Application Note

Instrument: Pegasus® BT and ChromaTOF® Sync

Comparison of Traditional Chardonnay and Buttery Chardonnay with Data Processing for Sample Sets

LECO Corporation; Saint Joseph, Michigan USA

Key Words: Wine, Aroma Profile, GC, MS, TOFMS, Solid Phase Microextraction, SPME, Retention Index, RI, Deconvolution, Peak Finding, Alignment, *ChromaTOF* Sync

Introduction

Gas chromatography (GC) and mass spectrometry (MS) are powerful analytical tools that can reveal individual analyte components in complex samples. Analytes are separated from each other with GC, and MS detection can provide analyte identifications by matching observed spectral data to library databases. Full m/z range TOFMS data also allows for deconvolution, which provides additional mathematical separation in instances of chromatographic coelution, often revealing even more chemical information about a sample. Chromatographic elution order and retention index (RI) matching can add additional support for these chemical identifications, leading to thorough and reliable sample characterizations. In order to extend this type of single sample characterization to sets of samples, it is usually necessary to link the relevant chemical information through the set of samples. Various software and data processing tools can facilitate this type of peak compilation, comparison, and characterization. *ChromaTOF* Sync is a data processing tool that compiles peak information through sets of samples by performing peak finding and deconvolution on the sample set. A composite sample set peak table is produced, and individual analyte trends through the sample set and overall sample trends can be observed and determined. This type of workflow and objective has broad applicability across many types of samples and markets. In this work, we explore the chemical composition of beverage samples. In particular, two chardonnay wine samples from the same vineyard and vintage were analyzed and compared. One of the wines was a traditional chardonnay and the other was a buttery chardonnay that had undergone additional processing, such as malolactic fermentation. Generally, buttery chardonnays tend to have more buttery, caramel, and rich fruit notes while traditional chardonnays tend to be more fruity, fresh, citrusy, and crisp. These descriptors were consistent with the specific wine samples that were analyzed here. In this work, GC-MS and *ChromaTOF* Sync were used to investigate specific chemical trends and to characterize these wine samples. Individual analytes that distinguished the wines and connected to their sensory attributes were observed, and representative examples are presented and described here.

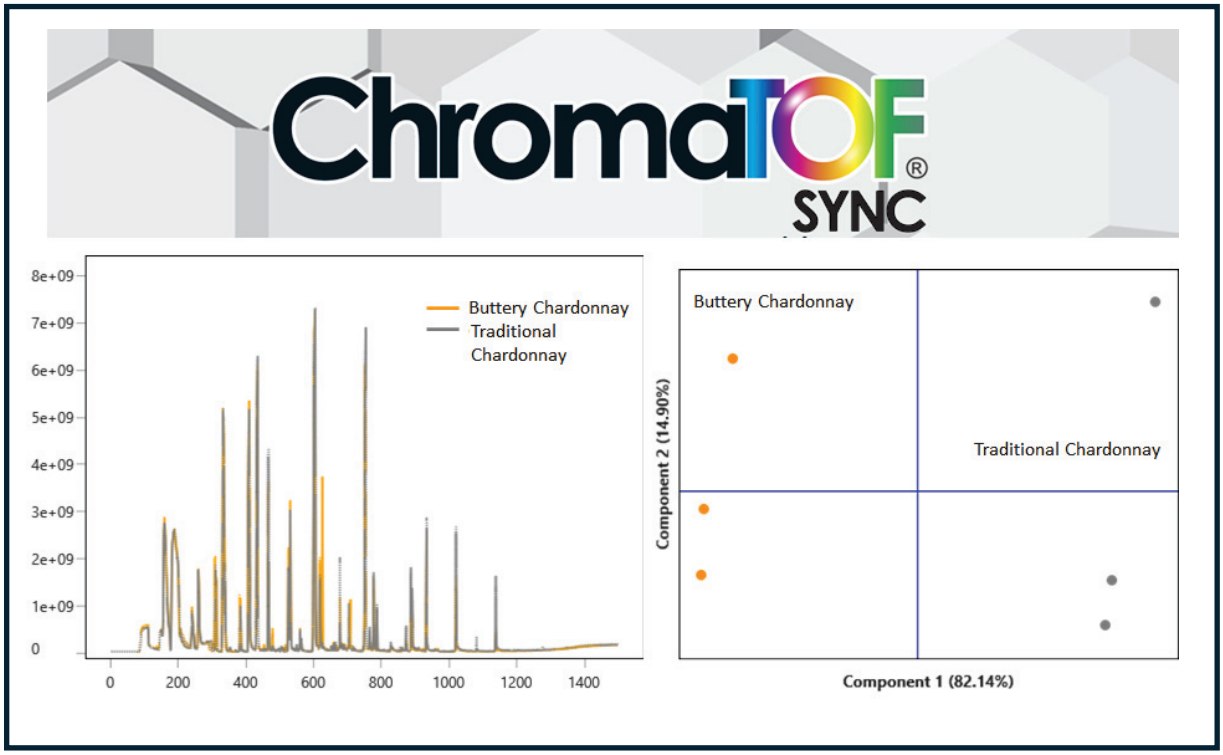

Figure 1. TIC chromatograms for three replicates of a butter chardonnay (orange) and three replicates of a traditional chardonnay sample (gray) are overlaid. PCA scores plot from compiled peak information shows the wine samples are distinguished on PC1.

