True Capabilities of UV Absorbance to Detect Organics in Water

Authors: Bernard Beemster, Roy McKnight, Scott Kahle and Jed Reemsnyder, ASA Analytics; Rod Wellings, Royce Water Technologies

Objective: Our objective is to show that UV Absorbance can be a useful method to detect and measure certain organic substances in water or wastewater, but is not a universal tool for general organic analysis under all circumstances.

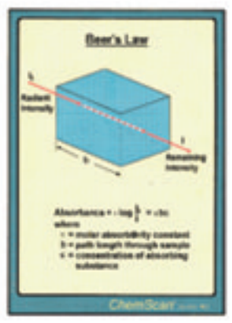
Methods:

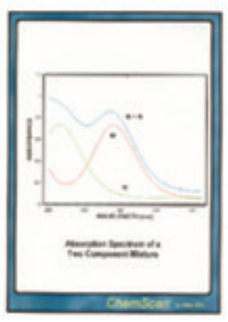
A. Define the theoretical interactions between light and matter that govern the use of UV absorbance for molecular analysis.
B. Define the theoretical limits for the use of UV absorbance as a method for analysis of specific organic substances.
C. Define the methods commonly used for aggregate organic analysis in water and wastewater.
D. Show baseline absorbance spectra for wastewater samples from different stages of treatment.
E. Show absorbance spectra for several water and wastewater samples with differing aggregate organic values, but similar absorbance spectra

A. Theoretical Interactions

1. Overall energy (E) associated with a molecule:
   $E = E_{electronic} + E_{vibrational} + E_{rotational} + E_{transitional}$
2. Light absorption in the UV, Visible and NIR range is mainly due to $E_{electronic}$ the energy associated with the outer orbital electrons in a molecule.
3. These include shared electrons that participate directly in bond formation and unshared electrons that are associated with atoms that tend to form strong ions or coordination compounds in water.
4. Beer's Law defines the functional relationship between measured absorbance and concentration in a sample, across a fixed path length.
5. For complex samples, the total absorbance at any wavelength is the sum of the individual absorbances for all components that exhibit an absorbance response at that wavelength. The total absorbance across a series of wavelengths defines the absorbance spectra for the sample across the wavelength range.

B. Theoretical Limits





1. Beer's Law is successful at describing absorption behavior of dilute solutions only. Close proximity between particles and interaction with electrolytes will affect absorbtivity.
2. Shared electrons in single bonds (carbon/carbon, carbon/hydrogen) require high excitation energy. Sufficient excitation energy is only available in the vacuum ultraviolet, below 180 nm. Many substances in this class are employed as solvents for spectrometric analysis because they are transparent in the UV-Visible wavelength range. Examples: water, ethanol, hexane, cyclohexane, carbon tetrachloride, diethyl ether, acetone, dioxane.
3. Shared electrons in double/triple bonds (unsaturated structures), unbonded electrons in some ions, and shared electrons in benzene rings can be excited by UV-Visible light.
4. Unsaturated organic groups that absorb UV and Visible light are termed *chromophores*. Examples: Alkenes and conjugated alkenes, alkynes, carbonyls, carboxyls, amidos, azos, nitros, nitrosos, organic nitrate, aromatics.

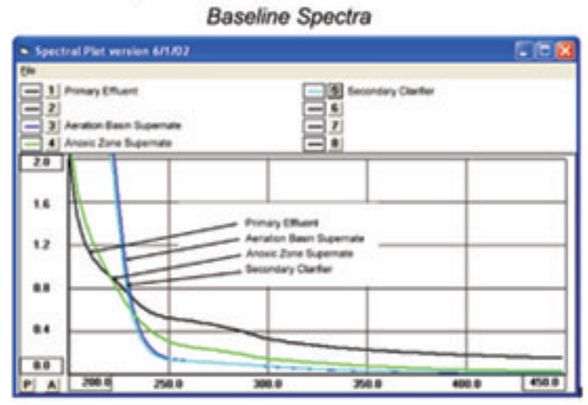
C. Aggregate Organic Analysis Methods

1. Measurements of the aggregate organic constituents in a sample rely on a common characteristic of the organics present in the sample. Different measurements define specific characteristics or fractions. The most common measurements are TOC, COD and BOD.
2. TOC measures the Total Organic Carbon in the sample, without regard to the oxidation state of the organic matter.
   a. It does not measure any inorganic matter and is not a measure of the oxygen demand in the sample.
   b. Measurement requires procedures to break down all organically bound carbon into a single molecular form.
   c. The original form of the organic molecules and their bond structure are not important for TOC analysis and are lost during the digestion process.
3. COD or Chemical Oxygen Demand measures the amount of a specific oxidant that reacts with any matter in the sample under controlled conditions.
   a. COD does not distinguish between organic or inorganic constituents. It is a measurement of reactivity to a reagent.
   b. The reactive substances in the sample may or may not have UV or Visible absorbance spectra.
4. BOD or Biochemical Oxygen Demand is a measurement of the oxygen consumed by microorganisms in the sample under controlled conditions plus the oxygen required to oxidize any inorganic material in the sample.
   a. Many BOD test variations exist, including longer and shorter incubation periods and various techniques to measure oxygen uptake rate.
   b. Alternative seeding, dilution and incubation conditions are chosen to mimic receiving water conditions.
   c. Microorganisms may be suspended in the sample or contained within biomass clusters or may be entrained within solids in the sample.
   d. Microorganisms that demand oxygen generally do not absorb UV or Visible light. Inorganic constituents may or may not absorb UV or Visible light. Suspended particles do tend to scatter transmitted light.

