Practical/ Analytical chemistry

Analytical chemistry

Analytical chemistry deals with the methods for the identification of one or more of the components in the sample of matter and determination of the relative amount of each. The identification process is called a qualitative analysis while the determination of amount is termed a quantitative analysis.

Application of chemical analysis

Application of chemical analysis found to be in the measurement of parts per million of hydrocarbons, nitrogen oxides, and carbon monoxides…..etc. Also for determination of the concentration of the ionized calcium in blood serum, the nitrogen content of break fast cereals and other foods can be directly related to their protein content and thus their nutritional qualities.

Standard solution

In analytical chemistry, a **standard solution** is a solution containing known concentration of an element or a substance i.e., a known weight of solute is dissolved to make a specific volume.

A simple standard is obtained by the dilution of a single element or a substance in a soluble solvent with which it reacts...

A solution of acid can be standardized by titrating it against a solution of alkali of known concentration. Once this has been calculated, it can in turn be used as a standard solution to find the concentration of a solution of alkali.

A standard solution can be prepared in either of two ways:

1. A primary standard is carefully weighed, dissolved, and diluted accurately to a known volume. Its concentration can be calculated from this data.A solution is made to an approximate concentration and then standardizedby titrating an accurately weighed quantity of a primary standard.

Primary standard properties

1-it must be easily obtained, purified, dried and preserved in pure state.

2-the material should be stable during storage.

3-the material should be neither hygroscopic nor efflorescent.

4- The material should not be affected by light.

5- The material should be pure (99.9%).

6- The material should not affected by O_2 and CO_2.

7- It should be readily water soluble and the condition of the experiment.

8-It should have high equivalence point to reduce weighting error.

9- It should be easily obtained and favorable cheep.

The requirements of a titration are:
1) The reaction between unknown and standard should be stoichiometric.
2) The reaction should be rapid.
3) There should be no side reactions, and the reaction should be specific.
4) There should be a marked change in some property of the solution when the reaction is complete.

5) The reaction should be quantitative which means the reaction should proceed to completion.

Terms to Know

Molarities (for solid) =moles of solute/Liters of solution

Molarities (for liquid) =sp.gr x 1000 x%/M.wt

Normality (for solid) =number of equivalents of solute/Liters of solution

Normality (for liquid) = sp.gr x 1000 x%/eq.wt

Parts per million=weight of solute/weight of solution x10^6

Percentage concentration= 1: weight of solute/weight of solution x100

2: volume of solute/volume of solution x100

3: weight of solute/volume of solution x100

Titration

Titration is the procedure used to determine the concentration of some substance by the controlled addition of a solution into a reaction vessel (flask) from a burette. By using titration, the volume of the solution delivered from the burette may be determined very precisely.

Indicator

An indicator is a substance used to signal when a titration reaches the point at which the reactants are stoic chimerically equal as defined by the balance reaction equation. For example in the acid-base titration between sodium hydroxide and hydrochloric acid.

$$NaOH_{(aq)} + HCl_{(aq)} ---> H_2O_{(l)} + NaCl_{(aq)}$$
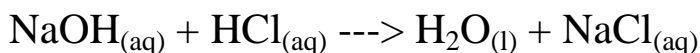
The indicator should tell when the number of moles of NaOH and HCl are exactly equal, matching the 1:1 ratio in the equation.

End Point

End point is the point at which the indicator changes color.

Our indicator, phenolphthalein changes from colorless to pink at the end point.

Equivalence Point

The equivalence point is the point in the titration in which enough standard solution has been added to react exactly with the substance being determined. The reactants are mixed in exact molar proportions represented by the balanced equation.

You should pick an indicator that has an end point that is the same as the equivalence point.

Standardizing or standardization

The process used to determine the concentration of a solution with very high accuracy is called **standardizing** a solution.

Reading the Burette
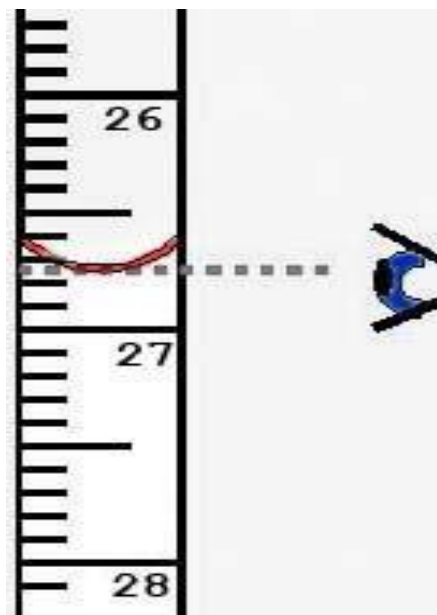
1. Make sure your eye is level with the bottom of the meniscus.

