Basics and Importance of Total Organic Carbon (TOC) Measurements in Environmental Samples

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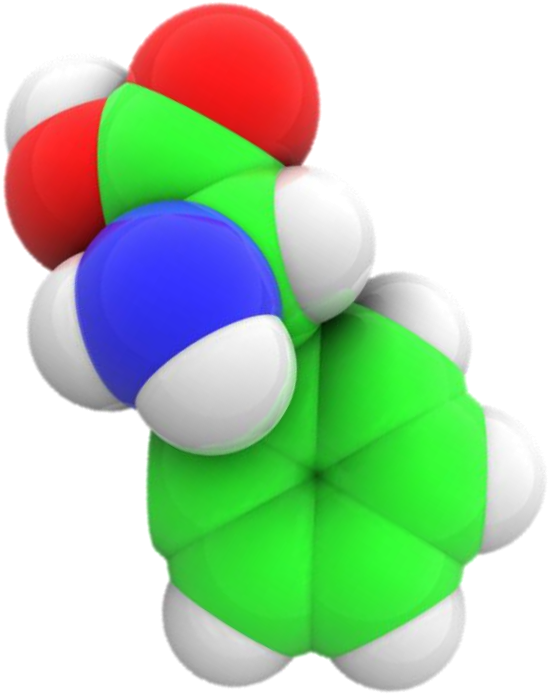
TOC is the measure of organic carbon in a sample

- measures all carbon converted to CO_2
- not source specific
- reacts with disinfectants to form THMs

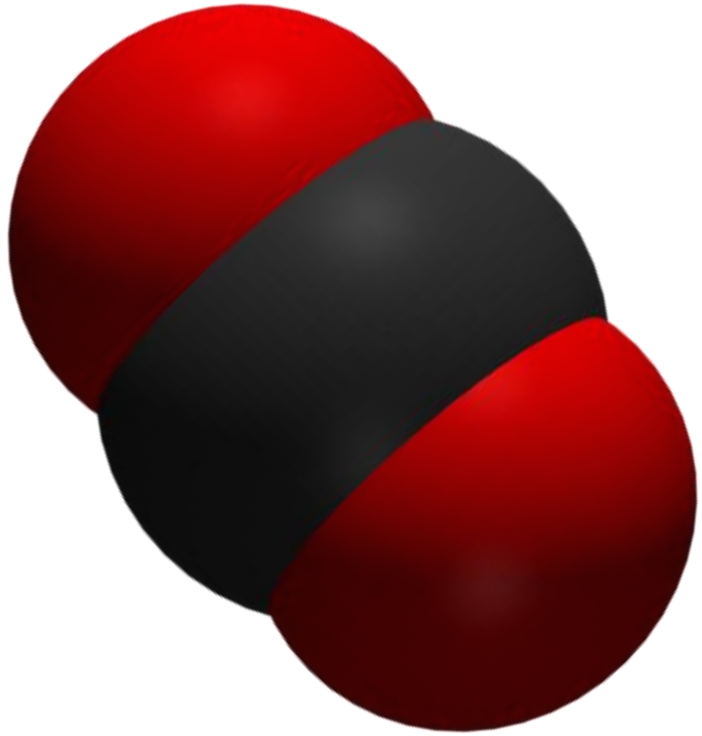
Organic carbon is derived from living molecules

- Sugars
- Metabolic Activities
- Decaying Vegetation
- Carbohydrates etc.

