# PRINCIPLES AND MODALITIES TO DIMINISH THE INFLUENCE OF THE CORK TAINT ON WINE QUALITY

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**Abstract:** The cork taint is a major problem of the winemaking, with the significant economic damages, in which the main responsible is considered the cork. Essential component of this defect is considered the compound 2,4,6-tricloroanisol (TCA) and its bromo/chloro derivatives that affects aromatic profile of the wine. The development of some methods rapid and efficient technologies led to the reduction of TCA in wine (INNOCORK process, Procork membranes, innovative filters, etc.) and the sterilization of corks with ionizing radiation, sulphur dioxide solutions (3-5% $SO_2$). The systems described do not change the aromatic character, the composition of wine and presents an efficiency of 90-95%.
**Key words:** wine, cork taint, 2,4,6-Trichloroanisole

## 1. Introduction

The wine industry is facing a multitude of problems of toxicological, with possible impact on the quality of wine, including cork taint (english – "Cork Taint"; french "Goût de Bouchon". According to the profile literature, a wine with a broken cork has a range of smell: mould, drugs, ground, cardboard or wet paper and cellar. Responsible for these anomalous smells is considered the cork, however, there were found wines with similar defects without being in contact with the cork and other products in the field of bottling so there are other sources of contamination of wine with this defect.

The cork taint is responsible for significant losses in the wine industry. Several researchers (Alvarez, Amon, Bertrand, Chatonnet, Margot, etc.), associate the cork taint with the presence in wine of the following compounds: geosmina, gaïacol, 1-octen-3-one, 1-octen-3-ol, metilisoborneol, 2,4,6-tricloroanisol (TCA) and its bromo/chloro derivatives: 2,3,4,6-tetracloranisol (TeCA), 2,3,4,5,6-pentacloranisol (PCA) and 2,4,6-tribromoanisol (TBA) (Teixeira M., Tanner H., and others, 2006). In most cases, 70-80%, the cork taint is attributed to the presence of TCA (Chatonnet P.; Dubourdieu D. ). In smaller quantities, the presence of TCA in wine masks its aromatic intensity.

According to the statistics, the quantities of wine affected by trichloroanisoli vary from one source to another. About 4-15% of the bottled wine is contaminated presenting cork taint. Several reasons may explain this variation number. One of them is the direct contamination of wine by trichloroanisoli. Having a threshold of perception in the range of 1,5 to 4 ng/L, trichloroanisoles give the wine an easily detectable smell of mould. As a rule, the wine consumers refuse the wine which contains an amount about 10 ng/L of TCA.

Analysis of the presence of TCA in wine, origin and its effects on human health have become recently targets of research, many aspects of these are still being studied. The necessity of researches result from a number of reasons, one being the economic. It is obviously, that the withdrawal from a contaminated consignment circuit creates a series of entrepreneurial problem, diminishing in a clearly way its effectiveness and efficiency. As

far as the consumer, he must be supplied with the harmless products, balanced, with high biological value and pleasant sensory properties.

## 2. Contamination of wines with chloroanisoles

Chloroanisoles can be synthesized by moulds based on chlorophenols derivatives which are used extensively as insecticides for wood treatment. Volatile enough, they may be spread in the cellar or in other places, condensed into the places where moulds are present. This defect is the result of enzymatic activity of methylation of chlorophenols, of some filamentous species. The transformation in chloroanisoles is performed in the chloroanisoles through a detoxification mechanism of species of moulds, having the basic process their methylation chloroanisoles correspondents. Genesis simplified scheme of chloroanisole compounds is:

*Phenolic substances + source of chlorine = 2, 4,6, trichlorophenol*

*2,4,6, trichlorophenol + mould (Aspergilius, Penicilium)= 2,4,6- trichloroanisole*

But not only fungicidal products are responsible for this cork taint. Chlorophenols can have other origins. Chlorine enter into the composition of many washing and disinfecting agents, used in wine-making, being present in different chemical forms, depending on the pH: $Cl^-$, HClO and $ClO^-$, but also in the form of free radicals, which can interact with phenols to form polychlorophenols.

Some fungal species of the genus *Penicillium* are able to synthesize the 2,4,6-trichlorophenol (TCP) on the shikimical acid way in the presence of free chlorine or embedded in methionine. Different ffilamentous fungi belonging to the different cork microflora: *Aspergilus sp*, *Penicillium sp*, *Actinomycetes sp*, *Botrytis sp*, *Cinerea sp*, *Neurospora sp*, *Mucor sp*, *Phiyobium sp* and *Streptomyces sp* are able to form numerous intermediate, volatile and soluble molecules in the water-alcoholic medium of wine. Under the influence of the O-methyltransferase on trichlorophenol takes place the formation of the compound 2,4,6-trichloroanizole (TCA). The conversion of other derivatives of anisoles occurs similarly.

