

Combining Sensory and Chemical Analyses (GC-MS) to Evaluate Shelf Stability Related to Storage Condition for an American IPA Beer

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INTRODUCTION

Shelf stability and how products change with storage is an area of interest across many markets. Changes in the product over the course of its shelf life are often apparent in the aroma profile, which can be monitored with a variety of tools. Chemical and sensory analyses are both common for this type of profiling. Gas chromatography (GC) with mass spectrometry (MS) is particularly well-suited for screening these volatile and semi-volatile analytes as a chemical analysis method. The sensory analyses are typically performed by a trained sensory panel. These are complementary techniques and, in this work, we combine both chemical and sensory approaches to investigate shelf stability for a bottled beer as it relates to storage condition.

METHOD

Samples: A time course series of an American IPA was acquired by collecting bottles directly from the packaging line at a brewery over a 10 week period. Bottles were collected 10, 4, 2, and 1 week ahead of analysis, as well as on the day of analysis. The bottles were stored on-site at the brewery with one set under refrigeration (maintained between 34-36 °F, cold), and the other set at room temperature (maintained between 68-70 °F, warm).

Sensory Analysis: Sensory analysis was performed by an expert panel of five tasters at the brewery. The panel was comprised of individuals from the quality and brewing departments that had undergone comprehensive training on beer oxidation and were very familiar with the brand being analyzed. Each sample was scored by the panel based on the scoring system outlined in Table 1.

Table 1. Sensory Scoring System for Freshness

Score	Description
8	Equivalent to fresh product with full flavor profile present
7	Some flavor profile has diminished, but no oxidation present
6	Diminished flavor profile, but no oxidation present
5	Beginning signs of aging with some flavor profile present
4	Moderate signs of aging with some flavor profile present
3	Extreme signs of aging with little flavor profile present
2	Extreme signs of aging, no longer resembles brand
1	Extreme signs of aging and change in appearance, no longer resembles brand
0	Infection, wrong brand, or not consumable

Chemical Analysis: The chemical analysis was performed with HS-SPME coupled to LECO's Pegasus® BT GC-TOFMS. For each sample, 5 mL of beer were transferred via pipet into a 20 mL glass vial, sealed with a septum cap. All samples were analyzed in triplicate with the method conditions listed in Table 2. Data for an alkane standard was also collected with the same methods, allowing for Retention Index determinations.

Table 2. GC-TOFMS Instrument Conditions

AS	LECO L-PAL3 Autosampler
SPME	10 minute incubation, 20 min extraction at 35 °C
SPME fiber	DVB/CAR/PDMS (Supelco)
Fiber conditioning	5 min at 250 °C between each sample
GC	Agilent 7890
Injection	Desorb fiber 3 min at 250 °C, splitless
Column	Stabilwax, 30 m x 0.25 mm i.d. x 0.25 µm coating (Restek)
Carrier Gas	He @ 1.40 mL/min, constant flow
Oven Program	3 min 40 °C, ramp 10 °C/min to 250 °C, hold 1 min
MS	LECO Pegasus BT
Ion Source Temp	250 °C
Mass range	33-500 m/z
Acquisition Rate	10 spectra/s

Data analysis: The chemical data were processed with LECO's ChromaTOF® brand software that includes deconvolution as part of the automated peak finding. Peak areas were determined with integration of a single m/z per analyte. Identifications are tentative, but determined by spectral matching to NIST library databases and by retention index matching of calculated values based on the alkane standard compared to NIST database values. Principle Component Analysis (PCA) was performed on the tabulated peak areas in MatLab.

SENSORY ANALYSIS

Each sample was scored by the sensory panel. As described in Table 1, higher scores indicated freshest samples. Scores between 8 and 6 showed decreased aroma, but no signs of aging; scores between 6 and 3 showed more significant decline in aroma along with increased signs of aging; and scores below 3 exhibited severe signs of aging and had little aroma remaining. The panelist's scores are shown in Figure 1. These results indicate that the beer quality decreases with age and does so more rapidly when stored at room temperature than when refrigerated.

