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Sensory Screening for Large-Format Natural Corks by "Dry Soak" Testing and Its Correlation to Headspace Solid-Phase Microextraction (SPME) Gas Chromatography/Mass Spectrometry (GC/MS) Releasable Trichloroanisole (TCA) Analysis

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Large-format natural corks were individually screened for trichloroanisole (TCA) taint and other non-characteristic cork odors by smelling the high relative humidity headspace of the jarred closure during expert panel sensory sessions. The method was coined "dry soak sensory screening". Out of a population of 2296 corks, 138 specimens [6% of the total population (TP)] were retained because of unusual odors, ranging from mild to severe. All retained corks were analyzed for releasable TCA (RTCA) by the solid-phase microextraction (SPME) gas chromatography/mass spectrometry (GC/MS) technique. Results indicated that 30 corks (1.3% TP) had concentrations between 1.0 and 5.0 ppt. Most of these corks had non-typical TCA odors described as ashtray, musty, moldy, dirty, and wet cardboard. A total of 13 retained corks (0.57% TP) had RTCA values higher than 5.0 ppt, mostly displaying the typical TCA odor. Dry soak screening has been determined to be a clean, fast, and most importantly, a nondestructive method ideal for screening large-format natural corks with off odors.

KEYWORDS: Large-format cork; retained cork; control cork; non-characteristic cork odor; trichloroanisole (TCA); releasable TCA (RTCA); solid-phase microextraction (SPME); gas chromatography/mass spectrometry (GC/MS); mass-to-charge ratio (*m/z*); parts per trillion (ppt); percentage of TCA recognition; non-typical TCA odor; percentage of musty odor recognition

INTRODUCTION

Natural cork, a bark material harvested from the *Quercus suber* oak tree, has been used by local winemakers and industry as a bottle closure for many centuries. In the last few decades, the use of cork material has been put in question because of its potential influence on the delicate flavor of wine. Cork material has been blamed for imparting off-flavors (cork taint) caused by compounds such as trichloroanisole (TCA) and its halogenated homologues, 2-methylisoborneol, geosmin, 1-octen-3-ol, 1-octen-3-one, guaiacol, and certain methoxy-alkylpyrazines (*1*−*3*). A more demanding and sophisticated global market has recently encouraged the appearance of new taint-free synthetic closure alternatives. This, in turn, has placed pressure on the cork industry to better understand the biogenesis of these undesirable compounds, as well as putting in place stricter quality control (QC) protocols during production.

"Healthy" cork material, like anything else in nature, has and releases volatile organic compounds (*4*, *5*). Consumer detection of these compounds depends upon the amount released by the cork matrix and the human threshold level of detection. In corkwood, intrinsic volatiles are generated when the material macroconstituents are broken down as a result of natural and industrial processes (thermal and chemical). Another group of volatiles originate from cross-contamination during material storage and transportation (*6*) caused by the remarkable adsorbing capabilities of the cork matrix toward organic compounds (hydrogen bonding and van der Waals interactions). A third and most widely publicized group of volatile compounds are generated by microbial activity lodged mostly in the lenticels and structural fissures of the cork material. This group of volatile compounds, particularly TCA (*7*), has been the main concern of the cork industry in recent times (*3*).

Since the discovery of the connection between TCA and cork taint during the early 1980s (*8*, *9*), a lot of work has been performed to detect, understand, and prevent the random incidence of taint in natural corks. A breakthrough was achieved when the industry was able to detect TCA in cork lots at the level of parts per trillion (ppt) by combining three powerful analytical tools: solid-phase microextraction (SPME) (*10*), capillary

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chromatography, and mass spectrometry under single-ion monitoring (SIM) (*11*, *12*). Releasable TCA (RTCA) analysis is a standard and well-recognized procedure to measure the presence of the analyte in cork material (*12*, *13*). TCA, on and near the surface of the cork, is extracted when the tested cork (or corks) is left in contact with an appropriate solvent; an apparent equilibrium is established between phases after a short (and fixed) period of time, usually 24 h. TCA is quantified in the headspace over the extracting solvent, and its value is then used as a marker for the potential taint that can affect the bottle of wine by the corresponding cork.

Today, cork lots are industrially tested for potential TCA contamination by implementing a statistically sound sampling plan (*14*, *15*). RTCA is measured by performing “bulk soaks” (usually 20−50 corks mixed with the solvent) on representative subsamples (*16*). Understandably, good results do not guarantee that every single cork in a lot will be taint-free (*12*, *3*).

