CORROSION OF CARBON STEEL OLC 45 AND STAINLESS STEEL AISI 304L IN WINES FROM BANAT COUNTY

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Abstract
In the present paper, results on the corrosion rate of carbon steel OLC 45 (similar to EU C 45) and stainless steel AISI 304L in a few species of wines from Banat County (Romania) have been emphasized. Corrosion rates have been determined using weight loss measurements, as well as Tafel plots method. The effect of wines on the surface of studied steels has been revealed using scanning electron microscopy. The obtained results show that the values of the corrosion rates in the wines tested for OLC 45 are close to the maximum allowed limit, which means that this type of steel cannot be used in the wine processing and storage. On the contrary, the corrosion rates for AISI 304L steel are extremely low in all the analyzed wines, which proves that they can be used both for wine processing and storage.

Introduction
In the last years, Romania has recorded significant successes in wine production, both in terms of quantity and especially in quality. According to the estimate data, in 2020, the production volume was 3.6 million hectoliters, our country being the 13th rank in the world's largest wine producers [1]. The essential condition in the obtaining of a high quality wines is the preservation of the organoleptic features. Containers used during the alcoholic fermentation process or for wine storage are made of different materials such as stainless steel, plastics and wood. These materials significantly influence the composition of the end product, increasing the metals ion content. In some cases, the relatively high level concentration of heavy metals ions (Mn, Ni, Cu) requires their partial extraction using ion exchangers. These metals ions have their origin not only in the soils of the vineyards, but also from metallic materials of the equipment used during the vinification process and storage [2]. According to the present paper, in order to improve the quality of the wines and ensure a low content of metal cations, the corrosion rates of some steels used in different stages of the technological wine process have been determined in some varieties of wines from Banat County.

Experimental
Materials
For the wine samples used in the experiments *pH*, conductivity and sulfur dioxide content were previously determined (Table 1).

Table 1. Characteristics of the wines used in the experiments.

No.	Wine type	Symbol	*pH*	Conductivity [S m^{-1}]	SO_2 content [mg L^{-1}]
1	Muscat Otonel 2016 half-sweet	W1	3.34	174 x 10^{-3}	160
2	Fetească Regală 2016 half-sweet	W2	3.24	194 x 10^{-3}	175
3	Sauvignon Blanc 2016 dry	W3	3.14	193 x 10^{-3}	180
4	Rose 2016 half-dry	R1	3.01	157 x 10^{-3}	145
5	Cabernet Sauvignon 2016 dry	R2	3.29	192 x 10^{-3}	125

In the experimental tests, two types of metallic samples were used: carbon steel OLC 45 and food grade stainless steel AISI 304L. Their elemental composition is given in the table 2 and table 3.

Table 2. Elemental composition of the carbon steel OLC 45.

Element	Fe	C	Si	Mn	P	S	Cr	Ni
wt %	96.98	0.4184	0.2510	0.7920	0.0132	0.0335	1.162	0.029
Element	Mo	Cu	Al	Ti	V	Co	Nb	W
wt %	0.2123	0.0234	0.0229	<0.004	0.0124	0.0222	<0.001	<0.010

Table 3. Elemental composition of AISI 304L stainless steel.

Element	Fe	C	Si	Mn	P	S	Cr	Ni
wt%	64.89	0.030	1.000	2.00	0.05	0.030	20.0	12.0

Corrosion rate evaluation by weight loss measurement

This method consists in the complete immersion of the metal sample in the corrosive environment and determination of the weight loss after 21 days using an analytical balance. The amount of corroded metal is obtained according to the relationship (1).

$$K = \frac{m_i - m_f}{S \cdot t} \qquad (1)$$

in which K is the corrosion rate, in g m^{-2} h^{-1}; m_i – initial mass of the metal sample, in g; m_f – final mass, in g; S – sample area, in m^2; t – test time, in h.

The accuracy of the method is conditioned by the possibility of complete removal of corrosion products from the sample surface.

Corrosion rate evaluation by Tafel plots method

The corrosion rate can also be expressed by the corrosion current density i_{cor}. This amount is determined by the Tafel slope method, based by drawing the metal sample potential in the corrosive environment as a function of the current density flowing through the interface [3,4]. By knowing the value of the corrosion current density, one can calculate the corrosion rate K, expressed in g m-2 h^{-1}, based on the relationship (2).

$$K = \frac{A}{zF} \cdot i_{cor} \cdot 3600 \qquad (2)$$

in which A is the atomic mass of the basic metal; z - metal ion charge; F – Faraday's constant, in C mol^{-1}; i_{cor} - corrosion current density, A m^{-2}.

