Technical Assistance
HYDROLOGY PROJECT

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Training module # WQ - 06

Understanding hydrogen ion concentration (pH)

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CSMRS Building, 4th Floor, Olof Palme Marg, Hauz Khas,
New Delhi – 11 00 16 India
Tel: 68 61 681 / 84 Fax: (+ 91 11) 68 61 685
E-Mail: dhvdelft@del2.vsnl.net.in

DHV Consultants BV & DELFT HYDRAULICS

with
HALCROW, TAHAL, CES, ORG & JPS

Table of contents

1 Module context

This module is a stand-alone module and no prior training in other modules is needed to complete this module successfully. It discusses basic concepts of hydrogen ion concentration in water. Other available, related modules in this category are listed in the table below.

While designing a training course, the relationship between this module and the others, would be maintained by keeping them close together in the syllabus and place them in a logical sequence. The actual selection of the topics and the depth of training would, of course, depend on the training needs of the participants, i.e. their knowledge level and skills performance upon the start of the course..

No.	Module title	Code	Objectives
1	*Basic water quality concepts*	WQ -01	• Discuss the common water quality parameters • List important water quality issues
2	*Basic chemistry concepts*	WQ -02	• Convert units from one to another • Discuss the basic concepts of quantitative chemistry • Report analytical results with the correct number of significant digits.
3	*How to prepare standard solutions*	WQ -04	• Select different types of glassware • Use an analytical balance and maintain it. • Prepare standard solutions.
4	*How to measure the pH of a water sample*	WQ -07	• Measure the pH of a water sample • Observe the effect of dissolved gasses on pH

2 Module profile

Title	:	Understanding hydrogen ion concentration (pH)
Target group	:	HIS function: Q1, Q2, Q3, Q5
Duration	:	1 session of 90 minutes
Objectives	:	After training, the participants will be able to: • Discuss about the concept of pH • Calculate pH
Key concepts	:	• Hydrogen ion concentration • pH scale • Buffer solution
Training methods	:	Lecture, discussion and exercises
Training tools required	:	OHS, flip chart
Handouts	:	As provided in this module
Further reading	:	• Analytical Chemistry: An introduction, D.A. Skoog and D. M. West/1986. Saunders College Publishing • Chemistry for Environmental Engineering, C.N. Sawyer, P.L. McCarty and C.F. Parkin. McGraw-Hill, 1994

3 Session plan

No	Activities	Time	Tools
1	**Preparations**		
2	**Concept of pH** Introduce the subject Ask participants to state the importance of hydrogen ion concentration Define and explain pH Explain dissociation of water molecule, equations and pH scale.	10 min	OHS
3	**Calculations** Demonstrate how to calculate pH for given concentrations of H^+ & OH^- ions.	25 min	OHS Board
4	**pH indicators** Explain the table for different indicators Explain the features of pH indicators.	10 min	OHS
5	**pH meter** Describe the working principle of pH meter Explain how to take care of electrodes.	15 min	OHS
6	**Buffer solutions & instrument calibration** Define buffer solution and its significance Explain how to prepare buffer solutions of known pH values Explain how to calibrate the instrument.	15 min	OHS
7	**Questions** Ask the participants for answers to questions listed in text section 8.7 orally Explain the answers one by one	15 min	Board

4 Overhead/flipchart masters

OHS format guidelines

Type of text	Style	Setting
Headings:	OHS-Title	Arial 30-36, Bold with bottom border line (not: underline)
Text:	OHS-lev1 OHS-lev2	Arial 26, Arial 24, with indent maximum two levels only
Case:		Sentence case. Avoid full text in UPPERCASE.
Italics:		Use occasionally and in a consistent way
Listings:	OHS-lev1 OHS-lev1-Numbered	Big bullets. Numbers for definite series of steps. Avoid roman numbers and letters.
Colours:		None, as these get lost in photocopying and some colours do not reproduce at all.
Formulas/ Equations	OHS-Equation	Use of a table will ease alignment over more lines (rows and columns) Use equation editor for advanced formatting only

