

MULTI-DIMENSIONAL GAS CHROMATROGRAPHY / MASS SPECTROMETRY / OLFACTOMETRY

ANALYSIS OF HEADSPACE GENERATED FROM GREEN COFFEE BEANS

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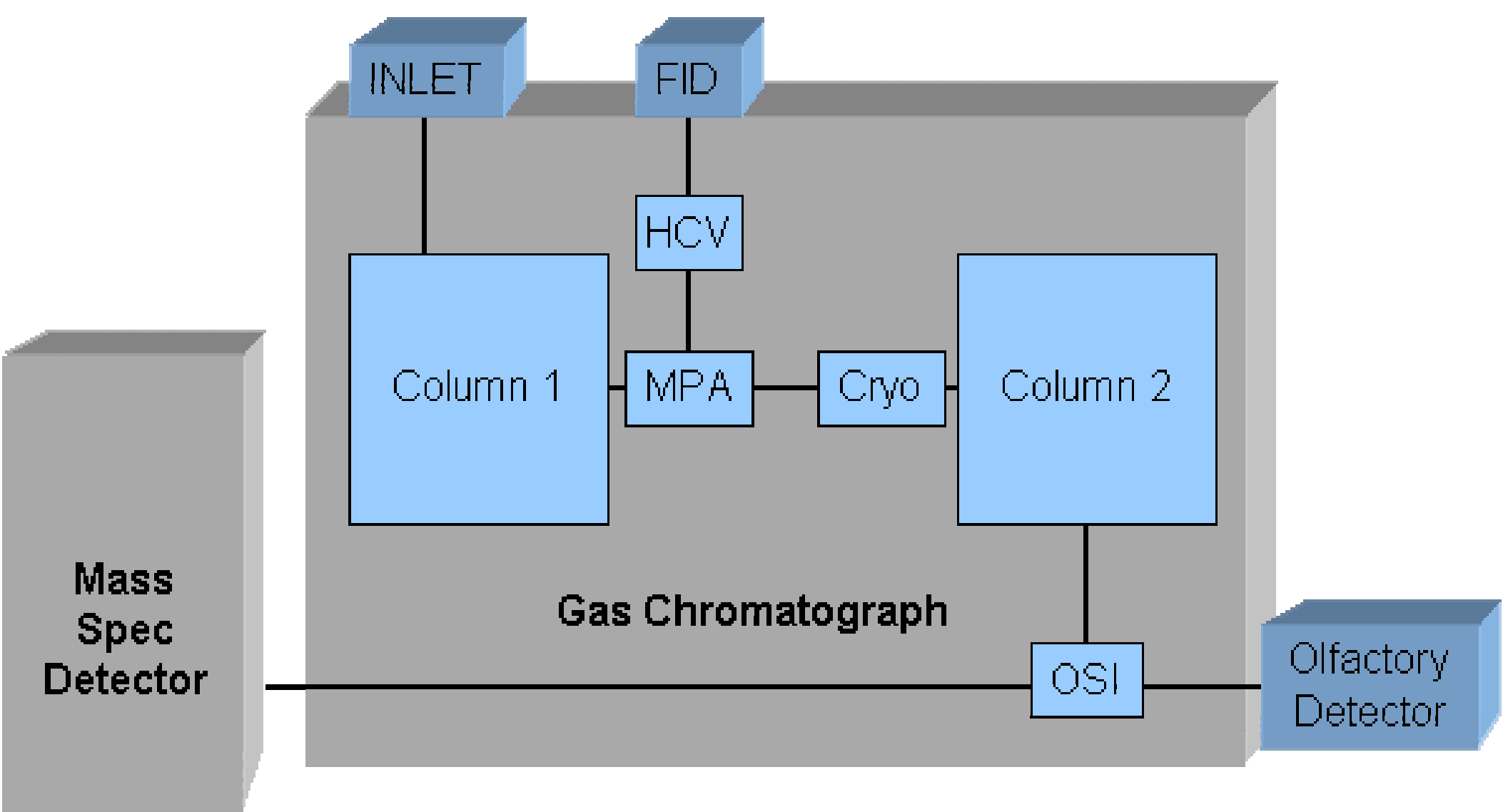
Introduction

Green coffee beans have an aroma which is vastly different from that of a typical cup of brewed coffee. During the roasting process, steam produced inside the green coffee bean reacts with numerous chemical compounds to yield a multitude of volatile aromatic chemical compounds. A brewed cup of coffee represents a complex chemical mixture that may contain well over 800 chemical compounds. Still, many of these compounds are odorless. Sensory analysis following the cupping protocol is an accepted method for evaluating the aroma and flavor of freshly roasted coffee beans. This process rates the quality of the coffee and hence the quality of the coffee beans. Sensory evaluation of the headspace created from green coffee beans would identify the volatile and semi-volatile aroma chemical compounds that are present. This could be a first step in establishing an instrumental analysis method to qualify the quality of the green coffee beans.

