Comparison of Static and Dynamic Headspace for Volatile Organic Compounds in Orange Juice

Application Note

Abstract

Volatile Organic Compounds (VOCs) play a major role in giving orange juice its flavor and aroma characteristics. Monitoring these VOCs are extremely important when controlling a manufacturing process. Differences in fruit varieties, fruit ripeness and processing techniques could cause undesirable and unacceptable variations in the orange juice's flavor and aroma.

This study presents a survey of VOCs found in fresh squeezed, reconcentrate and reconstituted powder for orange juice. This analysis will compare the VOC content in the three types of orange juice based on static and dynamic headspace techniques.

Introduction

The determination of VOCs is widely used in many fields of chemistry. Two common sample preparation techniques for this analysis are static and dynamic headspace. Static headspace is a relatively simple sampling method that is dependent upon the formation of equilibrium conditions in a closed system. Dynamic headspace continually sweeps the headspace of the sample concentrating the analytes onto a trap. They are retained on the trap until desorption to the GC/MS for separation and detection.

When dealing with flavor and aroma, the difference in fruit varieties, ripeness, and process techniques factor into the quality of the final product. In this study, 100% pure orange juice, orange juice from concentrate, and reconstituted orange drink powder samples were analyzed using static and dynamic headspace to profile their volatile flavor components.

Experimental-Instrument Conditions

The juice samples were analyzed using the static and dynamic headspace techniques of the Teledyne Tekmar HT3 Automated Headspace Analyzer. Commercially available orange juice samples were bought from the local grocery and kept refrigerated prior to analysis. The static headspace utilized a 5mL sample in a sealed 22mL headspace vial while the dynamic used only 1mL of sample in a 22mL headspace vial. When using the dynamic function a smaller amount of sample (1mL) can be utilized due to higher sensitivity. The headspace of the vial is swept using sweep gas to concentrate the analytes onto an analytical trap, where they are retained until desorption to the GC/MS for separation and detection.

Method parameters were optimized using M.O.M (Method Optimization Mode) for both static and dynamic techniques. The dynamic analysis was performed using a Vocarb 3000 (K) analytical trap.

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HT3 Headspace Instrument Parameters			
Static		Dynamic	
Variable	Value	Variable	Value
Valve Oven Temp	80 ˚C	Valve Oven Temp	150 ˚C
Transfer Line Temp	85 ˚C	Transfer Line Temp	150 ˚C
Platen/Sample Temp	40 ˚C	Platen/Sample Temp	40 ˚C
Sample Equil Time	20.0min	Sweep Flow Rate	40mL/min
Pressurize	10psig	Sweep Flow Time	10.0min
Loop Fill Pressure	5psig	Dry Purge Time	1.0min
Inject Time	1.0min	Dry Purge Flow	50mL/min
		Desorb Temp	250 ˚C
		Desorb Time	2.0min
		Trap Material	Vocarb 3000 (K)

Table 1: Static and Dynamic HT3™ Parameters

Thermo Focus GC/DSQ II MS Parameters	
Column	Retek Rtx® VMS, 20m, 0.18mm ID, 1µm; Constant Flow 0.90mL/min
Oven Program	35 °C for 1min; 14 °C/min to 100 °C, 30 °C/min to 200 °C hold for 5min
Inlet:	Split Flow 20mL/min, Temperature 220 °C, Helium Carrier Gas, Split Ratio 20:1
MS	Source and Transfer Line Temp 230 °C, Full Scan 25.0*m/z* to 270.0*m/z*

Table 2: Thermo Focus GC/DSQ II MS Parameters

Results and Chromatograms

1. Static Headspace Analysis

The static headspace option of the Tekmar HT3 Headspace Analyzer was used to profile the VOCs in each juice sample. Total Ion Chromatograms (TIC) were obtained for juice samples and can be found in Figures 1-3. Neat standards of ethanol (EtOH), hexanal, octanal, myrcene, limonene, α-pinene and β-pinene were used to verify the key VOC flavoring components. Retention times were established and confirmed by mass spectral library searches.

