Differences between Swedish, French and American oak when storing whisky analysed by GC-MS.

By: Carl Remmer
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Abstract (English)

This study describes how to analyse 12 different volatile oak related compounds in whisky using a gas chromatograph (GC) coupled to a mass spectrometer (MS). This is done in a way that makes it possible to characterize the properties of Swedish oak in comparison to American and French oak. The different parameters that contribute to the variation in these compounds studied in this report are the origin of the oak wood, the size of the barrel, the time the whisky is stored and the toasting degree of the barrel. Different diagrams are made to visualize the differences in compound concentration the different treatments and maturation periods in-between.

The results propose that differences between origins, toasting and barrel size could be made. But since the whiskies are still under maturation, no final taste profile could be made.

Abstract (Swedish)

Denna studie beskriver hur 12 olika volatila ämnen som finns i ek analyseras i whisky. Detta görs med en gaskromatograf (GC) kopplad till en masspektrometer (MS). Detta görs för att kunna karaktärisera svensk ek i jämförelse med amerikansk och fransk ek. De olika parametrarna som bidrar till olikheterna i koncentration av dessa ämnen är varifrån eken kommer, storleken på tunnan, hur länge whiskyn har lagrats och vilken rostningsgrad tunnan har. Det är dessa parametrar som undersöks i denna rapport. Olika diagram upprättas för att visualisera skillnaderna i koncentration mellan olika lagringstider och behandlingar av tunnorna. Eftersom whiskyn fortfarande lagras kunde inte en slutlig smakprofil fastställas.
1. Introduction

1.1 Aim

The aim of the project was to analyse the influence that different storage conditions have on the taste of whisky during maturation. Four different parameters where analysed. The first one was what kind of oak the barrel was made of, either Swedish oak (*Quercus Robur*), French oak (*Quercus Petraea*) or American white oak (*Quercus Alba*). The second was the size of the barrel either 25, 100 or 225 litres. The third one was the degree of toasting of the barrel (lightly burned, medium burned, hard burned or charred). The fourth one was the time the whisky had been in the barrel before the analysis. Twelve different target compounds where looked for in a gas chromatograph coupled to a mass spectrometer. Theses compounds where furfural, 5-methyl furfural, furfuryl alcohol, guaiacol, cis and trans whisky lactone, 4-methyl guaiacol, eugenol, syringol, 5-hydroxy methyl furfural, vanillin and syringol aldehyde.

1.2 Background to the project

In 2011 professor Bert van Bavel started a project together with the master cooper Johan Thorslund at Thorslundkagge AB. Professor van Bavel analysed the characteristics of Swedish oak in comparison to French and American Oak when making barrels for wine and whisky. The barrels for the project where filled in August 2011, and samples where taken from the barrels at various times, to be able to study the maturation process. In this report samples ranging from 13-11-11 to 14-08-12 will be analysed.

Keywords: Whisky, GC-MS, maturation, Swedish oak, volatile compounds
1.3 Background to whisky aging

To start the process of making whisky, barley is being germinated briefly to release the enzymes that convert starch to sugar, which finally is turned into alcohol. The aim is to turn as much of the starch into sugar as possible, because this gives the highest possible yield of alcohol. Then yeast is added and the mixture is let to ferment for about three days to concentrate the alcohol, before going into the next step of the process, distillation. After the distillation, this colourless liquid (which is not yet allowed to be called whisky) is tapped into oak barrels. This liquid already contains some of the compounds that contribute to the final flavour, for example phenols, esters, aldehydes and some nitrogen and sulphur containing compounds. (Gill 2008)

But it is in the barrel the interesting reactions happen. Maturation can be considered replacement of sharp, harsh, mushy and sour notes in new distillates with smooth, matured tenderness in the final beverage. (Lee 2011)

Oak has long been the wood of choice in barrels for wine and other alcoholic beverages, this is because of its physical and chemical properties. The mechanical properties because it’s a workable type of wood, hence making barrels of it is possible and the physical properties are just right for storing alcoholic beverages in containers made of it. (Cadahía 2014)

There are three main types of reactions that happen in the barrel, additive, subtractive and interactive. The subtractive reactions happen when compounds, for example sharp sulphur compounds like dimethyl sulphide, are lost through the pores of the timber. The additive reactions take place when oxygen diffuses into the barrel through the wood and reacts with both the spirit and the wood. Both alcohols and aldehydes are oxidised while acids react with ethanol to form some of the most aromatic whisky flavour compounds – esters. (Gill 2008)