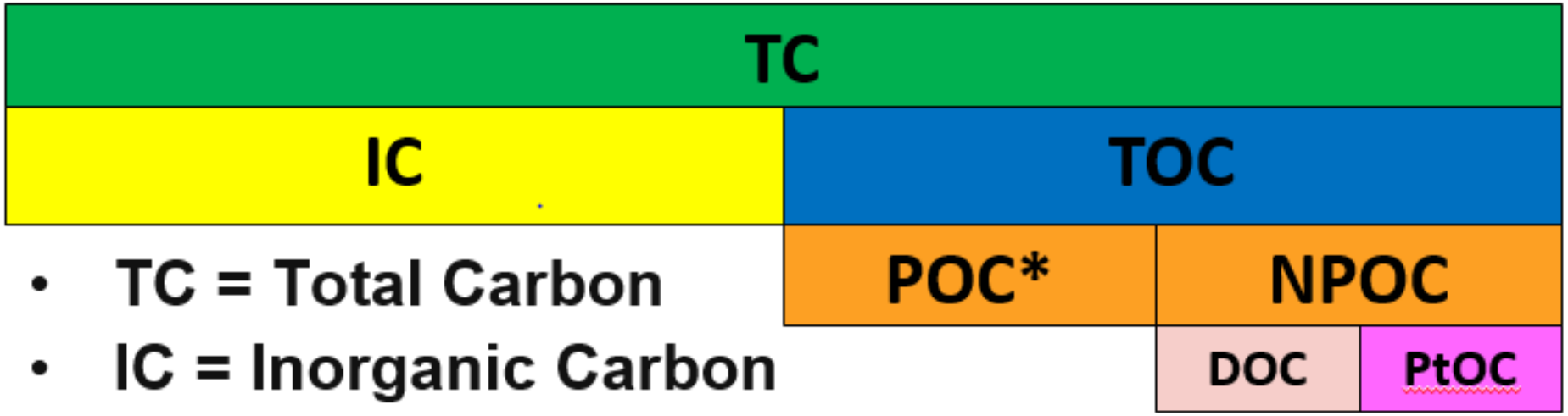


Inorganic Carbon is non-living carbon

- $CO_{(2)}$ [dissolved]
- Carbonates
- Bicarbonates
- Carbonyls etc.



Carbon Glossary



- TC = Total Carbon
- IC = Inorganic Carbon
- TOC = Total Organic Carbon
- POC = Purgable Organic Carbon
- NPOC = Non-Purgable Organic Carbon
- DOC = Dissolved Organic Carbon
- PtOC = Suspended (Particulate) Organic Carbon

Necessary definitions for TOC analyses

Purgable Organic Carbon

- organic carbon removed from an acidified sample by purging
- referred to as Volatile Organic Compounds (VOC)

Non-Purgable Organic Carbon

- organic carbon remaining in an acidified sample after purging

Dissolved Organic Carbon

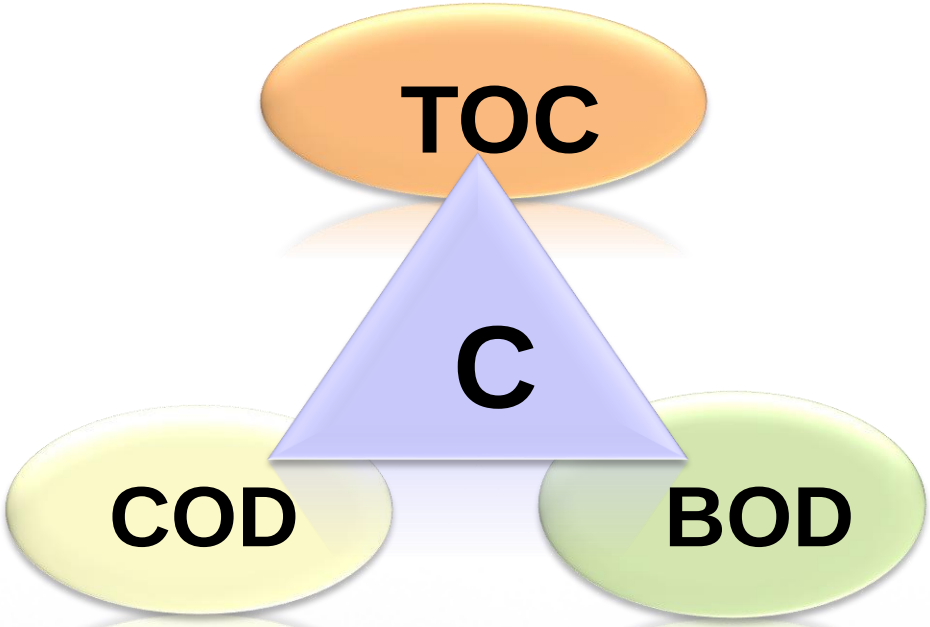
- organic carbon remaining in a sample after filtering the sample, typically using a 0.45 micrometer filter

