# DETERMINATION OF pH BY POTENTIOMETRY

## Tasks (goals):

1. Prepare the laboratory standard solution of NaOH by dilution of a stock solution and determine its exact concentration
2. What amounts of $H_3PO_4$ and $KH_2PO_4$ are included in your sample A (in grams)?
3. What is pH of your sample B?
4. Prepare Britton-Robinson buffer and estimate its dilution factor and buffer capacity

**Device for the measurement pH**

- pH meter pH8+DHS with the combined glass electrode

**A. Calibration of pH meter**

Calibration solutions used for the calibration of the glass-combined electrode are the following:

1. Tartrate (saturated solution) pH = 3.56 – buffer 1 (bottle „vinan“)
2. $Na_2B_4O_7$ (0.01 mol/L) pH = 9.22 – buffer 2 (bottle „borax“)

<u>If you start or finish work with an electrode</u>

A combined glass electrode is stored in an aqueous solution of potassium chloride to avoid the diffusion of chloride ions out of the electrode. Store the KCl solution at the safety place, rinse the electrode with water and do not leave the electrode on air for a long time. Immerse the electrode in water between individual measurements. When you finish work in lab give the electrode back to the KCl solution.

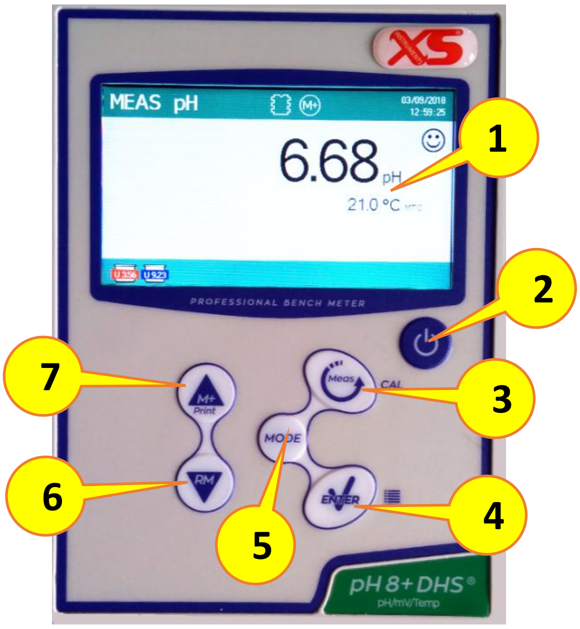


**Figure 1**. Front panel of pH-meter pH8+ DHS

1 – display, 2 – on/off, 3 – „back“ button when press or „calibration“ when hold for 3 s, 4 – „menu“ button during measurement or „OK“ button in menu, 5 – measurement mode (pH analog, pH digital, mV), 6,7 – arrows for menu or number settings

Procedure of pH meter calibration

1. **Set temperature.** Press button (6) or (7) for 3 seconds, use buttons (6) and (7) to set ambient temperature and confirm by button (4).
2. Press button (3) for 3 seconds; rinse and dry the electrode and confirm by button (4).
3. Insert the electrode to the **buffer 1** (tartrate (*czech* vinan)).
4. Set pH value of first calibration solution using buttons (6) and (7). The measurement stability is indicated with ☺ symbol. To confirm the value, press the button (4) As you have set first calibration point, you can see beaker symbol with pH value on display.
5. Rinse the electrode with distilled water and dry.
6. Insert the electrode to the **buffer 2** (borax).
7. Set pH value of second calibration solution using buttons (6) and (7). The measurement stability is indicated with ☺ symbol. To confirm the value, press the button (4) As you

have set second calibration point, you can see second beaker symbol with pH value on display. Press button (3) to finish the calibration.

You have prepared the pH meter for the measurement of pH.