2. Read the volume to the nearest 0.01 ml by reading between the lines. The burette is marked off in 0.1 ml so you must estimate the uncertain digit.

3. Read the burette from top (0.00 ml) to bottom (50.00 ml)

4. Burette read 26.75 ml

5. Volume used = final - initial.

EXP.NO. (1)

Preparation and Standardization of (~0.01N HCl)
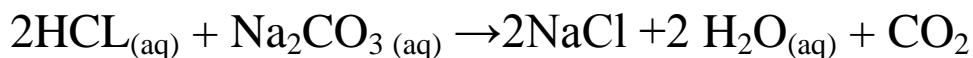
$$2HCL_{(aq)} + Na_2CO_{3\ (aq)} \rightarrow 2NaCl + 2\ H_2O_{(aq)} + CO_2$$

A-Preparation of ~0.010N HCl

1- Calculate the normality of the concentrated HCl (Normality forliquid) = sp.gr x 1000 x%/eq.wt

2 – Prepare~0.01NHCl (250ml) from the concentrated solution usingdilution law $N_1V_1=N_2V_2$

3 –Add about 50 ml of distilled water to the volumetric flask then add the concentrated HCl, mix it well and store it in a stopper bottle.

B-Preparation of standard 0.010N Na₂CO₃:

1 – Prepare0.01N **Na₂CO₃** (250ml) using

Normality (for solid) =number of equivalents of solute/Liters of solution(wt)g **Na₂CO₃** = Nx eq.wt xV/1000
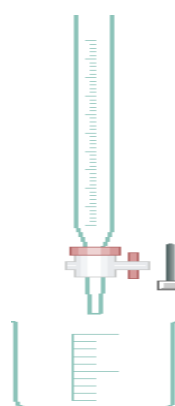
~ 0.01N HCl

10ml
(0.01NNa2CO3)

2-3drop indicator M.O

Titrating

Calculating the Normality of your HCl Solution

Once your titration is complete, you can calculate the normality of your HClsolution using the following equation:

$NxV_{(HCl)} = NxV$ (Na2C03)

$N_{HCl} = x$ eq/l or meq/ml

These types of titration are normally carried out in aqueous media and have applications in a variety of industries.
Common examples of being:

      1- Alkalinity of river, process and drinking water.2- Boric acid in cooling water.
      3- Acidity in soft "cola" type drinks.4- Acidity of Fruit Juices.

EXP. NO. (2)

PREPARATION and STANDARDIZATION of (~0.01N NaOH)

$HCL_{(aq)} + NaOH_{(aq)} \rightarrow NaCl + 2\,H_2O_{(aq)}$
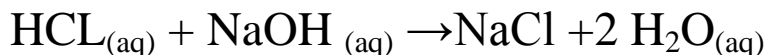
Why not use NaOH as the primary standard?

Why can't you weigh solid NaOH on the balance, dissolve and dilute it accurately to a known volume and then calculate its concentration from the data?

Solid NaOH has the property of absorbing water from the air so it is not possible to accurately weigh NaOH. Sodium hydroxide is unsuitable as aprimary standard because of this property.

A-Preparation of ~0.010N HCl

1- Calculate the normality of the concentrated HCl (Normality (for liquid) = sp.gr x 1000 x%/eq.wt

2 – Prepare~0.01NHCl (250ml) from the concentrated solution

usingdilution law $N_1V_1 = N_2V_2$

3 - Add about 50 ml of distilled water to the volumetric flask thenadd the conc. HCl, mix it well and store it in a stoppered bottle.

4- standarize the HCl with standard (Na_2CO_3).