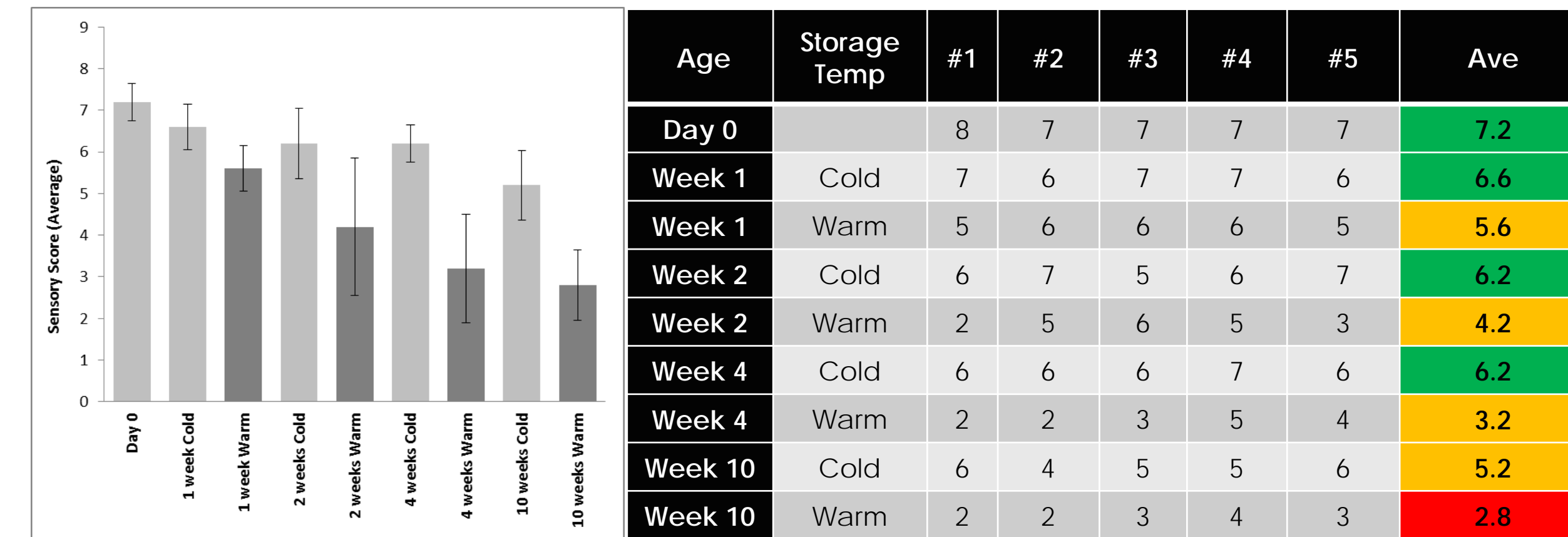


Figure 1. Sensory analysis results. Freshness shows a general decline with age with the change occurring more rapidly at room temperature storage than at refrigerated storage.

CHEMICAL ANALYSIS

Each beer sample was also subjected to chemical analysis. Representative TIC chromatograms for the samples are overlaid in Figure 2. Many analytes were chromatographically isolated, but coelution is common with complex samples. Deconvolution can often mathematically resolve coelutions and provide pure peak areas and spectral information for each unique analyte. An example is shown in Figure 2. What appeared as one analyte in the TIC was mathematically determined to be two analytes (an ester and a terpene). The ester did not change related to age or storage temperature, but the terpene had highest levels in the freshest sample and decreased with age, more rapidly at room temperature than when refrigerated.