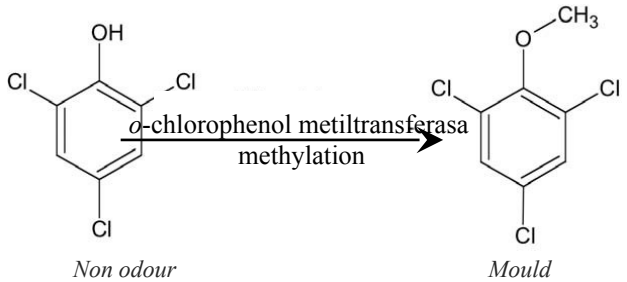



***Fig. 1.*** The mechanism of TCA formation by micro-organisms (Alvarez -Rodriguez M. 2002 and Rubio-Coque J. J. 2005)

## 3. Methods for the determination of TCA in wine

Determination of TCA in wine has a relatively complex method due to the extremely low level of sensory perception of it. The content of TCA in wine and its derivatives can be determined only by means of GC/MS, with headspace solid-phase microextraction (HS-SPME), method which possesses a great sensitivity and selectivity and is fully automated (Wang H. and others, 2010).

The extraction of 2,4,6-TCA from corks stoppers is accomplished with a solution of hydro-alcoholic and its adsorption on a fiber covered with a film of polydimethylsiloxane. It follows desorption of trichloroanisole in the chromatographic column and the detection by mass spectrometer (Figure 2).

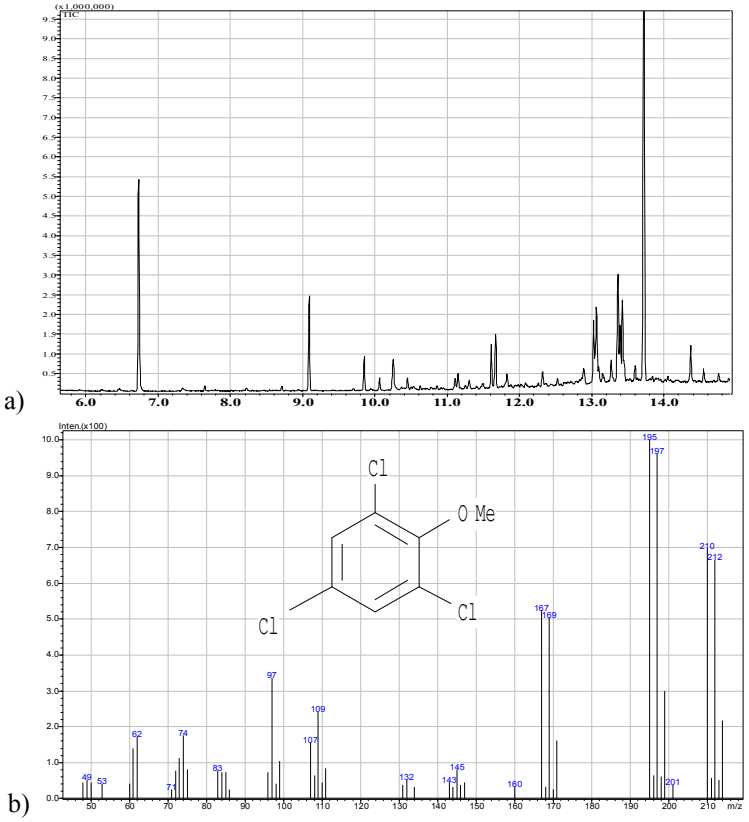



***Fig. 2.*** a) HS/SPME GC chromatogram of a red wine with cork taint ($t_R$(TCA)=10,06 min. (SPB5 25 m, 0,25 mm, 0,25 μm; 40 °C 2 min, 15 °C/min 250°C 10 min; He 49,2 cm/s ); b) the detection mass-spectrometric of the TCA (NIST-5)

## 4. Methods for reducing the risk of contamination of wine with TCA

The need to detect and to prevent the risk of contamination of the wine with TCA is required both economically and hygienic way. There are several possibilities for contamination of the cork stopper with TCA, which cause also the further contamination of wine during the storage of wine in bottles:

1) the contaminated cork - initial contamination, is certified a content of TCA to 1500 ng/ g of cork;

2) the infested cork which contaminates other corks – subsequent contamination during storage of wine in bottles;

3) the infested cork during storage - external contamination, the content of TCA lower than the TeCA and PCA.