Suspended Organic Carbon

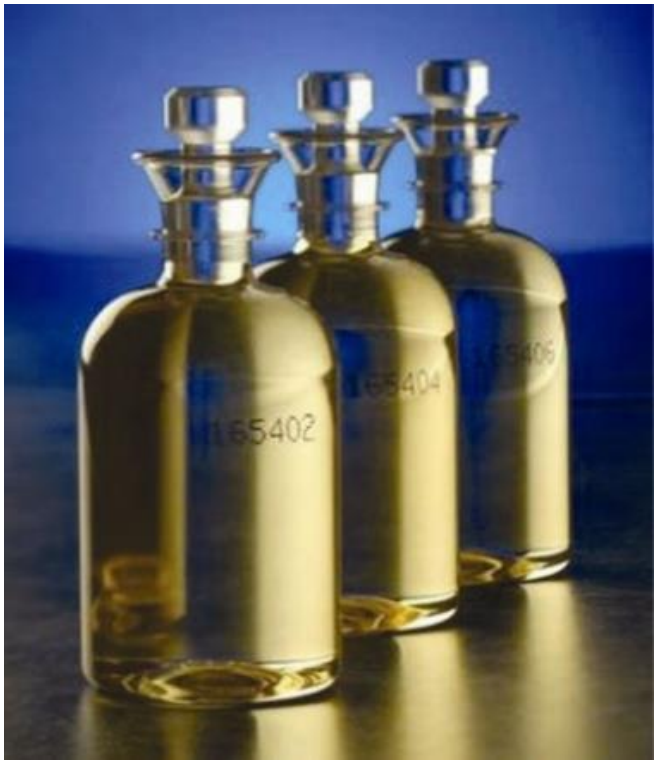
- the carbon in particulates too large to pass through a filter

Estimating Organic Carbon

Various methods are used to estimate organic carbon in environmental samples



BOD



Biological Oxygen Demand measures oxygen consumption by bacteria over 5 days

Also measures oxidation of NH_3 to NO_2 and NO_3,

COD

- **Chemical Oxygen Demand measures the oxygen required for chemical oxidation**

- **Organic matter, sulfide, iron, nitrogen all oxidize**

- **Some organic molecules do not oxidize**

COD and TOC

There is a theoretical correlation between COD and TOC

Theoretical COD = TOC x O_2/C

COD = TOC x 32/12

COD = TOC x 2.67

TOC and DBPs

Minimizing Disinfection byproducts requires TOC removal

Source Water TOC (mg/L)	Source Water Alkalinity (mg/L as $CaCO_3$)		
	0 – 60	60 – 120	Greater than 120
2.0 – 4.0	35.0 %	25.0 %	15.0 %
4.0 – 8.0	45.0 %	35.0 %	25.0 %
Greater than 8.0	50.0 %	40.0 %	30.0 %

Some CWA permits require TOC

TOC and Standard Methods

Technique	Method
High Temperature Oxidation	SM 5310B
Wet Chemical Oxidation	SM 5310C

To measure TOC you must have an Analyzer

- Measure organic and/or inorganic carbon in water or soil
- Used for DBP rule to estimate THM formation
- Correlate TOC with BOD and COD

