

Poster Reprint

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Qualitative and Quantitative Characterization of Whiskey with Accurate Mass Time of Flight LCMS

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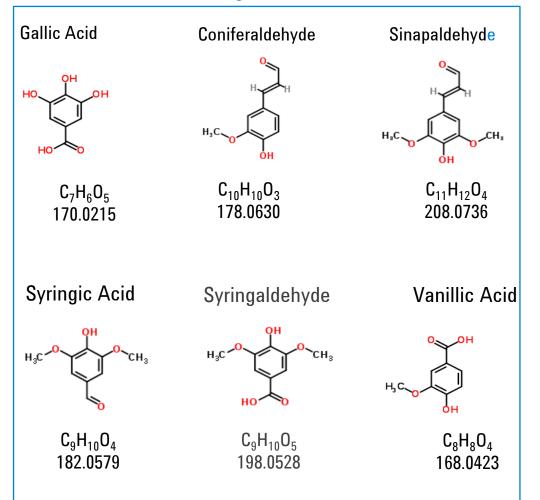
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Introduction

Many types of spirits are aged in oak barrels for the absorbance of color and flavors. The barrels are reused, moving from whiskies to bourbons to sherries and tequila. Ten compounds must be present for a spirit to be considered barrel aged. Counterfeiters market non barrel aged spirits as barrel aged. In order to prosecute these counterfeiters, there must be proof that a product is fake. Congeners are minor compounds other than ethanol that occur naturally in distilling and fermenting process. This method adds another level of confirmation to the presence of the congeners. With the addition of fragment confirmation, we have now ways to prove the authenticity of spirits can be proven by the simultaneous confirmation of fragments, retention time, isotopic fidelity and spacing and accurate mass. Congeners are quantified with reference standards.

Congeners



Experimental

One reference standard containing 10 nonvolatile congeners was run via LCMS TOF. A four-level calibration curve was created and run in triplicate. Seven samples of commercial whiskies were purchased and in quintuplicate for both quantitative and quantitative analysis. Known samples of nonaged spirits and long barrel aged spirits were analyzed. The multi-congener standard was included in this data set.

This data set was imported into Agilent Mass Profiler Professional software. The spirits were profiled by their mass characteristics. The experiment was repeated using all ion methodology. The all-ion method yielded LCMSMS-like spectral confirmation of the congeners in the spirits.

The samples were again rerun using all ions methodology with high and low fragmentor voltages. That data were analyzed against a Congener Agilent MassHunter Personal Compound Database and Library (PCDL) Manager for verification.

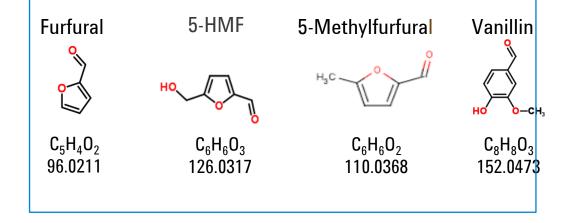


LC Parameters

TOF MS Parameters

Value
Dual ESI,
30-950 m/z
4 Hz
121.0509, 922.0098
9 L/min
300 °C
4000 V
145 V
100 V. 170 V 270 V
65 V
750

2

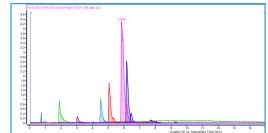


Prime UHPLC	Value
Column Temp	35 C
Injection volume	30-950 m/z
DAD Lambda	280
Flow Rate	0.5 ml/min
Mobile Phase A	0.1% Formic in H2O; Initial condition 95 %
Mobile Phase B	0.1% Formic Methanol; Initial condition 5%
Time 12 minutes	% A 5 [0.1% Formic in H20] % B 95 0.1% Formic Methanol
Run Times	Stop time = 15 minutes Post time = % minutes
Column	ZORBAX RRHT StableBond CN, 3.0 x 100 mm, 1.8 µm, 600 bar. 80Å,

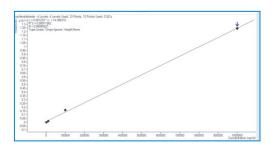
Results and Discussion

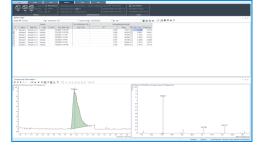
Quantitative Results

Extracted ions were used to create calibration curves from 1 ppm to 1000 ppm. 4 levels at 1, 10, 100, 1000 ppm.