8. Rinse electrode with distilled water and dry.
9. Insert electrode to the beaker with distilled water.

**B. Preparation of 500 mL 0.2 mol/L NaOH**

1. Calculate the volume of 1 mol/L NaOH required for preparing of 500 mL of 0.2 mol/L NaOH.
2. Use safety glasses, a volumetric cylinder and put the required amount of NaOH into a volumetric flask. Fill with distilled water to the mark, shake thoroughly. (Precise dilution to the mark is not necessary in this case because you will estimate the exact concentration in the next step but you can try yourself)

**C. Standardization of NaOH solution**

*Chemical reaction:*

$$H_2C_2O_4 + 2\ NaOH \rightarrow Na_2C_2O_4 + 2H_2O$$

*Procedure:*

1. Calculate how many $(COOH)_2.2H_2O$ should be weight for reaction with 25 mL of 0.2 mol/L NaOH.
2. Use an analytical balance and a pour boat (the glassware that is specially made for the dispensing of powdered materials) for weighing of of $H_2C_2O_4.2H_2O$. Dissolve the solid in 150-mL beaker in a small amount (approx. 50 mL) of distilled water. Put the electrode into a beaker (avoid the crash of the electrode) and add water, if needed, to cover the end of the electrode. Provide magnetic stirring. Position the burette so that reagent (NaOH) can be delivered without splashing. Titrate with NaOH in the range of pH 2 – 12 on the addition of NaOH 1 mL and record the meter reading. Draw a titration curve using MS Excel and determine the end point of titration.
3. Use two new amounts of $H_2C_2O_4.2H_2O$ (the maximum difference between individual amounts should be less than 0.001 g) and measure the titration curve more precisely – introduce fairly large volumes (about 5 mL) at the outset. Near the equivalence point, introduce the reagent in 1-mL increments and in the immediate vicinity (1 mL before and

after equivalence p.) in 0.2-mL increments. Continue the titration 3 mL beyond the equivalence point.

4. Estimate the exact concentration of NaOH from $2^{nd}$ and $3^{rd}$ measurement. Use MS excel to calculate differences of pH.

Calculate the volume of the NaOH solution in the equivalence point using following formula:

$$V_x = V_n + \Delta V_n \frac{\Delta^2 pH_n}{\Delta^2 pH_n - \Delta^2 pH_{n+1}}$$

$V_x$ – calculated volume of NaOH corresponding to the end point of titration,

$V_n$ – volume of NaOH corresponding to the last positive second difference of pH,

$\Delta V$ – constant addition of NaOH (in the close vicinity of the end of titration),

$\Delta^2 pH_n$ - last positive second difference of pH,

$\Delta^2 pH_{n+1}$ - first negative second difference of pH, where:

$\Delta^2 pH_n = \Delta^1 pH_{n+1} - \Delta^1 pH_n$ ,

$\Delta^1 pH_n = pH_n - pH_{n-1}$ .

**Table I.** Measured and calculated values of titration curve

| Volume of reagent [mL] | $\Delta V$ [ mL ] | pH | $\Delta^1$ pH | $\Delta^2$pH |
|---|---|---|---|---|
| 24.4 | | 5.13 | | |
| 24.6 | 0.2 | 5.34 | 0.21 | 0.07 |
| 24.8 | 0.2 | 5.62 | 0.28 | 0.10 |
| 25.0 | 0.2 | 6.00 | 0.38 | **2.18** |
| 25.2 | 0.2 | 8.56 | 2.56 | **- 1.21** |
| 25.4 | 0.2 | 9.91 | 1.35 | - 0.91 |
| 25.6 | 0.2 | 10.35 | 0.44 | - 0.91 |

$$V_x = 25{,}0 + 0{,}2 \cdot \frac{2{,}18}{2{,}18 + 1{,}21} = 25{,}13 \text{ mL}$$

Molarity of the NaOH solution calculate using following formula:

$n_{(NaOH)} = 2n_{(H2C2O4)}$

$$c_{NaOH} = 2\frac{m_{H2C2O4\cdot 2\,H2O}}{M_{H2C2O4\cdot 2\,H2O}\cdot V_{NaOH}} \quad (\frac{mol}{L})$$

***D. Determination of $H_3PO_4$ and $KH_2PO_4$ in the sample A***

<u>*Chemical reactions*</u>:

$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O$

$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$

$HPO_4^- + OH^- \rightarrow PO_4^{3-} + H_2O$

<u>Procedure:</u>

1. Fill the volumetric flask with your sample A (the number of sample and the number of your port should be the same) with distilled water to the mark and shake thoroughly.
2. Pipette 25 mL of this solution to the beaker (150 mL), add water to immerse the end of the electrode, provide stirring and adjust the burette filled with NaOH. Continue like in the case of the first titration of tartaric acid – use 1-mL increments of NaOH until the pH reach 12.
3. Use MS Excel to specify the end point of titration. Use 5-mL and 1-mL increments between the equivalence points and 0.2-mL increment in the 1-mL vicinity of the equivalence points.

