C15- Dosage of chlorine in water : Bunsen method

1. Principle

An excess of iodine ion is added to the sample volume containing chlorine
Dichlorine Cl_2 oxidise iodine I^- : $Cl_2 + 2\ I^- \longrightarrow I_2 + 2\ Cl^-$
Solution turns brown

I_2 is dosed by titrimetry with sodium thiosulphate : $I_2 + 2\ S_2O_3^{2-} \longrightarrow 2\ I^- + S_4O_6^{2-}$

Solution turns colourless

Equivalence :

$2\ n\ Cl_2 = n\ S_2O_3^{2-}$

V is the sample volume (L)
V_T is the volume of sodium thiosulphate poured (mL)
C is the unknown chlorine molar concentration (mol Cl_2 / L)
m is the mass of chlorine is the sample volume (mg Cl_2)
M is the chlorine molecular weight : 71 g / mol
C_T is the sodium thiosulphate concentration (mol / L) = 1 / 35.5 mol / L

Then : $2 * m * 10^{-3} / M = V_T * 10^{-3} * C_T$
$2*m / M = V_T * C_T$

$m = V_T * (1/35.5) * 71 / 2$

$m_{\text{mg Cl2}} = V_{T\ \text{ml thiosulphate}}$

At the equivalence, the weight of chlorine (mg Cl_2) in the sample volume is equals to the thiosulphate volume versed

This method is adapted for high chlorine concentration (> 100 mg Cl_2 / L) such as hypochlorite solution (Bleach…)

2. Procedure

Chose a sample volume which contains between 5 and 20 mg Cl_2 ; this volume generally is 10 mL.
All dilution must be carried out with drinking water, not with deionized water.
Add 20 mL of KI 10% (100g/L) and 10 mL of acetic acid : solution turns brown
Pour, with the burette, sodium thiosulphate 1/35.5 mol / L until solution turns colourless (just before solution turns colourless, add starch : solution turns black and the visual transition is easier)

3. Practical work

Determinate the chlorine concentration in the Javel water (Bleach) .
Data : 1°Cl (chlorometric degree) = 3.16 g Cl_2 / L

4. Report

Determination of chlorine concentration in bleach : $[Cl_2]$ =
Explain how you have chosen the sample volume, and / or the dilution of the bleach that you have carried out.
Indicate V and V_T .
Calculate the chlorine concentration in bleach, in g Cl_2/L and in chlorometric degree.

5. Required material and reagents

For one experiment :
250 mL of Bleach (Javel water, 12 or 48 °Cl)
100 mL of iodine potassium 10% (100 g KI / L)
50 mL of pure acetic acid
10 mL of starch

2. Dosage of chlorine in water : Titrimetric method with DPD

1. Principle

DPD : N,N-**D**iethyl**p**hénylene-1,4 **d**iamine is oxidised by chlorine (or free chlorine : Cl_2) :
DPD réd + 1/2 Cl_2 $\longrightarrow$ DPDox + Cl^-
The sample volume turns red

then DPDox is dosed by Mohr's salt Fe^{2+} :

DPDox + Fe^{2+} $\longrightarrow$ DPD réd + Fe^{3+}

At the equivalence, the solution turns colourless and :
$2nCl_2 = n_{mohr}$

$nCl_2 = n_{mohr} / 2$
If V_1 is the volume of Mohr's salt poured, in mL, at the equivalence
C_1 the concentration of Mohr' salt = 2.8 mmol / L
$C_{chlorine}$ the unknown chlorine concentration in the sample volume V = 100 mL

Then
$C_{chlorine} V = C_1V_1 / 2$

and $C_{chlorine}$ (mol / L) = C_1V_1 / 2V

C_{chlore} (mg/L) = 2.8 * V_1 * (35,5 * 2) / 2 * 100

and $C_{chlorine}$ (mg/L) = V_1 (mL)

In these conditions, the volume of Mohr's salt poured at the equivalence, in mL, is equal to the chlorine concentration in the sample volume, in mg Cl_2 / L.

This method is adapted for low chlorine concentration (< 25 mg Cl_2 / L, i.e. V_1 < 25 mL) such as drinking water (0.1 to 0.5 mg/L…).

☞ chlorine can be combined, for example with ammonia and other nitrogenous compounds, to give chloramines ($NHCl_2$, NH_2Cl , NCl_3) ; in order to dose total chlorine (free chlorine and chloramines) , add KI to the sample :
- chloramines oxidise I^- to give I_2 ;
- I_2 can react with DPD to give a red compound (same reaction between Cl_2 and DPD).

Then Fe^{2+} react with DPD issued from initial Cl_2 and from I_2.

☞ in order to dose chlorine, there is another method : spectrophotometric method

2. Procedure

In a 250 mL erlenmeyer flask, introduce 100 mL of sample.
Add 5 mL of pH 6.5 buffer and 5 mL of DPD : the solution turns red.
Pour Mohr's salt (burette) until solution turns colourless : V_1 mL.
Total chlorine : add 100 mL of sample, 5 mL of buffer, 5 mL of DPD and 1 g of KI and wait for 2 minutes. Verse Mohr's salt : V_1 correspond to the total chlorine concentration.

