EARTH LISTENER

Focus

Wine materials: ceramic

Wine, ceramic materials and sanitization. Let's make the point.

Research and development

Abstract

Ceramic is one of the most discussed materials of oenological interest in recent years. Amphorae, of different size and shape, as well as being the most ancient wine vessels are increasingly used by oenologists from all over the world for the interesting organoleptic characterization acquired by wines during the vinification and aging phase. Unlike concrete and steel, however, limited information on the complex phenomena involving the ceramic-wine binomial are currently available.

In recent years, considerable progress has been made in the development of winemaking protocols capable of fully exploiting the potential of these wine containers, but many aspects still need to be studied. The cleaning and sanitization of amphorae certainly represent one of the most important issues and a source of criticality for many wine producers.

The nature of the ceramic material, its porosity and the need to preserve its structural integrity lead to technical reflections on the suitability of the sanitization systems used in the wine sector, which allow to obtain the guarantee of organic, inorganic and microbiological cleanliness while respecting environmental sustainability.

Below the complete technical focus with the article "**Ceramic and wine, sanitizing experiences**" published in the n. **7 of November 2020 issue of the VVQ Vigne, Vini e Qualità Magazine**, in which the results of the research activity are reported in collaboration between **GiottoConsulting** and the **Fondazione Edmund Mach**, aimed at identifying new specific washing protocols for **TAVA amphorae**.

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“Ceramic and wine, sanitizing experiences”

Article published in the n° 7 of November 2020 of VVQ Vigne, Vini e Qualità Magazine

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Wine, materials and sanitization, three aspects not to be overlooked in order to get the best out of the grapes and the chemical-physical properties of each wine container. With experiments conducted in collaboration between Giotto Consulting and Fondazione Mach, we make the point of the sanitization of ceramic materials.

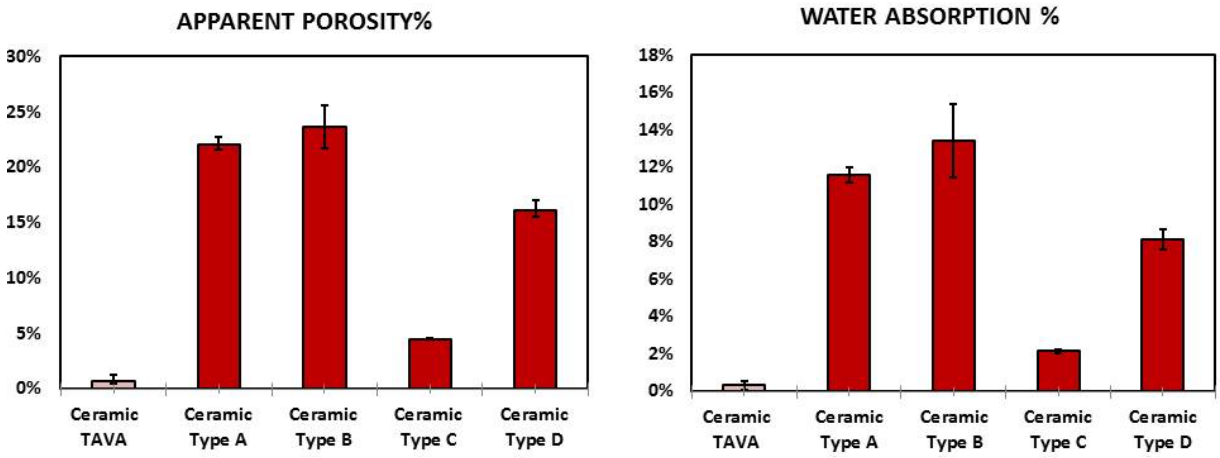
The material of the wine vessel is not a secondary detail in the winemaking process. Due to its hydroalcoholic nature, strong acidity and the presence of numerous compounds sensitive to the action of oxygen, wine interacts with the container which plays a fundamental role as an interface to the external environment. Depending on the characteristics of the grape variety, the enological variables to be adopted and the wine that you intend to produce, the material of the wine vessel must be carefully selected. In recent years there has been a growing attention towards cementitious materials and ceramic materials, including terracotta. If for cements, albeit with new technological contents, it is a return after the race to abandon in the 90s, for terracotta and ceramic materials in general, the use in oenology is recent history at least in Western countries such as Italy and France, although it goes back to ancient traditions. It is objectively difficult to describe the characteristics of these materials, given that the chemical composition and processing techniques vary enormously and there are still no recognized standards. However, cements and ceramics certainly have characters of interest including porosity and oxygen permeability modulated by the manufacturing process, generally intermediate between wood and steel, as well as a thermal inertia that makes them natural regulators of fermentation processes. Given the particularity of the aforementioned materials and the lack of specific studies in the literature, the washing of these containers is a critical aspect for many wine producers, often with the application of washing protocols that are not suitable for their correct cleaning and sanitization. The microbiological control of ceramic materials and their interactions with wine are the subject of this technical note, which summarizes a cycle of experiments conducted in collaboration between GiottoConsulting and the Technological Transfer Center of the Fondazione Mach. All tests were performed on ceramic specimens representative of the amphorae of the company manufacturer Tava srl (pic. Below). The cleaning and sanitizing products were supplied by the Piramide company, which helped to identify the optimal enzymatic formula for cleaning the ceramic material under study.

