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Using TDU-Pyrolysis-GC-MS to Investigate Aged Whiskey Samples and Their Oak Barrels

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Abstract
Pyrolysis GC-MS was used to profile residual solids after drying aged whiskey samples. The samples in question were both 20 years old from the same unaged parent distillate but matured in the very different wood species of *Quercus Robur* and *Quercus Alba*. Fractionated pyrolysis chromatograms generated at 450°C were obtained for both the different whiskey residues and samples of the respective wood species. The whiskey residues showed differences in peak pattern profiles and the same differences were observed between each residue and it's originating wood. Pyrolysis GC-MS could be applied to whiskey maturation investigations and can help to establish a link between the spirit non-volatile fraction and the type of wood used for maturation.

Introduction
A recent study presented a comparative analysis of one pot distillate at various intervals of barrel maturation extending to 20 years in new barrels made of *Quercus Alba* (American) and *Quercus Robur* (European) wood [1]. Using a large volume injection (LVI) technique for GC-MS combined with deconvolution techniques for data interpretation, a set of 47 compounds that originated from barrel storage were identified in the whiskey samples (A detailed description of the LVI process can be found in [2], [3] and [4]). It is stated that this type of profiling can be very useful for cask

quality assessment and also will have application in authenticity verification. The chromatographic profile of the volatile fraction, in terms of peak size pattern, obtained with "normal" GS-MS procedures is different for both whiskeys. But on the other hand substance spectra, in terms of identified compounds, are the same, although these two whiskeys have a different visual appearance and differ in aroma and taste.

In addition to the volatile and semi-volatile compounds found in whiskey as a result of the maturing process there is also a fraction of non-volatile compounds to be found. These non-volatile compounds originate from the degradation of wood lignin and macromolecules during barrel maturation. A feasibility study is presented in this paper to try to link this non-volatile fraction to the wood used for barrel maturation and to search for correlations. LC-MS was successfully applied to characterize the non-volatile high molecular fraction of whiskey compounds and significant differences were found depending on the wood species used for ageing [1]. In this paper pyrolysis-GC-MS is applied to get similar information about the solid residue of whiskey samples by analyzing thermal decomposition products of macromolecules in whiskey residues, Pyrolysis-GC-MS can provide information about the chemical nature of the whiskey residues and together with the pyrolysis of samples from the actual oak barrels, which were used for maturating the whiskeys, further correlations between aged whiskeys and the oak barrels they were stored in may be found.

Experimental

Whiskey and wood samples. Samples of 20 years aged whiskey matured in new *Quercus Alba* (QA) and *Quercus Robur* (QR) oak barrels together with wood segments from the corresponding QA and QR oak barrels were obtained from Irish Distillers-Pernod Ricard. The same parent distilled spirit was used for both whiskeys; the only difference was the type of wood used for barrel storage.

Five 20 µL samples of whiskey were pipetted separately into the pyrolysis sample holder (vial type holder with slit) using a manual microliter syringe. After each introduction, the volatile constituents were evaporated at room temperature facilitated by a vacuum pump. Figure 1a shows the picture of QA whiskey (left vial) and QR whiskey (right vial) and their residues in the pyrolysis sample holders. It can be seen clearly that the colour of QR whiskey is much deeper than the colour of QA whiskey, and correspondingly the QR whiskey gives a higher amount of solid residue when evaporated to dryness. For the barrel samples small pieces of wood were chipped off from a deeper layer of the oak barrel to ensure that the sample taken had not been in direct contact with whiskey. For analysis these small wood chips were placed into pyrolysis sample holders, figure 1b. For the wood samples no obvious difference in visual appearance was noticed.

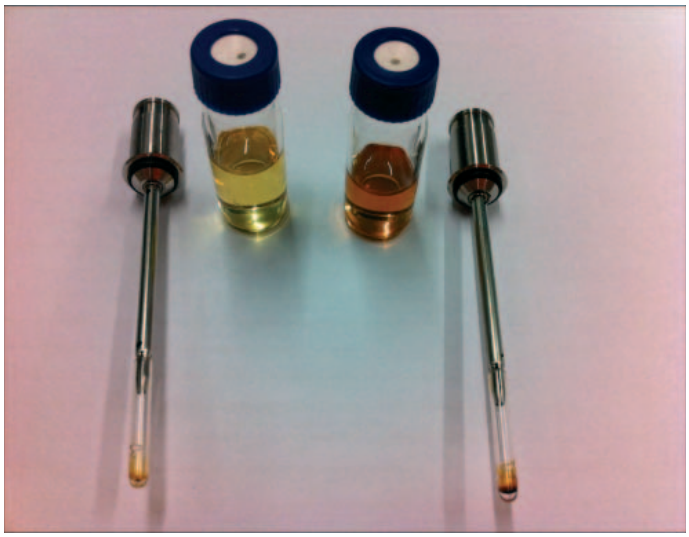

Figure 1a. QA whiskey (left) and QR whiskey (right) together with QA residue in pyrolysis sample holder (left) and QR whiskey residue in pyrolysis sample holder (right).

