agrovin

ORP in wine

In-depth analysis

Introduction

What do we know about the ORP?

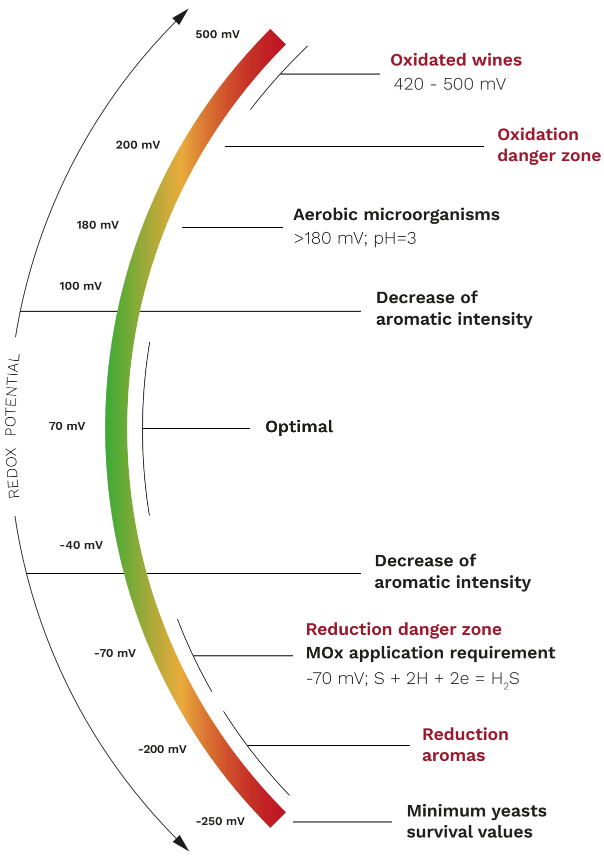
The chemical and biological processes in wine are multiple, but there are two balances among them that are particularly important because of their influence on the rest: the **acid-base** and **oxidation-reduction** balances.

The first of these is related to the acids in the wine, the measurement of the pH as well as the total acidity gives precise information on the real acidity of the wine.

Secondly, oxidation-reduction reactions involve a larger number of reactions than those of oxidation-reduction reactions of wine components, since they will involve all those molecules that can present an oxidized or reduced form. Knowledge of these molecules provides an image of the oxidation-reduction situation of the wine, as well as a forecast of its future trend.

pH	E (mV)
Electrode	Electrode
Buffer capacity	Buffer capacity
H^+	e^-
AT	OD
Dozens of compounds	Hundreds of compounds
Fast reactions reaching equilibrium	Slow reactions in constant evolution

Relationship between pH and ORP measurements.



The ORP influences a wide range of biochemical processes that affect the quality of the final wine, intervening in yeast metabolism, enzymatic activity, stability of phenolic compounds, as well as the production, perception and loss of aromas, etc.

The purpose of this document is to deepen the knowledge that the Agrovin group has developed over the last few years on how the ORP affects the different stages of winemaking.

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01. Alcoholic fermentation

02. Malolactic fermentation

03. Conservation

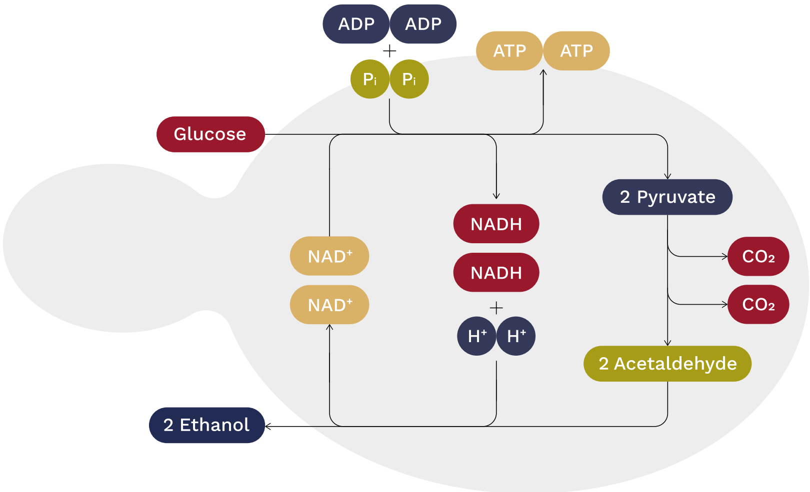
04. Monitoring

01. Alcoholic fermentation

During fermentation, yeasts break down sugars to produce ATP (adenosine triphosphate), their main source of cellular energy.

In the process of oxidation of sugars, electrons are released and transferred to electron transporters, such as NAD+, which is reduced to NADH. These electrons are then used to generate energy and synthesize new cellular components.

The accumulation of reduced compounds, such as NADH, can inhibit the activity of certain enzymes involved in fermentation, which can reduce the rate at which sugars are consumed.



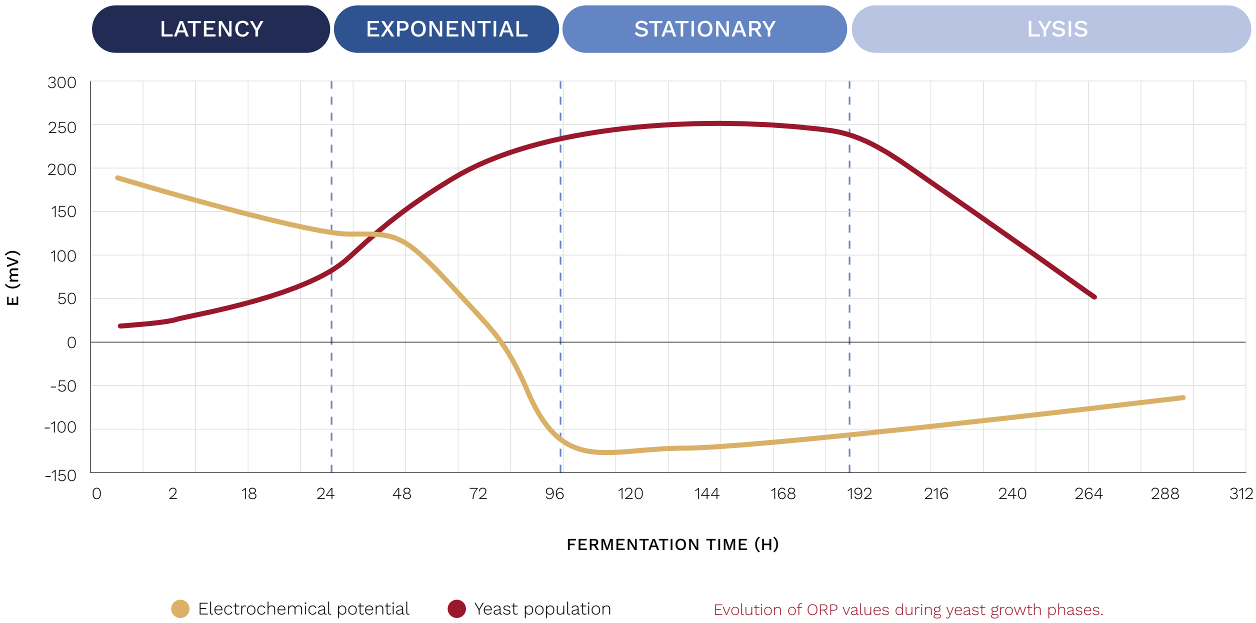
Internal ORP = -290 mV

This natural lowering of the redox potential during fermentation is also a microbiological self-protection by the *Saccharomyces cerevisae* yeasts, which guarantee their establishment in the medium against other microorganisms that require higher potential values.