Hydrogen ion concentration – pH

1. The concept
2. pH scale
3. pH concentration
4. Calculating pH
5. pH indicators
6. pH meter
7. Buffer solution

1.The concept

- Dissociation of water

$$\mathbf{H_2O \Leftrightarrow H^+ + OH^-}$$

- For pure water

  $[H^+] = 10^{-7}$ moles/L

  [ ] denotes moles/L

- pH = - log[H+]
- For pure water pH = 7

pH scale

- $[H^+]$ X $[OH^-]$ always equals 10^{-14}
- $\log [H^+] + \log [OH^-] = -14$
- pH scale

Acid **Neutral** **Alkaline**

1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**

H^+ concentration

Concentration of H^+ can be changed

$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$$

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+ + 3Cl^-$$

$$Na_2CO_3 + H_2O \longrightarrow 2Na^+ + HCO_3^- + OH^-$$

Calculating pH: example

Calculate the pH if $[H^{+}] = 0.001$

$$
\begin{aligned}
\mathbf{pH} &= -\log [H^{+}] \\
&= -\log [0.001] \\
&= -\log 10^{-3} \\
&= -(-3) \log 10 \\
&= 3 \times 1 \\
&= \mathbf{3}
\end{aligned}
$$

Calculating pH: example

Calculate the pH if $[OH^-] = 10^{-8}$

$$[H^+] \times [OH^-] = 10^{-14}$$

or $$[H^+] \times 10^{-8} = 10^{-14}$$

or $$[H^+] = 10^{-14} \div 10^{-8}$$

$$= 10^{-6}$$

$$\mathbf{pH} = -\log [H^+]$$

$$= -\log 10^{-6}$$

$$\mathbf{= 6}$$

Calculating pH: example

Calculate the pH if $[OH^{-}] = 0.00005$

$$\log [OH^{-}] = \log(5 \times 10^{-5})$$

$$= 0.7 - 5 = -4.3$$

$$\log [H^{+}] + \log [OH^{-}] = -14$$

or $$\log [H^{+}] = -14 + 4.3 = -9.7$$

$$\mathbf{pH} = -\log [H^{+}] = \mathbf{9.7}$$

pH indicators: features

- Colour changes over a wide range of pH values
- Interference due to colour of sample
- Interference due to turbidity of sample

pH indicators: properties

Indicator	Acid colour	Base colour	pH range
Methyl orange	red	yellow orange	3.1 – 4.6
Methyl red	red	yellow	4.4 – 6.2
Litmus	red	blue	4.5 – 8.3
Thymol blue	yellow	blue	8.0 – 9.6
Phenolphthalein	colourless	pink	8.2 – 9.8
Alizarin yellow	yellow	lilac	10.1 – 11.1

pH meter: features

- Consists of potentiometer, glass electrode, reference electrode
- Temperature compensation devise
- Measures potential difference
- Meter indicates pH value or milli volts
- Accuracy of $\pm$ 0.01 pH

pH meter: types of electrodes

- Glass electrodes
- Calomel electrodes

pH meter: maintenance

Glass electrode

- Do not scratch
- Immerse in pH 4.0 buffer, for short term storage
- Soak in water for 12 h before pH measurement

pH meter: calibration

- Calibration
  - Use two buffer solutions
  - Use a second buffer within 2 pH units of the sample pH

Buffer solutions

- Known pH
- Mixtures
  - *weak acids & their salts*
  - *weak bases & their salts*
- Dilution does not change pH
- Resist change of pH upon addition of small amount of acid or alkali