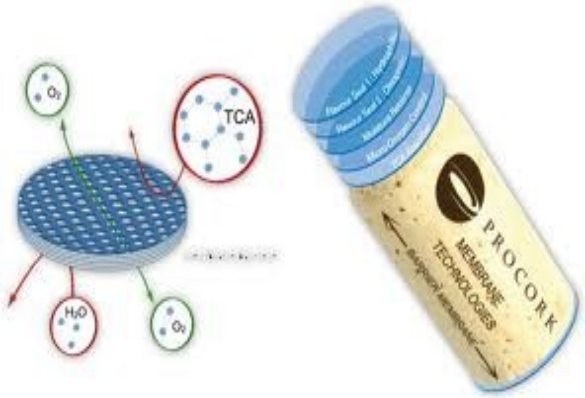
The content of TeCP, TeCA, PCP and PCA may increase by the winery operations - decanting, wine bottling, etc. In humid and unsanitary conditions; treatment of wood, with the pallets of the derivative sodium of 2,3,4,5,6 pentachlorinated phenol; the use of insecticides and pesticides in wine storage aries; bentonite used in the treatment of wine, stored in unsuitable conditions, all of these wine/corks contaminations with polychlorinated derivatives of phenol generate in bottled wine a content of TeCP, PCP, TeCA and PCA major (Bertrand A., Barrios M., 1994, Chatonnet P. 1995).

To avoid the present of these compounds in wine is recommended:

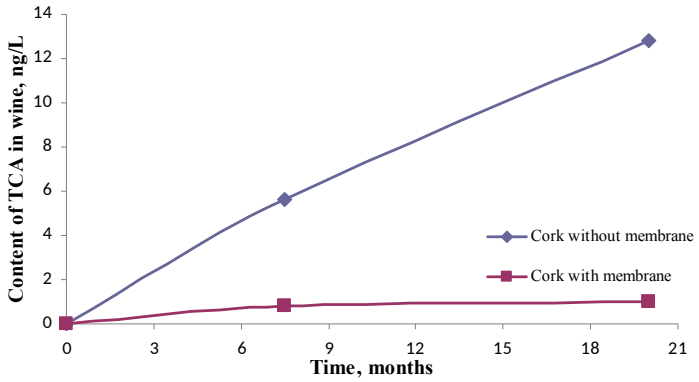
- avoiding the excess of moisture and the temperature increased during all stages of wine processing, as it facilitates the development of moulds;
- exclusion of insecticides, fungicides and all the compounds of treatment and disinfection containing chlorine (sanitary-hygienic maintenance of premises, and in particular the cork processing industry)
- surface treatment corks with polymethylsiloxane instead of compounds with nutritional character for moulds (fatty acids, wax, glue, etc.);
- the use of effective methods of cork treatment both on the surface and in the depth and even the removal of TCA from corks through modern methods (Innocork process);
- the atmospheric conditioning and hygienic control strictly in the production and storage aries of auxiliary products;
- the use of plastic and metal pallets for keeping bottles and corks.

An alternate solution would be the endowment of Corks, on the surface which is in the contact with wine, the silicon disc (Figure 3). That being neutral reduces the risk of a subsequent infection of wine.

This procedure not change the aromatic character, the composition of wine and presents an efficiency of 90-95% of reducing the content of 2,4,6-TCA in wine.




a)




b)

***Fig. 3.*** **a)** photo presentation of ProCork membrane type B (Procork Project); b) the evolution diagram of TCA in wine during the period of contact (20 months).

## Conclusions

Considering the potential contaminant of TCA in wine by both cork and through the wood of oak used for ageing, it is imperative to implement a new approach to detect their presence in cork and oak barrels before the technological use of their duration.

It is necessary to develop rapid and efficient methods and technologies to monitor primarily four groups of pollutants, namely: derivatives of benzene solvents, haloanisoles, halophenols and aromatic hydrocarbons. To ensure the full cycle traceability with risk measurement of wine pollution in general and especially with TCA, which is a problem not only theoretical but also practical matter.

Exclusion of sanitation compounds containing chlorine and the processes of preparation of corks and oak wood would effectively prevent the contamination with TCA. Corks endowment in contact with the wine surface of silicon discs (membrane Procork) it would reduce essentially the risk of contamination.

However, the most effective method of prevention would be sterilization by ionizing radiation of $Co^{60}$ and with the solutions of sulphur dioxide ($SO_2$ 3-5%). This method ensures the complete inactivation of fungi growth able to contaminate the cork and excludes the formation of TCA and other derivatives.

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