TARTARIC STABILIZATION BY ELECTRODIALYSIS

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The tartaric stability of wines

The need to produce wines that are stable where tartaric precipitations are concerned is currently felt, not only for wines that are destined for wide distribution, but also for niche products.
The tartaric stabilization of a wine can be obtained by using different techniques: traditional methods include the use of chilling and the addition of metatartaric acid.
However, the use of chilling to promote excessive bitartrate crystallization does not always, particularly in continuous processes, lead to certain stability and above all induces modifications in the medium (precipitation of colloid and color compounds) that may undermine the quality of the product.
The use of metatartaric acid, although economical and easy to apply, does not guarantee tartaric stability, if not for quite a limited period of time.
Other additives have been suggested: carboxymethylcellulose and mannoproteins.
Carboxymethylcellulose, an additive already used in many foods, is a colloid with inhibiting and protective action which, unlike metatartaric acid, does not undergo any deterioration over time and is stable over a broader range of temperatures.
Some Authors have evaluated the action of certain mannoproteins extracted by enzymatic hydrolysis from the cellular walls of yeasts; this preparation when properly purified, presents at doses of 25-50 g/hL, an inhibiting action towards precipitation of potassium bitartrate.
The active fraction of the mannoproteic complex, obtained by enzymatic means, is made up of strongly glycosylated molecules with a molecular mass of between 30,000 and 50,000 Da; the protection against tartrate crystallization by the mannoproteic preparation is prolonged over time.
Contrary to the action of metatartaric acid, which only inhibits the growth of crystals, mannoproteins impede the formation of the nuclei of crystallization but does not prevent the growth of tartrate crystals if nuclei are present or introduced into the medium by chance.
The efficacy of mannoproteins is still undergoing evaluation; from the results already obtained it is probable that the use of mannoproteins in conjunction with chilling may improve the stabilization of tartrate crystal formation but it is unlikely to replace the chilling method entirely.
More modern techniques for the separation of the unstable fraction of the bitartrate from the wine have been developed; they employ, alone or in combination, the use of selective membranes and of ion exchanging resins; the transport of matter may occur by using pressure, electrical fields, or ionic mobility.
The technique of membrane separation offers the possibility of identifying and removing certain molecules and to direct the flow of matter. The principle has been acknowledged for over a century, but the development in industrial applications is much more recent and essentially depends on the preparation of suitable membrane materials.
The use of electrodialysis in the stabilization of wines was legalized over a year ago in Europe but has been experimented with in France for quite some time and with satisfying results.

The Technique of Electrodialysis

Tartaric stabilization by electrodialysis is a separation technique that exploits an electrical field operating inside a membrane system as a means of transport.
The membranes used are selective and do not have a true filtering function in wine, but are needed to separate the ions found in the wine and to isolate the electrodes used to create the electrical field.
The principle of electrodialysis is based on the biochemical properties that membranes have of selectively allowing the passage of certain cations (e.g. Ca^{++} and K^{+}) or anions (e.g. tartrates) while preventing the passage of others.

An elementary electrodialysis unit is made up of two compartments: one for wine and the other for "brine", they are alternately separated by anionic and cationic membranes (Fig. 1).
A potential difference applied to opposite ends of the stack via electrodes promotes the migration of the ions.