Buffer solutions: preparation

Buffer solution of known pH

	Buffer solution	pH at 25°C	Amount of salts to be dissolved in 1000 ml freshly boiled & cooled distilled water
1	0.05M potassium hydrogen phthalate	4.00	10.12 g $KHC_8H_4O_4$
2	0.025M potassium dihydrogen phosphate + 0.025M disodium hydrogen phosphate	6.86	3.387 g KH_2PO_4 + 3.533 g Na_2HPO_4
3	0.01M sodium borate decahydrate	9.18	3.80 g $Na_2B_4O_7.10\ H_2O$

5 Evaluation

Questions

1. What is the relationship between pH and H^+ and between pH and OH^-?
2. What will be the pH of a solution containing 0.1008 g of hydrogen ion per litre?
3. What electrodes are used for pH measurement?
4. What is the normal range of pH of natural waters?
5. How will the pH value of a sample of water change when vinegar is added to it?

6 Handouts

Hydrogen ion concentration – pH

1. The concept
2. pH scale
3. pH concentration
4. Calculating pH
5. pH indicators
6. pH meter
7. Buffer solution

The concept

- Dissociation of water
  $H_2O \Leftrightarrow H^+ + OH^-$

- For pure water
  $[H^+] = 10^{-7}$ moles/L
  [ ] denotes moles/L

- pH = - log[H^+]

- For pure water pH = 7

pH scale

- $[H^+]$ X $[OH^-]$ always equals 10^{-14}

- log $[H^+]$ + log $[OH^-]$ = -14

- pH scale

Acid						Neutral							Alkaline
1	2	3	4	5	6	7	8	9	10	11	12	13	14

H^+ concentration

- Concentration of H^+ can be changed

$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$$

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+ + 3Cl^-$$

$$Na_2CO_3 + H_2O \longrightarrow 2Na^+ + HCO_3^- + OH^-$$

Calculating pH: example

Calculate the pH if $[H^+] = 0.001$

pH	=	$-\log [H^+]$
	=	$-\log [0.001]$
	=	$-\log 10^{-3}$
	=	$-(-3) \log 10$
	=	3×1
	=	**3**

Calculate the pH if $[OH^-] = 10^{-8}$

	$[H^+]$	x	$[OH^-]$	=	10^{-14}
or	$[H^+]$	x	10^{-8}	=	10^{-14}
or	$[H^+]$	=	10^{-14}	÷	10^{-8}
		=	10^{-6}		

pH	=	$-\log [H^+]$
	=	$-\log 10^{-6}$
	=	**6**

Calculate the pH if $[OH^-] = 0.00005$

	$\log [OH^-]$	=	$\log(5 \times 10^{-5})$		
		=	$0.7 - 5$	=	-4.3
	$\log [H^+]$	+	$\log [OH^-]$	=	-14
or	$\log [H^+]$	=	$-14 + 4.3$	=	-9.7
	pH	=	$-\log [H^+]$	=	**9.7**

pH indicators: features

- Colour changes over a wide range of pH values
- Interference due to colour of sample
- Interference due to turbidity of sample

Properties:

Indicator	Acid colour	Base colour	pH range
Methyl orange	red	yellow orange	3.1 – 4.6
Methyl red	red	yellow	4.4 – 6.2
Litmus	red	blue	4.5 – 8.3
Thymol blue	yellow	blue	8.0 – 9.6
Phenolphthalein	colourless	pink	8.2 – 9.8
Alizarin yellow	yellow	lilac	10.1 – 11.1

pH meter: features

- Consists of potentio meter, glass electrode, reference electrode
- Temperature compensation device
- Measures potential difference
- Meter indicates pH value or milli volts
- Accuracy of ± 0.01 pH

Types of electrodes

- Glass electrodes
- Calomel electrodes

Maintenance: glass electrode

- Do not scratch
- Immerse in pH 4.0 buffer, for short term storage
- Soak in water for 12 h before pH measurement

Calibration

- Use two buffer solutions
- Use a second buffer within 2 pH units of the sample pH

Buffer solutions

- Known pH
- Mixtures
  - weak acids & their salts
  - weak bases & their salts
- Dilution does not change pH
- Resist change of pH upon addition of small amount of acid or alkali

