USING HIGLY ABSORBENT YEAST HULLS IN WINE FOR ELIMINATING CORKED AND MUSTY TAINTS

Olivier FERNANDEZ, Céline FAUVEAU, Patrice PELLERIN DSM Food Specialties
Carole PUECH, Patrick VUCHOT, and Stèphane VIDAL, INTER RHÔNE

INTRODUCTION

Cork and musty taints are defects currently occurring in wine. This situation applies to all wine-growing areas and is not a new problem. In fact, the issue was raised by Georges Jacquemin in 1903 in his Modern Œnologie Treatise. Today it has been established that these alterations are not only due to cork contamination but can also come from products used in treating wood, and chlorinated products used for cleaning the winery. The molecules causing these defects are haloanisoles, and include chloroanisoles and bromoanisoles. Today, despite efforts by cork makers, and the care taken over hygiene in the winery, the taste of cork and mustiness are a serious commercial risk.
Preventive measures used today, although essential, fail to eliminate these wine contaminants. Authorized and tested enological products, do not provide an adequate curative treatment.

In this paper, we look at the adsorbent properties of the yeast hulls developed by DSM Food Specialties in respect the chloroanisoles (TCA, TeCA and PCA).

During the production process developed by DSM Food Specialties, HALO treated yeast hulls undergo a treatment that considerably increases their adsorption capacity. This unique process, owned by DSM, guarantees that HALO^{TM} (High Adsorption Low Odor) hulls are obtained, in other words, hulls that do not tranfer any odor to the wine, even when high doses are used!

Haloanisoles
Facts about chloroanisoles (TCA, TeCA, PCA) and bromoanisoles (TBA)

Haloanisoles include chloro- and bromoanisoles. Chloroanisoles are the main cause of corked and musty taints in wine, particularly 2,4,6-trichloroanisole (TCA), 2,3,4,6-tetrachloroanisole (TeCA) and pentachloroanisole (PCA).
TCA contamination found in bottled wine generally comes from a cork stopper that already harbours TCA. However, TCA found in wine that is still in the tank, comes either from using chlorine based cleaning products (such as bleach), or from using humidifiers that are run using highly chlorinated water. On contact with phenols in wood, wine residues, or some types of polymer resin floor coverings, chlorine reacts rapidly and forms trichlorophenol (TCP). Moulds found in the winery then turn the TCP into highly volatile TCA. Then, carried on air currents, the contamination can spread throughout the whole winery. In addition, if traces of chlorine get into the wine after inadequate tank rinsing, TCP forms on contact with the phenols in the wine, followed by TCA via microorganisms in the wine or on coming into contact with the cork.

Furthermore, many of the insecticides and fungicides used to treat wood (beams, palettes, doors and so on) contain tetra- and pentachlorophenol (TeCP and PCP). Moulds found in the winery can turn these into malodorous, highly volatile chloroanisoles, tetra- and pentachloroanisoles (TeCA and PCA), as explained by Maujean *et al.* (1985) and Alvarez-Rodriguez *et al.* (2002). The presence in the wine of the two latter molecules indicates aerial contamination. This type of spoiling will affect far greater volumes of wine than when the problem of TCA arises in bottles.

Other molecules causing a musty flavor in wines have been highlighted recently. These are bromoanisoles, particularly 2,4,6-tribromoanisole (TBA). Like chloroanisoles, they form on specific precursors with the action of moulds, most often bromophenols, as was demonstrated by Chatonnet *et al.,* 2004. Contamination is spread from treated wood through the air in the winery. It can also come from the metal caps on the stoppers (a varnish made from epoxybromide resins), from previously contaminated wood shavings and through aerial contamination from flame-retarded insulation containing flame retardants based on tetrabromobisphenol A.

These aerial contamination mechanisms are show diagrammatically on figure 1
The effectiveness of HALO treated yeast hulls in reducing haloanisoles, has been quantified in two stages. Firstly, by laboratory trials where dose/effect was measured, then by large volume trials to verify the results in actual working conditions.