Although, as we have already mentioned, yeasts have an important reducing effect, the lowering of the electrochemical potential during alcoholic fermentation must be controlled because too low ORP values can lead to fermentation deviations such as the formation of hydrogen sulfide and its derivatives by chemical means or even compromise the viability of the yeasts, causing fermentation to stop.

Yeasts and ORP

The relationship between yeast development and ORP follows a constant pattern that can be classified into four phases: dormancy, exponential growth, stationary and lysis.



Evolution of ORP values during yeast growth phases.

— **Latency phase:** first decrease in redox potential due to oxygen consumption.

— **Exponential phase:** the fact that there is a total consumption of oxygen and production of CO_2, at the same time that the yeast releases a large amount of reducing metabolites to regulate its intracellular potential, causes a pronounced drop in the ORP of the medium.

— **Stationary phase:** the accumulation of alcohol slows down cell metabolism and limits the rate of sugar consumption, the redox potential begins to stabilize.

— **Lysis phase:** with a high alcohol concentration and minimal sugar consumption, yeast metabolism begins to stop and oxygen dissolution becomes possible, leading to a progressive increase in potential.

Formation of reductive compounds

Volatile sulfur compounds constitute one of the most evident olfactory fractions of wine and their aromatic perception are strongly influenced by the redox potential. We differentiate between aromas with a positive sensory contribution, such as thiols, and those of a negative sensory nature that show a reductive character; these are the most common problem in both winemaking and bottled wine, since, apart from their presence in themselves, they hide the fruit and varietal characteristics of the wines.

Its formation is defined by two paths:

$SO_4^{2-} \rightarrow SO_3^{2-}$ (Sulfite) $\rightarrow H_2S$

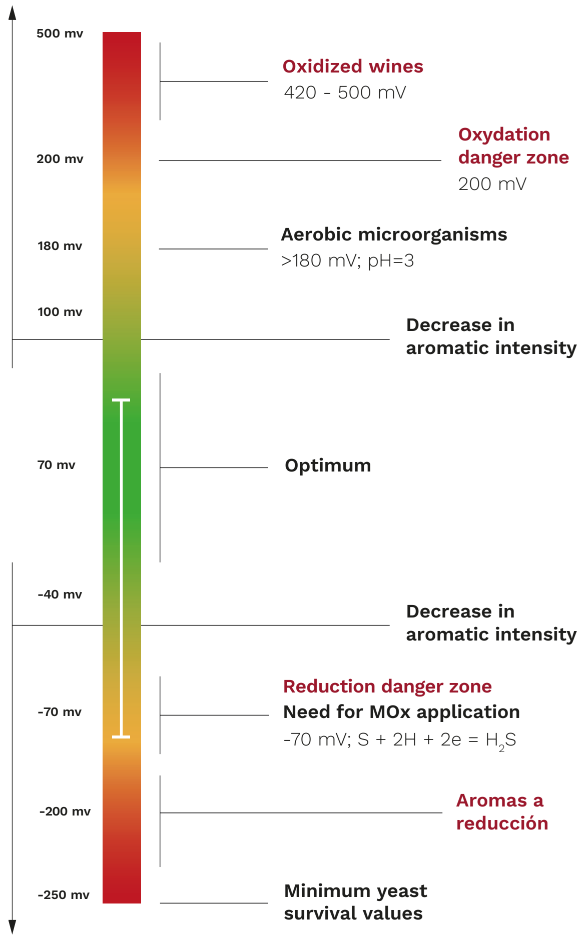
Yeast metabolic pathway that can form hydrogen sulfide (H_2S) as an intermediate product in the synthesis of sulfur amino acids if the must has no assimilable nitrogen compounds.

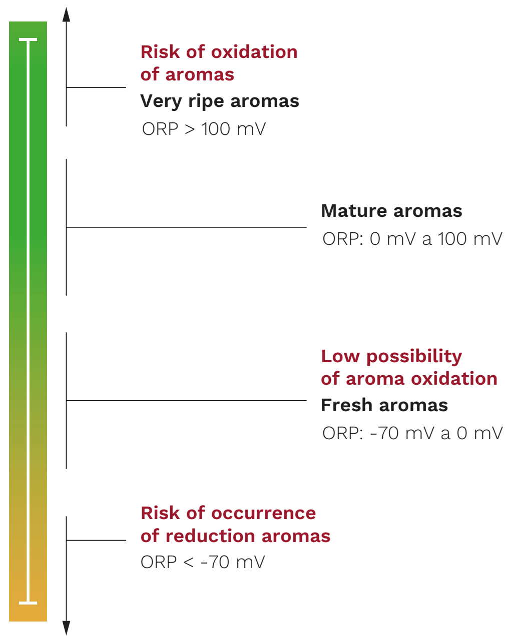
$S + 2H^+ + 2e^- \leftrightarrow H_2S$ E (pH = 3.5) = -70 mV

Spontaneous chemical pathway since at values below -70mV the risk of hydrogen sulfide (H_2S) formation from the elemental sulfur present in the must at wine pH begins.

In addition to this formation of sulfur compounds, ORP also plays an essential role in the aromatic expression of wines. We must seek the desired redox balance depending on the type of wine we want to make. We know that the ease of oxidation of aromas is determined by their nature, with thiol aromas being generally more easily oxidized, then terpenes and finally fermentative esters.

Therefore, in order to contribute to a greater aromatic expression by avoiding sulfur aromas and/or to direct the wine towards a specific profile, we must take into account the ORP level we want to bring the wine to at the time of bottling.





Scale of electrochemical potential values in winemaking.
Influence on aroma according to oxidation-reduction situation.

Why work on ORP during fermentation?

The experience gained in recent years thanks to the work carried out both in terms of measurement and oxygen supply has shown us that it is much easier to modify the ORP during alcoholic fermentation than after it. This point must be taken into account because, depending on the wine we want to obtain, white, rosé or young red wine for rapid rotation or wine for aging; depending on the varieties and their tendency to oxidation or reduction and depending on the ripening conditions, it will be convenient to be at lower or higher levels of redox potential. This will allow us to achieve a better aromatic expression as well as an optimal stabilization o f polyphenolic compounds.

Nutrition and ORP

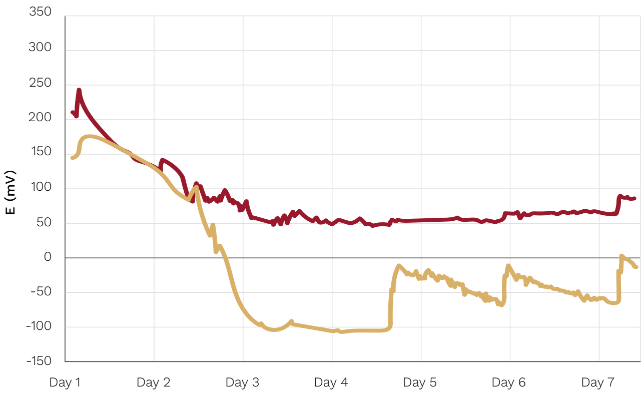
The rate of yeast multiplication will influence the decrease in electrochemical potential during alcoholic fermentation, and the change in trend can be associated with the end of the exponential phase. Therefore, variables that affect the rate of multiplication such as nutrition will have the ability to modulate the rate of lowering of the electrochemical potential.

