C8 - Water hardness and water alkalinity measure

1. Water hardness

1.1 Principles

Water hardness is the result of calcium and magnesium (Ca^{2+} and Mg^{2+}) presence.
Hard water is scale - forming ($CaCO_3$) in distribution network; it lathers with difficulties.
Soft water is aggressive, corrosive($Fe° \longrightarrow Fe^{2+}$, Fe^{3+}), induces rust formation ($Fe(OH_3)$) ; it lathers easily.

Calcium carbonate stability :

$$\begin{matrix} Ca(HCO_3)_2 \\ Mg(HCO_3)_2 \end{matrix} \quad \underset{2}{\overset{1}{\rightleftharpoons}} \quad \begin{matrix} CaCO_3 + CO_2 + H_2O \\ MgCO_3 \end{matrix}$$

dissolved Ca^{2+} and Mg^{2+} — scale

Temperature , Ca^{2+}, Mg^{2+} , HCO_3^- concentrations and pH } **increases** induce reaction **1** : water become **hard**

Temperature , Ca^{2+}, Mg^{2+} , HCO_3^- concentrations and pH } **decreases** induce reaction **2** : water become **soft**

Calcium and magnesium concentration can be expressed with many different units :
$mol_{ca, mg}$ / L
equivalent per liter ($eq_{ca, mg}$ / L)
$g_{ca, mg}$ / l and $mg_{ca, mg}$ / L
English, Deutsche or French degrees : these units won't be used in the course.
mg $CaCO_3$ / L or ppm $CaCO_3$

Correspondence between mol / L, eq / L and ppm $CaCO_3$
(mol / L) divided by valence is (eq / L)
(eq / L) multiplied by 50,000 is (ppm $CaCO_3$)

$$\textbf{mol / L} \xrightarrow{\text{x valence}} \textbf{eq / L} \xrightarrow{\text{x 50,000}} \textbf{ppm CaCO}_3$$

Example :
2.3 $*10^{-3}$ mol Ca^{2+} / L = 4.6 $*10^{-3}$ eq / L = 230 ppm $CaCO_3$
3.1 $*10^{-4}$ mol HCO_3^- / L = 3.1 $*10^{-4}$ eq / L = 15.5 ppm $CaCO_3$

Furthermore :
1 ° French = 0.56 ° Deutsche = 0. 7 ° English = 10 mg / L $CaCO_3$ = 10 ppm $CaCO_3$
1 ° Deutsche = 1.786 ° French = 1.25° English = 17.86 ppm $CaCO_3$
1 ° English = 1.438 ° French = 0. 8 ° Deutsche = 14.38 ppm $CaCO_3$

We will express these concentrations with
mol $_{ca, mg}$ / L
eq / L
mg $_{ca, mg}$ / L
or ppm $CaCO_3$.

Then 10 ppm $CaCO_3$ = 10^{-4} mol $_{ca, mg}$ / L = $0.5*10^{-4}$ eq $_{ca,mg}$ / L ; for a water containing both Ca and Mg the concentration expressed with mg / L can't be calculated : we don't know the calcium and magnesium proportions .

Hardness scale :

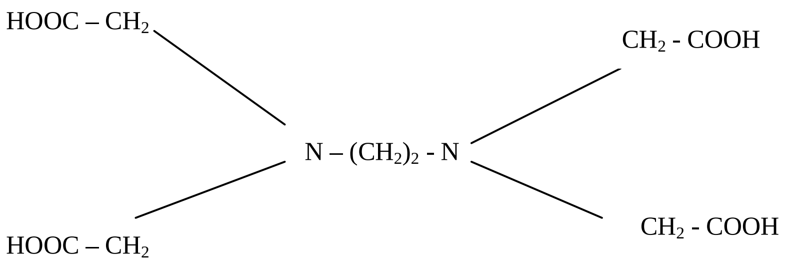
soft water		moderately hard water	hard water	very hard water
0	60	120	180	ppm $CaCO_3$
0	0.0006	0.0012	0.0018	$mol_{ca,mg}$ / L
0	0.0003	0.0006	0.009	eq $_{ca,mg}$ / L

Field of application : drinking water (the recommended allowances are 900 mg Ca and 400 mg Mg per day), industrial water.