Figure 1b. QA and QR wood chips in pyrolysis sample holders.

Instrumentation. Pyrolysis-GC-MS was performed using a Thermal Desorption Unit (TDU) with pyrolysis module (PYRO) combined with a Cooled Injection System (CIS 4) programmed temperature vaporization (PTV) type inlet with liquid nitrogen cooling (LN_2) (all from GERSTEL). Sample introduction was automated using a MultiPurpose Sampler (MPS) (GERSTEL). The TDU-PYRO system was coupled directly to an Agilent 6890N gas chromatograph with 5795B inert XL (triple axis) mass selective detector (MSD) (both from Agilent Technologies). The entire analysis system was operated under MAESTRO software control (GERSTEL) integrated in Agilent ChemStation software using one integrated method and one integrated sequence table.

The heart of the PYRO module is a platinum filament. Pyrolysis temperatures can be set from 350°C to 1000°C. PYRO fits into the heating tube of the Thermal Desorption Unit (TDU), which allows easy switching between Thermal Desorption operation and pyrolysis operation. Automation of all processes, such as transporting pyrolysis sample holders to and from the pyrolysis module in the TDU are performed using the GERSTEL MultiPurpose Sampler (MPS).

Analysis conditions.

Pyrolysis:	450°C pulsed pyrolysis
	Lead Time 20 sec
TDU:	50 mL/min, solvent vent (0.5 min)
	40°C (0.5 min); 720°C/min;
	300°C (4.43 min)
PTV:	quartz liner with quartzwool
	solvent vent
	100 mL/min (2.0 min) at 0 kPa
	40°C (2.2 min); 10°C/s;
	320°C (10.0 min)
Column:	25 m CP-SIL 5 CB (Varian)
	d_i = 0.15 mm d_f = 2.0 µm
Pneumatics:	He, constant flow = 0.5 mL/min
Oven:	60°C (2.0 min);10°C/min;
	150°C; 5°C/min; 320 °C (10.0 min)
MSD:	EI mode, scan, 30-350 amu,
	Threshold: 150

Results and discussion

Fractionated pyrolysis of QR whiskey residue at 300°C and 450 °C. The whiskey residue sample was twice thermally desorbed at 300°C to remove volatile and semi-volatile organic compounds (VOCs and SVOCs) in order to ensure that only the non-volatile solid residue was left. After each thermal desorption step, a GC/MS run was performed to determine which compounds were desorbed. These have been described in a previous publication [1]. As can be seen in figure 2, the chromatogram from the second run is very clean, indicating that the VOCs and SVOCs have been desorbed completely. Following thermal desorption, the whiskey residue was pyrolyzed at 450°C. In a series of fractionated pyrolysis experiments ranging from 400°C to 700°C, this had been found to be the optimum pyrolysis temperature. Generally for wood and lignin pyrolysis, a final temperature between 450°C and 510°C has previously been used [5,6].

Many well separated sharp peaks can be seen in the GC/MS pyrogram resulting from pyrolysis of the whiskey residue at 450°C (figure 2). A list of identified compounds can be found in table 1. A literature survey reveals that these compounds are known to be thermal degradation products from either wood, lignin or cellulose [5,6].

