CH3041 Tutorial 2 Answers

1. Explain the chemical basis for the BOD test and the similarities and differences to the COD test.

In the BOD test at time = 0 a DO measurement is made to ascertain the DO level in the water before oxidation of organic matter has taken place The sample is diluted with a BOD diluent containing nutrients (Mg, Ca, Fe, P) that has been fully aerated. A Winkler titration (which relies on a stoichiometric reaction between Mn^{2+} and O_2 followed by a subsequent $I_2 / S_2 O_3^{-2}$ titration) or an electrochemical DO probe are used to make the measurements (mg / L of dissolved oxygen).

The water sample is placed in a sealed BOD bottle and incubated at 20°C for 5 days and microbial oxidation of the organic matter in the water sample takes place. $\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O$

T = 5d a second DO measurement is made to ascertain the DO level after oxidation. The difference between the two DO measurements indicates the biochemical oxygen demand in the water, which is then related to the organic load of the water. Normal values in unpolluted water are around 2mg /L, high values are found in organically polluted water 1000s mg /L. A test which attempts to replicate the conditions found in natural waters and it best used for routine monitoring of water quality waterways as it takes 5 days per test.

The COD test is similar in that it involves oxidation of the residual DOC but it differs in that a strong chemical oxidant (e.g. H^+/Cr_2O_7) is added in excess and the amount in excess is determined by back titration with standard Fe²⁺ solution. The advantage of this is that it takes only two hours at reflux to carry out the test, it is most appropriate for testing industrial waste effluent.

2. Calculate the total alkalinity (meq/L) of a sample of river water which has a carbonate alkalinity of 3.0×10^{-4} M; the pH is 10.7; the bicarbonate ion concentration is equal to the hydroxide ion concentration due to equilibrium conditions.

(6 marks)

 $pH = -log_{10}[H^+] = 10.7$ $[H^+] = 10^{-pH} = 10^{-10.7} = 1.99 \text{ x } 10^{-11} \text{ M}$ pOH = 14 - 10.7 = 3.3 $[OH^-] = 10^{-pOH} = 10^{-3.3} = 5.01 \text{ x } 10^{-4} \text{ M}$ $[HCO_3^-] = 5.01 \text{ x } 10^{-4} \text{ M}$

 $[alk]_{tot} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$ $= 5.01 x 10^{-4} M + (2 x 3.0 x 10^{-4} M) + 5.01 x 10^{-4} M - 1.99 x 10^{-11} M$ $= 1.60 x 10^{-3} M$

[alk]_{tot} = **1.60 meq/L**

3. Explain the term Acid Neutralising Capacity. How does this parameter differ from the pH of a water sample?

Acid Neutralising Capacity $[ANC] = [A^{-}] + [OH^{-}] - [H^{+}]$ The major bases [A-] are: HCO₃⁻, CO₃²⁻.

ANC is the sum of all bases in a water that can be titrated to a fixed equivalent point using the strong acid HCl, it is the ability of the water to neutralise added acid.

This is also the working definition of the *alkalinity* of a water sample.

The total alkalinity is determined by titration to the methyl orange indicator endpoint (pH 4.3) while the titration of caustic alkalinity is found by titration to the phenolphthalein indicator endpoint (pH 8.2).

The units are meq / L (the mmol H^+ equivalents titrated per litre).

The pH of a sample indicates the available H^+ in the solution as an *intensity factor* of H^+ . Using $K_w = [H^+][OH^-]$ we know the concentration of the strong base OH, again as an intensity factor.

For a weak base it must have a high concentration to generate an appreciable OH⁻ intensity, due to weak proton transfer to the weak base to generate OH⁻ eg. NMe₃. A strong base may have a low concentration and yet display a appreciable OH⁻ intensity as it is fully dissociated eg. NaOH. In contrast a high ANC may be found with a weak base if it has a moderate concentration as this is a *capacity factor* that relates simply to the total concentration of the base not the liberated concentration of OH⁻. A strong base with an equivalent pOH will have a lower ANC as there will be a lower total concentration of the base.

