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 Brittanica

Chem M3LC
R. Corn

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Pacific Ocean Water Concentrations / mg L^{-1}	
Ion	CRC values [a]
Na^+	1.05×10^4
K^+	3.80×10^2
Mg^{2+}	1.35×10^3
Ca^{2+}	4.00×10^2
Cl^-	1.90×10^4
SO_4^{2-}	2.65×10^3
Br^-	6.5×10^1

[a] CRC Handbook of Chemistry and Physics, 61st ed.

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

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

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Concentrations

Cl^{-} - 536 mM

Na^{+} - 457 mM

Mg^{2+} - 56.3 mM

SO_4^{2-} - 27.6 mM

Ca^{2+} - 10.0 mM

K^{+} - 9.74 mM

Br^{-} - 0.823 mM

Chemists use molarity!

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Concentrations	Relative amounts
Cl^- - 536 mM	1000
Na^+ - 457 mM	853
Mg^{2+} - 56.3 mM	105
SO_4^{2-} - 27.6 mM	51.5
Ca^{2+} - 10.0 mM	18.7
K^+ - 9.74 mM	18.2
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

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Precipitation Reactions:	Detection Methods
$AgCl(s)$	Precipitation Titration
$BaSO_4(s)$	Turbidity
$(C_6H_5)4BK$	Turbidity

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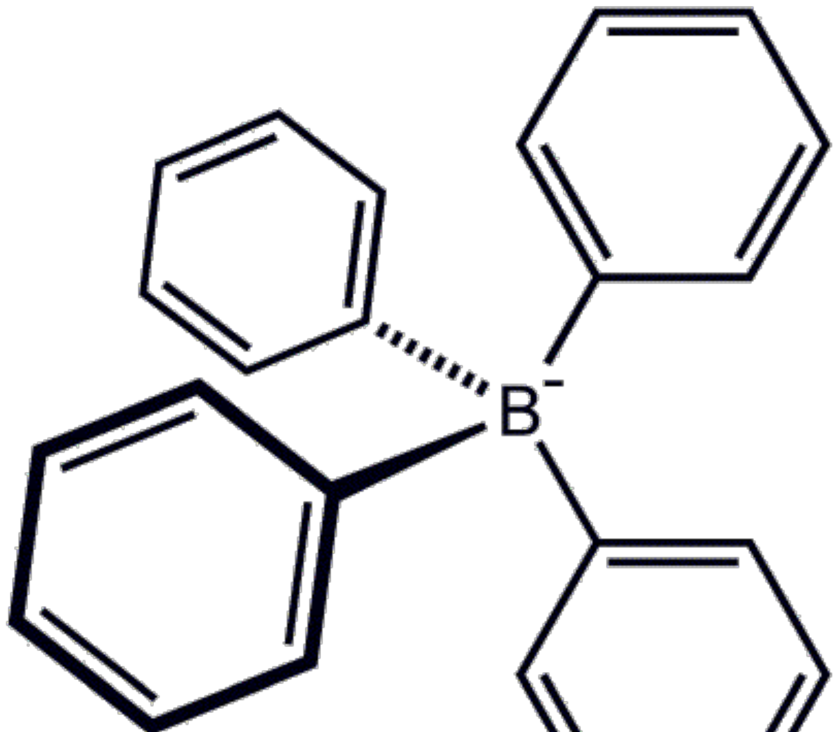
Precipitation Reactions:

AgCl(s)