Materials and methods

Treatment effectiveness

Trials were conducted in 2004 and 2005, on naturally contaminated red wine and fortified wine. We chose wine with a TCA content in excess of 5 ng/L, and TeCA in excess of 25 ng/L. These respective values are the commonly used perception thresholds for cork-mustiness and musty type tainting.
HALO treated yeast hulls were added in the laboratory at various doses: 0, 100, 200, 400 and 800 mg/L. Contact between the hulls and the wine was maintained for a period of 48 hours and stirred three times a day (morning, afternoon and evening).
Classic enological analyses were conducted on all the wine batches for chromaticity and haloanisoles using the SBSE/GC/MS method, which is COFRAC accredited at the Inter Rhône laboratory.

Large volume experiment

Large volume trials were conducted in order to verify the findings observed in the laboratory, in conditions where putting the hulls in suspension is more difficult to achieve.
Two sites were chosen for this trial. On both sites, a contaminated wine was treated. The first was a 2005 white wine contaminated by TBA and PCA, in two tanks. The second was a 2004 red wine contaminated by TeCA and PCA.
The yeast hulls were added in a single dose of 400 mg/L. Contact between the hulls and the wine was maintained for 48 hours to replicate the conditions previously validated in the laboratory. Circulation was achieved by pumping over three times a day.

Results and discussion

Effectiveness of the treatment

To carry out a statistical study, we show below the results obtained on the wines treated with HALO treated yeast hulls dosed at 400 mg/L, the mode for which we have the most data.

Table 1: Elimination of chloroanisoles. Two-factor variance analysis. Inter Rhône results.

	Number of wines treated	Control	Wine treated (+ 400 mg/L)	% variation	Overall risk
TCA (ng/L)	8	6.05	4.44	**- 27 %**	0.5 %
TeCA (ng/L)	6	33.98	15.22	**- 55 %**	0.6 %
PCA (ng/L)	6	25.21	6.94	**-72 %**	1.1 %

The statistical analysis revealed that for the 8 wines treated (Table 1), the addition of 400 mg/L yeast hulls enabled the level of TCA to be reduced by 27 % on average. These results have an error risk of 0.5 %.
The results were even better in respect of reducing TeCA. Here, hull treatment facilitated a reduction of over 55 % by comparison with the control (average over 6 wines). These differences are subject to an error risk of 0.6 %.
The effectiveness of the hull treatment is even more noticeable with PCA. The contamination level was reduced by over 72 %, a statistically significant result taking into account the error risk of 1.1 %.

Treatment dose/effect

In order to optimize cost-effectiveness of the treatment, different doses of HALO treated yeast hulls were tested (Figure 2).

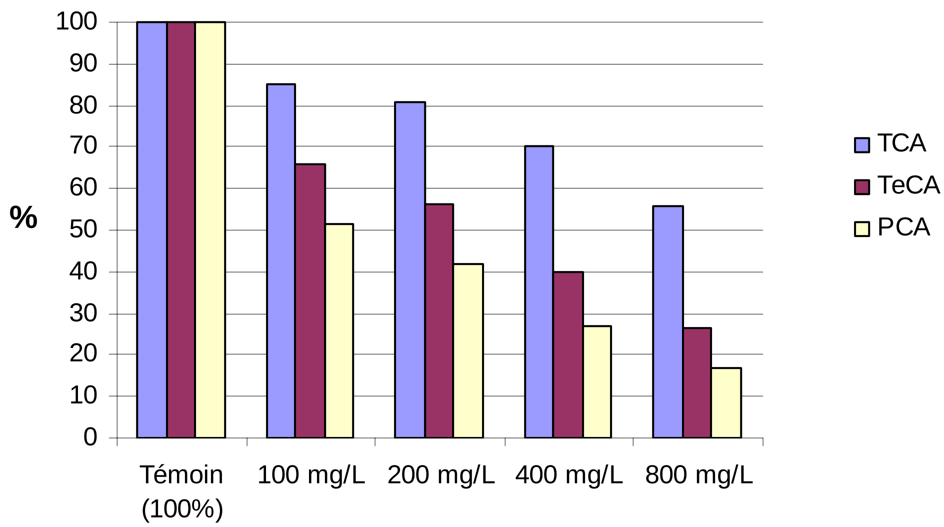

Figure 2: Elimination of chloroanisoles by increasing doses of HALO treated yeast hulls (average over two wines), expressed as a percentage of the contamination level in the wine. Inter Rhône results.