Before the barrel is ready for the liquid, it is toasted (or charred) over an open flame on the inside. The cooper does this process by hand and therefore every barrel is unique. This technique results in a layer of active carbon on the inside of the barrel that removes some of the unwanted compounds that contribute to an off taste. When introducing the barrel to the fire it also starts the breakdown of compounds such as lignin in the wood. (Gill 2008) Lignin then undergoes ethanolysis and form aromatic compounds (such as vanillin and phenols) that contribute to the taste of the whisky stored in the barrel. The golden brown/caramel colour of the final product is achieved by maturation in the toasted barrels, where Melanoidins from the cellulose breakdown during the toasting process reacts with the contents of the barrel. The barrels in which the whisky is stored cannot be too large, because the maturation process is dependent on the wood area versus the volume of the beverage. (Gill 2008)
First after three years of storage in the barrel the content can, legally, be called whisky. However storage for longer than three years is customary to achieve the right taste, Scottish whisky for example is often stored for a minimum of eight years. (Gill 2008)

1.4 Volatile compounds in oak

To be able to understand the final aroma of a beverage that has been matured in an oak barrel, the analysis of the volatile aroma compounds, for example lactones and volatile phenols (Cortés-Rojas 2014) released by the oak wood is the key. These volatile compounds have low aroma thresholds; therefore sensorial detection of these aromas takes place at very low concentrations in the mature beverage. They are also very important for some different fragrances of the mature beverage, like caramel, woody, vanilla etc. (Ducousso 2007). However the levels of the volatile compounds can vary depending on different parameters, for example the origin of the oak as well seasoning in the oak in open-air before the barrel making process starts. Another parameter that greatly can vary the levels of the volatile compounds is the degree of toasting of the oak barrel. (Cadahía 2014).

To be classified as a volatile compound it has to have an initial boiling point ≤ 250°C at standard atmospheric pressure, 101.3 kPa. (EU 2004/42/CE).

Trans Whisky lactone – woody, coconut taste (Lee 2011).

Cis Whisky lactone – Strong spicy coconut taste (Lee 2011).

Syringaldehyde – spicy, woody taste (Lee 2011).

Furfural – Cooked sugar taste. Aroma threshold 280 ppb-8ppm, taste threshold 30 ppm (Burdock 2002).

Guaiacol – smoky taste and sweet aroma. Aroma threshold 3-31 ppb (Burdock 2002).

Eugenol – spicy, clove leaf taste. Aroma threshold 6-100 ppb (Burdock 2002).

5-Methylfurfural – almond, caramel taste (Lee 2011).

Methylguaiacol – spicy, leather taste. Vanilla aroma threshold 90ppb, taste threshold 65 ppb (Fazzalari 1978).

Syringol – smoky, phenolic, bacon, woody taste. Aroma threshold 400 ppb – 1.85 ppm, taste threshold 60 ppm (Burdock 2002).

Hydroxymethylfurfural – sweet, caramel, coffee taste (Lee 2011).

Furfuryl alcohol – burning bitter aroma threshold 1-2 ppm, taste threshold 50 ppm (Burdock 2002).

All compounds are drawn at https://www.emolecules.com/.
2. Theory

2.1 Experimental design

Since this project is a continuation of the project that professor van Bavel started in 2011, the experiment will be set up in the same way so that the results are in a continuing time series from his work and can be compared to the results achieved now.

2.2 Gas Chromatography Mass Spectroscopy – basic principles

The traditional approach when analysing volatile compounds have been to use a gas chromatograph coupled to mass spectrometry. Together these two instruments can both detect and quantify compounds in complex mixtures.

To be able to analyse a compound in the GC it has to be volatile (meaning it must be able to vaporize without significant breakdown under 400°C), or else the compound can’t move through the column by the carrier gas.

2.3 The Gas Chromatograph

The gas chromatograph consists of an injector, a tank with carrier gas, an oven, a column and a detector.

The main principles of the gas chromatograph is the following, an inert gas (usually helium) flows continuously through the injector, the column and the detector, with a constant rate. This is the mobile phase, and the purpose of this gas is to carry the sample through the system without interacting with it. The sample is then injected with a microsyringe through a septum (which acts as a barrier between the high pressure inside the GC and the ambient pressure outside) into the heated injection port. The injection can either be done with an autosampler, which consists of a robotic arm that automatically injects the same volume of up to 100 samples or be done by hand (McNair 1998).

When the sample is injected it vaporises and moves into the column where the separation occurs. The separation occurs because the compounds in the sample move differently between the stationary phase and the mobile phase due to their properties. How fast a compound travels through the GC system is a function of its boiling point and its solubility with the stationary phase. The oven temp is increased during the time of analysis to be sure that the separation continues (McNair 1998).
2.4 The detector

After the column the compounds passes the detector that measures the quantity of the samples and generates an electrical signal (McNair 1998). The detector has to be in a high vacuum environment ($<10^{-5}$ torr), because electrons and ionized compounds cannot exist long enough to reach the detector if air is present. Because if air is present, the electrons and ionized compounds will collide with the air molecules in the analyser (McMaster 1998). This electrical signal is then transferred to a data system that generates a chromatogram. The signals from the detector are proportional to the amount of the analyte, therefore quantitative analyses are possible. The area of the peak determines how much of the compound is present, and the retention time is measured at the apex (highest point) of the peak.

