OIV-MA-BS-13 Determination of pH

Type IV method

1. **Presentation**

The pH is closely related to the concentration of hydrogen ions (H+) present in alcoholic beverages (the pH characteristics of alcoholic beverages depend on various parameters, such as the quality of the reducing water, the duration of maturation in casks, the nature of the aromatic raw materials, and of any additives).

Due to the presence of ethyl alcohol in alcoholic beverages, the pH should be measured according to specific procedures.

2. **Purpose**

The purpose of the present document is to describe the measurement of pH in alcoholic beverages by the potentiometric method, using a glass electrode.

On the one hand it specifies the essential characteristics required of the appliance in order to obtain comparable results, and on the other, standardises the operating instructions for the glass electrode and the techniques to follow in order to obtain satisfactory results.

3. **Scope**

The method is applicable in the case of measurements on beverages with an alcoholic strength by volume ranging between 15 and 50% vol.

4. **Principle of the method**

4.1. Definition of pH

The pH of a solution is the decimal cologarithm of the solution activity in hydrogen ions and is measured in pH units.

4.2. General principle

The potential difference between a glass electrode and reference electrode immersed in the same solution is a linear function of its pH. According to the laws of Nernst, the electrode potential is related to the activity of the H+ ions present as indicated by the relationship

H = k + RT Loa (H+l F

where

- R is the gas constant, in joules / degrees

- T is the absolute temperature (°K)
- F is the Faraday symbol (96,500 coulombs)
- (H+) is the activity of the H+ ions,
- k is a constant depending on the nature of the glass electrode and the measuring device.

Determining the pH is therefore equivalent to the accurate measurement of potential difference. This measurement is made using a potentiometric apparatus with amplifiers. The assembly is required because of the high resistance of the electrical circuit and, in particular, that of the glass electrode.

Given the influence of temperature on the measurement result, the electrometer used must be equipped with an apparatus for temperature compensation and the exact conversion of the electromotive force in pH units, at a temperature of the sample.

The asymmetry potential of the glass membrane and the junction and diffusion potentials between the reference electrode and the liquid being tested will be eliminated by calibrating the system using standard solutions of known pH. One these standard solutions will be considered as the primary standard.

4.3. Principle applied to alcoholic beverages

4.3.1. The measurement of pH in organic media

The traditional pH range extending from 0 to 14 is determined by the dissociation of water. If the water content of a solution is gradually reduced or the water is replaced by another solvent, it is the dissociation equilibrium, i.e. the latter’s ionic product which is taken into account instead of that of the water. This results in totally different concentration ranges for the "free" H+ ions (i.e. which are not chemically bound).

In non-aqueous media, it is not possible to carry out absolute measurements of pH. Only relative measurements can be made. In addition, partially aqueous media are often low-ion.

However, from a water content of at least 5%, the classic definition of pH can be used, i.e. expressed in terms of absolute values and not just relative values.

Under these operating conditions, at the interface between the electrolyte and solution to be measured a phase separation is often formed which makes the signal unstable. There is also a risk of precipitation at the membrane level. The same problem is also encountered when using concentrated solutions of KCl as the reference electrolyte.

4.3.2. Specific measurement conditions

To avoid the problems described above, the basic requirement is that the electrolyte solution to measure and form a homogeneous solution without phase separation or precipitation. This condition can be met using lithium chloride (LiCl) in an ethanol medium.

A second condition is the use of an electrode with cylindrical membrane and a ground-in diaphragm, to ensure optimum contact between the reference electrolyte and the solution to be measured.

5. **Apparatus**

1. pHmeter

pH meter calibrated in pH units, enabling measurements to a minimum accuracy of: ± 0.01 pH i.e. ± 1 mV.

The instrument is preferably to be equipped with an electronic device for the automatic compensation of the temperature to a minimum accuracy of ± 0.5°C.

The pH meter should be used in a place sheltered from pollutants, acid or alkaline vapours in particular, hydrogen sulphide (H2S) and ammonia (NH3).

5.2. Electrodes

5.2.1. Combined electrode

The electrodes marketed for this specific purpose are generally of the type: combined electrode.

The useful part of the electrode consists of a cylindrical membrane and a ground-in diaphragm made of Teflon.

The reference electrolyte is an ethanol solution at 95% vol. of lithium chloride (LiCl) to 1 mol/L. Its alcoholic strength should be close to that of the alcoholic beverage to be analysed.

5.2.2. Immerse the electrode tip when not used continuously, in an ethanol solution of lithium chloride to 1 mol/1, unless otherwise specified by the manufacturer of the electrode.