CERAMIC MATERIALS

The type of mixture and the production technique have a strong impact on the chemical-physical characteristics of ceramic materials and on their coloring (Figure A). The TAVA amphorae, thanks to the particular mixture and the processing technique that involves firing at higher temperatures than traditional techniques (up to 1280 ° C), are characterized by a low porosity and a high chemical inertness (recent is the Verte Excell certification) (Figure B). Thanks to the low levels of porosity, the contamination of the liquid in the ceramic material is superficial, facilitating the cleaning and sanitization processes.

Figure A - Ceramics obtained through different production techniques (different raw materials and firing at different temperature gradient). Below, the ceramic specimen representative of the TAVA amphorae under study

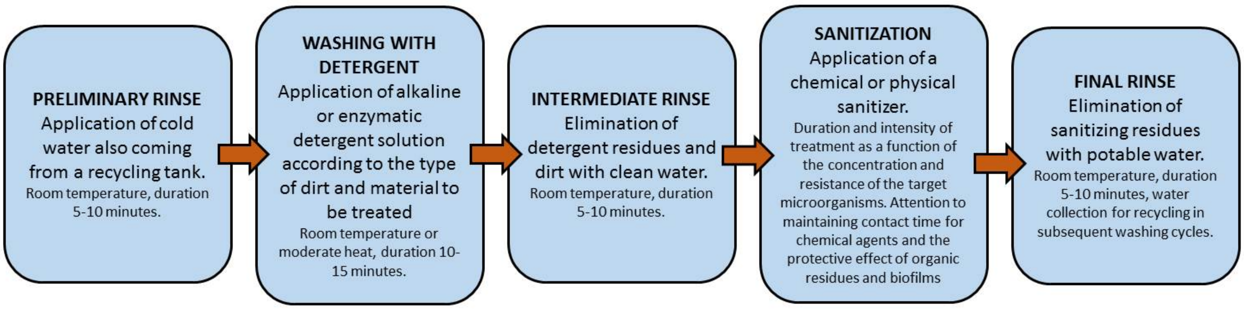
Figure B • Apparent porosity % and water absorption % (ASTM C373 Standard) of TAVA ceramic specimens compared to ceramic materials characterized by different mixture and / or different firing temperature



Sanitization: which is the correct practice

Obtaining adequate hygiene in the cellar, on surfaces and equipment, is not a simple practice. It should be considered that dirt is made up of a mixture of different phases and different materials, each of which requires a specific approach to removal. An error in the sequence of treatments or in the chemical and physical means used could make the dirt tougher, causing unwanted chemical reactions. To the dirt are then added the microorganisms that find protection and space for proliferation in it. Microorganisms are characterized by a very rapid and often unpredictable growth rate. To guarantee the hygiene of the working environment it is necessary to aim at their complete elimination, in particular where their presence can be critical for the stability or quality of the wine. A correct cleaning and sanitizing treatment must include several phases, five if the process is to be extremely summarized (Figure 1).