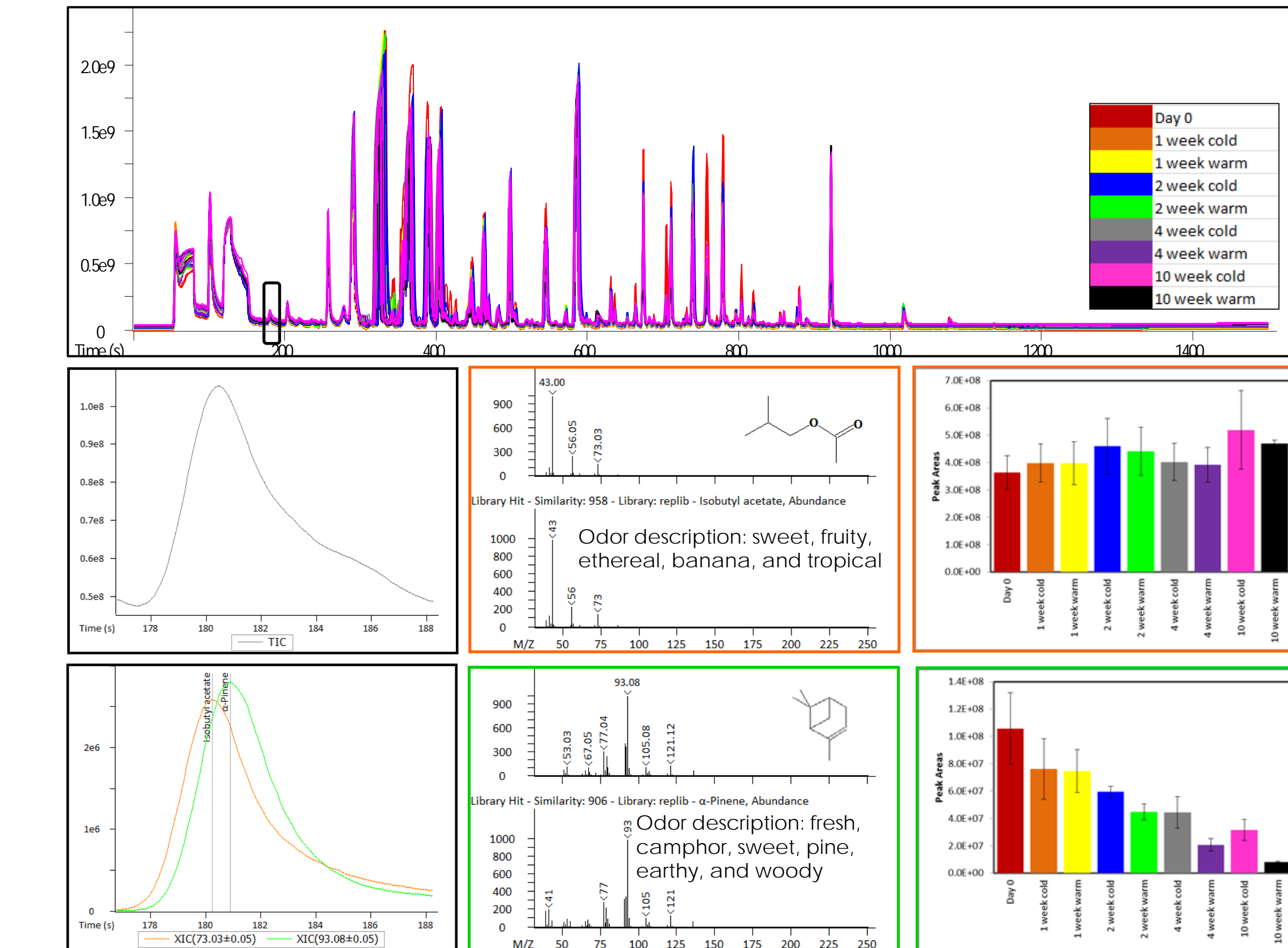
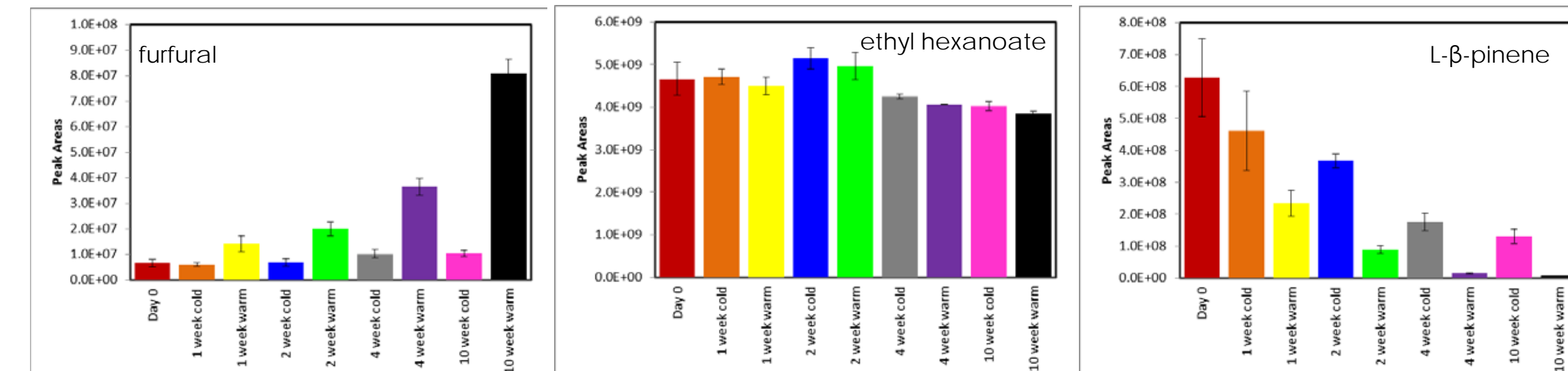