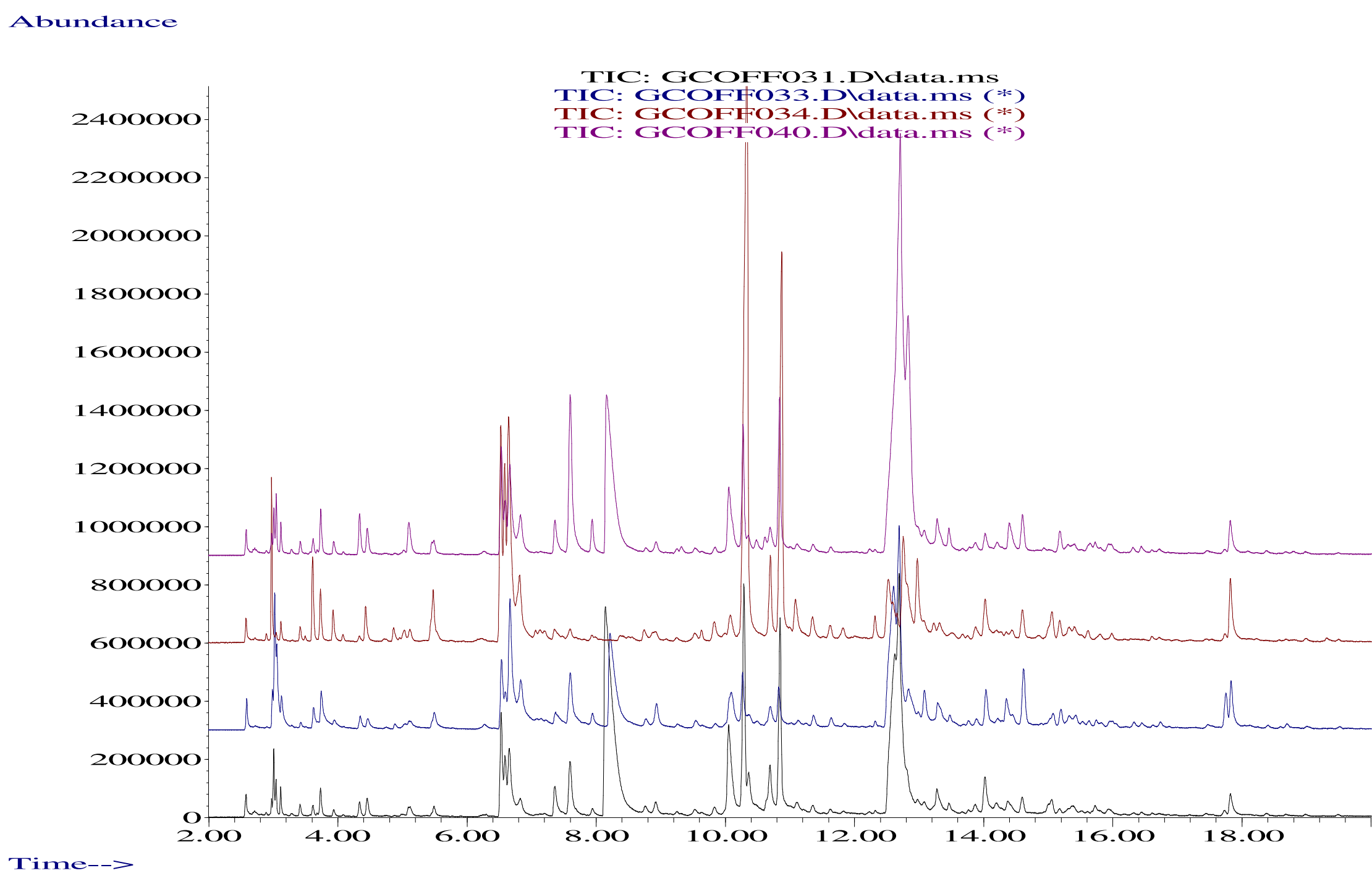
Experimental

- Four different green coffee bean samples
- 25 grams of beans enclosed in 125 ml glass bottle for headspace equilibration
- Volatile and semivolatile compounds collected from headspace using Solid Phase MicroExtraction (SPME) fibers (75 µm carboxen/polydimethylsiloxane)
- MDGC / MS / O analysis performed using AromaTrax® instrument (7820 Agilent GC / 5975 Agilent MSD / “Sniff Port” for olfactory analysis