$BaSO_4(s)$

$(C_6H_5)_4BK$



Tetraphenylboronate ion

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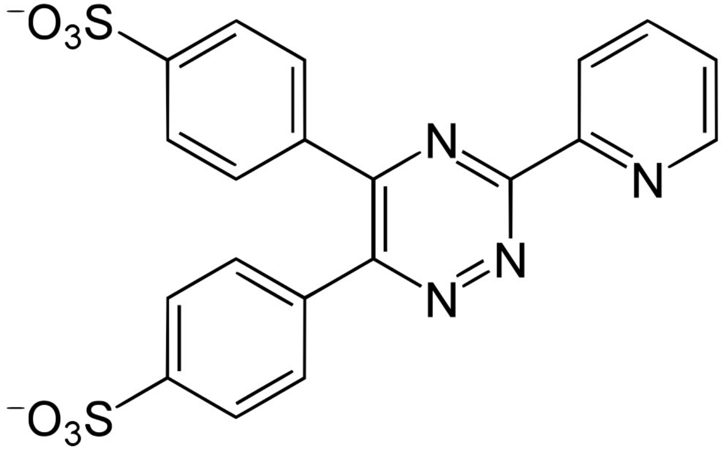
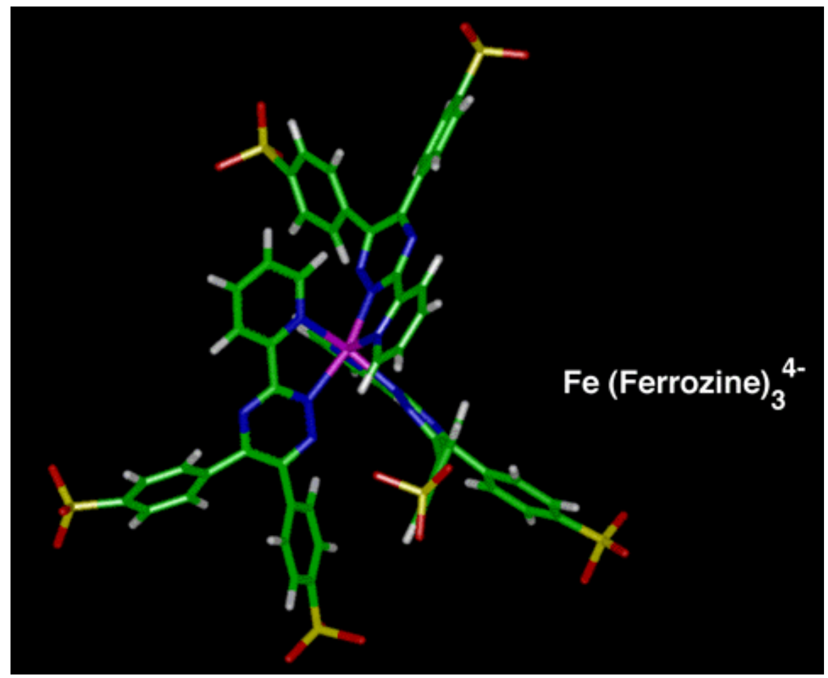
Metal-Ligand Complexation Equilibria

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

$$Fe^{2+} + 3\ Fz^{2-} \Rightarrow Fe(Fz)_3^{4-}$$



Ferrozine (Fz^{2-})
is a metal ligand



Three Ferrozine will form a metal-ligand complex with Fe^{2+}

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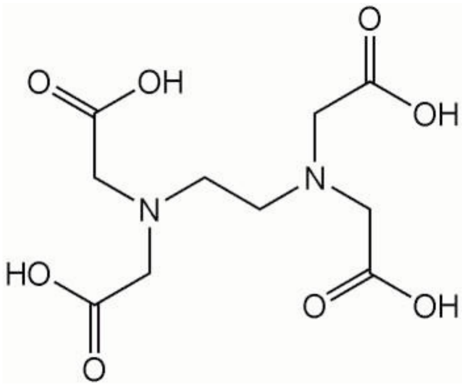
Complexation Reactions:	*Detection Methods*
Ca EDTA *Mg EDTA*	*Complexation Titration*
Mg - Hydroxyquinoline	*Fluorimetry*

EDTA Metal Ion Complexation Equilibria



Ethylene Diamine Tetra-acetic Acid (H_4Y)

EDTA - the world's best metal ion chelator

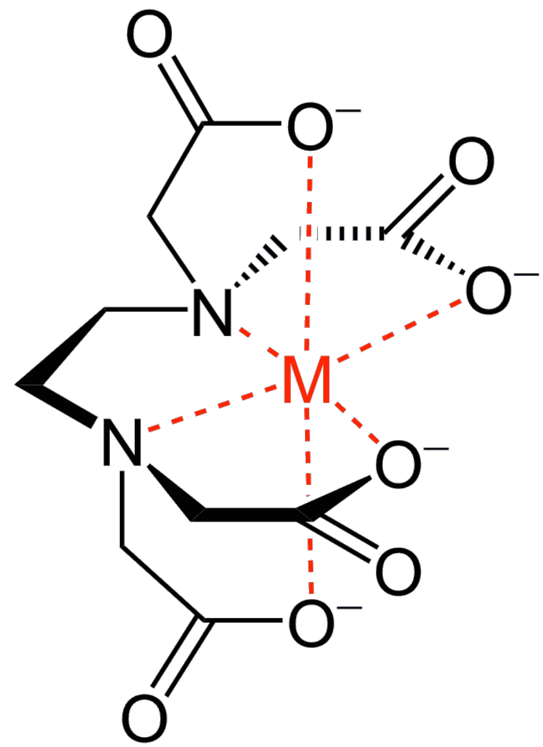
Metal complexation reactions with Y^{4-}:

$M^{n+} + Y^{4-} \rightarrow MnY^{(n-4)}$ K_f

Metal Ion	log K_f
Ag^{+}	7.32
Mg^{2+}	8.69
Ca^{2+}	10.70
Co^{2+}	16.31
Cd^{2+}	16.46
Al^{3+}	15.89
Fe^{3+}	25.10
V^{3+}	25.90

Conditional formation constant: $K'_f = \alpha_{Y4-} K_f$

Y^{4-}



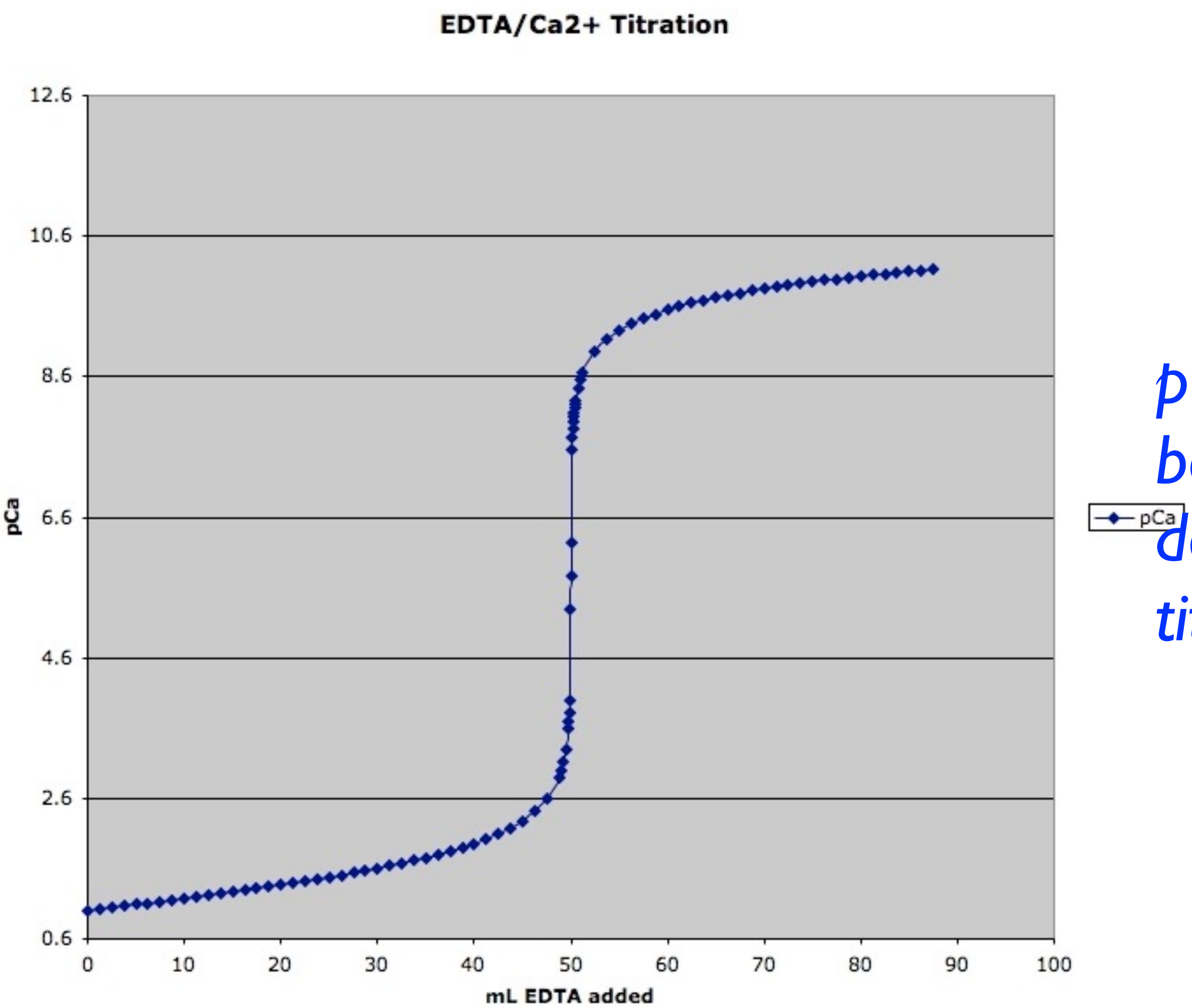
"Chelate"