The most commonly used detector is the Flame Ionization Detector (FID) that has characteristics such as high sensitivity, linearity, relative simplicity and is inexpensive.

The detector is the part of the GC that determines how low the LOD (Limit Of Detection) is. (McNair 1998)

3. Experimental

3.1 Chemicals

The chemicals used where furfural (99%), 5-methyl furfural (99%), furfuryl alcohol (99%), guaiacol, cis and trans whisky lactone (98%), 4-methyl guaiacol (99%), eugenol (99%), syringol (99%), 5-hydroxy methyl furfural (99%), vanillin (99%) and syringaldehyde (98%), all from Sigma Aldrich (USA). And ethanol absolute (99.96%) from VWR chemicals (USA).
3.2 Sample preparation

The whisky was sampled by professor van Bavel four times (2013-11-11, 2014-02-10, 2014-05-16) and by myself one time (2015-04-16). When I took the samples they were taken with a syringe directly out of the barrels at Thorslundkagge AB. The whisky samples had a volume of 0.5 ml and where diluted 1:4 with methanol to avoid saturation of the GC-MS. They were then stored in the freezer to avoid that the volatile compounds would evaporate. The samples where labelled as in table 1.

<table>
<thead>
<tr>
<th>Name of sample</th>
<th>Origin of oak</th>
<th>Toasting degree</th>
<th>Size of barrel</th>
</tr>
</thead>
<tbody>
<tr>
<td>SL 1-3</td>
<td>Swedish</td>
<td>Light</td>
<td>25 L</td>
</tr>
<tr>
<td>SM 1-3</td>
<td>Swedish</td>
<td>Medium</td>
<td>25 L</td>
</tr>
<tr>
<td>SH 1-3</td>
<td>Swedish</td>
<td>Hard</td>
<td>25 L</td>
</tr>
<tr>
<td>SK 1-3</td>
<td>Swedish</td>
<td>Charred</td>
<td>25 L</td>
</tr>
<tr>
<td>AL</td>
<td>American</td>
<td>Light</td>
<td>25 L</td>
</tr>
<tr>
<td>AM</td>
<td>American</td>
<td>Medium</td>
<td>25 L</td>
</tr>
<tr>
<td>AH</td>
<td>American</td>
<td>Hard</td>
<td>25 L</td>
</tr>
<tr>
<td>AK</td>
<td>American</td>
<td>Charred</td>
<td>25 L</td>
</tr>
<tr>
<td>FL</td>
<td>French</td>
<td>Light</td>
<td>25 L</td>
</tr>
<tr>
<td>FM</td>
<td>French</td>
<td>Medium</td>
<td>25 L</td>
</tr>
<tr>
<td>FH</td>
<td>French</td>
<td>Hard</td>
<td>25 L</td>
</tr>
<tr>
<td>FK</td>
<td>French</td>
<td>Charred</td>
<td>25 L</td>
</tr>
<tr>
<td>SL4</td>
<td>Swedish</td>
<td>Light</td>
<td>100 L</td>
</tr>
<tr>
<td>SM4</td>
<td>Swedish</td>
<td>Medium</td>
<td>100 L</td>
</tr>
<tr>
<td>SH4</td>
<td>Swedish</td>
<td>Hard</td>
<td>100 L</td>
</tr>
<tr>
<td>SK4</td>
<td>Swedish</td>
<td>Charred</td>
<td>100 L</td>
</tr>
<tr>
<td>SM5</td>
<td>Swedish</td>
<td>Medium</td>
<td>225 L</td>
</tr>
<tr>
<td>SK5</td>
<td>Swedish</td>
<td>Charred</td>
<td>225 L</td>
</tr>
</tbody>
</table>

*Table 1. Sample name, oak origin, toasting degree and barrel size.*

A standard stock solution was prepared that contained all the compounds mixed in ethanol. ~10 milligram of each solid compound was weighted and 10 µl of each liquid was put in a 10 ml volumetric flask, and the flask was filled with ethanol to the mark. This stock solution was diluted as shown in figure 2. This stock solution was always stored in the freezer to avoid that the volatile compounds would evaporate.
The dilutions with the concentrations 100, 10, 1, 0.1, and 0.01 were used in the calibration curve.

Before each run of samples, three vials with ethanol were run through the GC system to elute compounds that may have been present from previous analysis. After the ethanol the five calibration standards were run. Then three vials of methanol were ran again, to make sure that all the compounds from the calibration standards didn't interfere with the samples. Subsequently all the samples were run, with one methanol vial between samples from different origin. Finally the five calibration standards were run again.

