OCCURRENCE OF HALOANISOLE AND HALOPHENOL CONTAMINATION IN AGED RED WINES

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### OCCURRENCE OF HALOANISOLE AND HALOPHENOL CONTAMINATION IN AGED RED WINES

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OCCURRENCE OF HALOANISOLE AND HALOPHENOL
CONTAMINATION IN AGED RED WINES

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Abstract
This exhaustive study is the first to be carried out on the incidence of halophenols and haloanisoles in aged red wines, not only in terms of trichloroanisole. Nine hundred and sixty-six red wines of different ageing times (6, 12 and 24 months in oak barrels) and different Spanish production areas were analysed by stir bar sorptive extraction followed by GC/MS.

From the total sampling, 155 (16.1%) wines were contaminated with one or several compounds, with 7.6% of these corresponding to the aged-12 wine category, 6.9% to the aged-6 group and the rest to the aged-24 wines (1.5%). The most abundant compounds causing taint were 2,3,4,6-tetrachloroanisole and 2,4,6-trichloroanisol (6.8 and 5.3 %, respectively). No 2,4,6-tribromophenol was found in any of the samples. The contamination with halo- compounds was highest in the samples from the South-West of Spain, followed by those from the North. The mean concentration found for all compounds are always higher than their respective olfactory threshold, but neither of these halo compounds represent a health hazard to human subjects through the consumption of commercial red aged wines.

Keywords: Contamination, Haloanisoles, Halophenols, Aged red wine
Introduction

Musty taint, traditionally known as “cork taint”, is a serious problem for both wine and cork industries worldwide. This flavour-damaging effect is usually perceived as a mouldy, musty and/or earthy aroma that may mask the natural wine aroma and lessen its quality (Amon et al., 1989; Butzke et al., 1999; Fuller, 1995; Peña-Neira et al., 2000; Mazzoleni and Maggi et al., 2007). Although different compounds have been identified in relation to this alteration (guaiacol, geosmine or 2-metilisoborneol among others) (Maga, 1978), most authors agree that halophenols and haloanisoles, particularly chloroanisoles, are the primary compounds responsible for this problem (Butzke et al., 1999; Chatonnet et al., 2004; Silva-Pereira et al., 2000; Rubio-Coque et al., 2006). Other compounds such as 2,4,6-tribromoanisole (TBA) can be responsible for the “cork taint” when insufficient amounts of TCA or other chloroanisoles are detected in wines (Chatonnet et al., 2004).

Traditionally, and erroneously, the wine contamination with this off-flavour has been associated with the cork, and therefore the inappropriate used of the term “cork taint” has contributed to the spreading of the idea that contamination with chloroanisoles is always attributed to the cork stopper. Scientific data have shown that the true origin of the wine contamination by halophenols and haloanisoles is in fact a problem of environmental contamination. Blaming the cork stopper almost exclusively is too simplistic as there are many different sources of contamination. In fact, in some cellars, it is possible to detect contaminated wines that have never been in contact with cork, thus attributing the problem to other enological products that have been in contact with chlorine derivatives used as pesticides or cleaning products such as hypochlorite-based disinfectants (Chatonnet et al., 2004). These volatiles are easily transmitted through the air, and show a great capability for adhering and contaminating wood, cork and many other materials (plastic polymers, silicons, cardboard and paper, etc). Most studies also deal with chloroanisoles, especially TCA, due to their low olfactory thresholds, but chlorophenols are as important as they are considered their precursors. Chlorophenols may originate in several ways, the most accepted hypothesis being the O-methylation reaction by different microorganisms (especially fungi) (Álvarez-Rodriguez et al., 2002; Riu et al., 2002; Maggi et al., 2008). Many different microbes, e.g. common moulds such as Penicillium, Aspergillus, Trichoderma and even Botrytis cinerea can generate haloanisoles from halophenols (Lee and Simpson, 1993; Maggi et al., 2008). The most used halophenols have been especially pentachlorophenol (PCP) and 2,4,6-
trichlorophenol (TCP), which have been used as pesticides, although they were forbidden in
the European Union several years ago. However, they can persist in the ecosystems for a very
long time (Rubio-Coque et al., 2006). This problem also affects human health since the
precursors are considered as highly toxic (Armstrong et al., 1993; Fahrig et al., 1978; Jansson
Yet, international legislation only limits the content of some halophenols in drinking water (5
µg/L in TCP) (Iris, 1994), with nothing being said about haloanisoles. Soleas et al. (2002)
carried out a cytotoxicity study using TCA and TCP standard solutions up to a concentration
of 500 µg/L, with neither TCA nor TCP adversely affecting the viability of any of the cells
lines tested.