When ammonium and organic nutrients are added simultaneously during the early stages of fermentation, the yeast consumes the ammonium directly, causing excessive cell multiplication and premature yeast exhaustion, and rapidly reducing the ORP. For this reason, it is not recommended to add ammonium salts during the yeast multiplication phase, but rather the application of nutrients with a high amino acid content **(Actimax NATURA).**

The effect of nutrition on the evolution of the electrochemical potential during fermentation is shown below.

— **Actimax Natura (100% organic nutrition):** It shows a moderate downward trend without reaching values that could be considered a risk.

— **Complex nutrition:** The drop in electroche-mical potential is very pronounced, reaching very low values with appreciable organoleptic consequences in tasting.



Electro 1

Actimax Natura 30 g/hl (Start)
+
20 g/hl (D1080)

Electro 2

Nutrición compleja 30 g/hl (Start)
+
20 g/hl (D1080)

Electrochemical potential monitoring in two vinifications with different nutritional protocol.

Vintage 2021, Cabernet Sauvignon variety, Penedés.

Tasting

The effects of the difference in electrochemical potentials during fermentation are evident, with the wine made with **Actimax Natura** being much more varietal and fruity (presence of red and black fruits and a certain spicy touch) than the wine fermented with the complex nutrient, which has a much more neutral aroma with certain herbaceous touches.

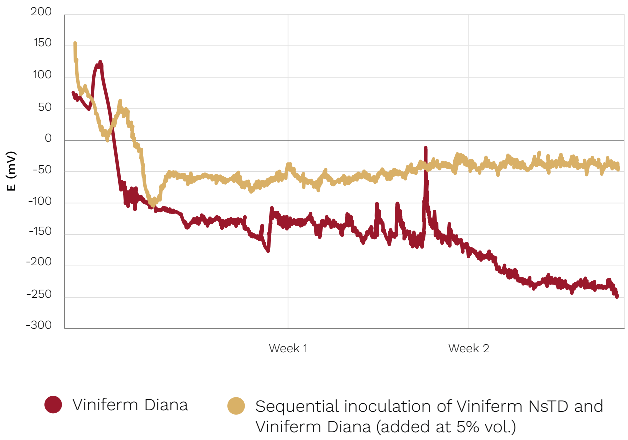
Influence of yeasts

Sequential inoculation strategy

The use of **Viniferm NSTD,** a non-*Saccharomyces* yeast, allows the consumption of sugars at a moderate rate, in combination with our range of Viniferm *Saccharomyces* yeasts, allows the control of potential decreases, with less probability of reaching values that lead to the risk of reduction aroma formation, in addition to promoting organoleptic improvements.

It should be noted that **Viniferm NSTD,** *Torulaspora delbrueckii,* has unusual sensory characteristics, demonstrated over several years of research and presented within of the NutriAroma Project, improving both aromatic sensations due to its high ß-lyase activity, and tactile sensations due to its high production of glycerol (cellular osmoregulator of the ORP).

The control of fermentation kinetics with controlled multiplication and sequential seeding makes it possible to obtain wines with maximum aromatic expression and complexity.



Monitoring and comparison of the electrochemical potential during fermentation between two identical Chardonnay musts (Puglia).

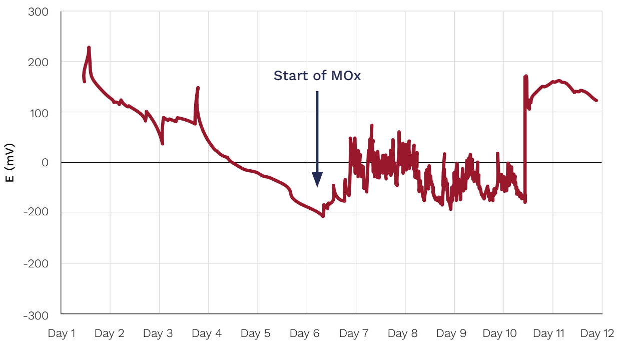
Oxygen supply

Oxygen has a great influence on AF development, both through its effect on yeast multiplication and viability and in the regulation of redox potential.

— **Latency and exponential phase:** in winemaking with a reductive tendency, oxygen supply should be minimized during the first 24-48 hours so as not to excessively stimulate multiplication and thus avoid reaching excessively low ORP values that could lead to aromatic deviations or even associated fermentation stoppages.

— **Stationary phase:** cell multiplication i s limited, small amounts of oxygen (5-25 ml/l/day depending on the oxidation-reduction tendency) can help to regulate the redox potential in fermentations with low oxidation-reduction potentials.

— **Cell lysis phase:** yeast activity is low, an oxygen supply (3-10 ml/l/day according to oxidative tendency) during this phase will favor a safer and more complete end of fermentation. It will also prevent the appearance of reduction aromas. On the other hand, the influence of these inputs on the redox potential will be greater, allowing greater control of it. A slight increase in redox potential at this stage will favor polyphenolic polymerization, will allow wines with more open and frank aromas and will also favor the subsequent MLF.



Monitoring of the electrochemical potential in fermentation with MOX.
Macabeo variety (Aragón).

Variety	E max.	E min.	O_2 supply
Macabeo	250 mV	-105 mV	10 ml/l/month

Tasting

Presence of reducing aromas in the situation of minimum electrochemical potential values.

The contribution of O_2 in the form of MOx increases the potential values and cleans the aroma to a fresher, floral and fruity profile.

ORP monitoring during a macro- or micro-oxygenation treatment in fermentation allows us to know the moment when the downward trend of the potential has been reversed and to decide objectively the end of the treatment, as well as the effective dose adjustment according to the fermentation needs.

This knowledge allows us to work not only on the polymerization of polyphenolic compounds in the case of red wines, but also on their aromatic expression. In white and rosé wines, which are more delicate in contact with oxygen, it will allow us to control their elaboration in a reductive way, increasing aromatic preservation and allowing us to control the redox potential values that allow us to reach their maximum aromatic expression.

Variety	E max.	E min.	O_2 supply	Pump over
Tempranillo	234 mV	-89 mV	2 ml/l/day + 3 ml/l/day	2 times/day

Monitoring of the electrochemical potential in fermentation with MOX.
Tempranillo variety (DO Mancha).

02. Malolactic fermentation

The control of the redox potential during the period between AF and MLF as well as during MLF will be vital to enhance the polymerization reactions of polyphenols, to minimize aromatic losses and even to favor the onset of MLF.

The redox potential actively influences the rate at which the polymerization reactions of phenolic compounds, mainly anthocyanins and condensed tannins, take place. A first transformation of ethanol into acetaldehyde is necessary to favor the binding between anthocyanins and tannins, providing greater colloidal stability and further reducing astringency.

