

Volumetric (Titrimetric) analysis

Volumetric analysis (or Quantitative chemical analysis) is determination the volume of a solution of accurately known concentration, which is required to react quantitatively with the solution of the substance being determined.

* The solution of accurately known strength is called the "**standard solution**". *The standard solution is usually added from a graduated vessel called a "**burette**"

* The process of adding the standard solution until the reaction is just complete is termed a "**titration**".

*The reagent of known concentration is called the "**titrant**" and the substance being titrated is termed the "**titrate**".

***Equivalent point** is the point in a titration where the amount of standard titrant added is chemically equivalent to the amount of analyte in sample.

***End point** is the point in a titration when an observable change that signals that the amount titrant added is chemically equivalent to the amount of analyte in sample.

***Indicator** is a reagent used to indicate when the end point has been reached.

* A primary standard is a highly purified compound that serve as a reference material in all volumetric titrimetric methods.

Important requirements for a primary standard are :

1. High purify.
2. Stability toward air.

3. Absence of hydrate water.
4. Ready availability at modest cost.
5. Reasonable solubility in the titration medium.
6. Reasonable large molar mass so that the relative error associated with weighing the standard is minimized.

Volumetric(titrimetric)analysis reaction must fulfill the following conditions:

1. There must be a simple reaction which can be expressed by a chemical equation and the substance to be determined should react completely with the reagent.
2. The reaction should be proceeding with very great speed.
3. An indicator should be available.
4. Equilibrium constant must be very large.



The following are required for volumetric analysis:

1. Calibrated measuring vessels, including burettes, pipettes, and measuring flasks.
2. Substances of known purity for the preparation of standard solution.
3. A visual indicator or an instrumental method detecting the completion of the reaction.

Classification of reactions in volumetric (titrimetric) analysis:

1. Neutralisation reaction or acidimetric and alkalimetric .(reaction between base and acid).

2. Complex formation reaction (Ions or compound combination to form stable-soluble slightly dissociated ion or compound).
3. Precipitation reactions.(form a simple precipitate).
4. Oxidation-reduction reactions (include all reactions involving change in oxidation number or transfer of electrons among the reaction substances).

Calculations of volumetric analysis:

Standard solution is one, which contains a known weight of the reagent in a definite volume of the solution.

Molar solution is one, which contains 1 gm molecular weight of the reagent per liter of solution.

$$M = \frac{\text{Weight}}{M.Wt} * \frac{1000}{\text{volume}(ml)}$$

Normal solution is one that contains 1 gm equivalent weight per liter of solution.

$$N = \frac{\text{Weight}}{eq.Wt} * \frac{1000}{\text{volume}(ml)}$$

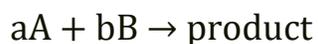
Part per million(ppm): Milligrams of solute per liter of solution.

$$ppm = \frac{\text{weight solute (mg)}}{\text{volume solution}(l)}$$

$$ppm = \frac{wt(g)}{V(ml)} * 10^6$$

$$ppm = M * M. wt * 1000$$

For titrimetric reaction:



titrant titrant

at equivalent point:

no.mmol of titrant(A) = no.mmol of titrant(B)

$$N_A * V_A = N_B * V_B$$

or
$$M_A * V_A * R = M_B * V_B \quad \left(R = \frac{b}{a} \right)$$

Equivalent weights

1. Equivalent weight in neutralization reactions.

The equivalent weight of acid is that weight of it which contains one-gram atom of replaceable hydrogen.

Ex:

equivalent weight of $H_2SO_4 = M. Wt H_2SO_4 / 2$

equivalent weight of $H_3PO_4 = M. Wt H_3PO_4 / 3$

$$eq. wt\ acid = \frac{M. Wt\ acid}{No. of\ active\ OH^+}$$

The equivalent weight of Base is that weight of it which contains one replaceable hydroxyl group.

Ex: equivalent weight of NaOH = M.Wt NaOH/1

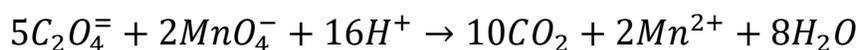
$$eq. wt\ acid = \frac{M. Wt\ base}{No. of\ active\ OH^-}$$

2. Equivalent weight in Oxidation -reduction reactions.

The equivalent weight of an oxidant or a reductant is the number of electrons which 1mol of the substance gains or loses in the reaction.

$$eq. wt = \frac{formula\ weight\ \left(\frac{gm}{mole}\right)}{No. of\ lost\ or\ gained\ electrons}$$

Ex:

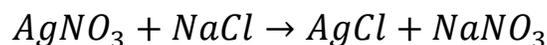


$$eq. wt\ MnO_4^- = \frac{f. wt\ MnO_4^-}{5} \qquad eq. wt\ C_2O_4^{2-} = \frac{f. wt\ C_2O_4^{2-}}{2}$$

3. Equivalent weight of complex formation and precipitation reactions.

Here the equivalent weight is the weight of the substance which contains or reacts with 1g. atm of a univalent cation M^+ .