Wineries promote their best creations by packaging part of the vintages in well-advertized oversized glass bottles (larger than the 0.75/1.50 L standard volumes). Double magnum (3.0 L) and larger bottles (*17*) require larger than regular (24 mm) diameter size closures; these are referred to as large-format corks. Because of the marketing exposure of these bottles of wine, cork companies have been asked to provide customers with taint-free large-format corks. RTCA screening with an ethanolic solution can obviously be performed on individual corks; however, the procedure would require a lot of preparation and analytical work, not to mention the fact that it is a destructive procedure that renders unattractive closures after drying because of tannin staining.

This report summarizes the experiences and results of cork dry soak screening, an old idea (*18*, *19*) that has been implemented by our organizations for the last 2 years with great success to provide natural corks with negligible risk for wine taint. It is a nondestructive, fast, and effective screening tool that does not require any cork-solvent contact and provides closures ready for printing and treatment.

MATERIALS AND METHODS

Cork Material. A total of 2296 large-format Portuguese natural corks from several lots were used in this work, including corks with the following dimensions: 54 × 33 mm (75%), 54 × 36 mm (24%), and 54 × 39 mm (1%). The corks were harvested and manufactured during the years of 2006 and 2007. All corks were grade “first” and processed using a peroxide wash. In addition, some cork lots were processed using the Innocork wash (*20*).

Chemicals and Reference Compounds. USP/EP purified water was used during sensory evaluation (Ricca Chemical Company, Arlington, TX).

HPLC water (Fisher Scientific, Fair Lawn, NJ), ACS reagent, absolute (200 proof) ethyl alcohol (ACROS, Geel, Belgium), and USP/FCC/EP/BP sodium chloride (Fisher Scientific) were used for SPME gas chromatography/mass spectrometry (GC/MS) sample preparation.

2,4,6-Trichloroanisole (100 μg/mL in methanol) from Supelco (Bellefonte, PA) was used to make RTCA SPME GC/MS calibration curves and 20 ng/L sensory standards.

Procedure for Sensory Evaluation. Corks were individually placed inside Teflon-lined cap 125 mL I-CHEM glass jars (Chase Scientific Glass, Inc., Rockwood, TN). Six drops of USP/EP water were placed inside the jars and next to the closures with a pipet. The jars were sealed with the cap and left to equilibrate at room temperature for a period of 24 h before any sensory screening was performed (*21*).

The 2296 corks were evaluated by four industry expert panelists, 200 corks at a time, through 12 individual sensory sessions for a period of 2 months. Corks were evaluated by opening the lid of the test jars and swiftly sniffing their headspaces in a systematic and fast-pace fashion throughout each session. Because all corks were assessed by all four panelists, a minimum of 1 h re-equilibration period was established between the previous and next panelist.

Sensory impressions were recorded *ad libitum*, with an emphasis on the typical TCA/haloanisole odor. Before the onset of each sensory session, a 20.0 ng/L solution of 2,4,6-trichloroanisole (CAS number 87-40-1) prepared in USP/EP purified water was used as an odor standard. At the end of each session, panelists discussed the results and developed a consensus on corks that had non-characteristic and questionable odors: Closures with unacceptable non-characteristic aromas were set aside and screened for RTCA by the SPME GC/MS technique. These corks were denoted as “retained corks”.

In addition, 100 corks that did not appear to have any unusual odors were also set aside for RTCA analysis. This second group of corks was denoted as “control corks”.

Corks that were deemed to have a normal odor by the expert panel were removed from their glass jars and dried for 30 min in an oven set at 55 °C to achieve product specification for final processing and commercial use.

Procedure To Quantify TCA by Analytical Instrumentation. Retained and control corks were analyzed for RTCA (*11*). These corks were individually soaked in approximately 75 mL of 12% ethanolic solution, inside the same I-CHEM jar used to assess them by sensory evaluation. Corks were soaked for 24 h before a 5 mL aliquot was removed and placed inside a 20 mL headspace vial containing 1 g of sodium chloride. Headspace vials were sealed with pre-assembled magnetic crimp caps and blue silicone/PTFE septa. Vials and caps were purchased from Gerstel, Inc. (Baltimore, MD).

Headspace vials were placed on a sample tray, part of a Gerstel multipurpose sampler system (MPS2). The sampler was interfaced to an Agilent 6890/5975 GC/MS system. The GC oven housed a 30 m × 0.25 mm DB-5MS capillary column, with a 0.25 μm coating (J&W Scientific, Folsom, CA). Each headspace vial was equilibrated at 50 °C for 20 min and sampled by placing a SPME fiber inside the vial and just above the liquid for another 20 min. The SPME fiber, housed inside a 23-gauge needle, was purchased from Supelco (Bellefonte, CA) with a 100 μm PDMS coating. After volatile collection, the fiber was introduced inside a Gerstel CIS four-injection port set at 260 °C. The volatiles were separated by applying a GC oven constant temperature of 45 °C for the first 2 min, followed by a temperature ramp of 17 °C/min until reaching a maximum temperature of 265 °C, and keeping the final temperature for an additional 5 min.