B-Preparation of ~0.010N NaOH

1 – Prepare ~0.01N **NaOH** (250ml) using

Normality (for solid) =number of equivalents of solute/Liters of

solution(wt) g **NaOH** = Nx eq.wt xV/1000

Add about x g of NaOH pellets weighed <u>on an watch glass</u>, mix it well and store it in a rubber Stoppered bottle. (<u>Caution : NaOH is very corrosive, do not spill and if you do, wash it off immediately with an excess of water.</u>)

Titrating

1- Standardization of HCI

2- Standardization of ~0.10M NaOH

NV(HCl)=NV(NaOH)
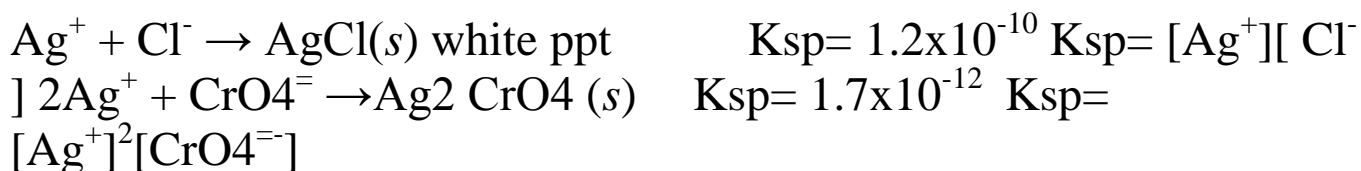NNaOH=xeq/l or meq/ml

standard HCl

~0.10M NaOH
+2-3drop indicatorPh.Ph

EXP.NO. (3)

Precipitation Titration
Determination of Chloride by the Mohr
Method

Introduction

Precipitation titrations are based upon reactions that yield ionic compounds of limited solubility. The most important precipitating reagent is silver nitrate. Titrimetric methods based upon silver nitrate are sometimes termed argent metric methods. Potassium chromate can serve as an end point indicator for the argent metric determination of chloride, bromide. The Mohr method uses chromate ions as an indicator in the titration of chloride ions with a silver nitrate standard solution. After all the chloride has been precipitated as white silver chloride, the first excess of titrant results in the formation of a silver chromate precipitate, which signals the end point. The reactions are:

$Ag^+ + Cl^- \rightarrow AgCl(s)$ white ppt $Ksp = 1.2 \times 10^{-10}$ $Ksp = [Ag^+][Cl^-]$ $2Ag^+ + CrO4^= \rightarrow Ag2\,CrO4\,(s)$ $Ksp = 1.7 \times 10^{-12}$ $Ksp = [Ag^+]^2[CrO4^{=-}]$

By knowing the stoichiometry and moles consumed at the end point, the amount of Chloride in an unknown sample can be determined.

Materials and Methods

Methods:

Preparation of 5% K2CrO4 (indicator): 1.0 g of K2CrO4 was

dissolved in 20 ml of distilled water.

Preparation of AgNO3 solution: (wt)g *AgNO3* = Nx eq.wt xV/1000

0.01N AgNO3

Preparation of NaCl solution: (wt)g **NaCl** = Nx eq.wt xV/1000

Standardization of AgNO3 (light reduce Ag$^+$ to Ag black ppt)

V_1= ml of **AgNO3 react with NaCl** and

indicator V_b = ml of **AgNO3 react with**

indicator

In a blank determination, all steps of the analysis are performed in the absence of the analyte.

$N \times V_{(NaCl)} = N \times (V_1 - v_b) \textbf{AgNO3}$

$N_{\textbf{AgNO3}} = x eq/L$ or meq/ml

Determination of Cl^- ***in solid sample (*Unknown):**

Titrate 10ml of Unknown with Standardized $AgNO_3$

$N \times V_{(NaCl)} = N \times (V_2 - v_b) \textbf{AgNO3}$

$N_{(NaCl)} = x$ eq /l

*The titration was carried out at a pH between 7 and 10 because chromate ion is the conjugate base of the weak chromic acid (2, 3). Therefore, when the pH is lower than 7, chromate ion is protonated and the chromic acid form predominates in the solution.

$$2H^+ + CrO_4^{=} \rightarrow 2HCrO^{4-} \leftrightarrow Cr_2 O_{7\ orange}^{=} + 2H_2 O$$
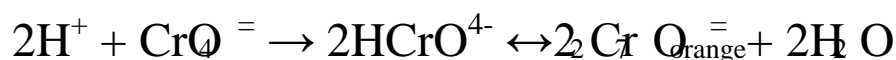
* In more acidic solutions the chromate ion concentration is too low to produce the precipitate at the equivalence point. If the pH is above 10, brownish silver hydroxide forms and masks the endpoint.

$$Ag^+ + OH^- \rightarrow AgOH \text{ brownish}$$

* Since the solubility's of silver chloride and silver chromate depend on temperature, all titrations were carried out at about the same temperature.