Congeners	R ²	m/z
Vanillic Acid	0.999	169.0495
Syringic Acid	0.999	199.0601
Vanillin	0.999	153.0546
Syringaldehyde	0.999	183.0652
Coniferaldehyde	0.999	179.0703
Sinapaldehyde	0.999	209.0808
5 - methylfuran	0.999	111.0441
Gallic Acid	0.999	170.0275
Furfural	0.999	96.0225
5 – Hydroxymethylfuraldehye (HMF)	0.999	126.0307

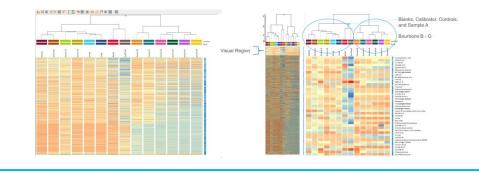


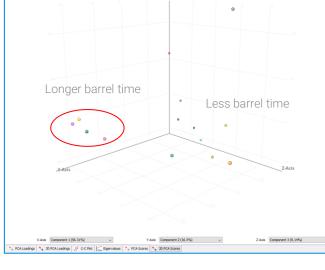


Sample	Compound	Concentration (ppm)	Sample	Compound	Concentration (ppm)
А	Vanillin	2.394	F	Vanillin	3.89
	5 HMF	1.609		Vanillic Acid	40.95
				Sryingic Acid	4.37
В	Vanillin	1.26		Syringaldehyde	13.46
	Vanillic Acid	45.21		Sinapaldehyde	6.98
	Sryingic Acid	2.34		Gallic Acid	12.57
	Syringaldehyde	10.59		5 HMF	0.96
	Sinapaldehyde	29.99			
	Gallic Acid	12.37	G	Vanillin	0.9
	5 HMF	2.02		Vanillic Acid	44.46
				Sryingic Acid	1.2
С	Vanillin	0.95		Syringaldehyde	8.01
	Vanillic Acid	45.41		Sinapaldehyde	20.25
	Sryingic Acid	1.603		Gallic Acid	8.23
	Syringaldehyde	7.74		5 HMF	7.83
	5 HMF	0.69			
			Е	Vanillin	0.92
D	Vanillic Acid	46.47		Vanillic Acid	45.33
	Sryingic Acid	0.38 ppm		Sryingic Acid	1.05
	Syringaldehyde	5.24		Sinapaldehyde	10.44
	Sinapaldehyde	0.47		5 HMF	0.63
	5 HMF	0.58		Gallic Acid	7.55
				Syringaldehyde	7.31

Data Analysis 3D PCA

Analysis via LC-TOF Calibrators, controls (Bourbons), blanks, samples N=5 for each, Total dataset = 97 files Feature Finding Agilent Profinder Data Analysis: 97 raw data files, "loose" parameters, non-recursive Statistical Analysis Agilent Mass Profiler Professional (MPP)





The workflow allowed characterization where all spirit samples clustered properly. Duplicate samples paired correctly. All analysis was done blindly and tacitly validating the MPP tools



Data base for Qualitative Evaluation



Compound Results 10 hits								
Name	Formula	Maas	Retention Time	Cation	Anion	CAS	ChemSpider	IUPAC
Vanilic acid	C8H9O4	168.04226	1.34			121-34-6	8155	4-Hydroxy-3-meth.
Vanilin	C8H8O3	152.04734	1.38			121-33-5	13860434	4-Hydroxy-3-meth.
Syringaldehyde	C9H1004	182.05791	1.64			134-96-3	8333	4-hydroxy-3,5-dim
Galic acid	C7H6O5	170.02152	0.83			149-91-7	361	3,4,5-Trihydroxyb
Conferaldehyde	C10H1003	178.06299	2.18					
Sinapaldehyde	C11H12O4	208.07356	2.48					
Symple add	C9H1005	198.05282	1.53					
Furfural	C5H4O2	96.02113	0.82					
5-HMF (hydroxymethylfuraidehyde)	C6H6O3	126.03169	0.72					
5-Methylfurfural	C6H6O2	110.03678	1					

