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium Hydrogen Phthalate (KHP)</td>
<td>2.05</td>
<td>102.0%</td>
<td>0.95 %</td>
<td>101.5%</td>
<td>2.03 %</td>
<td>99.4%</td>
<td></td>
</tr>
<tr>
<td>1,4-Benzoquinone</td>
<td>4.85</td>
<td>104.0%</td>
<td>5.79</td>
<td>98.0%</td>
<td>2.74 %</td>
<td>93.0%</td>
<td></td>
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<tr>
<td>Citric Acid</td>
<td>2.05</td>
<td>110.0%</td>
<td>1.41 %</td>
<td>101.0%</td>
<td>0.91 %</td>
<td>93.0%</td>
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<tr>
<td>Isocitric Acid</td>
<td>5.04</td>
<td>106.0%</td>
<td>2.75 %</td>
<td>95.9%</td>
<td>1.31 %</td>
<td>97.0%</td>
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<tr>
<td>L-glutamate</td>
<td>4.06</td>
<td>111.0%</td>
<td>0.77 %</td>
<td>95.6%</td>
<td>2.46 %</td>
<td>96.4%</td>
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<td>Na-Naphthalene-1-Sulfonate</td>
<td>2.22</td>
<td>106.0%</td>
<td>0.84 %</td>
<td>92.0%</td>
<td>1.46 %</td>
<td>92.7%</td>
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<td>Triphenylphosphine</td>
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<td>96.0%</td>
<td>2.44 %</td>
<td>95.2%</td>
<td>1.52 %</td>
<td>95.0%</td>
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<td>Lignosulfonic Acid</td>
<td>0.61</td>
<td>96.0%</td>
<td>0.40 %</td>
<td>96.1%</td>
<td>0.38</td>
<td>96.7%</td>
<td></td>
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</tbody>
</table>

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- To next lecture