Figure 1 - Theoretical diagram of a sanitization process and details of the process experimented in the sanitization of ceramic materials with the best antimicrobial efficacy



Cleaning must first of all include an abundant rinsing with water, aimed at removing coarse and easily soluble dirt. A detergent treatment will then follow to remove insoluble dirt and a rinse to eliminate traces of detergent. Once the dirt has been removed, the residual microorganisms will be attacked with a chemical or physical sanitizing agent. The choice of this tool will depend on both the nature of the microorganisms and the characteristics of the material, while the application time will have to be evaluated according to the characteristics of each reality, based on a well-defined mathematical theory which is easily available in specialized texts (box below).

SANITIZATION IN FOOD INDUSTRY

The theory of sanitization in the food sector is based on the calculation of the decimal reduction time, that is the treatment interval necessary to reduce the microbial load by 90%. Once this parameter has been defined, it is possible to compare different sanitization treatments, with chemical or physical means, or decide how long to apply a treatment according to the estimated contamination and the degree of sterility to be achieved.

At the end, a rinse with potable water will make the surface ready to come into contact with wine. As for the products used in cleaning and sanitizing, the wine sector has some peculiarities that lead to a rigorous selection of these preparations. Among the detergents, basic agents are usually used to break down the tartrate residues that are commonly formed in the wine vessels and which also act as an anchor point for the residues of wine or must, as well as the site of microbial proliferation. Alternatively, enzymatic detergents, non-corrosive preparations and therefore also suitable for more delicate materials, are of interest, which allow a good removal especially of organic polymers including biofilms produced by microorganisms.

Disinfection in the strict sense can be carried out by physical or chemical means. The use of chlorine derivatives (hypochlorites) is strongly not recommended in oenology, due to the risk of trichlorophenol formation resulting from the reaction between chlorine and phenolic compounds in grapes and considered one of the responsible for the “corking” defect. On the other hand, different organic acids are of certain interest such as peracetic acid and citric acid which, in addition to having good activity towards microorganisms, do not present problems of solubility in water and therefore can be easily rinsed.

Even ozone is a chemical disinfectant agent of great interest due to its high reactivity towards microbial forms and the absence of residues in the environment, with similar mechanism of action of other strong oxidizing agents derived from hydrogen peroxide. Among the physical means of disinfection, the most common is certainly heat which, however, has drawbacks linked to high energy costs, risks for operators and damage caused to materials. For homogeneous and non-porous materials, an interesting alternative is represented by UV radiation capable of causing serious damage to bacterial populations by altering key molecules for cellular life, such as nucleic acids, without damaging the materials with which it comes into contact. This basic information can guide the winemaker, however there are a myriad of possible variables to be evaluated with accurate experimental plans such as the one proposed.

The validation of sanitizing treatment of ceramic materials

As stated, the objective of the tests described was the development of an effective sanitizing treatment on ceramic materials for oenological use, after contamination with alterative microorganisms.