EDTA titrations for metal ions

$Ca^{2+} + Y^{4-} \rightarrow CaY^{2-}$ $K_f = 5.01 \times 10^{10}$

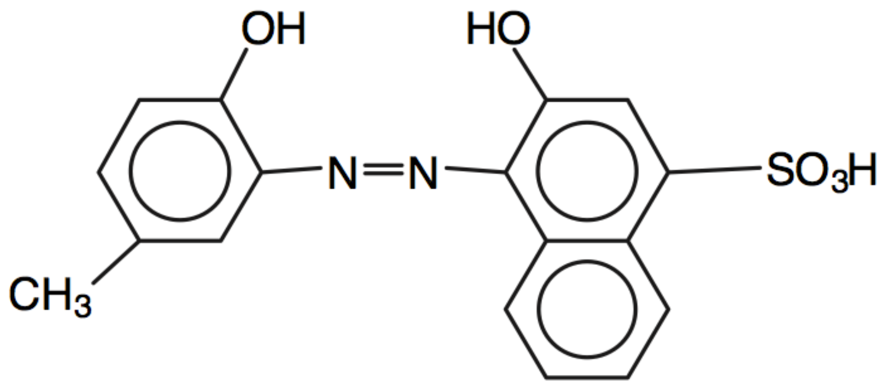
$Mg^{2+} + Y^{4-} \rightarrow MgY^{2-}$ $K_f = 4.90 \times 10^{8}$

pCa



pCa or pMg can be used to determine the titration endpoint.

EDTA titrations for metal ions

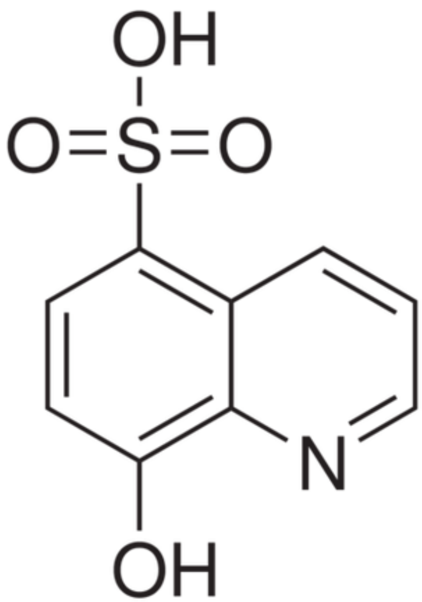


Calmagite (H_3In)

$MgIn^-$	+	HY^{3-}	$\rightleftharpoons$	MgY^{2-}	+	HIn^{2-}
metal ion/ indicator complex		titrant		metal ion/ EDTA complex		free indicator
(wine-red)		(colorless)		(colorless)		(blue)

EDTA will displace weaker ligands -- you will use this process with calmagite to determine the endpoint of an EDTA titration for Mg^{2+}

Hydroxyquinoline: a metal chelator that fluoresces upon binding!



