NEW PHYSICAL TECHNIQUES FOR THE TREATMENT OF WINE:
ELECTRODIALYSIS

Jean-Louis ESCUDIER
INRA, UE Œnologie, IPV-ISSV Pech Rouge, 11430 Gruissan

NOTE: THIS IS PART FOUR IN A FIVE PART SERIES BY ESCUDIER

2.2. Electrodialysis

The result of tartrate stabilization by electrodialysis is to avoid the formation of tartrate deposits in wines, which are not appreciated by consumers.

Electrodialysis is a subtractive technique well known and developed in the food and nutrition sector. It consists in extracting certain ions from wines, particularly potassium and calcium ions and tartaric acid, thus contributing to the decrease of supersaturated levels of tartaric acid salts.

2.2.1. Principle and definition of electrodialysis

The principle of electrodialysis is based on the properties of membranes to transfer exclusively either cations or anions.

The membranes

The membranes are dense, non-porous films of 100-200 µm thickness and several square decimeters of surface, which are composed of an organic polymer matrix with covalently bound, ionized functional groups grafted to them. Depending on the nature of these functional groups, we can distinguish:

⇒ membranes permeable to cations, which are called cationic membranes or anion exclusion membranes,
⇒ membranes permeable to anions, which are called anionic membranes or cation exclusion membranes.

Sulfonic and quaternary ammonium functional groups are most often used by producers for cationic and anionic membranes, respectively.

Under the effect of an electric field, the ions can move in the membranes from one place to the other in this network made up by the either positively or negatively charged functional groups. These movements are referred to as conduction itineraries (Gavach, 1992). The cationic membranes are only permeable to cations whereas the anionic membranes are only crossed by anions.

Working principle

Figure 4 illustrates the working principle of an electrodialysis cell. The elementary motifs of
Electrodialysis are two compartments "1" and "2" that are alternatively delimited by anionic and cationic membranes.

A difference in the electric potential applied to the electrode terminals placed on both sides of the cell will lead to ion migration: cations will migrate towards the negative electrode (the cathode), whereas anions will move towards the positive electrode (the anode). The cations in compartment "1" will be able to cross the cationic membrane and thus be eliminated in this compartment. However, they will not be able to leave compartment "2" since they would find an anionic membrane on their way. The anions can be exported from compartment "1" towards the neighbor cell to the left, but will remain in compartment "2" of the neighboring cell since they won’t be able to cross the next (cationic) membrane.

Figure 4: Electrodialysis, extraction of ions (K\(^+\), Ca\(^{++}\), tartaric acid) by membranes. The central motif is shown, which is repeated to both sides in an electrodialysis system.

Because of the alternating anionic and cationic membranes, one compartment ("1") exports its ions towards the neighboring circuits thus decreasing its ion concentrations. Therefore, this compartment is called “dilute”. The compartment that is enriched with ions is called "concentrate".

This method does not utilize the reactions that occur at the electrodes.

- **General description of an electrodialyzer**

An electrodialyzer is composed of a stack of elementary motifs or cells as described above.
Between every membrane, a divider-frame allows to maintain a uniform distance between the membranes, the flow of the fluids, as well as the rigidity and proofness of the stack.

The number of elementary cells can reach up to 800 pairs of membranes. They are assembled by a technology similar to the one used for pressed filters. The thickness of the compartments varies between 0.3 - 2 mm (0.011 - 0.078 in) depending on the producer of the electrodialyzer.

Two hydraulic circuits parallely feed the totality of the compartments of similar type. One line groups the "dilute" compartments of all elementary motifs, as well as the "concentrate" compartments are all connected.

The electrodialysis modules are all equipped with two electrodes (an anode and a cathode), which are generally placed at both ends of the stack. These ends are protected by a separate circuit containing an electrolyte, and are totally isolated from the product circuit.

The electrodes supply the current for the electrodialyzer. They produce a continuous electric current, which is transformed into an ion current because of the ion transfers in the solution and the membranes. The performance of electrodialysis is directly related to the quantity of electricity applied to the apparatus. The difference in the electric potential maintained across each membrane is generally in the order of 1 volt per cell and allows the selective passage of ions. The laws of Ohm and Faraday govern the phenomena.

2.2.2. Adaptation to wine treatment

The industrial implementation of electrodialysis goes back to the 1950’s. This membrane based separation technique was originally developed for desalination of water and the production of brine from seawater, particularly in Japan. More recently, electrodialysis has found applications in the food and pharmaceutical industries thanks to the emergence of new membranes. It has become widespread in the dairy sector for the demineralization of lactoserum, which is used for animal nutrition and for the production of infant milk formulas. This application today represents a global treatment capacity of 60 000 m$^2$ of installed membranes (Gavach, 1992). Approval is just being sought for the denitrification of drinking water. It is a clean technique that does create few polluting effluents.