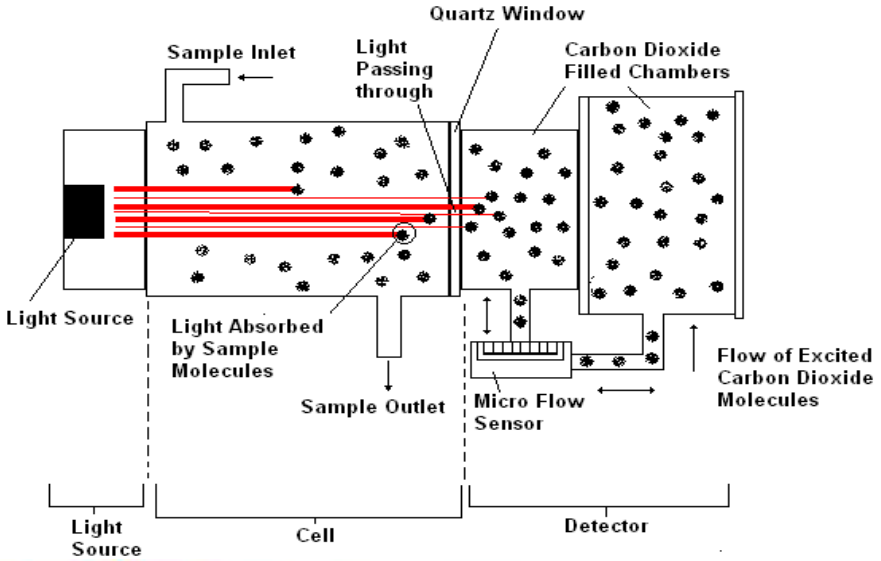
Measuring TOC

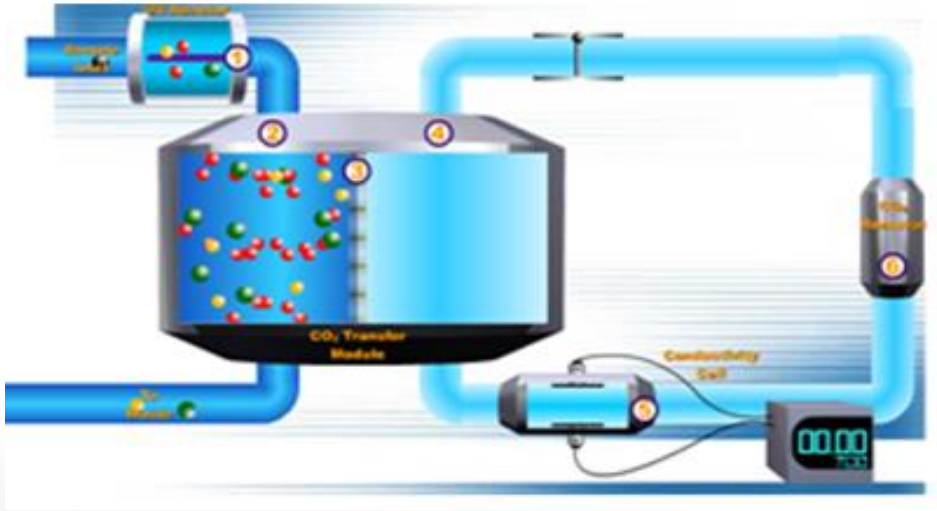
Most TOC analyzers remove TIC and measure NPOC

- NPOC = remove TIC with acid and measure remaining Carbon
- TOC = TC - TIC
  - Measure TC and TIC and subtract
  - Prone to error
  - Preferred for samples that foam