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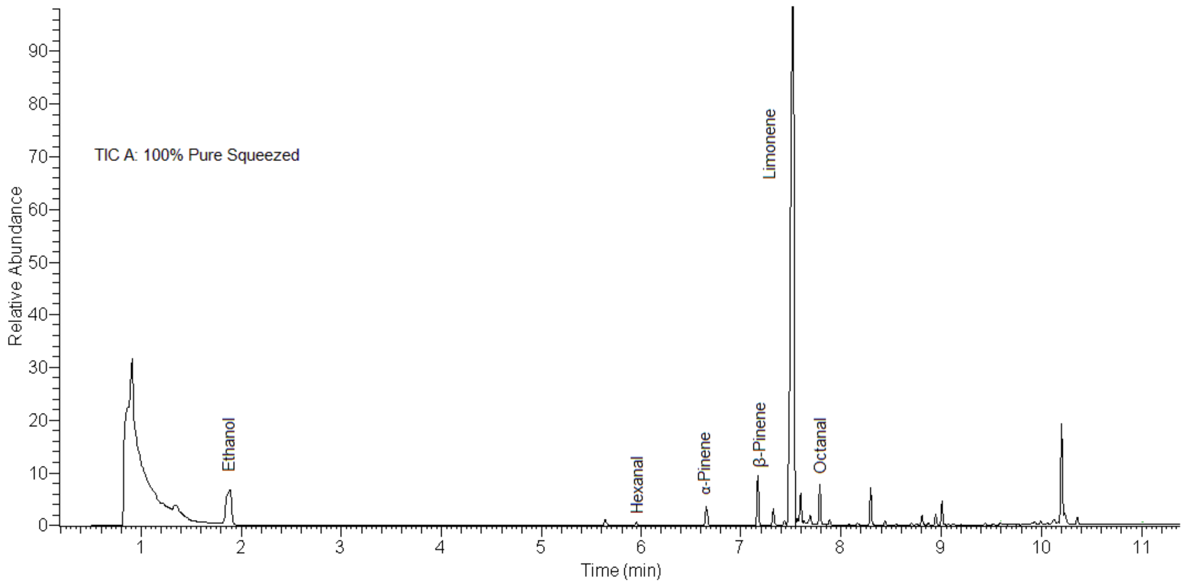