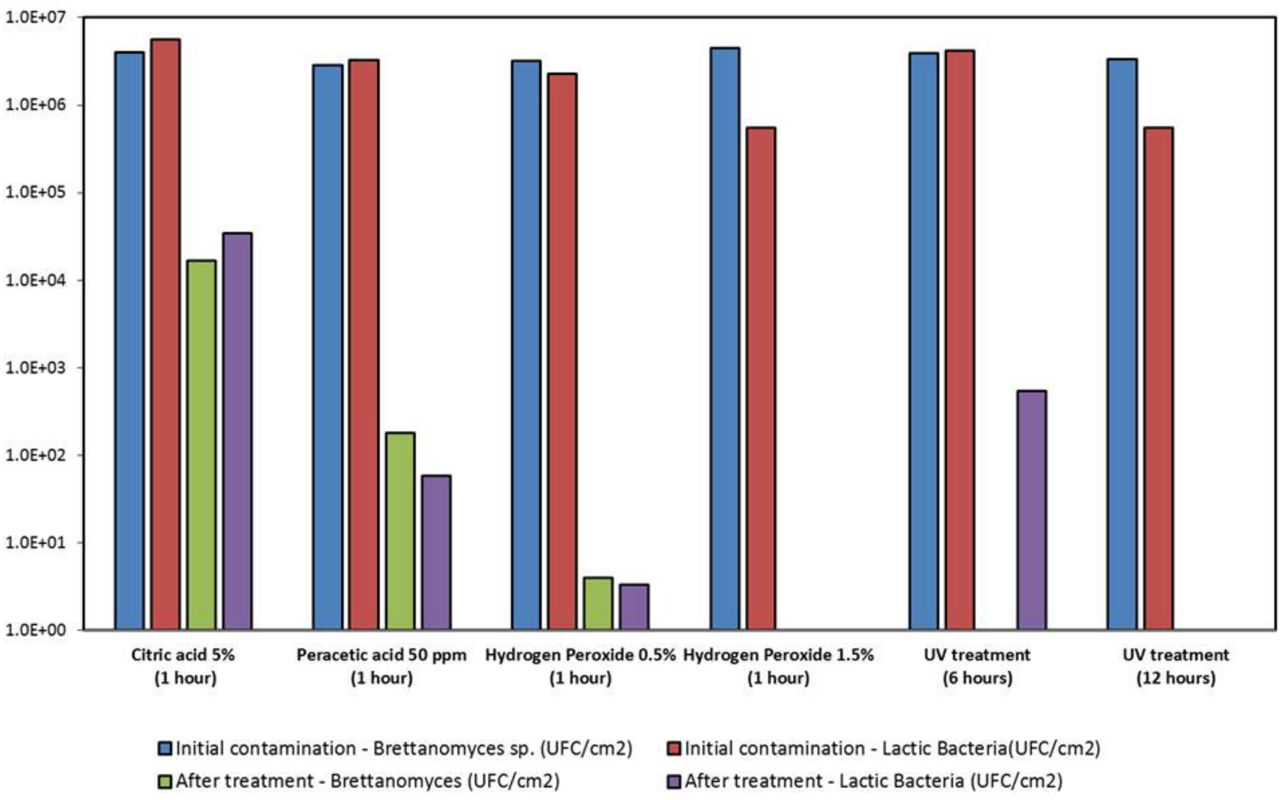
In particular, *Brettanomyces bruxellensis* and lactic bacteria were chosen as they can cause alterations in wines. Furthermore, they are able to resist on cellar surfaces for not negligible times, thanks to their ability to form biofilms and to resist even to incorrect sanitizing treatments (box below).

> *BIOFILM*
>
> *Biofilm is a layer of polysaccharides produced by some species of microorganisms to better adhere to the substrates and protect themselves from the action of physical or chemical agents that could limit their survival. In the food sector it is particularly feared because it reduces the effectiveness of sanitation treatments and makes microbial contamination unpredictable.*

In the first series of experiments (Test S1) a comparison was made between 4 sanitizing treatments on specimens in ceramic material contaminated with *Brettanomyces* and lactic bacteria at a nominal concentration higher than 10ˆ3 cell/mL for 5 days. Peracetic acid stabilized in solution with hydrogen peroxide (1 concentration, 1 hour of contact), an oxidizing chemical agent (a booster based on hydrogen peroxide, 2 concentrations, 1 hour of contact), citric acid (1 concentration, 1 hour of contact) and ultraviolet radiation (2 treatment times) were tested. The determination of the residual microbial load on the specimens of ceramic material was carried out by means of a sterile swab and seeding on specific culture media plates for *Brettanomyces sp*. and lactic acid bacteria, according to OIV standards. Having defined which was the most effective sanitizing treatment, it was decided to carry out a second series of tests (Test S2) in which the specimens were contaminated again with a mixture of the two alterative microbial species and the effectiveness of each step of the sanitization treatment was evaluated, from cleaning to final rinsing. The results, expressed as the average of the three determinations carried out on the ceramic material specimens, are shown in Figure 2 and Table 1. The surface swabs carried out on the ceramic specimens after contamination with bacterial cultures showed an initial contamination variable between the specimens used in the different tests, but always higher than 5 logarithmic units per cm ˆ2, therefore within the oenological range of contamination of wine vessels at end of vinification or wine storage.

In the Test S1 (Figure 2) treatments with hydrogen peroxideat 1,5% and UV radiation have proven to be more efficient towards *Brettanomyces*, making it untraceable after treatment. In the case of lactic acid bacteria, the same objective was achieved by treatment with UV for 12 hours and by treatment with hydrogen peroxide at 1.5%.

