Chemistry 203

Impurities in Natural Water

http://www.cnn.com/2000/NATURE/11/27/drinking.water.study.ap/

Purpose

- To learn some techniques for the purification of natural water.
- To test for the **contaminants** of natural water (mostly ions).
- To learn the technique of "**softening**" using ion-exchange *resins*.
- To learn about the properties of phosphate salts and their role as contaminants of natural water.
- To determine quantitatively (by spectrophotometric means), the phosphate content in a number of water samples and in an unknown.

Introduction

- Water is the most abundant substance on Earth.
- "Fresh water" constitute less than 3% of the earth's water.
- Water is capable of dissolving or suspending a tremendous variety of materials; therefore, there is simply no way to get "*pure*" spring water (H_2O and nothing but H_2O).
- The Environmental Protection Agency **EPA** has established Maximum Contaminant Levels (**MCL**s) for some of the most common and/or potentially dangerous identified water pollutants.

Are all water contaminants bad for our health?

- Not at all. Many of the naturally occurring compounds in water are benign or even good for our health.
- Some minerals, like calcium and magnesium are essential to human health.
- Also, sodium and potassium are essential to human health - in the correct amounts.
- Dissolved gases (oxygen, carbon dioxide, nitrogen, radon, methane, hydrogen sulfide, etc.) - no appreciable health effects, except for hydrogen sulfide and dissolved radioactive gases like radon.
- ***Drinking water must be free from harmful bacteria, suspended matter, odor, color and objectionable taste.***

Water Contaminants

- **Materials dissolved in water**:
  - **Inorganic Compounds**
    - Dissolved gases O_2, N_2, NH_3, H_2S, oxides of nitrogen (NO_x).
    - Metal and metalloid positive ions (aluminum, arsenic {MCL=0.05}, lead {MCL=0.015}, mercury {MCL=0.002}, calcium, magnesium, sodium, potassium, zinc, copper {MCL=1.3}, etc.)
    - Negative ions - (fluoride {MCL=4.0}, chloride, nitrate {MCL=10.0}, nitrite {MCL=1.0}, phosphate, sulfate, carbonate, cyanide {MCL=0.2}). As with the positive ions, some of these negative ions are necessary to life in proper concentrations (chloride and carbonate).

http://www.cyber-nook.com/water/contam.html

  - **Organic Compounds**
    - Synthetic Organic Chemicals, carbon tetrachloride {MCL=0.005}, and many other chemicals, like benzene {MCL=0.005} and vinyl chloride {MCL=0.002}
- **Materials suspended in water**
  - Sand, clay…
- **Microorganisms**
  - Viruses
  - Bacteria
  - Protozoans - Cryptosporidia and giardai. These are one celled organisms.

Phosphate: A Major Contaminant*

- Phosphorus is one of the most important elements to life. It is part of ATP, the most crucial molecule for the transfer and storage of cellular energy.
- In natural water and wastewaters, phosphorus exists almost exclusively in the form of phosphate.
- Phosphates may enter the water from agricultural runoff, or biological and industrial wastes.
- Phosphate is also a major ingredient in **detergents** and **fertilizers**, (it is estimated that detergent contributes 50% of the phosphate in domestic sewage),

- Phosphate in water can contribute to ***eutrophication***, excessive growth of algae.
- This rapid growth of algae causes the complete depletion of any dissolved oxygen in a body of water.
- Phosphate is also added to the water supply by the decompositions of dead organisms. For this reason, sediment on the bottom of lakes and rivers contain dissolved organic phosphate.

•http://webpages.charter.net/kwingerden/erhs/aquqrium/infophos.html

Tests and Purification Techniques

- Qualitative way: involves chemical reactions that produce visible colored products or precipitates.
- Quantitative way: involves
  - titrations (such as complexation of M^{2+} ions with ***ethylene diammine tetraacetic acid*** (EDTA))
  - or spectrophotometric analysis (such as the quantitative determination of phosphate ion PO_4^{3-} via complexation with ***ammonium molybdate*** under acidic conditions to form molybdophosphoric acid. A yellow compound vanadomolybdophosphoric acid, is formed in the presence of vanadium.

A. Distillation:

- Important purification technique:
  - Dissolve few crystals of cobalt chloride in water and distill.

Co^{2+}(anhydrous) $Co(H_2O)_6^{2+}$, $2Cl^-$ $CoCl_4^-$

blue *pink* *blue*

Note the color of the distillate.

Save the distillate; Label A1.

- Add conc. NH_3 to water and distill; Note the odor of the distillate. Is the distillate free of ammonia? Test with phenolphthleine.

  Save the remainder of the distillate; Label A2.