If the corrosion process is homogeneous, the corrosion rate can also be expressed by the penetration rate, expressed in mm $year^{-1}$, according to relationship (3).

$$K_p = \frac{24 \cdot 365 \cdot K}{\rho} \qquad (3)$$

in which ρ is the metal density, in g mm^{-3}.
The volume of the test solution has to be large enough so that changes of the concentration are minimal during the tests.

Scanning electron microscopy was used to study the morphology of the surfaces subjected to the action of wines. An SEM Quanta 250 FEG was used.

Results and discussion
The corrosion rates of OLC 45 and AISI 304L steels, determined by the weight loss measurements after 21 days are shown in Table 4.

Table 4. Corrosion rates determined by weight loss measurement.

No.	Wine type	Corrosion rate [g m^{-2} h^{-1}]	
		OLC 45	AISI 304 L
1	W1	0.0368	0.0002
2	W2	0.0314	0.0000
3	W3	0.0430	0.0002
4	R1	0.0974	0.0004
5	R2	0.0531	0.0000

It can be seen that OLC 45 carbon steel is much less corrosion resistant in the studied wines than AISI 304L stainless steel. For the last steel, in wines W2 and R2, the weight loss mass was below the detection limit.
Furthermore, the corrosion current densities were determined by plotting the Tafel polarization diagrams, shown in figures 1 - for the OLC 45 carbon steel and in figure 2 - for AISI 304L steel. The electrochemical parameters and the corrosion rate calculated based on the Tafel plots are shown in tables 5 and 6.

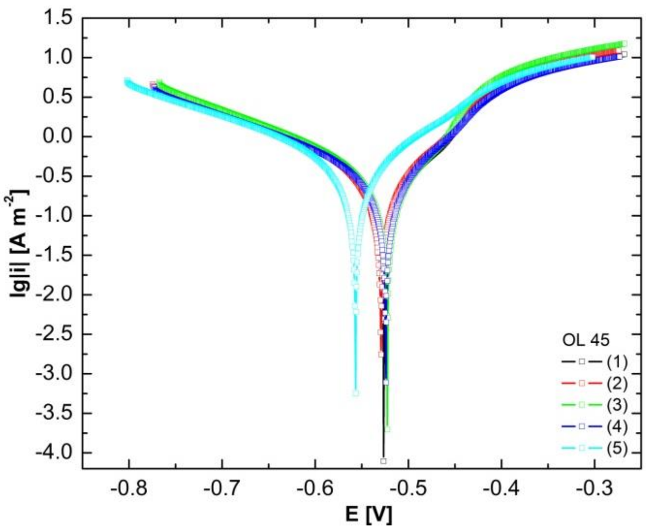

Figure 1. Tafel polarization plots drawn on OLC 45 carbon steel in different wine types, at a temperature of 25°C and scan rate of 1 mV s^{-1}.

Table 5. Electrochemical parameters determined by linear polarization on OLC 45.

Wine type	T [K]	i_{cor} [μA cm^{-2}]	E_{cor} [mV]	$-b_c$ [mV dec^{-1}]	b_a [mV dec^{-1}]	R_p [Ω]	v_{cor} [mm an^{-1}]
W1	298	35.3	-526	131	231	1260	0.414
W2		37.5	-528	129	234	1170	0.439
W3		35.0	-522	122	223	1201	0.411
R1		33.0	-521	128	235	1388	0.388
R2		49.1	-588	167	252	942	0.576

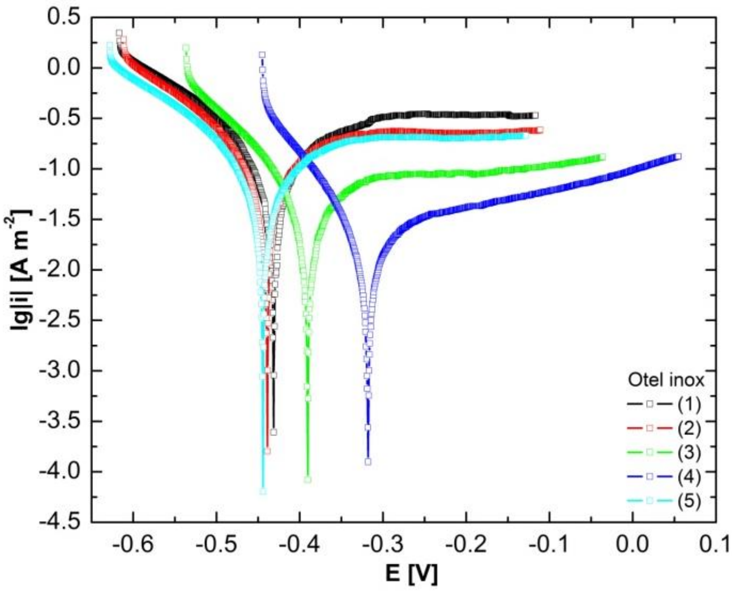

Figure 2. Tafel polarization diagrams drawn on stainless steel AISI 304L in different types of wine, at a temperature of 25°C and at a scan rate of 1 mV s^{-1}.