- Temperature program: 40°C (hold for 3 minutes), 7°C/min ramp to 240° C and 240°C (hold for 8.4 minutes)

Instrument Schematic



GCMS Total Ion Chromatograms

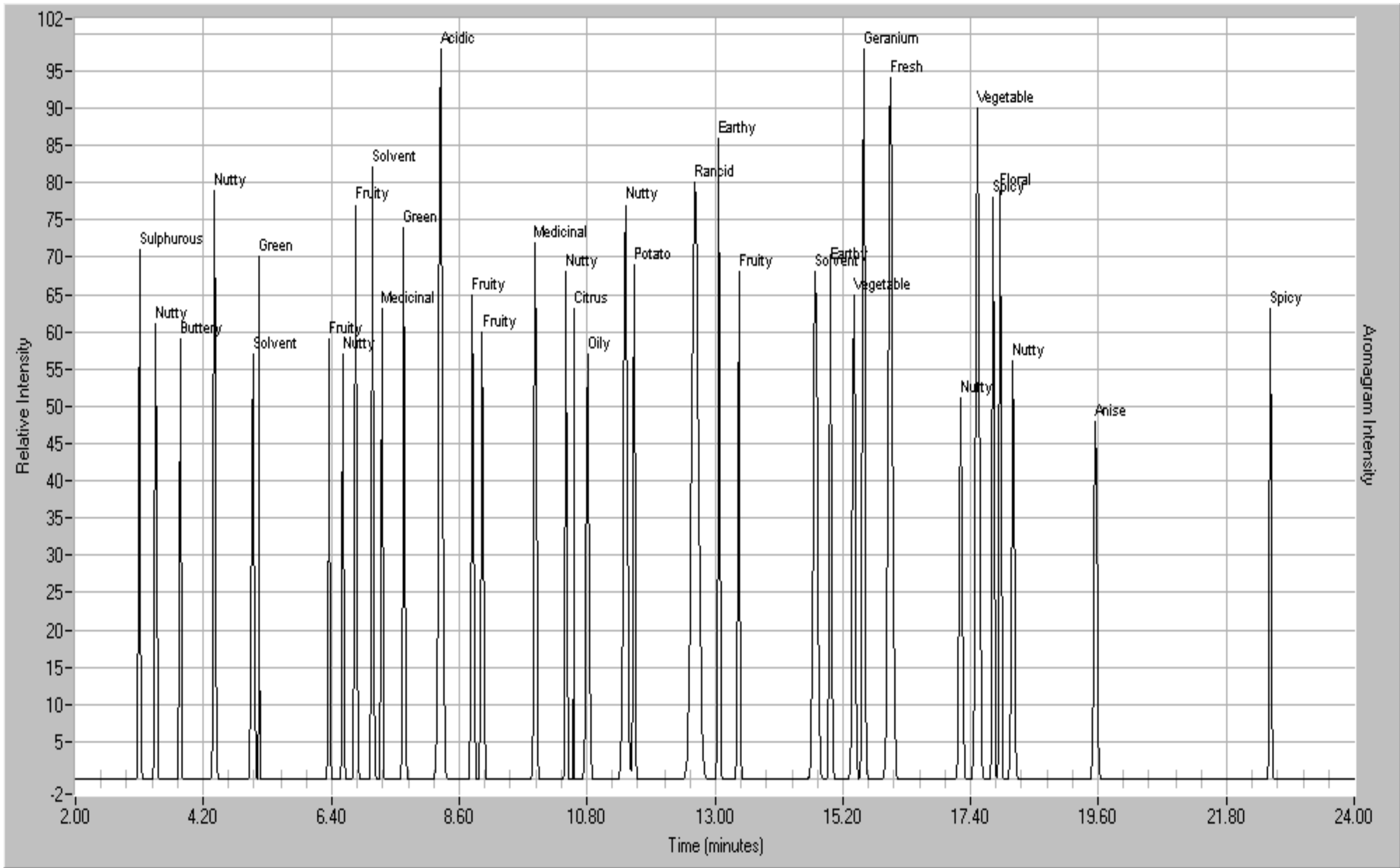


Comparison of GCMS total ion chromatogram results showing differences in the chemical compounds that are present in the headspace along with their relative intensities. (Sample 1, Sample 2, Sample 3, Sample 4)