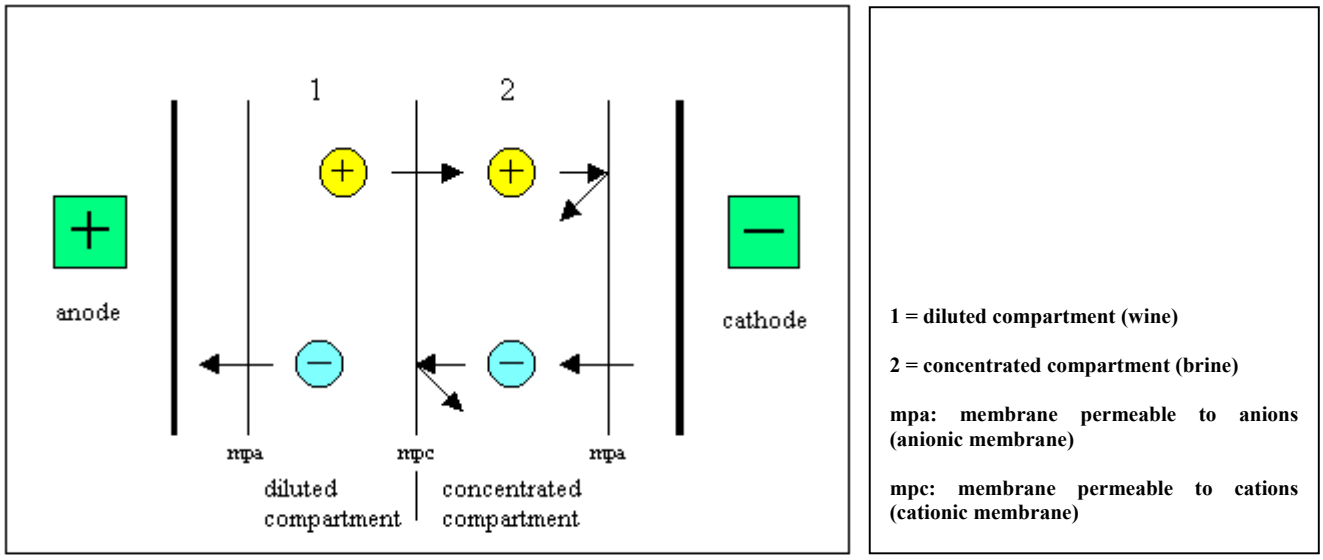

Fig. 1 – Schematic representation of the principle of electrodialysis.

Cationic membranes allow only cations to pass and are impermeable by anions while the anionic membranes prevent the passage of cations and are permeable only to anions. Fig. 1, illustrates the functioning principal of an electrodialysis cell. A basic constituent contains two compartments, 1 and 2, that are alternately separated by anionic and cationic membranes.
A potential difference applied via two electrodes allows the migration of ions. The cations flow toward the negative electrode (the cathode), the anions toward the positive electrode (the anode). The cations in the "wine" compartment (1) pass through the cationic membrane and move into the "brine" compartment (2) where, blocked by the next anionic membrane, they are concentrated. Likewise the anions migrate through the anionic membrane and concentrate in the "brine" compartment.
The permoselective ion exchanging membranes are made up of films of synthesized materials; they have a thickness of 100 to 200 microns. Ionized functional groups with a covalent bond are inserted into the polymeric matrix; where cationic membranes are concerned. They are made up of negatively charged functional groups (SO_3^-,or carboxylic groups COO^-), or in the case of anionic membranes, positively charged ions and may contain groups of quaternary ammoniums.
For cationic and anionic membranes to be used in electrodialysis, they must have certain characteristics.
In order to respect the qualitative integrity of wines, the selected pair of membranes must not affect the non-ionic components of the wine and have only a slight impact on their physico-chemical balance. In particular, a maximum decrease of the ethanol content limited to 0.1 vol %, (v/v), a lowering of the pH to less than 0.25 units and a decrease of the volatile acidity to less than 0.09 g/l (expressed as units of sulphuric acid) is sought.
To treat a wine by electrodialysis, it is necessary to measure its level of instability.
To do this, a sample of the wine that needs to be treated is taken and undergoes stability testing.
The test is based on the analysis of the conductivity of the sample, over a period of time, left at temperatures of less than 0 °C and inseminated with measured crystals of potassium acid tartrate while undergoing constant agitation.

During the formation of crystals the measurement in the fall of conductivity over time is recorded and expressed as a percentage; this is the value of the rate of deionization that will be applied to the wine during electrodialysis treatment.

The effects of electrodialysis on the composition of wines

Some experiments have been reported here to demonstrate an example of the treatment of wines by electrodialysis. Table 1 shows the data regarding electrodialysis carried out on IGT wine "Merlot delle Venezie". The wine was subjected to a deionization treatment of 12 % (the test required a rate of 14 %) corresponding to a decrease of 16 % in tartaric acid and 20 % in potassium. The tartaric stability measurements indicate that the product successfully reaches tartaric stability after electrodialysis. These indications are derived from the readings of the saturation temperature (TS = 13.8 °C) and of the critical saturation temperature (TCC = +1.8 °C): due to the effect of electrodialysis they are both decreased by 4.9 °C when compared to the wine before treatment. These results, combined with the isotherm at 25 °C (Δμs = 150), which indicates a moderate capacity of solubilization of the potassium bitartrate by the treated wine, demonstrate achievement ofsufficient tartaric stability.

It is interesting to note that the rate of decrease in potassium relative to that of tartaric acid is different when compared to stabilization by chilling. In fact, in the latter case as there is a crystallization of the potassium bitartrate there is also elimination from the medium of one part of potassium to every two parts of tartaric acid, which corresponds to a K/HTH (p/p) rate of 0.267. Experiments show this rate is 1.107 using electrodialysis leading to a lower deacidification of the wine than the chilling method and with only a slight reduction of the pH.