3.3 Identification of volatile oak related compounds

First the different compounds were identified in TIC (Total Ion Current) chromatograms (fig 3) by hand in Waters® Masslynx™ software. This was done by measuring the mass to charge ratio (m/z) and the retention times for each peak (table 2). This process was time consuming and was therefore automated using the computer program Quanlynx™ (v 4.1 by Waters®). This enabled much faster analysis of large amount of samples, with only minor modifications in the program between different sets of samples.
Figure 3. TIC Chromatogram of the 10µg/ml calibration standard, with all compounds identified.

Figure 4. Mass spectra of 5-methyl furfural, here it can be seen that the m/z value of 109 and 110 are the largest peaks.
<table>
<thead>
<tr>
<th>Name</th>
<th>CAS</th>
<th>m/z 1</th>
<th>m/z 2</th>
<th>Retention time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural</td>
<td>98-01-1</td>
<td>95</td>
<td>96</td>
<td>5.90</td>
</tr>
<tr>
<td>5- Methyl Furfural</td>
<td>620-02-0</td>
<td>109</td>
<td>110</td>
<td>6.55</td>
</tr>
<tr>
<td>Furfury alcohol</td>
<td>98-00-0</td>
<td>98</td>
<td>-</td>
<td>6.94</td>
</tr>
<tr>
<td>Guaiacol</td>
<td>90-05-1</td>
<td>109</td>
<td>124</td>
<td>8.00</td>
</tr>
<tr>
<td>Cis Whisky lactone</td>
<td>39212-23-2</td>
<td>99</td>
<td>-</td>
<td>8.24</td>
</tr>
<tr>
<td>4-methylguaiacol</td>
<td>93-51-6</td>
<td>123</td>
<td>138</td>
<td>8.46</td>
</tr>
<tr>
<td>Trans Whisky lactone</td>
<td>39212-23-2</td>
<td>99</td>
<td>-</td>
<td>8.57</td>
</tr>
<tr>
<td>Eugenol</td>
<td>97-53-0</td>
<td>164</td>
<td>-</td>
<td>9.39</td>
</tr>
<tr>
<td>Syringol</td>
<td>91-10-1</td>
<td>139</td>
<td>154</td>
<td>9.79</td>
</tr>
<tr>
<td>5-hydroxymethylfurural</td>
<td>67-47-0</td>
<td>97</td>
<td>126</td>
<td>10.88</td>
</tr>
<tr>
<td>Vanillin</td>
<td>121-33-5</td>
<td>151</td>
<td>152</td>
<td>11.34</td>
</tr>
<tr>
<td>Syringaldehyde</td>
<td>134-96-3</td>
<td>181</td>
<td>182</td>
<td>14.75</td>
</tr>
</tbody>
</table>

Table 2. The name of all compounds analyzed, their CAS-number, their retention time and the m/z value analyzed for each compound.

### 3.4 The GC-MS

The gas chromatograph was a Hewlett Packard 6890 Series, with a 7683 Series injector and Autosampler and a 5973 Mass Selective Detector.

### 3.5 The GC method

**Oven:** Initial temperature: 50°C  
**Ramps:**

<table>
<thead>
<tr>
<th>Rate</th>
<th>Final Temp</th>
<th>Final Time</th>
<th>Total run Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.00°C</td>
<td>240°C</td>
<td>7 min</td>
<td>16.60 min</td>
</tr>
</tbody>
</table>

**Back inlet:**

<table>
<thead>
<tr>
<th>Mode</th>
<th>Splitless</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial temperature</td>
<td>250°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>10.00 psi</td>
</tr>
<tr>
<td>Purge flow</td>
<td>45,9 ml/min</td>
</tr>
<tr>
<td>Purge time</td>
<td>2.00 min</td>
</tr>
<tr>
<td>Total flow</td>
<td>50.2 ml/min</td>
</tr>
<tr>
<td>Injection volume</td>
<td>1 µl</td>
</tr>
<tr>
<td>Syringe size</td>
<td>10 µl</td>
</tr>
</tbody>
</table>
4. Results

The results revealed that the different compounds varied as a result of aging, wood type (oak origin) barrel size and the toasting degree.

4.1 Calibration calculations

To calculate the concentrations of the different compounds a calibration curve for each compound had to be made. In order to decide which calibration concentrations to include in the calibration curve, all peak areas where correlated by their known concentrations. Then the average and the standard deviation of these values where calculated. The standard deviation from the curve was divided with the average, to get the relative standard derivation (RSD). First, the peaks from all the concentrations where included in the RSD, and then the peak from the highest concentration was taken away to see if the RSD increased or decreased. The same was done with the peak from the lowest concentration. In table 3 the example is Furfural (from 2014-02-10) where it can be seen that the RSD is 29% smaller if the peak from the highest concentration is removed. The RSD for all the calibration curves can be found in table 4.
### Table 3. Calculation of the standard deviation, average value and coefficient of variation.

