

# Seawater Analysis Project



“Seawater is a complex mixture of 96.5 percent water, 2.5 percent salts, and smaller amounts of other substances, including dissolved inorganic and organic materials, particulates, and a few atmospheric gases.”

-Encyclopedia Britannica

Chem M3LC  
R. Corn

# Seawater Analysis Project

Pacific Ocean Water Concentrations /  
mg L<sup>-1</sup>

Ion	CRC values <sup>a</sup>
Na <sup>+</sup>	1.05 × 10 <sup>4</sup>
K <sup>+</sup>	3.80 × 10 <sup>2</sup>
Mg <sup>2+</sup>	1.35 × 10 <sup>3</sup>
Ca <sup>2+</sup>	4.00 × 10 <sup>2</sup>
Cl <sup>-</sup>	1.90 × 10 <sup>4</sup>
SO <sub>4</sub> <sup>2-</sup>	2.65 × 10 <sup>3</sup>
Br <sup>-</sup>	6.5 × 10 <sup>1</sup>

## *Major ionic species in seawater*

“On average, seawater in the world's oceans has a salinity of about 3.5% (35 g/L, or 0.600 M).” - Wikipedia

<sup>a</sup>CRC Handbook of Chemistry and Physics, 61st ed.

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*We will measure six of the  
top seven ions in sea water!*

<sup>a</sup>CRC Handbook of Chemistry and Physics, 61st ed.

# Seawater Analysis Project

## Concentrations

$\text{Cl}^-$  - 536 mM

$\text{Na}^+$  - 457 mM

$\text{Mg}^{2+}$  - 56.3 mM

$\text{Ca}^{2+}$  - 10.0 mM

$\text{K}^+$  - 9.74 mM

$\text{SO}_4^{2-}$  - 2.76 mM

$\text{Br}^-$  - 0.823 mM

*Chemists use molarity!*

# Seawater Analysis Project

<i>Concentrations</i>	<i>Relative amounts</i>
$\text{Cl}^-$ - 536 mM	1000
$\text{Na}^+$ - 457 mM	853
$\text{Mg}^{2+}$ - 56.3 mM	105
$\text{Ca}^{2+}$ - 10.0 mM	18.7
$\text{K}^+$ - 9.74 mM	18.2
$\text{SO}_4^{2-}$ - 2.76 mM	5.15
$\text{Br}^-$ - 0.823 mM	1.54

*Chemists use molarity!*

# *Seawater Analysis Project*

1. Turbidity Measurements for Sulfate
2. Turbidity Measurements for Potassium
3. Magnesium Complexometric Fluorometry
4. EDTA titrations for Magnesium and Calcium
5. AgCl Precipitation titration for Chloride
6. Bromide Oxidation and Colorimetric Detection

# Seawater Analysis Project

*Precipitation Reactions:*

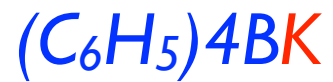
*Detection Methods*



*Precipitation Titration*



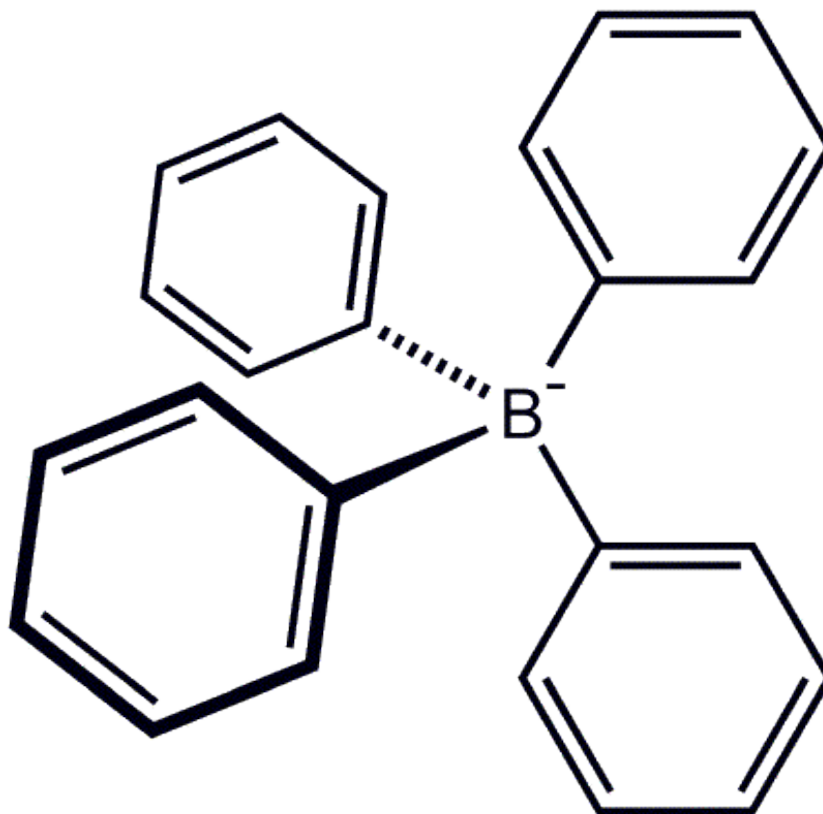
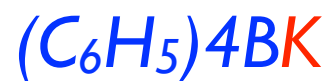
*Turbidity*