In treated wine there is also a decrease in the readings of another cation, calcium. Calcium, if present in excess, is responsible for the precipitation phenomena that are unavoidable with traditional techniques. In this application the decrease in calcium was 26 %, sufficient to give the wine under examination a certain stability as far as this metal is concerned. Other cations are subject to a certain reduction as well, but this does not raise any particular interest from a sensorial or technical perspective.

The reduction of ashes is of very little importance. Likewise, the extracts undergo a slight decrease and to a lesser extent than when compared to what happens in traditional processes which, due to chilling, promote not only the crystallization of the bitartrate but also the coagulation and the precipitation of phenolic substances and of colloids in general. To confirm this, it should be noted that the measurements of phenolic substances in wine that has undergone electrodialysis are identical to those of the product before treatment, thus demonstrating that this separation technique is extremely selective and removing from the medium only ions that are responsible for instability without depriving it of colloids which are useful for their stabilizing effect and/or for the positive action on the sensorial characteristics of the product.

Lastly, sensorial analysis has not highlighted any significant differences between the untreated wine and the sample treated by electrodialysis.

Table 2-3 reports the data regarding the analytical readings of two good quality red wines that have undergone a certain level of treatment (harvest of 1995).

In these cases, the rates with which potassium and tartaric acid K/HTH are subtracted from the medium are 0.447 (p/p) and 0.963 respectively for the Merlot wine (table 2), and the red "delle Venezie" wine (table 3). The data also suggests a deionization due more directly with the reduction of potassium than of tartaric acid when compared with crystallization methods.

The data concerning the parameters that characterize the susceptibility of the product to undergo tartaric precipitations indicate that the wines in question are sufficiently stable, especially when considering that the products examined are red wines.

The other assessments carried out on these wines do not indicate any significant modifications to their composition regarding the reduction of the content of ashes; Consequently, the extract

undergoes only a slight decrease; less than that found in the process of stabilization by chilling, where a noticeable decrease in colloids and of extractives in general can be seen.
The calcium content is decreased by 21 mg/L which, in the case of the wine in question, is enough to guarantee reasonable stability where this metal is concerned; a metal that was present in the product before treatment in such quantities as to create problems of stability (102 mg/L).
The alcohol does not undergo variations of any importance and data indicates that the materials are not permeable to this solvent, as foreseen by the CEE provisions on the matter. In addition, sensorial analysis has not indicated any relevant differences between wines treated by electrodialysis and untreated wines.
Table 4, shows the data concerning the experiments of electrodialysis treatment of Cabernet Sauvignon, a well-structured red wine.
The rate at which the potassium and the tartaric acid K/HTH are subtracted from the medium is 1.3 (p/p); so also in these wines there can be seen a deionization due, compared to crystallization, more to the subtraction of potassium rather than of tartaric acid from the medium.
The data concerning the parameters that characterize the susceptibility of the product to undergoing tartaric precipitations indicate that the wine in question is sufficiently stable. The other assessments carried out on the product do not indicate any significant modifications to its composition including that withregard to the reduction of the content of ashes; consequently the extract undergoes a slight decrease.
The other assessments carried out and reported in table 4 do not indicate any important modifications; including a sensorial analysis which determined there to be no significant effects on the organoleptic profile of wine treated by electrodialysis.
Table 5, shows the data regarding the experiments of electrodialysis treatment on a not very structured red wine that had previously been treated by tartaric stabilization using constant chilling,. The test was carried out by subjecting the same wine to further stabilization by chilling, using a continuous system, while treating another sample with electrodialysis.
The data concerning the parameters that characterize the level of tartaric stability of wines, indicate that the constant chilling treatment does not achieve, in this case, tartartic stability of the wine, even after the product has undergone two chilling treatments. On the other hand, the electrodialysis treatment leads to a secure tartaric stability of the wine under examination. In fact, the wine treated by electrodialysis has a TCC of –1.5 °C, while the wine treated by chilling has a TCC of +2.5 °C; with saturation temperatures, respectively, 13.5 and 17.5 °C. That the two techniques lead to quite different results on tartaric stability of the same wine is clearly illustrated by the reduction of conductivity which, in the case of electrodialysis, is 23 %, and for the wine stabilized by chilling is only 5 %.
Despite such a high rate of deionization during treatment by electrodialysis, the reduction of the pH is 0.10, not unlike that following treatment by constant chilling (0.07);. This is due to the lower reduction of the buffer capacity of the wine in the case of treatment by electrodialysis. The reduction of acidity is, as seen previously, more contained in the case of treatment with the membrane separation technique. In this case the rate at which the potassium and the tartaric acid K/HTH are subtracted from the medium is 0.540 (p/p). While on this subject, it should be noted that in the case of stabilization by chilling, the extraction of potassium and tartaric acid is at a rate of 0.344 (p/p) close, therefore, to the theoretical rate (0.267).
As always, during treatment by electrodialysis, the medium is deprived of a part of the calcium content, thus guaranteeing the stability of the wine where this element is concerned; magnesium is also reduced during electrodialysis (-7 %) but this reduction does not have, from an oenological point of view, any particular significance.
Therefore, it can be concluded that treatment by electrodialysis allows for the selective removal of the type and quantity of ions desired; at the same time making it possible to obtain secure tartaric stability even in wines characterized by difficult and slow crystallization kinetics and therefore unlikely to be stabilized by chilling.