Figure 1: TIC of 100% pure squeezed orange juice

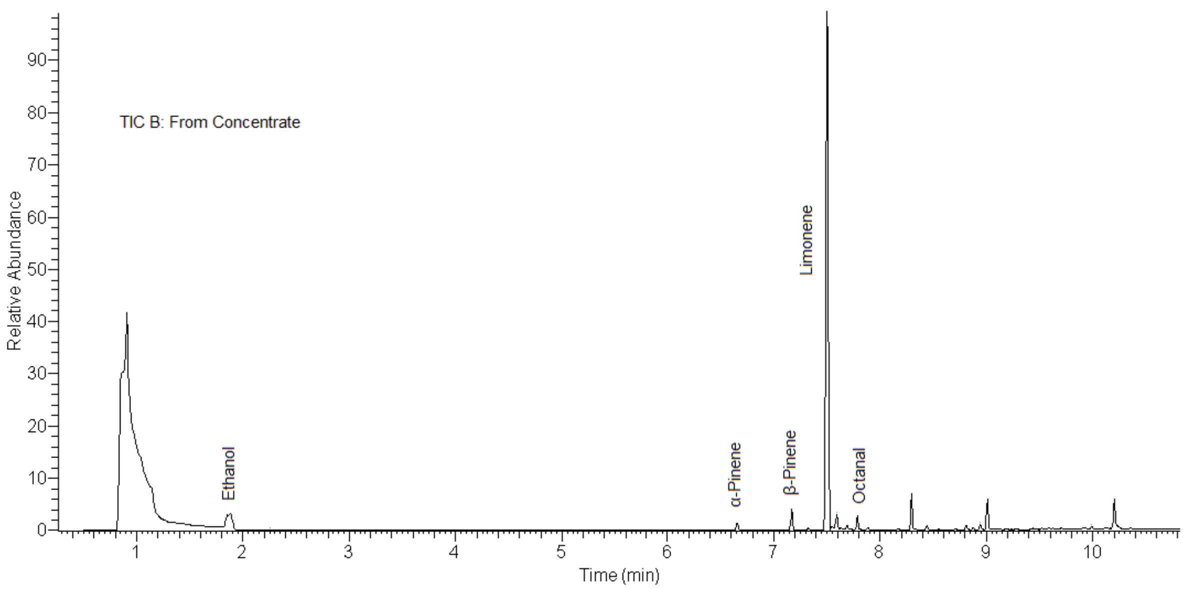

Figure 2: TIC of orange juice from concentrate

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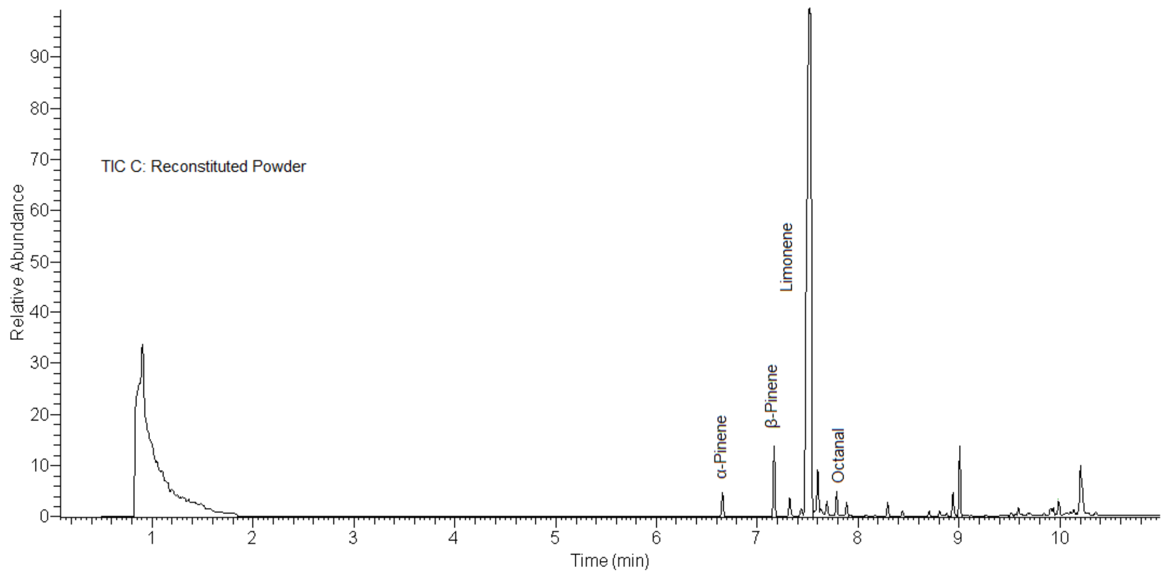

Figure 3: TIC of reconstituted orange drink powder

Figure 4 shows the differences between 100% pure squeezed and orange juice from concentrate. The flavoring compounds of interest were found in higher concentrations in the pure-squeezed orange juice, with the major difference being the concentration of limonene.