4. Humic and Fulvic acids are polyprotic, polymeric weak organic acids containing carboxyl, phenol and alcohol groups. Explain what this means and what are the differences between these two classes of acids.

A polyprotic acid has more than one dissociable acid functional group. A polymeric organic acid means that the carbon backbone of the organic compound is composed of simple repeating monomeric units which are repeated along the length of the polymer chain. The dissociable protons in the acids are found in the COOH (carboxyl), C_6H_4OH (phenol) and ROH (alcohol) functional groups. The humic acids are common in freshwater where they are formed by breakdown of lignins (complex plant biomolecules), they are yellow-brown in colour and are precipitated at a pH of 1. A typical humic acid structure would contain many fused organic rings. Fulvic acids have slightly lower molecular weights and are more important in marine waters where they are formed by fusion of simple triglyceride molecules, they are not precipitated at pH of 1. A typical structure would involve many long chains. Both humic and fulvic acids are refractory in nature resisting oxidation and have quite long lifetimes in water, they are important in complexing metals. The molecular weight of fulvic acids are typically lower (300s) than that of humic acids (1000s).

The origin of the humic matter is either through (i) being *imported* from the breakdown of: (A) higher plant material (lignins) or (B) microorganisms in the soils.

Alternatively (ii) the humic matter may produced *in-situ* in a water body by the decay of plant material and dead water microorganisms.

The actual formation of the humic molecules is either by:

(a) degradative transformation of lignins (+ waxes and other complex polymers) to humic matter in a number of oxidative steps.

(*b*) via total break down of macromolecules to small molecules followed by condensation polymerisation to form the humic matter polymers. In the oceans the route (b) involving triglycerides are thought to be important.

CH₂-O-C(=O)-R' | CH-O-C(=O)-R'' | CH₂-O-C(=O)-R'''

5. Rivers carry the products of chemical and physical erosion from the continental land mass

due to runoff, yet the river elemental chemical composition does not resemble the average

crustal elemental composition - why?

Rivers carry a mixture of dissolved solids ($\approx 20\%$) and suspended solids ($\approx 80\%$). The former result from chemical erosion and the latter from physical erosion. Chemical erosion, due largely to dissolved carbonic acid and harsh redox conditions, is more effective on minerals which are quite soluble, eg. Limestones CaCO₃, hence the higher ratio of Ca²⁺ and "CO₃" in the river water compared with other elements such as Al and Fe which have must higher crustal abundances. These other elements such as Al, Fe and Si are particularly insoluble in the common pH ranges found in natural waters and hence they have much lower concentrations in the river water than in the crust. This solubility may related to the charge / size ratio of the ions those with a high value will be quite insoluble while those with a low value will dissolve readily.

Al(OH)₃ gibbsite only becomes soluble under conditions of low or high pH. The equilibrium conditions dictate that Al remains out of solution.

 $Fe(OH)_3$ forms as an amorphous solid under normal pH conditions, Fe^{2+} is stable under conditions of normal pH but only under reducing anoxic conditions. The equilibrium conditions also dictate that Fe remains out of solution for most water bodies.

Silicate minerals such as quartz and feldspars weather slowly (they are framework silicates) to release silicic acid $H_2SiO_4(aq)$. In this case it is dissolution kinetics which dictate why the concentration of Si in solution is low.

| Crust | | 277g/kg | | <100g/kg | | | | |
|-------------|--------|-----------------|------|----------|----|----|----|---------------|
| | (0) | Si | Al | Fe | Ca | Na | Κ | Mg |
| River water | (O, H) | $C (HCO_3^{-})$ | Ca | Na | Cl | Si | Mg | $S(SO_4^{2})$ |
| | | 52mg/kg | <15n | ng/kg | | | - | |