The idea of stabilizing wines by electrodialysis regarding tartrate precipitations is old and its feasibility has been demonstrated (Okonov et al., 1975 ; Wucherfennig and Millies, 1976 ; Paronetto and Braido, 1977). Nevertheless, these works did not lead to industrial implementations. Naturally, the economic reasons are difficult to analyze. However, it is reasonable to assume that the lack of availability of high-performance membranes (high surface resistances) or membranes adapted to wine could have represented an initial limiting factor. Besides, a wine treatment allowing only the removal of fixed amounts of potassium probably represented a handicap to the industrialization of the procedure.

In spite of the progress achieved in the improvement of materials used for the cold stabilization of wines, and the development of control methods, the prevention of crystal precipitations in bottles has not been reached conclusively, at all. Many enologists also consider that the organoleptic qualities of wines can be affected by cold stabilizations, especially if they have a strong polyphenolic structure.
The international wine market is more and more competitive, and as a consequence, purchasers impose increasingly drastic requirements to be met: particularly, producers are required to confirm the absence of tartrate precipitations during the commercialization period.

This evolution has pushed the re-examination of the potential of electrodialysis to provide a truly efficient solution to existent problems while taking into account all technical, economic and regulatory considerations. In order to achieve this objective, it was necessary to study the behavior of electrodialysis membranes regarding wine (Cottereau, 1989), and to conceive a test allowing to adapt the treatment level to the instability of every wine. This option would thus lead to the automation of the procedure.

• **Criteria for the choice of membranes**

In principle, all cations and anions can be affected during electrodialysis. However, not all ions show the same behavior and their extraction depends on various factors. Within the limits of a sufficient ion charge, the transfer kinetics of ions follow a first order equation, so that $C_i = C_1^0 \exp(-\varpi t)$ where $C_i$ is the concentration in moles/l of the ion to be considered after a treatment duration of $t$, $C_1^0$ is the initial concentration, and $\varpi$ = the speed constant. The latter value is characteristic for every ion in the solution at specific medium conditions and temperatures (Audinos et al., 1979). In practice, the value depends essentially on the ion mobility and dimension, as well as on the nature of the membrane. These considerations explain the different extractions of every ion sort in the wines treated by electrodialysis.

The adjustment of electrodialysis membranes to the treatment of wines was built on the considerations for the regulatory agencies, the technological characteristics of the available membranes or membrane prototypes, and finally, on enological criteria.

1. The membranes to be used in enology have to be in agreement with the regulations regarding food additives and the materials that come into contact with foods. They also have to meet with the tests for migration in hydroalcoholic solutions at acid pH.

2. In order to ensure the efficiency of the stabilization at competitive costs, the selection of membranes was based on the evaluation of:

   - the global deionization kinetics adapted to the potassium and calcium cations and to the tartrate anions,
   - the mechanical resistance of the membranes,
   - and their resistance towards membrane fouling (secondary polarization), in order to guarantee a lifetime of at least 2000 hours for the anionic membranes, which generally are the most fragile.

3. To respect the qualitative integrity of wines, the membrane pair used must not affect the non-ionic wine constituents and must only lead to slight modifications of the physio-chemical equilibrium of wines.
While searching for the best membrane pair, the following limits have served as selection criteria:

- a maximum decrease of the ethanol content fixed to 0,1 % (v/v),
- a pH decrease lower than 0,25 units,
- a volatile acidity decrease lower than 0,09 g l\(^{-1}\) (expressed as sulfuric acid; or 0.14 g l\(^{-1}\) as tartaric acid).

This specification of requirements is only justified for the most instable wines.

Membrane pairs possessing the required properties and enological aptitudes were assembled in a pilot unit so as to validate the procedure under enological conditions.

**Tartrate stability tests and automatic control of the process**

**Test principle**

The test is based on the analysis of the variation of conductivity in a sample kept at sub zero temperatures (i.e. <0°C or <32°F) and inoculated with potassium hydrogentartrate crystals of a certain size under constant stirring (seeded conductivity test). The modeling of the phenomena, which are followed for approximately 4 hours, allows predicting the decrease in conductivity for a theoretically infinite period of time.

Different mathematical formulae can be suggested depending on the wine, the temperature used for the test, the eventual addition of ethanol to accelerate the precipitation, as well as the degree of filtration of the sample. The value given by the test therefore is the final conductivity at stability. An automatic and computer controlled device measures the extent of the decrease in conductivity that a wine has to undergo in order to become stable.