Despite being a great cause for concern for the wineries all around the world, there are many
discrepancies about its real incidence, and the quantification of the economic losses produced
by the contamination from these compounds. Most studies refer to TCA, and percentages
greater that the 7% have been not shown (Butzke et al., 1999; Fuller, 1995; Lee and Simpson,
1993; Pollnitz et al., 1996; Soleas et al. 2002). In the most exhaustive study, carried out by
Soleas et al. (2002), a panel of experts analysed more than 2,400 different wines from several
countries. The overall incidence of “cork taint”, only measured in terms of TCA, was 6.1%,
but those wines closed with composite corks demonstrated an incidence of 31.9%.
Differences were also observed between white and red wines with an incidence of 8.3% and
4.2%, respectively. Among red wines, the highest incidence was observed for Portugal (6.7%)
and Spain (6.5%), although only the 12.6% of the total sampling came from those two
countries.

For all these reasons, the occurrence of halophenols and haloanisoles, not only TCA, in nine-
hundred and sixty-six Spanish aged red wines has been analysed using SBSE-GC-MS. The
presence of the target compounds has been related to the different wine production areas and
other oenological parameters. Additionally, an estimation of halophenol and haloanisole
ingestion by Spanish red wine consumers has been carried out.

MATERIAL AND METHODS

Chemicals and reagents
Standards: 2,3,4,5,6-pentachloroanisole; 2,3,4,6-tetrachlorophenol; 2,3,4,6-tetracloroanisole; 2,4,6-tribromoanisole; 2,4,6-tribromophenol; 2,4,6-trichloroanisole; 2,4,6-trichlorophenol were obtained from Sigma-Aldrich (Madrid, Spain) and pentachloroanisole from LGC Promochem (Molsheim, France). Exact masses of the chemical standards were dissolved in absolute ethanol.

Solvents: ethanol (analytical-reagent grade) was obtained from Merk (Damstadt, Germany), while water was purified through a Milli-Q system (Millipore, Bedfords, MA, USA). Synthetic wine samples were prepared by an ethanol solution at 12 % (v/v) to which 5 g/l tartaric acid were added. Solution pH was adjusted to 3.6 with 1 M sodium hydroxide (Panreac, Barcelona, Spain).

Classical Oenological parameter analysis
The classic analyses of must and wines were performed according to the official methods established by the ECC (1990). The following parameters were analysed: pH, alcohol degree, and total acidity.

Stir Bar Sorptive Extraction (SBSE)
Compounds were extracted by introducing the polydimethylsiloxane coated stir bar (0.5 mm film thickness, 10 mm length, Twister, Gerstel, Mülheim and der Ruhr, Germany) into 10 ml of sample (either commercial wine or synthetic wine solution), to which 100 µl of internal standard γ-hexalactone solution at 6 µl/l in absolute ethanol was added. Samples were stirred at 700 rpm at room temperature for 60 min. The stir bar was then removed from the sample, rinsed with distilled water and dried with a cellulose tissue, and later transferred into a thermal desorption tube for GC/MS analysis (Zalacain et al., 2004).

TD-GC/MS analysis
The thermal desorption equipment (ATD 400 of Perkin-Elmer, Norwalk, USA) was coupled to the gas chromatograph. The stir bar was introduced into the thermal desorption tube and the volatile compounds were desorbed from the stir bar at the following conditions: oven temperature at 330 ºC; desorption time, 4 min; cold trap temperature, –30 ºC; helium inlet flow 45 ml/min. The compounds were transferred into the Hewlett-Packard 6890 gas
chromatograph coupled to an Hewlett-Packard mass detector (Palo Alto, USA) with a fused silica capillary column (BP21 stationary phase 50 m length, 0.22 mm i.d., and 0.25 µm film thickness) (SGE, Ringwood, Australia). The chromatographic program was set at 50 °C (held for 5 min), raised to 180 °C at 2.5 °C/min (held for 2 min) and to 230 °C (5 °C/min) and held for 20 min. For mass spectrometry analysis, electron impact mode (EI) at 70 eV was used. The mass range varied from 35 to 500 u and the detector temperature was 150 °C. Identification was carried out by comparing with their respective standards and using the NIST library. Quantification was carried out by using the extracted ion mode, with their respective m/z, and it was based on the calibration curves of standards in the synthetic wines (Zalacain et al., 2004). Triplicate analysis was carried out for all wines.