Summary of GCMS Results

- Numerous chemical compounds emitted from the coffee beans
- Over 120 chromatographic peaks or compounds observed among the 4 samples
- Many different classes of compounds represented: alkanes, alcohols, acids, aldehydes, esters, ketones, etc.
- For these collection conditions, each sample contained approximately 80 different compounds
- 37 compounds were present in all 4 of the samples
- Significant compositional differences among the 4 types of samples

Olfactory Analysis



Olfactory analysis is performed simultaneously with the GC analysis to detect the compounds that contribute to the aroma intensity of the green coffee beans. An aromagram is a graphical representation of this olfactory analysis. Each peak represents an aroma compound that was detected by the sensory scientist at the sniff port as it elutes from the GC column. (Aromagram shown from green coffee Sample 4).

Aroma Compound Comparison

RT (min)	Odor Character	Tentative MS Identification	Aroma Intensity			
			Sample 1	Sample 2	Sample 3	Sample 4
2.71	sweet, aldehydic	acetaldehyde		155	59	
2.82	foul, amine	trimethyl amine			419	
3.05	sulphurous, sharp, molasses	dimethyl sulfide	439	608	209	567
3.30	sharp, nutty, roasted	isobutanol	377	569	251	547
3.75	buttery, sweet	diacetyl	688	511	798	412
4.35	nutty, roasted	3-methyl butanal	1048	1118	801	788
4.99	solvent, petroleum, paper					682
5.15	green					209
6.31	sweet, fruity, fresh	ethyl isobutyrate	334	471	471	412
6.56	nutty, roasted			342	618	398
6.83	sweet, fruity, fresh	methyl isovalerate	808	858	868	768
7.06	solvent, fresh	2-methyl-3-pentanol	608	680		736
7.20	solvent, fresh, medicinal		898	766	845	440
7.60	green, grassy, aldehydic, herbaceous	hexanal	688	407	287	664
8.31	acidic, sour	acetic acid	1517	1578		1663
8.77	fruity, fresh, sweet	ethyl-2-methyl butyrate	765	768	852	713
8.92	fruity, fresh	ethyl isovalerate	199	461		659
9.85	solvent, fresh, medicinal, paper		1086	691	610	790
10.14	solvent		414			
10.41	nutty, roasted					475
10.53	citrus	1-heptanal				188
10.68	foul	isobutyric acid	766			
11.15	nutty, roasted	2,5-dimethyl pyrazine			299	
11.38	nutty, roasted, savory	2,4 or 2,6-dimethyl pyrazine	791	742	548	1383
11.58	potato	methional	582	898	547	619
12.54	rancid, foul, sweaty	isovaleric acid	1688	1102	1160	2475
12.67	herbaceous, green	gamma-butyrolactone		808	718	
12.79	foul, stale		664			
13.03	earthy, mushroom	1-octen-3-one				772
13.17	vegetable, herbaceous				341	
13.32	fresh, citrus	octanal	485	575	164	610
13.54	nutty, roasted	trimethyl pyrazine			299	
14.63	nutty, stale		718	1090	1054	
14.64	solvent, petroleum, oily					1289
14.95	earthy, mushroom					688
15.31	smoky, solvent			921		
15.35	vegetable, earthy	1-octene-3-ol 3-ethyl-2,5-dimethyl pyrazine	257		817	843
15.57	herbaceous, green, vegetable	linalool oxide	622	1018	1155	1076
15.94	fresh, medicinal, solvent	nonanal	619	709		1876
16.04	fruity, fresh, citrus	linalool		323	503	
17.18	smoky, sharp, roasted	guaiacol	913	1186	834	712
17.48	vegetable, herbaceous		730	674	1052	1527
17.74	vegetable, herbaceous, green	2-methoxy-3-(2-methylpropyl)pyrazine	973	874	349	700
17.83	floral, fresh, solvent	benzeneethanol	779	621	958	709
18.09	nutty, roasted					726
18.86	sharp					838
19.27	smoky, roasted					678
19.49	anise, sweet					670
21.65	musty, earthy, mushroom	2,4,6-trichloro anisole	519	766		
22.44	floral, cedar, smoky, foul	2-methoxy-4-vinylphenol	1132	1361	1119	566
		Number of aroma notes	30	31	32	35

