Peat, Phenol and PPM.

Malt whisky, until the mid 1960s, was made of the following ingredients: barley, water, yeast and peat. Until then, all the distilleries were using large amounts of peat for firing the stills and drying the barley in the kilns. At the turn of the 1960s, with the help of all the progresses in still firing (e.g., indirect firing, steam coils) and in maltings (e.g., large and industrial scale maltings), it became possible to produce large quantities of high quality malted barley without the use of peat. The Speyside and Lowlands distilleries were amongst the first to convert to non-peated whiskies. The change from peat to coke was made possible with the start of coke mining and the development of the railway network in order to convey the combustible to the distillery. Other areas, such as Islay maintained the traditional production of peated whiskies (at the exception of Bunnhahbhain, Bruichladdich and Caol IIa (to some extend with their highland style)). The influence and flavours of peat are easily recognized by the whisky drinker and the peating level expressed as phenol in parts per million (PPM, 1 PPM equals to 1 part (e.g., phenol) diluted in 1'000'000 parts (e.g., spirit).

Amongst the whisky enthusiasts, the terms peat, phenol and PPM are not well understood and this article will try to explain the meaning of these terms.

Peat:

Botany:

Peat is defined as follows on http://www.wildlifetrust.org.uk/facts/peat.htm: "Peat is an organic material that forms in the waterlogged, sterile, acidic conditions of bogs and fens. These conditions favour the growth of mosses, especially sphagnum. As plants die, they do not decompose. Instead, the organic matter is laid down, and slowly accumulates as peat because of the lack of oxygen in the bog.

In other terms, in wetlands or peatlands called also bogs, moors or mire in some countries, peat is the result of the decomposition of vegetal matter, composed mainly of Sphagnum. Spaghnum is the genus of bryophyte ("mosses") plant division and contains a few hundred species. It is a small plant of around 1-2 cm height with the main stem reaching 5-10 cm (reproductory organ) growing in very humid and wetlands. The content of water in the plant is very high, up to 70%. Under a microscope, you can see the chlorophyll floating in water. Because Spagnum is growing in wetlands, its decomposition do occur in absence of oxygen (anaerobic decomposition) and thus, the carbon trapped in the vegetal substance cannot be release as carbon dioxide (CO2). The resulting product of



In Scotland, in the islands, peat is still widely use as domestic fuel, such as here, on the Isle of Lewis.

this decomposition, the peat is black because of its rich carbon content.

Peat in distilleries:

Peat is abundant in the Northern countries (e.g., Russia, Canada, Scandinavia and United Kingdom (including Scotland) and in order to be used as fuel, it must be dried. In Scotland, peat was traditionally manually cut with spades. A flaughter spade is traditionally used to cut and remove the leaving mossy part, and then bands of peat are cut using a rutter and finally a tusker is used to cut the peat blocks. Once cut, the peat is stacked to form a peat stack, also called storrows, and left to dry. The upper part of the peat is then put back on top of the peat field in order to minimize



Macroscopic detail of a peat clump used in scottish distilleries.

the ecological impact of peat cutting.

Once dry, peat can be used as fuel for domestic and industrial use. Peat was the main fuel in Scotland and it is still an important one in some parts of Scotland such as the Outer Hebrides. Coal, coke, gas and petrol are better carburant. However, peat is still used in high quantities by the Scotch whisky industry. The distilleries of Highland Park, Springbank, Bowmore, Laphroaig and Kilchoman still use peat for the malting process, as well as Balvenie but in a much lower proportion. At Balvenie, in order to have little peat influence, there is a little peat fire adjacent to the kiln heated by coke and the peat smoke is mixed with the hot air generated by the coke fire. The other distilleries buy their peated malt directly from Maltings such a Port Ellen, Tamdhu or Glen Ord or from other Maltsers (Malters) such a Simpsons. In Maltings such as Port Ellen, as much as 5 tonnes of peat can be used per run and as little as 5 tonnes per year at Tadmhu. Drying the malted barley with peat gives some pleasant smoky flavours to the spirit and allows a better storage than non-peated malt, but might also reduce the yield (number of litres of pure alcohol by tonne of malt). Depending on the degree of peatiness, peat can be from any time for up to 48h. After 48h, the husk (envelope) of the barley grain will be dry and prolonging the exposure of the barley to the peat smoke will not increase the peaty character of the spirit. This treatment will result in an increase of a group of aromatic chemical compounds called phenols (see below). The so-called non-peated barley will contain a proportion of phenols in the range of 0.5-3 ppm (1 ppm=0.0001%) and the highly peated barley used for Ardbeg or for



A tusker at HighlandParkdistillery.

the Octomore of Bruichladdich, 50 and 80 ppm respectively. The ppm used for the different distilleries given in the different websites or books are usually the concentration of phenol of the barley used by the distillery, before milling and distillation. The concentration in phenols in the distillate flowing out of the still (new make) is between 30 and 50 percent of the initial barley concentration. For example, the barley for Ardbeg is peated to 54 ppm of phenol and the final concentration in the new make is between 17 and 24, depending on the milling and mashing process (1). For a second example, the barley used for the BenRiach Curiositas is peated to 55 ppm and the level of phenols is 35 ppm in the new make. An important property of the peat smoke is to make the barley more resistant to bacterial infection.