8-hydroxyquinoline-5-sulfonic Acid

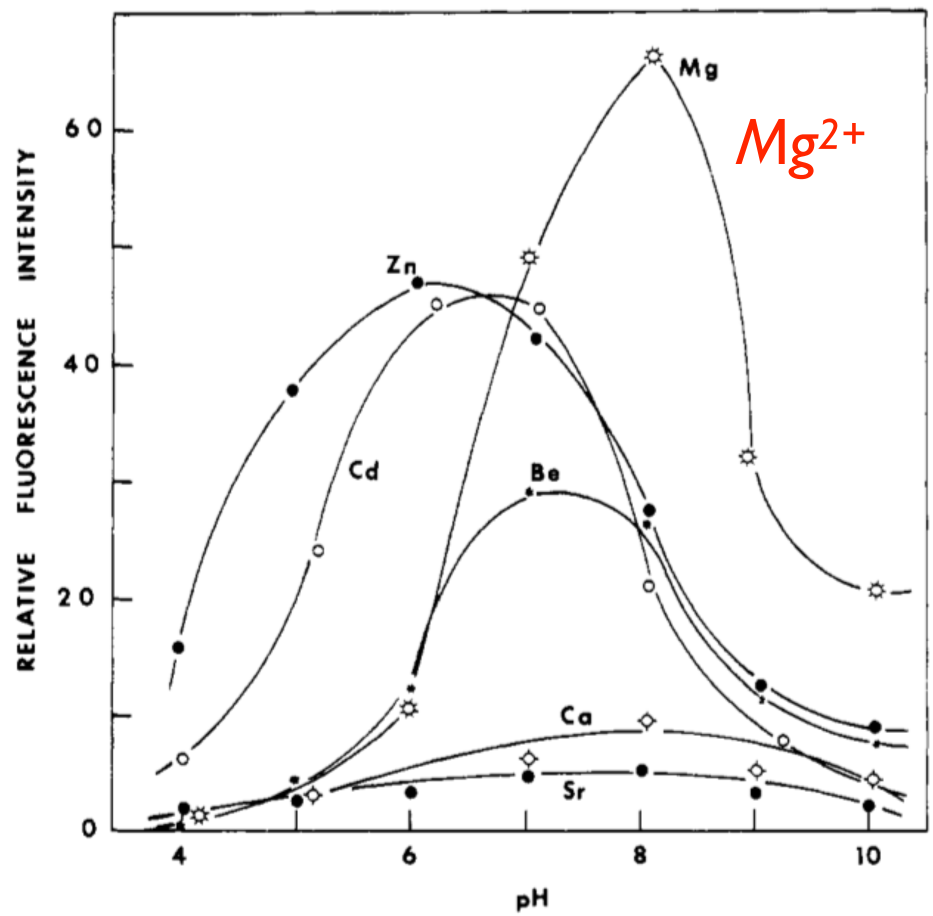
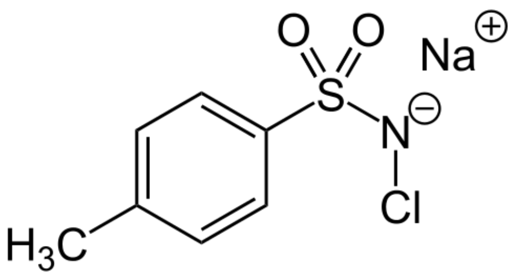


Figure 1. pH dependence of the fluorescnece intensities of group II metal–HQS chelates: Cd, 2 μM; all other metals in this and following figures, 20 μM; HQS, 1 mM.

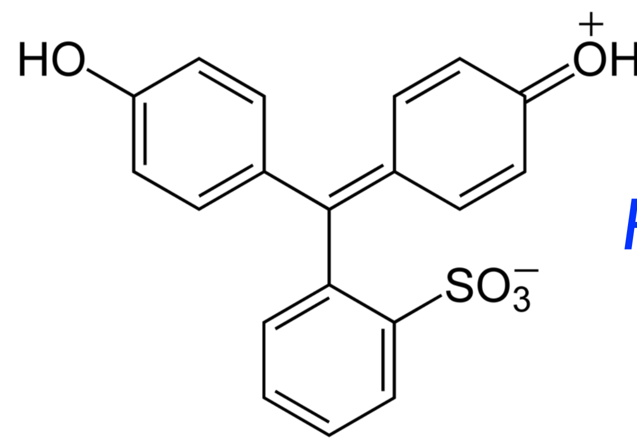
Fluorometric Detection of Mg^{2+} in Seawater

Seawater Analysis Project

Bromide: Bromination of Phenol Red

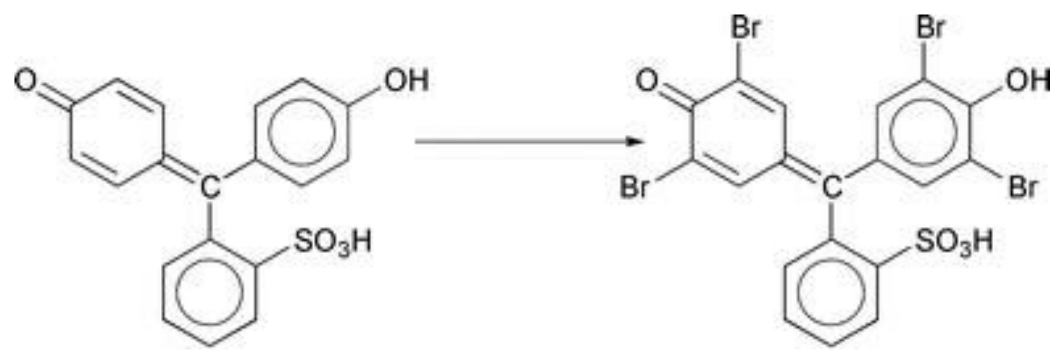


Chloramine T



Phenol Red

HOCl + Br- = HOBr + Cl-



Bromophenol Blue

Seawater Analysis Project

Bromide: Bromination of Phenol Red

Principle: When a sample containing bromide ions (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.