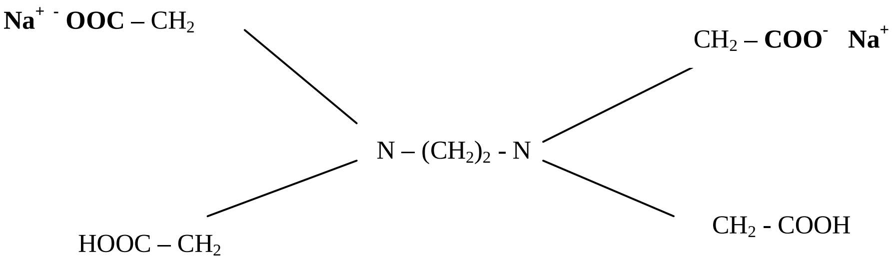
1.2. Water hardness measure

Ethylene diamine tetraacetic acid : EDTA is used during the complexometric dosage

EDTA = YH_4 at pH < 10



YH_2^{2-} at pH = 10



and at pH = 10 , YH_2^{2-} forms a complex with Ca^{2+} or Mg^{2+} (chelation) :

$$Ca^{2+} + H_2Y^{2-} \longrightarrow CaY^{2-} + 2\,H^+$$

First, Ca and Mg can react with NET, added in the tested solution (Volume V) :
Free NET is bleu : complexed with calcium or magnesium, NET is violet : the tested solution is violet

If are $n_{ca,\,mg}$ is the molar concentration (unknown) in the tested water (volume V)
Then EDTA, which concentration is precisely known (Cedta) , is added
EDTA has more affinity for Ca and Mg than NET

$ind + Ca^{2+} \longrightarrow ind - Ca$

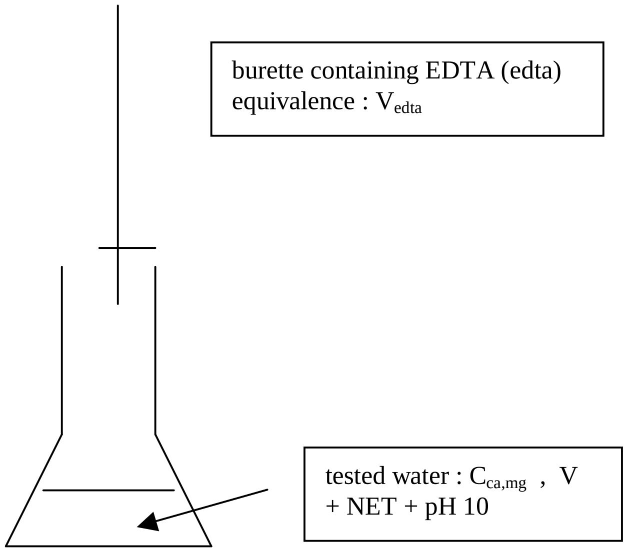
$ind - Ca + EDTA \longrightarrow EDTA - Ca + ind$

When the last Ca, Mg quantities linked to NET disappear, a volume V_{edta} has been poured and the solution turns blue (free NET) :

$n_{ca,mg} = n_{EDTA}$

$n_{ca,mg} = C_{ca,mg} * V_{pe} = C_{edta} * V_{edta}$

$C_{ca,mg} = C_{edta} * V_{edta} / V_{pe}$



Procedure :

The sample volume must contain a Ca, Mg quantity allowing a V_{edta} inferior to the burette maximum volume (20 or 25 mL).

example : V = 100 mL

Add 4 mL pH10 buffer and a bit of NET : solution is violet

Fill the burette with EDTA 0.01mol / L

Pour EDTA until solution turns blue.

Calcul example :

$V_{water\ sample}$ = 100 mL,

$V_{edta\ versed}$ = 18 mL

$C_{ca,Mg} = 18*10^{-3} * 0.01 / 0.1 = 18 * 10^{-4}$ mol / L = 180 ppm $CaCO_3$: hard water

☞ pH 10 buffer and NET in distillated water gives a blue solution : it allows to verify quickly the distillated water quality.

☞ the hardness measured after ebullition and filtration is called <u>permanent hardness</u> ; it consists of Ca and Mg linked with Cl^-, SO_4^{2-}…all anions but HCO_3^- , whereas scale has precipitated ; the other hardness is called <u>temporary</u> hardness

☞ the hardness measured at pH 12 (add 10 mL NaOH 2.5mol / L in place of pH 10 buffer) allows to determinate only <u>the Ca concentration</u> (at pH 12, $Mg(OH)_2$ precipitate).

<u>2. Water alkalinity</u>

<u>2.1. Principle</u>

Many ions (OH^-, CO_3^{2-} HCO_3^-….) can react with H^+ in water (buffer role) but at **neutral pH**, the HCO_3^- (hydrogen carbonate ion) are predominant :

HCO_3^- / CO_3^{2-} : pKa = 10.2 $\quad$ $Ka = (CO_3^{2-})(H^+) / (HCO_3^-) = 10^{-10.2}$

at pH=7, $\quad$ $CO_3^{2-} / HCO_3^- = 10^{-10.2} / 10^{-7} = 10^{-3.2} = 6.3 \cdot 10^{-4}$