In the same way it will influence the development of malolactic fermentation; too low redox potentials will hinder the multiplication and development of lactic acid bacteria, which may cause a delay in the onset of MLF. Therefore, wines with a high TPI content with a higher antioxidant capacity and a more reductive tendency have more difficulties in carrying out MLF.

How can we work the redox potential in MLF?

Micro-oxygenation between AF and MLF

Micro-oxygenation between AF and MLF is one of the most frequent processes to promote the formation of acetaldehyde by ethanol oxidation and thus encourage the polymerization reactions of the phenols in the wine.

Micro-oxygenation is usually carried out according to the experience acquired by winemakers and is stopped when acetaldehyde notes appear during tasting. However, by measuring the redox potential, we can see precisely how the oxidation-reductive tendency of the wine evolves, thus adjusting the micro-oxygenation dose according to the characteristics of each wine.

STABILIZATION

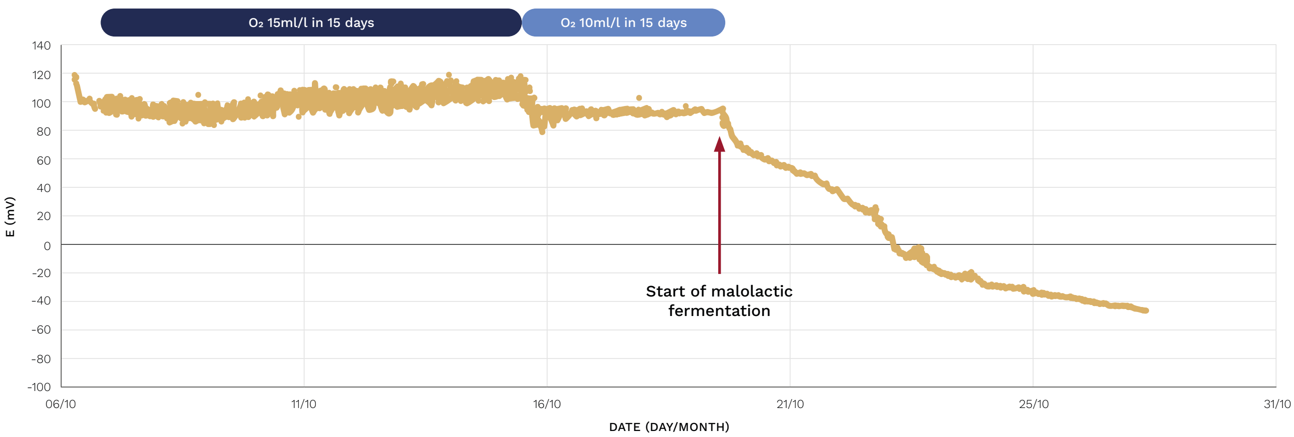
Micro-oxygenation

15-40 mL/L/month

TPI>70: 25-40 mL/L/month
TPI 50-70: 25-40 mL/L/month
TPI 30-50: 5-15 mL/L/month

15 days or until start of FML

The following shows the evolution of the redox potential of a wine between FA - MLF and how micro-oxygenation is modulated to decrease the oxidative tendency of the wine, thus avoiding possible aromatic losses due to oxidation.



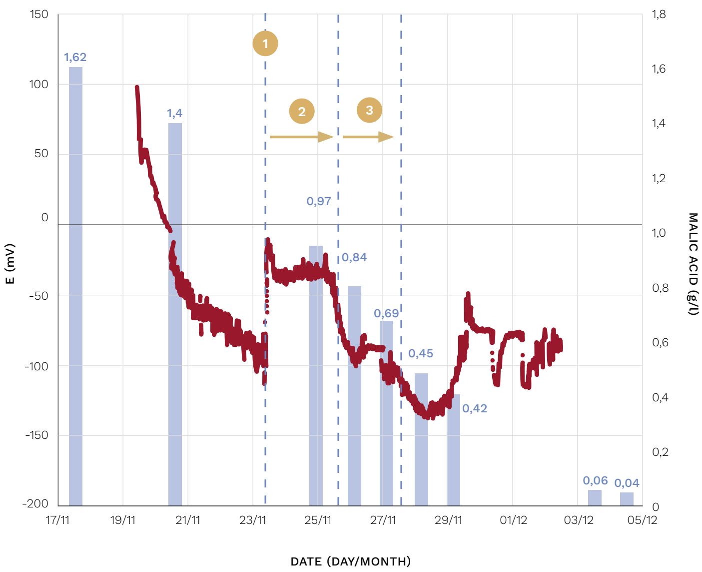
Synergy between the work with MOX and knowledge of electrochemical potential to adapt O_2 doses to the needs of the wine. Bull red wine (2020)

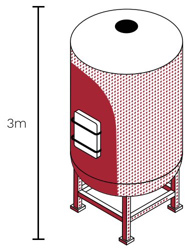
RedOx potential during the MLF

The effect of oxygen on the multiplication of lactic acid bacteria is variable, but in general, the best conditions for the development of malolactic fermentation are achieved with a non-strict anaerobiosis, i.e. with a slight amount of oxygen (Hidalgo Togores, 2003). Therefore, low redox potentials can delay or even inhibit the onset of MLF, so that control of this potential accompanied by micro-oxygenation, if necessary, can facilitate the development of MLF.

The correct management of the electrochemical potential, together with the application of bacteria from the **Viniferm OE** range, allows the realization of MLF even in the most unfavorable conditions.

In addition, once MLF has started, there is a reductive tendency due to the multiplication of lactic acid bacteria, which can lead to the formation of sulfur compounds in reduced form with a negative organoleptic impact. To avoid this phenomenon, we must modulate the drop in potential during MLF, and oxygen can be added until the malic acid value is half the initial value, after which oxygen doses should be limited, trying to maintain the redox potential between -50 and 30 mV.





Winemaking: Micro-oxygenation during MLF

ORP (mV) Malic acid

1 3 ml/l in 24h 2 1 ml/l/day 3 3 ml/l/month

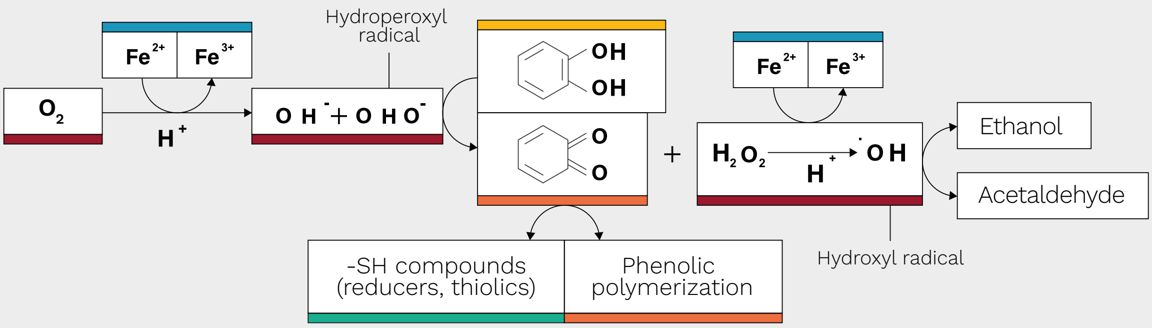
Work with oxygen during the MLF. Tempranillo (2020).