The elimination of the three types of chloroanisoles is proportional to the dose of yeast hulls employed. Treating with HALO treated yeast hulls at a dose of 100 mg/L, brought the level of TCA to less than 5 ng/L and that of TeCA to less than 25 ng/L. Although the perception thresholds are theoretical, it can be considered that the yeast hulls are an effective curative treatment for cork and musty taint.

Large volume experiment

On the first site, two white wine tanks of 18 and 3 hectoliters had high levels of TBA (respectively 5.5 and 2.8 ng/L). These wines were given a single does of 40 g/hL of DSM yeast hulls. In the smaller tank, where mixing in the hulls was easier, we were able to verify the effectiveness of the treatment. Following treatment, TBA content had greatly reduced to below the theoretical perception threshold (5 ng/l), down to 1.2 and 0.6 ng/L respectively, equating with a 78 % fall in both tanks (Figure 3). On tasting by the Inter Rhône Technical Service enologists, no defect was detected.

In addition, the TeCA was reduced by 23 % (from 2.6 to 2 ng/L) and PCA by 68 % (from 21.5 to 6.8 ng/L). These "residual" contamination levels are below perception thresholds.

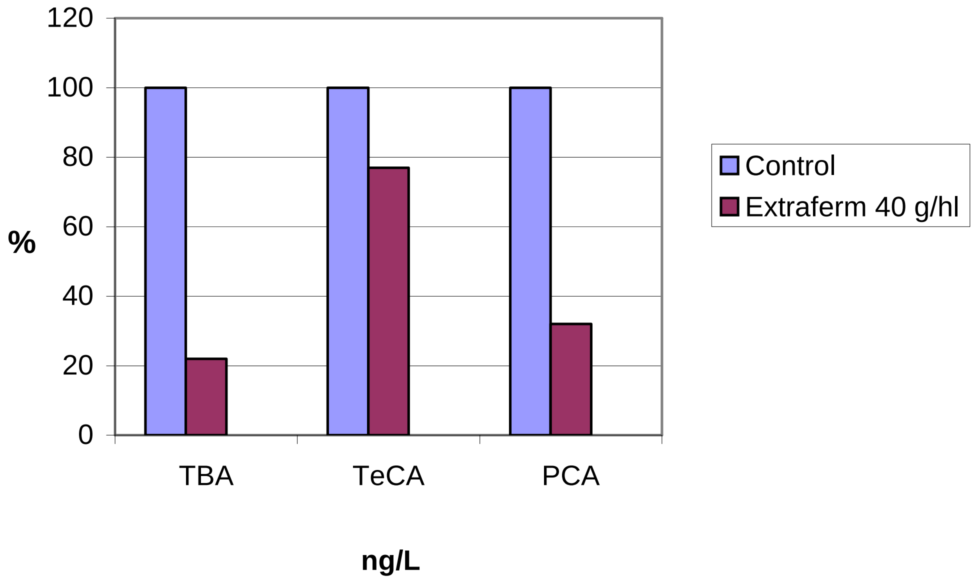

Figure 3: Reduction in haloanisoles content by HALO treated yeast hulls treatment in large volume white wine.

On the second site, a tank of red wine had high levels of TeCA and PCA (60 and 147 ng/L). A test treatment was conducted on a bottled quantity. Tasting by the Inter Rhône Technical Service enologists, proved entirely satisfactory in terms of eliminating musty taint and lack of yeast taste, compared with the control wine. The large volume treatment was conducted in the winery at 40 g/hL. The analyses showed a reduction in TeCA and PCA respectively of 60 and 61 %.

These large volume trials confirmed the effectiveness of yeast hull treatment for decontaminating wine containing haloanisoles.

A 48-hour period of contact between the hulls and the wine being treated, together with pumping over 2 or 3 times a day, facilitated the success of the decontamination treatment. This was achieved even though putting the hulls in suspension is more difficult in a large tank.

We were able, for the first time, to show the effectiveness of the treatment in reducing the TBA content, a molecule whose perception threshold is as low as that of TCA and gives the wine the same defect. We obtained a significant 78% reduction.