Experimental

Each wine sample was analyzed in triplicate with headspace solid phase microextraction (HS-SPME) and GC-TOFMS. For each replicate, 2 mL of wine were pipetted into a 20 mL headspace vial. The samples were incubated for 2 min at 40 °C in the LPAL-3 agitator and then extracted for 5 min at the same temperature with a tri-phase SPME fiber (DVB, C-WR, PDMS). Method details are shown in Table 1. An alkane standard was also analyzed with the same methods for retention index (RI) determinations. The GC-TOFMS data were processed and analyzed with LECO's *ChromaTOF* Sync software.

Table 1. Instrument (*Pegasus* BT) Conditions

Auto Sampler	**LECO L-PAL 3 Autosampler**
Injection	Desorb for 2 min in GC inlet, splitless
Gas Chromatograph	**LECO GC**
Inlet	250 °C
Carrier Gas	He @ 1.4 mL/min
Column	Stabilwax, 30 m x 0.25 mm i.d. x 0.25 µm coating
Temperature Program	40 °C (hold 2 min), ramp 10 °C/min to 250 °C (hold 2 min)
Transfer Line	260 °C
Mass Spectrometer	**LECO *Pegasus* BT**
Ion Source Temperature	250 °C
Mass Range	35-300 m/z
Acquisition Rate	10 spectra/s

Results and Discussion

TIC chromatograms for both of the wine samples are overlaid in Figure 1. The buttery chardonnay traces are shown in orange, and the traditional chardonnay traces are shown in gray. Initial visual review of these chromatograms seems to suggest that the samples are mostly similar, as many of the peaks overlay at similar levels in both of the wine types. Information on individual analytes can be determined with *ChromaTOF* Sync peak finding, which provides identification information for individual features and information on the relative trends for those features through the sample set.

Individual features can be explored from the results compiled by *ChromaTOF* Sync. One of the features in the sample elutes around tR=507 s, as shown in Figure 1. Peak find information for this feature is shown in Figure 2. The observed spectrum (bottom right of Figure 2) was matched to 3-methyl-1-pentanol in the NIST library database with a similarity score of 946. This identification was further supported with RI information. The calculated RI for this peak was 1323, showing good agreement with the library RI value of 1326. The analyte trends across the 6 samples can then be observed in the overlaid chromatogram plot (top left of Figure 2), the side-by-side plot (top right of Figure 2), and the bar chart (bottom left of Figure 2). Samples 1-3, shown in orange, are the buttery chardonnay and samples 4-6, shown in gray, are the traditional chardonnay. This particular analyte appears to be at fairly similar levels in both wine samples. Having a tentative identification and being able to observe the trends across the sample set can add insight to the characteristics of the wines and this analyte's potential contribution. For example, the aroma notes of 3-methyl-1-pentanol, observed in both wines, is fermented with descriptors like fusel, cognac, wine, cocoa, green, and fruity.[1] Both wines have fermented, wine, and fruity descriptors.

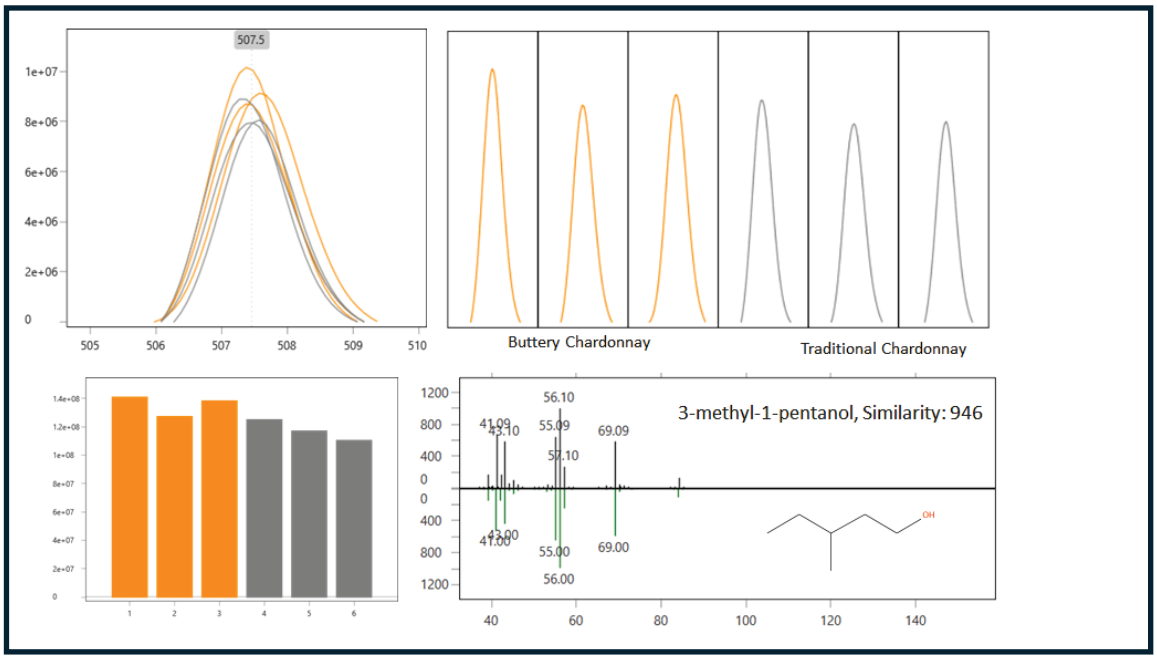

Figure 2. 3-methyl-1-pentanol was observed in both the buttery chardonnay (orange) and the traditional chardonnay (gray). ChromaTOF Sync peak find results are shown.