Preparation: Buffer solution of known pH

	Buffer solution		pH at 25°C	Amount of salts to be dissolved in 1000 ml freshly boiled & cooled distilled water
1	0.05M	potassium hydrogen phthalate	4.00	10.12 g $KHC_8H_4O_4$
2	0.025M 0.025M	potassium dihydrogen phosphate + disodium hydrogen phosphate	6.86	3.387 g KH_2PO_4 + 3.533 g Na_2HPO_4
3	0.01M	sodium borate decahydrate	9.18	3.80 g $Na_2B_4O_7.10\ H_2O$

Add copy of Main text in chapter 8, for all participants.

7 Additional handouts

These handouts are distributed during delivery and contain test questions, answers to questions, special worksheets, optional information, and other matters you would not like to be seen in the regular handouts.

It is a good practice to pre-punch these additional handouts, so the participants can easily insert them in the main handout folder.

8 Main text

Understanding hydrogen ion concentration (pH)

1. General

pH is a way of expressing the hydrogen ion concentration in water. It is related to the acidic or alkaline nature of water. Consideration of hydrogen ion concentration is important in almost all uses of water. In particular, pH balance is important in maintaining desirable aquatic ecological conditions in natural waters. pH is also maintained at various levels for efficient operation of water and wastewater treatment systems such as coagulation, disinfecting, softening, anaerobic decomposition of wastes, etc. The pH of most natural waters lies between 6.5 and 8.

2. The pH scale

Pure water dissociates to yield 10^{-7} moles/L of H^+ at 25 °C:

$$\mathbf{H_2O \Leftrightarrow H^+ + OH^-} \qquad \mathbf{(1)}$$

Since water dissociates to produce one OH^- ion for each H^+ ion. It is obvious that 10^{-7} OH^- ions are produced simultaneously.

The product of $[H^+]$ and $[OH^-]$ always remains constant even if the value for one of the species changes

$$\mathbf{[H^+] \times [OH^-] = 10^{-14}} \qquad \mathbf{(2)}$$

The large bracket sign, [ ], indicates molar concentration.

The concentration of H^+ ions can be increased when compounds are added which release H^+ ions such as H_2SO_4:

$$\mathbf{H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}} \qquad \mathbf{(3)}$$

Or preferentially combine with OH^- ions when added to water, such as $FeCl_3$:

$$\mathbf{FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ + 3Cl^-} \qquad \mathbf{(4)}$$

Note that in either case the product of $[H^+]$ and $[OH^-]$ ions remains constant at 10^{-14}.

Likewise the concentration of H^+ ions can be decreased when compounds are added which release OH^- ions, such as NaOH, or preferentially combine with H^+ ions, such as Na_2CO_3.

Expression of the molar concentration of hydrogen ions is rather cumbersome because of the extremely small values and large variations. To overcome this difficulty, the concentration is expressed in terms of pH value, which is negative logarithm of the concentration in moles/L.

$$\mathbf{pH = -\log [H^+]} \quad \mathbf{(5)}$$

or $$\mathbf{[H^+] = 10^{-pH}} \quad \mathbf{(6)}$$

Thus the pH value of a sample of water containing $10^{-7.5}$ moles/L H^+ is 7.5.
Since the product of $[H^+]$ and $[OH^-]$ is always a constant, Eq. (2) becomes

$$\mathbf{\log[H^+] + \log[OH^-] = -14}$$

or $$\mathbf{-\log[H^+] - \log[OH^-] = +14} \quad \mathbf{(7)}$$

The pH scale is usually represented as ranging from 0 to 14, with pH 7 at 25 °C representing neutrality. Acid conditions increase as pH values decrease and alkaline conditions increase as pH values increase.