The mass spectrometer was operated under SIM, screening for the four main TCA spectral ions (*m*/*z* 195, 197, 210, and 212). A standard curve was constructed out of four individually TCA-spiked 12% ethanolic solutions set at 1.0, 5.0, 10, and 20 ng/L. If an unknown sample produced a larger GC/MS peak area than the peak area produced by the largest standard, the unknown sample was diluted with more 12% ethanol solution until a peak area value fell between established standard values (interpolation).

RESULTS AND DISCUSSION

Characterization of the Analytical Method. To understand the relevance of the analytical data presented in this study, it is important to first describe and define the capability of the analytical equipment used to quantify RTCA.

The ion *m*/*z* 197 peak area was chosen for TCA quantitation because time and again it did not co-elute with other unknown ghost peaks while still providing a strong signal only surpassed by ion *m*/*z* 195 (MS electron impact base peak). TCA eluted from the capillary GC column at 9.02 min, and its identification was only confirmed when the *m*/*z* 197 peak was aligned with MS peaks at *m*/*z* 195, 210, and 212 at expected peak area ratios.

It was determined that the SPME GC/MS system used in this study had a TCA limit of detection (LOD) value of 0.2 ppt (ng/L), defined as 3 times the peak height of the background noise. Linear regression applied to the four calibrating standards (plus zero) produced a straight line with a slope value of 392 MSD $counts^{197}$/ppt and a correlation coefficient of 0.9994.

Cork soaks with peak areas reflecting very low TCA values, such as 0.2 ppt or less, were denoted as “non-detected”, while cork soaks with values ranging between 0.2 and 1.0 ppt were denoted

Table 1. List of the Most Frequently Mentioned Non-characteristic Cork Odor Remarks

sensory descriptor	frequency
musty	113
dirty (dirt, soil, earthy)	71
ashtray (caustic)	58
TCA (haloanisole)	56
moldy (mold, mildew)	52
cocoa (chocolate, milk chocolate)	47
minty (mint, menthol)	43
cardboard (wet cardboard)	35
vegetative (grassy, green, vegetal, aldehyde)	31
peppery (pepper, black pepper)	26
total	**847**

as less than 1.0 ppt (< 1.0 ppt). For practical purposes, values ≥1.0 ppt were segmented in three RTCA group ranges: 1.0−5.0 ppt (non-typical TCA odor), 5.0−20.0 ppt (TCA odor), and ≥20.0 ppt (high TCA odor).

Overall Sensory Results. During sensory evaluation sessions, the 2296 large-format corks triggered 9184 sensory responses (each cork causes four responses from four expert panelists), where the great majority was described as a weak cork/woody odor, typical of natural cork. However, in some cases, the panelists were also able to detect unusual aromas that differed from the expected background odor. These sensory impressions were denoted as non-characteristic cork odors.

Sensory evaluation sessions recorded a total of 847 non-characteristic cork odor remarks with a wide range of intensities, grouped under 86 odor descriptors. The 10 most frequently mentioned odor descriptors (representing 63% of all non-characteristic odor remarks) are shown in **Table 1**.

It is important to point out that the typical TCA/haloanisole odor was the only non-characteristic cork odor described as the effect of a unique chemical, i.e., 2,4,6-trichloroanisole. With an aroma identical to other less known haloanisoles (tetrachloroanisole, pentachloroanisole, and tribromoanisole), this is what most wine connoisseurs and enologists recognize as "corkiness" or cork taint (*22*). The other 85 descriptors used by the sensory panel originated from the elicited odor of common household and food products, as well as every day aromas (*23*). The panelists were encouraged not to overthink what they perceived and were not forced into specific sensory descriptors but rather were given ample freedom of verbal sensory expression.

Musty was found to be the non-characteristic sensory descriptor with the highest incidence, followed by other (negative) odors, such as dirty, ashtray, TCA, moldy, cocoa, and cardboard. The typical TCA/haloanisole odor was recorded 56 times at different intensities. Other not-so-negative descriptors, such as minty, vegetative, and peppery, were also among the most frequently cited non-characteristic cork odor descriptors.

