Analyzing the Flavors in Beer with the Polyarc System

Application Note

Foods and Beverages

Author

Charlie Spanjers, PhD.
Activated Research Company
7561 Corporate Way
Eden Prairie, MN 55344
charlie.spanjers@activatedresearch.com

Abstract

The Polyarc System combined with a mass spectrometer was used to identify and quantify flavor molecules in beer. Because of the complexity, the process for identifying and quantifying analytes in foods and beverages can be both challenging and time consuming with traditional methods. However, the method shown here is quick (< 1 hr) and only requires a single injection. A light lager and an india pale ale were analyzed by this method and found to contain more than 100 different flavor molecules.

Introduction

No two beers are the same. This is not necessarily by design, but rather from the molecular complexity that originates in the brewing process. This complexity begins with the molecular diversity of the grain and hops, and is magnified by the complex mixture of fermentation products produced by the yeast. The result are beers that can contain over 600 different molecules, each of which imparts its unique component of flavor to the overall taste. Descriptors used to describe these molecules include "sour", "fruity", "aromatic", "sweet", "musty", or even "geranium-like." Understanding the relationship between the recipes used to produce a beer and the concentration of the taste molecules in the final product helps brew masters craft the perfect beer. This, however, requires knowledge of the concentrations of the molecules.

The most common technique for quantifying the analytes in beer is gas chromatography. This process typically requires calibration to determine the response factor for each individual molecule before quantitative information can be determined.

Polyarc system (Figure 1) converts carbon-containing molecules to methane prior to detection in a flame ionization detector (FID) by performing the following reaction:

$$\underset{\text{Compounds}}{\text{Carbon-Containing}} + \text{Air} + H_2 \rightarrow \underset{(CH_4)}{\text{Methane}} + \underset{\text{Byproducts}}{\text{Non-Carbonaceous}}$$

Because all molecules are converted to methane, the response per carbon atom is equivalent for all carbon-containing compounds and calibration is not necessary. When paired with a mass spectrometer in a split setup, the combined system is capable of identifying and quantifying complex mixtures with a single injection. In this application note, we demonstrate the gas chromatography (GC) analysis of two beers with the Polyarc system.

Figure 1. Polyarc System installed in the back detector position next to an FID on an Agilent 7890 GC.

Experimental

An Agilent 7890A GC equipped with a split/splitless inlet (Agilent G3454-64000), capillary-optimized FID, mass spectrometer (Agilent 5973), and Polyarc® reactor (ARC PA-RRC-A02) were used for the analysis. Helium (99.999%, Praxair) was used for carrier and FID makeup. Air (zero grade, Praxair) and H_2 (99.999%, Praxair) were supplied to the ARC electronic flow control module (PA-MFC-A09) and to the FID. The effluent of the GC column was connected to an Agilent 3-way CFT splitter (G3183-60500). The MS was connected to the splitter via a retention gap column (Agilent, 160-2635-5, 0.61 m, 0.1 mm ID). The inlet capillary to the Polyarc® was connected directly to the splitter. The splitter was controlled by an EPC (with restrictor frit removed) set to 4 psig.

Two beer samples – a light lager and an India pale ale (IPA) – were injected directly into the GC without modification.

GC conditions

Front inlet	Split/splitless
Split ratio	10:1
Inlet temperature	260 °C
Inlet liner	Agilent 18740-80190
Carrier gas	He; 2.6 sccm constant flow
Septum purge flow	3 sccm
Oven	40 °C (hold 5 min) to 125 °C at 10 °C/min to 250 °C at 25 °C/min (hold 15 min)
Column	Phenomenex ZB-5 (30 m × 0.25 mm × 0.25 µm film)
Syringe	10 µL
Injection volume	0.5 µL

FID conditions

Temperature	400 °C
H_2	1.5 sccm
Air	350 sccm
Makeup	20 sccm (He)

Polyarc® System conditions

Setpoint	293 (450 °C actual temp.)
H_2	35 sccm
Air	2.5 sccm

Results and Discussion

The chromatograms for the two samples are shown in Figure 2. There are over 100 peaks present in each of the samples. Interestingly, they both display many of the same components at similar levels. While the light lager contains more glycerin, the IPA contains an elevated concentration of most flavor molecules compared to the lager. This beer is advertised as having "Magnum hops" and "lupulin dust". Perhaps it is the addition of these hops that give the beer its characteristic hoppy flavor and contribute to the elevated peak heights in the chromatogram.

Table 1 shows quantitative results for select peaks that were identified in the chromatogram. The carbon dioxide concentrations in the two samples are similar, at about 1.5 wt. %. Formic acid is only present in the IPA, and it is unclear if this is a desired or undesired component in the beer. 2-methylpropanal was found in both samples, but at almost two times the concentration in the IPA. This molecule is described as malty, grainy, husk-like, varnish, fruity, banana, melon, green malt, green leaves, bitter, and alcoholic. Glycerin is the most prevalent molecule that was detected, after carbon dioxide and methanol. The concentration of glycerin in the lager was nearly double that of the concentration in the IPA, but both were less than 1 %. Glycerin is produced during the fermentation process, and gives a sweet taste to beer.

Other compounds that were identified in both beers include acetic acid, 1-pentanol, furfuryl alcohol, phenylacetaldehyde, phenylethyl alcohol, and 5-hydroxymethylfurfural. 5-hydroxymethylfurfural contributes "stale" and "vegetable" notes to the beer, but it is unlikely that it is noticeable due to its low concentration and the overall complexity of the beer.

