Qualitative Comparison of Whisky Samples Using Fast GC/TOFMS

LECO Corporation; Saint Joseph, Michigan USA

Key Words: GC-TOFMS, Food, Flavors

1. Introduction

In quality control of alcoholic beverages it is often important to compare different production batches to detect possible changes in the fermentation and/or distillation process.

Additionally, the formation of chemicals due to the aging and storage of the raw liquor (e.g. Whisky) lactones are significant factors in the final taste and odor of the finished product.

This note describes the application of a simple and fast GC method with MS detection using the Pegasus II Time-of-Flight GC/MS detector. This, in combination with unique software algorithms for Automated Peak Find, Deconvolution, and sample comparison creates a powerful quality control instrumentation.

2. Experimental Conditions

An accelerated GC method requiring 11 minutes runtime was created using a column which was shorter and had a narrower inner diameter than used in common standard set-up.

GC-Parameters

Column:
J&W DB-WAX, 20 m x 0.18 mm x 0.18 µm

Oven Program:
50°C initial temperature, hold for 1.2 minutes, with 16°/minute to 150°C, then 66°/minute to 240°C, hold for 2.5 minutes

Split Ratio: 20:1

Flow Rate: 0.7 mL/minute Helium constant flow

MS-Parameters

Mass Range: 30 to 350 amu

Scan Rate: 20 spectra/second

Ion Source: 170°C

Total Run Time: 11.3 minutes

3. Results

Five commercial single malt Scottish Whisky samples and one Cognac sample were measured, processed and then automatically compared against each other.

The different brands were in detail:

Whisky (10 years, 40 vol %)
Whisky (10 years, 43 vol %)
Whisky (43 vol %)
Whisky (22 years, 43 vol %)
Whisky (60 vol %)
Cognac (40 vol %)

Figure 1 presents a typical chromatogram of a Whisky sample.

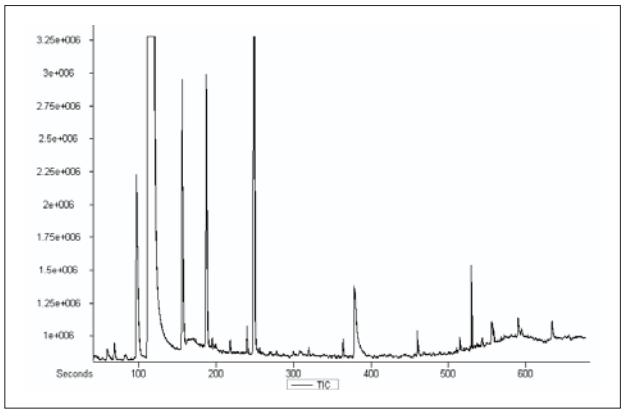

Figure 1. Enlarged Total Ion Chromatogram (TIC) of Whisky sample 1.

Some substances in the chromatogram were coeluting. The Pegasus deconvolution software can mathematically separate the spectra of the overlapping compounds and thus supplies undisturbed spectra as shown in Figure 2.

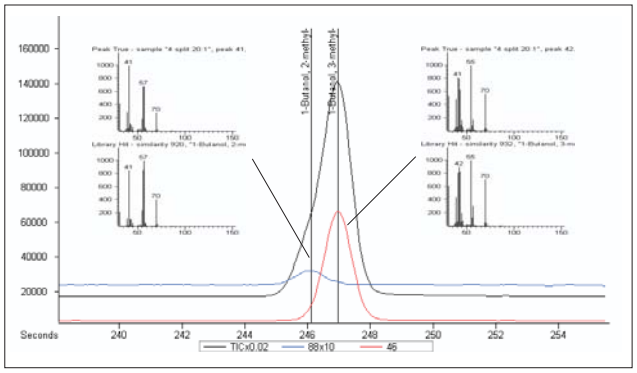

Figure 2. TIC and characteristic mass chromatograms of two coeluting compounds together with the deconvoluted mass spectra.

Other analytes were eluting within the tailing of the ethanol peak. The automatic peak finding and deconvolution also found and identified those compounds as shown in Figure 3 and 4.

