Deionization Degree Prediction for Wines Tartaric Stabilization

Inês Rodrigues Martins
ines.r.martins@tecnico.ulisboa.pt

Instituto Superior Técnico, Lisboa, Portugal

Maio 2019

Abstract

The aim of this work is the optimization and validation of the new controlled freeze-thawing test (CFT) to predict the deionization degree to impose in electrodialysis for wine tartaric stabilization.

In its optimization a variety of factors that could influence the deionization degree prediction were studied, using 5 wines from the regions of Setúbal, Bucelas and Douro. Factors like the agitation, the variation of the freezing temperature and the volume of water that promotes wine nucleation were studied.

It was demonstrated that it is possible to predict deionization degrees closer to wines effective stability with one measurement only, with previous agitation of 3 minutes/flask, using a portable agitator. It was proved that freezing temperature variations do not significantly affect the results. Also, the volume of water that promotes wine freezing should be between 1.3 L and 2.0L for 12 samples.

It was concluded that the optimization of the CFT decreases the overestimation of the deionization degree value, by the standard CFT, from 5-8% to 2-5%, allowing to obtain stable wines when processed by electrodialysis. This was proved using the freezer test, at -4°C for 6 days, for 3 different types, of wines from the regions mentioned above, processed by electrodialysis and subjected to the degree predicted by the optimized CFT. Therefore, the tartaric stabilization of wines by electrodialysis benefits from this validated test, the CFT, which provides deionization degrees that ensure its stability.

Keywords: Controlled Freeze-Thawing Test; Deionization Degree; Electrodialysis; Freezer Test; Tartaric Instability; Wine

1. Introduction

The tartaric instability is currently a huge concern for the wine industry, since it results in a unattractive wine, due to the precipitation of some salts, such as potassium bitartrate (KHT) and calcium tartrate (CaT)[Swarts, 2017]. Nowadays, there is an enormous diversity of techniques to stabilize the wine, thus preventing the precipitation of those salts. They are divided in 3 different categories, defined by [Gerbaud et al., 2010]:

- Processes that cause the precipitation through the refrigeration, followed by filtration: cold stabilisation (traditional process), contact method, between other continue contact processes;

- Ions removal processes: ion exchange and electrodialysis;

- Addition of crystallization inhibitors: metatartaric acid, carboxymethylcellulose (CMC), mannoproteins and polyaspartate.

Comparing all the existing methods, electrodialysis is considered one of the most promising for tartaric stabilization, mainly due to its versatility regarding the wine to be treated. In this process, wine flows through a rectangular channel confined by anionic and cationic selective membranes. By the action of an external electrical field normal to the membranes, the ions are forced to migrate to the electrodes, switching to the concentrated stream. Therefore, the wine stream becomes poorer in ions, diluate stream[Strathmann, 1986]. These two compartments, diluate and concentrate, alternate between each other, being held among two plates under high pressure. The ions that migrate more significantly are potassium (K^+) and bitartrate (HT^-). However, a considerable migration of calcium (Ca^{2+}) has also been recorded, ions involved in tartaric instability[Corti and Paladino, 2016]. Besides these ions, Na^+, Fe^{3+} and Cu^{2+} are also removed from wine, however in smaller amounts. The wine quality is preserved, or even improved because of the pH decrease. Also, the

losses of wine are minimal, as is energy consumption. Despite all the advantages mentioned, it is still not a very common method, due to the high initial investment needed for equipment and lack of familiarity with the method[Corti and Paladino, 2016].

