Analysis of Fragrance and Flavor Compounds in Spices by TD-GC/MS with a Pyroprobe 6200

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Application Note
Food and Flavor

Abstract
This application note demonstrates analysis of several spices by performing TD-GC-MS with a Pyroprobe 6200.

Introduction
Flavor is the sensory impression, determined by the senses of taste and smell. The correct spice combination added to food can enhance its flavor, making it more enjoyable to consume.[1] Individual spices each carry a unique fingerprint of chemical compounds contributing to its flavor, and these fingerprints can be studied using a CDS Pyroprobe 6200, when equipped for thermal desorption and dynamic headspace techniques. Several spices were characterized for flavor and fragrance compounds with a CDS Pyroprobe 6200.

Experiment Setup
Pieces of peppercorn were first added into a DISC (Drop-In-Sample Chamber) tube and analyzed using Evolved Gas Analysis (EGA) followed by multi-step pyrolysis as a screening step. Then, to get a more in-depth look of the volatile flavor and fragrance compounds, 55 mg of a peppercorn was added to a thermal desorption attachment and heated at 75°C to a sorbent trap. Cloves, cinnamon, and nutmeg were also studied with the same technique for a flavor profile comparison.

EGA
Pyroprobe with DISC
Initial: 50°C for 10min
Final: 800°C
Ramp Rate: 100°C per min
Interface: 300°C
Transfer Line: 300°C
Valve Oven: 300°C

GC-MS
Column: Fused silica (1m x 0.10mm)
Carrier: Helium 1.25mL/min
80:1 split
Injector: 360°C
Oven: 300°C
Ion Source: 230°C

Thermal Desorption
Pyroprobe 6200 with 1/4” Tube Desorber

TD Tube:	75°C 10min
Purge Gas:	He 20mL/min
Trap Contents:	Tenax
Trap Rest:	40°C
Trap Final:	300°C
Transfer Line:	300°C
Valve Oven:	300°C

GC-MS
Column: 5% phenyl (30m x 0.25mm)
Carrier: Helium 1.25mL/min, 80:1 split
Injector: 360°C
Oven: 40°C for 2 minutes
12°C/min to 320°C
Ion Source: 230°C
Mass Range: 35-600amu

Results and Discussion

Evolved gas analysis shows rises in baseline starting around 250°C, before a large peak at 350°C, and a second, smaller peak at 500°C (Figure 1). The evolution is due to both thermal desorption as well as degradation of the peppercorn. While volatile flavor compounds may outgas at this 75°C, EGA analysis is not sensitive enough to detect them.