Retained Corks. A total of 138 corks were retained because one or more panelists thought to detect TCA and/or any of the industry's well-known sensory descriptors that give away the presence of TCA at very low levels (ashtray, cardboard, dank, dirty, dusty, earthy, moldy, and musty), as well as other fully documented cork taints (*1*−*3*). Cork retention was also extended to corks with very strong aromas that are usually not typical of cork taint, such as minty, vegetative, and peppery (**Table 1**).

For the sake of result simplification, individual sensory remarks from all four expert panelists for all 138 retained cork samples will not be presented in this report. Each retained cork was not categorized as exuding a specific odor because very often panelists did not agree on the actual descriptor but always agreed on the presence of an objectionable non-characteristic cork odor.

Table 2. Releasable TCA Distribution in 138 Retained Corks

releasable TCA group	number of corks	percentage of total retained corks
non-detected	60	43.5
<1.0 ppt	35	25.5
1.0−5.0 ppt	30	21.5
5.0−20.0 ppt	10	7.5
≥20 ppt	3	2
total	**138**	**100**

Table 3. Releasable TCA Distribution in 100 Control Corks

releasable TCA group	number of corks	percentage of total control corks
non-detected	91	91
<1.0 ppt	9	9
total	**100**	**100**

The 138 retained corks represented 6% of the total cork population. The balance or 2158 large-format corks were approved and used for commercial purposes. Some of these corks, deemed as normal/typical, did sometimes own very faint non-characteristic cork odors (471 sensory remarks in total) but not serious enough to retain them.

Every retained cork was analyzed for RTCA, even if the non-characteristic cork odor was described as other than the typical TCA/haloanisole odor. **Table 2** shows the RTCA value distribution found for the totality of the retained corks. A total of 60 corks or 43.5% of the retained corks did not have any detectable RTCA (< 0.2 ppt). A total of 35 corks or 25.5% of the retained corks expressed RTCA values of < 1.0 ppt. A total of 30 corks or 21.5% of the retained corks were found to have values between 1.0 and 5.0 ppt. A total of 10 corks or 7.5% of the retained corks were found to have values between 5.0 and 20.0 ppt. Finally, only three corks had releasable RTCA values beyond 20.0 ppt (34, 46, and 174 ppt). This last small group represents about 2% of all retained corks.

Control Corks. A total of 100 samples pulled from the 2158 approved corks and deemed to own an acceptable (characteristic) cork odor were analyzed for RTCA in the same fashion as the retained corks. **Table 3** shows that all of the control corks were found to have RTCA values of < 1.0 ppt (91% reported no detectable levels, while 9% had actually < 1.0 ppt).

Retained Corks Because of TCA/Haloanisole Odor. All 138 retained corks were categorized on the basis of their RTCA results. **Table 4** shows the five retained cork groups, each with a corresponding number of corks (**Table 2**) and number of TCA sensory remarks by the four expert panelists. **Table 4** and **Figure 1** show the percentage of TCA recognition defined as the number of TCA sensory remarks divided by the maximum possible number of sensory remarks (number of corks multiplied by the number of sensory panelists) per cork group (or subgroup) and multiplied by 100, also computed by the following formula:

$$\%\ \text{TCA recognition} = \left[\frac{\text{TCA remarks}}{(\text{corks})(\text{panelists})}\right] \times 100$$

The percentage of TCA recognition is a practical concept, particularly for groups of corks with common attributes based on releasable TCA content. Because it is possible that not all sensory panelists would agree on a specific descriptor, the percentage of TCA recognition adds semi-quantitative strength to the sensory results. This concept can be applied to any other sensory descriptor, as long as the corresponding chemical marker can

Table 4. Percentage of TCA Recognition by Dry Soak Sensory Screening in 138 Retained Corks

RTCA group	number of corks (per TCA group)	number of corks (per TCA subgroup)	number of TCA sensory remarks	percentage of TCA recognition by group (subgroup)
non-detected	60		**4**	**1.7**
<1.0 ppt	35		**2**	**1.4**
1.0−5.0 ppt	30		**14**	**12**
		19 (1.0−1.9 ppt)	10	13
		4 (2.0−2.9 ppt)	2	13
		5 (3.0−3.9 ppt)	1	5
		2 (4.0−4.9 ppt)	1	13
5.0−20.0 ppt	10		**26**	**65**
		5 (5.0−5.9 ppt)	12	60
		1 (6.0−6.9 ppt)	3	75
		2 (10.0−10.9 ppt)	6	75
		1 (11.0−11.9 ppt)	1	25
		1 (17.0−17.9 ppt)	4	100
≥20.0 ppt	3		**10**	**83**
total	**138**		**56**	

be quantified by any analytical means and reconciled back to the sensory data (e.g., isoamyl acetate to banana aroma).