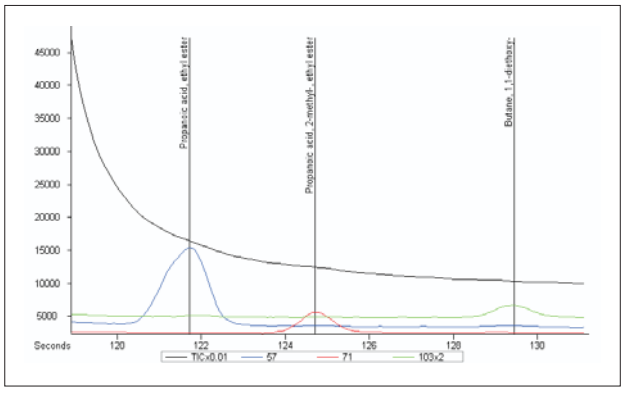

Figure 3. Three detected components in the ethanol tail. The TIC is presented at 1 percent of its original size.

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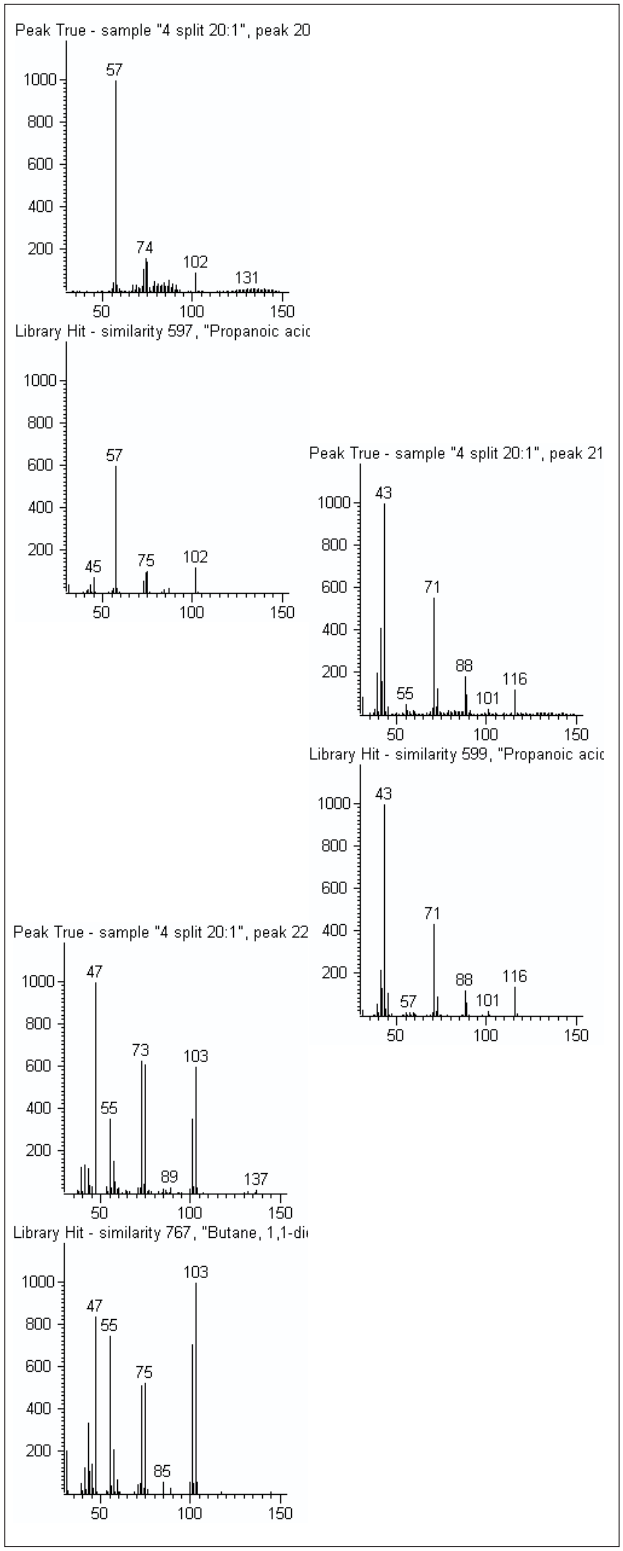

Figure 4. Spectra and library identification of compounds within the ethanol tailing.

Sample Comparison

Whisky Sample 1 had a very earthy, swampy taste. It contained more than 100 compounds with S/N ratios larger than 30 that were detected by the automatic peak finding algorithm of the Pegasus software. 64 compounds were selected and transformed into a reference list which was then automatically compared against the other Whisky samples.

