STUDY ON THE USE OF ACTIVATED MEMBRANES IN THE TARTARIC STABILIZATION OF WINES

Albert Gasull[a]; Fina Capdevila[b], Santiago Minguez[b], Ricard Garcia-Valls[a]

[a]*Departament d'Enginyeria Química, Escola Tècnica Superior d'Enginyeria Química,Universitat Rovira i Virgili, 43007 Tarragona, Spain (email: albert.gasull@urv.cat, ricard.garcia@urv.cat)*

[b]*Institut Català de la Vinya i el Vi (INCAVI) Estació de Viticultura i Enologia de Vilafranca del Penedès, Pl. Àgora, 2, polígon Domenys II, 08720 Vilafranca del Penedès, Barcelona, Spain (email: santiago.minguez@gencat.cat,, fcapdevila@gencat.cat)*

One of the most uncertain and problematic phases in the elaboration of the wine is the tartaric stabilization. The most usual way of stabilization is to precipitate the potassium hydrogen tartrate (*KHT*). It can be carried out through several alternatives: addition of tartars powder, Carboxymethyl cellulose, Mannoproteins, Meta-tartaric acid or by maintaining the wine at temperatures below 0ºC for 10-15 days. Only electrodialysis and cation-exchange resins, based on a physical procedure of the potassium cation removal, are actually practical. From these two alternatives just electroldialysis is nowadays authorized. Despite it presents advantages respect the other techniques, it is not a feasible alternative due to the high cost of the equipment. Thus, a new technique by using activated membranes (AM) has been studied in order to reduce the potassium cation concentration in wine. Activated membranes, based on the facilitated transport mechanism, have been developed and tested at laboratory scale in order to characterize the potassium cation transport. The AM were tested with different emulating-wine solutions prepared in the laboratory with the parameters of potassium, Calcium, Glucose, Malic acid, alcoholic content and pH determined. The results show that, in both cases, the AM presented an average decrease in potassium cations that depending on the operation conditions can reach a maximum value of 30%. According to these results we decided to go forward to a semi-pilot plant scale and testing real wine solutions.

1. INTRODUCTION

One of the most uncertain and problematic phases in the elaboration of the wine is the tartaric stabilization [5,10].The tartarate crystallization is one of the main causes of cloudiness and solid particles in the bottle. The tartaric stabilization refers to operations that prevent or minimize those effects. Despite the appearance of this crystals in the bottle is a natural process, which does not affect either odor or flavor, it is considered undesirable by both producers and consumers [1,13]. The most usual way of stabilization is to precipitate the potassium hydrogen tartrate (*KHT*). It can be carried out through several alternatives: addition of tartars powder, Carboxymethyl cellulose, Mannoproteins, Meta-tartaric acid or by maintaining the wine at temperatures below 0ºC for 10-15 days [10]. Only electrodialysis and cation-exchange resins, based on a physical procedure of the potassium cation removal, are actually practical [8, 12]. From these two alternatives just electroldialysis is nowadays authorized. Despite it presents advantages respect the other techniques, it is not a feasible

alternative due to the high cost of the equipment [9]. Thus, a new technique by using activated membranes (AM) has been studied in order to reduce the potassium cation concentration in wine.

In this document are presented the results obtained in a primary phase of the study of the AM in the tartaric stabilization process. The aim of this initial experimentation it is to prove the concept, this is to detect an exchange of K^+ from the wine to the stripping solution and proton (H^+) from the stripping solution to the wine through the AM and determine the concentration of K^+.

The AM have been tested, in an initial phase, by using known potassium concentration aqueous solutions. Later, the solutions have been changed to a varied emulating-wine matrix solutions, with a known potassium concentration. In order to verify and to compare the activity of the AM, they have been compared to not activated membranes, by using the same experimentation procedures.

2. EXPERIMENTAL

2.1 Reagents and solutions

For the preparation of the aqueous solutions, Hydrochloric acid, Panreac (Spain); sodium chloride, Panreac (Spain) and deionized water. For the analyses by means of the ion-selective electrodes, Ionic strength adjuster (5M NaCl), Orion, Germany; potassium Activity Pattern (KCl 0.1 M), Orion, Germany. In the case of the preparation of the AM the Reagents MET-VI-01, Meteor (Spain) have been used. The different emulating-wine solutions have been prepared by the Institut Català de la Vinya i el Vi (INCAVI) and the concentrations of the different parameters are shown in table 1.

