Water hardness tests: Ca^{2+} complexation with EDTA

Determining Ca^{2+} concentration in water

- Calcium and magnesium ions dissolved in water cause water hardness.

- Ethylenediaminetetraacetic acid (EDTA) is commonly used in a titration to determine the concentration of Ca^{2+} and Mg^{2+} ions in water, as both ions form complexes with EDTA.

- For Ca^{2+} analysis, Mg^{2+} must be removed first, usually by precipitation.

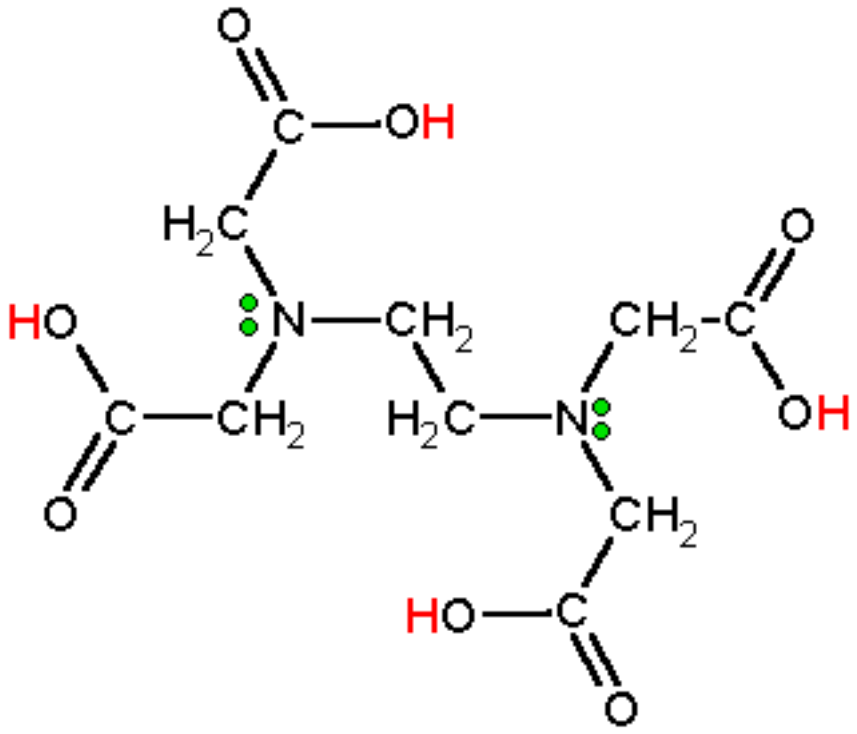
- Titration with EDTA determines the concentration of Ca^{2+}.

- The complex formed between Ca^{2+} and EDTA is colourless and soluble, so a suitable indicator must be used to show the endpoint of the titration.

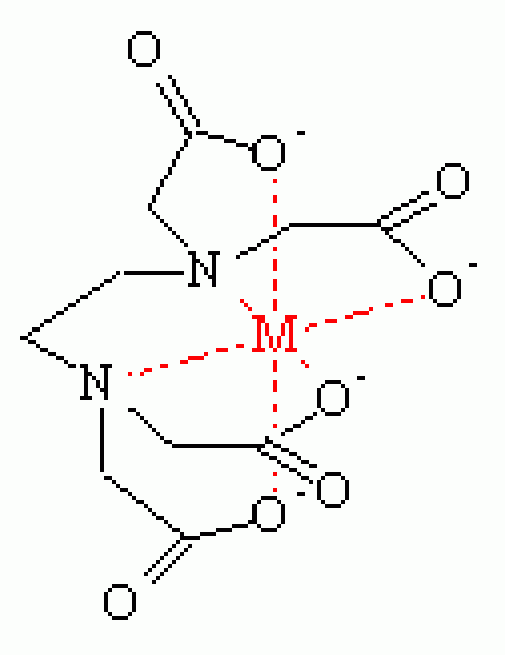
Complexation with EDTA

EDTA = ethylene diamine tetra-acetic acid

Polyprotic acid abbreviated H_4Y. It has five different charged states but only the Y^{4-} state forms stable complexes with metal cations.



