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POTENTIOMETRIC METHOD OF NATURAL ENVIRONMENTAL WATERS pH DETERMINATION

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The article deals with a general description of the potentiometric method of measuring of the pH medium reaction. The use of the method for determining the pH of surface waters is substantiated. The reaction of the environmental surface water was studied by students of the Faculty of Fisheries and Nature Management in the chemical laboratory of the Earth Science and Chemistry Department.

Modern fish farming deals with fresh water as a medium for fish production. Surface springs are characterized by changes in water quality at different times of a year, and that affects the results of fish farming. Among the chemical indicators of water quality the hydrogen index (pH) plays one of the most important role. The development and activity of aquatic organisms depends on the pH value. The pH value of environmental water ranges from 6.5 to 8.5. It depends on the season: in winter for the most river waters pH value decreases (6.8–7.4), and in summer it rises (7.4–8.2). There are few nutrients in waters with a low pH value. Fish can withstand pH in the range from 5.0 to 9.0. Basic medium with pH > 10 is dangerous for all fish. The reaction of the water from neutral to slightly basic is the most favorable for fish ponds. The optimal pH is at the range of 7.0–8.5, short-term pH changes up to 6.5 and 9.5 are allowed. In such cases we should take urgent actions to increase or decrease it. At pH below 7.0, i.e. with an acidic reaction of the environment, the life processes of fish and other hydrobionts are slowed down, which reduces their growth rate and can lead to their death. Therefore, it is necessary to monitor the pH of the aqueous medium constantly.

Keywords: hydrochemical studies, potentiometry, determination of pH, surface waters, the effect of pH on aquatic organisms.

Formulation of task. Justify the potentiometric method of measuring surface water pH.

Object of study. Surface waters.

Materials and methods of research. Pure water is a very weak electrolyte that partially dissociates into hydroxide ions OH^- and hydrogen ions H^+ :

$$H_2O \leftrightarrow H^+ + OH^-$$

The process of water dissociation is a reversible one that characterized by a dissociation constant: $K = [H^+]^* [OH^-]/[H_2O]$

The dissociation constant of water depends on temperature, with increasing temperature it increases. The product of concentrations $[H^+]^* [OH^-]$ is the ionic product of water. At a temperature of 22°C it is equal 10^{-14} and characterizes the acidity of the medium on a pH scale.

$$K_v = [H^+]^*[OH^-] = 1.8^*10^{-16} * 55.56 = 1^*10^{-14}$$

In pure water, the concentration of hydrogen ions is equal to the concentration of hydroxide ions:

$$[H^+] = [OH^-] = \sqrt{10^{-14}} = 10^{-7} \text{ mol/l}$$

The ionic product of water at certain temperature remains constant regardless of changes in ion concentrations, which allows to calculate concentrations of hydroxyde ions by numerical concentrations of H^+ and vice versa.

To characterize the water medium acidity it was proposed to use a pH value, which equals to the negative decimal logarithm of the hydrogen ions concentration:

$$pH = -lg [H^+]$$

In pure water the media is neutral and pH = 7. In acidic media pH <7 and in alkaline media pH> 7. The closer the pH value to zero, the higher the concentration of H^+ ions in solution and the acidity of the medium is higher too. On the contrary, the closer the pH value to 14, the higher the concentration of OH^- ions in the solution, the more basic is the medium.

Natural waters are divided into seven groups depending on pH:

– strongly acidic (pH <3);
– acidic (pH = 3 – 5);
– weakly acidic (pH = 5–6,5);
– neutral (pH = 6.5–7.5);
– slightly alkaline (pH = 7.5–8.5);
– alkaline (pH = 8.5–9.5);
– strongly alkaline (pH>9.5).

The acidity of natural waters depends mainly on the concentration of humic and other weak organic acids. On the other hand dissolution of natural limestone rocks gives the water an alkaline character.

The content of hydrogen ions in natural waters is defined by the content of hydrogen carbonate and carbonate ions:

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$$

If surface waters contain small amounts of carbon dioxide they characterized as alkaline. Due to the consumption of CO_2 by aquatic vegetation during the processes of photosynthesis substantial changes in pH may happen. The humic acids present in soils effect concentration of hydrogen ions as well. In

cases where significant amounts of iron, aluminum, copper and other metals sulfates enter the water hydrolysis of these salts plays a role:

$$Fe^{2+} + 2H_2O \leftrightarrow Fe(OH)_2 + 2H^+$$

Water can be contaminated and contain large amounts of strong acids or their salts due to the discharge of industrial wastewater. In these cases pH value may be below 4.5.

The value of pH in river waters usually varies from 5.9 to 8.5, in atmospheric sediments from 4.5 to 6.0, in swamps 5.5–6.0, in sea waters 7.8–8.3.