Analytical data at the beginning of MLF TPI: 72; CI: 19; AV: 0.40 and at the end of MLF TPI: 72; CI: 17; AV: 0.48.

03. Conservation

During storage, in white and rosé wines, we must take special care to avoid possible oxidation that could cause the wine's aromatic reduction or color evolution; in the case of red wines, during this stage of storage we can promote the polymerization of phenols and treatment with wood. In all these operations the measurement of the redox potential will be fundamental to know and control the correct evolution of the wines.

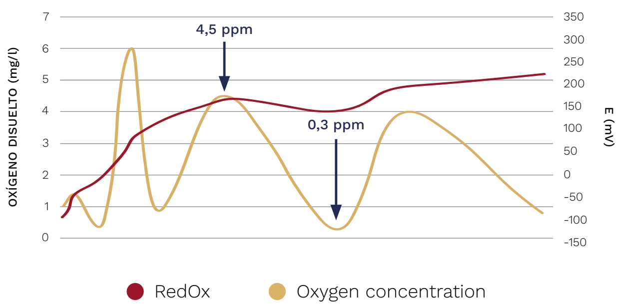
The oxidation process in wines is complex and depends on a large number of factors; there are compounds that act as substrates for oxidation and others as oxidants. Within this process, chain reactions occur that cause the oxidation of more compounds, even without the need for oxygen to be present. Oxygen by itself is not capable of oxidizing most of the compounds in wine; in order to oxidize them it needs a catalyst to perform the electron exchange. The main catalysts are Fe and Cu. Quinones are capable, on the one hand, of polymerizing with other quinones and producing browning, and on the other hand, of reacting with the -SH groups of thiols, considerably reducing the aromatic intensity of the wines.



Chemical oxidation process. Fenton reaction.

As mentioned above, oxygen initiates the oxidation reaction, but once it has started, the presence of this gas is not necessary for oxidation to occur.

For this reason, the measurement of dissolved oxygen must be accompanied by control of the redox potential, since this value will indicate the oxidative tendency of our wine. On certain occasions we can have low dissolved oxygen and high redox potentials, and therefore a high risk of oxidation.



Evolution of dissolved oxygen and ORP during storage.

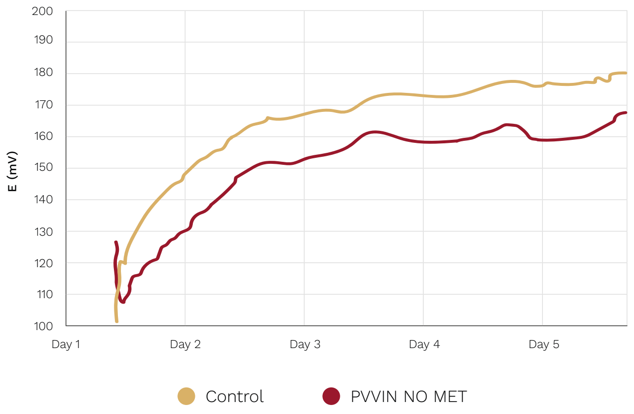
How can we work on the redox potential in conservation?

Metal removal

The role of catalysts in oxidation is decisive; it has been shown that oxygen is not capable of reacting with wines from which Fe and Cu have been totally eliminated. In practice, wines with lower levels of these metals are less oxidizable.

In the graph we can see how the wine treated with **PVVIN NO MET** and taken to forced oxidation, presents a lower redox potential compared to the wine that has not been treated with this oenological solution.

The use of **PVVIN NO MET** helps to reduce the concentration of Fe, Cu and phenolic compounds, thus reducing the risk of browning and aromatic losses by oxidation.



Comparison of the evolution of the electrochemical potential of a white wine under oxidation with and without PVVIN NO MET treatment.

Application of natural antioxidants
SuperBouquet Evolution

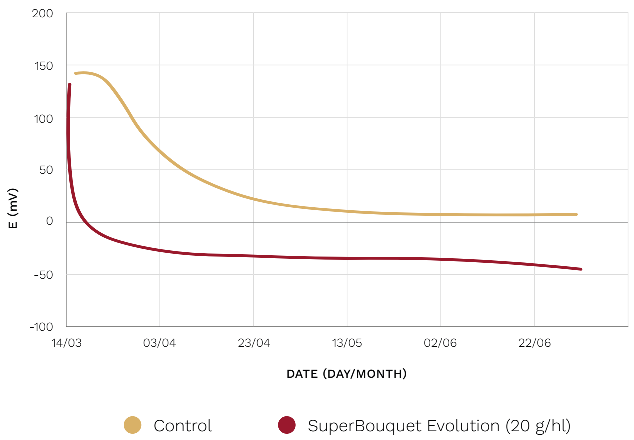
Glutathione is a tripeptide naturally present in yeast cells with a strong antioxidant power.

Its antioxidant action takes place at 3 levels:

01
Direct antioxidant. Due to its low RedOx potential, it is able to react with the oxidants present in the wine, protecting the desirable compounds from oxidation.

02
Color protection, GSH is able to bind to oxidized polyphenols giving rise to GRP (Grape Reaction Product), a colorless and stable compound whose formation paralyzes the cascade reactions that lead to wine browning.

03
Scent protection, quinones are highly reactive with thiols, leading to aroma degradation. GSH, by reacting with quinones, prevents them from reacting with thiols, thus protecting the aromas from oxidation.



Aged on exogenous lees in barrels. Tempranillo variety. DO Rioja.

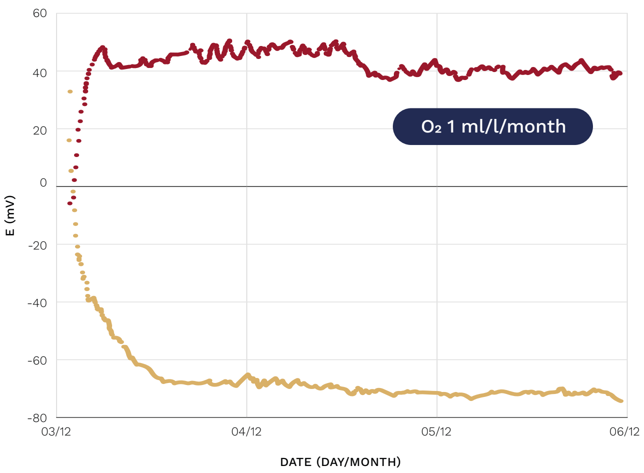
Tasting

The wine with lower electrochemical potential values has a fresher profile, with sharper acidity and fresher fruit.

Micro-oxygenation

On many occasions in the cellar, wines spend more time in tank than expected when they are ready for bottling. In these cases, it is possible to doubt, depending on the type of wine and the expected consumption time, whether it is more or less interesting to micro-oxygenate and to what extent.

On the one hand we know that wines with low redox potentials are more closed and less intense aromatically, and on the other hand we know what levels of micro-oxygenation will be optimal for the treatment of each wine, bearing in mind that even low doses of application can have a significant impact on the redox potential values.