Figure 5 shows examples of the necessary treatment intensities (expressed as % decrease of conductivity) required to obtain tartrate stability in a range of wines. The data in this table clearly shows that the initial conductivity of the wine (or its potassium content) is not correlated to the intensity of the stabilization treatment. Wines with a high initial conductivity (2,320 µS) only required weak treatments (-7%). By way of contrast, other wines with a low initial conductivity (1,590 µS) needed high treatment intensities (-24%).

Only the utilization of the test linked to an automatic control system allows the procedure to be operational.

**The automatic control system [Figure 6]**

The test device is linked to the electrodialyzer. It works either in measurement-mode or in process-mode. The measurement-mode allows the enologist to characterize the tartrate instability of a manually introduced wine sample. The process-mode allows the same characterization with a wine automatically sampled at the inlet of the electrodialyzer (the manual introduction is then impossible) and its identification by conductivity and pH at time zero of the test. The operation will only be authorized if the wine is determined to be unstable. The final conductivity at stability furnished by the test therefore represents the decisive value for the operation of the electrodialyzer.
2.2.3. Description of the process

A system for tartrate stabilization by electrodialysis is composed of a stack of electrodialysis membranes of two compartments filled with inert gas, feeding pumps, and two tanks allowing the return of the fluids (wine and concentrate) into their respective compartments. The wine return-tank (batch) is equipped with level sensors and the two circuits are both provided with a conductometer. With help of the conductivity probes, an automatic device conducts the circulation sequences and the concentration level of the discharge.

The wine is pumped into the treatment tank from where it circulates through the electrodialysis stack filled with inert gas. As soon as the conductivity of the circulating wine reaches the level determined by the instability test, the batch of stabilized wine is directed towards the reception tank by a set of electric valves. Subsequently, another batch of wine to be treated is introduced and stabilized under identical conditions. This corresponds to a short interrupted batch operation since the treatment is carried out in some minutes on a reduced amount of wine. The treatment time and thus, the performance of the installation are directly linked to the degree of potential instability of the wine. Globally, the procedure is continuous and does not require the immobilization of significant volumes of wine [Figure 6].

The ion concentration in the concentrate circuit, corresponding to the recovery of ions extracted from wine, is regulated through dilution by means of a conductivity threshold value in order to avoid that potassium hydrogen tartrate crystals precipitate in the compartments inside the membrane stack.

2.2.4. Procedure validation

The pilot plant which was set up for the realization of industrial trials, comprises 40 elementary cells, resulting in $3m^2$ of active cells, i.e. $3m^2$ of cationic membranes and $3m^2$ of anionic membranes. The wine circulates in the module in form of an ultra thin liquid film at a speed of 7 cm/s [2.7 in/s]. The treatment is carried out at low pressure (under 1 bar or 14.5 psi) at ambient temperature (10-25°C, 50-77°F). The wine is protected from contact with air and does not suffer excessive mixing in view of the low flow speed.

In this way, more than 20 000 hl (528,344 gal) white, rosé and red wines from different viticultural areas of France, Italy, Spain, Portugal and Germany were treated. The volume of wines stabilized by electrodialysis varied between 25 and 400 HL (660-10,500 gal) and the flow rates between 50 and 150 l/h/m$^2$ cells. Essentially, the flow rates depended on the quantity of ions to be extracted in order to assure stability. Considering an identical treatment degree, the performances were, however, higher with white than with red wines. The latter had a higher tendency to cause increased membrane surface resistances over time that, in conformity with Ohm's law, lead to reduced ion transfer speeds through the membranes. Anionic membranes are more sensitive regarding this phenomena and periodical rinsing and cleaning of the stack reduces the effects.

Different analyses carried out on electrodialysis treated wines have shown that the mineral cations are extracted efficiently. Calcium is the ion, which is removed most rapidly
(Figure 7). Basically, the reduction of the potassium content and the diminution of conductivity had a linear correlation. Other cations, such as iron, copper and lead were slightly reduced in concentration. This reduction was dependent on the treatment intensity. Anions were also extracted but with weaker kinetics as for potassium (Figure 7). For a reduction of 20% in conductivity, the decrease of tartaric acid concentrations was situated between 10 to 15%. The content in free and total SO₂ had the tendency to diminish slightly, such as the volatile acidity. As an example, the analytical results of a white and a red wine treated for tartrate stabilization by electrodialysis are compared in Tables 10 and 11.

