Migration of 2,4,6-TCA in still wines

Application to technological cork closures

Alain Bobé
Pure Environnement – Perpignan – France.

Extract from the Revue des Œnologues n° 133
www.oeno.tm.fr

TECHNICAL

Introduction

In 2004, a comparative study on the contents and homogeneity of 2,4,6-trichloranisole (TCA) in various cork closures available on the market, including natural closures, technical closures and technological closures, was published ***(1)***. It showed that technological closures were distinguished from the others owing to their much greater homogeneity within a given production batch. This remarkable homogeneity enables an evaluation of the truly high quality of the closure via quantification of the amount of releasable TCA.

The results below offer a more precise description of the TCA migration characteristics of technological cork closures made by the companies Sabaté and Œneo Bouchage: migration rates and migration kinetics under real conditions.

This study has also been the opportunity to compare the results obtained for total TCA and releasable TCA from the closure in order to better understand the migration rates, which are essential for good interpretation of results during expert audits.

Correlation between total TCA and releasable TCA from closures prior to bottling

Analyses were performed on different batches of closures BTD, BTR, BTE and BTO in order to measure either total TCA (ng/g) or releasable TCA (ng/L) in the closure. The total TCA content (ng/g) present in the closure is measured after grinding, extraction with an organic solvent and analysis by isotope dilution using gas chromatography (GC) coupled with mass spectrometry (MS) in fragmentometric mode (SIM).

The releasable TCA content (ng/L) of the closure is measured by headspace (HS) – solid-phase micro-extraction (SPME) – gas chromatography (GC) - mass spectrometry (MS) in fragmentometric mode (SIM) (isotope dilution) performed on macerates. The maceration of cork closures is done for 24 hours at ambient temperature in a model wine (solution of 12% vol. ethanol in water, acidified to pH 3.6) (methods available upon request).

■ **Figure 1: Correlation between total TCA and releasable TCA from new technological cork closures.**

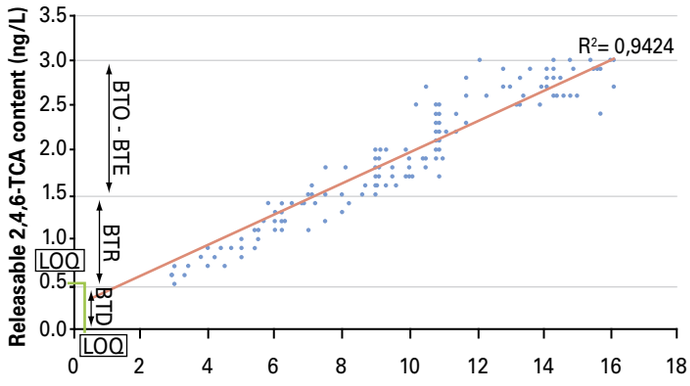


Figure 1 shows a satisfactory correlation between total TCA (ng/g) and releasable TCA (ng/L) for the different types of new technological closures. The correlation coefficient is 0.947. For these types of closures, the quantity of TCA likely to be released is low. It is evaluated at 3.8% of total TCA with good homogeneity (standard deviation of ± 0.5%).

Determination of migration rate under real conditions

The goal of this study is to quantify the migration rates of TCA from cork closures into wines under real conditions.
Analyses of still wines (red, white and rosé) and of the corresponding technological closures were performed on more

■ **Table 1: Evolution of the range of technological cork closures from Œneo Bouchage.**

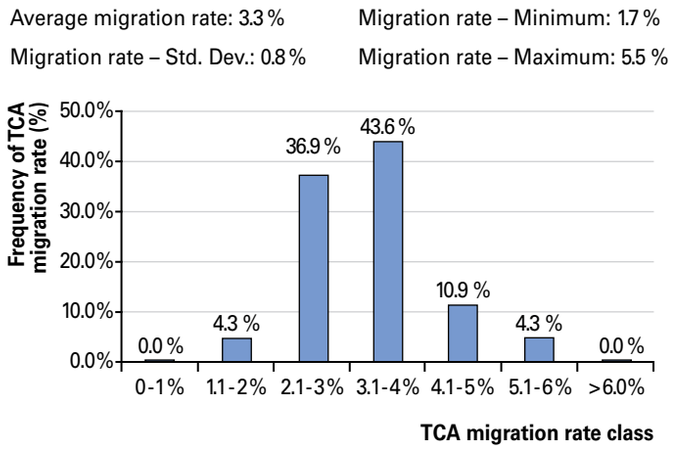
Trademark	Symbol	Year of release	Releasable TCA check	Comments
Altec®	BTA	1995	No guarantee	No treatment of cork powder
Original	BTO	2001	TCA ≤ 3.0 ng/L	No treatment of cork powder
Evolution	BTE	2003	TCA ≤ 3.0 ng/L	No treatment of cork powder
Reference	BTR	2005	TCA ≤ 1.5 ng/L	Steam cleaning process of cork (Revtech)
Diam®	BTD	2005	TCA ≤ LDQ (LDQ = 0,5 ng/L)	Supercritical CO_2 extraction process (Diamant – Patent EP 1216123BI in partnership with CEA)

than 200 bottles available on the market (bottling more than 12 months prior).
The principle for quantification of total TCA present in the closure is described in the preceding paragraph. The technique for quantification of 2,4,6-trichloroanisole in the corresponding wine samples is headspace (HS) – solid-phase micro-extraction (SPME) – gas chromatography (GC) – mass spectrometry (MS) in fragmentometric mode (SIM) (isotope dilution).
The total TCA contents measured are in a range from ≤ 5 to 213.2 ng/closure. The TCA contents measured in wine are in a range from ≤ 3 to 9.1 ng/bottle (750 mL bottle).