Two inflex points can be observed if the solution is consisted of $H_3PO_4$ only or $H_3PO_4$ and $KH_2PO_4$ mixture. They correspond with neutralization of $H_3PO_4$ to $H_2PO_4^-$ (pH of the solution is 3 – 6) and $H_2PO_4^-$ to $HPO_4^{2-}$ (pH of the solution is 8 – 11).

4. Calculate the volume of NaOH corresponding amount of $H_3PO_4$ and $KH_2PO_4$

   $V_{\text{total}} = 2\cdot V_1 + V_2$

   $V_{\text{total}}$ = total volume of NaOH corresponding amount of $H_3PO_4$ a $KH_2PO_4$

   $V_1$ = volume of NaOH corresponding amount of $H_3PO_4$

   $V_2$ = volume of NaOH corresponding amount of $KH_2PO_4$

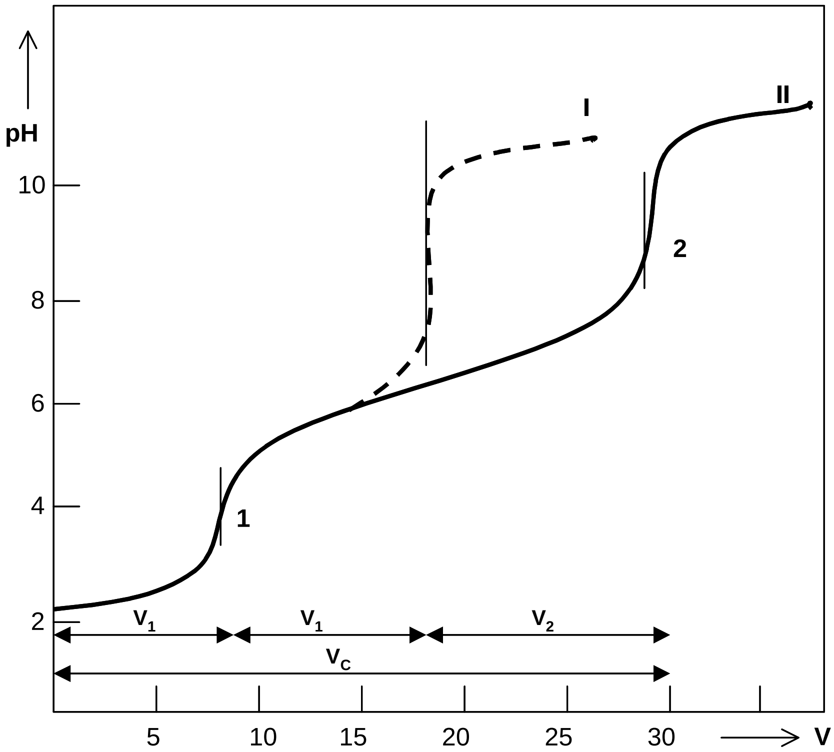


**Fig. 2.** Titration curve of $H_3PO_4$ (I) and the mixture of $H_3PO_4$+$H_2PO_4^-$(II)
$V_1$- volume of NaOH corresponding amount of $H_3PO_4$; $V_2$ – volume of NaOH corresponding amount of $H_3PO_4$ + $H_2PO4^-$; $V_c$ – total volume of NaOH

5. Calculate the amount of the $H_3PO_4$ and $KH_2PO_4$ in the sample A using following formula

$$m(A)_{vz} = c(NaOH) \cdot V(NaOH)_{ekv} \cdot \frac{V_{vz}}{V_x} \cdot M_A$$

where $m(A)_{vz}$ is total amount of $H_3PO_4$ or $KH_2PO_4$ contained in the original sample A; $V(NaOH)_{ekv}$ is corresponding volume of NaOH for the determination of amount $H_3PO_4$ and $KH_2PO_4$ ($V_1$ or $V_2$ , see **fig. 2**); $V_{vz}$ is total volume of a sample (100 mL); $V_x$ is aliquot volume of sample used for the titration (25 mL).