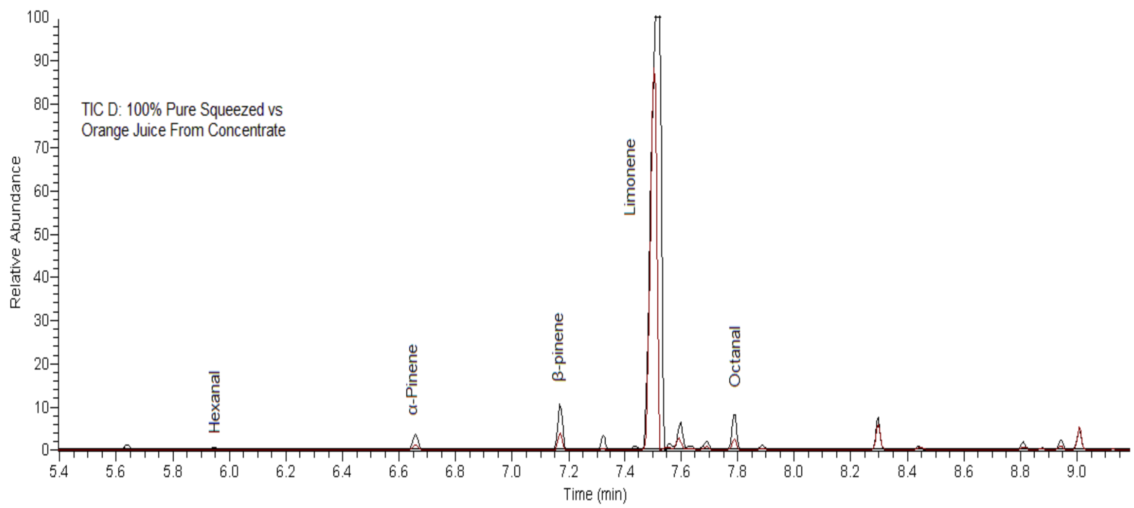

Figure 4: TIC overlay of 100% pure squeezed (black) compared to orange juice from concentrate (red).

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During the concentration process, the juice is heated to drive off water, and with it, some of the volatile compounds are lost as well. This explains why the flavoring compounds such as hexanal, octanal, myrcene, limonene, α-pinene and β-pinene are all reduced in the orange juice from concentrate.

Comparing the 100% pure squeezed orange juice to the reconstituted orange flavor powders there were a few differences between the amounts of compounds present. Figure 5 shows the TIC overlay for both samples.

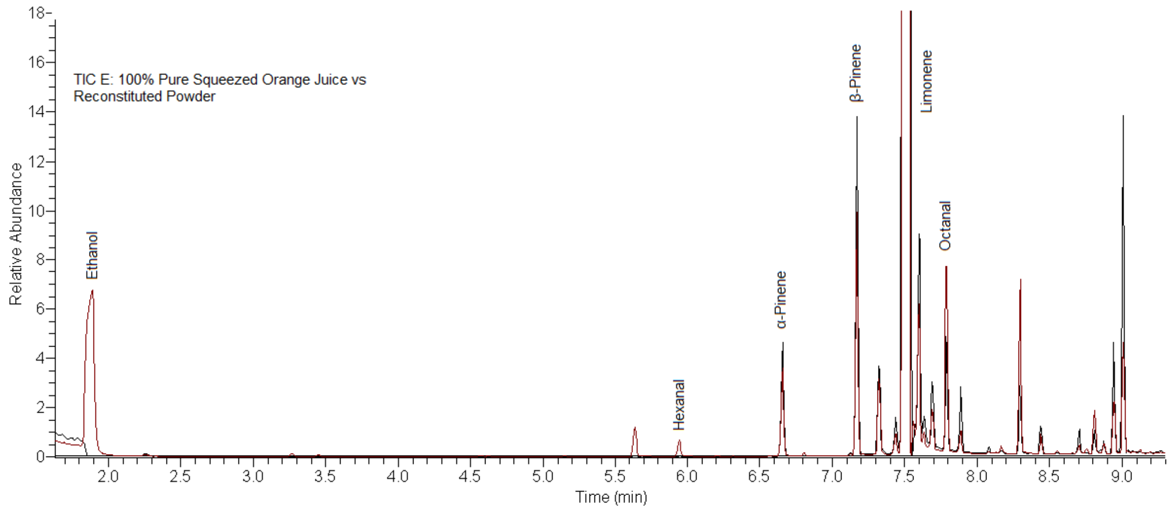

Figure 5: TIC overlay of 100% pure squeezed (red) compared to orange juice from reconstituted powder (black)

There is a considerable amount of ethanol in the pure juice that is not found in the reconstituted powder. Aldehydes such as hexanal and octanal were also found in higher amounts in the pure squeezed than the reconstituted powder. While the limonene concentration was consistent, the amounts of α-pinene and β-pinene were higher in the reconstituted powder.

2. Dynamic Headspace Analysis

The dynamic headspace options of the Tekmar HT3 Headspace Analyzer, the VOCs in the juice were profiled for each sample. When using the dynamic function, a smaller amount of sample (1mL) can be utilized due to higher sensitivity. The headspace of the vial is swept using sweep gas to concentrate the analytes onto an analytical trap, where they are retained until desorption to the GC/MS for separation and detection.