Wine Samples

One of the most tedious tasks of this study was the selection of samples, as the authors wanted to have the widest and most realistic wine sample distribution from the consumer point of view. A planned and randomised sampling taking into account the information provided by the Spanish Ministry of Agriculture, Fisheries and Food (MAPA, 2004) on domestic trade and wine production volume which affirmed that 95% of the Spanish Origin Designations (OD) produced more than 30,000 hl, was used for experimental sampling design. Wine selection was carried out in local supermarkets of 8 Spanish cities according to the data obtained, where four OD (Rioja, Mancha, Ribera del Duero and Valdepeñas) represented approximately 72% of all commercialized red wines. The selection of the other Spanish OD for this study was based on the information given by the MAPA, although an effort was made to include the different geographical wine production areas. Due to the great number of samples and the exhaustive consumption study of red wines obtained through ACNielsen consulting, all OD have been grouped according to the areas (ACNielsen, 2004) defined as follows: area 1: Priorato, Terra Alta, Costers del Segre, Cariñena, Penedés and Somontano; area 2: Jumilla, Valencia, Utiel-Requena; area 3: Guadiana; area 4: Mancha, Valdepeñas, Toro and Vinos de Madrid; area 6: Ribera del Duero, Navarra and Rioja. No wines from area 5 were bought as mainly white wines are produced.

For this study, only aged red wines of the highest quality have been chosen. According to the Spanish legislation and in agreement with the Regulatory Council for Origin Appellations, there are three oak-aged red wines categories. These categories establish a minimum period of
time in oak barrels of 6, 12 and 24 months, all of which require another period in bottle before
being eligible for sale at 18, 24 and 36 months, respectively. The total number of samples
analysed were 966 quality Spanish aged red wines from three different categories named as
aged-6, aged-12 and aged-24 (Table 1).

Statistical analysis

Data was processed by the Answer Tree 3.0, SPSS 14 and Unscrambler 9.0 using the CART
method (Classification And Regression Trees) which is an binary algorithm developed by
Breiman et al., (1984). CART divided the data into two subsets, so cases falling within each
of the subsets are more homogeneous than in the previous subset. It is a recursive process that
repeats itself until reaching the criterion of homogeneity or another criterion for stopping. The
same predicting variables can be used several times at different levels of the tree.