Properties of the metal-EDTA complex



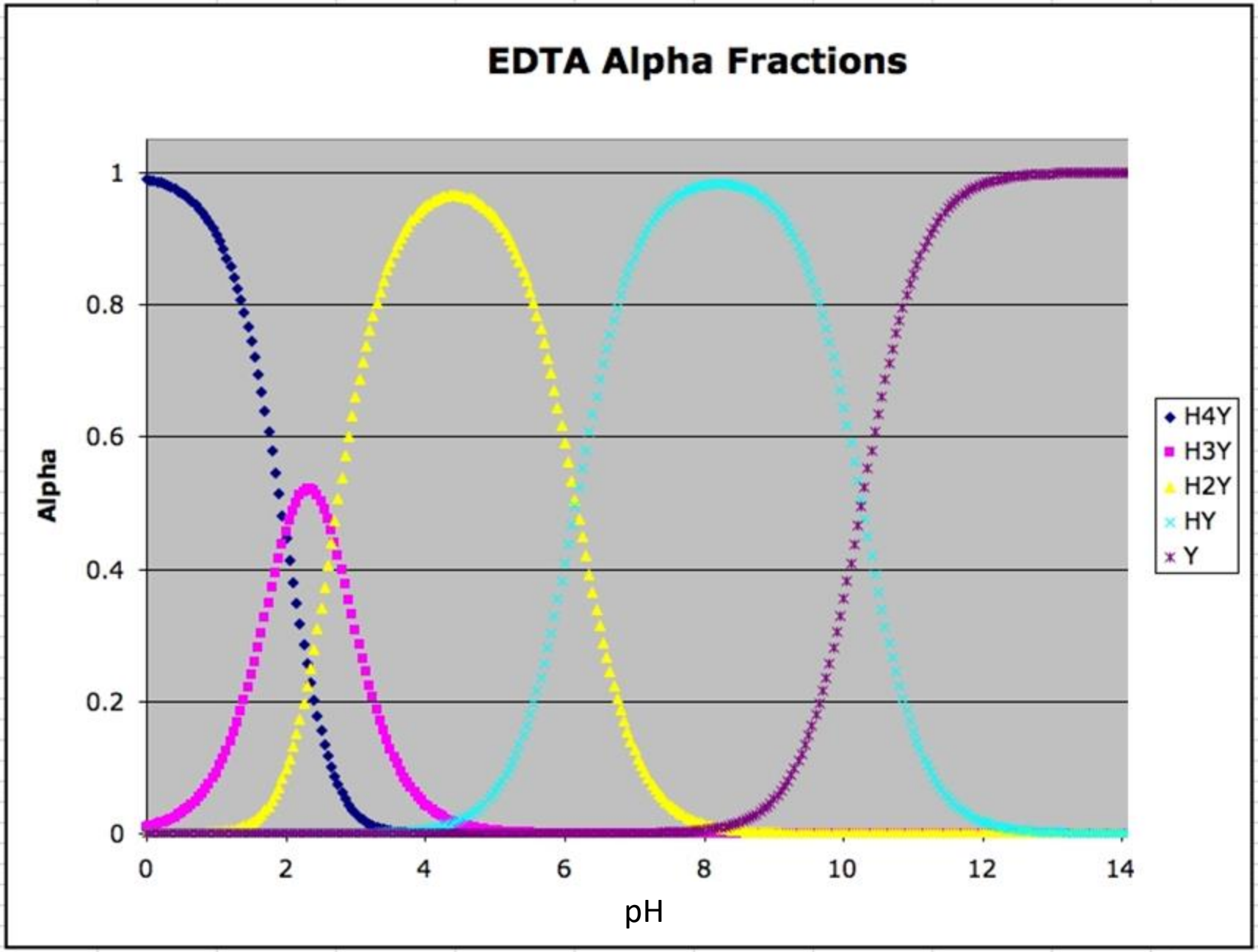
The chelation is “claw” type, with all new rings created by the chelation being 5-membered. The coordination of the metal ion itself is octahedral, with four of the ligands O^- and the other two to the lone pair on the N.