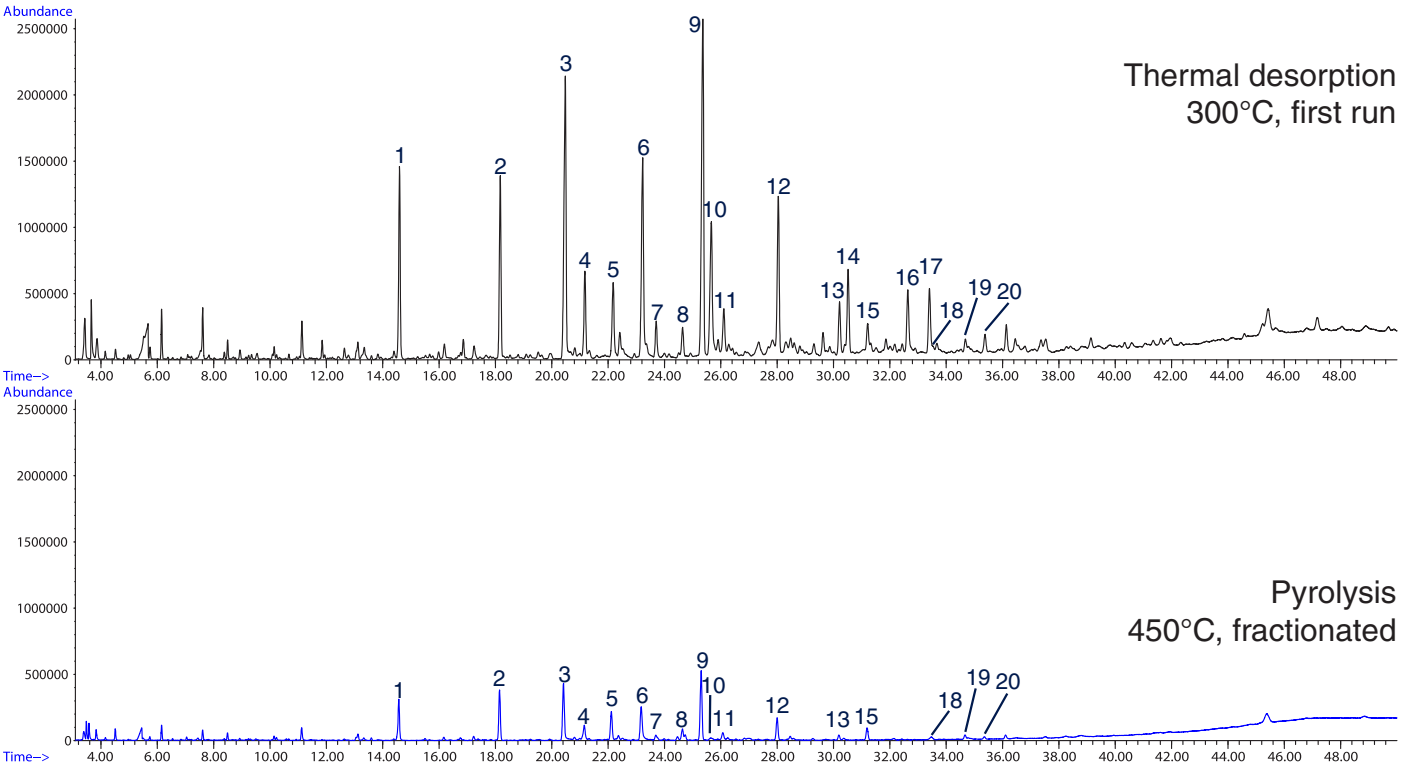

Figure 2. Comparison of TICs resulting from the first and second thermal desorption of QR whiskey residue at 300°C and from fractionated pyrolysis of the same sample at 450°C directly after the thermal desorption steps.

Table 1. List of 20 identified compounds in the pyrogram of whiskey residue at 450°C.

No.	Compound	Main Ion	Ion 1 (%RA)	Ion 2 (%RA)	Lignin [3]	Cellulose [3]	Wood [2]
1	Phenol	94	39(21)	66(20)	y	y	y
2	Guaiacol	109	124(85)	81(61)	y		y
3	1,2-Benzenediol	110	64(30)	63(11)		y	y
4	Guaiacol, 4-methyl-	138	123(96)	95(30)	y		y
5	1,4-Benzenediol	110	81(25)	53(17)		y	y
6	1,2-Benzenediol, 3-methoxy-	140	125(83)	97(54)		y	y
7	Guaiacol, 4-ethyl-	137	152(42)	122(11)	y		Y
8	Guaiacol, 4-vinyl-	150	135(83)	107(32)	y		y
9	Syringol	154	139(58)	111(29)	y	y	y
10	1,2,3-Benzenediol	126	108(26)	97(9)		y	y
11	Phenol, 3,4-dimethoxy-	154	139(68)	111(25)	y		y
12	Syringol, 4-methyl-	168	153(48)	125(27)	y		y
13	Benzene, 1,2,5-trimethoxy-3-methyl-	167	182(54)				
14	Naphthalene, 1,2,3,4-tetrahydro-2,2,5,7-tetramethyl-	132	188(36)	173(27)			
15	2,6-Dimethyl-3-(methoxymethyl)-p-benzoquinone	180	165(41)	137(29)			
16	Naphthalene, 1,6,7-trimethyl-	155	170(91)	115(8)			
17	Naphthalene, 1,4,5-trimethyl-	155	170(97)	115(8)			
18	Syringaldehyde	182	181(61)	167(13)	y		y
19	Methoxyeugenol	194	91(23)	119(16)	y		y
20	Acetosyringone	181	196(49)	153(13)	y		y