RESULTS AND DISCUSSION

Due to the discrepancies found about the impact of halophenols and haloanisoles
contamination in quality wines, 966 different aged red wines were analysed (Table 1). It is
important to point out that this study is not only concerned with TCA as most studies are, but
with the most important halophenols and haloanisoles related to this wine off-flavour defect
(Maarse et al., 1988, Tanner et al., 1981). The study has revealed that 155 wine samples were
contaminated with one or several compounds, which means the 16.1% of the total sampling.
Of these 155 tainted cases, the 7.6% correspond to the aged-12 wines category, the 6.9% were
aged-6 and the rest were aged-24 wines (1.5%). This tendency is not related with the
wineries’ belief that the longer the time in the oak barrels, the higher the possibility of
detecting such off-flavours (personal communications). No conclusions can be reached when
the different aged categories of contaminated wines were compared with the geographical
production areas (Table 1), as areas 1, 3 and 4 showed that aged-6 red wines where more
contaminated than the other categories and in areas 2 and 6 contamination was associated
with the aged-12 wines and aged-6 red wines. Without distinction of wine categories, area 3 is
the one with the highest incidence of tainting compounds (37.5%), followed by areas 6
(18.2%) and 1 (16.1%).
As it can be observed in Table 2, from the seven target compounds analysed, TCA and TeCA were the most abundant, 5.3% and 6.8% respectively, followed by TCP. The higher percentage of TeCA and TCP is quite surprising, as both are potential precursors of TCA although conversion takes place through different pathways (Maarse et al., 1988, Tanner et al., 1981). The higher occurrence of the tainting compounds was observed in aged-12 red wine (Table 3). Looking at Table 2, it is worthy of mention that in area 3, the most contaminated area, no TCA or TeCA was detected, but PCA (12.5%) and specially TCP (25%) were found. Those wines may be not be rejected by wine consumers for the moment as TCP and PCA olfactory thresholds are higher than TCA, but their evolution is of great importance in terms of TCP conversion into TCA. Area 6 has a 18.2% of their total wine sampling, with TeCA being the most abundant compound (9.3%) followed by TCA (5.9%), and with PCA, TCP and TBA (Table 2) showing lower values. The 16.1% of the wines analysed for area 1 have shown TCP as the one with the highest percentage (8.8%), whereas the remaining compounds (TCA, TeCA, PCA and TBA) do not surpass the 3.6%. In area 4, although the percentage of contamination is lower (11.5%) than area 6, the type of compounds found and the frequency at which they are detected are similar. In this case, TeCA is the most abundant haloanisole, followed by TCA, while under 4% of the wines analysed are contaminated with the other tainting compounds. Lastly, in area 2 showed a contamination of 9.8%, with TCA the most abundant (4.5%). Below 3%, TeCA, PCA and TCP are detected. Special mention should be made for TBA and TBP contamination, as Chatonnet et al., (2004) indicated that both compounds seem mainly to derive mainly from environmental pollution in wineries. TBP derivatives are often used as flame retardants in a broad range of materials, thus raising the risk of pollution. In this study, TBP has not been found in any of the wines analysed, but TBA has always been detected at a percentage lower than 3%.

A uniform contamination distribution in terms of geographical areas can be observed, as areas 1 and 6 are grouped within the northern zone of Spain followed by areas 2 and 4 which corresponded with the east-central zone of the Spanish mainland. It is not possible to affirm that cork stoppers are the only elements responsible for such contamination, as the contamination pattern found within this sampling in terms of wine production areas is not in accordance with such an affirmation. This does not mean that wineries from the north of Spain use stoppers of poorer quality than, for example, the centre-east. Such taint distribution, south-west of Spain (area 3) > northern (area 1 and 6) > centre-east (areas 2 and 4) may be attributed to the effect of the environmental conditions on the microorganism propagation...
when are exposed to polluted zones of halophenols in the wineries (Rubio-Coque et al., 2006). The western (area 3) and northern (areas 1 and 6) parts of Spain are characterized by their high humidity conditions (MAPA, 2004) (Table 4). The size of the microbial population significantly increases with humidity (Alvarez-Rodriguez et al. 2002), and may justify why these areas are the most contaminated of course if enough sources of precursors are present. Evidently it is not possible to conclude that the humidity conditions are the only responsible for the higher contamination, but wooden deposit use for winemaking in some cellars of these areas may be important on this occurrence.

In addition, the mean concentration of the compounds found in the contaminated wines are higher than their respective olfactory thresholds (Table 5), which means that consumers will perceived them with clarity in taste and smell, and therefore reject those wines. Such high concentrations suggest that cork stoppers are not the only factor responsible for this wine off-flavour, along with the fact that cork factories have diminished TCA by about 75% in recent years, a consequence of the many controls adapted to avoid such contamination (Rubio-Coque et al., 2006). Other studies reveal as well that cork stoppers can only contaminate the wine when the haloanisoles are located on the surface in contact with the wine (Pollintz et al., 1996). However, Capone et al. (1999, 2002) goes further by stating that only occasionally does more than the 10% of the TCA from the cork leach into the bottled wine and, in most cases, TCA cork does not leach into wine at all. In this way, the concentration found in the wines is again too high to be transferred from the cork stopper (Table 5).