* Good stirring during the addition of the silver nitrate is also required for a sharp and reproducible end point.

* The silver chloride precipitates formed were protected from light at all times because silver chloride decomposes according to

$$AgCl \longrightarrow Ag(s) + \tfrac{1}{2} Cl (g$$
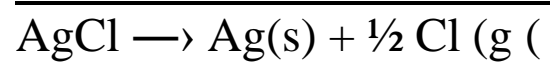
EXP.NO. (4)

A Redox titration

Determination of Iron by reaction with Permanganate

Potassium permanganate, KMnO4, is widely used as an oxidizing agent in volumetric analysis. A common task in analytical chemistry is the determination of the amount of a substance present in a sample or product. If the product contains a substance that can be oxidized, then it is possible to determine the number of moles of that substance by titrating the sample with a solution of a strong oxidizing agent. In this lab, a solution of an oxidizing agent will first be standardized and then used to determine the number of moles of iron, a reducing agent.
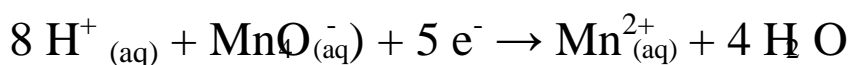
Standardize MnO_4^- with oxalic acid:
$$5H_2C_2O_4 + 2\ MnO_4^- + 6H^+ \;\square\; 10CO_2 + 2Mn^{2+} + 8H_2O$$

Redox titration:
$$5Fe^{2+} + MnO_4^- + 8H^+ \;\square\; 5Fe^{3+} + Mn^{2+} + 4H_2O$$

In acid solution, MnO^{4-} ion undergoes reduction to Mn^{2+} as shown in the following equation:

$$8\ H^+_{(aq)} + MnO_{4(aq)}^- + 5\ e^- \rightarrow Mn^{2+}_{(aq)} + 4\ H_2O$$

Since the MnO_4^- ion is violet and the Mn^{2+} ion is nearly colorless, the end point in titration using $KmnO_4$ as the tyrant can be taken as the first permanent pink color that appears in the solution.
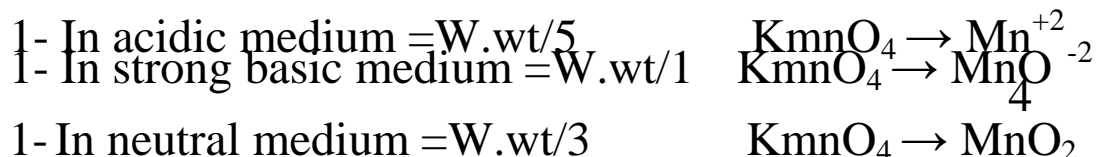
●$KMnO_4$ will be employed in this experiment to determine the percentage of iron in an unknown containing iron (II) ammonium sulfate,

$Fe\ (NH_4)_2(SO)_2 * 6H_2O.$

●The titration, which involves the oxidation of Fe^{2+} ion to Fe^{3+} by permanganate ion, is carried out in sulfuric acid solution to prevent the airoxidation of Fe^{2+}.

●The end point of the titration is sharpened markedly if phosphoric acid ispresent, because Fe^{3+} ion produced in the titration forms an essentially

colorless complex with the acid.

●Since potassium permanganate is very reactive; solutions containing this ionmust be standardized using a known primary standard before they are used.
●The eq. Wt. of KmnO$_4$:

1- In acidic medium =W.wt/5 $KmnO_4 \rightarrow Mn^{+2}$
1- In strong basic medium =W.wt/1 $KmnO_4 \rightarrow MnO_4^{-2}$
1- In neutral medium =W.wt/3 $KmnO_4 \rightarrow MnO_2$

Procedure:

1- Standardization of Permanganate Solution
In the first part of this experiment, you must standardize ~ 0.01NKMnO4, the permanganate solution (approximately 0.010) using   C2O4⁼(10ml) 1ml H$_2$SO$_4$, and acidified solution of ferrous ammonium sulfate hexa hydrate,
$FeSO_4 (NH_4)_2 SO_4 6H_2O$..
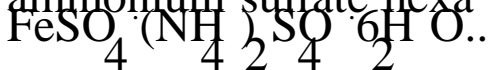
2- Determination of Iron Content in Unknown
Titrate to the end point which may be more difficult to observe depending onthe color of the pill.