While some analyte information stands out in visual review, data processing tools can uncover many more analytes than a visual review of the data would reveal. This is particularly the case when features are coeluting or at low levels and not apparent in the TIC. *ChromaTOF* Sync peak finding incorporates mathematical deconvolution to resolve chromatographic coelutions and reveal additional analytes in sets of samples. An example of deconvolution is shown in Figure 3. Acetic acid and isopentyl hexanoate coelute, as can be observed with the blue and green traces. Of note, even in instances where one feature is chromatographically overloaded (for example, acetic acid), deconvolution can often isolate it and the features that are buried beneath. Deconvolution effectively separates these features and provided spectra for each that were then matched to library databases. The spectra matched with similarity scores of 965 and 890 for acetic acid and isopentyl hexanoate, respectively. The identifications were also supported with RI. Acetic acid had an observed RI of 1455 compared to the library value of 1449, and isopentyl hexanoate had an observed RI of 1457 compared to the library RI of 1451. Relative trends for these features can be observed in the blue and green traces and also in the bar charts for each feature (orange bars are buttery chardonnay and gray bars are traditional chardonnay). These analytes also appear at relatively consistent levels in both chardonnay samples. Acetic acid has acidic aromas with sharp, pungent, sour, or vinegar descriptors and isopentyl hexanoate has fruity aromas with fruity, banana, apple, pineapple, and green descriptors.[1] These aromas descriptors connect with both wines and these features are likely important contributors.

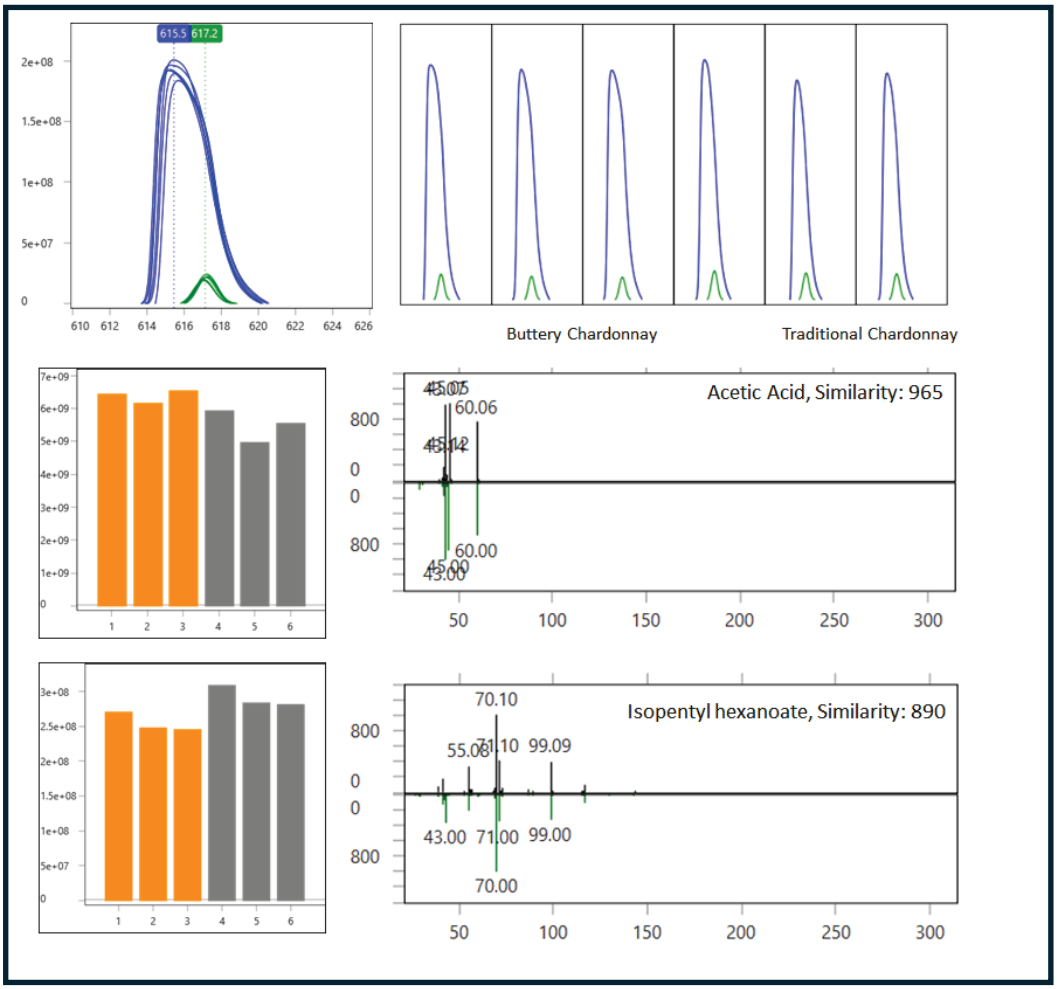

Figure 3. Deconvolution reveals information for 2 closely eluting features in the wine samples. Information for acetic acid (blue traces) and isopentyl hexanoate (green traces) is shown. Both analytes are observed at comparable levels in the buttery chardonnay (orange) and the traditional chardonnay (gray).