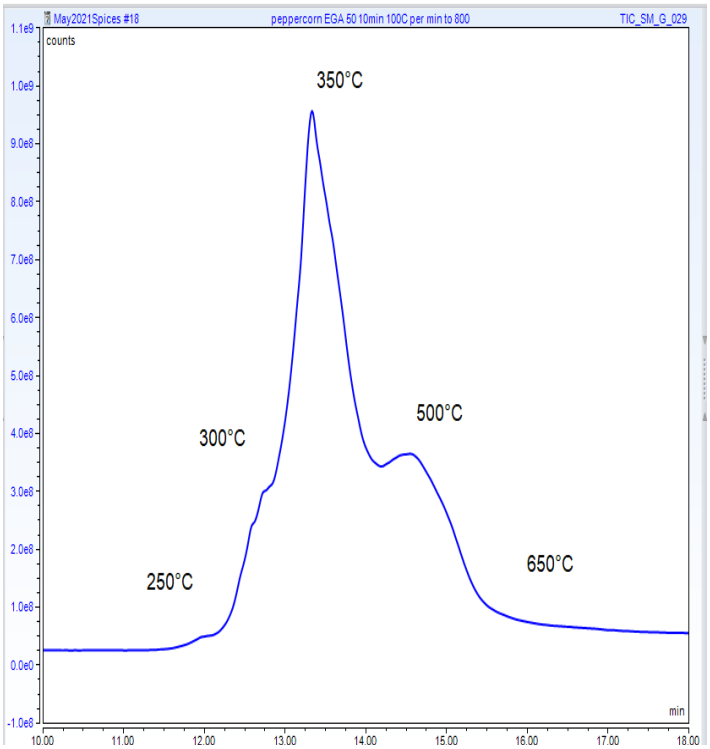
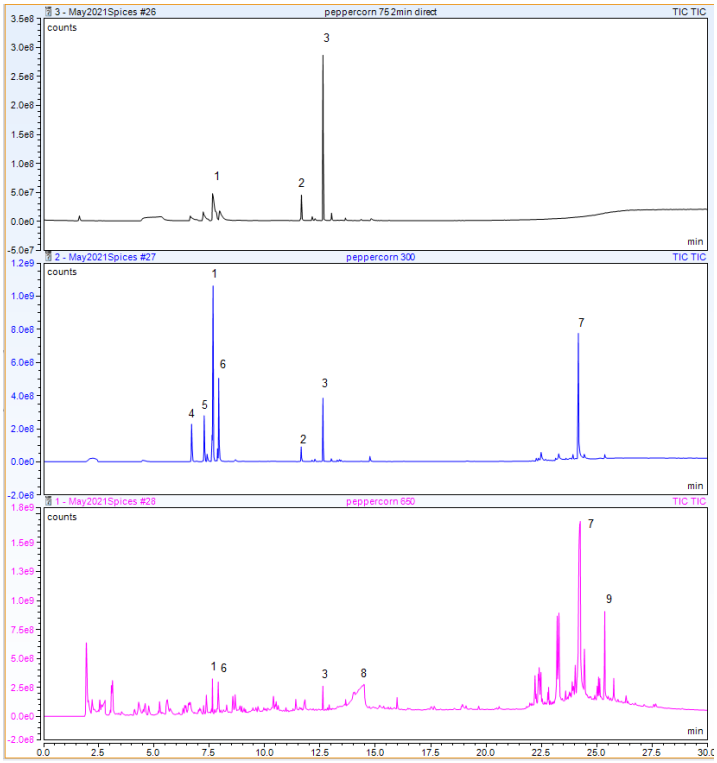


Figure 1. Evolved Gas Analysis of peppercorn from 50°C to 800°C at 100°C per minute.

After obtaining EGA results, multi-step pyrolysis was performed at 75°C, 300°C and 650°C. At 75°C, volatile compounds are seen. At 300°C the same volatile peaks are seen with greater intensity, along with semi-volatile compounds, including piperine, an alkaloid responsible for providing the sharp and penetrating quality of pepper.[2] Finally, at 650°C, pyrolysis products of the peppercorn, like levoglucosan, are evident, along with remaining semi-volatiles like piperine and pipersintenamide.

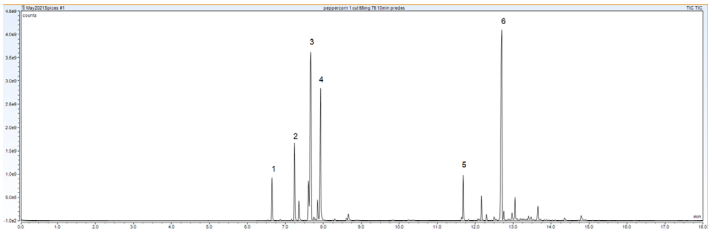
A tube desorber attachment was then attached to the Pyroprobe in order to peform thermal desorption with a larger sample size for exploring the flavor profile of peppercorn, and also clove, cinnamon, and nutmeg (Figures 2-6). With this configuration, the sample is purged to a sorbent trap within the 6200, which is then desorbed to the GC. This technique both concentrates and refocuses the compounds, resulting in good resolution for early eluting volatiles.

All 4 spices have distinctly different chemical profiles (Figures 2-6). Clove has a lot of m-Eugenol, Cinnamon stick is predominantly cinnamaldehyde, and nutmeg has the greatest variety of aromas and flavors. One compound, caryophyllene, is common to peppercorn, cloves, and cinnamon. This is a sesquiterpene