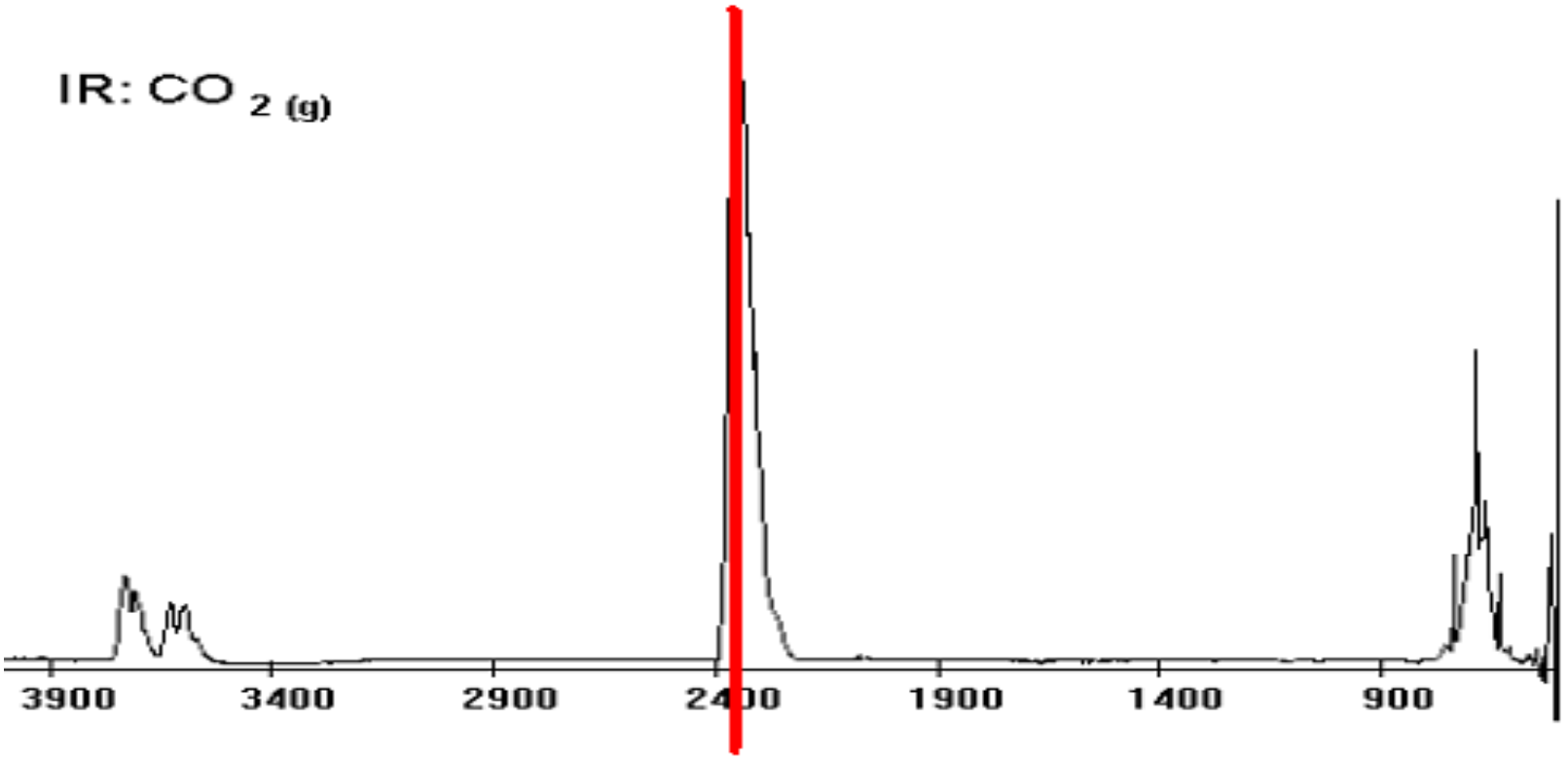
Detecting CO_2

- IR detection
  - requires carrier gas
  - specific to CO_2
- Membrane conductivity detection
  - Works by gas diffusion
    - Anything that passes through is detected
  - No carrier gas required





NDIR detection is practically interference free



Maximum Absorbance
2340 cm-1

TOC Oxidation Method

TOC analyzers oxidize carbon by high temperature or by chemical oxidation

- High Temperature
  - **Combustion**
  - **Catalyst assisted oxidation**

- Chemical Oxidation
  - **Persulfate**
    - **Catalyzed by heat**
    - **UV irradiation**
    - **Heat and UV irradiation**

