Analysis of Fragrance and Flavor Compounds in Citrus Peels by Dynamic Headspace with a Pyroprobe 6200

Application Note
Food and Flavor

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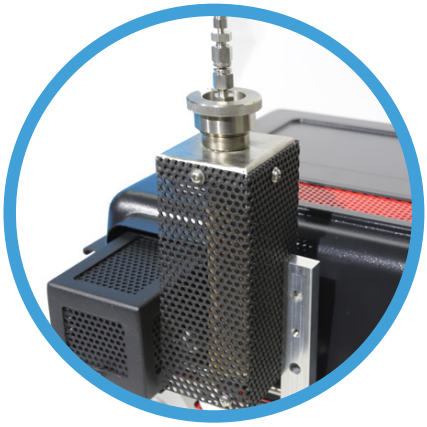
Abstract
This application note demonstrates analysis of fruit peels by performing DHS- GC-MS with a Pyroprobe 6200.

Introduction
Flavor is the sensory impression, determined by the senses of taste and smell. As citrus fruits are peeled, they release delicious, citrus scented aromas. The main compound in the fragrant vapor is limonene, which is a common ingredient flavorings, perfumes and even household cleaners[1]. Besides limonene, many individual flavor compounds together constitute the overall aroma profile of specific fruit, so that can distinguish between limes, oranges, and grapefruit. This can be studied using a CDS Pyroprobe 6200, when equipped with thermal desorption or dynamic headspace modules. Citrus peel was characterized for flavor and fragrance compounds using a CDS Pyroprobe 6200 with a dynamic headspace (DHS) module.

Experiment Setup
Citrus fruit was peeled and 1 gram of peel was added to a 25 mL test tube, which was placed in the DHS vessel attachment installed on a Pyroprobe 6200 interfaced to a GC-MS for multi-step dynamic headspace analysis at 50°C and 75°C.

Dynamic Headspace

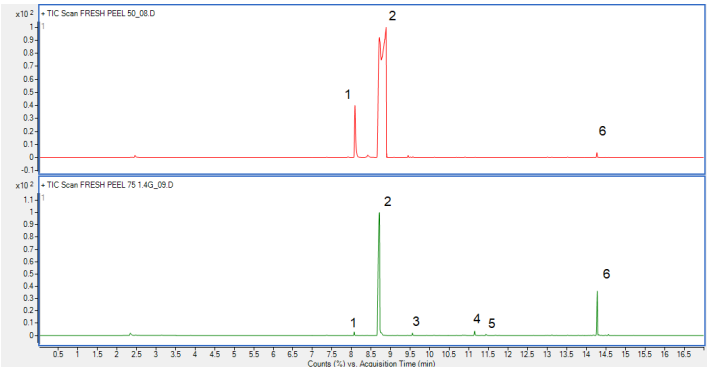
Pyroprobe 6200 with DHS		GC-MS
DHS Vessel:	50 °C, 75°C 10min	Column: 5% phenyl (30m x 0.25mm)
Purge Gas:	He 40mL/min	Carrier: Helium 1.25mL/min, 80:1 split
		Injector: 360°C
Trap Contents:	Tenax	Oven: 40°C for 2 minutes
Trap Rest:	40°C	12°C/min to 320°C
Trap Final:	300°C 3min	Ion Source: 230°C
Transfer Line:	300°C	Mass Range: 35-600amu
Valve Oven:	300°C	



Results and Discussion
A dynamic headspace (DHS) attachment was attached to the Pyroprobe 6200 in order to explore the aroma profile of citrus fruit peels. With this configuration, the peel is purged to a sorbent trap within the 6200, which is then desorbed to the GC. This technique both concentrates and refocuses, resulting in sufficient separaton and concentration for volatiles.