Since the extraction was slower for anions than for cations, a slight drop of the pH could be observed, which was limited to 0.15 units in the treated wines (compare Table 11).
Figure 5: Realization of the Tartrate Stability TEST

TEST temperature and decision table

<table>
<thead>
<tr>
<th>Product Type</th>
<th>Test Temperature</th>
<th>Modeled Level of Reduction</th>
<th>Reference Cold Stabilization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grape juice</td>
<td>-2°C</td>
<td>&lt;3% stable</td>
<td>0°C (32°F) 10 days</td>
</tr>
<tr>
<td>Still wine</td>
<td>-4°C</td>
<td>&lt;3% stable</td>
<td>-4°C (25°F) 6 days</td>
</tr>
<tr>
<td>Sweet wine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural sweet wines and wine based aperitifs</td>
<td>-9°C</td>
<td>&lt;6% stable</td>
<td>-9°C (16°F) 10 days</td>
</tr>
</tbody>
</table>
Figure 6: Automatic control system
Figure 7: Evolution of the contents of Ca++[ ], K+ [ ] and AT- [ ] in dependence on the extent of conductivity decrease.
Table 10: Average evolution of the physio-chemical composition of white wines

<table>
<thead>
<tr>
<th>% Conductivity decrease</th>
<th>Legislation</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 10 %</td>
<td>10 to 20 %</td>
</tr>
<tr>
<td>Alcohol % vol.</td>
<td>- 0.04</td>
</tr>
<tr>
<td>Volatile Acidity g/l H\textsubscript{2}SO\textsubscript{4}</td>
<td>- 0.03</td>
</tr>
<tr>
<td>pH</td>
<td>- 0.05</td>
</tr>
<tr>
<td>Potassium g/l</td>
<td>- 0.20 to – 0.40</td>
</tr>
<tr>
<td>Calcium mg/l</td>
<td>- 5 to – 15</td>
</tr>
<tr>
<td>Tartaric Acid g/l</td>
<td>- 0.20 to – 0.50</td>
</tr>
<tr>
<td>Polyphenols</td>
<td>0</td>
</tr>
<tr>
<td>Metals mg/l</td>
<td>- 1</td>
</tr>
<tr>
<td>Total SO\textsubscript{2} mg/l</td>
<td>- 15</td>
</tr>
<tr>
<td>Free SO\textsubscript{2} mg/l</td>
<td>- 5</td>
</tr>
<tr>
<td>CO\textsubscript{2} mg/l</td>
<td>- 50</td>
</tr>
</tbody>
</table>

Table 11: Evolution of the analytical composition of a moderately unstable red wine that was treated for tartrate instability by electrodialysis on an industrial unit of the company Jeanjean.

<table>
<thead>
<tr>
<th>Red wine – Variety: Merlot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before Electrodialysis</td>
</tr>
<tr>
<td>Conductivity (in mS)</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Total Acidity g/l H\textsubscript{2}SO\textsubscript{4}</td>
</tr>
<tr>
<td>Volatile Acidity g/l H\textsubscript{2}SO\textsubscript{4}</td>
</tr>
<tr>
<td>K\textsuperscript{+} g/l</td>
</tr>
<tr>
<td>Ca\textsuperscript{2+} mg/l</td>
</tr>
<tr>
<td>Tartaric Acid g/l</td>
</tr>
<tr>
<td>Free SO\textsubscript{2}</td>
</tr>
<tr>
<td>Total SO\textsubscript{2}</td>
</tr>
<tr>
<td>Alcohol % vol.</td>
</tr>
</tbody>
</table>

Regarding other wine constituents, detailed analyses suggested that polyphenols (anthocyanins and tannins), polysaccharides, amino acids and volatile compounds were not affected by the treatment. Comparative trials showed that color substances were
modified by cold treatment more than by electrodialysis. In fact, cold treatments do not only lead to tartrate precipitation but also to removal of color substances of colloidal nature. Under the working conditions described, all wines treated by electrodialysis turned out to be stable whereas this was not always the case for cold treatment. Every trial was subjected to sensory analysis and compared to control wines, either treated by electrodialysis or by refrigeration under the conditions normally used at the experimental site. It could not been shown that significant differences existed between the control and the electrodialysis treated wine (Riponi et al., 1992; Cottereau, 1993).

2.2.5 Technological interest

• **Reliability and control of the process**

The reliability of electrodialysis for the prevention of tartrate precipitations in wines relies on the utilization of selected membranes and a stability test, which are integrated in an automatic control system. The latter determines for every wine:

⇒ the necessity of a treatment

⇒ the degree of a treatment

Thus, the process is adapted to the physio-chemical equilibrium of every wine by removing only so much potassium and tartaric acid as to reach stability as determined in advance by the test. Therefore, the electrodialysis treatment intensity is adjustable to the instability of every wine, and is limited to preventing crystal formation in bottled wines.