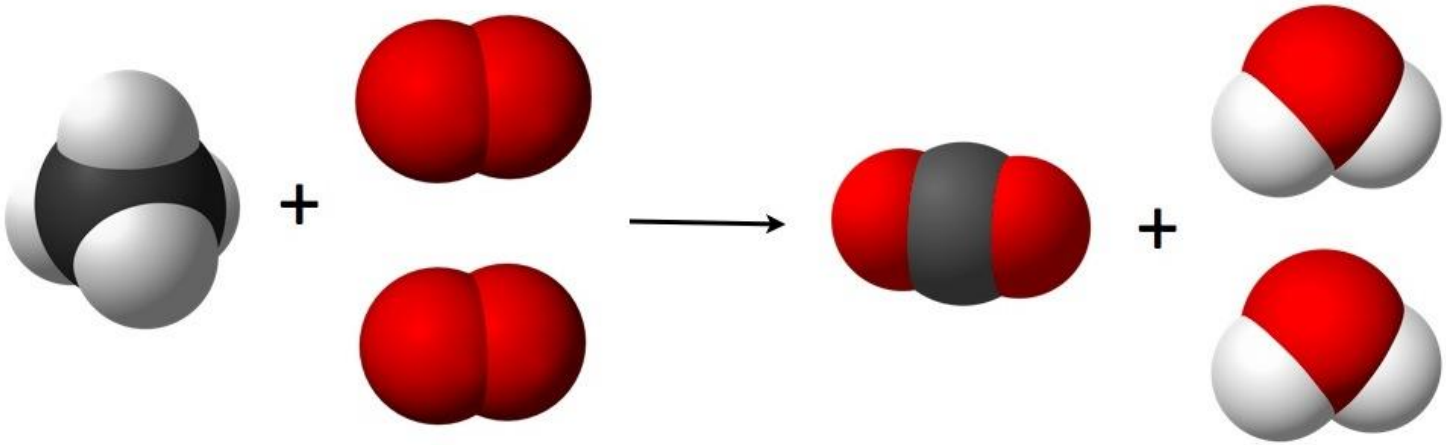
TOC is an Oxidation Reaction

When thinking about oxidation of TOC remember that:

For a reaction to happen a collision must occur…

TOC is an Oxidation Reaction

Combustion is a rapid form of oxidation that "burns" compounds to CO_2 and H_2O



$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

TOC is an Oxidation Reaction

For the reaction, we know:

- Oxygen and “fuel” must collide (vapor state)
- More oxygen = greater chance to collide
- Higher temperature = more collisions
- More time = more collisions

Combustion TOC Analyzer methods

Combustion TOC Analyzer methods are carried out in combustion tubes at 950°C or above