Table 6. Electrochemical parameters determined by linear polarization on AISI 304L.

Wine type	**T [K]**	**i_{cor} [μA cm^{-2}]**	**E_{cor} [mV]**	**$-b_c$ [mV dec^{-1}]**	**b_a [mV dec^{-1}]**	**R_p [kΩ]**	**v_{cor} [mm an^{-1}]**
W1	298	1.1	-322	222	108	25.3	0.013
W2		1.0	-304	179	102	29.5	0.011
W3		0.9	-291	172	105	31.6	0.010
R1		0.7	-254	134	113	34.2	0.009
R2		1.8	-362	284	107	17.1	0.021

It is found that the corrosion currents for AISI 304L are about 30 times lower than for OLC 45. As well, the same ratio is recorded for polarization resistance, that is proportional to the corrosion resistance of the metal in the studied environments. Based on the values of the corrosion currents, the corrosion rates expressed in mm year^{-1} were calculated. It is significant to emphasize the corrosive effects of wines on studied steels using the images obtained by scanning electron microscopy. Figures 3a and 3b show the SEM micrographs for OLC 45, respectively for AISI 304L.

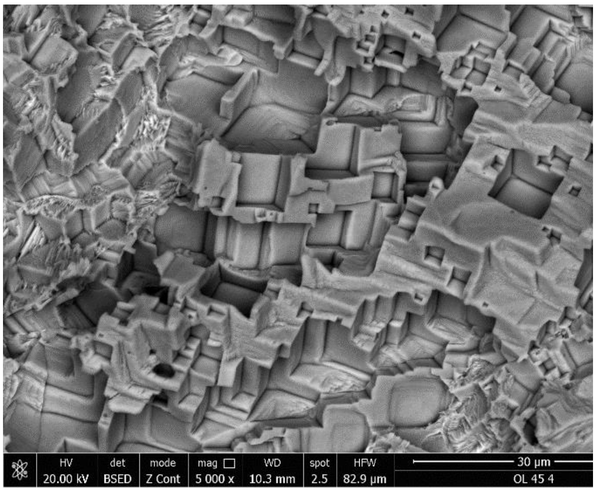

Figure 3a. SEM micrography of OLC 45.

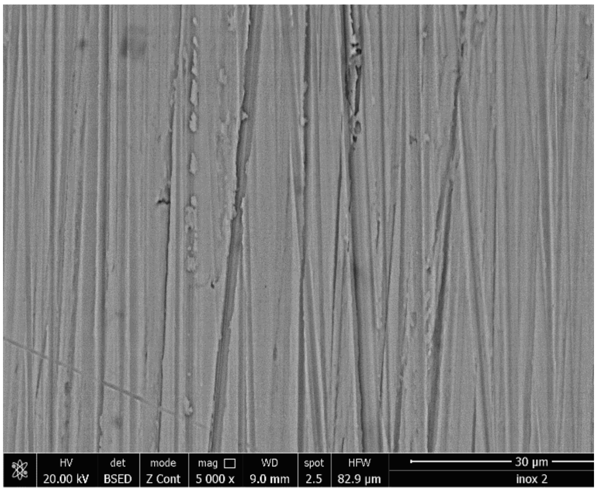

Figure 3b. SEM micrography of AISI 304L.

Additionally, SEM micrographs show that the surface of the carbon steel undergoes significant transformations in prolonged contact with the wine, while the surface of AISI 304L remains virtually unchanged.

Conclusion

Corrosion rates were determined by two methods for OLC 45 carbon steel and AISI 304L stainless steel. The corrosion rates obtained by the Tafel slope method are substantially higher as they represent quasi-instantaneous values from the beginning of the process, when the metal surface was not shielded by corrosion products. The obtained results show that the values of the corrosion rates in the wines tested for OLC 45 are close to the maximum allowed limit, which means that this type of steel cannot be used in the manufacturing of wine processing, storage devices and equipment. On the contrary, the corrosion rates for AISI 304L steel are extremely low in all the analyzed wines, which proves that they can be used both for processing and storing wines.

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