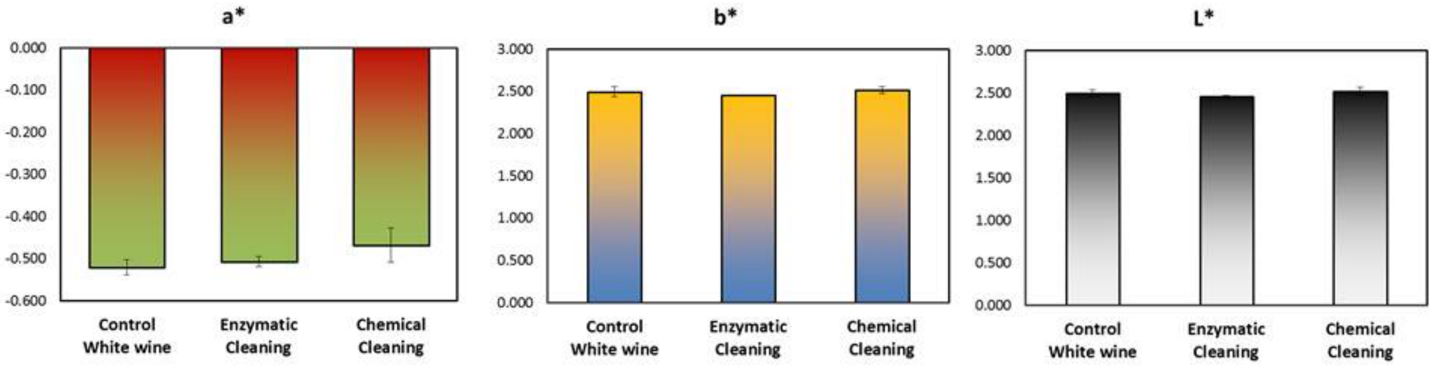
Figure 2 - Results of sanitizing treatments on ceramic materials conducted with different sanitizing agents (Test S1)



The other treatments revealed different efficacy, very good in the case of the treatment with hydrogen peroxide at 0.5% and peracetic acid at a concentration of 50 ppm, with only a few dozen surviving colony-forming units per cm ˆ 2, more modest in the case of citric acid and UV treatments applied for 6 hours. In these cases, a few hundred colony-forming units per cm ˆ 2 are residual on the surface of the ceramic specimens and therefore the material cannot be considered sanitized effectively.

The second series of tests compared two cleaning treatments, chemical and enzymatic, preliminary to the sanitizing treatment which was chosen in the form of UV irradiation for 12 hours considering its excellent environmental sustainability and the effectiveness demonstrated during the first series of tests. Precisely with a view to greater environmental sustainability in this study it was decided to compare the cleaning power of a chemical product commonly used for cleaning wine tanks (a complete formulation based on caustic soda) with a particular enzymatic formulation studied specifically for the ceramic material under study. The effectiveness of the detergency treatment was assessed by visual analysis of ceramic specimens immersed for a month in a highly tinted red wine and subjected to detergency with the chemical and enzymatic-based products. Subsequently, the specimens treated with different detergents were immersed in a white wine for fifteen days to understand the effectiveness of the discoloration and evaluate the possible absorption / release of detergent product in the wine, with consequent chromatic / chemical alterations of the same. The analysis of the color through the CIEL*a*b* method (OIV method) made it possible to evaluate any "transfers" of red wine residues, with a consequent increase of the chromatic parameter a * (red / green) over time. As shown in Figure 3, the CIEL*a*b* color parameters did not show significant differences compared to the control (white wine), testifying to the high cleaning power of both products tested. Furthermore, through the analysis of the general chemical parameters (FTIR analysis) of the wine, it was possible to exclude chemical alterations related to the release by the samples of chemical / enzymatic residues absorbed by the ceramic materials and then released into the wine (Table 2). The absence of enzymatic residues was also verified through appropriate tests performed by the manufacturer of the enzymatic formulations.

