PROFICIENCY-TESTING SCHEME FOR HALOANISOLES AND HALOPHENOLS IN OAK WOOD

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INTRODUCTION

Haloanisole contamination is a serious problem for wine quality, even trace amounts of 2,4,6-tricloroanisole (TCA), 2,3,4,6-tetrachloroanisole (TeCA), pentachloroanisole (PCA) and 2,4,6-tribromoanisole (TBA) can cause musty or moldy off-flavors in wine (1). Each of these haloanisoles has a similar odor but possesses different sensory thresholds. These compounds are not naturally occurring wine constituents. The origin of haloanisoles can be attributed to the biodegradation of 2,4,6-tricholorophenol (TCP), 2,3,4,6-tetrachlorophenol (TeCP), pentachlorphenol (PCP) and 2,4,6-tribromophenol (TBP) respectively, which can be found in winery environments. Several materials, including barrels' oak wood, may be contaminated and release these molecules into wine. The coopers' need to prove the quality of manufactured barrels increases the request of analyses of haloanisoles and halophenols (HAHP) in oak wood. However, coopers and laboratories face to difficulties in results interpenetration due to the lack of an official testing method. Different analytical methods, more or less comparable, have been implemented by laboratories. The main goal of setting up this PTS is to develop an evaluation process for the laboratories' performances, considering that laboratories can perform composition or migration analyses, which results are not equivalent. Both methods have advantages and disadvantages: analyses on corks, which have similar objectives than those on oak wood, are mostly migration ones, because the product impact makes the composition analysis less relevant for producers' needs; on the other hand, composition methods developed by each laboratory should give the same result which corresponds to the exact value of HAHP. Another challenge in developing these PTS is manufacturing stable and homogeneous samples of oak wood dipped in haloanisoles and halophenols. This work describes the design and the implementation of a PTS for the analyses of HAHP oak wood samples, with a focus on the results of the proficiency test of March 2018.

EXPERIMENTAL

Setting up of a PT can be schematized in 4 main steps: sample preparation, homogeneity and stability checks, analyses by the laboratories and statistical treatment of the data (figure 1).

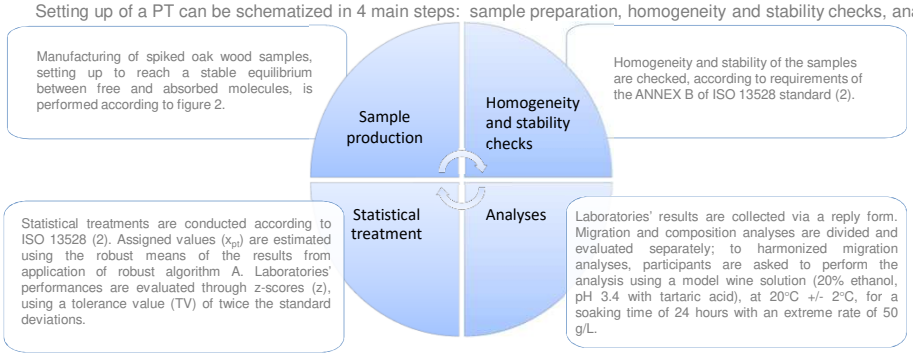

Figure 1. Description of main steps of "HAHP in oak wood" PTS

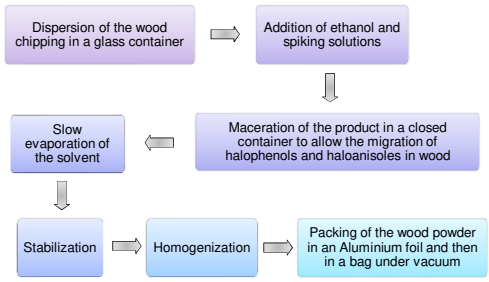

Figure 2. Manufacturing steps for oak wood samples spiked with HAHP

RESULTS & DISCUSSION

Since October 2013, 4 tests per year are proposed to laboratories. On average, 15 laboratories have been participating to PTS, with 10 results returned for composition analyses and 9 for migration ones. Laboratories' results are good, with, medially, less than 1 unsatisfactory result by analytical parameter. However, the range of dispersion may reach 100% according to the analyzed organo-halogenated, concentration levels and test and this can be mainly linked to the nature of product, the extraction and analysis methods. Figure 3 shows the graphs describing the dispersion of the results (twice the robust standard deviation) as a function of the assigned value for TeCA and TeCP from the test of March 2013 to the test of March 2019 (for composition and migration analyses). Values of the PT from March 2018 to March 2019 are represented in a different color, green: a reduction of the dispersion of all returned results can be noted on the last tests. As, for each PT, laboratories analyze the same sample for migration and composition tests, the difference between assigned values obtained from the two methods were estimated for each compound. Averagely, assigned values of migration analyses are between 90% and 60% lower than those of composition ones (see Table 1), that corresponds to the percentage of compound that can migrate from wood in the wine standard solution at 20°C for 24 hours. It has to be noted that this difference is not linked to contamination levels. Figure 4 summarizes graphically data obtained for composition and migration analyses of the test of March 2018. These results are coherent with those obtained in other tests, with a relative difference between -69% for TeCA and -94% for PCA analyses. Values of laboratories that returned quantitative results for both methods were also compared through z-scores. Figure 5 shows Youden plot confidence ellipse based on Jackson method comparing migration and composition laboratories' z-scores for TCA and TCP. Results are satisfactory for TCP, with only one laboratory out of the trueness region and the confidence ellipse at 5%. Concerning TCA, 3 laboratories are out of the trueness region with one out of the confidence ellipse at 1%.