Consumers are an important part of this problem. In 2004/05 red wine from OD was bought in 8,191,603 Spanish households, i.e. 55.5% of the total national, with areas 4 and 6 having the highest consumption percentage, 24.4 and 54.1% respectively (Table 6). For each purchase, 1.8 l of wine per person/month is calculated (MAPA, 2004). The average size of a Spanish household is 2.9 persons and, when considering the average consumption of red wine with OD and the average number of occupants per home, a common wine consumer will drink an average of 8.8 l / year. If this consumption data is related to the occurrence of halophenols and haloanisoles in aged red wines presented in Table 1 and considering the only toxicity normative available for TCP, 5 µg L⁻¹ in drinking water for TCP is acceptable, the mean concentration of tainting compounds found in those wines will never be a problem for quality red wine consumers, even if they are unfortunate enough to only buy contaminated wines from areas 1, 3 and 6. If these results are compared with a previous study done by...
Soleas et al., (2002) where the concentration limits are fixed at 500 µg/L (TCA and TCP), then we could conclude that neither of these halo compounds represent a health hazard to human subjects through the consumption of commercial aged red wines. It is important to point out that no other toxicity information has been found in relation to the other halophenols and haloanisoles in any other matrixes, and of course not in wines, leaving an via open for future research.

In order to get more information about the incidence on this problem, another statistical analysis was carried out including decision trees which related the percentage of contaminated wines with the areas studied, together with the aged wine categories (Figure 1). The first division is carried out according to the wine age category, finding significant differences between the aged-12 wines (20.7 %) and the other two aged wine categories (aged-6 and aged-24 wines, 13.4 %). Looking first at aged-12 wines, there is a variability which takes into account the geographical wine areas, where areas 1 and 6 (northern Spain) were the most contaminated (23.5 %) followed by 12.9 % in the remaining wine making areas. In relation to the other group of aged wines (6 and 24-aged), the statistical analysis revealed significant differences between the area 3 and the other areas studied, confirming the early data discussed. In fact, the 50% of the analysed wines from area 3 have any of the haloanisoles and halophenols studied, while this percentage is not higher than the 12.7% for the rest of the areas.

Classical wine parameters such as pH, total acidity and alcoholic degree were used within the decision trees as differentiating variables for contaminated wines in order to obtain more information about their possible effect on the wines. As there was too much data to process for each parameter, four sub-groups have been differentiated according to: alcohol (11-11.9%, 12-12.9%, 13-13.9% and 14-14.9%); pH (<3.2, 3.2-3.4, 3.4-3.6, > 3.6) and total acidity (between 4-4.9, 5-5.9, 6-6.9 and 7-7.9 g/l of tartaric acid). But no correlation was found and therefore no decision tree was shown. The same results were obtained by other authors when the extraction of TCA at different alcohol degrees was followed, but no conclusions could be obtained as the opposing effects of increased TCA extraction and loss of TCA volatility at high ethanol levels tend to cancel each other out (Hervé et al., 1999). This same effect is likely to hold for sensory analysis as well, as Mazzoleni and Maggi (2007) carried out an exhaustive sensory analysis and confirm that the detection level of TCA in red wines cannot
be correlated with analytical parameters such as character ethanol, sugar content, pH, and total acidity, whereas a positive differentiation can be carried out with white wines.

Conclusions

This exhaustive study is the first to be carried out on the incidence of all halophenols and haloanisoles in red aged wines, and not only in terms of TCA. The study has revealed that 16.1% of the total wine sampling was contaminated with one or several compounds, with the most contaminated wines being those aged for at least 12 months, followed by aged-6 and aged-24 months wines. Although the most abundant tainting compounds are TeCA and TCA, special attention should be given to the high concentrations of TCP, precursor of TCA. Due to the mean concentration of tainting compounds and the geographical areas distribution, the cork stopper is not the only factor responsible for such taint incidence since the south-western and northern areas of the Spanish mainland are the most contaminated, coinciding with the areas with the highest humidity conditions, ideal conditions for microorganism propagation. However, other sources of contaminations to be taking into account in these areas can be the wooden materials used during winemaking. Despite their possible economic damage to the wine industry, even the highest concentration encountered in commercial aged red wines is several orders of magnitude below the levels that may be harmful to human health.