Figure 2. Overlaid chromatograms from all samples are shown and a deconvolution example is noted. There appears to be one peak at 180 s (with a likely coelution in the tail around 185 s) in the TIC view. Using the full m/z range data, deconvolution determined that there were two analytes that elute at ~180 s. The first analyte is identified as isobutyl acetate and the second is alpha-pinene.

ANALYTE TRENDS

Hundreds of other analytes were determined in these samples by the automated peak finding tools. Analytes that were observed included hydrocarbons, esters, terpenes, alcohols, aldehydes, ketones, sulfur-containing analytes, nitrogen-containing analytes, etc. Specific analytes that are often associated with aging (for example, Strecker aldehydes, esters, Maillard reaction products, etc.) were also observed and individual trends could be discerned. The peak areas for over 350 analytes were compiled and compared across the sample set. Individual analyte trends were determined with some examples shown in Figure 3.



Analyte	Analyte Type	R.T. (s)	Similarity	CAS	Formula	RI	Library RI
fural	Maillard reaction product	611.981	943	98-01-1	C ₆ H ₄ O ₂	1464.2	1462
ethyl hexanoate	ester	404.247	954	123-66-0	C ₈ H ₁₆ O ₂	1229.1	1233
L-β-pinene	terpene	258.404	894	18172-67-3	C ₁₀ H ₁₆	1090.3	

Figure 3. Various trends across the sample set for individual analytes were observed.

CHEMICAL ANALYSIS SUMMARY

Overall chemical trends were also explored with Principle Component Analysis (PCA). PCA determines the similarities and differences between samples based on the inherent variability in the complete data. All 350 chemical compounds were used as variables and the associated scores plot is shown in Figure 4. Each sample is represented as a data point in this plot, and the proximity of the data points indicates the similarities between the samples when all variables are considered together. Some age and storage condition dependence is apparent. The scores on PC1, in particular, track with the age and storage condition as shown in Figure 4B, where the inverted PC1 score is plot vs sample. This plot parallels the trends in the sensory data, shown in Figure 1. This result indicates that the largest source of variation in the chemical data relates to the trends and variation that were determined by the sensory panel.