		(80.00)	133.05462	23 Pistive	821			
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iyy)		(8-11-	153.05490	23 Postive	ESI		2 5- 2 25-	
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ini	ln .	(8-10+	153.05493	43 Postive	651		100000000000000000000000000000000000000	85
							+59 MS2 GTOF FIV-159 CE-10 M-K1+	-
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	Varillo aoid	C8H804	168 54225	134			5 5 - 25.0 - 33.0 - 33.0 -	
	Vanilio	C84803	152.04734	1.08			1 0 4 6 6 7 6 6 10 10 10 10 10 10 10 10 10	-
	Sympathelyde	C\$H1304	102.05791	1.64			al la	
	Callc acid	C7H605	170.02152	0.83			+ESI W52 GTOF FV+150 CE+20 (M+H)+	
	Confienderlycke	C10H1003	178.06299	2.18			5 100- 05.02857 90.02049	
	Snapaldelyde	C11H1204	208 17296	2.48			8 N- 411 H0000	
	Syringic acid	C9H1305	198 05282	1.53			<	-
	Rutual	C5H402	96.62113	0.02			20 40 50 60 70 80 90 100 110 120 130 140 140 140 140 140 140 140	18
	5109 (tydosynethyflusidetyde)	CEHEOS	126 03103	0.72			+ER WS2 GTOF FILHIS2 CE+R0 (M+R)+	-
	5-Methyliationi	C6H602	110.03678				2 100-1 66.09867	
							51 51 51 51 51 51 51 51 51 51 51 51 51 5	1

A barrel aging PCDL has been created previously from all ions data. This data base has been used at sites in industry for qualification and of barrel aged spirits . The 100 ppm Congener standard was used to verify method performance. All Congeners were found with ion confirmation.