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>RSD (%) 2013-11-11</th>
<th>RSD (%) 2014-02-10</th>
<th>RSD (%) 2014-05-16</th>
<th>RSD (%) 2014-08-12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural</td>
<td>5%</td>
<td>4%</td>
<td>8%</td>
<td>2%</td>
</tr>
<tr>
<td>Furfuryl alcohol</td>
<td>2%</td>
<td>8%</td>
<td>29%</td>
<td>5%</td>
</tr>
<tr>
<td>5-methylfurfural</td>
<td>1%</td>
<td>2%</td>
<td>11%</td>
<td>1%</td>
</tr>
<tr>
<td>Guaiacol</td>
<td>10%</td>
<td>10%</td>
<td>5%</td>
<td>7%</td>
</tr>
<tr>
<td>Cis Whisky Lactone</td>
<td>2%</td>
<td>4%</td>
<td>14%</td>
<td>2%</td>
</tr>
<tr>
<td>4-methylguaiacol</td>
<td>4%</td>
<td>7%</td>
<td>2%</td>
<td>3%</td>
</tr>
<tr>
<td>Trans whisky lactone</td>
<td>4%</td>
<td>7%</td>
<td>12%</td>
<td>8%</td>
</tr>
<tr>
<td>Eugenol</td>
<td>4%</td>
<td>5%</td>
<td>9%</td>
<td>1%</td>
</tr>
<tr>
<td>Syringol</td>
<td>11%</td>
<td>20%</td>
<td>19%</td>
<td>15%</td>
</tr>
<tr>
<td>5-hydroxymethylfurfural</td>
<td>3%</td>
<td>10%</td>
<td>21%</td>
<td>6%</td>
</tr>
<tr>
<td>Vanillin</td>
<td>7%</td>
<td>10%</td>
<td>8%</td>
<td>11%</td>
</tr>
<tr>
<td>Syringaldehyde</td>
<td>10%</td>
<td>6%</td>
<td>3%</td>
<td>9%</td>
</tr>
</tbody>
</table>

The RSD values from all the calibration curves.

The calibration curve was then calculated from the concentrations that result in the lowest coefficient of variation, as seen in figure 5. Figure 6 shows the same calibration curve without the highest value removed.

The concentration of Furfural in all compounds was then calculated from the equation obtained from the calibration curve, by exchanging X in the equation with the peak area. Then the value was multiplied with four due to the dilution with methanol.
Figure 5. Calibration curve for Furfural from 2014-02-10.

\[
y = 6712.3x + 167.84 \\
R^2 = 0.99999
\]

Figure 6. Calibration curve for furfural from 2014-02-10, without the highest concentration removed.

\[
y = 4083.1x + 9350.6 \\
R^2 = 0.99644
\]

4.2 calculations of the concentration

When making the standard solution, all the compounds were threatned as if they would have a density of 1 g/ml to facilitate the process. When calculating the results, the real density had to be multiplied to the answer to obtain the real concentration. The densities for the compounds can be found in table 5.
### Table 5. The densities of all compounds (at 25°C).

<table>
<thead>
<tr>
<th>Compound name</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural</td>
<td>1,159 g/ml</td>
</tr>
<tr>
<td>5- Methyl Furfural</td>
<td>1,243 g/ml</td>
</tr>
<tr>
<td>Furfuryl alcohol</td>
<td>1,132 g/ml</td>
</tr>
<tr>
<td>Guaiacol</td>
<td>1,129 g/ml</td>
</tr>
<tr>
<td>Cis Whisky lactone</td>
<td>0,952 g/ml</td>
</tr>
<tr>
<td>4-methylguaiacol</td>
<td>1,095 g/ml</td>
</tr>
<tr>
<td>Trans Whisky lactone</td>
<td>0,952 g/ml</td>
</tr>
<tr>
<td>Eugenol</td>
<td>1,066 g/ml</td>
</tr>
<tr>
<td>Syringol</td>
<td>n/a</td>
</tr>
<tr>
<td>5-hydroxymethyl-furfural</td>
<td>1,107 g/ml</td>
</tr>
<tr>
<td>Vanillin</td>
<td>1,056 g/ml</td>
</tr>
<tr>
<td>Syringaldehyde</td>
<td>1,01 g/ml</td>
</tr>
</tbody>
</table>

4.3 Limit of detection (LOD)

The limit of detection was calculated using Waters® Masslynx™ computer program (v 4.1). It was calculated by measuring the signal to noise ratio (S/N), then dividing the S/N by 3. Then dividing the concentration of the sample with the value obtained from dividing S/N by 3. The concentration used when calculating the LOD was 0,1 µg/ml, except for vanillin and syringaldehyde where 1 µg/ml was used. All the LOD values can be found in table 6.