The TICs are presented in Figures 6-8 for each orange juice analyzed by dynamic headspace. Neat standards of ethanol (EtOH), hexanal, octanal, myrcene, limonene, α-pinene and β-pinene were used to verify the key VOC flavoring components. Retention times were established and confirmed by mass spectral library searches.

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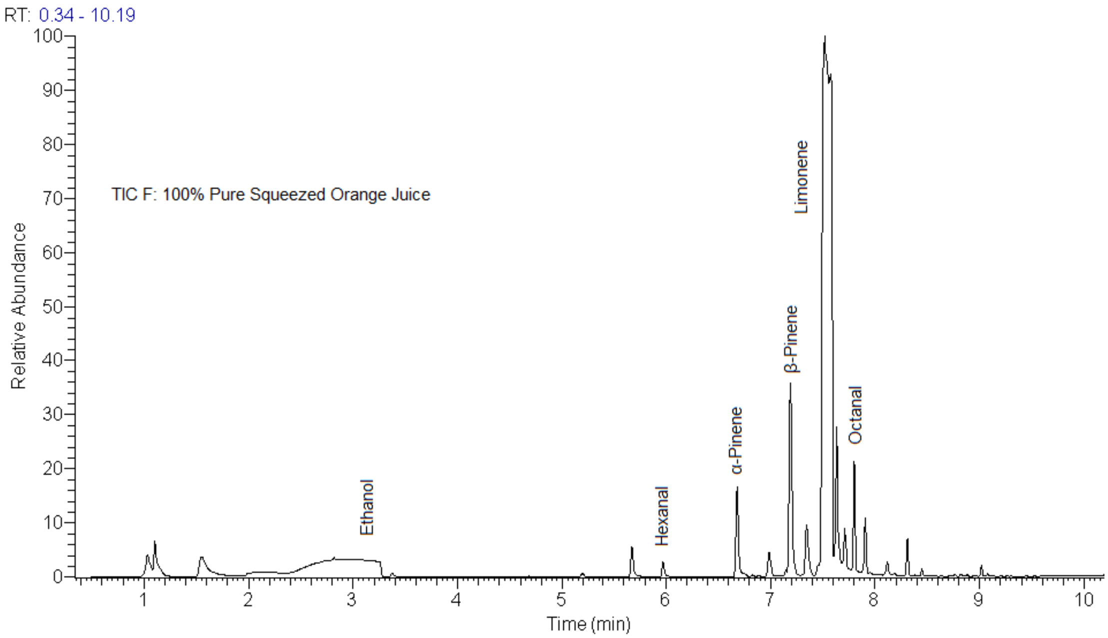