While the TIC chromatograms appear largely similar and the specific analytes shown in Figures 2 and 3 do not seem to differ between the types of wine, some analyte differences do stand out in the data. For example, a peak eluting at tR=624 is higher in the buttery chardonnay samples (orange traces) compared to the traditional chardonnay (gray traces). *ChromaTOF* Sync peak finding information is shown in Figure 4. The observed spectrum matched to furfural in the NIST library database with a similarity score of 924. Additionally, the calculated RI for this peak was 1466, showing good agreement with the library RI value of 1461 for furfural. This identification and the observed trends can add insight to the wine characteristics. Furfural aroma notes are bready with descriptors like sweet, woody, almond, and fragrant baked bread.[1] Furfural can also be associated with caramel notes and is often found in oak-aged wines, both of which connect to the description and process of the buttery chardonnay wine.

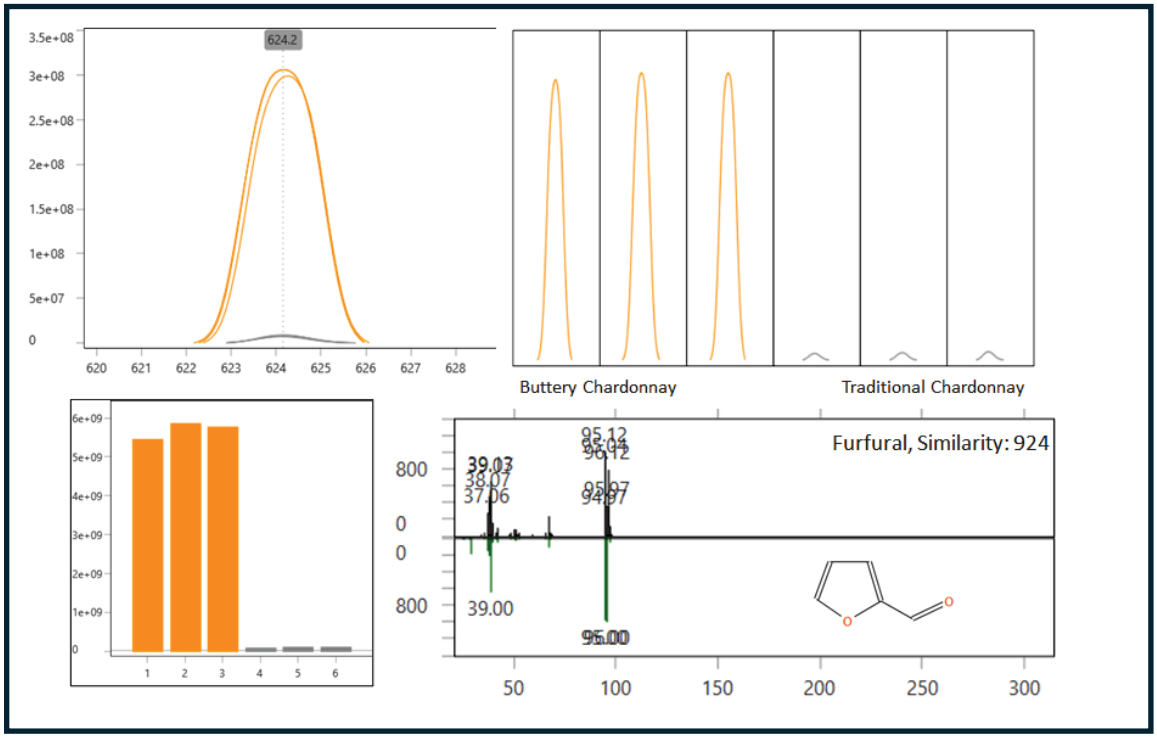

Figure 4. Furfural, higher in the buttery chardonnay (orange), was apparent from visual review of the overlaid chromatograms.

As more analyte information was uncovered through peak finding, more distinction between the samples became apparent. In fact, the two wine types were readily distinguished from each other when the overall chemical information was considered. Peak information for the sample set for features with S/N above 30 and similarity above 800 were compiled. When this peak information was used as the variables for PCA, shown in Figure 1, the two types of wine were distinctly separated on PC1. This suggests that there are clear analyte differences between the wines even though they were not always apparent in the TIC. Peak finding tools were crucial for finding these differences and understanding the chemical profiles of these wines. Some representative analytes are shown in Figure 5. These tentative analyte identifications are supported with mass spectral matching (similarity score) and with RI matching, as indicated. Representative analytes with various trends (higher in buttery chardonnay, similar in both wines, or higher in traditional chardonnay) are displayed in the heatmap (red is higher and blue is lower). The samples in columns 1-3 are buttery chardonnay and those in columns 4-6 are the traditional chardonnay. Additional detailed information for a few of these features is provided in Figures 6-8.