D. Baseline Absorbance Spectra for Wastewater Samples

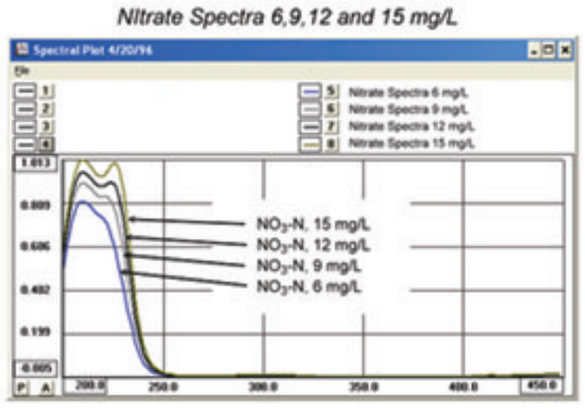
1. Different sample locations have substantially different optical and aggregate organic properties.

Baseline Spectra



2. A sample that has variation of concentration for a component exhibiting strong UV absorbance spectra, such as nitrate, has observable differences in sample spectra.

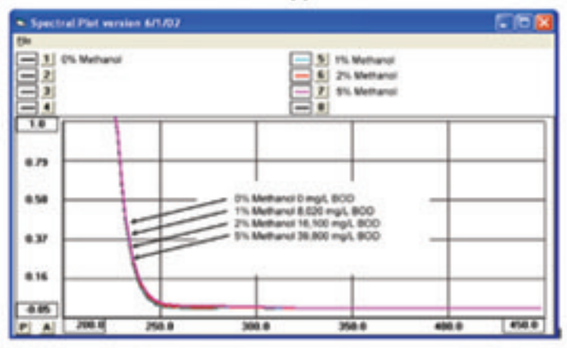
Nitrate Spectra 6,9,12 and 15 mg/L



E. Absorbance Spectra for Selected Samples with Organic Concentration Variation

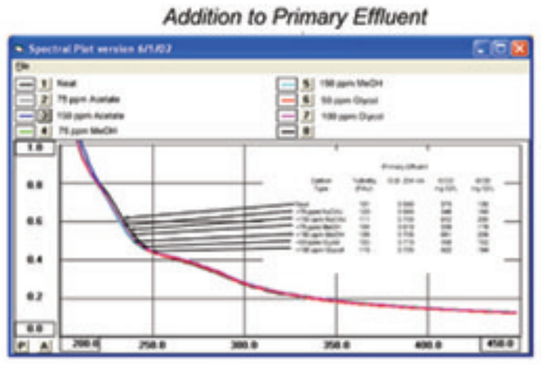
1. A non-absorbing component, such as methanol or ethanol, has little or no effect on the absorbance spectrum of a sample, but would have a substantial effect on the aggregate organic values.

Methanol Addition to 10 ppm Nitrate Solution

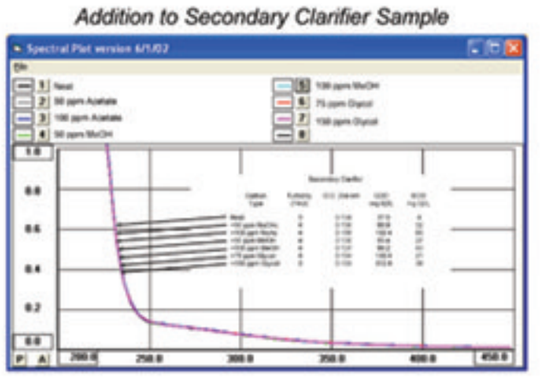


2. Many organic constituents are transparent in the UV or Visible wavelength range and have little or no impact on the absorbance spectra of water or wastewater.

Addition to Primary Effluent



Addition to Secondary Clarifier Sample



Conclusions

A. UV or Visible absorbance can be used to detect and measure certain kinds of molecular or ionic substances that possess certain types of bond structures and outer shell electrons.
B. Some substances that can be found in water or wastewater can have a substantial effect on aggregate organic values while having little or no effect on optical properties such as UV or Visible absorbance.
C. If the organic substances are in suspended form, such as in the form of biomass or solids, there may be some measurable optical properties such as changes in turbidity, TSS or UV-Visible absorbance that are momentarily proportionate to aggregate organic values.
D. Temporary relationships between UV absorbance and aggregate organic values may not continue to be valid if the distribution of organic components in samples is variable.

asa ANALYTICS

Applied Spectrometry Associates Inc.
2325 Parklawn Drive, Suite I
Waukesha, WI 53186
www.asaAnalytics.com

Royce Water Technologies
ABN 21 110 05f7 399
66 Rose Street
Wooloowin, Queensland 4030
www.RoyceWater.com.au