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Compound Link: 10 found											×	0.5-							
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		General							Compound life	dification			1 8	1 2 2	2 5	3 2	- A -	5 5	5 6
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and Tox Versilia and +; CEME OR 5220		90.0338 0.23				CE HE OA	191.023			121-54-6		C (arround	Chromatogram Result	N		Otomore	d Mi Spechami	insets.	
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BR-hogContex Set =Name =Formula = O Vanilin C3160 05 Constant C3160	153.0507 152.0436 gMassDi#pperi a 1643 2.6 5.4	152,0473 Rags(Rc)	-24.05 Qualified Qualified Qualified dence peaks	403 4.55 74 Givespt 4 170 747533 170 627594 270 491963 170 179923	4 D Abundar	norsjal) © mojali 900 650 125 1100	M+H 9 93,8352 80 65,2366 86 125,867 86 116,8561	bohiHeight(ME) 44 Con B434.7 13081.3 5222.9	43.9 Ispound Name + Vanilla Vanilla Vanilla Vanilla	Piero Pi	Fo SNR o 13 35369449 13 4133 13 3565 13 4653	50- 10- 5- 1- 0.5- 0.1-	7	-804	Prog 123 (600)	1- 05- 0- 70- 7, 85- 85- 85- 85- 8- 85- 8- 85- 8- 85- 8- 8- 8- 8- 8- 8- 8- 8- 8- 8- 8- 8- 8-	12 Vanilie, CB H	4004401 603.453411 100451 100451	0.000 +69 Sor
BR-hogContex Set =Name =Formula = O Vanilin C3160 05 Constant C3160	153.0507 152.0436 gMassDi#pperi a 1643 2.6 5.4	152,0473 Rags(Rc)	-24.05 Qualified Qualified Qualified dence peaks	403 4.55 74 Givespt 4 170 747533 170 627594 270 491963 170 179923	4 D Abundar	norsjal) © mojali 900 650 125 1100	M+H 9 93,8352 80 65,2366 86 125,867 86 116,8561	bohiHeight(ME) 44 Con B434.7 13081.3 5222.9	43.9 Ispound Name + Vanilla Vanilla Vanilla Vanilla	Piero Pi	Fo SNR o 13 35369449 13 4133 13 3565 13 4653	80- 10- 5- 0.5- 0.5- 0.05-	7	-804	Prog 123 (600)	1-05-0-0-0-0-0-0-0-0-0-0-0-0-0-0-0-0-0-0	2 Vanille, CB H	6 03 45 45 45 45 45 45 45 45 45 45 45 45 45	aasse -ea su
BR-hogContex Set =Name =Formula = O Vanilin C3160 05 Constant C3160	153.0507 152.0436 gMassDi#pperi a 1643 2.6 5.4	152,0473 Rags(Rc)	-24.05 Qualified Qualified Qualified dence peaks	403 4.55 74 Givespt 4 170 747533 170 627594 270 491963 170 179923	4 D Abundar	norsjal) © mojali 900 650 125 1100	M+H 9 93,8352 80 65,2366 86 125,867 86 116,8561	bohiHeight(ME) 44 Con B434.7 13081.3 5222.9	43.9 Ispound Name + Vanilla Vanilla Vanilla Vanilla	Piero Pi	Fo SNR o 13 35369449 13 4133 13 3565 13 4653	50- 10- 5- 1- 0.5- 0.1-	T	-804	Prog 123 (600)	1- 05- 0- 70- 7, 85- 85- 85- 85- 8- 85- 8- 85- 8- 85- 8- 8- 8- 8- 8- 8- 8- 8- 8- 8- 8- 8- 8-	12 Veniller, CBH	6 03. 454 1 6 03. 454 1 000 K1 000 K1 000 K1	0.0007 +69 Su
BR-hogContex Set =Name =Formula = O Vanilin C3160 05 Constant C3160	153.0507 152.0436 gMassDi#pperi a 1643 2.6 5.4	152,0473 Rags(Rc)	-24.05 Qualified Qualified Qualified dence peaks	403 4.55 74 Givespt 4 170 747533 170 627594 270 491963 170 179923	4 D Abundar	norsjal) © mojali 900 650 125 1100	M+H 9 93,8352 80 65,2366 86 125,867 86 116,8561	bohiHeight(ME) 44 Con B434.7 13081.3 5222.9	43.9 Ispound Name + Vanilla Vanilla Vanilla Vanilla	Piero Pi	Fo SNR o 13 35369449 13 4133 13 3565 13 4653	80- 10- 5- 0.5- 0.5- 0.05-	7		Pagiti 108 Ing 13. 800 Pagi 10. 2006	1-05-0-0-0-0-0-0-0-0-0-0-0-0-0-0-0-0-0-0		153 800 154 800 1758 803 441+	<u>}</u>
BR-hogContex Set =Name =Formula = O Vanilin C3160 05 Constant C3160	153.6507 152.0436 gt/455.01/#juent o 143 5.4 5.4 5.1 0	152.0473 Page/Rc) Inted/Mattgare ent	-2428 Calified Qualified Qualified Qualified dervor peaks Lorge RT off	403 433 % Givegiti 4 110 747533 110 427564 210 491963 110 119924 113484	a Albundar	norsjal) © mojali 900 650 125 1100	M+H 9 93,8352 80 65,2366 86 125,867 86 116,8561	bohiHeight(ME) 44 Con B434.7 13081.3 5222.9	43.9 Ispound Name + Vanilla Vanilla Vanilla Vanilla	Piero Pi	Fo SNR o 13 35369449 13 4133 13 3565 13 4653	80- 10- 8- 0.5- 0.1- 0.05- 0.05-	1 42 44	-804	Fragiti 1086 - Fragiti 1000 - Fragiti 10000 - Fragiti 10000 - Si 4 50	1-05-0-0-0-0-0-0-0-0-0-0-0-0-0-0-0-0-0-0	the	8 03.45411 102011 102011 102011	<u>}</u>

Results for 100 ppm standard

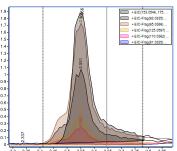
Qualitative analysis with All Ions Methodology

The known barrel aged Bourbon with all 10 congeners was run and analyzed with the Congener PCDL.