Figure 6: TIC of 100% pure squeezed orange juice

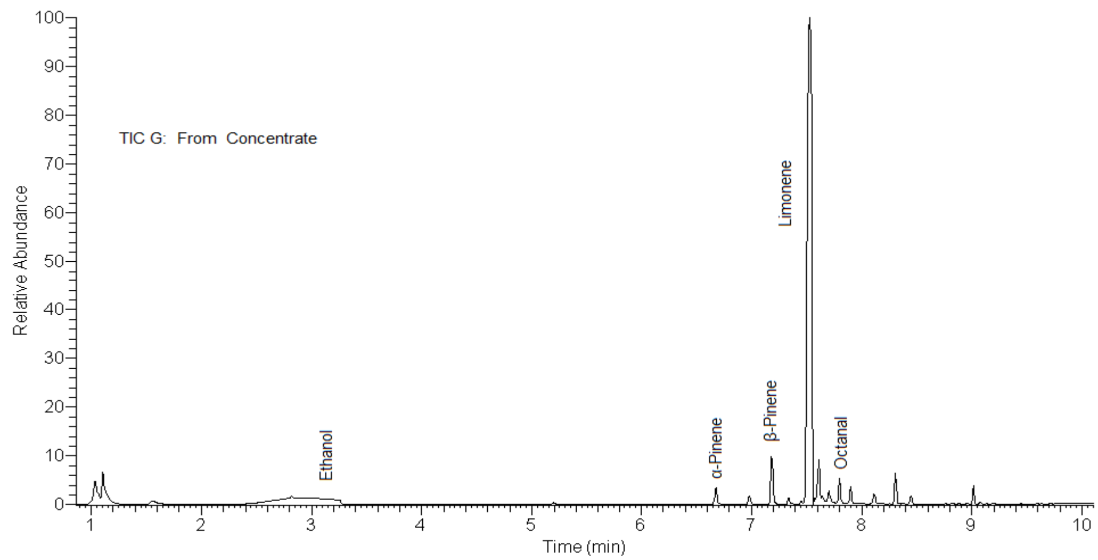

Figure 7: TIC of orange juice from concentrate

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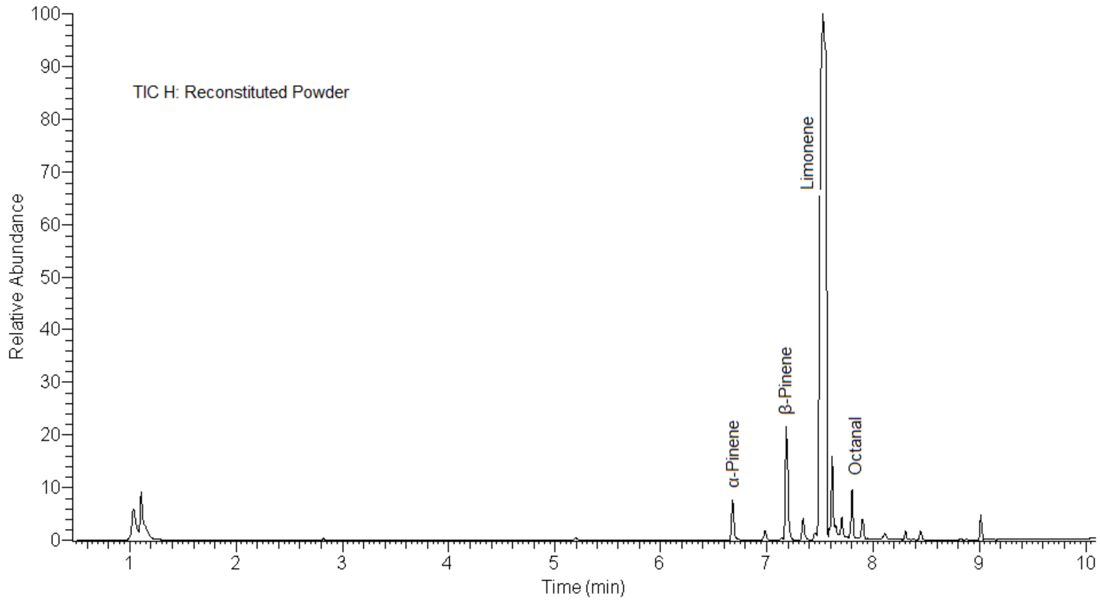

Figure 8: TIC of reconstituted orange powder

The trends observed in the dynamic analysis were consistent with those in the static analysis. The VOCs were again found in high concentration in the 100% pure squeezed juice. This is due to volatile flavor compounds being driven off during the concentration process. The comparison of these two samples can be seen in Figure 9.