B. Minerals in tap water: cations

- Hardness in Ca^{2+} and Mg^{2+}

  Complex with EDTA:

  $$M^{2+} + Y^{4-} \longrightarrow MY^{2-}$$

  Determine water *hardness* by Complexometric titration with EDTA.

  Use EBT indicator.

  Prepare a comparison solution.

  Report the total [Ca^{2+}, Mg^{2+}] in mol/L (M)

  Convert to mg $CaCO_3$/L solution.

C. Minerals in tap water: anions

- Chloride ion
  - Silver ion test:

    $$Ag^{+} (aq) + Cl^{-} (aq) \longrightarrow AgCl (s)$$
  - test on tap water and distillates A1 and A2

- Sulfate ion
  - Barium ion test:

    $$Ba^{2+} (aq) + SO_4^{2-} (aq) \longrightarrow BaSO_4 (s)$$
  - test on tap water and distillates A1 and A2

Carbonate

- Evaporation to dryness ⟶ ***scale***

$Ca(HCO_3)_{2(aq)} \xrightarrow{\Delta} CaCO_{3\ (s)} + H_2O_{\ (l)} + CO_{2\ (g)}$

$Mg(HCO_3)_{2(aq)} \xrightarrow{\Delta} MgCO_{3\ (s)} + H_2O_{\ (l)} + CO_{2\ (g)}$

At high T, solubility of CO_2 decreases: equilibrium driven to the right.

Test for the carbonates: Add HCl

$CaCO_{3\ (s)} + 2\ HCl_{(aq)} \rightarrow Ca^{2+} + 2Cl^{-} + CO_{2(g)} + H_2O$

$MgCO_{3\ (s)} + 2\ HCl_{(aq)} \rightarrow Mg^{2+} + 2Cl^{-} + CO_{2(g)} + H_2O$

Treat the solid with HCl ⟶ ***fizzing***

D. Water Softening using ion-exchange resins

- Resins are polymers with cross-linking (connections between long C chains in a polymer).
- A resin has active groups in the form of electrically charged sites.
- Ions are attracted at these sites, and are replaced by other ions.
- Two key factors:
  - Affinity for a specific ion
  - Number of active sites for exchange
- Activity (efficiency) depends on pH and temperature.

Resin-Softened Water

- By ion exchange, the resin captures all metal ions and releases Na^{+} ions in their place

  $Na_2R + CaCl_2 \rightarrow CaR + 2\,NaCl$

  R represents the negatively charged site of the cation exchange resin.

- On resin-softened water perform:
  - -hardness test
  - -Chloride ion test
  - -Sulfate ion test,
  - -Phosphate ion test.

E. Water Softening using De-ionizing type resins

- Both cation and anion exchange resins
- **Cations taken and replaced by H^{+}**
- **Anions taken and replaced by OH^{-}**

$$H^{+} + OH^{-} \longrightarrow H_2O$$

- De-ionization is less expensive than distillation due to lower energy requirements.

F. Determination of Phosphate

- Complexation with
  - molybdate $Mo_7O_{24}^{6-}$
  - vanadate VO_3^-

$$H_2PO_4^- + 6\ VO_3^- + Mo_7O_{24}^{6-} + 13\ H^+ \rightarrow$$

$$H_9Mo_6O_{40}PV_6 + MoO_3 + 3\ H_2O$$

$$Mo_6V_6(OH)_9O_{27}(PO_4)$$

Vanadomolybdo phosphoric acid

Procedure: Preparation of Standard Phosphate Solutions

- Obtain a sample of 3.230×10^{-3}M KH_2PO_4
- Pipet 1.00mL aliquot of this sample and transfer to a 50-mL volumetric flask.
- Make up the solution to the mark with distilled water. Stopper the flask, and mix well, then transfer to a beaker. Label the beaker.
- Repeat the above steps with 2.00, 3.00, 4.00 and 5.00mL aliquots.
- To each solution in the beaker, add 10mL of ammonium vanadate/molybdate reagent; A yellow color will appear (the intensity of the color depends on the concentration of phosphate).

Absorbance Measurements

- Measure the absorbance of each of the five standard solutions at 420nm.
- The blank is prepared by adding 10.0mL of ammonium vanadate/molybdate reagent to 50.0mL volumetric flask and diluting to the mark with distilled water.
- Plot a calibration curve and determine the slope (εb).

Phosphate in water samples

- Prepare a water sample (Tap water or Sea water) and an unknown:
  - Pipet 5.0mL aliquots of water sample (or unknown) into 50.0mL volumetric flask.
- Add 10.0mL of ammonium vanadate/ molybdate reagent and dilute to the mark with distilled water.
- Measure the absorbance of each sample.
- Determine the concentration of phosphate from the calibration curve.