standardKMnO4

Fe^{+2}(10ml)

1mlH$_2$SO$_4$+1ml
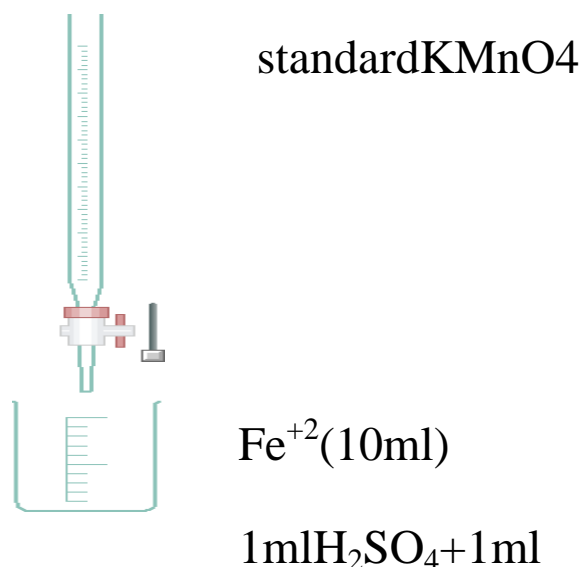
H3P

Analysis:

Show the following calculations:

Standardization

1.   Calculate the concentration of the permanganate solution.

Percent mass determination

1. Calculate the moles of permanganate reacted.

2. Relate moles of permanganate to Fe^{2+}.

3. Calculate grams of Fe^{2+}.

4. Calculate percent mass of iron in unknown ore sample.
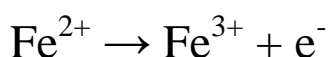
EXP. NO. (5)

Redox titration
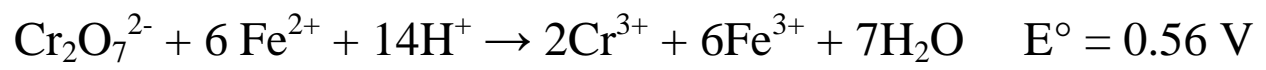## Determination of iron using potassium dichromate

Theory:

As an oxidant, dichromate has some advantages over permanganate, but, as it is less powerful, its use is much more limited. It is obtainable in a state of highpurity and can be used as a primary standard. Solutions of dichromate in waterare stable indefinitely. The half reaction for the dichromate system is:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

the most important application of dichromate is in its reaction with iron (II) inwhich it is often preferred to permanganate.
The relevant half reaction is:

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$
and the total reaction is:

$$Cr_2O_7^{2-} + 6\ Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \quad E° = 0.56\ V$$

Unlike permanganate, dichromate titrations require an indicator. There are three indicators that may be used for the titration of Fe^{2+} with $K_2Cr_2O_7$. These are diphenylamine, diphenyl Benzedrine and diphenylamine sulfonate. The colors change for all three indicators is green to violet .In this case, phosphoric acid is added to reduce the electrode potential for the $Fe^{3+} \rightarrow Fe^{2+}$ reaction by stabilizing the ferric ion.

Method:

1- Prepare a standard dichromate solution.

2- Transfer(10ml) of the iron(II) Into flasks accurately ,add 3 cm3 of dil. sulfuric acid, 10 cm3 of water, 2 cm3 of 85% phosphoric acid and 5 drops of diphenylamine sulfonate indicator. Titrate with dichromate to a purple colour. Calculate the percentage of iron in the solid.

- **Iron is one of the most frequently encountered elements in industrialanalyses. Potassium dichromate is an excellent oxidizing agent for iron
(II) since:**

1. Dichromate and iron (II) react quantitatively and with a known stoichiometry

2. The reaction is sufficiently fast to be practical for a titration.

3. The .E is large enough to produce a well-defined endpoint

4. Potassium dichromate is a primary standard; it can be purchased as a highpurity solid.

5. Standard solutions of potassium dichromate can be prepared from aweighed quantity of the dried solid and need not be standardized.

6. The prepared solutions are very stable.

EXP.NO. (6)

Complexo metric Titration

Determination of Water Hardness by Complexo metric Titration

Hard Water

Hard water is due to metal ions (minerals) that are dissolved in the ground
water. These minerals include Ca^{2+}, Mg^{2+}, Fe^{3+}_4, SO_4^{2-}, and HCO_3^-. Our hard
water is due to rain moving through the vast amount of limestone, $CaCO_3$ that occurs in our area to the aquifer. This is why we measure hardness in terms of $CaCO_3$. The concentration of the Ca^{2+} ions is greater than the concentration of any other metal ion in our water.