Top 10 Detected Aromas

RT (min)	Odor Character	Sample 1	
		Tentative MS Identification	Aroma Intensity
12.54	rancid, foul, sweaty	isovaleric acid	1688
8.31	acidic, sour	acetic acid	1517
22.44	floral, cedar, smoky, foul	2-methoxy-4-vinylphenol	1132
9.85	solvent, fresh, medicinal, paper		1086
4.35	nutty, roasted	3-methyl butanal	1048
17.74	vegetable, herbaceous, green	2-methoxy-3-(2-methylpropyl)pyrazine	973
17.18	smoky, sharp, roasted	guaiacol	913
7.20	solvent, fresh, medicinal		898
6.83	sweet, fruity, fresh	methyl isovalerate	808
11.38	nutty, roasted, savory	2,4 or 2,6-dimethyl pyrazine	791

RT (min)	Odor Character	Sample 2	
		Tentative MS Identification	Aroma Intensity
8.31	acidic, sour	acetic acid	1578
22.44	floral, cedar, smoky, foul	2-methoxy-4-vinylphenol	1361
17.18	smoky, sharp, roasted	guaiacol	1186
4.35	nutty, roasted	3-methyl butanal	1118
12.54	rancid, foul, sweaty	isovaleric acid	1102
14.63	nutty, stale		1090
15.57	herbaceous, green, vegetable	linalool oxide	1018
15.31	smoky, solvent		921
11.58	potato	methional	898
17.74	vegetable, herbaceous, green	2-methoxy-3-(2-methylpropyl)pyrazine	874

RT (min)	Odor Character	Sample 3	
		Tentative MS Identification	Aroma Intensity
12.54	rancid, foul, sweaty	isovaleric acid	1160
15.57	herbaceous, green, vegetable	linalool oxide	1155
22.44	floral, cedar, smoky, foul	2-methoxy-4-vinylphenol	1119
14.63	nutty, stale		1054
17.48	vegetable, herbaceous		1052
17.83	floral, fresh, solvent	benzeneethanol	958
6.83	sweet, fruity, fresh	methyl isovalerate	868
8.77	fruity, fresh, sweet	ethyl-2-methyl butyrate	852
7.20	solvent, fresh, medicinal		845
18.86	sharp		838

RT (min)	Odor Character	Sample 4	
		Tentative MS Identification	Aroma Intensity
12.54	rancid, foul, sweaty	isovaleric acid	2475
15.94	fresh, medicinal, solvent	nonanal	1876
8.31	acidic, sour	acetic acid	1663
17.48	vegetable, herbaceous		1527
11.38	nutty, roasted, savory	2,4 or 2,6-dimethyl pyrazine	1383
14.64	solvent, petroleum, oily		1289
15.57	herbaceous, green, vegetable	linalool oxide	1076
15.35	vegetable, earthy	1-octene-3-ol, 3-ethyl-2,5-dimethyl pyrazine	843
9.85	solvent, fresh, medicinal, paper		790
4.35	nutty, roasted	3-methyl butanal	788

Conclusions

- Extended SPME headspace collection followed by simultaneous MDGC / MS / Olfactometry analysis was utilized to acquire the GC Total Ion Chromatograms along with the Aromagrams
- GCMS results show compositional differences among the 4 samples
- Numerous compounds from many different classes are observed among the 4 samples
- Olfactory results indicate that more than half of the volatile compounds identified in the headspace by GCMS analysis are relatively odorless
- A total of 19 compounds are represented in the Top 10 Aromas
- Only 1 compound, isovaleric acid, is present in all four samples
- Six of these compounds are present in three different samples, while another six compounds appear in only one sample

Future Investigations

- Statistical analysis of green coffee aroma data
- MDCG/MS/O analysis of the roasted coffee samples from these same green coffee bean samples
- Perform analyses on additional green coffee bean samples