2.2 Instrumentation

2.2.1 Membrane modules

The equipment where the membranes have been tested is formed by two modules, made of Teflon ®, with a capacity of 200ml each. Each module is a cube geometrically. They are open in the top and one side they have a circular opening of 22,5 cm². The modules are united by the face where it is the circular overture and, in the middle, it is placed the membrane. The measurement devices are introduced through the openings in the top. Next you can see a scheme of the equipment.
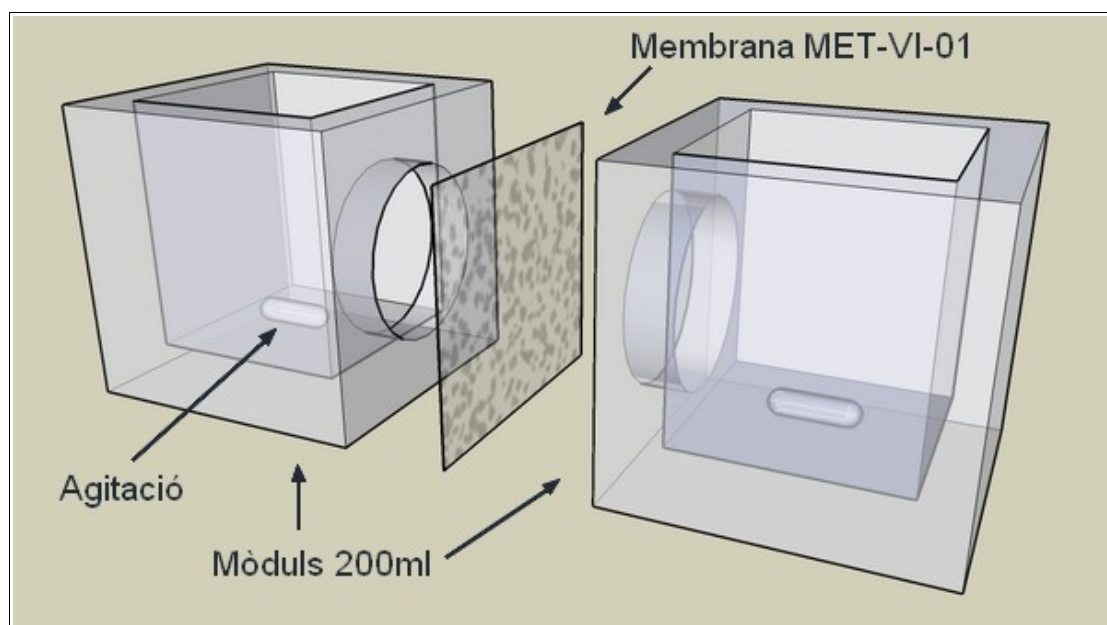
Figure 1: Scheme of the equipment used in the experimentation.

The agitation is performed by means of a multiple magnetic stirrer SBS ANM-10103, Spain.

2.2.2 Measurement devices

pH/Conductivity Dual Star meter, Thermo Scientific Orion, USA; pH/ISE Dual Star meter 8102, Thermo Scientific Orion, USA; potassium (K) Ionplus combined electrode, Orion, Germany.

3. PROCEDURE

3.1 Study on the transport of K^+ ions in the Activated Membranes MET-VI-01. Aqueous solutions.

The transport studies have been carried out by using the experimental equipment (membrane modules) as described before.

A piece of AM of uniform appearance is placed among the two modules. The modules will be adjusted carefully, trying not to shear the membrane. Before starting the experiment we must ensure that the assembly does not have defects that may cause losses or possible solutions exchanges between modules.

The active side of the membrane is oriented so that it is in contact with the stripping solution of potassium ions (K^+). The orientation is justified by the geometry of the modules and the nature of the membrane: 1. The face of the donor ion solution is not exposed to any excess of reagents present because of the activation treatment MET-VI-01, 2, Due to the geometry of the modules, and in case of its existence, the polarization layer in the stripping solution module is lower.

Once the modules are assembled, with the membrane placed in the middle, we can proceed to add the solutions. First, we add the stripping solution 200 ml 0.1 M HCl. We have to check out that there is no loss or transfer of solution to the other module. If everything is correct and there is no transfer of fluid, we can proceed to add the feed solution 200 ml of 0.1 M KCl and start the magnetic stirrer. Once the two solutions the pH and Conductivity meters are introduced to the modules and start the data recording.