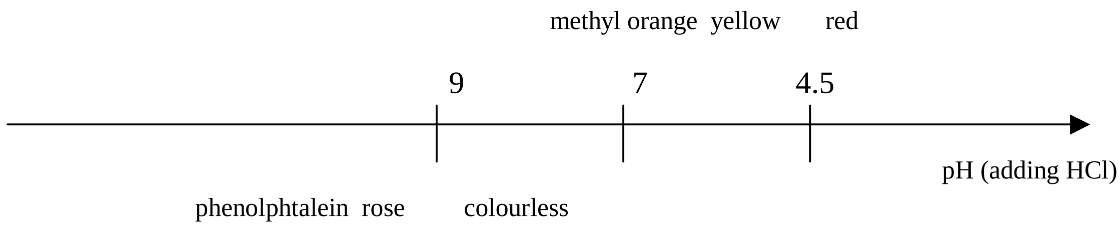
HCO_3^- react with acidity (H^+) to give CO_2

$$HCO_3^- + H^+ \longrightarrow H_2O + CO_2$$

<u>The origin of water alkalinity is the presence of HCO_3^-, at neutral pH</u>

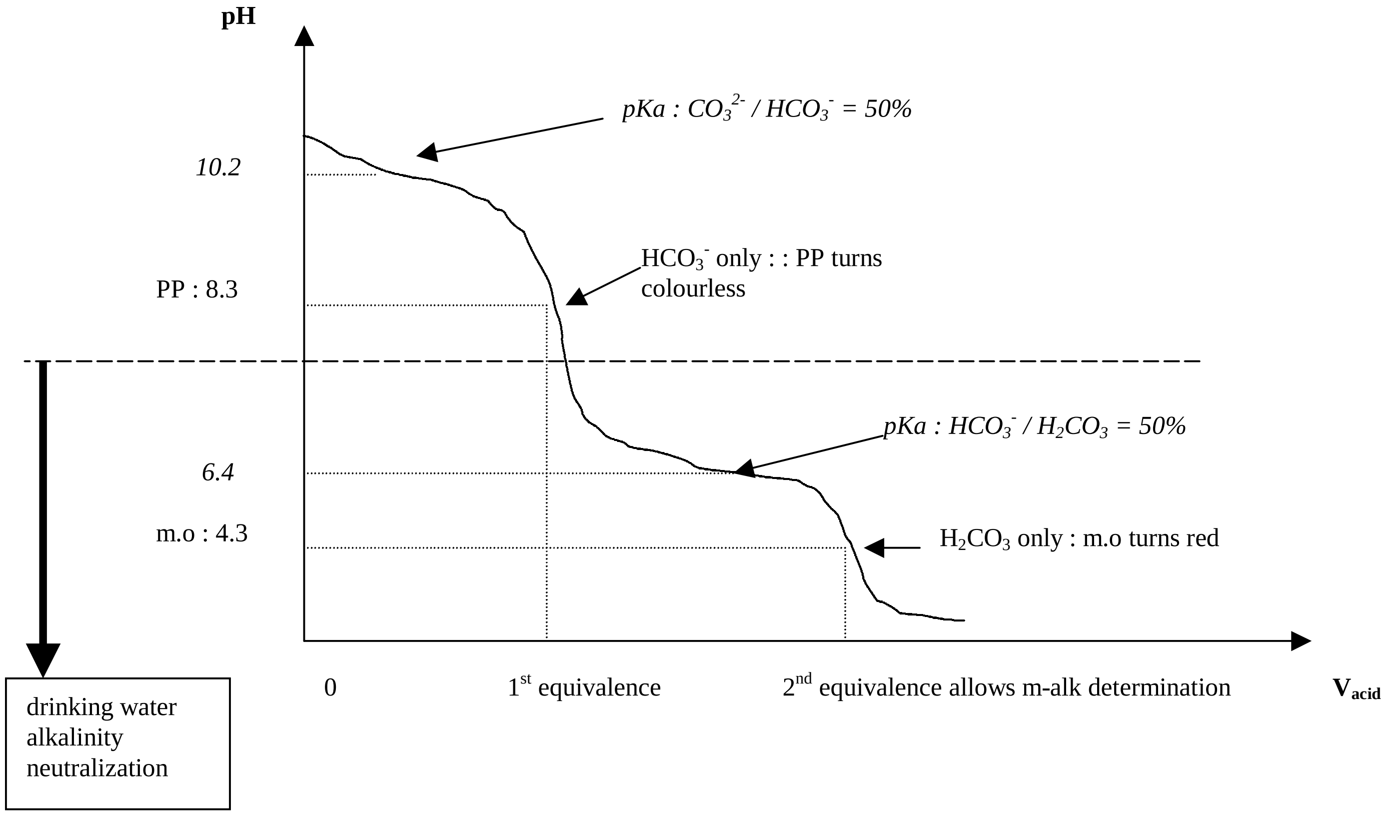
HCO_3^- concentration can be measured adding acid in the water sample, with coloured indicator :
- alkalinity, or methyl orange alkalinity (m-alk), is measured as adding HCl (hydrochloric acid) 0.04 mol / L in a 100mL tested water sample, with methyl orange (turns yellow to red, at pH = 4.5)