y=yes, means the compound is a pyrolysis product previously reported in literature.
RA = Relative Abundance

Comparative fractionated pyrolysis of QR whiskey residue and QA whiskey residue at 450°C. The fractionated pyrolysis process described above was also performed on solid residue from QA whiskey to determine if a difference in peak patterns could be found between the two whiskey residues. Figure 3 shows a comparison of the resulting pyrograms. The visual appearances are quite different, not only regarding peak size but also regarding compound pattern. Because both whiskey residues were obtained from 100 µL samples, peak areas can be semi-quantitatively compared. Here, the data was analyzed using the Agilent MassHunter Quantitative Analysis function based on retention time, target- and qualifier ion masses together with the relative abundance for each compound (see table 1).

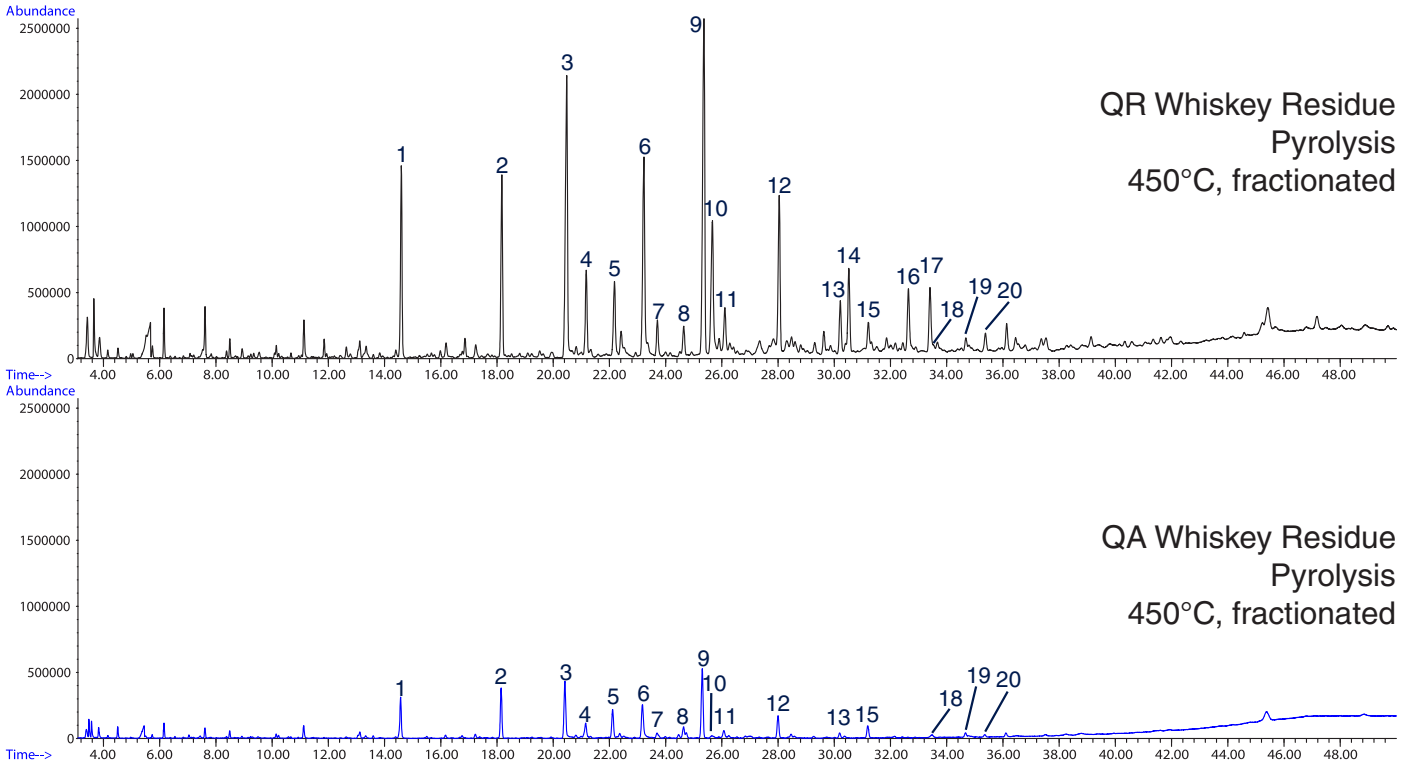

Figure 3. Comparison of pyrograms of QR and QA whiskey residues obtained from fractionated pyrolysis at 450°C.

Table 2. Peak response factors for the compounds listed in table 1 (QR whiskey residue / QA whiskey residue).

Peak Nr.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
P.R. QR whiskey residue /P.R. QA whiskey residue	5	4	6	6	3	6	7	2	6	49
Peak Nr.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.
P.R. QR whiskey residue /P.R. QA whiskey residue	6	9	11	n.d.	2	n.d.	n.d.	3	3	7

P.R. = Peak Response; n.d. = not detected in the QA whiskey

Based on the same amount of sample, peak response obtained from QR whiskey residue was much higher than from QA whiskey residue by a factor of 2 to 49. This is in good agreement with a previous study [1], in which the LC-MS chromatogram from the QR whiskey showed a much more complex peak pattern for the high molecular region. Additionally in the TICs compared in fig. 3, compounds 14, 16 and 17 were not found in the pyrogram of the QA whiskey residue, only in the pyrogram of the QR whiskey residue.

As a first conclusion from these experiments, it seems that pyrolysis-GC-MS can be used to obtain a quick characterization of whiskey residue, which could potentially be useful for cask quality assessment and authenticity verification.