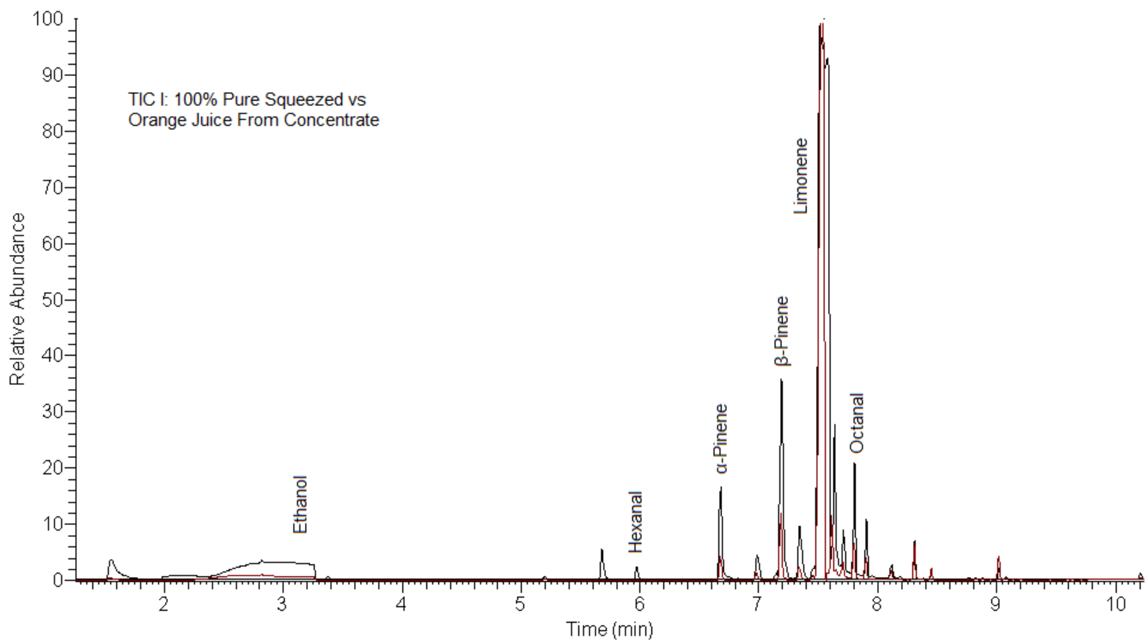

Figure 9: TIC overlay of 100% pure squeezed (black) compared to orange juice from concentrate (red).

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While the first comparison followed the same trend as the static technique, the second comparison did not. Results for the 100% pure squeezed and the reconstituted powder changed drastically, with the ability to trap the VOC flavor compounds. Figure 10 shows the TIC overlay for both samples.

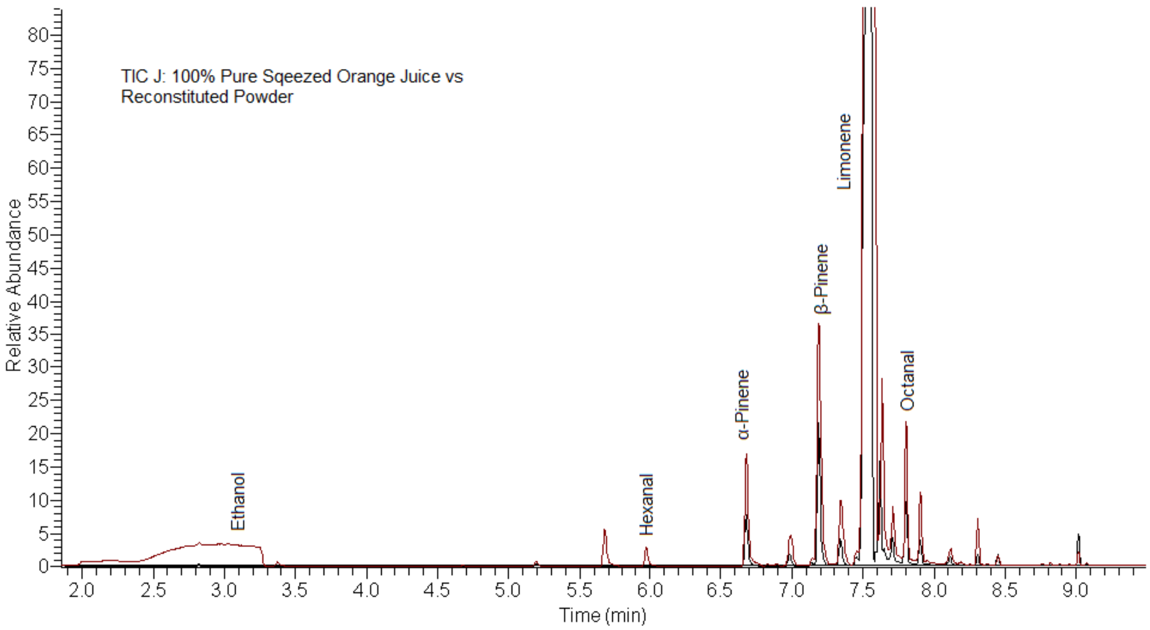

Figure 10: TIC overlay of 100% pure squeezed (red) compared to orange juice from reconstituted powder (black)

Much like the static analysis there was a significant difference in concentration in the ethanol between the two samples. Where the dynamic and static headspace results differ is in the α-pinene and β-pinene concentration. They are actually seen in greater amounts in the 100% pure squeezed than in the reconstituted powder.