Ex: When silver nitrate reacts with sodium chloride, to form silver chloride, the equivalent weight of $AgNO_3$ is:



$$eq. wt(AgNO_3) = \frac{f. wt AgNO_3}{1}$$

Experiment (1)

A: Preparation of approximately (0.1N) HCl

1. Calculate the normality of the concentrated HCl :

$$N = \frac{Sp. g * percentage * 1000}{equivalent weight}$$

$$N = \frac{1.19 * (37/100) * 1000}{36.5} = 12.0630$$

2. To prepare (500mL) Of 0.1N HCL:

$$N_1 * V_1 = N_2 * V_2$$

$$con. HCl \quad dil. HCl$$

Transfer distilled water to a glass-Stoppard bottle and add about 4.14 mL of conc.HCl. Mix the contents of the bottle thoroughly. Dilute to the mark with

distilled water and make a label.

B: Preparation of (0.1N) sodium carbonate:

1. Dry a quantity of primary-standard sodium carbonate for 2 hours at 110 °C, cool in a desiccator Weigh 1.325gm of the salt into a small beaker, and dissolve in 25 to 50 mL of distilled water.

2. Transfer this solution to a 250mL volumetric flask. Wash the beaker and transfer this washing water to the volumetric flask. Dilute to the mark with distilled water and mix thoroughly. Make a label.

$$N = \frac{\text{Weight}}{\text{equivalent weight}} * \frac{1000}{\text{Volume(mL)}}$$

Experiment (2)

Standardization of HCl solution with standard solution of Na₂CO₃

1. Clean the burette and rinse with HCl solution.
2. Fill the burette with HCl.
3. Pipet 10mL of standard solution(Na₂CO₃) into a 250mL conical flask. Add 3 drops of Methyl orange indicator.
4. Titrate by adding HCl drop wise until the solution just begins to change from yellow to red.
5. Repeat the titration a few times until you get approximate results. Take the average of the results and subtract 0.05mL. (This result represents the volume of extra drop which changes the color of indicator.)
6. Calculate the normality of HCl :

$$N_{\text{acid}} * V_{\text{acid}} = N_{\text{base}} * V_{\text{base}}$$

7. Make label.

Experiment (3)

Analysis of a mixture (sodium hydroxide + sodium carbonate)

1. Transfer a (10mL) of a mixture solution to 250 mL conical flask and add 1 drop of phenolphthalein indicator.
2. Clean the burette and rinse with hydrochloric acid.
3. Fill the burette with HCl.
4. Titrate with standard hydrochloric acid solution until the pink color disappears (the solution will be colorless).

* At this stage: all the hydroxide and half the carbonate have been neutralized. Let us assume that the volume of acid be "X" mL.

5. Now add 3drops of Methyl Orange indicator into the solution above and continue the titration until the solution just begins to change from yellow to red.

* At this stage :another half of carbonate has been neutralized. Let the volume of acid be "Y" mL.

6. Repeat the titration a few times until you get approximate results.

Calculations:

$$(X-Y)=Z \rightarrow \text{Volume of HCl which equivalent to OH} \dots\dots(1)$$

$$2*Y \rightarrow \text{Volume of HCl which equivalent to } CO_3^{=} \dots\dots\dots(2)$$

$$N_{\text{acid}} * V_{\text{acid}} = N_{\text{base}} * V_{\text{base}}$$

$$N_{\text{acid}} * Z = N_{\text{OH}} * 10 \dots\dots(1)$$

$$N_{\text{acid}} * 2Y = N_{\text{CO}_3} * 10 \dots\dots(2)$$

$$\text{Concentration of } [OH]_{(\text{ppm})} = N_{\text{OH}} * \text{eq.wt} * 1000$$

$$\text{Concentration of } [CO_3]_{(\text{ppm})} = N_{\text{CO}_3} * \text{eq.wt} * 1000$$

Experiment (4)

Analysis of a mixture (sodium bicarbonate + sodium carbonate)

1. Repeat the same steps of the experiment no.3.
2. Volume of acid at the end point of Ph.Ph indicator=X.
3. Volume of acid at the end point of M.O indicator=Y.

$$X = \text{Volume of HCl} = 1/2 \text{CO}_3^{2-}$$

$$Y = \text{Volume of HCl} = 1/2 \text{CO}_3^{2-} + \text{HCO}_3^{-}$$

$$(Y-X)=Z \rightarrow \text{Volume of HCl which equivalent to } \text{HCO}_3^{-} \dots\dots\dots (1)$$

$$2*X \text{ Volume of HCl which equivalent to } \text{CO}_3^{2-} \dots\dots\dots (2)$$

$$N_{\text{acid}} * V_{\text{acid}} = N_{\text{base}} * V_{\text{base}}$$

$$N_{\text{acid}} * Z = N_{\text{HCO}_3^{-}} * 10 \dots\dots\dots (1)$$

$$N_{\text{acid}} * 2X = N_{\text{CO}_3^{2-}} * 10 \dots\dots\dots (2)$$

$$\text{Concentration of } [\text{HCO}_3^{-}]_{(\text{ppm})} = N_{\text{HCO}_3^{-}} * \text{eq.wt} * 1000$$