Figure 3 - CIEL*a*b* color of a white wine after fifteen days of contact with the ceramic specimens, previously immersed for a month in a red wine characterized by a high coloring intensity, subjected to a chemical and enzymatic treatment. a *: red / green; b *: yellow / blue; L *: brightness. Analyzes performed in triplicate



From a microbiological point of view, as evident from the data in Table 1, the chemical cleaning treatment reduces the microbial population by 2 logarithmic units, the subsequent UV treatment eliminates any microbiological contamination making both *Brettanomyces* and lactic bacteria undetectable. The enzymatic treatment is even more effective with a zero microbial load already after cleaning, confirmed after UV sanitization. A two-stage sanitation process is therefore an advisable approach because in real cellar conditions deposits of an organic nature, such as tartrates or wine residues, can reduce the effectiveness of the sanitization treatment if not preceded by thorough cleaning.

TABLE 1- SUMMARY OF S2 TEST RESULTS, AIMED AT VALIDATING A CLEANING AND SANITIZING TREATMENT ON CERAMIC SPECIMENS

Test	Initial contamination		Contamination after cleaning		Contamination after sanitization	
	Brettanomyces	Lactic Bacteria	*Brettanomyces*	Lactic Bacteria	*Brettanomyces*	Lactic Bacteria
	(UFC/cm^2)					
Enzymatic cleaner + UV treatment for 12 hours	1.8E+05	5.0E+05	nr	nr	nr	nr
Chemical cleaner + UV treatment for 12 hours	1.9E+05	5.2E+05	nr	2.5E+03	nr	nr

nr: no microbial load detected (< 5 ufc/cm^2)

TABLE 2 - GENERAL CHEMICAL PARAMETERS (FTIR) OF A WHITE WINE AFTER FIFTEEN DAYS IN CONTACT WITH CERAMIC SPECIMENS, PREVIOUSLY IMMERSED FOR ONE MONTH IN A RED WINE CHARACTERIZED BY A HIGH COLORING INTENSITY AND SUBJECTED TO A CHEMICAL/ENZYMATIC DETERGENT TREATMENT. ANALYSIS CARRIED OUT IN TRIPLICATE

		Control White wine		Enzymatic cleaning		Chemical cleaning	
ANALYTICAL PARAMETERS	**u.m.**	*mean*	*dev.st.*	*mean*	*dev.st.*	*mean*	*dev.st.*
Relative density 20°C/20°C	a 20°C	0.995	0.000	0.995	0.000	0.995	0.000
Potential Alcohol	% vol	11.91	0.11	11.98	0.02	11.95	0.04
Actual Alcohol	% vol	11.56	0.11	11.63	0.02	11.60	0.04
Glucose + Fructose	g/l	5.72	0.05	5.71	0.02	5.80	0.06
Non-reducing extract	g/l	20.07	0.08	20.18	0.01	20.05	0.09
Total dry extract	g/l	25.82	0.10	25.89	0.02	25.85	0.03
Total acidity (tartaric acid)	g/l	5.68	0.03	5.74	0.03	5.73	0.02
pH		3.24	0.02	3.23	0.01	3.24	0.01
Volatile Acidity	g/l	0.37	0.01	0.39	0.01	0.39	0.01
Malic Acid	g/l	2.96	0.01	2.99	0.01	2.95	0.02
Lactic acid	g/l	0.04	0.06	0.08	0.01	0.02	0.01
Tartaric acid	g/l	1.48	0.02	1.47	0.03	1.49	0.01
Glycerine	g/l	5.41	0.02	5.35	0.06	5.35	0.05
Potassium	g/l	0.83	0.02	0.81	0.01	0.78	0.01

Conclusions

The ceramic material tested, thanks also to its low porosity, proved to be little susceptible to microbial colonization and easy to sanitize even in the presence of very high initial microbial contaminations. Ultraviolet radiation for at least 12 hours, preceded by adequate cleaning, proved to be the most appropriate sanitization strategy in the experimental conditions given. With a view to environmental sustainability, the use of an enzymatic detergent followed by sanitization with UV lamps represents the ideal solution for cleaning and sanitizing the TAVA amphorae under study, compared to traditional chemical products. It should be emphasized that the use of an enzymatic detergent allows greater respect for the ceramic material than more aggressive chemicals.