Comparative fractionated pyrolysis of whiskey residue and wood at 450°C. Because the solid residue of whiskey is generated entirely during the maturation process in the oak barrel, it can be assumed that all compounds in whiskey residue are directly or indirectly related to the wood. The compound pattern of the residue must also reflect the duration of the maturation process as well as other factors like the pre-treatment of wood (e.g. toasting), storage temperature, humidity and so on. However there is the additional complicating factor that macromolecules which originate from the wood will slowly be decomposed to simpler molecules during the long maturation period, and these can further react with the dominant ethanol or each other to produce new species. The possibility then exists that the residue, after the 300°C removal of the compounds amenable to GC, may represent an earlier degradation stage of wood lignin and this argument can be further extended to the actual wood itself.

Figure 4 and 5 show comparisons of pyrograms of whiskey residue and corresponding wood samples, each pyrolyzed at 450°C, for both the QR and QA sample types. Compounds found both in wood pyrograms and in whiskey residue pyrograms are marked. Among the 20 compounds identified in whiskey residue pyrograms and listed in table 1, the 17 were also found in both QR and QA wood pyrograms. With the exception of peak 15 [2,6-Dimethyl-3-(methoxymethyl)-p-benzoquinone] the other 16 compounds are known to be formed by thermal degradation of wood, lignin or cellulose (see table 1). This, together with the fact that the main components of wood are cellulose, hemicelluloses, lignin, proteins and small molecules, leads us to the conclusion that the degradation compounds from whiskey residue originate from the wood used for barrel maturation. The QA and QR wood pyrograms show fewer differences than the pyrograms of the respective resulting matured whiskeys. As discussed above, the intervening degradation of wood macromolecules in the spirit matrix over 20 years of maturation have not been taken into account. A natural extension of this work would be to obtain similar whiskey residue pyrograms at various earlier stages of maturation (2, 4, 6 years etc). In this way a detailed picture could be established, which could clarify the links between wood type and chemical as well as sensory properties of whiskeys.