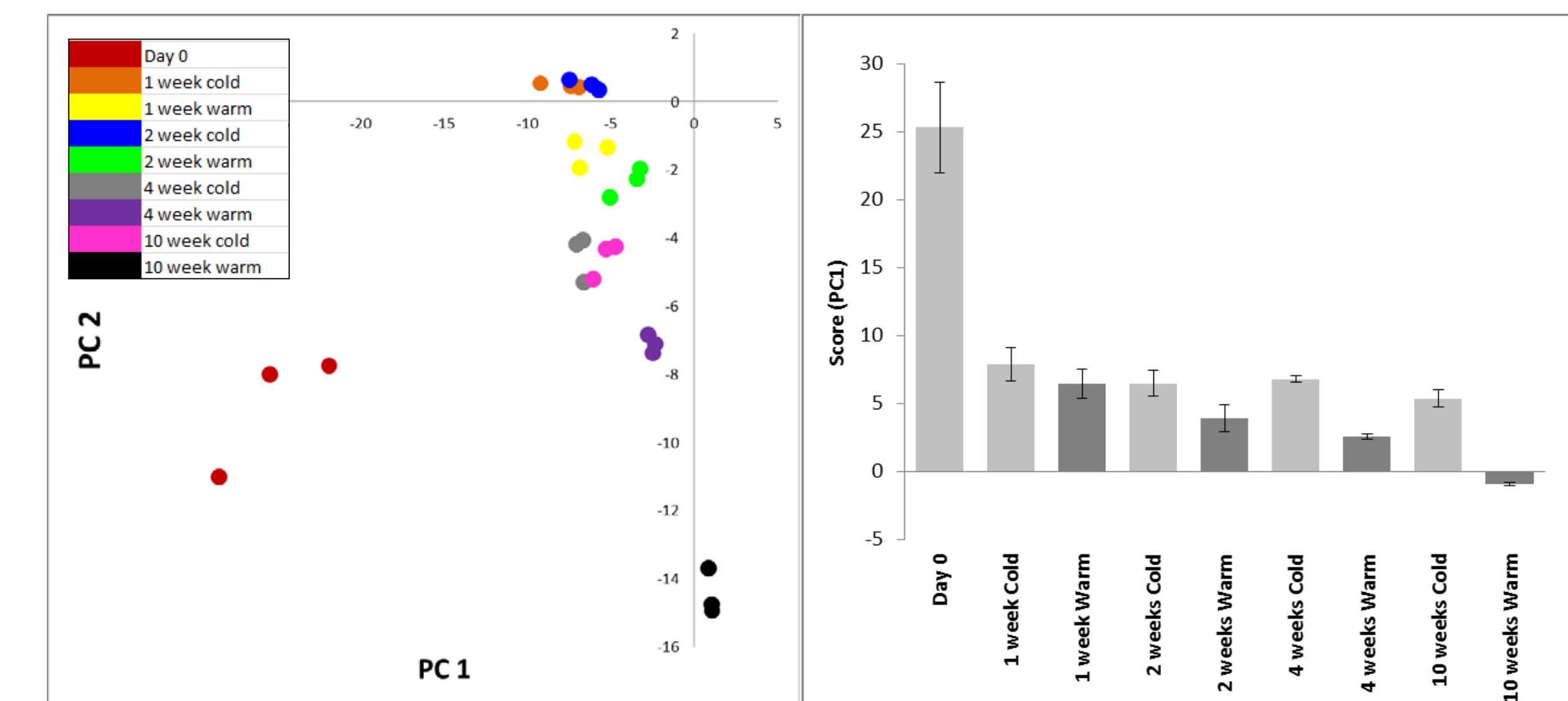


Figure 4. PCA Scores plot (left). Each sample is represented as a data point and the proximity of the data points indicates the similarities between the samples when all variables are considered together. The scores on PC1, in particular, track with the age and storage condition. The inverted PC1 score is plot vs sample (right). This plot parallels the trends in the sensory data, shown in Figure 1.

CORRELATION OF ANALYTICAL RESULTS

To further explore the parallels between the chemical and sensory data, the overall chemical score (PC1 in Figure 4) was compared to the overall sensory score (Figure 1), shown in Figure 5. The trend between the two analytical approaches is apparent. Some deviation can be observed in the freshest samples, which suggests that there were chemical changes at the earliest time point that did not impact the sensory score. The peak areas for each analyte were plotted against the overall sensory score and correlations were calculated for every analyte. A list of 36 analytes that correlate was determined. A heat map that represents the area trends is shown in Figure 6.