References


Maggi L, Mazzoleni V, Fumi MD, Salinas M R. 2008. Transformation ability of fungi isolated from cork and grape to produce 2,4,6-trichloroanisole from 2,4,6-trichlorophenol. Food Add Contam. DOI: 10.1080/02652030701522991


Contaminated wines

Node 0
Category | %  | n
---|---|---
no       | 83.95 | 811
yes      | 16.05 | 155
Total (100.00) | 966

Aged Wine Category
Improvement=0.0025

---

Node 1
Category | %  | n
---|---|---
no       | 79.28 | 532
yes      | 20.72 | 82
Total (63.56) | 614

Areas Improvement=0.0016

---

Node 2
Category | %  | n
---|---|---
no       | 86.84 | 532
yes      | 13.16 | 82
Total (83.56) | 614

Areas Improvement=0.0034

---

Node 3
Category | %  | n
---|---|---
no       | 76.45 | 198
yes      | 23.55 | 61
Total (26.81) | 259

Areas Improvement=0.0002

---

Node 4
Category | %  | n
---|---|---
no       | 87.10 | 81
yes      | 12.90 | 12
Total (9.63) | 93

---

Node 5
Category | %  | n
---|---|---
no       | 87.38 | 526
yes      | 12.62 | 76
Total (62.32) | 602

---

Node 6
Category | %  | n
---|---|---
no       | 50.00 | 6
yes      | 50.00 | 6
Total (1.24) | 12

Node 15
Category | %  | n
---|---|---
no       | 75.47 | 160
yes      | 24.53 | 52
Total (21.95) | 212

Node 16
Category | %  | n
---|---|---
no       | 80.85 | 38
yes      | 19.15 | 9
Total (4.87) | 47

---

Figure 1.- Decision tree which related the percentage of contaminated wines with the studied areas and the wine aged categories.
Table 1.- Distribution of aged red wine sampling and the percentage of contamination according to the aged wine category and geographical production area.

<table>
<thead>
<tr>
<th>AREA</th>
<th>Number of analysed wines</th>
<th>% of Contaminated Wines</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Aged-6</td>
<td>Aged-12</td>
</tr>
<tr>
<td>AREA 1</td>
<td>81</td>
<td>47</td>
</tr>
<tr>
<td>AREA 2</td>
<td>67</td>
<td>37</td>
</tr>
<tr>
<td>AREA 3</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>AREA 4</td>
<td>100</td>
<td>52</td>
</tr>
<tr>
<td>AREA 6</td>
<td>243</td>
<td>212</td>
</tr>
</tbody>
</table>

| Total | 503   | 352     | 111    | 966   |
Table 2.- Percentage of the contaminated wines depending on the area studied versus the total wine sampling

<table>
<thead>
<tr>
<th>AREA</th>
<th>TCA</th>
<th>TeCA</th>
<th>PCA</th>
<th>TCP</th>
<th>TeCP</th>
<th>TBA</th>
<th>TBP</th>
<th>% contaminated wines</th>
</tr>
</thead>
<tbody>
<tr>
<td>AREA 1</td>
<td>3.7</td>
<td>2.2</td>
<td>0.7</td>
<td>8.8</td>
<td>0</td>
<td>2.9</td>
<td>0</td>
<td>16.1</td>
</tr>
<tr>
<td>AREA 2</td>
<td>4.5</td>
<td>1.8</td>
<td>2.7</td>
<td>1.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>9.8</td>
</tr>
<tr>
<td>AREA 3</td>
<td>0</td>
<td>0</td>
<td>12.5</td>
<td>25.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>37.5</td>
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<tr>
<td>AREA 4</td>
<td>5.7</td>
<td>6.9</td>
<td>1.1</td>
<td>4.0</td>
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<td>5.9</td>
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<td>4.0</td>
<td>0.4</td>
<td>1.7</td>
<td>0</td>
<td>18.2</td>
</tr>
</tbody>
</table>

Note: TCA (2,4,6-trichloroanisole); TeCA (2,3,4,6-tetrachloroanisole); PCA (pentachloroanisole); TCP (2,4,6-trichlorophenol); TeCP (2,3,4,6-tetrachlorophenol); TBA (2,4,6-tribromoanisole); TBP (2,4,6-tribromophenol).
Table 3.- Percentage of cork taint wines according to the different aged wine categories and the compounds found.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Aged-6</th>
<th>Aged-12</th>
<th>Aged-24</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCA</td>
<td>2.1</td>
<td>7.7</td>
<td>0.8</td>
<td>5.3</td>
</tr>
<tr>
<td>TeCA</td>
<td>2.8</td>
<td>9.0</td>
<td>1.6</td>
<td>6.8</td>
</tr>
<tr>
<td>PCA</td>
<td>0.9</td>
<td>4.1</td>
<td>0.8</td>
<td>2.8</td>
</tr>
<tr>
<td>TCP</td>
<td>2.7</td>
<td>4.4</td>
<td>1.1</td>
<td>4.8</td>
</tr>
<tr>
<td>TeCP</td>
<td>0.2</td>
<td>0.3</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td>TBA</td>
<td>0.6</td>
<td>1.9</td>
<td>1.1</td>
<td>1.8</td>
</tr>
<tr>
<td>TBP</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>TOTAL</td>
<td>6.9</td>
<td>19.9</td>
<td>4.1</td>
<td>16.1</td>
</tr>
</tbody>
</table>