Acid range Neutral Alkaline range

1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**

3. Calculating pH

Example calculation

Calculate the pH value for the following cases:

A: $[H^+]$ = a. 0.001
b. 0.00005 and

B: $[OH^-]$ = a. 10^{-8}
b. 0.00005
c. 0.00001

A: $[H^+]$ a. 0.001 pH = $-\log 10^{-3} = 3$
b. 0.00005 pH = $-\log 0.00005 = -\log(5\times10^{-5}) = -0.7 + 5 = 4.3$

B: $[OH^-]$ a. 10^{-8} $[H^+] \times 10^{-8} = 10^{-14}$, or $[H^+] = 10^{-6}$
Therefore pH = 6
b. 0.00005 $-\log[H^+] - \log[OH^-] = 14$
Therefore pH = 14 – 4.3 = 9.7
c. 0.00001 pH = $14 + \log 10^{-5} = 14 - 5 = 9$.

4. pH indicators

A number of naturally occurring or synthetic organic compounds undergo definite colour changes in well-defined pH ranges. A number of indicators that are useful for various pH ranges are listed in Table 1. The indicators assume different hues within the specified pH range. These are used as liquid solutions or some as pH papers. The change in colour occurs over a wide range of pH change and therefore pH value cannot be measured accurately. Further, the turbidity and colour of the sample may cause interference.

Table 1

Indicator	Acid colour	Base colour	pH range
Methyl orange	**Red**	**Yellow orange**	3.1 – 4.6
Methyl red	**Red**	**Yellow**	4.4 – 6.2
Litmus	**Red**	**Blue**	4.5 – 8.3
Thymol blue	**Yellow**	**Blue**	8.0 – 9.6
Phenolphthalein	**Colourless**	**Pink**	8.2 – 9.8
Alizarin yellow	**Yellow**	**Lilac**	10.1 – 11.1

5. pH meter

The use of colour indicators for pH measurements has, to some extent, been superseded by development of glass electrode. pH meters employing glass-indicating electrodes and saturated calomel reference electrodes are now commonly used. Such meters are capable of measuring pH within $\pm$ 0.1 pH unit. The electrodes, connected to the pH meters are immersed in the sample and the meter measures the potential developed at the glass electrode due to hydrogen ion concentration in the sample and displays it directly in pH units. The pH meters are also equipped with a temperature-compensation adjustment.

The electrodes should be carefully handled and should not be scratched by butting against the sides of the beaker containing the sample. Follow the manufacturer’s instructions for their care during storage and use. For short-term storage, the glass electrode may be left immersed in pH 4 buffer solution., Saturated KCl is preferred for the reference electrode. The glass electrode needs to be soaked in water for at least 12 hours before it is used for pH measurement.

Buffer solutions & instrument calibration

pH meters have to be calibrated against solutions of known pH values. Standard buffers are used for this purpose. Buffers are solutions of chemicals of known pH which do not change their pH value upon dilution and resist change of pH when small amounts of acid or alkali are added to them. Buffer solutions usually contain mixtures of weak acids and their salts (conjugate bases) or weak bases and their salts (conjugate acids). Buffer has importance for life forms that usually can survive only within a narrow pH range. Table 2 gives the composition of some commonly used buffers. Buffers of different pH values are also available commercially.

Table 2 Buffer solutions of known pH

S. No.	Buffer solution	pH at 25°C	Amount of salt to be dissolved in 1000 ml freshly boiled and cooled distilled water
1	0.05 M potassium hydrogen phthalate	4.00	10.12 g $KHC_8H_4O_4$
2	0.025 M potassium dihydrogen phosphate + 0.025 M disodium hydrogen phosphate	6.86	3.387 g KH_2PO_4 and 3.533 g Na_2HPO_4
3	0.01 M sodium borate decahydrate	9.18	3.80 g $Na_2B_4O_7.10\ H_2O$

It is a good practice to calibrate the pH meter using two buffers. After calibrating with an initial buffer, use a second buffer within 2 pH units of the sample pH.