Why Be Concerned About Hard Water?

The determination of water hardness is a useful test that provides a measure of quality of water for households and industrial uses. Originally, water hardness was defined as the measure of the capacity of the water to precipitate soap. Hard water is not a health hazard. People regularly take calcium supplements. Drinking hard water contributes a small amount of calcium and magnesium toward the total human dietary needs of calcium and magnesium. The National Academy of Science states that consuming extremely hard water could be a major contributor of calcium and magnesium to the diet.

Hard water does cause soap scum, clog pipes and clog boilers.

Soap scum is formed when the calcium ion binds with the soap. This causes an insoluble compound that precipitates to form the scum you see. Soap actually softens hard water by removing the Ca^{2+} ions from the water.

When hard water is heated, $CaCO_3$ precipitates out; this then clogs

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pipes and industrial boilers. This leads to malfunction or damage and is expensive to remove.

Water Softeners

If you have hard water you may use a water softener to remove the hardness. Salt is mixed with water. The Na^+ ion from the salt replaces the Ca^{2+} ion, but

this causes the water to be too salty for drinking. Water that has been softenedshould be used only for laundry and bathing.

Types of Hardness

There are two types of water hardness, temporary and permanent.

Temporary Hardness is due to the bicarbonate $_3^-$, being present in ion, HCO
the water. This type of hardness can be removed by boiling the water to expelthe CO_2, as indicated by the following equation:

$$HCO_3^- \rightleftharpoons H_2O + CO_{2\,(g)}$$
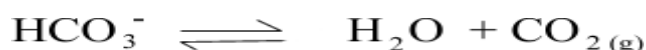
Bicarbonate hardness is classified as *temporary hardness*.

Permanent hardness is due to the presence of the ions Ca^{2+}, Mg^{+2}, Fe^{3+} and
SO_4^-. This type of hardness cannot be eliminated by boiling. The water with
this type of hardness is said to be *permanently hard*.

How Hard Is The Water?

The degree of hardness of the water is classified in terms of its calciumcarbonate concentration as follows:

Hardness rating	Concentration of Calcium Carbonate (mg/L)	Concentration of Calcium Carbonate (grains/US gallon)
Soft	0 to <75	0 to <5.2
Medium hard	75 to <150	5.2 to <10.5

|		
Hard	150 to <300	10.5 to <21
Very hard	300 and greater	21 and greater

Complexo metric Titration

Permanent hardness is usually determined by titrating it with a standard solution of ethylene diamin tetra acetic acid, EDTA. The EDTA is a complexing, or chelating agent used to capture the metal ions. This causes the water to become softened, but the metal ions are not removed from the water. EDTA simply binds the metal ions to it very tightly.

EDTA

EDTA is a versatile chelating agent. A **chelating agent** is a substance whose molecules can form several bonds to a single metal ion. Chelating agents are **multi-dentate ligands**. A **ligand** is a substance that binds with a metal ion to form a complex ion. **Multidentate ligands** are many clawed, holding onto the metal ion to form a very stable complex. EDTA can form four or six bonds with a metal ion.
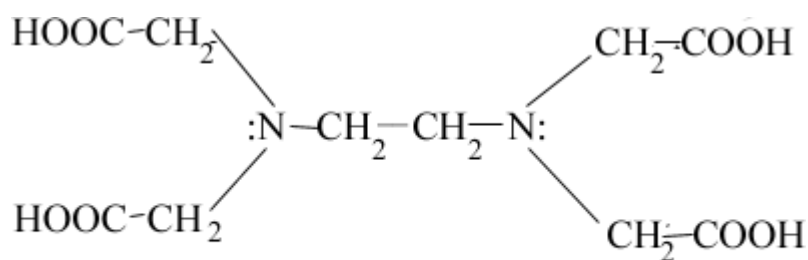
structure of EDTA

■ It is frequently used in soaps and detergents because it forms complexes with calcium and magnesium ions. These ions which are in hard water are bound to the EDTA and cannot interfere with the cleaning action of the soap or detergent.

■ EDTA is also used in foods. Certain enzymes are responsible for food spoilage. EDTA is used to remove metal ions from these enzymes.