It is clear to see in **Table 4** and **Figure 1** that, as the actual concentration of RTCA in the retained corks increases, the four expert panelists were able to improve their ability to recognize and screen for TCA cork taint. For cork groups with < 1.0 ppt in RTCA, the percentage of TCA recognition is low (1.7 and 1.4% for nondetected and < 1.0 ppt, respectively) because either these corks are tainted with very low levels of TCA or they were retained as a result of other objectionable non-characteristic cork odors.

The percentage of TCA recognition improves when the level of RTCA increases from < 1.0 ppt to a concentration range (called non-typical TCA odor) between 1.0 and 5.0 ppt (12% TCA recognition). For this TCA cork group, it was observed that most of the corks had RTCA values falling between 1.0 and 2.0 ppt (19 of 30 retained corks). It is interesting to point out that the five retained corks with releasable TCA values between 3.0 and 4.0 ppt exerted only 1 of 20 potential sensory TCA remarks. The corks of this subgroup were still retained because the sensory panel tagged to these specimens other sensory descriptors, such as strong cardboard, musty, moldy, dirty, and ashtray.

As the amount of TCA increases in corks with non-typical TCA odors to the next RTCA group level (RTCA values between 5.0 and 20.0 ppt), the percentage of TCA recognition significantly increased to 65%, with only one cork at 11.8 ppt revealed by only one of four panelists (25% TCA recognition). At 20.0 ppt or higher (high TCA odor), the percentage of TCA recognition reaches 83% for the three highest RTCA values.

Musty is also frequently used as a descriptor for TCA taint (*24*). Musty was the most commonly used sensory descriptor to reveal a cork with a non-characteristic odor (**Table 1**). This descriptor was used 113 times: 53 times with retained corks and 60 times with approved corks. **Figure 2** shows the percentage of musty odor recognition (calculated in the same fashion as the percentage of TCA recognition). For corks with nondetectable and < 1.0 ppt levels of RTCA, the percentage of musty odor recognition was 8.3 and 10%, respectively. As the level of RTCA increases (between 1.0 and 5.0 ppt), the musty descriptor is still cited by the sensory panel with a higher frequency than the typical TCA/haloanisole odor (**Figures 1** and **2**). It is at a RTCA level of 5.0 ppt and higher that the typical TCA odor takes over the musty descriptor, which is no longer used as often by the panelists (2.5 and 0% of musty odor recognition for groups 5.0−20.0 and 20.0 ppt or higher, respectively).

It is possible that low levels of some of the other well-known cork taints, such as 2-methylisoborneol, geosmin, 1-octen-3-ol, 1-octen-3-one, guaiacol, and methoxy-alkylpyrazines (*1−3*), might have been responsible for some of the cardboard, musty, moldy, dirty, and ashtray odor impressions recorded in corks with RTCA levels of < 5.0 ppt. However, the correlation found between musty odor and RTCA between 1.0 and 5.0 ppt indicates that any co-taint (other than TCA) will be masked by the halogenated anisole. It is very possible that many of the 95 retained corks with RTCA levels of < 1.0 ppt might have been rejected because of the presence of any of the other nonhaloanisole taint compounds (it was certainly unfortunate not to be able to screen for any of the other taint analytes).

On the basis of the data presented on previous paragraphs, a ruler for TCA sensory detection is presented in **Figure 3**. For corks "soaked" in a high relative humidity environment (dry soak), the point at which TCA can be significantly recognized is at or around a RTCA value of 5.0 ppt. Obviously, the chances for TCA recognition increases proportionally with the increasing amount of TCA present in the cork. Corks with RTCA values of 5.0 ppt or less can also be segregated by keeping in mind that, at such levels, TCA might no longer be recognized for its characteristic odor but rather by other sensory descriptors, such as ashtray, cardboard, dank, dirty, dusty, earthy, moldy, but especially musty. As the RTCA content decreases to levels below 1.0 ppt, other non-characteristic cork odors, if also present in the cork, could then be discerned (*24*).

Human odor detection and recognition levels of a specific aroma compound have to be defined within the context of the matrix from where the aroma chemical exudes. The previously reported "dry soak" sensory threshold levels (measured as RTCA) of ∼1 ppt (odor detection) and ∼5 ppt (odor recognition) would have been different if matrixes such as white or red wine (or even the popular "vodka soak" technique used by California wineries for large-format cork) were implemented as TCA-screening media (TCA released from a humid cork closure in contrast to TCA extracted and released by an alcoholic solution). Nevertheless, these "dry soak" threshold levels are in remarkably close approximation to the values reported by Pereira (*22*) for a TCA detection threshold range of 1−4 ppt and a recognition threshold range of 4−10 ppt in commercial wine and spirits, which is technically equivalent to the ethanolic RTCA testing protocol.