### Table 6. LOD (in µg) for all the analysed compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>LOD (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural</td>
<td>0,045</td>
</tr>
<tr>
<td>5-methylfurfural</td>
<td>0,073</td>
</tr>
<tr>
<td>Furfuryl alcohol</td>
<td>0,068</td>
</tr>
<tr>
<td>Guaiacol</td>
<td>0,098</td>
</tr>
<tr>
<td>Cis whisky lactone</td>
<td>0,111</td>
</tr>
<tr>
<td>4-methylguaiacol</td>
<td>0,06</td>
</tr>
<tr>
<td>Trans whisky lactone</td>
<td>0,185</td>
</tr>
<tr>
<td>Eugenol</td>
<td>0,104</td>
</tr>
<tr>
<td>Syringol</td>
<td>0,119</td>
</tr>
<tr>
<td>5-hydroxymethylfurfural</td>
<td>0,17</td>
</tr>
<tr>
<td>Vanillin</td>
<td>0,83</td>
</tr>
<tr>
<td>Syringaldehyde</td>
<td>2,27</td>
</tr>
</tbody>
</table>
4.4 Cyclic aldehydes

Four cyclic aldehydes were analysed; Furfural, 5-methylfurfural, Furfuryl alcohol and 5-hydroxymethylfurfural. The levels of Furfural in the non-matured whisky were 22 µg/ml. These levels had increased in all of the barrels over time except the lightly toasted barrels, which all had around 20 µg/ml. The highest levels were found in the Swedish and the American hard toasted barrels from 2014-12-08 (both around 110 µg/ml).

The levels of 5-methylfurfural were much lower than the furfural levels. Most of the matured samples had around 1 µg/ml while the non-matured whisky had a level of 1.5 µg/ml. The Swedish (25 and 100L) and French charred barrels from 2014-05-16 had concentrations between 3 and 5 µg/ml. However the highest value was found in a lightly toasted small Swedish barrel from 2014-05-16.

The levels of furfuryl alcohol were moderately higher in the lightly toasted barrels (around 0.7 µg/ml) than in the non-matured whisky, which had 0.2 µg/ml. All of the medium toasted, hard toasted and charred barrels had much higher concentrations, ranging between 1.2 µg/ml (in the Swedish medium toasted 100 and 225 L barrels and the Swedish charred 225 L barrel) to over 12 µg/ml (in the Swedish hard toasted 25 L barrel).

5-hydroxymethylfurfural had a concentration of 2.4 µg/ml in the non-matured whisky and were present in all of the samples. Most of the samples had a higher concentration than the non-matured, with the highest measured concentration in the Swedish medium toasted barrel from 2014-12-08 (over 50 µg/ml). All values are found in appendix 1, where the tables for the cyclic aldehydes are red.

4.5 Cyclic esters

The cyclic esters that were analysed are cis and trans whisky lactone. (These two are isomers to one another but are separated in the GC.) The non-matured whisky didn’t have any cis whisky lactone and 0.2 µg/ml trans whisky lactone.

Cis whisky lactone was present in all American oak barrels (ranging from 0.6 to 1.1 µg/ml), and in low concentrations in the Swedish light and medium toasted 25 L barrels, in the French medium, hard and charred 25 L barrels and in the Swedish charred 100 L barrel (ranging between 0.1 to 0.2 µg/ml). The highest concentration was found in the French lightly toasted barrel from 2014-02-10 (1.1 µg/ml).

Trans whisky lactone had significantly higher concentrations in the barrels of American oak than in any other sample were the concentration ranged between 8 to 15 µg/ml. It was also present in all of the barrels made of French oak but the concentrations were much lower.
ranging from 0.3 to 3 µg/ml. All values are found in appendix 1 where the tables for the cyclic esters are green.

4.6 Aromatic Phenols

Six aromatic phenols were analysed; Guaiacol, 4-methyl guaiacol, Eugenol, Syringol, Vanillin and Syringaldehyde.

Guaiacol was not present in the non-matured whisky and present at very low concentrations (around 0.1 µg/ml) in all other samples from 2013-11-11 and 2014-02-10. However, in all samples from 2014-05-16, 2014-12-08 and 2015-04-16 Guaiacol were present in much higher concentrations were the highest is in SL1 from 16-05-2014 (0.8 µg/ml).

4-methyl guaiacol was present in the non-matured whisky or in any of the samples from 2014-05-16 or 2015-04-16. In the samples from 2013-11-11, 2014-02-10 and 2014-12-08 4-methyl guaiacol is present in all the samples except the lightly toasted barrels, but at very low concentrations (ranging between 0.01 to 0.1 µg/ml).

The non-matured whisky had a concentration of 0.2 µg/ml Eugenol. All of the barrels made from Swedish oak had concentrations similar to the non-matured, ranging between 0.1 µg/ml (from 2014-12-08) to 0.3-0.4 µg/ml (from 2013-11-11). The American oak barrels all had concentrations over 0.2 µg/ml, ranging up to 0.7 µ/ml for the hardly toasted barrel.