Name	Formula	Similarity	CAS	RI. calc	RI. lib	S/N	Aroma	Notes	Med RT	1	2	3	4	5	6
Acetoin	$C_4H_8O_2$	862	513-86-0	1287	1285	28022.28	buttery	sweet buttery creamy dairy milky fatty	476.2	993.02	838.12	190.06	228.94	26.28	11.84
Furfural	$C_5H_4O_2$	924	98-01-1	1466	1461	45074.62	bready	sweet woody almond fragrant baked bread	624.2	854.53	774.64	842.68	820.43	84.74	78.68
Ethanone, 1-(2-furanyl)-	$C_6H_6O_2$	858	1192-62-7	1507	1499	3940.17	balsamic	sweet balsam almond cocoa caramel coffee	655.4	916.80	829.28	800.59	500.26	86.53	33.13
2-Furancarboxaldehyde, 5-methyl-	$C_6H_6O_2$	944	620-02-0	1577	1570	17280.68	caramellic	spice caramel maple	706.9	991.67	920.99	801.18	363.12	92.66	81.14
Creosol	$C_8H_{10}O_2$	897	93-51-6	1961	1956	2047.50	spicy	spicy clove vanilla phenolic medicinal leathery woody smoky burnt	960.4	978.82	890.41	107.86	375.93	32.97	60.80
2(3H)-Furanone, 5-butyldihydro-4-methyl-, cis-	$C_9H_{16}O_2$	954	55013-32-6	1967	1957	3575.72	spicy	sweet spicy coconut vanilla	964.4	952.29	829.70	116.63	356.66	10.12	68.13
Eugenol	$C_{10}H_{12}O_2$	862	97-53-0	2175	2169	375.98	spicy	sweet spicy clove woody	1082.7	932.60	826.24	313.62	915.53	60.29	62.23
Vanillin	$C_8H_8O_3$	954	121-33-5	2548	2568	517.53	vanilla	sweet vanilla creamy chocolate	1290.5	991.86	948.35	667.71	735.86	26.76	65.20
Benzaldehyde, 2-hydroxy-	$C_7H_6O_2$	936	90-02-8	1686	1670	1425.60	medicinal	medical spicy cinnamon wintergreen cooling	783.3	940.09	875.25	542.59	713.26	22.67	08.07
Phenol, 2-methoxy-	$C_7H_8O_2$	914	90-05-1	1866	1860	2030.93	phenolic	phenolic smoke spice vanilla woody	900.8	990.63	898.65	157.92	321.50	95.29	14.64
trans-3-Methyl-4-octanolide	$C_9H_{16}O_2$	959	39638-67-0	1898	N.A.	4058.02	coconut	spicy coconut clove celery incense	920.8	929.35	843.09	120.36	968.81	24.06	54.83
Benzaldehyde	C_7H_6O	957	100-52-7	1527	1520	4563.35	fruity	strong sharp sweet bitter almond cherry	670.5	975.82	949.50	155.44	397.18	28.08	04.22
Benzaldehyde, 4-methyl-	C_8H_8O	894	104-87-0	1630	1648	325.25	fruity	fruity cherry deep phenolic	744.0	962.35	942.25	235.32	733.29	11.74	01.18
Methyl 2-furoate	$C_6H_6O_3$	892	611-13-2	1580	1563	5318.14	fungal	fruity mushroom fungus tobacco sweet	708.8	901.61	887.17	740.50	818.65	94.72	96.34
Acetic acid, methyl ester	$C_3H_6O_2$	965	79-20-9	822	828	7020.43	ethereal	ether sweet fruity	131.7	911.18	862.79	420.40	868.23	01.03	31.83
Ethyl Acetate	$C_4H_8O_2$	882	141-78-6	884	888	26566.33	ethereal	ethereal fruity sweet weed green	156.0	996.44	890.05	330.97	302.51	90.48	53.84
1-Propanol, 2-methyl-	$C_4H_{10}O$	947	78-83-1	1095	1092	61939.22	ethereal	etherael winey corex	308.2	943.54	902.14	854.11	028.15	00.51	80.75
1-Butanol, 3-methyl-	$C_5H_{12}O$	852	123-51-3	1206	1209	39140.36	fermented	fusel oil alcoholic whiskey fruity banana	407.5	901.49	891.32	310.37	963.57	14.32	88.05