To stabilize the wine by electrodialysis, it is necessary to determine, in advance, the DD to be imposed, which corresponds to its instability degree. This determination is possible through several methods, such as the mini-contact test, the CFT and by the determination of the saturation temperature. Currently, the most used is the mini-contact test, due to its reduced testing time. This test consists in adding exogenous KHT crystals to the wine, at -4 °C, with constant stirring, for 4 hours. The crystallization of the wines KHT is monitored by conductivity measurement[Ribéreau-Gayon et al., 2006]. To improve the method, an exponential curve is adjusted to the conductivity evolution with time and the final conductivity is estimated by an extrapolation to infinite time. If during the wine treatment by electrodialysis it is only applied the DD predicted by this test, which just considers the KHT precipitation, it would result in an unstable wine. This happens, because the removal of other ions occurs, besides those involved in the precipitation of that salt. Therefore, it is necessary to always impose a safety margin, since the predicted degree demonstrates to be insufficient when wine stability is done by electrodialysis. If the degree is underestimated the wine has to be treated again, which increases the process time and complexity, therefore affecting the confidence in this method of stabilization[Corti and Paladino, 2016]. Furthermore, it requires more elaborated methods and equipments and the way the mini-contact test predicts the DD cannot be considered an absolute methods, since it predicts in 4 hours what takes a few weeks to complete[Ribéreau-Gayon et al., 2006]. It requires the extrapolation to infinite time through an empirical equation that has, as it is known, associated prediction errors, thus different parameters result in different DD[Henriques et al., 2019].

In order to minimize the errors associated with the mini-contact test and to decrease its costs, a new test has been introduced in the market that presents a lot of advantages when compared with this one[Henriques et al., 2019]: the CFT. This new test predicts the tartaric DD of wine with an additional safety margin, unlike the mini-contact test[Henriques et al., 2019], being ideal for electrodialysis. The CFT is a novelty in the wine market and as such, it is necessary to understand whether there is still room for improvement, for example checking if the overestimation associated with this test can be brought closer to the thermodynamic

equilibrium of wine. This test consists in freezing, at -20 °C for 24 hours, and thawing, at 0 °C for 30 minutes, in controlled conditions 12 wine samples of 10 μL. These two steps are essential to obtain reliable and reproductible results[Henriques et al., 2019].

The DD obtained by the CFT are always higher than those obtained by the mini-contact test. This difference may be due to the errors associated with the infinite time extrapolation or excess precipitated salt at -20 °C not having time to redissolve at 0 °C, during the interval studied by Henriques, et al., 2019. The fact that the mini-contact test stability is predicted for -4 °C and the CFT for 0 °C should not be a problem, since the cold stabilization method, that is performed at a temperature closer to the freezing point of wine, can be carried out in a range between 0 °C and -4 °C[Coulter et al., 2015]. This means that if the wine is considered stable at 0 °C then it must also be stable at -4 °C. The CFT has also the additional advantages of being a quick, simple and practical test that involves low cost equipment.

For wine quality control in terms of tartaric stability, one of the most commonly used tests in portuguese wine industry, considered simple, practical and that does not require special equipment, is the freezer test. However, it is not reproducible, since it is based in a spontaneous phenomenon, not induced crystallization, a slow and independent process. This test simulates the extreme conditions that wine is subjected during transportation or commercialization[Leske et al., 1996][Soares et al., 2009]. A sample of 100 mL of wine is kept at -4 °C, for 6 days. At the end of this time, the presence of crystalline structures or deposits is evaluated[Moutounet et al., 1999]. It is a qualitative test, that requires long periods of time, incompatible with certain low contact stabilization technologies, in which quick results are essential to guarantee treatments in real time.

This work intends to demonstrate that CFT is a good method to predict the DD of wine to apply in electrodialysis. The influence that some external factors can have is studied, in order to optimize and make it more robust. It is concluded that the introduction of agitation in this test brings the wine closer to its thermodynamic equilibrium, decreasing the DD previously predicted, considered overestimated. Factors like the added water volume on the freezing step and variation of the freezer temperature are not limiting, allowing to conclude that the improvements studied result in a more reliable test. This test can be used for different types of wines from different regions.

Applying the DD predicted by the optimized CFT to electrodialysis has proven to allow the produc-

tion of stable wines, using the freezer test. However, a small amount of samples were tested, being recommended an additional study on more wine types.

In conclusion, from this work results a validated tool, the optimized CFT, ready to be implemented in the treatment of wines by electrodialysis.

2. Materials and Methods

2.1. Wines

The wines used in this work were gently provided by the *Wineinova Lda* company, as well as their analyses. The physical-chemical properties and regions of origin for each wine are presented at Table 1.