Interactions between low TCA levels and desirable wine flavor components have been reported by the industry as responsible for wine fragrance masking. Herve et al. (*16*) calls wines (Chablis) with RTCA values between 1.0 and 4.0 ppt as "muted", which also coincides with the range of TCA sensory detection reported in the present work.

Taint in Cork Populations Based on TCA Incidence. The results found in this study, obtained from such a large sample size, could well be used to draw some conclusions about today's TCA taint incidence in the natural cork closure market, at least for high-end cork material.

All retained corks with some level of RTCA would certainly not taint an equal amount of wine bottles. Corks with releasable TCA levels of < 1.0 ppt (95 corks) were still retained because of the presence of other non-characteristic cork odors found above their sensory threshold levels. These corks are probably the bearers of other well-known cork taints (*1−3*), as well as other more benign compounds.

The good correlation between TCA/haloanisole sensory screening and the RTCA results seemed to be in good agreement with conclusions issued by scientists at the Australian Wine Research Institute (*3*, *25*). For cork closures, the typical

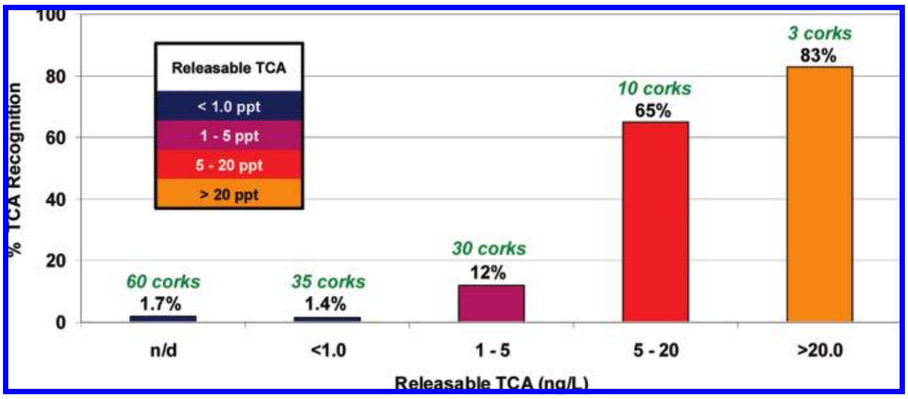

Figure 1. Percentage of TCA recognition in retained corks. RTCA: <1.0 ppt (blue bars), between 1.0 and 5.0 ppt (purple bar), between 5.0 and 20.0 ppt (red bar), and ≥20.0 ppt (orange bar). Bars also show the number of retained corks found in each RTCA group (**Table 4**).

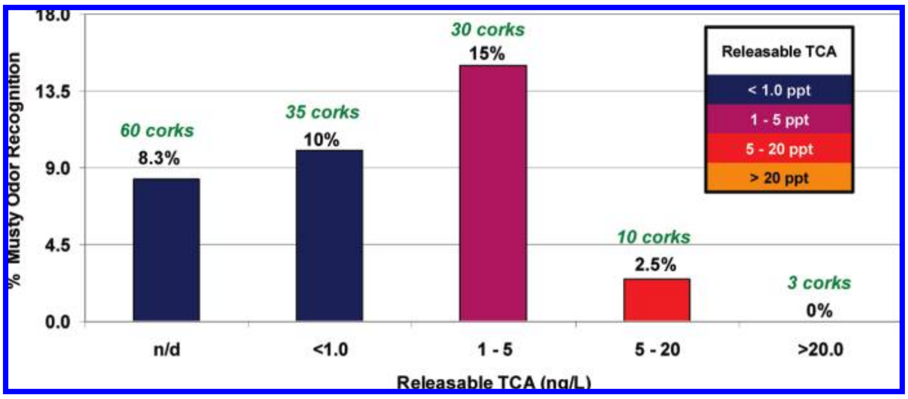

Figure 2. Percentage of musty odor recognition in retained corks. RTCA: <1.0 ppt (blue bars), between 1.0 and 5.0 ppt (purple bar), between 5.0 and 20.0 ppt (red bar), and ≥20.0 ppt (orange bar). Bars also show the number of retained corks found in each RTCA group (**Table 4**).