The non-matured whisky had a concentration of 0.4 µg/ml Syringol. All of the samples from 2014-12-08 had concentrations equal to or above this, ranging between 0.4 to 1.6 µg/ml. All of the hard toasted and charred 25 L barrels had values equal to or above the non-matured from all of the sampling dates.

Vanillin is not present in the non-matured whisky and only in low concentrations in the lightly toasted barrels (0.5 to 3.7 µg/ml). In all of the other samples the concentrations were significantly higher, ranging between 5 to 25 µg/ml.

The non-matured Syringaldehyde had a concentration of 3.3 µg/ml. All of the lightly toasted barrels and also the medium toasted 100 L barrel have concentrations similar to this. However the hard toasted and charred barrels all have concentrations ranging over 15 µg/ml up to 80 µg/ml. All values are found in appendix 1 where the tables for the aromatic phenols are blue.

4.7 Spider diagram

Spider diagrams where made to see the differences in concentration of the compounds in the different barrels and different treatments. Spider diagrams where made from the data obtained from all the barrels from 2013-11-11. The values had to be normalized or else the compounds with low concentrations would not have been visualized. Therefore furfural where divided by 40, furfuryl alcohol divided by 2, cis whisky lactone by 10, 5-hydroxymethylfurfural by 10, vanillin by 10 and Syringaldehyde by 20. These can be seen in figure 7-14.
The maturation in oak barrels are a continuous process and therefore these spiderdiagrams can be seen as a “snapshot” of an ongoing process.

Figure 7. Differences between Swedish light, medium, hard and charred 25 L barrel from 2013-11-11, as seen in spider diagrams. Note that there is not the same scale on the diagrams.
Figure 8. Differences between American light, medium, hard and charred 25 L barrel from 2013-11-11, as seen in spider diagrams. Note that there is not the same scale on the diagrams.
Figure 9. Differences between French light, medium, hard and charred 25 L barrel from 2013-11-11, as seen in spider diagrams. Note that there is not the same scale on the diagrams.
Figure 10. Differences between Swedish light, medium, hard and charred 100 L barrel from 2013-11-11, as seen in spider diagrams. Note that there is not the same scale on the diagrams.

Figure 11. Swedish charred 100L barrel from 2014-12-08, as seen in a spider diagram.
Figure 12. Differences between Swedish medium and charred 225 L barrel from 2013-11-11, as seen in spider diagrams. Note that there is not the same scale on the two diagrams.

Figure 13. Swedish charred 225L barrel from 2014-12-08, as seen in a spider diagram.
When comparing the spider diagrams to each other one can see that the Swedish small barrels all had the same character except for the light toasted. The light toasted did not have any furfuryl alcohol or vanillin.

The American medium toasted, hard toasted and charred all had the same character while the light toasted was rather different. The light toasted did not have any vanillin and the Cis whisky lactone was the most prominent.

The French medium toasted, hard toasted and charred all had similar characters while the light toasted was the most different. The light toasted was the only one were cis whisky lactone was present and the levels of furfuryl alcohol were a lot smaller than in the other three barrels. Furthermore vanillin was not present in the light toasted barrel.

The hard toasted and charred Swedish 100 L barrels had similar character and the light toasted and medium toasted had similar characters. Vanillin was not present in the light and medium toasted barrels and furfuryl alcohol was present at much lower concentrations in the light toasted than in the other barrels.

The Swedish charred 225 L barrel had a similar character to the charred 100 L barrel. The medium toasted 225 L barrel did not have any vanillin present.

The non-matured whisky was very different from the rest of the samples, containing almost only furfural and 5-methylfurfural.

The Swedish charred 100 and 225 L from 2014-12-08 shows that the maturation process continues in the barrels, resulting in higher concentrations of the compounds.
4.8 Concentration over time

Diagrams were made to see the differences in concentration of the compounds over time. They are made of the mean concentrations of the different compounds in the barrels. The date shown on the x-axis is the date the sample was taken out of the barrel at Thorslundkagge. All samples were put in the barrels in 2011. The samples were taken from the barrel on 2013-11-11, 2014-02-10, 2014-05-16 and 2014-12-08. This can be visualised in figure 15-26.

As can be seen, some of the compounds stay at approximately the same concentrations, for example cis whisky lactone (figure 19). However other compound concentrations varies greatly over time, for example vanillin (figure 26).

![Furfural](Figure 15. Mean furfural concentrations over time.)
Figure 16. Mean 5-methylfurfural concentrations over time.

Figure 17. Mean furfuryl alcohol concentrations over time.
Figure 18. Mean 5-hydroxymethylfurfural concentrations over time.

Figure 19. Mean cis whisky lactone concentrations over time.
Figure 20. Mean trans whisky lactone concentrations over time.

Figure 21. Mean 4-methylguaiacol concentrations over time.
Figure 22. Mean guaiacol concentrations over time.