2.2. Electrodialysis

The electrodialysis equipment from *Wineinova, Lda* has a nominal treatment capacity of 3000 L/h. The membrane module used is currently supplied by Suez (Paris, France) and is formed by 100 cationic (reference *CR67*) and anionic (reference *AR204*) membrane pairs. The total membranes effective area is 30 m^2. The equipment has a protective filter of 5 μ.

The wine was processed continuously with a density flow between 35 and 50 A/m^2 and a voltage of 0.8 to 1.2 V/membrane pair, depending on the wine being processed. All the wines were previously filtrated by tangential filtration.

2.3. Conductivity and Temperature Measurements

The temperature was measured using a thermocouple (model *AB*, *System Teknik*, Nørresundby, Dinamarca), it has a resolution of 0.001 °C, the temperature probe used is coupled with the thermocouple.

The specific conductivity was measured with a conductimeter (model *Primo 4*, *Hanna Instruments*, Rhode Island, USA), has a scale of 0.00 to 10.00 mS/cm. The calibration is done with a 5.00 mS/cm solution and makes the automatic compensation of temperature between 0 and 60 °C, however all the compensations were made using a temperature coefficient of 2.2 %/°C.

To register the temperature variation of the freezer during 6 hours a temperature logger was used (model *VL-1416-44V*, *Vaisala*, Vanda, Finlândia). The temperature probes used are coupled with the logger.

2.4. Controlled Freeze-Thawing Test (CFT)

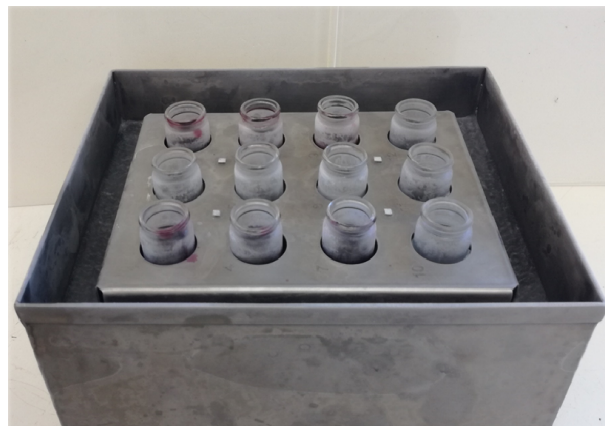The *StabilPro* equipment necessary for this test, Figure 1, was kindly provided by *Wineinova, Lda*.

Figure 1: *StabilPro* equipment.

Initially, a certain volume of water is added in the reservoir surrounding the flasks, that freezes during the night. Is extremely important that the level of water reaches the flasks base, allowing efficient heat exchanges. The *StabilPro* was put in the freezer (model *Medline*, *Liebherr*, Bulle, Switzerland), with a regulated temperature of -20°C, it has a resolution of 0.1°C.

In the following day, the *StabilPro* is put in an insulation box, to avoid heat losses. In all the flasks 100 μL of water are added followed by 10 mL of wine, except for one, that will serve as reference, where only the 100μL of water are added. The equipment goes back to the freezer, where it stays for 24 hours. After this time, the equipment goes back to the insulation box and 0.5 L of water are added in the reservoir, to thaw the samples. It is expected that the thawing of the samples is complete, it can take from 30 minutes to 1 hour, depending on the outdoor atmospheric conditions, and then the reference is added, a sample of 10 mL of wine, without treatment, in the free flask. The specific conductivity of the reference wine and the other samples is measured, the samples may or not have previous agitation, and its duration is variable.

The conductivity measurement will allow the determination of the DD, Equation 1, where the $\kappa_{initial}$ designates the reference specific conductivity and κ_{final} designates the specific conductivity of the samples, after being controlled freezed and thawed.

$$DD(\%) = \frac{\kappa_{initial} - \kappa_{final}}{\kappa_{initial}} \times 100\% \qquad (1)$$

The portable agitator (model *Grinder*, *KKMOON*, China) has an approximated speed of 2000 rpm. To optimize the agitation process two equipment parts were created (both in PLA material), using a 3D printer (model *2+*, *Ultimaker*, Gelderland, Netherlands). First, a new support was made that allowed the adjustment of the agitator to the flask,