**E. pH estimation of sample B**

1. Calibrate pH meter.
2. Fill a dry beaker with your sample B.
3. Insert the electrode into the solution.
4. Measure the pH value.

**F. Preparation of Britton-Robinson buffer on the required pH value**

Pipette 50 mL of Britton-Robinson solution to a dry beaker (100 mL) and mix it with NaOH that corresponds to required value of pH (ask the assistant) (see the table II.). Correct the volume of NaOH considering the different concentration of your NaOH (volumes of NaOH listed in the table II. correspond with exactly 0.2 mol/L NaOH). Measure the pH of this solution and compare it with pH in table II.

**Table II.** Preparation of Britton-Robinson buffers with the required pH value

50 mL solution containing a mixture of 0.04 mol·L$^{-1}$ $H_3PO_4$, 0.004 mol·l$^{-1}$ $CH_3COOH$ and 0.04 mol·l$^{-1}$ $H_3BO_3$ mixed with <u>*a*</u> ml of 0.2 mol·L$^{-1}$ NaOH

*a* … volume of 0.2000 mol·L$^{-1}$ NaOH

| **pH** | ***a*, mL** | **pH** | ***a*, mL** |
|---|---|---|---|
| 1.81 | 0.00 | 7.00 | 26.25 |
| 1.89 | 1.25 | 7.24 | 27.50 |
| 1.98 | 2.50 | 7.54 | 28.75 |
| 2.09 | 3.75 | 7.96 | 30.00 |
| 2.21 | 5.00 | 8.36 | 31.25 |
| 2.36 | 6.25 | 8.69 | 32.50 |
| 2.56 | 7.50 | 8.95 | 33.75 |
| 2.87 | 8.75 | 9.15 | 35.00 |
| 3.29 | 10.00 | 9.37 | 36.25 |
| 3.78 | 11.25 | 9.62 | 37.50 |
| 4.1 | 12.50 | 9.91 | 38.75 |
| 4.35 | 13.75 | 10.38 | 40.00 |
| 4.56 | 15.00 | 10.88 | 41.25 |
| 4.78 | 16.25 | 11.20 | 42.50 |
| 5.02 | 17.50 | 11.40 | 43.75 |
| 5.33 | 18.75 | 11.58 | 45.00 |
| 5.72 | 20.00 | 11.70 | 46.25 |
| 6.09 | 21.25 | 11.82 | 47.50 |
| 6.37 | 22.50 | 11.92 | 48.75 |
| 6.59 | 23.75 | 11.98 | 50.00 |
| 6.80 | 25.00 | | |

**G. Estimation of the dilution factor and buffer capacity**

1. Use a pipette and mix 25 mL of the prepared Britton-Robinson buffer and 25 mL of distilled water.
2. Measure the pH od a mixture. The dilution factor can be calculated by the following formula:

**$\Delta pH = pH_2 - pH_1$**

$pH_2$ – pH of Britton-Robinson buffer after dilution with distilled water

$pH_1$ – pH of Britton-Robinson buffer before dilution with distilled water.

3. Use a buret to add small additions (0.2 mL) of NaOH to the diluted Britton-Robinson buffer and record the pH until the value of pH increases by the unit pH. Calculate the buffer capacity β of the Britton-Robinson buffer by the following formula:

$$\beta = \frac{n(NaOH)}{V(buffer)} = \frac{c(NaOH) \cdot V(NaOH)}{V(buffer)}$$

*V*(buffer) = 50mL

## <u>Control questions</u>

1. Define $K_{H2O}$?
2. Define pH?
3. Describe the basic principle of potentiometric measurement
4. Describe electrodes contained in the cell for potentiometric analysis.
5. Define equation for the calculation of the potential of the cell.
6. Briefly describe or define electrode potential.
7. Briefly describe or define indicator electrode for the measurement pH.
8. Describe or define types of compounds that are used as buffer solutions?
9. Describe the equation of neutralization of $H_2C_2O_4$ with NaOH.
10. Which primary standards are used for the determination of NaOH?