Figure 23. Mean eugenol concentrations over time.
Figure 24. Mean syringol concentrations over time.

Figure 25. Mean vanillin concentrations over time.
4.9 Colour

The different treatments also resulted in different colours of the final product that could be seen with the naked eye. The harder the barrel had been toasted, the darker was the colour. Furthermore the larger the barrel was, the lighter was the colour of the final liquid. This can be seen in figure 27. The non-matured whisky is not present in figure 27 but it had a clear colour.

Figure 26. Mean syringaldehyde concentrations over time.

Figure 27.
2. Swedish oak, medium toasted, 25 L barrel.
5. Swedish oak, charred to light (top downwards), 100 L barrels.
6. Swedish oak, charred and medium (top downwards), 225 L barrels.
7. French oak, charred to light (top downwards), 25 L barrels.
8. American oak, charred to light (top downwards), 25 L barrels.

4.10 Sources of error

When the stock solution was made, the compounds that are solid in room temperature had to be weight to 10 milligram. Since the scale varies on the last digit the true weight of these compounds varies between 9.5 – 10.5 milligrams.

For those samples that had a peak area less than the m-value in the calibration curves equation, the trend line was “forced” to intersect 0 in the calibration curve. This resulted in an inferior $R^2$-value but positive concentrations. This was done on eugenol, 4-methylguaiacol and guaiacol from 2014-02-10 and guaiacol from 2013-11-11.

Discussion

When maturing in new toasted or charred barrels they impart high levels of colour and wood-derived aromas that contributes to the matured spirit. These aromas are described as woody, coconut, vanilla, pine, cedar and sap-like. They come from both the heartwood and the thermal degradation of wood polymers that occurs during toasting and charring (Bamforth 2003).

This can be seen in the results as the non-matured whisky received a lot of compounds while maturing in the barrels. Many of the compounds weren’t present in the non-matured whisky whilst abundant after maturation. However, some of the compounds were not present in a barrel from a certain origin, as for example Trans whisky lactone that was not present in the
Swedish oak barrels.
The different compound concentrations were often highest in the hard toasted and charred barrels and lowest in the light toasted. For example vanillin were not present at all in most of the light toasted barrels and also not in the medium toasted 100 and 225 L barrels. Vanillin is naturally present in oak wood, but these concentrations are greatly increased when heating the wood. This is because of the thermal lignin breakdown that results in more vanillin. The thermal breakdown of lignin also increases the concentrations of Syringaldehyde (Nishimura 1983, edited by Graham 2014).
The opposite can be said about 5-methylfurfural, which were present at higher levels in the light toasted barrels and non-matured whisky. This might be due to that 5-methylfurfural is broken down during the toasting process. It can be that either that the OH-group dissociates which will result in furfural or that the formaldehyde group (CH$_2$O) dissociates resulting in furfuryl alcohol.
Having this in mind, a hard toasted or charred barrel will give more taste to the final product. The size of the barrel also seemed to have a great influence on the final product and a small barrel often gave a much higher concentration of the different compounds. This has to do with the fact that in a small barrel the surface to liquid ratio is much higher, resulting in more reactions between the barrel and the liquid.
First fill barrels have a rapid extraction rate between the barrel and the liquid for the first six to twelve months thereafter the extraction rate is slowed down. However a steady increase color and cask constituent and is maintained during the whole maturation process. This is due to a combination of spirit hydrolysis and air oxidation (Bamforth 2003).
The majority of the compounds also increased over time, meaning that a barrel stored for 5 years will give more taste than a barrel stored for 3 years.
Regarding the final product, one must also have in mind that the different compounds have great differences in aroma and flavor threshold.
The aroma of the final product varies a lot from the non-matured distillate. The three compounds that contribute most to the final aroma are cis whisky lactone, eugenol and vanillin. It has been shown that omission of these three compounds will affect the flavor significantly. Furthermore, the compounds that contribute to the aroma of the distillate are not lost through the maturation process, but they are interfered by the compounds received during the maturation (Nishimura 1983, edited by Graham 2014).
Finally, the treatment of the barrel also gives an amber colored tone to the whisky, which is more consumer appealing than the non-colored non-matured distillate.
Conclusion

By looking at the spider diagrams one can see how the different treatments will affect the final product. The whisky stored in Swedish oak barrels (figure 7) are more similar to the whisky stored in French barrels (figure 9) than in the American barrels (figure 8). But there are still differences between the whisky stored in the French and the Swedish oak barrels. The larger the barrels are, the lower the concentrations of the compounds are compared to a smaller barrel at the same time. This has to do with the liquid to barrel surface ratio, which is smaller in the large barrels, therefore the maturation process is slower. This can be seen when comparing figure 7 with figure 13. The barrel in figure 13 has been in the barrel for about a year longer than figure 7.

Acknowledgement

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References