3. Practical work

Carry out the determination of the chlorine concentration of the sample noted "Cl_2"

4. Report

5. Required material and reagents

For one experiment :
50 mL of pH 6.5 buffer

(KH_2PO_4	*46g*
Na_2HPO_4	*24g*
EDTA,2Na ($C_{10}H_{14}N_2O_8Na_2 . 2H_2O$) 8 g/L	*100ml*
mercuric chloride $HgCl_2$	*0.02g*
deionized water until	*1000mL)*

5 g of KI
50 mL of DPD
(In 250 mL of deionized water, mix 2 mL of sulphuric acid (18 mol / L and 1.84 g/mL) and 25 mL of EDTA,2Na 8g/L*
** dissolve in this mixture, 1.1 g of anhydrous diethyl – p – phenylenediamine DPD sulphate [NH_2-C_6H_4-$N(C_2H_5)_2$ - H_2SO_4]*

** complete with deionized water until 1000mL*

☞ *maximum storage time : one month*

50 mL of Mohr's salt [$(NH_4)_2Fe(SO_4)_2$, 6 H_2O] 2.8 * 10^{-3} mol / L
([$(NH_4)_2Fe(SO_4)_2$, 6 H_2O] 1.106 g
sulphuric acid diluted 1/3 (V/V) 1mL
deionized water until 1000mL)

250 mL of diluted bleach (0.1 < [Cl_2] < 25 mg Cl_2 / L)
For example, if initial chlorine concentration in bleach is 48°Cl (152 g / L) : dilute it 10,000 times (until 15.2 mg / L : 100µL of bleach in one litre of drinking water , not in deionized water).

one microburette (0.1 to 1 mL or to 5 mL)

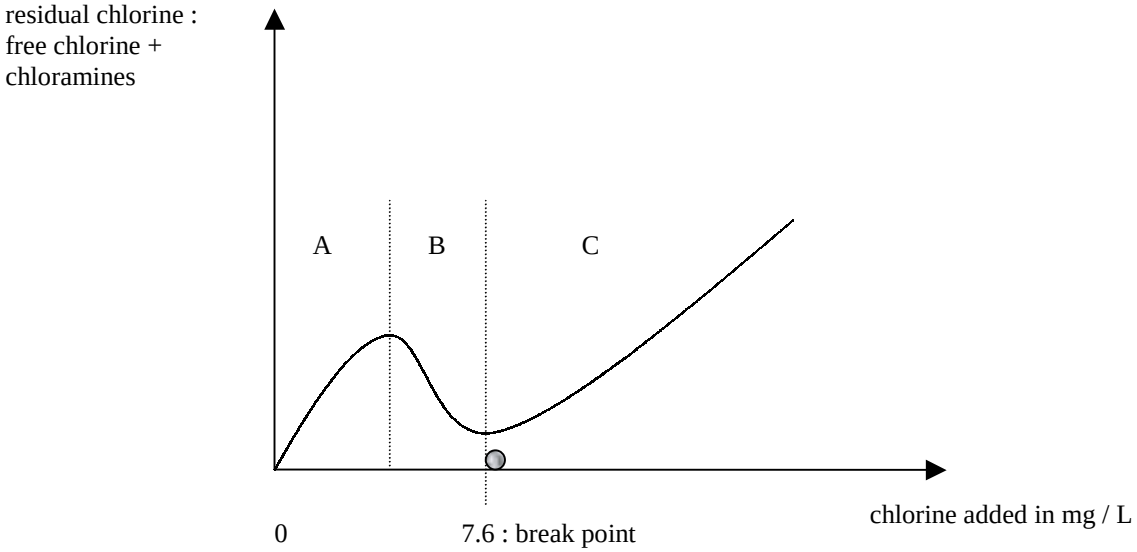
3. Determination of the break point

1. Principle

The break point is the amount of chlorine necessary to remove ammonia in water.
Chlorine first react with ammonia to give chloramines (A) :

$HClO + NH_3 \longrightarrow NH_2Cl + H_2O$

Beyond this formation, the chlorine added reacts with chloramines and destroy them (B) ; the amount of chlorine necessary to form and next to remove chloramines is the break point ; beyond this point, the amount of added chlorine remains in water as free chlorine (C) .



Evolution of residual chlorine in a sample of water containing 1 mg $N.NH_3$ / L, in wich chlorine is added

Global reaction : $2\ NH_3 + 3\ Cl_2 \longrightarrow 6HCl + N_2$
7.6 mg of dichlore are necessary to remove 1 mg $N.\ NH_3$.

2. Procedure

You have twelve 500 mL erlenmeyer flasks containing 500 mL of solution 1 mg $N.NH_4^+$ / L (3.82 g NH_4Cl / L).
Add these amounts of bleach :

flask n°	1	2	3	4	**5**	**6**	**7**	8	9	10	11	12
Bleach 1g/L (mL)	1.5	2	2.5	3	**3.5**	**3.75**	**4**	4.25	4.5	5	5.5	6
final $[Cl_2]$ mg/L	3	4	5	6	**7**	**7.5**	**8**	8.5	9	10	11	12

Keep the flask in the darkness during 2 hours.

Add 10 mL of acetic acid and 20 mL of KI 10% : solution must turns brown
Titrate total chlorine with sodium thiosulphate 1/35.5 mol / L until solution turns colourless : note V_T.

3. Report

Plot the curve representing $V_T = f([Cl]_2)$
Determinate the break point.

4. Material and reagent requirements

12 erlenmeyer flasks : 500 mL , containing 500 mL of 3.82 g NH_4Cl / L
200 mL of acetic acid
300 mL of KI 10%
Starch
1L of sodium thiosulphate 1/35.5 mol / L