Note: TCA (2,4,6-trichloroanisole); TeCA (2,3,4,6-tetrachloroanisole); PCA (pentachloroanisole); TCP (2,4,6-trichlorophenol); TeCP (2,3,4,6-tetrachlorophenol); TBA (2,4,6-tribromoanisole); TBP (2,4,6-tribromophenol).
Table 4.- Humidity data 2004/2005 of the different geographical production areas and the percentage of contaminated wines.

<table>
<thead>
<tr>
<th>AREA</th>
<th>Humidity (mm)</th>
<th>% contaminated wines</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>444.6</td>
<td>16.1</td>
</tr>
<tr>
<td>2</td>
<td>357.5</td>
<td>9.8</td>
</tr>
<tr>
<td>3</td>
<td>450.0</td>
<td>37.5</td>
</tr>
<tr>
<td>4</td>
<td>383.6</td>
<td>11.5</td>
</tr>
<tr>
<td>6</td>
<td>505.2</td>
<td>18.2</td>
</tr>
</tbody>
</table>
Table 5.- Mean concentrations of the halophenols and haloanisoles detected in the 966 quality red wines.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>OT [ng L⁻¹]</th>
<th>Mean Concentration [ng L⁻¹]</th>
<th>Concentration Range [ng L⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCA</td>
<td>5-10</td>
<td>76.5</td>
<td>546-2.6</td>
</tr>
<tr>
<td>TeCA</td>
<td>14-25</td>
<td>68.4</td>
<td>775-2.2</td>
</tr>
<tr>
<td>PCA</td>
<td>4000</td>
<td>64.9</td>
<td>454.3-2.3</td>
</tr>
<tr>
<td>TCP</td>
<td>Unknown</td>
<td>115.3</td>
<td>521.22-4.55</td>
</tr>
<tr>
<td>TeCP</td>
<td>Unknown</td>
<td>12.5</td>
<td>30.5-.3.4</td>
</tr>
<tr>
<td>TBA</td>
<td>8</td>
<td>272.5</td>
<td>847.3-10.6</td>
</tr>
<tr>
<td>TBP</td>
<td>Unknown</td>
<td>0.0</td>
<td>0</td>
</tr>
</tbody>
</table>

Note: TCA (2,4,6-trichloroanisole); TeCA (2,3,4,6-tetrachloroanisole); PCA (pentachloroanisole); TCP (2,4,6-trichlorophenol); TeCP (2,3,4,6-tetrachlorophenol); TBA (2,4,6-tribromoanisole); TBP (2,4,6-tribromophenol); OT (Olfactory Threshold)
Table 6.- Red wine distribution according to the different geographical areas and relation with the contaminated wines studied.

<table>
<thead>
<tr>
<th>AREA</th>
<th>% Red wine consumption</th>
<th>% Contaminated wines</th>
<th>Contaminates wines in the market</th>
</tr>
</thead>
<tbody>
<tr>
<td>AREA 1</td>
<td>11.8</td>
<td>16.1</td>
<td>1.9</td>
</tr>
<tr>
<td>AREA 2</td>
<td>9.4</td>
<td>9.8</td>
<td>0.9</td>
</tr>
<tr>
<td>AREA 3</td>
<td>0.3</td>
<td>37.5</td>
<td>0.1</td>
</tr>
<tr>
<td>AREA 4</td>
<td>24.4</td>
<td>11.5</td>
<td>2.8</td>
</tr>
<tr>
<td>AREA 6</td>
<td>54.1</td>
<td>18.2</td>
<td>9.9</td>
</tr>
</tbody>
</table>