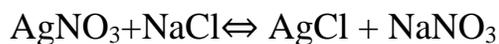
$$\text{Concentration of } [\text{CO}_3^{2-}]_{(\text{ppm})} = N_{\text{CO}_3^{2-}} * \text{eq.wt} * 1000$$

Experiment (5)

Determination of chloride ion by Mohr method

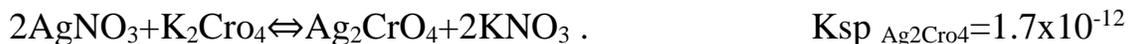
Precipitation titration: is titration depend upon the combination of ions to form a simple precipitate. Mohr method is a method depend upon formation a colored precipitate for the determination of chloride ion.

Chloride ion is reacted with silver nitrate solution to form AgCl precipitate.



$$K_{\text{sp}} \text{AgCl} = 1.2 \times 10^{-10}$$

A small quantity of potassium chromate (K_2CrO_4) solution is added to serve as indicator. The first excess of titrant results in the formation of a red silver chromate precipitate which signal the end point.



Procedure:

1. Clean the burette and fill it with silver nitrate(0.1N).
2. Pipet 10mL of chloride ion solution into 250mL conical flask, add 5drops of potassium chromate.
3. Titrate chloride solution against silver nitrate until arrive to equivalent point(the point in which the number of moles of $AgNO_3$ equal to the number of moles of chloride ion)[Notice a white precipitate in the yellow solution] After this point the excess of $AgNO_3$ will react with potassium chromate leading to formation of red precipitate Ag_2CrO_4 (the end point). The difference between equivalent and end point is the volume of $AgNO_3$ reacted with the indicator.
4. Repeat the titration and calculate the average and subtract the indicator blank(equal to 0.1mL).Calculate the normality.

$$N_{cl}^- * V_{cl}^- = N_{Ag}^+ * V_{Ag}^+$$

Concentration of $[Cl^-]_{(ppm)} = N_{cl}^- \times \text{eq.wt} \times 1000$

Questions:

1. Why is Mohr method carried out in neutral solution?
2. On which does Mohr method depend?
3. Enumerate methods used for determination of chloride ion?

Experiment (6)

Oxidation-reduction reactions

Oxidation-reduction reactions: are all the reactions involving change in oxidation number or transfer of electrons among the reacting substances.

* **Reduction agent:** is one that loses electrons and is oxidized to a higher valiancy conditions.

Ex: Ferrous, stannous compounds, sodium thiosulphate and oxalate ion.



* **Oxidation agent:** is one that gains electrons and is reduced to a lower valiancy conditions.

Ex: Potassium dichromate, potassium permanganate.

The permanganate ion in acid solution is a strong oxidizing agent, because the standard potential in acid solution E° has been calculated to be 1.51V.



$$eq. wt = 158.03/5 = 31.6 \text{ g/g. eq.}$$

Preparation of solutions:

A: Preparation of 0.1N potassium permanganate.

* Weigh out about 3.2gm of $KMnO_4$ on a watch glass and transfer it to a 1500mL beaker and add 1L distilled water, cover the beaker with a clock glass then heat the solution to boiling, boil gently for 1hr and allow the solution to cool to the laboratory temperature, filter the solution through a funnel containing a plug of purified glass wool, collect the filtrate in a vessel. The solution should be stored in a clean, glass stoppered bottle of a dark-brown-colored glass and kept in the dark.

B: Preparation of 0.1 N sodium oxalate ($Na_2C_2O_4$).

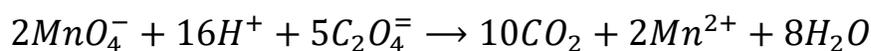
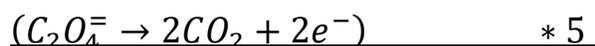
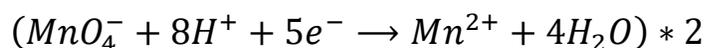
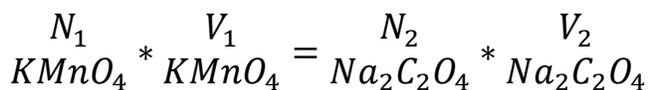
* Weigh out about 1.675gm of $\text{Na}_2\text{C}_2\text{O}_4$ and dissolved it in distilled water in a 250mL volumetric flask.