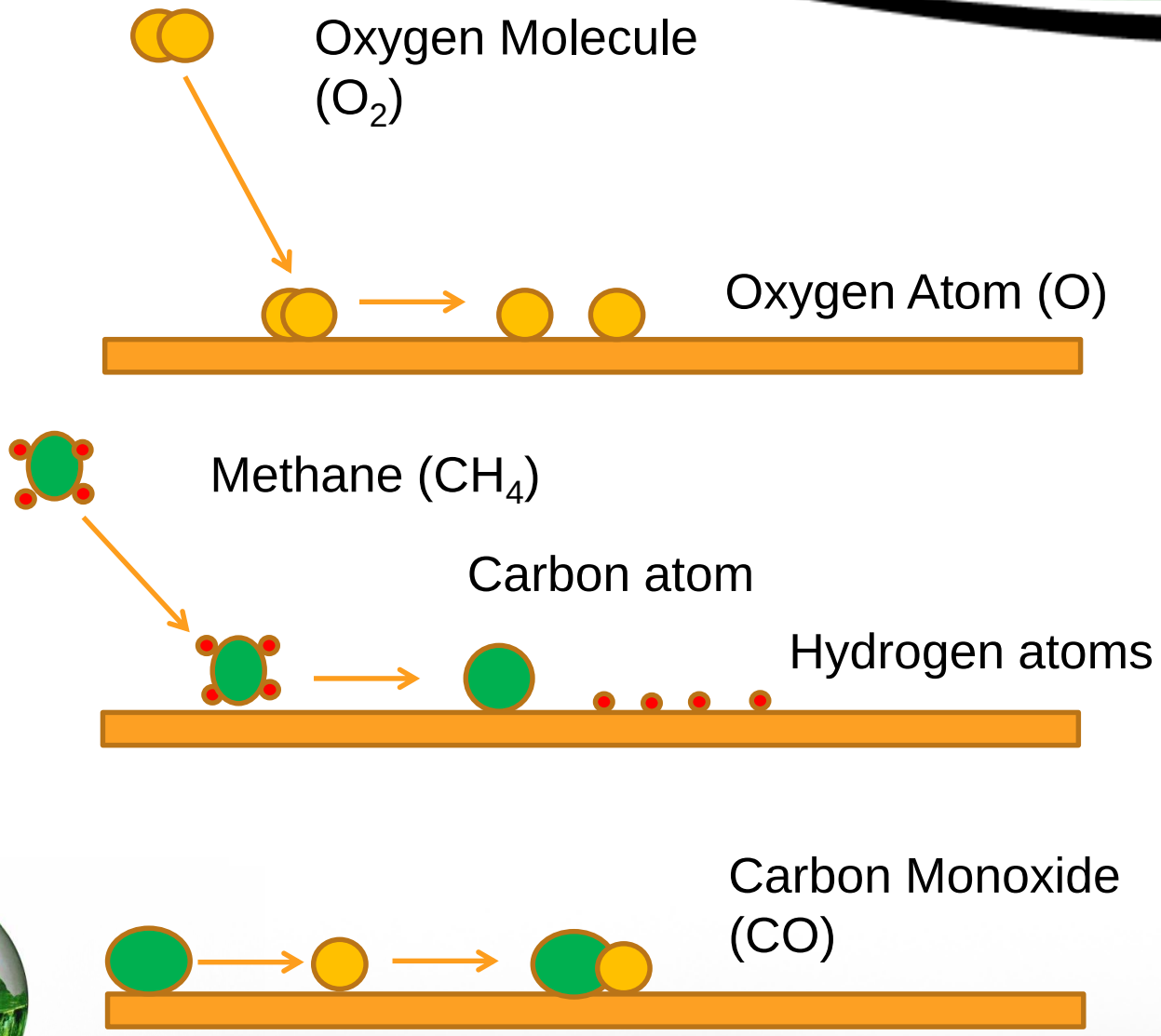
- Carrier gas is pure oxygen
- Detector is usually IR but can be Coulometric
- Combustion of carbonates…soil, rocks, or coal

Catalytic Combustion

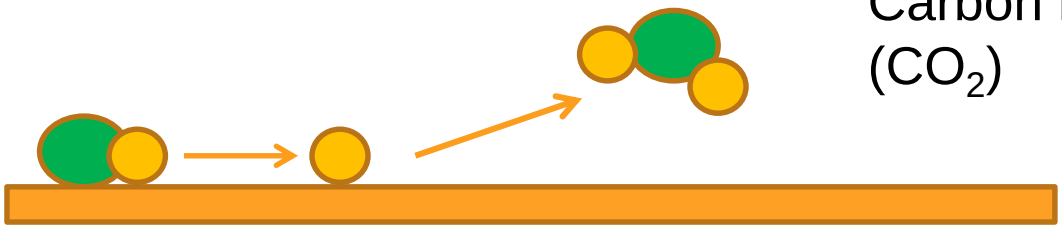
Catalytic Combustion oxidizes organic compounds to CO_2 and H_2O at lower temperatures