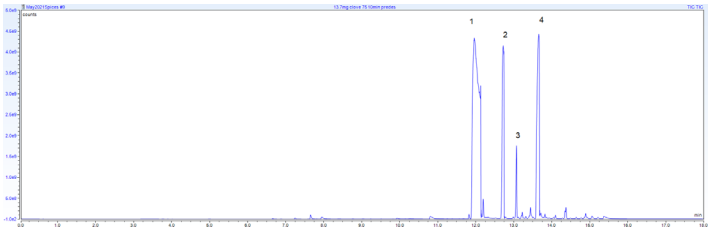
Peak	Identification	Peak	Identification
1	delta 3 carene	5	beta-pinene
2	delta elemene	6	sylvestrene
3	caryophyllene	7	piperine
4	alpha pinene	8	levoglucosan
		9	pipersintenamide

Figure 2. Multi-step pyrolysis of peppercorn, 75°C (top), 300°C (center), and 650°C (bottom).



Peak	Identification	Peak	Identification
1	alpha pinene	4	d limonene
2	beta pinene	5	gamma elemene
3	delta 3 carene	6	caryophyllene

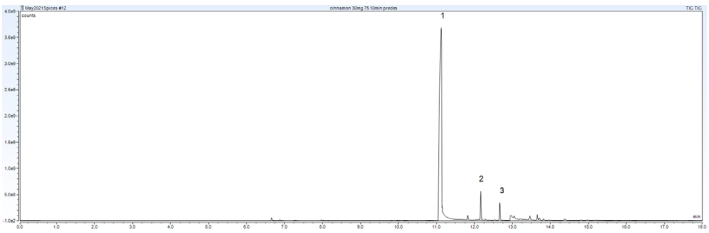
Figure 3. Peppercorn, on tube desorber attachment, 75°C



Peak	Identification	Peak	Identification
1	m-Eugenol	3	Humulene
2	caryophyllene	4	Eugenol Acetate

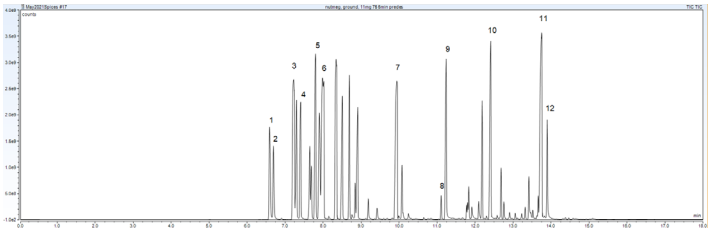
Figure 4. Clove, on tube desorber attachment, 75°C

found in many plants and is responsible for most of the aroma in peppercorn. Biologically active, it has anti-septic, anti-inflammatory, antioxidant, and antitumor qualities.[3]



Peak	Identification
1	Cinnamaldehyde
2	alpha-Copaene
3	caryophyllene

Figure 5. Cinnamon, on tube desorber attachment, 75°C



Peak	Identification	Peak	Identification
1	alpha-thujene	7	4- terpineol
2	alpha pinene	8	borneol acetate
3	sabinene	9	safrol
4	beta-pinene	10	methyl eugenol
5	gamma terpene	11	myristicin
6	delta limonene	12	elesmicin

Figure 6. Nutmeg, on tube desorber attachment, 75°C

Conclusions

Peppercorn, the spice of black pepper was analyzed using EGA and multi-step pyrolysis for screening. After which, the volatiles of peppercorn and three other commonly used spices were studied with a CDS 6200 Pyroprobe including a tube desorber attachment, demonstrating its usefulness in the profiling of flavor and aroma compounds.

References

1. https://www.scienceofcooking.com/what_is_flavor.htm
2. K. Srinivasan , Black pepper and its pungent principle-piperine: a review of diverse physiological effects, Crit Rev Food Sci Nutr. 2007;47(8):735-48. doi: 10.1080/10408390601062054
3. Keylla da Conceição Machado, Muhammad Torequl Islam, Eunüs S. Ali, Razina Rouf, Shaikh Jamal Uddin, Shrabanti Dev, Jamil A. Shilpi, Manik Chandra Shill, Hasan Mahmud Reza, Asish Kumar Das, Subrata Shaw, Mohammad S. Mubarak, Siddhartha Kumar Mishra, Ana Amelia de Carvalho Melo-Cavalcante. A systematic review on the neuroprotective perspectives of beta-caryophyllene. Phytotherapy Research. 2018; 2376-2388. https://doi.org/10.1002/ptr.6199