$$N = \frac{Wt}{eq.wt} * \frac{1000}{V(mL)}$$

$$0.1 = \frac{wt}{67} * \frac{1000}{250} \Rightarrow wt = 1.675 \text{ gm}$$

Standardization of permanganate solution with oxalate ion:

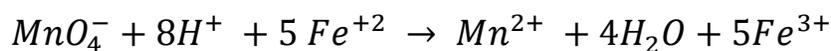
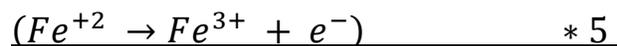
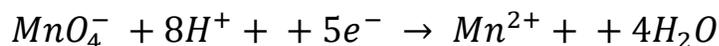
1. Pipet 10mL of 0.1 N of sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) in a 250mL conical flask
2. Add by a graduated cylinder 5mL of H_2SO_4 [1:8].
3. Add some drops of potassium permanganate and heat to 55-60°C and complete the titration by adding permanganate solution until a faint pink color persists for 30sec.
4. Calculate the normality of permanganate ion.



Determination the concentration of ferrous ion:

1. Pipet 10mL of ferrous ion solution in a 250mL conical flask.
2. Add 5mL of sulphuric acid H_2SO_4 [1:8].
3. Titrate the solution with standard (0.1N) KMnO_4 until the pink color persists.
4. Repeat the titration and then calculate the normality of ferrous ion.

$$V_{KMnO_4} * N_{KMnO_4} = \frac{wt Fe^{2+}}{\frac{55.85}{1000}}$$



Questions:

1. Why do we consider $KMnO_4$ as a strong oxidizing agent?
2. Why do we heat the prepared solution of $KMnO_4$ to a boiling boil for 1 hr?
3. Why do we not use an indicator in this experiment?

Experiment (7)

Complexometric titration

This kind of titration is called complexometric because it involved formation of complex especially by using the compound EDTA (Ethylene Diamine Tetra Actic acid) which forms a stable complex with metal ions especially with calcium and magnesium ions. In addition the users indicator with EDTA have also capable to form a complex with the same ions (Mg^{2+} and Ca^{2+}) but less stable than the complex formed between the metal ions and EDTA.

The total hardness of water is generally due to dissolved calcium and magnesium salts Water hardness was defined in terms of the capacity of cations in the water to replace the sodium and potassium ions in soaps and form sparingly soluble products.

There are two types of water hardness, temporary and permanent, **Temporary hardness** is due to the bicarbonate ion, HCO_3^- , (sodium and magnesium bicarbonate) being present in the water. This type of hardness can be removed by boiling the water to expel the CO_2 .

Permanent hardness is due to the presence of the ions Ca^{2+} , Mg^{2+} and SO_4 . This type of hardness cannot be eliminated by boiling.

Hardness is now expressed in terms of the concentration of calcium carbonate that is equivalent to the total concentration of all the multivalent cations in the sample. The determination of hardness is a useful analytical test that provides a measure of water quality for household and industries uses.

Determination of total hardness (permanent and temporary) of water

A: Determination of total hardness of water.

1. Prepare 250mL of 0.02N of EDTA solution.
2. Clean the burette and rinse with EDTA solution.
3. Pipet 10mL of hardness water and add 2mL of ammonia buffer solution (PH=10)[prepared from ammonium chloride +conc. ammonia].
4. Add 3-4 drops of Eriochrome black-T indicator and titrate with standard EDTA solution until the color changes from wine red to pure blue color.
5. Repeat the titration a few times and calculate the total hardness (V_A) of the sample of water ($Ca^{2+} + Mg^{2+}$).

Calculations

V_{EDTA} = Volume of EDTA which equivalent to $(Ca^{2+} + Mg^{2+}) \Rightarrow V_A$

$$\begin{array}{ccccccc} & N_1 & & N_1 & & N_1 & & N_1 \\ & \downarrow & & \downarrow & & \downarrow & & \downarrow \\ & EDTA & * & EDTA & = & Sample(?) & * & Sample \\ & (0.02N) & & & & & & \end{array}$$

$$\begin{array}{l} \text{Total hardness (ppm)} \\ \text{(Concentration of } Mg^{2+} + Ca^{2+}) \end{array} = N \times eq.wt_{CaCO_3} \times 1000$$

Or
$$\begin{array}{l} \text{Total hardness (ppm)} \\ \text{(Concentration of } Mg^{2+} + Ca^{2+}) \end{array} = (V_{EDTA}/V_{solution}) \times 2000$$

B: Determination of the permanent hardness

1. Pipet 10mL of the hardness water and add 2mL of sodium hydroxide solution 4N (PH=12) which is sufficiently high to precipitate the magnesium quantitatively as the hydroxide.
2. Add some crystals of Murexide indicator.
3. Stirr the solution and titrate it with standard EDTA solution until the color changes from pink to a purple.
4. Repeat the titration a few times and calculate the (V_B), which is the volume of EDTA equivalent to Ca^{2+} only.