The experiments have been performed with three different types of membranes, in order to check and compare the activity of the AM MET-01-VI. Tests have been done using membranes without any treatment (blanc), membranes with a pretreatment without a carrier agent (pretreatment) and activated membranes (MET-VI-01). In all cases 200 ml 0.1M KCl have been used as the feed solution and 200 ml 0.1M HCl as the stripping solution.

The experiments were performed using a magnetic stirring at an uniform speed of 600rpm in both modules and an average temperature of 24 ºC.

3.2 Study on the transport of K^+ ions in the Activated Membranes MET-VI-01. Emulating-wine solutions.

The procedure of this study is similar to the case study of transport in aqueous solutions. In this case, however, instead of a solution of 0.1 M KCl have been used emulating-wine solutions supplied by the Institut Català de la Vinya i el Vi (INCAVI). Only AM MET-VI-01 have been tested in this case. In this procedure, the concentration of potassium ions (K^+) have been measured by the potassium-selective electrode ion. pH was also measured throughout the experiment.

The experiments have been performed by means of a magnetic stirring at a uniform speed of 600rpm in both modules and an average temperature of 23 ° C

Table 1: Emulating-wine solutions used in the experimentation.

Solutions	pH	Total Acidity g/L	Theoretical K Concentration mg/L	Real K Concentration by EAA mg/L	Theoretical Ca Concentration mg/L
A1	2,73	4,6	200	213	no
B1	3,17	3,6	600	542	no
C1	3,51	2,8	1000	761	no
D1	3,55	3,2	1400	714	no
E1	2,65	5,5	200	213	no
F1	3,08	4,6	600	592	no
A2	2,73	4,5	200	213	50
B2	3,17	3,8	600	547	100
C2	3,51	2,8	1000	764	100
D2	3,54	3,2	1400	729	50
E2	2,66	5,5	200	210	50
F2	3,08	4,6	600	594	50

3.3 Transport Mechanism.

In order to quantify the transport we need an equation that describes the flow through the membrane. If we have into account the different types of transport and their flows in the diffusion layer, in the interphase and inside of the membrane, it is possible to define globally the flow through the membrane as a variation of the concentration in the feed solution as a function of time:

$$J = \frac{-V}{Q} \cdot \frac{d[A]}{dt}$$
[1]

where V is the volume of the feed solution and Q corresponds to the surface of the membrane [7, 11]. If we normalize the flow on the concentration of analyte A we obtain the Permeability Coefficient:

$$P = \frac{J}{[A]}$$
[2]

Combining the last two equations, and integrating between initial concentration and concentration C, initial time and time t, we find:

$$-\ln \cdot \left(\frac{[A]}{[A]_0} \right) = \frac{Q}{V} \cdot P \cdot t$$
[3]

This equation relates the permeability of the membrane with the decreasing of analyte A in the feed solution, on the concentration of A (in this case potassium) present initially.

4. RESULTS AND DISCUSSION

4.1 Transport of K+ ions on the blanc, pretreatment and activated (MET-VI-01) membranes. Aqueous solutions.

The feed solution contains 0,1M KCl (aq) and the streeping solution 0,1M HCl. Theoretically, the initial concentration in the solution is:

$[K^+]_0 = 0,1M$

$[H^+]_0 = 0,1M$

From:

pH=-log[H$^+$]
[4]

measuring the pH in the stripping solution it can easily be measured the final concentration of potassium in the stripping solution.

$[K^+]_{final} = [K^+]_0 - [H^+] = 0,1 - [H^+]$
[5]

Note that this operation is more effective in the case of the experiments run with AM VI-

MET-01 and pretreatment membranes, as in the case of blanc membranes due to a major porosity of the membrane species can exchange by convective transport.

Thus, performing experiments with AM MET-VI-01 and pretreatment membranes, can be determined the transport through the membrane. If transportation is effective and to what extent.