Table 1: Physical-chemical properties of the used wines

	Origin Region	Ethanol (v/v)	Total Acidity (g/L H_2T)	Volatile Acidity (g/L AcOH)	Free SO_2 (mg/L)	Sugars (Glu+Fru) (g/L)	Conductivity (μS/cm)	pH	Effective Deionization Degree (%)
White 1	Bucelas	12.8	5.8	0.5	65.0	<0.6	2393	32	*
White 2	Setúbal	12.5	5.5	0.5	81.0	1.2	2553	3.5	33.4
Rosé 1	Bucelas	13.0	6.5	0.3	78.0	1.6	1514	3.4	28.4
Red 1	Bucelas	13.5	4.8	0.6	95.0	<0.6	4054	3.8	*
Red 2	Douro	14.4	4.2	0.4	85.0	<0.6	3171	3.8	22.6

* Not subject to electrodialysis.

to diminish the human error factor and make the agitation more homogenous. Then, a fitting part was produced, to avoid wine sample contaminations.

During CFT optimization a chain study plan was defined: has conclusion were drawn in the studies carried out, they were applied in the following studies, allowing to obtain at the end an optimized CFT.

2.5. Freezer Test

In the freezer test, a sample of 100 mL of wine is cooled until -4 ⁰C, near is freezing point, for 6 days.

This test was made using a mixture of untreated and treated wine. This mixture allows to prepare wine samples with deionization percentages between the corresponding to the treated and untreated wine, in order to visually evaluate the appearance of KHT salts. If the samples do not present precipitate, they are considered stable, if otherwise it is concluded that they are unstable.

Samples with 1/2, 1/4 and 3/4 of the DD applied in electrodialysis, presented in Table 1 (effective deionization degree). Calculation of the treated and untreated volumes of wine that were necessary to add, to obtain the various DD, were made using the *Excel Solver* tool. After the mixtures were made with the calculated volume, the conductivity values was always evaluated to confirm that it equals the DD intended. If this requirement was not fulfilled, an adjustment was made with volume of treated or untreated wine, depending on each case, until the desired degree was obtained.

To keep the samples at -4 ⁰C for 6 days, a thermostatically-controlled ethylenoglicol bath (model *Polystat CC2*, *Huber*, New Jersey, USA) was used, with a resolution of 0.1 ⁰C.

3. Results and Discussion

3.1. Otimization of the CFT

In order to optimize the controlled freeze-thawing test (CFT), several factors that may influence KHT precipitation were studied. The factors studied were: the introduction of agitation of the wine samples and their duration, freezing conditions and the volume of water to freeze the samples.

To verify if the DD varies over time, several measurements have been made with a 30 minute interval between each other, performing various agitations.

3.1.1. Standard CFT

The CFT was performed without any alteration of the initial method, in order to allow comparison with the results of the optimized test.

In the CFT, without alterations, a volume of 2.0 L of water was used to form ice and allow the controlled freezing of the samples in the device *StabilPro*; the second drawer of the freezer was used, identified as B in Figure 2; the thawing lasted 30 minutes and only one measurement was performed at the end without any kind of prior agitation.

Table 2: Deionization degrees obtained with standard CFT.

	DD (%)
White 1	17.6
White 2	16.4
Rosé 1	27.2
Red 1	12.2
Red 2	11.2

The results shown in Table 2 are considered the reference values for the subsequent tests. To compare the DD obtained by the standard CFT with the results when evaluating the influence of some factors, allows to verify if they exert some type of consequence in the obtained values, allowing to achieve the most optimized method.

3.1.2. External Factors Influence

3.1.2.1. Introduction of Agitation

In the study of the influence of agitation, the CFT was performed using: a volume of 2.0 L of freezing water in the reservoir of the *StabilPro*; the second drawer of the freezer was used, identified as B in Figure 2; the thawing lasted 1 hour and several measurements were performed, with 30 minutes between them. For the first measurement, no previous agitation was performed. In the following, 3 of the 9 samples were maintained without agitation and in the remaining samples variable agitations

were performed: 3 with the use of a spatula and 3 with the portable agitator. Each agitation lasted 2 minutes per flask.