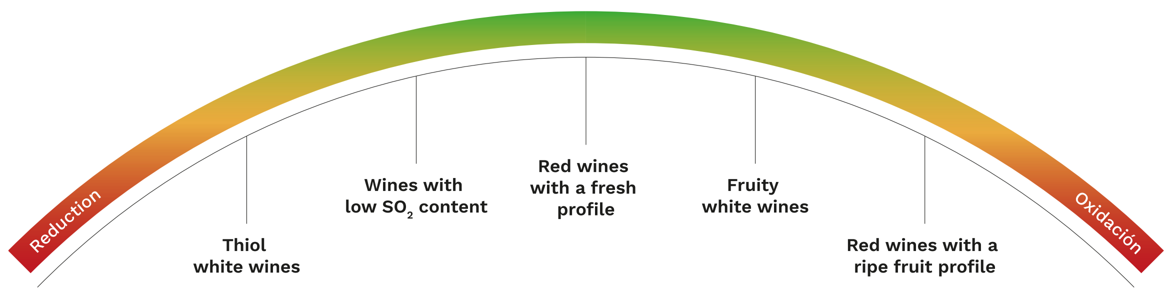
Comparison of the electrochemical potential values in a red wine with oxygen supply (red line) and without oxygen supply (yellow line).

Tasting

A comparison of the same wine with (red line) and without (yellow line) MOX treatment shows aromatic differences in which the wine with higher electrochemical potentials has a greater aromatic intensity, with a prevalence of red and black fruits. However, the wine maintained at low electrochemical potentials is neutral in aroma.

This will be an advantage for its conservation and preservation against oxidation, but will entail a lower aromatic expression in the case that it will be destined for immediate consumption..

The knowledge and modulation of the ORP of wines under preservation will allow to profile the character of the target wine.



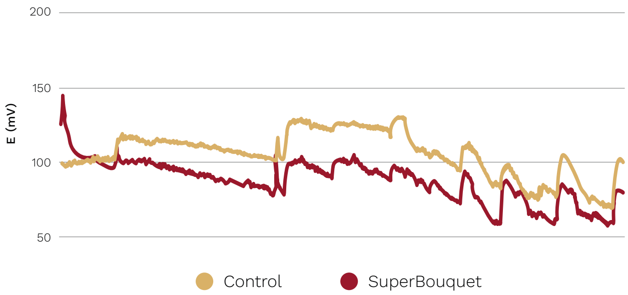
Aromatic profile of wines according to electrochemical potential values.

Aging on lees

Working on the lees of wines after alcoholic fermentation softens them by providing sweetness and reducing astringency.

During their lysis, yeasts increase the polysaccharide content and exert a protective action due to the reductive capacity of the lees themselves.

The preservation of wines in the presence of exogenous lees, although not specifically reductive, maintains the electrochemical potential values lower than in their absence.

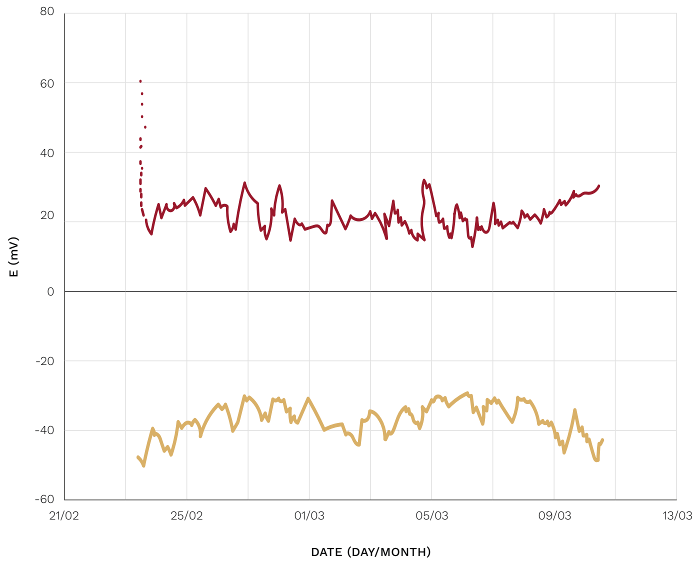


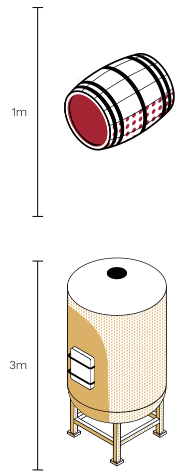
Comparison of electrochemical potential values of wine in the presence and absence of exogenous lees (SuperBouquet).

Aging with alternatives

Usually the work with oak alternatives is accompanied by the incorporation of oxygen in order to try to imitate the phenomena that occur inside the barrel. However, after the results obtained from different trials, the Agrovin group has detected that the micro-oxygenation provided in these treatments is usually lower than that which occurs naturally in the barrels, since, as can be seen in the graph, the redox potential reached in the barrel treatments is generally higher than the treatments with alternatives and micro-oxygenation in doses defined as equivalent.

Measuring the electrochemical potential at this point is essential to be able to adapt the oxygen supply to the real need according to the objective sought.





Variety: Tempranillo

Winemaking: Aging in barrels 2 months
2nd use

Variety: Tempranillo

Winemaking: 3 months of contact with staves
Post FML, stave aging

Comparison of the redox potential of barrel aging and treatment with oak staves and equivalent MOX.

04. ORP Monitoring

The measurement of redox potential during the winemaking process is an advantage in the knowledge of the processes, as well as in the decision making during the course of winemaking and storage.

AGROVIN offers you tools for the measurement of RedOx Potential during winemaking in different formats according to the needs of the winery, with the possibility of portable equipment and fixed installations:

Electrowine

It is a portable RedOx potential measuring device, designed to determine whether the wine is at risk of oxidation or reduction.

Technical characteristics

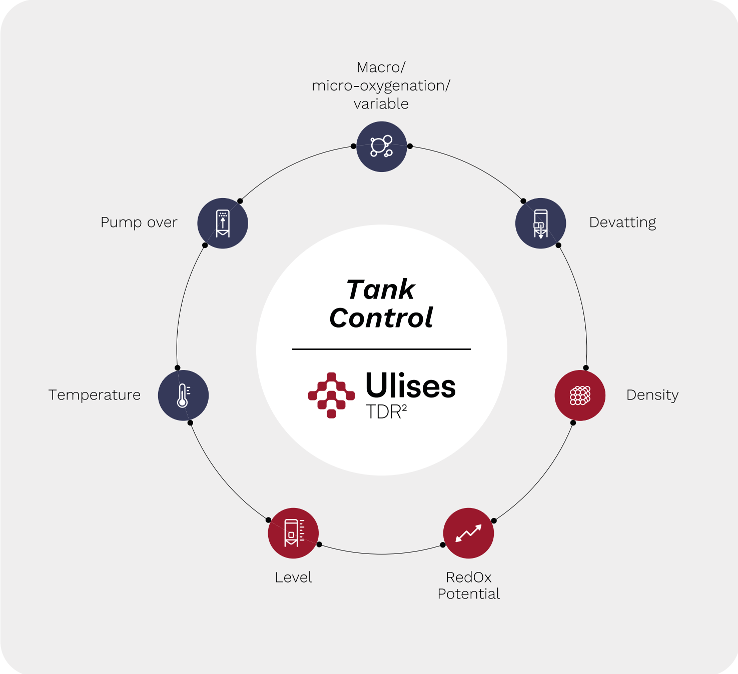
- Touch screen for the visualization and modification of the variables.
- Real-time display of measurements.
- Data storage.
- It allows working with up to 2 electrochemical potential probes.
- It allows the configuration of “single sensors” or “two sensors per tank” if we want to perform a stratified measurement at two heights.
- The Electrowine - Dosiox version has the option of working with 2 outputs for O_2 dosing.
- The synergy between O_2 dosing and electrochemical potential determination allows oxygen dosing within defined ranges.
- Remote connection system that allows the equipment to be controlled from mobile devices.