Distilleries prefer to use the upper part of the cut peat, because the top layers are richer and more rooty. The upper peat layer generates more smoke and is ideal for flavouring the barley. For domestic use, the lower part is preferred; since it will burn better, generate more heat and less smoke. Also, depending on the vegetation on the moorlands, the peat might have a different structure and composition, thus the peat coming from different locations might contribute to specific flavours. During the 1990s, Highland Distillery stopped using his malting floor and using only barley prepared by a maltser. It resulted in a change of the aromatic profile of the whisky and floor malting was repeated. At the beginning of this millennium, Laphroaig has distilled a spirit made exclusively on its malting floor. The result of this experiment will be delivered in a few A peat fire inside a kiln to years. The distilleries of Glendronach and Benriach have stopped using their dry the barley and to give a malting floors in the end of the 1990s. Although floor malting is uneconomical, smoky flavour to the spirit. BenRiach will restart the floor malting operations in 2008/2009. Hopefully,



Glendronach will restart again. At Highland park, they tried for a short period to buy only "commercially prepared malt" but this affected the quality of the spirit. Highland park is producing about 15% of all their barley on their malting floor. In the Speyside, one distillery is still keeping their floor malting for commercial reasons (as selling point).

Until the end of the 19th century, mainly in the highlands, peat was still in use for the heating of the stills. The heating of the stills was slower with the peat than with coke or coal and apparently resulted in a finer spirit (Insert ref).

Phenols and ppm:

As mentioned above, the Parts Per Million (ppm) is a measure of concentration. One ppm by definition is equivalent to the concentration of 1 molecule diluted in 1 a mixture of 1 million of other molecules.

During kilning, when peat is used as a combustible, the peat smoke (reek) will introduce a peaty character into the final distillate. The peatiness of the barley can be controlled by the amount of peat burnt, the duration of the peat smoke and by the humidity (moisture) of the barley. The optimal moisture is about 25% (2). As described by Lee et al. (3), the peaty character (e.g., burnt, smoky and medicinal) attributes originate primarily from phenolic compounds in peat smoke and the quantitatively important phenols are phenol, cresols, xylenols, ehtylphenols and guaiacol. In addition to the phenols originating from the peat smoke, some phenolic compounds are generated from the malting by the heat generated in the kiln (thermal degradation). Although

phenol dominates in peated barley malt, cresols can be more abundant in the final spirit. Changing the temperature of the peat fire between 400 and 750°C can significantly modify the balance of phenol and cresols versus guaiacol (2). Our nose is a very sensitive organ and the level of detection, the level at which a nose can detect the peaty flavour, is as low as 0.1 ppm of guaiacol according to the publication of Lee et al. (4).

As mentioned above, a common measure to report the peatiness of a whisky is to provide the ppm of the malted barley. The heavily peated single-malts are made of barley of more than 30 ppm of phenol, mediu-peated



barley of about 20 ppm and lightly peated below 15 ppm. Even "unpeated" barley contain phenols, but at a low level, between 0.5 and 2-3 ppm. The concentration of phenols contributing to the peaty character decreases with time. For example, Laphroaig's barley is 40 ppm, the new make spirit is 25 ppm. The phenol content drops to 8-10 ppm in the 10 years old (YO) and down to 6 ppm in the 30 YO (5).

The quantification of the phenolic compounds is done by UV/VIS spectroscopy or by 'direct-injection reversed-phase High Performance Liquid Chromatographic technique (HPLC).

In the case of UV/VIS spectroscopy, the whisky sample to be analyzed will be mixed with a reagent (e.g., Folin-Ciocalteu reagent), which will react with the phenolic compounds of the sample. This method is simple, straightforward, inexpensive and does not require much scientific expertise. However, because of heterogeneity and complexity of the chemical composition of the whisky, the specificity of the method is not 100%.

HPLC is a very powerful technique and allows a relatively accurate, precise and specific identification and quantification of the different classes/groups of phenolic compounds. Since whisky is composed of several hundreds of molecules, the identification of all the phenolic compounds is not (always) possible (e.g., coelution).

During these last years, new techniques such as Gas Chromatography/Mass spectrometry (GC/MS) or Gas Chromatography/Time-of-Flight Mass Spectrometry (GC/TOFMS) have been developed for the quality control of whisky.

To come back to the whisky, the most heavily peated whiskies is the Octomore produced at Bruichladdich. On their website (www.bruichladdich.com), the barley used for the Octomore distilled in 2002 had 80.5 ppm of phenol as measured by HPLC. The second Octomore, the Octomore II- Beast reached 167 ppm, as measured by HPLC. As written in Peat, Smoke and Spirit (5), the phenol level was 29.6 ppm in the 2002 run and 46.4 ppm in the 2003 run.

Conclusion:

Peat is a natural resource used since ages in Scotland as fuel. It is abundant and was used from the start in the whisky industry to dry the barley. Drying the barley over a peat fire protected the barley from moisture and bacterial infection. At the same time, the peat smoke gave a certain peatiness to the whisky. Peat is still largely used in Scotch distilleries, but mainly in the distilleries located in the islands of Skye, Orkney, Mull and Islay. Depending on the structure and the origin of the peat, the duration and temperature of the peat fire,

and the distillation, the peaty character might be quite different between the products of two distilleries. The peatiness, measured in ppm, is an indicator of the peatiness and commonly measured either by HPLC or by specrophotometry. The ppm values used by the distilleries to promote their product usually refer the concentration of total phenols in the barley, and not in the distillate.

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