To study the effect of agitation on determining the tartaric stability of the samples, it was considered the duration of the assay, this means, how many measurements would be necessary to perform until reached the conclusion that the sample were stabilized.

For White 1 the use of the portable agitator causes a decrease of about 2 % in the DD, between the first and second points, which shows that agitation enhances the KHT redissolution. This allows a faster approximation to thermodynamic equilibrium. For stirring with a spatula and without stirring, the value of the DD also decreases, but not as significantly as with mechanical stirring, between the first two points.

In the case of White 2, it is quite evident that both stirrings promote tartaric stabilization, through the slope between the first two points. The difference between the obtained DD values, in the second measurement, with a spatula and agitator is of only 0.4 %. However, the final DD obtained for agitation with a spatula ends up being lower than with the agitator. In the case of the agitator, there are not enough data to allow a comparison, since up to the point of abrupt descent, for agitation with a spatula, the values obtained with portable agitator are lower. It would be interesting to have more results with agitator, at least one more point, in order to verify if the degree would be equal or lower than the value obtained with spatula.

For Red 1 and Red 2 both samples present a lower DD value when using the portable agitator, when comparing with the other agitation variables. For Red 1, the DD value considered stable with the portable agitator coincides with one of the intermediate values for agitation with spatula. However, in the case of the spatula, a further measurement shows that the degree increases again and does not stabilise at the previously obtained value. Considering that none of the first points were subjected to any type of agitation, it should be noted that in the first point using a spatula a lower value was obtained, when compared to the value recorded for the first point using the agitator. Thus, is concluded that the results associated with the agitator are in line with expectations, since the degree decreases until it reaches the value recorded with the spatula. For Red 2, the first points of all the agitations have an approximately equal value, which allows a better comparison of the evolution of the DD for each type of agitation studied. It was found that, with the agitator, the DD stabilizes at a lower value, associated with the metastability of the solution. In addition, it is also with the agitator that

a greater slope between the first two points is verified, which is associated with a faster approximation to the wine thermodynamic equilibrium.

For Rosé 1, a slight difference is observed between the first points in the study of each agitation, although all were obtained without agitation. This may be the result of any measurement or conductimeter calibration errors. However, for all stabilised DD there is no significant difference between the values obtained. Again, the use of the portable agitator shows to stabilize the wine much faster. This is proved by the slope between the two initial values and by the fact that the DD considered stable has a lower value with this type of agitation. This indicates that a rapid KHT redissolution has occurred, which results in the approximation to the state of thermodynamic equilibrium of the wine.

Almost unanimously, for all the wine samples tested, the final DD obtained using the portable stirrer is lower, the only exception being White 2, using a spatula. Among the types of agitation studied, the DD varies between 1% and 3%, which is significant when considering the case of the most unstable wine, for example Rosé 1. Compared to the reference values, these values were clearly not the most correct to use in electrodialysis, since an excess of DD would be imposed, which varies between 3 and 6 %.

It is concluded that the use of the portable agitator in the measurements is beneficial. In the following studies, therefore, a 2 minute stirring was introduced.
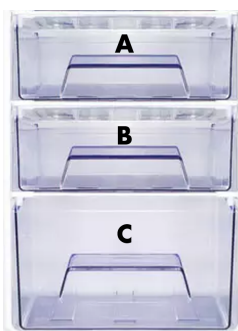
3.1.2.2. Freezing Temperature

As in the previous chapter is concluded that the introduction of agitation is beneficial, the experimental method described at the beginning was changed. Prior to the first measurement there is no stirring, however, the portable agitator is used for 2 minutes per flask for the following measurements.

Aiming to study the influence of freezer temperature variation, all freezer drawers were used, which were identified as: A for the upper drawer, B for the intermediate drawer, and C for the lower drawer, as shown in Figure 2.

A lower freezing temperature results in an increase in the concentration of alcohol in solution, which results in a decrease in the KHT solubility and, consequently, in an increase in the precipitation rate of this salt, thus increasing the DD of the sample. The aim is therefore to ascertain whether temperature fluctuations within the freezer affect the DD obtained.