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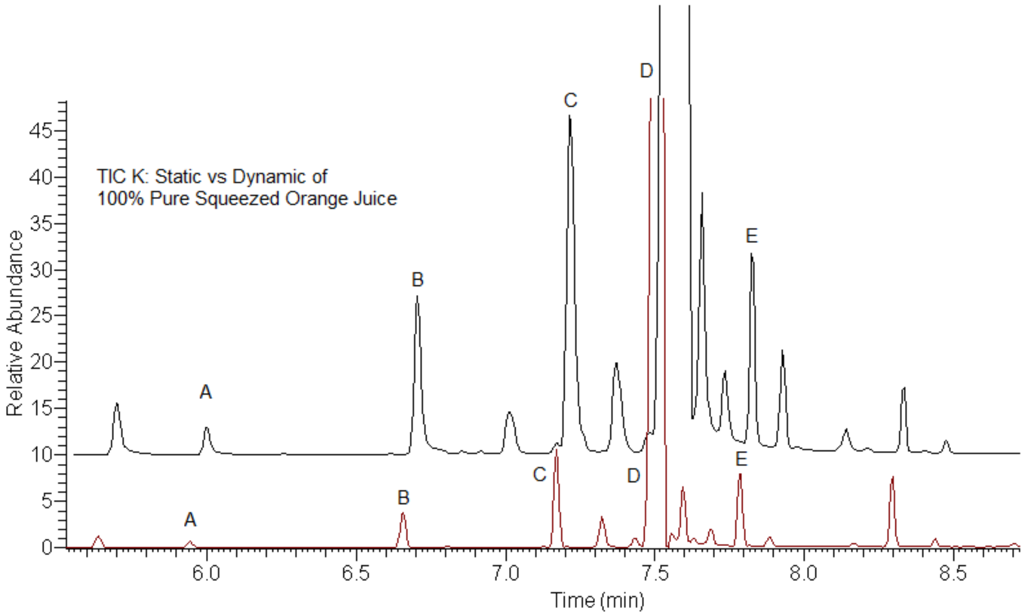

Figure 11: TIC overlay comparison of Static Headspace (red) vs Dynamic Headspace (black) (A-Hexanal, B-α-Pinene C-β-Pinene, D-Limonene, E-Octanal)

Figure 11 shows a TIC overlay of the static and dynamic analysis of the 100% pure squeezed orange juice. The dynamic mode allows for better recovery of the flavor and aroma compounds. Dynamic headspace enables for small amounts of sample (1mL) to be used, and gives detailed results that achieve lower detection levels than in static mode. The analytes are continually swept from the sample and trapped making the analysis much more sensitive.

Conclusion

Static and dynamic headspace analyses of volatile compounds are widely used techniques. Both can be used as valuable tools for analyzing a variety of matrices, and the dynamic option is highly beneficial to applications requiring lower (ppb) detection limits.

In this study, three orange juice samples were analyzed for their VOC flavor profile by both static and dynamic headspace the Tekmar HT3 Headspace Analyzer with a Thermo Focus GC/DSQ II MS. This enables a very detailed profile of these juices to be established. These flavor profiles can be used to recognize product purity, adulteration, or impurities. This analysis gives a detailed flavor profile of these juices and may be used to recognize product purity, adulteration, or impurities in these types of products. The HT3 is capable of performing both static and dynamic sampling of orange juice for volatile flavor compounds fast and efficiently to help ensure quality products.

References

1. Comparison of Gas-Sample and SPME-Sample Static Headspace for the Determination of Volatile Flavor Compounds. Michael E. Miller and James D. Stuart, Analytical Chemistry, Vol 71, NO.1, January 1, 1999
2. Profiling of Volatile Organic Compounds in Milk and Orange Juice Using Headspace Analysis, Teledyne Tekmar Application Note
3. Headspace Analysis and Stripping of Volatile Compounds from Apple and Orange Juice Using SIFT-MS, Application Note

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