1-Pentanol, 3-methyl-	$C_6H_{14}O$	946	589-35-5	1323	1326	4016.88	fermented	fusel cognac wine cocoa green fruity	507.5	959.20	911.38	216.62	711.10	62.95	33.47
Acetic acid	$C_2H_4O_2$	965	64-19-7	1455	1449	42113.64	acidic	sharp pungent sour vinegar	615.5	915.50	870.30	334.74	589.19	17.85	48.31
Benzeneacetic acid, ethyl ester	$C_{10}H_{12}O_2$	876	101-97-3	1789	1783	956.85	floral	sweet floral honey rose balsam cocoa	852.2	968.43	959.49	084.28	550.61	47.03	20.06
Phenylethyl Alcohol	$C_8H_{10}O$	943	60-12-8	1915	1907	28839.54	floral	floral rose dried rose flower rose water	932.0	966.43	947.36	590.14	982.22	42.20	65.85
Octanoic acid, ethyl ester	$C_{10}H_{20}O_2$	837	106-32-1	1438	1435	138360.60	waxy	fruity wine waxy sweet apricot banana brandy pear	602.1	951.81	896.25	039.62	359.79	21.52	81.44
Isobutyl acetate	$C_6H_{12}O_2$	951	110-19-0	1012	1012	14702.07	fruity	sweet fruity ethereal banana tropical	238.6	967.32	904.46	582.17	679.26	99.99	02.88
Butanoic acid, ethyl ester	$C_6H_{12}O_2$	937	105-54-4	1034	1036	29400.40	fruity	fruity juicy fruit pineapple cognac	257.0	919.67	830.13	276.28	088.58	45.49	35.81
Butanoic acid, 2-methyl-, ethyl ester	$C_7H_{14}O_2$	890	7452-79-1	1049	1052	2934.18	fruity	sharp sweet green appe fruity	269.5	991.61	899.38	018.59	135.58	52.99	47.44
Acetic acid, pentyl ester	$C_7H_{14}O_2$	957	628-63-7	1170	1176	1532.96	fruity	ethereal fruity banana pear banana apple	375.5	911.22	902.43	487.88	548.92	29.24	23.30
Acetic acid, hexyl ester	$C_8H_{16}O_2$	969	142-92-7	1272	1273	95014.43	fruity	fruit green apple banana sweet	463.8	922.86	902.73	753.06	017.80	01.94	81.99
Isopentyl hexanoate	$C_{11}H_{22}O_2$	890	2198-61-0	1457	1451	7477.12	fruity	fruity banana apple pineapple green	617.2	932.85	843.73	130.06	368.75	29.75	30.63
Acetic acid, heptyl ester	$C_9H_{18}O_2$	804	112-06-1	1371	1377	1637.77	green	fresh green rum ripe fruit pear apricot woody	548.4	996.58	847.42	311.97	788.21	28.69	03.38
Acetic acid, octyl ester	$C_{10}H_{20}O_2$	930	112-14-1	1473	1475	1135.78	floral	green earthy mushroom herbal waxy	629.3	978.19	857.68	394.66	171.87	11.55	13.22
Acetic acid, phenylmethyl ester	$C_9H_{10}O_2$	920	140-11-4	1733	1720	330.07	floral	sweet floral fruity jasmin fresh	814.7	928.19	837.64	771.88	832.13	90.04	33.48
Acetic acid, 2-phenylethyl ester	$C_{10}H_{12}O_2$	958	103-45-7	1820	1813	15813.03	floral	floral rose sweet honey fruity tropical	872.0	912.94	863.47	534.85	602.06	15.64	32.00
Cyclohexene, 1-methyl-4-(1-methylethylidene)-	$C_{10}H_{16}$	822	586-62-9	1282	1284	1211.65	herbal	fresh woody sweet pine citrus	472.0	932.07	877.41	961.20	348.61	39.90	23.88
Ethyl 9-decenoate	$C_{12}H_{22}O_2$	884	67233-91-4	1690	1694	9248.96	fruity	fruity fatty	785.7	992.03	905.74	139.67	551.41	09.95	93.24

