OIV-MA-AS2-06 Measurement of the oxidation-reduction potential in wines

Type IV method

1. **Purpose and scope of application**:

The oxidation-reduction potential (EH) is a measure of the oxidation or reduction state of a medium. In the field of enology, oxygen and the oxidation-reduction potential are two important factors in the pre-fermentation processing of the grape harvest, the winemaking process, growing, and wine storage.

Proposals are hereby submitted for equipment designed to measure the Oxidation-reduction Potential in Wines and a working method for taking measurements under normal conditions. This method has not undergone any joint analysis, given the highly variable nature of the oxidation-reduction state of a particular wine, a situation which makes this step in the validation process difficult to implement. As a result, this is a class 4 method[1] intended basically for production.

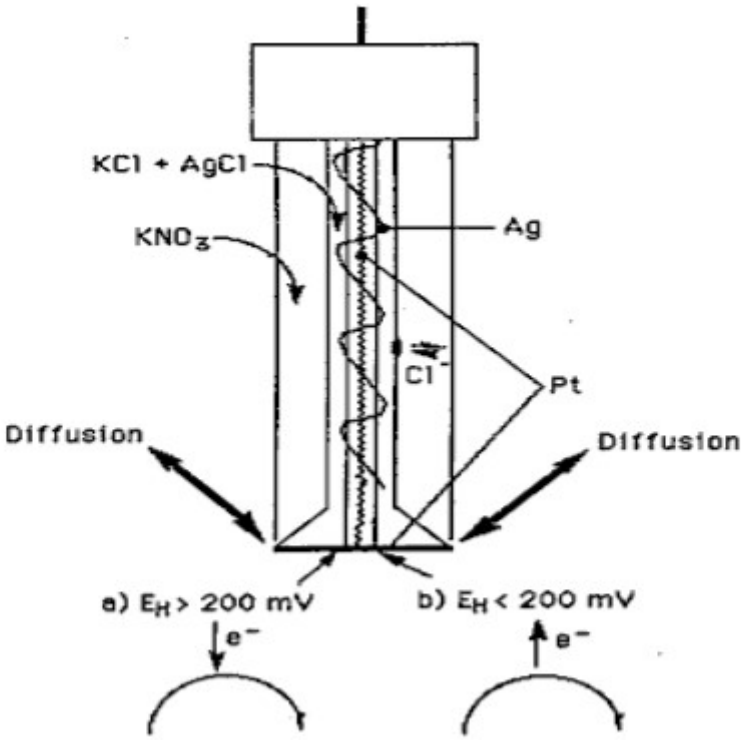
2. **Underlying principle**

The oxidation-reduction potential of a medium is defined as the difference in potential between a corrosion-proof electrode immersed in this medium and a standard hydrogen electrode linked to the medium. Indeed, only the difference in oxidation-reductions potentials of two linked systems can be measured. Consequently, the oxidation-reduction potential of the hydrogen electrode is considered to be zero, and all oxidation-reduction potentials are compared to it. The oxidation-reduction potential is a measurement value permitting expression of the instantaneous physico-chemical state of a solution. Only potentiometric volumetric analysis of the total oxidation-reduction pairs and an estimate of the oxidizing agent/reducing agent ratio can yield a true quantitative measurement. Oxidation-reduction potential is measured using combined electrodes, whether in wine or in another solution. This system usually involves the use of a platinum electrode (measuring electrode) and a silver or mercurous chloride electrode (reference electrode).

3. **Equipment**

Although several types of electrodes exist, it is recommended that an electrode adapted for measuring the EH in wine be used. It is recommended that use be made of a double-jacket combined electrode linked to a reference electrode (see figure). This system incorporates a measuring electrode, and a double-jacket reference electrode, both of which are linked to an ion meter. The inner jacket of the reference electrode is filled with a solution of 17.1% KNO_3; trace amounts of AgCl; trace amounts of Triton X-100; 5% KCL; 77.9% de-ionized water; and for the measuring electrode, the solution is made up of <1% AgCL; 29.8% KCL; and 70% de-ionized water.

Modified Combined Electrode



Oxidant Reduced Reductant Oxidized

4. Cleaning and calibration of the electrodes

4.1. Calibration

The electrodes are calibrated using solutions with known, constant oxidation-reduction potentials. An equimolar solution (10 mM/l) of ferricyanide and potassium ferrous cyanide is used. Its composition is: 0.329g of $K_3Fe(CN)_6$; 0.422g of $K_4FE(CN)_6$; 0.149g of KCl and up to 1000ml of water. At 20 °C this solution has an oxidation-reduction potential of 406 mV ($\pm$ 5 mV), but this potential changes over time, thus

requiring that the solution not be stored for more than two weeks in the dark.

4.2. Cleaning the Platinum in the Electrode

The electrode platinum should be cleaned by immersing it in a solution of 30% hydrogen peroxide by volume for one hour, then washing it with water. Complete cleaning in water is required after each series of measurement. The system is normally cleaned after each week of use.

5. Working method

5.1. Filling the Inner Jacket

The composition of the double jacket varies depending on the type of medium for which the EH is being measured (Table below).

Table

Composition of the Filler Solution in the Double Jacket of the Electrode as a Function of the Medium Measured

Medium to be measured	Solution Composition of the jacket
1 Dry wines	Ethanol 12% by vol., 5g tartaric acid, NaOH N up to pH 3.5, distilled water up to 1000 ml
2 Sweet wines	Solution 1 plus 20 g/l sucrose
3 Special sweet wines	Solution 2 plus 100 mg/l of $SO_2(KHSO_3)SO_2$
4 Brandies	Ethanol 50% by vol., acetic acid up to pH 5, distilled water up to 1000 ml.

5.2. Balancing the Electrode with the Medium to Be Measured

Before taking any measurements, the electrodes must be calibrated in Michaelis solution, then stabilized for 15 minutes in a wine, if the measurement s are to be taken in wines. Next, for measurements taken on site, measurements are read after the electrodes have been immersed in the medium for 5 minutes. For laboratory measurements, the stability index is the ΔEH(mV) / T (minutes) ratio; when this latter is $\leq$ 0.2, the potential can be read.

5.3. Measurements Under Practical Conditions

Measurements are systematically taken on site without any handling that could change the oxidation-reduction potential values. When taking measurements in storehouses, casks, vats, etc. care should be taken to record temperature, pH and

dissolved oxygen content (method under preparation) at the same time as the EH measurement is taken, as these measurements will subsequently be used to interpret results. For wines in bottles, the measurement is taken in the wine after letting it sit in a room whose temperature is 20 °C, immediately after the container is opened, under a constant flow of nitrogen, and after immersing the entire electrode unit in the bottle.

5.4. Expression of Results

Findings are recorded in mV as compared with the standard hydrogen electrode.

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[1] In conformity with the classification detailed in the Codex Alimentarius.