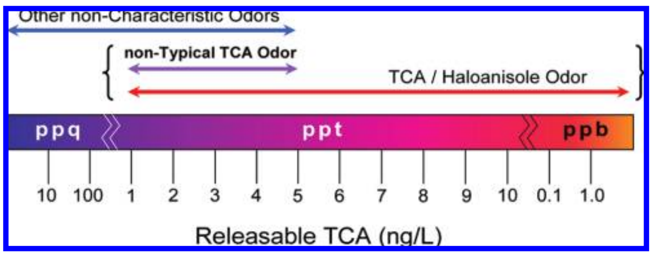

Figure 3. TCA odor was detected at RTCA above 1.0 ppt and recognized above 5.0 ppt. Non-typical TCA odors were recorded for RTCA values between 1.0 and 5.0 ppt. Other non-characteristic cork odors were recorded below the RTCA level of 5.0 ppt.

haloanisole taint aroma is indeed caused almost entirely by the presence of 2,4,6-trisubstituted chloroanisole, with very rare appearances of the di-, tetra-, and pentachloroanisoles. In comparison to the other halogenated anisoles, TCA is the major product of phenol chlorination (*7*), which is steered by the *ortho*- and *para*-directing hydroxyl (or methoxyl) group on the benzene ring (*26*).

By adding the 95 retained corks with RTCA levels of < 1.0 ppt (corks with nondetectable TCA and with RTCA levels of < 1.0 ppt) to the 2158 sensory accepted corks, a new total of 2253 corks (representing 98.1% of the total cork population) can be established exclusively on the basis of TCA cork taint. The balance or 1.9% of the total cork population (43 corks) could potentially exhibit different levels of cork taint caused by the presence of TCA. Of this number, 30 corks or 1.31% of the total cork population belong to the group of corks that contained RTCA levels between 1.0 and 5.0 ppt (non-typical TCA odor), 13 corks or 0.43% of the total population belong to closures with RTCA values between 5.0 and 20.0 ppt (TCA odor), and 3 corks or 0.13% of the total population belong to closures with RTCA values of 20.0 ppt or higher (high TCA odor). The new rearranged distribution of corks with various RTCA levels is shown in **Figure 4**.

Not all of the 43 corks with RTCA values higher than 1.0 ppt will inevitably taint their corresponding wine bottles. Pollnitz et al. (*25*) found no traces of TCA in few producer directly purchased wine bottles while recording significant amounts of RTCA in their corresponding corks. The authors attributed this discrepancy to the fact that the TCA on these corks was not homogeneously distributed all over the closure but rather localized, and the ultimate contamination would depend upon which end happens to be inserted into the bottle. This random event would definitely decrease the potential for cork taint outlined in the previous paragraph.

Finally, values reported in the past for taint incidence in wine bottles did not differentiate between actual TCA recognition and the effect of low TCA levels on wine aroma. TCA taint incidence studies have reported values as low as 0.5% and put in contrast frequencies of as high as 10% (*22*). However, frequently, no clarification is given to the type of taint, possible combination of recognized taint compounds and other non-characteristic cork odors, and even levels (concentration) of TCA present in the cork, which, as previously explained, can have diverse effects on the perceived cork odor. The relative low-frequency TCA taint found in this work (1.9% of the total population for corks with RTCA levels of 1.0 ppt or higher and 0.57% of the total population for