The concentration of hydrogen ions in water is subjected to seasonal fluctuations. An increase in the pH value to 9 and even more is often observed in summer in open water bodies. Especially during intensive photosynthesis when the concentration of CO_2 decreases because of its use in carbohydrates building. When photosynthesis weakens in winter, CO_2 content under the ice grows and pH value is decreasing. In winter, the most river waters have pH 6.9–7.5, in summer 7.5–8.2. The water pH in reservoirs to some extent is determined by the geology of the catchment basin. It depends on various factors and may change during a year and even during a day.

In accordance with the requirements for the composition and properties of drinking water from ponds the pH value of water for these purposes should not exceed the range of 6.5–8.5. This is especially true for water reservoirs in recreational areas, as well as for water from fishery ponds.

There are buffer systems in natural waters that capable to maintain a constant value of pH in the presence of strong acids or strong bases. The carbonate buffer system, which works at pH less than 6, is able to neutralize acidic or alkaline effluents brought in by rain. The buffering capacity of natural waters and reservoirs are different. It depends on the substances contained in the deposits, bottom sediments and so on. The content of carbon dioxide in water is also affected by mobility of sediments, large amount of leaf precipitation and its active destruction in the event of heavy rain.

Precipitation with a high acidity can lead to serious changes in the state of surface water systems. Content of hydrogen ions in a reservoir is rising and pH is decreasing.

It is possible to define some stages of water acidification process:

In a stable water body, even despite the of acid rain, the pH does not change at the first stage, bicarbonate ions have time to neutralize hydrogen ions completely. Total alkalinity in the reservoir may drop approximately 10 times to a size of less than 0.1 mMol/l. In this case, during the period of intensive inflow of acidic waters into the reservoir (in autumn from heavy rains, in spring from melting of snow) the pH value of surface water bodies may undergo to significant deviations. The reservoir returns to normal acidity with the cessation of intensive acid rain. pH numbers rise to its original values.

In the second stage of acidification of the reservoir, the pH of the water throughout the year usually does not rise above 5.5. Such reservoirs are referred to as moderately acidic. At this stage of acidification there are significant changes in the composition of living organisms species.

In the third stage of acidification, the pH of water bodies is stabilized at pH values < 5 (usually pH about 4.5), even if precipitation has higher pH values. This happens due to the presence of humic substances and Al compounds in natural waters and the soil layer.

The solubility of carbonates, sulfides, phosphates of heavy metals increases when pH lowers, increasing their migration and availability for assimilation by living organisms, poisoning. Acidified rainwater, flowing down the land surface and seeping into the lower layers of the soil, better dissolves carbonate and other rocks, increasing the content of ions of Calcium, Magnesium, Silicon in groundwater and river water. Depending on the pH value, the rate of chemical reactions, the degree of corrosion aggressiveness of water, the toxicity of pollutants can vary.

It is known that the ions of many heavy metals (Cadmium, Copper, Plumbum, Mercury, Aluminum) have high toxicity for many species of aquatic living organisms and humans. The solubility of heavy metal compounds depends on pH. For example, in an acidic environment, high mobility is characteristic of Mo, V, U, Se, Sr, Zn, Cu, Co, Ni, Hg, As, Cd and others, in an alkaline and neutral environment – Mg, F, Sr, Ra. It should be noted that in a neutral environment the mobility of such elements as Al, Ti, Sn, Ag, Te, Cr, Zn, Cu, Co, Ni, Hg is very low. An increase in the content of heavy metal ions in water can lead to death of the ecosystem. Thus, the acidity of the aquatic environment affects the state of pollution of natural waters.

Therefore, the concentration of hydrogen ions is of great importance for chemical and biological processes occurring in natural waters. The value of pH depends on the development and activity of aquatic plants, the stability of various forms of elements migration; the pH value of water also affects the conversion of various forms of nutrients, changes the toxicity of pollutants.

It is most convenient and most accurate to determine the pH of water by potentiometric method using a pH meter. For an approximate description of the acidity of the medium you can use a universal indicator paper and determine the pH on a color scale. Another way is to use different acid-base indicators, which change their color at different pH values.

Potentiometric pH measurement is an electrometric method for determining the activity of hydrogen ions, based on measuring the potential difference occurring at the outer surface of the pH-selective membrane of the glass electrode. In practice, potentiometric pH measurement is performed by measuring the potential difference of a circuit consisting of a glass pH electrode reversible

to activity of hydrogen ion and a silver chloride reference electrode with saturated potassium chloride solution.

The measurement of the potential difference of the electrode system is carried out by the compensation method using an ionomer, which is pre-calibrated in pH units according to standard buffer solutions with a precisely known pH value.