Electrodialysis removes tartrate and potassium ions at different rates compared to stabilization by chilling (rate of crystallization: 1:2 Eq K:HTH; with electrodialysis: from 1:1 to 1:0,5 Eq K:HTH). Consequently, with treatment by electrodialysis there is a lower reduction of the total acidity. The membrane separation technique also removes other ionic species in addition to potassium and tartrate: particularly interesting is the removal of calcium ions which, during these experiments, were reduced from between 21 to 43 %, while magnesium is removed with percentages ranging from 4 to 11 %.

More generally, tartaric stabilization using membranes, unlike the traditional chilling technique, stabilizes the product at room temperature, does not provoke the precipitation of color compounds, and does not modify the colloidal structures which are acknowledged as being important because they support the aromatic fraction and are a key element for the structure of the wine.

Table 1- IGT “Merlot delle Venezie.”

	TQ	AFTER ELECTRODIALYSIS			
			Δ	**Δ %**	**Δ meq/L**
Tartaric ac. g/L	1.525	1.282	- 0.243	- 16	- 3.24
K mg/L	1351	1082	- 269	- 20	- 6.90
Ca mg/L	87	64	- 23	- 26	- 1.15
Total acid g/L	5.70	5.55	- 0.15	- 3	- 2.00
Buffer capac. meq/L	39.2	35.9	- 3.3	- 8	- 3.3
pH	3,55	3,42	- 0,13		
Conductivity 25 °C µs	2476	2191	- 285	-12 (- 14)*	
Isotherm 25° C Δµs	65	150	+ 85		
TS °C	+18.7	+13.8	- 4.9		
TCC °C	+6.7	+1.8	- 4.9		

* The drop in conductivity present on the electrodialysis system is indicated in brackets.

	TQ	AFTER ELECTRODIALYSIS		
			Δ	**Δ %**
Alcohol %	12.48	12.42	- 0.06	- 0.5
Extract g/L	24.5	23.8	- 0.7	
Ashes g/L	2.49	2.15	- 0.34	
PFT mg/L	1039	1040		
Malic ac. g/L	0.695	0.624		
Lactic ac. g/L	1.709	1.662		
Fe mg/L	3.49	3.30		
Mg mg/L	97	66	- 31	- 32

Table 2 - IGT “Merlot delle Venezie” ‘95

	TQ	AFTER ELECTRODIALYSIS			
			Δ	Δ %	Δ meq/L
Tartaric ac. g/L	1.547	1.160	- 0.387	- 25	- 5.16
K mg/L	1233	1060	- 173	- 14	- 4.44
Ca mg/L	71	44	- 27	- 38	- 1.90
Total acid g/L					
Buffer capac. meq/L					
pH					
Conductivity 25° Cμs	2255	1991	- 264	-12 (- 14)*	
Isotherm 25° C Δμs	137	245			
TS °C	+ 17.5	+ 15	- 2.5		
TCC °C	+3.5	+ 1	- 2.5		

* The drop in conductivity present on the electrodialysis system is indicated in brackets

	TQ	AFTER ELECTRODIALYSIS		
			Δ	Δ %
PFT mg/L	1023	1015	- 7	- 1
Acetic ac. g/L	0.327	0.361		
Malic ac. g/L	0.483	0.458	- 0.025	- 5
Lactic ac. g/L	1.529	1.490	- 0.039	- 3
Fe mg/L	3.64	2.49	- 1.15	- 32

Table 3 - IGT red wine “delle Venezie” ‘95

	TQ	AFTER ELECTRODIALYSIS			
			Δ	Δ %	Δ meq/L
Tartaric ac. g/L	1.782	1.563	- 0.219	- 12	- 2.92
K mg/L	1295	1084	- 211	- 16	- 5.41
Ca mg/L	92	71	- 21	- 23	- 1.05
Total acid g/L	6.20	6.00	- 0.20	- 3	- 2.67
Buffer capac. meq/L	42.5	40.9	- 1.6	- 4	- 1.6
pH	3.48	3.42	- 0.06		
Conductivity 25° Cμs	2563	2412	- 151	-6 (- 10)*	
Isotherm 25° C Δμs	71	86			
TS °C	+22	+17	- 5		
TCC °C	+7	+2	- 5		