Calculations

V_{EDTA} = Volume of EDTA which equivalent to Ca^{2+} only $\Rightarrow V_B$

$$\begin{array}{ccccccc} & N_1 & & N_1 & & N_1 & & N_1 \\ & \downarrow & & \downarrow & & \downarrow & & \downarrow \\ & EDTA & * & EDTA & = & Sample(?) & * & Sample \\ & (0.02N) & & & & & & \end{array}$$

$$\text{Permanent hardness (ppm)} \\ (\text{Concentration of } Ca^{2+}) = N_{CaCO_3} \times eq. wt \times 1000$$

$$\underline{\text{Or}} \quad \text{Permanent hardness (ppm)} \\ (\text{Concentration of } Ca^{2+}) = (V_{EDTA}/V_{solution}) \times 2000$$

C: Determination of temporary hardness

Calculate the temporary hardness of water by subtracting the permanent hardness from the total hardness.

$$\text{Temporary hardness} \\ (Mg^{2+}) = \text{Total hardness} \\ (Mg^{2+} + Ca^{2+}) - \text{Permanent hardness} \\ (Ca^{2+}) = VA - VB$$

$$\begin{matrix} N_1 \\ \downarrow \\ EDTA \end{matrix} * \left(\begin{matrix} V_A \\ \downarrow \\ EDTA \end{matrix} - \begin{matrix} V_B \\ \downarrow \\ Sample(?) \end{matrix} \right) = \begin{matrix} N_2 \\ \downarrow \\ sample \end{matrix} * V_2$$

$$\text{Temporary hardness (ppm)} \\ (\text{Concentration of } Mg^{2+}) = N \times eq. wt_{CaCO_3} \times 1000$$

$$\underline{\text{Or}} \quad \text{Temporary hardness (ppm)} \\ (\text{Concentration of } Mg^{2+}) = (V_{EDTA}/V_{solution}) \times 2000$$

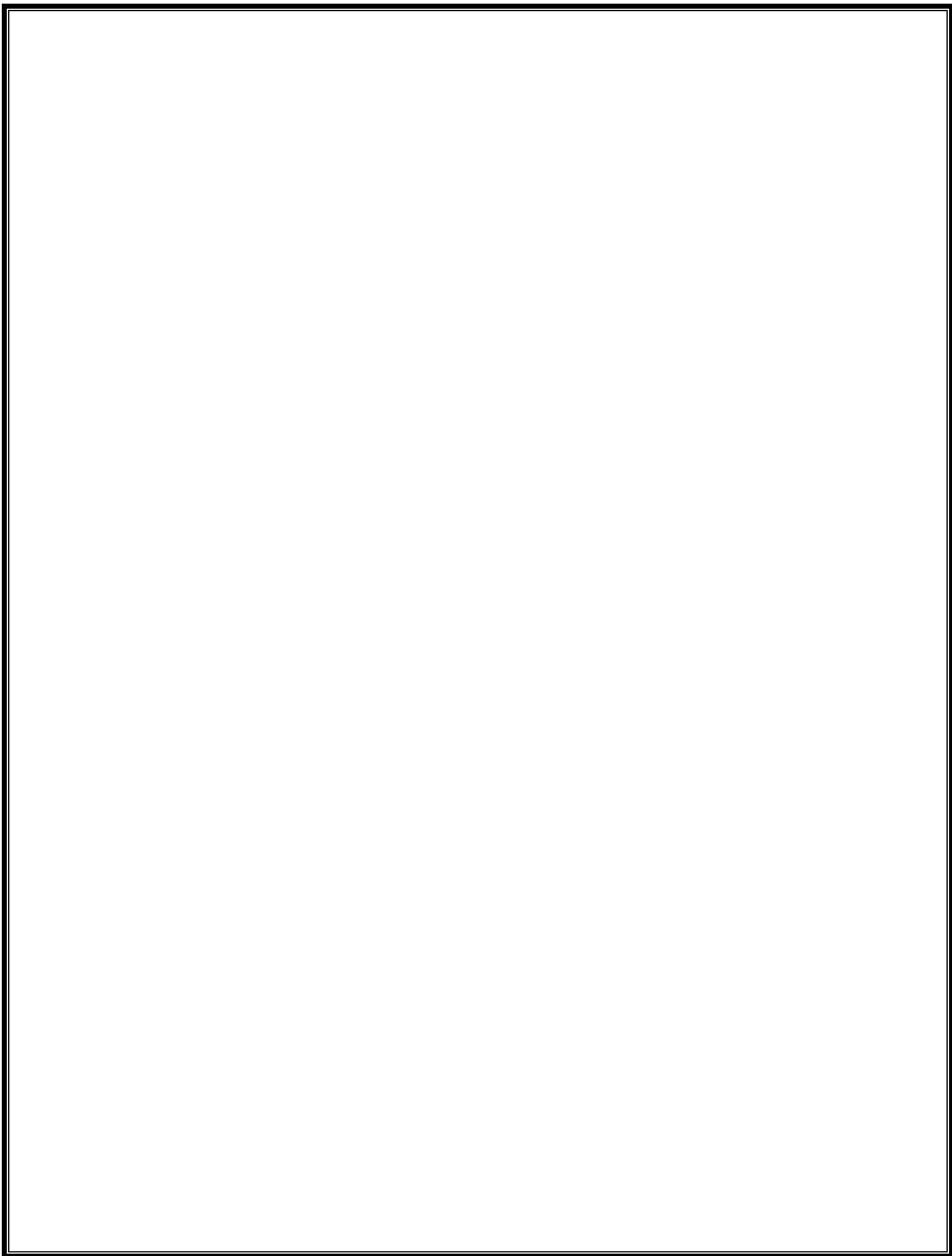
Questions:

1. What is the benefit of determination of water hardness?
2. Write the structure of EDTA compound and mention the ions that react with?
3. Why do we use Murexide and EBT as indicators in complexometric titrations?
4. Define the water hardness and give the main solutions to this problem?
5. Why should we prepare EDTA solution in ionized water?
6. Why do we use sodium hydroxide solution (PH=12) when we determine the permanent hardness?

No

1.	clamp	ماسك معدني
2.	Iron stand	حامل حديدي
3.	Water bath	حمام مائي
4.	Beaker	قدح
5.	Washing bottle	قنينة غسيل
6.	Balance	ميزان
7.	Conical flask	دورق مخروطي
8.	Glass rod or stirrer	محرك زجاجي
9.	Desiccator	مجفف
10.	Graduated cylinder	اسطوانة مدرجة
11.	spatula	ملعقة وزن
12.	pipet .	ماصة
13.	Burette clamp	ماسك سحاحة
14.	Burette	سحاحة
15.	Glass stoppered Bottle	قنينة بسداد زجاجي
16.	Separating funnel	قمع فصل
17.	Crucible	جفنة خزفية
18.	Dropper	قطارة
19.	Volumetric flask	قنينة حجمية
20.	Test tube	انبوبة اختبار
21.	Test tube Rack	حامل انابيب اختبار
22.	Test tube Brush	فرشة انابيب اختبار
23.	Reagent Bottle	قنينة كواشف
24.	Tong	ماسك يدوي
25.	Centrifuge	جهاز الطرد المركزي
26.	Evaporating dish (porcelain)	جفنة تبخير

27.	condenser	مكثف زجاجي
28.	Adapter	مكيف (وصلة زجاجية)
29.	Rubber tube	انبوب مطاطي
30.	Round bottom flask	دورق دائري القعر
31.	flat bottom flask	دورق مستو القعر
32.	Fractional column	عمود التقطير التجزيئي
33.	pipet	ماصة
34.	Burette clamp	ماسك سحاحة
35.	Burette	سحاحة
36.	Glass stoppered Bottle	قنينة بسداد زجاجي
37.	Separating funnel	قمع فصل
38.	Evaporating dish (porcelain)	جفنة تبخير
39.	Crucible	جفنة خزفية
40.	Dropper	قطارة
41.	Volumetric flask	قنينة حجمية
42.	Test tube	انبوبة اختبار
43.	Test tube Rack	حامل انابيب اختبار
44.	Test tube Brush	فرشة انابيب اختبار
45.	Reagent Bottle	قنينة كواشف
46.	Tong	ماسك يدوي
47.	Centrifuge	جهاز الطرد المركزي

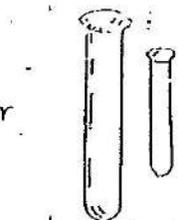




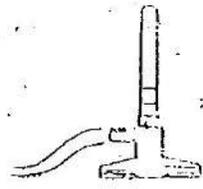
Crucible with cover
مقنة خزفية مع الغطاء



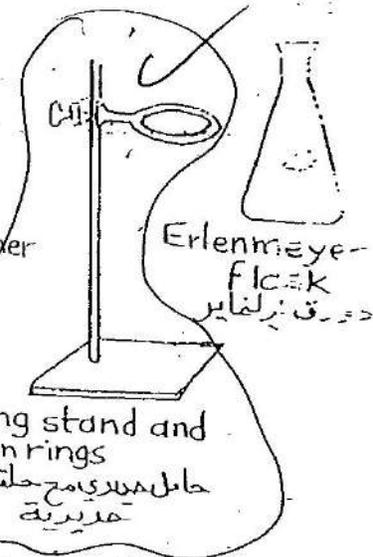
Evaporating dish
(porcelain)