Figure 5. ChromaTOF Sync outputs compiled peak table information for the sample set. Peak information for several representative analytes with various trends (higher in buttery chardonnay, approximately the same in both, and higher in traditional chardonnay) are shown. Relative trends are apparent in the heat map (red is higher and blue is lower). Aroma notes for these analytes have been added.

Analytes at the top of the table in Figure 5 were observed at higher levels in the buttery chardonnay. Detailed information for two of these features is provided in Figures 6 and 7. Acetoin, shown in Figure 6, was tentatively identified with a similarity score of 862, which was supported by RI (observed RI=1287 and library RI = 1285). This compound was described as having a buttery aroma with descriptors like sweet, buttery, creamy, dairy, milky, and fatty.[1]

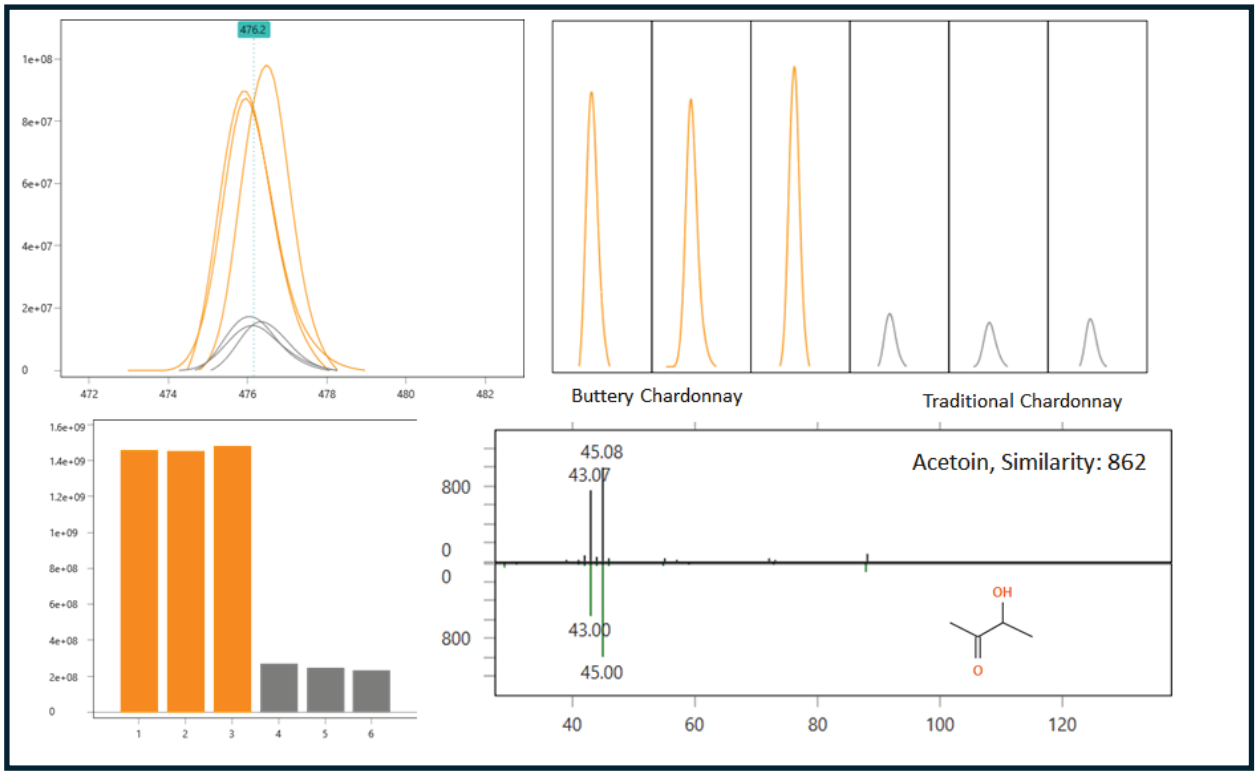

Figure 6. Acetoin, higher in the buttery chardonnay (orange), was determined with ChromaTOF Sync peak finding.

Creosol was also observed at higher levels in the buttery chardonnay and is shown in Figure 7. Creosol was tentatively identified with a similarity score of 897, which was also supported by RI (observed RI=1961 and library RI = 1956). This compound was described as having a spicy aroma with additional descriptors of spicy, clove, vanilla, phenolic, medicinal, leathery, woody, smoky, and burnt.[1]

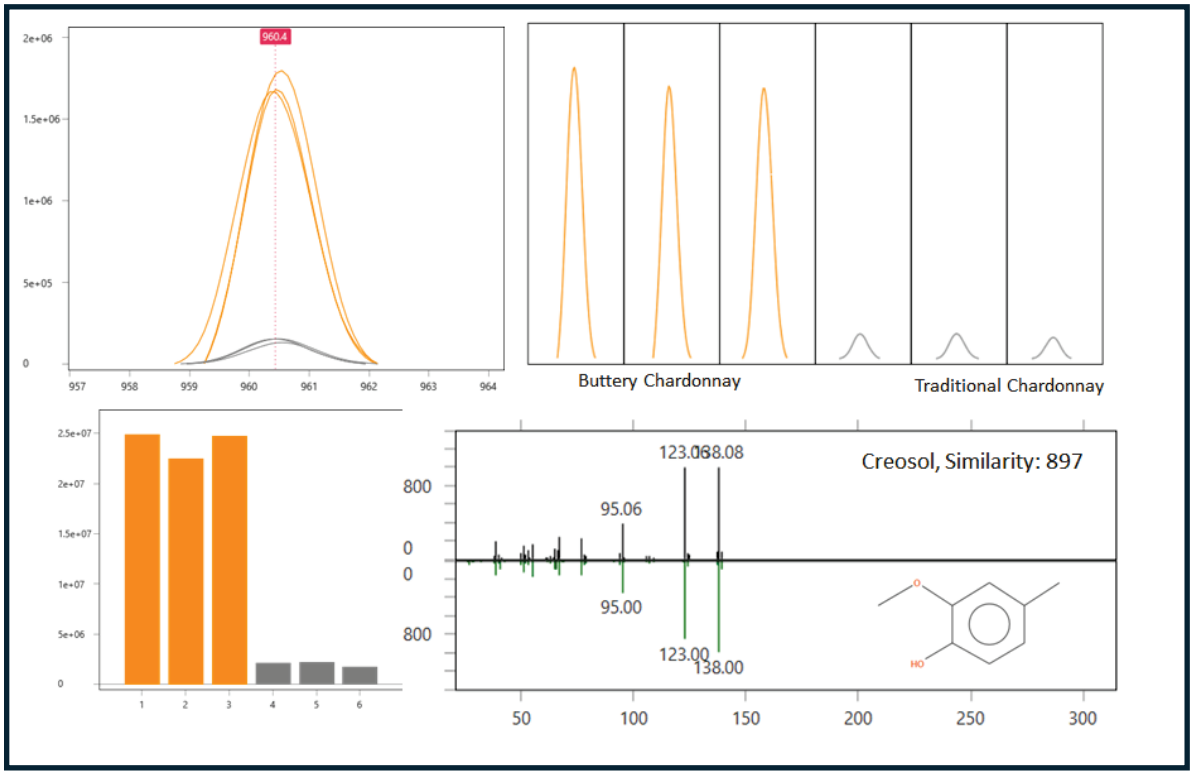

Figure 7. Creosol, higher in the buttery chardonnay (orange), was determined with ChromaTOF Sync peak finding.