- Samples are injected onto a metal, or metal oxide catalyst where collisions occur
- Reaction steps involve adsorption and desorption
- Organic compounds react with molecular oxygen on the surface of the catalyst
- Oxidation efficiency is a function of catalyst surface area and catalyst contact time

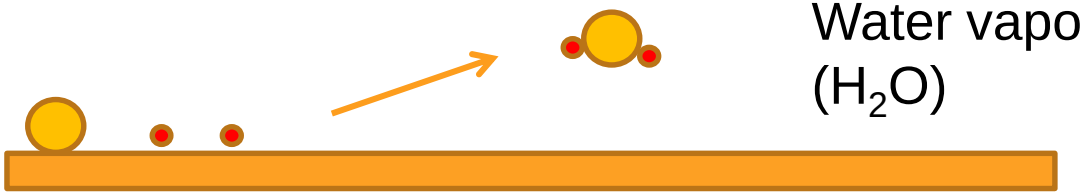
TOC is an Oxidation Reaction



TOC is an Oxidation Reaction



Carbon Dioxide
(CO_2)



Water vapor
(H_2O)

TOC is an Oxidation Reaction

- Oxidation of larger molecules proceeds stepwise as the organics travel through the catalyst.
- Oxidation efficiency ~= temperature (surface area / flow rate).
- As the surface area, flow rate, temperature increases so does the chance of collisions.
  - as temperature rises unwanted side reactions also increase

Why Temperature Matters

- Melting point of NaCL = 801^{o}C

- NaCL = H_2O → Na_2O + 2HCl
- Na_2O + SiO_2 → Na_2SiO_3

Why Temperature Matters

Catalytic Combustion TOC methods are carried out in combustion tubes at ≥ 680ºC

- Lower temperature increases detector life
- Lower temperature increases combustion tube life
- Catalytic Combustion is often used to determine TOC in drinking water, wastewater, and seawater.

Chemical Oxidation

Chemical oxidation reacts an oxidizing chemical with organic compounds to CO_2 and H_2O

- Homogenous reaction usually acid or basic persulfate
- Catalyst speeds the reaction
  - Heat
  - UV
- The catalyst converts $S_2O_8^{-2}$ to the $SO_4^{\bullet}$ radical
  - Stable persulfate + heat = free radical
  - The highest demand for radical is the matrix
- The number of collisions is proportional to temperature
  - Persulfate decomposes in high heat

Oxidation Techniques: Advantages and Disadvantages

Technique	Advantages	Disadvantages
Combustion (HTC)	High efficiency Soil, coal, solids	High detection limits Hazardous temperatures
Catalytic Combustion (HTCC)	High Efficiency Lower temperature than HTC Tolerates High Salt	Higher detection limit than PO Memory effects of catalyst Catalyst poisoning
Chemical Oxidation (PO)	Low Detection Limits No memory effects	Chloride interferes Lower oxidation efficiency

Auto Samplers Considerations

- High Sample Capacity
- Septum Piercing
- Stirring

- Lower Sample Capacity
- Fits Any Size Vial
- Stirring

Total Nitrogen Option

- TN add-on for TOC System
- Simultaneous Measurements of Carbon & Nitrogen
- 5 minute analysis

Options for Solid Sampling

- TC & IC Measurements
- Pt/CoO_3 Catalyst
- Adjustable Temperature

Online Options

- On-Line Continuous Monitoring
  Carbon, Nitrogen, Phosphorus
- Multi-Steam Particulate Sampler
  Up to 6 streams
- Remote Start, Stop and Alarms
- Same method as lab TOC

Northeast Environmental Seminar

November 6th

Shimadzu Scientific Instruments Headquarters, Columbia MD

Information at http://www.ssi.shimadzu.com/news/

Speakers from EPA, Restek, EST, Inorganic Ventures

Thankyou!

Any Questions?

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