test tubes
انابيب اختبار



Bunsen burner
مصباح بنزن



Ring stand and iron rings
حامل معدني مع حلقات معدنية



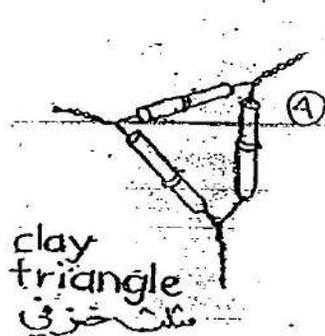
Erlenmeyer flask
دورق بيرلماير



Buret clamp
مساك ساعة



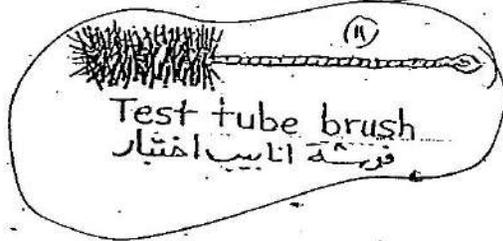
Watch glass
زجاجة ساعة



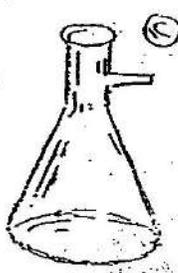
clay triangle
مثلث خزفي



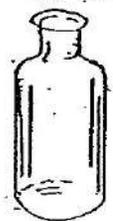
Wire gauze
شبكة سلكية



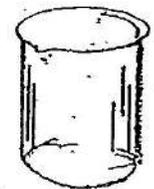
Test tube brush
فرشاة انابيب اختبار



Buchner or filter flask
دورق ترشيح



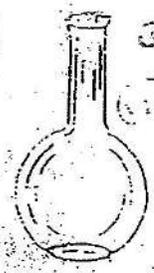
Reagents bottle
قسيحة كواشف



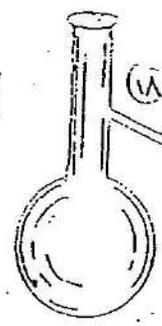
Beaker
مخبار (قدح)