* The drop in conductivity present on the electrodialysis system is indicated in brackets

	TQ	AFTER ELECTRODIALYSIS		
			Δ	Δ %
Alcohol %	12.66	12.58	- 0.08	- 0.6
Extract g/L	27.5	26.4	- 1.1	
Ashes g/L	2.88	2.52	- 0.36	
PFT mg/L	1188	1158	- 30	- 2.5
Acetic ac. g/L	0.340	0.334		
Malic ac. g/L	0.456	0.460		
Lactic ac. g/L	2.509	2.407		
Fe mg/L	3.76	3.55		
Mg mg/L	75	70	- 5	- 7

Table 4 – “Cabernet Sauvignon delle Venezie”

	TQ	AFTER ELECTRODIALYSIS			
			Δ	Δ %	Δ meq/L
Tartaric ac. g/L	1.861	1.622	- 0.239	- 13	- 3.19
K mg/L	1518	1204	- 314	- 21	- 8.05
Ca mg/L	102	81	- 21	- 21	- 1.05
Total acid g/L	6.45	6.35	- 0.10	- 2	- 1.33
Buffer capac. meq/L	43.10	41.35	- 1.75	- 4	- 1.75
pH	3.50	3.45	- 0.05		
Conductivity 25 °C µs	2534	2278	- 256	-10 (- 10)*	
Isotherm 25° C Δµs	69	89	+ 20		
TS °C	+ 18.5	+ 15,5	- 3		
TCC °C	+4	+1	- 3		

* The drop in conductivity present on the electrodialysis system is indicated in brackets

	TQ	AFTER ELECTRODIALYSIS		
			Δ	Δ %
Alcohol %	14.62	14.44		
Extract g/L	34.4	32.3		
Ashes g/L	2.90	2.63		
Alc. Ashes meq/L	23.2	20.4		
PFT mg/L	1516	1514		
Acetic ac. g/L	0.380	0.382		
Malic ac. g/L	0.185	0.157		
Lactic ac. g/L	1.863	1.829		
Fe mg/L	4.12	5.02		
Mg mg/L	82	79	- 3	- 4

Table 5 – IGT red wine "delle Venezie" '97

	TQ	AFTER ELECTRODIALYSIS				AFTER CONSTANT CHILLING STAB.			
			Δ	Δ %	Δ meq/L		Δ	Δ %	Δ meq/L
Tartaric ac. g/L	2.576	2.009	- 0.567	- 20	- 7.56	1.773	- 0.803	- 31	- 10.71
K mg/L	1089	783	- 306	- 28	- 7.84	813	- 276	- 25	- 7.08
Ca mg/L	93	53	- 40	- 43	- 2.00	89	- 4	- 4	- 0.2
Total acid g/L	6.00	5.75	- 0.25	- 4	- 3.30	5.50	- 0.50	- 8	- 6.67
Buffer capac. meq/L	40.6	36.5	- 4.1	- 10	- 4.1	35.3	- 5.3	- 13	- 5.3
pH	3.36	3.26	- 0.10			3.29	- 0.07		
Conductivity 25° Cμs	2183	1690	- 493	- 23 (- 25)*		2078	- 105	- 5	
Isotherm 25° C Δμs	28	280				183			
TS °C	+ 22.5	+ 13.5	- 9			+ 17.5	- 5		
TCC °C	+ 7.5	- 1.5	- 9			+ 2.5	- 5		

* The drop in conductivity preset on the electrodialysis system is indicated in brackets

	TQ	AFTER ELECTRODIALYSIS			AFTER CONSTANT CHILLING STAB.		
			Δ	Δ %		Δ	Δ %
Alcohol %	11.84	11.74	- 0.10	- 0.8	11.85	0	0
Extract g/L	22.9	21.9	- 1.0		22.0	- 0.9	
Ashes g/L	1.94	1.66	- 0.28		1.88	-0.06	
PFT mg/L	802	799	- 3	0	784	- 18	- 2
Acetic c. g/L	0.227	0.226			0.230		
Malic ac. g/L	0.13	0.14			0.12		
Lactic ac. g/L	1.85	1.87			1.91		
Fe mg/L	3.4	3.1			3.3		
Cu mg/L	0.1	0.1			0.1		
Mg mg/L	65	50	- 15	- 7	65	0	0