Next, two pairs of experiments with aqueous solutions of 0.1 M KCl as feed solution and 0.1 M HCl as stripping solution are shown. The figure shows how in the case of pretreatment membranes there is a null potassium ion transport. In contrast, the pair of experiments performed with the AM MET-VI-01 we can observe a significant transport of potassium. It can be observed how the concentration of potassium decreases over time.
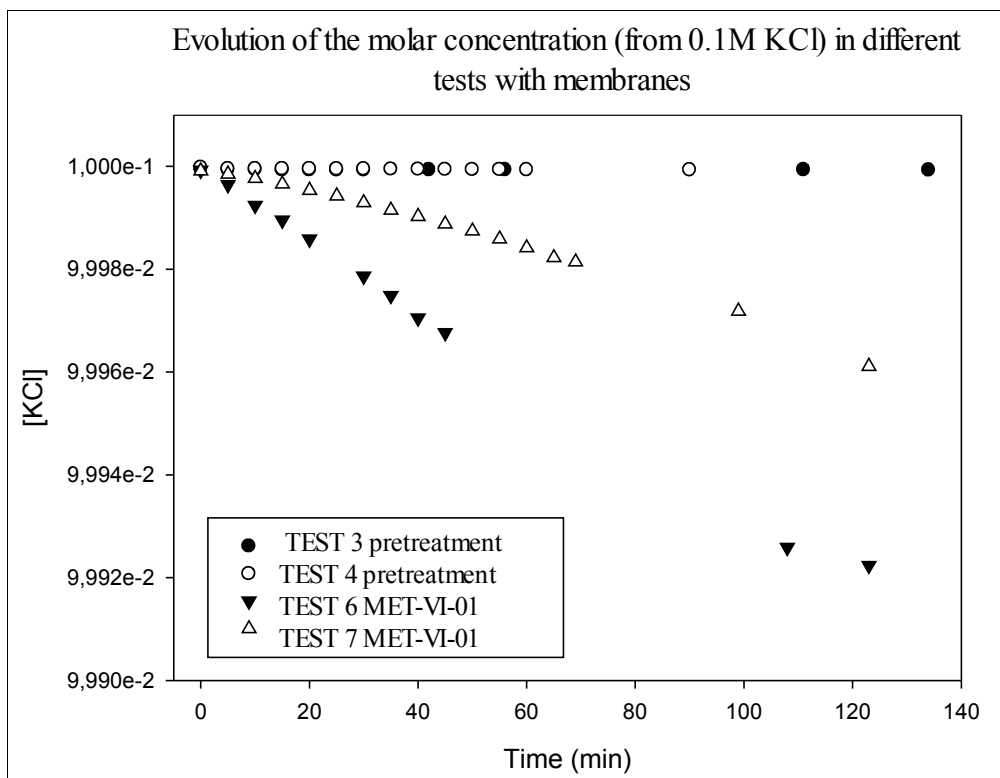

Figure 2. Comparison of two pairs of experiments with pretreatment and activated (MET-VI-01) membranes.