Table 1. Reference table from Sample 1.

Peak #	Name	R.T. (s)
1	Acetaldehyde	68.779
2	Propanal, 2-methyl-	81.712
3	Acetone	82.245
4	Formic acid, ethyl ester	83.645
5	Methane, diethoxy-	89.845
6	Ethyl Acetate	97.379
7	Ethane, 1,1-diethoxy-	99.245
8	Propanoic acid, 2-methyl-, ethyl ester	125.91
9	Butane, 1,1-diethoxy-	130.31
10	Acetic acid, 2-methylpropyl ester	143.91
11	Butanoic acid, ethyl ester	154.71
12	1-Propanol	156.51
13	Ethyl 2,3-epoxybutyrate	162.98
14	á-Pinene	186.31
15	1-Propanol, 2-methyl-	187.51
16	1-Butanol, 3-methyl-, acetate	195.31
17	1-Butanol	218.25
18	2-Propanol, 1-methoxy-	239.98
19	Methanesulfonyl chloride	241.51
20	Active Amyl alcohol	248.45
21	Isoamyl alcohol	249.51
22	Hexanoic acid, ethyl ester	256.18
23	Diethoxymethyl acetate	269.31
24	Heptanol	271.25
25	Pyrazine, methyl-	280.58
26	2-Butanone, 3-hydroxy-	292.45
27	2-Propanone, 1-hydroxy-	299.85
28	Acetaldehyde, hydroxy-	307.71
29	Propanoic acid, 2-hydroxy-, ethyl ester, (S)-	319.71
30	1-Hexanol	324.51
31	Acetic acid, hydroxy-, ethyl ester	357.78
32	Octanoic acid, ethyl ester	363.98
33	Acetic acid	378.45
34	Furfural	379.78
35	Acetylfuran	401.05
36	Dimethyl Sulfoxide	439.85
37	Propanoic acid, 2-methyl-	441.31
38	Decanoic acid, ethyl ester	459.85
39	Butanoic acid	466.91
40	2-Furanmethanol	467.98
41	Butanedioic acid, diethyl ester	472.85
42	2-Cyclopenten-1-one, 2-hydroxy-	500.51
43	Acetic acid, 2-phenylethyl ester	510.51
44	Pentadecanoic acid, ethyl ester	514.65
45	Hexanoic acid	521.98
46	Phenylethyl Alcohol	529.51
47	cis-3-Methyl-4-octanolide (Whisky-lactone)	538.65
48	Phenol, 2-methyl-	542.91
49	Phenol	543.65
50	Methyl 2-furoate	547.11
51	Phenol, 4-ethyl-2-methoxy-	548.71
52	Butanedioic acid, hydroxy-, diethyl ester, (ñ)-	549.25
53	Phenol, 2-ethyl-	553.18
54	Phenol, 2,4-dimethyl-	554.91
55	Octanoic Acid	555.51
56	Guaiol	558.65
57	Phenanthrene, 9-dodecyltetradecahydro-	559.98

All compound concentrations in the reference list were arbitrarily defined as 100%. Using the integration results of the compounds in the list a one point calibration was calculated for each analyte and then the other samples were quantified against the list.

Some individual results are described in the following. The complete comparison results are presented in Table 2.

Methylpyrazine was detected in Sample 1 as to be seen in Figure 5 (purple trace). The other samples only contained small, if any, amounts of this analyte. Only in Sample 3 (black trace) did the signal have a signal to noise ratio above the user defined threshold. The relative concentration was calculated to be 25%.

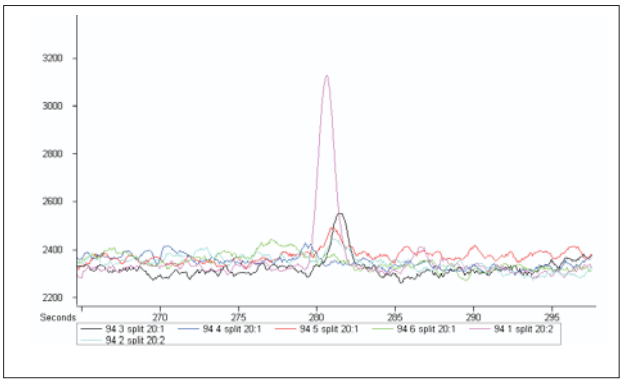

Figure 5. Characteristic mass trace 94 for Methylpyrazine in the six samples.