Tank Control - RedOx

The fixed electrochemical potential measurement systems are included in the Tank Control systems, an integrated winery management system where the winemaker can know, at any time and in each of the tanks, the key parameters during the winemaking and conservation of the wine.

Tank Control allows the integration of different tools, the components included being modular until reaching the total automation of the winemaking tanks:

- Automatic interventions
- Parameters monitored



The integrated software allows the control of all the tanks included in the technology, having a general preview screen of the tanks where basic information of each one of them is displayed.

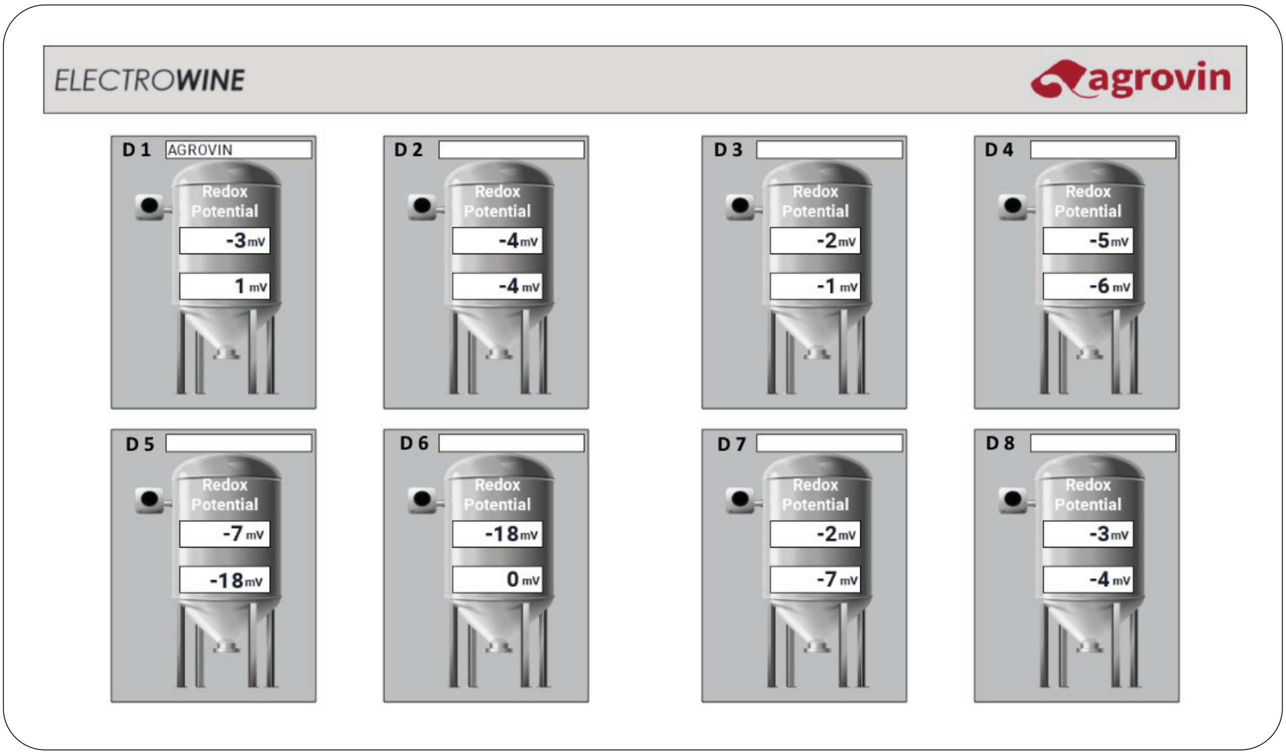


Image of the tank control screen

The evolution of the electrochemical potential of each of the stages is easily evaluated thanks to the graphical representation made by the management software. This allows us to visualize changes in trend or maintenance after the different cellar operations.

In addition, the alarm customization allows the establishment of optimal electrochemical potential ranges for each process, with a visual and acoustic warning when the measurement exceeds the established limits.

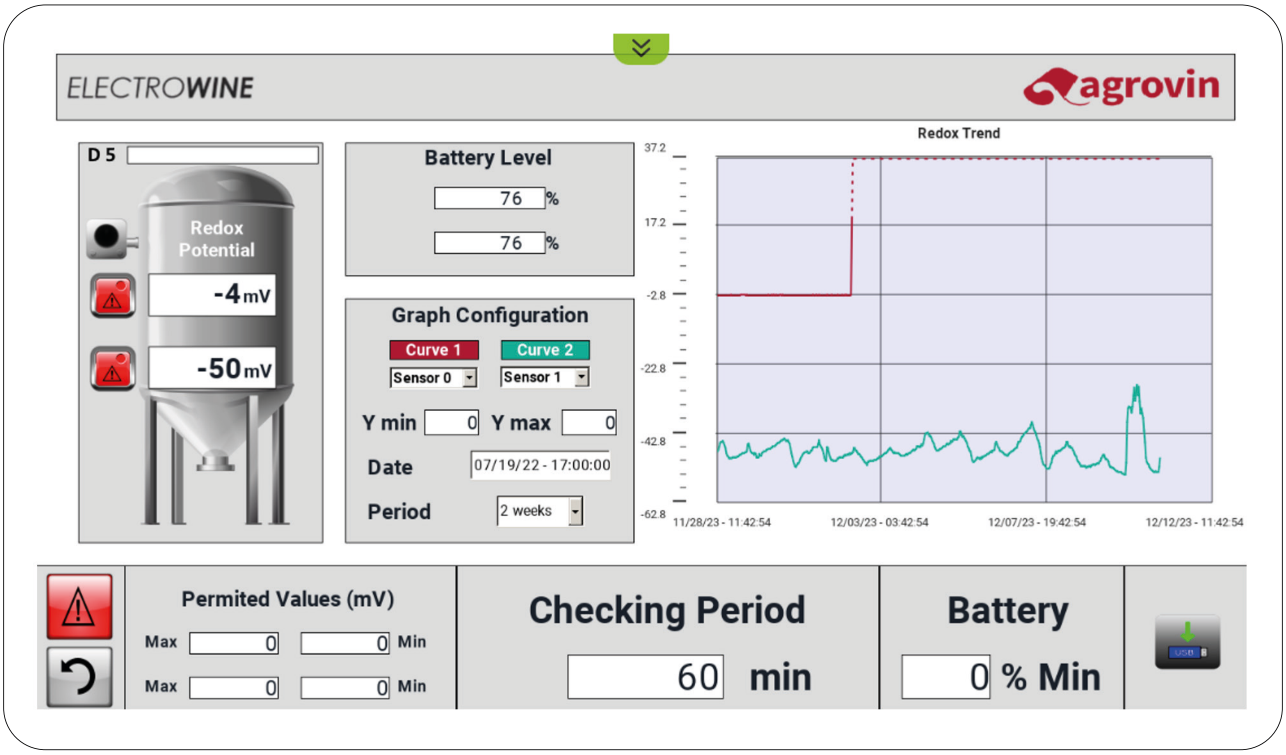
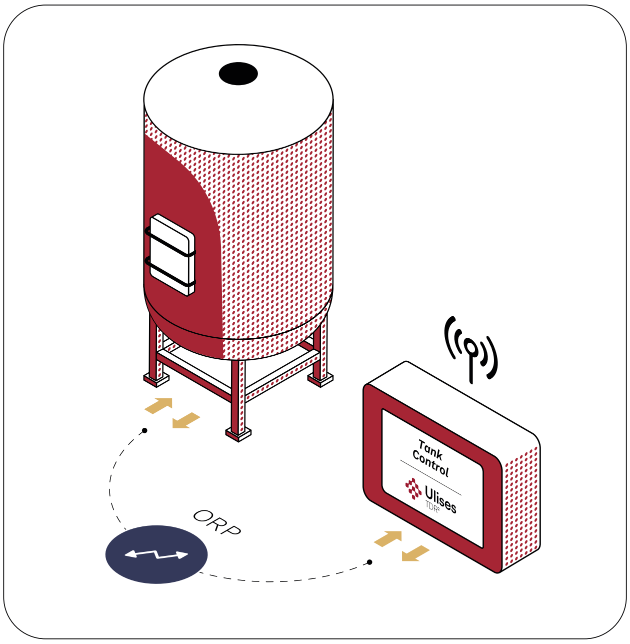