Analytes at the bottom of the table in Figure 5 were observed at higher levels in the traditional chardonnay. For example, 2-phenylethyl ester acetic acid is shown in Figure 8. This compound was tentatively identified with a similarity score of 958, which was also supported by RI (observed RI=1820 and library RI = 1813). This compound was described as having a floral aroma with additional descriptors of floral, rose, sweet, honey, fruity, and tropical.[1]

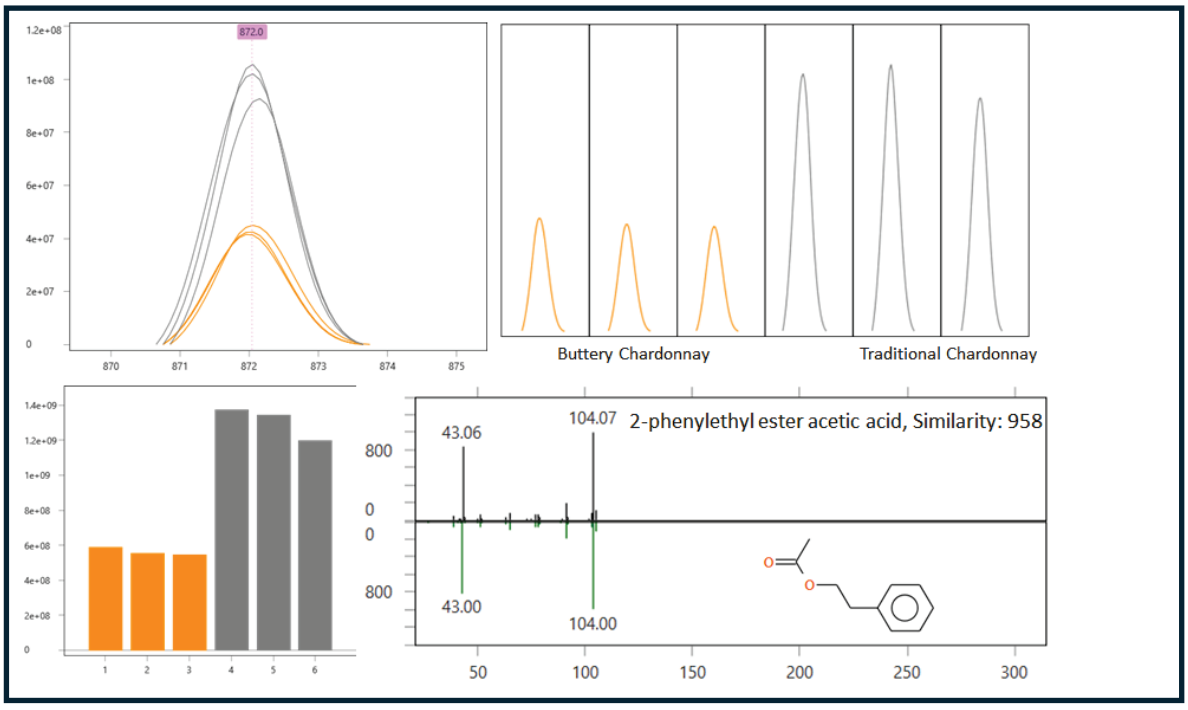

Figure 8. 2-phenylethyl ester acetic acid, higher in the traditional chardonnay (gray), was determined with ChromaTOF Sync peak finding.

Generally, many of the aroma notes for features that were higher in the buttery chardonnay had descriptors like buttery, milky, caramel, vanilla, maple, spicy, coconut, cherry, and fruity. Several analytes with fruity, floral, alcoholic, honey, and fermented notes were observed at similar levels in both wines. Other analytes with fresh, floral, fruity, and citrusy notes were observed at higher levels in the traditional chardonnay wine. Many of these analytes and aroma notes connect with the general observations and descriptions of the buttery chardonnay and traditional chardonnay wines. This deeper data review and comparison of the wine samples was facilitated by *ChromaTOF* Sync.

Conclusion

In this work, we used HS-SPME and GC-TOFMS to measure two related wine samples. A buttery chardonnay and traditional chardonnay from the same vineyard and vintage were compared. *ChromaTOF* Sync provided full sample set peak finding and helped reveal many specific analytes with aroma notes that connected with the overall descriptions of the wine samples. Several representative examples are highlighted and discussed.

References

[1]Good Scents database, http://www.thegoodscentscompany.com

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