Laboratory studies have confirmed precision of electrometric method of pH determination which is based on the measurement of the electromotive force (EMF) of an electrochemical circuit composed of a water sample, a glass electrode and a reference electrode. During electrometric pH determination, a laboratory pH meter with a glass measuring electrode and a silver chloride reference electrode is used.

When the glass electrode is immersed in the solution, between the surfaces of the glass electrode ball and the solution ion exchange occurs, as a result of which metal ions in the outer layers of the glass are replaced by hydrogen ions, so glass electrode becomes hydrogen one. Between the glass surface and the analyzing solution a potential difference (EMF) is forming proportional to the pH of the solution.

Water pH should be measured as soon as possible after sampling, as the pH changes rapidly due to various chemical, physical and biochemical processes in the sample. A laboratory pH meter is used for measurement.

Before determination, the electrodes are thoroughly washed with distilled water and dried with a paper filter. After determining the temperature we should set the handle "Solution temperature" of pH-meter in proper position. After determining the pH, the electrodes are immersed in a beaker with distilled water.

Potentiometric determination of pH is more accurate than colorimetric method and it makes it possible to measure the activity of hydrogen ions with an error of ± 0.02–0.05 pH in the range from 1 to 12 depending on the performance of the glass electrode and ionomer (pH meter).

Research results. Second-year students of the Faculty of Fisheries and Nature Management in the laboratory classes of the discipline «Biogeochemistry and Hydrochemistry» carried out a hydrochemical analysis of various samples of surface water by potentiometric method. The most effective teaching method in terms of developing of new competencies was the research method of projects. The results obtained in the study are shown in table 1.

Studies show that the water in all reservoirs has optimal pH values and is favorable for fish farming.

Conclusions. Water pH is one of the most important indicators of water quality, as it is of great importance for the formation of the chemical composition of water, its purification processes, providing living conditions for flora and fauna of the reservoir.

Table 1. **Hydrogen index of natural waters**

Name of the reservoir	pH	group
Dnipro R. (HBK)	7,2	Neutral waters
Dnipro R. (Hydropark)	7,9	Neutral waters
Dnipro R. (River port)	7,7	Neutral waters
Kosheva R.	7,0	Neutral waters
Ingulets R.	7,3	Neutral waters
Ingulets Canal	7,2	Neutral waters
Ingulka (Poniatovka village)	7,0	Neutral waters
Kakhovka Reservoir	7,1	Neutral waters

The acidity of natural waters depends mainly on the concentration of dissolved free carbon dioxide and the content of humic and other weak organic acids. But, as a result of pollution of fresh waters with acids, first of all, sulfate and nitrate, water pH decreases.

The potentiometric method is one of the main and accurate methods for determining the pH of the aqueous medium. The results of studies of the pH of the aquatic environment make it possible to control the hydrochemical regime of surface waters.

ПОТЕНЦІОМЕТРИЧНИЙ МЕТОД ВИЗНАЧЕННЯ pH ПРИРОДНИХ ВОД

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У статті розглядається загальний опис потенціометричного методу вимірювання реакції pH середовища. Обґрунтовано використання методу визначення pH поверхневих вод. Реакцію поверхневих вод навколишнього середовища вивчали студенти факультету рибного господарства та природокористування в хімічній лабораторії кафедри науки про Землю та хімії.

Сучасне рибництво розглядає прісну воду як засіб для виробництва риби. Поверхневі джерела характеризуються зміною якості води в різні періоди року, і це впливає на результати вирощування риби. Серед хімічних показників якості води водневий показник (pH) відіграє одну з найважливіших ролей. Розвиток та діяльність водних організмів залежить від значення pH. Значення pH природної води коливається від 6,5 до 8,5. Це залежить від пори року: взимку для більшості річкових вод значення pH знижується (6,8–7,4), а влітку воно піднімається (7,4–8,2). У водах з низьким значенням pH мало поживних речовин. Риба може витримувати pH в діапазоні від 5,0 до 9,0. Основне середовище з pH>10 небезпечно для всіх риб. Реакція води від нейтральної до слабоосновної є найбільш сприятливою для

рибних ставків. Оптимальний pH знаходиться в межах 7,0–8,5, допускаються короткочасні зміни pH до 6,5 та 9,5. У таких випадках нам слід вживати термінових заходів для його збільшення або зменшення. При pH нижче 7,0, тобто при кислій реакції навколишнього середовища, життєві процеси риб та інших гідробіонтів сповільнюються, що зменшує швидкість їх росту і може призвести до їх загибелі. Тому необхідно постійно контролювати pH водного середовища.

Ключові слова: гідрохімічні дослідження, потенціометрія, визначення pH, поверхневі води, вплив pH на водні організми.

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