Then, using the transport equations presented above, the results using the same solutions with three different membrane types: blanc, pretreatment and active MET-VI-01 membranes are shown. The experiments show that a higher slope of the regression line, a greater flow transport in a concrete time. So a higher permeability.
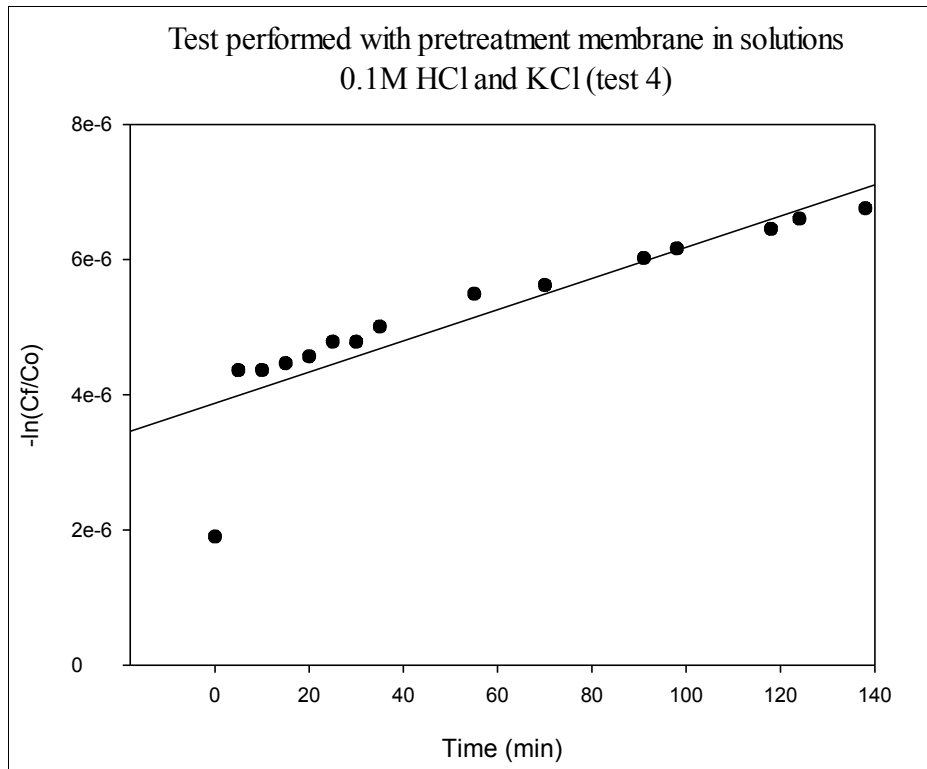
Figure3. Transport of potassium ions through a pretreatment membrane in test 4.
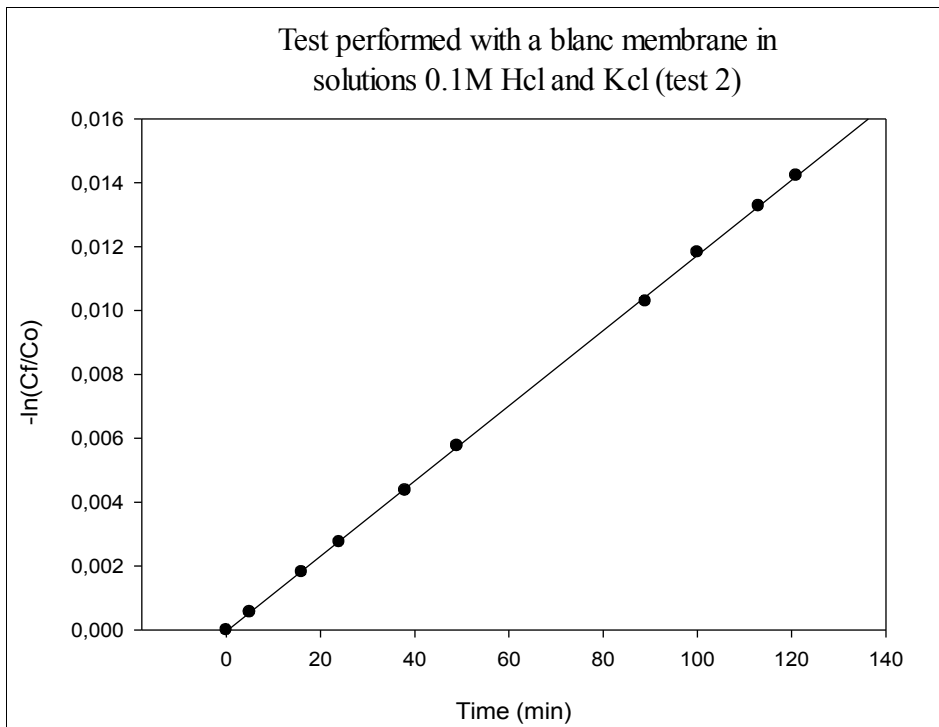