This study was not performed for White 1, due to the small amount of existing sample, which was

Figure 2: Labels of the freezer drawers.

necessary for the remaining tests.

It was concluded that in drawer A, closer to the cooling coil, the average temperature is the minimum recorded and there is a greater oscillation between minimum and maximum temperatures. In drawer B, the average temperature is slightly higher than in drawer A and for the further from the coil, drawer C, the average temperature is, as expected, the highest. For drawers B and C there are no major temperature fluctuations.

Verifying the ethanol concentration as a function of the average temperature of each drawer, it is observed that the wine would have a concentration in ethanol of about 30% for drawers A and B, and 28% for drawer C. These differences in concentration between drawers are not considered relevant. However, lower temperatures are preferable for nucleation kinetics.

The stabilized DD obtained for each drawer verify that there is no significant discrepancy between values. However, for drawer A it is observed, in most cases, that the DD registered is always lower than the others. This may be a consequence of the highest temperature oscillation, which affects the freezing control. The opposite happens for drawer C, where a lowest temperature fluctuation is registered, facilitating the nucleation, despite having the highest mean temperature. Nevertheless, it is considered that the ideal state, in this case happens in B, since the average temperature recorded is intermediate, but very close to the minimum value registered, and has less oscillation. Looking globally at the results, there is no considerable disparities between the DD recorded for the same type of wine.

3.1.2.3. Agitation Length

As previously shown, it is advisable to use drawer B of the freezer, the freezing stage will always be carried out there.

In order to reduce the experimental time, to make it more practical, it was tried to reduce the number of measurements required. Thus, only one

measurement was performed, with prior agitation (using the portable agitator) that lasted between 1 and 3 minutes per flask.

The agitation length should affect the KHT redissolution. Thus, increasing the duration of the agitation, it is expected that the DD obtained will decrease, since the redissolution results in the stabilization of the solution, as it approaches the thermodynamic equilibrium. The aim is to obtain a method that requires only one agitation and measurement, reducing the experimental time required to obtain reliable results.

The values obtained in this test are compared with the final values, considered stabilized, when agitation was introduced, in Chapter 3.1.2.1.

For White 1, White 2, Rosé 1 and Red 2 a longer agitation time results in a lower the DD, as expected. The variations between values, although not very evident in the case of more unstable wines, such as Rosé 1, can reach 3%, which is a considerable value considering that the resulting degree will be applied in electrodialysis. When compared to the values obtained by making multiple agitations, it is concluded that, for all cases, it is like stir only once for 3 minutes.

For Red 1 the opposite relation is observed than that for the other samples of wine analysed. As the agitation time increases, the DD increases, which would not be expected. This is due to some possible experimental errors, such as temperature variation during freezing, or possible contamination of samples with water used for defrosting. In this case, the result for 1 minute stirring coincides with the stabilized value obtained with several stirrings.

It is concluded that the introduction of agitation undoubtedly brings benefits that can be explored with the reduction of the test time, making the CFT faster. Compared to the reference values, stirring for 3 minutes decreases the DD between 1% and 6%, allowing a more reliable value to be applied to electrodialysis than what was assumed with the initial or standard method of the CFT.

In the following experiments only one measurement was made with previous agitation of 3 minutes per flask, using the portable agitator.

3.1.2.4. Freezed Water Volume

To study the influence of the volume of frozen water several volumes were tested: 1.3 L, 1.5 L and 2.0 L. The aim is to check the possibility of reducing the volume of water used in the freezing stage in order to save this valuable resource. The minimum volume tested was 1.3 L, because it is the required to reach the flasks bottom, in order to maintain the temperature of these homogeneous, at -20 ºC. Thus, when the wine samples are added, the

nucleation kinetics of the KHT crystals is initiated.

For White 1 and Red 1 it is observed a decrease in the DD proportional to the decrease in volume. However, for White 2 and Red 2 there is no apparent influence of the volume in the DD obtained. In the case of Rosé 1, there is an inverse relationship between the volume and the DD, when one increases the other decreases and vice versa.