There are many other peaks present that were not identifiable with this method, either because of the low signal-to-noise in the MS chromatogram, or because they are not present in the National Institute of Standards and Technology (NIST) database. A more sensitive method with the MS-only could be used to help identify additional compounds. Or, standards could be injected and used to identify the unknowns by retention time. Future work could explore these other techniques for applications where identification and quantification of additional compounds is required.

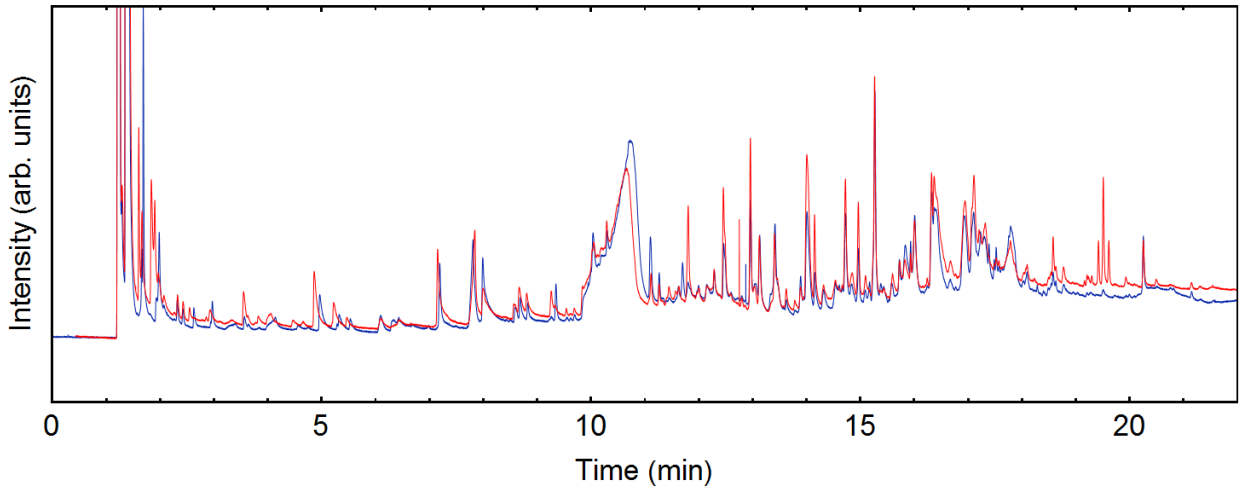

Figure 2. Polyarc/FID Chromatogram of light lager (blue) and an IPA (red).

Table 1. Quantitative analysis of two beers using the Polyarc system (only select molecules are shown below).

Molecule	Time (min)	Weight Concentration (%) IPA	Light Lager	Flavor Descriptors
Carbon Dioxide	1.23	1.45	1.50	sour
Ethanol	1.37	6.23	3.31	warming, strong, alcoholic
Formic acid	1.61	0.032	0.000	acidic
2-Methylpropanal	1.67	0.014	0.008	malty, grainy, husk-like, varnish, fruity, banana, melon, green malt, green leaves, bitter, alcoholic
Acetic Acid	1.90	0.026	0.035	acid, acetic, sour, pungent, vinegar
1-Pentanol	3.55	0.008	0.005	alcohol, medicinal, solvent-like
Furfuryl alcohol	7.16	0.026	0.025	sugar cane, woody
Glycerin	10.66	0.474	0.960	viscosity
PhenylAcetaldehyde	11.27	0.007	0.011	floral (hyacinth, roses, lilac), honey-like, sweet, aldehyde
Phenylethyl Alcohol	12.46	0.023	0.017	alcohol, flowery, honey-like, roses, sweet
5-Hydroxymethylfurfural	14.15	0.016	0.014	stale, vegetable oil, paper-like, vegetables, bready, caramel

Analysis Procedure

The area-per-mol of carbon is equivalent for all carbon-containing analytes because every molecule is completely converted to methane. This property allows for the determination of the concentration of any analyte using a single internal standard. For the data above, ethanol was used as the internal standard for calculation of the concentrations of the other analytes. The concentrations of all analytes were then calculated using the governing equation for the Polyarc:

$$C_A = C_S \left(\frac{Area_A}{Area_S}\right)\left(\frac{Mw_A}{Mw_S}\right)\left(\frac{\#C_S}{\#C_A}\right)$$

where:

C_A = Mass concentration of the analyte
C_S = Mass concentration of the standard
$Area_A$ = Integrated peak area of the analyte
$Area_S$ = Integrated peak area of the standard
Mw_A = Molecular weight of the analyte
Mw_S = Molecular weight of the standard
$\#C_S$ = Number of carbon atoms in standard
$\#C_A$ = Number of carbon atoms in analyte

Conclusions

After water, ethanol, and carbon dioxide, glycerin is the most prevalent component of beer at 0.5 to 1.0 wt. %. Beyond that, there are hundreds of flavor components present at levels of 0.1 wt. % or lower. Not surprisingly, the IPA contained higher levels of many flavor molecules, and this is presumably what gives it its characteristic hoppy flavor. As the beer industry becomes saturated with microbreweries, we hope that these companies will use the technique shown here to better understand their product and to help differentiate themselves from the competition. Compared to other methods, the Polyarc System allows for quicker and more accurate quantitative results to be obtained.

Contact Us

For more information or to purchase a Polyarc® system, please contact us at 612-787-2721 or contact@activatedresearch.com.

Please visit our website for details and additional technical literature.

Printed in the USA
March 27, 2018
PA-APP-1812