Besides the information whether the investigated samples either did or did not contain the compounds in the reference table, the automatic peak finding also detected components that are not present in the reference sample. One example for such an "unknown" compound is shown in Figure 6. Here, a pyrane derivative was found in the cognac which was not present in the reference sample. The identification is based on a standard NIST library search.

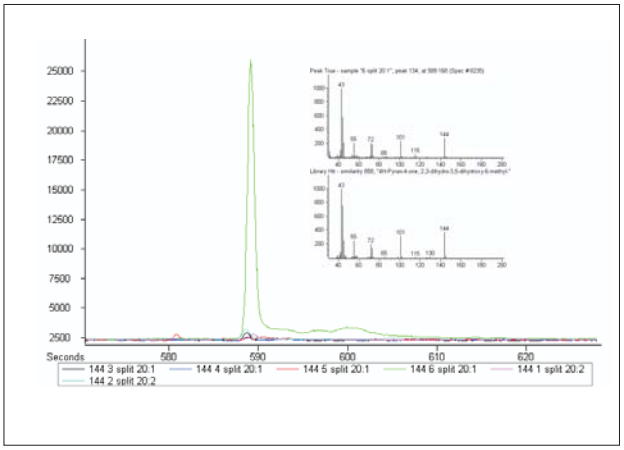

Figure 6. Characteristic mass trace and library identification of an "unknown" compound in the cognac sample.

Table 2. Comparison results from the other Whisky and Cognac samples. Fields in blue show the cause of the "muddy" taste of Sample 1, the phenols, which are not present in the other samples. Fields in red show major differences between Whisky and cognac.