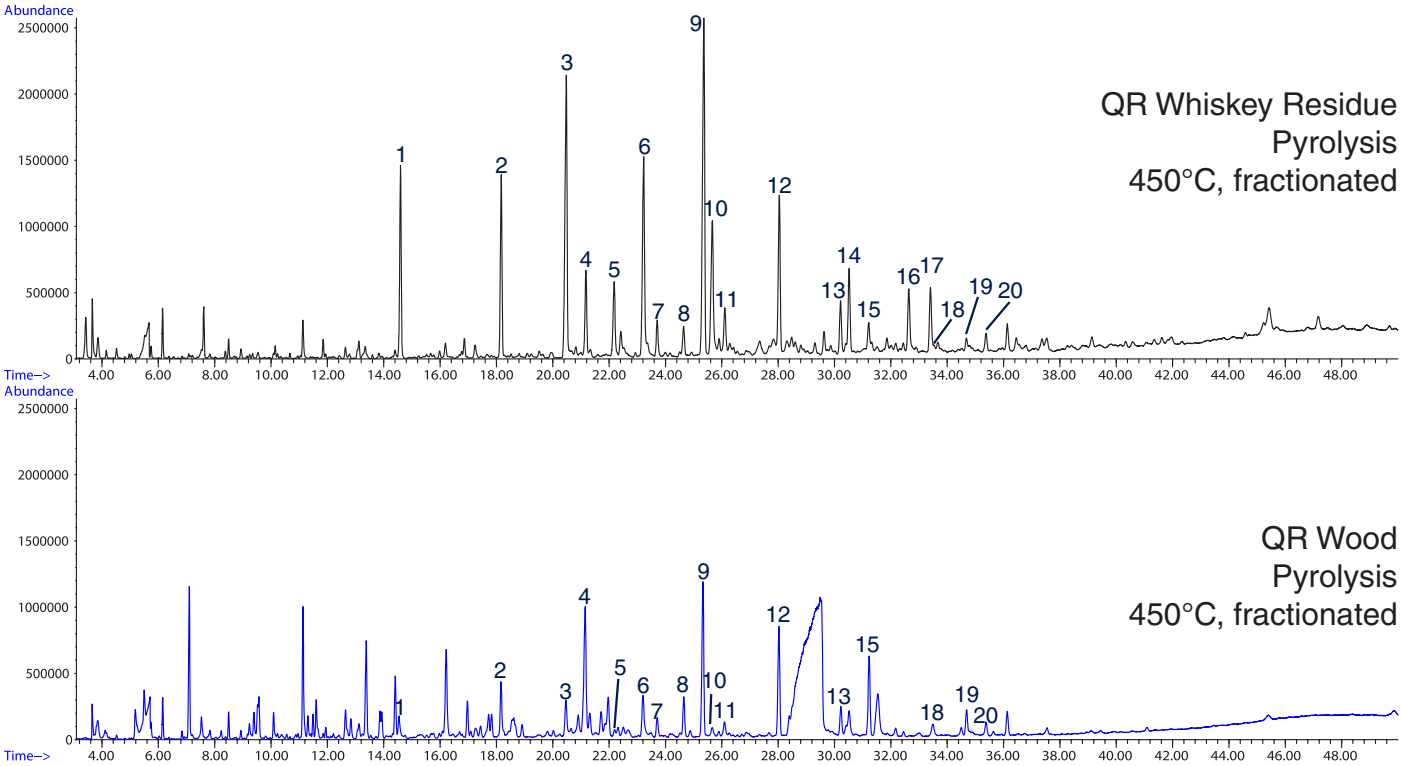

Figure 4. Comparison of pyrograms of QR whiskey residue and QR wood obtained from fractionated pyrolysis at 450°C.