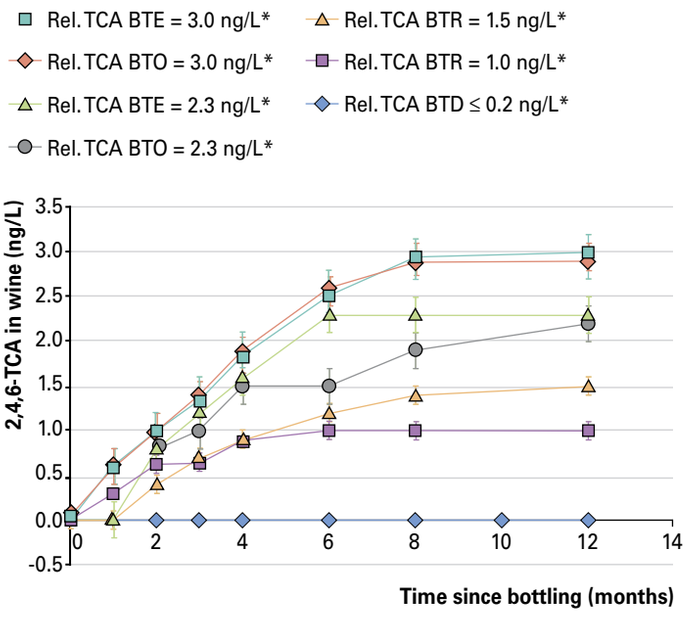
Figure 2 shows that under real conditions of use, the migration of TCA from technological closures is low, with an average migration rate of 3.3%, and this rate is equivalent to the average rate of release from new closures, which is found to be 3.8% (±0.5%).
It also shows that the migration is homogenous from one closure to another, with a standard deviation of ± 0.8%. The minimum and maximum migration rates, observed during this study, are 1.7 and 5.5%, respectively. This homogeneity of the migration rate demonstrates that there is a correlation between the total TCA of the closure and the TCA contamination of the corresponding wines.

For natural cork closures, the total TCA content present in the closures is not correlated with the appearance of a deviation in the wine (2). In other terms, two natural closures with the same quantity of total TCA can lead to different quantities of TCA in the bottled wine. The migration rates vary within a range from 10% to more than 35% of the total TCA, with a loose correlation between total TCA and the TCA present in the bottled wine.

■ Figure 2: TCA migration rate from the closure into the wine (more than 200 bottles and corresponding closures analyzed).



■ Figure 3: Monitoring of appearance of TCA released by the cork closure into the wine as a function of time.



** Releasable TCA contents from new closures.*

Determination of the kinetics of TCA migration under real conditions

The goal of this study is to analyze the evolution of TCA content over time, under real conditions, in different types of wine (stored horizontally) using different types of closures (BTO – BTE – BTR – BTD), with variable contents of releasable TCA (≤ 0.2 ng/L to 3.0 ng/L). The storage temperature of the bottle is controlled between 18 and 25°C.

Before bottling, the releasable TCA contents of new technological cork closures are measured on macerations of 25 closures in q.s. 1000 ml of ethanol-in-water solution (12% vol. acidified to pH 3.6) for 24 hours at ambient temperature. Monitoring of the TCA contents of wines was set up over time, at 0 (before bottling), 1, 2, 3, 4, 6, 8 and 12 months.

For each type of technological cork closure and each level of releasable TCA, 3 to 5 different types of wines (white – red – rosé with alcohol content between 11 and 14% vol.) were bottled and monitored over time.

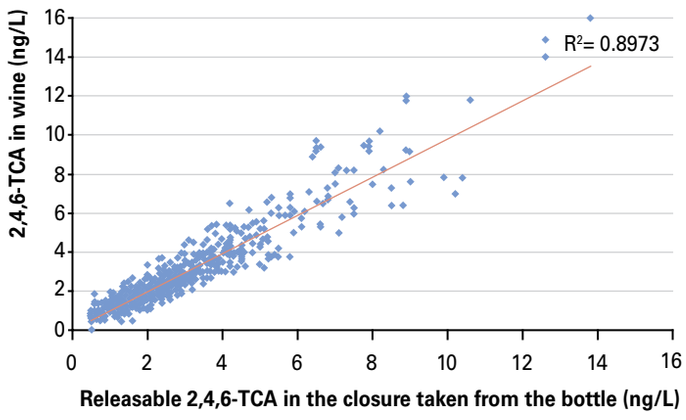
The results are presented in ***figure 3.*** Under real conditions of use of BTD closures (releasable TCA less than or equal to the limit of detection 0.2 ng/L), the different tests conducted on the different still wines have logically revealed the absence of TCA migration into the wines (contents below the limit of detection of the method: 0.2 ng/L).