Compound	Average relative difference (%)
TBA	-80
TCA	-71
TeCA	-82
PCA	-90
TBP	-78
TCP	-60
TeCP	-78
PCP	-87

Table 1. Average relative difference between composition and migration assigned values (%) of the PT performed from October 2013

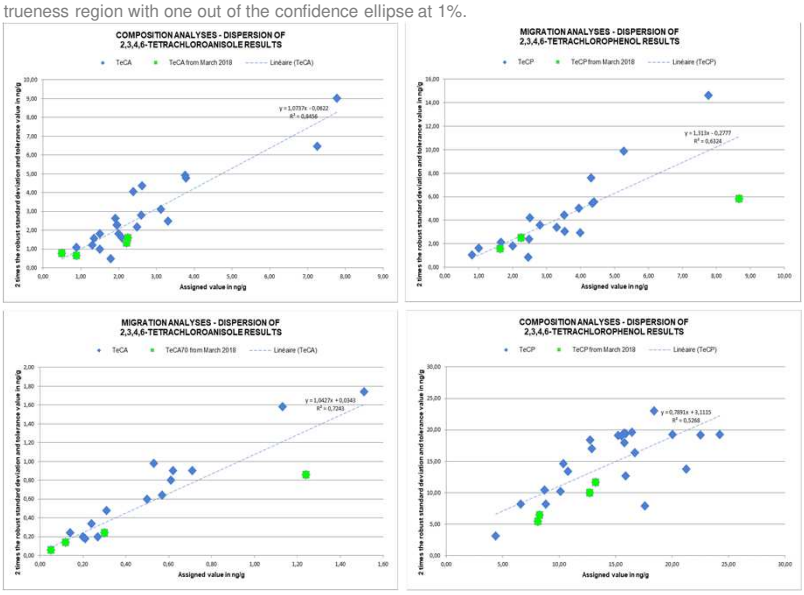

Figure 3. Results dispersion as a function of the assigned value for TeCA and TeCP, composition and migration analyses

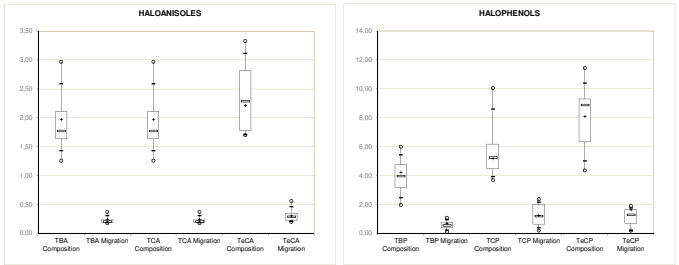

Figure 4. Results obtained for composition and migration analyses, test of March 2018 (ng/g) – Minimal value, median, maximal value, 1st quartile, 1st decile, 3rd quartile, 9th decile

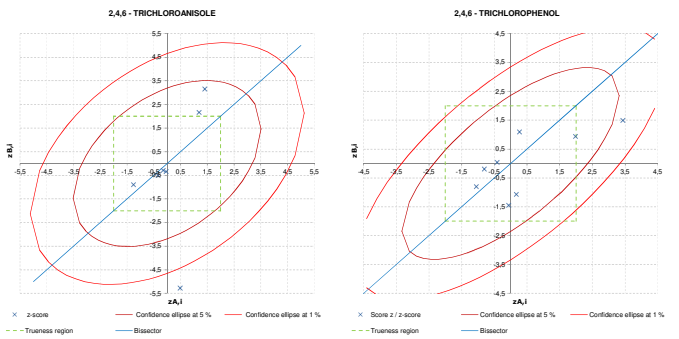

Figure 5. Youden plot confidence ellipse based on Jackson method comparing migration and composition laboratories' data for TCA and TCP, test of March 2018

CONCLUSION

A PTS for migration and composition analyses of haloanisoles and halophenols in oak wood has been implemented successfully, both from homogeneous and stable samples production and statistical point of view. These PT are an important tool for laboratories, answering to a lack of official methods and enabling participants to draw up a general inventory of their analytical skills in term of composition and migration analyses. A reduction of results' dispersion can be noted on the last tests This can be due to the fact that laboratories participating to regular PT can have a critical point of view on the performed methods and improve their analytical procedures to obtain values closer to the assigned ones. Laboratories can now monitor the reliability of their results and obtain recognition of their analytical procedures by coopers and accreditation bodies.

REFERENCES

(1) Buser H. R., Zanier C. and Tanner H. Identification of 2,4,6-trichloroanisole as a potent compound causing cork taint in wine. Agric. Food Chem. 30 (1982): 359-362.

(2) ISO 13528:2015 - Statistical methods for use in proficiency testing by interlaboratory comparisons.