

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 (H₂O and nothing but H₂O).
- The Environmental Protection Agency **EPA** has established **Maximum Contaminant Levels (MCLs)** 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 O₂, N₂, NH₃, H₂S, 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/aquarium/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 diamine 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 phenolphthaleine.
Save the remainder of the distillate; Label A2.

B. Minerals in tap water: cations

- Hardness in Ca²⁺ and Mg²⁺

Complex with EDTA:



Determine water *hardness* by Complexometric titration with EDTA.

Use EBT indicator.

Prepare a comparison solution.

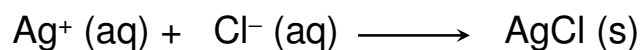
Report the total [Ca²⁺, Mg²⁺] in mol/L (M)

Convert to mg CaCO₃/L solution.

C. Minerals in tap water: anions

- Chloride ion

– Silver ion test:



– test on tap water and distillates A1 and A2

- Sulfate ion

– Barium ion test:



– test on tap water and distillates A1 and A2

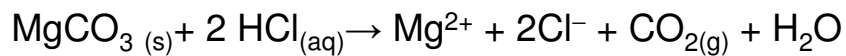
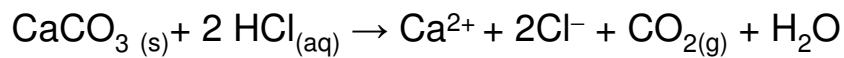
Carbonate

- Evaporation to dryness \longrightarrow **scale**



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

Test for the carbonates: Add **HCl**



Treat the solid with HCl \longrightarrow **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.

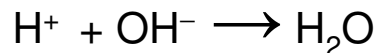
Resin-Softened Water

- By ion exchange, the resin captures all metal ions and releases Na^+ ions in their place
$$\text{Na}_2\text{R} + \text{CaCl}_2 \rightarrow \text{CaR} + 2 \text{NaCl}$$

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

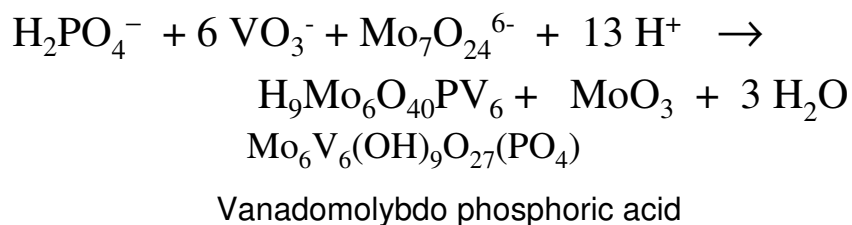
- Both cation and anion exchange resins
- **Cations taken and replaced by H^+**
- **Anions taken and replaced by OH^-**



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

F. Determination of Phosphate

- Complexation with
 - molybdate $\text{Mo}_7\text{O}_{24}^{6-}$
 - vanadate VO_3^-



Procedure: Preparation of Standard Phosphate Solutions

- Obtain a sample of $3.230 \times 10^{-3} \text{M}$ 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.