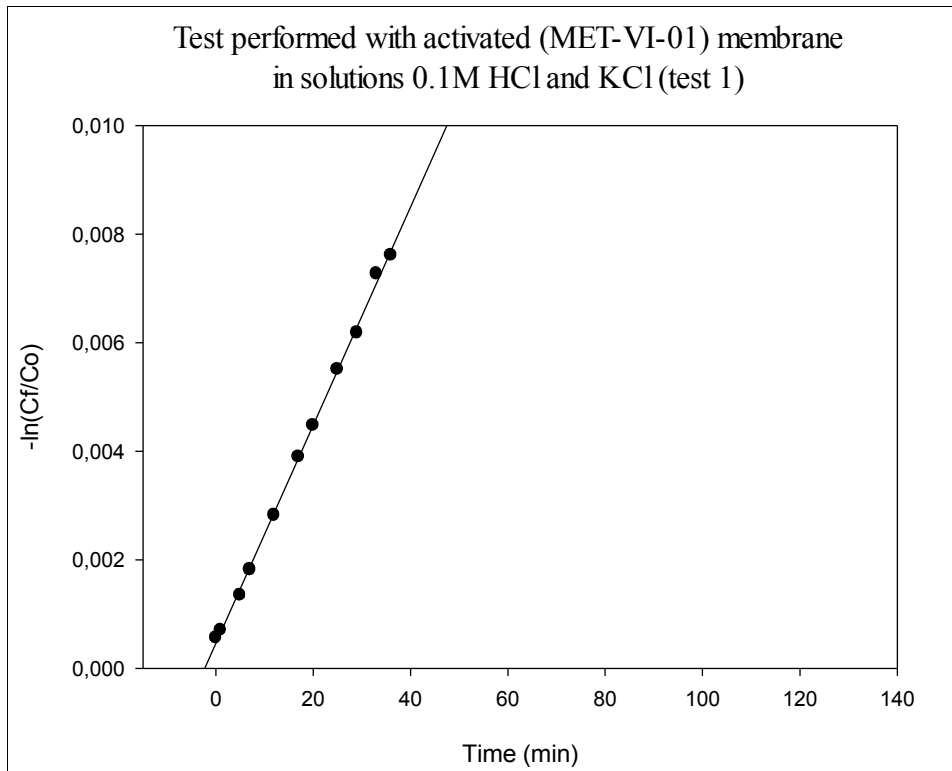*Figure 4. Transport of potassium ions through a blanc membrane in test 2.*

Figure 5: Transport of potassium ions through an activated (MET-VI-01) membrane in test 1.

As mentioned previously, the blank membrane lies sandwiched between a flux level of activated MET-VI-01 membranes and pretreatment membrane due to a high porosity, allowing the exchange of species freely.
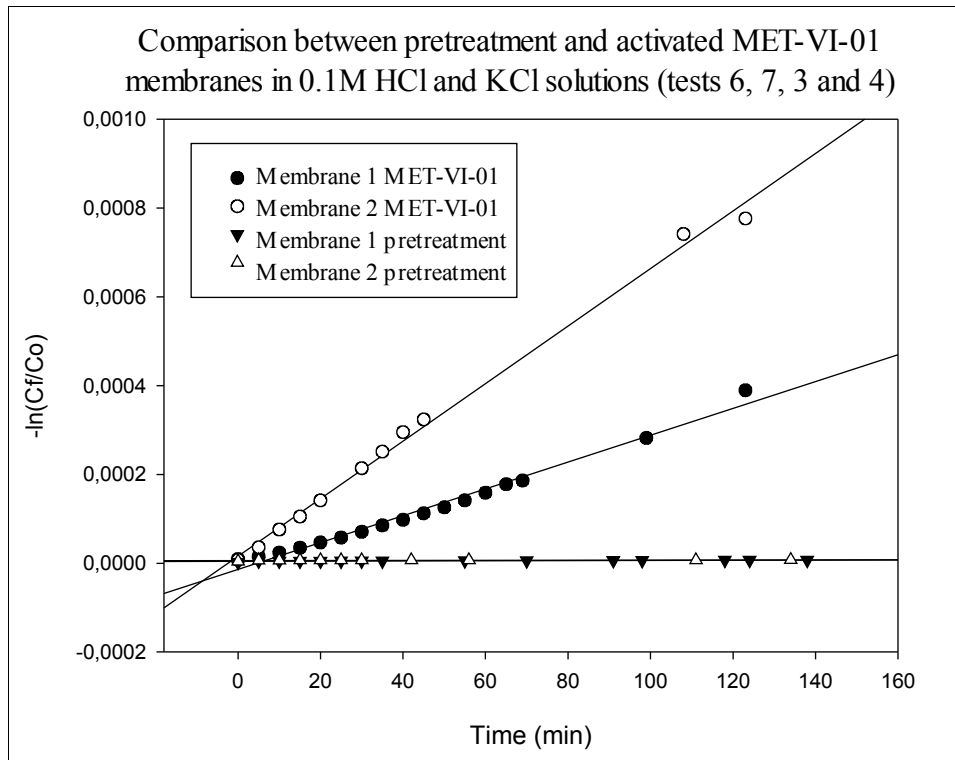
Figure 6: Comparison of two pairs of experiments with pretreatment and activated MET-VI-01 membranes.