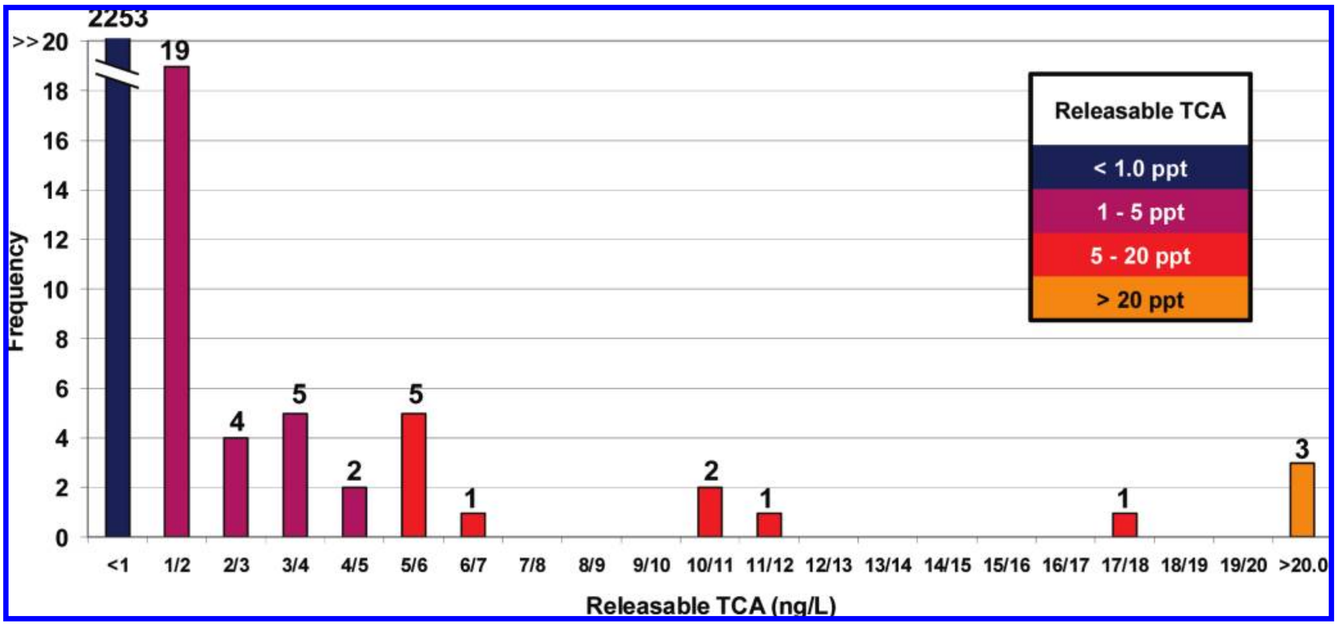

Figure 4. Releasable TCA distribution of 2296 large-format corks. RTCA: <1.0 ppt (blue bars), between 1.0 and 5.0 ppt (purple bar), between 5.0 and 20.0 ppt (red bar), and ≥20.0 ppt (orange bar).

corks with RTCA levels of 5.0 ppt or higher) is in part due to the good-quality cork material used by the industry to manufacture large-format corks. In addition, even though not all closures were treated with the Innocork process (*20*), the patented wash also contributed to the reduced TCA frequency in the overall cork population.

Other Non-characteristic Cork Odors. To the best of the authors' knowledge, most of the 471 sensory remarks (of a total of 847) recorded for the 2158 approved corks were inoffensive to the bottled wine. Most of the minty, vegetative, and peppery sensory remarks (**Table 1**) were found in approved corks. In addition to these odors, other descriptors of peculiar interest, such as buttery/dairy, eucalyptus, green pepper, medicinal/spicy, peanut, and woody, were also found at an appreciable frequency.

The origin and impact of these random non-characteristic cork odors on bottled wine is unknown. Natural corks bearing these types of odor descriptors could also be regarded as tainted. However, few winemakers believe these corks actually add serendipitous quality to individually selected bottles of varietals, with odors such as bell pepper for Cabernet Sauvignon wine and black pepper for Zinfandel wine (*27*). However, the cork industry is working diligently to eradicate them if not reducing their incidence. This will be the topic of a future research project.

Dry Soak Sensory Evaluation. Sensory screening by dry soak testing was found to be an effective method to identify and segregate tainted large-format corks. RTCA results of the 100 control corks proved that the method is effective against false-negative responses toward TCA taint, at least for the group of panelists used in this study.

A large number of corks were retained because of other non-characteristic cork odors different than the one caused by TCA. A total of 95 corks (60 with nondetected RTCA levels and 35 with RTCA levels of <1.0 ppt) only generated six TCA sensory remarks from six different corks, each with a 25% TCA recognition (one panelist in four). For the group of sensory panelists used in this work, this evidence proved that the method might have a small incidence of false-positive sensory responses toward TCA taint.

Dry soak screening for large-format corks was found to be a clean, quick, and, most important, a truly nondestructive method (compared to other methods used by the industry, such as vodka-soaking). The test could certainly be used for regular 24 mm diameter corks, but the requirements to meet industrial volumes would make it logistically impossible to implement.

Dry soak screening is not a quantitative method and, to a certain extent, can be used to qualify the culprit of a systemic taint in selected cork lots (either TCA or other nondesirable compound). The effectiveness of the method depends upon the make up of the sensory panel: size, industrial experience (training), and physiological capacities (*28*).

In the absence of GC/MS technology, dry soak sensory screening could well be used to determine cases of aroma-intense compound cross-contamination from packaging cardboard and wood materials (*29*, *30*, *6*). This method can be implemented for the approval of imported coffee beans, the material of another commodity industry that has suffered from TCA taint (*31*). The method could be suited as a QC protocol for the cooperage industry to approve incoming lots of oak wood (*32*).

ABBREVIATIONS USED

TCA, trichloroanisole; RTCA, releasable TCA; SPME, solid-phase microextraction; GC/MS, gas chromatography/mass spectrometry; ppt, parts per trillion; m/z, mass-to-charge ratio.

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