Comparing the DD obtained through the variation of the volume with those of the standard method, it is observed that: for a volume of 1.3 L there is a difference between degrees in the range of 5 and 2 %; for 1.5 L the difference recorded is between 4 and 2% and for 2.0 L between 6 and 1 %. It is concluded that using a volume of 1.5 L allows to obtain a DD less discrepant in relation to the obtained with the standard method.

In sum, the volume of freezing water does not significantly affect the DD obtained, and a slight error in the volume of added water is not a concern. However, it should be noted that the bottom of the flasks must always be in contact with the formed ice in order to enhance the nucleation kinetics. Therefore, the minimum volume of 1.3 L must always be respected.

3.2. Optimized CFT Validation

In order to validate the optimized CFT its results for the volume of 1.5 L are compared with those of the standard method and the freezer test, since the last-mentioned test is the most used by the wine industry to evaluate the stability of wine.

For the freezer test, after 6 days at -4ºC, it was possible to observe precipitate in some tested wines. This observation was undoubtedly more difficult in the red wine samples, due to the colour deposit.

In Table 3, the degree of instability of the samples is represented. All tested samples are presented, from the wine not subject to electrodialysis, 0%, up to the DD applied by electrodialysis, the effective deionization degree (EDD), presented in Table 1. Between these values, samples were prepared with intermediate percentages, of about 1/4, 1/2 and 3/4 of the value of EDD. It should be noted that not all the wines tested with CFT were subjected to electrodialysis, therefore only the results of 3 samples were used.

For terms of comparison with the standard and optimized CFT, the lowest DD in which no deposit occurred were considered for the refrigeration test, represented by ○ in Table 3. It should be noted that this test is merely qualitative and that the degree considered has a large associated error due to the margin of DD studied.

It is possible to observe, through Table 4, that the optimization of the CFT reduces the overestimation

inherent to it, this test continues to obtain higher DD than the freezer test, between 2 and 5 %. It is verified that the results obtained with the standard CFT are even higher than those obtained with the freezer test, between 5 and 8 %. It would be interesting to have tested more samples for comparison.

The results are in line with what was expected, since the CFT subjects the samples to extreme freezing conditions, reducing the solubility of KHT salts much more significantly. By decreasing the temperature to -20ºC, the ethanol concentration increases much more significantly than to -4ºC, the temperature used in the refrigeration test. When thawing the samples, the solution approaches its thermodynamic state of equilibrium, and the KHT redissolution is enhanced by the agitation used in the optimized CFT.

4. Conclusions

This work aimed the optimization and validation of the new test introduced in the market, the CFT, for the prediction of the DD of wine, to be applied in electrodialysis. To accomplish this, the influence of several external factors on its prediction was assessed, namely the introduction of agitation prior to the measurement of conductivity. The efficiency of this test for various types of wines from different regions was also verified through comparison with the traditional test, the freezer test.

The introduction of mechanical stir with an incorporated support makes the tests more practical and reduces the human error factor. This proved to be very beneficial, since it promotes the redissolution of KHT in solution, bringing the wine closer to its thermodynamic equilibrium. The agitation, carried out just before the measurement, should last 3 minutes/flask, ensuring more reliable results with one measurement only.

Regarding the freezing temperature of the wine, it was found that, although it does not have a significant influence on the results, its fluctuations showed to affect the samples nucleation. As a result, it is advisable to set the freezer set point to -20ºC. If the freezer used is the same as in this experimental work, drawer B should be chosen, illustrated in Figure 2.

For the volume of freezing water added to the base of *StabilPro*, in order to ensure the nucleation of the samples, it should be used a value between 2.0 and 1.3 L. The lower limit corresponds to the minimum volume necessary to reach the bottom of the flasks in order to promote the nucleation kinetics of the wine. It is advisable to use 1.5 L of water, as this allows a significant saving of this resource, respecting the minimum volume required,

Table 3: Recorded appearance of precipitate for the freezer test.

	DD(%)/Degree of Instability									
White 2	0	●	8	○	16	○	24	○	33	○
Rosé 1	0	●●●	7	●●	14	●	21	○	24	○
Red 2	0	●	6	○	12	○	18	○	24	○

Degree of Instability:
●●● Identification of crystalline structure.
●● Visualization of precipitate.
● Visualization of deposit.
○ Without any type of deposit.