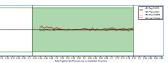
<u>+0</u>	Automatically Show Colum							
-		Formula V +				Diff (Tgt, ppm) マ+		
••	Cpd 1: <furfural></furfural>	C5 H4 O2	97.0286	96.0213	96.0211	2.14	87.59	Qualifie
)··	Cpd 2: <5-Methylfuran>	C6 H6 O2	111.044	110.0367	110.0368	-0.4	99.95	Qualifie
3 3 >	Cpd 3: <5-HMF>	C6 H6 O3	127.0389	126.0316	126.0317	-0.64	99.81	Qualifie
3+ 🕨	Cpd 4: Vanillin	C8 H8 O3	153.0546	152.0473	152.0473	-0.01	97.41	Qualifie
	Cpd 5: <vanillic acid=""></vanillic>	C8 H8 O4	169.0495	168.0423	168.0423	0.18	98.09	Qualifie
	Cpd 6: Gallic Acid	C7 H6 O5	171.0287	170.0214	170.0215	-0.83	99.57	Qualifie
	Cpd 7: <coniferaldehyde></coniferaldehyde>	C10 H10 O3	179.0702	178.0629	178.063	-0.53	99.38	Qualifie
	Cpd 8: <syringic acid=""></syringic>	C9 H10 O4	183.0651	182.0578	182.0579	-0.5	99.32	Qualifie
	Cpd 9: Syringaldehyde	C9 H10 O5	221.0421	198.0528	198.0528	-0.17	93.33	Qualifie
	Cpd 10: Sinapaldehyde	C11 H12 O4	209.0807	208.0734	208.0736	-0.97	99.35	Qualifie
4 5 4 3 2 2 1 0 4 8 6	03-\$385 03.\$250 10-032 -74-\$611 121-\$609 153.\$548					133.0047 ()Cd8ad9()+1;+		175 0364
4- 2-		ient sp	ectra	327.0829 280 300 310 320 330	s 375.0383 340 350 360 370 380 380 400	The com	do 182 184 186 188 1	()C8H803)+Na(+



Each of the 10 compounds in the mix was qualified by retention time, accurate mass, fragment matching, Isotopic spacing and pattern. When a compound was qualified, an overlay of fragment retention times is created along with a Coelution plot.



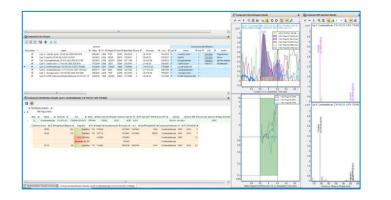
Overlay of EICs of fragment ions



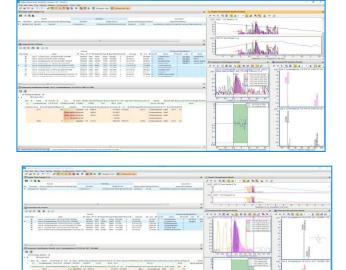
Coelution plot of fragment spectra retention times

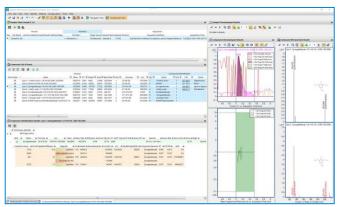


Sample A shows only 3 Congeners Matching a vodka sample and non aged bourbon.

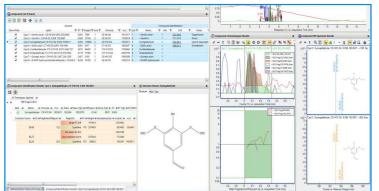


Sample B. C and D appear to be very similar. The congeners are found in low concentrations.

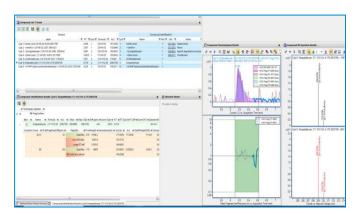




Sample E exhibits a golden color



Sample F, dark brown with rich aroma, shows definite presence of congeners. Sample F is a barrel aged whiskey



Sample G, darkest brown with rich aroma, shows definite presence of

with an aroma. Definite barrel aging is concluded.

congeners and is a barrel aged whiskey

Conclusions

We are able to use the time of flight for both qualitative and quantitative work. With all ion methodology, we see the ability to have MS/MS like spectral confirmation.

https://www.agilent.com/en/promotions/asms

This information is subject to change without notice.

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