5.3. Small laboratory equipment

5.3.1. Common glassware: beakers, crystallizers, etc.

5.3.2. Stirring device: magnetic stirrer and bar, for example.

5.3.3. Cleaning supplies: Joseph paper, etc.

6. **Reagents**

1. Deionised or distilled water.

Free from carbon dioxide and metal ions, with a maximum conductivity of 20°C 200 µS/m.

6.2. Standard buffer solution.

With reference to standard NFT 01012 "pH measurement - standard solutions for calibration of a pH meter"

6.2.1. pH buffer solution: 3.57 at 20°C

Saturated solution of potassium acid tartrate. Solution containing at least 5.7 g/1 of potassium acid tartrate (HOOC $C_2H_4O_2$ COOK) at 20°C. This solution can be kept for two months in the presence of 0.1 g of thymol per 200 ml.

pH	3.57 at 20°C
	3.56 at 25°C
	3.55 at 30°C

6.2.2. pH buffer solution: 4.00 at 20°C

- 0.05 M solution of potassium hydrogen phthalate. Solution containing 10.211 g/1 of potassium hydrogen phthalate (HOOC C_2 H_4 COOK) at 20°C (maximum storage time: 2 months).

pH	3.999 at 15°C
	4.003 at 20°C
	4.008 at 25°C
	4.015 at 30°C

6.2.3. pH buffer solution: 6.88 at 20°C

- Solution containing
- Dihydrogen phosphate, KH_2PO_4: 3.402 g
- Dipotassium phosphate, K_2HPO_4: 4.354 g
- Water q.s.p 1 L

- (Shelf life: 2 months)

pH	6.90 at 15°C
	6.88 at 20°C
	6.86 at 25°C
	6.85 at 30°C

6.2.4. pH buffer solution: 9.22 at 20°C Solution containing

- Decahydrated Borax, $B_4O_7Na_2.10\ H_2O$...: 3.810 g
- Water q.s.p: 1 L

(Basic buffer solutions are quickly altered by the carbon dioxide in the surrounding air, and it is therefore necessary to renew the solution for each calibration).

pH: 9.22 at 20°C

Note: market-available reference buffer solutions can also be used (according to the DIN 19266 standard and NBS, for example).

7. **Procedure**

1. Calibration of the measurement chain

    1. Two standard solutions are needed to calibrate the pH meter. Their pH should, if possible, be located on either side of the presumed pH value of the test solution; if this is not possible, one of them must not differ by more than one unit pH from the presumed value.

7.1.2. Zero setting the measurement chain (pH)

Operate in accordance with the instructions provided with the apparatus used.

Rinse the electrodes with the first standard buffer solution by pouring the liquid along them.

Introducing a sufficient volume of the same standard solution into the measuring vessel, which should be clean and dry, and immerse the electrodes.

Adjust the indication of the pH meter on the pH value of the standard solution taking into account its temperature (if necessary).

Remove the electrodes and discard the standard solution contained in the measuring vessel.

7.1.3. Setting the slope of the electrode

Rinse the electrodes with distilled or deionised water and then with the second standard buffer solution

Introduce a sufficient volume of the same standard buffer solution and immerse the electrodes.

If the result matches the known value of the pH of the standard solution, the unit is in working condition and is properly calibrated.

7.1.4. Calibration Check

Use a buffer solution with an intermediate pH value in relation those used for calibration.

7.2. pH measurements

Once the device has been calibrated, rinse the electrodes and the measuring vessel, first with deionised or distilled water, then with the test solution by proceeding as above. Homogenize the test solution, introduce a sufficient volume in the measuring vessel and immerse the electrodes.

Lightly stir the test solution.

Verify that the indication given by the pH meter is stable and record it.

8. Expression of results

In the operating conditions described above, the accuracy of the determination is ± 0.02 pH units

The results are expressed in units of pH, at a temperature of: 20°C, in the form

pH at 20 °C = xx, xx

9. Test report

Indicate in the test report:

- The method used,
- The specific details and any unforeseen events recorded during the measurement,
- Operations that were not scheduled or were optional.

10. Bibliography

- Method written with reference to the standards
- NFTO1-013 Mesure électrométrique du pH au moyen d'une électrode de verre - Vocabulaire et méthode de mesure –
- NFTO1-012 pH-métrie - Solutions étalons pour l'étalonnage d'un pH-mètre

Other sources

- Norme NF T 90-008 - Essais des Eaux. Mesure électrométrique du pH avec l'électrode de verre.
- Utilisation et entretien des instruments de mesure - Cahier technique - Fondation de l'eau - Ministère de l'Environnement –
- Théorie der Glaselektrode - K. Schwabe et H.D. Suschke-Angeur - Chem.76 (1964) 39-49

La pratique et la théorie de la Mesure du pH – Ingold Messtechnik AG.Compendium of International Methods of Analysis of Wines and Musts – International Office of Vine and Wine (OIV): Mesure du pH des vins et des moûts.