In the previous figure, you can see the difference between the transport present in pretreatment membranes and activated MET-VI-01 membranes. It can be observed clearly Flow is clearly present in the MET-VI-01 membranes in comparison of pretreatment membranes.

4.2 Transport of K^+ ions on the blanc, pretreatment and activated (MET-VI-01) membranes. Emulating-wine solutions.

From the solutions provided by the synthetic wine INCAVI (see Procedure) were performed the following experiments. Owing to technical difficulties due to several factors (Shearing of the membranes in the assembly, malfunction of measuring devices), and the limited volume of samples, we could not obtain results from all the samples present. However, the results we have obtained are clear and show a decrease in potassium. Therefore, transportation.
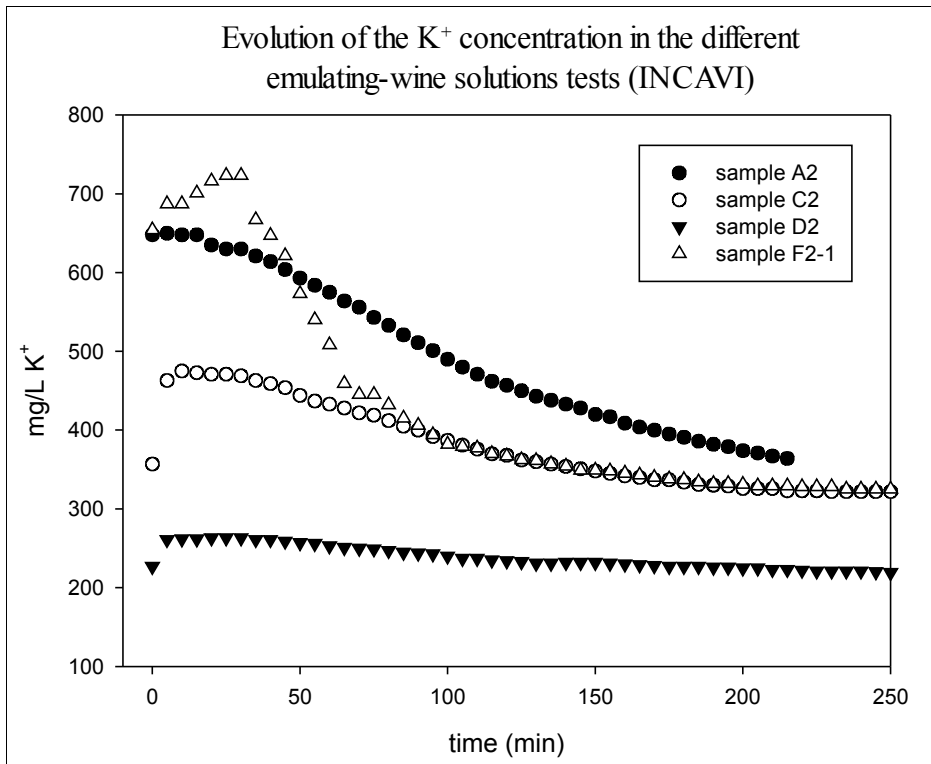
Figure 7: Diminution in the concentration of the different samples studied from different initial concentrations of potassium.
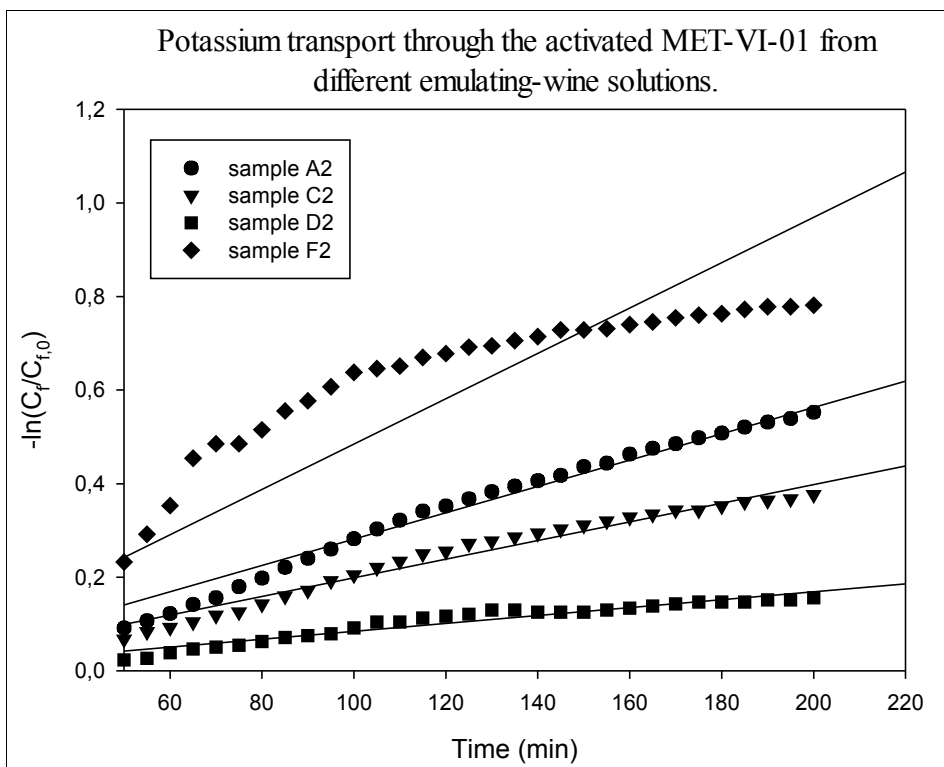