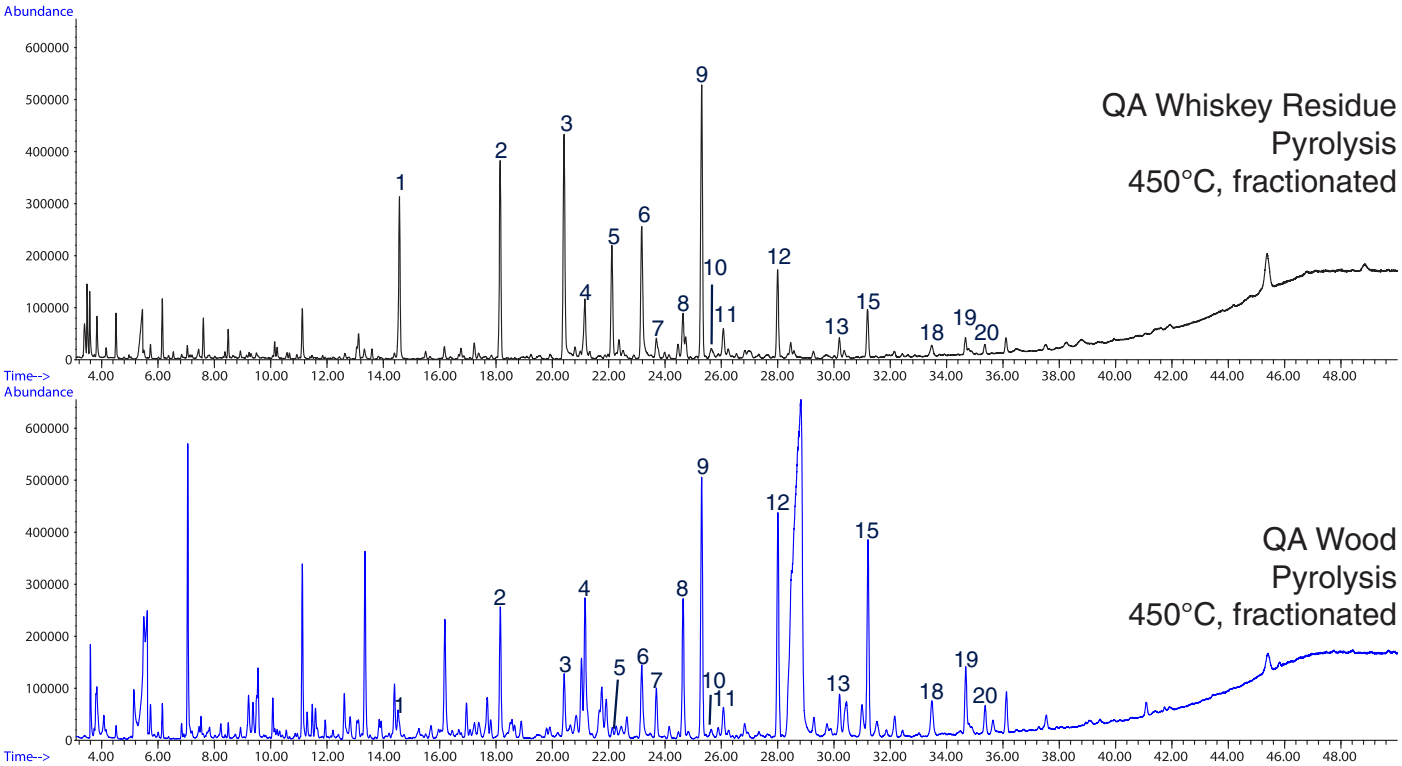

Figure 5. Comparison of pyrograms of QA whiskey residue and QA wood obtained from fractionated pyrolysis at 450°C.

Conclusions

Pyrolysis GC is a useful tool to get information on the chemical structure and composition of solid samples of organic origin, in this case whiskey residue and wood. This feasibility study has shown that the assessment of whiskey quality can be done quite easily by analyzing the solid residue of a whiskey using pyrolysis-GC-MS. Two whiskeys obtained from the same parent whiskey but matured in different oak barrels show totally different peak patterns in their pyrograms. These differences correlate to their difference in color, aroma and taste. The origin of the whiskey residue can be traced back to oak barrels used for maturation because most of the thermal decomposition products in pyrograms are also found in pyrograms of the corresponding wood materials. Finally, pyrolysis GC-MS only requires a simple addition to a GC-MS system already equipped with a thermal desorption unit (TDU). The same GC-MS unit can furthermore be used for LVI-GC-MS determination of semi-volatile degradation products of wood compounds already present in the spirit matrix.

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References

[1] K. MacNamara, D. Dabrowska, M. Baden, N. Helle. LCGC Europe,. Sep. 2011, (448-467).

[2] Y. Nie, E. Kleine-Benne, Determining Phenolic Compounds in Whiskey using Direct Large Volume Injection and Stir Bar Sorptive Extraction. GERSTEL AppNote 2/2012, www.gerstel.com

[3] T. Albinus, K. Mac Namara. Large Volume Injection with GC/MS Multi Column Switching for Direct Determination of Ethyl Carbamate in Alcoholic Beverages. GERSTEL AppNote 10/2012, www.gerstel.com

[4] A. Hoffmann, K. Mac Namara. Large Volume Injection with Solvent Venting - Application to Trace Detection of Analytes in Water. GERSTEL AppNote 15/2012. www.gerstel.com

[5] O. Faix, D. Meier, I. Fortmann, Thermal degradation products of wood, 48 (1990) 281.

[6] Serban C. Moldoveanu, Analytical Pyrolysis of Natural Organic Polymers, Elsevier

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