For the other technological cork closures (BTO, BTE and BTR), we observe a gradual increase in the TCA content in the different wines until equilibrium is reached, after about 8 months from bottling. At equilibrium, the TCA content in the wine corresponds to the releasable TCA content measured in the new closures.

Correlation between releasable TCA in the cork closure sampled from the bottle and TCA in the wine (greater than 12 months since bottling)

The goal of this study was to validate the relevance of the releasable TCA measurements on the used cork closures (sampled from bottles) during expert audits intended to determine the source of contamination of wines.
The results presented are a summary of analyses from more than 2000 bottles that

■ **Figure 4: Correlation between releasable TCA in the closure taken from the bottle and the TCA present in the still wine after more than 12 months of storage (more than 2000 bottles and closures analyzed).**



■ **References**

***(1)* Pascal Chatonnet**

Dosage du TCA extractible appliqué au contrôle de la qualité des bouchons ALTEC® : Particularités et interprétations

Revue des Œnologues n° 112.
July 2004.

***(2)* Pascal Chatonnet et Dominique Labadie**

Contrôle de la conformité des bouchons/ objectifs et paramètres à l'usage des professionnels

Revue Française d'œnologie.
January/February 2002.

***(3)* Éric Hervé, Steven Price – Gordons Burns and Peter Weber**

TCA in corks, Cork Soaks And Bottled wine

ASEV Annual Meeting Enology Session 7/2/99
Reno, Nevada.

have been stored for more than 12 months after bottling with various technological cork closures (BTA, BTO, BTE, BTR and BTD). None of the analyses performed on the used cork closures has revealed the presence of compounds of the 2, 3, 4, 6-tetrachloroanisole/2,4,6-tribromoanisole and pentachloroanisole type, thus confirming that storage was done under good conditions, without air contamination.

For the wines with BTD closures (more than 350 bottles analyzed) after a period of storage greater than or equal to 12 months, the TCA contents of the wines are non-detectable (less than the limit of detection = 0.2 ng/L). The releasable TCA contents of the used cork closures taken from the bottles are also non-detectable (less than the limit of detection = 0.2 ng/L).

For the other technological cork closures studied, ***figure 4*** shows a satisfactory correlation (R2 coefficient = 0.897) between the releasable TCA contents of the sampled bottles and the TCA in the corresponding wines.

Conclusion

The studies previously conducted by the Cork Quality Council and ETS (3) did not cover technological cork closures. The studies reported here enable us to determine the special TCA migration characteristics of technological cork closures into wine in bottles (in the case of these studies, the closures came from the Sabaté and Œneo Bouchage companies).
Under real conditions of use, the main results are:

– For BTD closures:
- Absence of TCA migration from the closure into wine (contents below the method's limit of detection).

– For the other technological cork closures with or without steam washing of the cork (BTA, BTO, BTE and BTR):
- Close correlation between TCA in the wine and the total TCA in the closure,
- A low and homogenous migration rate (average migration rate of 3.8%),
- Migration kinetics characterized by an equilibrium where the TCA value in the wine corresponds to the releasable TCA value of the new closure,
- Close correlation between TCA in the wine at equilibrium and releasable TCA measured in the closure sampled from the corresponding bottle.

This work demonstrates the advisability of determining the releasable TCA content when testing technological cork closures made from micro-agglomerated cork. The releasable TCA measurement provides an excellent assessment of the risk associated with micro-agglomerated cork closures.

The application of the releasable TCA method to used technological cork closures sampled from bottles is also a relevant tool to confirm whether or not the closure is responsible for contaminating a wine, as demonstrated by the satisfactory correlation, once equilibrium is reached, between the releasable TCA of the technological cork closure taken from the bottle and the TCA content of the incriminated wine.
This study also shows that the total TCA content of a technological cork closure (intrinsic TCA in ng/g) taken from a bottle can also be used, if we take into account that the average TCA migration rate into the wine is low (on the order of 3.8%). This relatively low migration rate can likely be explained by the homogenous and relatively compact structure of the micro-agglomerated cork closures studied here. ■

revue des œnologues
Sciences et techniques de la vigne et du vin

Article published with the authorization of the Journal the Revue des Œnologues

N° 133 October 2009 – pages 44 to 46 "Migration of 2,4,6-TCA in still wines – Application to technological cork closures" Alain Bobé.

The international reference for scientific and technical news on grape growing and winemarking, for more than 44 years in, France and 60 countries..

■ More than 1,200 articles archived by keywords www.oeno.tm.fr ■ Contact us: infos@mail.oeno.tm.fr ■