Figure 8: Transport in the different solutions studied.

According to equation [3], if we represent the logarithm of concentrations on time, knowing the surface of the membrane and volume of the feed solution, we can obtain the permeability of the membrane. Here are the values of permeability obtained:

Table 2. Permeability of the activated MET-VI-01 membranes from the different emulating-wine solutions.

Permeability	samples			
	A2	**C2**	**D2**	**F2**
cm/min	0,090	0,052	0,037	0,016
L/m²·h	54,079	31,404	22,216	9,423
µm/min	15,022	8,723	6,171	2,617

5. BIBLIOGRAPHY

1. Artigas, J. et al. 2003. Development of multiparametric analyser based on ISFET sensors applied to process control in the wine industry. Sensors and Actuators B, 89 (2003), 199-204.

2. Boulton, R. 1980. The general relationship between potassium, Sodium and pH in grape juice and wine. Am. J. Enol. Vitic., Vol. 31, No. 2.

3. Danesi, P.R. 1984. Membrane Science, 20, 231-248,

4. Esau, P.; Maynard, Amerine, M. 1966. Synthetic ion-exchange resins in wine research. Am. J. Enol. Vitic. 1966 17: 268-276.

5. Flanzy, C. 2003. Enología: fundamentos científicos y tecnológicos. Editorial Mundi-Prensa. ISBN: 848476074X / 9788484760740.

6. García Barceló, J. 1990.Técnicas Analíticas para vinos. Cap. 12, 12.10-12.17. ISBN 84-404-7827-5.

7. Garcia Valls, R. 1995. Ph.D Thesis. Nous Materials en Tècniques de Separació d'Elements Lantànids. Membranes Polimèriques Activades i Materials Inorgànics per a Cromatografia. Barcelona. ISBN: B-26993-2008 / 978-84-691-3775-8,

8. Gómez Benítez, J. et al. 2002. Comparison of electrodialysis and cold treatment on an industrial scale for tartrate stabilization of sherry wines. Journal of Food Engineering 58 (2003) 373–378.

9. Gómez Benítez, J. et al. 2002. Estimación de los costes directos de la estabilización

tartárica mediante tratamiento por frío, intercambio protónico y electrodiálisis. Tecnologia del vino, julio/agosto 2002, 45-49.

10. Margalit, Y. 2004. Concepts in Wine Technology. Wine Appreciation Guild. San Francisco, USA. ISBN: 9781891267512.

11. Mulder,M. 1991. Basic Principles of Membrane Technology. Kluwer Academic Publishers. The Netherlands.

12. Palacios, V.M. et al. 2001. Application of Ion Exchange Techniques to Industrial Process of Metal Ions Removal From Wine. Kluwer Academic Publishers. Adsorption 7: 131–138.

13. Usseglio-Tomasset, L. 1998. Química Enológica. Ediciones Mundi-Prensa. Madrid. ISBN: 978-84-7114-701-1.