*Turbidity*

# Seawater Analysis Project

## Precipitation Reactions:

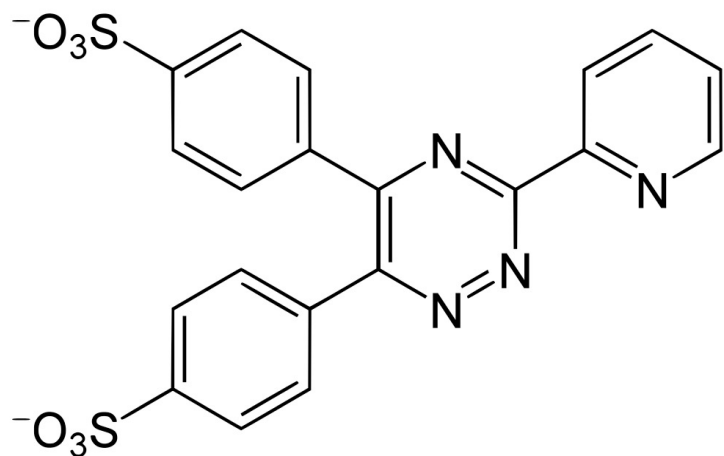
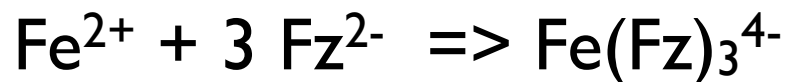


Tetraphenylboronate ion

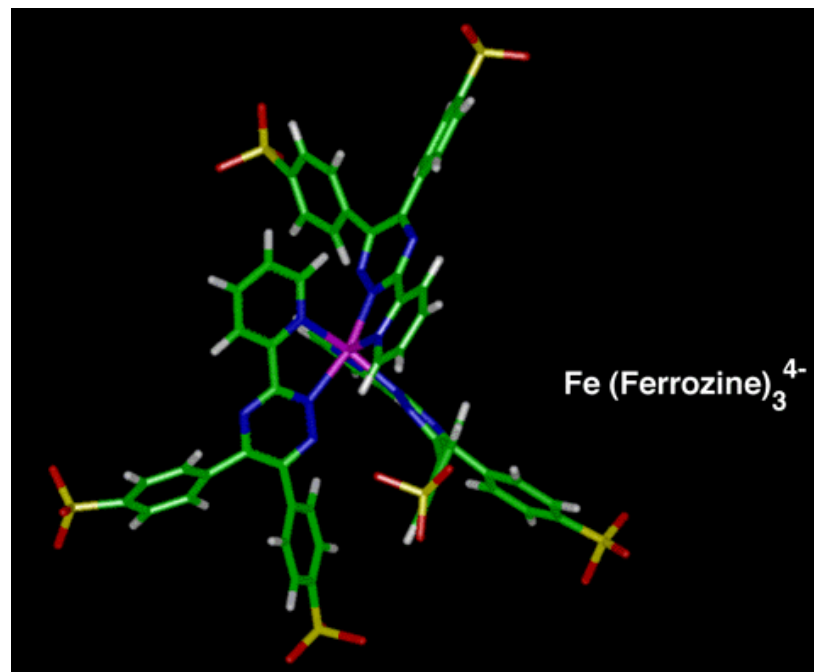


## Metal-Ligand Complexation Equilibria

We already used metal complexation in Week 2 for the Fe Colorimetry Experiment:



Ferrozine (Fz<sup>2-</sup>)  
is a metal ligand



Three Ferrozine will form a  
metal-ligand complex with Fe<sup>2+</sup>

# Seawater Analysis Project

*Complexation Reactions:*

*Ca EDTA*

*Mg EDTA*

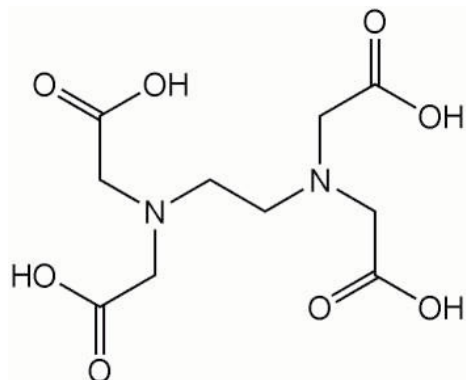
*Mg - Hydroxyquinoline*

*Detection Methods*

*Complexation Titration*

*Fluorimetry*

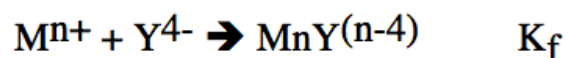
# EDTA Metal Ion Complexation Equilibria



## Ethylenediamine Tetra-acetic Acid (H<sub>4</sub>Y)

*EDTA - the world's best metal ion chelator*

Metal complexation reactions with Y<sup>4-</sup>:



Metal Ion                      log K<sub>f</sub>

Ag<sup>+</sup>                                      7.32

Mg<sup>2+</sup>                                      8.69

Ca<sup>2+</sup>                                      10.70

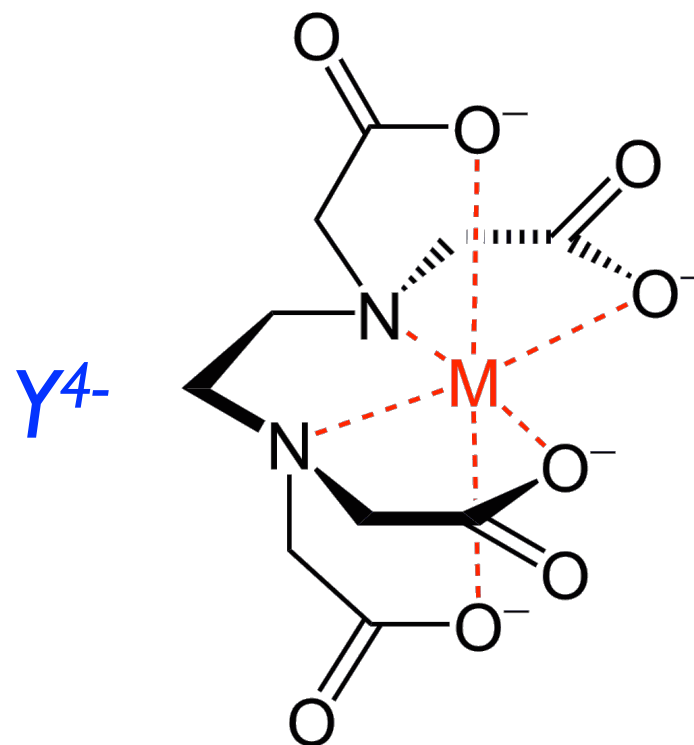
Co<sup>2+</sup>                                      16.31

Cd<sup>2+</sup>                                      16.46

Al<sup>3+</sup>                                      15.89

Fe<sup>3+</sup>                                      25.10

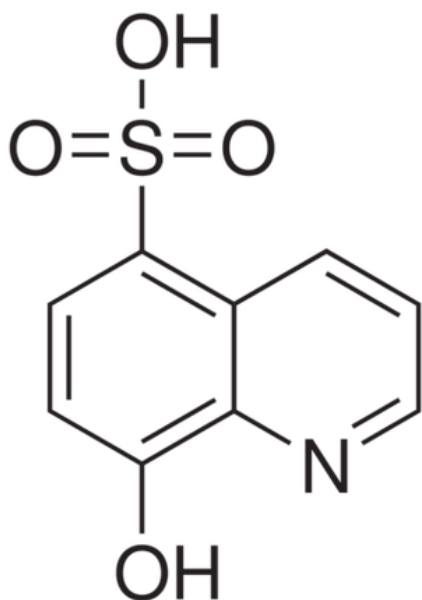
V<sup>3+</sup>                                      25.90