Dynamic headspace was performed using multiple temperatures. Multi-step analysis can simplify results by dividing volatiles into separate chromatograms. Therefore, each peel was run at 50°C and then at 75°C. Chromatograms of each peel are shown in Figures 1-4. At 50°C, limonene dominates the chromatograms,

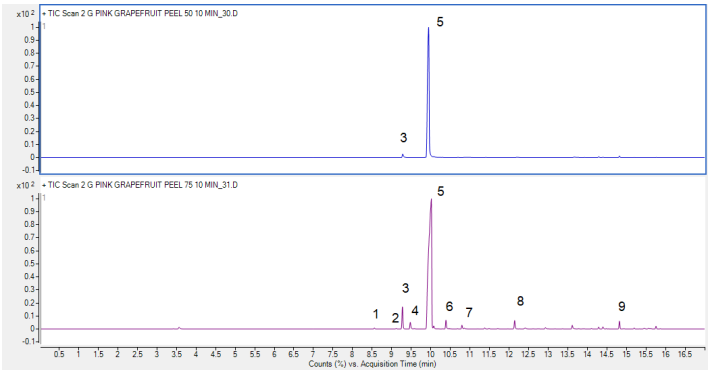
dwarfing the surrounding volatiles. Multi-step analysis allows much of the Limonene to outgas during this first step. Limonene is still dominant at 75°C, but other volatiles become more visible. Limonene, which provides a lemon-like odor, along with beta-Pinene, which is described as a woody- green aroma, and Linalool which emits floral and spicy wood notes, were common in all peels. In addition, orange peel had Valencene, which is abundant in Valencia oranges and gives a sweet citrus flavor reminiscent of fresh herbs or cut wood (Figure 1).



Peak	Identification	Peak	Identification
1	beta-Pinene	4	cis-Geraniol
2	Limonene	5	Geraniol
3	Linalool	6	Valencene

Figure 1. Dynamic Headspace of orange peel, 50°C (top), then 75°C (bottom).

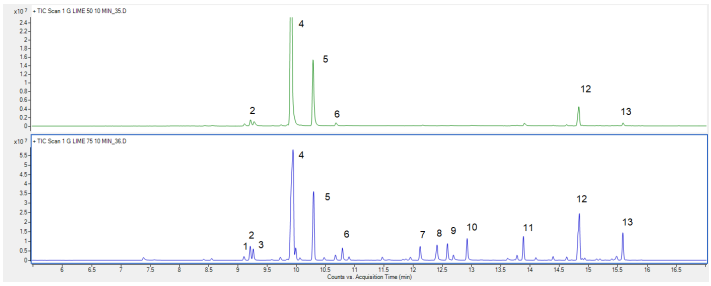
Pink grapefruit peel had compounds such as alpha-Pinene, Ylangene, Germancrene D, and Caryophyllene (Figure 2). Caryophyllene is also present in peppercorn[2] and is responsible for a "biting" quality.



Peak	Identification	Peak	Identification
1	alpha-Pinene	6	1-Octanol
2	Sabinene	7	Linalool
3	beta-Pinene	8	Decanal
4	Octanal	9	Caryophyllene
5	Limonene		

Figure 2. Dynamic Headspace of pink grapefruit peel, 50°C (top), then 75°C (bottom).

Lime peel had the most diverse aromatic profile which included beta-Myrcene, alpha- Terpineol, and Nerol. Nerol provides sweet, fresh rose odor[3]. Additionally, the lime peel had gamma-Terpinene, which can contribute to flavor deterioration when it degrades to para-Cymene[4].



Peak	Identification	Peak	Identification
1	Sabinene	8	Nerol
2	beta-Pinene	9	(S)-cis-Verbenol
3	beta-Myrcene	10	alpha-Citral
4	Limonene	11	Nerol acetate
5	gamma- Terpinene	12	alpha-Bergamotene
6	Linalool	13	beta-Bisabolene
7	alpha-Terpineol		

Figure 3. Dynamic Headspace of lime peel, 50°C (top), then 75°C (bottom).

Conclusion

The Pyroprobe 6200 is a versatile multi-function thermal injection system. Its modular design plus trapping capabilities expands the use of a pyrolyzer to techniques such as thermal desorption and dynamic headspace. The volatiles of citrus peels were studied with a CDS 6200 Pyroprobe including a dynamic headspace attachment, demonstrating its usefulness in the profiling of aroma compounds in citrus peels.

References

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3. Karl-Georg Fahlbusch, Franz-Josef Hammerschmidt, Johannes Panten, Wilhelm Pickenhagen, Dietmar Schatkowski, Kurt Bauer, Dorothea Garbe, Horst Surburg "Flavors and Fragrances" in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2002. doi:10.1002/14356007.a11_141

4. Ikeda,R., et al., "Monoterpene Hydrocarbon Composition of Citrus Oils", Journal of Food Science, Volume 27, Issue 6, November 1962, Pages 593-596.

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