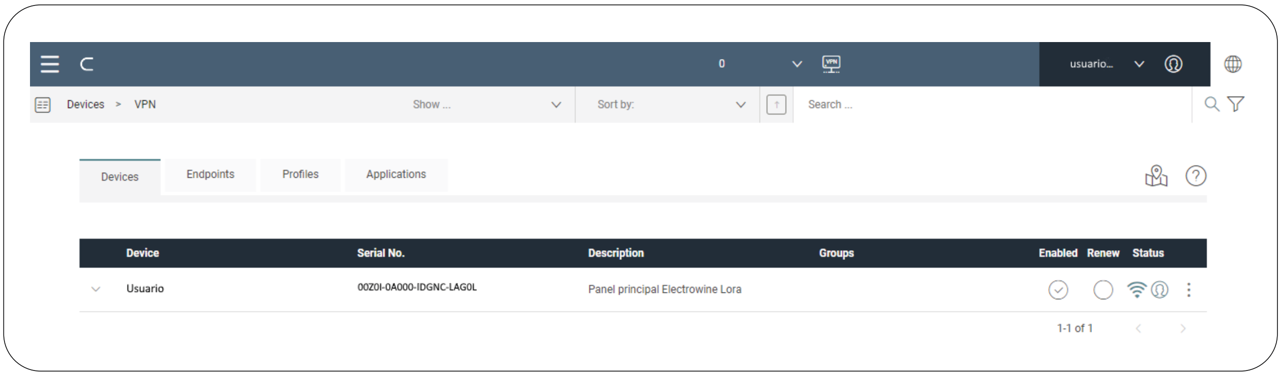
Image of the management screen by tank

The current technology developed by AGROVIN allows the option of wireless installations, without the need to run wiring between tanks, facilitating the installation and improving the signal reception capacity in large installations with significant distances between tanks. This is achieved thanks to the radiofrequency emission of the signal to the main control panel.



Both the visualization and control of the software can be done remotely through any electronic device (tablet or mobile) or from any computer in the winery.

The management will be done through the easy-to-use Corvina Cloud platform.



Remote management platform image

Notes

Calculations and conversion charts

Temperature conversions

°F	0	32	40	50	60	70	80	90
°C	-18	0	4	10	16	21	27	32
	°F = (°C x 9/5) + 32							

Dosage

g/hl	5	10	15	20	100
lbs/10³ gal	0.4	0.8	1.2	1.6	8
ppm	50	100	150	200	1000

Equivalent Units

1 gal = 3,785 L	**1 L = 0,264 gal**	1 lbs = 453,6 g
1 ml = 0,035 fl oz	1 fl oz = 30 ml	1 ppm = 1 mg/l
1 gal = 0,379 hl	1 hL = 26,4 gal	1° Brix = 1% sugar (wt/vol)
1 metric ton =2205 lb	1 metric ton = 1000kg	1 Vol % = 1 ml/ 100 ml
1 US ton = 2000 lb	1 US ton = 907 kg	1 barrel = 225 L = 59,4 gal = 25 cases

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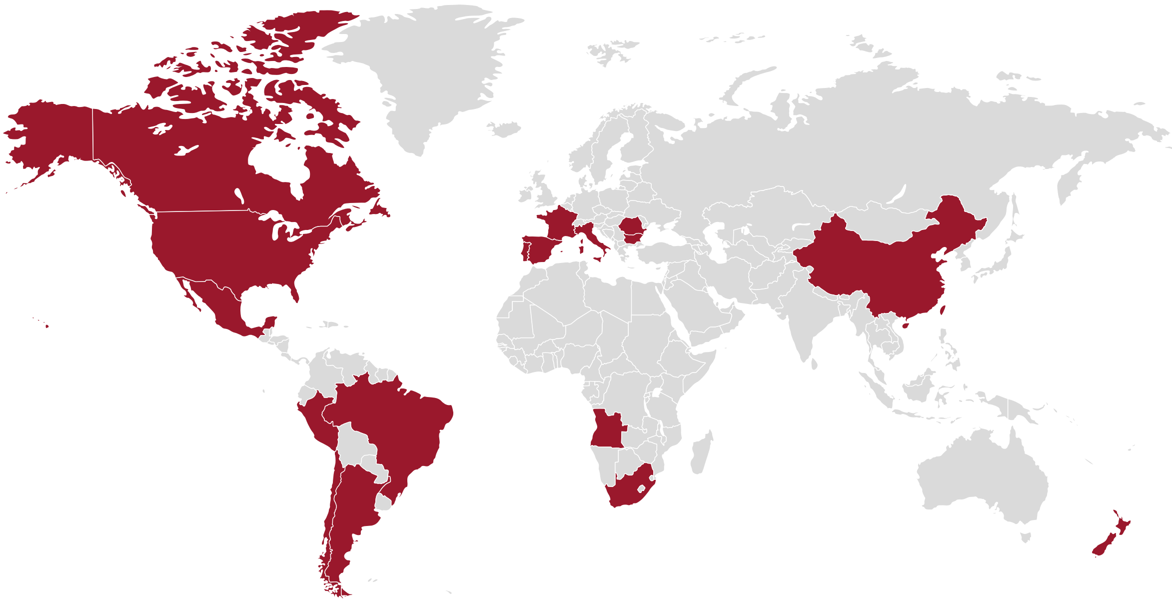

572 Martin Avenue - Suite A
94928 Rohnert Park (California)

Tel. 707-536-9934
agrovinusa@agrovin.com

agrovin.com

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