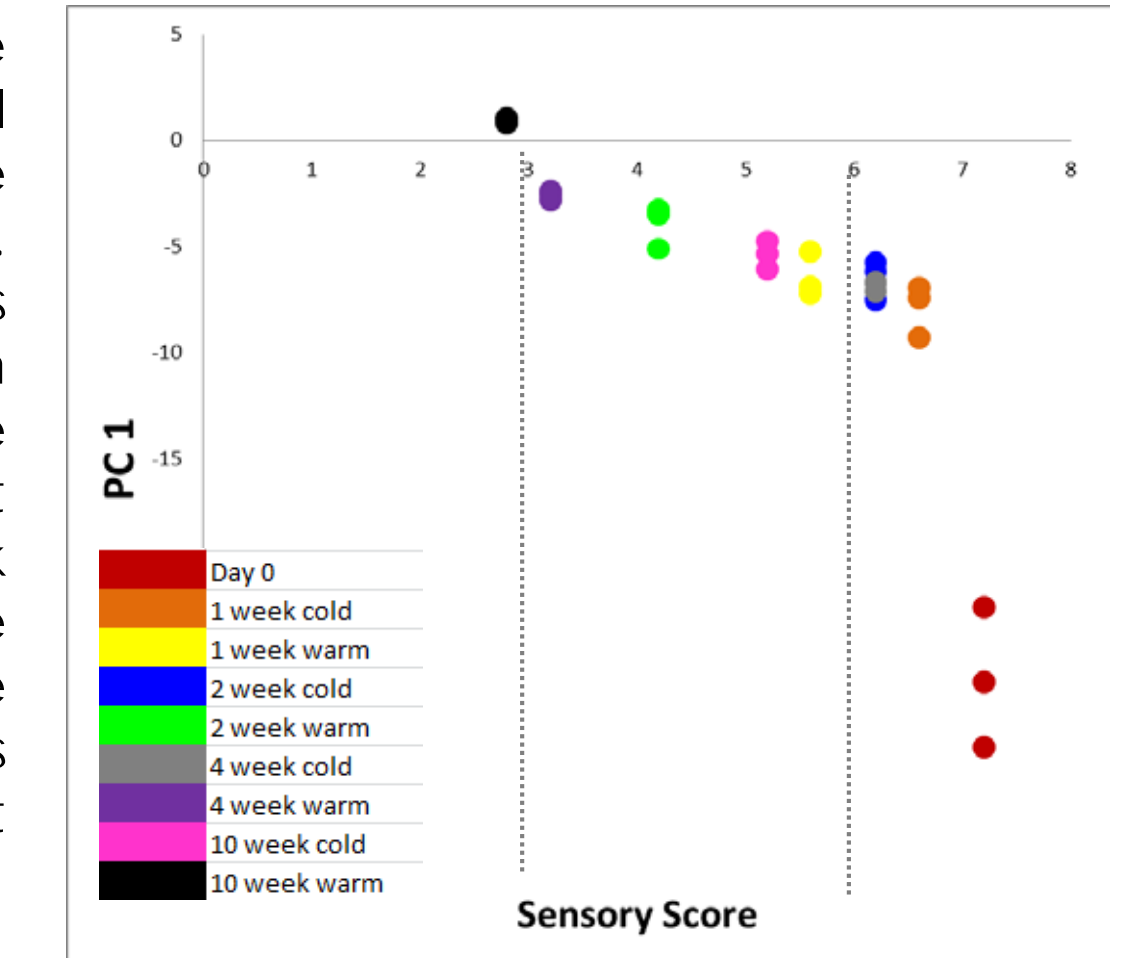


Figure 5. Sensory score compared to overall chemical score.