Impact on the composition of treated wines

The HALO^{TM} process enables hulls to be obtained that provide a reliable way of treating wines contaminated by haloanisoles. This treatment, which is very easy to employ and based on the use of an authorized enological product, gives new hope to many wine-makers.

Analyzing classic enological parameters shows that using HALO treated yeast hulls has a negligible effect on the composition of the wines treated, even at a maximal dose of 800 mg/L. The DO 280, 520, 420 and 620 nm measurement shows that the HALO treated yeast hull treatment only has a slight effect on wine color parameters. Of the six wines treated with a dose of 400 mg/L, there is an average reduction in DO 280 of 1.5 % and Color Intensity (the sum of DO at 420, 520 and 620 nm) of 3.1 %. These very small modifications are a matter of detail only, decontamination having rendered the wine drinkable.

Finally, yeast hull treatment appears particularly effective against TeCA, PCA and TBA molecules, whose presence in wine occurs through aerial contamination in the winery. Thus, when these components are detected by analysis, the contaminated wine is still housed in the tanks and the problem may affect very large volumes. At this stage, it is easier to treat the affected wine. (Where TCA contamination arises from bottling with poor quality corks, it is necessary to uncork the bottles to carry out the treatment.)

CONCLUSION

The series of experiments and the analysis carried out show the ability of a type of yeast hull to fix haloanisoles. Molecules can be classified according to their ability to be adsorbed by hulls, in descending order (Table 4).

Table 4: Results of haloanisoles elimination by Extraferm used at 400 mg/L.

Contamination reduction (%)	TBA	PCA	TeCA	TCA
In laboratory	-	-72.5 %	- 55.2 %	- 26.6 %
In winery	-78 %	-68 %	-23 %	-

For chloroanisoles, effectiveness is proportionally greater with a higher number of chlorine atoms. The increased number of chlorine atoms on the anisole nucleus increases the molecular apolarity. It would seem that the fixing mechanism of these molecules is based, at least in part, on hydrophobic adsorptions.
The large volume trials, where putting the hulls in suspension is not as easy as in the laboratory, particularly in large tanks, confirmed the feasibility of in-winery treatment.

The overall results indicate clearly that treatment with HALO treated yeast hulls has no negative effect on color or hue of the wine, nor does it cause any unpleasant flavor.
This study was carried out on a large number of red, white and fortified wines, of two vintages. The number of experiment repeats enabled statistical analysis to be conducted to confirm the validity of the results obtained. All the laboratory data has, moreover, been confirmed by large volume trials.

In fact, the high adsorption capacity of DSM HALO^{TM} hulls has proven ability to restart stuck fermentations, and clears toxicity in wines by reducing the rate of Ochratoxin A. This property also provides a curative treatment for unpleasant odors such as mustiness and cork taint caused by haloanisoles. The innovative results of this program are encouraging.
In order to optimize these treatments, it will now be of value to examine the best combinations of treatment dose, contact time, temperature and the frequency of putting the yeast hulls back into suspension in the wine. However, the data from the already completed research provide wine makers with an effective solution.

Bibliography

FERNANDEZ O., BAJARD-SPARROW C., PELLERIN P., LANKHORST P., **2005**. Arrêts de fermentation, une solution efficace. *(Stuck fermentation, an effective solution.)* Revue des Oenologues,116.

BONNET M.-L., VUCHOT P., RIOU C., VIDAL S., **2005**. Impact des alcalins chlorés sur la teneur en 2,4,6-trichlorophénol des vins. *(Impact of chlorinated alcalines on the 2,4,6-trichlorophenol content in wines.)* Revue des Œnologues,116.

MICHEL G., **2003**. Les goûts de bouchon, mise au point. *(Cork taint, update.)* Revue Française d'œnologie, 202, 20-22.

MIRABEL M., BEAUREGARD D., RIQUIER L., BERTRAND A., **2006**. Traitement des vins moisis, bouchonnés: le point sur la question. (*Treatment of musty, corked wines: update on the subject.)* Revue des Œnologues, 119, 31-33.

CHATONNET P., BONNET S., BOUTOU S., LABADIE M.-D., **2004**. Identification and responsibility of 2,4,6-tribromoanisole in musty, corked odors in wine. J. Agric. Food Chem., 52 (5), 1255-1262.