At neutral pH, the dominant form of EDTA in solution is HY^{3-}.

The complexation with calcium ions occurs through the unprotonated form of EDTA, Y^{4-}.

$$Ca^{2+} + Y^{4-} = CaY^{2-}$$

Calcium is determined at pH 12 where magnesium is quantitatively precipitated as the hydroxide and will not react with EDTA.


EDTA Alpha Fractions
Alpha
1
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
12
14
pH
H4Y
H3Y
H2Y
HY
Y

Precipitating the Magnesium Ions.

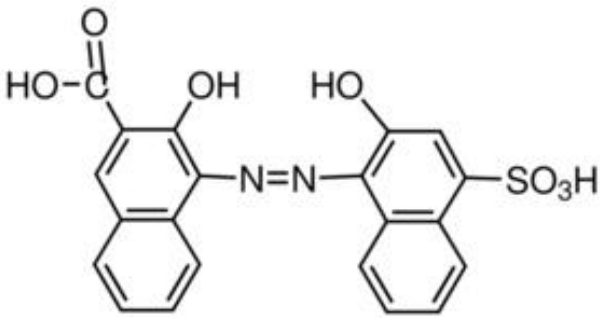
Reagent that will form a precipitate with magnesium but not with calcium.

An aqueous solution of sodium hydroxide can be used to precipitate out the magnesium hydroxide.

	K_{sp}	
	magnesium	**calcium**
carbonate	3.5×10^{-8}	2.8×10^{-9}
oxalate	1.0×10^{-8}	4.0×10^{-9}
fluoride	6.5×10^{-9}	4.0×10^{-11}
hydroxide	1.8×10^{-11}	5.0×10^{-6}

One type of titration

- The burette is filled with an EDTA solution of e.g. 0.010 mol/L.
- Typically 50.00 mL of water sample.
- A drop of indicator added to the water sample. For example, Patton and Reeder's Indicator will be *red* in the hard water sample and *blue* when excess EDTA has been added.



Titration no.	volume of EDTA (mL)
1	8.76 mL
2	8.80 mL
3	8.78 mL

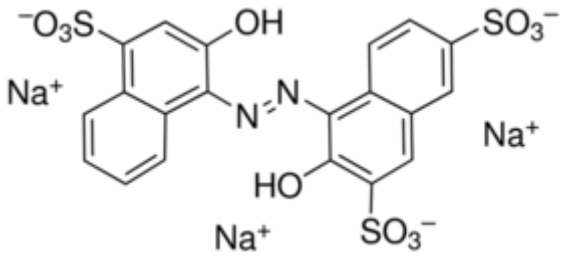
Another type of titration

USDA United States Department of Agriculture
Food Safety and Inspection Service

DETERMINATIVE METHOD

A. INTRODUCTION

1. Theory	Calcium is solubilized by acid hydrolysis forming calcium ion. The resultant hydrolyzate is diluted to a specific volume and an aliquot reacted with excess EDTA in alkaline media in the presence of cyanide and a hydroxy naphthol blue indicator. EDTA readily forms a chelated complex with the calcium ion. Excess EDTA is then titrated with calcium carbonate to a permanent purple end point. If phosphates are present they must be removed by passing an aliquot through an ion exchange column before the final titration steps.
2. Applicability	This procedure is applicable to the determination of calcium or bone in meat and poultry products.



http://www.fsis.usda.gov/wps/wcm/connect/280ccc0e-d197-4991-b7b0-5fcc1ca8e1ec/CLG_CAL.pdf?MOD=AJPERES

Example of calculation

To 50.00 mL of an unknown Ca^{2+} solution, 20.50 mL of a 0.010 M EDTA solution were added including excess EDTA, which was then titrated with 6.20 mL of a 0.0100 M calcium chloride solution.

Calculate the Ca^{2+} concentration of the unknown.

Other question

Would precipitation of Mg^{2+} ions be effective at pH 12, for a 1-L solution containing 500 ppm of $CaCl_2$ and 50 ppm of $MgCl_2$?