Table 4: Comparison between the freezer test, the standard CFT and the optimized CFT.

DD (%)	White 2	Rosé 1	Red 2
Freezer Test	8	21	6
Standard CFT	16	27	11
Optimized CFT	13	23	8

with some safety margin.

Comparing the DD obtained by the tests studied, it was verified that the optimised CFT allows to obtain more reliable results, reducing the overestimation of the DD inherent to the standard CFT and bringing it closer to its effective stability. It was also possible to conclude that, the application of the DD provided by the optimized CFT in electrodialysis allows to obtain stable wines, proving that no additional treatment is necessary. This test worked well for all the wine types tested, from different regions of the country.

In conclusion, from this work a validated test is obtained, the optimized CFT, ready to be implemented in the treatment of wines by electrodialysis. This test has also the additional advantage of being much more economic than the current most commonly used test, the mini-contact.

For future work it is suggested the creation of a matrix of stirrers to automate and speed up the agitation step; the study of the stabilization of calcium tartrate, applying to electrodialysis the DD predicted by the optimized CFT; and to better understand the importance of escalate the degree imposed in electrodialysis. Due to the comparison of a small amount of samples with the freezer test, it is advisable to be applied to a larger variety of wines in order to confirm the results.

References

[Corti and Paladino, 2016] Corti, S. V. and Paladino, S. C. (2016). Estabilización tartárica en vinos: comparación entre electrodiálisis y tratamiento de frío por contacto. *Revista de la Facultad de Ciencias Agrarias*, 48(1):225–238.

[Coulter et al., 2015] Coulter, A., Holdstock, M., Cowey, G., Simos, C., Smith, P., and Wilkes, E. (2015). Potassium bitartrate crystallisation in wine and its inhibition. *Australian Journal of Grape and Wine Research*, 21(1):627–641.

[Gerbaud et al., 2010] Gerbaud, V., Gabas, N., Blouin, J., and Crachereau, J. (2010). Study of Wine Tartaric Acid Salt Stabilization by Addition of Carboxymethylcellulose (CMC) : Comparison With the « Protective Colloids » Effect. *Journal International des Sciences de la Vigne et du Vin*, 44(4):231–242.

[Henriques et al., 2019] Henriques, P., Alves, A. M. B., Rodrigues, M., and Geraldes, V. (2019). Controlled freeze-thawing test to determine the degree of deionization required for tartaric stabilization of wines by electrodialysis. *Food Chemistry*, 278:84–91.

[Leske et al., 1996] Leske, P. A., Bruer, N. G. C., and Coulter, A. D. (1996). Proceedings of the ninth Australian wine industry technical conference. In *Potassium tartrate - how stable is stable?*, pages 39–45.

[Moutounet et al., 1999] Moutounet, M., Battle, J. L., Saint-Pierre, B., and Escudier, J. L. (1999). Stabilisation tartrique. Détermination du degré d'instabilité des vins. Mesure de l'efficacité des inhibiteurs de cristallisation.

[Ribéreau-Gayon et al., 2006] Ribéreau-Gayon, P., Dubourdieu, D., Donèche, B., and Lonvaud, A. (2006). *Handbook of Enology Volume 2 The Chemistry of Wine Stabilization and Treatments*. Bourdeaux, 2nd edition.

[Soares et al., 2009] Soares, P., Geraldes, V., Fernandes, C., Santos, P., and Pinho, M. (2009). Wine Tartaric Stabilization by Electrodialysis: Prediction of Required Deionization Degree. *American Society for Enology and Viticulture*, 60(2):183–188.

[Strathmann, 1986] Strathmann, H. (1986). Electrodialysis. In *Synthetic Membranes: Science,*

Engineering and Applications, pages 197–223. Springer Netherlands, Dordrecht.

[Swarts, 2017] Swarts, A. (2017). *A Look at Tartrate Stabilisation Of Wine In The South African Wine Industry*. PhD thesis, The Cape Wine Academy.