Another kind of alkalinity exists, concerning basic waters (containing CO_3^{2-} and OH^-) :
- phenolphtalein alkalinity (p-alk) is measured as adding HCl (hydrochloric acid) 0.04 mol / L in a 100mL tested water sample, with phenolphtalein ,(turns rose to colourless, at pH = 8.3)



H_2CO_3 / HCO_3^- : pKa = 6.4 $\quad$ $Ka = (HCO_3^-)(H^+) / (H_2CO_3) = 10^{-6.4}$

pH evolution in a basic solution in which Hcl is added, with PP and next methyl orange



Then, in drinking waters, pH = 7 and the main reaction is

$H^+ + HCO_3^- \longrightarrow H_2CO_3$

at the equivalence, $n_{H+} = n_{HCO3-}$

If Ca is the acid concentration and Va the acid volume versed at the equivalence (about pH = 4 and m.o turning yellow to red)

If C_{hco3} is the hydrogen carbonate concentration un known in the tested water sample and V the sample volume :

$Ca * Va = C_{hco3} * V$

C_{hco3} = CaVa / V

Alkalinity is expressed in mol HCO_3^- / L or mg $CaCO_3$ / L (ppm $CaCO_3$, as hardness) :
10^{-4} mol HCO_3^- / L = 10^{-4} eq / L (valence = 1) = 5 ppm $CaCO_3$

Procedure :
V = 100 mL
Add a bit of methyl orange : solution is yellow
Pour HCl 0.04 mol / L until solution turns red

Example :
Va = 14,3 mL
C_{hco3} = CaVa / V = 0.04 * 14.3 / 100 = 5.72 * 10^{-3} mol HCO_3^- / L = 5.72*10^{-3} eq / L = 286 ppm $CaCO_3$

m-alk = 286 ppm $CaCO_3$

Water table, drinking waters must present a high m-alk : they won't be aggressive and present high buffer proprieties : generally, m-alk is about 50 (aggressive water) to 400 ppm $CaCO_3$ (water with calcium carbonate alkalinity) ; here, m-alk = 286 ppm and is enough to present calcium carbonate stability.

3. Practical work : bottling water analysis verification

3.1. Hardness measurement

Read the bottling water analysis and sample a volume (10 to 100mL) which allows a coherent EDTA versed volume (5 to 25 mL) ; a dilution can be necessary
Add 4 mL pH 10 buffer and NET
Pour EDTA until solution turns blue
Calculate water hardness in ppm $CaCO_3$ and verify your result (bottle etiquette)

Carry on that experiment again : $\Delta A / A_{average}$ must be < 0.03 (precision test)

3.2. Alkalinity measurement

Read the bottling water analysis and sample a volume (10 to 100mL) which allows a coherent HCl versed volume (5 to 25 mL) ; a dilution can be necessary
Add methyl orange (4 -5 drops) : solution is yellow
Introduce pH meter
Pour HCl 0.04mol/ L until solution turns red ; read pH at the equivalence point
Calculate m-alk, in ppm $CaCO_3$ and mg HCO_3^- / L and verify your result (bottle etiquette)
Carry on that experiment again : $\Delta A / A_{average}$ must be < 0.03 (precision test)

3.3. Report

3.3.1. Water hardness
- EDTA poured volumes (mL)
- Test precision interpretation
- hardness determination (ppm $CaCO_3$)
- interpretation of your analysis in comparison with bottling water etiquette one
- is it a soft or a hard water ?

3.3.2. Water alkalinity
- HCl poured volumes (mL)
- pH equivalence
- Test precision interpretation
- m-alk determination (ppm $CaCO_3$ and mg HCO_3^- / L)
- interpretation of your analysis in comparison with bottling water etiquette one
- is this water buffered enough ?

4. Material and reagents requirements (12 students)

4L of bottling water (with indicated chemical composition)
6 flasks with 100 mL of EDTA 0.01mol / L

6 flasks with 100mL of pH10 buffer
dissolve 67.5 g of NH_4Cl in 570 mL of ammonia solution 13 mol / L (25% m/m)
add 5 g of EDTA $C_{10}H_{14}N_2O_8$ ***Na_2 Mg***
complete to 1000 mL with deionized water

6 flasks with 50 mL of methyl orange 5g/L
6 flasks with 100 mL of HCl 0.04 mol / L
12 pH meter + reference solutions (pH 7 and 4) + notice