Name	Whisky 2	Whisky 3	Whisky 4	Whisky 5	Cognac
Acetaldehyde	197.4%	293.4%	93.8%	222.6%	123.3%
Propanal, 2-methyl-	233.5%	207.6%	46.1%	231.6%	329.1%
Acetone	100.0%	145.7%	56.5%	198.4%	82.3%
Formic acid, ethyl ester	197.7%	249.8%	137.0%	354.5%	234.3%
Methane, diethoxy-	110.6%	462.6%	186.0%	107.3%	289.7%
Ethyl Acetate	232.9%	223.5%	130.3%	324.0%	112.6%
Ethane, 1,1-diethoxy-	230.1%	360.9%	189.9%	654.8%	128.0%
Propanoic acid, 2-methyl-, ethyl ester	177.7%	337.7%	117.7%	236.7%	125.9%
Butane, 1,1-diethoxy-	324.3%	274.1%	76.5%	843.7%	352.6%
Acetic acid, 2-methylpropyl ester	189.4%	115.9%	66.1%	421.3%	78.1%
Butanoic acid, ethyl ester	206.2%	198.6%	69.7%	287.4%	75.8%
1-Propanol	195.8%	154.7%	52.0%	179.1%	57.6%
Ethyl 2,3-epoxybutyrate	114.4%	not found	127.5%	not found	70.4%
á-Pinene	38.4%	383.1%	73.5%	62.4%	23.9%
1-Propanol, 2-methyl-	143.4%	181.9%	83.9%	228.2%	200.6%
1-Butanol, 3-methyl-, acetate	228.6%	76.1%	44.2%	367.3%	29.1%
1-Butanol	172.6%	135.6%	20.2%	175.3%	26.4%
2-Propanol, 1-methoxy-	139.8%	161.5%	123.4%	221.8%	93.0%
Methanesulfonyl chloride	144.5%	122.2%	31.0%	131.1%	138.3%
Active Amyl alcohol	143.9%	158.9%	50.7%	200.1%	140.5%
Isoamyl alcohol	150.2%	162.4%	55.9%	189.2%	170.2%
Hexanoic acid, ethyl ester	216.8%	344.5%	94.0%	251.3%	94.9%
Diethoxymethyl acetate	123.4%	239.0%	101.5%	159.1%	123.9%
Heptanol	162.2%	197.5%	60.8%	202.5%	31.8%
Pyrazine, methyl-	not found	25.3%	not found	not found	not found
2-Butanone, 3-hydroxy-	249.7%	149.5%	97.5%	415.7%	108.8%
2-Propanone, 1-hydroxy-	139.0%	66.4%	not found	40.1%	381.6%
Acetaldehyde, hydroxy-	165.4%	18.1%	11.5%	55.9%	2039.0%
Propanoic acid, 2-hydroxy-, ethyl ester, (S)-	603.8%	633.3%	56.7%	2245.3%	939.0%
1-Hexanol	173.6%	212.2%	56.2%	213.5%	545.5%
Acetic acid, hydroxy-, ethyl ester	88.7%	132.5%	21.4%	69.8%	73.4%
Octanoic acid, ethyl ester	201.5%	366.2%	108.3%	297.2%	68.0%
Acetic acid	19.9%	71.1%	78.7%	401.1%	142.6%
Furfural	294.5%	236.7%	62.1%	388.4%	191.9%
Acetylfuran	101.7%	129.6%	21.9%	240.7%	54.6%
Propanoic acid, 2-methyl-	216.9%	453.8%	302.1%	394.8%	93.6%
Dimethyl Sulfoxide	222.3%	not found	not found	20.6%	not found
Decanoic acid, ethyl ester	268.3%	354.1%	117.1%	543.6%	34.1%
Butanoic acid	149.5%	not found	not found	323.9%	not found
2-Furanmethanol	215.6%	106.5%	40.3%	265.2%	1813.3%
Butanedioic acid, diethyl ester	276.4%	522.0%	57.9%	1214.2%	216.9%
2-Cyclopenten-1-one, 2-hydroxy-	220.1%	127.0%	38.3%	120.8%	841.9%
Acetic acid, 2-phenylethyl ester	212.4%	61.2%	11.2%	356.6%	5.5%
Pentadecanoic acid, ethyl ester	358.5%	382.7%	153.0%	1138.8%	30.2%
Hexanoic acid	174.7%	184.6%	31.9%	211.3%	58.3%
Phenylethyl Alcohol	138.9%	181.7%	38.7%	265.4%	33.5%
cis-3-Methyl-4-octanolide (Whisky-lactone)	77.6%	151.4%	12.7%	63.7%	not found
Phenol, 2-methyl-	not found	10.9%	3.9%	not found	not found
Phenol	not found	14.5%	5.9%	not found	not found
Methyl 2-furoate	not found	83.7%	not found	not found	631.0%
Phenol, 4-ethyl-2-methoxy-	25.1%	not found	not found	not found	not found
Butanedioic acid, hydroxy-, diethyl ester, (ñ)-	118.9%	390.2%	75.6%	193.9%	118.6%
Phenol, 2-ethyl-	not found	not found	27.1%	not found	not found
Octanoic Acid	1.9%	not found	not found	not found	not found
Phenol, 2,4-dimethyl-	6.7%	not found	not found	4.7%	not found
Guaiol	98.3%	433.8%	93.3%	105.2%	not found
Phenanthrene, 9-dodecylte-tradecahydro-	88.4%	308.4%	75.8%	108.5%	67.3%
Phenol, 4-ethyl-	not found	10.8%	not found	19.3%	not found
n-Decanoic acid	186.0%	103.8%	12.4%	185.2%	20.8%
Glycerin	589.8%	1646.8%	237.7%	992.4%	146.3%
Dodecanoic acid	218.3%	46.9%	8.7%	50.8%	not found
2-Furancarboxaldehyde, 5-(hydroxymethyl)-	98.1%	25.2%	not found	not found	1313.8%
Cedar aldehyd	88.5%	198.3%	82.0%	408.5%	180.3%
Vanillin	79.9%	111.3%	21.8%	147.8%	96.8%

Delivering the Right Results

4. Conclusion

As demonstrated in this application, the Pegasus is ideal for performing fast, sensitive determination of complex samples. The data processing software detects and identifies the target compounds by comparison of complete spectra (even when the components are buried in the baseline) as well as performing a search for unknown substances after separating overlapping spectra. A proper library identification can also be achieved using derived (background subtracted) spectra. Further acceleration and increase in sensitivity could easily be accomplished by means of higher scan rates, larger injection volume, etc.

The application outlines not only the potentials of creating fingerprint type information of different samples but also implies the possibility of creating an effective tool for quality control purposes within the production process.

5. Acknowledgements

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LECO Corporation • 3000 Lakeview Avenue • St. Joseph, MI 49085 • Phone: 800-292-6141 • Fax: 269-982-8977
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