Since the treatment, among others, also removes part of the calcium, the wines will be more stable regarding calcium tartrate precipitations. Consequently, stabilization by electrodialysis turns out to be an available tool that can be integrated into the quality control strategies of wine producing companies.

• **Position in the wine treatment sequence**

Electrodialyzers admit products that are simply cleared of micronic particles, that is, solid elements of cloudiness. Consequently, procedures using electrodialysis eliminate the need for filtrations, which are imperative for cold treatments. The precipitation of potassium hydrogen tartrate by temperature reduction is more efficient the better the wines were clarified. Therefore, tight filtrations are a prerequisite for the application of low temperatures. These successive clarification steps are often detrimental to wine quality. They tend to result in “thinning” the wines and loss of aromatic perception. The tartrate stabilization by electrodialysis, therefore, does not present these disadvantages.

On the other hand, because electrodialysis preserves the colloidal structure of wines, it should be indicated that the wines would not be protected against eventual risks of color precipitation; various technological solutions exist to treat wines that possibly will display this problem. Electrodialysis is well suited to be coupled with cross-flow microfiltration. The overall aspects of clarification, and microbiological and tartrate stability thus can be realized continuously.

If a fining has to be realized, it should be carried out beforehand and eventually followed by centrifugation in order to eliminate the floculates from the fining reaction. For example, the new outline for short and qualitative wine treatments could be:
Fining ➔ Racking or Centrifugal Clarification ➔ Electrodialysis ➔ Cross-Flow Microfiltration ➔ Bottling with low microbial count

- **Economic advantages**

Compared with classic treatments, electrodialysis allows saving on filter aids, seeding tartrates or metatartaric acid, depending on the technologies used. Therefore, the waste caused by wine treatment will also be reduced. It will be limited to membrane cleaning (1-2 times per 24h; acid, basic and saline cycles) and the water used to dilute the salt concentrate circuit. This water contribution will represent a consumption of 10 to 20 liters for 100 liters of wine (i.e. 10-20%). This water can be directly recycled for cellar cleaning.

The chemical oxygen demand (COD) of this waste is between 2-3.5 g/l, which is very low. This effluent contains 1-1.5 g tartaric acid, 1-1.5 g potassium, 0.5 g sulfates, 0.1 g calcium and 0.5-1 g alcohol. This corresponds to an average polluting load of 30 g COD per 100 l (26.4 gal) of treated wine. This value represents only 10% of the estimated polluting load linked to the elaboration of 100 l of wine.

Further recycling treatments could be used for this liquid waste if this was necessary on certain sites, particularly in order to reduce water consumption.

The energy expenditures for tartrate stabilization by electrodialysis are particularly low, since the global power consumption is between 0.5 and 1 kWh per m³ (264 gal) per liter of wine treated, including pumping costs. The power consumption is approximately 10 times lower as compared with the costs required for cold energy in traditional treatments where the economy depends on the refrigeration system used (continuous or cold stabilization), as well as the insulation of the tanks or the energy recovery modalities.

The automation of the procedure also allows reducing labor costs significantly. Table 12 indicates the necessary investment for electrodialysis as well as the costs for consumables and operation. These figures have been established by the Eurodia and Boccard companies who market electrodialysis stacks and complete units for wine treatment.

The comparative evaluation under consideration of the fixed costs (redemption of equipment in 5 years, financial expenses) and the operation costs (power consumption, consumables, membrane renewals, labor, maintenance costs) are in favor of electrodialysis. The costs per treated hectoliter (26.4 gal) can be reduced 50 - 70 % compared with the cold stabilization at -3°C (26.6°F) for 10 days, depending on the size of the electrodialysis installation, the degree of automation of the various tasks (filling, emptying, rinsing, management of process security) and the frequency of membrane renewals.

*Table 12: Economic data*
Sources: EURODIA (91320 WISSOUS) and BOCCARD (69007 LYON) companies

1 values in gallons/h in parentheses
2 approximate values in thousand USD in parentheses
3 thousand French Franc
4 approximate value in USD/1000 gal

• Industrial validation

Since 1997, ten units with capacities varying between 40 and 100 hl/h (1056 - 2641 gal/h) are operational in France at different negociants and producers, and including appellation of controlled origin areas.

The sensory evolution has allowed validating the organoleptic neutrality of the process over the long study period and the multitude of products treated: it is very difficult to distinguish untreated from treated wines.

The establishment of mobile units (see photo) renders the treatment accessible to the winery.