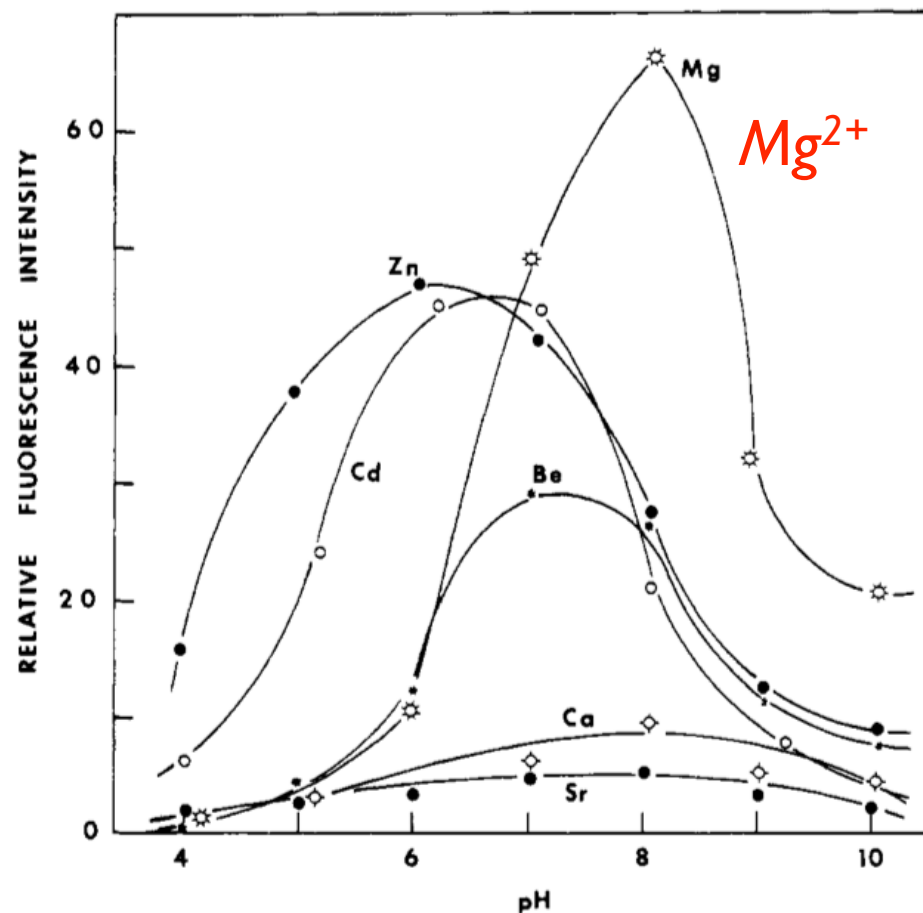
*“Chelate”*

Conditional formation constant:       $K'_f = \alpha_{Y^{4-}} K_f$

*Hydroxyquinoline: a metal chelator that fluoresces upon binding!*



*8-hydroxyquinoline-5-sulfonic Acid*

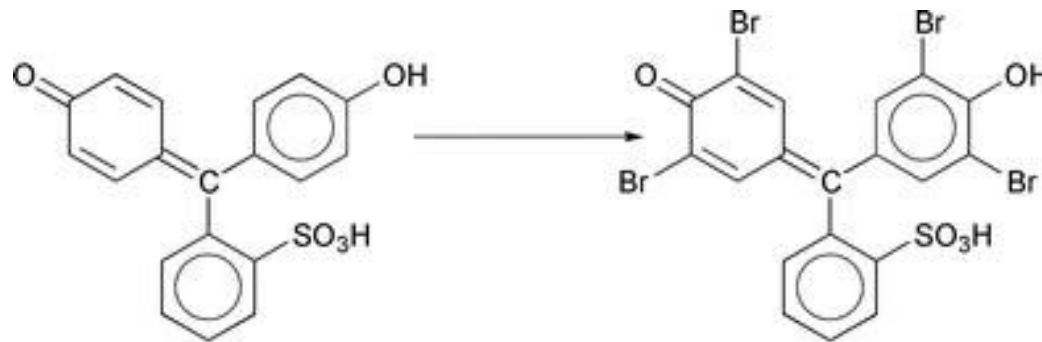
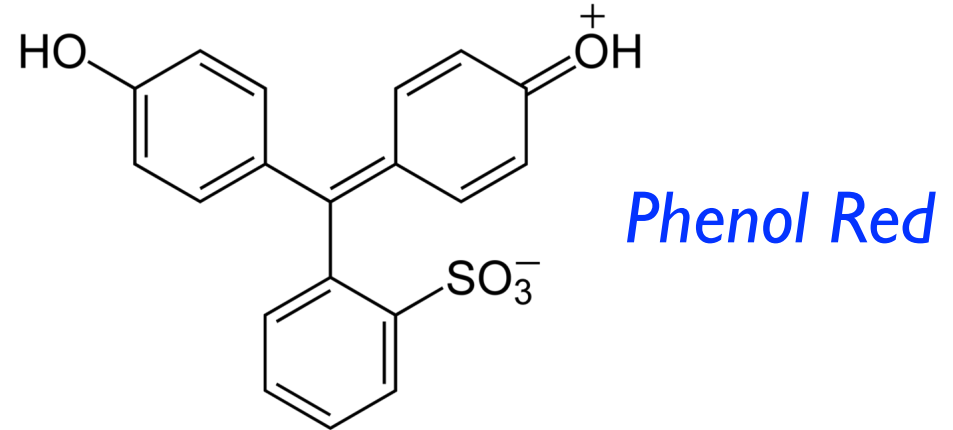
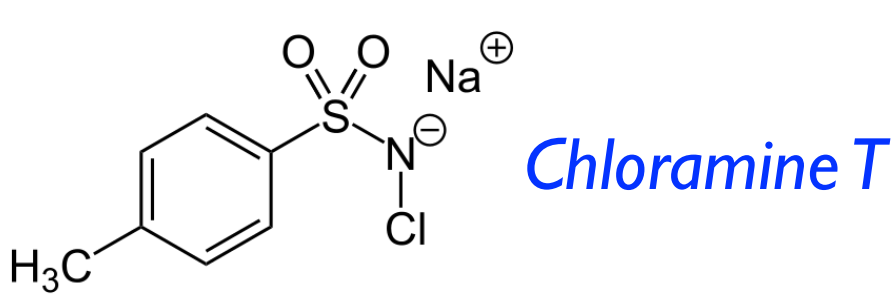


**Figure 1.** pH dependence of the fluorescence intensities of group II metal-HQS chelates: Cd, 2  $\mu\text{M}$ ; all other metals in this and following figures, 20  $\mu\text{M}$ ; HQS, 1 mM.

*Fluorometric Detection of  $\text{Mg}^{2+}$  in Seawater*

# Seawater Analysis Project

## Bromide: Bromination of Phenol Red



*Bromophenol Blue*

# Seawater Analysis Project

## *Bromide: Bromination of Phenol Red*

Principle: When a sample containing bromide ions ( $\text{Br}^-$ ) is treated with a dilute solution of chloramine-T in the presence of phenol red, the oxidation of bromide and subsequent bromination of the phenol red occur readily. If the reaction is buffered to pH 4.5 to 4.7, the color of the brominated compound will range from reddish to violet, depending on the bromide concentration. Thus, a sharp differentiation can be made among various concentrations of bromide. The concentration of chloramine-T and timing of the reaction before dechlorination are critical.

Chloride interference is reduced by the addition of sodium thiosulfate. Chloramine-T dissociates in aqueous solution to form hypochlorous acid, which can then react with chloride, causing substitution of chloride at positions ortho to the hydroxy groups on phenol red, just as in bromination. Sodium thiosulfate reacts with chlorine to reduce this interferent to a selectivity (ratio of analyte to interferent concentration) of  $>28\ 000$ .