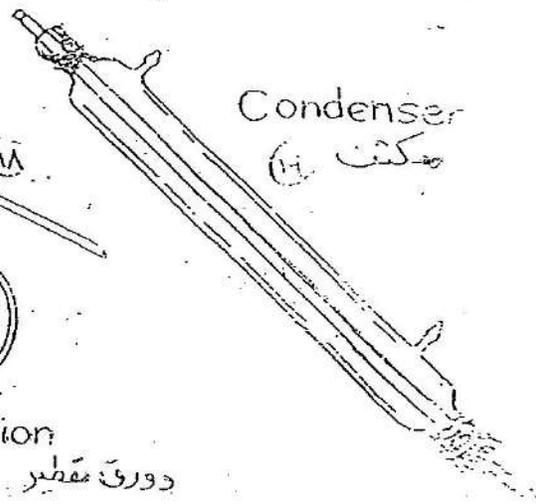
Round bottom flask
دورق دائري القعر



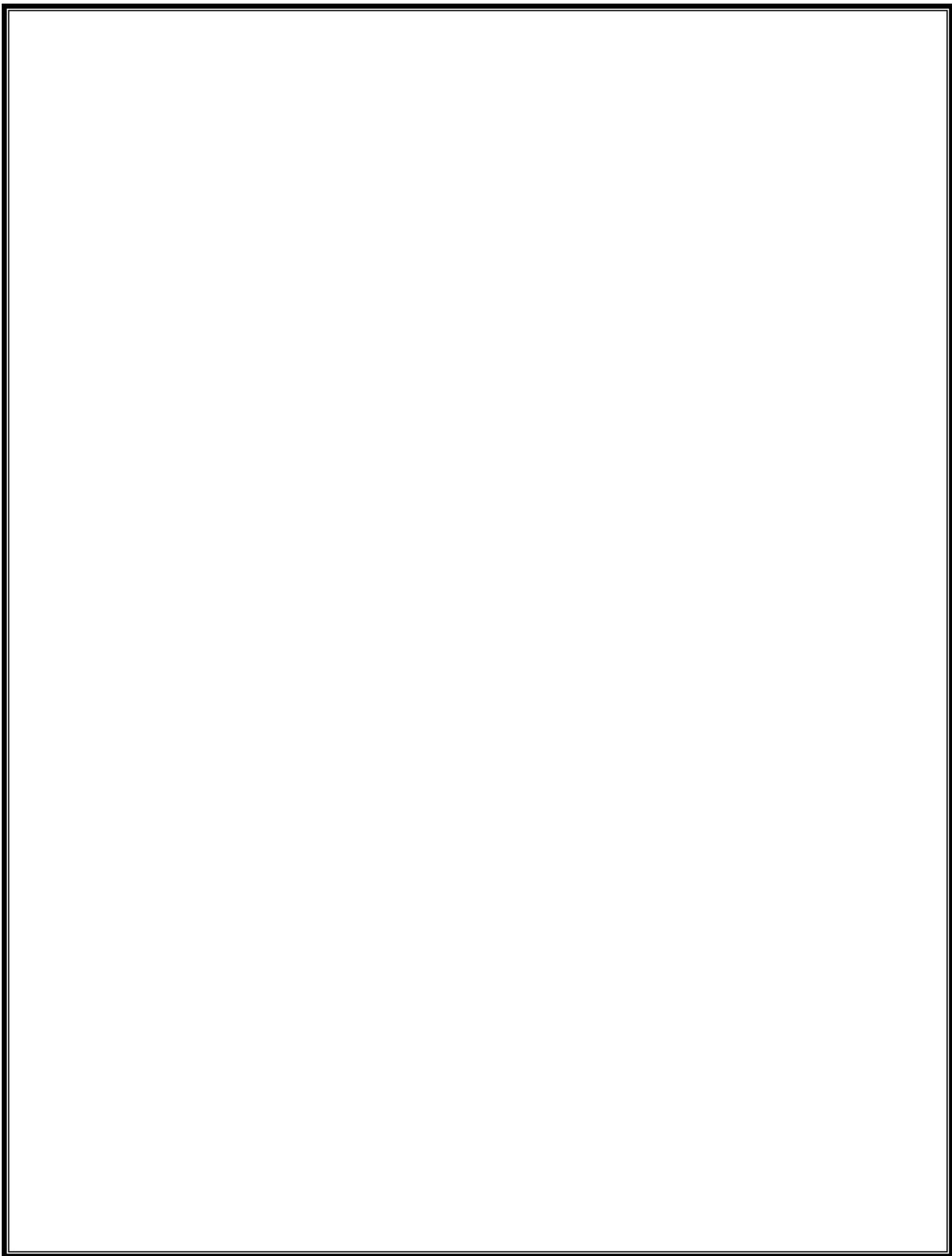
Florence flask
دورق القعر الواسع

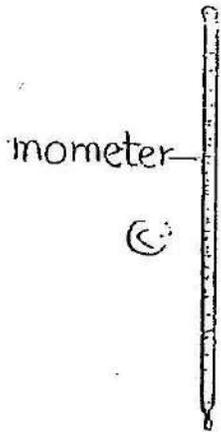


Distillation flask
دورق تقطير



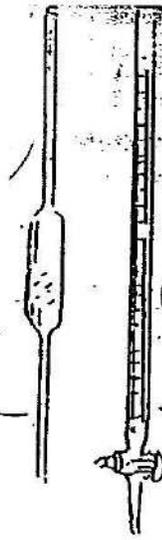
Condenser
مكثف



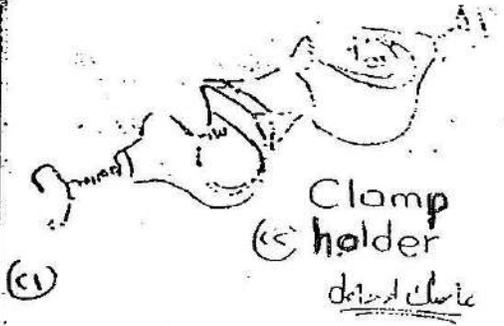


Thermometer

1

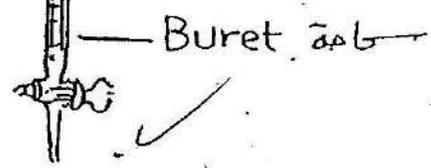


Pipet
قاصة

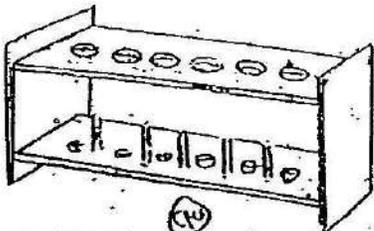


Clamp holder

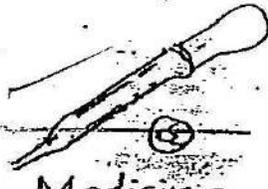
حامل المشبك



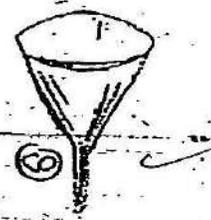
Buret
بurette



Test tube rack
حامل انابيب الاختبار



Medicine dropper
قطارة طبية



Funnel
قمع



Buchner funnel
قمع بوشنر

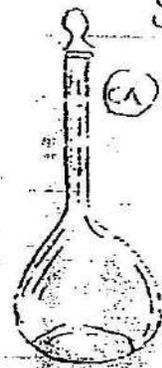
Separatory funnel
قمع فصل



Graduated cylinder
Funnel



Graduated cylinder
اسطوانة مدرجة



Volumetric flask
قبة حجمية

Separatory

Volume