■ It is used to promote color retention in dried bananas, beans, chick peas, canned clams, pecan pie filling, frozen potatoes and canned shrimp.

■ It is used to improve flavor retention in canned carbonated beverages, beer,salad dressings, mayonnaise, margarine, and sauces.

■ It inhibits rancidity in salad dressings, mayonnaise, sauces and saladspreads.

Why Do We Heat the Water?

We heat the water to make sure all the calcium ions and other metal ions are dissolved in the water. If they are not dissolved in the water, the indicator cannot form a complex with them and your end point will not be the true end point of the titration.

Total Permanent Hardness

In this lab you will be asked to determine the total permanent hardness. EDTA grabs all the metal ions in the water, not just the Ca^{2+} ions. This gives us a value that is not truly the concentration of Ca^{2+} ions. This causes an experimental error of about 1% which is acceptable due to the "fuzzy" endpoints in this type of titration.
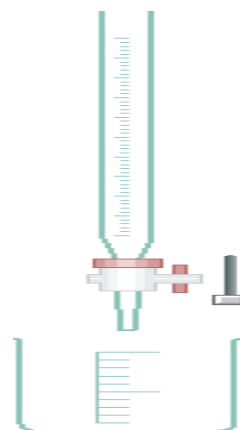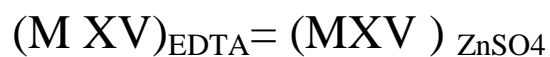
Erio - T Indicator
EDTA ENDPOINT COLOR CHANGE

Erio - T indicator or Eriochrome Black-T indicator is used in this titration. When it is chelated or acidifies, it produces a **PINK RED** solution. When it is not chelated and under basic conditions it is **BLUE**.
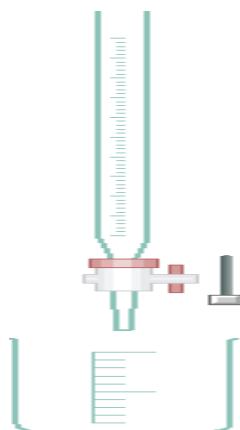
Procedure:

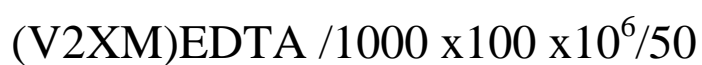1- Prepare approximate 0.01MEDTA.2- Prepare 0.01M ZnSO4.

3- Standardization of EDTA.

EDTA

5ml Zn^{+2}
0.2gm EBT
40ml H_2O
2ml PH10

$$(M \times V)_{EDTA} = (M \times V)_{ZnSO4}$$

Determination of total hardness

EDTA

50ml tap water
0.2gm EBT
2ml PH10

$$(V_2 \times M)_{EDTA} / 1000 \times 100 \times 10^6 / 50$$

Determination of permanent hardness

Boil (250ml) of tap water in a beaker and boil it at for 30-45 min, cool and filter it. Complete the volume with distilled water to 250ml. Use the same procedure of total hardness.

Temporary hardness = total hardness-permanent hardness

Sample Problem

You are using EDTA with a molarity of .0080 for the titration. You titrate
50.00 ml of water sample using 10.68 m of EDTA.

What is the CONCENTRATION of Ca^{2+} ion?

$$\frac{moles\ Ca^{2+}ion}{1\ L} = \frac{(molarity\ EDTA)\ (mL\ EDTA\ added)}{50.00\ mL\ of\ water\ sample\ titrated}$$

$$\frac{moles\ Ca^{2+}ion}{1\ L} = \frac{(.0080\ M)\ (10.68\ mL)}{50.00\ mL\ water} = .0017\ M$$

What is the hardness?

$$ppm\ CaCO_3 = \frac{(mol\ Ca^{2+})\ (1\ mol\ CaCO_3)\ (100.1\ g\ CaCO_3)\ (10^3\ mg)}{(1\ L)\quad (1\ mol\ Ca^{2+})\quad (1\ mol\ CaCO_3)\quad (1\ g)}$$

$$ppm\ CaCO = \frac{(.0017\ moles)(1\ mol\ CaCO_3)(100.1\ g\ CaCO_3)(10^3\ mg)}{(1\ L)\ (1\ mol\ Ca^{2+})(1\ mol\ CaCO_3)(1\ g)} = 170\ ppm$$

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