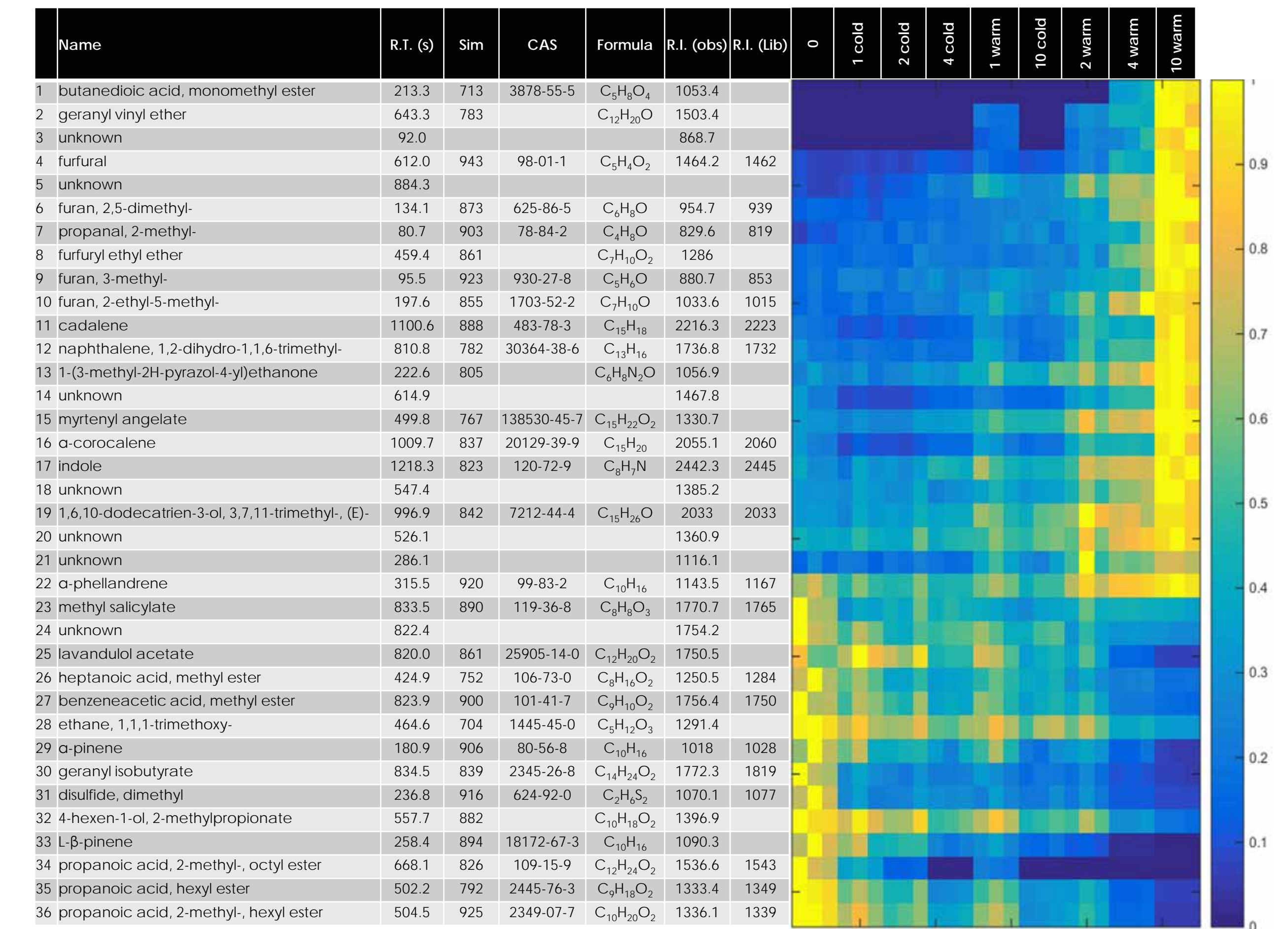


Figure 6. Analytes that correlate. Many of the analytes that are at the top of the heat map (that negatively correlated with sensory scores) are furans, Maillard reaction products, and Strecker aldehydes. Some of the associated aroma characteristics for these analytes are bread, animal, meaty, and gassy. The analytes at the bottom of the heat map (that positively correlate with sensory score) are analytes like esters and terpenes. These have odor descriptors like fruity, honey, herbal, floral, and green.

CONCLUSIONS

In this work, we aimed to investigate the impact of storage temperature on the shelf life of an American IPA. Chemical and sensory data were combined, and we observed that freshness generally declines with age and that this degradation occurs at a faster rate with higher temperature storage compared to lower temperature storage. The sensory analysis gave good information on the quality of the samples overall and provided important context to probe the chemical data. The chemical analysis uncovered specific analytes that were related to the sensory observations and that correlate with sensory score. We also demonstrated an effective way to connect data from these complementary analysis techniques. Using both data sets together, we were able gain a better understanding of these samples than was possible with either data set independently.